Study of Perovskite Structure Cathode Materials and Protective Coatings on Interconnect for Solid Oxide Fuel Cells

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ABSTRACT

Solid oxide fuel cells (SOFCs) are promising devices to convert chemical energy to electrical energy due to their high efficiency, fuel flexibility, and low emissions. However, there are still some drawbacks hindering its wide application, such as high operative temperature, electrode degradation, chromium poisoning, oxidization of interconnect, and so on.

Cathode plays a major role in determining the electrochemical performance of a single cell. In this dissertation, three perovskite cathode materials, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF), Ba$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (BSCF), and Sm$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (SSCF), are comparatively studied through half-cells in the temperature range of 600-800 °C. Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (SDC) block layer on the yttria-stabilized zirconia (YSZ) electrolyte can lead to smaller polarization resistances of the three cathode materials through stopping the reaction between the cathodes and the YSZ electrolyte. SDC is also used as a catalyst to increase the oxygen reduction reaction (ORR) rate in the LSCF cathode.

In addition, interconnect is protected by Co$_x$Fe$_{1-x}$ oxide and Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coatings separately. These coatings are demonstrated to be effective in decreasing the area specific resistance (ASR) of the interconnect, inhibiting the Cr diffusion/evaporation, leading higher electrochemical performance of the SSCF-based half-cell. Only 1.54 at% of Cr is detected on the surface of the SSCF cathode with the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect and no Cr is detected with the Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coated interconnect.

Finally, single cells with LSCF, BSCF, and SSSF as the cathodes are operated in the temperature range of 600-800 °C fueled by natural gas. BSCF has the highest power density of 39 mW cm$^{-2}$ at 600 °C, 88 mW cm$^{-2}$ at 650 °C, and 168 mW cm$^{-2}$ at 700 °C; LSCF has the highest power density of 263 mW cm$^{-2}$ at 750 °C and 456 mW cm$^{-2}$ at 800 °C. Activation energies calculated from the cathode ASR are 0.44 eV, 0.38 eV, and 0.52 eV for the LSCF, BSCF, and
SSCF cathodes respectively, which means the BSCF cathode is preferred. The stability test shows that the BSCF-based single cell is more stable at lower operative temperature (600 °C) while the LSCF-based single cell is more stable at higher operative temperature (800 °C).
Study of Perovskite Structure Cathode Materials and Protective Coatings on Interconnect for Solid Oxide Fuel Cells

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GENERAL AUDIENCE ABSTRACT

Solid oxide fuel cells (SOFCs) are promising devices to convert chemical energy to electrical energy due to their high efficiency, fuel flexibility, and low emissions. However, there are still some drawbacks hindering its wide application, such as high operative temperature, electrode degradation, chromium poisoning, oxidization of interconnect, and so on.

A single cell is composed of an anode, electrolyte, and cathode. Interconnect can connect individual single cell to stack to increase voltage and current. In order to improve the electrochemical performance, such as resistance and power density, cathode materials and protective coatings to interconnect are studied. Three perovskite cathode materials, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF), Ba$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (BSCF), and Sm$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (SSCF), are comparatively studied in 600-800 °C to obtain the optimal cathode at different operating temperatures. BSCF has the smallest resistance at 600 °C, LSCF at 700 °C, and SSCF at 800 °C. A thin Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (SDC) block layer on the yttria-stabilized zirconia (YSZ) electrolyte can lead to smaller resistances of the three cathode materials through stopping the reaction between the cathodes and the YSZ electrolyte. SDC is also used as a catalyst by three methods to lower the resistances of the LSCF cathode.

In addition, interconnect is protected by Co$_x$Fe$_{1-x}$ oxide and Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coatings separately. They are demonstrated to be effective in decreasing the resistance of the interconnect, inhibiting the Cr diffusion/evaporation outward to poison cathodes. Only 1.54 at% of Cr is detected on the surface of the SSCF cathode with the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect and no Cr with the Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coated interconnect.

Finally, single cells with LSCF, BSCF, and SSCF as the cathodes are operated in 600-800 °C fueled by natural gas. BSCF has the highest power densities at lower operating temperatures while LSCF has the highest power densities at higher operating temperatures. Activation energies are
0.44 eV, 0.38 eV, and 0.52 eV for the LSCF, BSCF, and SSCF cathodes respectively, which means the BSCF cathode is preferred. The stability test shows that the BSCF-based single cell is more stable at 600 °C while the LSCF-based single cell is more stable at 800 °C.
DEDICATION

To my parents and sister
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This has been quite a tough but meaningful time in my life. I can’t express how grateful I am. First of all, my family is always the source of power in my life. They never made me feel pressured but always let me keep independent even when I was a kid. They never expressed their miss to me in the past several years when I was out of my hometown, but I know they love me.

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>ASR</td>
<td>Area Specific Resistance</td>
</tr>
<tr>
<td>BSCF</td>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_3$</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>DPB</td>
<td>Double Phase Boundary</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic Deposition</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic Acid</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field-Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>GDC</td>
<td>Gadolinium-Doped Ceria</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>I-P</td>
<td>Current-Power Density</td>
</tr>
<tr>
<td>LSCF</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_3$</td>
</tr>
<tr>
<td>LSM</td>
<td>Lanthanum Strontium Manganite</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>PAA</td>
<td>Peracetic Acid</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SDC</td>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{1.9}$</td>
</tr>
<tr>
<td>SSCF</td>
<td>Sm$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_3$</td>
</tr>
<tr>
<td>SSC</td>
<td>Sm$<em>x$Sr$</em>{1-x}$CoO$_3$</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>TPB</td>
<td>Triple-Phase Boundary</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria-Stabilized Zirconia</td>
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</table>
Chapter 1. Introduction

1.1 Solid oxide fuel cell overview

Solid oxide fuel cells (SOFCs) are promising electrochemical devices which can produce electricity via the conversion of chemical energy to electrical energy \(^{1-3}\). In a SOFC, reactions of oxidizing a gaseous fuel (e.g. hydrogen, methane or ethanol) and reducing an oxidant gas (e.g. oxygen) occur on the anode and cathode respectively, with the active charge carriers (e.g. H\(^+\) or O\(^2-\)) going through an ion conducting electrolyte. An external circuit can release these electrons to generate electricity. SOFC has a higher efficiency to utilize fuels compared to conventional combustion.

SOFCs are complex electrochemical devices. A single cell is usually composed of an anode, electrolyte, and cathode, the three basic components. Cells can be constructed in planar cells and tubular cells. Each component of the SOFC serves several functions and must therefore meet certain requirements. A typical planar SOFC structure is shown in Fig. 1-1.

![Fig. 1-1. Schematic of SOFC.](image)

The cathode is a thin porous layer, contacting the electrolyte where oxygen reduction reactions (ORRs) occur. ORR is essentially an electrochemical reaction involving the charge transfer process and believed to occur at triple-phase boundaries (TPBs), which are the adjoining portions of the electrode, electrolyte, and oxygen gas. The ORR can be simply expressed as follows \(^4\):

\[
O_2(gas) + 4e^- (cathode) \rightarrow 2O^{2-} (cathode)
\]  

(1-1)
Perovskite cathode materials have attracted much attention and have had great significance since La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ was first reported as a cathode for SOFCs by Button and Archer in 1966. Perovskites are oxides with the formula ABO$_3$ in which A sites are mainly occupied by rare and alkaline earth metals, such as La, Ba, and Ca, with larger ionic radius while B sites are occupied by higher valence transition metal cations, such as Co, Fe, and Ni with smaller ionic radius. They are usually poor ionic conductors before doping. At present, there are many choices for cathode materials.

The ceramic electrolyte lies between the cathode and anode to separate the fuel and air. There are several requirements for the electrolyte:

a) It has to be dense to prevent the fuel and air meeting;
b) It must be an ionic conductor so that oxygen ions can transfer from the interface of the cathode and electrolyte to the interface of the anode and electrolyte;
c) Its electronic conductivity must be as low as possible to prevent a leakage current;
d) It has to be compatible with the cathode and anode, including chemical stability and matching the coefficient of thermal expansion (CTE);
e) It has to be stable in both oxidizing and reducing atmospheres;
f) Its mechanical properties must be reliable.

Oxygen ions transfer through the electrolyte from the cathode side to the anode side, and at the same time, oxygen vacancies migrate in the electrolyte from the opposite direction. The oxygen ions conduct through the oxygen vacancy hopping mechanism, which is a thermally activated process. The function of the electrolyte in ORR can be simply written as follows:

$$O^{2-}(\text{cathode}) \rightarrow O^{2-}(\text{electrolyte}) \rightarrow O^{2-}(\text{anode})$$

Fluorite structure oxides, such as ZrO$_2$ and CeO$_2$, are candidate electrolyte materials. Pure ZrO$_2$ does not possess sufficient amount of oxygen vacancies to conduct ions, but doping can increase its ionic conductivity and stability. For YSZ electrolyte, the acceptor dopant cation, Y$^{3+}$, not only stabilizes the cubic phase of ZrO$_2$ crystal lattice but also enhances its ionic conductivity. Among the various Y$_2$O$_3$-ZrO$_2$ systems, 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ has the highest ionic conductivity of around 0.1 S cm$^{-1}$ at 1000 °C. CeO$_2$ also needs to be doped to exhibit higher ionic conductivity. Acceptor cations with lower valence, such as Gd$^{3+}$, Sm$^{3+}$, and Y$^{3+}$, can be introduced into the structure through substitution. Its ionic conductivity reaches a maximum with 10-20 mol%
doping. SDC (or GDC) has a higher ionic conductivity than YSZ, which is suitable to be operated in intermediate temperatures (~500-800 °C).

The anode must also be porous to allow fuel to reach the anode and electrolyte interface. The transferred $O^{2-}$ from the cathode side reacts with hydrogen and produces water and electrons. Taking hydrogen fuel as an example, the reaction mechanism can be described as follows:

$$H_2(gas) + O^{2-}(anode) \rightarrow H_2O(gas) + 2e^- (anode) \quad (1-3)$$

Ni and YSZ (or SDC, GDC) composites are the most commonly used anode material. Ni is electrochemically more active than Pt and has attracted extensive research. Plentiful Ni metal can provide enough electrical conductivity and catalytic activity, and at the same time, the second phase, YSZ (SDC, or GDC), is helpful to obtain enough ionic conductivity for oxygen ions and prevent the sintering of the Ni particles during the anode operation at high temperature 8. In addition, the YSZ (or SDC, GDC) phase, also as the ceramic electrolyte phase, can decrease the CTE mismatch between the electrolyte and anode.

Except oxygen-ionic conducting electrolyte, protonic conductor is another option for the solid electrolyte since its first observation by Iwahara 9. Its application has received considerable attention. Among the various perovskite structure electrolytes, rare earth such as Y, Nd, and Sm-doped BaCeO$_3$ oxides exhibit a good protonic conductivity in H$_2$ atmosphere 10. This is because the protonic conductivity of those electrolytes is dependent on the concentration of oxygen vacancies in the perovskite oxides, which is similar to oxygen ionic conductivity. The oxygen vacancies of perovskite oxides can be considerably increased by acceptor doping, such as doping lower valence elements at the B-site 11. The process of H$_2$ oxidation and transfer can be expressed as follows:

**Anode**

$$H_2(gas) \rightarrow 2H^+(anode) + 2e^- (anode) \quad (1-4)$$

**Electrolyte**

$$H^+(anode) \rightarrow H^+(electrolyte) \rightarrow H^+(cathode) \quad (1-5)$$

**Cathode**

$$O_2(gas) + 4H^+(cathode) + 4e^- (cathode) \rightarrow 2H_2O(gas) \quad (1-6)$$

Usually, the activation energy of proton transport is around 0.3-0.6 eV 12-13, which benefits the proton-conducting SOFCs. Moreover, H$_2$O is generated at the cathode side and fuel at the
anode will be pure. However, the electrochemical performance of proton-conducting SOFCs at intermediate temperature is still worse than that of oxygen ion-conducting SOFCs.

Coming back to the oxygen ion-conducting SOFCs, the gradient in the oxygen partial pressure \( P_{O_2} \) across the electrolyte provides the driving force for the ORR, oxygen ion transfer, and hydrogen oxidation reaction \(^7\). The theoretical reversible voltage \( E_{th} \) of the SOFCs can be given by the Nernst equation:

\[
E_{th} = \frac{RT}{4F} \ln \left( \frac{P_{O_2 \, cathode}}{P_{O_2 \, anode}} \right)
\]

(1-7)

where ‘\( R \)’ is the gas constant, ‘\( T \)’ is an absolute temperature, and ‘\( F \)’ is the Faraday’s constant. The coefficient ‘\( 4 \)’ means there are 4 electrons transferred per oxygen molecule reacted in the process. If air is fed in the cathode side and pure hydrogen gas is fed in the anode side, the equilibrium constant \( K_{eq} \) for the reaction can be expressed as follows:

\[
K_{eq} = \frac{P_{H_2O}}{(P_{H_2})(P_{O_2})^{1/2}}
\]

(1-8)

Then the Gibbs free energy change \( \Delta G_T \) and oxygen partial pressure \( P_{O_2} \) can be simply written as follows:

\[
\Delta G_T = \Delta H_T - T\Delta S_T = -RT\ln(K_{eq})
\]

(1-9)

\[
P_{O_2} = \left( \frac{P_{H_2O}}{P_{H_2}} \right)^2 \exp \left[ \frac{2(T\Delta S_T - \Delta H_T)}{RT} \right]
\]

(1-10)

where \( \Delta H_T \) is heat change, \( \Delta S_T \) is entropy change. Since \( P_{O_2 \, cathode} \) is equal to 0.21 atm if air flow is supplied and \( P_{O_2 \, anode} \) can be calculated with Eq. (1-10), then the theoretical Nernst potential at any operating temperature can be estimated with Eq. (1-7). The actual voltage, however, is always lower than the theoretical value due to some polarization losses.

The voltage for a single cell is little, on the order of 1 V \(^{14}\), which is insufficient for most applications. Metal or ceramic interconnects can connect single cells in series to increase voltage while also separate air from fuel. They also serve for electron conduct. Various geometries for the cell design were investigated but the most developed is the Siemens-Westinghouse tubular configuration, whose design has been demonstrated successfully at the 100 kW scale \(^{14}\). In this work, only planar structure will be discussed. Fig. 1-2 shows the schematic of a SOFC stack. The unit of interconnect/single cell can be repeated to increase voltage and current. As shown in Fig. 1-2, the interconnect is designed to have separate channels for the oxygen and fuel flows for the
adjoining cells. Therefore, the selection criteria for interconnect materials are more stringent than other components of the SOFC stacks. It has to meet the following requirements:\(^{15}\):

- a) It should be highly conductive with an area specific resistance (ASR) less than 0.1 Ω cm\(^2\);
- b) It should be stable in aggressive environments, including chemically and structurally stable at operating temperatures of ~600-1000 ºC in both oxidizing and reducing atmospheres with long term operation;
- c) It should be dense enough to stop oxygen and fuel meeting;
- d) Its CTE needs to match the other components of SOFC stacks;
- e) It should have no poisoning elements coming out at high operating temperature to react with the other components in the SOFC stack;
- f) Also, it should be easy to fabricate and shape;
- g) Low cost is the basic necessity for all products which have a potential of commercial application.

**Fig. 1-2. Schematic of SOFC stack.**

Ceramics, such as LaCrO\(_3\) and its related materials, have potential to be interconnect materials. Their conductivity is an increasing function of temperature, making them suitable for high temperatures. However, their conductivity at low temperatures, such as below 600 ºC, is not appreciable. Doping is effective to improve the electrical conductivity of these ceramic interconnects at relatively low operating temperatures. The bad formability of ceramics is another
issue hindering their wide application. Metallic interconnects are more attractive due to their low cost, ease of fabrication, and availability. Among metallic alloys, Cr-containing alloys, such as AISI 441 and SUS 430, are being extensively used as interconnect materials owing to their high melting point, low volatility, and similar CTEs to the other components of the SOFC stacks. Oxidization causing an increase in ARS and Cr outward diffusion/evaporation to poison the cathode are the two major issues for Cr-containing metallic interconnects. Protective coatings to improve their resistance to oxidize and inhibit Cr outward diffusion/evaporation have attracted much attention now.

Single cells are connected by interconnects in planar design SOFC stacks and sealant materials play a key role in avoiding leakage of oxygen and fuel in this aspect. Similar to interconnects, sealant materials are always exposed to oxidizing and reducing atmospheres at high temperature. Thus, there are some similar requirements to interconnect for sealant, such as high stability at high temperature and the two atmospheres, compatible CTE with the other components, and no contaminating elements volatilized. Moreover, sealant materials need high toughness and high bond strength. Metals, glass powders, ceramics, and mica-based composites are some of the sealant materials often used.

SOFCs usually work at the temperature range of 500 °C-1000 °C, so all components need to be stable at these temperatures. The high operating temperature accelerates rapid electro-catalytic activity for ORR, and generates high quality byproduct heat for co-generation or combined cycle applications. These special properties make the efficiency of SOFCs able to reach over 70% with fuel regeneration. It has been reported by Yokoo that an electrical conversion efficiency of 56% was achieved by a 25 anode-supported SOFC stack with an internal manifold structure. Powell studied a small-scale SOFC power system operating on methane with an efficiency of 55% in 2012.

Fuel choice, such as hydrogen, natural gas, and carbon monoxide, is flexible, which is another advantage for SOFCs. Low emissions in the exhaust gases enhances its potential to be widely used. As interest in renewable energy, CO2 emission reduction, and portability requirements grow, interest in SOFCs grows as well. They are currently under development for use in transportation as well as stationary and mobile applications.

1.2 Cathode material research development
Cathode, as an important component of a SOFC, contributes the most to the polarization during operation. A porous platinum electrode on yttria-stabilized zirconia (YSZ) was first studied over 100 years ago, and it helped to understand the kinetics and mechanism of cathode working. Decades ago, SOFCs operating at 1000 °C using a YSZ electrolyte, a La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) cathode which is a perovskite structure material, and a nickel-YSZ cermet anode were developed. Perovskite and perovskite-related structure oxides have attracted much attention as promising cathode materials for SOFCs because of their high electronic conductivity and high oxygen reduction activity based on disorder-free oxygen ion migration mechanism. The crystal structure of ABO$_3$ is shown in Fig. 1-3. A$^{n+}$ cation has a 12-fold oxygen coordination while B$^{n+}$ cation has a six-fold (octahedral) oxygen coordination.

SOFCs cannot yet compete with conventional combustion systems in terms of cost and durability. In recent years, the focus of SOFC development has been on lowering the operating temperatures of SOFCs to intermediate temperatures (500-800 °C), which can reduce costs and degradation and extend the range of acceptable material selection.

Lowering the operating temperature can increase the durability of SOFC systems by reducing problems associated with thermal cycling and performance degradation because of interdiffusion or reaction between the individual components. A key obstacle lowering the operating temperature for SOFC is the poor ionic conductivity of YSZ electrolyte. Another one is the poor catalytic activity of LSM for the electrochemical reduction of oxygen at these low temperatures. Reducing the operating temperature from 1000 to 500 °C brings an increase in the polarization resistance of
LSM from <1 to 2000 Ω cm², way outside of the practical range. Moreover, LSM is not a mixed ionic and electronic conductor, whose ionic conductivity is reported to be as low as 4×10⁻⁸ S cm⁻¹ at 800 ºC. Thus, new cathode materials exploration is significant.

SmₓSr₁₋ₓCoO₃ (SSC) is another ABO₃ structure compound and has very good properties both as a single phase material and in SSC composite cathodes consisting of SSC-La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂ₓCoₓO₃ or SSCF-Gd₀.₁Ce₀.₉O₁.₉₅. La₁₋ₓSrₓCo₁₋ₓFeₓO₃ is another example with perovskite structure. Electronic conductivity of its one stoichiometry, LSCF, is as high as 269 S cm⁻¹ at 800 ºC with ionic conductivity at 5.8×10⁻² S cm⁻¹. The larger rare earth ions La and Sr occupy the A-sites and Co and Fe occupy the B-sites. Park et al. reported the total resistance of 0.55 Ω cm², 0.86 Ω cm², and 1.56 Ω cm² at 730 ºC, 680 ºC, and 630 ºC respectively for a Ni-YSZ/YSZ/Gadolinium-doped Ceria (GDC)/LSCF cell. Ba₁₋ₓSrₓCo₁₋ₓFeₓO₃ was reported by Shao and Haile to give very low area specific resistances of 0.055-0.071 Ω cm² at 600 ºC, and 0.51-0.6 Ω cm² at 500 ºC based on the Sm₀.₂Ce₀.₈O₁.₉ (SDC) electrolyte.

Mixed electronic-ionic conductors, such as LSCF, can expand the ORR sites from TPB to double-phase boundary (DPB). Fig. 1-4 shows the mechanism of ORR for LSM and LSCF cathodes. For LSM cathode, ORR occurs at TPB. However, the reduction reaction occurs not only at TPB but also at DPB in five steps for LSCF cathode:

a) Oxygen adsorption and dissociation;
b) Ionization of the oxygen atom;
c) Incorporation of adsorbed oxygen in the bulk;
d) Surface diffusion;
e) Bulk diffusion;

These five steps show how the ORR occurs at DPB, which improves the electrochemical performance of cathode.
Ln\textsubscript{2}NiO\textsubscript{4} (Ln=La, Pr, Nd) is also an interesting cathode material because of its high diffusivity of the interstitial oxygen ions. The structure of Ln\textsubscript{2}NiO\textsubscript{4} can be described as a succession of LaNiO\textsubscript{3} perovskite layers alternating with LaO rock salt layers. La\textsubscript{2}NiO\textsubscript{4} was found to have an oxygen diffusivity higher than that of LSCF. The single cell based on SDC electrolyte showed a maximum power density of 295 mW cm\textsuperscript{-2} at 800 °C \textsuperscript{34}.

The double perovskites are another interesting class of cathode materials, but at present only limited research has been reported. The general formula can be expressed as AA’Co\textsubscript{2}O\textsubscript{5} (A=rare earths and A’=Ba, Sr) \textsuperscript{35}. In order to prevent the random distribution of the two cations in A and A’ sites, the ionic radii difference between the elements occupying A and A’ site should be significant. Among double perovskites, PrBaCo\textsubscript{2}O\textsubscript{5} thin films and bulk materials were both measured and showed high oxygen diffusivity and rapid surface exchange kinetics, which are reflected in the low ASR \textsuperscript{36}. Jiang has reported the ASR of a symmetrical cell based on a GDC electrolyte to be 0.113 Ω cm\textsuperscript{2} at 600 °C, 0.054 Ω cm\textsuperscript{2} at 650 °C, and 0.028 Ω cm\textsuperscript{2} at 700 °C \textsuperscript{37}. In other studies, the electrochemical performance of GdBaCo\textsubscript{2}O\textsubscript{5} has also been investigated and its stability was found to be very good in a CO\textsubscript{2} atmosphere at temperatures up to 700 °C \textsuperscript{38-39}.
1.3 Challenges

There still have many challenges for the commercial use of SOFCs. These include the high operating temperatures to improve the activities of the electrodes and the ionic conductivity of the electrolyte, as well as the degradation of cell materials because of the high temperature and long operating time. To make SOFCs commercially competitive, it is necessary to develop new electrode materials with high activity and stability between 500-800 °C. In addition, the stacks must meet a lifetime goal of 40,000 hours with performance degradation of less than 0.1% per thousand hours of operation.

1.3.1 High operating temperature

At present, SOFCs can work at temperature range of 800-1000 °C, which are still high for wide use. They bring multiple materials problems which include electrode sintering, catalyst poisoning, interfacial diffusion between electrolyte and electrode materials, thermal instability, and thermal stresses due to the CTE mismatch of the cell components. Lower operating temperatures can effectively relieve these limitations, but come with poorer ORR activities and lower ionic conductivities. New materials and catalysts are focused on decreasing the operating temperature with enhanced or at least comparable electrochemical performance. Further, reduction of the operating temperature can allow selection among a wider choice of interconnect materials with lower cost.

