

V.9 SECA Coal-Based Systems Core Research

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Objectives

- Determine how contaminants found in coal gas will affect the performance of nickel-based solid oxide fuel cell (SOFC) anodes, with an emphasis on those contaminants expected to form secondary solid phases with nickel. This information is needed to help establish clean-up criteria for coal gas intended to fuel large SOFC systems.
- Establish the role of pressure on SOFC electrode activity and stability. Pressures in the range of 1 to 15 bar are emphasized, which are most relevant to SOFC integration with gasifier and turbine technology.
- Develop contact paste compositions and forms aimed at providing a more reliable electrical connection between the cathode and interconnect plate, and can be processed at temperatures less than 1,000°C.

Accomplishments

- Irreversible losses in SOFC performance of approximately 10 percent per 100 hours were observed when exposed to low concentrations of phosphine (PH_3) in simulated coal gas and in humidified hydrogen. Phosphine, expected to be present at about 2 ppm in coal gas following warm gas clean-up, interacts strongly with Ni in the anode to form stable secondary phases such as Ni_3P and Ni_5P_2 . In contrast, sulfur forms no secondary phases with Ni at similar concentrations. No interactions

of phosphorus-containing species with either zirconia or ceria were observed.

- Low concentrations of arsine (AsH_3) in simulated coal gas also led to irreversible losses in SOFC performance of approximately 10 percent per 100 hours, similar to results obtained for phosphine. Arsine concentrations of approximately 0.6 ppm are expected in coal gas following warm gas clean-up. Like phosphorus, arsenic reacts to form stable, secondary phases with nickel (primarily Ni_3As_2). No interactions with either zirconia or ceria were observed.
- The performance of lanthanum strontium manganite (LSM) and LSM-ceria composite electrodes were shown to improve considerably with increased pressure up to at least 100 bar. For LSM electrodes, polarization losses decreased as the square root of the oxygen partial pressure, which was shown by electrochemical impedance spectroscopy (EIS) to be dominated by gas adsorption processes. More active LSM-ceria composite electrodes also improved with increased pressure but more slowly due to a greater contribution of charge transfer processes.
- Enhanced densification of LSM was induced by thermal and oxygen partial pressure, at temperatures hundreds of degrees lower than typical processing temperatures. Enhanced sintering is the result of the creation of transient oxygen vacancies by thermal and oxygen partial pressure cycles, which interact with metal vacancies already present in LSM. This behavior potentially offers a way to densify LSM-based cathode contact pastes at low temperatures.

Introduction

The purpose of this project is to address key barrier issues of relevance to the operation of solid oxide fuel cells on gasified coal, in support of the Solid State Energy Conversion Alliance (SECA) Coal-Based Systems Program. The interaction of contaminants known to be present in gasified coal with nickel-based SOFC anodes is being investigated, with an emphasis on those contaminants that are expected to form secondary phases with anode components. This information is needed to help establish criteria for coal gas cleanup. Because integration of SOFC stacks with gasifiers and turbines may require operation at elevated pressures, this project is evaluating how the activity and stability of SOFC electrodes are affected by high pressure. Contributions to electrode losses include charge transfer,

gas adsorption, and concentration polarization, all of which show pressure dependence. High steam partial pressures on the anode side are expected to affect the stability of the nickel electrode. Finally, contact paste compositions and forms are being developed to provide a more reliable electrical connection between the porous cathode and the interconnect plate. To minimize degradation of metallic components during stack assembly, it is considered essential that the contact pastes be processed at temperatures less than 1000°C.

