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One-Step Infiltration of Mixed Conducting Electrocatalysts for Reducing Cathode Polarization of a Commercial Cathode-Supported SOFC

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Infiltrating fine-grained electrocatalyst particles of either ion conducting or mixed electron and ion conducting (MEIC) material into a ceramic porous electrode scaffold has proven a very effective way to improve electrode performance for low to intermediate temperature solid oxide fuel cells (SOFCs). We report here one-step infiltration of MEIC fine particles, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCo) and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF), into a commercial cathode substrate. A comparative study shows that the cathode polarization can be considerably reduced by a factor of 17 to 28 and 28 to 49 from 1000 to 700°C by the infiltrated LSCF and SCF electrocatalysts, respectively, demonstrating an effective solution to improve the electrode performance without altering mechanical properties of the electrode substrate.

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Reducing the operating temperature of a SOFC is widely recognized as the solution to meet the foremost challenges in cost and reliability of the technology.^{1,2} Strategies to lower the operating temperature of a SOFC include not only the development of high conductivity solid electrolytes, but also high-performance electrode materials, particularly cathode.³ The importance of attaining high-performance electrode materials is best manifested by the fact that cathodic polarization resistance of a doped LaMnO_3 , the most commonly used cathode material for SOFC, can increase by three orders of magnitude if the temperature is lowered from 1000 to 500°C.³ Therefore, enhancing the electrode performance, particularly the cathode performance, is a very demanding task for the development of intermediate temperature solid oxide fuel cells (IT-SOFCs).

The cathode-supported tubular SOFCs developed by Siemens' (formerly Westinghouse's) were based on Ca- and Ce-doped LaMnO_3 . Although there have many unique design features such as no-gas-seals, Ni-based cell-to-cell connections in reducing atmospheres, Cr-poisoning-free LaCrO_3 -based ceramic interconnect and non-constraint bundle/stack design to ensure excellent durability,⁴⁻⁶ the performance of a Siemens' SOFC is generally low, particularly at temperatures <900°C. On the other hand, infiltration of electrochemically active fine-grained catalysts of either ion conducting or mixed electron and ion conducting (MEIC) material into a ceramic porous electrode scaffold is a methodology developed in recent years to enhance electrode performance of SOFCs.⁷⁻¹¹ More importantly, infiltration of fine particles of electrocatalysts would not alter the mechanical properties of a substrate, which is critically important to the development of a reliable and robust product. It is, therefore, a logical step to apply the electrochemically active MEIC particles into the Siemens cathode substrate by the infiltration technique as a means to improving the cell performance.

However, conventional infiltration process requires many repetitive impregnation steps of low-concentration aqueous nitrate solutions in order to reach desirable loading and to form percolated network,^{7,8,10} significantly increasing the manufacturing cost. In this study, we describe a one-step procedure of infiltrating MEIC materials, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCo) and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF), into the cathode porous scaffold of a Siemens cathode-supported SOFC. A comparative study on the cathode polarization resistance between infiltrated and baseline cell is particularly conducted to illustrate the beneficial effect of the infiltrated electrocatalysts.

Experimental

Simplified one-step infiltration of LSCo and SCF.— The substrates we used in this study are tubular segments of a cathode-supported SOFC, provided by the courtesy of Siemens. The cathode substrate has an average pore size and porosity of 10 μm and 30%, respectively.¹² The cathode is comprised of 30mol% Ca and 10mol% Ce doping on the La-site and minor Ni and Cr doping (<1mol%) on the Mn-site of LaMnO_3 perovskite. Details on the materials perspective of Siemens' cathode-supported tubular SOFCs can be found in ref. 12.

The infiltration process used in this study is primarily based on the procedure described in the reference 6, but with a first-time reported simplification of how the precursor solution is impregnated into the porous scaffold. Detailed description is given as follows. A solution containing $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCo) or $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) precursor is first prepared by dissolving appropriate amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Triton-X100 (3wt%) in DI water. The concentration of LSCo/SCF in the starting solution is 1.0M. Then a cathode-supported tubular SOFC segment is immersed into the prepared solution, followed by heating it to 80°C. During the heating, the air trapped in the pores gradually escapes, allowing the precursor solution to penetrate deep into the interface of cathode/electrolyte. At the same time, the precursor solution becomes viscous and gradually reaches the nitrate solubility limit. The infiltrated cell is then removed from the solution, dried at room temperature and in 110°C-oven, and finally fired in air at 1000°C for 2h to decompose the precursor into LSCo and SCF nanoparticles. No degassing step is needed during the entire infiltration process. The phase purity and microstructural features of the infiltrated LSCo and SCF were examined with Rigaku D/max-A X-ray Diffractometer (Cu Kα radiation) and captured by Zeiss Ultra plus FE-SEM, respectively.

