IV.A.15 SOFC Cathode Materials Development at PNNL

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Objectives

- Develop and optimize solid oxide fuel cell (SOFC) cathode materials and microstructures offering low polarization losses and long-term stability at intermediate SOFC operating temperatures (650-850ºC).
- Improve understanding of mechanisms affecting cathode performance, including both intrinsic factors (e.g., composition, microstructure) and extrinsic factors (e.g., Cr poisoning).

Accomplishments

- Performed baseline testing on Sr-doped lanthanum manganite (LSM), LSM/yttria-stabilized zirconia (LSM/YSZ), and LSM/samarium-doped ceria (LSM/SDC) cathodes.
- Initiated development of composite cathodes prepared using mechanofusion process.

Introduction

Minimization of cathodic polarization losses represents one of the greatest challenges to be overcome in obtaining high, stable power densities from SOFCs. Cathodic polarization typically exhibits high activation energy relative to other internal power losses, so the need to improve cathode performance becomes increasingly important as the targeted SOFC operating temperature is reduced. For high-temperature SOFCs operating at around 1,000ºC, the preferred cathode material is doped lanthanum manganite, which offers adequate electrical conductivity and electrocatalytic activity, reasonable thermal expansion, and stability in the SOFC cathode operating environment. For SOFCs operating at substantially lower temperatures, modified or alternative cathode materials may be required. For example, alternative perovskite compositions containing La on the A site and transition metals such as Co, Fe, and/or Ni on the B site have received attention. In general, they offer higher oxygen ion diffusion rates and exhibit faster oxygen reduction kinetics at the electrode/electrolyte interface than lanthanum manganite, but tend to exhibit significant degradation of performance over time. During FY 2007, PNNL's cathode development work was focused on development of LSM-based composite cathodes intended to provide improved performance in the 650-850ºC temperature range.

Approach

Cathode performance was measured by screen-printing and sintering the cathode material onto anode-supported YSZ membranes. In some cases, an SDC interlayer was included between the cathode and YSZ. After attachment of current collectors, the resulting cells were placed into test fixtures, and their current-voltage characteristics were evaluated using DC and impedance spectroscopy measurements. Cells were tested in air vs. moist (~3% H_2O) hydrogen at low fuel utilizations. After cell tests were completed, the cells were analyzed by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and other techniques as appropriate.

Results

Cathode compositions under study were $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM), LSM/YSZ (50/50 vol% mixture of LSM and 8YSZ), and LSM/SDC (50/50 vol% mixture of LSM and $Ce_{0.8}Sm_{0.2}O_2$). For each cathode composition, a range of sintering temperatures was evaluated in order to determine effects of sintering temperature of cathode performance. All of the cells were tested at 750ºC and at 0.7 V, with periodic current-voltage and impedance spectroscopic analysis. Although this study is still in progress, results to date are summarized in this report.

LSM Cathodes. For LSM cathodes sintered directly onto anode-supported YSZ electrolyte membranes, cell power densities were relatively low and quite variable even for nominally identical cathodes sintered at the same temperature. This result suggests that the performance of the LSM cathode may be highly dependent on slight changes in the cathode microstructure. In general, somewhat higher cell power densities were observed for LSM cathodes sintered onto SDC interlayers (Figure 1), but again the results for nominally identical cells showed considerable

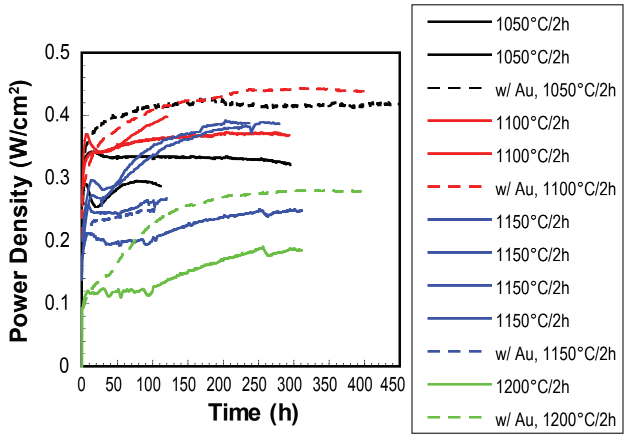

FIGURE 1. Anode-supported button cell test results for LSM cathodes sintered onto SDC interlayers at the indicated temperatures and tested at 0.7 V and 750°C. LSM contact paste was used except where Au is indicated.