Approach

This project is addressing three principal topics: (1) interaction of SOFC anodes with coal gas contaminants, (2) the influence of elevated pressures on SOFC electrode performance, and (3) electrical contact paste development. Coal gas contaminant studies emphasize those trace species expected to remain after warm gas cleanup and possibly form secondary phases with nickel, following the results of a recent study by Trembly, Gemmen, and Bayless [1], as summarized in Table 1. The tendency for adsorption and second phase formation was evaluated using zirconia test coupons, onto which anode materials were screen-printed, which were exposed to contaminants of interest in a coal gas matrix. Anode-supported button cells were similarly exposed, and changes in performance evaluated by direct and alternating current methods. Post-test analyses were conducted with analytical electron microscopy and surface electron spectroscopies to evaluate the extent of adsorption and secondary phase formation. To evaluate the effect of pressure on SOFC electrode performance, a high-pressure cell was constructed that is capable of operation to 950°C and 130 bar. Cells with thick (~2 mm) electrolytes were employed, which enabled an embedded reference electrode to be used. Electrode performance under cathodic and anodic polarization was evaluated by direct and alternating current methods. LSM and LSM composite electrodes were emphasized in initial studies. Contact paste compositions that were considered include the layered calcium cobaltites and

TABLE 1. Trace Species in Coal Gas Expected to Affect SOFC Performance and Concentrations Following Warm Gas Cleanup (from Trembly, Gemmen, and Bayless [1]).

Component	Concentration, ppmv
Antimony	0.07
Arsenic	0.6
Cadmium	0.011
Lead	0.26
Mercury	0.025
Phosphorus	1.9
Selenium	0.15

LSM. Layered calcium cobaltites exhibit a misfit layered structure, consisting of an oxygen octahedral layer and a Co-O layer. These materials yield an unusually stable electrical conductivity over a wide temperature regime, a good thermal expansion match to other fuel cell components, and a favorable processing temperature. Oxygen partial pressure cycling was employed to lower the sintering temperature of LSM, effective because of the unique defect structure of that material.

Results

Coal Gas Contaminant Studies: In this study, SOFC operation on simulated coal gas was evaluated in the presence of certain impurities that are expected to remain in low concentration after warm gas cleanup. Phosphorus, arsenic and antimony compounds were emphasized because of their ability to form secondary phases with Ni in the SOFC anode in low concentration.

It was found that the SOFC did not show immediate degradation upon exposure to PH_3 or AsH_3 . After 30-50 hours of exposure, cell area specific resistances (ASR) began to increase at the rate of 10-20%/100 hours, as shown in Figure 1 for PH_3 exposure. This process was irreversible and returning to moist hydrogen without contaminants in the stream did not lead to a decrease in the ASR. Post-mortem microstructural and surface analysis revealed secondary nickel phase formation, mainly on the metal nickel current collecting grid on the Ni/YSZ anode. Depending on the time of exposure and proximity to the gas channel, Ni was partially or entirely converted either into nickel phosphides or nickel arsenide. Scanning electron microscopy/energy dispersive spectrometer (SEM/EDS) identified the presence of only one form of the arsenide, Ni_3As_2 , while several forms of nickel phosphides, Ni_3P , Ni_5P_2 and Ni_2P , were found. Although conductive, nickel phosphides have much lower melting temperature than metallic

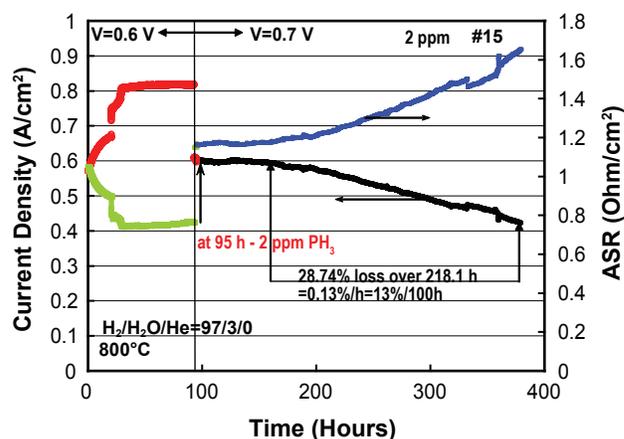


FIGURE 1. Anode Supported Cell Performance at 800°C When Exposed to 2 ppm PH_3 in Hydrogen/Steam

Ni. This resulted in the current collector surface reorganization followed by densification.