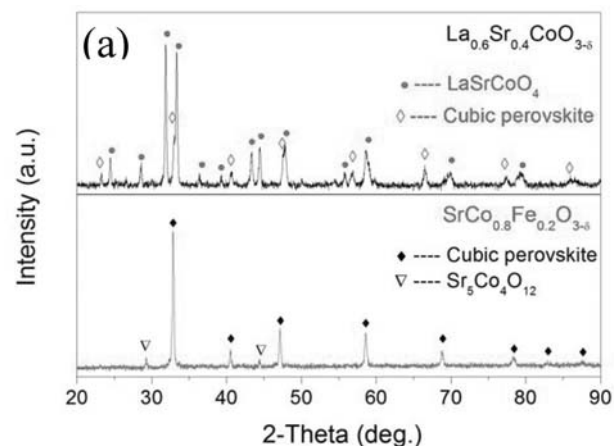
Comparative study on cathode polarization.— The comparative study was conducted on a half-cell fashion of the cathode-supported SOFC consisting of only cathode and electrolyte. Platinum was used as the counter electrode (CE). It is understood that the measured polarization resistance by AC impedance spectroscopy will include contributions from both cathode and Pt-CE, of which only cathode contribution is the interest to this study. However, if a change is only made to the cathode such as infiltration of electrocatalysts, the corresponding change in polarization resistance observed on impedance spectrum should only reflect the change made on the cathode while the Pt-CE remains the same. This thinking has become the basis for the comparative study of cathode polarization between infiltrated and baseline cells.

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Results and Discussion



Characterization of infiltrated catalysts.— The phase identity of the prepared LSCo and SCF (in absence of the cathode substrate) after calcining at 1000°C for 2 hours was examined with XRD, and is shown in Fig. 1a. For the LSCo catalyst, there are two phases found after calcinations: primary LaSrCoO₄ (space group: *I4/mmm*) and secondary cubic perovskite LSCo. Although the starting solution of LSCo was prepared according to the chemical formula of La_{0.6}Sr_{0.4}CoO_{3-δ}, the cubic perovskite structure was not formed as the dominant phase. It is most likely due to the lower calcinations temperature of LSCo, e.g., 1000°C, which is unfavorable to the formation of the cubic LSCo-phase.¹³ For SCF, the cubic perovskite is the dominant phase with trace Sr₅Co₄O₁₂.

The morphology of the LSCo and SCF particles in the cathode porous scaffold after calcining at 1000°C for 2 h is illustrated in Fig. 1b and 1c by FE-SEM near the electrolyte/cathode interface. The LSCo and SCF particles are evidently nano-sized, discrete and uniformly distributed; these features play an important role in the following observed reduction of polarization resistance.

Comparison of cathode polarization.— The AC impedance spectra of cathode/electrolyte/Pt cells measured from 1000 to 700°C under the OCV condition are compared in Fig. 2. The polarization resistance recorded as the length between the high-frequency and the low-frequency intersections with the Z'-axis is substantially reduced by the infiltrated LSCo and SCF catalysts. The ohmic resistance as represented by only the high-frequency intersection with Z'-axis was also decreased by the infiltration of LSCo and SCF, see the inserts in Fig. 3, but not as significant as those of polarization resistance.

A side-by-side comparison of polarization resistance (including both cathode and Pt-CE in this case) suggests a factor of 17 to 28 reductions from 1000 to 700°C between baseline and LSCo-infiltrated cells. Much better results were obtained when the cell was infiltrated with the SCF catalyst. The polarization resistance is decreased by a factor of 28 to 49 from 1000 to 700°C. The observed reductions are clearly the results of increased reactive sites provided by the infiltrated LSCo and SCF nanoparticles. The intrinsically higher MEIC conductivity and dominant perovskite phase in SCF are believed to be responsible for the observed better performance than LSCo.¹⁴

The pronounced reduction of cathode polarization by the presence of electrocatalysts is a strong indication of the oxygen-molecule-activation being the rate-limiting step in the cathode polarization process. Additional evidence includes the observation of a higher degree reduction at lower temperatures than higher temperatures since the cathode activation is a thermally activated process. This assertion agrees with the previous conclusion that the cathode polarization, particularly charge-transfer process, is the performance-limiting factor for cathode-supported SOFCs.¹⁵

Arrhenius plots of area specific electrode resistances, R_p , of the infiltrated and baseline cells are shown in Fig. 3a. The activation energies are $E_a = 1.92$ eV for the baseline cell, 1.81 eV for the LSCo-infiltrated one and 1.52 eV for the SCF-infiltrated one. A gradual reduction of E_a from baseline to LSCo- and to SCF-infiltrated cells suggests that the oxygen reduction process become more activated in the presence of better performing MEICs.

Similarly, Arrhenius plots of area specific ohmic resistances of the infiltrated and baseline cells are shown in Fig. 3b. The obtained activation energies are close in the range of 0.75-0.87 eV, all in good agreement with that reported value.⁶ Although no significant difference in the activation energies can be discerned from the data, the absolute values for the LSCo- and SCF-infiltrated cells are smaller than that of the baseline cell. The higher electronic conductivity in LSCo and SCF than LaMnO₃ helps the electronic conduction through the substrate and is most likely the reason for the lowered ohmic resistance.

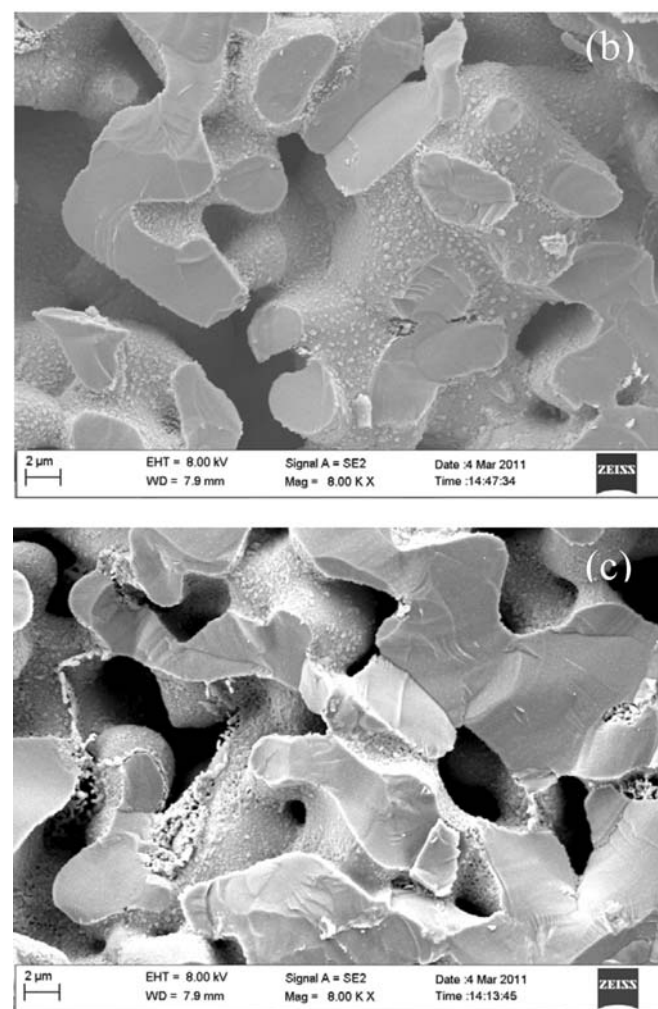


Figure 1. (a) XRD pattern of the prepared LSCo and SCF powders; SEM images of the infiltrated half-cells. (b) LSCo; (c) SCF.

The Pt-CE coating on the electrolyte surface was prepared from a commercial Pt paste along with Pt-meshes/leads serving as the current collectors by curing at 800°C for 0.5h. The effective cell surface area was kept at 1cm². The AC impedance measurements were carried out in a flowing 100scm air from 1000 to 700°C with a Zahner IM6 Electrochemical Workstation.