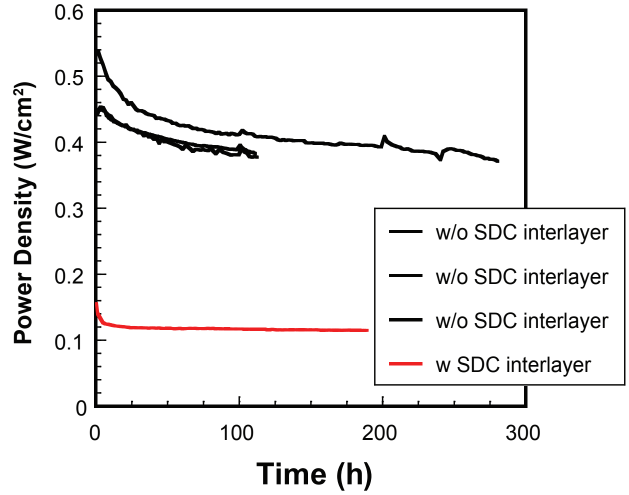

FIGURE 2. Anode-Supported Button Cell Test Results for LSM/YSZ Cathodes Sintered at 1,150°C and Tested at 0.7 V and 750°C

variability. Nyquist plots from impedance spectroscopic analysis indicated that, for cells with or without the SDC electrolyte interlayer, higher sintering temperatures tended to result in lower initial power densities, presumably due to increased densification and therefore reduction in triple phase boundary (TPB) length at the cathode/electrolyte interface. It will be noted that the ohmic resistance of samples with the SDC interlayer was higher than those sintered directly onto YSZ, which suggests that insulating zirconate phases were not formed at the cathode/YSZ interface during cell fabrication.

It was observed that, for a given sintering temperature, cathodes sintered directly onto YSZ tended to be denser than cathodes sintered onto an SDC interlayer. The enhanced densification of the cathodes on YSZ may be related to diffusion of Ni (from the NiO/YSZ anode) through the YSZ electrolyte into the LSM cathode. It has been established by SEM/EDS analysis that Ni diffusion from the anode into the YSZ during anode/electrolyte co-sintering at 1,375°C results in a Ni content of ~2-3 at% in the YSZ membrane. Similarly, SEM/EDS analysis on as-fabricated cells indicated that ~1-2 at% of Ni was present in an LSM cathode sintered at 1,150°C, and ~2-3 at% was present in an LSM cathode sintered at 1,250°C. In contrast, no Ni was detected in LSM cathodes sintered at those temperatures onto an SDC interlayer, suggesting that the SDC substantially blocks diffusion of Ni out of the YSM electrolyte into the cathode. The mechanism behind the enhanced sinterability of the LSM cathode containing Ni is not clear, but may be related to presence of free manganese oxide formed when Mn was displaced by Ni from B-sites in the LSM perovskite lattice.

LSM/YSZ Cathodes. Results for LSM/YSZ cathodes sintered at 1,150°C (with and without the SDC interlayer) are shown in Figure 2. LSM-YSZ on an SDC interlayer exhibited very poor performance, while LSM/YSZ sintered directly onto YSZ (no SDC interlayer) gave high initial performance followed by significant degradation. Overall the LSM/YSZ cathodes without the SDC layer demonstrated better consistency in performance, suggesting that a performance of a mixture of electronically conducting LSM and ionically conducting YSZ is less sensitive to subtle changes in microstructure compared to cathodes consisting of the electronically conducting LSM alone. The higher initial performance of the LSM/YSZ cathodes (compared to LSM) is probably associated with an expanded active region for oxygen reduction due to the mixed-conducting nature of the composite, but a more porous microstructure for the composite compared to LSM alone may also contribute. Figure 3 shows the difference in microstructure for LSM and LSM/YSZ cathodes sintered under identical conditions (1,200°C for 2 hours). It is frequently observed that, under identical conditions, and in the absence of liquid phase formation, multi-phase mixtures of oxide powders exhibit reduced densification relative to the single phase components on their own. Results from impedance spectroscopy analysis of the cells with LSM/YSZ cathodes revealed that the decrease in performance over time was predominantly associated with an increase in the ohmic resistance of the cell. It is possible that the increased resistance is a result of the formation of an insulating phase such as lanthanum zirconate during cell operation.

LSM/SDC Cathodes. Results for cells with SDC interlayer and LSM/SDC cathodes, sintered at the indicated temperatures, are shown in Figure 4. The cells typically showed some performance conditioning which was associated with a decrease in the non-ohmic component of the cell impedance. Ohmic resistance was relatively high, but remained stable over time. Similar

