CATHODE/ELECTROLYTE INTERACTIONS AND THEIR EXPECTED IMPACT ON SOFC PERFORMANCE

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ABSTRACT

The cathode characteristics and cathode/electrolyte interactions were studied. Both dense and porous cathode films have been deposited on ZrO$_2$ and CeO$_2$-based electrolyte substrates by using a novel spin coating technique. La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) and La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) were found compatible with (CeO$_2$)$_{0.8}$(SmO$_{1.5}$)$_{0.2}$ (CSO) substrates at temperatures up to 1200°C. However, LSCF and LSM reacted with (ZrO$_2$)$_{0.8}$(Y$_2$O$_{1.5}$)$_{0.16}$ (YSZ), forming La$_2$Zr$_2$O$_7$ and SrZrO$_3$. The impact of interfacial reactions on cell performance was studied by AC impedance spectroscopy. The LSCF/CSO system showed the lowest electrode resistance and overpotential. Interactions were observed between LSCF (or LSM) and YSZ in the 1000°C to 1200°C range, which resulted in high interfacial resistance. If indeed YSZ is the electrolyte of choice, both operating and processing temperatures must be maintained below 800°C. The introduction of CSO buffer layer between LSCF (or LSM) and YSZ alleviates this limitation. Our results show that this layer impedes interfacial reactions which, in turn, affect cell performance.

1. INTRODUCTION

The state-of-the-art solid oxide fuel cells (SOFC) operate at 1000°C and their components are processed at even higher temperature. The high temperature operation and processing cause interactions and interdiffusion that lead to reduced cell performance (1). Recently, Schroeder and Anderson used a mixture of LSM and CeO$_2$ to reduce the LSM/YSZ interface resistance (2). Chen et al. successfully deposited a CSO buffer layer between LSM and YSZ. This buffer was found compatible with both LSM and YSZ, and eliminated the interactions that occur at high temperature (3). For development and commercialization of SOFC that compete with other fuel cells (e.g. molten carbonate) it is desirable that the operating temperature should be reduced to 600 ~ 800°C. This can be achieved...
by either reducing the thickness of the electrolyte, thus lowering its internal resistance, or by developing new electrolyte and cathode materials with reduced interactions and lower interfacial resistance.

In order to operate at these lower temperatures, the cathode should possess low polarization and high catalytic activity. Our recent findings (4) and those of others (5,6) indicate that La$_{1-x}$Sr$_x$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) compositions are expected to be candidates for this application.

The objective of this study is to evaluate the compatibility between the cathode and electrolyte materials and to determine the effect of their interactions on the characteristics of the interface at various temperatures. AC impedance spectroscopy was used for this purpose. Both LSM and LSCF cathode material were tested with YSZ and CSO. The following bi- and trilayers were studied:

- LSM/YSZ
- LSM/CSO
- LSCF/YSZ
- LSCF/CSO
- LSCF/CSO/YSZ

From AC impedance measurements, equivalent electrical circuits can be obtained and the components resolved. The results are expected to provide a better understanding of the electrode/electrolyte processes. The impact of their interaction on cell performance can also be identified.

2. EXPERIMENTAL PROCEDURES

(A) **Electrolyte Substrates**

Both dense YSZ and CSO were used. The CSO powder was prepared by the mixed oxide technique using CeO$_2$ and Sm$_2$O$_3$. The oxide were ground and calcined for 24 hours twice at 1350°C to insure the presence of a single phase fluorite structure. Disk-shaped pellets were then pressed isostatically and sintered at 1700°C for 10 hours. Tape cast YSZ electrolyte was supplied by Cerametec Inc. Samples 1 cm$^2$ were cut and used for this study.

(B) **Dense Electrode Films**

Thin film electrodes of LSM and LSCF were deposited on the dense CSO and YSZ substrates using a spin coating technique (7) in order to make interaction studies. This technique involves chelation of specific cations in a polymeric precursor. Dense thin films with required thickness were obtained by careful control of polymerization, viscosity of solution and the spinning rate. The spun-on film was densified at temperatures not exceeding 600°C as described elsewhere (8). The film thickness was controlled in the range of 0.4 ~ 0.6 μm. These films were
thin enough that the interfacial reactions between the dense films and the substrates could be studied by XRD analysis of the surface of the films.

