Structural, Interfacial, and Electrochemical Properties of Pr2NiO4+δ – Based Electrodes for Solid Oxide Fuel Cells

Emir Dogdibegovic
University of South Carolina

Follow this and additional works at: http://scholarcommons.sc.edu/etd
Part of the Chemical Engineering Commons

Recommended Citation

This Open Access Dissertation is brought to you for free and open access by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact SCHOLARC@mailbox.sc.edu.
STRUCTURAL, INTERFACIAL, AND ELECTROCHEMICAL PROPERTIES OF \( \text{Pr}_2\text{NiO}_{4+\delta} \)-BASED ELECTRODES FOR SOLID OXIDE FUEL CELLS

by

Emir Dogdibegovic

Bachelor of Arts
Hood College, 2012

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
Chemical Engineering
College of Engineering and Computing
University of South Carolina

2017

Accepted by:
Xiao-Dong Zhou, Major Professor
Harry Ploehn, Committee Member
Bihter Padak, Committee Member
John Weidner, Committee Member
Kenneth Reifsnider, Committee Member

Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

To my parents Fadila and Sulejman, my sister Azra, and my entire family.
ACKNOWLEDGMENTS

I would like to acknowledge many individuals and teams for helping me reach this stage of academic development. First and foremost, I would like to thank my parents and my sister for their unconditional love, support, and advisement. Second, I would like to thank my entire family for believing in me all these years and never having any doubts in my personal goals. Third, I would like to thank my friends who helped me retain the balance between academic development and personal life.

I would like to express my gratitude and appreciation to those individuals who sparked my love for science, math, and engineering since a young age including Prof. Radojka, Prof. Dushanka, Prof. Cecilija, Prof. Ema, and Prof. Muslija. I would also like to thank Nelson Mandela, Queen Noor, and Shelby Davis foundation for the establishment of an impeccable and internationally spirited United World College (UWC) and their continuous support through my studies. Furthermore, I would like to acknowledge many UWC professors who pushed my limits of academic development further than I could ever imagine. Equally important, I would like to thank many professors at Hood College including Dr. Flora, Dr. Ensel, Dr. Stromberg, Dr. Bennett, and Dr. Stewart for preparing me for the graduate studies.

This thesis would not be possible without contributions from many individuals and collaborators at industry, national laboratories, research centers, and academic institutions. In particular, I would like to thank Dr. Cai, Dr. Yan, Dr. Chen, Dr. Stevenson, Dr. Hardy, Chris Coyle, Rich Goettler, Dr. Liu, Dr. Jung, and Dr. Taghi. Furthermore, I would like to
thank Dr. Minh, Dr. Torabi, and Dr. Elangovan for selflessly sharing their knowledge on the current challenges in SOFC industry and future industrial prospects.

A significant part of this thesis would not be completed without unselfish help from Chris Wright. Our work at a synchrotron source provided further insights into complexity of materials discussed in this thesis. Significant help during the past four years also came from over 25 undergraduate trainees and group members who contributed to parts of this work not only with their skills but also with their wonderful personalities. In particular, I would like to thank Nawf, Sam, Yudong, Sterling, Seth, Olivia, Madison, Scott, John, and Salim.

Finally, I would like to thank Dr. Zhou for his continuous support and guidance during my Ph.D. candidacy. Without his help I would not be able to publish numerous papers, be granted multiple patents, and attend many professional conferences. I would also like to thank the committee members Dr. Reifsnider, Dr. Ploehn, Dr. Padak, and Dr. Weidner for their encouragement and guidance during my Ph.D. training. Lastly, I would like to thank the Electrochemical Society, in particular the high temperature materials division, and the University of South Carolina for numerous travel grants and for funding my trips to Argonne National Laboratory.
Currently, the electrochemical performance and performance durability of solid oxide fuel cells (SOFCs) are limited by cathode materials. The high polarization resistance and phase instability of the cathode are two major challenges to hinder the commercialization of SOFC systems. Two families of oxides are presently known as potential cathode materials for SOFCs: (1) the perovskite family of oxides with a general formula of \( \text{ABO}_3 \), and (2) the Ruddlesden-Popper (RP) family of oxides (e.g. nickelates) with a general formula of \( \text{A}_2\text{BO}_4 \). The electron-hole conduction in these materials occurs simultaneously with oxygen ion conduction based on either oxygen vacancies (e.g. \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \), LSCF), cation vacancies (e.g. \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta} \), LSM), or oxygen interstitials (\( \text{Ln}_2\text{NiO}_{4+\delta} \), where \( \text{Ln} = \text{La, Pr, Nd} \)). Among these candidates, the \( \text{Pr}_2\text{NiO}_{4+\delta} \) (PNO) shows the highest surface exchange and diffusion coefficients, lowest activation energy for oxygen reduction reaction, and lowest electrode polarization, making it a potential candidate for the next generation SOFC systems (Chapter 1).

However, the phase transformation in PNO is of a concern as the structural instability has been linked to the long-term performance degradation (Chapters 3-4). Therefore, it is of a great scientific interest to find ways to stabilize the phase while retaining the activity in PNO. In this thesis, a new series of compositions (\( \text{Pr}_{1-x}\text{Nd}_x\text{NiO}_{4+\delta} \) and \( \text{Pr}_{1-x}\text{Nd}_x\text{Cu}_y\text{NiO}_{4+\delta} \) are introduced as phase and performance stable cathodes (Chapters 5-8). Detailed x-ray diffraction and in situ synchrotron studies showed that combination of doping on A- and B-sites provides structural rigidity, which in turn leads
to suppressed phase transformations and stabilized performance, as evaluated via long-term durability studies in powders, electrodes, and full cells.

This thesis also presents an in-depth comparison between phase transformation in thermal vs. electrochemical systems (Chapters 9-10). A discrepancy was found between the rates of phase transformation in thermally annealed nickelates when compared to their operation in full cells. Therefore, the thermodynamics and electrochemical potential driving forces were addressed respectively. Furthermore, the accelerated tests protocols were developed (Chapter 11) which can simulate the long-term cell operation (10,000-20,000 hours) within a fraction of time (1,000-2,000 hours). Finally, a deeper understanding behind the use of an interlayer (a buffer layer between the cathode and the electrolyte) was obtained (Chapter 12). It was found that by manipulating the interlayer chemistry the phase transformation in nickelates can be fully suppressed with a remarkable performance improvement of 48%. These combined studies provide deeper fundamental understanding behind structure - phase stability - electrochemical property relationship and can serve as a platform for future cathode and interlayer development.
Solid oxide fuel cells (SOFCs) directly convert chemical energy stored in fuels (e.g. natural gas) into electricity and heat without any combustion or harmful products. The process involves a series of electrochemical reactions at elevated temperatures (e.g. 600-750 °C) that lead to the reduction of oxygen and oxidation of chemical fuels. SOFCs are flexible systems and can utilize a variety of fuels ranging from hydrocarbons to ammonia to carbon monoxide. Their efficiencies in combined heat and power systems can exceed 70%, since they are not limited by the theoretical Carnot efficiency. Furthermore, SOFCs can operate in a reversible electrolysis mode to convert CO₂ and/or H₂O to fuels and oxygen. Overall, these systems can potentially decrease the carbon footprint, provide electricity and heat more efficiently, and replace current coal-fired power plants and electrical generators that are based on internal combustion engines.

However, to reach these goals many technical and industrial challenges have to be resolved within the SOFCs. This thesis focuses on many fundamental questions surrounding the SOFC operation such as: (1) What materials allow operation at reduced temperatures while retaining high mixed conducting properties? (2) What is the role of crystal structure in cathodes on phase stability and electrochemical performance? (3) What is the role of phase transformation on electrochemical performance? (4) What is the origin behind stable electrochemical performance? (5) Can thermal phase transformation behavior in cathode materials simulate the behavior in full cells? (6) Can the material
screening process be accelerated along with the SOFC operation? (7) What is the role of an interlayer (a.k.a. buffer) towards phase stability and electrochemical performance?

The current SOFC operation is limited by the cathode due to its large polarization resistance in a single cell and relatively slow oxygen kinetics. To improve on these factors structural (crystal structure), interfacial (contact with other cell components), and electrochemical (synergy of all factors during electrochemical operation) properties have to be considered. Layered Pr$_2$NiO$_{4+\delta}$-based electrodes are discussed due to their low polarization resistance, structural flexibility, and superior kinetics over commonly used materials.

Due to required ~40,000 hours of continuous operation, the long-term durability studies are essential in SOFC field. Unfortunately, they are often not reported in open literature, which leaves doubts regarding the potential of new materials for long-term SOFC operation. In this thesis, the novel cathode materials are studied in a great detail including their crystal structure, phase stability, kinetics, conduction properties, and prolonged electrochemical operation. Deeper fundamental knowledge was obtained on the structure - phase stability - electrochemical property relationship, allowing for easier development of the next generation cathode materials, interlayers, and SOFC systems.
# TABLE OF CONTENTS

**DEDICATION** ........................................................................................................ iii

**ACKNOWLEDGEMENTS** .......................................................................................... iv

**ABSTRACT** ............................................................................................................... vi

**PREFACE** ................................................................................................................ viii

**LIST OF TABLES** ..................................................................................................... xv

**LIST OF FIGURES** .................................................................................................. xix

**CHAPTER 1: RUFFLESDEN-POPPER-TYPE OXIDES AS OXYGEN ELECTRODES FOR SOLID OXIDE FUEL CELLS** ................................................................. 1

1.1 **BACKGROUND ON SOLID OXIDE FUEL CELLS** ........................................... 2

1.2 **OXYGEN ELECTRODES FOR SOLID OXIDE FUEL CELLS** .............................. 6

1.3 **OXYGEN CONTENT AND MIXED CONDUCTION IN NICKELATES** ................. 16

1.4 **PHASE FORMATION AND CRYSTAL STRUCTURE IN NICKELATES** ............. 32

1.5 **PHASE TRANSFORMATION IN RP NICKELATES** ........................................... 48

1.6 **ELECTROCHEMICAL PERFORMANCE IN RP NICKELATES AND CUPRATES** .... 59

1.7 **FUTURE RESEARCH DIRECTIONS** ................................................................. 80

1.8 **SUMMARY** ....................................................................................................... 84

**CHAPTER 2: EXPERIMENTAL PROCEDURES** .................................................... 102

2.1 **MATERIAL SYNTHESIS** ..................................................................................... 102

2.2 **DENSE CERAMIC BAR MANUFACTURING** .................................................... 104

2.3 **ELECTRODE MANUFACTURING** ..................................................................... 104
2.4 INTERLAYER SYNTHESIS AND SYMMETRIC CELL MANUFACTURING ..............104
2.5 FABRICATION OF FULL CELLS ..................................................................106
2.6 ELECTROCHEMICAL TESTS ........................................................................107
2.7 QUANTIFICATION OF PHASE EVOLUTION IN FULL CELLS ......................109
2.8 SEM AND EDS ANALYSIS ..........................................................................109
2.9 IN OPERADNO X-RAY STUDIES ON ELECTROCHEMICAL CELLS ..........110
2.10 IN SITU X-RAY STUDIES AT A SYNCHROTRON SOURCE ..................111

CHAPTER 3: COMPATIBILITY OF PRASEODYMIUM NICKELATES WITH OTHER CELL COMPONENTS .................................................................................................114

3.1 COMPATIBILITY OF Pr2NiO4 AND La0.8Sr0.2CoO3 (LSC) CURRENT COLLECTOR .................................................................114

3.2 COMPATIBILITY OF Pr2NiO4 AND (La0.8Sr0.2)0.95MnO3-x (LSM) CURRENT COLLECTOR ..................................................................................................................117

3.3 COMPATIBILITY OF Pr2NiO4 AND CERIA ..........................................................................................................................119

3.4 ELECTROCHEMICAL PERFORMANCE AND PERFORMANCE STABILITY OF Pr2NiO4 ELECTRODE ..................................................................................121

CHAPTER 4: QUANTIFICATION OF PHASE EVOLUTION IN PRASEODYMIUM NICKELATE CATHODES ........................................................................................................124

4.1 INTRODUCTION TO QUANTIFICATION CHALLENGES ..........................124

4.2 CELL DESIGN AND QUANTIFICATION OF PHASE TRANSITION ............125

4.3 ELECTROCHEMICAL PERFORMANCE AND CELL DURABILITY ...........130

CHAPTER 5: ELECTROCHEMICAL PERFORMANCE AND PERFORMANCE DURABILITY OF (Pr1-xNdx)2NiO4 AS CATHODES FOR SOLID OXIDE FUEL CELLS .................................................................134

5.1 POWER DENSITY AND AREA SPECIFIC RESISTANCE IN PNNO ..........134

5.2 ANALYSIS OF THE DISTRIBUTION OF THE RELAXATION TIMES (DRT) ..138

5.3 PERFORMANCE STABILITY .........................................................................142
CHAPTER 6: CRYSTAL STRUCTURE, ELECTRICAL PROPERTIES, AND MICROSTRUCTURAL ANALYSIS OF \((\text{Pr}_{1-x}\text{Nd}_x)\text{NiO}_4\) CATHODES ..................................................147

6.1 STRUCTURAL AND ELECTRICAL PROPERTIES OF PNNO ..........................................................147

6.2 PHASE EVOLUTION IN PNNO POWDERS AND ELECTRODES.......................................................155

6.3 MICROSTRUCTURAL ANALYSIS OF THE ELECTRODES ..............................................................160

CHAPTER 7: THE ROLE OF A- AND B-SITE DOPANTS ON THE STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF \((\text{Pr}_{1-x}\text{Nd}_x)\text{Ni}_{1-y}\text{B}_y\text{O}_4\) CATHODES ...............167

7.1 STRUCTURAL CHARACTERIZATION ..................................................................................................168

7.2 PHASE STABILITY ..........................................................................................................................171

7.3 THE ROLE OF ANNEALING TEMPERATURE ON THE STRUCTURAL STABILITY ....174

7.4 ELECTROCHEMICAL PERFORMANCE AND AREA SPECIFIC RESISTANCE .................176

7.5 ANALYSIS OF THE DISTRIBUTION OF RELAXATION TIMES (DRT) .........................179

7.6 LONG-TERM PERFORMANCE DURABILITY .................................................................................180

CHAPTER 8: IDENTIFYING THE ORIGIN OF PHASE TRANSFORMATION AND STRUCTURAL STABILITY IN \((\text{Pr}_{1-x}\text{Nd}_x)\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}\) CATHODES .................................................................185

8.1 STRUCTURAL CHARACTERIZATION AT ROOM TEMPERATURE ..................................................185

8.2 IN SITU STRUCTURAL CHARACTERIZATION AT THE SYNCHROTRON SOURCE.....189

8.3 ON THE ORIGIN OF STRUCTURAL CHANGES IN PRASEODYMIUM NICKELATES ..192

CHAPTER 9: WHAT IS THE DRIVING FORCE FOR RETAINED ACTIVITY AND STABLE LONG-TERM PERFORMANCE IN \(\text{Pr}_2\text{NiO}_4\)? .................................................................197

9.1 PERFORMANCE DEGRADATION IN PNO ....................................................................................198

9.2 PHASE EVOLUTION IN PNO AND SYNCHROTRON STUDIES .............................................200

9.3 MICROSTRUCTURAL ANALYSIS AND FORMATION ON NANOCLUSTERS..............202

9.4 \(\text{Pr}_3\text{Ni}_2\text{O}_7\) PHASE AS AN ADDITIONAL CONTRIBUTOR TO RETAINED ACTIVITY OF \(\text{Pr}_2\text{NiO}_4\) ..........................................................................................................................207
CHAPTER 10: ELECTROCHEMICALLY DRIVEN PHASE TRANSFORMATION IN PRASEODYMIUM NICKELATES

10.1 ELECTROCHEMICALLY DRIVEN PHASE TRANSFORMATION AND A PROPOSED THEORY

10.2 PERFORMANCE STABILITY AND IN OPERANDO DRT ANALYSIS

10.3 PHASE TRANSFORMATION IN ELECTROCHEMICAL CELLS

10.4 MICROSTRUCTURAL ANALYSIS ON ELECTROCHEMICAL CELLS

CHAPTER 11: ACCELERATED TEST PROTOCOLS (ATPS) IN SOLID OXIDE FUEL CELLS

11.1 ACCELERATED TEST PROTOCOLS-THEORETICAL ANALYSIS

11.2 INITIAL PERFORMANCE AND CELL DURABILITY

11.3 PERFORMANCE STABILITY UNDER ATPS AND DRT ANALYSIS

11.4 ACCELERATED PHASE TRANSFORMATION IN PNNO

11.5 ATPS ON STABLE Nd₂NiO₄ ELECTRODE

CHAPTER 12: UNRAVELING THE ROLE OF INTERLAYER ON PHASE STABILITY AND CATALYTIC ACTIVITY IN NICKELATE CATHODES

12.1 BRIEF HIGHLIGHTS ON THE ROLE OF DOPED CERIA INTERLAYER

12.2 INTRODUCTION TO INTERLAYER CHALLENGES

12.3 DEVELOPMENT OF THE NEXT GENERATION INTERLAYERS

12.4 THE ROLE OF INTERLAYER ON PHASE TRANSFORMATION IN NICKELATES

12.5 KINETICS OF PHASE TRANSFORMATION IN NICKELATES

12.6 THE ROLE OF INTERLAYER ON CATHODE PERFORMANCE

12.7 THE ROLE OF INTERLAYER ON CATHODE DURABILITY

12.8 IN OPERANDO XRD ANALYSIS IN ELECTROCHEMICAL CELLS

12.9 THE ROLE OF INTERLAYER ON PHASE TRANSFORMATION IN OPERATING ELECTRODES
APPENDIX A – SUPPLEMENTARY INFORMATION TO CHAPTER 7.................................262
APPENDIX B – SUPPLEMENTARY INFORMATION TO CHAPTER 12.........................266
APPENDIX C – AUTHOR’S PUBLICATIONS, PATENTS, AND PRESENTATIONS...............273
LIST OF TABLES

Table 1.1 Total conductivity ($\sigma_{\text{tot}}$) of monolithic nickelate ceramics measured in air at various temperatures. Oxygen over-stoichiometry ($\delta$) measured in air at room temperature (RT) and 600 °C (HT) is also listed. .................................................................24

Table 1.2 Total conductivity ($\sigma_{\text{tot}}$) of doped Pr$_2$NiO$_{4+\delta}$ nickelate ceramics measured in air at various temperatures. The measured $\delta$ in air at room temperature (RT) and 600 °C (HT) is listed. .................................................................27

Table 1.3 Total conductivity ($\sigma_{\text{tot}}$) of doped La$_2$NiO$_{4+\delta}$ nickelate ceramics measured in air at various temperatures. The measured $\delta$ in air at room temperature (RT) and 600 °C (HT) is listed. .................................................................28

Table 1.4 Total conductivity ($\sigma_{\text{tot}}$) of doped Nd$_2$NiO$_{4+\delta}$ nickelate ceramics measured in air at various temperatures. Oxygen over-stoichiometry ($\delta$) measured in air at room temperature (RT) and 600 °C (HT) is also listed. .................................................................29

Table 1.5 Calculated lattice parameters for Pr$_2$NiO$_{4+\delta}$-based compositions at room temperature. The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{\text{syn}}$: XRD at a synchrotron source, ND: neutron diffraction). .................................................................41

Table 1.6 Calculated lattice parameters for La$_2$NiO$_{4+\delta}$-based compositions at room temperature (A-site doping). The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{\text{syn}}$: XRD at a synchrotron source, ND: neutron diffraction). .................................................................42

Table 1.7 Calculated lattice parameters for La$_2$NiO$_{4+\delta}$-based compositions at room temperature (B-site doping). The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{\text{syn}}$: XRD at a synchrotron source, ND: neutron diffraction). .................................................................43

Table 1.8 Calculated lattice parameters for Nd$_2$NiO$_{4+\delta}$-based compositions at room temperature. The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{\text{syn}}$: XRD at a synchrotron source, ND: neutron diffraction). .................................................................44
Table 1.9 The cell configuration and calculated activation energy for electrode reaction for monolithic cathodes. Cells with similar configuration and operating temperatures were compared ................................................................. 64

Table 1.10 The cell configuration and calculated activation energy between 650 – 850 °C for electrode reaction for doped PNO, LNO, and NNO cathodes. ............................ 70

Table 3.1 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSC current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented. ................. 116

Table 3.2 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSM current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented. The highlighted region 16 corresponds to LSM-cathode interface. ................................................................. 118

Table 3.3 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSM current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented. ......................... 120

Table 4.1 The Percentage of Pr$_6$O$_{11}$ in Pr$_2$NiO$_4$ treated at various conditions. .......... 127

Table 6.1 Refinement parameters of (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ at room temperature. x,y,z are fractional position coordinates. All samples are orthorhombic structure with space group Bmab. $\chi^2$ is $[R_{wp}/R_{exp}]^2$, where $R_{wp}$ is the residual error of the weighted profile and $R_{exp}$ is statistically expected residual error of the entire measured diffraction patterns. ................................................................. 150

Table 6.2 Conductivity maximum for (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ series. ................................. 154

Table 6.3 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell. For the simplicity reasons only atomic percentages for Pr, Nd, and Ni are presented. ................................................................. 161

Table 7.1 Refinement parameters of (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_4$ at room temperature. x,y,z are fractional position coordinates. All samples are orthorhombic structure with space group Bmab. $\chi^2$ is $[R_{wp}/R_{exp}]^2$, where $R_{wp}$ is the residual error of the weighted profile and $R_{exp}$ is statistically expected residual error of the entire measured diffraction patterns. ................................................................. 170

Table 9.1 Elemental analysis on nanoclusters and surrounding regions of operated PNO electrode (500 hours, 0.80V and 750 °C). Exemplary EDS spectrum on point 1 is also provided. ................................................................. 206
LIST OF FIGURES

**Figure 1.1** Operating principle of a solid oxide fuel cell ........................................... 3

**Figure 1.2** Schematic V-I curve for a typical SOFC, which shows OCV, cathodic polarization loss, anodic polarization loss, and ohmic loss. ...........................................5

**Figure 1.3** (a) Power density vs. current density for several cathodes at 750°C on the same batch of electrolyte/anode bilayers. The peak power density increases substantially by changing the cathode. (b) Power density vs. time for several cathodes at 750°C at constant voltage 0.8 V. ................................................................. 7

**Figure 1.4** A schematic of cathode surface reacting with oxygen. ................................. 8

**Figure 1.5** Comparison between three typical SOFC oxygen electrodes. Acronym definition: LSM: (La,Sr)MnO$_3$; LCM: (La,Ca)MnO$_3$; LSCF: (La,Sr)(Co,Fe)O$_3$; BSCF: (Ba,Sr)(Co,Fe)O$_3$ ........................................................................................................ 10

**Figure 1.6** A typical perovskite structure. Note the repeating units are based on rigid oxygen octahedron, which can tolerate a variety of local chemical and structural changes, such as distortion, rotation, or redox reaction. ...................................................... 13

**Figure 1.7** Ruddlesden-Popper structures for n = 1 (a), 2 (b) and 3 (c); A atoms shown in green, BO$_6$ in blue/red. The Pr$_2$NiO$_4$ unit cell without octahedral canting (d). The interstitial defect site is shown along with an outline of the tetrahedral Pr coordination environment. The interstitial site is also tetrahedrally coordinated by apical oxygen ions. ................. 16

**Figure 1.8** Thermal variation in $\delta$ in air for the LNO, PNO, NNO and other compounds. .......................................................................................................................... 18

**Figure 1.9** Structure and nuclear density distribution of (Pr$_{0.90}$La$_{0.10}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_{4+\delta}$ at room temperature analyzed via neutron diffraction, synchrotron x-ray diffraction, maximum entropy method (MEM), and Rietveld refinement. (a) Nuclear density distribution on the $bc$ plane. (b) Electron density distribution on the $bc$ plane. (c) A corresponding valence electron density distribution obtained using DFT calculations. (d) Optimized structure used for DFT calculations. (e) Isosurface of highest occupied molecular orbitals (HOMO) of optimized structure ................................................. 19

**Figure 1.10** (a) Total conductivity for the series of PNNO bars measured in air between 50 – 850 °C. (b) Conductivity in bars with x=0, 0.50, 1.0 as function of oxygen partial pressure. .................................................................................................................. 22
Figure 1.11 The total conductivity of La$_{2}$Ni$_{0.9}$Co$_{0.10}$O$_{4}$ as function of oxygen content. .................................................................31

Figure 1.12 Calculated vertical section of the La-Ni-O phase diagram along the La$_2$NiO$_4$-LaNiO$_3$ join in air. The experimental measured results (marked) are also superimposed. .................................................................33

Figure 1.13 (a) XRD patterns on a single phase PNNO powders matched against the standard reflections. (b) Rietveld refinement on selected PNNO compositions. (c) Rietveld refinement on PNNO(50/50)-Cuy compositions. Dots are raw data and solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves. ..........................36

Figure 1.14 (a) Cell volume for Nd-substituted Pr$_2$NiO$_{4+\delta}$ powders obtained from the Rietveld refinement. (b) Calculated cell parameters as function of Nd substitution and compared against results obtained by Boehm et al. ..........................38

Figure 1.15 Refined a, b, and c lattice parameters (a), and unit cell volume for (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+\delta}$ powders at RT (b). .................................39

Figure 1.16 Thermal variation in lattice parameters and unit cell volume in air for (a-b) PNO, (c-d) LNO, and (e-f) NNO compositions in LNO and NNO. The variation in oxygen stoichiometry measured by TGA is also shown. ..................................................40

Figure 1.17 Refined average (Ni,Cu)-O bond lengths for (Ni,Cu)O$_e$ (equatorial) and (Ni,Cu)-O$_f$ (focal) arrangements (a), and O-(Ni,Cu)-O bond angles for the same series (b). Refined average (Pr,Nd)-O bond lengths for (Pr,Nd)O$_e$ (c), and (Pr,Nd)-O$_f$ arrangements (d). .................................................................46

Figure 1.18 Quantified M-O distances from PDF measurements as function of composition and temperature for (a) (Ni, Cu)-O$_f$ atomic distance and (b) (Pr, Nd)-O$_f$ atomic distance. .................................................................47

Figure 1.19 (a) Thermal stability of PNNO powders at 750 °C in air. (b) Phase evolution in PNO and (c) PNNO electrodes in symmetric cells (YSZ/GDC/cathode) as function of time and temperature. .................................................................50

Figure 1.20 Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours. .................................................................53

Figure 1.21 (a) Phase purity and phase stability in PNNO(50/50) powders with various dopants on the Ni-site including Cr, Mn, Fe, Co, and Zn. (b) Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours. .................................................................55
Figure 1.22 Quantified phase evolution in PNN05050-Cu$_y$ electrodes at elevated temperatures .................................................................55

Figure 1.23 Phase evolution in thermally annealed (750 °C) and electrochemically operated (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ electrodes after 500 hours at 750 °C and 0.80 V. .........................58

Figure 1.24 Representation of nickelate reports between 1990-2017. Percentage of reports on nickelate material studies (conductivity, diffusion, surface exchange), cathode materials on symmetric cells, and performance in symmetric and full cells (a). Percentage of reports presenting only initial studies, performance stability between 25-100 hours, and long term operation over 500 hours (b) .................................................................60

Figure 1.25 Monolithic electrode ASR at OCV from the 1190-2017 literature reports in the temperature region between 600-850 °C (a). Initial power density of monolithic electrodes measured at 0.80 V and 0.70 V at various temperatures (b). Respective references are provided on the side legend. .................................................................61

Figure 1.26 Measured (a) surface exchange and (b) diffusion coefficients on nickelates when compared to commonly used LSCF and LSFN materials. .................................63

Figure 1.27 (a) Electrode resistance ln (ASR$_e$) as a function of 1/T for all cathode compositions at OCV obtained from i-V curves. (b) Similar plot obtained from the DRT analysis and taking into consideration the anodic ASR. .................................63

Figure 1.28 (a) Reproducible operation for multiple cells. (b) Power density as function of temperature. .................................................................................65

Figure 1.29 Initial i-V and power density curves for selected (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cathodes, as function of x, operated between 650 and 850 °C. .................................................................66

Figure 1.30 Doped monolithic electrode ASR at OCV from the year 1190-2017 literature reports in the temperature region between 600-850 °C on PNO-based electrodes (a), LNO-based electrodes (b), and NNO-based electrodes (c). PNO, LNO and NNO baselines are provided on each figure. Respective references are provided in parentheses. ...............67

Figure 1.31 Initial power density of doped monolithic electrodes measured at 0.80 V and 0.70 V at various temperatures for PNO-based compositions (a), and LNO, NNO-based compositions (b). Respective references are provided in parentheses. ...............72

Figure 1.32 Performance stability for (a) (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cathodes operated at 0.80 V and 750 °C, and (b) (Pr$_{1-x}$Nd$_x$)$_2$Ni$_{1-y}$Cu$_y$O$_4$ cathodes operated at 0.80 V and 790 °C for 500 hours ...............................................................................73

Figure 1.33 EIS plots on PNO cell under (a) +100 mv (OER), and (b) -100 mV (ORR) as function of oxygen partial pressure at 750 °C. (c) Quantified electrode polarization at various potentials and partial pressures in a single cell ........................................79
Figure 2.1 A schematics showing experimental procedures utilized to characterize and evaluate cathode materials for SOFCs. .................................................................103

Figure 2.2 (a) Electrolyte supported cells for thermal annealing studies. Electrodes were printed on both sides of the cell. At least two cells (4 electrodes) for each cathode composition were tested. Tests were performed on cells without an interlayer, or with an interlayer as shown in (b). .................................................................105

Figure 2.3 (a) Electrolyte supported cells with sintered GDC-20 buffer, and with 10 and 20 drops of PrO_x spin coating solution on top of the GDC-20 interlayer. (b) PGCO interlayer after sintering. .................................................................106

Figure 2.4 (a) Electrolyte and anode supported cells with printed cathodes and Au grids (Au grinds were not sintered). (b) The cell setup used to perform electrochemical tests. .................................................................107

Figure 2.5 Designed and built SOFC laboratory at University of South Carolina (property of USC). Single cell tests high throughput setups are shown in top figures and the bottom left figure. The furnaces used for powder and cell thermal annealing studies are shown in bottom middle figure. The setup used for conductivity and/or and pressurized studies is shown at the bottom right. .................................................................108

Figure 2.6 (a) Solartron 1470E Multistat and 1255B Frequency Response Analyzer. (b) Biologic VMP3 potentiostat with external current boosters. ....................................................109

Figure 2.7 (a) A top view on initial cells with sintered Au grid. In this set of cell the interlayer was screen printed. (b) A top view on operated full cells used for post-operation phase transition studies. In this case interlayer was sprayed. The cathode was not damaged during cell assembly and disassembly and the cells were preserved. ........................................110

Figure 2.8 (a) Bruker D8 Advance XRD at Pacific Northwest National Laboratory. (b) Anton Paar HTK 1200 heating chamber. (c) In-situ SOFC setup with an open cathode center for phase evolution studies. .................................................................110

Figure 2.9 (a) APS and Argonne National Laboratory. (b) Experimental setup for XRD synchrotron studies at 11-ID-B beamline at APS. Details are described in Chapter 10. .................................................................112

Figure 3.1 XRD of the Pr_2NiO_4 and a) LSC or b) LSM mixtures annealed at 750 °C for times between 0-500 h. LSC or LSM were used as cathode contacts and LaB_6 was added to evaluate potential peak shifts. .................................................................115

Figure 3.2 (a) SEM image of a button cell with LSC current collector, Pr_2NiO_4 cathode and SDC-20 buffer layer. EDS line scan of elemental distribution across the cell layers is shown. b) Multiple regions of EDS area scan used for analysis. ........................................116
Figure 3.3 Partial SEM image of a button cell with LSM current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer. (a) Cathode and LSM current collector are shown together with EDS area scan regions. b) Functional anode layer and ceria layer are shown with EDS area scan regions.

Figure 3.4 XRD of the Pr$_2$NiO$_4$ and (a) GDC or (b) SDC mixtures annealed at 750 °C for times between 0-500 h. GDC or SDC were used as an interlayer between the cathode and YSZ. LaB6 was added to evaluate potential peak shifts.

Figure 3.5 (a) Electrochemical impedance spectra for a button cell with Pr$_2$NiO$_4$ cathode measured at 750 °C and 0.8 V. (b) Power density vs. time spectra at 750 °C and 0.8 V for multiple cells tests with Pr$_2$NiO$_4$ cathode. Note that ohmic resistance changed, but electrode resistance remained stable over ~ 1200 hours measurements.

Figure 4.1 (a) A fuel cell configuration of an anode-supported cell, doped ceria/YSZ/Ni–YSZ, with the cathode covered by Au metal grid. (b) A top view of cells with Au grid and visible cathode for phase evolution studies.

Figure 4.2 XRD patterns on an operated cell (a). Standard XRD reflections are shown for Ni/YSZ/GDC/nickelate/Au cell configuration. Cathode signal reproducibility after sintered Au grid (b). The LCOS fitted against the XRD patterns in initial cell and after the electrochemical operation (c). Standardization of nickelate/Pr$_6$O$_{11}$ powder mixtures (volume and mole percent), with calculated signal intensity ratio between nickelate and Pr$_6$O$_{11}$ (d).

Figure 4.3 XRD signal comparison for the physical powder mixtures of Pr$_2$NiO$_4$ and Pr$_6$O$_{11}$.

Figure 4.4 (a) I–V and power density curves for cells with nickelate electrodes and Au grids. (b) I–V curves of cells with Au, LSC, and LNF current collectors measured at 790°C. (c) impedance spectra of the cells with Au, LSC, and LNF current collectors measured at 790°C.

Figure 4.5 (a) A long-term performance (I–V and powder density) of Pr$_2$NiO$_4$ measured up to 500 h. (b) Impedance spectra of Pr$_2$NiO$_4$ measured up to 500 h. (c) A backscattered SEM image of Ni/YSZ/GDC/nickelate/Au-based cell after a 500-h measurement. (d) The images of cell surface after 500-h operation.

Figure 5.1 (a-e) Initial i-V and power density curves for (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cathodes as a function of $x$, operated between 650 and 850 °C, and (f) power density measured at 0.80 V as function of temperature for each composition.

Figure 5.2 Total cell ASR as a function of current density for (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cells calculated from dc measurements at 750 °C.
Figure 5.3 A comparison of the electrode ASR obtained from i-V and EIS measurements at 750 °C. Ohmic ASR was obtained by using the equivalent circuit presented in Figure 3.5 (c). .................................................................137

Figure 5.4 (a) Electrode resistance ln (ASR_e) as a function of 1/T for all cathode compositions at OCV obtained from i-V curves. (b) A similar plot obtained from the DRT analysis while subtracting the anodic ASR. .................................................................138

Figure 5.5 (a) DRT analysis on cells as a function of Nd content. (b) DRT analysis on a cell with x = 0.25 exposed to air and oxygen environments. (c) A schematic equivalent circuit model for PNNO cells. .................................................................139

Figure 5.6 (a-f) Plots of i-V and power density curves for (Pr_1-xNd_x)2NiO_4 cells as a function of time, measured at 0.8 V and 750 °C along with corresponding EIS spectra measured at 0, 250th, and 500th hours. .................................................................141

Figure 5.7 Resistance for each process obtained from the equivalent circuit model in Figure 5(e). .................................................................142

Figure 5.8 Performance stability for (Pr_1-xNd_x)2NiO_4 cathodes measured at 0.8 V and 750 °C. .................................................................143

Figure 5.9 (a) Electrode ASR and (b) ohmic ASR of the cells measured at 0.50 A cm^-2 for (Pr_1-xNd_x)2NiO_4 cathodes at 0.8 V. .................................................................144

Figure 6.1 XRD of raw, single phase (Pr_1-xNd_x)2NiO_4+δ powders. ...............148

Figure 6.2 Rietveld refinement on (Pr_1-xNd_x)2NiO_4+δ cathode materials using the FullProf code. Dots are raw data. Solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves. .................................................................149

Figure 6.3 (a) Cell volume for Nd-substituted Pr_2NiO_4+δ powders obtained from the Rietveld refinement. (b) Calculated cell parameters as function of Nd substitution and compared against literature values. .................................................................151

Figure 6.4 (a) Total conductivity for the series of PNNO bars measured in air between 50 – 850 °C. (b) Conductivity in bars with x=0, 0.50, 1.0 as function of oxygen partial pressure. .................................................................153

Figure 6.5 Thermal stability of PNNO powders at 750 °C in air. ..................156

Figure 6.6 (a) Phase evolution in PNO and (b) PNNO electrodes in symmetric cells (YSZ/GDC/cathode) as function of time and temperature. .................................................................157
Figure 6.7 Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours. .......................................................................................... 159

Figure 6.8 (a) A cell cross section showing configuration of all components. Inserted figure shows a top view of the cells. (b) Gas assisted etching was performed via FIB to verify elemental composition at the cathode/GDC interface. Numbered boxes show the areas used for EDS studies. .................................................................................................. 160

Figure 6.9 Initial electrode microstructure and porosity (a), and the changes in electrode microstructure and porosity after 500 hours of operation in full cells at 750 °C and 0.80 V (b). .................................................................................................................. 162

Figure 6.10 (a) TEM image on a single phase PNO electrode, and (b) on electrochemically operated PNO electrode. The electrode was operated in full cells for 500 hours at 750 °C and 0.8V. The regions shown in a high angle annular dark field image (b) on operated PNO electrode were used for elemental mapping analysis (c-f). ................................................................. 163

Figure 6.11. (a) TEM image on a single phase PNNO50-50 electrode, and (b) on electrochemically operated PNNO50-50 electrode. The electrode was operated in full cells for 500 hours at 750 °C and 0.8V. The regions shown in a high angle annular dark field image (b) on operated PNNO50-50 electrode were used for elemental mapping analysis (c-f). ................................................................. 163

Figure 7.1 Rietveld refinement using the FullProf code on (Pr0.50Nd0.50)2Ni1-yCu0.4+yO4+δ powders where y=0, 0.05, 0.10, and 0.20, respectively. Dots are the raw data and solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves. .................................................................................. 168

Figure 7.2 (a) Refined a, b, and c lattice parameters, (b) and the unit cell volume for PNNO5050-Cu0 powders at RT. ............................................................................................................. 171

Figure 7.3 Phase purity and long-term phase stability in (a) PNO, (b) PNNO50, (c) PNNO5050-Cu5, and (d) PNNO5050-Cu10 powders at 790 °C and 870 °C. ......................... 172

Figure 7.4 (a) Quantified phase evolution in PNNO5050-Cu0 electrodes at elevated temperatures. (b) Quantified phase evolution in thermally annealed PNNO5050-Cu0 powders, where the mole fraction y=0.05, 0.10, 0.20, and 0.30, respectively. Percentage of Pr6O11 was calculated from the calibration curves on physical powder mixtures. ................................................................. 173

Figure 7.5 The role of annealing temperature on phase evolution in PNNO5050-Cu0 at (a) 790 °C, and (b) 870 °C. ............................................................................................................. 175
Figure 7.6 (a-c) Initial I-V and power density curves PNNO5050-Cu_y, as function of y. (d) Cell reproducibility at 790 °C. (e) EIS spectra for the same series. (f) Power density measured at 0.80 V as function of temperature for each composition.

Figure 7.7 (a) Total ASR as a function of current density for PNN5050-Cu_y cells calculated from dc measurements at 790 °C. (b) A comparison of the electrode ASR obtained from i-V and EIS measurements at 790 °C. Ohmic ASR was obtained by using the equivalent circuit model.

Figure 7.8 (a) Electrode resistance ln (ASRe) as function of 1/T for all cathode compositions at OCV obtained from i-V curves. The ohmic resistance, obtained from the circuit model fitted against the EIS spectra at OCV, was subtracted from the total cell ASR. (b) A similar plot obtained from the DRT analysis while subtracting the anodic ASR.

Figure 7.9 (a) DRT analysis obtained at OCV and 790 °C identifying four peaks associated with cathodic and anodic processes. (b) Equivalent circuit model generated via Zview software using initial values obtained from the DRT spectra.

Figure 7.10 (a-c) I-V and power density curves PNNO5050-Cu_y series during 500h operation. (d-f) Corresponding EIS spectra for the same series of cells.

Figure 8.1. (a) Refined average (Ni,Cu)-O bond lengths for (Ni,Cu)O_e (equatorial) and (Ni,Cu)-O_f (focal) arrangements. (b) O-(Ni,Cu)-O bond angles for the same series. Refined average (Pr,Nd)-O bond lengths for (Pr,Nd)O_e (c), and (Pr,Nd)-O_f arrangements (d).

Figure 8.2. (a) Illustration showing the orthorhombic layered structure in (Pr_{0.50}Nd_{0.50})_2NiO_{4+δ} where perovskite layers (oxygen octahedral packed layer) alternate with the rock-salt M-O layers. (b) Resulting structural changes with Cu-doping on the Ni-site leading to increase in volume via expansion in the z-direction and shrinkage in the a-b plane. Shrinkage in oxygen ion conduction paths is highlighted.

Figure 8.3. (a) 2D masked data obtained on PNNO powder at 11-ID-B beamline at APS source. Generated PDFs for in-situ measurements on PNNO powder for (b) short-range ordering and (c) long-range ordering. Stacked PDF plots correspond to discrete temperature values listed on the right side. (d) Rw distribution (difference in PDF) as function of temperature.

Figure 8.4. (a) In-situ PDF patterns for PNNO(50/50)-Cu_{10} powder at selected temperatures highlighting “frozen” M-O atomic pair distances. (b) In-situ PDF patterns on PNNO powder showing changes in M-O distances.

Figure 8.5. Quantified M-O distances from PDF measurements as function of composition and temperature for (a) (Ni, Cu)-O_f atomic distance and (b) (Pr, Nd)-O_f atomic distance.
Figure 8.6. Phase purity in Pr$_{2}$Ni$_{1-y}$Cu$_{y}$O$_{4+\delta}$ (PNO-Cu$_{y}$) powders (a-c), where $y$=0.05, 0.10, and 0.20, respectively. Evolution or PrO$_{x}$ is marked with (+). Standard XRD patterns are included. .................................................................193

Figure 8.7. Phase stability in PNO-Cu$_{y}$ powders after 150 hour annealing at 790 °C (a-c) and 870 °C (d-f), where $y$=0.05, 0.10, and 0.20, respectively. .................................................................194

Figure 9.1. Illustration showing relatively low performance degradation but substantial phase degradation (according to XRD) in Pr$_2$NiO$_4$. Formation of nanoclusters may provide link for retained activity during long-term operation in electrochemical cells. .............197

Figure 9.2. (a) i-V and power density curves for PNO full cells as function of time. (b) EIS spectra as function of time measured at 0.50 A/cm$^2$ and 750 °C. (c) in operando DRT analysis on PNO electrode. (d) Quantified DRT spectra showing resistance of each process shown in (c). .................................................................199

Figure 9.3. (a) XRD patterns illustrating phase evolution in PNO powder for various thermal annealing temperatures. (b) Phase evolution in PNO electrode on YSZ/GDC/nickelate configuration as function of time. (c) Phase evolution on PNO electrode in full electrochemical cell operated at 750 °C and 0.80 V for 500 hours. ........200

Figure 9.4. (a) Generated XRD patterns for in-situ measurements on PNO electrode. Stacked XRD plots correspond to discrete temperature values listed on the right side. (b) In-situ diffraction data obtained on PNO electrode before, during, and after thermal annealing. .................................................................201

Figure 9.5. SEM images on PNO electrode (a) before and (b) after electrochemical operation at 750 °C and 0.80 V for 500 hours. The insert image shows direct exposure window for XRD studies on cathode. .................................................................202

Figure 9.6. (a) TEM image on a single phase PNO electrode. (b) HR-TEM diffraction pattern on single phase PNO. (c-d) Thermally annealed PNO powder at 750 °C for 150 hours. (e-f) PNO electrode held at OCV and 750 °C for 500 hours. (g-h) Electrochemically operated PNO electrode at 750 °C and 0.80V for 500 hours. .................................................................204

Figure 9.7. TEM image on nanocluster formation on electrochemically operated PNO electrode at 750 °C and 0.80V for 500 hours. d-spacing is shown. .................................205

Figure 9.8. (a-b) TEM images on nanoclusters and designated regions used for point scan elemental analysis listed in Table 9.1. .................................................................205

Figure 9.9. i-V and power density curves for Pr$_3$Ni$_2$O$_7$ full cells as function of time. .................................................................207

Figure 9.10. Phase evolution in Pr$_3$Ni$_2$O$_7$ electrodes operated in full electrochemical cell at 750 °C and 0.80 V for 200 hours. .................................................................208
Figure 9.11. Phase evolution in Pr$_3$Ni$_2$O$_7$ + PrO$_x$ (50 vol.% mixture) pellet thermally annealed in air at 750 °C for 200 hours. .................................................................209

Figure 10.1. Phase evolution in thermally annealed (750 °C) and electrochemically operated (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ electrodes after 500 hours at 750 °C and 0.80 V. .......................215

Figure 10.2. i-V and powder density curves as function of time for cells operated under continuous current at (a) 0.25 A/cm$^2$, (b) 0.50 A/cm$^2$, and (c) 0.75 A/cm$^2$. (d) Performance stability as function of time under various current density. .................................217

Figure 10.3. (a) Representative DRT analysis on operating cell measured at 790 °C and 0.50 A/cm$^2$. (b) Quantified evolution of cathodic peaks as function of time at various operating current density. ......................................................218

Figure 10.4. Phase evolution in PNNO electrodes operated under different current densities at (a) 700 °C, (b) 750 °C, and (c) 790 °C. Standard XRD patterns for Ni-YSZ/GDC substrate are shown in (a). .................................................................220

Figure 10.5. Quantified phase evolution in PNNO powders and electrodes. Powders and electrodes at OCV were thermally annealed at 790 °C for 500h in air. Phase evolution in electrochemically operated electrodes is illustrated as function of current density at various temperatures and operating times. .........................................................221

Figure 10.6. (a) A cross section image showing the configuration for all cell components. The three highlighted regions were used for quantification of elemental composition. (b) Quantified elemental distribution of Pr and Nd at the three regions shown in (a). .................................................................222

Figure 10.7. SEM images of the electrodes before operation (a) and after 300 hours of operation at 790 °C at (b) 0.25 A/cm$^2$, (c) 0.50 A/cm$^2$, and (d) 0.75 A/cm$^2$. .................................224

Figure 10.8. TEM images on PNNO electrodes (a) before operation, (b) after thermal annealing at 790 °C for 500 hours, and (c-d) after electrochemical operation at 0.75 A/cm$^2$ for 300 hours at 790 °C. .................................................................224

Figure 10.9. (a-b) TEM images on PNNO electrodes after electrochemical operation at 0.75 A/cm$^2$ for 300 hours. (c) to (f) are elemental maps of the electrode after operation shown in (b). .................................................................225

Figure 11.1 Quantified phase transformation in PNNO electrodes undergoing thermal annealing and continuous electrochemical operation at 0.50 A/cm$^2$ at various temperatures including 700 °C, 750 °C, and 790 °C. Multiple runs with full cells were conducted to ensure reproducibility.................................................................229
Figure 11.2 (a) i-V and power density curves in PNNO cells measured at various temperatures. (b) Performance reproducibility with multiple PNNO cells measured at 700 °C, 750 °C, and 790 °C. (c) Power density as function of temperature at 0.80 V for multiple PNNO cells. (d) EIS spectra at 750 °C and 0.50 A/cm² on multiple PNNO cells. ……233

Figure 11.3 Cell voltage as function of time for various current density values including 0.25 A/cm², 0.50 A/cm², and 0.75 A/cm² at 790 °C for 300 hours. Constant hold vs. accelerated protocols were compared. ……………………………………234

Figure 11.4 In operando (at 0.50 A/cm²) DRT analysis as function of time on (a) cell operated at constant current density of 0.75 A/cm² for 300 hours, and (b) cell undergoing accelerated cycling at 0.75 A/cm². Quantified (c) P3c peak area, and (d) P2c peak area as function of time for both testing methods. ……………………………………………………………………235

Figure 11.5 XRD patterns on PNNO electrodes in full cells before and after electrochemical operation at: (a) constant current density of 0.75 A/cm² for 150 hours, (b) cycling current density of 0.75 A/cm² for 150 hours, and (c) cycling current density of 0.75 A/cm² for 300 hours. Standard XRD patterns for each cell component and possible products are shown in (a). …………………………………………………………………………………237

Figure 11.6 Quantified percentage of phase transformation on PNNO powders and electrodes undergoing thermal annealing tests and two types of electrochemical operation: (1) constant hold, and (2) accelerated tests at various current densities and time. ……238

Figure 11.7 (a) Voltage vs. time for NNO cells operated at 0.25 A/cm² and 750 °C for 1,100 hours. ATPs result in over one 1.3 million cycles within 1,100 hours of operation. Two NNO cells were measured to ensure reproducibility. (b) In operando (at 0.25 A/cm²) DRT analysis on NNO cells as function of time. ……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………… 
Figure 12.3 (a) XRD patterns collected continuously at 86.7 keV during heating to 850 °C, holding at 750 °C, and cooling to RT on PNO electrode. The background contribution was subtracted for each temperature condition. A transition from orthorhombic to tetragonal structure occurs at ~450 °C during heating. Tetragonal phase prevails during operation and transitions back to orthorhombic structure upon cooling. (b) Selected XRD patterns for phase transformation comparison in PNO/GDC20 cell. Evolution of PrO_x occurs in-situ (as indicated with evolution of PrO_x peaks with higher intensity than the parent reflections) and is retained upon cooling. (c) The PNO cell with PGCO interlayer shows significantly lower percentage of PrO_x. (d) Selected XRD patterns for PNNO/GDC cells showing a small percentage of PrO_x formation. (e) Retained initial structure in PNNO/PGCO cell and preserved peak intensity ratios indicate preserved parent phase. Accelerated formation of PrO_x at nickelate/GDC20 interface promotes phase transformation in nickelate cathodes.

Figure 12.4 Quantified long-term phase evolution in (a) PNO, and (b) PNNO electrodes with the three different interlayers at 750 °C. Accelerated phase transformation was measured in cells with GDC20 interlayer, while PGCO interlayer leads to substantial phase stabilization.

Figure 12.5 (a) Initial i-V and power density curves for a PNO electrode on various interlayers. Two cells per each condition were measured to examine the data reproducibility. (b) Power density as a function of temperature measured at 0.80 V. An increase in power density was measured in cells with PGCO interlayer across all measured temperatures. (c) Degradation rate in cells operated at 750 °C and 0.80 V. The cells with PGCO interlayer show zero degradation when compared to substantial degradation in cells with GDC20 interlayer. (d) Impedance measurements showing ohmic and electrode area specific resistance vs. time for cells with GDC20 and PGCO interlayer configurations.

Figure 12.6 Phase evolution in (a) PNO and (b) PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours. The flux was normalized and peak positions were calibrated with multiple external (Ni-YSZ, single phase PNO and PrO_x) and internal (Au) standards. An XRD pattern illustrated at the bottom shows initial cathode/GDC/YSZ/Ni-YSZ cell. Shown progressively from bottom to top are the final XRD patterns on cells with various interlayers. The cells with PGCO interlayer show preserved nickelate phase. (c) In-situ XRD patterns on operating PNNO electrode. Phase transformation from orthorhombic to tetragonal occurs at operating conditions. The parent nickelate phase in PNNO was fully preserved after operation.