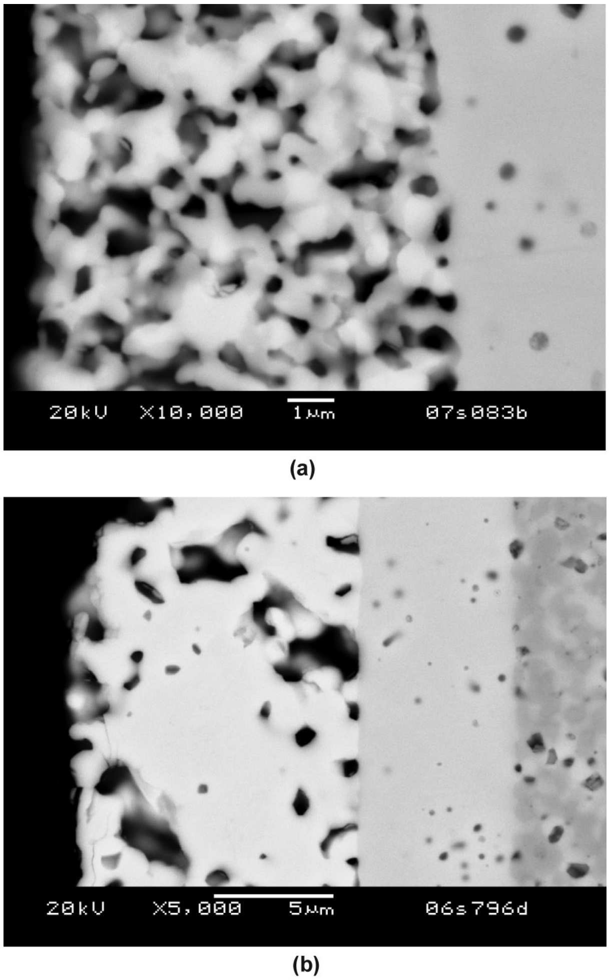

FIGURE 3. SEM Micrographs of a) LSM/YSZ and b) LSM Cathodes after Sintering at 1,200°C for 2 Hours

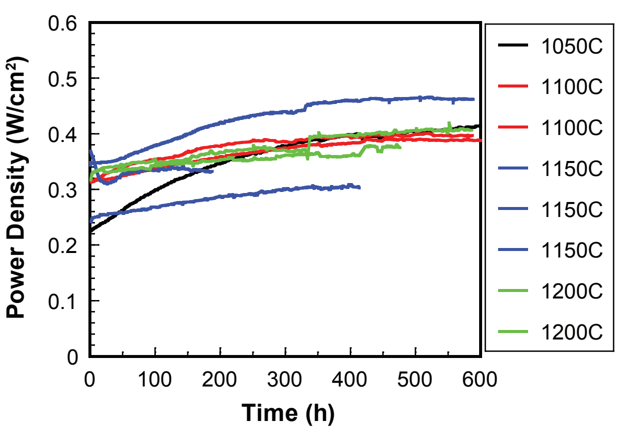

FIGURE 4. Anode-Supported Button Cell Test Results for LSM/SDC Cathodes Sintered onto SDC Interlayers at the Indicated Temperatures and Tested at 0.7 V and 750°C

to the LSM/YSZ cells, the LSM/SDC cells showed better performance consistency than the LSM-only cells. Overall, performance of the LSM/SDC cells was more stable than that of the LSM/YSZ cells. It is anticipated that future work directed towards a) optimizing the LSM/SDC microstructure via mechanofusion, and/or b) increasing cathode activity by insertion of electrocatalytic materials via infiltration may result in improved, stable performance for anode-supported cells with LSM/SDC or LSM/YSZ cathodes.

Conclusions and Future Directions

- LSM cathodes exhibited relatively poor performance and low reproducibility compared to composite (LSM/YSZ, LSM/SDC) cathodes.
- LSM/YSZ cathodes exhibited relatively high initial performance but the performance degraded over time, possibly due to the formation of insulating phases.
- LSM/SDC cathodes exhibited improved stability compared to LSM or LSM/YSZ cathodes.
- Future work will focus on optimizing LSM-based composite cathode microstructures via mechanofusion and/or other techniques to obtain improved, stable cathode performance at intermediate SOFC operating temperatures.

FY 2007 Publications/Presentations

Publications

1. S.P. Simner, M.D. Anderson, J.W. Templeton, and J.W. Stevenson, "Silver-Perovskite Composite SOFC Cathodes Processed via Mechanofusion," J. Power Sources, 168, 236 (2007).

Presentations

1. S.P. Simner, M.D. Anderson, and J.W. Stevenson, "Performance of a Novel La(Sr)Fe(Co)O_3-Ag SOFC Cathode," MS&T 2006, Cincinnati, OH, October 15–19, 2006.

2. S.P. Simner, M.D. Anderson, and J.W. Stevenson, "SOFC Cathode Degradation Mechanisms", MS&T 2006, Cincinnati, OH, October 15–19, 2006.

3. S.P. Simner, M.D. Anderson, and J.W. Stevenson, "SOFC Cathode Development at Pacific Northwest National Laboratory," 31st Int. Conference on Advanced Ceramics & Composites (American Ceramic Society), Daytona Beach, FL, January 21–26, 2007.