1.3.2 Cathode degradation

Cathode degradation is another obstacle hindering the large-scale application of SOFCs. Degradation of SOFC cathodes is affected by both intrinsic, as well as extrinsic factors. Intrinsic factors arise from the material itself during operation at high temperature. The major intrinsic factors responsible for cathode degradation are phase transformation, coarsening of particles while undergoing thermal treatment, decomposition, interdiffusion between cell components, and chemical reactions with other components. Extrinsic factors arise from the operation, which includes chromium poisoning from Cr-containing metallic interconnect materials and contaminants from sealing materials.
1.3.2.1 Reaction with electrolyte

At high operating temperature, perovskites are highly active to react with other components, especially with electrolytes. Solid state reactions between the cathode and the YSZ electrolyte due to the elemental diffusion are widely accepted as the reason for the instability of perovskite cathode materials. The reactions contribute to the electrochemical performance degradation with time. It has been frequently reported that the voltage and power density heavily degraded with long time operation due to the cathode and electrolyte reacting to form insulating products. Insulating phases, such as La$_2$Zr$_2$O$_7$ and SrZrO$_3$, at the interface of the LSM or LSCF cathode and the YSZ electrolyte have been detected and are partially responsible for the long term degradation of the SOFC. Furthermore, a significant dissolution of Mn was detected in YSZ. The solubility of Mn in YSZ ranges from 5.1% at 1000°C to 11.4% at 1300 °C. In the YSZ matrix, Mn was observed to be either in divalent or trivalent states.

1.3.2.2 Chromium poisoning

Perovskite structure cathodes can be poisoned by chromium species which diffuse from the interconnects at high operating temperatures. The diffusion can be realized through vapor evaporation or solid diffusion. In SOFC, the interconnect experiences high temperatures and a chemically aggressive environment. The cathode side is particularly corrosive as it contains oxygen and often water. Because of the oxygen inlet flow and the high operating temperature, SOFC interconnects containing chromium release a chromium oxide vapor into the cathode which severely degrades the performance of the fuel cell. The reaction can be simply written as follows:

\[ \text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) \rightarrow 2\text{CrO}_3(g) \]  \hspace{1cm} (1-11)

As known, Cr-containing alloys produce different gaseous chromium species in moist air compared with those in dry air and the reaction is described as follows:

\[ \text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{CrO}_2(\text{OH})_2(g) \]  \hspace{1cm} (1-12)

The CrO$_3$ and Cr(OH)$_2$O$_2$ vapors enter the cathode’s pores and react at the TPB sites. As a result, the reverse reactions of Equations. (1-11) and (1-12) happen, as Equations. (1-13) and (1-14). Solid Cr$_2$O$_3$ is then deposited on the electrochemically reactive site, and blocks the active TPB sites and impedes the reduction reaction of oxygen.

\[ 2\text{CrO}_3(g) + 6e^- \rightarrow \text{Cr}_2\text{O}_3(s) + 3\text{O}^{2-} \]  \hspace{1cm} (1-13)
1.4 Objectives and significance of study

The aim of this study is to improve the electrochemical performance of cathodes at intermediate temperatures. Several aspects are applied to achieve this aim:

- The electrochemical performance of three perovskite cathode materials, LSCF, BSCF, and SSCF, at 600, 700, and 800 °C operating temperatures will be compared based on half-cells and will know which material is more suitable to work at low operating temperature.

- Composite electrodes, which typically consist of a mixed ionic and electronic conductor and an ionic conductor, exhibit higher performance than pure-phase electrodes. The ionic conductivity of LSCF cathode is not high enough. The ionic conductivity of SDC is as high as $8.4 \times 10^{-2}$ S cm$^{-1}$ around 800 °C, which is much higher than that of YSZ. SDC catalyst will be applied on LSCF cathode by three methods, including mechanical mixture, infiltration, and dip coating to enhance the oxygen reduction rate and reduce the activation loss, leading high electrochemical performance of SOFCs.

- The reaction between the perovskite cathode and the YSZ electrolyte in long term run is one of the reasons lowering the electrochemical performance of SOFCs. The approaches to minimize resistive losses across the electrolyte have included replacing YSZ with alternative electrolyte materials (such as SDC) with much higher ionic conductivity, or making a thin solid oxide electrolyte sandwich. But the advantages of the YSZ electrolyte, matched CTE with LSCF cathode, moderate mechanical strength, phase stability in both oxidizing and reducing atmospheres, and excellent gas tightness, are still attractive. SDC is inert to perovskite materials at 800 °C, which can block the reaction between the perovskite cathode and the YSZ electrolyte if a SDC layer is deposited on YSZ electrolyte.

- Cr-containing ferritic stainless steels are the most promising candidates as interconnects due to their appropriate thermal expansion behaviors and low cost. However, chromium will diffuse and evaporate to poison the cathode at high operating temperature, which is another serious issue for cathode degradation. Moreover, the electrical conductivity of the ferritic interconnects will decrease because of the oxidation in long term run. It’s significant to deposit a protective coating, such as $\text{Co}_x\text{Fe}_{1-x}$ oxide coating or $\text{Co}_3\text{O}_4$/SDC/$\text{Co}_3\text{O}_4$ tri-layer coating on ferritic steel to improve its resistance to oxidation.
and inhibit chromium diffusion/evaporation. The elements in these coatings would not bring in contamination to the cathodes.

- The previous cathode electrochemical performance studies are based on half-cells. Single cell testing is more convincing because voltage and power density can be shown and it includes an anode. Natural gas is used as a fuel because it has a wider availability, safer storage, and lower cost than H₂. Single cells with three cathode materials are conducted at different temperatures to measure their maximal power densities and stability. The best cathode candidate at different operating temperatures will be unveiled.

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Chapter 2. Temperature and Chromium Poisoning Study on Perovskite-type Cathode Materials

Abstract

In the pursuit for SOFC cathode materials that can operate over a wide temperature range, especially at low temperatures such as 600 °C, perovskite structure materials LSCF, BSCF, and SSCF are studied. Their electrochemical performance is compared by EIS at 600 °C, 700 °C and 800 °C for 100 hrs through an AISI 441 interconnect/cathode/YSZ electrolyte half-cell structure. The BSCF cathode has the smallest polarization resistance at 600 °C, closely followed by the SSCF cathode; the LSCF cathode has the smallest polarization resistance working at 700 °C; the SSCF cathode has the smallest polarization resistance working at 800 °C, closely followed by the LSCF cathode. From 600-800 °C, SrCrO$_4$ phase forms on the SSCF cathodes near the interconnect while BaCrO$_4$ phase forms on the BSCF cathodes near the interconnect. For the LSCF cathodes, however, SrCrO$_4$ phase is only detected at 700 °C and 800 °C. Cr species diffusion to and poisoning of the cathodes do not directly correlate with the half-cell performance. Lattice constant, stoichiometry, particle size, Cr deposition, and working temperature are important factors to consider.

2.1 Introduction

Mixed ionic-electronic conductors are promising cathode materials for SOFCs, considering that the ORR is not just limited to the TPB sites between electrolyte, cathode, and gas but can be extended to DPB sites between the cathode and gas $^{1-3}$. They also have much higher oxygen ionic conductivity than the conventional (LaSr)MnO$_3$ cathode material $^{4-5}$.

Iron-cobalt-based ABO$_3$ perovskite oxides are promising cathode materials for intermediate temperature SOFCs because of their high electronic conductivity and high oxygen reduction activity based on disorder-free oxygen ion migration mechanism $^6$. Among them, LSCF and BSCF are frequently reported $^7$-$^8$. SSCF is also a cathode material and can be obtained through Sm substitution of Ba in BSCF; however, this material has not gained much attention $^9$-$^{10}$. Lv et al. showed that the polarization resistance of SSCF is 0.17 Ω cm$^2$ at 800 °C with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ as the electrolyte $^{11}$. So far, there has been no systematic comparative study of these three cathodes working at different temperatures.
Cr-containing alloy is the most commonly used metallic interconnect material due to their high electronic conductivity, high thermal conductivity, easy workability, and low cost\textsuperscript{12-14}. However, Cr poisoning can cause dramatic electrochemical performance degradation of cathodes\textsuperscript{15-16}. With the continuing interest of developing new cathode materials, understanding of their interaction tendency and mechanism with Cr species is needed in order to develop Cr-tolerant cathode materials. In addition, high SOFC operating temperature causes the degradation of cathode materials and the reaction at the interface of cathode and interconnect\textsuperscript{17}. Lowering working temperature of SOFCs is one of the major objectives for its commercialization. The behaviors of new cathodes at different operating temperature need to be understood.

2.2 Experimental procedures

2.2.1 Chemicals

La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, Sr(NO\textsubscript{3})\textsubscript{2}, Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Ba(NO\textsubscript{3})\textsubscript{2}, Sm(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, ethylenediaminetetraacetic acid (EDTA), citric acid, NH\textsubscript{4}NO\textsubscript{3}, sucrose, and NH\textsubscript{3}·H\textsubscript{2}O were purchased from Alfa Aesar (Ward Hill, MA). α-terpineol as solvent was purchased from Sigma-Aldrich (St. Louis, MO). Microcrystalline cellulose as a pore forming agent was purchased from Spectrum Chemical Manufacturing Corporation (Gardena, CA). Ethyl cellulose as a binder was purchased from Acros Organics (Morris Plains, NJ). YSZ was purchased from Nextech Materials (Lewis Center, OH). AISI 441 was produced by ATI Allegheny Ludlum Corporation (Brachenridge, PA).

2.2.2 Synthesis of LSCF, BSCF, and SSCF powders

LSCF powder was synthesized by a combustion method\textsuperscript{18}. The molar ratio of La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, Sr(NO\textsubscript{3})\textsubscript{2}, Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O was 6:4:2:8 and the molar ratio of metal ions, EDTA, citric acid, ammonium nitrate, sucrose was 2:1:2:10:0.75. In the first step, the metal nitrates were dissolved in distilled water in a beaker; EDTA, citric acid, ammonium nitrate, and sucrose were added. The pH value was adjusted by ammonium hydroxide to 6 to completely dissolve EDTA. With the usage of a mesh on the top of a beaker the solution was placed in a pre-heated furnace at 450 °C. After 10 min the combustion process was completed and the beaker was taken out to cool down. The reaction equation was as follows\textsuperscript{19};
The combusted powder was calcined at 900 °C for 2 hrs and ball milled before use. For the synthesis of BSCF and SSCF powders, the above procedure was followed with the exception of the raw materials and molar ratios of metal ions. La(NO$_3$)$_3$·6H$_2$O was substituted by Ba(NO$_3$)$_2$ and Sm(NO$_3$)$_3$·6H$_2$O for BSCF and SSCF respectively. The final LSCF, BSCF, and SSCF stoichiometries were La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$, Ba$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$, and Sm$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$. The LSCF stoichiometry had the best compromise between high electrical conductivity and good CTE match with the electrolyte material. The BSCF and SSCF stoichiometries showed the highest electrical conductivity and crystal structure stability.

2.2.3 Electrical conductivity test

For electrical conductivity measurement, the powders of LSCF, BSCF, and SSCF were cold pressed at 200 MPa into cylindrical pellets (12.7 mm in diameter and about 6 mm in thickness) using a uniaxial press. The green pellets were further sintered at 1300 °C, 1150 °C, and 1250 °C for 10 hrs at a heating/cooling rate of 5 °C min^{-1} respectively. Ag-Pd paste was subsequently painted onto both sides of the pellets as electrodes. The electrical conductivities were measured in air by a four-probe DC potentiostat (VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN). The voltage was scanned from 0 to 1 V and the corresponding current was evaluated over a temperature range of 300-900 °C. Resistance was obtained through the slope of I-V curve.

2.2.4 Assembly of AISI 441/cathode/YSZ structure

The cathode material (56.8 wt%) was mixed and ball-milled with microcrystalline cellulose (5.7 wt%), ethyl cellulose (1.1 wt%), and α-terpineol (36.4 wt%) for 1 hr to make pastes for screen printing. The prepared pastes were screen printed on 8 mol% YSZ substrates, using a #330 mesh. The screen printed pastes were square-like with ~0.5 cm$^2$ area. The cathode/YSZ structure was kept at 200 °C for 3 hrs and at 600 °C for 1 hr to partially burn the binder and solvent and was then kept at 950 °C for 2 hrs to complete binder removal and bond with YSZ; a heating and cooling rate of 1 °C min$^{-1}$ was used.
AISI 441 ferritic stainless steel pieces were used as the interconnect material and were cut into square substrates (area: 10 x 10 mm$^2$). In order to remove the oxidized layer and obtain a scratch-free flat surface, the steel pieces were polished to optical finish and ultrasonically cleaned with water and ethanol. The polished AISI 441 alloy piece was placed on the cathode side and the configuration was shown in Fig. 2-1.

![Half-cell configuration diagram](image)

**Fig. 2-1. Half-cell configuration.**

### 2.2.5 Thermal treatment under current load

In order to investigate the electrochemical behaviors of the LSCF, BSCF, and SSCF cathodes, the AISI 441/cathode/YSZ half cells were heated to 600 °C, 700 °C, and 800 °C respectively, using a tube furnace (1730-20 HT Furnace, CM Furnace Inc. Bloomfield, NJ) in dry air environment. Afterwards, the half cells were cathodically polarized using a potentiostat (VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN). A platinum mesh was placed in-between the porous cathode layer and the AISI 441 interconnect to optimize the current distribution, and the electrodes were connected by Pt wires with a Pd paste. The working electrode was positioned at the center of the YSZ electrolyte with about the same area as the cathode. The reference electrode was painted as a ring around the working electrode. The counter electrode was positioned at the center of the interconnect and the reference electrode was painted on the edge. The EIS testing program used was a multi-loop process with the frequency from 100 kHz to 0.025 Hz. The amplitude was 10 mV. After that, a current density of 200 mA cm$^{-2}$ was applied to mimic the working condition of an actual fuel cell. EIS data were recorded every 2 hrs during the thermal treatment.

### 2.2.6 Characterization

X-ray diffraction (XRD, X’Pert PRO diffractometer, PANalytical B.V., EA Almelo, The Netherlands) analysis was employed to characterize the crystal structure of the synthesized
powders. The microstructures of the cathodes before and after the thermal treatment were examined by a field-emission scanning electron microscope (FESEM, LEO (Zeiss) 1550, Oberhochem, Germany) with a carbon layer applied before imaging.

2.3 Results and discussion

2.3.1 Electrochemical behaviors

The electrical conductivities of LSCF, BSCF, and SSSF in air were measured in the temperature range of 300-900 °C as shown in Fig. 2-2. The conductivities here were extracted to full density values by considering the relative densities of the corresponding cylindrical pellets. LSCF has the largest electrical conductivity while BSCF has the smallest electrical conductivity. The detailed values are shown in Table 2-1. Overall, the electrical conductivities first increase and then decrease with the measurement temperature for these three cathode materials. The maximal electrical conductivities are located between 600-700 °C for the three electrode materials. As a comparison, the electrical conductivity for the classical cathode material $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is reported to be 110 $\text{S cm}^{-1}$ at 800 °C $^{22}$, which is only higher than that of BSCF but much lower than those of LSCF and SSSF. This means these cathode materials have high application potentials.

![Graph showing electrical conductivities of LSCF, BSCF, and SSSF](image)

**Fig. 2-2. Electrical conductivities of LSCF, BSCF, and SSSF from 300 °C to 900 °C in air.**

**Table 2-1. Detailed electrical conductivities of LSCF, BSCF, and SSSF.**
The conductivity difference of these three cathode materials can be understood as follows. The ionic radii of Sm$^{3+}$, La$^{3+}$, and Ba$^{2+}$ are 1.24 Å, 1.36 Å, and 1.61 Å respectively. Smaller ionic radius means smaller lattice constant for the same crystal structure. The lattice constants of the SSCF, LSCF, and BSCF powders can be calculated to be 3.85 Å, 3.87 Å, and 3.95 Å, which are in agreement with earlier reports\textsuperscript{11, 19, 23}. In general, the electrical conductivity from the smaller unit cell is greater than that from the larger unit cell. Here, BSCF and SSCF have the same stoichiometry and the ionic radius of Ba$^{2+}$ is larger than that of Sm$^{3+}$, so the conductivity of BSCF is smaller than that of SSCF. For LSCF, its electrical conductivity is affected also by its different stoichiometry from BSCF and SSCF and cannot be compared directly.

Since the above conductivity measurement is from direct current mode, it can only provide ohmic resistance information for the cathodes. In order to understand the fundamental process in different half-cells and correlate the electrochemical behaviors with the cathode evolution, an equivalent circuit $R_Ω(R_H CPE_H)(R_L CPE_L)$ under alternating current (AC) mode, shown in Fig. 2-3, has been used to fit the EIS spectra and obtain deconvoluted arcs at different frequencies. In the circuit, $R_Ω$ is the ohmic resistance from the cathode, the Pt wires, the Pd paste, the contact between each layer and the cathode, and the electrolyte; however, the major contribution and especially the changes are from the contact resistance between each layer, and the electrolyte. $R_H$ and $R_L$ refer to the polarization resistances at high and low frequencies, while $CPE_H$ and $CPE_L$ are constant phase elements corresponding to each frequency range. The high frequency resistance $R_H$ corresponds to O$^{2-}$ incorporation into the electrode and its transport in the cathode; and the low frequency resistance $R_L$ in the impedance spectra is attributed to oxygen adsorption and dissociation as well as its surface diffusion\textsuperscript{24}.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>LSCF</th>
<th>BSCF</th>
<th>SSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma@300$ °C (S cm$^{-1}$)</td>
<td>176</td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>$\sigma_{\text{max}}$ (S cm$^{-1}$)</td>
<td>252</td>
<td>46</td>
<td>185</td>
</tr>
<tr>
<td>$T@\sigma_{\text{max}}$ (°C)</td>
<td>650</td>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>$\sigma@900$ °C (S cm$^{-1}$)</td>
<td>220</td>
<td>16</td>
<td>122</td>
</tr>
</tbody>
</table>
Fig. 2-3. Equivalent circuit used for fitting the EIS.

Considering that the cathode requires time to activate and stabilize at the intended operating temperatures, the electrochemical data after the initial starting points are more representative of the cathode behaviors. Accordingly, the electrochemical performance after 2 hrs of testing is presented to demonstrate the fundamental difference of the cathode materials. Fig. 2-4(a) shows the electrochemical behavior of the LSCF cathode under a current density of 200 mA cm$^{-2}$ at 600 °C, 700 °C, and 800 °C after 2 hrs of the thermal treatment. With the operating temperature increase from 600 °C, to 700 °C, and to 800 °C, the ohmic resistance decreases from 7.1 Ω cm$^2$, to 2.5 Ω cm$^2$, and to 0.9 Ω cm$^2$ and the polarization resistance (sum of $R_H$ and $R_L$) decreases dramatically from 47.0 Ω cm$^2$, to 3.2 Ω cm$^2$, and to 2.1 Ω cm$^2$. From 600 °C to 700 °C, the ohmic resistance decreases the most, which is partly attributed to the ohmic resistance decrease of the YSZ electrolyte, as YSZ has poor ionic conductivity at 600 °C. More importantly, the polarization resistance drastically decreases from 47.0 Ω cm$^2$ to 3.2 Ω cm$^2$. This is because its catalytic activity for oxygen exchange reaction and the ionic conductivities of the cathode and the electrolyte are enhanced. Fig. 2-4(b) shows the electrochemical behavior of the BSCF cathode after 2 hrs of the thermal treatment. With the working temperature increase from 600 °C, to 700 °C, and to 800 °C, the ohmic resistance decreases from 20.3 Ω cm$^2$, to 5.8 Ω cm$^2$, and to 2.5 Ω cm$^2$ and the polarization resistance decreases gradually from 10.0 Ω cm$^2$, to 2.8 Ω cm$^2$, and to 2.0 Ω cm$^2$. Again, the drastic ohmic resistance decrease can be partly attributed to the ohmic resistance decrease of the YSZ electrolyte. The large polarization resistance decrease from 10.0 Ω cm$^2$ to 2.8 Ω cm$^2$ is due to the enhanced catalytic activity for the oxygen exchange reaction and the ionic conductivities of the LSCF cathode and the YSZ electrolyte. Fig. 2-4(c) shows the electrochemical behavior of the SSCF cathode after 2 hrs of the thermal treatment. With working temperature increase from 600 °C, to 700 °C, and to 800 °C, the ohmic resistance decreases from 11.2 Ω cm$^2$,
to 3.6 $\Omega$ cm$^2$, and to 2.5 $\Omega$ cm$^2$ and the polarization resistance decreases gradually from 21.4 $\Omega$ cm$^2$, to 3.0 $\Omega$ cm$^2$, and to 1.8 $\Omega$ cm$^2$. Again, the ohmic resistance decrease is partly due to the ohmic resistance decrease of the YSZ electrolyte. The polarization resistance decrease is due to its higher catalytic activity for the oxygen exchange reaction and higher conductivities of SSCF and YSZ at the elevated temperatures.

Fig. 2-4. Electrochemical impedance spectroscopic plots of (a) LSCF cathodes, (b) BSCF cathodes, and (c) SSCF cathodes tested at 600 °C, 700 °C, and 800 °C respectively after 2 hrs.

With the acknowledgment of the ohmic resistance contribution from other cell components, the relative magnitude of the total ohmic resistance is consistent with the ohmic resistance for individual cathode materials shown in Fig. 2-2. The LSCF cathode has the smallest ohmic resistance at all temperatures due to its largest electrical conductivity among all three materials,
while the BSCF cathode has the largest ohmic resistance due to its smallest electrical conductivity. The oxygen vacancy concentration is determined by the stoichiometry of the cathode. The polarization resistance difference can be partially explained based on the oxygen vacancy. Here, for LSCF, BSCF, and SSCF, their oxygen vacancy concentrations can be calculated to be 6.7%, 16.7%, and 8.3% respectively based on the chemical stoichiometries. Higher oxygen vacancy concentration from BSCF means higher oxygen ionic conductivity and lower polarization resistance, as shown in Fig. 2-4.

To better understand the electrochemical performance of the cathodes, the polarization resistance changes with time are shown in Fig. 2-5. Fig. 2-5(a) is for 600 °C testing temperature and all the polarization resistances at this temperature first decrease dramatically and then stabilize, which can be related to the slow cathode activation at 600 °C, taking about 50 hrs for the three cathodes to achieve their optimal performance. After 50 hrs of the thermal treatment, BSCF and SSCF have about the same low polarization resistance of 5 Ω cm² while LSCF has much higher polarization resistance of 8 Ω cm². Fig. 2-5(b) is for the 700 °C results and all the polarization resistances first decrease and then increase gradually. At this temperature, the cathodes are activated in about 6 hrs, which is much faster than that at 600 °C. After that, the small polarization resistance increases are believed to be from cathode degradation and chromium deposition. Among them, LSCF has the smallest polarization resistance and SSCF has the largest polarization resistance. Fig. 2-5(c) is for the 800 °C results and all the polarization resistances first increase dramatically and then stabilize/increase gradually. At this temperature, no drop for polarization resistances is observed, which means the activation process completes in 2 hrs at 800 °C. The higher operating temperature accelerates cathode degradation, microstructure change, and chromium deposition, resulting in large polarization resistances after cathode activation. This can explain why the LSCF and BSCF cathodes have larger polarization resistances when working at 800 °C than working at 700 °C. Among them, SSCF has the smallest polarization resistance in long term operation, while BSCF has the largest polarization resistances.

Based on Fig. 2-5, it can also be stated that in the long term use of the SOFCs, the electrochemical performance of cathodes is different from their initial state. The cathode performance is not only affected by their intrinsic properties, such as electrical conductivity and oxygen vacancy concentration, but also by their microstructure evolution and interaction with other foreign species.
Fig. 2-5. Polarization resistance changes for the LSCF, BSCF, and SSCF cathodes at (a) 600 °C, (b) 700 °C, and (c) 800 °C with the thermal treatment time.

The polarization resistances for the three cathodes after working at 600 °C, 700 °C, and 800 °C for 100 hrs are shown in Table 2-2. The polarization resistance of the BSCF cathode (5.1 Ω cm²) is the smallest and comparable to the SSCF cathode (6.0 Ω cm²) at 600 °C; the polarization resistance of the LSCF cathode (3.3 Ω cm²) is the smallest at 700 °C; the polarization resistance of the SSCF cathode (4.5 Ω cm²) is the smallest and comparable to the LSCF cathode (4.6 Ω cm²) at 800 °C. Overall, BSCF is preferred for working at 600 °C; LSCF is preferred for working at 700 °C; and SSCF is preferred for working at 800 °C.
Table 2-2. Resistances for the three cathodes after working at the three studied temperatures for 100 hrs.