(C) Porous Electrode Coatings

Porous electrode films were prepared by a slurry painting technique. Powders of LSM and LSCF were made by the Pechini method (9). The perovskite structures of the synthesized powders were confirmed by XRD. The powders were then mixed with ethylene glycol using a vibratory mixer with plastic containers and balls. The LSM and LSCF slurries were painted onto YSZ and CSO substrates and fired at 1100°C for 2 hrs. The film morphology was examined by a JOEL T330A Scanning electron microscope (SEM). In another experiment a CSO buffer layer was applied onto YSZ substrates using our multiple spin coating technique. A LSCF electrode was then slurry painted onto the CSO layer. The developed trilayer was tested and compared with the previously prepared double layers.

(D) AC Impedance Spectroscopy

AC impedance spectroscopy (Schlumberger 1260) was used to study the electrode resistance and oxygen activation at the cathode/electrolyte interface. With the frequency sweep, equivalent electrical circuits of the electrode processes were obtained and the components resolved thus identifying the electrode/electrolyte processes. In this study, the measurements were performed on the slurry painted electrode/electrolyte bilayers and on the previously described trilayers. A two electrode measuring method (a two symmetric-electrode cell) was used (10). Pt mesh, pressed to the sample by a spring, was used as current collector. The measurements were carried out using small a.c. signal (< 10 mV) without a d.c. bias voltage.

3. RESULTS AND DISCUSSION

(A) Interaction Studies

The structural evolution of the as deposited amorphous films of LSM and LSCF on YSZ and CSO substrates (after annealing at temperature between 600°C and 1200°C) was monitored by x-ray diffraction. (Fig. 1-4) Fine-grained polycrystalline film was detected at annealing temperatures as low as 600°C. For the LSM/YSZ system, a reaction occurred at 1100°C, where the major reaction product formed at the interface was La₂Zr₂O₇. A small amount of SrZrO₃ was also detected. However, in the LSCF/YSZ system a reaction occurred at temperatures as low as 1000°C as shown in Fig.2, and even at lower temperatures upon prolonged exposure (11). The major compound formed at the interface was
SrZrO$_3$. At 1200°C the reaction between LSCF and YSZ became so rapid that the LSCF film dissolved into the substrate. For the LSCF/CSO and LSM/CSO system, no second phases were detected at temperatures between 600°C and 1200°C (See Figs. 3,4). This indicates that the CSO electrolyte is compatible with both LSCF and LSM electrodes.

(B) Electrode Characteristics

Figs. 5 and 6 show typical surface and cross-section SEM images of LSM/YSZ and LSCF/CSO bilayers, respectively, after heating at 1100°C for 2 hrs. Although these micrographs provide information on the electrode morphology, they do not show the initial stages of interactions at the interface. AC impedance spectroscopy is a sensitive technique by which minor changes in the interfacial characteristics can be identified. The interfacial electrode characteristics were investigated using AC impedance spectroscopy on samples which consisted of two symmetric electrodes of either LSM or LSCF deposited on YSZ or CSO.

The complex impedance diagrams are represented in terms of imaginary vs. real components. A high frequency semicircle indicates parallel combination of the electrolyte resistance and capacitance, with the high frequency intercept of the real axis corresponding to the electrolyte resistance. Low frequency arcs are generally due to electrode or interfacial resistance (10,11). The complex impedance for LSM/YSZ, LSM/CSO and LSCF/YSZ cells consisted of only one arc between 600°C and 1000°C which corresponds to the interfacial resistance. In the LSCF/CSO system, at 820°C a new arc appeared at the low-frequency end of the previously observed arc. The two semi-circle arcs were well separated at 1025°C. Fig. 7 shows the complex impedance plot of the LSCF electrode with CSO electrolyte at various temperatures. In this system, no interactions were detected up to 1200°C. Hence, the impedance results can be explained in terms of two processes that occur at the interface. One is related to activation polarization (charge transfer), the other is due to concentration (diffusion) polarization (12). Usually, the latter process dominates at lower temperature and diminishes with increasing temperature. Accordingly, these two processes are well resolved at higher temperatures. The observed two slopes of activation energy in the LSCF/CSO system, within this temperature range, supports this hypothesis. The mechanism is still under investigation. Fig. 8 shows the Arrhenius plots of interfacial resistance/cm$^2$ for these systems. The activation energies calculated from Fig. 8 are listed in Table I. As can be seen, these results are in agreement with Takeda et al.’s calculations using the current interruption technique for some systems (13). (See table II)

