

IV.A.19 Novel Composite Materials for SOFC Cathode-Interconnect Contact

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Objectives

- Elucidation of the mechanism of Ag evaporation at elevated temperatures.
- Alloy design and development of new Ag-based alloys with significantly reduced Ag evaporation/migration.
- Optimization of the processing and the microstructures of Ag alloy/perovskite composites.
- Demonstration/assessment of performance of the new contact materials in the solid oxide fuel cell (SOFC) operating conditions.

Accomplishments

- A number of Ag-base alloys have been prepared using both the arc-melting/drop-casting technique and the powder metallurgical route. These alloys were pressed into 1-mm sheets for Ag evaporation testing.
- Pd, Pt, and Au have been found to be effective in reducing the Ag evaporation rate; however, these elements are too expensive. The effects of other low-cost alloying additions on the Ag evaporation are being studied.
- The perovskite-containing composite contact layer has been demonstrated to effectively reduce the Cr migration from the interconnect to the porous cathode.
- With the increase of Ag in the composite contact layer, both the area specific resistance (ASR) of and thermal cycling-induced damage in the interconnect/contact/cathode test cells decreased.

Introduction

To reduce the electrode/interconnect interfacial resistance in SOFC stacks, electrical contact layers are often applied between the interconnect and electrodes during construction of an SOFC stack by compensating for the corrugations present on their respective surfaces. Some of the major criteria for SOFC contact materials are (1) sufficiently high electrical conductivity over the SOFC lifetime; (2) chemical stability under high current conditions and compatibility with other cell components, especially negligible effects on the formation of protective oxides on interconnect alloy; and (3) reasonable match in coefficient of thermal expansion (CTE) with other cell components. In addition, it is highly desirable for the contact materials to have some damage tolerance (possible self-healing if thermal cycle-induced cracking occurs in the contact layer) and to act as a Cr “sponge” by absorbing the Cr species migrating from the interconnect to the cathode and therefore reducing the Cr “poisoning” of the cathode. Because of the stringent criteria, finding a suitable material for the interconnect-cathode contact is very challenging.

The materials currently under consideration for cathode/interconnect contact application include low melting-point ceramics (such as doped LaCoO₃), noble metals (e.g. Ag or Pt), and their composites [1-2]. Pt, Au, and Pd are not desirable for this application because of their high raw material cost. However, Ag is an exception due to its relatively low price. An Ag-ceramic composite is one of the very promising candidates for a SOFC contact due to the inherent properties of Ag, such as high chemical stability, high electrical conductivity, high ductility, and relatively low melting point. The perovskite component in the composite is expected to provide a more desirable CTE match and potentially act as a Cr absorbent and/or a barrier for Cr migration to the cathode. One major drawback of Ag as a SOFC interconnect/cathode contact material is its tendency to evaporate at the SOFC operating temperatures, while for the perovskite material, thermal cycle-induced cracking and damage accumulation might be an issue.

Approach

Ag would be a wonderful contact material if its evaporation/migration can be reduced. Since Ag evaporation is determined by the bonding of Ag atoms, alloy design should focus on identifying suitable alloying elements that drastically affect the bonding in Ag or finding surface-active elements that segregate to and thus block the Ag sites on the Ag surface. What is desired

of the alloying elements is to effectively reduce Ag evaporation/migration without significantly altering the overall properties of Ag. A number of alloying additions have been selected based on these considerations and the Ag evaporation rate of each of these alloys is being determined using the optimized evaporation parameters identified last year. Another approach to reduce the Ag evaporation rate as well as improve the other properties of the contact material is to form a Ag/perovskite composites. By selecting the right perovskite material and optimizing the Ag-to-perovskite ratio, a composite material might address all the issues facing the interconnect-cathode contact material development.

The Ag-base alloys were prepared using both the arc-melting/drop-casting technique and the powder metallurgical route. These alloys were pressed into 1-mm sheets for Ag evaporation testing. The composite materials with different Ag-to-perovskite ratios were also synthesized and the performance of the composite materials as interconnect/cathode contact was assessed using a special testing rig.

Results

The effects of a number of alloying additions on Ag evaporation were investigated. The noble metals such as Pt, Pd, and Au noticeably reduced the Ag evaporation rate. Figure 1 shows the weight losses of the Ag-Pd alloys after exposure at 850°C for 40 hours in flowing air with a flow rate of 1.5 cm/s. It can be seen that the weight loss due to Ag evaporation decreased significantly as the content of Pd in the alloys increased. The weight loss of Ag decreased from about 0.28 mg/cm² for pure Ag to 0.08 mg/cm², less than one third of that of pure Ag, with a Pd content of 25 wt.% after exposure. Similar results were obtained for Ag-Au

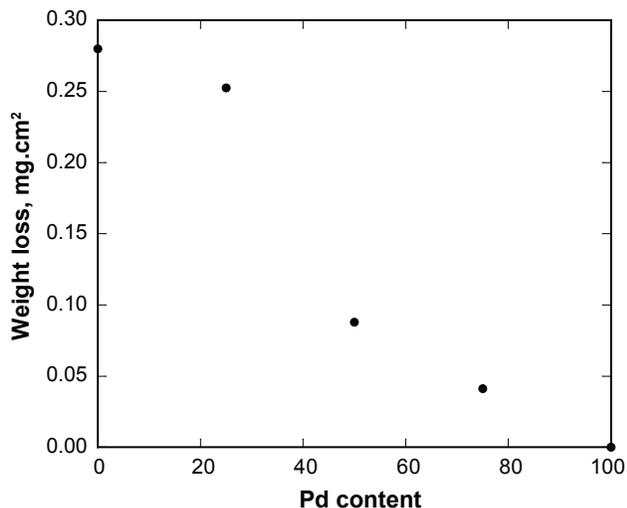


FIGURE 1. Weight Losses of Various Ag-Pd Alloys after Thermal Exposure at 850°C for 40 Hours in Air with a Flow Rate of 1.5 cm.s⁻¹

and Ag-Pt alloys. Obviously, the noble metal additions can reduce the evaporation rate of Ag. However, the reduction was more significant when the Pt, Pd, or Au additions were higher than 50%. Considering the cost of these elements, they are not suitable choices as alloying additions. Low-cost alloying additions with similar or further improved performance should be identified. Initial work indicates that micro-alloying with non-noble elements Cu, Ce, and Y had very little effect on the evaporation of Ag. The Ag alloys with Ce and Y additions even showed a slightly larger weight loss than pure Ag. A systematic study on the effects of other elements on Ag evaporation is currently underway.

Two types of Ag-perovskite composites are being evaluated, with the Ag contents of 0, 25, 50, 75, and 100% (in volume) in the composites. The first type is with La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF-6428) as the perovskite, while the second type is with La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ (LSCF-6482). Both Ag and the perovskite had very fine particle size of around 1 μm. The powders with the desired Ag-to-perovskite ratio were thoroughly mixed before pastes were made for screen printing. To evaluate the performance of various contact materials in a simulated SOFC environment, a special interconnect/contact/cathode test cell was constructed. Analysis with energy-dispersive spectroscopy (EDS) indicates that the amount of perovskite in the composite contact materials had a significant effect on chromium migration to the cathode from the interconnect alloy. Figure 2 shows that the amount of Cr detected in the center of the porous cathode layer as a function of the volume % of Ag in the Ag-(LSCF-6428) composite contact layer after the test cells were thermally exposed to air for 300 hours at 800°C. The increase of the LSCF content (and therefore the reduction of silver) in the contact material led to a significant decrease in chromium migration, as more Cr was absorbed by the perovskite phase.

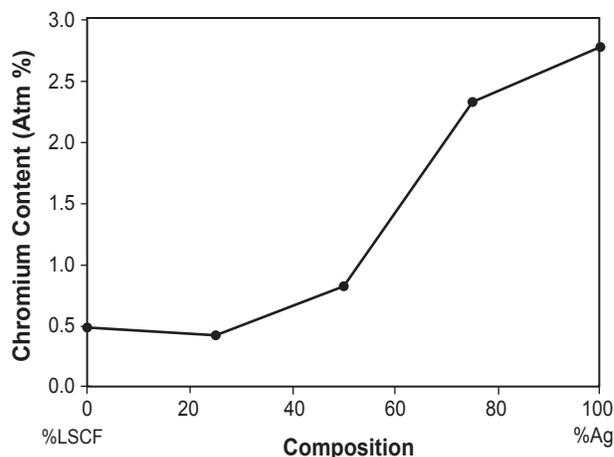


FIGURE 2. Chromium Content in the Porous LSM Cathode Layer vs. Volume % of Ag in the Ag-LSCF-6428 Composites

The ASR of the test cells with different Ag-LSCF contact materials as a function of exposure time and thermal cycling is shown in Figure 3. The data clearly indicate that the amount of perovskite in the composite contact materials had a significant effect on the ASR stability of the test cell as well as the cell resistance to thermal cycle-induced damage. For the pure perovskite contact material, after the initial “break-in” period, the ASR increased significantly during thermal cycling. This implies the damage was introduced in the contact layer during the cycling due to the brittleness of the perovskite material, leading to the jump in the ASR curve. Interestingly, the contact layer seemed to undergo a “self-healing” process during additional isothermal holding at 800°C, as the ASR value dropped continuously in this period of time. Nevertheless, the recovery in ASR was not complete; the accumulation of the residual damage led to a significant rise in ASR value, over 50 mΩ·cm², which is the targeted ASR limit for SOFC. From these results, it appears that pure LSCF contact materials are not adequate for interconnect-cathode contact application. With the increase in Ag content in the contact material, the ASR dropped continuously, as shown in Figure 3. The ASR value dropped from about 75 mΩ·cm² for the pure perovskite contact material to about 6 mΩ·cm² for the pure Ag contact material after 450 hours of thermal exposure at 800°C. Furthermore, the increase in ASR with thermal cycling was much lower for the Ag-containing contact materials. The Ag-containing contact materials are less prone to thermal cycle-induced damage, which might be a result of good ductility of the metal Ag. While pure

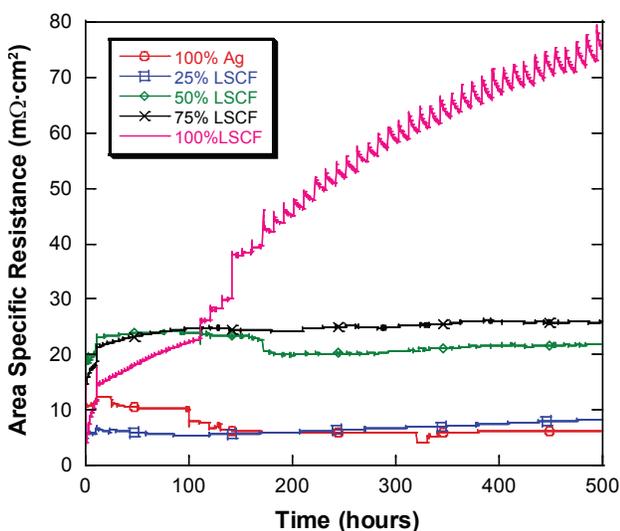


FIGURE 3. ASR of the Test Cell during Thermal Cycling for the Cells with Different Amounts of LSCF in the Contact Material (initial firing of 850°C x 10 h; “break-in” of 800°C x 100 h; 40 cycles with 800°C x 10 h holding plus furnace cooling to 250°C)

Ag contact material exhibited the best performance with regard to ASR stability and damage tolerance, it alone is not considered a good contact material, due to its high evaporation rate as well as ineffectiveness in blocking the Cr migration from the interconnect to the cathode. Based on these results, it seems that a Ag-composite material with about 50 vol% Ag and 50 vol% LSCF might be a good contact material that deserves further investigation.

Conclusions and Future Directions

The following conclusions can be drawn based on this study:

- Noble metals Pd, Pt, and Au were effective in reducing the evaporation rate of Ag. Micro-alloying with Y, Ce, or Cu had little effect on the evaporation of Ag.
- The perovskite in the contact material decreased the Cr migration from the interconnect to the porous cathode.
- While the pure perovskite LSCF is prone to thermal cycle-induced damage and ASR increase during thermal exposure, the addition of Ag to form a Ag-LSCF composite is effective in reducing the thermal cycling effect.

The future directions for this project are listed below:

- The evaporation rate of a number of binary and ternary Ag alloys with various alloying additions will be measured and potential alloying elements which can significantly reduce the Ag evaporation will be identified.
- The evaporation behavior of Ag+perovskite composites with different Ag-to-perovskite ratios will be studied.
- Electrical characterization and thermal cycling of the interconnect/contact/cathode test cells will be continued to identify the desired Ag-to-perovskite ratio as well as the best perovskite materials for achieving stable electrical conductivity of the cells.

FY 2007 Publications/Presentations

1. “Thermal Evaporation of Pure Ag in SOFC-Relevant Environments”, *Electrochemical and Solid-State Letters*, in press, 2007.
2. “Evaporation of Pure Ag under SOFC Operation Conditions”, Presented at the Symposium Fuel Cells and Energy Storage Systems: Materials, Processing, Manufacturing and Power Management Technologies, MS&T 06, Cincinnati, Ohio, October 15-19, 2006.

3. "Development and Characterization of Ag-LSCF Composite Contact Material for SOFC", Presented at the Symposium Fuel Cells and Energy Storage Systems: Materials, Processing, Manufacturing and Power Management Technologies, MS&T 06, Cincinnati, Ohio, October 15-19, 2006.

References

1. S. Koch, and P.V. Hendriksen, Solid State Ionics, 168, 1 (2004).
2. Z. Yang, G. Xia, P. Singh, J.W. Stevenson, J. Power Sources, 155, 246 (2006).