<table>
<thead>
<tr>
<th>Resistance $R_p$ (Ω cm$^2$)</th>
<th>LSCF</th>
<th>BSCF</th>
<th>SSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 °C</td>
<td>9.4</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td>700 °C</td>
<td>3.3</td>
<td>5.2</td>
<td>5.3</td>
</tr>
<tr>
<td>800 °C</td>
<td>4.6</td>
<td>5.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

2.3.2 Microstructures

The microstructures of the cathode/interconnect interface after 100 hrs of the thermal treatment at 600 °C, 700 °C, and 800 °C are shown in Fig. 2-6. Figs. 2-6(a), (b), and (c) are for the LSCF, BSCF, and SSCF cathodes respectively before testing. As expected, all the electrode layers are porous. The initial particle sizes of LSCF, BSCF, and SSCF are about 100 nm, 400 nm, and 50 nm respectively. Usually, smaller particle size means larger specific surface area, and thus larger DPB and TPB. This is to say, smaller particles are desired for better electrochemical performance.

For the LSCF cathode, after 100 hrs at 600 °C (Figs. 2-6(d)), a few larger particles appear, of which the size is about 300 nm. At 700 °C for 100 hrs (Fig. 2-6(g)), there are more large particles forming at about 500 nm. At 800 °C for 100 hrs (Fig. 2-6(j)), the larger particles keep coarsening and the size is around 1 μm. For the BSCF cathode (Figs. 2.6(b), (e), (h), and (k)), at 600 °C for 100 hrs, the cathode becomes denser but the particles do not coarsen. At 700 °C and 800 °C after 100 hrs respectively, the particles also stay about the same, which is partly ascribed to the larger starting particle size. For the SSCF cathode (Figs. 2-6(c), (f), (i), and (l)), at 600 °C for 100 hrs, many large particles can be seen and their size is about 400 nm. The same happens for the SSCF cathode working at 700 °C. At 800 °C, the large particles coarsen to 1 μm. The other particles still maintain their original size.
Fig. 2-6. Surface morphology of LSCF cathodes ((a), (d), (g), (j)), BSCF cathodes ((b), (e), (h), (k)), and SSCF cathodes ((c), (f), (i), (l)). (a), (b), (c) are from the initial samples before testing; (d), (e), (f) are from the tested cathodes at 600 °C for 100 hrs; (g), (h), (i) are from the tested cathodes at 700 °C for 100 hrs; (j), (k), (l) are from the tested cathodes at 800 °C for 100 hrs. All images have the same scale.

XRD is used to examine the phase evolution after 100 hrs of the thermal treatment (Fig. 2-7). The main peaks at (110) direction are located at 32° for BSCF, 32.7° for LSCF, and 33° for SSCF, which demonstrates the peak shift from right to left for SSCF, LSCF, and BSCF. The lattice constants of the SSCF, LSCF, and BSCF powders can be calculated to be 3.85 Å, 3.87 Å, and 3.95 Å, which are in agreement with earlier reports 11, 19, 23. This result shows that replacing La with Ba
increases the lattice constant of the perovskite crystal structure for about 2.1%; while replacing La with Sm decreases the lattice constant of the perovskite crystal structure for about 0.5%. It has to be admitted that the more ratio of La$^{3+}$ to Sr$^{2+}$ in LSCF makes its lattice constant decreases a little. Thus, the actual lattice constant increase for replacing La with Ba is less than 2.1% and the actual decrease for replacing La with Sm is larger than 0.5%.

Fig. 2-7(a) shows the evolution of the LSCF cathode. After working at 600 °C for 100 hrs, only LSCF peaks are detected. For the cathodes tested at 700 °C and 800 °C, however, SrCrO$_4$ phase is found. This is consistent with the SEM results, indicating that Cr deposition on the LSCF surface is through interaction with Sr rather than with La, Co, or Fe. It has been demonstrated that these large particles are SrCrO$_4$ and they mainly reside on the surface of the cathode$^{25-26}$. The formation of the poorly conductive SrCrO$_4$ (1.8×10$^{-5}$ and 1.8×10$^{-4}$ S cm$^{-1}$ at 700 °C and 800 °C respectively$^{27}$) increases the electrode ohmic resistance by blocking the electrical conductivity path. Also, SrCrO$_4$ formation extracts Sr species from the LSCF lattice, leading to Sr deficiency at the A-site. Thus the electrical conductivity of LSCF is further reduced. As a result, the activity of the LSCF cathode for the oxygen reduction reaction and DPB are reduced substantially. This process is embodied by the significant increase in $R_p$ of LSCF after activation. The absence of SrCrO$_4$ formation at 600 °C also explains the slight polarization resistance increase shown in Fig. 2-5(a). At 700 °C and 800 °C, however, the polarization resistance increases substantially. Fig. 2-5(b) shows the evolution of the BSCF cathode. Instead of SrCrO$_4$, BaCrO$_4$ phase is detected. BaCrO$_4$ is reported to be more stable compared to SrCrO$_4$ $^{27}$. Therefore, the Cr deposition (CrO$_3$, Cr$_2$O$_3$) on the BSCF takes place by interacting with Ba$^{2+}$ rather than with Sr$^{2+}$ with the presence of BaO. The extraction of Ba$^{2+}$ species from the BSCF cathode can also reduce the activity of the BSCF cathode for the oxygen reduction reaction and DPB substantially, supported by the significant increase in $R_p$ of BSCF after activation. The formation of BaCrO$_4$ phase does prevent the reaction of Sr$^{2+}$ with the poisonous CrO$_3$ vapor or Cr$_2$O$_3$. Moreover, the extraction of the Ba species from the BSCF lattice leads to Ba deficiency at the A-site and changes its stoichiometry, leading to the cathode performance degradation. The electrical conductivity of BaCrO$_4$ has been reported to be 4.5×10$^{-3}$ S cm$^{-1}$ at 800 °C, which is almost 25 times higher than that of SrCrO$_4$ $^{27}$.

Fig. 2-7(c) shows the evolution of the SSCF cathode. It is similar to that of the LSCF cathode, moreover, SrCrO$_4$ phase is formed on the cathode after working at 600 °C for 100 hrs, indicating that SSCF is more susceptible to Cr poisoning than LSCF because the smaller ionic radius of Sm$^{3+}$
cannot retain Sr\(^{2+}\) in the lattice structure as well. The easy and fast Cr accumulation on the cathode surface for SSCF causes faster polarization resistance increase (shown in Figs. 2-5(b) and (c)) after its activation, compared with LSCF. For all the cathodes, very weak SrO\(_2\) peaks are detected due to the degradation of cathodes\(^\text{13,28}\).

![XRD patterns of (a) LSCF cathodes, (b) BSCF cathodes, and (c) SSCF cathodes at initial state and after 600 °C, 700 °C, 800 °C testing.](image)

**2.3.3 Fundamental cathode behaviors**

Based on the above results, the factors affecting the electrochemical performance of the cathodes can be summarized as follows:

- Lattice constant: Smaller lattice constant means larger electrical conductivity, leading to smaller ohmic resistance.
Stoichiometry: Stoichiometry affects the electrical conductivity and oxygen vacancy concentration. Higher oxygen vacancy usually means higher ionic conductivity. Stoichiometry also affects lattice constant and crystal structure stability. Usually, more atoms in A-site means smaller lattice constant.

Particle size: Smaller particle size means larger DPB and TPB, leading to smaller $R_p$.

Cr deposition: Cr deposition increases polarization resistance through formation of $\text{SrCrO}_4$ on LSCF and SSCF and $\text{BaCrO}_4$ on BSCF, which decrease their conductivity and oxygen vacancy. TPB and DPB are blocked by Cr deposition. SSCF is more prone to Cr deposition.

Temperature: Higher working temperature means faster cathode activation, microstructure evolution, and more Cr deposition, leading to faster increase of $R_p$. The peak conductivities for all three cathodes are around 600-700 °C.

The above five factors affect the electrochemical performance of the cathodes through conductivity, oxygen vacancy, TPB, and DPB. An illustration of their interrelationship is shown in Fig. 2-8. Lattice constant can be changed through elemental substitution, to a certain extent stoichiometry variation, and extraction of cations from the cathodes. Stable crystal structure is essential for high electrochemical performance. Particle size is usually determined by the synthesis temperature and the intrinsic properties of the material; smaller particle sizes increase TPB and DPB but may make the cathode more susceptible to degradation. Cr deposition decreases cathode performance through extraction of Sr for LSCF and SSCF and Ba for BSCF, forming poor conductive phases, especially for the LSCF and SSCF cathodes. Higher temperature accelerates initial cathode activation but also Cr deposition, leading to worse electrochemical performance for the cathodes in short term operation.
As explained above, besides cathode degradation, Cr deposition also decreases the electrochemical performance of cathodes. The Cr deposition process in the LSCF, BSCF, and SSCF systems can be expressed as follows:\textsuperscript{29}:

In the LSCF and SSCF systems (Sr segregation):

\[ CrO_3(g) + SrO(s) \rightarrow Cr - Sr - O(nuclei) \] (2-2)
\[ Cr - Sr - O(nuclei) + CrO_3(g) \rightarrow Cr_2O_3(s) \]  \hspace{1cm} (2-3)

\[ Cr_2O_3(s) + CrO_3(g) + SrO(s) \rightarrow SrCrO_4(s) \]  \hspace{1cm} (2-4)

In the BSCF system (Ba segregation):

\[ CrO_3(g) + BaO(s) \rightarrow Cr - Ba - O(nuclei) \]  \hspace{1cm} (2-5)

\[ Cr - Ba - O(nuclei) + CrO_3(g) \rightarrow Cr_2O_3(s) \]  \hspace{1cm} (2-6)

\[ Cr_2O_3(s) + CrO_3(g) + BaO(s) \rightarrow BaCrO_4(s) \]  \hspace{1cm} (2-7)

Based on the products of Cr deposition, BSCF is preferred than LSCF and SSCF as the cathode material since its reaction product has relatively higher conductivity. Moreover, a protective coating layer on the interconnect to inhibit Cr diffusion and lower working temperature are viable options for SOFCs.

Usually, initial stoichiometry can be controlled by the ratio of reaction precursors. The optimal stoichiometry is the tradeoff between conductivity and structure stability. Lattice constant is affected by compositions and stoichiometry. More atoms in A-sites lead to smaller lattice constant \(^ {30} \). Smaller lattice constant can lead to larger conductivity. Particle size is affected by many factors, such as synthesis method and temperature. Smaller particle size is beneficial for electrochemical performance. These factors play a major role on the initial cathode performance because Cr deposition is not significant at this point. At high temperature operation, Cr deposition is more significant and play a major role in the cathode performance. Also, stoichiometry, lattice constant, and particle size change with thermal treatment should be separately evaluated. Higher working temperature accelerates cathode activation and increases polarization resistance; however, the stabilized polarization resistance is smaller.

### 2.4 Conclusions

Three cathode materials, LSCF, BSCF, and SSCF, are compared for their electrochemical performance working at 600 °C, 700 °C, and 800 °C and the corresponding microstructure and phase changes. The electrical conductivity of LSCF is the highest while that of BSCF is the lowest across this temperature range. All the cathodes reach the maximal electrical conductivity at 600-700 °C. The BSCF cathode has the smallest polarization resistance at 600 °C, comparable to the SSCF cathode; the LSCF cathode has the smallest polarization resistance working at 700 °C; the SSCF cathode has the smallest polarization resistance working at 800 °C, comparable to the LSCF cathode. SrCrO\(_4\) forms on the LSCF and SSCF cathodes next to the interconnect after 100 hrs of
the thermal treatment. For the BSCF cathode, only BaCrO$_4$ is detected after working at 600-800 ºC for 100 hrs, which is related to the larger atomic radius of Ba$^{2+}$ ions. SSCF is more prone to chromium deposition than that of LSCF because of its smaller ionic radius.

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Chapter 3. LSCF Cathode Incorporated with SDC by Three Different Methods

Abstract

The incorporation of SDC into LSCF is carried out by three methods: mechanical mixing, infiltration, and dip coating. The effects of SDC on the electrochemical performance of the LSCF cathodes are studied by EIS at 800°C for 100 h. LSCF mechanically mixed with SDC as the cathode decreases the electrochemical performance of the half-cell; the LSCF cathode infiltrated with SDC offers faster activation and decreased resistance with thermal treatment time; and the LSCF cathode dip coated with SDC has the smallest polarization resistance. These cathodes also show clear microstructure differences at the cathode/interconnect interface after 100 hrs of thermal treatment. SrCrO$_4$ phase still forms on all the cathodes near the interconnect. Reactions between the mechanically mixed cathode and the YSZ electrolyte destroy the electrolyte. The influence of SDC catalyst on oxygen adsorption, dissociation, and incorporation is explained for each type of cathodes. Overall, dip coating method is recommended for incorporation of SDC into the LSCF cathode.

3.1 Introduction

There are many challenges for the commercial use of SOFCs. These include the high operating temperatures to improve the activities of the electrodes and the ionic conductivity of the electrolyte, as well as the degradation of cell materials because of the high temperature and long operating time. To make SOFCs commercially competitive, it is necessary to develop electrode materials with high activity and stability between 500-800°C.

LSCF is widely used for intermediate temperature SOFCs. Unfortunately, the development of LSCF cathode has been hindered by its performance degradation. Several possible degradation mechanisms have been proposed, such as the instability of LSCF material, the coarsening of LSCF particle, the reaction between the LSCF cathode and YSZ electrolyte, and the chromium poisoning from the interconnect. In addition, the oxygen reduction reaction is mainly confined to the electrode/electrolyte interface due to the relatively low ionic conductivity of LSCF, which results in low electrocatalytic activity. Considerable efforts have been devoted to improve the stability and electrocatalytic activity of LSCF cathode. For example, a SDC interlayer
on the YSZ electrolyte has been reported to enhance the stability of LSCF. Introduction of oxygen ion conducting phases is another option.

Rare earth doped ceria has been considered as one of the most promising electrolyte materials for intermediate temperature SOFCs because of its high ionic conductivity and low electronic conductivity. Also, doping rare earth oxide into ceria can slightly improve its mechanical properties. Among the various dopants, Gd$^{3+}$ and Sm$^{3+}$ doped ceria have been studied extensively owing to their higher conductivity and stability in reducing environments. This results from the small association enthalpy between the trivalent dopant cation and the oxygen vacancy as well as the optimum radii of the dopants. SDC is also incorporated into cathode materials to improve the stability of the cathodes. The ionic conductivity of SDC is as high as $1.7 \times 10^{-2}$ S cm$^{-1}$ at ~800 °C, much higher than that of LSCF. When introduced into the cathode, SDC can offset the low ionic conductivity of the cathode materials, promote the ionic exchange processes, and expand the electrochemically active area, such as TPBs. These permit electrochemical reactions to occur within the electrodes, thus reducing the polarization resistance.

There are many methods to incorporate SDC into the LSCF cathode, such as mechanical mixing and infiltration. The electrochemical performance of LSCF mixed with SDC showed small polarization resistance, even though SDC pellets or YSZ pellets coated by SDC were used as the electrolytes. Also, coating a porous LSCF cathode with a thin layer of SDC using a one-step infiltration process dramatically reduced the polarization of the LSCF cathode. However, neither of the approaches studied the long term performance of the cathodes.

### 3.2 Experimental procedures

#### 3.1.1 Chemicals

Ce(NO$_3$)$_3$·6H$_2$O were purchased from Alfa Aesar (Ward Hill, MA). The other precursors are the same as what used in Chapter 2.

#### 3.1.2 Synthesis of SDC powder

SDC powder was synthesized by a sol-gel method. First, stoichiometric amounts of Sm(NO$_3$)$_3$·6H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O (according to the molecular composition of the oxides) were mixed into water. EDTA and citric acid were used as the chelating agents. The molar ratio of total...
metal ions, EDTA, and citric acid was 1:1:2. The ammonium hydroxide was used to adjust the pH value of the solution to 6. Water was evaporated from the solution while stirring at 80 °C, creating transparent gels which were kept at 200 °C for 2 hrs and calcined at 800 °C for 4 h. The SDC powder was milled before use.

### 3.1.3 SDC incorporation into LSCF cathodes by mixture, infiltration, and dip coating

For the mechanical mixing of SDC and LSCF, 10 wt% of SDC and 90 wt% of LSCF were mixed by vibratory milling for 1 hr. The mixture was used as the cathode material and the procedures afterwards were the same as that of pure LSCF cathode.

Infiltration and dip coating were carried out on the screen printed LSCF cathodes which were sintered at 950 °C prior. The weight percentage of SDC was also kept at ~10 wt%. Aqueous nitrate solutions of SDC precursors with 0.25 mol L⁻¹ concentration were prepared by dissolving 0.5 mmol Sm(NO₃)₃·6H₂O and 2 mmol Ce(NO₃)₃·6H₂O in water. Propanol was added into water with a ratio of 0.6:1. Glycine was also added to the solution as a complexing agent. The ratio of metal ions and propanol was 1:1. 4 µL of the solution was then infiltrated into the porous LSCF cathode by using a microliter syringe to control the amount of SDC loading under vacuum. The half-cell was heated at 800 °C for 4 hrs to crystallize SDC.

The SDC sol for dip coating was prepared by 2 mmol diluted commercial ceria colloidal dispersion and 0.5 mmol Sm(NO₃)₃·6H₂O in 10 mL water. The LSCF cathode was completely dipped into the SDC sol for 3 mins and dried at room temperature. After removing the SDC sol extending the LSCF cathode, it was then heated at 600°C for 2 hrs. This cycle was repeated five times to increase the amount of SDC in the LSCF cathode to ~10 wt%.

### 3.1.4 Characterization

XRD (X’Pert PRO diffractometer, PANalytical B.V., EA Almelo, The Netherlands) analysis was employed to characterize the crystallinity of the cathodes after 100 hrs of thermal treatment. The microstructures of the cathodes before and after 100 hrs of thermal treatment were examined by a FESEM (LEO (Zeiss) 1550, Oberhochem, Germany), with a carbon layer coating applied before imaging. The cross section line scan was conducted by an environmental scanning electron microscope (ESEM, FEI Quanta 600 FEG, Hillsboro, USA) attached with an EDS module (BrukerAXS, MicroanalysisGmbH, Berlin, Germany).
3.3 Results and discussion

3.3.1 Electrochemical behaviors

Figs. 3-1(a), (b), (c) and (d) show the $R_\Omega$, $R_H$, and $R_L$ changes for half-cells with the pristine LSCF, LSCF mixed with SDC, LSCF infiltrated by SDC, and LSCF dip coated by SDC respectively. For the pristine LSCF cathode shown in Fig. 3-1 (a), the value of $R_\Omega$ increases slightly with thermal treatment time, from 0.9 Ω cm$^2$ to 1.3 Ω cm$^2$. The value of $R_H$ first increases from 0.8 Ω cm$^2$ to 1.2 Ω cm$^2$ after 20 hrs of the thermal treatment, then decreases to 0.1 Ω cm$^2$ at the end of the 100 hrs thermal treatment. Additionally, the value of $R_L$ increases tremendously, from 1.3 Ω cm$^2$ to 4.5 Ω cm$^2$. For the LSCF mixed with SDC cathode (Fig. 3-1 (b)), the value of $R_\Omega$ decreases from 4.2 Ω cm$^2$ to 2.4 Ω cm$^2$. The values of $R_H$ and $R_L$ range from in 4.2-7 Ω cm$^2$ and 5.4-7.6 Ω cm$^2$ respectively, which are much larger than that of the pristine LSCF cathode. For the LSCF infiltrated by SDC as the cathode (Fig. 3-1 (c)), the value of $R_\Omega$ decreases from 4.1 Ω cm$^2$ to 1.3 Ω cm$^2$. The value of $R_H$ almost remains constant at ~0.3 Ω cm$^2$. The value of $R_L$ first increases from 3.2 Ω cm$^2$ to 4.5 Ω cm$^2$, then decreases to 3.5 Ω cm$^2$. For the LSCF dip coated by SDC as the cathode (Fig. 3-1 (d)), the value of $R_\Omega$ increases from 1.1 Ω cm$^2$ to 1.5 Ω cm$^2$. The value of $R_H$ first remains almost constant at 0.1 Ω cm$^2$, then increases to 0.3 Ω cm$^2$. The value of $R_L$ first increases tremendously from 1.6 Ω cm$^2$ to 3.3 Ω cm$^2$ after 20 hrs of the thermal treatment, then increases slightly to 3.8 Ω cm$^2$, and then decreases slightly to 3.6 Ω cm$^2$. For all the half-cells, the values of $R_L$ are much higher compared to the values of $R_\Omega$ and $R_H$ throughout the thermal treatment.
Fig. 3-1. Half-cell ohmic resistance as well as high and low frequency polarization resistances for (a) pristine LSCF; and LSCF with SDC by (b) mechanical mixing, (c) infiltration, and (d) dip coating methods after different time of the thermal treatment.

Clearly, different methods of introducing SDC into the LSCF cathodes have a significant impact on the cathode electrochemical performance. This can be fundamentally linked to oxygen reduction activation and electronic/ionic conductivity of the LSCF cathode.

In order to compare the electrochemical performance of different half-cells, the polarization resistance (sum of $R_H$ and $R_L$) changes with thermal treatment time are shown in Fig. 3-2. The contrast is obvious. For the half-cell with the pristine LSCF, the polarization resistance increases all the time from 2.1 $\Omega$ cm$^2$ to 4.6 $\Omega$ cm$^2$. After 70 hrs of the thermal treatment, the increase is slower. For the LSCF mixed with SDC half-cell, the polarization resistance is the highest and fluctuates; it is larger than 10 $\Omega$ cm$^2$ for the entire 100 hrs thermal treatment process. For the half-cell with the LSCF infiltrated by SDC, the polarization resistance increases from 3.3 $\Omega$ cm$^2$ to 4.7 $\Omega$ cm$^2$ after 30 hrs of the thermal treatment. However, it decreases to 3.7 $\Omega$ cm$^2$ after that, being larger than that of the pristine LSCF cathode half-cell in the first 60 hrs of the thermal treatment and smaller than that after 60 hrs of the thermal treatment. For the half-cell with the LSCF dip coated by SDC, the polarization resistance increases quickly from 1.6 $\Omega$ cm$^2$ to 3.4 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment and then slowly increases to 3.9 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment. It is higher than that of the pristine LSCF cathode half-cell between 10 hrs and 30 hrs of the thermal treatment, but smaller than that for the rest of the testing time.
Fig. 3-2. Polarization resistance changes after different time of the thermal treatment.

Through the comparison of the polarization resistances from different half-cells, it can be seen that mixing SDC with LSCF as the cathode not only decreases the electrochemical performance but causes large impedance fluctuation, while infiltration or dip coating of SDC into LSCF improves the electrochemical performance. For long term cathode performance, both infiltration and dip coating of SDC into the LSCF cathode are feasible methods, even with the consideration of the ohmic resistance (Figs. 3-1(c) and (d)).

3.3.2 Microstructures of LSCF cathodes with SDC

To understand the electrochemical performance difference shown above, Fig. 3-3(a) shows the microstructure of the LSCF nanoparticles synthesized by the combustion method. The particle size is about 100 nm. The microstructure of SDC nanoparticles synthesized by the sol-gel method is shown in Fig. 3-3(b). The SDC particle size is about 40 nm, which is only used in the mixture method. Based on the particle size, the SDC particles should be able to mix with the LSCF particles or stay on the surface of the LSCF particles.

Fig. 3-3(c) shows the crystal structures of different LSCF-SDC half-cells after 100 hrs of the thermal treatment on the YSZ electrolytes. The XRD pattern of the synthesized SDC nanoparticles by the sol-gel method is also shown to identify the SDC phase in the half-cells. Face centered cubic
SDC phase is formed for the infiltration and dip coating samples. However, SrCrO$_4$ is detected after 100 hrs of the thermal treatment for all the cathodes. This means that even though LSCF and SDC are compatible, Cr from the interconnect still interacts with the LSCF cathode at all conditions as explained next.

![Microstructures of LSCF and SDC nanoparticles](image)

**Fig. 3-3.** Microstructures of (a) LSCF by the combustion method and (b) SDC nanoparticles by the sol-gel method; (c) XRD patterns of SDC particles, pure LSCF cathode, LSCF cathodes with SDC by mixing, infiltration, and dip coating methods.

Figs. 3-4(a) and (b) show the typical microstructures of the cathode/interconnect interface of the pure LSCF cathode before and after 100 hrs of the thermal treatment. Before the thermal treatment, the LSCF shows homogeneous microstructure with similar pore size among the LSCF...
particles, which is led by similar particle size, minimal agglomeration, and homogeneous microstructure. The particle size is the same as the LSCF particle size, ~100 nm, even though necking of the LSCF particles is prevalent. After 100 hrs of the thermal treatment, some larger particles appear on the LSCF surface, with sizes >1 µm. The relative elemental concentrations from spots 1 (large particles) and 2 (small particles) in Table 3-1 show that the relative Sr and Cr concentrations from larger particles are higher than those from smaller particles, indicating the formation of a SrCrO$_4$ phase (consistent with Fig. 3-3(c)). SrCrO$_4$ formation is common in Sr-containing cathodes and they preferentially distribute at the cathode/interconnect interface to compromise the cell performance. This cathode microstructure change can be correlated to the electrochemical performance shown in Fig. 3-1(a). First of all, the large particles are not electrochemically active and decrease oxygen vacancies and polarons in the cathode. This causes the LSCF cathode ohmic resistance to increase with the thermal treatment time. Second, SrCrO$_4$ formation leads to fewer DPBs between the cathode and the gas phase, then less O$_2$ is adsorbed and the low frequency resistance $R_L$ increases. This hinders the oxygen adsorption and dissociation as well as its diffusion on the cathode surface and thus increases the low frequency resistance $R_L$. The microstructure of the LSCF cathode bulk after 100 hrs of the thermal treatment are shown in Fig. 3-4(c). There is no noticeable change in the microstructure of the LSCF bulk, meaning that SrCrO$_4$ formation mainly occurs at the cathode/interconnect interface.
Fig. 3. Microstructures of the pure LSCF cathode: the cathode/interconnect interface (a) before and (b) after the thermal treatment; (c) LSCF bulk and EDS line scan after the thermal treatment.

Figs. 3-5(a) and (b) show the typical microstructures of the cathode/interconnect interface before and after the thermal treatment when the cathode is from LSCF mixed with SDC. Before the thermal treatment, the cathode microstructure is also uniform with pores. After 100 hrs of the thermal treatment, some larger particles appear, while the other particles remain the same size as the initial particles. These large particles are similar to those of the pure LSCF cathode; however, the top surface is much denser. Unexpectedly, the YSZ electrolyte becomes brittle and always fractures after 100 hrs of the thermal treatment. Even the color of the YSZ covered by the cathode is changed from white to black. We believe that reactions occur among YSZ, LSCF, and SDC. The EDS line scan in Fig. 3-5(c) also reveals the reactions, as Cr and Ce are detected on the YSZ side and Zr is detected on the cathode side. Moreover, only a very small amount of Sr is detected in the cathode bulk. The reactions most likely lead to the destruction of the YSZ electrolyte and increase ohmic resistance and polarization resistance as shown in Fig. 3-1(b). Fig. 3-5(c) shows huge microstructure changes (coarsened large grains) for the LSCF cathode bulk. There is no obvious boundary line between the YSZ and the LSCF. The EDS results (Table 3-1) from spots 3 (large particles) and 4 (small particles) demonstrate the enrichment of Sr and Cr in the large particles, which means that SrCrO$_4$ phase forms. However, since the involved species are the same for all the LSCF-SDC cathodes and the reaction with the YSZ electrolyte is only observed for this cathode, the exact mechanism is unclear.
Fig. 3-5. Microstructures of the LSCF cathode with SDC by mixing: the cathode/interconnect interface (a) before and (b) after thermal treatment; (c) cathode bulk microstructure and EDS line scan after the thermal treatment.

Table 3-1. Relative elemental concentrations from the locations shown in Figs. 3-4 to 3-7.

<table>
<thead>
<tr>
<th>No.</th>
<th>Atomic percent (%)</th>
<th>La</th>
<th>Sr</th>
<th>Co</th>
<th>Fe</th>
<th>Cr</th>
<th>Ce</th>
<th>Sm</th>
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<tr>
<td>1</td>
<td></td>
<td>21.56</td>
<td>24.71</td>
<td>7.31</td>
<td>31.25</td>
<td>15.18</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>25.02</td>
<td>20.78</td>
<td>8.49</td>
<td>35.91</td>
<td>9.82</td>
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<tr>
<td>3</td>
<td></td>
<td>13.68</td>
<td>29.08</td>
<td>4.71</td>
<td>21.17</td>
<td>27.71</td>
<td>2.54</td>
<td>1.13</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>21.97</td>
<td>15.19</td>
<td>6.91</td>
<td>32.57</td>
<td>18.73</td>
<td>3.49</td>
<td>1.15</td>
</tr>
<tr>
<td>5</td>
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<td>31.48</td>
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<td>20.85</td>
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</tr>
<tr>
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<td>25.97</td>
<td>11.68</td>
<td>25.09</td>
<td>15.05</td>
<td>4.13</td>
<td>1.29</td>
</tr>
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</table>
Figs. 3-6(a) and (b) show the typical porous microstructures of the cathode/interconnect interface before and after the thermal treatment when LSCF is infiltrated by SDC. Before the thermal treatment, the microstructure is homogeneous. After the infiltration with SDC, SDC uniformly distributes as a layer on the LSCF backbone. The SDC particle size is much smaller than that of the SDC particles used in the mixture method, which should increase the TPBs of the cathode. After 100 hrs of the thermal treatment, larger particles than those of the pure LSCF cathode appear, and the surface next to the interconnect become very dense with low porosity (Fig. 3-6(b)). EDS results (Table 3-1) from spots 5 (large particles) and 6 (small particles) also demonstrate the enrichment of Sr and Cr in the large particles. The microstructure of the cathode bulk (Fig. 3-6(c)) shows no noticeable change, which is similar to that of the pristine LSCF cathode. The SDC layer evolves into isolated small particles. EDS line scan shows that SDC is present in the cathode bulk, not just on the surface.
Fig. 3-6. Microstructures of the LSCF cathode with SDC by infiltration: the cathode/interconnect interface (a) before and (b) after the thermal treatment; (c) cathode bulk microstructure and EDS line scan after the thermal treatment.

Figs. 3-7(a) and (b) show the microstructure of the cathode/interconnect interface before and after the thermal treatment when the cathode is made from the porous LSCF dip coated by SDC. Fine SDC particles are deposited on the surface of the LSCF backbone. The SDC particle size is about 20 nm, smaller than that of the synthesized SDC particles by the sol-gel method. The microstructures of the SDC dip coated LSCF cathode, however, change significantly after 100 hrs of the thermal treatment (Fig. 3-7(b)). Few small particles are observed but the large particles coarsen together into a fully dense layer on the cathode surface. The microstructure of the cathode bulk (Fig. 3-7(c)) shows no noticeable change, which is also similar to that of the pristine LSCF cathode. EDS results (in Table 3-1) from a typical location 7 demonstrate the high concentration of Sr and Cr. EDS line scan also shows that SDC is in the cathode bulk, not just on the surface.
Based on the electrochemical performance and microstructures of the four different kinds of cathodes, we note that LSCF mixed with SDC as the cathode reacts with the YSZ electrolyte and leads to dramatically increased ohmic and polarization resistances. When SDC is introduced by infiltration, the resistances are large at the beginning of EIS test because the LSCF backbone is covered by the less electronically conductive SDC layer. With the thermal treatment, the continuous SDC layer transforms into isolated particles and the ohmic resistance decreases gradually. Additionally, the electrocatalytic property of SDC enlarges the TPBs and contributes to oxygen adsorption and dissociation, leading to a smaller low frequency resistance $R_L$. Moreover, SDC is beneficial for $O^{2-}$ incorporation into the electrode and transport in the cathode due to its larger ionic conductivity than that of LSCF. Hence $R_H$ is smaller than that of the pure LSCF cathode half-cell. When SDC is introduced into LSCF by the dip coating method, the SDC particles are discontinuous, and the transport of electrons between the LSCF and the interconnect is not compromised. Thus, the ohmic resistance is about the same as that of the half-cell with pure LSCF as the cathode. For its polarization resistance, it has the same change trend as that of the half-cell with SDC infiltration in the first 40 hrs of the thermal treatment but reverses after that, which is shown in Fig. 3-1. The increase in polarization resistance after 40 hrs of the thermal treatment is attributed to the more susceptibility to SrCrO$_4$ formation on the cathode top surface shown in Fig. 3-7(b). The large amount of SrCrO$_4$ formed at the cathode/interconnect interface contributes to the electrochemical performance degradation via the following two mechanisms: a) blocking of the electrochemically active sites (TPBs and DPBs), which decreases oxygen adsorption, dissociation and its surface diffusion, and as a result, $R_L$ deteriorates; b) the decomposition of the cathode, which deteriorates $R_\Omega$, $R_H$ and $R_L$. The second mechanism seems to have a small contribution to the total performance degradation because only a small portion of cathode was decomposed. Although the half-cell with dip coating method has the best performance during the 100 hrs of the thermal treatment, for longer term SOFC operation, a protective layer on the interconnect that can prevent the diffusion and evaporation of chromium oxide to the cathode is desirable.
Overall, the introduction of SDC into LSCF by infiltration and dip coating can enhance the electrochemical performance of the half-cells. In all three cathodes, LSCF dip coated with SDC is most susceptible to SrCrO$_4$ formation and pristine LSCF is least susceptible. However, LSCF dip coated with SDC has the best electrochemical performance since the formation of SrCrO$_4$ is not the only factor that deteriorates the half-cell electrochemical performance. For the mixed cathode, reactions with the electrolyte destroy the electrolyte and are a major contributor to the performance deterioration. For the LSCF cathode infiltrated with SDC, the resistances generally decrease with the thermal treatment even though the continuous SDC layer increases the ohmic and polarization resistances at the beginning of the thermal treatment. Therefore, from the long-term perspective, the LSCF cathode infiltrated with SDC would have better electrochemical performance than the LSCF cathode dip coated with SDC. The trends of ohmic and polarization resistances shown in Figs.3-1(c), (d) and 2 support this observation.

### 3.3.3 Fundamental process

When LSCF is used as the cathode material, the oxygen reduction reaction not only happens at the TPBs of the cathode, the electrolyte, and the gas phase, but also at the DPBs between the cathode and the gas phase due to its mixed ionic-electronic conductivity. Oxygen incorporation at the TPBs is much easier than that at the DPBs$^{26}$ and plays a dominating role in the electrochemical process. Therefore, the introduction of a second ionic conductor, such as SDC, should form new TPBs with the LSCF and the gas phase and improve the electrochemical performance of the cathode. The surface reaction, which is usually the limiting process and can be expressed as the following three steps$^{27}$, plays an important role in the electrochemical performance:

- **Adsorption**
  \[ O_{2,g} \rightarrow (O_2)_{ad,LSCF} \quad (3-1) \]

- **Dissociation**
  \[ \frac{1}{2} (O_2)_{ad,LSCF} + 2e_{LSCF}^{\prime} \rightarrow O_{ad,LSCF}^{\prime\prime} \quad (3-2) \]

- **Incorporation**
  \[ O_{ad,LSCF}^{\prime\prime} + V_{O,LSCF}^{-} \rightarrow O_{O,LSCF}^{\times} \quad (3-3) \]

where \( e_{LSCF} \) is the electron from the LSCF cathode, \( V_{O,LSCF}^{-} \) is the oxygen vacancy in the LSCF cathode, and \( O_{O,LSCF}^{\times} \) is the lattice oxygen in the LSCF cathode.
After the introduction of SDC, the incorporation step can be conducted with an oxygen vacancy from SDC, and the oxygen ion transfers to LSCF cathode through diffusion:

\[ O_{ad,\text{LSCF}}^{\dagger} + V_{\text{O,SDC}}^{\ddagger} \rightarrow O_{\text{SDC}}^{\ddagger} \]  

Equation (3-4)

The schematics for LSCF incorporated with SDC by the three methods are shown in Fig. 3-8 respectively. TPBs and oxygen ion transfer are also shown.

![Schematics of LSCF incorporated with SDC by (a) mixing; (b) infiltration; (c) dip coating methods.](image)

Fig. 3-8. Schematics of LSCF incorporated with SDC by (a) mixing; (b) infiltration; (c) dip coating methods.

For the LSCF-SDC mixed cathode, although SDC creates more LSCF-SDC-gas TPBs, the reaction with YSZ destroys the LSCF-YSZ-gas TPBs. The total oxygen reduction reaction sites
are actually decreased. This explains the decreased electrochemical performance compared with that of the pure LSCF cathode.

For the LSCF cathode with SDC by infiltration, there is no obvious reaction that can destroy the YSZ electrolyte. The LSCF-YSZ-gas TPBs are reserved and the total amount of the TPBs is increased. At the beginning, the LSCF surface is covered by the SDC layer, which limits the electron transfer from the cathode to the interconnect. With the thermal treatment, the continuous SDC coating layer transforms into isolated particles, electrons can directly transfer from the LSCF cathode to the interconnect, and the number of LSCF-SDC-gas TPBs increases gradually to enhance the electrochemical performance.

For the LSCF cathode with SDC by dip coating, there is no obvious reaction to destroy the YSZ electrolyte either. Also the total amount of the TPBs is increased. The isolated SDC particles do not block the contact between LSCF and the interconnect, so the ohmic resistance is very small at the beginning of the thermal treatment. This contributes to its best electrochemical performance. After 40 hrs of the thermal treatment, the largest amount of SrCrO$_4$ forms at the cathode/interconnect interface, increasing the polarization resistance, although SrCrO$_4$ also forms for all the other half-cells.

3.4 Conclusions

The incorporation of SDC into the LSCF cathodes is accomplished by mechanical mixing, infiltration, and dip coating methods. SDC incorporated by mixing destroys the YSZ electrolyte and thus decreases LSCF-YSZ-gas TPBs by reactions with YSZ. As a result, the electrochemical performance decreases compared with that of pure LSCF. The infiltrated SDC evolves from a continuous layer before the thermal treatment to isolated small particles after the thermal treatment, while the dip coated SDC evolves from particles before the thermal treatment to being covered by a SrCrO$_4$ layer on the surface after the thermal treatment. SDC incorporation into the LSCF cathode by infiltration leads to large ohmic and polarization resistances at the beginning of the EIS test, but they decrease with the thermal treatment because the LSCF-SDC-gas TPBs are gradually induced. The same process happens to the half-cell with the dip coating method, which has the best electrochemical performance. All the cathodes form a SrCrO$_4$ phase at the cathode/interconnect interface. Even though LSCF dip coated with SDC is most susceptible to form SrCrO$_4$ phase which leads to increase high frequency and low frequency resistances after 40
hrs of the thermal treatment, it still has the best electrochemical performance in 100 hrs of the thermal treatment.

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Chapter 4. Effect of SDC Block Layer on Cathode Degradation

Abstract

SDC block layer with thickness of ~3 µm is spin coated on the YSZ electrolyte to stop the reaction between the three cathodes and the YSZ electrolyte, leading to lower polarization resistances. It means the SDC layer can effectively inhibit the reaction between the cathodes and the electrolyte. For BSCF half-cell, the SDC block layer can also compensate the mismatch of the CTEs between the BSCF cathode and the YSZ electrolyte. The SDC block layer would not affect the microstructures of the LSCF, BSCF, and SSCF cathode.

4.1 Introduction

Several possible degradation mechanisms for cathode materials have been proposed, such as phase transformation 1, coarsening of particles 2, chromium poisoning from the interconnect 3, and reaction between the cathode and the electrolyte 4. Solid state reaction between the cathode and the YSZ electrolyte due to the elemental diffusion is widely accepted as the reason for the instability of perovskite cathode materials. The introduction of a SDC block layer can separate the cathode and the YSZ electrolyte and prevent reactions during both the cell fabrication and the cell operation. The ionic conductivity of SDC is as high as 8.4×10⁻² S cm⁻¹ around 800 °C, which is much higher than that of YSZ 5. Moreover, the CTE of SDC is ~12.2×10⁻⁶ K⁻¹ 6, which can decrease the difference in the TECs between the YSZ electrolyte and the cathodes.

4.2 Deposition of SDC block layer

The SDC block layer was deposited by spin coating. Before spin coating, a SDC suspension was prepared. NH₃·H₂O was used as the solvent with pH at 11. The solid content of SDC was 10 vol%, 6 wt% of peracetic acid (PAA, Thermo Fisher Scientific, Waltham, MA)) was added as a dispersant. Then the suspension was obtained after vibratory milling (8000 Mixer/Mill, SPEX SamplePrep, Metuchen, NJ) for 1 hr. The spin coating process was set at 500 rpm s⁻¹ for 5 s then at 3000 rpm s⁻¹ for 60 s. After the spin coated layer dried at room temperature, it was calcined at 1200 °C for 4 hrs with a heating and cooling rate of 2 °C min⁻¹. The second SDC layer was deposited with the same spin coating and calcination process.
4.3 Results and discussion

4.3.1 Microstructures

Fig. 4-1(a) shows the XRD patterns of the synthesized LSCF, BSCF, and SSCF powders. They have the same crystal structure, showing pure perovskite phase. In order to show the differences of the diffracted peaks in these three materials, the main (110) peaks are enlarged and shown in Fig. 4-1(b). They are located at $32.7^\circ$ for LSCF, $32^\circ$ for BSCF, and $33^\circ$ for SSCF, which demonstrates the peak shift from right to left for SSCF, LSCF, and BSCF. This means replacing La with Ba increases the lattice constant of the perovskite crystal structure; while replacing La with Sm decreases the lattice constant of the perovskite crystal structure. The (110) peak shift is due to the ionic radius difference from La$^{3+}$ (1.36 Å), Ba$^{2+}$ (1.61 Å), and Sm$^{3+}$ (1.24 Å) with the relationship of Ba$^{2+}$>La$^{3+}$>Sm$^{3+}$. The lattice parameters of the synthesized perovskite LSCF, BSCF, and SSCF are calculated to be 3.8666 Å, 3.9495 Å, and 3.8410 Å, respectively, which are smaller than the reported values, 3.8973 Å$^7$, 3.9495 Å$^8$, and 3.8547 Å$^9$ but are fairly close.

![Fig. 4-1. (a) XRD patterns of LSCF, BSCF, and SSCF particles and (b) the enlarged (110) peaks.](image)

The top surface microstructure and the cross section of the SDC block layer are shown in Fig. 4-2. According to the top surface shown in Fig. 4-2(a), the SDC layer is not fully dense, so two layers were spin coated to increase its thickness. The particle size of the SDC is about 40 nm and the pore size shown in the inset is also about 40 nm. The total thickness of the SDC block layer is about 3 µm (Fig. 4-2(b)).
Fig. 4-2. Top surface (a) and cross section (b) of one SDC block layer on the YSZ electrolyte. The inset in (a) shows the high resolution image of the top surface.

The microstructures of the cathode/interconnect interface after 100 hrs of the thermal treatment at 800°C are shown in Figs. 4-3(a)-(c). As expected, all the electrode layers are porous. For the LSCF cathode shown in Fig. 4-3(a), some larger particles appear after 100 hrs of the thermal treatment, while the other particles remain the same size as the initial particles. The large particle size is over 1 µm. For the BSCF cathode shown in Fig. 4-3(b), particles remain the same size as that before the thermal treatment, which is about 700 nm. However, the particles neck together because of the diffusion in the contact regions during the EIS test. For the SSCF cathode shown in Fig. 4-3(c), the microstructure change is similar to that of the LSCF cathode. Larger particles and smaller particles co-exist and the large particle size is even as large as 2 µm.
Fig. 4-3. Microstructures of the cathode/interconnect interface and cathode bulks after 100 hrs of the thermal treatment: (a) (d) LSCF, (b) (e) BSCF, and (c) (f) SSCF cathodes.

Through the comparison of the microstructures of the cathode/interconnect interface after 100 hrs of the thermal treatment at 800 °C, it is clear that the BSCF particles are more resistant to large particle formation than the LSCF and SSCF particles. The electrochemical performance of these cathodes would be affected by the changes in their microstructures. In order to distinguish the elemental changes from small particles to large particles, EDS is used to detect the relative elemental concentrations. The detected locations are shown in Figs. 4-3(a)-(c) and the relative elemental concentrations are shown in Table 4-1. For the LSCF and SSCF cathodes, the relative Sr and Cr concentrations from larger particles (1 and 5) are higher than those from smaller particles.
(2 and 6). The difference is especially obvious for Cr. This means that Sr and Cr are enriched in the larger particles, which is consistent with the results in Chapter 2 and Chapter 3. Surprisingly, for the BSCF cathode, because no coarsened particles are found at the cathode/interconnect interface, there is not much elemental concentration difference for the two random spots 3 and 4. It is possible that Ba$^{2+}$ has large enough atomic radius (1.61 Å) at the A sites in the BSCF perovskite structure, which can effectively accommodate the Sr$^{2+}$ ions and prevent the reaction of Sr$^{2+}$ with the poisonous CrO$_3$ vapor in the dry air environment used for the study.

Table 4-1. Relative elemental concentrations detected from the locations shown in Figs. 4-3(a)-(c).

<table>
<thead>
<tr>
<th>No.</th>
<th>Atomic percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La/Ba/Sm</td>
</tr>
<tr>
<td>1</td>
<td>22.04</td>
</tr>
<tr>
<td>2</td>
<td>24.56</td>
</tr>
<tr>
<td>3</td>
<td>22.42</td>
</tr>
<tr>
<td>4</td>
<td>25.64</td>
</tr>
<tr>
<td>5</td>
<td>17.46</td>
</tr>
<tr>
<td>6</td>
<td>22.94</td>
</tr>
</tbody>
</table>

The microstructures of the LSCF, BSCF, and SSCF cathode bulks after 100 hrs of the thermal treatment are shown in Figs. 4-3(d)-(f). There are few coarsened particles found. The microstructures of LSCF and SSCF are similar but considerably different from BSCF. This can be explained as follows. La and Sm are lanthanide and have very similar physical and chemical properties, such as close ionic radii (1.36 Å and 1.24 Å, respectively). Ba is not lanthanide and has much larger ionic radius (1.61 Å). Generally, smaller particles mean larger specific surface area and more double phase boundaries between the cathode and the gas phase. This is to say, as mixed ionic-electronic conductors for LSCF, BSCF, and SSCF, smaller particle size should improve oxygen adsorption area on the cathode. After 100 hrs of the thermal treatment, the particle sizes almost remain unchanged. This means that only some particles at the cathode/interconnect interface have grown for LSCF and SSCF.
4.3.2 Electrochemical behaviors

Figs. 4-4(a)-(c) shows the $R_\Omega$, $R_H$, and $R_L$ changes for the half-cells with LSCF, BSCF, and SSCF as the cathode without the SDC block layer respectively. For the LSCF cathode (Fig. 4-4(a)), the $R_\Omega$ value increases slightly with the thermal treatment time, from 0.9 $\Omega$ cm$^2$ to 1.3 $\Omega$ cm$^2$. The $R_H$ value first increases slightly from 0.8 $\Omega$ cm$^2$ to 1.2 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment, then decreases to 0.1 $\Omega$ cm$^2$ at the end of the thermal treatment. Additionally, the $R_L$ value increases drastically, from 1.3 $\Omega$ cm$^2$ to 4.5 $\Omega$ cm$^2$. For the BSCF cathode (Fig. 4-4(b)), the value of $R_\Omega$ is high at 3.1 $\Omega$ cm$^2$ and decreases gradually to 2.5 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment. The value of $R_H$ first decreases quickly from 1.4 $\Omega$ cm$^2$ to 0.7 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment, then almost stays flat at 0.7 $\Omega$ cm$^2$. In addition, the value of $R_L$ increases from 2.5 $\Omega$ cm$^2$ to 4.4 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment, then increases gradually to 4.9 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment. For the SSCF cathode (Fig. 4-4(c)), the value of $R_\Omega$ decreases from 3.5 $\Omega$ cm$^2$ to 2.0 $\Omega$ cm$^2$ after 30 hrs of the thermal treatment, then stays at that value until the end of the testing. The value of $R_H$ first increases from 0.7 $\Omega$ cm$^2$ to 1.8 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment, then decreases to 0.2 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment. Additionally, the value of $R_L$ increases significantly, from 1.4 $\Omega$ cm$^2$ to 4.3 $\Omega$ cm$^2$. 

![Graphs showing $R_\Omega$, $R_H$, and $R_L$ changes for LSCF, BSCF, and SSCF cathodes.](image)
Fig. 4-4. Ohmic, high frequency, and low frequency polarization resistance changes for (a) (d) LSCF, (b) (e) BSCF, and (c) (f) SSCF cathodes without and with the SDC block layer after different time of the thermal treatment.

Fig. 4-3 shows that LSCF and SSCF have much smaller particle sizes than BSCF. This should contribute to higher $R_\Omega$ for the corresponding cathodes. However, intrinsically LSCF and SSCF have higher electrical conductivities than BSCF. Most importantly, the mismatch of CTEs between BSCF and YSZ causes poor contacts (Fig. 4-5(b)) and thus larger resistance than that of the LSCF/SSCF cathode half-cell. Figs. 4-4(a)-(c) also shows that the low frequency polarization resistance changes of LSCF are similar to that of SSCF, but different from that of BSCF. This is consistent with the microstructure changes of the cathodes shown in Fig. 4-3. For the LSCF and SSCF cathodes, it seems that the overall process of $O_2^-$ incorporation and transport is easier than that in the BSCF cathode. The $R_H$ of the LSCF and SSCF cathodes is smaller than that of the BSCF.
cathode after the thermal treatment. This observation is inconsistent with the ionic conductivities and atomic radii. It is possible that the dominating influence is from the $O^{2-}$ incorporation in the cathodes.

The half-cells with the SDC block layers are also measured by EIS and the deconvoluted resistances are shown in Figs. 4-4(d)-(f). For the LSCF cathode (Fig. 4-4(d)), the value of $R_{\Omega}$ decreases all the time, from 1.5 $\Omega$ cm$^2$ to 1.3 $\Omega$ cm$^2$. Compared with the resistance of the LSCF cathode without the SDC block layer, the change trend of $R_{\Omega}$ is reversed, although the value for the sample with the SDC layer is slightly higher than that of the sample without the SDC layer. At the end of the 100 hrs thermal treatment, they are the same at 1.3 $\Omega$ cm$^2$. The value of $R_H$ first increases from 0.5 $\Omega$ cm$^2$ to 0.9 $\Omega$ cm$^2$ after 60 hrs of the thermal treatment, then decreases to 0.5 $\Omega$ cm$^2$. The obvious bump of $R_H$ without the SDC layer shown in Fig. 4-4(a) from the beginning to 50 hrs of the thermal treatment does not appear here. The SDC layer stabilizes the $O^{2-}$ incorporation and transport process, at least near the cathode/electrolyte interface, even though it does not improve the process. Additionally, the value of $R_L$ first decreases slightly from 2.2 $\Omega$ cm$^2$ to 2.1 $\Omega$ cm$^2$ after 20 hrs of the thermal treatment, then increases to 3.5 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment, which is much smaller than that of the half-cell without the SDC layer. This means that the SDC layer is conducive to the oxygen adsorption and dissociation as well as its surface diffusion near the cathode/electrolyte interface even though such effect diminishes with the thermal treatment time.

Fig. 4-4(e) shows the resistance changes of the BSCF cathode. The value of $R_{\Omega}$ decreases from 2.3 $\Omega$ cm$^2$ to 1.7 $\Omega$ cm$^2$ and the value of $R_H$ decreases from 0.6 $\Omega$ cm$^2$ to 0.1 $\Omega$ cm$^2$ after 100 hrs of the thermal treatment. $R_L$ increases from 1.6 $\Omega$ cm$^2$ to 3.6 $\Omega$ cm$^2$. Compared with Fig. 4-4(b), all the resistances of the half-cell with the SDC layer (Fig. 4-4(e)) are smaller than those of the half-cell without the SDC layer. The SDC layer effects on the ohmic resistance, cathode oxygen reduction, and ionic transport process can be explained similarly.

For the SSCF cathode shown in Fig. 4-4(f), the value of $R_{\Omega}$ decreases from 2.4 $\Omega$ cm$^2$ to 1.7 $\Omega$ cm$^2$, which is slightly smaller than that of the half-cell without the SDC layer. Also, the value of $R_H$ decreases slightly from 0.6 $\Omega$ cm$^2$ to 0.4 $\Omega$ cm$^2$, and is more stable than that of the half-cell without the SDC layer (Fig. 4-4(c)). There is no bump from the beginning to 40 hrs of the thermal treatment. For the value of $R_L$, it almost linearly increases from 1.0 $\Omega$ cm$^2$ to 2.6 $\Omega$ cm$^2$ after 40
hrs of the thermal treatment, then to $3.0 \ \Omega \ \text{cm}^2$, which is smaller than that of the sample without the SDC layer. Overall, the SDC layer remains beneficial to reduce the ohmic resistance and facilitate the cathode oxygen reduction and ionic transport process.

To compare the electrochemical performance of different half cells, the polarization resistance (sum of $R_H$ and $R_L$) changes with the thermal treatment time are shown in Fig. 4-5. For the LSCF cathode without the SDC layer (Fig. 4-5(a)), the polarization resistance increases from $2.2 \ \Omega \ \text{cm}^2$ to $4.6 \ \Omega \ \text{cm}^2$. For the half cell with the SDC layer, it decreases from $2.8 \ \Omega \ \text{cm}^2$ to $2.6 \ \Omega \ \text{cm}^2$ after 20 hrs of the thermal treatment, then increases to $4 \ \Omega \ \text{cm}^2$. For the BSCF cathode without the SDC layer (Fig. 4-5(b)), the polarization resistance fluctuates. The smallest value is $3.8 \ \Omega \ \text{cm}^2$ and the largest value is $5.8 \ \Omega \ \text{cm}^2$. For the half cell with the SDC layer, it increases from $2.2 \ \Omega \ \text{cm}^2$ to $3.8 \ \Omega \ \text{cm}^2$, then decreases to $3.6 \ \Omega \ \text{cm}^2$. For the SScF cathode without the SDC layer (Fig. 4-5(c)), the polarization resistance increases from $2.2 \ \Omega \ \text{cm}^2$ to $3.9 \ \Omega \ \text{cm}^2$, then decreases to $3.7 \ \Omega \ \text{cm}^2$, then increases to $4.5 \ \Omega \ \text{cm}^2$. For the half cell with the SDC layer, it increases from $1.6 \ \Omega \ \text{cm}^2$ to $3.4 \ \Omega \ \text{cm}^2$. Overall, the polarization resistances of the half-cells with the SDC layer are smaller than that of the half-cells without the SDC layer, especially for the BSCF cathode. The introduction of the SDC block layer contributes to the oxygen reduction reaction as SDC is known as an electrocatalyst. Because SDC has a higher ionic conductivity than YSZ, the generated $O^{2-}$ ions from the three phase boundaries can be quickly transferred to the electrolyte.
Fig. 4-5. Polarization resistance changes of (a) LSCF cathode, (b) BSCF cathode, and (c) SSCF cathode after different time of the thermal treatment.

4.3.3 Fundamental process

The cross sections and EDS line scans of the cathode/electrolyte interface are presented in Figs. 4-5(a)-(c). There was no noticeable change in the microstructure of the LSCF layer except for the thin layer on the top surface next to the interconnect. The thickness of the thin layer is about 3 µm. Compared with the top surface shown in Fig. 4-3(a), the relative dense layer on the top surface consists of both large and small particles. The large particles have been demonstrated to be SrCrO$_4$ phase $^{10-11}$. The same is true for the SSCF cathode shown in Fig. 4-5(c). One consequence of Cr deposition is removal of Sr from the perovskite crystal structure by the formation of SrCrO$_4$, which leads to decreases in oxygen vacancies and polarons and thus electrochemical performance. For the BSCF cathode (Fig. 4-5(b)), however, there is no such thin layer shown on the top surface, which is consistent with the top surface microstructure of the BSCF cathode shown in Fig. 4-3(b).
Fig. 4-6. Cross section SEM images and corresponding EDS line scan of (a) (d) LSCF, (b) (e) BSCF, and (c) (f) SSCF cathodes without and with the SDC block layer after 100 hrs of the thermal treatment.

The LSCF and SSCF cathodes have good contact with the YSZ electrolyte. For the BSCF cathode, however, there is a small gap between the BSCF cathode and the YSZ electrolyte as shown in Fig. 4-6(b). As mentioned before, this is due to the mismatch of CTEs between BSCF and YSZ, which are $20 \times 10^{-6}$ K$^{-1}$ and $10.8 \times 10^{-6}$ K$^{-1}$ respectively $^{12-13}$. For LSCF and SSCF, their TECs are about $15 \times 10^{-6}$ K$^{-1}$ and $16 \times 10^{-6}$ K$^{-1}$ respectively $^{9,14}$, which are more comparable with that of YSZ. The poor contact of the BSCF cathode with the YSZ electrolyte is one of the reasons for the larger resistance shown in Fig. 4-4(b).

The cross sections and EDS line scans of the electrolyte/block layer/cathode tri-layer are given in Figs. 4-5(d)-(f). The microstructures of the cathodes are not affected by the SDC layer. The LSCF and SSCF cathodes near the interconnect are still covered by a relatively dense thin layer while this is absent for the BSCF cathode, mainly because Cr-related SrCrO$_4$ formation is a result of the cathode-interconnect interaction. The SDC block layer can effectively prevent the contact of the cathodes with the electrolyte and decrease the elemental diffusion between them. For the BSCF cathode shown in Fig. 4-5(e), no gap is found in the BSCF/SDC/YSZ structure. This means
that the SDC block layer decreases the mismatch of the TECs between BSCF and YSZ. The reason is that the TEC of SDC is \(12.2 \times 10^{-6} \text{ K}^{-1}\), in-between those of BSCF and YSZ.

### 4.4 Conclusions

The deposition of the SDC block layer can effectively prevent the contact of the cathode materials and the electrolyte, resulting in better electrochemical performance. The improvement of the electrochemical performance is most obvious for the BSCF cathode, because the SDC block layer can not only prevent the contact of the cathode and the electrolyte but also decrease the mismatch of TECs between BSCF and YSZ. The SDC block layer does not affect the microstructures of the LSCF, BSCF, and SSCF cathode after 100 hrs of the thermal treatment.

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Chapter 5. Co$_x$Fe$_{1-x}$ Oxide Coatings on AISI 441 Interconnect for Solid Oxide Fuel Cells

Abstract

In this chapter, CoFe alloy coatings with Co:Fe ratios of 9:1, 8:2, 7:3, 6:4, and 5:5 are deposited by electrodeposition and then oxidized to Co$_x$Fe$_{1-x}$ oxide coatings with a thickness of ~6 µm as protective layers on the interconnect. The ASR of the coated interconnect increases with the Fe content. Higher Co content oxide coatings are more effective in limiting the growth of the chromia scale while all coatings are effective in inhibiting Cr diffusion and evaporation. With the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect, the electrochemical performance of the SSCF cathode is improved. Only 1.54 at% of Cr is detected on the surface of the Sm$_{0.5}$Sr$_{0.5}$Co$_{0.2}$Fe$_{0.8}$O$_3$ cathode while no Cr is detected 0.66 µm or more into the cathode. Co$_x$Fe$_{1-x}$ oxide coatings are promising candidates for solid oxide fuel cell interconnects with the advantage of using existing cathode species for compatibility and performance enhancement.

5.1 Introduction

The interconnect is a critical part in SOFCs, which connects individual cells, provides electrical conductivity, and separates fuels and oxidizing gases. Usually, ceramic and metal alloy can both work as the interconnect. Ceramic interconnect has high performance, but it’s expensive. Compared with ceramic interconnect, metal alloy is much easier to fabricate and cheaper, both of which decrease the manufacturing cost. Besides, Cr-containing metallic alloys have higher electrical conductivity and excellent thermal conductivity. Cr-containing stainless steels, such as AISI 441 and Crofer 22 APU, have high thermal conductivity and similar CTE to the electrodes and are the most promising interconnect candidates. However, the long-term use of the Cr-containing stainless steels in SOFCs is still challenged by two major issues. First, the electrical conductivity is almost always lowered due to oxidation. Second, Cr diffusion and evaporation through the formation of volatile Cr species, such as CrO$_3$ and CrO$_2$(OH)$_2$, poison the cathode and block the ORR sites.

The oxidation when exposed to oxygen and chromium evaporation to poison cathode are two major challenges. The growth of the oxide scale obeys the parabolic law:

$$
\varepsilon^2 = k_p t = \frac{k_g}{(y\rho)^{\frac{1}{2}}} = \frac{t}{d^2}k_g^0 e^{-E_{OX}/kT}
$$

(5-1)
where, $\varepsilon$ is the oxide scale thickness at time $t$; $k_p$ and $k_g$ are the rate constants in thickness and weight respectively; $\gamma$ is the weight fraction of oxygen in the oxide; $\rho$ is the oxide density; $E_{OX}$ is the activation energy for the oxide scale growth; $K$ is the Boltzmann constant and $T$ is the absolute temperature

The parabolic law can be used to calculate the thick and homogeneous oxide scale. Low $k_p$ metallic alloy is preferred. In order to decrease oxide scale growth rate and inhibit chromium diffusion and evaporation, efforts have been focused on coating layers on metal alloys.

The application of a protective coating on the stainless steel surface has been demonstrated to lower the rate of ASR increase. Low $k_p$ metallic alloy is preferred. In order to decrease oxide scale growth rate and inhibit chromium diffusion and evaporation, efforts have been focused on coating layers on metal alloys.

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A (La,Sr)CrO$_3$ coating was reported to have good adhesion to the interconnect and acceptable ASR. Spinel materials are also promising protective layers because they have relatively high electrical conductivity and can be doped with a wide range of transition metal cations to improve their performance. For example, Co$_3$O$_4$ was reported as protective coatings for metallic interconnects even though the accumulative chromia scale between the substrate and the coating layer was thick and the electrical conductivity was relatively low (6.7 S cm$^{-1}$ at 800 ºC). In addition, the Co$_3$O$_4$ coating is unstable after long term operation at high temperatures, voids were reported within the grains. Worse yet, the CET of Co$_3$O$_4$ is $\sim$40x10$^{-6}$ K$^{-1}$ at 800 ºC, which is almost three times larger than that of AISI 441 steel. Doping Fe in the Co$_3$O$_4$ spinel is beneficial. (Mn,Co)$_3$O$_4$, (Cu,Mn)$_3$O$_4$, and (Cu, Mn,Co)$_3$O$_4$ have been demonstrated as promising protective coatings because of their high conductivity, stability, and oxidation resistance, even though Mn is not desired for Mn-free cathodes. Fortunately, the CTE of spinel can be adjusted by doping of species that are intrinsic to the cathode. For example, CoFe$_2$O$_4$ spinel has a CTE of 19x10$^{-6}$ K$^{-1}$ at 800 ºC, which is much closer to that of AISI 441.

A number of coating techniques have been utilized to deposit coating layers, including sputtering, plasma spray, physical vapor deposition, slurry coating, screen painting, and electroplating with thermal oxidation. Among various reported coating techniques, electroplating is a simple and cost-effective approach, and can deposit dense structures. The electroplated metallic layer can be oxidized to produce a dense oxide layer. Desirably, Co and Fe
can be co-deposited because of their relatively close standard electrode potentials (-0.28 V_{SCE} for Co^{2+}/Co and -0.44 V_{SCE} for Fe^{2+}/Fe). In addition, coating compositions can be controlled by adjusting the corresponding ion concentrations in the electroplating bath solution and deposition temperature. However, the study of Fe-doped Co$_3$O$_4$ has been mainly focused on the CoFe$_2$O$_4$ phase. Systematic study of the Co to Fe ratio effect on the protective coatings has not been reported yet.

To address the interconnect stability needs, especially in light of the acceptance of the new generation Co- and Fe-containing cathodes, in this chapter CoFe alloy coatings with the Fe content from 10 at% to 50 at% were electroplated followed by oxidation at 800 ºC for 5 hrs. The electrical property of the coated and bare interconnects was assessed via ASR measurement at 800 ºC. The oxidation behavior was evaluated based on the chromia scale thickness between the coating layer and the steel substrate. Cr diffusion in the coating layer was investigated using EDS and X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Kanagawa, Japan) depth profiling. The effect of the coating layer on the electrochemical performance of the interconnect/SSCF cathode/YSZ electrolyte half-cell was investigated using EIS at 800 ºC for 100 hrs.

5.2 Experimental procedures

5.2.1 Chemicals

CoSO$_4$·H$_2$O, CoCl$_2$·6H$_2$O, FeCl$_2$·6H$_2$O, and H$_3$BO$_3$ were purchased from Alfa Aesar (Ward Hill, MA). The other precursors are the same as what used in Chapter 2.

5.2.2 Electrodeposition of CoFe alloy

The Co$^{2+}$ and Fe$^{2+}$ solutions consisted of CoSO$_4$·6H$_2$O, CoCl$_2$·6H$_2$O, FeCl$_2$·6H$_2$O, and H$_3$BO$_3$. The details for the five solutions with the Co:Fe molar ratios of 9:1, 8:2, 7:3, 6:4, and 5:5 are shown in Table 5-1. The pH was adjusted to 3.6 using a HCl solution. A fine polished AISI 441 steel with a size of 15 mm×10 mm×1 mm was used as the cathode during the electrodeposition. It was connected to the negative port of a power source with a 4 mA·cm$^{-2}$ constant current density. The process continued for 35 min at 40 ºC. The coated steel was then oxidized at 800 ºC for 5 hrs to form CoFe oxide coatings.

Table 5-1. Compositions of the five solutions used for CoFe electrodeposition.
<table>
<thead>
<tr>
<th>Fe/(Fe+Co) (at%)</th>
<th>CoSO₄·6H₂O (mM)</th>
<th>CoCl₂·6H₂O (mM)</th>
<th>FeCl₂·6H₂O (mM)</th>
<th>H₃BO₃ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>10</td>
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</tr>
<tr>
<td>50</td>
<td>15</td>
<td>10</td>
<td>25</td>
<td>10</td>
</tr>
</tbody>
</table>

5.2.3 ASR measurements

ASR measurements were performed using a four-point probe method, whose schematic is shown in Fig. 5-1. All samples, including the bare interconnect, were run at the same conditions. An interconnect specimen (with or without the coating) was placed between two Pt meshes. A Pd-Ag paste was used to ensure good electrical contact between the interconnect and the meshes. The assembly was then put in a horizontal furnace at 800 °C for 100 hrs. A constant current density of 500 mA·cm⁻² was applied to mimic the actual cell operation and resistances were obtained based on a voltage scan from 0 to 3 V. The measurement was taken every half hour. ASR values were then calculated using the resistance multiplied by the area covered by the paste and divided by two due to the symmetrical test design:

\[
ASR = \frac{1}{2} R \times S
\]

Fig. 5-1. Schematic of four-probe method.

5.3 Results and discussion

5.3.1 Effect of bath temperature on Fe content in the coating layers

The compositions of the electroplated CoFe layers from three different bath solutions at 25 °C, 40 °C, and 55 °C were determined by EDS and plotted as a function of the Fe atomic
concentration in the bath solutions as shown in Fig. 5-2. When the CoFe layer is deposited at room temperature, the Fe contents in the coating layer are 7.5 at%, 15.5 at%, and 37.4 at%, corresponding to the Fe contents of 10 at%, 20 at%, and 50 at% respectively in the baths. The Fe contents in the coating layers deviate significantly from their original contents. When the bath temperature is increased to 40 ºC, the Fe contents in coating layer are 10.0 at%, 19.4 at%, and 45.5 at% respectively, much closer to their original contents in the baths, especially for the coating layer with lower Fe contents. The effect of temperature on the Co to Fe ratio in the coatings can be explained on the basis of two dominant factors, polarization and diffusion. In a typical alloy co-deposition system, the more noble metal (Co in the case) is preferentially deposited; polarization and diffusion both increase the content of the more noble metal. This explains why the Fe content (less noble) deviates from the bath composition at 25 ºC electrodeposition temperature. Higher temperature increases the concentration of all metal ions in the diffusion layer by increasing the rates of diffusion and convection. At 40 ºC, both polarization and diffusion should enhance the deposition of the more noble metal (Co). However, with further bath temperature increase, opposite effects from polarization and diffusion have been reported in anomalous co-deposition systems; polarization increases the content of the more noble metal while diffusion decreases it. The tradeoff between polarization and diffusion determines the composition of the coatings. This explains why when the bath temperature is raised to 55 ºC, the Fe contents in the coating layer are 11.3 at%, 19.3 at%, and 45.7 at% respectively, without much Fe content change compared to that at 40 ºC, indicating that the temperature effect on the composition of the coatings is not significant when the bath temperature is higher than 40 ºC. Therefore, the CoFe coating layers are all electrodeposited at 40 ºC in the following study.
5.3.2 Electrodeposited layer analysis before and after oxidation

The XRD patterns of the deposited CoFe coatings after oxidation at 800 °C for 5 hrs are shown in Fig. 5-3(a). The peaks of the steel substrates can still be detected. The crystal structures of the CoFe oxide coatings change gradually with the increase of the Fe content in the coating layers. For the Co$_{0.9}$Fe$_{0.1}$ oxide coating, strong Co$_3$O$_4$ peaks are detected with minor CoFe$_2$O$_4$ peaks. For the Co$_{0.8}$Fe$_{0.2}$ oxide coating, the intensity of the Co$_3$O$_4$ peaks decreases and that of the CoFe$_2$O$_4$ peaks increases. This trend continues for the Co$_{0.7}$Fe$_{0.3}$ oxide coating. For the Co$_{0.6}$Fe$_{0.4}$ oxide and Co$_{0.5}$Fe$_{0.5}$ oxide coatings, the Co$_3$O$_4$ peaks completely disappear and only CoFe$_2$O$_4$ phase exists in the coatings. Meanwhile, weak Fe$_2$O$_3$ peaks are detected in the Co$_{0.8}$Fe$_{0.2}$ oxide, Co$_{0.7}$Fe$_{0.3}$ oxide, Co$_{0.6}$Fe$_{0.4}$ oxide, and Co$_{0.5}$Fe$_{0.5}$ oxide coatings.

The phase concentrations of Co$_3$O$_4$, CoFe$_2$O$_4$, and Fe$_2$O$_3$ are calculated based on the XRD peak areas in Fig. 5-3(a) and plotted as a function of the initial Fe content, as shown in Fig. 5-3(c). At 10 at% Fe, Co$_3$O$_4$ takes up 73.9 wt% in the Co$_{0.1}$Fe$_{0.9}$ oxide coating and CoFe$_2$O$_4$ takes up the remaining 26.1 wt%. Then the Co$_3$O$_4$ content decreases and the CoFe$_2$O$_4$ and Fe$_2$O$_3$ contents increase. At 50 at% Fe, no Co$_3$O$_4$ is detected in the Co$_{0.5}$Fe$_{0.5}$ oxide coating while CoFe$_2$O$_4$ takes up to 92.2 wt% and Fe$_2$O$_3$ increases to 7.8 wt%. The main peak (311) for the CoFe$_2$O$_4$ phase is enlarged and shown in Fig. 5-3(b). The peak intensity increases with the Fe content. Left shift of
the peak is observed, especially for the coatings with a higher Fe content (30 at%, 40 at%, and 50 at%). This means that the Fe content in the coatings affects the CoFe$_2$O$_4$ crystal structure. The lattice constant of cubic CoFe$_2$O$_4$ is calculated to be 8.3259±0.0026 Å, 8.3302±0.0019 Å, 8.3359±0.0022 Å, 8.3581±0.0017 Å, 8.3815±0.0037 Å respectively based on Fig. 5-3(b). This means that higher doping of Fe makes the peaks shift more from cubic Co$_3$O$_4$ (8.1514±0.0021 Å) to cubic Fe$_3$O$_4$ (8.4242±0.0028 Å). It should be pointed out that the CoFe$_2$O$_4$ content increase has a significant impact on the coating performance. The electrical conductivity of CoFe$_2$O$_4$ is reported to be 0.85 S cm$^{-1}$, which is much lower than that of pure Co$_3$O$_4$ (6.7 S cm$^{-1}$). More CoFe$_2$O$_4$ phase in the coating would decrease its electrical conductivity. Also, we believe the electrical conductivity of CoFe$_2$O$_4$ decreases with the increase of its lattice constant because larger radius leads to lower conductivity in the same crystal structure and the radius of Fe$^{3+}$ is larger than that of Co$^{3+}$. Co$_3$O$_4$ and CoFe$_2$O$_4$ are p-type semiconductors and their electrical conductivities are achieved by the electron hopping. Smaller ions, e.g., Co$^{3+}$ has a smaller resistance to electron transport than larger ions, e.g., Fe$^{3+}$ in the same crystal structure. The specific effect can be seen in Table 5-2. In addition, the continuous increase of the Fe$_2$O$_3$ content should significantly decrease the electrical conductivity of the coating because its electrical conductivity is as low as $\sim 10^{-2}$ S cm$^{-1}$ at 800 °C.
At the lowest Fe content, the microstructure of the electrodeposited Co$_{0.9}$Fe$_{0.1}$ coating layer before oxidation is shown in Fig. 5-4(a). The coating layer is porous with mesh structures. After oxidation at 800 °C for 5 hrs, the Co$_{0.9}$Fe$_{0.1}$ oxide coating shows dense polycrystalline structures, shown in Fig. 5-4(c). The oxidization of Co$_{0.9}$Fe$_{0.1}$ alloy causes volume expansion due to the lower densities for the oxides (Co$_3$O$_4$, CoFe$_2$O$_4$, Fe$_2$O$_3$) than the metals (Co, Fe). The volume expansion transforms the porous coating into a fully dense structure with an average grain size of about 200 nm. At the highest Fe content (the Co$_{0.5}$Fe$_{0.5}$ coating), several morphologies appear before oxidation, including cauliflowers, tetrahedral, and crosses, as shown in Fig. 5-4(b). This is different from that of the Co$_{0.9}$Fe$_{0.1}$ coating shown in Fig. 5-4(a), because Co, CoFe alloy, and Fe co-exist in the Co$_{0.5}$Fe$_{0.5}$ coating while only Co and Fe co-exist in the Co$_{0.9}$Fe$_{0.1}$ coating. After oxidation at 800 °C for 5 hrs, however, the microstructure is similar to that of the Co$_{0.9}$Fe$_{0.1}$ oxide coating except that some discrete, bright clusters form on the surface, as shown in Fig. 5-4(d). The bright clusters are characterized to be Fe$_2$O$_3$ particles by EDS mapping. Due to the low conductivity of Fe$_2$O$_3$, the conductivity of the Co$_{0.5}$Fe$_{0.5}$ oxide coating is compromised as shown in Table 5-2. Nonetheless, the dense coatings are expected to prevent oxygen gas inward diffusion, which should reduce the oxidation of the steel substrate and the formation of volatile Cr species. The thickness
of all the coatings after oxidation is controlled at ~6 µm, which has been confirmed by the SEM cross section examination.