It is suggested that phosphorus and arsenic adsorb immediately on the Ni surface, both in hydrogen and the coal gas. Because of the strong Ni-P and Ni-As interactions, the main changes occurred on the surface and not in the anode bulk. At the same time, x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) analyses revealed gradients in P and As from the top of the anode to the anode/electrolyte interface, as is shown in Figure 2. In particular, after the test at 800°C in the presence of 5 ppm of PH₃, Ni₃P was observed up to 70 μm from the top. Nickel secondary phases at the electrode/electrolyte interface were not detectable by the techniques used. Thus, cell degradation could be ascribed to changes in the current collector (the mass transport limitations because of the current collector densification and perhaps the difference in conductivities of Ni and Ni₃P).

Pressure Dependence of Cathode Performance:

The performance of LSM and LSM/ceria composite electrodes was found to improve substantially with increases in pressure. Polarization curves for an LSM electrode in both cathodic and anodic directions are given in Figure 3 at different oxygen partial pressures, and show typical Tafel behavior with two electrons transferred in the rate-limiting step. Exchange currents for LSM electrodes, calculated from polarization curves, were found to increase as the square root of the oxygen partial pressure to at least 100 bar, as is shown in Figure 4. Two principal features were observed in the EIS spectra for LSM electrodes: a dominant low frequency arc associated with gas adsorption processes and a much smaller arc at high frequency associated with charge transfer processes. These results suggest rate control by a dissociative oxygen adsorption mechanism, and show that the surface of LSM is not saturated with oxygen adatoms even to very high pressures. In contrast, platinum electrodes do become saturated with oxygen adatoms below 1 bar, and actually become less active with further increases in pressure.

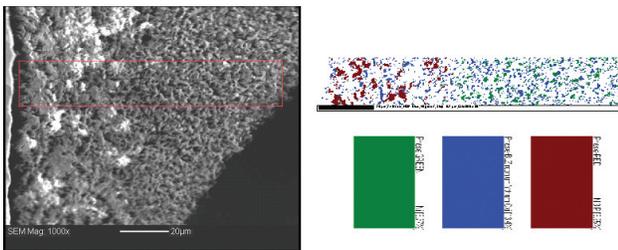


FIGURE 2. Electron backscatter diffraction (EBD) characterization of the Ni/YSZ anode after the SOFC test at 800°C in H₂/H₂O=97/3 with 5 ppm of PH₃ for 166 hours. Left side is the top part of the anode (closest to the fuel channels). Red is Ni₃P, blue is YSZ, green is Ni.

LSM-ceria composite electrodes also improved with increased pressure but more slowly, the results of which are also included in Figure 4. The composite electrode is a mixed electron and ion conductor, and more active than LSM alone. At 850°C, a clear change in slope was apparent at higher pressures. For oxygen pressures less than 10 bar, exchange currents followed a square root of pressure dependence, while a P^{1/4} dependence was followed for pressures greater than that value. A P^{1/4} oxygen partial pressure dependence is expected for dissociative charge transfer-limited reactions, where surface sites are not saturated. Electrochemical impedance results for the composite electrode again showed two principal features, dominated by a high frequency charge transfer feature, in agreement with the observed pressure dependence. This is the first such investigation of SOFC cathode performance at elevated pressures conducted with a DC bias, and shows that significant improvements in SOFC performance may