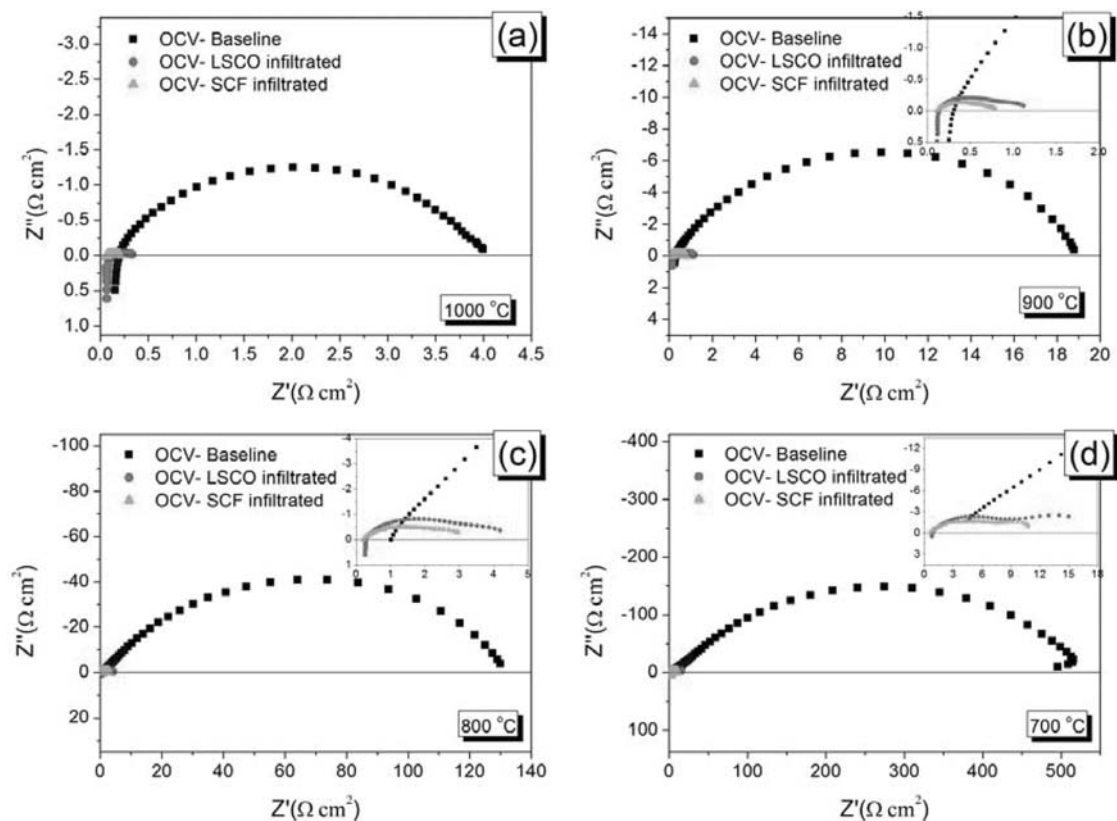


Figure 2. Comparison of impedance spectra between baseline and infiltrated half-cells. (a) 1000 °C; (b) 900 °C; (c) 800 °C; (d) 700 °C. Inserts represents the details at low resistance regime.

Conclusions

Fine particles of MEIC electrocatalysts LSCo and SCF have been successfully infiltrated into a commercial cathode porous scaffold by a first-time reported simplified one-step approach. The morphology of the impregnated LSCo and SCF particles are nano-sized, discrete and well-dispersed throughout the cathode substrate. A comparative

electrochemical study shows that the cathode polarization can be considerably reduced by a factor of 17 to 28 and 28 to 49 from 1000 to 700 °C by the infiltrated LSCF and SCF, respectively. These results strongly suggest that the poor cathode performance of a commercial cathode-supported SOFC can be significantly enhanced by the infiltration of MEIC materials without compromising the structural properties of the substrate.

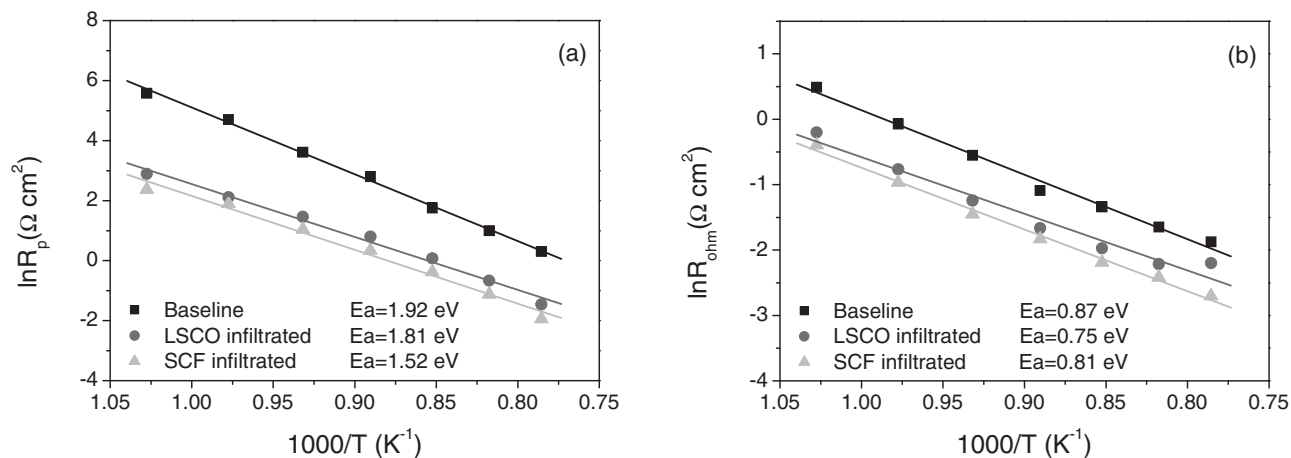


Figure 3. Arrhenius plots of (a) area specific ohmic resistance and (b) area specific polarization resistance.

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