![Fig. 5-4. Surface morphologies of the coatings: (a) (c) Co_{0.9}Fe_{0.1}; (b) (d) Co_{0.5}Fe_{0.5}, at as-deposited state and after oxidation at 800 °C for 5 hrs respectively.](image)

**5.3.3 ASR measurements**

ASR is an effective parameter to compare the coating layer properties since the electrical resistance of the un-oxidized steel is negligible compared with the coating layer. An important requirement for the protective coating on the interconnect is low ASR. Fig. 5-5 shows the ASR comparison of the bare steel and the Co_{x}Fe_{1-x} oxide coated steels. The ASR of the bare interconnect increases from 0.9 mΩ cm² to 13.7 mΩ cm² after 100 hrs of the ASR testing. For the Co_{0.9}Fe_{0.1} oxide coated interconnect, the ASR increases from 2.0 mΩ cm² to 7.6 mΩ cm², similar to that of the Co_{0.8}Fe_{0.2} oxide coated interconnect (2.0 mΩ cm² to 8.3 mΩ cm²) and that of the Co_{0.7}Fe_{0.3} oxide coated interconnect (2.3 mΩ cm² to 10.9 mΩ cm²). However, the ASR of the Co_{0.6}Fe_{0.4} oxide coated interconnect increases from 4.0 mΩ cm² to 13.8 mΩ cm². For the highest Fe content...
coating, Co$_{0.5}$Fe$_{0.5}$ oxide, its ASR increases from 7.5 mΩ cm$^2$ to as high as 31.4 mΩ cm$^2$. It is obvious that the ASR increases with the Fe content in the coating. The ASR of the Co$_{0.9}$Fe$_{0.1}$, Co$_{0.8}$Fe$_{0.2}$, and Co$_{0.7}$Fe$_{0.3}$ oxide coated interconnects are smaller than that of the bare interconnect due to their relatively small initial ASR and low increasing rates; the ASR of the Co$_{0.6}$Fe$_{0.4}$ oxide coated interconnect is comparable to that of the bare interconnect, but its increasing rate is still lower than that of the bare interconnect; the ASR of the Co$_{0.5}$Fe$_{0.5}$ oxide coated interconnect is much higher than that of the bare interconnect, indicating that the Fe content limit in the Co$_x$Fe$_{1-x}$ oxide coating should be less than 50 at%.

![ASR comparison graph](image)

**Fig. 5-5. ASR comparison for the bare and Co$_x$Fe$_{1-x}$ oxide coated interconnects at 800 °C for 100 hrs.**

The above results can be explained from two aspects. The first is the internal conductivity of the coating. As reported, the conductivity of CoFe$_2$O$_4$ is almost one order of magnitude lower than that of Co$_3$O$_4$. More CoFe$_2$O$_4$ in the coating results in higher ASR. Second, the accumulated chromia scale between the coating and the substrate contributes to the total ASR. The thickness of the chromia scale is critical, which will be discussed in the next section.

### 5.3.4 Oxidation kinetics and Cr diffusion

After 100 hrs of the ASR testing, the microstructures of the coatings change significantly, two of which, Co$_{0.9}$Fe$_{0.1}$ oxide and Co$_{0.5}$Fe$_{0.5}$ oxide, are shown in Fig. 5-6. The Co$_{0.9}$Fe$_{0.1}$ oxide coating
(Fig. 5-6(a)) is still dense and the average grain size increases from ~200 nm to ~1 µm. The microstructure of the Co$_{0.5}$Fe$_{0.5}$ oxide coating (Fig. 5-6(b)), however, is not as dense. Serious phase separation, CoFe$_2$O$_4$ and Fe$_2$O$_3$, leads to the less dense coating. The distribution of the particles is heterogeneous. The large size particles (CoFe$_2$O$_4$) are up to 3 µm while the small size particles (Fe$_2$O$_3$) are just ~100 nm. The porous coating shown in Fig. 5-6(b) cannot prevent O$_2$ from reaching the steel substrate and inducing oxidation to increase the ASR, to as high as 31.4 mΩ cm$^2$. Moreover, some Co$_{0.5}$Fe$_{0.5}$ oxide coating peels off from the AISI 441 substrate surface after 100 hrs of the ASR testing, which further demonstrates that the coating is less effective. These small Fe$_2$O$_3$ particles are spalled off due to the excessive Fe in the coating. Thus, low Fe content is needed in order to obtain a dense coating and low enough ASR.
Fig. 5-6. Surface morphologies of (a) Co$_{0.9}$Fe$_{0.1}$ oxide and (b) Co$_{0.5}$Fe$_{0.5}$ oxide coatings; (c) changes of the chromia scale thickness with the Fe content in the coatings after 100 hrs of the ASR testing.

As mentioned earlier, the oxidation of the interconnect with the formation of chromia contributes to the increase of the ASR. For the bare AISI 441, Cr oxide vapors is released as volatile CrO$_3$ or CrO$_2$(OH)$_2$ (depending on the presence of water vapor) to lose the passivating layer. Then Fe is oxidized. Thus, the large ASR of the bare steel shown in Fig. 5-5 is ascribed to the oxidation of Fe and its delamination from the substrate. For the CoFe oxide coated interconnect, the formation of the chromia scale is ascribed to two aspects. One is direct oxidation during the CoFe alloy→Co$_x$Fe$_{1-x}$ oxide conversion before any electrochemical testing. In this process, a dense Co$_x$Fe$_{1-x}$ oxide layer has not fully formed. The activity of Co, Fe, and Cr has a relationship of Cr>Fe>Co, which means Cr is the easiest to be oxidized. The passivating chromia layer on the surface of AISI 441 limits the oxidation of Fe by acting as a diffusion barrier.

In order to compare the coating resistance to oxidation, the chromia scale thicknesses on the interconnect are given in Fig. 5-6(c) for the five coatings studied. The corresponding Cr distributions (blue) in the five coatings are also illustrated. The chromia scale thickness increases with the increase of the Fe content, from ~0.84 µm for 10 at% Fe, to ~0.96 µm for 20 at% Fe, to ~1.24 µm for 30 at% Fe, to ~1.46 µm for 40 at% Fe, and finally to ~1.55 µm for 50 at% of Fe. The electrical conductivity of the chromia scale, such as Cr$_2$O$_3$, is as low as 1.5×10$^{-2}$ S cm$^{-1}$ at 800 °C$^{32}$, which is over two orders of magnitude lower than that of Co$_3$O$_4$ (6.7 S cm$^{-1}$ at 800 °C) and one order of magnitude lower than that of CoFe$_2$O$_4$ (0.85 S cm$^{-1}$ at 800 °C). The ASR can be calculated based on the parallel resistance of the coating and the chromia scale, as shown in Table 5-2. The calculation can be expressed as the follows:

$$ASR_{Chromia} = \frac{t_{Chromia}}{\sigma_{Chromia}}$$ \hspace{1cm} (5-3)

$$ASR_{Coating} = \frac{t_{Coating}}{\sigma_{e,Coating}}$$ \hspace{1cm} (5-4)

$$ASR_{Total} = ASR_{Chromia} + ASR_{Coating}$$ \hspace{1cm} (5-5)

where $t_{Chromia}$ is the average chromia thickness, which is shown in Fig. 5-5(c); $\sigma_{Chromia}$ is the electrical conductivity of chromia, which is 1.5×10$^{-2}$ S cm$^{-1}$; $t_{Coating}$ is the thickness of the coating,
which is around 6 µm; \( \sigma_{e,Coating} \) is the effective conductivity of the coating, which can be calculated with Equation (5-6) based on the Bruggeman model:

\[
\sum_i \delta_i \frac{\sigma_i - \sigma_{e,Coating}}{\sigma_i + 2\sigma_{e,Coating}} = 0
\]

(5-6)

where \( \delta_i \) is the volume fraction of each phase, which can be calculated from Fig. 5-3(c); \( \sigma_i \) is the electrical conductivity of each phase, 6.7 S cm\(^{-1}\) for Co\(_3\)O\(_4\), 0.85 S cm\(^{-1}\) for CoFe\(_2\)O\(_4\) and \(~10^{-2}\) S cm\(^{-1}\) for Fe\(_2\)O\(_3\). The effective conductivity for each coating is also shown in Table 5-2. The calculated resistance is smaller than the measured resistance, especially for the high Fe content coating, because the Bruggeman model considers the coating as dense with all the phases homogeneously distributed. In addition, no interdiffusion is considered here which could increase the ASR.

<table>
<thead>
<tr>
<th>Fe concentration (at%)</th>
<th>ASR(_{\text{Chromia}}) (mΩ·cm(^2))</th>
<th>( \sigma_{e,\text{Coating}} ) (S·cm(^{-1}))</th>
<th>ASR(_{\text{Coating}}) (mΩ·cm(^2))</th>
<th>ASR(_{\text{Total}}) (mΩ·cm(^2))</th>
<th>ASR(_{\text{Measured}}) (mΩ·cm(^2))</th>
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<tr>
<td>10</td>
<td>5.6</td>
<td>4.38</td>
<td>0.1</td>
<td>5.7</td>
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</tr>
<tr>
<td>20</td>
<td>6.4</td>
<td>2.28</td>
<td>0.3</td>
<td>6.7</td>
<td>8.3</td>
</tr>
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<td>30</td>
<td>8.3</td>
<td>1.06</td>
<td>0.6</td>
<td>8.9</td>
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<td>40</td>
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<td>50</td>
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<td>0.75</td>
<td>0.8</td>
<td>11.1</td>
<td>31.4</td>
</tr>
</tbody>
</table>

The calculated resistance is smaller than the measured resistance, especially for the high Fe content coating, because the Bruggeman model considers the coating as dense with all the phases homogeneously distributed. In addition, no interdiffusion is considered here which could increase the ASR.

Table 5-2. Comparison of the calculated and measured ASR for the Co\(_x\)Fe\(_{1-x}\) oxide coated interconnects.

The reason for the increase of the chromia scale is oxygen diffusion in the Co\(_x\)Fe\(_{1-x}\) oxide coatings. The chromia scale is not desired and its growth should be limited in order to maintain the desirable conductivity. The coatings with low Fe contents are dense and can prevent O\(_2\) from reaching the steel. These coatings keep the thin passivated chromia scale in place, which protects Fe from being oxidized. Based on the microstructures in Fig. 5-6, a dense coating layer with less Fe content contributes to low ASR.

The elemental distributions of Fe, Cr, and Co along the cross section of the Co\(_{0.9}\)Fe\(_{0.1}\) oxide and Co\(_{0.5}\)Fe\(_{0.5}\) oxide coating layers after 100 hrs of the ASR testing are shown in Fig. 5-7. For the
Co\textsubscript{0.9}Fe\textsubscript{0.1} oxide coated interconnect shown in Fig. 5-7(a), an intense Cr peak is located in the dark thin layer between the AISI 441 substrate and the coating. It demonstrates the Cr accumulation on the AISI 441 surface and the effectiveness of the coating in preventing its evaporation after the long-term operation. The process can be understood as follows. During the high temperature testing, oxygen diffuses inward through the oxygen vacancies in the coating layer to oxidize the substrate. Due to the higher activity of Cr than Fe, Cr is oxidized prior to Fe. When there is no outer coating layer, Cr\textsubscript{2}O\textsubscript{3} layer would increase fast and a thick chromia layer might even detach from the steel substrate. If the Co\textsubscript{x}Fe\textsubscript{1-x} oxide layer is porous, Cr\textsubscript{2}O\textsubscript{3} can also be oxidized further into volatile CrO\textsubscript{3} (dry air was used as stated earlier), which is the Cr species that poisons the cathode. Since almost no Cr is detected in the coating layer, it means that the Co\textsubscript{0.9}Fe\textsubscript{0.1} oxide coating is effective in inhibiting the Cr solid state diffusion. Meanwhile, a significant amount of Fe is detected in the middle of the coating. A high concentration of Co is also distributed along the coating. This means that the Co\textsubscript{0.9}Fe\textsubscript{0.1} oxide coating is intact. For the Co\textsubscript{0.5}Fe\textsubscript{0.5} oxide coated interconnect shown in Fig. 5-7(b), the chromia scale grows thicker to 1.55 µm, indicating that more oxygen diffuses inward due to the porous nature of the coating. A Co peak is detected in the steel substrate, confirming that Co diffuses into the metallic substrate after more Cr oxidation, which has been reported before\textsuperscript{14, 21, 34-36}. Still, almost no Cr is detected in the coating layer, which means that the Co\textsubscript{0.5}Fe\textsubscript{0.5} oxide coating continues to be effective in inhibiting the Cr solid state diffusion, even with its porous nature. High concentration of Fe and low concentration of Co are distributed uniformly along the coating.
5.3.5 Interconnect coating effects on the SSCF cathode

In this work, Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect is taken as an example to study the coating effect on the half-cell performance. The ohmic resistances and polarization resistances for the SSCF cathode with the coated and bare interconnects are shown in Fig. 5-8. Ohmic resistance, $R_\Omega$, is from the cathode, the Pt wires, the Pd paste, the contact between the interconnect and the cathode, and the electrolyte; The high frequency resistance, $R_H$, corresponds to $O^{2-}$ incorporation into the electrode and its transport in the cathode; and the low frequency resistance, $R_L$, is attributed to oxygen adsorption and dissociation as well as its surface diffusion. The ohmic resistance $R_\Omega$ for the coated interconnect increases from 1.1 $\Omega$ cm$^2$ to 1.5 $\Omega$ cm$^2$ and is smaller than that with the bare interconnect (2.0 $\Omega$ cm$^2$ at stabilized state after ~20 hrs of testing). This means that less or no low conductivity phase, such as SrCrO$_4$, is deposited on the cathode for the former. The high frequency polarization resistance $R_H$ gradually increases to 3.1 $\Omega$ cm$^2$ for the coated interconnect half-cell after 100 hrs of the thermal treatment, which is still smaller than that with the bare interconnect (4.1 $\Omega$ cm$^2$). This is because without Cr poisoning the path for $O^{2-}$ incorporation and transport is more available. The low frequency polarization resistances $R_L$ are initially smaller except for the stabilized value (0.3 $\Omega$ cm$^2$), which is comparable to that of the half-cell without the coating on the interconnect (0.2 $\Omega$ cm$^2$). This means that the oxygen adsorption and dissociation are almost unchanged by the coating.
Fig. 5-8. Electrochemical performance of the SSCF cathode with the (a) bare (b) Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnects.

It has been demonstrated that SrCrO$_4$ forms on the cathode side next to the interconnect when bare interconnects are applied in the previous work. In this study, after 100 hrs of the thermal treatment, the XRD pattern of the SSCF cathode with the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect is shown in Fig. 5-9(a). No SrCrO$_4$ peaks are detected and the SSCF cathode is stable after 100 hrs of the thermal treatment. This further proves that the Co$_{0.8}$Fe$_{0.2}$ oxide coating is effective in inhibiting the Cr diffusion and evaporation. SrCrO$_4$ phase is a poor electrical conductor (1.8$\times$10$^{-5}$ and 1.8$\times$10$^{-4}$ S cm$^{-1}$ at 700 °C and 800 °C respectively $^{38}$). If it forms on the cathode, the SSCF cathode ohmic resistance will eventually increase. In addition, SrCrO$_4$ formation leads to fewer two phase boundaries between the cathode and the gas phase, thus the rate of ORR will be lowered. This explains why the high frequency polarization resistance $R_H$ decreases for the coated interconnect half-cell.

XPS depth profiling is used to detect the Cr concentration on the SSCF cathode after 100 hrs of the thermal treatment with the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect. When an XPS scan is conducted on the top surface, a small Cr2p3 peak is detected as shown in Fig. 5-9(b). The Cr concentration is calculated to be 1.54 at%, which is much less than that with the bare interconnect (6.8 at% on the top surface and 9.39 at% after 0.60 µm of sputtering). When another XPS scan is conducted after 0.66 µm of sputtering, no Cr peak is detected. Even three more scans are conducted after deeper sputtering, still no Cr is detected. This means that only a small amount of Cr accumulates on the surface of the SSCF cathode after 100 hrs of the thermal treatment. The Co$_{0.8}$Fe$_{0.2}$ oxide coating can effectively inhibit the Cr diffusion and evaporation during 100 hrs of the thermal treatment.
Fig. 5-9. (a) XRD pattern and (b) XPS scans (cathode surface and after 0.66 µm of sputtering) of the SSCF cathode thermally treated with the Co$_{0.8}$Fe$_{0.2}$ oxide coated interconnect.

5.4 Conclusions

In this chapter, five coatings (Co$_{0.9}$Fe$_{0.1}$, Co$_{0.8}$Fe$_{0.2}$, Co$_{0.7}$Fe$_{0.3}$, Co$_{0.6}$Fe$_{0.4}$, and Co$_{0.5}$Fe$_{0.5}$) are created by electrodeposition followed by oxidation at 800 °C for 5 hrs. Coatings with lower Fe (<30 at%) contents have smaller ASR and are more effective in limiting the growth of the chromia scale on the AISI 441 substrate. EIS testing also demonstrates the effectiveness of the coatings. Low Fe content coatings improve the electrochemical performance of the SSCF cathode compared with the SSCF cathode with the bare interconnect. Very little Cr is detected on the SSCF cathode surface after the EIS testing and no Cr is detected in the SSCF cathode. Thus, low Fe-containing CoFe oxide coatings (Fe≤30 at%) are effective in protecting the interconnect oxidation and the Cr diffusion and evaporation and are desirable coatings for SOFCs.

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Chapter 6. Co₃O₄/SDC/Co₃O₄ Tri-layer Coating on AISI 441 Interconnect for Solid Oxide Fuel Cells

Abstract

In this work, a novel Co/SDC/Co tri-layer of ~6 µm is deposited by alternating electrodeposition and electrophoresis and oxidized to a Co₃O₄/SDC/Co₃O₄ tri-layer structure. This coating is unique and effective in the following aspects: a) The ASR of the coated interconnect is more stable and lower than that of the uncoated interconnect after thermal treatment at 800 ºC for 400 hrs; b) The Co₃O₄/SDC/Co₃O₄ coating layer can effectively inhibit the Cr diffusion and evaporation and significantly slow the oxidation rate of the interconnect; c) The SSCF cathode in the electrolyte/cathode/interconnect half-cell retains its initial stoichiometry after 100 hrs of the thermal treatment. Subsequently, the ohmic resistance $R_\Omega$, high frequency polarization resistance $R_{hf}$, and low frequency polarization resistance $R_L$ of the half cell with the Co₃O₄/SDC/Co₃O₄ coated interconnect are all smaller than those of the half cell with the bare interconnect. The Co₃O₄/SDC/Co₃O₄ coating layer has great advantages to be used as a protective layer for the metallic interconnect in SOFCs to improve the cell performance, stability, and durability.

6.1 Introduction

Spinel coatings such as CoFe₂O₄, (Mn,Co)₃O₄, (Cu,Mn)₃O₄, and (Cu, Mn,Co)₃O₄ have been demonstrated as promising protective coatings because of their relatively high conductivity and oxidation resistance ⁴⁻⁵, even though Mn is not desired for Mn-free cathodes. Spinel Co₃O₄ is another promising candidate with high conductivity (6.7 S cm⁻¹ at 800 ºC ⁵) even though the accumulative chromia scale between the substrate and the coating layer is thick ⁶. A dense Co₃O₄ coating layer can also improve the oxidation resistance and inhibit the Cr diffusion and evaporation from the interconnect. However, the diffusion of cations (such as Cr³⁺) in the Co₃O₄ layer, especially along the grain boundaries, cannot be ignored even at moderate temperatures ⁶. In addition, the Co₃O₄ coating is unstable after long term operation at high temperatures, voids were reported within the grains ⁸. As it is known, all those coatings cannot inhibit the Cr diffusion and evaporation completely in long term operation. Additionally, the CoₓFe₁-x oxide coatings in Chapter 5 are not effect enough, because little Cr (1.54%) is still detected on the SSCF cathode.
A SDC layer with high ionic conductivity (5.5-9.5×10^{-2} \text{ S cm}^{-2} \text{ at } 800 \text{ °C}) can help to inhibit the Cr diffusion by cutting off Co\textsubscript{3}O\textsubscript{4} grain boundaries, the paths for the Cr diffusion in the dense Co\textsubscript{3}O\textsubscript{4} layer. To create an oxide layer such as SDC on the interconnect, electrophoretic deposition (EPD) is a promising technique. It provides a feasible process to form coatings with a controllable thickness. With a well-controlled suspension, SDC nanoparticles can be deposited on conducting substrates. Several methods have been utilized for Co\textsubscript{3}O\textsubscript{4} spinel layer deposition, including slurry coating, dip coating, physical vapor deposition, and electroplating. Among these methods, electroplating is attractive due to its low cost and simplicity. The electroplated metallic layer can be oxidized to produce a dense oxide layer. When these two procedures are combined, a Co/SDC/Co tri-layer coating can be created on the metal interconnect followed by oxidation to form a Co\textsubscript{3}O\textsubscript{4}/SDC/Co\textsubscript{3}O\textsubscript{4} structure.

In this chapter, AISI 441 steel substrates were coated with Co/SDC/Co by electroplating and electrophoresis in consecutive steps followed by oxidation at 800 °C for 5 hrs in air atmosphere. Cr diffusion and evaporation can be completely inhibited by the Co\textsubscript{3}O\textsubscript{4}/SDC/Co\textsubscript{3}O\textsubscript{4} tri-layer coating. The inner, dense Co\textsubscript{3}O\textsubscript{4} layer was designed to inhibit the Cr diffusion and evaporation, prevent oxygen gas inward diffusion, and ensure CTE match with the ferritic substrate; the intermediate SDC layer was intended to inhibit Cr diffusion by providing a physical barrier to solid state diffusion; the outer Co\textsubscript{3}O\textsubscript{4} layer should fill the pores in the SDC layer, fix the SDC layer, and connect with the inner Co\textsubscript{3}O\textsubscript{4} layer to improve the conductivity of the tri-layer coating. The electrical property was assessed via ASR at 800 °C. The oxidation behavior was evaluated using the chromia scale between the coating layer and the steel substrate. Cr diffusion in the coating layer was investigated via EDS and XPS depth profiling. The effect of the coating layer on the interconnect/SSCF cathode/YSZ electrolyte half-cell electrochemical performance was investigated using EIS at 800 °C.

6.2 Electrodeposition of Co and electrophoretic deposition of SDC

The inner Co layer was made by an electrodeposition method. Co plates were used as the two anodes and an AISI 441 substrate was used as the cathode located between the two anodes. The Co\textsuperscript{2+} solution consisted of 27 mM CoSO\textsubscript{4}·6H\textsubscript{2}O, 6 mM CoCl\textsubscript{2}·6H\textsubscript{2}O, and 9 mM H\textsubscript{3}BO\textsubscript{3}. The pH was adjusted to 3.6 by a HCl solution. A well-polished AISI 441 steel with a size of 15 mm×10 mm×1 mm, as the cathode during the electrodeposition, was connected to the negative port of a
power source with 4 mA cm\(^{-2}\) constant current density. The process continued for 10 min. The Co coated steel was rinsed by DI water.

The intermediate porous SDC layer was deposited by an electrophoretic deposition method. 0.1 g SDC particles were dispersed in 100 mL NH\(_3\)\(\cdot\)H\(_2\)O at pH 11. 0.005 g PAA was added, followed by vibratory milling for 30 min. The Co coated steel was connected to the positive port of the power source with 50 mA cm\(^{-2}\) constant current density. The process continued for 2 min.

The outer Co layer was electrodeposited in a similar manner as for the inner Co layer. The process also lasted for 10 min. The coated steel was oxidized at 800 °C for 5 hrs to form the Co\(_3\)O\(_4\)/SDC/Co\(_3\)O\(_4\) tri-layer coating.

6.3 Results and discussion

6.3.1 Microstructures

Fig. 6-1 shows the top surface microstructures of the deposited Co/SDC/Co layer and its oxidized state after 800 °C for 5 hrs, namely the Co\(_3\)O\(_4\)/SDC/Co\(_3\)O\(_4\) layer. Before the oxidation, the coating layer is porous and the SDC particles are invisible as they are covered by the outer Co layer. After 5 hrs of oxidation at 800 °C, the coating (Fig. 6-1(b)) shows fully dense polycrystalline structures. The theoretical densities of Co and Co\(_3\)O\(_4\) are reported to be 8.9 and 6.1 g cm\(^{-3}\) respectively. Thus, the volume expansion is calculated to be 98.5% after the oxidation, which makes the Co\(_3\)O\(_4\) layer dense. Pores disappear because of the volume expansion after oxidation. The outer Co\(_3\)O\(_4\) layer is dense and the average grain size is around 180 nm. During use, the dense Co\(_3\)O\(_4\)/SDC/Co\(_3\)O\(_4\) layer is expected to prevent oxygen gas inward diffusion, which should reduce the oxidation of the ferritic substrate and the formation of volatile Cr species.
Fig. 6-1. Microstructures of (a) Co/SDC/Co coating top layer and (b) Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating top layer after oxidization at 800 °C for 5 hrs.

The SEM cross section image of the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer is shown in Fig. 6-2. The total thickness of the coating layer is about 6 µm. The thicknesses of the inner Co$_3$O$_4$ layer, the intermediate SDC layer, and the outer Co$_3$O$_4$ layer are ~2.5 µm, ~1 µm, and ~2.5 µm respectively. From the cross section, the SDC middle layer (the bright layer) is uniformly distributed between the two Co$_3$O$_4$ layers. A thin chromia scale (marked by two vertical lines in Fig. 6-2) with a ~280 nm thickness forms between the steel substrate and the inner Co$_3$O$_4$ layer, which is attributed to the interconnect oxidation before the Co layer is oxidized into the dense Co$_3$O$_4$ layer. The electrical conductivity of the chromia scale, such as Cr$_2$O$_3$, is reported to be low at elevated temperatures ($1.5\times10^{-2}$ S cm$^{-1}$ at 800 °C$^{19}$), which is over two orders of magnitude smaller than that of Co$_3$O$_4$ ($6.7$ S cm$^{-1}$ $^5$). Thus, the chromia scale is not desired and its growth should be limited in order to maintain desirable electrical conductivity.

Fig. 6-2. Cross section of the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer after oxidation at 800 °C for 5 hrs.

6.3.2 ASR and oxidation kinetics
An important requirement for the coating layer is to avoid the decrease of the electrical conductivity of the interconnect. Fig. 6-3 shows the ASR results of the bare AISI 441 steel and the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coated AISI 441 steel. ASR is an effective parameter to compare the coating layer effectiveness since the electrical resistance of the un-oxidized steel is negligible compared to that of the coating layer. In this work, the ASR of the uncoated steel increases from 1.1 mΩ cm$^2$ to 25.3 mΩ cm$^2$ after 400 hrs of the ASR testing. For the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coated steel, the ASR increases from 2.0 mΩ cm$^2$ to 8.2 mΩ cm$^2$ after 400 hrs of the ASR testing. In the first 23 hrs of the testing, the ASR of the coated steel increases to 4.9 mΩ cm$^2$, which is larger than that of the bare steel. This is because the oxidation of the bare steel is not severe enough at the beginning and the fast ASR increase of the coated steel can be attributed to the fast Cr accumulation at the interface of the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer and the substrate. After that, the ASR increase of the coated steel is nearly linear with a rate of 8.5×10$^{-3}$ mΩ cm$^2$ h$^{-1}$. The ASR increase of the bare steel, however, is nearly parabolic, with slower oxidation increasing rate over time.

![Graph showing ASR comparison](image)

Fig. 6-3. ASR comparison for the bare and Co$_3$O$_4$/SDC/Co$_3$O$_4$ coated AISI 441 steels at 800 °C for 400 hrs.

In order to demonstrate the resistance to oxidation from the coating layer, the changes of the chromia scale thickness between the coating layer and the substrate are given in Fig. 6-4. The chromia scale thickness increases fast at the beginning, but then decreases over time. Specifically, it increases from 0.28 µm at 5 hrs, to 0.43 µm at 20 hrs, to 0.79 µm at 100 hrs, to 0.86 µm at 200
hrs, and to 0.94 µm at 400 hrs. A semi-logarithmic equation (Equation (6-1)) can be used to fit the chromia scale thickness.

\[ d = -0.2242 + 0.20813 \ln(t + 6.14946) \]  

(6-1)

where \( d \) is the chromia scale thickness and \( t \) is the oxidation time. Based on this empirical equation, with the oxidation time increase to 4000 hrs, the thickness of the chromia scale is predicted to be \(~1.50 \mu m\) and stays relatively stable. The corresponding cross section images of the chromia layers for different oxidation hours are also shown in Fig. 6-4. The increase of the chromia scale thickness contributes to the ASR increase shown in Fig. 6-3, due to the low electrical conductivity of chromia. For the bare AISI 441 after 400 hrs of the ASR testing, a chromia scale with \(~3 \mu m\) thickness is formed on the top surface. This is three times thicker than that with the \( \text{Co}_3\text{O}_4/\text{SDC}/\text{Co}_3\text{O}_4 \) coating. This layer also delaminates, as shown in the lower inset in Fig. 6-4. Also, \( \text{Fe}_2\text{O}_3 \) phase is detected by XRD, which supports the claim that the bare AISI 441 substrate is oxidized after 400 hrs of the ASR testing.

Fig. 6-4. Increase of chromia scale with oxidation time for the \( \text{Co}_3\text{O}_4/\text{SDC}/\text{Co}_3\text{O}_4 \) try-layer coated AISI 441; the upper inset shows the corresponding SEM cross section images of the chromia scales (between two red vertical lines); the lower inset shows the cross section of the bare AISI 441 after 400 hrs of the ASR testing.
Without considering interdiffusion, a simplified schematic of the coated AISI 441 after oxidation can be illustrated as Fig. 6-5. The total ASR of the specimen, $R_T$, can be expressed as follows:

$$R_T = R_0 + R_1 + R_2 + R_3 + R_4$$  \hspace{1cm} (6-2)

where $R_0$ is the ASR of the AISI 441, which can be ignored due to its high electrical conductivity; $R_1$ is the ASR of the chromia scale; $R_2$ is the ASR of the inner Co$_3$O$_4$ layer; $R_3$ is the ASR of the mixed SDC and Co$_3$O$_4$ layer; $R_4$ is the ASR of the outer Co$_3$O$_4$ layer. For the sample after 400 hrs of the ASR testing, $R_1$ can be calculated to be 6.3 mΩ cm$^2$ according to its thickness (0.94 µm) and electrical conductivity ($1.5 \times 10^{-2}$ S cm$^{-1}$). $R_2 + R_4$, which is the total ASR of the Co$_3$O$_4$, can be calculated to be 0.07 mΩ cm$^2$ according to its thickness (5 µm) and electrical conductivity (6.7 S cm$^{-1}$). For $R_3$ from the mixed SDC and Co$_3$O$_4$ layer with the thickness of 1 µm, 40 vol% of the SDC layer is assumed to be porous and fully filled by Co$_3$O$_4$, so $R_3$ is calculated to be 0.04 mΩ cm$^2$. Thus, $R_T = 6.4$ mΩ cm$^2$, which is smaller than the measured value (8.2 mΩ cm$^2$). It is obvious from the calculation that the chromia scale contributes most of the resistance. To achieve low ASR, it is vital to limit the increase of the chromia scale.

![Schematic of the coated AISI 441 after oxidation.](image)

The formation of the chromia scale is ascribed to two aspects. One is direct oxidation during the Co→Co$_3$O$_4$ conversion. In this process, a dense Co$_3$O$_4$ layer has not fully formed. The activity of Co, Fe, and Cr has a relationship of Cr>Fe>Co, which means Cr is the easiest to be oxidized. The passivating chromia layer on the surface of AISI 441 limits the oxidation of Fe by acting as a diffusion barrier. If O$_2$ is supplied continually, such as for the bare AISI 441, Cr oxide vapors will
be released as Equations (1-8) or (1-9) (when moisture is present), to lose the passivating layer \(^{20-21}\). Then Fe will be oxidized.

Thus, the large ASR of the bare steel shown in Fig. 6-3 is ascribed to the delamination and the thick passivating chromia scale. Specifically, \(\text{Fe}_3\text{O}_4\) phase is detected by XRD, which means Fe is oxidized for bare steel. It should be noted that, the activation energies for Equations (1-11) and (1-12) are higher than that of the Co oxidation reaction. Therefore, with the presence of the Co/SDC/Co layer, the formation of \(\text{Co}_3\text{O}_4\) occurs faster. Eventually, a dense \(\text{Co}_3\text{O}_4\) coating layer can prevent \(\text{O}_2\) from reaching the steel. For the coated steel, the \(\text{Co}_3\text{O}_4/\text{SDC}/\text{Co}_3\text{O}_4\) coating layer keeps the thin passivating chromia scale in place, which protects Fe from being oxidized. The reason for the increase of the chromia scale is oxygen diffusion in \(\text{Co}_3\text{O}_4\) through oxygen vacancies. Nonstoichiometric \(\text{Co}_3\text{O}_{4.5}\) can be the carrier of oxygen and oxygen vacancies contribute to the diffusion of oxygen. Thus, the oxygen inward diffusion cannot be neglected considering the thin coating layer and long term operation.

Long term SOFC operation requires the chromia scale to grow slowly or have no growth to maintain low electrical resistance over the interconnects. Furthermore, the thickness of the chromia scale must be limited to prevent the delamination from the AISI 441 substrate. Otherwise, the mismatch of CTEs between the AISI 441 substrate (~11.3\(\times\)10\(^{-6}\) K\(^{-1}\)) and the chromia scale (5.4-7.5\(\times\)10\(^{-6}\) K\(^{-1}\) \(^{22}\)) will lead to defective coatings and decreased performance. Desirably, the \(\text{Co}_3\text{O}_4/\text{SDC}/\text{Co}_3\text{O}_4\) coating layer should inhibit the growth of the chromia scale by limiting the oxygen inward diffusion.

### 6.3.3 Cr diffusion

The elemental distribution along the cross section of the coating layer is shown in Fig. 6-6. Fig. 6-6(a) shows the distribution for the involved elements before the ASR testing (after oxidation at 800 °C for 5 hrs). A thin chromia scale accumulates at the interface between the steel substrate and the coating layer. Fe diffuses into the \(\text{Co}_3\text{O}_4\) layer to form the \(\text{CoFe}_2\text{O}_4\) phase (reported to be 0.85 S cm\(^{-1}\)), which has lower electrical conductivity than that of \(\text{Co}_3\text{O}_4\). Without considering this species, it likely results in the smaller calculated ASR in Fig. 6-5 than the measured value. A small chromium peak exists in the coating layer, which coincides with the cerium peak. This means that the SDC layer plays a role in inhibiting the Cr diffusion. Hypothetically, Cr diffusion can occur in three ways: 1) Cr\(^{3+}\) ions diffuse through \(\text{Co}_3\text{O}_4\) unit cells, which is impossible because
interatomic distance (< 0.1 Å) in Co₃O₄ is much smaller than the radius of Cr³⁺ (0.615 Å). 2) Cr³⁺ partially substitutes Co³⁺ in the spinel structure, which mostly possibly occurs at the interface of the inner Co₃O₄ layer and the chromia layer. However, the low content of Co at the interface indicates that this process is unlikely. 3) Cr³⁺ diffuses along the grain boundaries of Co₃O₄, which is believed to be the most likely mechanism for Cr outward movement. In this work, Co₃O₄ grain boundaries decrease dramatically with the creation of the SDC layer; it is possible that the paths are cut off totally in the intermediate SDC layer, so the Cr³⁺ diffusion beyond the SDC layer is starved. The elemental distribution from the interconnect to the coating layer after 400 hrs of the ASR testing is shown in Fig. 6-6(b). The thickness of the chromia layer located at the interface (between the steel substrate and the coating layer) increases from 0.28 µm to 0.94 µm (as shown in Fig. 6-4). More Fe diffuses into the Co₃O₄ layer to create CoFe₂O₄ phase and decreases the electrical conductivity of the coating. Nonetheless, only a small chromium peak locates at the SDC position. The thickness of the coating layer decreases, especially for the outer Co₃O₄ layer, which means some Co₃O₄ has escaped after 400 hrs of the ASR testing. The SDC intermediate layer not only inhibits the Cr diffusion but also block the inner Co₃O₄ from escaping due to its high stability at 800 ºC.

6.3.4 Effects on SSCF cathode

The ohmic resistances and polarization resistances for the SSCF cathode with the coated and bare interconnects are shown in Fig. 6-7. The ohmic resistance R_Ω for the coated interconnect
stabilizes at 1.5 Ω cm² and is smaller than that with the bare interconnect (2.0 Ω cm² at stabilized state after ~20 hrs of testing). This means less low conductivity phase, such as SrCrO₄, is deposited on the cathode for the former. The high frequency resistance R_H gradually increases to 2.2 Ω cm² after 100 hrs of the thermal treatment, which is also smaller than that with the bare interconnect (4.1 Ω cm²). This is because without Cr poisoning the path for O²⁻ incorporation and transport is more available. The low frequency resistances R_L are smaller for the half-cell with the coated interconnect (0.1 Ω cm²) than that for the half cell with the bare interconnect (0.2 Ω cm²), and the hump of the low frequency resistance for the coated interconnect is smaller than that with the bare interconnect and decreases at an earlier thermal treatment time. This means that the oxygen adsorption and dissociation are enhanced with the coating. Thus, R_Ω, R_H, and R_L all decrease when the Co₃O₄/SDC/Co₃O₄ coated interconnect is used.

Fig. 6-7. Electrochemical performance of the SSCF cathode with the coated and bare interconnects.

It has been demonstrated that SrCrO₄ forms on the cathode side next to the interconnect when bare interconnects are applied. In this study, after 100 hrs of the thermal treatment, the XRD patterns of the SSCF cathode on the YSZ electrolyte with the coated and bare interconnects are shown in Fig. 6-8. No SrCrO₄ peaks are detected. The SSCF cathode is stable after 100 hrs of the thermal treatment. This demonstrates that no Cr has diffused or evaporated from the interconnect. For the SSCF cathode with the bare interconnect, the formation of SrCrO₄ leads to the
microstructure change and decomposition of the SSCF cathode and eventually the degradation of the electrochemical performance. This is because SrCrO$_4$ phase is a poor electrical conductor ($1.8 \times 10^{-5}$ and $1.8 \times 10^{-4}$ S cm$^{-1}$ at 700 °C and 800 °C respectively$^{25}$) and causes the increase of the SSCF cathode ohmic resistance. In addition, SrCrO$_4$ formation leads to fewer two phase boundaries between the cathode and the gas phase, thus the rate of ORR will be lowered. This hinders the oxygen dissociation and diffusion on the cathode surface and thus increases the low frequency resistance $R_L$. Moreover, $O_2^-$ incorporation into the electrode is blocked by the formation of SrCrO$_4$ on the cathode surface, which contributes to the increase of the high frequency resistance $R_H$.

![XRD patterns of the SSCF cathode on the YSZ substrate with coated and bare interconnects after 100 hrs of the thermal treatment.](image)

Fig. 6-8. XRD patterns of the SSCF cathode on the YSZ substrate with coated and bare interconnects after 100 hrs of the thermal treatment.

The microstructures of the SSCF cathodes tested with the bare and coated interconnects are shown in Figs. 6-9(a) and (b) respectively. The large particles in Fig. 6-9(a) are SrCrO$_4$ (such as the circled location)$^{23-24}$, which is absent in Fig. 6-9(b). Based on Figs. 6-8 and 6-9, it can be concluded that no Cr poisoning reaction happens between the SSCF cathode and the coated interconnect after 100 hrs of the thermal treatment at 800 °C.

The elemental concentrations of the SSCF cathode are obtained by EDS and given in Table 6-1. Only 0.30 at% Cr is detected on the SSCF cathode with the coated interconnect. This is due to the background noise of the EDS analysis. However, 20.23 at% Cr is detected for the cathode
with the bare interconnect. This means that the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer can effectively inhibit Cr diffusion and evaporation. Equally importantly, the Sm:Sr:Co:Fe ratio in the SSCF cathode with the coated interconnect is 0.47:0.46:0.2:0.81, which is close to the initial ratio of 0.50:0.50:0.20:0.80. However, for the SSCF cathode with the bare interconnect, the elemental ratio is 0.48:0.90:0.20:0.85, which is significantly Sr-rich. This means the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer can retain the initial stoichiometry of the SSCF cathode.

![Fig. 6-9. Microstructures of the SSCF cathodes with (a) the bare interconnect and (b) the coated interconnect after 100 hrs of the thermal treatment. A SrCrO$_4$ particle is circled in (a).](image)

<table>
<thead>
<tr>
<th>Atomic (%)</th>
<th>Sm</th>
<th>Sr</th>
<th>Co</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare interconnect</td>
<td>15.84±0.93</td>
<td>29.44±2.34</td>
<td>6.54±0.74</td>
<td>27.95±2.48</td>
<td>20.23±1.81</td>
</tr>
<tr>
<td>Coated interconnect</td>
<td>23.79±0.32</td>
<td>24.25±1.23</td>
<td>9.95±0.51</td>
<td>41.71±0.61</td>
<td>0.30±0.02</td>
</tr>
</tbody>
</table>

Through XPS depth profiling, Fig. 6-10 also shows that the Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coating can effectively block the Cr diffusion. After 25 min of sputtering with Ar$^+$, the Cr concentration in the SSCF cathode with the bare interconnect is around 8 at%. However, no Cr is detected in the SSCF cathode with the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coated interconnect after 25 min of sputtering. Even in the coating, no Cr is detected in the ~0.7 µm depth after 25 min of sputtering. Thus, it further demonstrates that the Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coating is effective in inhibiting the Cr diffusion and evaporation.
Fig. 6-10. Cr concentration changes with Ar$^+$ sputtering time in the SSCF cathodes with the bare and Co$_3$O$_4$/SDC/Co$_3$O$_4$ coated interconnects as well as the interconnect with the coating.

6.4 Conclusions

In this study, a simple yet extremely effective tri-layer coating for the interconnect of solid oxide fuel cells is deposited. It can be used for the wide range of new generation Co-containing cathodes over 600-800 °C. The Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coating is created by electrodeposition and electrophoresis followed by oxidation at 800 °C for 5 hrs. It is extremely effective in inhibiting the ASR increase of the coated AISI 441 and limiting the growth of the chromia scale on the AISI 441 surface. EIS testing also demonstrates the effectiveness of the coating in improving the half-cell performance. In addition, no Cr is detected in the SSCF cathode after 100 hrs of the thermal treatment, even after sputtering with Ar$^+$ for ~3.2 μm. Thus, the Co$_3$O$_4$/SDC/Co$_3$O$_4$ coating layer can effectively improve the oxidation resistance as well as inhibit the Cr diffusion and evaporation. It also can retain the cathode stoichiometry and inhibit the formation of the SrCrO$_4$ phase on the SSCF cathode surface.

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Chapter 7. Properties of Natural Gas Fueled Solid Oxide Fuel Cells with Perovskite Cathodes

Abstract

The electrochemical performance of the previous research is based on half-cells with an electrolyte/cathode/interconnect structure. Anode is not considered in the half-cells, but instituted by Pd-Ag paste. Single cell test can reflect not only the ohmic and polarization resistances but also voltage and power density. It involves anode, electrode, cathode, fuel, oxygen and sealing in the system. This paper compares the electrochemical performance of three perovskite cathode materials, LSCF, BSCF, and SSCF at different operating temperatures with natural gas as a fuel. Based on the electrochemical performance of the single cells, BSCF has the highest power density of 39 mW cm\(^{-2}\) at 600 ºC, 88 mW cm\(^{-2}\) at 650 ºC, and 168 mW cm\(^{-2}\) at 700 ºC; LSCF has the highest power density of 263 mW cm\(^{-2}\) at 750 ºC and 456 mW cm\(^{-2}\) at 800 ºC. The cathode overpotentials have the same trend as the power densities. Activation energies calculated from the cathode ASR are 0.44 eV, 0.38 eV, and 0.52 eV for the LSCF, BSCF, and SSCF cathodes respectively. Stability test for 100 hrs shows that the open circuit potentials (OCVs) of the LSCF and BSCF cathodes drop 16.1% and 22.9% at 800 ºC respectively, as well as 15.3% and 11.3% at 600 ºC respectively, which means the LSCF cathode is more stable at 800 ºC while the BSCF cathode is more stable at 600 ºC.

7.1 Introduction

Among various types of fuel cells, SOFCs have the advantages of high energy conversion efficiency and high electrode performance without Pt catalyst\(^{1-4}\). However, SOFCs are generally operated at ~800 ºC, resulting in severe performance degradation and increased cost over time\(^{5-7}\). Great efforts have been devoted to develop high performance and stability cathode materials due to the key role of cathodes in SOFCs. Mixed ionic-electronic conductors are promising cathode materials, considering that the oxygen reduction reaction is not just limited to the TPB sites but can be extended to DPB sites\(^{8-10}\). In addition, cathode materials play an important role in lowering the operating temperature for SOFCs through determining the rate of oxygen reduction reaction. Thus, it is essential to compare cathode materials at different temperatures and identify the optimal cathode material at a given temperature.
LSCF, BSCF, and SSCF are used as the cathodes in the study. They were studied based on half-cells. However, there has been no comparative study of their full cell performance at different temperatures.

Hydrogen is a basic fuel for SOFCs \cite{11,12}. However, flammability as well as difficulty in handling, storage and transportation hinder its wide application in SOFCs \cite{13}. Among other fuels, such as hydrocarbon, natural gas, biogas, methanol, and ammonia \cite{14-15}, natural gas is of interest due to its wide availability, higher energy density than H\textsubscript{2}, and well-developed infrastructure \cite{16}. Replacing H\textsubscript{2} with natural gas can extend the applications of SOFCs and make them more economically viable. However, with natural gas, SOFC anode materials are required to have higher electrocatalytic activity, coking resistance, and H\textsubscript{2}S tolerance \cite{17}. Decomposition of natural gas at the anode can produce a carbon layer that may block the active sites of the anode and reduce the cell performance.

This study is focused on evaluating the thermophysical and electrochemical characteristics of three cathode materials: LSCF, BSCF, and SSCF. Their electrochemical performance at 600 °C, 650 °C, 700 °C, 750 °C, and 800 °C is analyzed in order to identify the optimal cathode material at different operating temperatures. The cathode overpotentials at different operative temperatures are presented. The stability of the LSCF and BSCF-based single cells at 800 °C and 600 °C is evaluated through OCV changes for 100 hrs of cell operation.