Figure 12.7 (a) An SEM image of a cell cross section after 500 hours of operation at 750 °C and 0.80 V. The cells were prepared via FIB etching, showing each cell layer and the three regions used for EDS studies. Quantified results are presented in Table B.1. (b) A backscattered SEM image on nickelate/PrO_x-GDC interface. Dark phase is PrO_x, as shown via EDS analysis in Table B.2. Numbered circles show the locations used for EDS studies.
CHAPTER 1
RUDDLESDEN-POPPER-TYPE OXIDES AS OXYGEN ELECTRODES FOR SOLID OXIDE FUEL CELLS

During past 60 years significant efforts have been taken to understand the mixed conducting properties in Ruddlesden-Popper (RP) nickelates through numerous modifications of the A-and and B-sites (e.g. in Pr$_2$NiO$_4$, A-site is Pr, and B-site in Ni). Such modifications involved substitution and doping with various elements of similar size and charge such as Pr, La, Nd, Ca, Sr on the A-site, and various d-block dopants (Cr, Mn, Fe, Co, Ni, Cu, Zn) on the B-site. Along with their mixed conductivity, the respective structures have also been investigated. Better understanding behind electron-hole conduction and oxygen ion transport in RP nickelates was obtained through rigorous x-ray diffraction (including synchrotron sources) and neutron diffraction studies. Although much has been done in terms of substituting cations and tuning the structure, a lot is still unknown in this field with respect to correlating the structure, phase stability, and electrochemistry in solid oxide fuel cells. Furthermore, tailoring the electrochemical properties by tuning the structures has also remained largely unknown due to complexity of the fuel cells and the synergy of various factors contributing towards fuel cell operation. In this chapter an attempt was made to extend the knowledge on RP nickelates through detailed structural studies (both ex situ and in situ), long-term phase stability and phase transformation studies.
under thermal and electrochemical potential gradients, and long-term electrochemical operation in full cells. Detailed summary of the most important findings on RP nickelates in last 60 years have been compiled in this single chapter along with new findings reported by our research group. This review is divided into 8 main sections. Sections 1-2 provide the background on solid oxide fuel cells and electrodes. Sections 3-4 discuss the developments in RP nickelates from their intrinsic structure to mixed conduction properties. Section 5 embodies phase stability and phase transformation behavior. Section 6 provides detailed summary on electrochemical performance of RP nickelates in solid oxide fuel cells. Finally, sections 7 and 8 provide the summary and address future directions in development and understanding of oxygen electrodes.

1.1 BACKGROUND OF SOLID OXIDE FUEL CELLS

Solid oxide fuel cells (SOFCs) directly convert chemical energy in fuels (e.g. natural gas) to electricity through a series of electrochemical reactions at elevated temperatures; combustion processes are not involved. ¹⁻⁵ As a result, fuel cell efficiencies are not limited by theoretical Carnot efficiencies since the electrical work is directly converted from a substantial fraction of the enthalpy associated with the electrochemical oxidation of the fuel to water and/or carbon dioxide. Hence, fuel cells can deliver higher electrical conversion efficiencies when compared with traditional technologies such as coal-fired power plants and electrical generators based on internal combustion engines. In addition to high efficiency, SOFC, when compared with other fuel cells, has two particular advantages, owing to its high operating temperature: (1) SOFC allows the use of a variety of fuels, ranging from hydrogen to carbon monoxide to hydrocarbons, and (2) operation at
elevated temperatures produces high-quality heat, which makes combined heat and power (CHP) systems possible. The overall efficiency of a CHP may exceed 70%.2-4, 6-7

Shown in Figure 1.1 is a typical SOFC, which essentially consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte. In an operating SOFC, oxygen gas molecules on the oxygen electrode (cathode) side react with incoming electrons coming from the external circuit to form oxygen ions, which migrate through the oxide ion conducting electrolyte to the fuel electrode (anode). At the anode, oxygen ions react with the fuel to form H₂O (and/or CO₂), liberating electrons, which flow from the anode through the external circuit to the cathode to produce electricity. Provided that both fuels and oxygen are supplied constantly, the continuous electrochemical reactions can steadily generate electricity. The essence of SOFCs lies in their high operating temperature, which enables their cermet anode (typically a mixture of yttria-stabilized zirconia (YSZ) and Ni) to be catalytically active for oxidation of a variety of fuels, from H₂ to CO to hydrocarbons, without the poisoning effects (particularly from CO) observed in polymer electrolyte membrane fuel cells.

![Figure 1.1 Operating principle of a solid oxide fuel cell.](image)
Quantitatively speaking, the electromotive force (EMF) of a cell is determined by activity of reacting species on the two electrodes which is expressed by the Nernst Equation as:

$$EMF = \Gamma \frac{RT}{4F} \ln\left(\frac{pO_2^a}{pO_2^b}\right)$$  \hspace{1cm} (1)

where $\Gamma$ is the ionic transference number (i.e. ionic conductivity/total conductivity of the electrolyte), $T$ is operation temperature, $F$ is Faraday constant, the activity on the cathode involves the oxygen activity ($pO_2$) on the oxidant side and activity on the anode involves the oxygen activity ($pO_2$) on the fuel side. In the case without external circuit, the EMF is corresponding to open circuit voltage (OCV). For instance, an OCV $\sim 1.1$ V can be calculated for an SOFC operating at 800°C with air as oxidant ($pO_2 = 0.2$ atm) and room-temperature humidified $H_2$ as fuel.

Under cell operating conditions, i.e., when a current passes through a cell, a fingerprint characteristic of fuel cells is the relationship between voltage and current density. Figure 1.2 illustrates a schematic of voltage-current (V-I) curve for a typical SOFC, which represents OCV ($E^o$), cathodic polarization loss, anodic polarization loss, and ohmic loss. The cell voltage ($V$) is given by:

$$V = E^o - iR - \eta_A - \eta_F$$  \hspace{1cm} (2)

where $i$ is the current passing through the cell, $R$ is the electrical resistance of the cell, and $\eta_A$ and $\eta_F$ are the polarization voltage losses associated with the air electrode (cathode) and the fuel electrode (anode), respectively. These electrode polarizations are related to three primary elementary physical processes: gas diffusion, gas-solid interaction, and ion migration. These processes will be analyzed from the viewpoints of structure and chemical bonding. First, the analysis will be performed at the atomic scale, with the emphasis on
the charge exchange and transport with respect to crystal structure and local chemical bonding/ordering. On the micro-scale, emphasis will be on gas diffusion and triple phase boundary.

Figure 1.2 Schematic V-I curve for a typical SOFC, which shows OCV, cathodic polarization loss, anodic polarization loss, and ohmic loss.

The high operation temperature of SOFCs may result in degradation of cell performance due to instability of the constituent materials at high temperatures. This instability could result from oxidation, diffusion, phase transformation, or chemical reaction processes. Consequently, research on SOFCs has been driven by the recognition of the need to lower the operation temperature to intermediate region (600-750°C). As the operating temperature is lowered, however, the polarization due to oxygen reduction at the cathode – a thermally activated process with an activation energy ~100 kJ/mol – becomes substantial. Hence, the challenge is to fundamentally understand materials chemistry of solid-state cathodes, which governs chemical activity and polarization stability in SOFCs, as illustrated by workshops carried out by US DOE – Basic Energy Sciences and Fossil Energy.
1.2 OXYGEN ELECTRODES FOR SOFCs

The importance of the cathode in an SOFC is shown in Figure 1.3a, in which power density (W/cm$^2$) is plotted as a function of current density (A/cm$^2$) for a variety of cathodes. The electrolyte/anode bilayers (YSZ/Ni-YSZ) for all these cells were from the same batch. More than three cells were tested for each cathode to provide statistical significance and reproducibility. The peak power density shown in Figure 1.3a can be increased by several times, simply by changing the cathode, suggesting that the highest polarization loss in these anode-supported SOFCs is associated with the cathode. Figure 1.3b shows power density as a function of time to illustrate the stability of electrochemical activity of several cathodes. Two points need to be emphasized: (1) excellent reproducibility was observed for all cathodes, indicating that substrates of these cells were indeed identical and data can be used for statistical comparison of electrochemical activity of different cathodes; and (2) there exists significant difference in temporal stability for the cathodes. Stable power density has been observed for SOFCs with (La,Sr)MnO$_3$ (LSM) based cathodes, but power density tends to be relatively low. For example, Figure 1.3b shows data for an LSM/SDC-based cell, which had a low power density (~ 0.3 W/cm$^2$), but was stable over the >1,000 hour testing period. Higher cathode activity can be obtained using mixed electronic and oxygen ionic conductors (MIECs), such as (La,Sr)(Fe,Co)O$_3$ (LSCF) and (Ba,Sr)(Co,Fe)O$_3$ (BSCF). It is known that LSCF is very active at T >650°C, resulting in a power density of ~0.9 W/cm$^2$ at 750°C. BSCF, an even more active material developed by Haile’s group, yielded a peak power density of ~ 1 W/cm$^2$ at 650°C. However, the cells with both LSCF and BSCF cathodes were found to degrade rapidly during operation. The degradation mechanism is unknown, but may be related to segregation of Sr.
other hand, cells with a Pr$_2$NiO$_4$ cathode exhibited similar initial power density as the LSCF-based cells, but considerably better stability during the 1,000 hour test.$^{28}$ The degradation rate for these Pr$_2$NiO$_4$-based cells was ~ 3% per 1,000 hours, whereas the degradation rate of LSCF-based cells was in the range of 10 to 20% per 1,000 hours. The bilayers, YSZ/Ni-YSZ, were from the same batch. Different results may be obtained, depending on the factors such as electrolyte/substrate chemistry and specimen geometry.$^5$, $^{33, 36-37}$

![Figure 1.3](image)

**Figure 1.3** (a) Power density vs. current density for several cathodes at 750°C on the same batch of electrolyte/anode bilayers. The peak power density increases substantially by changing the cathode.$^{28}$ (b) Power density vs. time for several cathodes at 750°C at constant voltage 0.8 V. Recent discovered Pr$_2$NiO$_4$ showed high chemical activity and polarization stability.$^8, 28$ SDC: Sm-doped ceria.

Understanding electrochemical phenomena shown in **Figure 1.3a** and **Figure 1.3b** raises the following questions: (1) what is the origin of activity and stability of cathodes? (2) why are active cathodes not stable; and stable cathodes are not active – the so-called activity/stability conjugation?, and (3) how can we design materials with unique chemistry to de-conjugate activity-stability relationships? This section will address these three questions.
1.2.1 ELECTROCHEMICAL ACTIVITY

Oxygen reduction pathways involve a series of physiochemical processes on the cathode side, as shown in Figure 1.4. Each process is addressed separately in the following sections and the sum of these processes is the activity.

![Reduction and Oxidation Directions](image)

**Figure 1.4** A schematic of cathode surface reacting with oxygen. Due to the distribution of oxygen vacancies and holes, it is reasonable to assume that $M^1$ has a different valance state from $M^2$.

1. **Diffusion of oxygen molecules to the surface of catalytic active cathodes.** In this process, bulk diffusion can be characterized with known porosity, tortuosity, pore size and grain size. This is known as the extrinsic effects – microstructural effects on activity. The polarization resistance given in equation can thus be written in terms of intrinsic, microstructural and adsorption parameters as follows:

$$R_{\text{Chem}} \sim \frac{\tau}{\sqrt{(1-\varepsilon)a}}$$  \hspace{1cm} (3)

where $R_{\text{Chem}}$ is the chemical reaction induced resistance; $\tau$ is tortuosity; $\varepsilon$ is fractional porosity; and $a$ is the surface area per unit volume. Equation 3 explicitly shows the role of microstructure on the resistance induced by interfacial chemical reactions between the
cathode and the electrolyte. Similar derivation was developed by Virkar’s group.\textsuperscript{39-41} Tailoring microstructure has been an effective approach to improve activity through control over the extrinsic microstructural factor.\textsuperscript{5, 18, 42-50}

(2) \textit{Physi-chemisorptions and dissociation of oxygen molecules}. From chemistry point of view, the oxygen reduction reaction consists of several elementary electrochemical steps including physisorption and chemisorption of oxygen molecules, and the reduction and dissociation of the adsorbed molecules. \textbf{Figure 1.5} shows the three kinds of cathodes:

(a) LSM-based cathode functions through the interaction between surface oxygen vacancies and bulk cation vacancies; oxygen reduction is through surface oxygen vacancies and microstructure design. The activity is relatively low. Our recent work on anomalous diffusion in LSM clearly showed that cation defects indeed governed the electrochemical properties of LSM based materials.\textsuperscript{51-53}

(b) LSCF, BSCF, and SSC cathodes have a large amount of oxygen vacancies at high temperatures (> 600\textdegree C). It has been shown in open literature that the activity of LSCF and BSCF is related to fast surface exchange and bulk diffusion.

(c) The oxygen reduction reaction in Ruddlesden-Popper type complex oxides (nickelates) is based on oxygen interstitials. The chemisorption for these materials is due to exchange between oxygen gaseous molecules and oxygen interstitials in the solids.
In general, oxygen reduction involves a number of elementary electrochemical reactions that contain several intermediate oxygen species on the oxide surface. Oxygen adsorption may be either associative or dissociative:

\[
O_{2(g)} + \text{ad} \leftrightarrow O_{2-ad}; \quad \frac{\theta_{O_2}}{(1-\theta_{O_2})} = k(p_{O_2}) \quad \text{(associative)} \tag{4}
\]

\[
O_{2(g)} + 2\text{ad} \leftrightarrow 2O_{\text{ad}}; \quad \frac{\theta_{O}}{(1-\theta_{O})} = k(p_{O_2})^{1/2} \quad \text{(dissociative)} \tag{5}
\]

where \(O_{2-ad}\) and \(O_{ad}\) represent adsorbed oxygen molecule and an adsorbed oxygen atom, respectively. Experimental results of exchange current densities in LSM were in favor of the dissociative adsorption. Assuming that surface coverage \(\theta\) can be expressed in the form of a Langmuir isotherm and only neutral species are present, in the case of \(1-\theta_o \gg \theta_o\), the polarization resistance \(R_{ad}\) is given by:

\[
R_{ad} \propto p_{O_2}^{-1/2} \tag{6}
\]
In the case of mixed conducting composite cathode, the exchange current densities are limited by charge transfer. $R_{ad}$ was found to be dependent upon $pO_2$ to a power of $-1/4$.\textsuperscript{55-57} Following oxygen adsorption, diffusion to the active site and charge transfer are likely two other rate-limiting processes, although as many as five have been suggested in LSM-based cathode.\textsuperscript{55, 58-60}

(3) Diffusion of oxygen ions. The diffusion of as-dissociated oxygen ions depends on the amount of available sites (oxygen vacancy concentration) and the mobility.\textsuperscript{61-62} The polarization induced by diffusion ($R_d$) is inversely proportional to the mobility ($\mu$), which is expressed as:

$$R_d \propto \mu^{-1} = \left[ \frac{Aq^2a_0^2}{kT}\exp\left(\frac{\Delta S_m T - \Delta H_m}{kT}\right) \right]^{-1}$$  \hspace{1cm} (7)

where $A$ is a constant, $\nu$ is the defect vibrational frequency ($s^{-1}$), $a_0$ is the distance between two equivalent sites (m), $k$ is the Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K), $T$ is the temperature (K), $\Delta S_m$ (J/K) is the entropy, and $\Delta H_m$ (J) is the enthalpy of ionic motion. Oxygen ion diffusion can be improved by tailoring the parameters in Eq. 2.4 to subsequently increase the mobility. For instance, composite electrodes comprised of LSM and YSZ offer considerably lower electrode resistance than monolithic LSM electrodes.\textsuperscript{63-64} Overall, reversible oxygen reduction at the electrolyte/electrode interfaces can be given by Eq. 2.5 in Kröger-Vink notation:\textsuperscript{65}

$$\frac{1}{2}O_2 + 2M^{\ast}_m + V^{\ast\ast}_0 \rightarrow 2h^\ast + O_0^\ast$$  \hspace{1cm} (8)

The activity is related to microstructures (extrinsic factor), and surface-exchange and bulk-diffusion coefficients (intrinsic factors) of the cathodes.
1.2.2 ELECTROCHEMICAL STABILITY

Degradation/failure of the physiochemical properties and electrochemical activity of SOFCs constituents, particularly the cathodes, are correlated and bridged by the electrode reaction mechanisms. In literature, studies of stability of cathodes have overwhelmingly been focused on chemical interaction with other constituents, particularly chromium species. For an active electrode, such as LSCF, the mechanism of activity degradation is rarely reported and the origin is unknown. As a consequence, as Yokokawa concluded in his review article, work on more stable and still-highly performing cathode materials has to be conducted. That is the purpose of this review.

1.2.3 CANDIDATE COMPOUNDS BASED ON OXYGEN ION VACANCIES: LSCF and BSCF

LSCF adopts the perovskite (ABO$_3$) structure in which A, the large cation site, may be an alkali, alkaline earth, or rare earth ion, while B, the small cation site, is a transition metal cation (Figure 1.6). The large cations are in 12 fold coordination with oxygen while the small cations fit into octahedral positions. Since these two sites are very different in size (as shown in Figure 1.6), the occupancy of these sites is determined primarily by ionic size rather than valency, so it is possible to substitute selectively for either the A or B ion by introducing isovalent or aliovalent cations. This provides materials scientist an opportunity to alter the properties of a given oxide by substituting different cations onto either the A or B site. Research on LSCF dates back to early 1980 by Matsumoto as the oxygen evolution catalyst in alkaline solutions. Terasota further evaluated oxygen adsorption and permeation properties of LSCF. The important findings from their research were that perovskite-type ABO$_3$ compositions containing more than two types of
transition metal ions on the B site are always more reactive (for oxygen reduction) than those with only one type of transition metal ion. But the reason behind this was not clear until seminal research by Anderson and his colleagues, who extensively investigated crystal structure and nonstoichiometric chemistry of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$, and the role of crystal chemistry and defect chemistry on electron and ion transport properties.\(^85-88\) They concluded that Co ions on the B site appear to have a smaller binding energy for oxygen than do Fe ions, which, along with charge disproportionation of Co ions and preferential electronic compensation of Fe over Co ions, resulted in a higher degree of oxygen deficiency in LSCF than in LSF. Hence, the high electrochemical activity of LSCF toward oxygen reduction can be attributed to the active site on Co ions and large number of oxygen vacancies.\(^89-93\) There has been a recent work on Ba replacing La, which showed great electrochemical performance, possibly associated with faster oxygen exchange and diffusion in BSCF.\(^{33}\) Recent work by Maier and his colleagues\(^94\) showed that significant improvement of oxygen reduction activity in BSCF over LSCF was primarily contributed by faster oxygen ion diffusion in BSCF.

![Figure 1.6](image.png)

**Figure 1.6** A typical perovskite structure. Note the repeating units are based on rigid oxygen octahedron, which can tolerate a variety of local chemical and structural changes, such as distortion, rotation, or redox reaction.
1.2.4 CANDIDATE COMPOUNDS BASED ON CATION VACANCIES: LSM and LSM/YSZ

(La,Sr)MnO$_3$ is a unique perovskite-type oxide in that the O/Mn ratio is greater than 3. Hence, precisely, LSM should be written as (La,Sr)MnO$_{3+\delta}$. Indeed, excess oxygen in LSM compounds at high oxygen activity has been observed. Conductivity increases are not observed with the addition of excess oxygen. Therefore, it seems that the excess oxygen is not compensated by electron holes. Moreover, it is known that perovskite structure cannot adopt oxygen interstitials because of the large ionic radii of oxygen ions that do not fit interstitially into the close packed perovskite structure (see Figure 1.6). Hence, the negative charge species are cation vacancies in LSM bulk. Cation vacancies can be understood as oxygen excess through a restructuring of the chemical formula of LSM as:

$$\text{La}(\text{Mn}^{3+}_{1.2\delta} \text{Mn}^{4+}_{2\delta})\text{O}_{3+\delta} \rightarrow \frac{3+\delta}{3}[\text{La}_{3(3+\delta)}\text{(V)}_{\delta/3(3+\delta)}\text{(Mn)}^{4+}_{\delta/3(3+\delta)}\text{(Mn)}^{3+}_{6\delta/3(3+\delta)}\text{(V)}^{-}_{\delta/3(3+\delta)}\text{O}_{3}]$$

Hence, the improvement of the electrochemical catalytic activity is expected to be different for LSM and LSCF at higher oxygen partial pressures ($p_{O_2} > 1$ atm) and elevated temperatures (>700°C). Mitchell et al. observed an increase of $\delta$ for the specimens annealed in O$_2$/Ar mixture, up to $p_{O_2} = 1$ atm. Computer coupling of phase diagrams and thermochemistry was used by Grundy et al. to calculate the defect population and significantly higher values of nonstoichiometry were found at oxygen partial pressure $p_{O_2} = 5$ bar. In terms of oxygen reduction, ab initio calculation was conducted by Kotomin et al. on oxygen absorption on LSM surface. They found that surface oxygen vacancies are key to promote oxygen reduction on (001) LSM surfaces. Experimental work based on composite electrodes suggested that a large portion of the charge transfer reaction must be
occurring at (or very close to) gas phase-electrocatalyst-electrolyte three-phase boundaries (TPB).

1.2.5 CANDIDATE COMPOUNDS BASED ON OXYGEN INTERSTITIALS: RARE EARTH NICKELATES

The building block in perovskite structure shown in Figure 1.6 can be modified by replacing one layer of oxygen octahedron with an element of NaCl-type structure to form a new type of perovskite-like structure, usually named after their first researchers – the Ruddlesden-Popper phase.\textsuperscript{102-103} The general formula of the Ruddlesden-Popper phases can be written as $A_{n-1}A'_2B_nO_{3n+1}$, where A, A' and B are cations, and n is the number of the layers of octahedra in the perovskite-like stack (Figure 1.7a to 1.7c).\textsuperscript{104-105} In this structure, the stoichiometric compound, such as La$_2$NiO$_4$, has two different oxygen lattice sites (Figure 1.7d),\textsuperscript{106} the 4$c$ site at 0.0, 0.5, 0.0 and the 4$e$ site at 0.0, 0.0, 0.1773. This structure can accommodate excess lattice oxygen as interstitials, which locate in the A$_2$O$_2$ site. Pr$_2$NiO$_4$, with oxygen interstitials, was found to have an order of magnitude faster surface exchange and diffusion coefficients than LSCF (e.g. $D = 8 \times 10^{-8}$ cm$^2$/s; $k = 2 \times 10^{-6}$ cm/s at 700 °C) making it an attractive candidate as the cathode.\textsuperscript{107-109} The Ruddlesden-Popper phase exhibits a number of different structures, depending on temperatures and stoichiometry. For instance, Pr$_2$NiO$_4$ goes through subtle changes from Pr$_2$NiO$_4$, to Pr$_3$Ni$_2$O$_7$, and to Pr$_4$Ni$_3$O$_{10}$. The results shown in Figure 1.3 are very encouraging; the monolithic Pr$_2$NiO$_4$ can potentially have simultaneous high chemical activity and polarization stability. The following sections will focus in detail on the structure, phase stability, and electrochemical performance in nickelates.
Figure 1.7 Ruddlesden-Popper structures for \( n = 1 \) (a), \( 2 \) (b) and \( 3 \) (c); \( A \) atoms shown in green, \( BO_6 \) in blue/red. The \( \text{Pr}_2\text{NiO}_4 \) unit cell without octahedral canting (d). The interstitial defect site is shown along with an outline of the tetrahedral \( \text{Pr} \) coordination environment. The interstitial site is also tetrahedrally coordinated by apical oxygen ions.\(^{106}\)

1.3 OXYGEN CONTENT AND MIXED CONDUCTION IN NICKELATES

The layered structures found in \( \text{La}_2\text{NiO}_{4+\delta} \) (LNO), \( \text{Pr}_2\text{NiO}_{4+\delta} \) (PNO), and \( \text{Nd}_2\text{NiO}_{4+\delta} \) (NNO) are intriguing due to their ability to store excess oxygen in the \( \text{Ln}_2\text{O}_2 \) site (\( \text{Ln}=\text{La}, \text{Pr}, \text{Nd} \)). Figure 1.8 shows over-stoichiometry for the three monolithic materials ranging from \( \delta=0.16 \) (LNO) to \( \delta=0.23 \) (PNO) and \( \delta=0.24 \) (NNO) at room temperature.\(^{107}\) In the stoichiometric \( \text{Ln}_2\text{NiO}_4 \) compounds, the value of the Goldschmidt factor (which is used to calculate the stability or distortions of crystal structures) is low and close to the theoretical limit of the stability of the \( \text{K}_2\text{NiF}_4 \) type structure (e.g. 0.87 for PNO).\(^{110}\) This is because of the relatively small size of the rare earth cations (e.g. \( r_{\text{Pr}^{3+}} = 1.13 \) Å, 8-fold coordination) and large ionic radius of the \( \text{Ni}^{2+} \) transition metal cation. The result are the structural stresses arising in the structure. The natural oxygen incorporation into the Ruddlesden-Popper (RP) structures can be linked to tendency of the structure to reduce the mismatch between the perovskite and rock-salt layers.\(^{111}\) As a result, natural oxygen incorporation oxidizes \( \text{Ni}^{2+} \) into a smaller \( \text{Ni}^{3+} \) cation (e.g. \( r_{\text{Ni}^{3+}} = 0.60 \) Å, \( r_{\text{Ni}^{2+}} = \)
0.69 Å in 6-fold coordination) and makes Ln-O distances longer according to the reaction:\(^{110}\)

\[
\text{Ln}_2\text{Ni}^{2+}\text{O}_4 + \frac{1}{2}\delta\text{O}_2 \rightarrow \text{Ln}_2\text{Ni}^{2+}_{1-2\delta}\text{Ni}^{3+}_{2\delta}\text{O}_{4+\delta}
\]  

(10)

Therefore, prepared RP nickelates under air are over-stoichiometric. The unique conduction behavior through oxygen interstitials has been investigated in detail in multiple reports.\(^{109,112}\) The apical oxygen atoms undergo highly anisotropic thermal motion which leads to the migration of oxide ions to the nearest-neighbor interstitial position. This process continues as long as there is over-stoichiometric oxygen present. Furthermore, it was also found that due to repulsion of Ln (La, Pr, Nd) and O atoms the oxygen diffusion paths in the \(a-c\) plane are curved.\(^{109}\)

Minervini et al.\(^{113}\) calculated the oxygen migration in LNO using energy minimization techniques and found that the migration energy in \(a-c\) plane (0.29 eV) is 10x lower than in the \(b\) direction. It was also found that the distance between Ln and oxygen atoms is approximately constant along the diffusion path, which suggested that the large cations at the A site in \(A_2\text{BO}_4\) type conductors are effective in improving the oxygen ion conduction.\(^{109}\) Furthermore experimental electron density maps showed electron-hole conduction via B-site atoms in the Ni-O layer, indicating that in addition to the oxygen diffusion layer, there also exists a two dimensional electron-hole conductive layer.\(^{114}\)
1.3.1 ON THE ORIGIN OF MIXED CONDUCTIVITY IN NICKELATES

Figure 1.9\textsuperscript{115} shows the structure, nuclear and electrode density distributions of an RP nickelate at room temperature. Nuclear and electron density distribution in Figure 1.9a-b confirm the interstitial O3 site. The theoretical valence electron density map, Figure 1.9c, also confirms the interstitial O3 atom. Furthermore, Yashima et al.\textsuperscript{115} demonstrated that the nuclear density at the O3 site decreased with increase in temperature, which is consistent with the decrease in occupancy factor at the O3 site and in the 4+δ value in RP nickelates. Simultaneously, Figure 1.9a-c provide a clear representation of a 2D oxide-ion diffusion and electron-hole conduction path. The chemical bonding is also shown with these representations, where the covalent bonds between the Ni-site (Ni,Cu,Ga) and O1 atoms are observed on the 2D planes, while the (Pr,La) atoms are more ionic, as shown...
Figure 1.9 Structure and nuclear density distribution of (Pr\textsubscript{0.90}La\textsubscript{0.10})\textsubscript{2}(Ni\textsubscript{0.74}Cu\textsubscript{0.21}Ga\textsubscript{0.05})O\textsubscript{4+δ} at room temperature analyzed via neutron diffraction, synchrotron x-ray diffraction, maximum entropy method (MEM), and Rietveld refinement. (a) Nuclear density distribution on the bc plane. (b) Electron density distribution on the bc plane. (c) A corresponding valence electron density distribution obtained using DFT calculations. (d) Optimized structure used for DFT calculations. (e) Isosurface of highest occupied molecular orbitals (HOMO) of optimized structure.\textsuperscript{115}
by A in Figure 1.9b-c. The covalent bond on the Ni-site is formed by the overlap of Ni 3d, Cu 3d, and O1 2p orbitals, leading to a 2D network of B-O1. Figure 1.9d shows the respective paths in 3D representation of an optimized structure generated via density functional theory (DFT) calculations. Figure 1.9e shows the isosurface of highest occupied molecular orbital (HOMO), obtained via DFT, which confirms the conduction path of electron-hole occurring in 2D planes of the perovskite part of the RP structure. These experimental findings further confirm the mixed ionic and electronic (MIEC) properties of layered nickelates. The oxygen over-stoichiometry allows for unique oxygen ion conducting capabilities (see Figure 5.3), which relate to high oxygen surface exchange and diffusion coefficients. With increase in temperature the oxygen occupancy decreases and different behavior in the curves can be linked to oxygen loss and phase transitions, which will be discussed in more detail. Such changes will also influence the electron-hole conduction and ultimately lead to changes in mixed conducting properties of the material.

1.3.2 TOTAL CONDUCTIVITY IN MONOLITHIC AND DOPED NICKELATES

Temperature dependency of the electronic conductivity, $\sigma_e$, in nickelate ceramics (in particular $(Pr_{1-x}Nd_x)_{2}NiO_4$, PNNO) is given by:

$$\sigma_e = N\mu q$$  \hspace{1cm} (11)

where $\mu$ is the mobility, $q$ is the carrier charge, and $N$ in the carrier concentration. Since the mobility of either electrons or holes is much higher than the mobility of oxygen ions, the total conductivity in PNNO is dominated by hole conduction. In PNNO series, oxygen transport is known to occur via oxygen interstitials, $O'_i$. The defect chemistry reaction between oxygen gas and oxygen interstitials is given by:
\[ O_{2(g)} = 2O_i'' + 4h^0. \]  
(12)

The charge neutrality equation is:

\[ 2[O_i''] = p. \]  
(13)

**Figure 1.10(a)** illustrates the \( \sigma_e \) measured in air on the series of PNNO ceramics between 50 and 850 °C. With an increase in temperature from 50 to ~ 500 °C, the \( \sigma_e \) increases for the entire PNNO series. The results can be attributed to thermally activated polaron hoping process, which follows:

\[ \mu = \mu_0 \exp\left(\frac{-E_{a,m}}{kT}\right). \]  
(14)

There are three regions in the plot: (i) the low temperature region (T ≤ 600 °C) corresponding to thermally activated hopping process;\(^{118}\) (ii) high temperature region (T > 750 °C), at which conductivity decreases due to the rapid loss of oxygen interstitials, thus a decrease in carrier density, \( p \), which overwhelms the increase in mobility; as a result, the electrical conductivity decreases; and (iii) a transition region between 500 and 750 °C, where the decrease in carrier density started to influence electrical conductivity upon heating. The highest conductivity (90 S cm\(^{-1}\) at 600 °C) was measured for PNO and decreased with an increase in Nd content (54 S cm\(^{-1}\) at 500 °C for NNO). The entire PNNO series exhibits a \( p \)-type conducting behavior, with a conductivity maximum observed between 500-600 °C. With an increase in Nd content the conductivity maximum shifts to lower temperatures. The shift in temperature is attributed to the lower activation energy for polaron hoping of NNO (\( E_a \approx 0.06 \text{ eV} \)) than that of PNO (0.11 eV). As a result, the loss of oxygen interstitials influences the electrical conductivity of NNO at lower temperature. The greater activation energy in PNO likely results from the presence of Pr4+, which
creates additional phonon cloud to reduce the hole mobility. Consequently, the $\sigma_{e,\text{max}}$ for PNO, PNNO7525, PNNO5050, and PNNO2575 are similar.

Figure 1.10 (a) Total conductivity for the series of PNNO bars measured in air between 50 – 850 °C. (b) Conductivity in bars with $x=0, 0.50, 1.0$ as function of oxygen partial pressure.

NNO exhibits the lowest $\sigma_e$ over the entire temperature region. Measurements on a single crystal NNO showed a lower oxygen mobility when compared to PNO.\textsuperscript{117} Reduced apical oxygen mobility at lower temperatures ($T < 500$ °C) was attributed to low energy specific phonon modes, which are required for the conduction at lower temperatures.\textsuperscript{119-120} Because of smaller $c$-axis parameter when compared to PNO (as will be discussed in the following section), there is less vibrational motion of oxygens along the (a,c)-plane in the rock-salt layer, leading to lower oxygen mobility.\textsuperscript{117} Figure 1.10(b) shows an increase in $\sigma_e$ for all compounds with increasing oxygen activity, consistent with $p$-type conduction behavior. Higher oxygen activity leads to a higher hole concentration, as shown in Eq. (12); therefore, a higher $\sigma_e$ was measured for all PNNO ceramics in pure oxygen. Less pO$_2$ dependency in NNO (4.0% at 600 °C and 5.6 % at 850 °C) vs. PNO (5.1% at 600 °C and 8.4% at 850 °C) further indicates a higher $E_{a,m}$ in NNO ceramics, as shown in Eq. 14.
Therefore, due to a smaller cell volume (as will be discussed in the next section), a lower oxygen mobility, and a smaller conductivity, the mixed-ionic-electronic-conduction (MIEC) properties are suppressed in NNO. The transport data are in agreement with electrochemical operation in full cells,\textsuperscript{121} as shall be discussed in chapter 6, showing a much lower performance (decrease by fourfold at 750 °C and 0.80 V) and a 29-38\% increase in the activation energy for ORR in Nd-rich PNNO electrodes.

The conductivity values for monolithic nickelate electrodes found in open literature, Table 1.1, are in good agreement with results presented in Figure 1.10. It can be seen that among the three composition PNO on average has the highest total conductivity ($\sigma_{\text{tot}}$) in the temperature region between 600-800 °C. The $\sigma_{\text{tot}}$ tends to vary among different reports, which can be attributed to different annealing temperatures, which effectively influence the oxygen content in the material. For instance, for measured LNO dense ceramics $\delta$ varies by ~30\% among the different reports, which in turn is expected to lead to different $\sigma_{\text{tot}}$ values based on Eq. 13, as the amount of oxygen content in the material directly governs the concentration of the charged carriers. Furthermore, the processing temperature of the ceramic bars, used for conductivity measurements, will govern the overall density and porosity of the bar. Higher sintering temperature allows for better material contact but may lead to more oxygen loss; therefore, finding the appropriate conditions is of fundamental importance. However, the overall results show substantially lower $\sigma_{\text{tot}}$ in LNO and NNO materials. For instance, for PNO and NNO materials there is up to 33\% of oxygen loss at 600 °C in air.
Table 1.1 Total conductivity ($\sigma_{\text{tot}}$) of monolithic nickelate ceramics measured in air at various temperatures. Oxygen over-stoichiometry ($\delta$) measured in air at room temperature (RT) and 600 °C (HT) is also listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Annealing Temp ($^\circ$C)</th>
<th>$\sigma_{\text{tot}}$ (S/cm)</th>
<th>Ref.</th>
<th>$\delta$ RT</th>
<th>$\delta$ HT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 °C</td>
<td>700 °C</td>
<td>800 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$NiO$</em>{4+\delta}$</td>
<td>1080</td>
<td>90.2</td>
<td>84.4</td>
<td>73.9</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>90</td>
<td>81</td>
<td>69</td>
<td>110, 122</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>-</td>
<td>125.9</td>
<td>-</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>107.2</td>
<td>-</td>
<td>-</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>92</td>
<td>80</td>
<td>-</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>134.9</td>
<td>120.2</td>
<td>109.6</td>
<td>108</td>
</tr>
<tr>
<td>La$<em>2$NiO$</em>{4+\delta}$</td>
<td>1350</td>
<td>-</td>
<td>67.6</td>
<td>-</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>38</td>
<td>31</td>
<td>-</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>71</td>
<td>68</td>
<td>61</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>58</td>
<td>53</td>
<td>48</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>95.5</td>
<td>91.2</td>
<td>83.2</td>
<td>108</td>
</tr>
<tr>
<td>Nd$<em>2$NiO$</em>{4+\delta}$</td>
<td>1150</td>
<td>50.6</td>
<td>46.2</td>
<td>42.8</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>39</td>
<td>32</td>
<td>-</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>109.6</td>
<td>95.5</td>
<td>89.2</td>
<td>212, 213</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>82</td>
<td>80</td>
<td>78</td>
<td>183</td>
</tr>
</tbody>
</table>

In order to further improve the MIEC properties in monolithic RP nickelates, various dopants on Pr and Ni sites have been screened by numerous research groups. Table 1.2, Table 1.3, and Table 1.4 summarize the literature reports on doped PNO, LNO, and NNO ceramics, respectively. The respective $\delta$ for each composition (if available) has also been listed at room temperature (RT) and at 600 °C (HT). Doping with Sr on the Ln site seems to be a common approach to increase the $\sigma_{\text{tot}}$ in RP nickelates, which results in $\sigma_{\text{tot}}\sim100$ S/cm, and is sufficient towards cathode applications for SOFCs. For all three monolithic compositions the Sr doping seems to improve the total conduction of the
system. Such change in $\sigma_{\text{tot}}$ can be mainly attributed to the 2+ charge on Sr when compared to 3+ charge on Ln. With increase in Sr content the overall conductivity seems to increase, which has been correlated with changes in oxidation of nickel induced by introduction of Sr cation,\textsuperscript{110,123} which effectively leads to increase of the carrier (holes)\textsuperscript{124} concentration according to: \textsuperscript{110}

$$2\text{SrO} + 2\text{Pr}^{2+} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{Sr}^{+} + 2\text{h}^+ + \text{Pr}_2\text{O}_3$$ \textsuperscript{(15)}

This effect is prevailing at elevated temperatures. A few anomalies were also recorder (e.g \(x=0.3, 0.4\) in \(\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}\), Table 1.2) where increase in Sr content leads to lower $\sigma_{\text{tot}}$ when compared to compositions with less Sr doping. A possible explanation behind these anomalies involves charge-spin ordering that results from interaction of holes with a 2D antiferromagnetic spin lattice.\textsuperscript{125-126} Furthermore, as is the case for PNNO series, the maximum $\sigma_{\text{tot}}$ occurs at different temperatures: at $T\sim400 \, ^\circ\text{C}$ for $x=0, 0.1$, at $T\sim600 \, ^\circ\text{C}$ for $x=0.20$, and at $T\sim800 \, ^\circ\text{C}$ for $x=50$. Such behavior can again be attributed to decrease of the charge carrier concentration due to oxygen loss at increasing temperatures and reduction of Ni\textsuperscript{3+} to Ni\textsuperscript{2+}.\textsuperscript{110,127}

By replacing Ln\textsuperscript{3+} with larger Sr\textsuperscript{2+} in Ln\textsubscript{2-x}Sr\textsubscript{x}NiO\textsubscript{4+\delta} leads to: (1) an increase in Ln-Sr-O distance (as will be addressed in more detail later), (2) increase in the Goldschmidt factor and “stabilization” of the initial structure, and (3) decrease in oxygen over-stoichiometry.\textsuperscript{110} As shown in Table 1.1, with increase in Sr content in PNO the $\delta$ decreases and becomes 0 when $x=0.5$, which is consistent with other reports on Nd\textsubscript{2-x}Sr\textsubscript{x}NiO\textsubscript{4+\delta} and La\textsubscript{2-x}Sr\textsubscript{x}NiO\textsubscript{4+\delta},\textsuperscript{128-129} and can also be seen in Table 1.3 and Table 1.4, where $\delta$ decreases substantially when compared to rich over-stoichiometry at RT. Some authors have also measured surface exchange coefficient ($k$) as function of Sr doping and found a substantial
decrease in $k$ by one or two orders of magnitude for \( \text{La}_{1.90}\text{Sr}_{0.10}\text{NiO}_{4+\delta} \) and \( \text{La}_{1.80}\text{Sr}_{0.20}\text{NiO}_{4+\delta} \), respectively.\textsuperscript{130-131} Detailed comparison and analysis of surface exchange and diffusion coefficients are not a scope of this work, but have been addressed recently in a comprehensive review by Gao et al.\textsuperscript{116} Therefore, the complexity behind substitution and/or doping on RP nickelates requires consideration not only for the conductivity of material, but also oxygen content, kinetics of oxygen exchange, and even the crystal structure (which will be addressed in the following sections).

The Ca doping on the Ln site has also been reported as a method to increase $\sigma_{\text{tot}}$ in \( \text{Ln}_{2}\text{NiO}_{4} \), Table 1.3 and Table 1.4. \( \text{La}_{1-x}\text{Ca}_{x}\text{NiO}_{4} \) shows similar $\sigma_{\text{tot}}$ to monolithic PNO (~100 S/cm at 600 °C),\textsuperscript{132-133} while the conductivity in \( \text{Nd}_{1-x}\text{Ca}_{x}\text{NiO}_{4} \) (~80 S/cm at 600 °C) is acceptable.\textsuperscript{134} However, as was the case for Sr doping the $\delta$ decreases with increase in Ca content (e.g. $\delta$ decreases by whopping 65% in \( \text{La}_{1.60}\text{Ca}_{0.40}\text{NiO}_{4} \) and by 54.5% in \( \text{Nd}_{1.80}\text{Ca}_{0.20}\text{NiO}_{4} \)).\textsuperscript{107, 133} At elevated temperatures the role of Ca dopant is even more evident as losses in $\delta$ reach up to 82% (e.g. $\delta=0.22$ (RT) and $\delta=0.18$ (HT) for \( \text{Nd}_{2}\text{NiO}_{4} \) vs. $\delta=0.10$ (RT) and $\delta=0.04$ (HT) for \( \text{Nd}_{1.80}\text{Ca}_{0.20}\text{NiO}_{4} \)).

The role of substitution of d-block ions on the Ni-site in \( \text{Ln}_{2}\text{NiO}_{4} \) has been investigated by numerous groups. Table 1.2 and Table 1.3 summarize the role of Ni-site dopants (e.g. Cu,\textsuperscript{20, 115, 132, 135-137} Fe,\textsuperscript{135, 138-139} Co,\textsuperscript{136, 138, 140} and Mn\textsuperscript{141}) on $\sigma_{\text{tot}}$ and $\delta$. There seems to exist a discrepancy in the literature reports on the role of B-site dopants on the conductivity in PNO. Although lower $\sigma_{\text{tot}}$ was obtained with Cu, Co, and Fe doping in PNO\textsuperscript{136} (e.g. $\sigma_{\text{tot}}\sim112.2$ S/cm for \( \text{Pr}_{2}\text{Ni}_{0.80}\text{Cu}_{0.10}\text{O}_{4+\delta} \) at 600 °C) when compared to PNO baseline ($\sigma_{\text{tot}}\sim130$ S/cm at 600 °C) from multiple reports,\textsuperscript{136} Kovalevsky et al.\textsuperscript{135} reports the
Table 1.2 Total conductivity ($\sigma_{\text{tot}}$) of doped Pr$_2$NiO$_4$+$\delta$ nickelate ceramics measured in air at various temperatures. The measured $\delta$ in air at room temperature (RT) and 600 °C (HT) is listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Annealing Temp (°C)</th>
<th>$\sigma_{\text{tot}}$ in air (S/cm)</th>
<th>Ref. #</th>
<th>$\delta$ in air (RT)</th>
<th>$\delta$ in air (600 °C)</th>
<th>Ref. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$_2$NiO$_4$-based ceramics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>700 °C</td>
<td>800 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sr-doping on Pr-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.90}$Sr$</em>{0.10}$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>120</td>
<td>108</td>
<td>98</td>
<td></td>
<td>110,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.16,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>Pr$<em>{1.80}$Sr$</em>{0.20}$NiO$_4$</td>
<td>1200</td>
<td>120</td>
<td>106</td>
<td></td>
<td></td>
<td>122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Pr$<em>{1.70}$Sr$</em>{0.30}$NiO$_4$</td>
<td>1250</td>
<td>76</td>
<td>72</td>
<td>71</td>
<td></td>
<td>157</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Pr$<em>{1.60}$Sr$</em>{0.40}$NiO$_4$</td>
<td>1350</td>
<td>78</td>
<td>76</td>
<td>75</td>
<td></td>
<td>122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>122</td>
</tr>
<tr>
<td>Pr$<em>{1.50}$Sr$</em>{0.50}$NiO$_4$</td>
<td>1200</td>
<td>156</td>
<td>160</td>
<td>159</td>
<td></td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>95</td>
<td>92</td>
<td>85</td>
<td></td>
<td>157</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>122</td>
</tr>
<tr>
<td>Pr$<em>{1.20}$Sr$</em>{0.80}$NiO$_4$</td>
<td>1250</td>
<td>139</td>
<td>125</td>
<td>121</td>
<td></td>
<td>157</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>122</td>
</tr>
<tr>
<td><strong>Nd-doping on Pr-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.75}$Nd$</em>{0.25}$)$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.25}$Nd$</em>{0.75}$)$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>80.8</td>
<td>76.6</td>
<td>66.7</td>
<td></td>
<td>this</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cu, Fe, Co-doping on Ni-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.90}$Cu$_{0.10}$O$_4$</td>
<td>1200</td>
<td>-</td>
<td>112.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.75}$Cu$_{0.25}$O$_4$</td>
<td></td>
<td>-</td>
<td>112.2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.77}$Cu$<em>{0.22}$Ga$</em>{0.05}$O$_4$</td>
<td></td>
<td></td>
<td>90.5</td>
<td></td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.75}$Cu$<em>{0.20}$Fe$</em>{0.05}$O$_4$</td>
<td></td>
<td></td>
<td>78</td>
<td>76</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.80}$Cu$_{0.20}$O$_4$</td>
<td>1400</td>
<td>200</td>
<td>190.5</td>
<td>182</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>Pr$<em>2$Ni$</em>{0.90}$Fe$_{0.10}$O$_4$</td>
<td>1300</td>
<td>173.8</td>
<td>169.8</td>
<td>162</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>(Pr$<em>{0.90}$La$</em>{0.10}$)$_2$NiO$_4$</td>
<td>1300</td>
<td>30.9</td>
<td>27.54</td>
<td>24</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>(Ni$<em>{0.74}$Cu$</em>{0.21}$Ga$_{0.05}$)$_2$O$_4$</td>
<td>1400</td>
<td>-</td>
<td>60.3</td>
<td>-</td>
<td></td>
<td>135</td>
</tr>
</tbody>
</table>
Table 1.3 Total conductivity \((\sigma_{\text{tot}})\) of doped La\(_2\)NiO\(_{4+\delta}\) nickelate ceramics measured in air at various temperatures. The measured \(\delta\) in air at room temperature (RT) and 600 °C (HT) is listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ann. T (°C)</th>
<th>(\sigma_{\text{tot}}) (S/cm)</th>
<th>Ref</th>
<th>(\delta) RT</th>
<th>(\delta) HT</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sr-doping on La-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(<em>{1.50})Sr(</em>{0.50})NiO(_4)</td>
<td>950</td>
<td>175</td>
<td>167</td>
<td>160</td>
<td>138</td>
<td>-</td>
</tr>
<tr>
<td>(La(<em>{0.50})Sr(</em>{0.50}))(_2)NiO(_4)</td>
<td>1200</td>
<td>118</td>
<td>115</td>
<td>-</td>
<td>153</td>
<td>≈0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>153</td>
</tr>
<tr>
<td><strong>Ca-doping on La-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(<em>{1.90})Ca(</em>{0.10})NiO(_4)</td>
<td>1300</td>
<td>71</td>
<td>68</td>
<td>61</td>
<td>55.3(^{132})</td>
<td>0.15</td>
</tr>
<tr>
<td>La(<em>{1.80})Ca(</em>{0.20})NiO(_4)</td>
<td>1350</td>
<td>86</td>
<td>81</td>
<td>77</td>
<td>63(^{132})</td>
<td>131</td>
</tr>
<tr>
<td>La(<em>{1.70})Ca(</em>{0.30})NiO(_4)</td>
<td>1350</td>
<td>89</td>
<td>85</td>
<td>81</td>
<td>61(^{132})</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(<em>{1.60})Ca(</em>{0.40})NiO(_4)</td>
<td>120</td>
<td>115</td>
<td>114</td>
<td>83.7(^{132})</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td><strong>Cu, Fe, Co, Mn-doping on Ni-site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(<em>{2})Ni(</em>{1.00})Cu(_{0.20})O(_4)</td>
<td>1000</td>
<td>54</td>
<td>52</td>
<td>47</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{2})Ni(</em>{1.00})Cu(_{0.40})O(_4)</td>
<td>1320</td>
<td>77</td>
<td>70</td>
<td>56</td>
<td>50</td>
<td>137</td>
</tr>
<tr>
<td>La(<em>{2})Ni(</em>{1.00})Cu(_{0.60})O(_4)</td>
<td>1450</td>
<td>34</td>
<td>28</td>
<td>25.5</td>
<td>49</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>La(<em>{2})Ni(</em>{1.00})Mn(_{0.10})O(_4)</td>
<td>1270</td>
<td>-</td>
<td>46.8</td>
<td>44.7</td>
<td>139</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>139</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>139</td>
</tr>
<tr>
<td><strong>Doping on La- and Ni-sites simultaneously</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(<em>{1.50})Sr(</em>{0.50})Ni(<em>{0.70})Fe(</em>{0.30})O(_4)</td>
<td>1350</td>
<td>175</td>
<td>167</td>
<td>160</td>
<td>138</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{1.50})Sr(</em>{0.50})Ni(<em>{0.50})Fe(</em>{0.50})O(_4)</td>
<td>1350</td>
<td>115</td>
<td>118</td>
<td>119</td>
<td>138</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{1.00})Ca(</em>{0.30})Ni(<em>{0.90})Cu(</em>{0.10})O(_4)</td>
<td>1350</td>
<td>135</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{1.00})Ca(</em>{0.30})Ni(<em>{0.80})Cu(</em>{0.20})O(_4)</td>
<td>1350</td>
<td>149</td>
<td>145</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{1.70})Ca(</em>{0.30})Ni(<em>{0.70})Cu(</em>{0.30})O(_4)</td>
<td>1350</td>
<td>160</td>
<td>157</td>
<td>-</td>
<td>152</td>
<td>-</td>
</tr>
<tr>
<td>(La(<em>{0.50})Sr(</em>{0.50}))(<em>2)Ni(</em>{0.50})Mn(_{0.50})O(_4)</td>
<td>1350</td>
<td>34</td>
<td>38</td>
<td>40</td>
<td>92</td>
<td>95</td>
</tr>
<tr>
<td>La(<em>{1.50})Sr(</em>{0.70})Ni(<em>{0.90})Mn(</em>{0.10})O(_4)</td>
<td>1350</td>
<td>92</td>
<td>95</td>
<td>96</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>La(<em>{1.50})Sr(</em>{0.80})Ni(<em>{0.90})Mn(</em>{0.10})O(_4)</td>
<td>1400</td>
<td>102</td>
<td>103</td>
<td>104</td>
<td>140</td>
<td>-</td>
</tr>
</tbody>
</table>

---

28
Table 1.4 Total conductivity ($\sigma_{\text{tot}}$) of doped Nd$_2$NiO$_{4+\delta}$ nickelate ceramics measured in air at various temperatures. Oxygen over-stoichiometry ($\delta$) measured in air at room temperature (RT) and 600 °C (HT) is also listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Annealing Temp. (°C)</th>
<th>$\sigma_{\text{tot}}$ (S/cm)</th>
<th>Ref #</th>
<th>$\delta$ RT</th>
<th>$\delta$ HT</th>
<th>Ref #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$NiO$_4$-based ceramics</td>
<td>600 °C</td>
<td>700 °C</td>
<td>800 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr-doping on Nd-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.50}$Sr$</em>{0.50}$)$_2$NiO$_4$</td>
<td>1250</td>
<td>190.5</td>
<td>177.8</td>
<td>162.2</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.60}$Sr$</em>{1.40}$)$_2$NiO$_4$</td>
<td></td>
<td>245.5</td>
<td>223.9</td>
<td>195</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.60}$Sr$</em>{1.60}$)$_2$NiO$_4$</td>
<td></td>
<td>159.2</td>
<td>117.5</td>
<td>141.3</td>
<td>213</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca-doping on Nd-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.80}$Ca$</em>{0.20}$NiO$_4$</td>
<td>1250</td>
<td>81</td>
<td>76</td>
<td>71</td>
<td>133</td>
<td>0.10</td>
</tr>
</tbody>
</table>

very opposite trend, where the overall conduction in Pr$_2$Ni$_{0.80}$Cu$_{0.20}$O$_{4+\delta}$ and Pr$_2$Ni$_{0.90}$Fe$_{0.10}$O$_{4+\delta}$ is significantly higher (e.g. $\sigma_{\text{tot}}$~223 S/cm and 178 S/cm at 600 °C, respectively) when compared to the parent PNO composition ($\sigma_{\text{tot}}$~ 141 S/cm at 600 °C). However, it is imperative to note that different annealing temperatures, dense ceramic bar preparations for conductivity measurements, and different $\delta$ could significantly influence the material behavior and ultimately the measurements. The report by Kovalevsky et al. involved quenching of a high temperature phase (~1000 °C), while other reports use a more common approach of slow material cooling in air before the measurements.