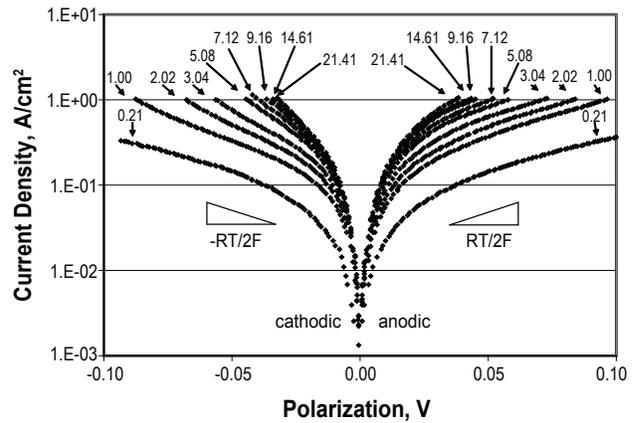


FIGURE 3. Polarization Curves for an LSM-20 Cathode on Yttria-Zirconia at 850°C at the Indicated Oxygen Partial Pressures, Determined Using Current Interrupt Methods

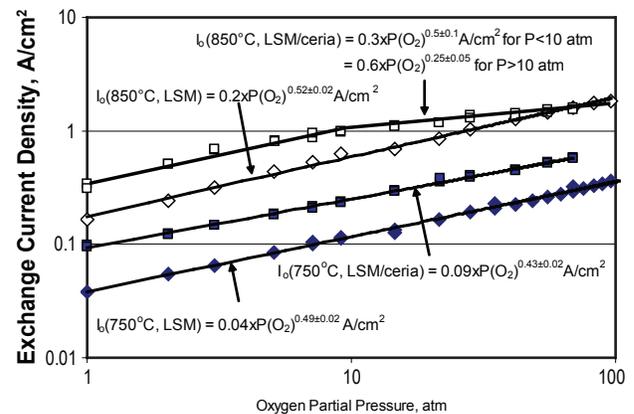


FIGURE 4. Relation of Exchange Current Density to Oxygen Partial Pressure for an LSM-20 Cathode and for an LSM-20/Ceria Composite Cathode

be expected when operated at greater than atmospheric pressure.

Enhanced Sintering of LSM by Oxygen Partial Pressure Cycling: Exposure of $(\text{La}_{0.90}\text{Sr}_{0.10})_{0.98}\text{MnO}_{3+\delta}$ (LSM-10) to repeated oxygen partial pressure cycles (air/10 ppm O_2) resulted in enhanced densification rates, similar to behavior shown previously due to thermal cycling. Shrinkage rates in the temperature range of 700 to 1,000°C were orders of magnitude higher than Makipirtti-Meng model estimations based on stepwise isothermal dilatometry results at high temperature, as is shown in Figure 5. A maximum in enhanced shrinkage due to oxygen partial pressure cycling occurred at 900°C. Shrinkage was greatest when LSM-10 bars that were first equilibrated in air were exposed to gas flows of lower oxygen fugacity than in the reverse direction. The former creates transient cation and oxygen vacancies well above the equilibrium concentration, resulting in enhanced mobility. These vacancies annihilate as Schottky equilibria is re-established, whereas the latter condition does not lead to excess vacancy concentrations.

These principles were applied in developing a method to densify LSM-based contact pastes at low temperatures. Figure 6 provides fracture strengths for two spinel-coated Crofer 22 coupons bonded together with an LSM slurry. Two sets of samples were evaluated: the first was held in air at 900°C (control) and the second was subjected to alternating air/10 ppm O_2 cycles. The control set developed no significant bond strength, while the second gave fracture strengths of several MPa. LSM is a preferred contact paste composition because of relatively good stability and compatibility with other fuel cell components, however