Fig. 9 shows the plots of interfacial resistance/cm$^2$ (Ri) versus temperature for various systems. LSCF/CSO possessed the lowest overpotential and electrode
resistance at temperatures between 600°C and 800°C as compared to the other potential materials. Fig. 9 also shows that upon application of CSO buffer (∼0.1μm) on the LSCF/YSZ system, a significant reduction in electrode interfacial resistance was observed. This indicates that the CSO film can be a protective layer which impedes the interactions between LSCF on YSZ electrolyte thus improving cell performance at lower temperature.

4. CONCLUSIONS

The interactions of perovskite-type oxides, LSM and LSCF, with YSZ and CSO electrolytes have been studied by depositing dense electrode films (∼0.5 μm) on dense electrolyte substrates. XRD results showed that LSM and LSCF were compatible with CSO at temperatures to at least 1200°C, but after annealing at 1100°C for 2 hrs LSM reacted with YSZ to form La2Zr2O7 and SrZrO3. At 1000°C for 2 hrs LSCF reacted with YSZ to form SrZrO3. The electrode resistance and the effect of interactions on interface characteristics were investigated by AC impedance spectroscopy. LSCF/CSO system possessed lowest electrode resistance and overpotential. The interactions between LSCF (or LSM) and YSZ at higher processing temperatures result in high interfacial resistance. The CSO film merits application as a protective and buffer layer on YSZ electrolyte for high and intermediate temperature SOFCs. A two-layered thin film of YSZ and CSO on LSCF cathode substrate is suggested for intermediate temperature SOFC applications.

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Table I: Activation Energy of Electrode/Electrolyte Interface (This Study)

| System         | Activation Energy (KJ/mole) |
|----------------|-----------------------------|
| LSM/YSZ        | 136.24                      |
| LSM/CSO        | 144.09                      |
| LSCF/YSZ       | 124.01                      |
| LSCF/CSO       | 79.16 (High Temp.)          |
|                | 168.58 (Low Temp.)          |

Table II: Activation Energy of Electrode/Electrolyte Interface
(From Takeda) (13)

| System                          | Activation Energy (KJ/mole) |
|---------------------------------|----------------------------|
| La_{0.3}Sr_{0.7}MnO_{3-x}/YSZ   | 110                        |
| La_{0.5}Sr_{0.5}MnO_{3-x}/YSZ   | 180                        |
| La_{0.7}Sr_{0.3}MnO_{3-x}/YSZ   | 180                        |
| La_{0.3}Sr_{0.7}FeO_{3-x}/YSZ   | 90                         |
| La_{0.5}Sr_{0.5}FeO_{3-x}/YSZ   | 105                        |
| La_{0.7}Sr_{0.3}FeO_{3-x}/YSZ   | 160                        |
| La_{0.3}Sr_{0.7}CoO_{3-x}/YSZ   | 220                        |
| La_{0.5}Sr_{0.5}CoO_{3-x}/YSZ   | 220                        |
| La_{0.7}Sr_{0.3}CoO_{3-x}/YSZ   | 220                        |
Fig. 1: XRD patterns of the as-deposited LSM film on YSZ substrate after annealing between 800°C and 1100°C for 2 hrs.
Fig. 2: XRD patterns of the as-deposited LSCF film on YSZ substrate after annealing between 600°C and 1000°C for 2 hrs.
Fig. 3: XRD patterns of the as-deposited LSM film on CSO substrate after annealing between 800°C and 1200°C for 2 hrs.
Fig. 4: XRD patterns of the as-deposited LSCF film on CSO substrate after annealing between 800°C and 1200°C for 2 hrs.
Fig. 5: Typical surface and cross-section SEM images of a LSM/YSZ bilayer after firing at 1100°C for 2 hrs.
Fig. 6: Typical surface and cross-section SEM images of a LSCF/CSO bilayer after firing at 1100°C for 2 hrs.
Fig. 7: Complex impedance diagrams of the LSCF/CSO bilayer at various temperatures.
Fig. 8: Arrhenius plots of interface resistance/cm² for various systems.

Fig. 9: Plots of interface resistance/cm² (R_i) versus temperature for various systems.