However, as shown in multiple reports, the measured conductivity in LNO-based compositions was also lower than in monolithic material. It can be immediately seen that overall $\sigma_{\text{tot}}$ decreases with doping on the Ni-site in Ln$_2$NiO$_4$ monolithic compounds, Table 1.3, which may indicate that the substitution on the Ni-site in Pr$_2$NiO$_4$ also likely plays a negative role on the $\sigma_{\text{tot}}$. Ultimately, the electrochemical operation in SOFCs can provide the most accurate comparison among different nickelate compositions as the synergy of all variables ($\sigma_{\text{tot}}$, $\delta$, k, D, $E_a$,ORR, structure) in an operating system will provide
a direct comparison between different nickelate materials. Such approach will be discussed in section 6 of this review.

Although the $\delta$ values are rarely reported for these sets of compositions, a few reports on La$_2$Ni$_{0.9}$Co$_{0.10}$O$_4$ and La$_2$Ni$_{0.90}$Fe$_{0.10}$O$_4$ show that Co and Fe do not greatly influence the oxygen content in LNO-based compositions. However, even minor changes in $\delta$ may lead to substantial changes in $\sigma_{\text{tot}}$. Figure 1.11 shows the dependency of $\sigma_{\text{tot}}$ on $\delta$ in La$_2$Ni$_{0.9}$Co$_{0.10}$O$_4$ measured at various temperatures. With increase in $\delta$ (which has been adjusted via various synthesis conditions) from 0.08 to 0.14 the $\sigma_{\text{tot}}$ also increases by twofold at all measured temperatures (700-1000 °C), which is in agreement with Eq. 13 due to increase in concentration of charge carriers (holes). Therefore, the oxygen content and dopant charge greatly influence the concentration of the charge carries, leading to respective changes in $\sigma_{\text{tot}}$. It is imperative to note however that such results do not necessarily apply for other dopants or compositions. Hence, detailed studies are necessary to investigate the role of each dopants on $\delta$ and $\sigma_{\text{tot}}$, as each dopant carries different ionic size and charge, and might prefer different structural arrangement in a sixfold coordination (e.g. octahedral vs. square planar), which would in turn influence the structure and ultimately the oxygen content. Furthermore, each B-site dopant will effectively influence the overall charge on B site cations as $d$ block ions can carry a range of oxidation states, which will in turn influence the electron-hole conduction in the perovskite layer, as shown in Figure 1.9.
The total conductivity of $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.10}\text{O}_4$ as function of oxygen content.

The complexity behind the role of doping on $\sigma_{\text{tot}}$ and $\delta$ is further reflected in Table 1.3, where doping on Pr and Ni sites was performed simultaneously. Although doping on the Ni site in LNO alone does not seem to lead to significant increase in $\sigma_{\text{tot}}$, the combination of doping on both sites seems to provide more encouraging results with conductivity reaching $\sim160$ S/cm for $\text{La}_{1.70}\text{Ca}_{0.30}\text{Ni}_{0.70}\text{Cu}_{0.30}\text{O}_4$ and $\sim150$ S/cm for $\text{La}_{1.0}\text{Ca}_{0.30}\text{Ni}_{0.80}\text{Cu}_{0.20}\text{O}_4$ at 600 °C. Such increase in $\sigma_{\text{tot}}$ when compared to baseline LNO ($\sigma_{\text{tot}}\sim70$ S/cm, 600 °C, Table 1.1) and $\text{La}_{1-x}\text{Ca}_x\text{NiO}_4$ compositions ($\sigma_{\text{tot}}\leq120$ S/cm at 600 °C, Table 1.3) indicates additional driving force towards materials properties besides the competing carrier concentration and immediate change in $\delta$. Therefore, a better understanding of change in crystal structure with substitution and doping in $\text{Ln}_2\text{NiO}_4+\delta$ is of fundamental importance, and as such is discussed in the following sections.
1.4 PHASE FORMATION AND CRYSTAL STRUCTURE IN NICKELATES

The thermal phase formation of a desirable RP nickelate phase is a rather complex challenge. Depending on the thermal annealing history, oxygen content, annealing environment, and temperature, different RP phases may be formed. Hence, in order to obtain monolithic composition, each composition should be studied separately until optimal conditions for single phase synthesis are developed. Out of the three monolithic systems (PNO, LNO, NNO) the thermodynamics of phase formations of LNO system (under temperatures of interest for SOFC operation) have been studied considerably in open literature. However, the recent interest for PNO and NNO as cathodes in SOFCs require further studies at elevated temperatures.

1.4.1 PHASE FORMATION IN NICKELATES

The topology of the ternary Ln-Ni-O system is not very well known. However, a recent report by Zinkevich et al.\textsuperscript{143} provided more basic understanding of the thermodynamics of the ternary systems. Zinkevich et al. conducted thermodynamic analysis of the ternary La-Ni-O system by analytically minimizing the Gibbs energy of individual phases in terms of state variables (temperature, pressure, composition) and comparing the calculations to experimental data. Figure 1.12 shows La-Ni-O phase diagram as function of temperature in air, in which solid lines represent calculated patterns and discrete symbols are experimental data.\textsuperscript{143} The complexity of phase transformation can be immediately seen, where multiple phases can be present providing a very narrow window for a synthesis of a single LNO phase. The LNO composition sits on the vertical line (indicated by 2La:1Ni ratio). Any deviations from this line lead to phase transformation and presence of two or more phases, which is of a concern in SOFCs as the
properties of the material will also change and could lead to performance degradation (as will be discussed in the last section). Both temperature and La:Ni ratio could cause distinct phase variation. Similar phase diagrams can be constructed for PNO and NNO compositions, which also result in a single phase under specific experimental conditions.\textsuperscript{118, 144}

Figure 1.12 Calculated vertical section of the La-Ni-O phase diagram along the La$_2$NiO$_4$-LaNiO$_3$ join in air. The experimental measured results (marked) are also superimposed.\textsuperscript{143}

It is also imperative to note that the constructed phase diagram treats all nickelate phases as stoichiometric compounds, which in reality is challenging to obtain. Therefore, further refinement of the present thermodynamic description is necessary with oxygen non-stoichiometry taken into account. To the best of authors knowledge, similar phase diagrams for PNO and NNO have not been reported, which further presents the necessity for better
understanding of phase formation in RP nickelates. Fortunately, the current synthesis sol-gel methods (such as glycine-nitrate combustion process),\textsuperscript{118} 144\textasciitilde147 or citrate method\textsuperscript{148} allow for a synthesis of a single phase RP nickelates. However, it is imperative to note that thermodynamically stable phases may not necessarily be stable under operating conditions in a SOFC, since the role of electrochemical potential comes into play. Unfortunately, the majority of the literature reports strictly focus on phase stability studies under thermal annealing conditions, giving very little attention to phase transformation under operating conditions. Section 1.5 will provide more insight into this phenomena, but has been discussed in great detail in chapters 10-11 of this thesis.

1.4.2 CRYSTAL STRUCTURE IN NICKELATES

The crystal structure of Ln\textsubscript{2}NiO\textsubscript{4} has been extensively studied from monolithic compounds to doped compositions, where both Ln and Ni sites have been modified. In parallel to development of higher conducting MIECs which effectively lead to lower polarization resistance in a single cell, the crystal structure was also investigated to obtain better understanding behind changes in conduction properties and oxygen content. Furthermore, changes in lattice parameters and crystal structure also influence the thermal expansion coefficient (TEC), which is of essential importance in SOFCs, as different cell components must be mechanically compatible. Therefore the RP nickelates, used as cathodes in SOFC, must be in good thermal compatibility with common electrolytes such as yttria stabilized zirconia (YSZ) and doped ceria (usually doped with Gd, GDC). Typical TEC for electrolyte materials is between 11\textasciitilde13 \times 10\textsuperscript{-6} K\textsuperscript{-1} (TEC\textsubscript{YSZ}\sim11\times10\textsuperscript{-6} K\textsuperscript{-1}, and TEC\textsubscript{GDC}\sim13\times10\textsuperscript{-6} K\textsuperscript{-1}); hence, the doping and substitutions on the Ln and Ni sites should aim to retain TEC within this range. Numerous RP nickelate compositions that provide
acceptable \( \sigma_{\text{tot}} \) (between 50-100 S/cm), and are mechanically compatible with common electrolyte materials have been structurally studied, and are summarize in this section.

1.4.2-1 UNIT CELL PARAMETERS AND CELL VOLUME IN MONOLITHIC AND DOPED COMPOUNDS

Due to structural flexibility in RP nickelates, when compared to rigid structure of perovskites, the Ln and Ni sites in RP structure can be doped and/or substituted with various cations of similar size and charge.\(^{149}\) Figure 1.13a\(^{144}\) shows raw XRD patterns of PNNO powders. Single phase in an orthorhombic structure was obtained for each composition. The Rietveld refinement in Bmab symmetry results in an agreement between the experimental and calculated patterns, which can be seen from their difference depicted in blue line, as shown in Figure 1.13b. The highest intensity diffraction peak shifts to higher 2\( \theta \) values with increase in Nd content, indicating changes in structural parameters. Fractional position coordinates on heavy metal cations (Pr,Nd) indicate a compression in both \( z \) and \( y \) direction with an increase in Nd content,\(^{144}\) accompanied by a compression of O2(f) and O1(e) atomic positions, respectively. Therefore, the substitution of Nd on the Pr-site does not change the crystal structure itself but changes the relative atomic positions, which in turn affects the lattice parameters described by using Vegard’s Law:

\[
a_{A_{1-x}B_x} = (1 - x) a_A + x a_B
\]  

(1)

where \( a_{A_{1-x}B_x} \) is the lattice parameter of a PNNO solution, \( a_A \) and \( a_B \) are lattice parameters of the pure constituents, PNO and NNO, respectively, and \( x \) is the molar fraction of Nd in the solution. Shrinkage in the cell volume with increase in Nd content can be expressed as:

\[
V = 364.69 - 3.23x
\]  

(2)
and is illustrated in Figure 1.14a. The volume contraction is driven by a fast rate of
decrease in the c parameter, with a negative slope of $m = -3.18$ (which is within 1.60% of
the slope in volume change), while $a$ and $b$ lattice parameters decrease at much slower
rates, $m = -0.016, m = -0.0045$, respectively, as shown in Figure 1.14b. A steeper slope
for the volume contraction, when compared to a decrease in the c lattice parameter, may
be associated with the change in oxygen occupancy, as suggested in previous studies on

![Figure 1.13 (a) XRD patterns on a single phase PNNO powders matched against the
standard reflections. (b) Rietveld refinement on selected PNNO compositions. (c) Rietveld
refinement on PNNO(50/50)-Cuy compositions. Dots are raw data and solid lines are the
calculated profiles. Thick marks below the profiles mark the positions of the allowed
reflections. Solid lines below the thick marks are the difference curves.](image)

PNO and NNO. A decrease in the c parameter from 12.4303 Å (PNO) to 12.3686 Å
(NNO) is equivalent to 0.50%, which is in an agreement with the work (0.55%) performed
by Boehm and Bassat et al. Similarly, Wahyudi and Ceretti et al. calculated a
significant decrease in the c parameter in single crystals of PNO and NNO from 12.4402
Å (PNO) to 12.3652 Å (NNO), which is equivalent to 0.60%. The ionic radii of Pr$^{3+}$ and
Nd$^{3+}$, with the coordination number of 8, are within 1.8% (1.13 Å and 1.11 Å,
respectively), hence the shrinkage in the cell volume with an increase in Nd content at room temperature seems mainly driven by the size difference between the two cations.

Tables 1.5, 1.6 and 1.8 summarize similar calculations obtained on a number of different Ln$_2$NiO$_4$ compositions (PNO-, LNO-, and NNO-based, respectively) with modifications on the Ln site including doping and/or substitutions with Pr, La, Nd, Ca, and Sr. The cell volume is within 2.2% for all monolithic compositions (PNO, LNO, NNO) among the literature reports that conducted refinement in orthorhombic (Bmab, Fmmm) symmetry. A few reports claimed refinement of LNO in tetragonal structure (I4/mmm) at room temperature. The reason behind refinement in I4/mmm symmetry is of no surprise as the $a$ and $b$ lattice parameters are within a fraction of a percent difference from each other, see Table 1.6 and Figure 1.16c. Furthermore, with increase in temperature the structure is known to undergo phase transition from orthorhombic to tetragonal, as illustrate in Figure 1.16. Figure 1.16a,c,e show increase in lattice parameters in PNO, LNO, and NNO with increase in temperature in air, followed in parallel by linear increase in cell volume, Figure 1.16b,d,f. A linear rise in the $c$ lattice parameter and cell volume implies that an increase in cell volume in air from 30 °C to 1000 °C (e.g. 4.26% for PNO and 2.76% for NNO) is independent of the structural transition from Bmab to I4/mmm, but largely dependent on $\delta$ in the system. The change in phase has also been linked with loss in $\delta$ occurring between ~200-450 °C, depending on the composition, Figure 1.8. However it still remains obscure how these few reports show significantly smaller (by twofold, ~180-190 Å$^3$) unit cell volume when compared to tetragonal structure in majority of reports, which has volume only slightly
Figure 1.14 (a) Cell volume for Nd-substituted Pr$_2$NiO$_{4+\delta}$ powders obtained from the Rietveld refinement. (b) Calculated cell parameters as function of Nd substitution and compared against results obtained by Boehm et al.

higher than in orthorhombic symmetry. Such large discrepancy of results may be a result of experimental uncertainty when specifying the unit cell, as doubled volume would be equivalent to volume obtained with orthorhombic symmetry.

Doping with various cations on Ln site leads to respective changes in the lattice parameters, which is mainly governed by the difference in charge and size of dopants and the change in $\delta$. By doping larger cations (Sr$^{2+}$, Ca$^{2+}$) on the Ln$^{3+}$ site one might expect volume expansion. However, the change in $\delta$ must not be overlooked (as shown in Tables 1.2-1.4) and will effectively influence the change in cell volume. Due to substantial decrease in $\delta$ with doping of Sr$^{2+}$, Ca$^{2+}$ the rate of change in cell volume may be rather complex, as shown in Tables 1.5-1.8. Since the lattice parameters are changing the M-O bond lengths in oxygen octahedra (perovskite layer) also change, which in turn will affect the 2D electron-hole transport, and result in changes in $\sigma_{\text{tot}}$. However, due to lack of studies on thermal variation in structure of doped nickelates, it is difficult to say what specific structural behavior these compositions will undergo at operating conditions. Therefore, further studies are necessary.
The change in TEC is also influenced by doping. For instance, Pr$_{2-x}$Sr$_x$NiO$_4$-based materials undergo TEC changes from $13.2 \times 10^{-6}$ K$^{-1}$ ($x=0$) to $12.05 \times 10^{-6}$ K$^{-1}$ ($x=0.3$).$^{158}$ Such significant change has been attributed to the loss of lattice oxygen (Table 1.2) and the formation of oxygen vacancies.$^{158}$ Similar mechanism can be associated with Ln$_{2-x}$Ca$_x$NiO$_4$, in which loss in $\delta$ occurs with Ca doping on the Ln site (Table 1.3 and Table 1.4). Doping on the Ni-site is of comparable complexity with regards to the role of dopants on changes in material properties. Figure 1.13c shows the refined structure for Cu doped PNN050-50 compositions. Tables 1.5-1.8 summarize the structural parameters for the B-site doped Ln$_2$NiO$_4$ compositions. It appears that doping with Cu and Fe leads to increase in cell volume. Figure 1.15 shows the Rietveld refinements in orthorhombic symmetry (Bmab) on (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+\delta}$ powders where $y = 0$, 0.05, 0.10, and 0.20, respectively. With an increase in Cu content there is a 0.30% increase in $a$ and a 0.70% decrease in $b$, as shown in Figure 1.15a. However, the most significant change was calculated for the $c$ lattice parameter with a 0.90% increase for PNN05050-Cu$_{20}$. Due to an overall increase in the lattice parameters, the cell volume increased by 0.40%, as shown
Figure 1.16 Thermal variation in lattice parameters and unit cell volume in air for (a-b) PNO, (c-d) LNO, and (e-f) NNO compositions in LNO and NNO. The variation in oxygen stoichiometry measured by TGA is also shown.

in Figure 1.15b. Combination of doping on both Ln- and Ni-sites is also common (see Table 1.5 and Table 1.7) as it may lead to interesting properties. A few prospective candidates developed by our group are discussed in the following section with regards to detailed structural changes and M-O distances.
Table 1.5 Calculated lattice parameters for Pr$_2$NiO$_{4+δ}$-based compositions at room temperature. The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{syn}$: XRD at a synchrotron source, ND: neutron diffraction).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Space group</th>
<th>Ref. #</th>
<th>TEC (ppm)</th>
<th>Ref. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$_2$NiO$_4$</td>
<td>a = 5.38435 (20), b = 5.44870 (32), c = 12.43025 (45)</td>
<td>364.675 (30)</td>
<td>Bmab</td>
<td>this work (XRD)</td>
<td>151 (XRD)</td>
<td>13.2</td>
</tr>
<tr>
<td>(Pr$<em>{0.75}$Nd$</em>{0.25}$)$_2$NiO$_4$</td>
<td>a = 5.38075 (35), b = 5.44758 (42), c = 12.41688 (50)</td>
<td>363.9356 (33)</td>
<td>Bmab</td>
<td>143</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$_2$NiO$_4$</td>
<td>a = 5.37673 (15), b = 5.44646 (28), c = 12.39882 (31)</td>
<td>363.0661 (25)</td>
<td>Bmab</td>
<td>108 (XRD)</td>
<td>13.11</td>
<td>108</td>
</tr>
<tr>
<td>(Pr$<em>{0.25}$Nd$</em>{0.75}$)$_2$NiO$_4$</td>
<td>a = 5.37234 (22), b = 5.44533 (25), c = 12.3815 (60)</td>
<td>362.2261 (35)</td>
<td>Bmab</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd-doping on Pr-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe, Cu-doping on Ni site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Doping on Pr- and Ni-sites simultaneously</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.95}$Cu$_{0.05}$O$_4$</td>
<td>a = 5.37824(25), b = 5.43124(15), c = 12.41546(36)</td>
<td>362.5255(31)</td>
<td>Bmab</td>
<td>this work (XRD, XRD$_{syn}$)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.90}$Cu$_{0.10}$O$_4$</td>
<td>a = 5.38145(21), b = 5.41831(35), c = 12.45074(45)</td>
<td>363.0132(28)</td>
<td>Bmab</td>
<td>108 (ND, XRD$_{syn}$)</td>
<td>13.6</td>
<td>108, 13.2, 13.3, 217</td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.85}$Cu$_{0.15}$O$_4$</td>
<td>a = 5.38078(23), b = 5.40055(38), c = 12.4998(30)</td>
<td>363.6591(25)</td>
<td>Bmab</td>
<td>115, 215</td>
<td>13.7</td>
<td>216</td>
</tr>
<tr>
<td>Fe, Cu-doping on Ni site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Doping on Pr- and Ni-sites simultaneously</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.75}$Cu$<em>{0.25}$Co$</em>{0.05}$O$_4$</td>
<td>a = 5.37824(25), b = 5.43124(15), c = 12.41546(36)</td>
<td>362.5255(31)</td>
<td>Bmab</td>
<td>this work (XRD, XRD$_{syn}$)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.70}$Cu$_{0.10}$O$_4$</td>
<td>a = 5.38145(21), b = 5.41831(35), c = 12.45074(45)</td>
<td>363.0132(28)</td>
<td>Bmab</td>
<td>108 (ND, XRD$_{syn}$)</td>
<td>13.6</td>
<td>108, 13.2, 13.3, 217</td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.65}$Cu$_{0.20}$O$_4$</td>
<td>a = 5.38078(23), b = 5.40055(38), c = 12.4998(30)</td>
<td>363.6591(25)</td>
<td>Bmab</td>
<td>115, 215</td>
<td>13.7</td>
<td>216</td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.60}$Cu$<em>{0.25}$Co$</em>{0.05}$O$_4$</td>
<td>a = 5.37824(25), b = 5.43124(15), c = 12.41546(36)</td>
<td>362.5255(31)</td>
<td>Bmab</td>
<td>this work (XRD, XRD$_{syn}$)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.55}$Cu$<em>{0.30}$O$</em>{0.50}$O$_4$</td>
<td>a = 5.38145(21), b = 5.41831(35), c = 12.45074(45)</td>
<td>363.0132(28)</td>
<td>Bmab</td>
<td>108 (ND, XRD$_{syn}$)</td>
<td>13.6</td>
<td>108, 13.2, 13.3, 217</td>
</tr>
<tr>
<td>(PrNd)$<em>2$Ni$</em>{0.50}$Cu$<em>{0.25}$Co$</em>{0.05}$O$_4$</td>
<td>a = 5.38078(23), b = 5.40055(38), c = 12.4998(30)</td>
<td>363.6591(25)</td>
<td>Bmab</td>
<td>115, 215</td>
<td>13.7</td>
<td>216</td>
</tr>
</tbody>
</table>
Table 1.6 Calculated lattice parameters for La$_2$NiO$_{4+\delta}$-based compositions at room temperature (A-site doping). The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{syn}$: XRD at a synchrotron source, ND: neutron diffraction).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Space group</th>
<th>Ref. #</th>
<th>TEC (ppm) 50-1000 °C</th>
<th>Ref. #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monolithic La$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$_2$NiO$_4$</td>
<td>5.467</td>
<td>5.468</td>
<td>12.672</td>
<td>378.81</td>
<td>Fmmm 151 (XRD)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.456(2)</td>
<td>5.462(3)</td>
<td>12.691(2)</td>
<td>378.2</td>
<td>153 (XRD)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.4499(3)</td>
<td>5.4574(3)</td>
<td>12.6724(5)</td>
<td>376.9061</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.467(7)</td>
<td>5.462(7)</td>
<td>12.693(8)</td>
<td>379.023</td>
<td>214 (XRD)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.4482(10)</td>
<td>5.4773(4)</td>
<td>12.6668(8)</td>
<td>377.9954</td>
<td>132 (XRD)</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>3.8611(8)</td>
<td>12.6465(4)</td>
<td>188.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.86464(8)</td>
<td>12.6914(3)</td>
<td>189.5517</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr, Sr, Ca-doping on La-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.40}$Pr$</em>{0.60}$NiO$_4$</td>
<td>5.4505</td>
<td>5.451</td>
<td>12.592</td>
<td>374.117</td>
<td>Fmmm 151 (XRD)</td>
<td>-</td>
</tr>
<tr>
<td>(La$<em>{0.50}$Pr$</em>{0.50}$)$_2$NiO$_4$</td>
<td>5.445</td>
<td>5.447</td>
<td>12.552</td>
<td>372.279</td>
<td>Bmab</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.60}$Pr$</em>{1.40}$NiO$_4$</td>
<td>5.415</td>
<td>5.459</td>
<td>12.508</td>
<td>369.743</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(La$<em>{0.50}$Sr$</em>{0.50}$)$_2$NiO$_4$</td>
<td>3.824(7)</td>
<td>12.464(8)</td>
<td>182.3</td>
<td>153 (XRD)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3.8236(1)</td>
<td>12.4723(4)</td>
<td>182.344</td>
<td>140 (XRD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.8520(9)</td>
<td>12.6343(9)</td>
<td>187.48</td>
<td></td>
<td></td>
<td>13.3</td>
</tr>
<tr>
<td>La$<em>{1.50}$Sr$</em>{0.50}$NiO$_4$</td>
<td>3.8347</td>
<td>12.718(7)</td>
<td>186.948</td>
<td>138 (XRD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.90}$Ca$</em>{0.10}$NiO$_4$</td>
<td>3.8622(4)$^{P107}$</td>
<td>12.6712(12)</td>
<td>189.01</td>
<td></td>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>L$<em>{3.8}$Ca$</em>{2.2}$NiO$_4$</td>
<td>3.8491(8)$^{P107}$</td>
<td>12.5617(3)</td>
<td>186.11</td>
<td></td>
<td></td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>3.849(4)$^{P107}$</td>
<td>12.6427(13)</td>
<td>187.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$NiO$_4$</td>
<td>3.8353(3)</td>
<td>12.6338(8)</td>
<td>185.84</td>
<td>I4/mmm (XRD)</td>
<td></td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>3.8350(3)$^{P107}$</td>
<td>12.6141(12)</td>
<td>185.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.60}$Ca$</em>{0.40}$NiO$_4$</td>
<td>3.8128(1)</td>
<td>12.5942(8)</td>
<td>183.09</td>
<td>152 (XRD)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3.8195(6)$^{P107}$</td>
<td>12.5892(14)</td>
<td>183.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$NiO$_4$</td>
<td>3.824(6)</td>
<td>12.594(21)</td>
<td>190.554(7)</td>
<td>I4/mmm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.7 Calculated lattice parameters for La$_2$NiO$_{4+\delta}$-based compositions at room temperature (B-site doping). The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{syn}$: XRD at a synchrotron source, ND: neutron diffraction).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Space group</th>
<th>Ref.</th>
<th>TEC (ppm) 50-1000 °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Doping on Ni-site in Ln$_2$NiO$_4$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.80}$Cu$_{0.20}$O$_4$</td>
<td>5.4502(1)</td>
<td>12.7901(5)</td>
<td>379.92(2)</td>
<td>F4/mmm</td>
<td>13.9 13.3$^{139}$</td>
<td>20</td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.60}$Cu$_{0.40}$O$_4$</td>
<td>5.43333(6)</td>
<td>12.8788(2)</td>
<td>380.195(9)</td>
<td>20 (ND)</td>
<td>13.0</td>
<td>13$^{107}$</td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.40}$Cu$_{0.60}$O$_4$</td>
<td>5.41070(5)</td>
<td>12.9701(2)</td>
<td>379.708(7)</td>
<td>20 (ND)</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.50}$Co$_{0.50}$O$_4$</td>
<td>3.8711(4)</td>
<td>12.656(5)</td>
<td>189.655</td>
<td>Fmmm</td>
<td>12.8</td>
<td>218</td>
</tr>
<tr>
<td><strong>Doping on Pr- and Ni-sites simultaneously</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$Ni$<em>{0.70}$Cu$</em>{0.30}$O$_4$</td>
<td>3.802(4)</td>
<td>12.770(2)</td>
<td>184.645(4)</td>
<td>I4/mmm</td>
<td>152 (XRD)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.50}$Sr$</em>{0.50}$Ni$<em>{0.70}$Fe$</em>{0.30}$O$_4$</td>
<td>3.835(5)</td>
<td>12.714(2)</td>
<td>187.075</td>
<td></td>
<td>138 (XRD)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.50}$Sr$</em>{0.50}$Ni$<em>{0.50}$Fe$</em>{0.50}$O$_4$</td>
<td>3.837(8)</td>
<td>12.734(1)</td>
<td>187.557</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(La$<em>{0.90}$Sr)$<em>2$Ni$</em>{0.10}$Mn$</em>{0.10}$O$_4$</td>
<td>3.8264(2)</td>
<td>12.4918(6)</td>
<td>182.8967</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(La$<em>{0.90}$Sr)$<em>2$Ni$</em>{0.50}$Mn$</em>{0.10}$O$_4$</td>
<td>3.8264(2)</td>
<td>12.4918(6)</td>
<td>182.8967</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(La$<em>{0.90}$Sr)$<em>2$Ni$</em>{0.50}$Mn$</em>{0.50}$O$_4$</td>
<td>3.8426(1)</td>
<td>12.5646(3)</td>
<td>185.5235</td>
<td></td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>(La$<em>{0.90}$Sr)$<em>2$Ni$</em>{0.30}$Mn$</em>{0.70}$O$_4$</td>
<td>3.8426(2)</td>
<td>12.652(1)</td>
<td>186.678</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.30}$Sr$</em>{0.70}$Ni$<em>{0.90}$Mn$</em>{0.10}$O$_4$</td>
<td>3.8138(2)</td>
<td>12.660(1)</td>
<td>184.1406</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.20}$Sr$</em>{0.80}$Ni$<em>{0.90}$Mn$</em>{0.10}$O$_4$</td>
<td>3.8194(1)</td>
<td>12.6081(7)</td>
<td>183.9246</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.10}$Sr$</em>{0.90}$Ni$<em>{0.90}$Mn$</em>{0.10}$O$_4$</td>
<td>3.8203(3)</td>
<td>12.550(1)</td>
<td>183.1634</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 1.7 is continuation to Table 1.6.*
Table 1.8 Calculated lattice parameters for Nd$_2$NiO$_{4+\delta}$-based compositions at room temperature. The space group assigned to refinement is provided along with thermal expansion coefficient (TEC) of the respective compositions. The experimental methods used are also indicated (XRD: x-ray diffraction, XRD$_{syn}$: XRD at a synchrotron source, ND: neutron diffraction).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell lattice parameters (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Space group</th>
<th>Ref.</th>
<th>TEC (ppm) 50-1000 °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$NiO$_4$</td>
<td>a 5.36842 (18) b 5.44421 (23) c 12.36856 (55)</td>
<td>361.4935 (28)</td>
<td>Bmab</td>
<td>this work (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a 5.3642(2) b 5.4586(2) c 12.3739(6)</td>
<td>362.3204</td>
<td></td>
<td>133 (XRD)</td>
<td>12.7 13.5$^{187}$ 133</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a 5.378(3) b 5.457(1) c 12.379(1)</td>
<td>363.363</td>
<td>Fmmm</td>
<td>214 (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a 5.374(4) b 5.458(5) c 12.376(0)</td>
<td>363.0</td>
<td>Bmab</td>
<td>153 (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr, Ca-doping on Nd-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.9}$Sr$</em>{0.1}$NiO$_4$</td>
<td>a 3.81(2) b 12.35(2)</td>
<td>179.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.8}$Sr$</em>{0.2}$NiO$_4$</td>
<td>a 3.81(2) b 12.37(1)</td>
<td>179.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.7}$Sr$</em>{0.3}$NiO$_4$</td>
<td>a 3.81(2) b 12.38(1)</td>
<td>179.71</td>
<td></td>
<td>181 (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.6}$Sr$</em>{0.4}$NiO$_4$</td>
<td>a 3.81(2) b 12.41(2)</td>
<td>180.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.5}$Sr$</em>{0.5}$NiO$_4$</td>
<td>a 3.80(2) b 12.43(2)</td>
<td>180.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.5}$Sr$</em>{0.5}$)$_2$NiO$_4$</td>
<td>a 3.795(4) b 12.30(5)</td>
<td>177.2</td>
<td></td>
<td>153 (XRD)</td>
<td>12.3 213</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a 3.795(1) b 12.3183(1)</td>
<td>177.417(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.8}$Sr$</em>{1.2}$)$_2$NiO$_4$</td>
<td>a 3.8037(1) b 12.2587(1)</td>
<td>177.358(2)</td>
<td></td>
<td>213 (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.6}$Sr$</em>{1.4}$)$_2$NiO$_4$</td>
<td>a 3.8064(1) b 12.2528(1)</td>
<td>177.527(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Nd$<em>{0.4}$Sr$</em>{1.6}$)$_2$NiO$_4$</td>
<td>a 3.8038(1) b 12.2957(1)</td>
<td>177.906(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.90}$Ca$</em>{0.10}$NiO$_4$</td>
<td>a 5.3611(1) b 5.4205(1) c 12.3504(3)</td>
<td>358.9007</td>
<td>Bmab</td>
<td>133 (XRD)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.80}$Ca$</em>{0.20}$NiO$_4$</td>
<td>a 5.3773(1) b 5.3702(1) c 12.3214(2)</td>
<td>355.8072</td>
<td>Fmmm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.4.2-2 M-O DISTANCES AND BOND ANGLES IN THE UNIT CELL

The fractional position coordinates on heavy metal cations (Pr, Nd) indicate an elongation in the z direction and overall compression in the y direction while the orthorhombic Bmab symmetry was retained.\textsuperscript{144} Hence, to further investigate the role of Cu-doping on the crystal structure in PNN05050-Cu\textsubscript{y}, the changes in lattice parameters were further studied by refinement of the average bond lengths in the perovskite and rock-salt layers.

Figure 1.17a shows average (Ni,Cu)-O bond lengths for equatorial (e) and focal (f) oxygen positions in the perovskite layer. While the (Ni, Cu)-O\textsubscript{e} bond length decreases (by 0.30, 0.40 and 0.50\%, respectively) the (Ni, Cu)-O\textsubscript{f} increases by 2.80\%, which is equivalent to sixfold larger expansion in the focal direction. These results show that Cu doping within the oxygen octahedra forces equatorial oxygen atoms to arrange closer to the transition metal, which in turn creates steric strain between equatorial and focal oxygens, and leads to repulsion of focal oxygens towards the rock-salt layer. Smaller size of Cu\textsuperscript{2+} cation (0.57 Å) when compared to larger Ni\textsuperscript{2+} (0.63 Å) allows for such modifications in the perovskite layer. Furthermore, as shown by multiple studies on lanthanum cuprates,\textsuperscript{159-161} Cu tends to arrange in a metastable square planar structure at RT but transforms at elevated temperatures to K\textsubscript{2}NiF\textsubscript{4}-type structure forming elongated CuO\textsubscript{6} octahedra.\textsuperscript{159} Consequently, the focal oxygens on one side of (Ni,Cu)O\textsubscript{6} octahedra tend to tilt away from the adjacent interstitial oxygen site to minimize the oxygen-oxygen Columbic repulsion. However, due to increase in the distance between the oxygen transport sites, more energy (higher temperature) will be required for further oxygen hopping. As oxygen octahedra tilt the angle strain formations are produced, which are the most
pronounced for $O_e$-(Ni,Cu)-$O_f$ arrangement, resulting in 3.40% increase in bond angle, \textbf{Figure 1.17b}. Simultaneously, the focal oxygens on the opposite side of the (Ni,Cu)O$_6$ octahedra move closer together towards vacant oxygen interstitial sites and likely reduce their availability for further oxygen transport.$^{162}$

These combined steric effects and angle strains in oxygen octahedra lead to respective changes in the rock-salt layer, bringing to changes in oxygen ion conduction paths and concentration of oxygen interstitials.$^{144}$ \textbf{Figure 1.17c} shows refined average (Pr, Nd)-O$_e$ bond lengths. With increase in Cu content the overall (Pr,Nd)-O$_e$ bond lengths decrease. Since Pr and Nd cations are heavy and do not undergo as nearly as much movement as oxygen ions do, the decrease in bond lengths can be explained by tilts in oxygen octahedra due to aforementioned steric and angular strains. A 3.0% decrease in (Pr,Nd)-O$_f$ bond length (\textbf{Figure 1.17d}) is even more evident and further indicates the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.17.png}
\caption{Refined average (Ni,Cu)-O bond lengths for (Ni,Cu)O$_e$ (equatorial) and (Ni,Cu)-O$_f$ (focal) arrangements (a), and O-(Ni,Cu)-O bond angles for the same series (b). Refined average (Pr,Nd)-O bond lengths for (Pr,Nd)O$_e$ (c), and (Pr,Nd)-O$_f$ arrangements (d).}
\end{figure}
Figure 1.18 Quantified M-O distances from PDF measurements as function of composition and temperature for (a) (Ni, Cu)-O$_f$ atomic distance and (b) (Pr, Nd)-O$_f$ atomic distance.

The largest overall decrease in (Pr,Nd)-O bond lengths was measured for 5 and 10 mol.% Cu doped PNNO. Unfortunately, due to limitations of XRD the precise oxygen content could not be determined and our group is conducting efforts to obtain such information utilizing a synchrotron source and neutron diffraction.

The structural information obtained at room temperature was used as a baseline for in-situ studies at a synchrotron source. A pair distribution function (PDF)\textsuperscript{163} was utilized to generate the plots from 2D masked data collected at discrete temperatures during heating, and cooling on RP nickelates. The PDF allows to plot the distance between any two atoms of interest, and by taking advantage of a high resolution and high flux synchrotron radiation the peak shifts in the measured region can be studied, which correspond to changes in M-O distance.

Figure 1.18 summarizes quantified M-O distance of interest as function of composition and temperature. The largest changes occur in PNO, with 7% increase in Ni-O$_f$ and 3.2% decrease in Pr-O$_f$. With PNNO composition the changes are partially
suppressed with 4% increase in Ni-O₁ and 1.4% decrease in Pr-O₁, while for PNNO-Cu₁₀ and PNNO-Cu₂₀, the changes in M-O distances are fully suppressed. With 5% Cu doping some changes in M-O distances are still present. These results are in agreement with the ex situ studies and show promising compositions to stabilize structural changes in RP nickelates, which could in turn lead to stabilized phase during SOFC operation (as confirmed in section 6, Figure 1.32).

1.5 PHASE TRANSFORMATION IN RP NICKELATES

The need for stable long-term performance in SOFCs stems from a target operation of five years (~40,000 hours) during which the performance degradation should not be higher than 4%/1,000 hours. Simultaneously, the cathode activity for oxygen reduction reaction (ORR) should be high enough to provide sufficient cell performance. Section 1.3 summarized various attempts to improve the MIEC properties of RP nickelates which could enhance electron-hole and oxygen ion transport, thus reducing the $E_a$ for ORR. Equally challenging is to stabilize the crystal structure (phase) in RP nickelates, which is known to undergo changes (as briefly discussed in section 1.4.1).

Although the crystal structure has been extensively studied in monolithic and doped RP nickelates (section 1.4.2), there is a lack of phase stability studies. For instance, multiple reports point to phase transition behavior in RP nickelates¹⁰⁷, ¹⁴³, ¹⁵⁵, ¹⁶⁴ based on the thermodynamics and phase diagram (Figure 1.12), but do not perform systematic work comparing thermal annealing studies to electrochemical operation in full cells. Instead, only initial phase is often reported along with the initial cell performance of a few hours of operation (addressed in great detail in the section 1.6). However, such a narrow window of
study (thermal effects only), and a short time frame for structural analysis do not provide a clear representation of an electrode behavior in SOFCs.

For instance, the perovskite structures (e.g. PrNiO$_3$, NdNiO$_3$) are known to exhibit interesting properties such as high-$T_c$ superconductivity and magnetoresistance. Moreover, they show unique low-temperature magnetic ordering (antiferromagnetic). It was found that the changes in electronic properties have been associated with the degree of structural distortions in NiO$_6$ octahedra, due to respective tilts and rotations. The changes in the RP structures have also been extensively studied as function of temperature and oxygen partial pressure, and undergo rather substantial changes when compared to their perovskite relatives. Due to less structural rigidity and the presence of rock-salt layers, the phase transition in PNO leads to formation of Pr$_6$O$_{11}$ (PrO$_x$) and Pr$_3$Ni$_2$O$_7$. However, the systematic studies in SOFCs are missing and have been addressed by extensive research in our group. Detailed studies are reported in chapters 4-9 of this thesis but the most important findings have been summarized in this section.

1.5.1 PHASE TRANSFORMATION IN DOPED RP NICKELATES (A-SITE)

Besides the challenging design of active cathodes for ORR, equally challenging, is to generate compositions with stable phase, since phase transformations have been linked to performance degradation. Therefore, designing new and stable nickelate structures is crucial in SOFC cathode development. In previous sections the PNNO series has been addressed in detail as potential candidates for SOFCs. As such, their phase stability has been extensively studied by our group; Figure 1.19 shows phase evolution behavior in PNNO powders (Figure 1.19a) and electrodes (Figure 1.19b-c) as function of time and temperature in 3% humidified air.
Predominant evolution of Pr$_6$O$_{11}$ (PrO$_x$), measured via XRD, indicates 30% transition of the parent PNO phase after only 150 hours at 700 °C. With 50% Nd substitution on the Pr-site (PNNO50-50), the phase was significantly stabilized, showing only 3 mol% of PrO$_x$ after 500 hours at 750 °C. With a further increase in Nd content, the long-term studies up to 2,500 hours at 750 °C show the preservation of parent (Pr$_{0.25}$Nd$_{0.75}$)$_2$NiO$_{4+δ}$ (PNNO25-75) phase. Phase evolution was further examined in electrodes at various temperatures, as shown in Figure 1.19b-c. PNO undergoes a rapid phase transformation, within 150 hours, at all tested temperatures. The rate of phase

![Figure 1.19b](image1)

![Figure 1.19c](image2)

Figure 1.19 (a) Thermal stability of PNNO powders at 750 °C in air. (b) Phase evolution in PNO and (c) PNNO electrodes in symmetric cells (YSZ/GDC/cathode) as function of time and temperature.\textsuperscript{144} increases with increasing temperatures. At lower temperatures, a two region plot evolves: (i) a slow phase transformation for $t \leq 75$ h and, and (ii) a rapid phase evolution beyond
100 hours of thermal annealing. The sixfold increase in rate of phase transformation at 700 °C, and threefold at 750 °C may be initiated by a sufficient amount of PrO$_x$ being formed, which tends to accelerate phase transformation due to considerable (69%) thermal mismatch between PNO (TEC=13.2 x 10$^{-6}$ °C$^{-1}$) and PrO$_x$ (TEC=22.3 x 10$^{-6}$ °C$^{-1}$). There seems to be a relationship between phase transformation and formation of PrO$_x$.

Although the parent PNN50-50 phase remains stable at 700 °C and up to ~200 hours at 750 °C, a significant phase transformation follows reaching 24.4% after 500 hours, Figure 1.19c. The phase evolves slowly between 150-300 h and then accelerates, as in the case for PNO. Therefore, a higher Nd concentration on the Pr-site was utilized to further suppress phase transformation. As a result, PNNO25-75 and NNO electrodes had fully preserved phase after long-term thermal annealing at all temperatures, as shown in Figure 1.19c.

In order to investigate the kinetics of thermal phase transformation, an early kinetic model developed by Avrami$^{171-173}$ was adopted. The model is based on a sigmodial increase in volume of a new crystal phase as a function of time, where slow crystallization initiates followed by a rapid increase. Such a behavior is similar to the phase evolution in praseodymium nickelates shown in Figure (6), hence the model by Avrami is appropriate for this study. The experimental data has been fitted using the equation:

$$x = 1 - \exp[-kt^n]$$  \hspace{1cm} (7)

where $x$ is the fraction of parent phase transformed, $k$ is the reaction rate, $t$ is time, and $n$ is the exponent that describes geometry of the growth of a new phase. By arranging the Eq. (7) and expressing it in natural logarithm form as:

$$\ln[-\ln(1-x)] = \ln(k) + n \ln(t)$$  \hspace{1cm} (8)
the isothermal linear plots were generated to determine the values of \( k \) and \( n \) from the least squares fitting. The order of phase transformation in PNO decreases with increase in temperature, with \( n \) decreasing from 2.43 (700 °C), to 2.10 (750 °C), to 1.65 (790 °C), further indicating thermally driven phase transformation. By expressing the reaction rate in its Arrhenius form:

\[
k = k_0 \exp\left(-\frac{E_a}{RT}\right)
\]

where \( k_0 \) is the pre-exponential factor and \( E_a \) is the activation energy for phase transformation, the activation energy can be extrapolated from the logarithmic expression of this equation. A high activation energy, \( E_a \approx 4.40 \text{ eV} \), can be attributed to cation mobility within the structure,\(^{174-175}\) which in turn leads to atomic rearrangements and phase transformation.

**Figure 1.20** illustrates raw XRD plots on phase evolution in electrochemically operated PNNO electrodes. Gold grids\(^{169}\) were used as cathode current collectors providing an exposure window for phase quantification studies. Evolution of PrO\(x\), NiO (in 2\(\theta = 38-42^\circ\)), and new peaks (2\(\theta < 24^\circ\)) shows major transition in PNO phase. Respective magnitude of an arrow at a high intensity nickelate peak (2\(\theta \approx 32^\circ\)) shows a relative drop in nickelate signal after operation, when compared to initial signal in each cell. With an increase in Nd content, the phase evolution is significantly suppressed resulting in fully preserved NNO phase after 500 hours of electrochemical operation. Reproducible results were obtained with multiple cells for each cathode composition. With an increase in Nd content, the phase transformation is suppressed by 40, 65, 75, and 100 %, respectively. The TEM analysis on operated PNO electrode also confirmed formation of PrO\(x\), and even NiO
Figure 1.20 Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours.\textsuperscript{144}

phase, while for PNNO50-50 composition the phase transformation was significantly suppressed.\textsuperscript{144}

1.5.2 PHASE TRANSFORMATION IN DOPED RP NICKELATES (A,B-SITES)

However, as shown in section 1.6 (Figure 1.32a) the tradeoff between power density and phase stability is rather costly. NNO electrode shows up to 4x lower power density at 750 °C when compared to PNO, which stems from suppressed MIEC properties discussed in section 1.3. Therefore, further RP nickelate development was necessary to stabilize the phase but also retain majority of the activity in PNO. Consequently, the Ni site was also manipulated with $d$-block dopants. Figure 1.21a shows phase purity and stability in PNNO(50/50) doped with various B-site cations including Cr, Mn, Fe, Co, and
Zn. The represented molar content for each cation provided the best results among various tested concentrations. Single phase was only obtained with Co and Fe doping, while doping with Cr, Mn, and Zn lead to formation of a secondary PrO_x phase. However, thermal stability studies on PNNO(50/50)-Fe_5(Co_5) showed significant phase transformation after only 150 hours at 790 °C and 870 °C in 3% humidified air. On the other hand, Cu doping provided the most promising results. Figure 1.21b shows selected PNNO(50/50)-Cu_{10} composition retaining single phase after thermal annealing up to 500 hours. Such tremendous phase stability also lead to stable electrochemical operation in full cells (Figure 1.32b), while retaining 75% of activity when compared to PNO. The 5% and 10% Cu doping provided the most promising results as depicted in Figure 1.22.

Aforementioned structural studies show that phase evolution in praseodymium nickelates is in-situ phenomenon and can be linked to respective changes in M-O distances in perovskite and rock-salt layers. However, a question remains on how a structure (M-O distances) can be “frozen” in PNNO-Cu_y during the heating process (Figure 1.18). Through the molecular dynamics simulations of oxygen transport in PNO, Parfitt et al.\textsuperscript{162} showed that oxygen diffusivity has a weak dependence upon the concentration of oxygen interstitials due to a rise in the effective migration barrier, which is in agreement with neutron scattering studies in related RP structure materials.\textsuperscript{176} Since the cathode materials addressed in this chapter follow the general de-intercalation of interstitial oxygen with increase in temperature,\textsuperscript{134} then a possible explanation for the retained shrinkage of oxygen ion conduction paths in PNNO(50/50)-Cu_y can be associated with the proposed stiffening of the NiO_6 perovskite layer due to effective pinning of oxygen interstitials.\textsuperscript{162}
Figure 1.21 (a) Phase purity and phase stability in PNNO(50/50) powders with various dopants on the Ni-site including Cr, Mn, Fe, Co, and Zn. (b) Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours.

Figure 1.22 Quantified phase evolution in PNNO5050-Cu_y electrodes at elevated temperatures.
This mechanism reduces the ease at which the octahedra can tilt, and therefore do not further impact the conduction paths in the rock-salt layer. Furthermore, the Cu$^{2+}$/Cu$^{3+}$ redox couple may also be responsible for the octahedral stiffening. This would explain a narrow concentration window of Cu that can be used to stabilize the phase. In absence of Cu the Ni$^{2+}$/Ni$^{3+}$ redox couple alone cannot suppress structural changes, while higher Cu concentration may yield excess of Cu$^{3+}$ which leads to additional strain, hence the inability to refine PNNOCu$_{30}$ in orthorhombic Bmab symmetry.

Obtaining a single orthorhombic phase with 5, 10, and 20 mol.% Cu doping in PNO was challenging at various temperatures. In all cases at least ~1 mol.% of PrO$_x$ was detected during thermal annealing (see chapter 8 of this thesis). The phase transformation occurred in all samples (indicative by substantial evolution of PrO$_x$ phase) within 150 hours at 790 °C and 870 °C in 3% humidified air. These results also show that Cu-doping alone is not sufficient in stabilizing the PNO phase. Therefore, based on our results we propose that less available Pr cations for oxidation, due to Nd substitution on the Pr-site, and shrinkage in oxygen ion conduction paths, due to Cu-doping on the Ni-site, mutually suppress the formation of PrO$_x$ and phase transformation in praseodymium nickelates. Due to shrinkage of the rock-salt layer (decrease in oxygen occupancy)$^{177}$ and decrease in (Pr,Nd)-O$_i$ distance, the Pr is less likely to be oxidized and more energy is required (higher temperature) to remove it from the structure. This leaves a very narrow phase transformation window, as 1150 °C was the annealing temperature for PNNOCu$_y$. Consequently, the suppressed formation of PrO$_x$ leads to less local stress between the two phases, due to 68% thermal mismatch, and stable long-term phase.
1.5.3 PHASE TRANSFORMATION IN THERMAL VS. ELECTROCHEMICAL SYSTEMS

During long-term phase durability and performance studies\textsuperscript{121, 169} our group observed that phase transformation in electrodes after electrochemical operation did not equate to those thermally annealed in symmetric cells. Since the phase transformation in operating praseodymium nickelate electrodes is rarely reported, this discrepancy has not been addressed in the open literature. Instead, the conventional approach to evaluate phase evolution in praseodymium nickelates includes thermal annealing studies on powders and electrodes in symmetric cells. After annealing, the resulting materials are cooled down and studied via XRD. However, this method is based on thermodynamics of phase transformation, and may not necessarily represent phase evolution behavior in operating cells. During thermal annealing the material eventually reaches thermal equilibrium, and the phase evolution is governed by the thermodynamic variables. On the other hand, a SOFC does not operate in equilibrium regime due to exchange of matter and energy with the surroundings. Consequently, the thermodynamics may no longer dominate and the role of electrochemical potential on the phase transformation requires further consideration.