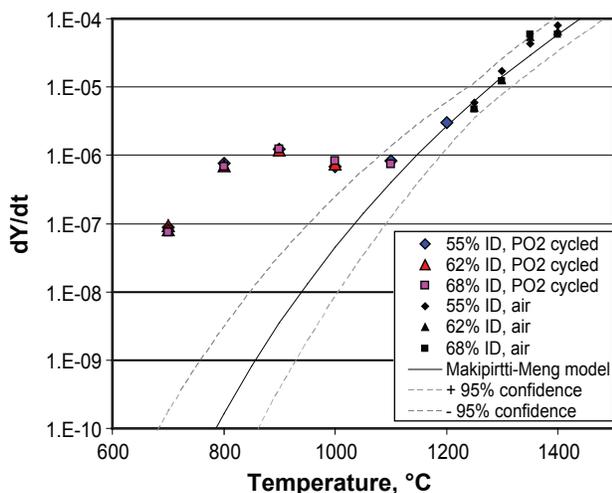


FIGURE 5. Volumetric shrinkage rate for LSM-10 as a function of temperature for samples with initial densities (ID) ranging from 52 to 68 percent of theoretical. Air/10 ppm O_2 cycles resulted in a significant increase in sintering rate compared to sintering in air alone.

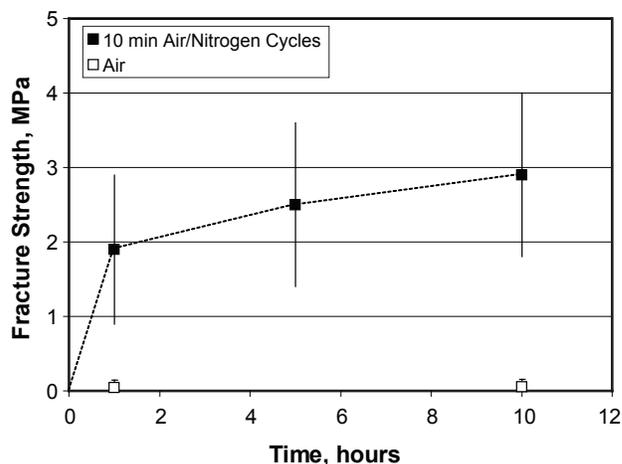


FIGURE 6. Fracture strength of two coated Crofer 22 plates that had been bonded together with an LSM-10 contact paste. Samples exposed to air/10 ppm O_2 cycles developed substantially greater fracture strengths than those exposed only to air at 900°C.

its high sintering temperature limits its use in stacks with metallic interconnects. Though considerable work remains to be done to optimize contact paste compositions and bonding schedules, this work demonstrates that low temperature processing of LSM contact pastes is possible.

Conclusions and Future Directions

- Exposure of nickel-based SOFC anodes to phosphorus and arsenic compounds of 1 to 5 ppm in a coal gas matrix led to irreversible performance losses of ~10 percent per 100 hours. Secondary phases were formed with both these coal gas contaminants, particularly involving the nickel-based current collector paste. Future studies will address degradation reactions involving these and other high priority coal gas contaminants, as well as synergistic effects.
- Elevated pressures, which may be necessary when integrating SOFCs with gasifiers and turbines, were shown to lead to significantly improved cathode performance. The improvement followed a $P^{1/2}$ dependence for LSM, which is dominated by dissociative oxygen adsorption reactions. Mixed electronic and ionic conductors such as an LSM/ceria composite improved more slowly with increased pressure, reflecting a greater dependence on charge transfer reactions. Future work will address the role of pressure on anode reaction kinetics and stability.
- Densification of LSM was accomplished in a cyclical oxygen partial pressure environment at temperatures hundreds of degrees lower than typical processing temperatures, an outgrowth of the unique

defect structure of LSM. Using these principles, a processing schedule for LSM contact pastes was developed that provided fracture strengths between two Crofer 22 coupons of several MPa in a matter of hours. Future work will be directed towards optimizing contact paste compositions and processing conditions.

FY 2007 Publications/Presentations

1. Zhou XD, Pederson LR, Cai Q, Yang J, Scarfino BJ, Kim M, Yelon WB, James WJ, Anderson HU, Wang C. "Structural and magnetic properties of $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0 < x < 1.0$).” *J. Appl. Phys* 99 (8): Art. No. 08M918 2006.
2. Pederson LR, Singh P, and Zhou XD. "Application of vacuum deposition methods to solid oxide fuel cells – a review.” *Vacuum* 80: 1066–1083 (2006).
3. Marina OA, