Surface Science and Engineering of Nano-Structured Cathodes for Intermediate Temperature Solid Oxide Fuel Cells

Yeting Wen

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SURFACE SCIENCE AND ENGINEERING OF NANO-STRUCTURED CATHODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

by

Yeting Wen

Bachelor of Material Science and Engineering
University of Science and Technology Beijing, 2012

Master of Material Science and Engineering
University of Science and Technology Beijing, 2015

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University of South Carolina
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Accepted by:
Kevin Huang, Major Professor
Ralph E. White, Committee Member
Xinyu Huang, Committee Member
Fanglin Chen, Committee Member
Cheryl L. Addy, Vice Provost and Dean of the Graduate School
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ABSTRACT

The bulk-to-surface Sr-segregation can seriously compromise the stability of oxygen electrocatalysis in Sr-doped perovskite oxides such as $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ and limit their practical applications as cathode materials in solid oxide fuel cells. Although such chemical instability has been actively studied in recent years, fundamental understanding of Sr-segregation process vs temperature and time, particularly under real-world conditions, as well as the suppression method, are still needed. This PhD dissertation aims to acquire fundamental knowledge of Sr-segregation process under practical conditions in solid oxide fuel cells and develop suppression method to ensure the long-term stability through surface modifications.

To gain scientific understanding, the pristine and ZrO$_2$ atomic layer deposition (ALD) modified $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCo) epitaxial films were used as the model system to investigate how the temperature, time and surface coating affect the surface concentration of Sr via in situ synchrotron-based ambient pressure XPS. This information was also correlated with their electrochemical performances characterized by electrochemical impedance spectroscopy. From an engineering perspective, ALD-ZrO$_2$ overcoat was also applied on nano-structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) to study the effect of Sr-segregation suppression on its electrochemical performance. EIS results showed that the ALD-ZrO$_2$ indeed reduced the performance degradation rate of LSCF and the modification was also optimized by adjusting the thickness of the overcoat. In
addition, the Sr-segregation-free SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ (SCT) which is reported with high oxygen permeability and good chemical stability was studied as a multifunctional coating on a benchmark cathode LSCF-GDC (SCT@LSCF-GDC) to enhance ORR activity and mitigate coarsening and Sr-segregation. We also observed significant performance improvement against Cr-poison of SCT@LSCF-GDC composite due to its Sr-segregation-free feature.
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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-Ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>GDC</td>
<td>Gd_{0.1}Ce_{0.9}O_{2-δ}</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscope</td>
</tr>
<tr>
<td>LCC</td>
<td>Ca_{0.0125}Ce_{0.5}O_{2-δ}</td>
</tr>
<tr>
<td>LSCF</td>
<td>(La,Sr)(Co,Fe)O_{3-δ}</td>
</tr>
<tr>
<td>LSM</td>
<td>Sr-doped LaMnO_3</td>
</tr>
<tr>
<td>MIECs</td>
<td>Mixed ionic and electronic conductors</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>R_o</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>R_p</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SCT10</td>
<td>SrCo_{0.9}Ta_{0.1}O_{3-δ}</td>
</tr>
</tbody>
</table>
SOFC ................................................................. Solid oxide fuel cell
STEM ............................................................ Scanning transmission electron microscope
TEC .............................................................. Thermal expansion coefficient
TPB ................................................................ Triple phase boundary
XPS ............................................................... X-ray photoelectron spectroscopy
APXPS ......................................................... Ambient pressure X-ray photoelectron spectroscopy
YDC .................................................................. \( Y_{0.2}Ce_{0.8}O_{1.9} \)
YSZ .................................................................. \( Y_2O_3 \) stabilized zirconia
CHAPTER 1

INTRODUCTION

1.1 Fuel Cells

Energy always plays a critical role for human survival and the world development in human history. The total consumption of energy along the world will expand from 549 quadrillion British thermal units (Btu) in 2012 to 815 quadrillion Btu in 2040: a 48% increase from 2012 to 2040.\(^1\) Due to the fact that the fossil fuels including coal, natural gas and liquid fuels are the dominant energy sources, a couple of serious problems has come along with the increasing world energy demand. Firstly, the fossil fuels are non-renewable energy resources which are facing fast depletion. And the rapid consumption of fossil fuels has released a vast amount of pollutant gases which can cause serious problems. For example, the SO\(_x\) and NO\(_x\) will produce the acid rain damages buildings and contaminates soil and water sources and CO\(_2\) as greenhouse gas can cause global climate change. As those problems are becoming a great threat to the sustainable development for our society, it is urgent to seek new energy technologies which can both meet the growing energy requirement and reduce the level of pollutant gas emissions.

Electric energy is central to our life, and almost everything we do depends on it one way or another because it is clean, convenient and has multiple sources. Thus using electricity as a fuel has attracted extensive efforts. Many new energy generation
techniques such as dam system, wind farm and solar cells are developed. However, those techniques are greatly dependent on topography and weather which limits their practical applications. Fuel cell as an energy generation system can effectively produce electricity from electrochemical reaction of fuel and oxidant gases and provide reliable energy supplies. The efficiency of fuel cell can be up to 85% in a combined heat and power (CHP) system, much higher than that of the conventional distributed energy systems which is around 20-30%). Another important feature of fuel cell is fuel adaptability and the resulted low emissions. For hydrogen fuel cell system, the only product is water. For other nature gas fuel cell systems, even the product still contains greenhouse gas, the emission per unit electricity is lower than conversion systems. In addition, the modularity of fuel cell can meet a variable range of power input requirement. Considering the fact that the fossil fuels will still be the dominant source in the near future, it is necessary to put efforts in fuel cell technology and make high efficient use of these sources.

1.2 Solid Oxide Fuel Cells

The fuel cells can be classified into six groups based on different type of fuel and electrolyte: proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), direct methanol fuel cell (DMFC) and solid oxide fuel cell (SOFC). They have different operating temperature, applications, efficiency and costs. Among them, SOFC has the highest operation temperature (600-1000 °C) which gives many advantages, e.g., use of nonprecious, no liquids involved in the fuel cell, and invariant electrolyte. The use of a solid electrolyte eliminates material corrosion and electrolyte management problems, and makes it possible to fabricate the cell components into unique shapes. The high operating
temperature leads to rapid reaction kinetics, allows reforming of hydrocarbon fuels within the fuel cell and provides high-quality byproduct heat. Thus, the solid oxide fuel cells have more variable applications and higher efficiency than many other technologies.

- **1.2.1 Operation Principles**

Solid oxide fuel cells consist of a solid oxide-ion conductor as electrolyte sandwiched by porous anode and cathode, the configuration is shown in Figure 1.1. The typical process includes oxygen reduction at cathode, oxygen-ion transportation through electrolyte and fuel oxidation at anode. The electrons transport through the external circuit to generate electricity. The cathode obtains electrons by catalyzing the oxygen reduction reaction:

\[
\frac{1}{2} O_2(g) + 2e^- \rightarrow O^{2-}(s) \quad (1-1)
\]

The anode gives electrons by catalyzing the oxidation of fuel such as hydrogen or hydrocarbons:

\[
H_2(g) + O^{2-}(s) \rightarrow H_2O(g) + 2e^- \quad (1-2)
\]

\[
CO(g) + O^{2-}(s) \rightarrow CO_2(g) + 2e^- \quad (1-3)
\]

The electrolyte is used to separate air and the fuel. It transports only the oxygen-ion from cathode to anode, and forces the electrons to the external circuit.
Figure 1.1 The schematic representation of SOFC working principle using H$_2$ as fuel.

- 1.2.2 The reversible cell potential of SOFC

The maximum electrical work $W_{e,\text{max}}$ available from a fuel cell is determined by the Gibbs free energy change across the electrolyte membrane, $\Delta G$. When all electrochemical reactions are reversible with no losses, for a reaction under constant pressure and temperature:

$$W_{e,\text{max}} = -\Delta G$$

(1-4)

The total charge ($q$) carried by the reaction is:

$$q = nF$$

(1-5)

where $n$ is the number of moles of electrons involved and $F$ is Faraday constant (96485 C/mol). The maximum electrical work done by moving the charge of $q$ under reversible potential ($E$) is given by:

$$W_{e,\text{max}} = qE$$

(1-6)
So combine the equations (1-4), (1-5) and (1-6), we have:

\[ \Delta G = -nFE \]  

(1-7)

If all the reactants and products are in their standard conditions, the standard state Gibbs free energy change \( \Delta G^0 \) can be found, and then the reversible standard potential \( E^0 \) can be calculated. For the hydrogen-oxygen SOFC, the reaction is:

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \]  

(1-8)

The standard potential:

\[ E^0 = \frac{-(-237300 \text{ J} \cdot \text{mol}^{-1})}{2 \times (96485 \text{ C} \cdot \text{mol}^{-1})} = 1.229V \]

Other than the standard condition, the reversible potential \( E \) can be obtained by Nernst equation:

\[ E = E^0 + \frac{RT}{4F} \ln \frac{P_{\text{O}_2}}{P_{\text{H}_2\text{O}}} + \frac{RT}{2F} \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \]  

(1-9)

where \( T \) is the absolute temperature, \( R \) is the gas constant and \( p \) is the partial pressure of each gas.

- 1.2.3 SOFC electrode voltage losses

SOFC will be working when there is a current passing through the cell, and its actual working potential is always smaller than the theoretical reversible potential because of the losses in electrodes and electrolyte. The loss, which is also known as polarization or over-potential, is the drop of actual potential from the theoretical potential. There are three types of polarization: activation polarization (\( \eta_{\text{act}} \)), ohmic polarization (\( \eta_{\text{ohm}} \)) and concentration polarization (\( \eta_{\text{conc}} \)). So the cell voltage \( V \) is given by:

\[ V = E_0 - \eta_{\text{act}} - \eta_{\text{ohm}} - \eta_{\text{conc}} \]  

(1-10)

1) Activation polarization
The electrochemical reactions in SOFC have to overcome an activation-energy barrier that will cause a loss of the reversible cell voltage. For the single electron transfer reaction, the Bulter-Volmer equation can be used to express the relationship between activation polarization ($\eta_{act}$) and working current density. Assuming the reaction rate does not affect the concentration of reactant and product, the Bulter-Volmer equation can be expressed as:

$$i = i_0 \left( e^{nF\eta_{act}l(RT)} - e^{-(1-\alpha)nF\eta_{act}l(RT)} \right)$$

where $i$ is current density, $n$ is the number of moles of electrons in the reaction, $i_0$ is the exchange current density which represents the rate of forward or reverse electrode reaction under equilibrium, $\alpha$ is charge transfer coefficient (range from 0.2 to 0.5 for most electrochemical reactions). Although the Butler-Volmer is used for single electron transfer reaction, and the electrochemical reactions in SOFC normally have multiple steps, it can also serve as a good approximation since the one rate-limit step is much slower than the rest. From (1-11), it can be easily found that increasing the exchange current density can lower the activation polarization which requires: 1) decrease the activation-energy barrier; 2) increase the concentration of reactants; 3) increase the operation temperature; 4) increase the reaction sites. For SOFC, the activation polarization is greatly dependent on oxygen reduction reaction (ORR) activity at the cathode. So the cathode performance is very important for the development of SOFCs.

(2) ohmic polarization

The ohmic polarization is caused by the resistance for conduction of ions and electrons, and the contact resistance at the interfaces. The ohmic polarization ($\eta_{ohm}$) can be expressed as:
\( \eta_{\text{ohm}} = iR_{\text{ohm}} \)  

(1-12)

where \( R \) is the total resistance including ionic, electronic, and contact resistances. For SOFC, the resistance is denoted in terms of area specific resistance (ASR) with the unit \( \Omega \text{cm}^2 \).

(3) **Concentration polarization**

Concentration polarization is caused by the insufficient transport of reactant on the reaction interface compared to consumption rate. It can decrease the Nernst cell voltage and the kinetic reaction rate, and thus lower the cell voltage. Concentration polarization \( (\eta_{\text{conc}}) \) can be expressed as:

\[
\eta_{\text{conc}} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_L}\right)
\]

(1-13)

where \( i_L \) is the limiting current density, which represents the current density when the electrode reaction is completely governed by mass transfer. The diffusion rate of \( \text{O}_2 \) in cathode is much slower than that of \( \text{H}_2 \) in anode, so the concentration loss at cathode is normally large than that for anode when they have similar thickness.

1.3 Perovskite Materials as Cathode for SOFCs

Many of the recent studies on SOFCs are focused on seeking cathode materials with high performance under intermediate-temperature range. The cathode materials need to have the properties such as high electronic conductivity, ionic conductivity, high oxygen reduction reaction (ORR) activity, and chemical stability during cell operation, and high compatibility with other cell components. Platinum and other noble metals were used as cathode materials for SOFC in the early stage of development. Since they are too...
expensive and less compatible with electrolyte, the less expensive perovskites that meet the required properties have attracted much interest. The general formula of perovskite structure is $\text{ABO}_3$, in which the B-ion is coordinated by six oxygen-ions to form a $\text{BO}_6$ octahedra, the larger A-ion is surrounded by $\text{BO}_6$ octahedra and sits in the center of a cuboctahedra cage formed by 12 oxygen-ions. A-site normally contains rare earth or alkaline ions and in B-site are transition metal ions. The different combination of cations in A and B-site will generate oxygen vacancies ($V_0^-$) which serve as charge carries to provide ionic conductivity. In addition, the ORR activity in perovskites is greatly affected by the defects state and electronic structure.$^5$

- 1.3.1 The perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3-\delta$ (LSM) as cathode in SOFC

Among various cathode materials, lanthanum strontium manganite (LSM)-based perovskites are one of the most investigated cathode materials for SOFCs.$^6$ Undoped $\text{LaMnO}_3$ is orthorhombic at room temperature and shows an orthorhombic/rhombohedral crystallographic transformation at $\sim$600 °C which is attributed to the oxidation of some $\text{Mn}^{3+}$ to $\text{Mn}^{4+}$ ions. Thus doping lower-valence cations such as $\text{Sr}^{2+}$ for the La-sites can increase the $\text{Mn}^{4+}$ concentration and lower the transformation temperature.$^7$

$\text{LaMnO}_3$ is an intrinsic $p$-type conductor and its electronic conductivity can be enhanced by substitution of $\text{La}^{3+}$ site with $\text{Sr}^{2+}$. When a $\text{La}^{3+}$ ion at the A-site is replaced by a $\text{Sr}^{2+}$ ion, an electric hole is formed on the B-site to maintain the electroneutrality, leading to the increased electrical conductivity.$^8$ The thermal expansion coefficient (TEC) of undoped $\text{LaMnO}_3$ is approximately $12.5 \times 10^{-6} \text{K}^{-1}$, which is slightly higher than that of the most commonly used $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ (YSZ) electrolyte ($10.3 \times 10^{-6} \text{K}^{-1}$ in the temperature range from 50 to 1000 °C in air).$^9$ It was found that the TEC value can be slightly
reduced by substitution of $\text{La}^{3+}$ site with $\text{Sr}^{2+}$. The electronic conductivity and TEC of selected $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.3$) perovskites are given in Table 1.1.$^{10-12}$

Table 1.1 The electronic conductivity and TEC of selected $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.3$) perovskites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>TEC ($10^{-6} \text{K}^{-1}$)</th>
<th>Conductivity ($\text{Scm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LaMnO}_3$</td>
<td>12.5</td>
<td>83 (800 °C)</td>
</tr>
<tr>
<td>$\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{MnO}_3$</td>
<td>11.2</td>
<td>120 (800 °C)</td>
</tr>
<tr>
<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{MnO}_3$</td>
<td>12.0</td>
<td>190 (900 °C)</td>
</tr>
<tr>
<td>$\text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{MnO}_3$</td>
<td>11.7</td>
<td>178 (800 °C)</td>
</tr>
</tbody>
</table>

Although $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has excellent electronic conductivity, it shows very low ionic conductivity ($10^{-7} \text{ S·cm}^{-1}$) which limits its application at lower temperatures ($<800 \text{ °C}$).$^{13}$ In order to improve its performance at intermediate temperature, the composite cathode of LSM-YSZ, LSM-GDC ($\text{Gd-doped CeO}_2$) and LSM-ESB ($\text{Er}_2\text{O}_3$ stabilized $\text{Bi}_2\text{O}_3$) were used where the additional triple-phase boundary can be added in the mixture cathode. Murray et al.$^{14}$ synthesized composite cathodes consisting of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and Ce$^{0.8}$Gd$_{0.2}\text{O}_{2-x}$ (GDC) on GDC electrolyte. The polarization resistance of 50 wt. % GDC composite was about 7 times lower than pure LSM. Zhang et al.$^{15}$ examined the performance of composite electrode of LSM-ESB which was prepared with an infiltration method. The polarization resistance of the infiltrated LSM cathode was 2.31 $\Omega\text{cm}^2$ at 600 °C, which was compared with 380 $\Omega\text{cm}^2$ for the non-infiltrated LSM cathode. The low electrode resistance could be explained by the formation of high oxide ion conductivity $\text{Er}_2\text{O}_3$-doped $\text{Bi}_2\text{O}_3$ on the LSM particles.
1.3.2 The perovskite \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (LSCo) and \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \) (LSCF) as cathode in SOFC

To further lower the polarization resistance of cathode in SOFC, the perovskites containing cobalt were developed as cathode material due to the high electronic and ionic conductivity. \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (LSCo) has an electronic conductivity of 1600 Scm\(^{-1}\) and ionic conductivity of 0.22 Scm\(^{-1}\) at 800 °C\(^{16}\) which makes it a promising candidate for the SOFC cathode. However, thermal expansion coefficient (TEC) of LSCo is much larger than that of electrolyte such as YSZ (23×10\(^{-6}\) vs. 10.3×10\(^{-6}\) K\(^{-1}\) ) which will cause cell cracking and degradation of cell performance.\(^{17}\) Huang et al.\(^{17}\) used the low-temperature impregnation method to prepare the LSCo-YSZ composite and achieved the TEC as low as 12.6×10\(^{-6}\) K\(^{-1}\).

There are also other efforts made to eliminate such TEC mismatch. By substituting Co with Fe in LSCo, a low TEC (14.8×10\(^{-6}\) K\(^{-1}\) ) was achieved for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \).\(^{18}\) Unfortunately, the decrease in thermal expansion for LSCF is accompanied by the decreasing in conductivity with low cobalt contents. Specifically at 600 °C, the conductivity of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) is only 77 S cm\(^{-1}\) whereas the conductivity is 1689 S cm\(^{-1}\) for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta} \).\(^{18}\) However, since LSCF has better ionic conductivity and electrocatalytic activity than LSM, it is still a very promising candidate for the SOFC cathode. The enhancement of electrochemical performance of LSCF can be achieved through the nanostructure approach. A sol-gel method was used to synthesize LSCF nano-powders and a maximum power density of 0.99 Wcm\(^{-2}\) was achieved on \( \text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95} \) (GDC) electrolyte cell.\(^{19}\) The composite of LSCF with some ionically
conductive material such as GDC also have better electrocatalytic activity than pure LSCF cathodes.\textsuperscript{20-22}

1.4 Surface Engineering of Nano-structured Cathodes for Solid Oxide Fuel Cells

The basic requirements for functional SOFC cathodes including high ORR electrocatalytic activity, good chemical compatibility and adequate thermal expansion match with the electrolyte lead to two major categories of perovskite oxides as modern SOFC cathodes: La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (LSM) and La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3-δ} (LSCo) or La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ} (LSCF). LSM suffers from its poor ionic conductivity, which requires the formation of a composite cathode like LSM-YSZ or LSM-ESB. The application of LSCo and LSCF is limited by a higher TEC than electrolytes which can be mitigated by introducing nanosized electrodes. The nano-structure can minimize chemical reactions between highly active cathodes and electrolytes due to low processing temperatures, and ensure thermal expansion compatibility among the structural components. However, the nano-structured LSCo or LSCF generally have fast performance decay because of the thermal coarsening of nanoparticles during high temperature operation and the intrinsic Sr-segregation. Thus the nanoscale surface engineering was introduced as a method of mitigation.

- 1.4.1 Metal Salt Solution Infiltration as a Surface Engineering Technique.

Engineering of nano-structured cathode via metal salt solution impregnation or infiltration attracts increasing attention as an effective way to develop highly active and advanced electrode structures for SOFCs with mitigation of thermal expansion mismatch or reactions between electrode and electrolyte materials.\textsuperscript{23} Infiltration method is a two-step sintering process including the formation of porous electrode or electrolyte
scaffold/framework and the precipitation and decomposition of a metal salt solution inside a porous electrode or electrolyte structure. It can lower the process temperature required to achieve good contact between electrode and electrolyte which avoids the grain growth and achieves nano-sized particles on the scaffold. Figure 1.2 shows the schematic of infiltration process on pre-sintered porous electrode or electrolyte. Firstly, the porous electrode/electrolyte scaffold needs to be prepared by firing at high temperatures to ensure an excellent connectivity for oxygen ion transportation and a good structural stability of the cathode under operating temperatures. The properties of the scaffold such as morphology and porosity can seriously influence the infiltration process and the SOFC performance. Typically, the high porosity will lead to an easier infiltration process and improve the infiltration efficiency. Secondly, the stoichiometric metal salt liquid solution will be introduced into the pre-sintered scaffold and followed with thermal treatment under a lower temperature compared to the need to form the backbone. The infiltration process will be repeated for a dozen of times to ensure enough loading of the catalyst. The infiltrate solution can be engineered to control the infiltrate morphology to obtain either discrete particles or a conformal thin film.²⁴

Figure 1.2 Schematic of the infiltrated nano-structured electrodes on pre-sintered porous electrode or electrolyte scaffold.
The most distinctive advantage of the infiltration method is the flexibility in the selection and combination of scaffold and infiltrate with high electronic or ionic conductivity to meet stringent requirements of SOFCs. The infiltration strategy can be simply classified by the scaffold material which could be electrolyte or mixed ionic and electronic conductor. The infiltration into electrolyte backbone can minimize the thermal expansion mismatch and enlarge the triple phase boundary (TPB), which is important for the electronic conductor like LSM. LSM can serve as an infiltrate on YSZ scaffold to form nano-structured LSM-YSZ cathode which achieved 0.83 Wcm\(^{-2}\) at 750°C in H\(_2\)/air, more than 4 times higher than that on similar cells with conventional LSM-YSZ composite cathode.\(^{25}\) For the infiltration using MIEC backbone, it has the advantages include: there are mature manufacturing and processing techniques to fabricate the backbone; the infiltration is an additive process which can minimize the fabrication. As indicated before, LSCF is a promising cathode material for SOFC but limited by surface catalytic properties. So a lot of infiltration modifications were developed onto LSCF to improve its electrochemical performance. Sm-doped ceria nano-particles were deposited on LSCF backbone by infiltration and significantly lowered the Rp than the pristine LSCF: 0.074 and 0.44 Ωcm\(^2\) vs 0.15 and 1.09 Ωcm\(^2\) at 750 and 650 °C.\(^{26}\) The similar performance improvement was also found in Y\(_{0.2}\)Ce\(_{0.8}\)O\(_{1.9}\) (YDC)\(^{27}\) and Ca\(_{0.0125}\)Ce\(_{0.5}\)O\(_{2-δ}\) (LCC)\(^{28}\) infiltration into porous LSCF cathodes. In other studies, LSM can also serve as scaffold because of its good compatibility with electrolyte and good electronic conductivity, and the infiltration with MIEC or ionic conductor can enlarge the TPB length. The Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-δ}\) (BSCF) infiltrated BSCF-LSM cathode exhibited the power density of 1.21 Wcm\(^{-2}\) at 800°C, substantially higher than 0.51 Wcm\(^{-2}\) for the cell
with pure LSM cathode. Jiang et al did a series of study about Gd-doped ceria (GDC) infiltrated LSM cathode and determined that the optimized GDC-LSM cathode possessed Rp of 0.21 $\Omega \text{cm}^2$ at 700, while the baseline LSM was approximately 12 $\Omega \text{cm}^2$. Apart from the nano-particle infiltration, thin film can also be achieved by infiltration method. The continuous LSM films have been fabricated by non-aqueous and water-based method.