Figure 1.23 shows quantified\textsuperscript{169} phase evolution in PNNO series on thermally annealed electrodes for 500 hours at 750 °C, and electrochemically operated electrodes in full cells at 0.80 V. Two sets of full cells show reproducible phase transformation. However, it is imperative to note that phase transformation in thermally annealed electrodes is substantially lower than in operated electrodes. This finding brings to a question as to what extent do operating conditions on PNNO materials influence the phase transformation, which has been linked to performance degradation in full cells.
Figure 1.23 Phase evolution in thermally annealed (750 °C) and electrochemically operated \((Pr_{1-x}Nd_x)_{2}NiO_4\) electrodes after 500 hours at 750 °C and 0.80 V.

Electrochemical operation generates difference in electrochemical potential across the fuel cell, which can be considered as analogous to temperature gradients or pressure differences that drive phase transformations in other systems. Therefore, better understanding of such behavior in solid oxide fuel cells is of fundamental importance.

During thermal annealing, the changes on the electrode surface and in the bulk are only affected by fluctuations in the thermodynamic parameters (e.g. temperature, pressure, molar number, and the chemical potential). However, an operating SOFC is a non-equilibrium system subjected to continuous and non-linear flux across the material. During electrochemical reaction, the electrode undergoes a transfer of matter and energy with the surroundings and is also subject to external thermodynamic forces. Furthermore, the presence of electrochemical potential, as a dominating driving force in operating cells,
cannot be overlooked. An attempt to further obtain understanding of this phenomena has been addressed in detail in chapters 10 and 11 of this thesis.

1.6 ELECTROCHEMICAL PERFORMANCE IN RP NICKELATES AND CUPRATES

Unlike the abundant conduction and structural studies of RP nickelates, discussed in sections 1.3 and 1.4, the performance evaluation reports are rather limited. This may stem from the complexity of measurements of SOFCs and difficulty in obtaining reproducible measurements, which would allow statistically significant comparison between different cathode materials. In this section, an attempt was made to combine the relevant results from the literature reports and further expand on our findings. **Figure 1.24a** shows the distribution of the literature reports on nickelates from 1990 to 2017. Majority of the studies (~92%) were focused on materials properties (e.g. phase purity, phase transformation, conductivity). However, the performance reports account for less than 8% of total research in the field of nickelates, with 4% of reports involving research on symmetric cells. Since the common electrolyte thickness in electrolyte supported cells is between 100-250 μm, the ohmic resistance of the cell is high, allowing only relatively low current density to be injected into the cell, which is rather unusual in SOFC stacks. Furthermore, the two electrodes in symmetric cells will undergo two different processes under electrochemical potential, the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), which brings to a question if the contribution from the two electrodes can be considered equal during quantification studies. During prolonged operation or at elevated currents the OER electrode undergoes delamination due to the pressure buildup at the electrolyte/electrode interface. This occurrence does not allow
systematic studies since both electrodes are changing, hence it is challenging to isolate the contributions of individual electrodes towards area specific resistance (ASR) measurements.

As a result, the majority of the performance reports (~85%) present only the initial cell performance without much consideration towards performance stability and cell durability, Figure 1.24b. It is imperative to note that these reports only address the cell and electrode ASR measured within a few hours from the cell startup, without the actual power density measurements. Unfortunately, such approach does not provide a full representation of the materials activity and durability in SOFCs. On the contrary, it only provides the very initial cathode resistance and activity, which from industrial perspective, is of significantly less interest when compared to stable long-term operation in full cells. It is well know that the targeted SOFC operation of ~40,000 hours requires stable operation with less than 4%/1,000 hour degradation. A very few performance reports (~10%) actually address the power density within at least 25 hours of operation, while only 5% of the performance

![Figure 1.24](image-url) Representation of nickelate reports between 1990-2017. (a) Percentage of reports on nickelate material studies (conductivity, diffusion, surface exchange), cathode materials on symmetric cells, and performance in symmetric and full cells. (b) Percentage of reports presenting only initial studies, performance stability between 25-100 hours, and long term operation over 500 hours.
reports address the prolonged electrochemical operation beyond 500 hours. The majority of performance stability reports originate from our research group with the exception of a handful of studies from other researchers.

1.6.1 PERFORMANCE IN MONOLITHIC ELECTRODES

Figure 1.25a shows combined (1190-2017) electrode ASR for PNO, LNO, and NNO electrodes measured predominantly in symmetric cells, with the exception of our work which was performed on full anode supported cells. The selected reports showed the smallest ASR for PNO electrode in a single cell, while the ASR for NNO electrode was up to two orders of magnitude higher at low temperatures. With increase in temperature the activity for ORR increase, hence the discrepancy among the electrode ASR is reduced to within an order of magnitude. The high activity towards ORR of PNO stems from its unique properties over a wide temperature range, including a high oxygen diffusion coefficient (e.g. $8 \times 10^{-8}$ cm$^2$ s$^{-1}$ at 750 °C), and a high surface exchange coefficient ($D$, e.g. $2 \times 10^{-6}$ cm s$^{-1}$ at 750 °C).

Figure 1.26a-b shows orders of magnitude higher $k$ for PNO when compared to commonly used LSCF and LSNF materials. Furthermore, $D$ is
also an order of magnitude higher over the entire temperature region of interest. Among the monolithic nickelates, PNO has the highest $k$ and $D$, making it a superior candidate for ORR. **Figure 1.25b** shows the initial power density for the monolithic electrodes measured between 650-850 °C at 0.70 V and 0.80 V. It can be immediately seen that only a few reports show initial power density for LNO cells, which were primarily measured in electrolyte supported (GDC) cells at low temperature. Furthermore, only a handful of reports show the power density sweep over the temperature region of interest for PNO and NNO cells. The power density for PNO cells is 6x higher when compared to NNO. Although the power density for NNO cells increases by an order of magnitude with increase in temperature, its activity for ORR is substantially smaller.

The higher power density of PNO stems from its lower activation energy ($E_a$) for ORR. **Figure 1.27a** shows the ln(ASR$_{e}$) as a function of 1/T for all (Pr$_{1-x}$Nd$_{x}$)$_2$NiO$_4$ (PNNO) electrodes measured at OCV in anode supported full cells. The electrode ASR decreases with increasing temperature for each cathode composition. PNO electrode has comparably smaller ASR than other NNO cells between 650 °C and 800 °C at all measured currents. This can be attributed to smaller activation energy for the overall electrode reaction for PNO (0.87 ± 0.02 eV vs. 1.15 ± 0.02 eV). Extrapolated activation energy values from the distribution of relaxation time (DRT) analysis$^{121}$ (Figure 1.27b) further show the increase in Ea in NNO. The greater activation energy in NNO results in more active electrode at temperature >800 °C. Therefore, a desirable compositions can be formulated while retaining relatively stable long-term performance, based on the operating conditions of SOFC stacks (e.g. temperature and voltage).
The measured $E_a$ values are in good agreement with the literature reports on monolithic electrodes. Table 1.9 shows the cell configurations used along with the calculated $E_a$. Our work on PNO electrodes shows among the lowest $E_a$ values, while NNO electrode is in good agreement with majority of the reports. The $E_a$ for LNO electrode ranges between 1.08-1.3 eV, which is still significantly higher when compared to PNO. It is imperative to note that majority of tabulated values come from the measurements on
symmetric cells, as previously discussed, while our work is based on anode supported full cells. The agreement between the literature values and the results on full cells at OCV allowed us to generate systematic work on SOFCs.

**Table 1.9** The cell configuration and calculated activation energy for electrode reaction for monolithic cathodes. Cells with similar configuration and operating temperatures were compared.

<table>
<thead>
<tr>
<th>Monolithic Cathode</th>
<th>Cell Configuration</th>
<th>Electrode Thickness (µm)</th>
<th>Ea for ORR (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PNO</strong></td>
<td>Ni-YSZ/YSZ/GDC/nickelate full cells</td>
<td>20</td>
<td>0.87 ± 0.02</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>nickelate/GDC/YSZ symmetric cells</td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nickelate/YSZ symmetric cell</td>
<td>15-20</td>
<td>0.90</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>BaCeYO3/nickelate symmetric cells</td>
<td>*/</td>
<td>0.95</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>nickelate/BCY10 symmetric cells</td>
<td>20</td>
<td>0.85</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>nickelate/GDC/YSZ symmetric cells</td>
<td>25-30</td>
<td>0.92</td>
<td>210</td>
</tr>
<tr>
<td><strong>LNO</strong></td>
<td>Nickelate/YSZ pellet symmetric cells</td>
<td>7</td>
<td>1.2</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>nickelate/GDC/YSZ symmetric cells</td>
<td>15-20</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nickelate/YSZ symmetric cell</td>
<td>25-30</td>
<td>1.30</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>nickelate/GDC/YSZ symmetric cells</td>
<td>20</td>
<td>1.15</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>nickelate/BCY10 symmetric cells</td>
<td>25-30</td>
<td>1.08</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>nickelate/SDC symmetric cells</td>
<td>*/</td>
<td>1.1</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>nickelate/YSZ symmetric cells</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td><strong>NNO</strong></td>
<td>Ni-YSZ/YSZ/GDC/nickelate full cells</td>
<td>20-25</td>
<td>1.15 ± 0.02</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>Nickelate/YSZ pellet symmetric cells</td>
<td>7</td>
<td>1.3</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>Nickelate/YSZ pellet symmetric cells</td>
<td>*/</td>
<td>1.0</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>Ni-YSZ/nickelate full cell</td>
<td>20</td>
<td>1.12</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>nickelate/YSZ symmetric cells</td>
<td>20</td>
<td>1.2</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>nickelate/BCY10 symmetric cells</td>
<td>20</td>
<td>1.12</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>nickelate/GDC/YSZ symmetric cells</td>
<td>25-30</td>
<td>1.1</td>
<td>210</td>
</tr>
</tbody>
</table>

* the electrode thickness or sufficient SEM images were not provided
1.6.2 PERFORMANCE IN DOPED ELECTRODES

A common approach towards manipulating the cell performance in praseodymium nickelates involves substitution and doping on Pr and Ni sites. However, such attempt requires tedious and reproducible SOFC studies, which allow for statistically significant results. Figure 1.28 illustrates reproducibility of SOFC measurements on (Pr$_{0.50}$Nd$_{0.50}$)$_2$NiO$_4$ (PNNO50-50) electrodes at various temperatures. The performance, Figure 1.28a, is within 2% for all cells. The consistent OCV values of 1.10 ± 0.04 V indicate quality seals and consistent cell assembly. The calculated power density as function of temperature, Figure 1.28b, further illustrates the confidence in our full cell studies, which granted studies on the entire (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ (PNNO) series. Figure 1.27

![Figure 1.28 (a) Reproducible operation for multiple cells. (b) Power density as function of temperature.](image)

shows the $E_a$ for the PNNO series. With increase in Nd content the activation energy increases by 28%. Such difference in $E_a$ for overall ORR was reflected in the performance studies. Figure 1.29 shows i-V and power density curves on PNO, PNNO50-50, and NNO cells, respectively, measured between 650-850 °C. It is evident that with increase in Nd content the performance decreases substantially at all temperatures. However, for Nd-rich
Figure 1.29 Initial i-V and power density curves for selected (Pr<sub>1-x</sub>Nd<sub>x</sub>)<sub>2</sub>NiO<sub>4</sub> cathodes, as function of x, operated between 650 and 850 °C.

Electrodes the temperature increase leads to significantly larger performance changes (up to an order of magnitude for NNO). For instance, the performance increases by threefold in PNO and by 13x in NNO cells when increasing temperature from 650 °C to 850 °C.

Various changes on the A and B sites on monolithic PNO, LNO, and NNO electrodes were performed over the course of last 26 years. Figure 1.30a shows the ASR<sub>electrode</sub> as function of temperature on PNO-based cathodes. The three baselines (PNO, LNO, and NNO) are also shown. The substitution with Sr on the Pr-site was studied by multiple groups. It was found that 25-40% Sr substitution seems to further reduce the ASR<sub>electrode</sub> at OCV down to 0.1 Ω cm<sup>2</sup> at 800 °C. Such change can be mainly attributed to smaller size and charge of Sr<sup>2+</sup> when compared to larger Pr<sup>3+</sup>, and its...
effect on the oxygen occupancy in the structure. The activation energy for ORR is higher for Sr-doped PNO (Table 1.10), ranging from 1.35 eV for 15% Sr doping to 1.45 eV for 45% Sr doping. However, the phase stability studies on these compositions are rarely reported, which is of a great concern, as Sr containing compounds are known to undergo cation segregation and demixing, as is the case in LSCF and LSM electrodes. Other notable compositions include doping on the Ni site with Cu and Co. However, in both cases the ASR\textsubscript{electrode} increases and can be attributed to increase in $E_a$ for overall ORR (1.05 ± 0.02 eV for 5% Cu doping in PNNO50-50 and 1.08 ± 0.02 eV for 10% Cu doping), which stems from decrease in mixed conducting properties (conductivity). Nomura et al.\textsuperscript{136}

Figure 1.30 Doped monolithic electrode ASR at OCV from the year 1190-2017 literature reports in the temperature region between 600-850 °C on PNO-based electrodes (a), LNO-based electrodes (b), and NNO-based electrodes (c). PNO, LNO and NNO baselines are provided on each figure. Respective references are provided in parentheses.
reported low ASR values (e.g. 0.13 Ω cm² at 700 °C) with 10% Co doping in Sm-doped ceria supported full cells. However, the phase stability studies were not addressed, nor was the long-term performance studied. Our work on Co-doped PNNO compositions (Figure 1.21a) showed that although a single phase can be obtained with Co doping, the phase transformation occurs with substantial formation of PrOₓ under operating temperatures. On the other hand, Cu doping is a promising solution to stabilized long-term performance.

Similar approach was taken towards decreasing the ASR_{electrode} in LNO composition. Figure 1.30b shows the ASR_{electrode} as function of temperature on LNO-based cathodes. In this case however, Sr doping¹³³ on the La-site did not yield significantly lower ASR_{electrode} when compared to the parent compound.¹³³ On the contrary, with 15-20% Sr doping the resistance increased by 30x, surpassing the resistance of NNO.¹³³ The main difference between the two sets of measurements is the presence of GDC interlayer in Sr-doped LNO cells,¹³³ Table 1.10. Perhaps the presence of an ionic conductor (GDC interlayer) along with 10-15 μm thinner electrodes overshadowed the changes in electrode resistance with Sr doping. The overall activation energy for ORR is higher when compared to 1.1 eV on average for LNO. For LaSrNiO₄, the Eₐ reaches 1.41 eV. Ca doping on the La-site also showed increase in ASR_{electrode}. With increase in Ca content the electrode resistance continuously increased (by 3x for 10% Ca doping, 5x for 15% Ca doping, and 30x for 20% Ca doping), which can be attributed to increase in Eₐ,ORR (1.29 eV for 20% Ca doping). Cu doping leads to relatively similar Eₐ values when compared to LNO baseline. Combination of doping on both Pr- and Ni-sites showed more promising results. The series of La₁.7₀Ca₀.₃₀Ni₁.₃₅CuₓO₄ was studied with varying Cu content.¹⁵³ It was found that with increase in Cu concentration the ASR_{electrode} decreased, especially at higher temperature.
reaching whopping 0.04 Ω cm² at 850 °C with 30% Cu doping. The 20% Cu doping yielded comparable results to the parent LNO compound. However, as was the case with PNO doping, the phase stability studies on electrodes were not addressed. It is also imperative to note that \((\text{La}_{0.9}\text{Sr}_{0.1})\)(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{3-\delta}\) (LSGM) electrolyte was used as support for these cathode compositions (Table 1.10), when compared to typical YSZ. Since our group has not conducted systematic and reproducible work on LNO-based electrode, it is rather difficult to say where the \(\text{ASR}_{\text{electrode}}\) baseline should be relatively to other compositions, as doping with Sr is expected to reduce the electrode resistance (due to increase in \(\sigma_{\text{tot}}\), discussed in section 1.3.2) as is the case with PNO.

According to the literature reports, modifications to NNO electrode composition show a range of \(\text{ASR}\) values; from low resistance comparable to PNO electrode, to substantially higher resistance in a single cell, Figure 1.30c. The activation energy for ORR is higher for all compositions when compared to the baseline NNO compound (Table 1.10), indicating that structural changes and changes in oxygen occupancy govern the performance of these materials. Similar to PNO doping with Sr, the \(\text{ASR}_{\text{electrode}}\) decreases with Sr doping. The 10% and 40% Sr concentration provides the lowest \(\text{ASR}_{\text{electrode}}\), which is close to matching the values for PNO. Doping with low concentration of Cu (5-15%) provides the most promising results. The minimum \(\text{ASR}_{\text{electrode}}\) was obtained for 5% Cu doping (0.18 Ω cm² at 850 °C), with fivefold decrease in electrode resistance. However, further increase in Cu content leads to increase in electrode resistance, which is higher than the baseline NNO. The \(\text{Nd}_2\text{CuO}_4\) leads to an order of magnitude increase in \(\text{ASR}_{\text{electrode}}\). In all three cases (PNO, LNO, NNO) the \(\text{ASR}_{\text{electrode}}\) seems to be highly dependent on the type and the concentration of the dopants. The origin of such changes have not yet been fully
Table 1.10 The cell configuration and calculated activation energy between 650 – 850 °C for electrode reaction for doped PNO, LNO, and NNO cathodes.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Cell configuration</th>
<th>Electrode thickness (μm)</th>
<th>Calculated Ea (eV) at 600-850 °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PNO-based</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.75}$Nd$</em>{0.25}$)$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$_2$NiO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.25}$Nd$</em>{0.75}$)$_2$NiO$_4$</td>
<td>Ni-YSZ/YSZ/GDC/ nickelate full cells</td>
<td>20</td>
<td>1.14 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$<em>2$Ni$</em>{0.95}$Cu$_{0.05}$O$_4$</td>
<td></td>
<td></td>
<td>1.05 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$<em>2$Ni$</em>{0.90}$Cu$_{0.10}$O$_4$</td>
<td></td>
<td></td>
<td>1.08 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.2}$Sr$</em>{0.8}$NiO$_4$</td>
<td></td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.2}$Sr$</em>{0.8}$NiO$_4$</td>
<td>Nickelate/Sm$<em>{0.2}$Ce$</em>{0.8}$O$_4$</td>
<td>~15</td>
<td>1.44 ± 0.02</td>
<td>157</td>
</tr>
<tr>
<td>Pr$<em>{1.2}$Sr$</em>{0.3}$NiO$_4$</td>
<td>镍叶/Sm$<em>{0.2}$Ce$</em>{0.8}$O$_4$</td>
<td>1.9 symmetric cells</td>
<td>1.24 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.2}$Sr$</em>{0.5}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.35 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Pr$<em>{1.5}$Sr$</em>{0.7}$NiO$_4$</td>
<td>Nickelate/YSZ</td>
<td>~20</td>
<td>1.43 ± 0.02</td>
<td>181</td>
</tr>
<tr>
<td>Pr$<em>{1.5}$Sr$</em>{0.9}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.45 ± 0.02</td>
<td></td>
</tr>
<tr>
<td><strong>LNO-based</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.8}$Cu$_{0.2}$O$_4$</td>
<td></td>
<td>1.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.6}$Cu$_{0.4}$O$_4$</td>
<td>Nickelate/YSZ</td>
<td>/</td>
<td>1.15 ± 0.02</td>
<td>20</td>
</tr>
<tr>
<td>La$<em>2$Ni$</em>{0.4}$Cu$_{0.6}$O$_4$</td>
<td>symmetric cells</td>
<td></td>
<td>1.10 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>LaCuO$_4$</td>
<td></td>
<td></td>
<td>1.10 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.90}$Sr$</em>{0.10}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.16 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.80}$Sr$</em>{0.20}$NiO$_4$</td>
<td>Nickelate/GDC/YSZ</td>
<td>15</td>
<td>1.14 ± 0.02</td>
<td>182</td>
</tr>
<tr>
<td>La$<em>{1.70}$Sr$</em>{0.30}$NiO$_4$</td>
<td>symmetric cells</td>
<td></td>
<td>1.28 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.60}$Sr$</em>{0.40}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.29 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>LaSrNiO$_4$</td>
<td>nickelate/BCY10</td>
<td>20</td>
<td>1.41 ± 0.02</td>
<td>153</td>
</tr>
<tr>
<td>La$<em>{1.90}$Ca$</em>{0.10}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.16 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.80}$Ca$</em>{0.20}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.14 ± 0.02</td>
<td>132</td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$NiO$_4$</td>
<td>nickelate/SDC</td>
<td>25-30</td>
<td>1.28 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.60}$Ca$</em>{0.40}$NiO$_4$</td>
<td>symmetric cells</td>
<td></td>
<td>1.29 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$NiO$_4$</td>
<td></td>
<td></td>
<td>1.26 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$Ni$<em>{0.90}$Cu$</em>{0.10}$O$_4$</td>
<td>nickelate/LSGM</td>
<td>30</td>
<td>1.30 ± 0.02</td>
<td>152</td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$Ni$<em>{0.80}$Cu$</em>{0.20}$O$_4$</td>
<td>symmetric cells</td>
<td></td>
<td>1.53 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>La$<em>{1.70}$Ca$</em>{0.30}$Ni$<em>{0.70}$Cu$</em>{0.30}$O$_4$</td>
<td></td>
<td></td>
<td>1.52 ± 0.02</td>
<td></td>
</tr>
<tr>
<td><strong>NNO-based</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.80}$Sr$</em>{0.20}$NiO$_4$</td>
<td></td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.60}$Sr$</em>{0.40}$NiO$_4$</td>
<td>nickelate/YSZ</td>
<td>20</td>
<td>1.21 ± 0.02</td>
<td>110</td>
</tr>
<tr>
<td>Nd$<em>{1.40}$Sr$</em>{0.60}$NiO$_4$</td>
<td>symmetric cells</td>
<td></td>
<td>1.15 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{1.20}$Sr$</em>{0.80}$NiO$_4$</td>
<td></td>
<td>1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.90}$Cu$_{0.10}$O$_4$</td>
<td></td>
<td></td>
<td>1.52 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.80}$Cu$_{0.20}$O$_4$</td>
<td></td>
<td></td>
<td>1.43 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.70}$Cu$_{0.30}$O$_4$</td>
<td></td>
<td></td>
<td>1.43 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.60}$Cu$_{0.40}$O$_4$</td>
<td>nickelate/SSZ/Ni-YSZ full cells</td>
<td>15</td>
<td>1.70 ± 0.02</td>
<td>183</td>
</tr>
<tr>
<td>Nd$_{2}$NiCuO$_4$</td>
<td></td>
<td></td>
<td>1.64 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.40}$Cu$_{0.60}$O$_4$</td>
<td></td>
<td></td>
<td>1.77 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Nd$<em>{2}$Ni$</em>{0.20}$Cu$_{0.80}$O$_4$</td>
<td></td>
<td></td>
<td>1.77 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>NdCuO$_4$</td>
<td></td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* the electrode thickness or sufficient SEM images were not provided
understood for each composition (for instance why does increase in Cu concentration beyond 15% in NNO leads to sharp increase in $\text{ASR}_{\text{electrode}}$) but seem to stem from the changes in materials intrinsic properties (electronic and ionic conductivity), and the structural changes as discussed in section 1.3 (see also chapter 8 of this thesis). By introducing dopants with different physical properties (size and charge) into the monolithic system, the intrinsic response of a material will change. Furthermore, different size of cations will lead to changes in the overall atomic structure, not necessarily the phase transformation, that will influence the ionic transport and oxygen occupancy. The results show that although the $\text{ASR}_{\text{electrode}}$ may be reduced with doping, the entire set of materials properties should be considered, as the synergy of all property changes influence the electrode performance in SOFCs.

**Figure 1.31** shows initial power density for cells with doped electrodes measured at various temperatures and voltages. The highest power density was measured by our group for monolithic PNO, closely followed by PNNO75-25 and PNNO50-50 electrodes, **Figure 1.31a.** Sr, Co, and Cu- doped PNO electrodes show lower performance (in increasing order), which is in agreement with calculated $E_a$ values. Due to lack of full cell measurements only the measurements at 700 °C were presented from the open literature, while the rest of the data was obtained by our group. **Figure 1.31b** illustrates similar plot for LNO and NNO-based electrodes. The highest power density was obtained for NNO, 10% Cu doped NNO, and 5% Cu doped NNO (in descending order). On the other hand, the highest performance (700 – 800 °C) for LNO-based electrodes was obtained for compositions with simultaneously modified La and Ni-sites. Co and Fe- doping shows improved (up to 2x) power density at 600 °C when compared to LNO. However, the
question arises on the performance stability of these electrodes, as SOFC systems require relatively stable long-term operation.

1.6.3 PERFORMANCE STABILITY IN FULL CELLS

Figure 1.32a shows the long-term performance stability for PNNO cathodes, including monolithic PNO and NNO, operated at 0.8 V and 750 °C in full cells. Cell performance for each cathode composition was within 9% among multiple cells measured. A rapid initial degradation rate of 3.50% occurs for PNO cells within first 150 hours of operation, after which the performance remains constant. This can be attributed to relatively fast phase evolution in PNO.\(^{169}\) For cells with Nd substituted cathodes, the degradation rates are relatively constant. However, due to slower kinetics\(^{144}\) and lower \(E_a\)\(^{121}\) (due to suppressed mixed conduction properties),\(^{144}\) the power density for NNO cells is 4x lower than in PNO. The 6.40%/1,000 hours performance degradation in PNO cells is of a concern; hence, Nd substitution was employed to alleviate phase transformation in PNO (Figure 1.20). As a result, the NNO cells show a remarkable 0.06%/1,000 hour
degradation. However, due to low power density in NNO, the highest potential for SOFC application seem to show the midrange composition (PNNO50-50), which has 26x lower performance degradation than PNO while retaining ~75% of its activity. Multiple cells for each cathode composition show reproducible operation, ensuring statistical significance of the results. Combined doping on the Pr and Ni-sites, Figure 1.32b, shows further improvements in performance stability. With 5% and 10% Cu doping in PNNO50-50 electrodes the cell performance remains stable for 500 hours, without any degradation. These results provide a narrow window of promising cathode composition that retain majority of activity of PNO, while enhancing the long-term durability. More detailed studies are reported in chapters 5 through 7 of this thesis.

![Figure 1.32](image.png)

**Figure 1.32** Performance stability for (a) \((Pr_{1-x}Nd_x)_{2}NiO_4\) cathodes operated at 0.80 V and 750 °C, and (b) \((Pr_{1-x}Nd_x)_{2}Ni_{1-y}Cu_yO_4\) cathodes operated at 0.80 V and 790 °C for 500 hours.

1.6.4 COMPOSITE AND IMPREGNATED ELECTRODES

Another approach towards lowering the ASR\(_{\text{electrode}}\) and stabilizing the cell performance is through composite electrodes. Although in its early stages of development in nickelates, the composited electrodes with perovskite mixed conductors such as
LSM/YSZ and LSCF/GDC have been widely investigated. Composite electrodes consists of a mixed conducting material (monolithic or doped electrode) mixed with an oxygen ion conductors (e.g. GDC, YSZ). If ionic conductor has much higher $D$ than the mixed conductor, then it provides a shorter pathway for ionic transport within the cathode. Furthermore, the effective thickness of the electrode can be increased which leads to larger active surface area for ORR.

Impregnated electrodes involve wet infiltration of a solvent solution containing metal salts precursors into a pre-fired and porous backbone of mixed conductor. Upon drying and calcination a metal oxide coating is formed on the particle surface of mixed conductor. One approach towards infiltration is to introduce catalytic material that enhances the performance of a mixed conductor. Another approach is to infiltrate an ionic conductor (eg. GDC) with a mixed conductor (e.g. LNO) to produce a composite cathode. In both cases a nano-scale particles are deposited onto the particle surface of a porous base which effectively increases the catalytic properties of a material. A key advantage towards infiltrating a pre-fired and porous backbone is that the particle morphology (nano-scale) of infiltrated metal oxide can be retained, as it does not require high temperature calcination. Therefore, the catalytic area for ORR can be substantially increased.

Nicollet et al. showed that the calcination temperature of infiltrated LNO into the GDC backbone plays a substantial role towards reducing the $R_{\text{electrode}}$. Measurements on YSZ supported symmetric cells show $R_{\text{pol}}$ of 40 $\Omega$ cm$^2$ for infiltrated electrodes annealed at 1100 °C. However, with annealing at 900 °C the $R_{\text{pol}}$ was substantially reduced by tenfold to 4 $\Omega$ cm$^2$ at 500 °C and to 0.15 $\Omega$ cm$^2$ at 600 °C. The reduced $R_{\text{electrode}}$ has been attributed to reduced diffusion length of infiltrated electrode when compared to the
GDC backbone.\textsuperscript{187} The Arrhenius plots of the polarization resistance show reduced $E_a$ from 1.12 eV (GDC) to 0.96 eV for the infiltrated GDC backbone.\textsuperscript{187}

Similarly, NNO impregnated Sc-stabilized zirconia (SSZ) composite electrode allows reduction of $ASR_{\text{electrode}}$ in full cells to 0.5 $\Omega$ cm$^2$ at 750 °C and 0.15 $\Omega$ cm$^2$ at 800 °C at OCV.\textsuperscript{188} It is imperative to note that a large discrepancy in $ASR_{\text{electrode}}$ was measured in symmetric and full cells.\textsuperscript{188} In symmetric cells the NNO-SSZ electrode showed substantially lower ASR of 0.04 $\Omega$ cm$^2$ at 800 °C and OCV.\textsuperscript{188} Such discrepancy further indicates the necessity for full cell configuration to evaluate the cell performance and electrode polarization. The NNO-SSZ composite electrode exhibited maximum power densities of 1.26 W cm$^{-2}$ (800 °C) and 0.73 W cm$^{-2}$ (700 °C), which is substantially higher when compared to 0.07 W cm$^{-2}$ at 700 °C for single phase NNO (Figure 1.29c).\textsuperscript{188} The measured power density in microtubular NNO-YSZ impregnated cells at 800 °C was also high, 0.76 W cm$^{-2}$.\textsuperscript{189} The electrical conductivity was enhanced by 2.8x at 750 °C (125.8 S cm$^{-1}$ in NNO-GDC\textsuperscript{188} vs. 45 S cm$^{-1}$ for NNO),\textsuperscript{144} which can be attributed to reduced length of conduction paths. However, prolonged heat treatments of NNO-SSZ showed separation of NiO and Nd$_2$O$_3$ phases, which could effectively negatively influence the long-term performance.\textsuperscript{188} Furthermore NNO-YSZ electrodes shower reaction between the two phases creating an insulating Nd$_2$Zr$_2$O$_7$ phase.\textsuperscript{188} However, since the long-performance studies are rarely reported on composite electrodes, additional studies are required to understand electrode behavior under electrochemical conditions in SOFCs.

Another notable example of composite electrodes is the PNO infiltration into LSGM backbone,\textsuperscript{190} which also showed lowered electrode polarization of 0.11 $\Omega$ cm$^2$ at 650 °C with 14 vol.% PNO loading. Furthermore, after thermal aging for 100 hours at 650
°C in air the PNO-LSGM retains a parent phase with marginal formation of PrO\textsubscript{x} and higher order phase.\textsuperscript{190} The phase preservation upon thermal annealing was associated with a physical volume constraint on any phase transformation, due to direct contact between the infiltrate electrode and LSGM. Alternatively, an interdiffusion of La, Sr, Gd from LSCG into the PNO could help stabilize the parent PNO phase.\textsuperscript{190} Both La and Gd have been shown to increase the low temperature stability of the PNO phase.\textsuperscript{190-192} However, as discussed in more detail in chapters 10 and 11 of this thesis, the thermal annealing studies cannot fully simulate the electrode behavior in SOFCs since they overlook the role of electrochemical potential as the main driving force towards structural changes in electrode and the cell performance. The stability of R\textsubscript{pol} measured in symmetric cells with PNO-LSGM electrodes\textsuperscript{190} further confirms this statement as R\textsubscript{pol} increases by 25% after only 500 hours of tests at 650 °C.

1.6.5 SOLID OXIDE ELECTROLYSIS AND OXYGEN EVOLUTION REACTION

Besides the heat and power generation in SOFCs the ceramic fuel cells can also operate in a reversible mode, known as solid oxide electrolysis cells (SOECs), by simple change in the current direction. Before hydrogen can become an alternative fuel, a massive production via clean and environmentally friendly process is required with low or no CO\textsubscript{2} emissions. The high temperature steam electrolysis is one of the most promising ways to reach this goal, with a substantially higher efficiencies when compared to low temperature processes. By splitting water into hydrogen and oxygen gasses using electricity and heat, no environmentally detrimental products are generated. Since the electrode polarization remains as one of the limiting factors towards development of high efficiency systems, the interest for nickelates has also grown towards SOEC applications due to a low R\textsubscript{pol} in a
single cell. Although not as intensively studied as commercial LSCF electrodes, the recent interest for nickelates towards SOEC applications resulted in handful of literature reports.

With change in current direction the voltage of the cell increase from ~1.1 V (OCV) to higher values, based on the injected current density. Although now an endothermic system, the SOEC allows for electrolysis of widely spread CO/CO₂ fuels, syngas, and steam. Therefore, nickelates as oxygen evolution electrodes in SOEC cells are no exception to advanced research development. The main attribute towards nickelate studies as OER electrodes is their ability to accommodate excess oxygen (over-stoichiometry) in the structure (in forms of oxygen interstitials), especially under oxidizing conditions. This property allows to alleviate stress at the triple phase boundary (TPB, electrolyte/nickelate/gas interface) due to possible inability of electrode to accommodate excess oxygen species transported by oxide ion conducting electrolyte. Therefore, less pO₂ buildup is generated at TPB, thus mitigating the problem of electrode delamination at the nickelate/electrolyte interface. Recently, it was reported that under anodic polarization (nickelate undergoing OER) the Rₚₒˡ in LNO was lower than under cathodic polarization. Our preliminary work also seems to point in the same direction for PNO electrode, as injection of positive potentials (OER) generates lower Rₚₒˡ in a single cell. Figure 1.33a-b shows EIS plots for YSZ supported PNO cell tested under positive and negative potentials while changing the pO₂. At both 100 mV and 250 mV the measured Rₚₒˡ in a single cell was lower when compared to injection of negative potential (ORR), Figure 1.33c.

Ogier et al. demonstrated 58% steam to hydrogen conversion ratio at 800 °C in an electrolyte supported full cell (Ni-YSZ/YSZ/GDC/PNO), utilizing 90 vol.% H₂O -10
vol.% H₂ as fuel and LNO and PNO electrodes for OER. The measured current density at 1.3 V (800 °C) reached relatively high -0.9 A cm² with PNO electrode, which is comparable to commercial LSCF cells. Reversible operation in cells with NNO electrode,¹⁹⁶ and similar cell configuration (Ni-CGO/YSZ/NNO), also shows promising results. The NNO has higher oxygen over-stoichiometry than LNO-based oxides¹⁰⁷; hence, it attracts interest for potentially improved SOEC performance. At 1.3 V and the fuel ratio mixture of p(H₂O)/p(H₂)=0.9 the measured current densities were 0.40 A cm², 0.64 A cm², and 0.87 A cm² at 750, 800, and 850 °C, respectively. The corresponding steam to hydrogen conversion was 14, 23, and 31%, which is significant improvement over cells with LSM electrodes.¹⁹⁶ Indeed, at 1.3 V the current density (the magnitude) in NNO cells was 1.7x, 3x, and 4.2x higher than from the LSM cells at 850 °C, 800 °C, and 750 °C, respectively. Furthermore, the ASR electrode in SOEC mode was lower than in SOFC mode,¹⁹⁶ which is in agreement with LNO and PNO electrodes. In particular, ASR electrode(NNO) at 750 °C, 800 °C, and 850 °C in SOFC mode was 1.09 Ω cm², 0.74 Ω cm², and 0.60 Ω cm², respectively, when compared to 0.96 Ω cm², 0.58 Ω cm², and 0.43 Ω cm² in SOEC mode, respectively.

Composite electrodes are no exception to SOEC studies. Chen et al.¹⁹⁷ showed that cells with impregnated nano-structured NNO into SSZ exhibit current densities of 1.08 A cm², 0.68 A cm², 0.44 A cm², and 0.23 A cm² at 800 °C, 750 °C, 700 °C, and 650 °C, respectively, when operated at 1.3 V. Up to 69% higher current densities (measured at 1.3 V) when compared to screen printed NNO electrode (0.64 A cm² at 800 °C and 0.4 A cm⁻² at 750 °C),¹⁹⁷ and up to 20% higher current density (measured at 800 °C) when
Figure 1.33 EIS plots on PNO cell under (a) +100 mV (OER), and (b) -100 mV (ORR) as function of oxygen partial pressure at 750 °C. (c) Quantified electrode polarization at various potentials and partial pressures in a single cell.

compared to PNO\textsuperscript{195} shows promising avenue of composite electrodes in development of state-of-the-art SOECs. Comparable results were measured for various fuel compositions ranging from 80/20 to 50/50 H\textsubscript{2}O/H\textsubscript{2} ratio, without major deviations in performance. The measured ASR\textsubscript{electrode} at 800 °C, 750 °C, 700 °C, and 650 °C was 0.15 A cm\textsuperscript{2}, 0.3 A cm\textsuperscript{2}, 0.55 A cm\textsuperscript{2}, and 1.1 A cm\textsuperscript{2} under 50/50 H\textsubscript{2}O/H\textsubscript{2} fuel mixture, which is up to 5x lower than in NNO electrodes operated at 1.3 V\textsuperscript{196}.

These results indicate that that nickelate electrodes are suitable candidates for high temperature electrolysis. However, the lack of long-term durability tests still do not provide
a full story regarding the performance stability of nickelates as OER electrodes in SOEC. Only a short-term stability measurements were provided by a few groups. For instance, Chen et al. performed 25 hour measurements at 0.37 A cm$^{-2}$ and 700 °C on NNO-SSZ composite cells with 7.2% voltage degradation. Such significant degradation requires further durability and structural studies.

1.7 FUTURE RESEARCH DIRECTIONS

1.7.1 The origin of high surface exchange coefficient and the chemical activity toward oxygen reduction

High activity and stability in Pr$_2$NiO$_4$ have not been extensively reported, as discussed in Section 1.2, and therefore warrant further investigation. (1) On-surface exchange and bulk diffusion in high oxygen partial pressures have to be investigated. Measurements in pure oxygen at high pressure (up to 1000 psi) will enable us to solve a discrepancy in activation energies in migration of oxygen interstitials. The discrepancy is most likely related to unpredictable amounts of oxygen interstitials at high temperatures in ambient pressure. Non-stoichiometry will be directly determined by quenching experiments, which were found very reliable to analyze defect concentration in perovskite type oxides. It is necessary to utilize other indirect approaches, including structure refinements of neutron diffraction data, conductivity measurements, and modeling. (2) It is necessary to conduct creep and trace diffusion experiments to determine diffusion coefficient of Ni and possibly Pr. The stability data will be correlated with research work on kinetic demixing in Pr$_2$NiO$_4$. (3) For oxygen reduction process, it is necessary to investigate p(O$_2$) dependence of exchange currents (see discussion in Section
1.2) to investigate possible steps of oxygen adsorption and dissociation processes with active sites as oxygen interstitials.

1.7.2 The origin of retained activity and performance stability in Pr$_2$NiO$_4$

Relatively small performance degradation in PNNO electrodes is inconsistent with significant phase transformation occurring under operating conditions. The best example is Pr$_2$NiO$_4$ phase which after 500 hours of operation at 0.80 V and 750 °C undergoes major phase transformation (up to 100% according to XRD). However, such large phase transformation does not seem to greatly influence the performance stability in full cells, with measured 6.40%/1,000 hours degradation. This brings to a question of how such a significant phase transformation, also confirmed via TEM analysis, could not play a larger role on the performance stability in SOFCs. To address this question high resolution TEM and high flux synchrotron studies are required. Detailed TEM studies may provide better insight into microstructural changes in the material, while the synchrotron studies can detect even the smallest presence of a parent phase. The studies will allow to identify any additional mechanisms that may be responsible for retained activity and performance stability in Pr$_2$NiO$_4$ cells. Chapter 9 of this thesis will address this question in detail.

1.7.3 Electrochemically driven solid-state reaction and phase transformation

The phase transformation in electrodes after electrochemical operation does not equate to those thermally annealed in symmetric cells (see section 1.5.3). Since the phase transformation in operating praseodymium nickelate electrodes is rarely reported, this discrepancy has not been addressed in open literature. During thermal annealing the material eventually reaches thermal equilibrium, and the phase evolution is governed by the thermodynamic variables. On the other hand, a SOFC does not operate in equilibrium
regime due to exchange of matter and energy with the surroundings. Consequently, the thermodynamics may no longer dominate and the role of electrochemical potential on the phase transformation requires further consideration. The driving force for the solid-state reaction and phase transformation is related to the change of local electronic transference numbers with position due to flux of electrons and oxygen ions. As a consequence, local internal oxidation or reduction will take place, which can subsequently result in reactions or phase transformations. Hence, the specimen under operating conditions may be different with what is quenched or naturally cooled. This brings to a new avenue in SOFC field where phase transformation can be electrochemically manipulated. Furthermore, accelerated electrochemical protocols can be developed which can significantly reduce operation time and simulate the long-term operation in fuel cells. More detailed discussion is provided in chapters 4, 7, 10, and 11 of this thesis.

1.7.4 The origin of the difference in chemical activity between composite and monolithic cathodes.

There is no question that composite electrodes are potentially superior to single phase cathodes, because microstructures in two-phase materials are usually finer than in single-phase materials due to the Zener pinning mechanism,\textsuperscript{204-205} in which particle coarsening is suppressed due to the presence of another phase. Laberty et al.\textsuperscript{206} reported that the chemical activity of composite of La\textsubscript{2}NiO\textsubscript{4} and ceria was substantially better than that of monolithic La\textsubscript{2}NiO\textsubscript{4} compound. Pr\textsubscript{2}NiO\textsubscript{4} monolithic composition, however, showed superior activity. In general, if a monolithic cathode material is used, its defect chemistry must be carefully manipulated to ensure mixed conduction in a quite wide range of temperatures and atmospheres. The chemical activity in a composite electrode, comprising
Pr$_2$NiO$_4$ and ceria based oxides, is unknown. Our group is currently working on development of composite electrodes along with long-term studies in full cells.

1.7.5 The role of interlayer on phase transformation in RP phases

The direct contact between an active cathode and YSZ is challenging due to the thermal expansion mismatch between YSZ (11×10$^{-6}$ K$^{-1}$) and cathodes (e.g. 13.2×10$^{-6}$ K$^{-1}$ for Pr$_2$NiO$_{4+\delta}$ and 14.9×10$^{-6}$ K$^{-1}$ for La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$FeO$_{0.8}$O$_3$)\textsuperscript{145, 180} and the formation of an insulating zirconates (e.g. La$_2$Zr$_2$O$_7$)\textsuperscript{207} at the interface. A common attempt to circumvent this challenge is to use doped ceria (e.g. Gd$_{0.20}$Ce$_{0.80}$O$_{1.90}$, GDC20) as an interlayer between the cathode and the electrolyte.\textsuperscript{118, 145, 180, 208-211} The role of the interlayer (aka. buffer) is threefold: (1) to prevent reaction between a cathode and YSZ, (2) to reduce the thermal expansion mismatch, and (3) to maintain oxygen ion transport. For instance, the thermal expansion mismatch between Pr$_2$NiO$_{4+\delta}$ (PNO) and GDC20 (13×10$^{-6}$ K$^{-1}$) is significantly smaller (~1.5%), when compared to ~17% mismatch between PNO and YSZ, resulting in a more stable interface.

Although the interlayer is shown to be capable of preventing cathode/YSZ reaction and suppressing electrode delamination, its role on the cathode phase stability and catalytic activity has remain obscure. To the best of author’s knowledge, this has not been reported in open literature. Our preliminary work shows that the diffusion of Pr occurs from PNO cathode into the interlayer bulk (chapters 3, 4 and 6 of this thesis).\textsuperscript{145} Consequently, it is unknown whether or not the interlayer accelerates the phase decomposition in PNO to form Pr$_6$O$_{11}$ and high-ordered nickelates. A new approach is required to develop an interlayer capable of suppressing the phase decomposition and ideally promote the cathode
performance. This avenue of research has been greatly investigated by our group and is addressed in detail in chapter 12 of this thesis.

1.8 SUMMARY

This review chapter demonstrated the true complexity of RP nickelate systems in which the mixed conduction properties, oxygen content, crystal structure, phase transformation, and electrochemical operation are all interconnected. Separate studies on each one of these properties allows for better understanding towards material operation in SOFCs. Although the total conductivity of a material may be enhanced with elemental substitution and/or doping on A- and B-site in RP nickelates, the integrity of the crystal structure may be violated, which would in turn results in phase transformation. Since the properties of single phase materials are easier to reproduce and study, any phase transformation would lead to a new set of properties that may be difficult to reproduce via simple synthesis. Therefore, retaining active and stable RP nickelate phase is of fundamental importance when applied in SOFCs. The Pr$_2$NiO$_4$-based compounds seem to be the most promising candidates for SOFC applications due to their superior mixed conduction properties (~90 S/cm at and high $\delta=0.22$ at room temperature), high activity towards oxygen reduction reaction ($E_a = 0.87$ eV vs. 1.3 eV for La$_2$NiO$_4$ and 1.15 eV for Nd$_2$NiO$_4$), superior $D$ and $k$ (e.g. $D = 8\times10^{-8}$ cm$^2$/s; $k = 2\times10^{-6}$ cm/s at 700 °C), and low polarization resistance ($R_{pol} = 0.01$ at 600 °C to $R_{pol} = 0.03$ at 800 °C) in a single cell.

However, the phase stability is an issue under operating conditions. The attempts of our group to stabilize the parent Pr$_2$NiO$_4$ phase through substitution with Nd on the Pr-site and Cu on the Ni-site seem to provide the most promising results. The parent (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+\delta}$ compositions retained stable phase up to 500 hours under
electrochemical operation in full cells, while retaining 75% of activity when compared to Pr$_2$NiO$_4$ cells. Due to lack of long-term performance and phase stability studies in open literature it is difficult to say if any other Ln$_2$NiO$_4$-based systems meet this benchmark and as such can also serve as promising candidates for the state of the art SOFC cathodes. Prolonged SOFC operation also pointed out that phase transformation in RP nickelates is greatly dependent on the operating conditions. Although a nickelate composition might seem phase stable during thermal annealing studies (where thermodynamics dominates), it may not be the case during electrochemical operation in full cells (where electrochemical potential as a driving force dominates). This is specifically true for the (Pr$_{1-x}$Nd$_x$)$_2$NiO$_{4+\delta}$ series in which after electrochemical operation, up to 70% larger phase transformation was detected with XRD when compared to thermal annealing studies.

Although some attempts have been made to study the performance of composite/infiltrated electrode (e.g. Ln$_2$NiO$_4$/GDC) the long-term stability studies have not been reported, which requires further analysis. However, initial results show that $R_{pol}$ can be reduced by tenfold when using composite instead of monolithic electrodes, which brings $R_{pol}$ close to the values of monolithic Pr$_2$NiO$_4$. Such remarkable decrease in $R_{pol}$ has been attributed to reduced diffusion length of composite electrode, which stems from high $D$ of an ionic conductor (e.g. GDC). Upon mixing with mixed conductor (e.g. Ln$_2$NiO$_4$) a shorter pathway for ionic transport within the cathode is created.

Recent applications of PR nickelate electrodes towards electrolysis and oxygen evolution reaction has also been investigated by a handful of reports. The interest for RP nickelate studies as OER electrodes stems from their low $R_{pol}$ and their ability to accommodate excess oxygen in the structure, especially under oxidizing conditions. This
unique property allows to alleviate stress at the triple phase boundary due to possible inability of electrode to accommodate excess oxygen species transported by oxide ion conducting electrolyte. Therefore, less pO$_2$ buildup is generated at TPB, thus mitigating the problem of electrode delamination at the nickelate/electrolyte interface. Up to date, the SOEC operation of Pr$_2$NiO$_4$ electrode resulted in 58% steam to hydrogen conversion ratio at 800 °C in an electrolyte supported full cell. The measured current density at 1.3 V (800 °C) reached relatively high 0.9 A cm$^2$ with PNO electrode, which is comparable to commercial LSCF cells. These results indicate that that nickelate electrodes are suitable candidates for high temperature electrolysis. However, the lack of long-term durability tests still do not provide a full story regarding their phase and performance stability.
REFERENCES

10. Mitterdorfer, A.; Gauckler, L. J., La2Zr2O7 formation and oxygen reduction kinetics of the La0.85Sr0.15Mn3O7, O2(g) vertical bar YSZ system. Solid State Ion. 1998, 111 (3-4), 185-218.


34. Zhou, W.; Ran, R.; Shao, Z. P., Progress in understanding and development of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$-based cathodes for intermediate-temperature solid-oxide fuel cells: A review. *J. Power Sources* **2009**, *192* (2), 231-246.


53. McCarthy, B. P.; Pederson, L. R.; Williford, R. E.; Zhou, X. D., Low-
Temperature Densification of Lanthanum Strontium Manganite (La\(_{1-x}\)Sr\(_x\)MnO\(_{3+\delta}\)), x=0.0-0.20. J. Am. Ceram. Soc. 2009, 92 (8), 1672-1678.


67. Millar, I.; Taherparvar, H.; Filkin, N.; Slater, P.; Yeomans, J., Interaction of (La\(_{1-x}\)Sr\(_x\))(1-y)MnO\(_3\)-Zr\(_{1-z}\)Y\(_2\)O\(_{2-\delta}\) cathodes and LaNi\(_{0.6}\)Fe\(_{0.4}\)O\(_3\) current collecting layers for solid oxide fuel cell application. Solid State Ion. 2008, 179 (19-20), 732-739.

80. Yang, L.; Wang, S.; Blinn, K.; Liu, M.; Liu, Z.; Cheng, Z.; Liu, M. L., Enhanced sulfur and coking tolerance of a mixed ion conductor for SOFCs: BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$-$\chi$Yb$_{\chi}$O$_{3-d}$. *Science* **2009**, *326*, 126-129.
87. Tai, L. W.; Nasrallah, M. M.; Anderson, H. U.; Sparlin, D. M.; Sehlin, S. R., Structure and electrical properties of La$_{1-x}$Sr$_x$Co$_{1-x}$Fe$_2$O$_3$. 2. The system La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$. *Solid State Ion.* **1995**, *76* (3-4), 273-283.
88. Chen, C. C.; Nasrallah, M. M.; Anderson, H. U., Immittance response of La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$ based electrochemical cells. *Journal of the Electrochemical Society* **1995**, *142* (2), 491-496.
89. Kim, J. H.; Prado, F.; Manthiram, A., Characterization of GdBa$_{1-x}$Sr$_x$Co$_2$O$_{5+\delta}$ (0 <= x <= 1.0) double perovskites as cathodes for solid oxide fuel cells. *Journal of the Electrochemical Society* **2008**, *155* (10), B1023-B1028.
92. Lee, K. T.; Manthiram, A., Characterization of Nd$_{1-x}$Sr$_x$CoO$_{3+\delta}$ (0 <= x <= 0.5) cathode materials for intermediate temperature SOFCs. *Journal of the Electrochemical Society* **2005**, *152* (1), A197-A204.
93. Lee, K. T.; Manthiram, A., Comparison of Ln$_{0.6}$Sr$_{0.4}$CoO$_{3+\delta}$ (Ln = La, Pr, Nd, Sm, and Gd) as cathode materials for intermediate temperature solid oxide fuel cells. *Journal of the Electrochemical Society* **2006**, *153* (4), A794-A798.


115. Yashima, M.; Sirikanda, N.; Ishihara, T., Crystal Structure, Diffusion Path, and Oxygen Permeability of a Pr$_2$NiO$_4$-Based Mixed Conductor (Pr$_{0.9}$La$_{0.1}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_4$+$\delta$. *J. Am. Chem. Soc.* **2010**, *132* (7), 2385-2392.


140. Patrakeev, M. V.; Naumovich, E. N.; Kharton, V. V.; Yaremchenko, A. A.; Tsipis, E. V.; Nunez, P.; Frade, J. R., Oxygen nonstoichiometry and electron-hole transport in La2Ni0.9Co0.1O4+delta. *Solid State Ion.* **2005**, *176* (1-2), 179-188.


Lou, X. Y.; Wang, S. Z.; Liu, Z.; Yang, L.; Liu, M. L., Improving La0.6Sr0.4Co0.2Fe0.8O3-delta cathode performance by infiltration of a Sm0.5Sr0.5CoO3-delta coating. *Solid State Ion*. **2009**, *180* (23-25), 1285-1289.


Haynes, W. M.


Shen, Y. N.; Zhao, H. L.; Swierczek, K.; Du, Z. H.; Xie, Z. X., Lattice structure, sintering behavior and electrochemical performance of La1.7Ca0.3Ni1-xCuxO4+delta as cathode material for intermediate-temperature solid oxide fuel cell. *J. Power Sources* **2013**, *240*, 759-765.


186. Philippeau, B.; Mauvy, F.; Nicollet, C.; Fourcade, S.; Grenier, J. C., Oxygen reduction reaction in Pr2NiO4+delta/Ce0.9Gd0.1O1.95 and La0.6Sr0.4Co0.2Fe0.8O3-delta/La0.8Sr0.2Ga0.8Mg0.2O2.80 half cells: an electrochemical study. *J. Solid State Electrochem.* 2015, 19 (3), 871-882.
190. Railsback, J. G.; Gao, Z.; Barnett, S. A., Oxygen electrode characteristics of Pr2NiO4+delta-infiltrated porous (La0.9Sr0.1)(Ga0.8Mg0.2)O3-delta. *Solid State Ion.* 2015, 274, 134-139.


200. Yang, J. B.; Yelon, W. B.; James, W. J.; Chu, Z.; Kornecki, M.; Xie, Y. X.; Zhou, X. D.; Anderson, H. U.; Joshi, A. G.; Malik, S. K., Crystal structure, magnetic properties, and Mossbauer studies of La0.6Sr0.4FeO3-δ prepared by quenching in different atmospheres. *Phys. Rev. B* 2002, 66 (18), 184415.


214. Philippeau, B.; Mauvy, F.; Mazataud, C.; Fourcade, S.; Grenier, J. C., Comparative study of electrochemical properties of mixed conducting Ln(2)NiO(4) (+) (delta) (Ln = La, Pr and Nd) and La0.6Sr0.4Fe0.8Co0.2O3 (-) (delta) as SOFC cathodes associated to Ce0.9Gd0.1O2 (-) (delta), La0.8Sr0.2Ga0.8Mg0.2O3 (-) (delta) and La9Sr1Si6O26.5 electrolytes. Solid State Ion. 2013, 249, 17-25.


217. Kharton, V. V.; Tsipis, E. V.; Yaremchenko, A. A.; Frade, J. R., Surface-limited oxygen transport and electrode properties of La(2)Ni(0.8)Cu(0.2)O(4+delta). Solid State Ion. 2004, 166 (3-4), 327-337.

218. Yaremchenko, A. A.; Kharton, V. V.; Patrakeev, M. V.; Frade, J. R., p-type electronic conductivity, oxygen permeability and stability of La2Ni0.9Co0.1O4+delta. J. Mater. Chem. 2003, 13 (5), 1136-1144.


CHAPTER 2

EXPERIMENTAL PROCEDURES

The general schematics for experimental procedures is shown in Figure 2.1, and is composed of three stages following a material standardization and synthesis: (1) screening process on single phase cathode powders and XRD characterization, (2) material characterization with dense ceramic bars, and (3) cell manufacturing and electrochemical tests.

2.1 MATERIAL SYNTHESIS

Starting materials including Pr(NO₃)₃, Nd(NO₃)₃, and Ni(NO₃)₂ (99.9%, Alfa Aesar, Haverhill, MA) were standardized using thermogravimetric analysis and used in glycine nitrate combustion process.[1] The same procedure was utilized for the B-site doped compounds. The synthesized powders were calcined in air with 3°C per minute heating and cooling rates. PNO was calcined at 1080 °C for 10 hours, while the PNNO series was calcined at 1150 °C for 5 hours. Crystal structure of the calcined powders was studied via x-ray diffraction (XRD) analysis using a Rigaku Miniflex II (Houston, TX) diffractometer equipped with scintillating and high speed silicon strip (D/teX) detectors. External Al sample holder, Ni/YSZ/GDC ceramic substrates (or YSZ/GDC substrates for symmetric cells), and single phase PNO and Pr₆O₁₁ (PrO₃) powders were used as external standards to ensure a proper peak positioning and normalized flux.
Figure 2.1 A schematics showing experimental procedure utilized to characterize and evaluate cathode materials for SOFCs.
2.2 DENSE CERAMIC BAR MANUFACTURING

Conductivity measurements were performed on dense ceramic bars. Single phase PNNO powders were mechanically milled with V006 vehicle (Heraeus Inc, PA, 19067) in isopropanol to obtain a particle size of 200 - 300 nm. The respective powders were dried and sieved before uniaxial pressing (≈150 MPa). The bars were sintered at 1200 °C for 5 hours with intermittent binder burning at 300 °C. The resulting bars were in 96% of theoretical density range, as verified by the Archimedes’ method. Four Pt wires were wrapped (two on edges and two evenly spaced in the middle) around the bars and Au paste was used to improve the contact. Resulting bars were heated to 900 °C for 30 min to cure Au paste.

2.3 ELECTRODE MANUFACTURING

Micrometer carbon powders were added to single phase cathode powders as pore formers, which were then ball milled with 2mm zirconia grinding media at 560 rpm for 15h (1:10 powder to grinding media wt. ratio) to obtain a mean particle size of 270 ± 60 nm. This particle size distribution was used in cathode ink manufacturing.

2.4 INTERLAYER SYNTHESIS AND SYMMETRIC CELL MANUFACTURING

The 1” diameter electrolyte (8-YSZ obtained from Fuel Cell Materials, Columbus, Ohio 43035) supported symmetric cells were used for thermal annealing studies with nickelate/interlayer//8-YSZ//interlayer/nickelate configurations. An example of electrolyte supported cells are shown in Figure 2.2(a). Nano-sized GDC20 ceria was prepared by precipitation method from standardized Gd(NO₃)₃·xH₂O (99.9% REO, Alfa Aesar, Haverhill, MA) and Ce(NO₃)₃·xH₂O (99.998%, Alfa Aesar, Haverhill, MA).²⁴ The produced powders were dried and mixed (10 wt%) with 100nm (90 wt%) GDC20 powder
(Fuel Cell Materials, Columbus, Ohio 43035). The resulting powder mixture (bimodal ceria) was used for interlayer ink manufacturing, Figure 2.2(b). The cells without an interlayer and cells with bimodal GDC20 were used as controls for thermal annealing studies.

In cells with Pr$_6$O$_{11}$/GDC20 (PrO$_x$-GDC) interlayer additional steps were required. First bimodal GDC20 interlayer was sintered at 1200 °C for 2h. Synthesized PrO$_x$ powder was mixed with V006 (Heraeus Inc, PA, 19067) vehicle (10 wt%) and dissolved in acetone. The solution was then ultrasonicated using FB 120 sonic dismembrator (Fisher Scientific, Pittsburgh, Pa 15275) for 30 min, to ensure uniform particle dispersion. Thin film deposition of PrO$_x$ on GDC20 was performed by spin coating the cells with the solution at 1,700 rmp using SCK-100 spin coater (Instras Scientific, New Jersey, 07660), followed by drying and sintering at 1200 °C for 2h. The resulting cells is shown in Figure 2.3(a). A bimodal Pr$_{0.10}$Gd$_{0.10}$CeO$_{1.90±δ}$ (PGCO) interlayer was prepared in similar way to bimodal GDC20 with addition of in-house synthesis of PGCO (glycine-nitrate combustion). The resulting interlayer is shown in Figure 2.3(b). All interlayers were sintered at 1200 °C for
2h, and then the cathode was screen printed and sintered under same conditions. Thermal annealing tests on cells were conducted between 700-870 °C in air.

Figure 2.3 (a) Electrolyte supported cells with sintered GDC-20 buffer, and with 10 and 20 drops of PrO$_x$ spin coating solution on top of the GDC-20 interlayer. (b) PGCO interlayer after sintering.

2.5 FABRICATION OF FULL CELLS

The 1" diameter anode supported button cells were used for performance evaluation (Figure 2.4a). The Ni-YSZ bilayers with YSZ electrolyte were co-sintered at 1350 °C for 2h in air. The bimodal interlayers were screen printed and sintered at 1200 °C for 2h together with anode current collector composed of Ni paste and Pt wires imbedded into Ni mesh. Cathode inks were screen printed and sintered at the same condition resulting in 25-µm thickness. The electrode active area was 2 cm$^2$. Gold metal grids were then screen-printed and sintered at 900 °C, resulting in a thickness of 10 µm. Pt wires were co-sintered with gold grids allowing the four probe measurements. The cells prepared for electrochemical measurements are shown in Figure 2.4(b). Each full cell was electrically connected to the test fixture with Pt wires, and then sealed on a tubular alumina stand with G-18 glass paste. Figure 2.4(c) shows the cell assembly. Anode was provided with 3% humidified H$_2$ at a flow rate of 200 sccm, and cathodes were supplied with 400 sccm air. Up to 30 button cells were run simultaneously using a uniquely designed cell stands which allowed fast material evaluations (Figure 2.5). These single cell tests high throughput
setups allowed for individual cell control. For instance, the environment(s) on cathode and anode sides could be modified accordingly for each cell and were independent of other cells. The humidification could also be adjusted on both electrodes along with different operating conditions.

2.6 ELECTROCHEMICAL TESTS

Electrochemical measurements were performed using two instruments. In all cases the performance was verified on both instruments to ensure safe data comparison. The first option was 8 channel Solartron 1470E Multistat and 1255B Frequency Response Analyzer (Solartron Analytical, Oak Ridge, TN, 37830), (Figure 2.6a). The second option was a 16 channel Biologic VMP3 potentiostat (Bio-Logic USA, Knoxville, TN) with external current boosters (Figure 2.6b). The i-V measurements were performed with 5 mV/s scan rate, and EIS was measured between 0.1 Hz and 50 kHz, with a scan rate of 30 points per decade. The \( dc \) and \( ac \) measurements were performed every 25 hours of operation.

![Figure 2.4](image)

**Figure 2.4** (a) Cell configuration and schematics of operation. (b) Electrolyte and anode supported cells with printed cathodes and Au grids (Au grinds were not sintered). (c) The cell setup used to perform electrochemical tests.
Figure 2.5 Designed and built SOFC laboratory at University of South Carolina. Single cell tests high throughput setups are shown in top figures and the bottom left figure. The furnaces used for powder and cell thermal annealing studies are shown in bottom middle figure. The setup used for conductivity and/or pressurized studies is shown at the bottom right.
Figure 2.6 (a) Solartron 1470E Multistat and 1255B Frequency Response Analyzer. (b) Biologic VMP3 potentiostat with external current boosters.

2.7 QUANTIFICATION OF PHASE EVOLUTION IN FULL CELLS

Having a normalized flux for XRD studies, the intensity of PNO peaks can be quantified before, during, and after electrochemical measurements. Quantification of the phases was performed by the least-squares fitting of the linear combination of the XRD standards (LCOS) against the experimental XRD patterns. The intensity and the width of the initial XRD peaks for each standard were preserved, thus allowing an accurate quantification even with overlapped peaks. As a result, LCOS enables PNO phase to be separated from higher ordered nickelate phases. Tested cells were preserved without any manipulations on the cathode and current collector surfaces (Figure 2.7). Details are discussed in Chapter 4 of this thesis.

2.8 SEM AND EDS ANALYSIS

Surface and cross sectional images on cells were obtained using the Tescan Vega-3 (Brno, Czech Republic) SEM with EDS capability. Focused ion beam (FIB) and EDS analysis was performed on nano DUE’T double beam NB5000 microscope (Hitachi, NY, 10591).
Figure 2.7 (a) A top view on initial cells with sintered Au grid. In this set of cell the interlayer was screen printed. (b) A top view on operated full cells used for post-operation phase transformation studies. In this case interlayer was sprayed. The cathode was not damaged during cell assembly and disassembly and the cells were preserved.

2.9 IN OPERANDO X-RAY STUDIES ON ELECTROCHEMICAL CELLS

In-situ XRD studies on electrochemical cells were performed using Bruker D8 Advance XRD with Anton Paar HTK 1200 heating chamber, Figure 2.8(a-b), at Pacific Northwest National Laboratory. The XRD was outfitted with a Cu K$_{\alpha1}$ radiation source, a Göbel mirror, a 0.12° diffracted beam Soller slit, and a Sol-X energy dispersive x-ray detector (Bruker AXS) that filters out K$_{\beta}$ peaks and the fluorescence background due to the presence of Co and Fe. Small-scale (13 mm) diameter button cells were used with 0.50 cm$^2$ cathode active area. The middle of the cathode was left open for incoming x-rays and built-in Au

Figure 2.8 (a) Bruker D8 Advance XRD at Pacific Northwest National Laboratory. (b) Anton Paar HTK 1200 heating chamber. (c) In-situ SOFC setup with an open cathode center for phase evolution studies.
was used as an internal standard, Figure 2.8(c). The cell was assembled on a test fixture and fed into the heating chamber. XRD patterns were collected before, during, and after electrochemical operation at 750 °C.

2.10 IN SITU X-RAY STUDIES AT A SYNCHROTRON SOURCE

In-situ XRD studies were performed at Advanced Photon Source (APS), Argonne National Laboratory, beamline 11-ID-B (Figure 2.9a). The high energy and high flux x-rays allowed detailed analysis of phase evolution in nickelates and their phase transformation products. Ceria standard was used for detector and exposure calibration. An empty quartz tube (blank) was fixed in a flow furnace\textsuperscript{[2]} (composed of a stainless steel frame, heating elements, a quartz tube, and heat shields) and run through the entire temperature profile, providing the background for powder sample studies at all experimental conditions. Similar studies were performed on YSZ/interlayer cells to ensure the background collection for electrochemical tests (Figure 2.9b).

A sample was then centered in front of a beam using a built in camera and laser. Experimental data was collected via QXRD continuously at 86.7 keV and 95 cm detector distance. In-situ studies (T \leq 900 °C) were then performed in a controlled atmosphere, and respective data was continuously collected during heating and cooling. The data was processed using PDFgetX2 and in-house Python code. The background data was subtracted from the sample data. The analysis involved Rietveld, PDF, and Monte Carlo methods.
Figure 2.9 (a) APS and Argonne National Laboratory. (b) Experimental setup for XRD synchrotron studies at 11-ID-B beamline. Details are described in Chapter 10 and Appendix D.
REFERENCES

CHAPTER 3

COMPATIBILITY OF PRASEODYMIUM NICKELATES WITH OTHER CELL COMPONENTS

Despite the intrinsic advantages of Pr$_2$NiO$_4$ (as discussed in Chapter 1), the elevated operation temperature may result in degradation of cell performance due to instability of the constituent materials at high temperatures.\textsuperscript{[1]} This instability can result from oxidation, diffusion, phase transformation, or chemical reaction processes. As a result, research on SOFCs has been driven by the recognition of the need to lower the operation temperature to intermediate region (650-800°C). Pr$_2$NiO$_4$ is a candidate for this approach, hence its compatibility with other cell components needs investigation. Here a compatibility with various oxide current collectors and electrolytes (or buffers) has been addressed.

3.1 COMPATIBILITY OF Pr$_2$NiO$_4$ AND La$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSC) CURRENT COLLECTOR

The compatibility between the Pr$_2$NiO$_4$ cathode and LSC current collector was investigated using XRD and EDS line and area scans. XRD scans, shown in Figure 3.1(a), were performed on Pr$_2$NiO$_4$-LSC mixture annealed at 750 °C between 0 to 500h. Peak shifting was not observed as a function of time in either phase in the mixture. Microstructural analysis for a button cell operated at 750 °C up to 500h is presented in Figure 3.2(a) showing the EDS line scan of elemental distribution in Pr$_2$NiO$_4$ cathode and LSC current collector. The results indicate possible interdiffusion between Pr$_2$NiO$_4$ and
LSC layers. Praseodymium La1 signal intensity decreased from 200 a.u. in cathode layer to 60 a.u. through ~5 μm of LSC layer. Therefore, there was a steady concentration of Pr across narrow region of LSC layer after 500h. Nickel, however, was not present in LSC layer as the intensity decreased from 50 a.u. in cathode layer to zero in LSC layer. Small amount of cobalt was identified in very narrow region at interface between cathode and LSC but the intensity dropped down to zero in the cathode region. Lanthanum was not detected in the cathode region and cerium and zirconium were not detected in Cathode-LSC interface region.

Figure 3.1 XRD of the Pr$_2$NiO$_4$ and a) LSC or b) LSM mixtures annealed at 750 °C for times between 0-500 h. LSC or LSM were used as cathode contacts and LaB6 was added to evaluate potential peak shifts.

Nevertheless, further EDS analysis, using the area scan, showed no presence of Pr and Ni in the narrow 5 μm LSC region, region 4 in Figure 3.2(b), which indicated minimal to zero diffusion between the cathode and LSC layers. In the interface region of Pr$_2$NiO$_4$ and LSC (region 5) the normalized signal intensity for Co and La were 1.83 and 1.69, respectively (Table 3.1). For both elements, such signal intensity was at minima in the LSC and cathode-LSC regions. The signal intensity for the two elements decreased to zero.
Figure 3.2 a) SEM image of a button cell with LSC current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer. EDS line scan of elemental distribution across the cell layers is shown. b) Multiple regions of EDS area scan used for analysis.

Table 3.1 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSC current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>O</th>
<th>Co</th>
<th>Ni</th>
<th>Sr</th>
<th>Y</th>
<th>Zr</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>48.65</td>
<td>1.17</td>
<td>6.57</td>
<td>43.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>37.63</td>
<td>20.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>37.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>30.62</td>
<td>33.33</td>
<td>4.95</td>
<td></td>
<td></td>
<td>31.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>39.38</td>
<td>1.83</td>
<td>17.39</td>
<td>5.04</td>
<td></td>
<td></td>
<td>1.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Yes</td>
<td>37.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Yes</td>
<td>35.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Max.        | 48.65 | 33.33 | 22.24 | 5.04 | 6.57 | 43.61 | 31.10 | 40.24 | 44.21 | 7.51 |
Min.        | 30.62 | 1.83  | 1.17  | 4.95 | 6.57 | 43.61 | 1.69  | 40.24 | 14.92 | 7.51 |

in the cathode layer (region 2). The Sr intensity in the cathode-LSC region was 5.04, which was 1.8% higher than the 4.95 detected in LSC region. It has been previously reported that Sr segregation from LSC layer might result in Sr enrichment in the cathode region.[2] Since
diffusion detected at thin cathode-LSC interface region was insignificant, and peak shifting was not observed in either phase in the mixture, it is considered that there was no interdiffusion between the cathode and LSC current collector. Hence, the Pr$_2$NiO$_4$ cathode is compatible with LSC current collector when measured at 750 °C up to 500 hours.

3.2 COMPATIBILITY OF Pr$_2$NiO$_4$ AND (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3-x}$ (LSM) CURRENT COLLECTOR

XRD measurement on Pr$_2$NiO$_4$-LSM mixture annealed at 750 °C between 0 to 500h was carried out and the results are shown in Figure 3.1(b). Peak shifting vs. time was not observed in either phase in the mixture. Figure 3.3(a) shows EDS area scan results on the button cell operated at 750 °C up to 500 h with LSM as a current collector. Pr and Ni were not detected in the entire LSM layer including region 15, Table 3.2. Furthermore, Mn and Sr did not diffuse into the cathode layer (regions 17-22). On the other hand, lanthanum slowly diffused across regions 17-22 in the cathode layer. Low La concentration was
detected across the entire cathode region. Furthermore, in cathode-LSM interface region (region 16) the expected diffusion occurred between the two layers. All elemental signals had the lowest value when compared to cathode and LSM layers.

Strontium segregation was not observed at the cathode-LSM interface. Diffusion across the whole cathode-LSM region was zero except at the very narrow, region 16. Therefore, since peak shifting was not observed for either phase of Pr\textsubscript{2}NiO\textsubscript{4}-LSM mixture and diffusion between the cathode and LSM at 750 °C was zero, the Pr\textsubscript{2}NiO\textsubscript{4} cathode is compatible with LSM current collector when measured up to 500 hours. Chlorine poisoning was also detected in a button cell with LSM electrolyte, with normalized intensity of 1.40 (Table 3.2). It has been previously reported that a cell performance might drop by exposure to only 1 ppm Cl\textsubscript{2}(g) at 750 °C.\textsuperscript{[3]} Due to a cell operating temperature at 750 °C used in this research it is possible that chlorine gas yielded the largest poisoning effect.

Table 3.2 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSM current collector, Pr\textsubscript{2}NiO\textsubscript{4} cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented. The highlighted region 16 corresponds to LSM-cathode interface.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>O</th>
<th>Cl</th>
<th>Mn</th>
<th>Ni</th>
<th>Sr</th>
<th>La</th>
<th>Pr</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>9</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>10</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>11</td>
<td>Yes</td>
<td>32.84</td>
<td>33.73</td>
<td>3.02</td>
<td>29.64</td>
<td></td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Yes</td>
<td>34.84</td>
<td>32.30</td>
<td>3.58</td>
<td>29.28</td>
<td></td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Yes</td>
<td>34.62</td>
<td>32.08</td>
<td>3.11</td>
<td>30.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Yes</td>
<td>35.59</td>
<td>31.35</td>
<td>3.30</td>
<td>29.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Yes</td>
<td>32.46</td>
<td>33.09</td>
<td>3.65</td>
<td>30.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Yes</td>
<td>33.75</td>
<td>20.60</td>
<td>9.51</td>
<td>2.08</td>
<td>20.78</td>
<td>13.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Yes</td>
<td>35.29</td>
<td>20.94</td>
<td>1.28</td>
<td>42.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Yes</td>
<td>35.56</td>
<td>20.20</td>
<td>1.44</td>
<td>41.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Yes</td>
<td>36.51</td>
<td>20.66</td>
<td>0.74</td>
<td>42.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Yes</td>
<td>36.07</td>
<td>20.57</td>
<td>1.05</td>
<td>42.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Yes</td>
<td>36.28</td>
<td>20.89</td>
<td>0.00</td>
<td>42.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Yes</td>
<td>35.66</td>
<td>21.58</td>
<td>0.80</td>
<td>41.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max.</td>
<td>36.51</td>
<td>1.40</td>
<td>33.73</td>
<td>21.58</td>
<td>3.65</td>
<td>30.80</td>
<td>42.83</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Min.</td>
<td>32.46</td>
<td>1.40</td>
<td>20.60</td>
<td>9.51</td>
<td>2.08</td>
<td>0.00</td>
<td>13.28</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>
3.3 COMPATIBILITY OF Pr$_2$NiO$_4$ AND CERIA

XRD results for both cathode-GDC and cathode-SDC mixtures are reported in Figure 3.4. Peak shifting in either phase of the mixtures was not observed. EDS line scan of the elemental distribution in a button cell with Pr$_2$NiO$_4$ cathode, LSC current collector, and SDC-20 interlayer (buffer layer between the cathode and YSZ) operated at 750 °C up to 500 h is shown in Figure 3.2(a). Ceria diffused to the narrow cathode-ceria interface region and continued to diffuse ~1 μm into the cathode layer. On the other hand, praseodymium diffused much slower across the whole ceria layer. Nickel concentration was zero across the ceria layer, however. EDS area scan confirmed interdiffusion between the cathode and ceria layer. In ceria layer, region 3 in Figure 3.2(b) and Table 3.1, the Pr signal was 14.92 which is 37.1% of ceria signal. Nickel did not diffuse across the ceria layer and samarium was not detected in the cathode layer. Ceria was not detected by EDS area scan in region 6 which revealed its very narrow region of diffusion. Moreover, for a button cell with Pr$_2$NiO$_4$ cathode, LSM current collector and SDC-20 interlayer, EDS results confirmed the Pr diffusion into ceria layer in regions 1 and 2 (Figure 3.3(b) and Table 3.3) which further supports the presence of interdiffusion between Pr$_2$NiO$_4$ cathode and ceria interlayer at 750 °C. Due to diffusion of ceria and praseodymium across the two layer interface, further cell performance and stability measurements were required.
Figure 3.4 XRD of the Pr$_2$NiO$_4$ and a) GDC or b) SDC mixtures annealed at 750 °C for times between 0-500 h. GDC or SDC were used as an interlayer between the cathode and YSZ. LaB6 was added to evaluate potential peak shifts.

Table 3.3 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell (LSM current collector, Pr$_2$NiO$_4$ cathode and SDC-20 buffer layer) are shown. Normalized signal intensity for each elements is presented.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>O</th>
<th>Ni</th>
<th>Y</th>
<th>Zr</th>
<th>Ce</th>
<th>Pr</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>43.45</td>
<td></td>
<td></td>
<td></td>
<td>43.47</td>
<td>4.04</td>
<td>9.04</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>40.46</td>
<td></td>
<td></td>
<td></td>
<td>47.95</td>
<td>1.86</td>
<td>7.49</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>38.26</td>
<td></td>
<td></td>
<td></td>
<td>50.38</td>
<td>0.00</td>
<td>11.36</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>39.22</td>
<td>0.00</td>
<td></td>
<td></td>
<td>50.26</td>
<td>0.00</td>
<td>10.52</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>37.86</td>
<td>7.49</td>
<td></td>
<td></td>
<td>45.35</td>
<td>0.00</td>
<td>9.30</td>
</tr>
<tr>
<td>6</td>
<td>Yes</td>
<td>47.10</td>
<td>4.20</td>
<td>27.25</td>
<td></td>
<td>15.94</td>
<td></td>
<td>5.51</td>
</tr>
<tr>
<td>7</td>
<td>Yes</td>
<td>49.51</td>
<td>1.14</td>
<td>6.05</td>
<td>43.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max.</td>
<td></td>
<td>49.51</td>
<td>1.14</td>
<td>6.05</td>
<td>43.29</td>
<td>50.38</td>
<td>4.04</td>
<td>11.36</td>
</tr>
<tr>
<td>Min.</td>
<td></td>
<td>37.86</td>
<td>1.14</td>
<td>4.20</td>
<td>0.00</td>
<td>15.94</td>
<td>0.00</td>
<td>5.51</td>
</tr>
</tbody>
</table>
3.4 ELECTROCHEMICAL PERFORMANCE AND PERFORMANCE STABILITY OF Pr$_2$NiO$_4$ ELECTRODE

There is no question that composite electrodes are potentially superior to single phase cathodes, because microstructures in two-phase materials are usually finer than in single-phase materials due to the Zener pinning mechanism$^{[4-5]}$ in which particle coarsening is suppressed due to the presence of another phase. Laberty et al.$^{[6]}$ reported that the chemical activity of composite of La$_2$NiO$_4$ and ceria was substantially better than that of monolithic La$_2$NiO$_4$ compound. Pr$_2$NiO$_4$ monolithic composition, however, showed superior activity. Figure 3.5(a) shows that after operating for 1250h at 750 °C with 3% water humidified H$_2$, the ohmic resistance increased from 0.14 to 0.17 Ω·cm$^2$, while the polarization resistance remained almost unchanged. The increase in ohmic resistance arose most likely from the formation of less conductive phase at the cathode-ceria-electrolyte interface due to interdiffusion, as supported by the EDS results. The fact that polarization resistance remained almost constant indicates good stability of monolithic Pr$_2$NiO$_4$ cathode. As shown in Figure 3.5(b), at 750 °C, 0.8 V and 3% water humidified H$_2$ the

![Figure 3.5](image)

**Figure 3.5** (a) Electrochemical impedance spectra for a button cell with Pr$_2$NiO$_4$ cathode measured at 750 °C and 0.8 V. (b) Power density vs. time spectra at 750 °C and 0.8 V for multiple cells tests with Pr$_2$NiO$_4$ cathode. Note that ohmic resistance changed, but electrode resistance remained stable over ~ 1200 hours measurements.
degradation rate of Pr$_2$NiO$_4$ was only marginal, ~ 3% per 1000 hours up to 2000 hours. Multiple cells were tested and similar results were obtained. Therefore, to further improve the stability of SOFC with Pr$_2$NiO$_4$ cathode, it is necessary to suppress the interdiffusion of Pr, either by depositing dense ceria buffer layer, or improving the cathode material itself for better elemental stability. In general, if a monolithic cathode material is used, its defect chemistry must be carefully manipulated to ensure mixed conduction in a quite wide range of temperatures and atmospheres.

CONCLUSIONS

High performance Pr$_2$NiO$_4$ cathode was reported, as well as its compatibility with various cathode current collectors and electrolytes. At 750 °C, Pr$_2$NiO$_4$ is compatible with LSC or LSM current collectors up to 500 hours with minimum diffusion across the narrow interface region. Interdiffusion between Pr$_2$NiO$_4$ and ceria layer occurred; however, even with the presence of interdiffusion, the degradation rate at 0.8 V was marginal, ~ 3% per 1000 hours up to 2000 hours.
REFERENCES

CHAPTER 4

QUANTIFICATION OF PHASE EVOLUTION IN PRASEODYMIUM NICKELATE CATHODES

4.1 INTRODUCTION TO QUANTIFICATION CHALLENGES

Quantification of phase evolution in Praseodymium nickelate (Pr$_2$NiO$_4$) operating single cell is challenging because of the overlap of X-ray diffraction (XRD) peaks between the cathode and oxide current collector. However, it is necessary to quantify the degree of phase evolution in the cathode in order to study the structure–electrochemical property relationship. X-ray diffraction (XRD) has been extensively used to investigate the structural evolution of nickelates. Unfortunately, the XRD peaks of nickelates overlap with these from oxide current collectors. Furthermore, a thick oxide current collector suppresses the signal intensity from the cathodes making the quantification of phase evolution in the cathode unattainable.[1] An alternative approach to expose the cathode for post-test XRD studies involves mechanical removal of a thick oxide current collector layer from the cathode surface, which may overlook the structural interactions between the cathodes and current collector, and can often lead to surface damage or full cathode delamination.[1]

Therefore, in order to quantify the phase evolution in Pr$_2$NiO$_4$ (PNO) as an SOFC cathode, it is necessary to replace the oxide current collector with another material which can meet the requirements, including mechanical stability under operating conditions, high electrical conductivity, and chemical compatibility with the cathode. In this work, Au metal
grids\textsuperscript{[2]} were used as the current collector. The grid design provides electrochemical properties comparable to the oxide current collectors while simultaneously exposing parts of the cathode for direct XRD studies. The quantification of phase evolution in cathodes was achieved using a linear combination of XRD standards (LCOS) fitted against the experimental XRD patterns, obtained using the grid current collectors. Reproducibility of measurements was studied in multiple cells with various current collectors.

4.2 CELL DESIGN AND QUANTIFICATION OF PHASE TRANSITION

Figure 4.1(a) shows a schematic of an anode-supported cell with the cathode covered with a gold grid as the current collector. Figure 4.1(b) illustrates the multiple cells used in this work. Au grids expose ~ 45% of the cathode area for phase quantification studies. The XRD patterns of the oxide current collectors (LaNi\textsubscript{0.6}Fe\textsubscript{0.4}O\textsubscript{3}, La\textsubscript{0.80}Sr\textsubscript{0.20}CoO\textsubscript{3}, and La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3})\textsuperscript{[3-5,6-10]} overlap with Pr\textsubscript{2}NiO\textsubscript{4}, while Au and Pr\textsubscript{2}NiO\textsubscript{4} exhibit distinct XRD reflections.\textsuperscript{[1-2]} An extensive study on compatibility of Pr\textsubscript{2}NiO\textsubscript{4} with oxide current collectors and ceria is reported in Appendix B. The use of Au grids eliminates complex peak deconvolution procedures. Figure 4.2(a) shows the initial XRD patterns of the anode/YSZ substrate with a GDC layer, a single-phase PNO and Pr\textsubscript{6}O\textsubscript{11} powders. The area and intensity of PNO peaks remained constant after sintering the Au grid, as shown in Figure 4.2(b). A linear background subtraction was then carried out over the 2h region of interest. The standards, aluminum and Ni/YSZ/GDC substrates, were used for the calibration of the peak positions and flux normalization. Having a normalized flux, the intensity of PNO peaks can be quantified before and after electrochemical measurements. The least-squares method was used to generate the LCOS using the following equation:

\[
LCOS = \sum_i \alpha_i \cdot Std_i
\]

(1)
Figure 4.1 (a) A fuel cell configuration of an anode-supported cell, doped ceria/YSZ/Ni–YSZ, with the cathode covered by Au metal grid. (b) A top view of cells with Au grid and visible cathode for phase evolution studies.

where $i$ is the index of a given standard, $\alpha_i$ is a scale coefficient for the $i$th pattern, and $Std_i$ is the $i$th standard XRD pattern. The least squares method was then used to minimize the residual ($\sum_\theta (Exp - LCOS)^2$) between the difference of experimental XRD patterns ($Exp$) and LCOS over the 2$\theta$ region of interest.

The bottom patterns in Figure 4.2(c) refer to the residual (light gray), and the top patterns are the least-squares fit (dark gray). The calculated fit is in agreement with the XRD pattern of the nickelate cathode in initial cell (black) with a ~1% residual for the highest intensity nickelate peak. The area and intensity of the two nonoverlapping nickelate reflections (113) and (111) at $2\theta = 24^\circ$ and $32^\circ$ decreased after operation while Pr$_6$O$_{11}$ peaks at $2h = 28^\circ$, $33^\circ$, and $47^\circ$ appeared due to the phase transformation. Emerging new peaks at $2\theta = 23^\circ$, $27^\circ$, and $46^\circ$ indicate the formation of higher order nickelate phase, as shown in Figs. 2(a) and (c). Once the intensity of Pr$_6$O$_{11}$ (+) is calculated, the nickelate versus Pr$_6$O$_{11}$ intensity ratio from the physical powder mixture [Figure 4.2(d)] can be used.
Figure 4.2 XRD patterns on an operated cell (a). Standard XRD reflections are shown for Ni/YSZ/GDC/nickelate/Au cell configuration. Cathode signal reproducibility after sintered Au grid (b). The LCOS fitted against the XRD patterns in initial cell and after the electrochemical operation (c). Standardization of nickelate/Pr$_6$O$_{11}$ powder mixtures (volume and mole percent), with calculated signal intensity ratio between nickelate and Pr$_6$O$_{11}$ (d).

Table 4.1 The Percentage of Pr$_6$O$_{11}$ in Pr$_2$NiO$_4$ treated at various conditions.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Thermal annealing of the electrode for 150 h</th>
<th>Operated Pr$_2$NiO$_4$ electrode for 150 h 790 °C at 0.5 A/cm$^2$</th>
<th>Operated Pr$_2$NiO$_4$ electrode for 500 h 790 °C at 0.8 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powders</td>
<td>750 °C 790 °C 850 °C</td>
<td>Pores</td>
<td>Pores</td>
</tr>
<tr>
<td>Electrode</td>
<td>0 0 1.1 5.6</td>
<td>5.0</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td>0 0 1.2 5.9</td>
<td>5.9</td>
<td>26.3</td>
</tr>
</tbody>
</table>
to quantify the mole percent of Pr$_6$O$_{11}$ in the mixture. A detailed signal intensity comparison between nickelate and Pr$_6$O$_{11}$ is shown in Figure 4.3.

**Figure 4.3** XRD signal comparison for the physical powder mixtures of Pr$_2$NiO$_4$ and Pr$_6$O$_{11}$.

The major advantage of the LCOS method over a comparison of the single peak intensity is the preservation of the initial intensity and width of the peaks of each standard, thus allowing an accurate quantification even with overlapped peaks. In this work, LCOS method enables PNO phase to be separated from higher ordered nickelate phases, making the quantification possible. **Table 4.1** summarizes the degrees of phase evolution in nickelates under various conditions.

Quantification from the LCOS is compared to the direct signal intensity ratio between the PNO and Pr$_6$O$_{11}$ phases. The mole concentration of Pr$_6$O$_{11}$ phase is obtained for each condition utilizing the calibration curves in Figure 4.2(d). The direct signal ratio quantification was obtained by the deconvolution of the highest intensity Pr$_6$O$_{11}$ peak ($2\theta \approx 28^\circ$) from the PNO peak using a pair of Voigt profiles via LMFt[11] and compared against
the highest intensity PNO peak (113). Unlike LCOS, this method does not distinguish between different nickelate phases that have direct peak overlaps, such as PNO and Pr$_3$Ni$_2$O$_7$. On the other hand, the generated LCOS fit uses only PNO standard, so the presence of other nickelate phase(s) should be reflected in the residual for the entire XRD pattern. Consequently, the direct signal ratio provides up to 20% lower mole percentage of Pr$_6$O$_{11}$ when compared to the values obtained from LCOS fits in operated cells since Pr$_3$Ni$_2$O$_7$ phase may contribute to the nickelate peak intensity. Figure 4.2(d) shows the final fits which were calculated and compared to the verification curve obtained from the LCOS method.

The question arises as whether or not Pr$_6$O$_{11}$ is formed from PNO or a further phase transition originated from Pr$_3$Ni$_2$O$_7$. In order to answer this question, it was necessary to start with a pure PNO cathode, thus the LCOS fit on the cell after operation provides the value of 1–x, where x is the fraction of the decomposed parent phase. The value of x was obtained utilizing the ratio of the $\alpha_i$ values for the PNO phase in final and initial XRD patterns. This approach accounts for the percentage of preserved parent phase and the total percentage of all byproducts. Comparing the alpha scale factors for the initial and final LCOS fits showed decrease in the amount of parent nickelate phase. Since LCOS method takes into consideration only PNO phase, while direct signal ratio method also considers Pr$_3$Ni$_2$O$_7$ phase, then changes in the percentage of Pr$_6$O$_{11}$ between these two methods might be associated with the formation of Pr$_6$O$_{11}$ from Pr$_3$Ni$_2$O$_7$ phase decomposition. This indicates that majority of the Pr$_6$O$_{11}$ is formed from PNO, while up to 3 mol% of additional Pr$_6$O$_{11}$ is generated from Pr$_3$Ni$_2$O$_7$ phase in long-term operated cells.
The second question is whether or not LCOS can be applied to study the reaction between nickelates and GDC.\(^1\) In this work, LCOS fits from the overlapping reflections at \(\theta = 29^\circ - 30^\circ\), and \(33^\circ - 34^\circ\) [Figure 4.2(a)] result in large residuals, indicating a reaction between the nickelates and GDC. Due to the reaction at the cathode/GDC interface, and the respective peak shifts, the least-squares method was not used in this 2\(\theta\) range. The role of ceria on phase transition and performance stability will be addressed extensively in Chapter 7.

4.3 ELECTROCHEMICAL PERFORMANCE AND CELL DURABILITY

Figure 4.4(a) show that Au grids can provide reproducible cell performance, which is within 5\% of those with oxide current collectors (LNF and LSC) as shown in Figure 4.4(b). The ohmic resistance [Figure 4.4(c)] in cells with Au grids is comparable (7\% lower) to cells with LNF and LSC current collectors, suggesting that the current collector of Au forms slightly better interfaces with the cathode than LSC or LNF. Over a wide temperature range (650\(^\circ\)C–850\(^\circ\)C), all cells exhibit a reproducible performance.

![Figure 4.4](image)
Figure 4.4 (a) I–V and power density curves for cells with nickelate electrodes and Au grids. (b) I–V curves of cells with Au, LSC, and LNF current collectors measured at 790\(^\circ\)C. (c) impedance spectra of the cells with Au, LSC, and LNF current collectors measured at 790\(^\circ\)C.

Figure 4.5(a) illustrates a long-term performance of PNO up to 500 h. The power densities measured at 0, 250, and 500th hour are 0.68, 0.68, and 0.66 W/cm\(^2\) at 0.8 V. Impedance measurements illustrated in Figure 4.5(b) show that the slow degradation of
the cell performance is consistent with an increase in electrode polarization, both of which are resulted from the evolution of the electrode. Backscattered SEM of a cell with Au current collector after 500 h of operation at 0.8 V is shown in Figure 4.5(c). The EDS analysis on cells tested with Au grids did not show any Au deposition at the cathode/GDC interface. A stable ohmic resistance during the long-term operation is indicative of good mechanical compatibility and interfacial contact between the cell components. This observation is consistent with the previous work,\textsuperscript{[1,3]} which showed the mechanical

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.5.png}
\caption{(a) A long-term performance (I–V and powder density) of Pr\textsubscript{2}NiO\textsubscript{4} measured up to 500 h. (b) Impedance spectra of Pr\textsubscript{2}NiO\textsubscript{4} measured up to 500 h. (c) A backscattered SEM image of Ni/YSZ/GDC/nickelate/Au-based cell after a 500-h measurement. (d) The images of cell surface after 500-h operation.}
\end{figure}
compatibility of PNO cathode with the GDC buffer layer, allowing for a long-term study. The results suggest that Au grids are capable for the studies of phase evolution and cathode durability in SOFCs without a significant performance interference.

CONCLUSIONS

The Au grid can be used as the cathode current collector for the quantification of phase evolution in PNO in an operating SOFC. Low chemical reactivity and mechanical stability of Au during cell operation make it suitable for such application. Quantification of the phase evolution in PNO was performed by the least-squares fitting of the LCOS against the experimental XRD patterns. Multiple cells were tested to study the reproducibility of the measurements. High performance was observed in cells with Au metal grids, extending the application of this method to cathode durability studies in state-of-the-art SOFCs.
REFERENCES


CHAPTER 5

ELECTROCHEMICAL PERFORMANCE AND PERFORMANCE DURABILITY OF (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ AS CATHODES FOR SOLID OXIDE FUEL CELLS

PNO partially decomposes to praseodymium oxide (PrO$_x$) and a higher order layered structure (Pr$_3$Ni$_2$O$_7$) during operation,$^{[1]}$ which presents a concern because of possible structural collapse and long-term performance degradation.$^{[1-2]}$ Current approaches to stabilize the PNO phase focus on substituting A and/or B-site ions.$^{[3-4]}$ Both La$_2$NiO$_4$ and Nd$_2$NiO$_4$ (NNO) are more stable than PNO$^{11}$, but have lower power density.$^{[5]}$ This work reports an attempt to stabilize the long-term cell performance in praseodymium nickelate. (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ (PNNO, x = 0, 0.25, 0.50, 0.75, and 1.0) cathodes were synthesized and electrochemically evaluated in anode supported cells. Nd was chosen as an A-site substituent due to its similar physical properties to Pr and its ability to suppress the formation of PrO$_x$ and higher order phases. The i-V and electrochemical impedance spectroscopy (EIS) measurements were performed between 650-850 °C, while the performance stability was measured at 750 °C and 0.8 V for 500 hours.

5.1 POWER DENSITY AND AREA SPECIFIC RESISTANCE in PNNO

Figure 5.1 shows i-V and power density curves for PNNO cells operated between 650 °C and 850 °C. The open circuit voltage (OCV) for all tested cells was in a range of 1.10 ± 0.02 V, suggesting reproducible assembly and quality seals. The i-V curves show
nonlinear behaviors as a function of current density, which is consistent with the previous measurements on PNO electrodes.\textsuperscript{[1,6-8]} With an increase in Nd content, the overall cell performance decreases. For instance, the power densities at 0.7 V at 750 °C are 0.85,

Figure 5.1 (a-e) Initial i-V and power density curves for (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cathodes as a function of $x$, operated between 650 and 850 °C, and (f) power density measured at 0.80 V as function of temperature for each composition.
0.63, and 0.14 W·cm\(^{-2}\) for PNO, PNNO5050 and NNO, respectively. This may be attributed to the slower kinetics in NNO\(^{11}\) because of its smaller surface exchange coefficient than PNO (e.g. \(4 \times 10^{-7}\) cm s\(^{-1}\) in NNO vs. \(2 \times 10^{-6}\) cm s\(^{-1}\) in PNO at 750 °C).\(^{[9]}\)

Figure 5.1(f) illustrates the power density as a function of temperature for all cathodes measured at 0.8 V. The power density increases with temperature by threefold for PNO cells, and by an order of magnitude for NNO cells. Therefore, higher operating temperatures are desirable to enhance ORR and ionic transport \(^{[9]}\) in Nd rich PNNO cathodes.

The total cell ASR as a function of current density at 750 °C is shown in Figure 5.2, which was calculated from the slope of \(i-V\) curves. The activation polarization region was observed between 0 and ~ 0.25 A·cm\(^{-2}\) with a large negative slope. In the ohmic polarization region, the total cell ASR is nearly linear with the current density. A positive slope would suggest the existence of the concentration polarization region. PNO was found...
to have the lowest ASR with a global minimum occurring at 0.80 V. With an increase in Nd content, the cell ASR increases, especially at low current densities, which is attributed to the reaction rate losses in electrodes.

Additionally, the total cell ASR can be obtained from the analysis of impedance spectra by using an equivalent circuit shown in Figure 5.5(c). Figure 5.3 shows a comparison of the electrode ASR determined from EIS and i-V measurements. The results for the two testing regimes (i-V vs. EIS) were reproducible and within 5% for each cathode composition. With an increase in current density, the overall electrode resistance decreases at 750 °C in air. Figure 5.4 shows ln(ASR_e) as a function of 1/T for all compositions measured at OCV. The electrode ASR decreases with increasing temperature for each cathode composition. PNO and PNNO7525 electrodes have comparably smaller ASR than

![Figure 5.3](image-url)

Figure 5.3 A comparison of the electrode ASR obtained from i-V and EIS measurements at 750 °C. Ohmic ASR was obtained by using the equivalent circuit presented in Figure 3.5 (c).
Figure 5.4 (a) Electrode resistance \( \ln(\text{ASR}_e) \) as a function of \( 1/T \) for all cathode compositions at OCV obtained from i-V curves. (b) A similar plot obtained from the DRT analysis while subtracting the anodic ASR.

other PNNO compositions between 650 °C and 800 °C at all measured currents. This can be attributed to smaller activation energy for the overall electrode reaction for PNO and PNNO7527 (0.87 ± 0.02 eV and 0.91 ± 0.02 eV, respectively). Extrapolated activation energy values from the DRT analysis (Figure 5.4b) further show the trend of an increase in \( E_a \) in Nd rich compounds. The greater activation energy in Nd-rich compounds results in more active electrodes at temperature > 800 °C. Therefore, a desirable PNNO composition can be selected while retaining relatively stable long-term performance, based on the operating conditions of SOFC stacks (e.g. temperature and voltage).

5.2 ANALYSIS OF THE DISTRIBUTION OF THE RELAXATION TIMES (DRT)

The evolution of DRT spectra for Nd-rich electrodes (\( \alpha = 0.75 \) and 1.0) is even more profound than Pr-rich electrodes. The advantage of DRT analysis lies in its high frequency resolution ability, \(^{10-13}\) since it allows to separate neighboring electrode processes which resonate within a half a decade. Consequently, relatively small frequency shifts can be
deconvoluted and a unique equivalent circuit model can be constructed for each impedance spectrum. **Figure 5.5(a)** shows the cathodic peaks P1c, P2c, and P3c dominate in the spectra. The high frequency impedance arc shifts to 5 kHz, as shown in **Figure 5.6(f)**. The shift is accompanied by corresponding changes in DRT spectra including a shift of P3c peak to higher frequency and an evolution of an additional cathodic process at 35 Hz. A twofold increase in the electrode polarization is consistent with a decrease in performance maxima, as illustrated in **Figure 5.1**.

**Figure 5.5(b)** shows DRT spectra on a cell with the cathode exposed to air and oxygen environments. Since anode conditions were kept constant, the changes in DRT spectrum were dominated by the evolution of cathodic processes. The peak at low frequency (P4a) does not significantly change and is associated with the anodic polarization. With an increase in Nd content from $x = 0$ to $x = 0.50$, there is a 20% increase in P3c (10 Hz) peak area. Such changes indicate higher resistance in cathodic processes. The arcs between 5 and 100 Hz (P3c and P2c) are generally assigned to change transfer
resistance and double layer capacitance in a cathode, consistent with the DRT analysis at different temperatures\textsuperscript{15} and under different oxidative environments\textsuperscript{10} in LSM and LSCF electrodes. The emergence of the low frequency arc at 0.5 Hz, as shown in Figure 5.6(d), is associated with slower adsorption/desorption of oxygen on the electrode surface\textsuperscript{11-12}, which is in agreement with an order of magnitude higher surface exchange coefficient for PNO (e.g. $2\times10^{-6}$ cm s\textsuperscript{-1} vs. $4\times10^{-7}$ cm s\textsuperscript{-1} in NNO at 750 °C).\textsuperscript{6} The high frequency (1 kHz) peak also increases with an increase in Nd-content and is attributed to slower oxygen ion transport from the electrode to the cathode/electrolyte interface.\textsuperscript{13}

Using the combined EIS and DRT results, a general equivalent circuit model was also constructed for PNNO cells, as shown in Figure 5.5(c). Based on the DRT analysis, the suppressed arcs in EIS spectra (corresponding to P2c and P3c) were fit with the neighboring equivalent circuits, with two parallel sets of resistors and constant phase elements (RCPE). Generated secondary DRT signals of a small intensity were an indication of neighboring RCPE elements. The P1c and P4a peaks were fit with corresponding RC elements. The initial resistance values were given using the DRT results, and the corresponding frequency range for each physical process was used for circuit fitting in ZView software.\textsuperscript{14} In contrast to DRT analysis, EIS has a low frequency resolution ability and can only recognize two neighboring electrode processes which have relaxation frequency difference of two or three orders of magnitude. Such a low resolution may not provide enough details while constructing the equivalent circuit model. Hence, the DRT analysis in this work shows gradual peak shifts to higher frequency with increasing Nd content followed by an increase in area of cathodic peaks, which corresponds to an increase in resistance of physical processes.
Figure 5.6 (a-f) Plots of i-V and power density curves for (Pr\textsubscript{1-x}Nd\textsubscript{x})\textsubscript{2}NiO\textsubscript{4} cells as a function of time, measured at 0.8 V and 750 °C along with corresponding EIS spectra measured at 0, 250\textsuperscript{th}, and 500\textsuperscript{th} hours.