### 7.2 Experimental procedures

#### 7.2.1 Single cells preparation

SDC particles were synthesized by a sol-gel method, which has been reported in Chapter 3. SDC block layers on both sides of YSZ (~20 mm diameter and ~250 μm thickness) electrolyte were deposited by spin coating. Before spin coating, a SDC suspension was prepared. NH\textsubscript{3}H\textsubscript{2}O was used as the solvent with pH at 11. The solid content of SDC was 10 vol% and 6 wt% of PAA (relative to SDC, Thermo Fisher Scientific, Waltham, MA) was added as a dispersant. Then the suspension was mixed for 2 hrs using a vibratory mill. The spin coating was carried out at 500 rpm s\textsuperscript{-1} for 5 s then at 2000 rpm s\textsuperscript{-1} for 60 s. The SDC layer was then dried at 80 °C for 30 min. The other side of the YSZ electrolyte was spin coated with the same process. The SDC coated YSZ electrolyte was calcined at 1300 °C for 2 hrs with heating and cooling rates of 2 °C min\textsuperscript{-1}. 

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The anode was composed of 60 vol% Ni and 40 vol% SDC. NiO (Sigma-Aldrich, St. Louis, MO) and SDC were ball milled with ethyl cellulose and α-terpineol and then tape cast on one side of the SDC coated YSZ electrolyte. The anode had \(0.5\) cm\(^2\) area in square and was bonded with the YSZ electrolyte at 1300 °C for 2 hrs.

LSCF, BSCF, and SSCF powders were synthesized by a combustion method and have been described in Chapter 2. Each cathode was screen printed on the other side of the YSZ electrolyte with microcrystalline cellulose, ethyl cellulose, and α-terpineol as a pore forming agent, binder, and solvent respectively. The printed pastes were again square-like with \(0.5\) cm\(^2\) area and bonded with the YSZ electrolyte at 950 °C for 2 hrs. The cross section structure of a single cell with LSCF as the cathode is shown in Fig. 7-1 as an example. The thickness of the Ni/SDC anode, LSCF cathode, and SDC coating layer was ~70 µm, ~25 µm, and ~1.5 µm respectively.

Fig. 7-1. (a) Cross section structure of a single cell with LSCF as the cathode; (b) (c) The enlarged anode/electrolyte and cathode/electrolyte interfaces respectively.

### 7.2.2 Sealing and electrochemical measurement

A commercial glass-ceramic powder (EG03118, Ferro Corporation, Cleveland, OH) was used as the sealing material for the single cell tests at 600-800 °C. The glass-ceramic powder was mixed with polyvinyl butyral (PVB, Alfa Aesar, Ward Hill, MA) and 1-propanol (Alfa Aesar, Ward Hill, MA) as the binder and solvent respectively. The mixture was ball milled for 1 hr to obtain a homogeneous slurry. The slurry was cast on an alumina tube cross-section with a diameter of \(21\) mm. Then a single cell was stacked and pressed on the slurry. After drying at room temperature for 20 min, the set-up was heated using a tube furnace to 850 °C for 10 min at 2 °C min\(^{-1}\), and then
cooled to the cell testing temperature with 2 °C min⁻¹. The sealing tightness was tested through giving a pressure in the tube and detecting gas bubble for the sealed end in water so that there was no leakage in the cell testing process. The schematic of the home-made set-up is shown in Fig. 7-2(a).

Fig. 7-2. Schematic of (a) a home-made set-up with an alumina tube and (b) a single cell and its Pt wire connections.

In order to investigate the electrochemical behaviors of the single cells with LSCF, BSCF, and SSCF cathodes, the current density-potential curves, current density-cathode overpotential curves, and EIS were measured with a four-probe DC potentiostat. EIS was measured in a frequency range of 25 mHz to 100 kHz with an amplitude of 10 mV. Before the testing, the anode was reduced at 800 °C for half an hour in H₂ to achieve the complete reduction of NiO to Ni. Platinum mesh and paste were used as current collectors at the both cathode and anode sides. A platinum paste ring around the cathode was set as the reference electrode (shown in Fig. 7-1(b))
for the cathode overpotential measurement. For the cell potential and EIS measurements, probe connections were realized with Pt-1, Pt-2, Pt-3, and Pt-4; while for the cathode overpotential measurement, probe connections were conducted with Pt-1, Pt-2, Pt-3 (or Pt-4), and Pt-5. Air and natural gas were introduced into the cathode and anode, respectively. The air and fuel flow rates were kept constant at 200 and 100 mL min\(^{-1}\) respectively and at constant atmospheric pressure of 1 atm. The operating temperatures were set as 600 °C, 650 °C, 700 °C, 750 °C, and 800 °C.

7.3 Results and discussion

7.3.1 I-V and I-P curves

The single cells consist of perovskite cathode, SDC coated YSZ electrolyte, and Ni/SDC composite anode with natural gas as a fuel. The electrochemical performance for each cell type is shown in Fig. 7-3. In Fig. 7-3(a), the I-V and I-P curves for the single cells with the LSCF cathode show that the OCVs are ~1.1 V at all measured temperatures, close to the theoretical one, confirming that a gas-tight and poor current leakage electrolyte as well as hermetic sealing. The maximum power densities are 456 mW cm\(^{-2}\) at 800 °C, 263 mW cm\(^{-2}\) at 750 °C, 140 mW cm\(^{-2}\) at 700 °C, 70 mW cm\(^{-2}\) at 650 °C, and 34 mW cm\(^{-2}\) at 600 °C. Fig 7-3(b) shows the electrochemical performance of the single cells with BSCF as the cathode. The OCVs are still ~1.1 V at all measurement temperatures and the maximum power densities are 327 mW cm\(^{-2}\) at 800 °C, 239 mW cm\(^{-2}\) at 750 °C, 168 mW cm\(^{-2}\) at 700 °C, 88 mW cm\(^{-2}\) at 650 °C, and 39 mW cm\(^{-2}\) at 600 °C. For the single cells with the SSCF as cathode shown in Fig. 7-3(c), the OCVs are also ~1.1 V at all measurement temperatures and the maximum power densities are 366 mW cm\(^{-2}\) at 800 °C, 208 mW cm\(^{-2}\) at 750 °C, 116 mW cm\(^{-2}\) at 700 °C, 74 mW cm\(^{-2}\) at 650 °C, and 34 mW cm\(^{-2}\) at 600 °C. Therefore, the single cells with LSCF as the cathode have the highest power densities at 800 °C and 750 °C and the single cells with the BSCF as the cathode have the highest power densities at 700 °C, 650 °C, and 600 °C. The change of the power density with the cell operating temperature is shown in Fig. 7-4. Obviously, the power densities for all single cells decrease with temperature. LSCF has the highest decrease rate while BSCF has the lowest decrease rate. At 600 °C, all the power densities are close and small. From 800 °C to 600 °C, the power densities decrease by 92.5%, 88.1%, and 90.7% for the single cells with LSCF, BSCF, and SSCF as the cathodes respectively.
Fig. 7-3. I-V and I-P curves of single cells at different testing temperatures with (a) LSCF, (b) BSCF, and (c) SSCF as cathodes.
7.3.2 Cathode overpotential and resistance

The drop of the cell potential with current is ascribed to the internal resistance of a cell, which is composed of polarization resistances of the cathode \( R_{\text{Cathode}} \) and anode \( R_{\text{Anode}} \), and the ohmic resistance \( R_{\text{Ohmic}} \). \( R_{\text{Cathode}} \) and \( R_{\text{Anode}} \) lead to the overpotentials of the cathode and anode respectively. The contributions to \( R_{\text{Ohmic}} \) are from the electrolyte, connecting wire, and so on. For a single cell operated at a current density of \( I \), its potential can be defined as follows:

\[
U(I) = U(0) - \eta_{\text{Anode}} - \eta_{\text{Cathode}} - \Delta U_{\text{Electrolyte}}
\]  

(7-1)

\[
\Delta U_{\text{Electrolyte}} = I \times R_{\text{Electrolyte}}
\]

(7-2)

where \( U(0) \) means OCV, \( \eta_{\text{Anode}} \) means anode overpotential, \( \eta_{\text{Cathode}} \) means cathode overpotential. \( R_{\text{Electrolyte}} \) can be simplified as \( R_{\text{Ohmic}} \). Usually, overpotential can be categorized into activation overpotential, concentration overpotential, and ohmic resistance \(^{18}\). The activation overpotential originates from the irreversibility of the electrochemical reaction, which refers to the activation energy for transferring an electron from the cathode to the anode through redox reaction. For the cathode, the activation overpotential is an indicator of the activation energy of the \( \text{O}_2 \) to \( \text{O}_2^- \) conversion process. It is significantly influenced by the TPB \(^{19-20}\), a function of the microstructure of the cathode. For mixed ionic-electronic conductors, such as LSCF, BSCF, and
SSCF, DPB can also enable the \( \text{O}_2 \) to \( \text{O}^{2-} \) conversion process. The concentration overpotential is generated from the mass transport gradient in the electrodes \(^{21,22}\), to which the thickness of the cathodes is critical. Ohmic overpotential is generated by the charge-transfer resistances, which is determined by the electronic conductivity of the cathode material.

In order to quantify the contribution of the cathode to the total cell potential loss, direct measurements of the cathode overpotential as a function of the current density are conducted. Only the cathode overpotentials are measured because the overpotentials from the anodes and the potential loss from the electrolytes are the same for different cathodes. The results are shown in Fig. 7-5. The cathode potentials dramatically increase and become more non-linear with decreasing temperature for all the cathodes. They are 0.36 V, 0.44 V, and 0.41 V respectively with the current density of 1.2 A cm\(^{-2}\) at 800 °C for LSCF, BSCF, and SSCF respectively. Based on Eq. (7-1), lower overpotential means higher cell potential and power density. The lowest overpotential for the LSCF cathode coincides with the highest peak power density shown in Fig. 7-3. At 750 °C, the cathode overpotentials of the three cathodes are 0.43 V, 0.46 V, and 0.48 V respectively with the current density of 0.8 A cm\(^{-2}\), which also agrees with the highest and lowest peak power densities for LSCF and SSCF cathodes in Fig. 7-3. The same observations can be made for the cathodes at 700 °C, 650 °C, and 600 °C respectively. The detailed cathode overpotentials are shown in Table 1. The ohmic overpotential is in inverse relationship to the electrical conductivity of the cathode material. The electrical conductivities of the LSCF, BSCF, and SSCF cathode materials have been shown in Chapter 2, which states that LSCF has the highest conductivity and BSCF has the lowest conductivity. When the cell testing temperature decreases from 800 °C to 600 °C, the conductivity of LSCF is in the range of 237-252 S cm\(^{-1}\) with a little change; the conductivity of BSCF increases from 16 S cm\(^{-1}\) to 37 S cm\(^{-1}\), which contributes to the smaller ohmic overpotential at the lower temperature; the conductivity of SSCF is in the range of 160-185 S cm\(^{-1}\), which is relatively stable. As to the activation overpotential, lower operating temperature slows the electrochemical reactions, such as the electrocatalytic activity for oxygen reduction, leading to higher overpotential. In addition, the particle sizes of LSCF, BSCF, and SSCF are 100 nm, 400 nm, and 50 nm respectively, as shown in Chapter 2. The larger particle size of BSCF contributes to its higher overpotential at 800 °C due to reduced TPBs. For the concentration overpotential, lower operating temperature also slows the oxygen transportation in the cathode, which is related to the oxygen vacancy concentration. Here, oxygen vacancy concentrations of LSCF, BSCF, and
SSCF can be calculated to be 6.7%, 16.7%, and 8.3% respectively based on their chemical stoichiometries. Higher oxygen vacancy concentration from BSCF contributes to smaller concentration overpotential.
Fig. 7-5. Dependence of the cathode overpotentials of (a) LSCF, (b) BSCF, and (c) SSCF on the current density at different test temperatures.

Table 7-1. Cathode overpotentials (V) at different testing temperatures.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>600 °C@ 0.2 A cm(^{-2})</th>
<th>650 °C@ 0.32 A cm(^{-2})</th>
<th>700 °C@ 0.6 A cm(^{-2})</th>
<th>750 °C@ 0.8 A cm(^{-2})</th>
<th>800 °C@ 1.2 A cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>1.00</td>
<td>0.83</td>
<td>0.60</td>
<td>0.43</td>
<td>0.36</td>
</tr>
<tr>
<td>BSCF</td>
<td>0.67</td>
<td>0.63</td>
<td>0.54</td>
<td>0.46</td>
<td>0.44</td>
</tr>
<tr>
<td>SSCF</td>
<td>0.99</td>
<td>0.88</td>
<td>0.66</td>
<td>0.48</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Impedance spectra measured between the cathode and the reference electrode are shown in Fig. 7-6. The EIS can be deconvoluted by an equivalent circuit \( R_\Omega (R_H \text{CPE}_H)(R_L \text{CPE}_L) \) under AC mode, shown in Fig. 2-2. It can be interpreted that the ohmic overpotential is caused by \( R_\Omega \), the activation overpotential and the concentration overpotential are caused by the polarization resistance \( R_p \) (sum of \( R_H \) and \( R_L \)). With operating temperature decrease, ohmic and polarization resistance both increase gradually for the cathode materials.
Fig. 7-6. EIS curves measured between the cathode of (a) LSCF, (b) BSCF, and (c) SSCF and the reference electrode in natural gas at open circuit.
The deconvoluted cathode ASR, which is polarization resistance because the EIS of cathode was in-situ measured between the cathode and the reference electrode, is indicated in Fig. 7-7. Based on the Arrhenius plots and their fittings, activation energies for the three cathodes are calculated to be 0.44 eV, 0.38 eV, and 0.52 eV. This means that the energy to active the reaction for BSCF cathode is the smallest, which is the most suitable cathode. The high activation energy leads to large enhancement of the polarization resistance with a reduction of the operating temperature. The overall process in the cathode involves oxygen reduction, diffusion, and transfer. The higher ionic conductivity of the BSCF cathode results in faster oxygen transfer and consequently lower ASR. In addition, the ORR rate, the oxygen bulk diffusion coefficient, and the oxygen surface exchange coefficient are all critical to determine the activation energy.

\[
\begin{align*}
\text{Ln}(R_p) &= \frac{E_s}{nF} + \ln(1000/T) \\
E_{s, \text{LSCF}} &= 0.44 \text{ eV} \\
E_{s, \text{BSCF}} &= 0.38 \text{ eV} \\
E_{s, \text{SSCF}} &= 0.52 \text{ eV}
\end{align*}
\]

Fig. 7-7. Arrhenius plots of the temperature dependence of the three cathodes and their fittings.

### 7.3.3 Stability test

The LSCF-based single cells have the highest power densities at 800 and 750 °C and the BSCF-based single cells have the highest power densities at 700, 650, and 600 °C, so the stability of the OCVs for the LSCF and BSCF-based single cells at 800 °C and 600 °C is studied and shown in Fig. 7-8. The OCV of the LSCF-based single cell at 800 °C decreases with the testing time from ~1.11 V to ~0.93 V after 100 hrs of the testing, with a degradation of 16.1%. The OCV of the
BSCF-based single cell decrease slowly from ~1.11 V to ~1.08 V in the first 15 hrs of the testing, then decreases dramatically to ~0.85 V, around 23.3% after 100 hrs of the testing. The LSCF-based single cell is more stable than the BSCF-based single cell at 800 °C. BSCF has a greater distortion of the lattice and leads to more serious instability of the perovskite structure at high operating temperature since the radius mismatch of the Ba\(^{2+}\) (1.61 nm) and Sr\(^{2+}\) (1.44 nm) cations is larger than that of the La\(^{3+}\) (1.36 nm) and Sr\(^{2+}\) cations \(^{23}\). This instability reduces reactant sites and consequently lows OCV. The drop of OCVs can be ascribed to the degradation of the single cells. Actually, carbon powder has been found on the anode side after 100 hrs of the testing for both single cells. When H\(_2\) is introduced into the anode side for 5 min after 100 hrs of the testing, the OCVs recover to 1.05 V and 1.01 V for the LSCF and BSCF-based single cells respectively, which are also shown in Fig. 7-8. This means that Ni in the anode is partly oxidized in the long term operation. For the testing at 600 °C, the OCV from the LSCF-based single cell drops from ~1.13 V to ~0.96 V, 15.3% degradation, and it from the BSCF-based single cell drops from ~1.12 V to ~1.00 V, 11.3% degradation. It means that the BSCF-based single cell is more stable than the LSCF-based single cell at 600 °C as the instability of the BSCF cathode is relieved at this temperature. Moreover, both single cells working at 600 °C are more stable than the two working at 800 °C. This is because higher operating temperature leads to more serious degradation of the single cells, including cathode degradation, interdiffusion, coking, and so on. Only a small amount of carbon powder is found on the anode side after 100 hrs of the testing at 600 °C for both single cells. When the same H\(_2\) reduction process is applied to these two single cells, the OCVs recover to 1.06 V and 1.09 V. The EIS testing shows that both ohmic and polarization resistances decrease after the H\(_2\) reduction, but all of them are still 10-50% larger than that before the stability testing due to the degradation of electrode and interdiffusion.
Fig. 7-8. OCV changes with the testing time for the LSCF and BSCF-based single cells at 800 °C and 600 °C; The open symbols represent the OCVs after 100 hrs of the stability testing and H\textsubscript{2} reduction to the anodes.

The maximum power densities after 100 hrs of the testing and H\textsubscript{2} reduction to the anodes are shown in Table 7-2. All the power densities are much smaller than those before the stability testing even though the H\textsubscript{2} reduction recovers some of the cell potentials due to the enhancement of the ohmic and polarization resistances. This means that the degradation of the single cells in the long term operation is still a serious issue.

Table 7-2. Maximum power densities for the LSCF and BSCF-based single cells both at 800 °C and 600 °C after 100 hrs of the testing and H\textsubscript{2} reduction.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>After 100 hrs</th>
<th>After 100 hrs+H\textsubscript{2} reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 °C</td>
<td>600 °C</td>
</tr>
<tr>
<td>LSCF</td>
<td>46 (mW cm\textsuperscript{-2})</td>
<td>18 (mW cm\textsuperscript{-2})</td>
</tr>
<tr>
<td>BSCF</td>
<td>38 (mW cm\textsuperscript{-2})</td>
<td>20 (mW cm\textsuperscript{-2})</td>
</tr>
</tbody>
</table>

7.4 Conclusions
This study evaluates the single cell performance when LSCF, BSCF, and SSCF are used as cathodes. Electrochemical measurements show that BSCF has the highest power densities of 39 mW cm\(^{-2}\) at 600 °C, 88 mW cm\(^{-2}\) at 650 °C, and 168 mW cm\(^{-2}\) at 700 °C and LSCF has the highest power densities of 263 mW cm\(^{-2}\) at 750 °C and 456 mW cm\(^{-2}\) at 800 °C. The cathode overpotentials demonstrate the same trend as the power density. The activation energies are 0.44 eV, 0.38 eV, and 0.52 eV for the LSCF, BSCF, and SSCF cathodes respectively. The LSCF cathode is more stable than BSCF at 800 °C, while the BSCF cathode is more stable than the LSCF cathode at 600 °C. Thus, LSCF is the deserved cathode at high temperatures (such as 800 °C) and BSCF is the deserved cathode at low temperatures (such as 600 °C).

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Chapter 8. Conclusions and Future Work

8.1 Conclusions

In this dissertation, three perovskite cathode materials, LSCF, BSCF, and SSCF are comparably studied at different temperatures. The SDC catalyst and the SDC block layer between the cathode and the YSZ electrolyte are involved respectively to improve the electrochemical performance of the cathode. The Co\(_x\)Fe\(_{1-x}\) oxides and the Co\(_3\)O\(_4\)/SDC/Co\(_3\)O\(_4\) tri-layer protective coatings are applied on the interconnect to inhibit the chromium diffusion/evaporation to poison the SSCF cathode, slow the oxidation of the interconnect, and decrease its ASR.

First, the BSCF cathode has been demonstrated to have the smallest polarization resistance at 600 ºC, closely followed by the SSCF cathode; the LSCF cathode has the smallest polarization resistance working at 700 ºC; the SSCF cathode has the smallest polarization resistance working at 800 ºC, closely followed by the LSCF cathode. From 600-800 ºC, a SrCrO\(_4\) phase forms on the SSCF cathodes near the interconnect while a BaCrO\(_4\) phase forms on the BSCF cathodes near the interconnect. For the LSCF cathodes, however, the SrCrO\(_4\) phase is only detected at 700 ºC and 800 ºC. Cr species diffusion to and poisoning of the cathodes do not directly correlate with the half-cell performance. Lattice constant, stoichiometry, particle size, Cr deposition, and working temperature are important factors to consider. Three methods, mechanical mixing, infiltration, and dip coating are used to incorporate SDC catalyst into the LSCF cathode to improve the performance of the cathodes. LSCF mechanically mixed with SDC as the cathode decreases the electrochemical performance of the half-cell; the LSCF cathode infiltrated with SDC offers faster activation and decreased resistance with thermal treatment time; and the LSCF cathode dip coated with SDC has the smallest polarization resistance. These cathodes also show clear microstructure differences at the cathode/interconnect interface after 100 hrs of thermal treatment. Overall, dip coating is recommended for incorporation of SDC into the LSCF cathode. The SDC block layer on the YSZ electrolyte can stop the reaction between the perovskite cathode and the YSZ electrolyte as well as decrease the polarization resistance. The SDC layer can effectively decrease the mismatch of the CTEs between BSCF and YSZ.

Second, CoFe alloy coatings with Co:Fe ratios of 9:1, 8:2, 7:3, 6:4, and 5:5 are deposited on the metallic interconnect by electrodeposition and then oxidized to form Co\(_x\)Fe\(_{1-x}\) oxide coatings. The ASR of the coated interconnect increases with the Fe content, and the Fe content limit in the
Co$_x$Fe$_{1-x}$ oxide coating should be less than 50 at%. Higher Co content oxide coatings are more effective in limiting the growth of the chromia scale. The Co$_{0.8}$Fe$_{0.2}$ oxide coating is demonstrated to be effective in decreasing the poisoning of the SSCF cathode by chromium diffusion/evaporation, leading to an increase on the electrochemical performance of the cathode. Also, the Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer coating is demonstrated to have a better performance than any Co$_x$Fe$_{1-x}$ oxide coating. The Co$_3$O$_4$/SDC/Co$_3$O$_4$ tri-layer protective coating can eliminate the Cr deposition on the SSCF cathode while the Co$_{0.2}$Fe$_{0.8}$ oxide coating only decrease the deposited Cr content to 1.54 at%.

Finally, single cell testing with natural gas as a fuel shows that BSCF has the highest power density of 39 mW cm$^{-2}$ at 600 ºC, 88 mW cm$^{-2}$ at 650 ºC, and 168 mW cm$^{-2}$ at 700 ºC; LSCF has the highest power density of 263 mW cm$^{-2}$ at 750 ºC and 456 mW cm$^{-2}$ at 800 ºC. Activation energies calculated from the cathode ASR are 42, 37, and 50 kJ mol$^{-1}$ for LSCF, BSCF, and SSCF cathodes respectively. The OCV of the single cell with BSCF as the cathode decreases 22.9% after 100 hrs of testing.

### 8.2 Future work

Single cell testing shows the BSCF cathode has the highest power density at relatively low temperatures compared to the LSCF and SSCF cathodes and the LSCF cathode has the highest power density at relatively high temperatures compared to the other two cathodes. However, the measured power densities are still low, especially at the relatively low temperature. The major contribution to the high ohmic resistance at relatively low temperatures, such as 600 ºC, is from the YSZ electrolyte, because YSZ has a week ionic conductivity at 600 ºC. It can be improved from two aspects.

First, the YSZ electrolyte can be replaced by the SDC electrolyte which has a better performance at relatively low temperatures. Actually, a single cell with SDC as the electrolyte has been tried. It has a smaller resistance than the YSZ electrolyte and the potential drop with current increase is also smaller, but the OCV is only ~0.9 V. It means the tried SDC electrolyte has a leakage current due to its electronic conductivity or pores. Pure phase and higher density can help to reduce its electronic conductivity. Moreover, the mismatch of the CTEs between the SDC electrolyte and the Al$_2$O$_3$ tube is larger than that between the YSZ electrolyte and the Al$_2$O$_3$ tube.
Thus, a YSZ tube with a CTE close to the SDC electrolyte is an option to replace the Al₂O₃ tube, but it will increase the cost.

Second, the present construction of the single cell is electrolyte-supported. The thickness of the YSZ electrolyte is 250-300 µm. An anode-supported construction would be helpful to decrease its resistance because the anode material is usually more conductive and the thickness of the YSZ electrolyte can be as thin as tens of micron.

Except the decrease of the high resistance of the YSZ electrolyte, the oxygen reduction reaction can be enhanced by incorporation of the SDC catalyst, which has been demonstrated to be effective in the half-cells. The combination of the catalyst and even an coated interconnect can increase the power density of these SOFCs.
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Journal papers


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Patent