- **1.4.2 Atomic Layer Deposition as a Surface Engineering Technique.**

Atomic layer deposition (ALD) is a powerful tool that capable of producing conformal and homogeneous nano-scaled films of a variety of materials. It is a process related to chemical vapor deposition but with self-limiting surface reactions to deposit a film onto a substrate surface one atomic layer at a time. Based on such features, ALD offers advantages such as exceptional conformity on complex structures, thickness control at the Angstrom level, low deposition temperature and tunable film composition. It is widely used in many industrial and research areas.

A general ALD process is presented in Figure 1.3. It includes sequential alternating pulses of gaseous chemical precursor and oxidant. During each pulse, the precursor is pulsed into the chamber under vacuum with a certain amount of time to ensure a full coverage on the substrate. Then the chamber is purged with an inert gas to remove the unreacted precursor and leave one monolayer. This is followed by another pulse of oxidant with same sequence. This process can be cycled to achieve conformal thin films with certain thickness. Because of its self-limiting characteristic, which restrains the reaction at the surface of substrate, the precursor can disperse into deep trenches, allowing a complete reaction with the entire surface. Another advantage is the thickness
control of the thin films. Due to the layer-by-layer deposition, the thickness of the film can be controlled by the number of ALD cycles. The growth rate of different thin films can be found in previous studies. ALD can also control the composition to form materials such as zinc tin oxide and SrTiO. Those composite materials were obtained by the ALD super-cycle which contains multiple types of precursor.

Figure 1.3 Schematic of ALD process: a) before the ALD process; b) precursor pulse is introduced to the chamber; c) the excess precursor is purged by inert carrier gas; d) oxidant pulse is introduced to the chamber; e) the reaction between precursor and the oxidant; f) the excess precursor is purged by inert carrier gas.

For SOFC, the construction of functional thin layers plays an important role of improving the properties of electrode surface or electrode-electrolyte interface. The thin electrolyte layers can reduce the resistance; the interfacial layer between electrode and electrolyte can prevent some side reactions or serve as diffusion or electronic barriers; thin layer on the surface of electrode can serve as a protection or catalyst. Many of the
electrolytes and electrodes for SOFC were successfully synthesized by ALD such as YSZ,\textsuperscript{42,43} GDC,\textsuperscript{44} LSM\textsuperscript{45} and LSCO.\textsuperscript{46} In addition, ALD can deposit a protective layer on the surface of SOFC cathodes and improve their long-term stability.\textsuperscript{47}

1.5 Objectives

La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3-δ} and La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ} are very promising cathodes since they have mixed ion conductivity and good electrocatalytic activity. But their application is limited by the bulk-to-surface Sr-segregation which can seriously compromise the stability of the oxygen electrocatalysis. Although such chemical instability has been actively studied in recent years, fundamental understanding of Sr-segregation process \textit{vs} temperature and time, particularly under real-world conditions are still needed. The pristine and ZrO\textsubscript{2} atomic layer deposition (ALD) modified La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3-δ} epitaxial films were used as the model system to investigate the fundamental knowledge about Sr-segregation via \textit{in situ} synchrotron-based ambient pressure XPS. Their electrochemical performances were also characterized by electrochemical impedance spectroscopy. In addition, the infiltration method and ALD as the advanced surface engineering technologies were employed on La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ} to increase its long-term stability and electrocatalytic activity.
CHAPTER 2

SURFACE Sr-SEGREGATION IN PRISTINE AND ATOMIC LAYER DEPOSITION MODIFIED La_{0.6}Sr_{0.4}CoO_{3-δ} EPITAXIAL FILMS

2.1 Introduction

One of the major issues associated with La_{1-δ}Sr_{δ}CoO_{3-δ} is the strong bulk-to-surface Sr-segregation at elevated temperatures. The main compositions of the segregated Sr-rich phase identified so far are insulating SrO, SrCO_{3} and/or Sr(OH)_{2}^{48-50}, a coverage of which rapidly diminishes the original high ORR activity stemming from the strong O-2p and Co-3d orbital covalent mixing, causing performance decay.\textsuperscript{51-54} Such chemical and thermal instability has severely limited practical applications of those highly ORR active Sr-doped perovskite cobaltites in IT-SOFCs.

Although the exact driving force for the Sr-segregation is still under investigation, some early studies have shown that elastic and electrostatic interactions between Sr and the lattice are the two major mechanisms for the Sr-segregation.\textsuperscript{55, 56} Specifically, the electrostatic force is related to the charged defect interactions between the positively charged oxygen vacancy $V_{O}^{\bullet \bullet}$ and the negatively charged dopant Sr'_{La} as shown in Figure 2.1. Normally, the surface (and sub-surface) concentration of $V_{O}^{\bullet \bullet}$ for oxygen-deficient perovskites is high, thus forming a positively charged skin to attract the negatively
charged dopant $\text{Sr}^{' \text{La}}$ to the surface.\textsuperscript{57} Fister et al \textsuperscript{58} confirmed this mechanism with total reflection x-ray fluorescence (TXRF) technique, by which the Sr surface concentration of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ under different oxygen partial pressures ($pO_2$) was probed. The Sr-segregation was indeed found to increase with decreasing $pO_2$. On the other hand, the elastic force introduced by the size mismatch between the dopant and host cations has also been proposed as a driving force for Sr-segregation. For the case of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, the ionic radius of $\text{Sr}^{2+}$ (144 pm, CN=12) is larger than that of $\text{La}^{3+}$ (136 pm, CN=12)\textsuperscript{59} so that the dopant $\text{Sr}^{2+}$ ions are under compressive stress when substituting on the La-site and could be driven to the surface under much less stress. Lee et al\textsuperscript{55} studied the lattice strain effect on the surface cation segregation; the lattice strain were created by doping $\text{Ba}^{2+}$ (161 pm, CN=12), $\text{Sr}^{2+}$ (144 pm, CN=12) and $\text{Ca}^{2+}$ (134 pm, CN=12) into the host $\text{La}^{3+}$ in $\text{LaMnO}_3$. The authors found that the larger dopants $\text{Ba}^{2+}$ and $\text{Sr}^{2+}$ would result in more cation rearrangements leading to surface segregation, while the closer dopant $\text{Ca}^{2+}$ would have a relatively less surface segregation. By lowering $pO_2$, the authors also managed to ease the lattice under compressive stress by chemical expansion and observed a reduced surface segregation. However, this finding is contradictory to the electrostatic attraction mechanism that suggests a stronger surface Sr-segregation under lower $pO_2$. The controversy may be related to the fact that the compressive stress could be relieved at higher temperatures regardless of cation size mismatch, thus making oxygen stoichiometry the major factor influencing the Sr-segregation.
To mitigate the Sr-segregation and enhance long-term performance stability, Gong et al.\textsuperscript{60} first demonstrated by overcoating a conformal nanoscale ZrO\textsubscript{2} layer via atomic layer deposition (ALD) on La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3-δ} nanoparticles (NPs) that the original high ORR activity of LSCo NPs can be effectively retained for 4,000 h at 700 °C. The authors proposed that the porosity in the ALD-ZrO\textsubscript{2} layer, interdiffusion between Zr and Co and confinement of NPs coarsening are the three leading reasons for the ORR activity retention. The authors particularly argued that the interdiffusion-induced substitution of Zr into Co-site has led to the creation of point defect Zr\textsubscript{Co}\textsuperscript{*}, which can decrease the concentration of surface oxygen vacancies V\textsubscript{O}\textsuperscript{**} required by the charge neutrality, thus reducing the electrostatic driving force for Sr\textsubscript{La}' migration towards surface. In a recent study, Tsvetkov et al.\textsuperscript{61} further confirmed the idea that a fixed, higher-valent and less reducible cation such as Hf\textsuperscript{4+} and Zr\textsuperscript{4+} can suppress Sr\textsubscript{La}' migration in LSCo by reducing the concentration of surface V\textsubscript{O}\textsuperscript{**}, thus the driving force to attract Sr\textsubscript{La}'. By modifying the surface of La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3-δ} epitaxial thin films grown on YSZ single crystal substrates with less reducible oxides derived from metal chloride solutions, the authors showed reduced surface Sr-concentration with improved electrochemical stability.
While the Sr-segregation in La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ epitaxial films has been actively studied in recent years, quantification of Sr-segregation process vs temperature and time, particularly under real-world conditions, is rare in the literature. Therefore, the aim of the present study is to investigate how the temperature, time and surface coating affect the surface concentration of Sr in a La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ epitaxial film. The tool to attain the surface Sr-concentration is a cutting-edge surface analysis technique, in situ synchrotron-based ambient pressure XPS (APXPS). To precisely control the thickness and chemistry of the surface coating, atomic layer deposition (ALD) is applied to make a nanoscaled ZrO$_2$ layer over the La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ epitaxial films. We expect that epitaxial thin films with ALD-overcoat will provide a well-defined platform for in-depth fundamental understanding of surface chemistry without the interference from structural and kinetic complexities encountered in porous and polycrystalline samples. To complement the understanding of APXPS results, electrochemical impedance spectroscopy (EIS) has also been performed on the sister samples under similar conditions for hundreds of hours.

2.2 Experimental

The epitaxial La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSCO) thin films in a thickness of 50 nm were grown on (001)-oriented YSZ by pulsed laser deposition (PLD). Single crystal 9.5 mol% YSZ wafers with the (001) cubic orientation and dimensions of $10 \times 5 \times 0.5$ mm (MTI corporation, USA) were used as the substrate. To prevent the formation of La$_2$Zr$_2$O$_7$ at the interface, a layer of 5 nm thick Gd-doped CeO$_2$ (GDC) buffer layer was also deposited by PLD between YSZ single crystal and LSCO epitaxial film. The YSZ substrate was affixed to the PLD substrate holder using a small amount of silver paint for thermal contact. PLD was performed using a KrF excimer laser at $\lambda = 248$ nm, 10 Hz
pulse rate, and 50 mJ pulse energy under a $pO_2$ of $6.6 \times 10^{-5}$ atm (50 mTorr). For GDC film, a total of 500 pulses were applied to YSZ single crystal substrate at 550 °C, and for LSCo film, a total of 5,000 pulses was applied to GDC/YSZ-substrate at 650 °C. After completing the LSCo film deposition, the samples were cooled down to room temperature (RT) in the PLD chamber in ~1 h under the same $pO_2$.

A precise 0.8 nm thick ZrO$_2$ layer was further coated on top of the PLD-grown LSCo epitaxial film by ALD in a flow-type reactor (Ultratech Savannah 200 series). Tetrakis (dimethylamido) zirconium (IV) (electronic grade, ≥ 99.99%, Sigma-Aldrich) and deionized (DI) water were used as Zr-precursor and oxidant, respectively. The reactor temperature was controlled at 180 °C. For a typical cycle, the reactor chamber was first pumped down to 50 mTorr, and then the Zr-precursor was introduced into the chamber by a 0.4 s pulse and stayed for 20 s to completely cover the surface of the sample. Then, a pure N$_2$ gas at a flow rate of 15 sccm was introduced into the chamber to purge out the residual Zr-precursor. The chamber was then pumped down to 50 mTorr again, followed by a 0.015 s pulse of DI water and holding for 20 s to oxidize the precursor. A typical cycle can be summarized in Figure 2.2. The pre-determined deposition rate is 0.1 nm/cycle for ALD-ZrO$_2$, which requires 8 cycles to yield a 0.8 nm thick layer of ZrO$_2$.

Figure 2.2 The schematic representation of a typical ALD cycle for ZrO$_2$ deposition.

Oxide phase purity and orientation of the deposited thin films were investigated via high resolution X-ray diffraction (HRXRD) using a four-circle diffractometer.
Measurements were performed in normal and off-normal configurations. The in-plane $a$ lattice parameters of LSCO were determined from the off-normal $(202)_{pc}$ peak position (where “pc” denotes the pseudocubic) and the out-of-plane $c$ lattice parameters were determined from the $(002)_{pc}$ peak position. Details of lattice parameter calculations can be found elsewhere.\textsuperscript{66-68} The surface morphology and roughness of the films synthesized was also checked by atomic force microscopy (AFM, XE-100, PARK System) under a non-contact mode.

The \textit{in-situ} APXPS spectra were collected at Beamline 9.3.2 of Advanced Light Source at Lawrence Berkeley National Laboratory.\textsuperscript{69} A schematic of the ambient pressure XPS spectrometer at ALS beamline 11.0.2 which has the similar working principle is shown in Figure 2.3. The sample was first placed on a heater on which a thermocouple was attached to measure the temperature. One set of the pristine and overcoated samples were used to investigate the temporal evolution of surface Sr as the temperature was raised from 25 to 520 °C. The heating rate was controlled at 3~5 °C per minute, and there was a holding period of roughly 3 h at 200, 350, 450 and 520 °C under a constant oxygen partial pressure of $1 \times 10^{-3}$ atm. The spectra collection started with two survey scans (BE = 10 – 590 eV) at a photon energy of 690 and 695 eV to remove the Auger peaks and continued with low-resolution scans of Sr 3d and La 4d spectra in every 3 min during the entire heating process to capture the fast-changing surface Sr-concentration.

Another set of samples was used to study the isothermal equilibrium concentration of specific element at temperatures of 25, 250, 350, 450 and 520 °C under oxygen partial pressure of $1 \times 10^{-3}$ atm. A 30-min hold was given at each temperature before data collection. The data collection began with two survey scans (BE = 10 – 590 eV) at a
photon energy of 690 and 695 eV, followed by a high-resolution scan of Sr 3d, O 1s, La 4d, Co 2p and particularly Zr 3d for the coated sample at a photon energy of 690 eV. The inelastic mean free path (IMFP) of photoelectrons in this measurement was about 1 nm, which becomes the assumed probe depth for this study. The photon energy change in survey scans may cause a shift of peak position in the following scans. So we used La 4d peak as a calibration standard in the analysis. CasaXPS software was used to analyze and deconvolute the spectra.

Figure 2.3 The schematic representation of the ambient pressure XPS spectrometer.

The electrochemical impedance spectroscopy (EIS) was employed to measure the ohmic and polarization resistances of Ag/LSCo/GDC/YSZ/Ag and Ag/ZrO$_2$/LSCo/GDC/YSZ/Ag half-cells (GDC: Gd$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$) using an electrochemical workstation (Solartron 1255/1287 system) at 550°C in ambient air as a function of time.
To avoid experimental variability, the two cells were loaded side-by-side in the same furnace and EIS measurements were taken sequentially. The sweeping frequency range was varied from $10^6$ to 0.005Hz with an AC stimulus amplitude of 10 mV. Both sides of the sample were covered with silver paste (C8829, Heraeus) and silver mesh as current collector. The equivalent circuit method in ZSimDemo software was used to extract the resistance values from the collected Nyquist plots.

2.3 Results and discussion

- 2.3.1 Thin film HRXRD patterns

The HRXRD $\theta$-$2\theta$ patterns collected at RT are shown in Figure 2.4a, where only (00$l$) ($l$ is integer) peaks of LSCo, GDC, and YSZ can be seen, implying that the LSCo films were grown epitaxially with the (001) orientation of the single-crystal YSZ substrate: (001)$_{pc}$LSCo//(001)$_{cubic}$GDC//(001)$_{cubic}$YSZ. With the 0.8 nm thick ZrO$_2$ overcoat, no discernible change in the XRD pattern of LSCo was observed. Off-normal $\phi$ scan analysis of the multilayer with and without ZrO$_2$ overcoat shown in Figure 2.4b reveals only {202} plane family for LSCo, GDC and YSZ layers, suggesting a 4-fold cubic symmetry and a cube-on-cube alignment of GDC on YSZ and 45° in-plane rotation of LSCo on GDC. Like previous studies, the relaxed lattice parameters, $\tilde{a}$ of the epitaxial LSCo films with and without ZrO$_2$ overcoat obtained in this study vary slightly in the range of 3.828 – 3.831 Å. This observation implies that a very thin ZrO$_2$ layer has no influence on in-plane and out-of-plane strains of the LSCo thin film underneath. Therefore, we can ignore the strain effect of ZrO$_2$ overcoat on the LSCo film.
2.3.2 Surface morphology of epitaxial films.

The surface morphologies of pristine and coated samples after APXPS experiments are examined by AFM and shown in Figure 2.5. Some “humps or islands” with a height of ~10 nm are apparent on the surface of the pristine sample after APXPS testing. Given the fact that Sr-enriched particles have been previously observed on the surface of the epitaxial La$_{0.8}$Sr$_{0.2}$CoO$_{3-δ}$ thin films after annealing at 550 °C for 6 h,$^{67, 72, 73}$ it is reasonable to assert that these “islands” are associated with segregated Sr phases. On the contrary, the ALD-ZrO$_2$ coated sample after APXPS testing shows a much flatter and smoother surface with no obviously large “islands” on the surface, suggesting that the growth of surface Sr-phase has been suppressed by the ZrO$_2$ overcoat.
2.3.3 In situ APXPS analysis

**Time-dependent surface Sr-concentration.** The low-resolution Sr 3d and La 4d spectra of the first set of pristine and ALD-coated LSCo films were collected in every 3 min within a temperature range of 25 to 520 °C at a fixed oxygen partial pressure of $1 \times 10^{-3}$ atm. The Sr 3d spectra were used to determine the time needed to reach equilibrium concentration at each selected temperature. The La 4d spectra were used to ensure a proper compensation of unstable beam energy and to calibrate the peak positions. This correction sometimes makes binding energies of the same element slightly different in pristine and coated samples or at different temperatures.

In general, the Sr 3d peaks can be divided into 2 sets of Sr 3d$_{5/2}$ and 3d$_{3/2}$ doublets that belong to surface and lattice Sr. The lower-energy set of Sr 3d is assigned to lattice Sr, whereas the higher set can be assigned to surface Sr that is associated with SrO and Sr(OH)$_2$. The presence of SrCO$_3$ phase can be ruled out because of the lack of C 1s peak when the temperature was above 250 °C. The time-dependent Sr 3d spectra of both samples under 350°C are shown in Figure 2.6a and 6b as an example. The shape of the spectra remains almost unchanged from 0 to 0.6 h after the temperature was increased to

Figure 2.5 AFM images of a) pristine and b) coated sample after APXPS test
350 °C. The obtained peak area ratios of the surface Sr (we here used peak area ratio instead of atomic fraction to illustrate the trending because of low-resolution data. We will present more accurate compositions in atomic fractions when dealing with equilibrium concentration later) are further shown as a function of time in Figure 2.6c and 2.6d for pristine and coated samples, respectively. It is obvious that the surface Sr area ratio of both samples were increasing with the temperature and stabilized as soon as the temperature reached the set point, implying that the surface Sr-segregation process is rather fast. The fast Sr-segregation kinetics was also observed by the other study.\textsuperscript{61} In a separate ToF-SIMS study, Kubicek et al also concluded that Sr-segregation kinetics in the same LSCO epitaxial film on YSZ-single crystal as this study is very fast because of the enhanced chemical diffusion coefficient of Sr, instead of tracer self-diffusion coefficient, by the mobile oxygen vacancy during the ambipolar transport.\textsuperscript{74}

**Temperature-dependent Surface Sr-content.** To attain a more accurate analysis of the chemical state in the near surface region of the LSCO thin films, high-resolution Sr 3d and O 1s spectra of another group of pristine and coated LSCO films were collected and the results are shown in Figure 2.7 and 2.8 as a function of temperature. The peak positions at different temperatures were calibrated with the La 4d spectra as well. The O 1s spectra were divided into 3 sets that can be associated with lattice Sr, SrO and absorbed -(OH) with the binding energy of 534.3, 535.6 and 537.0 eV, respectively.\textsuperscript{75, 76} The binding energies (BE), full-width-half-maximum (fwhm), and peak area for each component of the high-resolution scans are listed in Table 2.1 and 2.2.
**Figure 2.6** Time-dependent low-resolution Sr 3d spectra for a) pristine and b) coated sample at 350°C; time-dependent area ratio of surface Sr for c) pristine and d) coated sample during the heating process from 200 to 520 °C in an oxygen pressure of $1 \times 10^{-3}$ atm.

For the pristine sample, Figure 2.7b shows that the content (area ratio) of lattice Sr is less than the surface Sr at RT; however, at 250 °C the content of lattice Sr increases drastically, which could be due to the removal of the carbon-containing species on the surface. As the temperature is further increased to 350 °C, the content of surface Sr shows a significant increase, suggesting the onset of Sr segregation as similarly reported in other work \(^{56}\). From 350 to 520 °C, the content of surface Sr continues to increase, and it is worth noticing that the peak position of surface Sr continues to shift towards higher binding energy. Although the surface components were described as one set of Sr 3d\(_{5/2}\) and 3d\(_{3/2}\) doublets in many early studies on chemical state in the near-surface region of LSCO films,\(^{61, 70, 77}\) there could be more than one species such as SrO and Sr(OH)$_2$. Due
to the close Sr peak position of SrO with other surface components, we cannot obtain a precise quantification analysis from Sr spectra. But the existence of Sr(OH)\textsubscript{2} at lower temperature and its decomposition at higher temperatures would explain the energy shift and thus give a better description of the surface compositions at different temperatures. The maximum surface Sr content at 520 °C is 76% of the total Sr in the near-surface region for the pristine sample.

Table 2.1 The fitting parameters (binding energy, fwhm and peak area) of all elements (La 4d, Sr 3d, Co 3p and O1s) in pristine sample at different temperatures.

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<th>fwhm / eV</th>
<th>Peak area</th>
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Table 2.2 The fitting parameters (binding energy, fwhm and peak area) of all elements (La 4d, Sr 3d, Co 3p, O 1s and Zr 3d) in coated sample at different temperatures.

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Figure 2.7 a) Schematic of surface states in the pristine sample at different temperatures; b) Sr 3d and c) O 1s spectra of the pristine sample at different temperatures in an oxygen pressure of $1 \times 10^{-3}$ atm.
For the O 1s spectra of the pristine sample, Figure 2.7c shows the same trend as Sr. At RT, the peak at around 537 eV is much higher than the other two peaks, indicating a large amount of surface contaminations. As the temperature is raised to 250 °C when the contaminations are quickly removed, the content of lattice oxygen is increased in the same way as Sr. From 250 to 520 °C, the oxygen in SrO keeps increasing and finally becomes the dominant component, making the lattice oxygen less pronounced. The oxygen peak of -(OH) starts to fade at 350 °C and finally disappears at 520 °C, corresponding to the decomposition of Sr(OH)$_2$. Overall, the Sr 3d and O 1s spectra show a clear evidence of Sr segregation and variations of surface compositions with temperature in the pristine sample.

The Sr 3d and O 1s spectra of the ALD-coated sample are shown in Figure 2.8. In general, Figure 2.8b shows that Sr 3d peak intensities of the coated sample are much lower that of the pristine sample. At RT, one can still see the same 2 sets of Sr-spectral components. At 250 °C, the intensity of both surface Sr and lattice Sr peaks become stronger because of the removal of surface carbon species. From 250 to 520 °C, the surface Sr keeps increasing while the lattice Sr keeps decreasing. The peak position of surface Sr remains unchanged, suggesting the surface component on the coated sample is mainly SrO. This is different from what was observed on the pristine sample, implying that the ALD process (at 180 °C) may remove some surface species. At 520 °C, the content of surface Sr components is ~75%, which is similar to that of pristine sample. But the actual amount of surface Sr components should be presented by a proper quantification analysis, which will be discussed later.
Figure 2.8 a) Schematic of surface states in the ALD-coated sample at different temperatures; b) Sr 3d and c) O 1s spectra of the coated sample at different temperatures in an oxygen pressure of $1 \times 10^{-3}$ atm.

The O 1s spectra for the ALD-coated sample shown in Figure 2.8c are more complicated. At RT, there seems to be 4 sets of spectral peaks: 530.5 eV for the lattice O,
531.8 eV for O associated with surface Sr, 531.2 eV and 532.1 eV for lattice O associated with Zr, and 533.4 eV for surface carbon species. As the temperature is raised to 250 °C, the peak at 533.4 eV disappears, confirming the removal of carbon species. While from 250 to 520 °C, a clear trend of changes in surface and lattice O cannot be observed because those O peaks are too close to discern; a small shift of binding energy in the analysis could lead to a significant difference and make it very hard to produce reliable results. However, since the O 1s peak of the coated sample can be well fitted with 4 sets of oxygen peaks, it can still be considered as a good indicator of the existence of surface and lattice Sr components, which makes the analysis for Sr-chemistry valid.

**Equilibrium surface Sr concentration vs temperature.** Due to the existence of ZrO₂ layer on the surface of the coated sample, the surface-to-lattice Sr-ratio cannot fairly represent the degree of surface Sr-segregation in both the pristine and coated samples. So, the atomic fraction of La, Sr, Co, O and Zr (denoted as [La], [Sr]₉₀, [Co], [O] and [Zr], respectively) were calculated based on their normalized intensities that were obtained by normalizing the peak area with photoionized cross-section and inelastic mean free path of each elements; this is a technique that has been used elsewhere. The equation used for normalizing the peak area can be expressed as:

\[ I_{\text{nor}} = \frac{I}{\sigma \lambda} \]  
(2-1)

where \( I_{\text{nor}} \) is the normalized peak area, \( I \) is the original peak area, \( \sigma \) is the photoionized cross-section obtained from the database, and \( \lambda \) is the IMFP calculated based on the Gries inelastic scattering mode. The constants used and the calculated IMFPs are listed in Table 2.3. For the pristine sample, only La and Co are considered as the lattice component in the bulk of perovskite LSCo; Sr and O are normalized separately as in
LSCO and SrO based on the content obtained from Figure 2.7. For the coated sample, La, Sr and Co are normalized in the same way as the pristine sample, while Zr and O are considered as in ZrO$_2$. The atomic fraction of each component was calculated according to their normalized peak areas (denoted as $I^A_{nor}$, A = La, Sr$_{tot}$, Co, Zr or O). For the pristine sample, the atomic fraction of element A in LSCO can be determined using the following expression,

$$[A] = \frac{I^A_{nor}}{(I^\text{La}_{nor} + I^{\text{Sr}}_{nor} + I^{\text{Co}}_{nor} + I^{\text{O}}_{nor})}$$

(2-2)

where A = La, Sr$_{tot}$, Co or O. For the coated sample, the atomic fraction of element A can be determined using the following expression,

$$[A] = \frac{I^A_{nor}}{(I^\text{La}_{nor} + I^{\text{Sr}}_{nor} + I^{\text{Co}}_{nor} + I^{\text{Zr}}_{nor} + I^{\text{O}}_{nor})}$$

(2-3)

where A = La, Sr$_{tot}$, Co, Zr or O. For Sr in both samples, [Sr]$_{lat}$ and [Sr]$_{surf}$ were calculated separately based on the $I_{nor}$ in LSCO and SrO; [Sr]$_{tot}$ is the sum of them. The results from 250 to 520 °C (RT data was not included due to the adsorbed carbon-containing species) are shown in Figure 2.9a and 9b, where the atomic fraction of each element is compared for the two samples.

For the pristine sample at RT, [Sr]$_{tot}$ is larger than [La] and [Co] because of the existence of rich surface Sr components. From 250 to 520 °C, [Sr]$_{tot}$ is increased gradually because of the migration of Sr in the bulk towards the near surface region where XPS can detect. For the coated sample, [Zr] and [O] are dominant over the entire temperature range studied; this is because XPS is only sensitive to the near surface region and the thickness of ZrO$_2$ is close to the probe depth. The ratio of [Co]/[lattice] ([lattice]=[$\text{La}]+[\text{Sr}]_{lat}+[\text{Co}]$) and [Sr]$_{surf}$/[lattice] for both samples were calculated and presented in Figure 2.9c. The ratio of [Co]/[lattice] for both samples varies from 0.50-
0.55, which is close to the stoichiometry of LSCO, despite the increase in temperature and low atomic fractions of La, Sr and Co in the coated sample, indicating the validity of spectral analysis and quantification process. The ratio of $[\text{Sr}]_{\text{surf}}/[\text{lattice}]$ for both samples increases with temperature, but it is obvious that the ratio in the pristine sample increases faster and ends up with a higher value at 520 °C.

To the interest of this study, we present the equilibrium atomic fractions of surface Sr ($[\text{Sr}]_{\text{surf}}$) of the two samples in Arrhenius format, $\ln([\text{Sr}]_{\text{surf}}) vs 1/T$, from 250 to 520 °C in Figure 2.9d. It is evident that $[\text{Sr}]_{\text{surf}}$ of both samples increases from 250 to 520 °C, and $[\text{Sr}]_{\text{surf}}$ of the coated sample is much smaller than that of the pristine sample (~4% vs ~22% at 520 °C). The plots in Figure 2.9d are found to follow the Arrhenius relationships:

For the pristine sample:  
\[ [\text{Sr}]_{\text{surf}} = 1.06 \exp\left(-\frac{10808}{RT}\right) \]  
(2-4)

For the coated sample:  
\[ [\text{Sr}]_{\text{surf}} = 0.205 \exp\left(-\frac{11307}{RT}\right) \]  
(2-5)

where, R is the gas constant, 8.314 J/mole/K; T is absolute temperature, K. The activation energy $E_a$ (J/mol) for the coated sample is a slightly higher than that of the pristine sample, implying that it is a little more difficult for Sr to migrate to the surface in the coated sample than in the pristine sample. The major determining factor is the pre-exponential factor for the two samples. However, the overall magnitude of $E_a$ is much smaller than other similar thermally-activated process such as Sr diffusion in SrTiO$_3$ (~372 kJ/mol)\textsuperscript{84} or Mg segregation in Al-Mg alloy (64 kJ/mol),\textsuperscript{85} suggesting that the Sr-segregation in LSCO is an easy diffusion process that does not need significant thermal energy to activate. This finding is also supported by another study.\textsuperscript{74}
Table 2.3 The atomic volume calculated from the density of each compound and the obtained IMFP for all elements.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Elements</th>
<th>Atomic volume (cm$^3$/mol)</th>
<th>IMFP (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$CoO$_3$</td>
<td>La</td>
<td>57.9</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>Sr</td>
<td>86.8</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>34.7</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>11.6</td>
<td>0.48</td>
</tr>
<tr>
<td>SrO</td>
<td>Sr</td>
<td>22.0</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>22.0</td>
<td>2.08</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zr</td>
<td>21.7</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>10.8</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Figure 2.9 Temperature-dependent atomic concentrations of a) pristine and b) ALD-coated samples; c) Temperature-dependent [Co]/[lattice] and [Sr]surf/[lattice] ratio; d) Arrhenius plots of atomic fractions of surface Sr in both samples.
The presence of high concentration of surface oxygen vacancies in the pristine LSCo is the driving force for the easy Sr-segregation. For the coated LSCo, the Zr-substitution on the Co-site near the surface region creates positive charged defect \( \text{Zr}^+_\text{Co} \), thus decreasing \([\text{V}^+_{\text{O}}]\) on the surface as required by the local charge neutrality, and thus the electrostatic attraction to pull the negatively charged Sr-defect (Sr\(_{\text{La}}^+\)) towards the surface. The present study supports this hypothesis rather than “strain-effect” hypothesis because the thin-film HRXRD results did not reveal any strains in the thin films with or without ZrO\(_2\) overcoat.

- 2.3.4 EIS analysis

To the time-dependent EIS measurements were performed to characterize the thermal stability of the pristine and coated LSCo films. The EIS spectra are shown in Figure 2.10a with the equivalent circuit as the inset for fitting \( R_o \) and \( R_p \); \( R_o \) is the highest-frequency intercept with the \( Z' \)-axis, representing the ohmic resistance; \( R_p \) is the length between highest and lowest frequency on the \( Z' \)-axis, representing the polarization resistance; CPE in the equivalent circuit is the constant phase element used for fitting the impedance spectra. The obtained \( R_p \) values for the two samples are compared in Figure 2.10b for 300 h. From the beginning, \( R_p \) of the pristine sample was larger than that of the coated one. From APXPS data, we know that the pristine sample already has a large \([\text{Sr}]_{\text{surf}}\) at 520 °C, which is responsible for the higher \( R_p \). As the time elapses, \( R_p \) of the pristine sample grows precipitously with time at a rate of 4.3 ohm·cm\(^2\)/h; for the coated sample, the \( R_p \) increases at a much smaller rate of 0.9 ohm·cm\(^2\)/h, further demonstrating of beneficial effect of ALD-ZrO\(_2\) coating in suppressing Sr-segregation and thus stabilizing the polarization resistance.
Figure 2.10 a) Comparison of Nyquist plots of pristine and coated samples for select time intervals, inset is the equivalent electrical circuit for EIS spectra simulation; b) time-dependent $R_p$ values and c) surface oxygen exchange coefficients vs time of the pristine and coated samples measured at 550 °C in ambient air.

The low-frequency $R_{p(LF)}$ is associated with the oxygen adsorption/dissociation process, \textit{i.e.} surface oxygen exchange process\textsuperscript{86, 87} and can be used to calculate the surface exchange coefficient $k^q$ by\textsuperscript{88}:

$$k^q = \frac{RT}{4F^2R_{p(LF)}Ac_0}$$ \hspace{2cm} (2-6)

where R and T have their usual meanings; F is the Faraday’s constant; A is the electrode area; $c_0$ is the lattice oxygen concentration in LSCO, 0.089 mol/cm\textsuperscript{3} in this study\textsuperscript{77}. The $k^q$ of the coated sample is in reasonable range of the reported value\textsuperscript{66, 68} and about 2\times higher.
than that of pristine sample at the beginning of the test and 4\times higher at 300h marker. For the thin film sample, there is no structural complexity, meaning that such difference should not be attributed to geometrical effects, but to the true chemical state in the near-surface region. Therefore, a much stable \( R_p \) of the coated samples is another strong evidence of the suppressed Sr segregation by the ZrO\(_2\) layer, consistent with the APXPS results. It is to be noted that \( R_p \) values of the thin-film samples are much higher than practical three-dimensional porous electrodes due to the limited reactive areas.

2.4 Conclusions

In summary, the oxygen-deficient LSCO epitaxial films fabricated by PLD exhibit the desirable (001) normal and (202) off-normal crystallographic orientations with and without ALD-ZrO\(_2\) overcoat. There is no in-plane and out-of-plane strains in the LSCO thin film imposed by the ALD-ZrO\(_2\)-overcoat from the relaxed lattice parameter analysis. The Sr bulk-to-surface segregation of pristine and ALD-ZrO\(_2\)-overcoated LSCO epitaxial films investigated by \textit{in-situ} APXPS as a function of time and temperature at a fixed oxygen partial pressure of \( 1 \times 10^{-3} \) atm show fast kinetics, but the amount of surface Sr in the coated sample is significantly lower than that of the pristine sample. The equilibrium surface Sr concentration is found to follow Arrhenius relationship, but with a small activation energy, suggesting that Sr bulk-to-surface migration is a weak thermally-activated diffusion process. The concentration-dependent pre-exponential term plays a major role in the Sr-segregation process. The suppressed Sr surface migration in the coated film is resulted from the cation exchange between Zr and Co near the sub-surface region, thus reducing surface \([V_0^*]\) and the electrostatic force to pull Sr-defect (\(Sr_{La}^-\)) to
the surface. Correspondingly, EIS study reveals that the coated sample exhibits a more stable and higher ORR activity than the pristine sample at 550 °C in ambient air over 300 h. Overall, it is concluded that the ALD-ZrO₂ thin layer is effective in suppressing bulk-to-surface Sr segregation in oxygen-vacancy-rich Sr-doped perovskites and thus improving their thermal and electrochemical stability as a cathode for IT-SOFCs.
CHAPTER 3

ATOMIC LAYER DEPOSITION MODIFIED La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} AS CATHODE OF SOLID OXIDE FUEL CELL

3.1 Introduction

The mixed oxide-ion and electron conducting perovskite oxide La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) is a promising cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs) because of its high intrinsic electrocatalytic activity to the oxygen reduction reaction (ORR) and manageable thermal expansion coefficient (TEC). The Nicholas Group\textsuperscript{89, 90} has discovered a novel processing method, infiltrate precursor solution desiccation, which allows the La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} infiltrate particle sizes to be reduced from the ~50 nm average particle sizes common in the literature to ~22 nm. This reduced infiltrate particle size has resulted in an excellent 0.17 $\Omega$cm$^2$ open circuit polarization resistance at 540 °C in air.

However, the LSCF cathode with excellent performance still experienced a 1.2%/khr degradation rate which is larger than the DOE SOFC program’s 0.2%/khr degradation rate target.\textsuperscript{91} The performance decay in LSCF can be possibly linked to the surface Sr-segregation which can introduce an insulating layer of SrO to block the ORR-active sites and nano-particle thermal coarsening which can cause the loss of surface area.
In our previous study, the ALD-ZrO$_2$ overcoat has been proved to mitigate the Sr-segregation. Therefore, it was also applied on nano-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ to study the effect of Sr-segregation suppression on its electrochemical performance.

3.2 Experimental

The symmetrical cells used for electrochemical performance test were prepared as follows: first, 0.8 g of GDC powder was pressed to a 0.75 inch pellet and heated to 1475 °C for ~10 h; the obtained dense pellets (relative densities >95%) were then polished using 240 grit SiC sandpaper until the thicknesses were ranging from 430 to 480 mm.

A GDC ink contains the mixture of Rhodia GDC powder and V-737 electronic vehicle (Heraeus Circuit Materials Division; West Conshohocken, PA) was screen printed on both sides of the GDC electrolyte pellets. A total of three layers of GDC ink with a circular 0.5 cm$^2$ open area were screen printed onto both sides of the GDC electrolyte pellets using a patterned 80 mesh stainless steel screen. The scaffolds were then air-heated to 1050 °C for 3 h.

The LSCF precursor solution used for infiltration was prepared by dissolving 99.999% pure La(NO$_3$)$_3$*6.84 H$_2$O, 99.9965% pure Sr(NO$_3$)$_2$, 99.999% pure Co(NO$_3$)$_2$*5.9 H$_2$O and 99.999% pure Fe(NO$_3$)$_3$*9.84 H$_2$O (Alfa Aesar; Ward Hill, MA) in 18.2 MΩ water. (These precise nitrate water of hydration contents were determined prior to nitrate weighing by measuring the mass loss that occurred inside a Q500 thermogravimetric analyzer (TA Instruments; New Castle, DE) with heating under nitrogen up to 850 °C.) Then the LSCF precursor solution and 0.75 mol of citric acid
per mole of metal nitrates were combined as LSCF precursor solutions. After the infiltration process, the LSCF-GDC cathodes were heated to 700 °C for 1 h.

The ZrO$_2$ layers were further coated on the nano-structured LSCF cells by ALD in a flow-type reactor (Ultratech Savannah 200 series). Tetrakis (dimethylamido) zirconium (IV) (electronic grade, ≥ 99.99%, Sigma-Aldrich) and deionized (DI) water were used as Zr-precursor and oxidant, respectively. The reactor temperature was controlled at 180 °C. The ALD process is the same as demonstrated in chapter 2: the reactor chamber was first pumped down to 50 mTorr, and then the Zr-precursor was introduced into the chamber by a 0.4 s pulse and stayed for 20 s to completely cover the surface of the sample. Then, a pure N$_2$ gas at a flow rate of 15 sccm was introduced into the chamber to purge out the residual Zr-precursor. The chamber was then pumped down to 50 mTorr again, followed by a 0.015 s pulse of DI water and holding for 20 s to oxidize the precursor. The predetermined deposition rate is 0.1 nm/cycle for ALD-ZrO$_2$, which requires 10 to 100 cycles to yield the 1 nm to 10 nm thick layer of ZrO$_2$ on different cells.

The morphology of the infiltrated cathode was evaluated using a Auriga Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) (Carl Zeiss Microscopy GmbH; Jena, Germany) operated with a 30 mm aperture, a 40 s scan speed, a 1.4 mm working distance, and 20 kV beam voltage. The high-resolution transmission electron microscope (HRTEM, Hitachi H-9500) and a scanning transmission electron microscope (STEM, Hitachi HD-2000) equipped with EDX was also used to obtain images and analyze chemical compositions. The electrochemical impedance spectroscopy (EIS) was employed to measure the ohmic and polarization resistances using an electrochemical
workstation (Solartron 1255/1287 system) at 650 °C in air as a function of time. The sweeping frequency range was varied from $10^5$ to 0.1Hz with an AC stimulus amplitude of 10 mV. Both sides of the cell were covered with gold paste (C5756, Heraeus) and Pt sheet as current collector. The obtained EIS spectra were analyzed by an equivalent circuit model using ZSimpWin Demo software.

3.3 Results and discussion

To determine the quality of the ZrO$_2$ coating, XPS analysis and TEM images were taken on 3 nm and 5 nm coated cells. Table 1 shows the relative atomic concentrations of the possible elements. For both cells, Zr is the dominant cation element and the amount of Zr increases with the coating thickness, suggesting the ZrO$_2$ coating was successfully deposited on the cells. Because of the surface-sensitivity feature of XPS analysis, the amounts of other cation elements are too small to give other detailed information. Figure 3.1 shows the TEM images of the post-test 3 nm and 5 nm ZrO$_2$ coated cells. A conformal thin layer can be clearly seen on both cells and the thicknesses of the layers are very close to 3 nm and 5 nm, respectively. To further identify the element constituents of the thin layer, the STEM and STEM-line scanning were taken from the 5 nm ZrO$_2$ coated cell and shown in Figure 3.2. The results of STEM-line scanning show that the intensity of La, Sr, Co, Fe and O are all decreasing on the edges between two particles; only the intensity of Zr peak is increasing, suggesting Zr is more concentrated on the particle surface. Combining the XPS and TEM results, we can conclude that the conformal ZrO$_2$ layers with the precise thickness were successfully deposited on different cells.
Table 3.1 XPS-determined relative atomic concentrations from ZrO$_2$ coated LSCF after time–dependent electrochemical test at MSU.

<table>
<thead>
<tr>
<th></th>
<th>3nm ZrO$_2$ coated cell (%)</th>
<th>5nm ZrO$_2$ coated cell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>25.1</td>
<td>24.3</td>
</tr>
<tr>
<td>O</td>
<td>40.1</td>
<td>38.2</td>
</tr>
<tr>
<td>Zr</td>
<td>26.8</td>
<td>35.1</td>
</tr>
<tr>
<td>La</td>
<td>5.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Sr</td>
<td>2.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figure 3.1 TEM images of a) 3 nm and b) 5 nm coated cells after time-dependent electrochemical test at USC.

Figure 3.2 a) STEM image of the post-test 5 nm coated cell and b) the STEM-line scanning results across two particles, the dash lines represent the adjacent edges between two particles.
This is a collaboration work with Michigan State University (MSU), so the cells with different ZrO$_2$ coating were tested simultaneously in two places. The time-dependent EIS test was performed on pristine LSCF, 1nm, 3nm and 5nm ZrO$_2$ coated cells in USC under 650°C in ambient air for 860h. The resistance ratio was used to represent the performance degradation. For ohmic and polarization resistance, the ratio was obtained by dividing $R_o$ or $R_p$ with the initial value of $R_o$ or $R_p$. The $R_o$ of all cells are very stable with the degradation rate less than 3%/khrs as shown in Figure 3.3a. Figure 3.3b shows the $R_p$ degradation for all cells. For the baseline LSCF, there is a rapid increase of $R_p$ during the first 12h (0-12%), then the $R_p$ ratio increases gradually with time from 12%-50%. For the 1nm coated cell, there is no rapid increasing of $R_p$ at the beginning of the test, and the $R_p$ increases in a relatively lower rate with time (30%/khrs). For 3 nm and 5 nm coated cells, neither of them have that “break-in” region with the accelerated $R_p$ increase, and the degradation rate continues to reduce as the coating thickness increases: 20%/khrs for 3 nm coated cell and 12%/khrs for 5 nm coated cell. The Nyquist plots of selected time for four cells are shown in Figure 3.3c-f. For the spectra of all cells, there are three features shown as high frequency (HF), medium frequency (MF) and low frequency (LF) impedance. The HF impedance can be assigned to the electrode/electrolyte interfacial oxygen transport because for each cell, the HF arcs for selected time are almost overlapped with each other. For all the cells, the LF impedance are very similar and do not change with time, so we assume those low frequency semi-circles are related with the gas diffusion problem introduced by our push-contact test rig. The most distinguished $R_p$ increase is from MF feature which should represent the ORR activity. It is obvious that the coated cells have a lower MF impedance.
increase than pristine LSCF, and the 5 nm coated cell exhibits the most stable electrochemical performance.

Figure 3.3 EIS results from baseline, 1 nm, 3 nm and 5 nm ZrO2 coated LSCF cells: a) $R_o$ and b) $R_p$ increasing ratio at 650 °C in air for 860 h, Nyquist plots of c) baseline LSCF cell, d) 1 nm coated cell, e) 3 nm coated cell and f) 5 nm coated cell ($R_o$ is normalized to zero).

The parallel EIS measurement was performed in Michigan State University to ensure the validity of the performance improvement introduced by ALD-ZrO2. Figure 3.4a and 3.4b show the $R_o$ and $R_p$ increasing ratio for baseline, 1 nm, 2 nm and 5 nm of ZrO2 coated cells at 650 °C in air for 1000 h. The $R_o$ degradation is similar with that of USC cells. The rapid increase of $R_p$ is also observed for the uncoated LSCF cell during the first 48 hours of test and its degradation rate is about 37%/khrs. All of the coated
cathodes do not show this “break-in” behavior and the polarization resistance increases almost linearly at a rate of 28%/khrs, 18%/khrs, and 12%/khrs for 1 nm, 2 nm and 5 nm of ZrO2 coated cells, respectively. The degradation rates are very similar to those obtained from USC. Figure 3.4c compares the temperature-dependent, open-circuit polarization resistance values of the uncoated, 1 nm, 2 nm, 5 nm and 10 nm ZrO2 coated cells tested at MSU. The 1 nm, 2 nm and 5 nm coated cells have similar Rₚ with the uncoated cell, while the 10 nm coated cell has a higher Rₚ. It should be noted that the initial Rₚ values for different cells obtained from USC and MSU are not exactly the same. We assume such difference is introduced by the way of printing the current collector in two places. In USC, the current collector was hand-printed and the thickness could be different for each cell. In MSU, a printer and gold grid were used to ensure the consistency for all the cells and the absolute Rₚ value from MSU should be more reliable. Despite the small difference of initial Rₚ, the degradation trend achieved from two places are very close and it can be easily concluded that the coating below 5 nm can improve stability of LSCF nano-particles without hurting the Rₚ performance.

Figure 3.5 shows SEM images for LSCF infiltrate cell before and after 1000 hours at 650 °C. A direct comparison of average particle sizes from Figure 3.5a-d is difficult due to local particle size variations. However, the larger distribution of particle sizes observed in Figure 3.5b-e, compared to Figure 3.5a, suggests that nano-particle thermal coarsening may be severe in the uncoated and 1 nm ZrO2 coated cells, but less active in the 2 nm and 5 nm ZrO2 coated cells.
Figure 3.4 EIS results from baseline, 1 nm, 2 nm and 5 nm ZrO$_2$ coated LSCF cells: a) R$_o$ and b) R$_p$ increasing ratio at 650 °C in air for 1000 h, and c) comparison of temperature-dependent, open-circuit polarization resistance values of the uncoated, 1 nm, 2 nm, 5 nm and 10 nm ZrO$_2$ coated cells.

Figure 3.5 SEM images of a) standard cell before test, b) standard cell after 1000 h at 650 °C, c) 1 nm ZrO$_2$ coated cell after 1000 h at 650 °C, d) 2 nm ZrO$_2$ coated cell after 1000 h at 650 °C and e) 5 nm ZrO$_2$ coated cell after 1000 h at 650 °C.
The rapid increasing $R_p$ of baseline cell should be attributed to Sr segregation which is an easy chemical diffusion process;\textsuperscript{74} such trend was also reported by other publication.\textsuperscript{61} The ZrO$_2$ overcoat can effectively suppress the Sr segregation and thus eliminated the sudden increase of $R_p$. The suppression mechanism is similar with our previous study since Sr-segregation mechanism in LSCF is similar with LSCO. The following increase of $R_p$ vs time should be related to the particle coarsening because the baseline and 1nm coated cell have close degradation rate while the 2 nm and 5 nm coated cells showed a more stable performance. Combining the EIS and SEM results, we can conclude that the ZrO$_2$ film can effectively improve the long-term stability of LSCF nano-particles, and the optimized thickness of the film is 5 nm for this study.

3.4 Conclusions

The nano-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$–Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-x}$ (LSCF-GDC) cells were prepared and overcoated by ZrO$_2$ thin film with the thickness ranging from 1 nm to 10 nm via atomic layer deposition. TEM and STEM images revealed that the thin films were deposited around the nano-particles with the uniform morphology and their thicknesses were well controlled. The EIS results at 650 °C during 1000 h showed that the long-term stability of LSCF-GDC has been improved by the ZrO$_2$ coating and this improvement in degradation rate followed the trend of the film thickness increasing from 1 nm to 5 nm. Specifically, the removal of the rapid increasing $R_p$ for the coated cells indicates that the ZrO$_2$ overcoat can suppress the Sr-segregation in LSCF and the thicker overcoat can also mitigate the particle coarsening. The 5 nm coated cell yields the best performance and reduced the degradation rate from $\sim 38\%$/khrs to $12\%$/khrs.
CHAPTER 4

ISO-STRUCTURED SrCo$_{0.9}$Ta$_{0.1}$O$_{3.8}$@La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3.8}$−Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$

COMPOSITE AS CATHODE OF SOLID OXIDE FUEL CELL

4.1 Introduction

In the previous chapter, we employed the ALD-ZrO$_2$ overcoat to improve the stability of nano-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3.8}$. Although the performance degradation rate of LSCF was reduced by the ZrO$_2$ overcoat, the oxygen reduction reaction (ORR) activity was not effectively improved. Moreover, the application of LSCF cathode is also limited by the H$_2$O and CO$_2$ in ambient air and Cr-poison from metal interconnects. H$_2$O and CO$_2$ can compete with O$_2$ on LSCF surface for adsorption and oxygen reduction reaction (ORR),$^{92}$ or lead to the formation of carbonates and hydroxides.$^{93-95}$ The Cr vapor from the surface of metallic components of SOFC stacks can condense into SrCrO$_4$ at the cathode surface and block the ORR active sites.$^{96-99}$ Thus it is necessary to find a highly active nano-scaled thin film to coat on top of LSCF to increase its electrochemical performance along with the electrochemical stability against H$_2$O, CO$_2$ and Cr-poison. Recently, SrCo$_{0.9}$Ta$_{0.1}$O$_{3.8}$ (SCT) was found to have very good oxygen diffusion coefficients and surface exchange rate. What is more, due to the lack of negatively charged dopant Sr$_{La}^-$ in materials like LSCo and LSCF, it is free of Sr-
segregation. By infiltrating a thin layer of SCT on the LSCF skeleton, the core-shell SCT@LSCF structure was successfully formed. In the previous study, the SCT@LSCF exhibited a much lower polarization resistance and a better long-term stability compared to the pristine LSCF.

However, in former study, the GDC electrolyte used in the electrochemical test was corroded by bismuth which was introduced by the current collector. Such “bismuth attack” brings along some uncertainties and makes it hard to reveal the true insight of the benefit from SCT coating. Additionally, the more comprehensive evaluation is needed to fully exploit the advantages obtained from SCT overcoat. Herein SCT was infiltrated on the benchmark LSCF-GDC composite to form Iso-structured SCT@LSCF-GDC electrode and its long-term electrochemical performance was re-evaluated with Bi-free current collector. We also investigated its performance in H$_2$O and CO$_2$-contained air and the durability against Cr-poison.

4.2 Experimental Procedure

The SCT@LSCF-GDC cell was first fabricated by screen printing an LSCF-GDC ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{−Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$) ink (purchased from Fuelcellmaterials, 50:50 of weight ratio) on both side of a 300 µm thick Gd$_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC10, Fuelcellmaterials) dense pellet, followed by firing at 1100 °C for 2 h to form the LSCF-GDC skeleton with the thickness of ~25 µm. The infiltration solution was made by the following procedures: citric acid (Sigma-Aldrich) was first dissolved in a de-ionized water, then mixed with a stoichiometric amount of Sr(NO$_3$)$_2$ (Alfa Aesar) and Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar). A separate solution containing ethylene diamine tetraacetic acid (EDTA, Sigma-Aldrich)
and diluted ammonia water was then added into the above solution and adjust the pH to 8. A stoichiometric amount of Ta(OC$_2$H$_5$)$_5$ (Sigma-Aldrich) was dissolved into pure ethanol and then slowly added into the above solution to achieve the solution for infiltration. The total metal-ions concentration was 0.2 M. Citric acid, EDTA and metal ions have the molar ratio of 2:1:1. Water and ethanol have a volume ratio of 5:1 in the final solution. Then the SCT solution was dropped into the LSCF-GDC skeleton and followed by thermal treatment at 500 °C for 1 h. The infiltration process was repeated for about 10 times to reach 20% SCT loading (based on the weight of LSCF) and followed by the calcination at 1000 °C for 2 h. A schematic showing the formation of the bilayer structure is given in Figure 4.1.

![Figure 4.1](image)

Figure 4.1 The schematic presentation of forming bilayer structured cathode particles

The electrochemical impedance spectroscopy (EIS) was collected under different circumstances using an electrochemical workstation (Solartron 1470/1455B system). The sweeping frequency range was varied from $10^6$ to 0.1 Hz with an AC stimulus amplitude of 10 mV. The long-term electrochemical stability test was performed at 700 °C in
ambient air as a function of time. For Cr-tolerance test, a pair of pristine LSCF-GDC and SCT@LSCF-GDC cells were loaded side-by-side in the same furnace at 700 °C in ambient air for 200 h; then a piece of 430 stainless steel (McMaster-Carr, 16-18% chromium content) was put aside of the cells and the EIS performance was carried out sequentially. For H₂O tolerance test, the temperature range was from 550 to 700°C and the dry air, ~2.5% and ~5.5% humidified air were introduced to the furnace under each temperature. Similarly for the CO₂ tolerance test, the temperature range was the same and clean air, 0.5% and 1% CO₂-contained air were used. The bismuth-free gold paste (C5756, Heraeus) and bismuth-contained silver paste (C8829, Heraeus) were used in the long-term electrochemical stability test for comparison and only the gold paste was used for the rest of the tests. The silver mesh was used as current collector. The equivalent circuit method in ZSimDemo software was used to extract the resistance values from the collected Nyquist plots.

The microstructures of electrodes were characterized by a field emission scanning electron microscope (FESEM, Zeiss Ultraplus). EDX was also employed to analyze the chemical composition.

4.3 Results and Discussion

- 4.3.1 Long-term stability of SCT@LSCF-GDC electrode

One pristine LSCF-GDC and two SCT@LSCF-GDC cells were used for long-term stability test. The pristine and one of the coated cells were covered with gold paste (denoted as LSCF-GDC-Au and SCT@LSCF-GDC-Au) and the other coated cell was covered with silver paste (denoted as SCT@LSCF-GDC-Ag) to compare the performance effect from “bismuth attack”. Figure 4.2a presents the comparison of R₀ for
coated cells. SCT@LSCF-GDC-Au and SCT@LSCF-GDC-Ag have similar initial ohmic resistance, but SCT@LSCF-GDC-Ag experiences a much larger increase than that of SCT@LSCF-GDC-Au: 0.051 vs 0.013 Ωcm² during 300h, corresponding to the effect of “bismuth attack”. The time-dependent R_p for the three cells are shown in Figure 4.2b, from which SCT@LSCF-GDC-Au exhibits an excellent performance compared to LSCF-GDC-Au. It has a much lower initial Rp of 0.15 vs 0.46 Ωcm², and a lower increase of 0.13 vs 0.36 Ωcm²/khrs compared with pristine LSCF-GDC. The initial R_p of SCT@LSCF-GDC-Ag is higher than that of SCT@LSCF-GDC-Au, considering the skeleton was made by LSCF-GDC composite, the “bismuth attack” may also corrode the porous GDC and compromise its performance. The morphology of electrolyte for the post-test cells is shown in Figure 4.3. The corroded GDC layer with thickness of ~13 μm can be clearly seen at the electrode/electrolyte interface of SCT@LSCF-GDC-Ag cell. While for the cells using gold paste as current collector, the electrode/electrolyte interface remains intact. The electrolyte morphology of post-test cells can be well related with their R_o degradation and such “bismuth attack” phenomenon is further proved.

Figure 4.2 Comparison of a) ohmic resistance and b) polarization resistance for LSCF-GDC-Au, SCT@LSCF-GDC-Au and SCT@LSCF-GDC-Ag at 700 °C in air for 1000 h.
Figure 4.3 SEM images of a) SCT@LSCF-GDC-Ag, b) SCT@LSCF-GDC-Au and c) LSCF-GDC-Au after EIS test at 700 °C in air for 1000 h.

- 4.3.2 H$_2$O, CO$_2$ and Chromium-tolerance study on SCT@LSCF-GDC electrode

The Nyquist plots of LSCF-GDC and SCT@LSCF-GDC cells under dry and humid air in 550-700 °C are shown in Figure 4.4a-d. For LSCF-GDC cell, the performance obviously decreases with introducing H$_2$O at all temperatures. Specifically, at temperature below 600 °C, the ~2.3% and ~5.5% humid air have the similar effect, suggesting H$_2$O is easily saturated on the surface of LSCF-GDC. At higher temperatures, the performance degradation increases with the H$_2$O content, indicating that H$_2$O molecules can be more active at higher temperatures and it is harder for them to occupy
the ORR active sites. The detailed comparison of $R_p$ increase ($\Delta R_p$) introduced by H$_2$O at different temperatures for both cells are presented in Figure 4.4e. For SCT@LSCF-GDC cell, it is obvious the performance degradation cause by H$_2$O is much less than that of LSCF-GDC not only in comparison of the increased $R_p$ value, but also the relative ratio. It is also worth mentioning that the performance degradation of SCT@LSCF-GDC increases with H$_2$O content at all temperatures, suggesting that H$_2$O could not easily take place on the surface of SCT@LSCF-GDC even under lower temperature. It is, therefore, reasonable to postulate that the SCT coating can provide a noticeable improvement for H$_2$O-resistance to LSCF-GDC composite.

The Nyquist plots for CO$_2$ effect are shown in Figure 4.5a-d and the comparison of $\Delta R_p$ introduced by CO$_2$ at different temperatures is shown in Figure 4.5e. The major trend is same with the H$_2$O effect: the $R_p$ of both samples are increased with CO$_2$ content and such increase is less pronounced at higher temperatures. However, SCT@LSCF-GDC electrode reacts differently to CO$_2$ compared to H$_2$O. The $R_p$ increase ratio of SCT@LSCF-GDC does not change with CO$_2$ content at 550 and 600 °C, suggesting CO$_2$ can be easily absorbed on its surface. CO$_2$ also causes a higher performance degradation ratio. So SCT may have different affinity for H$_2$O and CO$_2$ which will be discussed later. However, the SCT@LSCF-GDC still has less $\Delta R_p$ than LSCF-GDC, exhibiting a better resistance against CO$_2$.

The ln ($R_p$) vs 1000/T plots of LSCF-GDC and SCT@LSCF-GDC cells under H$_2$O and CO$_2$ effect are shown in Figure 4.6. The activation energy under different circumstances was calculated by Arrhenius equation:

$$\ln R_p = \ln A - \frac{E_a}{RT}$$

(4-1)
where $R$ is the gas constant, 8.314 J/mole/K; $T$ is absolute temperature, K. $A$ is the pre-exponential term; $E_a$ is the activation energy, eV. It seems neither $\text{H}_2\text{O}$ nor $\text{CO}_2$ has a noticeable effect on $E_a$ for both cells especially if we take the errors into consideration, suggesting $\text{H}_2\text{O}$ and $\text{CO}_2$ have blocked some of the active sites but not compromised the entire structure with such lower content. The SCT@LSCF-GDC has a much lower $E_a$ than LSCF-GDC, reaffirms the excellent ORR activity introduced by SCT layer.

Figure 4.4 Nyquist plots of LSCF-GDC and SCT@LSCF-GDC cells under dry, 2.3%, and 5.5% humid air in a) 550, b) 600, c) 650 and d) 700 °C; e) the comparison of $\Delta R_p$ of LSCF-GDC and SCT@LSCF-GDC introduced by 2.3% and 5.5% $\text{H}_2\text{O}$. 
Figure 4.5 Nyquist plots of LSCF-GDC and SCT@LSCF-GDC cells under air, 0.5%, and 1.0% CO₂-contained air in a) 550, b) 600, c) 650 and d) 700 °C; e) the comparison of $\Delta R_p$ of LSCF-GDC and SCT@LSCF-GDC introduced by 0.5% and 1% CO₂.

Figure 4.6 ln ($R_p$) vs 1000/T for LSCF-GDC and SCT@LSCF-GDC cells under a) H₂O effect and b) CO₂ effect.
The different response of LSCF-GDC and SCT@LSCF-GDC to H₂O and CO₂ is possibly attributed to the surface reactions which involve SrO. It is known that there is considerable amount of SrO on the surface of LSCF due to Sr-segregation. In humid air, H₂O could react with SrO to form Sr(OH)₂ and lead to a more serious SrO segregation. Similarly, SrO can also react with CO₂ and form SrCO₃. The segregated SrO and those productions block the ORR active sites and cause the performance degradation. For SCT@LSCF-GDC, SCT layer cannot provide SrO for the formation of Sr(OH)₂ or SrCO₃ because of its Sr-segregation-free feature. However, oxygen vacancies also play a substantial role towards the carbonate formation on the surface of perovskites, and thus lead to more serious performance degradation for SCT layer under CO₂ effect.

The comparison of R_p collected from the electrochemical chromium poisoning experiment is shown in Figure 4.7. For the first 200 h without Cr, both cells exhibit a relatively stable performance. After the cells are exposed to Cr-contained alloy, the R_p of LSCF-GDC experienced a significant increase from 0.51 to 1.35 Ωcm². The increase is very high at the beginning and followed with a lower increase which is in agreement with the other study. The effect of Cr is quite different for SCT@LSCF-GDC: there is only a slight increase of R_p when Cr was added and the total performance degradation after 1000h test is only 0.1 Ωcm² which is very similar with the previous long-term test. From the aspect of electrochemical performance, SCT@LSCF-GDC is almost free of Cr poisoning. Figure 4.8 shows the morphology of the post-test LSCF-GDC and SCT@LSCF-GDC electrodes and the chemical component analysis by EDX. The weight ratio of Cr and Sr was used to represent the relative amount of Cr. Some large clusters as shown in Figure 4.8a can be found on the surface of LSCF-GDC, and the corresponding
EDX analysis in Figure 4.8b reveals the presence of Cr. The particles seem to be locked by Cr species and lost activity. For SCT@LSCF-GDC, the similar clusters can also be found but the particles are less accumulated. The Cr peak and the Cr/Sr ratio are much smaller, indicating the Cr deposition in SCT@LSCF-GDC is less severe than it is in LSCF-GDC.

The significant difference in electrochemical performance degradation and Cr deposition for LSCF-GDC and SCT@LSCF-GDC reveals the excellent durability against Cr-poison introduced by SCT coating. A lot of efforts have been given to understand the Cr-poison mechanisms. It is commonly believed that the formation of Cr-containing secondary phase such as SrCrO$_4$ serves as an insulator covering the cathode surface.\textsuperscript{105-108} Also, it has been found out that the segregated Sr from the LSCF bulk can greatly enhance the deposition of Cr species.\textsuperscript{109} SrO was identified to be the nucleation agent for Cr deposition and the mechanism can be expressed as\textsuperscript{110,111}:

\begin{equation}
SrO + CrO_3 \rightarrow Cr - Sr - O_x \text{ (nuclei)}
\end{equation}

\begin{equation}
Cr - Sr - O_x + CrO_3 + SrO \rightarrow SrCrO_4
\end{equation}

As a conformal layer, the SCT coating can separate LSCF from gaseous Cr species, and there is no SrO on the surface of SCT to initiate Cr deposition due to its Sr-segregation-free feature. The excellent resistance of SCT coating against H$_2$O, CO$_2$ and especially Cr-poison has a profound meaning for the practical application of SCT@LSCF-GDC composite as cathode of SOFC.
Figure 4.7 Time-dependent $R_p$ values for LSCF-GDC and SCT@LSCF-GDC electrodes unexposed and exposed to Cr-contained alloy at 700°C in air for 1000h.

Figure 4.8 a) SEM image and b) EDX analysis of LSCF-GDC surface; c) SEM image and d) EDX analysis of SCT@LSCF-GDC surface after the electrochemical chromium poisoning experiment. The inserts are the magnified images of selected areas.
4.4 Conclusions

From the study on the iso-structured SCT@LSCF-GDC composite cathodes, the SCT coating has greatly improved the ORR activity and the long-term stability of LSCF-GDC. Different current collectors were used to study the “bismuth attack” and the Bi-free current collector can effectively retain the stability of the ohmic resistance and decrease the polarization resistance. The SCT coating also shows great resistance against H₂O and Cr-poison due to its Sr-segregation-free feature. The initial polarization resistance of SCT@LSCF-GDC at 700 °C is only 20% of pristine LSCF-GDC and the performance degradation is only 0.1 vs 0.84 Ωcm² under Cr-poison. With the high ORR activity and long-term stability in practical conditions, the iso-structured SCT@LSCF-GDC composite can be a promising cathode material for commercial IT-SOFC.
CHAPTER 5

SUMMARY

*In-situ* synchrotron-based ambient pressure XPS (APXPS), atomic layer deposition (ALD), metal salt solution infiltration and electrochemical test are employed to acquire fundamental knowledge of Sr-segregation process under practical conditions in solid oxide fuel cells as well as the suppression methods to ensure the long-term stability of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta$ (LSCo) and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3-\delta$ (LSCF).

The Sr bulk-to-surface segregation of pristine and ALD-$\text{ZrO}_2$-overcoated LSCo epitaxial films investigated by *in-situ* APXPS as a function of time and temperature at a fixed oxygen partial pressure of $1 \times 10^{-3}$ atm show fast kinetics, but the amount of surface Sr in the coated sample is significantly lower than that of the pristine sample. The equilibrium surface Sr concentration is found to follow Arrhenius relationship, but with a small activation energy, suggesting that Sr bulk-to-surface migration is a weak thermally-activated diffusion process. The concentration-dependent pre-exponential term plays a major role in the Sr-segregation process. The suppressed Sr surface migration in the coated film is resulted from the cation exchange between Zr and Co near the sub-surface region, thus reducing surface $[\text{V}_0^{\text{**}}]$ and the electrostatic force to pull Sr-defect ($\text{Sr}_{\text{\small La}}^-$) to the surface. Correspondingly, EIS study reveals that the coated sample exhibits a more stable and higher ORR activity than the pristine sample at 550 °C in ambient air over 300
h. Overall, it is concluded that the ALD-ZrO$_2$ thin layer is effective in suppressing bulk-to-surface Sr segregation in oxygen-vacancy-rich Sr-doped perovskites and thus improving their thermal and electrochemical stability as a cathode for IT-SOFCs.

The nano-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$-Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-x}$ (LSCF-GDC) cells are overcoated with conformal ZrO$_2$ thin films with the thickness ranging from 1 nm to 10 nm via ALD. The EIS results at 650 °C during 1000 h show that the long-term stability of LSCF-GDC has been improved by the ZrO$_2$ coating and this improvement in degradation rate follows the trend of the film thickness increasing from 1 nm to 5 nm. Specifically, the removal of the rapid increasing $R_p$ for the coated cells indicates that the ZrO$_2$ overcoat can suppress the Sr-segregation in LSCF and the thicker overcoat can also mitigate the particle coarsening. The 5 nm coated cell yields the best performance and reduces the degradation rate from ~38%/khrs for the uncoated cell to 12%/khrs.

The Sr-segregation-free SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ (SCT) is coated on benchmark LSCF-GDC composite by infiltration method. The SCT coating has greatly improved the ORR activity and the long-term stability of LSCF-GDC. The SCT coating also shows great resistance against H$_2$O and Cr-poison due to its Sr-segregation-free feature. The initial polarization resistance of SCT@LSCF-GDC at 700°C is only 20% of pristine LSCF-GDC and the performance degradation is only 0.1 vs 0.84 Ωcm$^2$ under Cr-poison. With the high ORR activity and long-term stability in practical conditions, the iso-structured SCT@LSCF-GDC composite can be a promising cathode material for commercial IT-SOFCs.
REFERENCES