Figure 5.7 illustrates the resistance for each process identified via DRT. With an increase in Nd content, the resistance for each process increases. A new emerging peak for NNO electrode at ~35 Hz carries a capacitance value of 3.9×10\textsuperscript{-4} F cm\textsuperscript{-2}, which lies within
the capacitance range for electrochemical reactions on cathodes.\textsuperscript{[15-16]} The $R_{3c}$ value also increases as expected from results obtained in Figure 3.4. After 500 hours of operation, the resistance of $P_{3c}$ peak in PNO cells increases by 5%, while stable R values were measured in cells with NNO cathodes.

5.3 PERFORMANCE STABILITY

Figure 5.6 shows i-V and EIS measurements at a function of time at 0.8 V. The performance degradation in PNO-based cells is more rapid than other compositions. The current density of PNO cathode at 0.8 V decreases from 1.12 A cm$^{-2}$ to 1.03 A cm$^{-2}$ after 250 hours, and to 0.90 A cm$^{-2}$ after 500 hours of operation, while the Nd substituted cathodes retain stable i-V and impedance responses, as shown in Figures 5.6(c-f). With an increase in Nd content, the total cell polarization increases by 29% for $x = 0.50$ and by
twofold for $x = 1.0$. **Figure 5.8** shows the long-term performance stability for all PNNO cathodes operated at 0.8 V and 750 °C. Cell performance for each cathode composition was within 9% among multiple cells measured.

A rapid initial degradation rate of 3.50% occurs for PNO cells within first 150 hours of operation, after which the performance remains constant. This can be attributed to relatively fast phase evolution in PNO. For cells with Nd substituted cathodes, the degradation rates are relatively constant. An unexpected increase in initial cell performance (2-3%) was observed within first 125 hours of operation in cells with platinum current collector. Pt current collector is known to enhance the electrode performance due to its inherent activity towards ORR. Indeed, the migration of Pt to the GDC/cathode interface was observed via SEM-EDS analysis. On the other hand, cells with gold current collector did not show changes in initial performance due to its excellent mechanical compatibility with cathodes.

**Figure 5.8** Performance stability for $(\text{Pr}_{1-x}\text{Nd}_x)_2\text{NiO}_4$ cathodes measured at 0.8 V and 750 °C.
Figure 5.9 illustrates the evolution of electrode and ohmic resistance as a function of time. Performance degradation in PNO is accompanied by increase in electrode resistance by 5.80%/1,000 hours (measured at 0.50 A cm$^{-2}$) and by 13.5%/1,000 hours (measured at 1 A cm$^{-2}$), while ohmic resistance remained stable. The cells with Nd-substituted cathodes show remarkable improvements in performance stability accompanied with a decrease in maximum power density, as shown in Fig. 5.8. A 7% reduction in power density for $x=0.25$ was compensated by an order of magnitude increase in performance stability (degradation of 0.56%/1,000 hours). With further Nd substitution, the degradation becomes marginal (a fraction of a percent), indicating that A-site substitution with Nd is a promising solution to stabilize the long term performance in PNO.

![Figure 5.9](image)

Figure 5.9 (a) Electrode ASR and (b) ohmic ASR as a function of time measured at 0.50 A cm$^{-2}$ for (Pr$_{1-x}$Nd$_x$)$_2$NiO$_4$ cathodes at 0.8 V.

The performance stability for Nd-rich electrodes was also studied with oxide CCs. (Pr$_{0.25}$Nd$_{0.75}$)$_2$NiO$_4$ cells were measured with LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) and (La$_{0.80}$Sr$_{0.20}$)$_{0.95}$CoO$_{3-x}$ (LSC) oxide CCs (Fig. 5.9, cells 9-10) and NNO cells were measured with LSC current collector (cell 12) and showed consistent power density maxima with those obtained with metal CCs (0.25 W cm$^{-2}$ for PNN02575 cells and ~0.20
W cm\(^{-2}\) for NNO cells at 750 °C and 0.8 V). The performance remained stable, with a degradation rate of 0.13% and 0.06%/1,000 hours for PNNO2575 and NNO, respectively.

CONCLUSIONS

Electrochemical performance and performance stability of PNNO series as the SOFC cathodes were studied. A reproducible performance, within 9% for each cathode composition, was observed. While Pr\(_2\)NiO\(_4\) cells undergo degradation rate of 6.40%/1,000 hours, each Nd-substituted cathode show improved performance stability, regardless of the current collector used. EIS and DRT analysis showed that an increase in total cell ASR is governed by the increase in electrode polarization, which in turn leads to lower performance maxima. With increase in Nd content at temperatures ≤ 750 °C, the electrode ASR increases due to lower kinetic parameters of cathodes. At 800-850 °C, a significant reduction in the electrode ASR for all Nd substituted compositions was observed, and is consistent with a higher activation energy towards oxygen reduction reaction in Nd doped compounds. Therefore, depending on the systems requirements, PNNO can operate at wide temperature regions to provide a simultaneously stable and active performance.
REFERENCES

CHAPTER 6

CRYSTAL STRUCTURE, ELECTRICAL PROPERTIES, AND
MICROSTRUCTURAL ANALYSIS OF (Pr\textsubscript{1-x}Nd\textsubscript{x})\textsubscript{2}NiO\textsubscript{4+C} CATHODES

Performance measurements in Chapter 3 showed that an increase in Nd content led to more stable long-term performance, but a substantial decrease in the electrode activity in Nd-rich (Pr\textsubscript{1-x}Nd\textsubscript{x})\textsubscript{2}NiO\textsubscript{4+δ} (PNNO) electrodes. This brings to a question of how a simple substitution on the Pr-site, with a cation of similar size and charge, can lead to considerable changes in electrode properties. An approach taken in this work involves a systematic study involving Nd substitution (x = 0, 0.25, 0.50, 0.75, and 1.0) on the Pr-site. In parallel to this study, a detailed investigation was conducted on the structural and electrical properties of the materials. Characterization was performed at room temperature and operating conditions. The long-term phase evolution in PNNO series was studied in powders, electrodes, and full electrochemical cells. The results were used to complement our previous studies on the electrochemical properties of PNNO series used as the cathodes in SOFCs. Microstructural characterization of electrodes was also conducted and used to understand the phase evolution and performance stability.

6.1 STRUCTURAL AND ELECTRICAL PROPERTIES OF PNNO

**Figure 6.1** shows raw XRD patterns of (Pr\textsubscript{1-x}Nd\textsubscript{x})\textsubscript{2}NiO\textsubscript{4} (PNNO) powders (x = 0, 0.25, 0.50, 0.75, and 1) together with the standard diffraction files for PNO and Nd\textsubscript{2}NiO\textsubscript{4} (NNO). Single phase in an orthorhombic structure was obtained for each composition. The
Rietveld refinement of XRD patterns was performed using a FullProf code and Bmab symmetry, resulting in an agreement between the experimental and calculated patterns, which can be seen from their difference depicted in blue line, as shown in Figure 6.2. The

![Figure 6.2](image)

**Figure 6.1** XRD of raw, single phase (Pr$_{1-x}$Nd$_x$)$_2$NiO$_{4+\delta}$ powders

constraint of full elemental occupancy was made with (Pr+Nd)/Ni equal to two, allowing the atomic positions to vary. The refinement parameters for all PNNO samples at room temperature are listed in Table 6.1. The refinement in orthorhombic structure gives encouraging results. For instance, the fit for the entire series does not deviate much, $2.70 \leq \chi^2 \leq 4.10$. The highest intensity diffraction peak shifts to higher 2θ values with increase in Nd content, indicating changes in structural parameters. Fractional position coordinates
Figure 6.2 Rietveld refinement on (Pr_{1-x}Nd_x)_{2}NiO_{4+δ} cathode materials using the FullProf code. Dots are raw data. Solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves.

on heavy metal cations (Pr,Nd) indicate a compression in both z and y direction with an increase in Nd content, accompanied by a compression of O2(f) and O1(e) atomic positions, respectively. The decrease in magnitude of the fractional position coordinate indicates closer distance to the origin of the system, which is a Ni atom in oxygen octahedral with coordinates (0,0,0). As the magnitude of the fractional position coordinate is decreasing, the atoms are closer to the Ni (origin of the system). For instance, the magnitude of the (-)ve y coordinate on Pr/Nd position decreases (closer to origin) while the z coordinate become less positive (closer to origin), both indicating compression. Similarly,
Table 6.1. Refinement parameters of \((\text{Pr}_{1-x}\text{Nd}_x)\text{NiO}_4\) at room temperature. \(x, y, z\) are fractional position coordinates. All samples are orthorhombic structure with space group Bmab. \(\chi^2\) is \([R_{wp}/R_{exp}]^2\), where \(R_{wp}\) is the residual error of the weighted profile and \(R_{exp}\) is statistically expected residual error of the entire measured diffraction patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(x=0)</th>
<th>(x=0.25)</th>
<th>(x=0.50)</th>
<th>(x=0.75)</th>
<th>(x=1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>5.38435 (20)</td>
<td>5.38075 (35)</td>
<td>5.37673 (15)</td>
<td>5.37234 (22)</td>
<td>5.36842 (18)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>5.44870 (32)</td>
<td>5.44758 (42)</td>
<td>5.44646 (28)</td>
<td>5.44533 (25)</td>
<td>5.44421 (23)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>12.43025 (45)</td>
<td>12.41688 (50)</td>
<td>12.39882 (31)</td>
<td>12.38315 (60)</td>
<td>12.36856 (55)</td>
</tr>
<tr>
<td>(\text{Vol} (\text{Å}^3))</td>
<td>364.675 (30)</td>
<td>363.9356 (33)</td>
<td>363.0661 (25)</td>
<td>362.2261 (35)</td>
<td>361.4935 (28)</td>
</tr>
<tr>
<td>(\text{Pr/Nd})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(y)</td>
<td>-0.00318 (2)</td>
<td>-0.00302 (1)</td>
<td>-0.00293 (3)</td>
<td>-0.00258 (1)</td>
<td>-0.00117 (2)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.35918 (5)</td>
<td>0.35899 (5)</td>
<td>0.35893 (5)</td>
<td>0.35875 (6)</td>
<td>0.35848 (5)</td>
</tr>
<tr>
<td>(\text{Pr Occ})</td>
<td>0.50</td>
<td>0.375</td>
<td>0.25</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>(\text{Nd Occ})</td>
<td>0.125</td>
<td>0.25</td>
<td>0.25</td>
<td>0.375</td>
<td>0.50</td>
</tr>
<tr>
<td>(\text{Ni})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Ni Occ})</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(\text{O1(e)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(y)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(z)</td>
<td>-0.00911 (1)</td>
<td>-0.01219 (1)</td>
<td>-0.002124 (2)</td>
<td>-0.00327 (1)</td>
<td>-0.00568 (2)</td>
</tr>
<tr>
<td>(\text{O2(f)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(y)</td>
<td>0.05968 (2)</td>
<td>0.05123 (1)</td>
<td>0.04876 (1)</td>
<td>0.04816 (1)</td>
<td>0.04490 (1)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.17591 (6)</td>
<td>0.17552 (8)</td>
<td>0.17515 (4)</td>
<td>0.17508 (5)</td>
<td>0.17470 (4)</td>
</tr>
<tr>
<td>(R_p) (%)</td>
<td>5.67</td>
<td>5.15</td>
<td>5.65</td>
<td>4.01</td>
<td>5.03</td>
</tr>
<tr>
<td>(R_{wp}) (%)</td>
<td>7.45</td>
<td>6.66</td>
<td>7.52</td>
<td>5.26</td>
<td>6.75</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>3.52</td>
<td>3.20</td>
<td>4.10</td>
<td>2.70</td>
<td>3.90</td>
</tr>
</tbody>
</table>
the magnitude of the $z$ coordinate for O1(e) decreases, as is the case for O2(f). Therefore, the substitution of Nd on the Pr-site does not change the crystal structure itself but changes the relative atomic positions, which in turn affects the lattice parameters. Furthermore, the change in oxygen occupancy,\cite{1} which could not be precisely determined via XRD, is another factor influencing the lattice parameters. Therefore, detailed $M$-$O$ bond lengths and angles will be reported in Chapter 8 using high resolution and high flux synchrotron radiation.

With an increase in Nd content, the cell volume decreases linearly by 0.87\% ($m = -3.23$) for $x = 1$, as shown in Figure 6.3(a). The lattice parameter change can be described by using Vegard’s Law:

$$a_{A_{1-x}B_x} = (1 - x) a_A + x a_B$$

(1)

where $a_{A_{1-x}B_x}$ is the lattice parameter of a PNNO solution, $a_A$ and $a_B$ are lattice parameters of the pure constituents, PNO and NNO, respectively, and $x$ is the molar fraction of Nd in the solution. Shrinkage in the cell volume with increase in Nd content can be expressed as:

$$V = 364.69 - 3.23x.$$ 

(2)

Figure 6.3 (a) Cell volume for Nd-substituted Pr$_2$NiO$_{4+\delta}$ powders obtained from the Rietveld refinement. (b) Calculated cell parameters as function of Nd substitution and compared against literature values.
The volume contraction is driven by a fast rate of decrease in the $c$ parameter, with a negative slope of $m = -3.18$ (which is within 1.60% of the slope in volume change), while $a$ and $b$ lattice parameters decrease at much slower rates, $m = -0.016$, $m = -0.0045$, respectively, as shown in Figure 6.3(b). A steeper slope for the volume contraction, when compared to a decrease in the $c$ lattice parameter, may be associated with the change in oxygen occupancy, as suggested in previous studies on PNO and NNO.\cite{1} A decrease in the $c$ parameter from 12.4303 Å (PNO) to 12.3686 Å (NNO) is equivalent to 0.50%, which is in an agreement with the work (0.55%) performed by Boehm and Bassat et al.\cite{1} Similarly, Wahyudi and Ceretti et al.\cite{2} calculated a significant decrease in the $c$ parameter in single crystals of PNO and NNO from 12.4402 Å (PNO) to 12.3652 Å (NNO), which is equivalent to 0.60%. The ionic radii of Pr$^{3+}$ and Nd$^{3+}$, with the coordination number of 8, are within 1.8% (1.13 Å and 1.11 Å, respectively), hence the shrinkage in the cell volume with an increase in Nd content at room temperature seems mainly driven by the size difference between the two cations. A linear increase in $c$ lattice parameter in both PNO and NNO with an increase in temperature was observed,\cite{1} implying that an increase in cell volume in air from 30 °C to 1000 °C (4.26% and 2.76%, respectively) was independent of the structural transition from Bmab to I4/mmm.\cite{3, 4}

Temperature dependency of the electronic conductivity, $\sigma_e$, in PNNO ceramics is given by:

$$\sigma_e = N\mu q$$ (3)

where $\mu$ is the mobility, $q$ is the carrier charge, and $N$ in the carrier concentration. Since the mobility of either electrons or holes is much higher than the mobility of oxygen ions, the total conductivity in PNNO is dominated by hole conduction. In PNNO series, oxygen
transport is known to occur via oxygen interstitials, $O_i''$. The defect chemistry reaction between oxygen gas and oxygen interstitials is given by:

$$O_{2(g)} = 2O_i'' + 4h^0$$

(4).

The charge neutrality equation is:

$$2[O_i''] = p$$

(5).

**Figure 6.4(a)** illustrates the $\sigma_e$ measured in air on the series of PNNO ceramics between 50 and 850 °C. With an increase in temperature from 50 to ~ 500 °C, the $\sigma_e$ increases for the entire PNNO series. The results can be attributed to thermally activated polaron hoping process, which follows:

$$\mu = \mu_0 \exp\left(-\frac{E_{a,m}}{kT}\right)$$

(6)

There are three regions in the plot: (i) the low temperature region ($T \leq 600$ °C) corresponding to thermally activated hopping process;[5] (ii) high temperature region ($T > 750$ °C), at which conductivity decreases due to the rapid loss of oxygen interstitials, thus a decrease in carrier.

**Figure 6.4** (a) Total conductivity for the series of PNNO bars measured in air between 50 – 850 °C. (b) Conductivity in bars with x=0, 0.50, 1.0 as function of oxygen partial pressure.
density, \( p \), which overwhelms the increase in mobility; as a result, the electrical conductivity decreases; and (iii) a transition region between 500 and 750 °C, where the decrease in carrier density started to influence electrical conductivity upon heating. The highest conductivity (90 S cm\(^{-1}\) at 600 °C) was measured for PNO and decreased with an increase in Nd content (54 S cm\(^{-1}\) at 500 °C for NNO). The entire PNNO series exhibits a \( p \)-type conducting behavior, with a conductivity maximum observed between 500-600 °C. With an increase in Nd content the conductivity maximum shifts to lower temperatures. Since the maximum conductivity range falls within the transition region (iii) the decrease in carrier density in NNO seems to play a larger role on the electrical conductivity, resulting in lower temperature for the conductivity maximum (\( \sigma_{e,\text{max}} \)). Table 6.2 summarizes the \( \sigma_{e,\text{max}} \) and its \( T(\sigma_{e,\text{max}}) \).

Table 6.2 Conductivity maximum for \((\text{Pr}_{1-x}\text{Nd}_x)\text{NiO}_4\) series.

<table>
<thead>
<tr>
<th>( x ) (Nd fraction)</th>
<th>( \sigma_{e,\text{max}} ) (S cm(^{-1}))</th>
<th>( T(\sigma_{e,\text{max}}) ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90</td>
<td>600</td>
</tr>
<tr>
<td>0.25</td>
<td>81</td>
<td>595</td>
</tr>
<tr>
<td>0.50</td>
<td>73</td>
<td>590</td>
</tr>
<tr>
<td>0.75</td>
<td>68</td>
<td>580</td>
</tr>
<tr>
<td>1.0</td>
<td>54</td>
<td>500</td>
</tr>
</tbody>
</table>

NNO exhibits the lowest \( \sigma_e \) over the entire temperature region. Measurements on a single crystal NNO showed a lower oxygen mobility when compared to PNO.\(^{[6]}\) Reduced apical oxygen mobility at lower temperatures (\( T < 500 \) °C) was attributed to low energy specific phonon modes, which are required for the conduction at lower temperatures.\(^{[7, 8]}\) Because of smaller \( c \)-axis parameter when compared to PNO (Figure 6.3(a)), there is less vibrational motion of oxygens along the (a,b)-plane in the rock-salt layer, leading to lower oxygen mobility.\(^{[6]}\) Figure 6.4(b) shows an increase in \( \sigma_e \) for all compounds with
increasing oxygen activity, consistent with $p$-type conduction behavior. Higher oxygen activity leads to a higher hole concentration, as shown in Eq. (4); therefore, a higher $\sigma_e$ was measured for all PNNO ceramics in pure oxygen. Less $pO_2$ dependency in NNO (4.0% at 600 °C and 5.6 % at 850 °C) vs. PNO (5.1% at 600 °C and 8.4% at 850 °C) further indicates a higher $E_{a,m}$ in NNO ceramics, as shown in Eq. (6). Therefore, due to a smaller cell volume, a lower oxygen mobility, and a smaller conductivity, the mixed-ionic-electronic-conduction (MIEC) properties are suppressed in NNO. The transport data are in agreement with electrochemical operation in full cells in our previous work,[9] showing a much lower performance (by fourfold at 750 °C and 0.80 V) and a 29-38% increase in the activation energy for ORR in Nd-rich PNNO electrodes.

6.2 PHASE EVOLUTION IN PNNO POWDERS AND ELECTRODES

Figure 6.5 demonstrates phase evolution in thermally annealed PNNO powders. Predominant evolution of PrO$_x$, measured via XRD, indicates 30% transition of the parent PNO phase after only 150 hours at 700 °C. With 50% Nd substitution on the Pr-site (PNNO50-50), the phase was significantly stabilized, showing only 3 mol% of PrO$_x$ after 500 hours at 750 °C. With a further increase in Nd content, the long-term studies up to 2,500 hours at 750 °C show the preservation of parent ($Pr_{0.25}Nd_{0.75}$)$_2$NiO$_{4+\delta}$ (PNNO25-75) phase.

Phase evolution in electrodes was examined at various temperatures, as shown in Figure 6.6(a). PNO undergoes a rapid phase transition, within 150 hours, at all tested temperatures. The rate of phase evolution increases with increasing temperatures. At lower temperatures, a two region plot evolves: (i) a slow phase transition for $t \leq 75$ h and, and (ii)
Figure 6.5 Thermal stability of PNNO powders at 750 °C in air.

A rapid phase evolution beyond 100 hours of thermal annealing. The sixfold increase in rate of phase transition at 700 °C, and threefold at 750 °C may be initiated by a sufficient amount of PrO$_x$ being formed, which tends to accelerate phase transition due to considerable (69%) thermal mismatch between PNO (TEC=13.2 x 10$^{-6}$ °C$^{-1}$),$^{[10]}$ and PrO$_x$ (TEC=22.3 x 10$^{-6}$ °C$^{-1}$).$^{[11]}$ There seems to be a linear relationship between phase transition and formation of PrO$_x$.$^{[12, 13]}$ Although the parent PNNO50-50 phase remains stable at 700 °C and up to ~200 hours at 750 °C, a significant phase transition follows reaching 24.4 % after 500 hours, Figure 6.6(b). The phase evolves slowly between 150-300 h and then accelerates, as in the case for PNO. Therefore, a higher Nd concentration on the Pr-site was utilized to further suppress phase transition. As a result, PNNO25-75 and NNO electrodes
had fully preserved phase after long-term thermal annealing at all temperatures, as shown in Figure 6.6(b).

![Figure 6.6](image)

**Figure 6.6** (a) Phase evolution in PNO and (b) PNNO electrodes in symmetric cells (YSZ/GDC/cathode) as function of time and temperature.

In order to investigate the kinetics of thermal phase transition, an early kinetic model developed by Avrami\(^{[14-16]}\) was adopted. The model is based on a sigmodial increase in volume of a new crystal phase as a function of time, where slow crystallization initiates followed by a rapid increase. Such a behavior is similar to the phase evolution in praseodymium nickelates shown in Figure 6.6; hence, the model by Avrami is appropriate for this study. The experimental data has been fitted using the equation:

\[
x = 1 - \exp[-kt^n]
\]  

where \(x\) is the fraction of parent phase transformed, \(k\) is the reaction rate, \(t\) is time, and \(n\) is the exponent that describes geometry of the growth of a new phase. By arranging the Eq. (7) and expressing it in natural logarithm form as:

\[
\ln[-\ln(1-x)] = \ln(k) + n \ln(t)
\]  

the isothermal linear plots were generated to determine the values of \(k\) and \(n\) from the least squares fitting. The order of phase transition in PNO decreases with increase in temperature, with \(n\) decreasing from 2.43 (700 °C), to 2.10 (750 °C), to 1.65 (790 °C),
further indicating thermally driven phase transition. By expressing the reaction rate in its Arrhenius form:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

(9)

where $k_0$ is the pre-exponential factor and $E_a$ is the activation energy for phase transition, the activation energy can be extrapolated from the logarithmic expression of this equation. A high activation energy, $E_a = 4.40$ eV, can be attributed to cation mobility within the structure,[17, 18] which in turn leads to atomic rearrangements and phase transition.

**Figure 6.7** illustrates raw XRD plots on phase evolution in electrochemically operated PNNO electrodes. Gold grids[13] were used as cathode current collectors providing an exposure window for phase quantification studies. Evolution of PrO$_x$, NiO (in $2\theta = 38$-$42^\circ$), and new peaks ($2\theta < 24^\circ$) shows major transition in PNO phase. Respective magnitude of an arrow at a high intensity nickelate peak ($2\theta \approx 32^\circ$) shows a relative drop in nickelate signal after operation, when compared to initial signal in each cell. With an increase in Nd content, the phase evolution is significantly suppressed resulting in fully preserved NNO phase after 500 hours of electrochemical operation. Reproducible results were obtained with multiple cells for each cathode composition. With an increase in Nd content, the phase transition is suppressed by 40, 65, 75, and 100 %, respectively. It is imperative to note that phase transition in operated PNNO electrodes is significantly higher when compared to thermally annealed powders (**Figure 6.5**), as was the case in symmetric cells. At 750 °C the phase degrades by additional 28.0% in PNNO50-50 electrode. Such increase can be attributed to significant reaction with GDC barrier layer.[10]
Figure 6.7 Phase evolution in PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours.

The reaction with GDC buffer was studied via SEM/EDS analysis on operated full cells. The cell cross section along with cell components is shown in Figure 6.8(a). FIB was also used for sample etching to further expose the GDC/cathode interface for the elemental analysis, as shown in Figure 6.8(b). Three regions were studied including the GDC buffer layer (region 1), cathode/GDC interface (region 2), and cathode bulk (region 3). Suppressed reaction with GDC was observed with increase in Nd content, which can be seen from a decrease in Pr diffusion into GDC bulk. Table 6.3 summarizes the elemental distribution across multiple regions of a button cell for Pr, Nd, and Ni in all PNNO cathodes. With only 25% Nd substitution on the A-site, the Pr diffusion into GDC is suppressed by twofold (region 1), sixfold for x=0.50, and fully suppressed for compositions
with higher Nd content. The stoichiometric Pr:Nd:Ni ratios in cathode bulk indicate that reaction occurs at a narrow cathode/GDC interface.

Figure 6.8 (a) A cell cross section showing configuration of all components. Inserted figure shows a top view of the cells. (b) Gas assisted etching was performed via FIB to verify elemental composition at the cathode/GDC interface. Numbered boxes show the areas used for EDS studies.

6.3 MICROSTRUCTURAL ANALYSIS OF THE ELECTRODES

Figure 6.9(a) shows SEM analysis on all electrode microstructures before operation. The initial microstructures are similar for the entire series. However, a substantial decrease in electrode porosity was observed after 500 hours of operation. The rate of electrode densification seems to be dependent upon Nd substitution. Figure 6.9(b) shows larger decrease in electrode porosity in PNNO electrodes (in particular PNNO75-25, PNNO50-50) and NNO when compared to PNO. Therefore, there might be a link between a substantial phase transition in PNO and slower rate of electrode densification. Overall, with Nd substitution the particle agglomeration is faster, which might be attributed to the absence of secondary phases (PrOₓ and higher order nickelates) and better thermal expansion match. On the other hand, formation of PrOₓ and the thermal mismatch against PNO may slow down the densification process. A large phase evolution and a decrease in electrode porosity in PNO appear counterintuitive when compared to ~ 6.40%/1,000 hours
performance degradation. This brings to a question of the role of phase transition on performance stability because a 98% phase transition in PNO (according to XRD analysis) is expected to lead to a sharp performance decrease in a cell. Therefore, a deeper understanding on the role of phase evolution and microstructural changes on the electrochemical performance was required to bridge the two sets of results.

TEM images and elemental mapping on single phase PNO electrode show uniform phase distribution, as shown in Figure 6.10(a). Figure 6.10 (b), however, shows noticeable contrasted phases, which were formed after electrode operation. STEM analysis on an operated PNO electrode shows regions of fully extruded PrO$_x$ and NiO phases, Figure 6.10(c-f). Analysis on operated PNN050-50 electrode (Figure 6.11) also shows multiple phases but with significantly smaller presence of PrO$_x$ and NiO. The results confirm phase transition, as supported by XRD analysis in Figures 6.5 and 6.7. However, regions with nickelate phase(s) were also detected through the entire electrode bulk with reduced particle size (60-70 nm). The regions of preserved nickelate phase(s) and substantial

Table 6.3 Quantified EDS area scan results of elemental distribution across multiple regions of a button cell. For the simplicity reasons only atomic percentages for Pr, Nd, and Ni are presented.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Region 1 (GDC)</th>
<th>Region 2 (GDC/cathode interface)</th>
<th>Region 3 (cathode bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Pr</td>
<td>Nd</td>
<td>Ni</td>
</tr>
<tr>
<td>Pr$<em>2$NiO$</em>{4+δ}$</td>
<td>11.17</td>
<td>/</td>
<td>3.70</td>
</tr>
<tr>
<td>(Pr$<em>{0.75}$Nd$</em>{0.25}$)$<em>2$NiO$</em>{4+δ}$</td>
<td>5.25</td>
<td>0</td>
<td>2.96</td>
</tr>
<tr>
<td>(Pr$<em>{0.50}$Nd$</em>{0.50}$)$<em>2$NiO$</em>{4+δ}$</td>
<td>2.30</td>
<td>3.87</td>
<td>1.51</td>
</tr>
<tr>
<td>(Pr$<em>{0.25}$Nd$</em>{0.75}$)$<em>2$NiO$</em>{4+δ}$</td>
<td>0</td>
<td>3.15</td>
<td>1.43</td>
</tr>
<tr>
<td>Nd$<em>2$NiO$</em>{4+δ}$</td>
<td>/</td>
<td>2.82</td>
<td>0.96</td>
</tr>
</tbody>
</table>
microstructural change may provide further insights for retained electrode activity towards ORR, which warrants a further study.

Figure 6.9 Initial electrode microstructure and porosity (a), and the changes in electrode microstructure and porosity after 500 hours of operation in full cells at 750 °C and 0.80 V (b).
Figure 6.10 (a) TEM image on a single phase PNO electrode, and (b) on electrochemically operated PNO electrode. The electrode was operated in full cells for 500 hours at 750 °C and 0.8V. The regions shown in a high angle annular dark field image (b) on operated PNO electrode were used for elemental mapping analysis (c-f).

Figure 6.11 (a) TEM image on a single phase PNNO50-50 electrode, and (b) on electrochemically operated PNNO50-50 electrode. The electrode was operated in full cells for 500 hours at 750 °C and 0.8V. The regions shown in a high angle annular dark field image (b) on operated PNNO50-50 electrode were used for elemental mapping analysis (c-f).
CONCLUSIONS

The structural, electrical, and microstructural properties in PNNO series were investigated. A decrease in the unit cell volume (0.87%) and total electrical conduction (40%) suppress the mixed conduction properties in NNO, which is in agreement with lower power density in full cells and an increase in activation energy for ORR. Long-term electrochemical operation of PNNO electrodes shows suppressed phase transition with an increase in Nd content. STEM analysis confirms multiple phases present in PNO electrode including fully extruded PrO$_x$ and NiO phases, while suppressed phase transition was detected with an increase in Nd content. Nickelate phase(s) was also detected via STEM through the entire electrode bulk and undergoes microstructural change. Decrease in particle size (60-70 nm) may provide a better understanding towards retained electrode activity, regardless of decrease in electrode porosity and phase transition. Reaction with GDC buffer layer was also suppressed with an increase in Nd content, which was confirmed by significant reduction of Pr elemental diffusion into GDC bulk.
REFERENCES

13. Dogdibegovic, E., C.J. Wright, and X.-D. Zhou, Stability and Activity of (Pr1-xNd)2NiO4 as Cathodes for Solid Oxide Fuel Cells: I. Quantification of Phase


CHAPTER 7

THE ROLE OF A- AND B-SITE DOPANTS ON THE STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF (Pr$_{1-x}$Nd$_x$)$_2$Ni$_{1-y}$B$_y$O$_4$

CATHODES

A task to develop a compositional window which results in both stable structure and desirable catalytic activity has been a fundamental challenge. Chapters 5 and 6 show that A-site substitution with Nd in (Pr$_{1-x}$Nd$_x$)$_2$NiO$_{4+\delta}$ cathodes is a promising solution to stabilize the cell performance. However, with a low Nd-content (≤ 50 mol%), a long-term operation leads to phase transition. In contrast, a high Nd content results in a stable phase during a 2,500-hour test,[1] but with a much lower performance (fourfold decrease). Therefore, further compositional modifications are required to simultaneously obtain high catalytic activity and stable crystal structure.

An approach taken in this work was to manipulate the Ni-site in a promising (Pr$_{0.50}$Nd$_{0.50}$)$_2$NiO$_{4+\delta}$ (PNN05050) electrode, which is known to have 26× lower performance degradation (0.25%/1,000h) when compared to PNO.[2] The screening process included multiple d-block ions in various concentrations (Table A.1, Appendix A). It was found that Cu doping at the Ni-site can fully stabilize the performance, suppress phase transition, and retain relatively high power output.[3] The (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+\delta}$ (PNN05050-Cu$_y$) powders were synthesized and evaluated thermally at various conditions. Quantification of phase changes was performed through long-term studies and
compared against PNNO5050 composition. Current-voltage sweep (i-V scan) and electrochemical impedance spectroscopy (EIS) measurements were performed between 650-850 °C, while the performance stability was measured at 790 °C and 0.80 V for 500 hours.

7.1 STRUCTURAL CHARACTERIZATION

Figure 7.1 shows the Rietveld refinements on (Pr\textsubscript{0.50}Nd\textsubscript{0.50})\textsubscript{2}Ni\textsubscript{1-y}Cu\textsubscript{y}O\textsubscript{4+δ} powders where y = 0, 0.05, 0.10, and 0.20, respectively. Dots are the raw data and solid lines are the calculated profiles. Thick marks below the diffraction profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves. Single

![Rietveld refinement using the FullProf code on (Pr\textsubscript{0.50}Nd\textsubscript{0.50})\textsubscript{2}Ni\textsubscript{1-y}Cu\textsubscript{y}O\textsubscript{4+δ} powders where y = 0, 0.05, 0.10, and 0.20, respectively. Dots are the raw data and solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves.](image)

**Figure 7.1** Rietveld refinement using the FullProf code on (Pr\textsubscript{0.50}Nd\textsubscript{0.50})\textsubscript{2}Ni\textsubscript{1-y}Cu\textsubscript{y}O\textsubscript{4+δ} powders where y = 0, 0.05, 0.10, and 0.20, respectively. Dots are the raw data and solid lines are the calculated profiles. Thick marks below the profiles mark the positions of the allowed reflections. Solid lines below the thick marks are the difference curves.
phase powders were in an orthorhombic structure for PNNO5050-Cu\textsubscript{y} compositions, as indicated by the red line. The Rietveld refinement of XRD patterns was performed using a FullProf code\cite{4} and Bmab symmetry, resulting in an agreement between the experimental and calculated patterns, which can be seen from their difference depicted in a blue line. The constraint of full elemental occupancy was made with (Pr+Nd)/(Ni+Cu) equal to two, allowing the atomic positions to vary. The refinement parameters for all PNNO5050-Cu\textsubscript{y} samples at room temperature are listed in Table 7.1. The fit for the entire series does not deviate much, $3.90 \leq \chi^2 \leq 4.70$, indicating a proper symmetry. With an increase in Cu-content, the doubles at $2\theta \approx 33^\circ$ merge, indicating changes in structural parameters. However, the highest intensity diffraction peaks do not shift and there are no new emerging peaks, indicating a retained parent phase.

Fractional position coordinates on heavy metal cations (e.g. Pr and Nd) indicate an elongation in the $z$ direction and overall compression in the $y$ direction with an increase in Cu content, accompanied by a compression of O1(e) and elongation of O2(f) atomic positions. Therefore, the Cu doping ($y \leq 0.20$) on the Ni-site in PNNO5050 does not change the crystal structure itself but changes the relative atomic positions, which in turn affect the lattice parameters. The refinement for PNNO5050-Cu\textsubscript{30} was not possible in Bmab symmetry due to large structural changes, as seen by the change in the relative peak intensity ratio and by full merging of the doublets at $33^\circ$ and $44^\circ$. With an increase in Cu content, the unit cell parameters change results in a 0.30% increase in $a$ and a 0.70% decrease in $b$, as shown in Figure 7.2(a). However, the most significant change was calculated for the $c$ lattice parameter with a 0.90% increase for PNNO5050-Cu\textsubscript{20}. Due to an overall increase in the lattice parameters, the cell volume increases by 0.40%, as shown.
Table 7.1 Refinement parameters of \((\text{Pr}_{0.50}\text{Nd}_{0.50})_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4\) at room temperature. \(x, y, z\) are fractional position coordinates. All samples are orthorhombic structure with space group Bmab. \(\chi^2\) is \([R_{wp}/R_{exp}]^2\), where \(R_{wp}\) is the residual error of the weighted profile and \(R_{exp}\) is statistically expected residual error of the entire measured diffraction patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(y=0)</th>
<th>(y=0.05)</th>
<th>(y=0.10)</th>
<th>(x=0.20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>5.37473 (30)</td>
<td>5.37824 (25)</td>
<td>5.38145 (21)</td>
<td>5.38708 (23)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>5.44012 (25)</td>
<td>5.43124 (15)</td>
<td>5.41831 (35)</td>
<td>5.40055 (38)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>12.38508 (32)</td>
<td>12.41546 (36)</td>
<td>12.45074 (45)</td>
<td>12.4998 (30)</td>
</tr>
<tr>
<td>Vol (Å³)</td>
<td>362.12954 (38)</td>
<td>362.52549 (31)</td>
<td>363.01321 (28)</td>
<td>363.6591 (25)</td>
</tr>
<tr>
<td>Pr/Nd</td>
<td>-0.00293 (2)</td>
<td>-0.00254 (1)</td>
<td>-0.00212 (1)</td>
<td>-0.00178 (2)</td>
</tr>
<tr>
<td>(y)</td>
<td>0.35894 (5)</td>
<td>0.35898 (3)</td>
<td>0.35912 (2)</td>
<td>0.359314 (6)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Pr Occ</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Nd Occ</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Ni/Cu</td>
<td>0.25</td>
<td>0.2375</td>
<td>0.225</td>
<td>0.20</td>
</tr>
<tr>
<td>Ni Occ</td>
<td>0.25</td>
<td>0.0125</td>
<td>0.025</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu Occ</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>O1(e)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>O2(f)</td>
<td>0.0125</td>
<td>0.025</td>
<td>0.025</td>
<td>0.05</td>
</tr>
<tr>
<td>(y)</td>
<td>0.04490 (2)</td>
<td>0.04486 (1)</td>
<td>0.04492 (2)</td>
<td>0.04502 (2)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.17591 (5)</td>
<td>0.17623 (3)</td>
<td>0.17684 (2)</td>
<td>0.17725 (1)</td>
</tr>
<tr>
<td>(R_p) (%)</td>
<td>5.25</td>
<td>4.25</td>
<td>4.25</td>
<td>5.33</td>
</tr>
<tr>
<td>(R_{wp}) (%)</td>
<td>6.30</td>
<td>5.40</td>
<td>6.23</td>
<td>5.95</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>4.30</td>
<td>3.90</td>
<td>4.32</td>
<td>4.70</td>
</tr>
</tbody>
</table>
in Figure 7.2(b). An increase in the cell volume with increasing molar fraction of Cu (x) can be expressed as:

\[ V = 362.1 + 7.692x \] (1)

The change in oxygen occupancy is another factor influencing the lattice parameters. For instance, our separate \textit{in situ} neutron studies on Cu-doped LaFeO\textsubscript{3} system\textsuperscript{[4]} showed that changes in both bond lengths and angles were found to be strongly dependent on the oxygen positions and were shown to compensate for internal strain induced by Cu doping.\textsuperscript{[5]} However, in this study the oxygen content cannot be precisely determined via XRD.

**Figure 7.2** (a) Refined \(a\), \(b\), and \(c\) lattice parameters, (b) and the unit cell volume for PNNO5050-Cux powders at RT.

7.2 PHASE STABILITY

**Figure 7.3** shows the phase evolution in nickelate electrodes, in which PNNO5050 (Figure 7.3b) shows remarkable improvements in phase stability when compared to PNO, as shown in **Figure 7.3(a)**. Favoring oxidation state changes in Pr\textsuperscript{3+} (PNO) when compared to Nd\textsuperscript{3+} (NNO) can be linked to increasing nuclear charge. The \(f\)-electrons become more tightly bound to Nd, which decreases overlap with neighboring atoms and leads to reduced
gain in binding energy.\textsuperscript{[6]} As a result, a decreasing affinity for the tetravalent configuration from CeO\textsubscript{2} to Nd\textsubscript{2}O\textsubscript{3} was found and indicates trivalent configuration on Nd as energetically more favorable.\textsuperscript{[6]} This may explain why NdO\textsubscript{2} does not occur naturally and the difficulty in oxidizing Nd\textsuperscript{3+}. As a result, only 4 mol\% of PrO\textsubscript{x} was generated in PNNO5050 at 870 °C after 150 hours. However, extended operation (500 h) leads to accelerated phase evolution resulting in 24\% phase transition, as shown in Figure 3b. Therefore, with an attempt to fully suppress phase transition, a series of systematic studies were performed on a family of praseodymium nickelates.

\textbf{Figure 7.3} Phase purity and long-term phase stability in (a) PNO, (b) PNNO5050, (c) PNNO5050-Cu\textsubscript{5}, and (d) PNNO5050-Cu\textsubscript{10} powders at 790 °C and 870 °C.
Since Nd substitution on the Pr-sites takes place only in the rock-salt layer, an attempt was made to manipulate the oxygen octahedron layer and test its role on phase evolution. Therefore, a number of transition metals were screened as dopants on the Ni-site. Doping PNN05050 phase with Cu showed the most promising results. Figures 7.3(c-d) illustrate suppressed phase transition with 5 and 10 mol% Cu doping on the Ni-site, respectively. PNN05050-Cu10 retains stable phase, while PNN05050-Cu5 undergoes 6% phase transition at 870 °C after 500 hours. Compositions with various Cu contents were also tested, but the aforementioned chemistry provided the most promising results. Raw data and phase stability on 20 and 30 mol% Cu doping is provided in Figure A.1 (Appendix A). The most notable changes occur at 870 °C where the phase transition in PNN05050 was suppressed by fourfold with 5% Cu doping, and fully suppressed for 10% Cu doping on the Ni-site. A narrow window of Cu doping on the Ni-site (predominantly 5 and 10 mol%) appears to suppress the initial formation of Pr₆O₁₁ (PrOₓ), resulting in more homogeneous phase distribution and suppressed phase transition.

**Figure 7.4** (a) Quantified phase evolution in PNN05050-Cu₁ₓ electrodes at elevated temperatures. (b) Quantified phase evolution in thermally annealed PNN05050-Cu₁ₓ powders, where the mole fraction ₁ₓ=0.05, 0.10, 0.20, and 0.30, respectively. Percentage of Pr₆O₁₁ was calculated from the calibration curves on physical powder mixtures.
Figure 7.4(a) summarizes the quantification of phase evolution in PNNO5050-Cu_y electrodes. The raw data are shown in Figure A.2 (Appendix A). Quantification was performed against the calibration curves obtained from the physical mixture of the nickelate and PrO_x.[7] PNNO5050 was used as a baseline for phase transition studies, which exhibited a degradation during 500-h tests. PNNO5050-Cu_{10} retains a stable phase at both annealing temperatures (790 and 870 °C) after 500 hours; while PNNO5050-Cu_{5} is stable at 790 °C, but partially decomposes at 870 °C after 500 hours. With a further increase in Cu content, the structural changes (evident by the merging doublets) occur and lead to the formation of PrO_x. The evolution of PrO_x (for Cu ≥ 20 mol%) reaches 9 mol% after only 150 hours, as shown in Figure 7.4(b). These results bring to a question as whether or not doping with Cu on the Ni-site in PNO can stabilize the parent PNO phase without modifications on the Pr-site. We found that it was challenging to obtain a single orthorhombic phase with 5, 10, or 20 mol% Cu doping in PNO (Figure A.3, Appendix A). In all cases, at least 1 mol% of PrO_x was detected at various annealing temperatures (1050, 1080, 1100, and 1150 °C), which was then accompanied with the phase transition at operating conditions. Figure A.4 (Appendix A) shows the raw data and Table A.2 (Appendix A) presents the summary of findings and comparison between PNNO5050-Cu_y and PNO-Cu_y electrodes.

7.3 THE ROLE OF ANNEALING TEMPERATURE ON THE STRUCTURAL STABILITY

The ability to produce a cathode material in the shortest time and at the lowest cost is of fundamental industrial importance. Similarly, finding the appropriate synthesis conditions for a material with the highest catalytic yield is essential. Figure 7.5 illustrates...
the importance of annealing temperature during the preparation of PNN05050-Cu$_y$. A synthesis at four different temperatures was followed by annealing for 150 hours in 3% humidified air. Powder calcination at 1150 °C generated the least amount of PrO$_x$ at 790 °C (Figure 7.5a). A large synthesis temperature window for Cu-rich ($y \geq 0.10$) cathodes, with marginal variations in PrO$_x$ content, was detected at 870 °C as shown in Figure 7.5(b). For a lower Cu content ($y \leq 0.10$), the calcination at 1150 °C suppressed the formation of PrO$_x$ and was used for long-term studies.

![Figure 7.5](image)

**Figure 7.5** The role of annealing temperature on phase evolution in PNN05050-Cu$_y$ at (a) 790 °C, and (b) 870 °C.

Detailed XRD studies on phase purity show that the layered structure in PNN05050-Cu$_y$ tends to form in the temperature window between 1050 and 1150 °C in air. Longer calcination time is required at lower temperatures (e.g. 10 hours at 1080 °C for PNO vs. 5 hours at 1150 °C for PNN05050) to obtain a single orthorhombic phase. With Cu doping, the calcination time is further reduced to 2 hours at 1150 °C. Therefore, not only was the parent phase stabilized with modifications of the Pr- and Ni-sites, but also the material synthesis process was substantially simplified.
7.4 ELECTROCHEMICAL PERFORMANCE AND AREA SPECIFIC RESISTANCE

Figures 7.6(a-c) show initial i-V and power density curves for PNNO5050-Cu_y operated between 650 and 850 °C. The power density increases with temperature for each cathode composition. The open circuit voltage (OCV) for all tested cells was in a range of 1.10 ± 0.03 V and the i-V curves were reproducible with multiple cells for each

![Graphs showing i-V and power density curves](image1)

**Figure 7.6 (a-c)** Initial I-V and power density curves PNNO5050-Cu_y, as function of y. (d) Cell reproducibility at 790 °C. (e) EIS spectra for the same series. (f) Power density measured at 0.80 V as function of temperature for each composition.
composition, as shown in Figure 7.6(d). In compassion with PNNO, Figure 7.6(e) shows that the electrode polarization increases by 25% for PNNO5050-Cu_5 and by 45% for PNNO5050Cu_{10}. In order to further understand this behavior, it is key to study the change in power density as a function of temperature. Figure 7.6(f) illustrates power density measured at 0.80V, for PNNO5050-Cu_y. With an increase in temperature from 650 to 850 °C, the power density increases by fourfold for PNNO5050 and by threefold for PNNO5050-Cu_y electrodes. Furthermore, the difference in power density between undoped and Cu doped cells increases with temperature.

Figure 7.7(a) shows the total cell ASR, calculated from the slopes of the i-V curves, as a function of current density measured at 790 °C. The activation polarization region, indicative by a negative slope at low current densities (i ≤0.25 A/cm²) is followed by the linear ohmic polarization region. PNNO5050 was found to have the lowest ASR with a global minimum occurring between 0.85-1.05 A/cm². With an increase in Cu content, the

Figure 7.7 (a) Total ASR as a function of current density for PNN5050-Cu_{y} cells calculated from dc measurements at 790 °C. (b) A comparison of the electrode ASR obtained from i-V and EIS measurements at 790 °C. Ohmic ASR was obtained by using the equivalent circuit model.
cell ASR increases; while the most notable change was observed in PNNO5050-Cu$_{10}$. A higher ASR at low current densities can be attributed to the reaction rate losses in electrodes. A positive slope at high current densities would suggest the existence of the concentration polarization region. The total ASR was also obtained from the analysis of the impedance spectra by using an equivalent circuit, which is discussed in more detail in our previous report on PNNO series.[2] Figure 7.7(b) shows a comparison of the electrode ASR (cathode exposed to air) determined from the i-V and EIS measurements at 790 °C. The results from the two testing regimes were within 4% for each cathode composition. With an increase in current density, the total cell ASR decreases. A decrease in cell performance with an increase in Cu content can be attributed to an increase in the activation energy ($E_a$) for overall electrode reaction.

Figure 7.8(a) shows a plot of ln(ASR$_e$) as a function of 1/T for all compositions measured at OCV. With a 10% increase in Cu content, the $E_a$ increases by 8% (1.00 ± 0.02 eV vs.1.08 ± 0.02 eV). The results were consistent with the extrapolated energy values from the DRT analysis, as shown in Figure 7.8(b). A higher activation energy for Cu doped electrodes results in more active electrodes at temperatures ≥ 800 °C, in consistency with the phase stability zone shown in Figure 7.4(b). Consequently, PNNO5050-Cu$_y$ electrodes can retain stable phase at higher operating temperatures when compared to the parent PNO phase. The increase in activation energy can also be linked to changes in oxygen occupancy. It has been shown in many cases that the substitution on the A or B sites of A$_2$BO$_{4+\delta}$ can simultaneously affect the transport properties and oxygen overstoichiometry ($\delta$).[8-12] For instance, Grenier et al.[8] demonstrated that 25 mol% Cu substitution on the
Ni-site in \( \text{La}_2\text{NiO}_{4+\delta} \) led to a decrease in \( \delta \) (by \( \sim 30\% \) at 800 °C) and a lower oxygen diffusion coefficient. The structural refinement on PNNO5050-Cu\(_y\) shows that the cell volume increases with increasing Cu content (mainly driven by the increase in the \( c \) parameter) and is accompanied with the unit cell elongation in a \( z \) direction. However, the \( b \) parameter simultaneously decreases. This may lead to the compression in the \( x\)-\( y \) plane of oxygen octahedra, which in turn leads to the repulsion of oxygens towards the rock-salt layer, \( z \)-direction. The combination of these two effects might be responsible for the compression of the oxygen ion conduction paths in the rock-salt layer and a change in oxygen occupancy.

7.5 ANALYSIS OF THE DISTRIBUTION OF RELAXATION TIMES (DRT)

The evolution of DRT spectra for PNNO5050-Cu\(_y\) electrodes is shown in Figure 7.9(a). Details behind the process and circuit modeling were described in our previous work on the PNNO series.[2] The same circuit model was used here since the identified
DRT peaks fall within the similar frequency range and no additional processes were identified. The analysis shows dominating cathodic (P1c, P2c, P3c) peaks and one peak at a low frequency (P4a), which has been attributed to the anodic polarization due to the absence of a change with pO2 switch on the cathode side.[2] The arcs between 5 and 100 Hz (P3c and P2c) are generally assigned to a change in the transfer resistance and double layer capacitance in a cathode, consistent with the DRT analysis at different T[2, 13] and pO2[14] in LSM and LSCF electrodes. The change in a high frequency (1 kHz) peak is attributed to a slower oxygen ion transport from the electrode to the cathode/electrolyte interface.[2, 14]

With an increase in Cu content, the area of cathodic peaks increases by 42% (10 mol.% Cu), indicating a higher resistance in cathodic processes. This increase is consistent with the higher electrode polarization in Cu doped electrodes, as shown in Figures 7.10 (d-f) at 0th hour.

7.6 LONG-TERM PERFORMANCE DURABILITY

Since the industrial requirements impose a stable long-term performance in SOFCs, it is necessary to identify a cathode which exhibits high activity and durability
simultaneously. **Figures 7.10(a-c)** show i-V and power density curves for PNNO5050-Cu\textsubscript{y} during 500 hour operation at 790 °C and 0.80 V. The cells were measured every 25 hours,

![Figure 7.10](image)

**Figure 7.10** (a-c) I-V and power density curves PNNO5050-Cu\textsubscript{y} series during 500h operation. (d-f) Corresponding EIS spectra for the same series of cells.
but for simplicity reasons the measurements in 100 hour increments are shown. The
degradation rates were marginal, at most a fraction of a percent (0.04%) per 1,000 hours.
The i-V measurements were in agreement with EIS measurements, as shown in Figures 7.10(d-f), in which stable ohmic and electrode polarization were observed. Results shown in Figure 7.10 are in congruence with DRT analysis (Figure 7.9b), which shows minor changes in cathodic peaks at 500th hour of operation at 790 °C.

CONCLUSIONS

The crystal structure and phase stability in PNNO-Cu$_y$ was reported. Doping with 5 and 10 mol.% Cu on the Ni-site showed the most promising results, leading to a stable parent phase after 500 hours of thermal annealing at 790 and 870 °C in 3% humidified air. A reproducible performance was obtained with multiple full cells for each cathode composition. A stable long-term performance was measured on Cu doped electrodes with a marginal degradation rate (0.04%/1,000 hours) at 790 °C and 0.80 V. EIS and DRT analyses showed an increase in total cell ASR with increasing Cu content, which is governed by the increase in electrode polarization. An 8% increase in activation energy for overall electrode reaction leads to lower performance maxima, which is in an acceptable range when compared to threefold decrease in performance with a further increase in Nd content on the Pr-site. Therefore, a superior phase stability over PNO and a wide operating temperature window in PNN05050-Cu$_y$ allow for long-term operation in SOFCs.
REFERENCES


CHAPTER 8
IDENTIFYING THE ORIGIN OF PHASE TRANSFORMATION AND STRUCTURAL STABILITY IN (Pr$_{1-x}$Nd$_x$)$_2$Ni$_{1-y}$Cu$_y$O$_4$ CATHODES

The results in Chapter 7 showed that Cu doping on the Ni-site in (Pr$_{0.50}$Nd$_{0.50}$)$_2$NiO$_{4+\delta}$ (PNNO) electrodes resulted in stable long-term operation, when compared to 6.4%/1,000 hours degradation in PNO cells. This chapter is an extension to electrochemical studies with an attempt to correlate performance stability to structural behavior in (Pr$_{1-x}$Nd$_x$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+\delta}$ (PNNO-Cu$_y$), where $y=0.05, 0.10, 0.20$. As a result of manipulations on the Ni-site the changes in the perovskite layer (oxygen octahedra) were expected but their role on the oxygen ion transport paths in the rock-salt layer was unknown. Detailed study of M-O bond lengths behavior was performed at room temperature and in-situ at synchrotron source, and the findings were used to correlate the structure, phase stability, and electrochemical stability. A strong correlation was found between the stiffening of the oxygen octahedra and shrinkage in oxygen ion conduction paths, leading to stabilized phase and stable electrochemical performance.

8.1 STRUCTURAL CHARACTERIZATION AT ROOM TEMPERATURE

The refinement on PNNO-Cu$_y$ series, reported in our preceding work, showed an increase in the cell volume with increasing molar fraction of Cu, mainly driven by 0.90% increase in the $c$ lattice parameter. In addition, the fraction position coordinates on heavy metal cations (Pr, Nd) indicated an elongation in the $z$ direction and overall compression
in the y direction while the orthorhombic Bmab symmetry was retained. In order to further investigate the role of Cu-doping on the crystal structure, the changes in lattice parameters were further studied by refinement of the average bond lengths in the perovskite and rock-salt layers.

**Figure 8.1(a)** shows average (Ni,Cu)-O bond lengths for equatorial (e) and focal (f) oxygen positions in the perovskite layer, represented with positions 1 and 2 (Figure 8.2a), respectively. While the (Ni, Cu)-O_e bond length decreases (by 0.30, 0.40 and 0.50%, respectively) the (Ni, Cu)-O_f increases by 2.80%, which is equivalent to sixfold larger expansion in the focal direction. These results show that Cu doping within the oxygen octahedra forces equatorial oxygen atoms to arrange closer to the transition metal, which in turn creates steric strain between equatorial and focal oxygens, and leads to repulsion of focal oxygens towards the rock-salt layer. Smaller size of Cu^{2+} cation (0.57 Å) when compared to larger Ni^{2+} (0.63 Å) allows for such modifications in the perovskite layer. Furthermore, as shown by multiple studies on lanthanum cuprates,^{1-3} Cu tends to arrange in a metastable square planar structure at RT but transforms at elevated temperatures to K_{2}NiF_{4}-type structure forming elongated CuO_6 octahedra.^{1} Consequently, the focal oxygens on one side of (Ni,Cu)O_6 octahedra tend to tilt away from the adjacent interstitial oxygen site to minimize the oxygen-oxygen Coulombic repulsion. However, due to increase in the distance between the oxygen transport sites, more energy (higher temperature) will be required for further oxygen hopping. As oxygen octahedra tilt the angle strain formations are produced, which are the most pronounced for O_e-(Ni,Cu)-O_f arrangement, resulting in 3.40% increase in bond angle, **Figure 8.1(b)**. Simultaneously, the focal oxygens on the opposite side of the (Ni,Cu)O_6 octahedra move closer together towards
vacant oxygen interstitial sites and likely reduce their availability for further oxygen transport. These combined steric effects and angle strains in oxygen octahedra lead to respective changes in the rock-salt layer, bringing to changes in oxygen ion conduction paths and concentration of oxygen interstitials.

Conduction of oxygen in PNNNO-Cu_{y} occurs via natural exchange of oxygen atoms between interstitial and apical sites, which allow for oxygen propagation via hopping mechanism in the \textit{a-b} plane. Therefore, obtaining a better understanding of the structural changes in oxygen ion conduction paths is of fundamental importance with respect to material’s transport properties. Figure 8.1(c) shows refined average (Pr, Nd)-O_{e} bond lengths. With increase in Cu content the overall (Pr,Nd)-O_{e} bond lengths decrease. Since
Figure 8.2. (a) Illustration showing the orthorhombic layered structure in (Pr<sub>0.50</sub>Nd<sub>0.50</sub>)<sub>2</sub>NiO<sub>4+δ</sub> where perovskite layers (oxygen octahedral packed layer) alternate with the rock-salt M-O layers. (b) Resulting structural changes with Cu-doping on the Ni-site leading to increase in volume via expansion in the z-direction and shrinkage in the a-b plane. Shrinkage in oxygen ion conduction paths is highlighted.

Pr and Nd cations are heavy and do not undergo as nearly as much movement as oxygen ions do, the decrease in bond lengths can be explained by tilts in oxygen octahedra due to aforementioned steric and angular strains. A 3.0% decrease in (Pr,Nd)-O<sub>i</sub> bond length (Figure 8.1d) is even more evident and further indicates the shrinkage of oxygen ion conduction paths, as illustrated in Figure 8.2(b). The largest overall decrease in (Pr,Nd)-O bond lengths was measured for 5 and 10 mol.% Cu doped PNNO.
8.2 IN SITU STRUCTURAL CHARACTERIZATION AT THE SYNCHROTRON SOURCE

The structural information obtained at room temperature was used as a baseline for in-situ studies. Figure 8.3(a) shown an example of a 2D masked data which was used to generate the PDF plots. The PDFs obtained on PNNO powder in air during heating and cooling regimes are also shown (Figure 8.3b-c). Each PDF pattern was collected at a discrete temperature profile, as shown on the right. Figure 8.3(b) shows a short-range PDF (atomic distances within a single unit cell) while Figure 8.3(c) shows the long-range PDF (atomic distances beyond a single unit cells). Each peak in PDF (G(r) plot) represents an atomic pair distance, hence the respective peak shifts indicate changes in distance between any two atoms of interest. The advantage of a high resolution and high flux synchrotron radiation allows to study any peak shifts in the measured region.

At first the shifts are mostly noticeable for metal-metal pairs at r(Å) > 8 (Figure 8.3b) and for distances larger than a single unit cell (>12.50 Å, Figure 8.3c). However, a closer examination will show that at r(Å) < 8 a significant changes in the structure occur. At atomic distances beyond the single unit cell the peak shifting also occurs, which may indicate turbostratic displacement between the layers, as these are extended structures. However, the changes in metal-oxygen (M-O) distances and structural changes beyond a single unit cell dimension are not a focus of this study, hence will be reported in a separate work. A general peak shifting occurs during heating to, or cooling from, ~450 °C, and is associated with orthorhombic to high temperature tetragonal (HTT) phase transition.4, 8 Upon cooling the phase transitioned back to orthorhombic structure with Bmab symmetry. In the temperature window between 450-850 °C in air the peak shifting does not occur.
indicating thermodynamically stable phase, which has been confirmed via *in-situ* XRD studies on PNNO electrodes.

**Figure 8.3.** (a) 2D masked data obtained on PNNO powder at 11-ID-B beamline at APS source. Generated PDFs for *in-situ* measurements on PNNO powder for (b) short-range ordering and (c) long-range ordering. Stacked PDF plots correspond to discrete temperature values listed on the right side. (d) Rw distribution (difference in PDF) as function of temperature.

The relative changes of entire PDF patterns during the heating and cooling regimes were also studies. **Figure 8.3(d)** illustrates the differences in PDFs as function of temperature. The green/yellow regions indicate larger differences, while blue regions indicate a good match. Substantial differences were observed when comparing low vs. high temperature PDFs on PNNO-Cuy. However, during hold at 750 °C the PDFs are not changing indicating stable phase. Using this approach the PDFs at selected temperatures were studied in more detail and compared to result before and after thermal annealing,
Figure 8.4. For the PNNO-Cu_y compositions (Cu_{10} is shown) the metal-oxygen atomic pair distances do not show any shifts during thermal annealing (peak shifts were not detected), Figure 8.4(a). The (Ni, Cu)-O_{f,e} and (Pr, Nd)-O_{f,e} distances are not changing indicating rigid octahedra and retained (but also compressed) oxygen ion conduction paths, respectively. Such stable structure consequently leads to stabilized phase, as reported in our preceding work. On the other hand, PNNO composition with the absence of Cu but with Nd substituted Pr-site show substantial changes in PDF patterns (Figure 8.4b), indicating phase transition.\(^5\) Similarly, the in-situ PDFs on PNO powder show substantial changes in M-O distances.

Figure 8.5 summarizes quantified M-O distances of interest as function of composition and temperature. The largest changes occur in PNO, with 7% increase in Ni-O_{f} and 3.2% decrease in Pr-O_{f}. Such substantial changes in M-O distances can be linked to considerable phase transition.\(^5\) With PNNO composition the changes are partially suppressed with 4% increase in Ni-O_{f} and 1.4 % decrease in Pr-O_{f}, while for PNNO-Cu_{10} and PNNO-Cu_{20}, the changes are fully suppressed. With 5% Cu doping some changes in
M-O distances are still present indicating insufficient amount of Cu content to stabilize the phase. These results are in agreement with a few percent phase transition in PNNO-Cu$_5$ after long term operation, as reported in our preceding work.

![Graphs showing quantified M-O distances from PDF measurements as function of composition and temperature for (a) (Ni, Cu)-O$_{\text{f}}$ atomic distance and (b) (Pr, Nd)-O$_{\text{f}}$ atomic distance.](image)

**Figure 8.5.** Quantified M-O distances from PDF measurements as function of composition and temperature for (a) (Ni, Cu)-O$_{\text{f}}$ atomic distance and (b) (Pr, Nd)-O$_{\text{f}}$ atomic distance.

### 8.3 ON THE ORIGIN OF STRUCTURAL CHANGES IN PRASEODYMIUM NICKELATES

Aforementioned structural studies show that phase evolution in praseodymium nickelates is *in-situ* phenomenon and can be linked to respective changes in M-O distances in perovskite and rock-salt layers. However, a question remains on how a structure (M-O distances) can be “frozen” in PNNO-Cu$_y$ during the heating process. Through the molecular dynamics simulations of oxygen transport in PNO, Parfitt et al.$^4$ showed that oxygen diffusivity has a weak dependence upon the concentration of oxygen interstitials due to a rise in the effective migration barrier, which is in agreement with neutron scattering studies in related K$_2$NiF$_4$ structure materials.$^6$ Since the cathode materials studied in this work follow the general de-intercalation of interstitial oxygen with increase in temperature,$^9$ then a possible explanation for the retained shrinkage of oxygen ion
conduction paths in PNNO(50/50)-Cu<sub>y</sub> can be associated with the proposed stiffening of the NiO<sub>6</sub> perovskite layer due to effective pinning of oxygen interstitials. This mechanism reduces the ease at which the octahedra can tilt, and therefore do not further impact the conduction paths in the rock-salt layer. Furthermore, the Cu<sup>2+</sup>/Cu<sup>3+</sup> redox couple may also be responsible for the octahedral stiffening. This would explain a narrow concentration window of Cu that can be used to stabilize the phase. In absence of Cu the Ni<sup>2+</sup>/Ni<sup>3+</sup> redox couple alone cannot suppress structural changes, while higher Cu concentration may yield excess of Cu<sup>3+</sup> which leads to additional strain, hence the inability to refine PNNO-Cu<sub>30</sub> in orthorhombic Bmab symmetry.

**Figure 8.6.** Phase purity in Pr<sub>2</sub>Ni<sub>1.7</sub>Cu<sub>y</sub>O<sub>4+δ</sub> (PNO-Cu<sub>y</sub>) powders (a-c), where y=0.05, 0.10, and 0.20, respectively. Evolution or PrO<sub>x</sub> is marked with (+). Standard XRD patterns are included.

This brings to a question if Cu doping on the Ni-site can stabilize the parent PNO phase without Nd substitution on the Pr-site. Therefore, it is imperative to study the role of Cu-doping in PNO and the long-term phase stability. Obtaining a single orthorhombic phase with 5, 10, and 20 mol.% Cu doping was challenging at various temperatures. In all
cases at least ~1 mol.% of PrO$_x$ was detected during thermal annealing. **Figure 8.6.** The phase transformation occurred in all samples (indicative by substantial evolution of PrO$_x$ phase) within 150 hours at 790 °C and 870 °C in 3% humidified air, **Figure 8.7.** These results also show that Cu-doping alone is not sufficient in stabilizing the PNO phase.

**Figure 8.7.** Phase stability in PNO-Cu$_y$ powders after 150 hour annealing at 790 °C (a-c) and 870 °C (d-f), where $y=0.05$, 0.10, and 0.20, respectively.

Therefore, we propose that less available Pr cations for oxidation, due to Nd substitution on the Pr-site, and shrinkage in oxygen ion conduction paths, due to Cu-doping on the Ni-site, mutually suppress the formation of PrO$_x$ and phase transition in praseodymium
nickelates. Due to shrinkage of the rock-salt layer (decrease in oxygen occupancy)\textsuperscript{10} and decrease in (Pr,Nd)-O\textsubscript{f} distance, the Pr is less likely to be oxidized and more energy is required (higher temperature) to remove it from the structure. This leaves a very narrow phase transition window, as 1150 °C was the annealing temperature for PNNO-Cu\textsubscript{y}. Consequently, the suppressed formation of PrO\textsubscript{x} leads to less local stress between the two phases, due to 68\% thermal mismatch, and stable long-term phase.

CONCLUSIONS

An attempt to identify the origin of structural changes and phase evolution in praseodymium nickelates has been addressed. The Rietveld refinement and atomic pair distribution function at the synchrotron source were utilized to investigate the structural changes. The Cu doping on the Ni-site in PNNO leads to formation of steric and angular strain in the perovskite layer resulting in bond elongation between the transition metal and focal oxygen in the perovskite layer. This bond elongation forces shrinkage in oxygen ion conduction paths in the rock-salt layer, by decreasing the (Pr,Nd)-O\textsubscript{f} atomic distance. A strong correlation exists between the shrinkage in oxygen ion conduction paths, phase stability, and electrochemical performance in PNNO-Cu\textsubscript{y}. The superior phase stability of PNNO-Cu\textsubscript{y}, when compared to PNO, and a wide operating temperature window allow for stable long-term operation in electrochemical cells. The structural approach towards designing active and stable praseodymium nickelate cathodes provides a promising avenue in development of robust SOFC cathodes.
REFERENCES

CHAPTER 9

WHAT IS THE DRIVING FORCE FOR RETAINED ACTIVITY AND STABLE LONG-TERM PERFORMANCE IN Pr$_2$NiO$_4$?

The origin of retained activity of Pr$_2$NiO$_4$ (PNO) electrode during long-term electrochemical operation remains obscure. PNO undergoes substantial phase evolution under operating conditions, resulting in formation of Pr$_6$O$_{11}$ and higher order Pr$_3$Ni$_2$O$_7$ phase, Figure 9.1. Furthermore, SEM analysis in chapter 6 showed significant decrease in electrode porosity after operation, which would in turn result in less oxygen delivery to the mixed conducting bulk. Such significant phase transformation and decrease in electrode porosity is expected to play a detrimental role on the cell performance. However, even after

**Figure 9.1** Illustration showing relatively low performance degradation but substantial phase degradation (according to XRD) in Pr$_2$NiO$_4$. Formation of nanoclusters may provide link for retained activity during long-term operation in electrochemical cells.
the long-term electrochemical operation, where XRD analysis shows majority of the parent phase transformed, the performance degradation in PNO cells is only 6.40%/1,000 hours. Therefore, there must exist another mechanism preserving the catalytic activity of the electrode. In this work an attempt was made to unravel the origin of retained activity and performance stability in PNO electrode.

It is also imperative to note that commonly used in-house x-ray diffractometers do not have high flux and high resolution capability to detect small percentage of phase(s) or to distinguish highly overlapping XRD patterns, as is the case in PNO and Pr$_3$Ni$_2$O$_7$. Therefore, in-situ XRD studies at a synchrotron source were employed to further verify the phase transformation behavior in PNO electrode. In an attempt to complement the XRD studies and to address the retained catalytic activity in PNO, a series of systematic TEM studies were performed along with detailed microstructural analysis of the electrodes. The correlation was made between the startling microstructural changes and generated nanocluster matrix to relatively stable operation in electrochemical cells.

9.1 PERFORMANCE DEGRADATION IN PNO

Figure 9.2(a) shows i-V and power density curves for PNO cell operated at 750 °C for 500 hours. During operation the power density, measured at 0.80 V, decreases from 0.87 W/cm$^2$ (0th hour) to 0.83 W/cm$^2$ (250th hour) and to 0.80 W/cm$^2$ (500th hour). The decrease in power density can be associated with increase in electrode polarization ($R_{pol}$) as illustrated in EIS spectra in Figure 9.2(b), where $R_{pol}$ increases by 7.6% after 500 hours. In order to understand the origin of the degradation, a distribution of relaxation times (DRT) analysis was performed on collected EIS spectra to identify respective changes in
Figure 9.2. (a) i-V and power density curves for PNO full cells as function of time. (b) EIS spectra as function of time measured at 0.50 A/cm² and 750 °C. (c) in operando DRT analysis on PNO electrode. (d) Quantified DRT spectra showing resistance of each process shown in (c).

Since EIS has a low frequency resolution ability and can only recognize two neighboring electrode processes which have relaxation frequency difference of two or three orders of magnitude, the DRT was employed as the relaxation frequency during PNO operation is not changing to such large extent. The advantage of DRT analysis lies in its high resolution ability, since it allows to separate neighboring electrode processes which resonate within a half a decade. Consequently, relatively small frequency shifts can be deconvoluted, as illustrated in Figure 9.2(c). Four resolved peaks are shown, as previously discussed in more detail, with P1c-P3c behind associated with cathodic processes and P4a is an anodic peak. The cathodic peaks are shifting to higher frequency and increasing in magnitude (Figure 9.2d), with P3c undergoing the largest increase of 5.2%, indicating...
increase in resistance in cathodic oxygen reduction processes. Consequently, the increase in $R_{\text{pol}}$ is consistent with decrease in the cell performance.

9.2 PHASE EVOLUTION IN PNO AND SYNCHROTRON STUDIES

In coherence with respective changes in $R_{\text{pol}}$, the phase evolution in PNO electrodes was also studied. Figure 9.3(a) shows phase evolution in PNO powders as function of thermal annealing at various temperatures. With increase in temperature the phase evolution in PNO is promoted, resulting in dominating formation of PrO$_x$, which has been previous attributed as an indicator of phase transformation in praseodymium nickealtes.$^{6-7}$ Similar behavior was also recorded in YSZ/GDC/PNO cell configuration on electrodes, Figure 9.3(b). In both cases PrNiO$_3$ is also generated further indicating the structural degradation. The long-term electrochemical operation in full cells shows majority of the parent phase transformed along with formation of PrNiO$_3$ and NiO, Figure 9.3(c). When

Figure 9.3. (a) XRD patterns illustrating phase evolution in PNO powder for various thermal annealing temperatures. (b) Phase evolution in PNO electrode on YSZ/GDC/nickelate configuration as function of time. (c) Phase evolution on PNO electrode in full electrochemical cell operated at 750 °C and 0.80 V for 500 hours.
compared to dominating PrO$_x$ signal, the NiO peaks carry low intensity, but were observed for the first time after electrochemical operation, further supporting the magnitude of phase transformation. It is possible that lower concentrations of NiO (<1%) are present in thermally annealed powders and cells, but could not be detected with XRD.

With the majority of the parent phase transformed and relatively stable cell performance, the question arises of whether the phase transformation occurs *in-situ* or is a result of thermal cycle(s), since the aforementioned XRD patterns were obtained upon cooling. To address this question *in-situ* XRD studies at the synchrotron source were carried out. Figure 9.4(a) shows stacked XRD patterns collected continuously during heating, thermal holding, and cooling of a PNO electrode. Each XRD pattern is associated with a discrete temperature value in time. A closer examination of the patterns shows formation of new peaks (marked with arrows) during heating. Figure 9.4(b) shows selected XRD patterns on PNO electrode. Initial pattern is a single PNO phase while at 750 °C the PrO$_x$ evolves. With further increase in temperature
the formation of PrO$_x$ was suppressed by a few percent, as can be seen by decrease in intensity of PrO$_x$ peaks. However, this pattern is expected as the temperature is reaching the sintering temperature (1080 °C) of PNO at which a single phase was obtained. After prolonged holding at 750 °C the XRD patterns upon cooling show a remarkable resemblance to *in-situ* phase distribution, allowing for direct comparison to XRD patterns obtained after cell operation.

9.3 MICROSTRUCTURAL ANALYSIS AND FORMATION OF NANOCLUSTERS

With reproducible results from the in-house XRD and the synchrotron source, the question remains on how a considerable phase transformation in PNO does not play such a detrimental role on the performance stability. In order to provide a link between the two aforementioned sections a detailed microstructural analysis was performed. Figure 9.5 shows SEM images on PNO electrode before and after electrochemical operation in full cell. There is a substantial decrease in electrode porosity after operation, which in turn would allow less oxygen delivery to the active sites of the mixed conducting bulk. Perhaps a larger performance degradation with increase in current density (Figure 9.2a) can indeed

![Figure 9.5. SEM images on PNO electrode (a) before and (b) after electrochemical operation at 750 °C and 0.80 V. for 500 hours. The insert image shows direct exposure window for XRD studies on cathode.](image)
be associated with the concentration polarization region. A low magnification TEM image on a single phase PNO electrode (Figure 9.6a) shows uniform contrast and phase distribution. An exemplary diffraction pattern is shown in Figure 9.6(b). The thermally annealed powder (Figure 9.6c-d) at 750 °C for 150 hours shows some initial phase transformation (~5%). However, a PNO cell held at OCV for 500 hours at 750 °C undergoes significant changes in microstructure, shown by the decrease in particle size and multiple contrasted phases present, Figure 9.6(e-f). Quantification of phase evolution shows up to 20% of parent phase transformation. Furthermore, the formation of nanoclusters (boxed region) was observed within 20-60 nm range. Electrochemically operated electrode undergoes majority of the parent phase transformation, with ~1% of PNO detected via XRD. The formation of nanoclusters (5nm in size) was further promoted in electrochemical cells, generating a nano-matrix through the entire electrode bulk, Figure 9.6(g-h). The nanoparticles appear as randomly oriented with consistent size and the number of reflection planes. Figure 9.6(h) also reveals that the interface between the nanoclusters and the rest of the electrode bulk is abrupt, as there is no obvious elemental intermixing at the interface. The formation of nanoclusters, Figure 9.7, is most likely the self-preservation mechanisms of the PNO system that reduces the residual stress from the thermal expansion mismatch formed during phase transformation and then rearranges to form new grain boundaries.
Figure 9.6. (a) TEM image on a single phase PNO electrode. (b) HR-TEM diffraction pattern on single phase PNO. (c-d) Thermally annealed PNO powder at 750 °C for 150 hours. (e-f) PNO electrode held at OCV and 750 °C for 500 hours. (g-h) Electrochemically operated PNO electrode at 750 °C and 0.80V for 500 hours.

In order to characterize the nanoclusters the characteristic lattice spacing was calculated using the relationship between the \( d \)-spacing, Miller indices and the lattice parameters for the orthorhombic Bmab symmetry:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  

(1)

where \( h, k, \) and \( l \) are Miller indices for a single reflection in the XRD pattern (as shows in Figure 9.3), and \( a, b, \) and \( c \) are the calculated lattice parameters of PNO obtained from the Rietveld refinement.\(^7\) The calculated theoretical \( d \)-spacing of 2.812 Å corresponds to the highest intensity PNO (1 1 3) reflection. The experimental \( d \)-spacing of 2.81 ± 0.08 Å on average is within 2.8 \% of the theoretical value, confirming that the nanoclusters are indeed orthorhombic structure of an active PNO phase. With changes in microstructure to form...
nanoclusters the active area for ORR increases and may counterbalance the significant phase transformation in PNO, leading to relatively stable long-term operation in full cells.

Figure 9.7. TEM image on nanocluster formation on electrochemically operated PNO electrode at 750 °C and 0.80V for 500 hours. d-spacing is shown.

Figure 9.8. (a-b) TEM images on nanoclusters and designated regions used for point scan elemental analysis listed in Table 1.
Figure 9.8(a-b) shows selected nanocluster regions used for the point scan elemental analysis. The elemental distribution on nanoparticles is presented in Table 9.1 along with the EDS spectrum on one of the nanoparticle regions. The uniform elemental distribution and proper Pr:Ni ratio in nanoclusters further indicates the localized PNO matrix surrounded by physically extruded PrO$_x$ and NiO phases, as demonstrated in more detail in previous chapters.

Table 9.1 Elemental analysis on nanoclusters and surrounding regions of operated PNO electrode (500 hours, 0.80 V and 750 °C). Exemplary EDS spectrum on point 1 is also provided.

<table>
<thead>
<tr>
<th>Atom. %</th>
<th>Pr</th>
<th>Ni</th>
<th>O</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>37.42</td>
<td>18.15</td>
<td>44.43</td>
<td></td>
</tr>
<tr>
<td>Point 2</td>
<td>30.89</td>
<td>14.43</td>
<td>54.68</td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>45.03</td>
<td>23.04</td>
<td>31.39</td>
<td>PNO</td>
</tr>
<tr>
<td>Point 4</td>
<td>32.54</td>
<td>15.12</td>
<td>52.34</td>
<td></td>
</tr>
<tr>
<td>Point 5</td>
<td>29.14</td>
<td>15.2</td>
<td>55.66</td>
<td></td>
</tr>
<tr>
<td>Point 6</td>
<td>34.61</td>
<td>-</td>
<td>65.39</td>
<td>PrO$_x$</td>
</tr>
<tr>
<td>Point 7</td>
<td>-</td>
<td>48.07</td>
<td>51.93</td>
<td>NiO</td>
</tr>
</tbody>
</table>
9.4 Pr$_3$Ni$_2$O$_7$ PHASE AS AN ADDITIONAL CONTRIBUTOR TO RETAINED ACTIVITY OF Pr$_2$NiO$_4$

It is imperative to note that formation of Pr$_3$Ni$_2$O$_7$ phase is difficult to detect via XRD due to significant peak overlap with PNO phase, as discussed in more detail in one of our previous reports. However, we have previously shown that up to 3 mol% of PrO$_x$ in PNO is generated from phase transformation of Pr$_3$Ni$_2$O$_7$. Although the EDS analysis predominantly indicates PNO phase in nanoparticles, a small presence of Pr$_3$Ni$_2$O$_7$ phase is also possible, and should not be ignored. In addition, PrNiO$_3$ and Pr$_2$Ni$_2$O$_7$ phases could be mixed in a certain ratio, making it difficult to identify phases separately. To account for its presence, Pr$_3$Ni$_2$O$_7$ phase was synthesized and evaluated in SOFCs. Figure 9.9 shows the i-V and power density curves for two Pr$_3$Ni$_2$O$_7$-based cells. Although the activity is reduced by twofold when compared to PNO, the performance is relatively stable after 200 hours of operation at 750 ºC and 0.80 V. However, a similar phase transformation behavior

![Graph](image-url)  
**Figure 9.9.** i-V and power density curves for Pr$_3$Ni$_2$O$_7$ full cells as function of time.
occurs, where PrOₓ dominates in operated electrodes (Figure 9.10), indicating similar microstructural changes as is the case for PNO. A minor presence of PNO and Pr₄Ni₃O₁₀ phases was also detected from phase transformation of Pr₅Ni₂O₇, which further indicates the complexity of phase transformation in praseodymium nickelates.

![Figure 9.10. Phase evolution in Pr₅Ni₂O₇ electrodes operated in full electrochemical cell at 750 °C and 0.80 V for 200 hours.](image)

To further investigate the role of PrOₓ on phase transformation, a physical mixture of PrOₓ and Pr₅Ni₂O₇ phase (50% vol. mixture) was evaluated through thermal annealing studies on pressed pellets. Initial XRD patterns show presence of both phases, Figure 9.11. However, after only 25 hours of thermal annealing at 750 °C, the PrOₓ signal dominates, and similar pattern is retained up to 200 hours. The measured phase transformation behavior may indicate that PNO and Pr₅Ni₂O₇ phases reach phase transformation
equilibrium where both phases coexist during operation, but due to the substantial microstructural changes in electrodes the activity remains relatively stable, as confirmed

Figure 9.11. Phase evolution in Pr$_3$Ni$_2$O$_7$ + PrO$_x$ (50 vol.% mixture) pellet thermally annealed in air at 750 °C for 200 hours.

through the elemental analysis of nanoparticles. The XRD alone is simply not a sufficient experimental method to characterize the phase transformation behavior in PNO since the PrO$_x$ signal dominates. However, the initial crystal structure of the nickelate is of crucial importance as it governs the activity and performance stability in SOFCs, as shown with performance evaluation studies.
CONCLUSIONS

In this work, an attempt was presented to unravel the origin of retained activity and performance stability in PNO electrode. Thermal annealing and electrochemical studies on electrodes show significant phase transformation (also confirmed via *in-situ* synchrotron studies), reaching up to 99% in full cells after operation at 0.80 V and 750 °C for 500 hours. Furthermore, the SEM analysis of electrodes shows significant decrease in porosity after operation, which in turn leads to less oxygen delivery to the active sites. However, the measured performance degradation rate was only 6.40%/1,000 hours with multiple cells, proposing the existence of another mechanism that allows for preservation of the catalytic activity. High-resolution TEM analysis shows significant microstructural changes in electrodes where nanocluster matrix is formed through the entire electrode bulk, and is localized in the 20-60 nm region. The nanoparticles of 5 nm in diameter were found to be the PNO phase with (113) reflection, which corresponds to the highest PNO diffraction peak. Consequently, a surface of PNO nanoparticles is exposed for direct ORR. Due to formation of PNO nanoparticles, the catalytic area increases, which may account for the losses in catalytic activity from phase transformation and lead to stable long-term operation in electrochemical cells. EDS analysis shows 2:1 ratio for Pr:Ni in nanoparticles, further confirming the presence of the parent phase after operation.
REFERENCES


211
CHAPTER 10

ELECTROCHEMICALLY DRIVEN PHASE TRANSFORMATION IN PRASEODYMIUM NICKELATES

The need for stable long-term performance in SOFCs stems from a target operation of five years (~40,000 hours) during which the performance degradation should not be higher than 4%/1,000 hours. Simultaneously, the cathode activity for oxygen reduction reaction (ORR) should be high enough to provide sufficient cell performance. Equally challenging, is to reduce the cell operating temperature, typically below 800 °C. Lower operating temperature has multiple advantages including: (1) increased mechanical stability at interfaces\textsuperscript{1-2} and improved material durability,\textsuperscript{3-4}, (2) suppressed structural changes in electrodes\textsuperscript{3} and interdiffusion/reaction between the cell components,\textsuperscript{5} and (3) reduced startup time and fabrication costs. Therefore, the replacement of typical SOFC cathode materials such as lanthanum strontium manganite (LSM) is necessary, since it leads to substantial performance losses at temperatures lower than 800 °C.\textsuperscript{6} With the operating temperature region of 600 – 750 °C and high catalytic properties of PNO for ORR (at least fourfold increase in performance at 750 °C when compared to LSM),\textsuperscript{7} the Pr\textsubscript{2}NiO\textsubscript{4} (PNO)-based electrodes attract a broad interest.

Chapters 5-8 showed that phase transformation behavior can be drastically modified by substitution and doping on the Pr and Ni sites in PNO, and also provided the fundamental understanding behind the structure-electrochemical-property relationship.
However, these studies also shed a light on an unusual discrepancy in phase transformation in praseodymium nickelates. It was found that phase transformation in electrodes after electrochemical operation did not equate to those thermally annealed in symmetric cells. Since the phase evolution and phase transformation kinetics at the electrode level may affect the cell performance and stability in unexpected ways, it is necessary to obtain the fundamental understanding behind the difference in phase transformation in different system configurations.

However, as phase transformation in operating praseodymium nickelate electrodes is rarely reported, this discrepancy has not been addressed in the open literature. Instead, the conventional approach to evaluate phase evolution in praseodymium nickelates includes thermal annealing studies on powders and electrodes in symmetric cells. After annealing, the resulting materials are cooled down and studied via XRD. However, this method is based on thermodynamics of phase transformation, and may not necessarily represent phase evolution behavior in operating cells. During thermal annealing the material eventually reaches thermal equilibrium, and the phase evolution is governed by the thermodynamic variables. On the other hand, a SOFC does not operate in equilibrium regime due to exchange of matter and energy with the surroundings. Consequently, the thermodynamics may no longer dominate and the role of electrochemical potential on the phase transformation requires further consideration. The generated difference in electrochemical potential across the fuel cell can be considered as analogous to temperature gradients or pressure differences that drive phase transformations in other systems. Therefore, better understanding of such behavior in solid oxide fuel cells is of fundamental importance.
In this chapter phase transformation in thermally annealed \((\text{Pr}_{1-x}\text{Nd}_x)_2\text{NiO}_4\) electrodes was compared to phase transformation in electrodes operated in full cells at 0.80 V and 750 °C for 500 hours. In addition, multiple \((\text{Pr}_{0.50}\text{Nd}_{0.50})_2\text{NiO}_4\) (PNNO) cells were tested at various temperatures and current densities to study the role of electrochemical potential on phase evolution in PNNO. Extended operation up to 300 hours was conducted and post XRD patterns were compared to results obtained on powders and thermally annealed electrodes. It is imperative to note that the detailed \textit{in situ} study at a synchrotron source (chapter 12) showed that the quantity of phase transformation at operating conditions in full cells is in agreement to phase transformation recorded upon cooling. Hence, the quantification of phase transformation in praseodymium nickelates after operation is justified and reflects the actual phase evolution behavior in full cells.

10.1 ELECTROCHEMICALLY DRIVEN PHASE TRANSFORMATION AND A PROPOSED THEORY

In the preceding chapters a stabilized long-term performance with Nd substitution on the Pr-site\(^8\) in PNO was achieved, along with suppressed phase transformation.\(^3\) However, the extent of phase transformation in thermally annealed PNNO electrodes (for \([\text{Nd}] \leq 50\%) deviated from the results obtained after operation in full cells. Figure 10.1 shows quantified\(^5\) phase evolution in PNNO series on thermally annealed electrodes for 500 hours at 750 °C, and electrochemically operated electrodes in full cells at 0.80 V. Two sets of full cells show reproducible phase transformation. However, it is imperative to note that phase transformation in thermally annealed electrodes is substantially lower than in operated electrodes. This finding brings to a question as to what extent do operating
conditions on PNNO materials influence the phase transformation, which has been linked to performance degradation in full cells.

![Phase evolution](image)

**Figure 10.1.** Phase evolution in thermally annealed (750 °C) and electrochemically operated \((Pr_{1-x}Nd_x)NiO_4\) electrodes after 500 hours at 750 °C and 0.80 V.

In order to answer this question, a brief theoretical perspective was developed. The phase transformation in thermal annealing studies is bound by the laws of thermodynamics. Annealed materials will effectively reach thermal equilibrium that will govern the phase evolution. In other words, the changes on the electrode surface and in the bulk are only affected by fluctuations in the thermodynamic parameters (e.g. temperature, pressure, molar number, and the chemical potential). However, an operating SOFC is a non-equilibrium system subjected to continuous and non-linear flux across the material. During electrochemical reaction, the electrode undergoes a transfer of matter and energy with the surroundings and is also subjected to external thermodynamic forces. Furthermore, the presence of electrochemical potential, as a dominating driving force in operating cells, cannot be overlooked.
The flux density will be dependent on the concentration and mobility of mobile species, along with the driving force (electrochemical potential) according to:

\[ J_i = -C_i B_i \nabla \mu_i \]  

where \( J_i \) is the flux density of species \( i \), \( C_i \) is the concentration, \( B_i \) is the mobility, and \( \nabla \mu_i \) is the electrochemical potential. In PNNO ceramics the conduction process is known to occur via oxygen interstitials (\( O_i^{\prime\prime} \)) and holes (\( h^0 \)).

Hence, with the injection of the current a substantial flux is created causing \( O_2^- \) and \( h^0 \) to move across the material.

For short-term measurements of only a few hours, as commonly reported in the literature, the effects of the electrochemical potential on phase transformation in nickelates may not play a significant role. However, with sufficiently long operation the local oxidation and reduction may take place since the conducting species move under substantial flux and will chose the paths of the least resistance, possibly creating a gradient inside the grains that form the electrode. In such case a starting homogeneous electrode may evolve into inhomogeneous form, which could in turn promote phase transformation.

10.2 PERFORMANCE STABILITY AND IN OPERANDO DRT ANALYSIS

The aforementioned theory was studies via systematic tests on multiple full cells. Figure 10.2(a-c) shows i-V and power density curves on PNNO cells operated at various current densities (0.25, 0.50, and 0.75 \( \text{A/cm}^2 \)) at 790 °C. The performance remains stable after 300 hours of continuous operation. Figure 10.2(d) shows reproducible results on three cells at each current density. We have also previously demonstrated relatively stable operation in PNNO cells (0.25%/1,000 hours performance degradation) held at 750 °C and 0.8 V for 500 hours, but detected phase transformation after operation. The retained activity and performance stability was linked to startling formation of PNNO nanoclusters.
(chapter 9), which lead to increase in active area for oxygen reduction reaction (ORR) and exposed surface for direct ORR. However, the focus of this work is to manipulate phase transformation with electrochemical operation since the phase transformation may not be evident from the DC measurements. Consequently, a closer look was given to EIS spectra\(^8\) with an attempt to identify any changes in the electrodes.

![Figure 10.2. i-V and powder density curves as function of time for cells operated under continuous current at (a) 0.25 A/cm\(^2\), (b) 0.50 A/cm\(^2\), and (c) 0.75 A/cm\(^2\). (d) Performance stability as function of time under various current density.](image)

*In operando* distribution of relaxation times (DRT) analysis\(^9\)\(^{-12}\) was obtained from the inverse Fourier transform of impedance spectra. DRT allows different processes on electrode to be separated based on their relaxation frequency. Therefore, instead of having a single or double EIS arc,\(^8\) each process will be show as a separate peak in DRT plot, Figure 10.3(a).\(^9\) Furthermore, DRT has high resolution ability and can separate processes
that resonate within half a decade, while EIS can only separate processes that resonate at frequencies within two to three orders of magnitude. As a result, different processes associated with electrode can be studied. An increase in polarization of cathodic peaks (P1c-P3c) was detected along with shifts to higher frequency, Figure 10.3(a). This behavior has been previously associated with increase in resistance for overall ORR in PNNO electrodes. The area specific resistance (ASR) for the cathodic peaks that experience the largest change is shown in Figure 10.3(b). Both P2c and P3c (associated with ORR) increase over time. The rate of increase is promoted by fourfold with increase in current density from 0.25 A/cm² to 0.75 A/cm². The evolution of cathodic peaks clearly indicates increase in electrode resistance, which is not evident from the i-V and power density curves. Therefore, detailed analysis of EIS spectra could potentially provide some insights into phase transformation.

Figure 10.3. (a) Representative DRT analysis on operating cell measured at 790 °C and 0.50 A/cm². (b) Quantified evolution of cathodic peaks as function of time at various operating current density.
10.3 PHASE TRANSFORMATION IN ELECTROCHEMICAL CELLS

In order to correlate changes in electrode polarization with the structural changes, the phase transformation was studied via XRD before and after cell operation. First, a baseline was developed where phase transformation in PNNO was not influenced by electrochemical potential. Figure 10.4(a) shows that operation at 700 °C and 0.10 A/cm² for 300 hours does not lead to phase transformation, as shown by preserved parent phase (indicated with ●). However, once the current density is raised to 0.50 A/cm² a clear phase transformation follows with formation of PrOₓ (+). Therefore, the phase transformation is evidently driven by the electrochemical potential and must not be overlooked when quantifying phase transformation in praseodymium nickelates. With greater confidence in the proposed theory, a systematic work at various temperatures and current densities was performed. Figure 10.4(b) shows phase evolution after electrochemical operation at 750 °C at 0.10 A/cm² and 0.50 A/cm². With increase in current density the phase transformation also increases. Similarly, the electrochemical tests in full cells at 790 °C show major phase transformation at 0.50 and 0.75 A/cm², Figure 10.4(c). It is evident that with increase in current density the formation of PrOₓ is promoted. Furthermore, the phase transformation can be further accelerated at elevated temperatures, which may be due to increased mobility of oxygen ions in the structure. It is imperative to note that thermally annealed PNNO powder (between 700 – 790 °C) does not show significant phase transformation after 300 hours. In fact, only ~1 mol. % of PrOₓ is formed after 300 hours of annealing at 790 °C, Figure 10.4(c).
Figure 10.4. Phase evolution in PNNO electrodes operated under different current densities at (a) 700 °C, (b) 750 °C, and (c) 790 °C. Standard XRD patterns for Ni-YSZ/GDC substrate are shown in (a).

Figure 10.5 shows quantified phase evolution in thermally annealed PNNO powder and electrodes, along with electrochemically operated cathodes. The plot was divided into two regions: (1) a region of thermally driven phase transformation where thermodynamics dominates, and (2) a region of electrochemically driven phase changes, where electrochemical driving force dominates. After 500 hours of annealing at 790 °C both powders and electrodes (YSZ/GDC/PNNO configuration) show only a few percent of phase transformation. A 1-2% larger phase transformation in electrode was detected due to previously discussed reaction with GDC interlayer. However, it is evident that the electrochemical operation significantly enhances phase transformation in PNNO. At 700 °C the electrodes operated at 0.50 A/cm² undergoes 10.6 % phase transformation. With further increase in temperature the phase transformation reached 15.5% at 750 °C and 0.50...
Figure 10.5. Quantified phase evolution in PNNO powders and electrodes. Powders and electrodes at OCV were thermally annealed at 790 °C for 500h in air. Phase evolution in electrochemically operated electrodes is illustrated as function of current density at various temperatures and operating times.

A/cm². Even more evident results were obtained at 790 °C, where phase transformation was 60x larger than in thermal annealing studies at the same temperature. The baseline studies (0.10 A/cm² and 700 °C) which provided zero phase transformation also show enhanced phase degradation with increase in temperature and operation time, further indicating the magnitude of the driving force (electrochemical potential).

Based on these results, the formation of PrOₓ seems to be promoted with increase in current density. PrOₓ is formed due to oxidation of Pr³⁺ to Pr⁴⁺ since the effective nuclear charge on Pr cannot hold the f electrons as tightly as perhaps is the case for Nd³⁺.⁵,¹⁴ This may explain why the phase transformation in Nd₂NiO₄ and (Pr₀.25Nd₀.75)₂NiO₄ does not occur even after electrochemical operation, Figure 10.1. However, with high Nd content
in the structure, the activity of the electrode decreases substantially. The generated Pr$^{4+}$ in PNNO is too small to stabilize in the parent structure and leaves the lattice forming PrO$_x$, which has ~69% thermal mismatch (TEC=22.3 ppm) when compared to PNNO phase. As a result, the local stress in a material will be induced. During electrode operation more PrO$_x$ is generated and the area of the thermal mismatch increases, effectively leading to enhanced phase transformation. With increase in electrochemical potential across the electrode local oxidation and reduction occurs at a faster rate (2x higher phase transformation at 0.75 A/cm$^2$ vs 0.25 A/cm$^2$ at 790 °C), as illustrated in Figure 10.5, creating inhomogeneous phase and leading to enhanced phase transformation. Therefore, the obtained results seem to closely follow the proposed theory.

Figure 10.6(a) shows an SEM image of the cell cross section after operation. EDS analysis was performed on the three regions of the cell, from the GDC interlayer bulk to the cathode/interlayer interface. The quantification of the elemental composition in the three regions,
with respect to cathode bulk, is shown in Figure 10.6(b). Quantified percentage of Pr and Nd is illustrated against the cell held at OCV. There is a threefold increases of Pr and Nd diffusion into GDC interlayer with increase in current density from OCV to 0.75 A/cm², which further confirms enhanced phase transformation in PNNO electrodes. It seems that electrochemical potential not only promotes the phase transformation, but also accelerates the reaction with interlayer, which could not be taken into consideration in thermal annealing tests on electrodes.

10.4 MICROSTRUCTURAL ANALYSIS ON ELECTROCHEMICAL CELLS

Figure 10.7(a) shows the microstructure of electrode before operation. After operation and with increase in current density the porosity of the electrode decreases, as illustrated in Figure 10.7(b-d). The results indicate that electrode microstructure can also be electrochemically manipulated. The TEM analysis shows a single PNNO phase before electrode operation, Figure 10.8(a). After thermal annealing at 790 °C for 500 hours a formation of contrasted phases indicates some formation of PrOₓ, Figure 10.8(b). Figure 10.8(c) shows that after electrochemical operation at 0.75 A/cm² for 150 hours the contrasted regions are clearly separated, indicating presence of multiple phases. With increase in operation time (Figure 10.8(d)) the nanoclusters are formed, which have been addressed in detail previously (chapter 9), and are associated with the active PNNO phase. Elemental mapping on electrodes operated at 0.75 A/cm² for 300 hours is shown in Figure 10.9. STEM analysis in Figure 10.9(c-f) shows fully extruded PrOₓ and NiO phases, along with majority of the PNNO phase throughout the electrode bulk. Hence, the TEM results confirm electrochemically enhanced phase transformation, which supports the XRD studies shown in Figure 10.4 and Figure 10.5.
Figure 10.7. SEM images of the electrodes before operation (a) and after 300 hours of operation at 790 °C at (b) 0.25 A/cm$^2$, (c) 0.50 A/cm$^2$, and (d) 0.75 A/cm$^2$.

Figure 10.8. TEM images on PNNO electrodes (a) before operation, (b) after thermal annealing at 790 °C for 500 hours, and (c-d) after electrochemical operation at 0.75 A/cm$^2$ for 300 hours at 790 °C.
Figure 10.9. (a-b) TEM images on PNNO electrodes after electrochemical operation at 0.75 A/cm² for 300 hours. (c) to (f) are elemental maps of the electrode after operation shown in (b).

CONCLUSIONS

Phase evolution in praseodymium nickelate electrodes during thermal annealing and electrochemical operation has been addressed. Electrochemically operated PNNO electrodes show up to 60x higher phase transformation when compared to thermal annealing studies. Such large discrepancy was attributed to dominating electrochemical potential in full cells, which is not present in thermal annealing studies. Since the phase transformation during thermal annealing is under equilibrium and driven by the thermodynamic variables (pressure, temperature, molar number, and chemical potential), it cannot account for the electrochemical operation in full cells. The results show that for the accurate phase stability studies in praseodymium nickelate electrodes both thermal annealing and electrochemical operation in full cells should be performed. TEM analysis shows promoted phase transformation in PNNO electrodes with increase in current density.
along with physically extruded PrO$_x$ and NiO phases, as confirmed with STEM analysis. SEM-EDS analysis shows promoted interdiffusion (by threefold) between the electrode and GDC interlayer, which further indicates accelerated phase transformation in PNNO; which has been discussed in a great detail in Chapter 12.
REFERENCES


CHAPTER 11

ACCELERATED TEST PROTOCOLS (ATPs) IN SOLID OXIDE FUEL CELLS

With time consuming and costly long-term SOFC operation, the approach towards development of new phase-stable cathodes has been mostly oriented towards thermal annealing studies. However, in the preceding chapter it was shown that thermal annealing studies cannot simulate phase transformation behavior in praseodymium nickelates in

![Figure 11.1](image)

**Figure 11.1** Quantified phase transformation in PNNO electrodes undergoing thermal annealing and continuous electrochemical operation at 0.50 A/cm² at various temperatures including 700 °C, 750 °C, and 790 °C. Multiple runs with full cells were conducted to ensure reproducibility.
operating cells. The presence of electrochemical potential as a dominating force must be considered in SOFC. In this chapter the cells operated at constant current density were compared to cells undergoing newly developed accelerated test protocols (ATPs), which include intermittent current injections to the cell.

**Figure 11.1** shows quantified phase transformation in PNNO electrodes at various temperatures during thermal annealing and electrochemical operation. It can be clearly seen that electrochemical operation at all temperatures promoted phase transformation. At 700 and 750 °C thermal annealing on electrodes shows preserved parent phase. However, with electrochemical operation at 0.50 A/cm² the phase transformation increases to 12% after 300 hours. Even more evident is the operation at 790 °C, where phase transformation reaches remarkable 40%, which is 40x increase when compared to thermal annealing studies at 790 °C for 300 hours. In the preceding chapter a detailed and systematic work showed similar patterns for various current densities. It was found that with increase in current density the phase transformation was further promoted. Having confirmed the electrochemically driven phase transformation behavior in PNNO, an approach was taken to further accelerate the cell life and simulate the long-term cell operation in a fraction of the cost.

Since SOFCs are targeted for ~40,000 hour operation (5 years) with only a few percent degradation per thousand hours, finding a way to screen materials in a faster and more effective way is highly desired. Since thermal annealing studies show only ~1% phase transformation in PNNO after 500 hours of annealing at 790 °C,[1] finding the ways to accelerate the phase transformation is of outmost importance, as phase transformation has been previously linked to performance degradation in praseodymium nickelates.[1, 2]
Having confirmed that electrochemical potential can indeed accelerate phase transformation, the ATPs were developed to simulate and mimic the long-term cell operation (10,000-20,000 hours) in significantly shorted periods of time (1,000-2,000 hours).

11.1 ACCELERATED TEST PROTOCOLS-THEORETICAL ANALYSIS

Our preceding work showed that electrochemical potential, which can be indirectly measured through the chemical potential of oxygen and electrical potential, can indeed promote phase transformation in PNNO. Since the conduction process in PNNO is known to occur via oxygen interstitials ($O_i^+$) and holes ($h^0$), the flux density is dependent on the concentration and mobility of these mobile species, along with the driving force (electrochemical potential) according to:

$$J_i = -C_i B_i \nabla \mu_i$$  \hspace{1cm} (1)

where $J_i$ is the flux density of species $i$, $C_i$ is the concentration, $B_i$ is the mobility, and $\nabla \mu_i$ is the electrochemical potential. Hence, with the injection of the current a substantial flux is created causing $O^{2-}$ and $h^0$ to move across the material. However, the interaction between all the species in the system cannot be overlooked during long-term SOFC operation. The exchange transport coefficients play a negligible role on the measurements during a short period of time, which is on the order of hours. However, in the case of sufficiently long operation (e.g. several thousand hours) or the presence of a very high driving force ($-\nabla \mu_i$) the effect of the flux of cation ($j_{cation}$) cannot be overlooked. Consequently, a net current of cations is generated and subsequently accounts for the phase transformation in praseodymium nickelates. In other words, if one of the cations in a material is more mobile than the other, the originally homogeneous material becomes inhomogeneous; indicating
that kinetic de-mixing takes place. The consequent work will show that the net current of cations during prolonged operations also accounts for segregation of SrO in LSCF, and the anomalous grain growth in LSM. The author emphasizes that further understanding of this theory is necessary, but its current state provides a new avenue in electrochemical measurements, which is the development of accelerated test protocols. As a result, shorted operation times and faster material screening have potential to significantly cut down the operation cost, and subsequently lead to design of better electrodes, in which cation migration can be suppressed. In this work, the ATPs were demonstrated on PNNO electrodes.

11.2 INITIAL PERFORMANCE AND CELL DURABILITY

Figure 11.2(a) shows i-V and power density curves for PNNO cell at temperatures between 600 - 850 °C. The power density reaches 0.70 W/cm² at 750 °C, 0.87 W/cm² at 800 °C, and over 1 W/cm² at 850 °C. In order to ensure accuracy of the results multiple cells were tested as each operating condition, as shown in Figure 11.2(b). The i-V curves for the three PNNO cells are within a good agreement (1-2% difference). The measured open circuit voltage (OCV) of 1.10 ± 0.04 V shows reproducible and quality seals. Figure 11.2(c) show power density as function of temperature at 0.80 V for multiple cells. With increase in temperature from 650 °C to 850 °C the power density increase by fourfold. Higher operating temperatures are desirable for PNNO electrode to enhance oxygen reduction reaction (ORR) and ionic transport.[1, 2] Figure 11.2(d) shows in operando AC impedance spectra on three PNNO cells at 750 °C and 0.50 A/cm². Consistent ohmic resistance (R_{ohm}) of 0.1 Ω·cm² indicates consistent manufacturing techniques and stable
interfaces. The polarization resistance ($R_{pol}$) of electrode is 0.21 $\Omega \cdot \text{cm}^2$, which is a reasonable value for PNNO electrode at intermediate temperature. By obtaining the

![Graphs showing i-V and power density curves, performance reproducibility, and EIS spectra for PNNO cells.](image)

Figure 11.2 (a) i-V and power density curves in PNNO cells measured at various temperatures. (b) Performance reproducibility with multiple PNNO cells measured at 700 °C, 750 °C, and 790 °C. (c) Power density as function of temperature at 0.80 V for multiple PNNO cells. (d) EIS spectra at 750 °C and 0.50 A/cm$^2$ on multiple PNNO cells.

required cell reproducibility, which eliminates the effects of variations in $R_{ohm}$ and $R_{pol}$ between the cells, allowed for applications of ATPs. Their role on performance stability and phase transformation in PNNO was studied.

11.3 PERFORMANCE STABILITY UNDER ATPs AND DRT ANALYSIS

Figure 11.3 shows the performance stability as function of time at various current densities (0.25 A/cm$^2$, 0.50 A/cm$^2$, and 0.75 A/cm$^2$). PNNO cells operated under constant
current density show stable operation after 300 hours at 790 °C (chapter 10). However, ATPs show clear performance degradation (up to 4%/1,000 hours) at all current densities.

**Figure 11.3** Cell voltage as function of time for various current density values including 0.25 A/cm², 0.50 A/cm², and 0.75 A/cm² at 790 °C for 300 hours. Constant hold vs. accelerated protocols were compared.

With increase in current density the rate of performance degradation with ATPs increases (by threefold at 0.75 A/cm² when compared to 0.25 A/cm² cycling). It is also advantageous to mention that PNNO operation at 750 °C and 0.80 V only showed 0.25%/1,000 hours degradation (chapter 5). Hence, with ATPs the performance degradation was accelerated by 16x.

Distribution of relaxation times (DRT) analysis[^3-6] of EIS spectra is shown in **Figure 11.4.** **Figure 11.4(a)** illustrates four peaks, where P1c-P3c are associated with cathodic processes and P4a is an anodic peak, as described in detail in one of our preceding studies.[^2] Evolution of in operando DRT spectra (measured at 0.50 A/cm²) for a cell held at constant current density of 0.75 A/cm² shows minor changes in the peaks after 300 hours of operation. However, a quantified peak area shows some increase in P3c and P2c peaks.
Figure 11.4(b) shows 4.3% increase in P3c and 2.4% increase in P2c. Such changes in cathodic peaks are associated with increase in resistance for overall ORR, which can be linked with phase transformation in PNNO (chapter 5-6). On the other hand, the cell undergoing ATPs at 0.75 A/cm² shows significant changes in DRT spectra. The resistance of cathodic peaks increases substantially along with shifts to higher frequency. The accelerated increase in $R_{\text{pol}}$(cathode) becomes evident when compared to constant operation. Therefore, to provide a link between the changes in electrode resistance and performance degradation a detailed phase evolution analysis was performed on full cells before and after electrochemical operation. It is also imperative to note that in situ studies

![DRT Analysis](image)

**Figure 11.4** In operando (at 0.50 A/cm²) DRT analysis as function of time on (a) cell operated at constant current density of 0.75 A/cm² for 300 hours, and (b) cell undergoing accelerated cycling at 0.75 A/cm². Quantified (c) P3c peak area, and (d) P2c peak area as function of time for both testing methods.
at a synchrotron source (chapter 12) on PNNO electrodes showed that the quantity of phase transformation at operating conditions in full cells is in agreement to phase transition recorded upon cooling. Hence, the quantification of phase transformation in praseodymium nickelates after operation is justified and reflects the actual phase evolution behavior in full cells.

11.4 ACCELERATED PHASE TRANSFORMATION IN PNNO

The role of ATPs on phase transformation in PNNO electrodes is illustrated in Figure 11.5. Figure 11.5(a) shows XRD patterns on common standards along with initial full cell. The parent layered structure can be clearly seen (marked as ●). After constant operation at 0.75 A/cm² for 150 hours at 790 °C, the phase transformation occurs showing decrease in intensity of nickelate peaks along with formation of PrOₓ (+). Figure 11.5(b) shows initial and final XRD diffraction patterns on the cell undergoing ATPs at the same conditions. The phase transformation is substantially higher, with the parent nickelate peaks being overshadowed with formation of PrOₓ and a higher order Pr₃Ni₂O₇[7] and Pr₄Ni₃O₁₀ phases (marked as x, as indicated by evolution of new peaks in 2θ region of 22-27°). Furthermore, the operation after 300 hours (Figure 11.5c) shows further phase transformation. The arrows on the highest intensity nickelate peak (2θ=32.15°) show the magnitude of phase transformation with ATPs. In addition, another new peak evolves at 2θ=27.5°, further indicating the formation of higher order Pr₄Ni₃O₁₀ phase. The Pr₄Ni₃O₁₀ phase⁸ is known to have a number of distinctive reflections between 20-27° while the Pr₃Ni₂O₇ mainly overlaps with the PNO phase.⁷ Vibhu et al.⁸ showed that Pr₄Ni₃O₁₀ electrode could potentially have high activity in SOFCs under oxidizing conditions; however, the phase transformation after electrochemical operation was not reported.
Furthermore, the highest intensity PrO\textsubscript{x} reflection directly overlaps with Pr\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10} phase\textsuperscript{8} further questioning the initial phase purity. Instead, thermal annealing studies at 800 °C for one month on Pr\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10} were performed\textsuperscript{8} (which from this work are known to fail to

![Figure 11.5 XRD patterns on PNNO electrodes in full cells before and after electrochemical operation at: (a) constant current density of 0.75 A/cm\textsuperscript{2} for 150 hours, (b) cycling current density of 0.75 A/cm\textsuperscript{2} for 150 hours, and (c) cycling current density of 0.75 A/cm\textsuperscript{2} for 300 hours. Standard XRD patterns for each cell component and possible products are shown in (a).](image)

simulate the phase transformation during electrochemical operation) and showed some phase transformation and formation of PrO\textsubscript{x}. Accelerated phase evolution and the mechanism of phase transformation in praseodymium nickelates show that ATPs may provide further insights on the complexity of the system in a significantly shorter time frame. It is also imperative to note that cell operation under constant current density does not yield formation of Pr\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10} phase (which has also been demonstrated in our preceding
report), hence the ATPs may shed a light on an additional phase transformation mechanism(s) in SOFCs; however, further work is required.

The effectiveness of ATPs on the phase transformation in praseodymium nickelates is best illustrated through the quantitative analysis. Figure 11.6 shows quantified phase evolution in thermally annealed PNNO powder and electrodes, along with electrochemically operated cathodes undergoing standard operation (constant current injected for the duration of experiments) and ATPs with alternating current injection (2 seconds at selected current, and 1 second at OCV). The plot was divided into two regions:

1. a region of thermally driven phase transition where thermodynamics dominates, and
2. a region of electrochemically driven phase changes, where electrochemical driving force dominates, as discussed in more detail in chapter 10. The standard electrochemical operation leads to significantly lower phase transformation when compared to ATPs. Even
after only 150 hours of operation the rate of phase transformation in full cells was accelerated by additional 50% with ATPs. With increase in operation time, the power of ATPs was further demonstrated by 67% increase in phase transformation when compared to standard electrochemical operation. Evidently the ATPs are a promising avenue in electrode evaluation, which take into account the role of electrochemical potential on phase transformation in praseodymium nickelates.

The transformation of parent PNNO phase is clearly promoted with electrochemical operation (chapter 10) and increase in current density. Furthermore, ATPs can further accelerate phase transformation by enhancing the net current of cations (in particular the Pr\textsuperscript{4+} formed during phase transformation, which is too small to stabilize in the parent structure and effectively leaves the lattice and forms the PrO\textsubscript{x} and higher order phases). Such effect is commonly overlooked in short-term measurements due the absence of a significant driving force (-\nabla \mu\textsubscript{i}). By simulating the prolonged operations and stimulating the net current of cations in the structure, ATPs can provide fundamental knowledge of electrode and system behavior in a fraction of the time and cost when compared to long-term thermal annealing studies and standard cell operation.

11.5 ATPs ON STABLE Nd\textsubscript{2}NiO\textsubscript{4} ELECTRODE

To further attest the power of ATPs, a highly stable Nd\textsubscript{2}NiO\textsubscript{4} (NNO) electrodes were also investigated. Thermal annealing studies (up to 2,500 hours) on NNO electrodes at the temperature range between 700-790 °C did not show any phase transformation in air (Chapter 6). Furthermore, electrochemical operation at 0.80 V and 750 °C showed preserved NNO phase after 500 hours of operation with 0.06%/1,000 hour performance degradation (Chapters 5-6). These results show the rigidity of the NNO phase and stable
Figure 11.7 (a) Voltage vs. time for NNO cells operated at 0.25 A/cm$^2$ and 750 °C for 1,100 hours. ATPs result in over one 1.3 million cycles within 1,100 hours of operation. Two NNO cells were measured to ensure reproducibility. (b) In operando (at 0.25 A/cm$^2$) DRT analysis on NNO cells as function of time.

![Voltage vs. time graph](image)

Figure 11.8 XRD patterns on two NNO electrodes in full cells before and after accelerated electrochemical operation at 0.25 A/cm$^2$ for 1,100 hours. Standard XRD patterns for NNO, NiO, and Nd$_2$O$_3$ products are shown on the bottom.

![XRD patterns](image)

Nd$^{3+}$ oxidation state, which stems from high effective nuclear charge holding the $f$ electrons tightly bound and less available for orbital overlaps.$^1$ The retained performance stability can be linked to stable NNO phase. However, ATPs on NNO electrodes in full cells show a remarkable sixfold increase in performance degradation (0.37%/1,000 hours) after 1,100
hour operation at 750 °C and 0.25 A/cm², Figure 11.7(a). Two NNO cells show reproducible degradation rates. The DRT analysis confirmed increase in cathode ASR, as can be seen from the increase in area of cathodic peaks and shifts to higher frequency, Figure 11.7(b). Even more evident effects of ATPs are shown in phase transformation studies in Figure 11.8. The XRD analysis on operated NNO electrodes shows clear phase transformation with formation of Nd₂NO₃ oxide and an additional nickelate phase. The authors postulate a possible formation of a higher order phase (*), as NdNiO₃ reflections do not match the newly emerged peaks in the 2θ range between 20-25°. The results further attest to effectiveness of ATPs on the entire (Pr₁₋ₓNdₓ)₂NiO₄ series.

CONCLUSIONS

In this work cells operated at constant current density were compared to cells undergoing ATPs, which are composed of intermittent current injection to the cell. The performance degradation was accelerated by 16x in PNNO electrodes when compared to standard cell operation. DRT analysis showed clear increase in cathode ASR, which has been linked to phase transformation. ATPs demonstrated 67% increase in phase transformation when compared to standard electrochemical operation in PNNO cells. Furthermore, highly stable NNO electrodes were also tested with ATPs and underwent surprising sixfold increase in performance degradation (0.37%/1,000 hours) after 1,100 hour operation at 750 °C and 0.25 A/cm². The parent NNO phase also underwent phase transformation in multiple cells, with formation of Nd₂O₃. Evidently the ATPs are a promising avenue in electrode evaluation, which take into account the role of electrochemical potential on phase transformation in praseodymium nickelates.
REFERENCES


CHAPTER 12
UNRAVELING THE ROLE OF INTERLAYE ON PHASE STABILITY
AND CATALYTIC ACTIVITY IN NICKELATE CATHODES

12.1 BRIEF HIGHLIGHTS ON THE ROLE OF DOPED CERIA INTERLAYER

Figure 12.1 Performance stability in praseodymium nickelate cells with common interlayer (GDC-20) when compared to a new interlayer (PGCO). Insert shows stabilized parent phase with a new interlayer, while GDC-20 promotes phase transformation.

The use of doped ceria as an interlayer in solid oxide fuel cells (SOFCs) is ubiquitous, which provides a better thermal expansion match and prevents the interaction between cathode (e.g. LSCF) and electrolyte (e.g. YSZ). However, the role of ceria interlayer on the cathode phase durability and catalytic activity remains obscure. This is particularly true in nickelate cathodes (e.g. Pr$_2$NiO$_4$). Here, we report that traditional Gd-
doped ceria (GDC) interlayer substantially accelerates the phase decomposition in Pr$_2$NiO$_4$ to form Pr$_6$O$_{11}$ and Pr$_3$Ni$_2$O$_7$, which leads to cell performance degradation. Two new interlayer designs were investigated in order to circumvent the phase evolution by using (1) a thin Pr$_6$O$_{11}$ film deposited on the surface of GDC and (2) a Pr-doped ceria interlayer. The latter design not only suppresses the phase decomposition, but also results in a 48% increase in cathode performance; and more importantly, it leads to a zero degradation over long-term measurements. *In operando* x-ray diffraction and a synchrotron source were used to elucidate the origin of interlayer functionality.

### 12.2 INTRODUCTION TO INTERLAYER CHALLENGES

A state-of-the-art solid oxide fuel cell consists of Ni/Ni-YSZ bilayer as an anode, a yttria-stabilized zirconia (YSZ) electrolyte, and a cathode.\[^1\] The direct contact between an active cathode and YSZ is challenging due to the thermal expansion mismatch between YSZ (11×10^{-6} K^{-1}) and cathodes (e.g. 13.2×10^{-6} K^{-1} for Pr$_2$NiO$_{4+\delta}$ and 14.9×10^{-6} K^{-1} for La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$FeO$_{0.8}$O$_{3}$)\[^2, 3\] and the formation of an insulating zirconates (e.g. La$_2$Zr$_2$O$_7$)\[^4\] at the interface. A common attempt to circumvent this challenge is to use doped ceria (e.g. Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$, GDC20) as an interlayer between the cathode and the electrolyte.\[^2, 3, 5-9\] The role of the interlayer (i.e. buffer) is threefold: (1) to prevent reaction between a cathode and YSZ, (2) to reduce the thermal expansion mismatch, and (3) to maintain oxygen ion transport. For instance, the thermal expansion mismatch between Pr$_2$NiO$_{4+\delta}$ (PNO) and GDC20 (13×10^{-6} K^{-1}) is significantly smaller (~1.5%), when compared to ~17% mismatch between PNO and YSZ, resulting in a more stable interface.

Although the interlayer is shown to be capable of preventing cathode/YSZ reaction and suppressing electrode delamination, its role on the cathode phase stability and catalytic
activity has remained elusive. To the best of authors knowledge, this has not yet been reported in open literature. Our preliminary work shows that the diffusion of Pr occurs from PNO cathode into the interlayer bulk. Consequently, it is unknown whether or not the interlayer accelerates the phase decomposition in PNO to form \( \text{Pr}_6\text{O}_{11} \) and high-ordered nickelates. A new approach is required to develop an interlayer capable of suppressing the phase decomposition and ideally promote the cathode performance.

It must be pointed out that the use of \( \text{Pr}_2\text{NiO}_4 \)-based cathodes stems from the necessity to develop an active and stable oxygen electrode over the intermediate temperature region (e.g. 500 to 750 °C). Indeed, PNO exhibit a much higher diffusion coefficient and surface exchange coefficient than LSCF over a wide temperature range between 500 and 900 °C, and thus a superior activity towards oxygen reduction reaction (ORR). Moreover, the layered structure in PNO, consisting of alternating rigid oxygen octahedra and metal-oxygen (MO) rock-salt layers (i.e. Ruddlesden-Popper structure), allows for a certain degree of flexibility to various substituents at Pr and Ni sites. This allows for the improvement of electrical properties, phase stability, and thus the cell performance. \( \text{Pr}_2\text{NiO}_4 \), however, is known to go through structural changes to form a higher order phase (\( \text{Pr}_3\text{Ni}_2\text{O}_7 \)) and \( \text{Pr}_6\text{O}_{11} \). The structure change has been a concern in developing commercial SOFC systems because of the possible consequence of performance degradation. Our recent work showed that phase decomposition in PNO can be significantly suppressed with Nd substitution on the Pr-site. However, two questions remain as: (1) whether or not the interlayer can accelerate the phase decomposition and (2) what is the role of interlayer on the cathode activity and durability. The aim of this chapter is to address these two questions.
12.3 DEVELOPMENT OF THE NEXT GENERATION INTERLAYERS

Initial research focused on the design of new interlayers. Figure 12.2(a) illustrates a standard cell configuration with a conventional GDC20 interlayer. Oxygen ions resulted from ORR move through the interlayer and electrolyte to reach the anode for fuel oxidation.

![Diagram](image)

**Figure 12.2** Schematics showing the overall electrochemical reaction in fuel cells and a nickelate electrode printed on (a) GDC20 (b) PrO₅-GDC, and (c) PGCO interlayers in full cell configuration. (d) Representative SEM image of a cell cross section showing respective thickness of each layer. A top view of Au grid (insert) is shown, which provides an exposure window for phase quantification studies.

at Ni-YSZ interfaces. The first approach to design new interlayers involved a deposition of a thin Pr₆O₁₁ film (~ 0.2 μm) on the top of GDC20 (named as PrO₅-GDC), as shown in **Figure 12.2(b)**. The thin PrO₅ layer was designed to act as a diffusion barrier by enriching the GDC20/cathode interface with Pr. The second approach is to tune the interlayer chemistry by using Pr/Gd co-doped ceria, Pr₀.₁₀Gd₀.₁₀Ce₀.₈₀O₁.₉₀±δ (PGCO), a bulk form rich with Pr, as shown in **Figure 12.2(c)**. These cell configurations were then used to study
the role of the interlayer on phase decomposition and performance stability of the cathodes. **Figure 12.2(d)** shows a scanning electron microscope (SEM) image of a cell cross section, illustrating a respective thickness of each layer and a gold grid current collector,\(^5\) which allows for *in operando* phase evolution studies in cathodes.

### 12.4 THE ROLE OF INTERLAYER ON PHASE TRANSFORMATION IN NICKELATES

The baseline studies were carried out on cells with and without conventional GDC20 interlayer, which enabled us to investigate the magnitude of phase decomposition accelerated by the interlayer. **Figure B.1** (Appendix B) shows the phase decomposition in PNO and \((\text{Pr}_{0.50}\text{Nd}_{0.50})_2\text{NiO}_{4+\delta}\) (PNNO) electrodes in the absence (**Figures B.1a,c**) and presence (**Figures B.1b,d**) of GDC20, respectively. An accelerated formation of PrO\(_x\) and a higher order nickelate phase was detected in cells with GDC20 interlayer. This accelerated phase decomposition (~20\% for different electrodes) is due to the interaction between the cathode and interlayer.

In order to understand the role of the interlayer on the phase decomposition of the cathode, *in operando* synchrotron studies were performed on nickelate electrodes with various interlayers. The experimental setup shown in **Figure B.2** was used in this study at the Advanced Photon Source at Argonne National Laboratory. **Figure 12.3(a)** shows a phase transformation from the orthorhombic to high temperature tetragonal (HTT) phase at ~450 °C during the heating process.\(^{19, 20}\) Upon cooling, the HTT phase underwent a reversible phase transformation to the orthorhombic structure. **Figure 12.3(b)** illustrates the phase decomposition in PNO electrode with the GDC20 interlayer when the electrode was held at 750 °C. PrO\(_x\) signal intensity (+) surpassed the intensity of the highest nickelate
Figure 12.3 (a) XRD patterns collected continuously at 86.7 keV during heating to 850 °C, holding at 750 °C, and cooling to RT on PNO electrode. The background contribution was subtracted for each temperature condition. A transition from orthorhombic to tetragonal structure occurs at ~450 °C during heating. Tetragonal phase prevails during operation and transitions back to orthorhombic structure upon cooling. (b) Selected XRD patterns for phase transformation comparison in PNO/GDC20 cell. Evolution of PrOₓ occurs in-situ (as indicated with evolution of PrOₓ peaks with higher intensity than the parent reflections) and is retained upon cooling. (c) The PNO cell with PGCO interlayer shows significantly lower percentage of PrOₓ. (d) Selected XRD patterns for PNNO/GDC cells showing a small percentage of PrOₓ formation. (e) Retained initial structure in PNNO/PGCO cell and preserved peak intensity ratios indicate preserved parent phase.

peak after 150 hours at 750 °C in air, indicating substantial phase decomposition. Furthermore, the formation of a higher order Pr₃Ni₂O₇ nickelate phase (*) was also detected; while NiO was not. With a PGCO interlayer, the formation of PrOₓ was significantly suppressed, as shown in Figure 12.3(c). More interestingly, when PNNO was placed on GDC20 interlayer the PrOₓ was also formed, Figure 12.3(d). On the contrary, a PGCO interlayer led to a complete absence of PrOₓ, thus a stable layered phase, as shown in Figure 12.3(e). It is imperative to note that PNNO powders, or PNNO electrodes printed directly on YSZ (Figure B.1c), did not show formation of PrOₓ after annealing for 150
hours at 750 °C in air (~1% of PrO\textsubscript{x} was detected only after 500 hours), further indicating the promoted reaction in cells with GDC20.

The quantified phase decomposition in PNO and PNNO electrodes is shown in Figure 12.4 with three different interlayers. Quantification was performed using standardization curves generated from the physical mixtures of nickelate and PrO\textsubscript{x} powders.\textsuperscript{[5]} Figure B.3 shows the raw XRD patterns for PNO electrodes on GDC20, PrO\textsubscript{x}-GDC, and PGCO interlayers, respectively, measured at OCV as a function of time. The most noticeable changes occur at T ≤ 750 °C. With the presence of PGCO interlayer, the phase decomposition was suppressed by threefold at 750 °C and by an order of magnitude at 700 °C (Figure B.4a). In addition, there was no indication of new phase(s) evolving in cells with PGCO (Figure B.3c), while a small percentage of Pr\textsubscript{3}Ni\textsubscript{2}O\textsubscript{7} phase\textsuperscript{[5]} was detected with PrO\textsubscript{x}-GDC (Figure B.3b). The phase decomposition in cells with PrO\textsubscript{x}-GDC interlayer was suppressed by twofold at 750 °C and by threefold at 700 °C. When compared to cells with GDC20 interlayer (Figure B.3a), a tremendous improvement in phase stability was obtained with the new interlayer designs. At elevated temperatures (e.g. T ≥ 790 °C),

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.4.png}
\caption{Quantified long-term phase evolution in (a) PNO, and (b) PNNO electrodes with the three different interlayers at 750 °C. Accelerated phase transformation was measured in cells with GDC20 interlayer, while PGCO interlayer leads to substantial phase stabilization.}
\end{figure}
thermally driven phase decomposition dominates,[5] so the role of interlayers becomes secondary (Figure B.4a).

An addition of Nd is known to suppress the phase decomposition in PNO.[16] The higher nuclear charge in Nd atom holds f-electrons more tightly, which decreases their overlap with neighboring atoms.[21] As a result, there is a decreased electron affinity of Nd which is in favor of the trivalent configuration, in comparison to the tetravalent in Pr. Consequently, the effect of interlayer on the phase decomposition in PNNO is more profound, as shown in Figure 12.4(b). The parent phase was fully preserved up to 500 hours at 750 °C in cells with PGCO and PrOx-GDC interlayers. This is a remarkable improvement when compared to 8% phase decomposition (750 °C, 500th hour) with GDC20. Furthermore, 17% of phase decomposition was detected after 500 hours at 790 °C in cells with GDC20 interlayer (Figure B.4b). However, the cells with PGCO retained stable phase at all measured temperatures. Considering the superior ability of PGCO to suppress phase decomposition at T ≤ 750 °C, the new interlayer design may play a critical role in developing the intermediate temperature SOFCs, during which a metal interconnect can be used and a reduced performance degradation is expected.

12.5 KINETICS OF PHASE TRANSFORMATION IN NICKELATES

The phase decomposition shown in Figure 12.4(b) and B.4(b) can be divided into two regions: (1) a detection limit region below 150 hours and (2) a detectable region (t > 150 hours). For instance, at 750 °C with GDC20, x-ray diffraction (XRD) detects the formation of PrOₓ after 150 hours. It is likely that low percentages (≤ 1%) of PrOₓ do exist, but are not shown in XRD patterns. The percentage of phase decomposition becomes more profound at 790 °C, where marginal phase decomposition at the 100th hour (2.2%/100h)
slowly evolves up to 250 hours. Then, the phase decomposition accelerates (14.9%/100-h). An early model by Avrami[22-24] was used to study the kinetics of phase decomposition in this work. Avrami’s model was based on a sigmodial increase in volume of new crystal phase as a function of time, where a slow crystallization initiates, followed by a rapid increase. Such behavior is in congruence with observations in nickelate cathodes. The mathematic description to fit the experimental data is:

\[ x = 1 - \exp[-kt^n] \]  

where \( x \) is the fraction of parent phase transformed, \( k \) is the reaction rate, \( t \) is time, and \( n \) is the exponent that describes the geometry of the growth of a new phase. By arranging the Eq. (1) and expressing it in natural logarithm form as:

\[ \ln[-\ln(1-x)] = \ln(k) + n\ln(t) \]  

the isothermal linear plots can be generated to determine the values of \( k \) and \( n \) from the least squares fitting. At 700 °C the \( n \) increases from 2.40 (GDC20) to 3.30 (PGCO), indicating suppressed phase decomposition. By expressing the reaction rate in its Arrhenius form:

\[ k = k_0 \exp\left(-\frac{E_a}{RT}\right) \]  

where \( k_0 \) is the pre-exponential factor and \( E_a \) is the activation energy for phase decomposition. It was found that \( E_a \) for PNO increases substantially with the new interlayer, from 4.40 eV (GDC20) to 7.80 eV (PGCO), indicating much higher energy barrier for the decomposition within the structure,[25,26] which in turn leads to fewer atomic rearrangements and suppressed structural changes.
12.6 THE ROLE OF INTERLAYER ON CATHODE PERFORMANCE

**Figure 12.5(a)** shows a series of plots for initial current-voltage (i-V) scans and power density with PNO electrodes on three interlayer configurations. Switching from GDC20 to PGCO, the cell performance was improved. A 48% increase in power density was obtained at 650 °C, 27% at 750 °C, and 13% at 850 °C for PNO/PGCO cell configuration, as shown in **Figure 12.5(b)**. With an increase in temperature, the power densities for three cell configurations tend to converge, which can be attributed to thermally
thermally activated ORR process in cathodes. At lower temperatures, the greater difference in power density results from the presence of Pr in the interlayer.

It is known that Pr doping into ceria lowers the activation energy for electronic conduction, which can be attributed to an additional Pr(4f) level placed closer to the Fermi energy. Due to the virtually constant concentration of oxygen vacancies in ceria, the chemical potential of oxygen ions is constant, hence the position of the Fermi level with respect to the conduction and valance band edges can be assumed to be only a function of oxygen activity at a constant temperature. With Pr-doping, a small fraction of Pr$^{4+}$ is formed under oxidizing conditions which leads to an increase in p-type conduction. When compared to only narrow Pr-enriched zone in PrO$_x$-GDC interlayer (2 µm thick zone with 3-5 atom.% of Pr), the PGCO interlayer has Pr-enriched bulk (8 µm) which further improves the conduction properties. By introducing a mixed conductor (e.g. PrO$_x$-GDC and PGCO) at the triple phase boundary (TPB), the TPB expands to the entire particle surface of the mixed conductor, resulting in a highest performance with the presence of PGCO interlayer.

12.7 THE ROLE OF INTERLAYER ON CATHODE DURABILITY

Figure 12.5(c) shows the current density as a function of time for PNO cathodes on various interlayers at 0.8 V. Remarkable performance stability was observed in cells with PGCO interlayer, with 0% degradation during 500 hour tests. Furthermore, the current density at 750 °C and 0.80 V was increased by 27% (1.4 A/cm$^2$) with PGCO, in comparison to conventional GDC interlayer. The cells with PrO$_x$-GDC interlayer exhibited performance degradation, but still lower than with GDC. Figure 12.5(c) and B.5 show that
the measurements were consistent and reproducible in multiple cells on different electrodes.

Results measured from electrochemical impedance spectroscopy (EIS) are illustrated in Figure 12.5(d). The PGCO interlayer reduces electrode polarization ($R_{pol}$) by 20%, when compared to GDC20. Furthermore, the ohmic resistance ($R_{ohm}$) is 16% lower. A decrease in total cell resistance can be attributed to the extended mixed conduction zone in PGCO. Both $R_{pol}$ and $R_{ohm}$ were stable after 500 hours of operation. On the other hand, a significant degradation in $R_{pol}$ (18%) was measured in cells with GDC20 interlayer. The PrO$_x$-GDC interlayer does reduce $R_{pol}$, but does not fully suppress the degradation (Figure B.6). This brings to a question if the stabilized long-term operation in nickelate/PGCO cells can be linked to suppressed phase decomposition in the cathode during electrochemical operation. In an attempt to address this question, a series of in operando XRD studies were performed.

12.8 IN OPERANDO XRD ANALYSIS IN ELECTROCHEMICAL CELLS

Figure 12.6(a) illustrates the phase evolution in PNO cathodes in operated full cells. With GDC20, 45% of phase decomposition occurs, confirmed by evolution or PrO$_x$ (+) and a higher order Pr$_3$Ni$_2$O$_7$ phase (*). With PrO$_x$-GDC, the Pr diffusion was not fully suppressed due to its initial thickness (0.2 µm) was much thinner than that of of Pr-free bulk (6 µm). However, the cells with PGCO layer provide the most promising results. After 500 hours of electrochemical operation, the majority (87%) of the PNO phase (●) was preserved, while PNNO cathode retained stable structure (initial ratio of peak intensities was preserved), as shown in Figure 12.6(b). Despite the absence of formation of Pr$_3$Ni$_2$O$_7$ phase in PNNO electrodes on GDC20 interlayer, the evolution of PrO$_x$ peak (2θ ≈ 29°) is
a clear indication of phase decomposition and interaction with ceria interlayer. These results along with a long-term electrochemical operation shown in Figure 12.5(c) clearly establish a correlation between stable performance and suppressed phase decomposition. Proper selection of the interlayer seems to play a significant role on stabilizing the parent phase.

*In operando* XRD analysis in full cells (Figure B.7) at 750 °C and 0.80 V also confirms a transition from orthorhombic to HTT phase, as shown in Figure 12.6(c), suggesting the active phase at high current densities (i ≥ 1.0 A/cm²) is the prevalent HTT phase. PrOₓ was not formed in PNNO electrode after 150 hours of electrochemical operation, which is in agreement with results shown in Figure 12.4(b). On the other hand, operating PNO electrode showed a steady evolution of PrOₓ as seen in Figure 12.3(b) and Figure 12.4(a).

**Figure 12.6** Phase evolution in (a) PNO and (b) PNNO electrodes operated in full cells at 750 °C and 0.80 V for 500 hours. The flux was normalized and peak positions were calibrated with multiple external (Ni-YSZ, single phase PNO and PrOₓ) and internal (Au) standards. An XRD pattern illustrated at the bottom shows initial cathode/GDC/YSZ/Ni-YSZ cell. Shown progressively from bottom to top are the final XRD patterns on cells with various interlayers. The cells with PGCO interlayer show preserved nickelate phase. (c) In-situ XRD patterns on operating PNNO electrode. Phase transformation from orthorhombic to tetragonal occurs at operating conditions. The parent nickelate phase in PNNO was fully preserved after operation.
12.9 THE ROLE OF INTERLAYER ON PHASE TRANSFORMATION IN OPERATING ELECTRODES

Elemental analysis on electrochemical cells after operation is summarized in Table B.1 (Appendix B) to address the role of nickelate/interlayer reaction on phase decomposition in electrodes. Figure 12.7(a) shows an SEM image of the cell cross section after 500 hours of electrochemical operation at 750 °C and 0.80 V. The cells were prepared via focused ion beam (FIB) etching. The three regions used for EDS analysis are depicted and include: (1) the nickelate bulk, (2) the nickelate/interlayer interface, and (3) the interlayer bulk. The electrode bulk shows a proper Pr:Nd:Ni ratio with all three interlayer configurations; however, the elemental distribution varies widely at the cathode/interlayer interfaces. When PNO was used, elemental diffusion of Pr into ceria interlayer was suppressed by 34% with an addition of PrO\textsubscript{x} thin film, while PGCO interlayer suppressed the diffusion of Pr by tenfold in PNO. With PNNO electrode, the diffusion was suppressed

Figure 12.7 (a) An SEM image of a cell cross section after 500 hours of operation at 750 °C and 0.80 V. The cells were prepared via FIB etching, showing each cell layer and the three regions used for EDS studies. Quantified results are presented in Table B.1. (b) A backscattered SEM image on nickelate/PrO\textsubscript{x}-GDC interface. Dark phase is PrO\textsubscript{x}, as shown via EDS analysis in Table B.2. Numbered circles show the locations used for EDS studies.
by 48% with PrO$_x$-GDC, and fully suppressed with PGCO layer. Furthermore, Pr diffusion from PGCO into YSZ was not observed, indicating highly stable interlayer chemistry.

Since the Pr diffusion is initiated at the cathode/interlayer interface, the origin of accelerated phase decomposition in the conventional GDC20 can be linked to the chemistry at this interface. Due to substantial elemental interdiffusion with GDC20 interlayer (Figure 12.7b), some of the parent phase undergoes phase decomposition, leading to the formation of PrO$_x$ (a dark phase). A small percentage of PrO$_x$ formed at the interface after a few hundred hours further accelerated phase decomposition, as shown in Figure 12.4. The local stress$^{[32]}$ resulting from considerable thermal expansion mismatch ($\sim 69\%$) between the nickelate and PrO$_x$ (TEC=22.3 ppm)$^{[33]}$ may play a role in a decrease of mechanical integrity of the interfaces, which is consistent with an increase in ohmic resistance observed in EIS measurements (Figure 12.5d and Figure B.6). With PrO$_x$-GDC interlayer, the reaction is suppressed to some extent, as shown by PrO$_x$ accumulation at the interface (Figure 12.7b). Table B.2 shows EDS analysis on the interface regions with PrO$_x$-GDC interlayer. PrO$_x$ phase was detected along the interface with a full absence of Ni, and propagates towards the nickelate bulk. However, with PGCO interlayer the initial reaction is fully suppressed since the PrO$_x$ is not generated at the interface, leading to suppressed phase decomposition in nickelates.

12.10 CONCLUSIONS

In summary, this chapter has shown that traditional Gd-doped ceria promotes the phase transformation in nickelate electrodes, leading to performance degradation. A new interlayer chemistry was presented to obtain a stable long-term cell operation. The reaction with GDC20 was shown to be irreversible and thermally driven. Newly developed PGCO
interlayer can fully suppress the reaction with cathodes and consequent phase transformation. Furthermore, due to Pr-enrichment of the interlayer bulk the mixed conducting zone is extended, which in combination with stabilized cathode structure leads to increased cell performance by 48%. Stable long-term performance was measured at 750 °C and 0.80 V for 500 hours in cells with PGCO interlayer. In-situ and post-operation XRD analysis on full cells show 100% preservation of a parent nickelate phase. This is a tremendous improvement when compared to a 45% structural change in nickelate cathodes with a common ceria interlayer. A transition to tetragonal phase during electrochemical operation at high current densities (i ≥ 1 A/cm²) sheds a light, for the first time, on an electrochemically active phase in nickelate cathodes. The combination of the next generation interlayers and high performing and stable nickelate electrodes could have a profound effect on the current SOFC systems.
APPENDIX A
SUPPLEMENTARY INFORMATION TO CHAPTER 7

Table A.1 B-site metal cation screening. A pure phase was obtained with Fe and Cu ions while rest of dopants did not provide a single phase. Due to instability of Fe-doped compositions, only the Cu-doped compounds were studied in detail. Thermal annealing in 3% humidified air was performed at 790 °C and 870 °C.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure phase was obtained</td>
<td>NO</td>
<td>NO</td>
<td>YES (5% and 10%)</td>
<td>YES (5% to 30%)</td>
<td>YES (5% to 30%)</td>
<td>NO</td>
</tr>
<tr>
<td>Phase stability at 790 °C</td>
<td>N/A</td>
<td>N/A</td>
<td>5% Fe has a marginal second phase ~1%</td>
<td>not stable after 150h</td>
<td>stable (specific comp.)</td>
<td>N/A</td>
</tr>
<tr>
<td>Phase stability at 870 °C</td>
<td>N/A</td>
<td>N/A</td>
<td>not stable after 150h</td>
<td>not stable after 150h</td>
<td>stable (specific comp.)</td>
<td>N/A</td>
</tr>
<tr>
<td>Favors which structure</td>
<td>octahedral</td>
<td>layered</td>
<td>square planar or tetrahedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coordination #</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Charge and Ionic radius (Å)</td>
<td>Cr³⁺</td>
<td>Mn³⁺</td>
<td>Fe²⁺</td>
<td>Co³⁺</td>
<td>Cu²⁺</td>
<td>Zn²⁺</td>
</tr>
<tr>
<td></td>
<td>0.755</td>
<td>0.645</td>
<td>0.78</td>
<td>0.61</td>
<td>0.57</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Figure A.1 Phase purity and phase stability in (Pr$_{0.50}$Nd$_{0.50}$)$_2$Ni$_{1-y}$Cu$_y$O$_{4+δ}$ powders at 790 °C and 870 °C, where (a) $y=0.20$, and (b) $y=0.30$. Standard XRD patterns are included.

Figure A.2 Phase purity and long-term phase stability in PNNO(50/50) (a), (PNNO(50/50)-Cu5 (b), and (PNNO(50/50)-Cu10 (c) powders at 790 °C and 870 °C. The samples were annealed in 3% humidified air.
Figure A.3 Phase purity in Pr$_2$Ni$_{1.3}$Cu$_y$O$_{4+\delta}$ (PNO-Cu$_y$) powders (a-c), where $y=0.05$, 0.10, and 0.20, respectively. Evolution of PrO$_x$ is marked with (+). Standard XRD patterns are included.

Figure A.4 Phase stability in PNO-Cu$_y$ powders after 150 hour annealing in 3% humidified air at 790 °C (a-c) and 870 °C (d-f), where $y=0.05$, 0.10, and 0.20, respectively.
Table A.2 The summary of phase purity and phase stability in PNO-Cu$_y$ and PNNO5050-Cu$_y$ electrodes. Thermal annealing was performed in 3% humidified air at 790 °C and 870 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pr$<em>2$Ni$</em>{0.95}$Cu$<em>{0.05}$O$</em>{4+\delta}$</th>
<th>Pr$<em>2$Ni$</em>{0.9}$Cu$<em>{0.1}$O$</em>{4+\delta}$</th>
<th>(PrNd)$<em>2$Ni$</em>{0.95}$Cu$<em>{0.05}$O$</em>{4+\delta}$</th>
<th>(PrNd)$<em>2$Ni$</em>{0.9}$Cu$<em>{0.1}$O$</em>{4+\delta}$</th>
<th>(PrNd)$<em>2$Ni$</em>{0.8}$Cu$<em>{0.2}$O$</em>{4+\delta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions for obtaining a pure phase after glycine-nitrate combustion process + annealing in air</td>
<td>All annealing temperatures lead to formation of Pr$<em>6$O$</em>{11}$ phase; however, 1080 °C results in the lowest percentage of Pr$<em>6$O$</em>{11}$.</td>
<td>All annealing temperatures lead to formation of Pr$<em>6$O$</em>{11}$ phase; however, 1150 °C results in the lowest percentage of Pr$<em>6$O$</em>{11}$.</td>
<td>1) 1h at 1050 °C, or 1080 °C, or 1100 °C; 2) 2h at 1150 °C</td>
<td>1) 1h at 1050 °C, or 1080 °C, or 1100 °C; 2) 2h at 1150 °C</td>
<td>1h at 1050 °C or 1080 °C this compositions was not annealed at higher temperatures</td>
</tr>
<tr>
<td>Presence of Pr$<em>6$O$</em>{11}$ phase</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Percentage of Pr$<em>6$O$</em>{11}$ phase present at indicated annealing temperatures</td>
<td>1080 °C - 6%</td>
<td>1080 °C - 7%</td>
<td>1080 °C - 9.5%</td>
<td>sample annealed at 1200 °C shows presence of Pr$<em>6$O$</em>{11}$ phase (~6%) at ~28°</td>
<td>N/A</td>
</tr>
<tr>
<td>Comments</td>
<td>From XRD patterns, a higher order phase formation was detected by a low intensity peak emerging at 2θ = ~23°.</td>
<td>Possible structural change due to doublets at 2θ = 33° and 44° merging into singlets.</td>
<td>doublets at ~33°, ~44° and ~45° are poorly resolved (probably due to changes in atomic positions with increase in Cu content)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO presence</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

Figure A.5 (a) Phase purity in Cu-doped PNNO25-75 electrodes. Phase stability in 3% humidified at (b) 790 °C and (c) 870 °C after 150 hours. Nd$_2$O$_3$ phase was indicated by two peaks at ~28° plane (002) and 31° (101) region and the presence of (102) and (103) at 41° and 53°, respectively. Additional Nd$_2$O$_3$ peaks overlap with Pr$_2$NiO$_4$ reflections. Electrodes were phase-stable after thermal annealing.
Figure B.1 Thermal stability studies on PNO electrodes annealed at 700 °C for 150 hours in the electrolyte supported cells: (a) in the absence of a interlayer, and (b) with GDC20 interlayer. Long-term thermal stability on PNNO electrodes annealed at 750 °C for 500 hours in the electrolyte supported cells: (c) in the absence of an interlayer, and (d) with GDC20 interlayer. Standard XRD patterns on YSZ and YSZ/interlayer substrates, PrOx and nickelate powders are shown at the bottom.
Figure B.2 Experimental setup for XRD synchrotron studies at 11-ID-B beamline at Advanced Photon Source. A hutch containing the 2D detector and a flexible sample chamber used for powder and cell studies is shown. High flux and high resolution x-rays (86.7 keV) were used for XRD analysis. In-line laser and a camera were used to center the sample in front of the beam. Thermocouples were used to monitor the temperature of a sample. Electrolyte supported cells used for interlayer studies are also shown (bottom right). Test stations are also depicted (bottom left). See methods section for further details.

Figure B.3 Phase evolution in PNO electrodes at 700 °C on various interlayers: (a) GDC20, (b) PrO$_x$-GDC, and (c) PGCO.
Figure B.4 Quantified long-term phase evolution in (a) PNO, and (b) PNNO electrodes with the three different interlayers at various temperatures 700 °C and 790 °C. Colors indicate the temperature, while distinctive squares designate the types of interlayers. Accelerated phase transition was measured in cells with GDC20 interlayer, while PGCO interlayer leads to substantial phase stabilization.

Figure B.5 Degradation rate in PNNO full cells operated at 750 °C and 0.80 V. Two cells per each condition are shown. The cells with PGCO interlayer show zero degradation when compared PNNO/GDC20 cells.
Figure B.6 Impedance measurements showing ohmic and electrode resistance over time for a single full cell with PrO\textsubscript{x}-GDC interlayer configuration. Ohmic and electrode polarization resistance were decreased when compared to cells with GDC20 interlayer but the R\textsubscript{pol} was increasing.

Figure B.7 (a) Bruker D8 Advance XRD at Pacific Northwest National Laboratory. (b) Anton Paar HTK 1200 heating chamber. (c) In-situ SOFC setup with an open cathode center for phase evolution studies.
Figure B.8 (a) PNO/GDC20/YSZ cell annealed at 790 °C for 200 hours and reheated to 1080 °C for 10h, and (b) PNO/PGCO/YSZ cell undergoing the same conditions.
Table B.1 Quantified energy dispersive x-ray spectroscopy (EDS) area scan results of elemental distribution across multiple regions of a button cell with PNO and PNNO electrodes on various interlayers. For the simplicity reasons only Pr, Nd, and Ni atomic percentages are presented. Gas assisted etching was performed via focused ion beam (FIB) to verify elemental composition at the cathode/interlayer interface. Numbered boxes show the areas used for EDS studies, as illustrated in the SEM image below.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Region 1 (cathode)</th>
<th>Region 2 (cathode/interlayer)</th>
<th>Region 3 (interlayer bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compo-</td>
<td>Pr</td>
<td>Nd</td>
<td>Ni</td>
</tr>
<tr>
<td>sition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNO</td>
<td>GDC</td>
<td>40.1</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>PrO&lt;sub&gt;x&lt;/sub&gt;-GDC</td>
<td>42.3</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>PGCO</td>
<td>43.2</td>
<td>/</td>
</tr>
<tr>
<td>PNNO</td>
<td>GDC</td>
<td>15.0</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>PrO&lt;sub&gt;x&lt;/sub&gt;-GDC</td>
<td>20.6</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>PGCO</td>
<td>24.2</td>
<td>23.6</td>
</tr>
</tbody>
</table>

![SEM image of the button cell with labeled regions](image)
Table B.2 Quantified EDS point scan results of elemental distribution across multiple regions at the PNO/interlayer interface. For the simplicity reasons only Pr, Ni, and O atomic percentages are presented. Numbered circles show the points used for EDS studies, as illustrated in Figure 12.7b.

<table>
<thead>
<tr>
<th>Atom. %</th>
<th>Pr</th>
<th>Ni</th>
<th>O</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>28.24</td>
<td>1.21</td>
<td>70.55</td>
<td>-</td>
</tr>
<tr>
<td>Point 2</td>
<td>16.29</td>
<td>-</td>
<td>67.45</td>
<td>16.26</td>
</tr>
<tr>
<td>Point 3</td>
<td>57.0</td>
<td>-</td>
<td>15.7</td>
<td>27.29</td>
</tr>
<tr>
<td>Point 4</td>
<td>47.7</td>
<td>-</td>
<td>15.9</td>
<td>36.39</td>
</tr>
<tr>
<td>Point 5</td>
<td>36.7</td>
<td>5.31</td>
<td>57.98</td>
<td>-</td>
</tr>
</tbody>
</table>
APENDIX C

AUTHOR’S PUBLICATIONS, PATENTS, AND PRESENTATIONS

PUBLICATIONS


3. **E. Dogdibegovic**, C.J. Wright, and X.D. Zhou, “Activity and Stability of \((Pr_{1-x}Nd_x)_{2}NiO_{4+\delta}\) as Cathodes for Solid Oxide Fuel Cells: I Quantification of Phase Evolution in \(Pr_2NiO_{4+\delta}\)”. *Journal of American Ceramic Society*, 99(8), 2737-2741 (2016).


Evolution and Structural Stability in \((\text{Pr}_{1-x}\text{Nd}_x)\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}\) Electrodes”- submitted to the *Journal of The Electrochemical Society*


14. **E. Dogdibegovic** and X.D. Zhou, “Accelerated Electrochemical Tests on the Phase Transition in \((\text{Pr}_{0.50}\text{Nd}_{0.50})\text{Ni}_4\text{O}_{4+\delta}\) and \(\text{Nd}_2\text{NiO}_4\) Electrodes”- in preparation

15. **E. Dogdibegovic**, S. A. Horlick, S. Reese, and X.D. Zhou, “Accelerated Electrochemical Tests and Degradation Mechanisms in \((\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}(\text{Co}_{0.20}\text{Fe}_{0.80})_{3-x}\) and \((\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{MnO}_3-x\) Electrodes”- in preparation


**PATENTS AND INVENTIONS**


2. X.D. Zhou, and **E. Dogdibegovic**, “Accelerated Test Protocols in Solid Oxide Fuel Cells”, University of South Carolina.-invention application filed

**PROFESSIONAL PRESENTATIONS**

1. **E. Dogdibegovic**, N. S. Alabri, C.J. Wright, and X.D. Zhou, “The Role of Doped Ceria Buffer Layer on Phase Evolution in \(\text{Pr}_2\text{NiO}_{4+\delta}\)”. *Electrochemical Society Meeting*, October 2016, Honolulu, HI.

2. **E. Dogdibegovic**, C.J. Wright, and X.D. Zhou, ”X-ray Diffraction and in-situ Synchrotron Studies on Phase Evolution in \(\text{Pr}_2\text{NiO}_{4+\delta}\): Understanding the Local Structure Changes”. *Electrochemical Society Meeting*, October 2016, Honolulu, HI.


274
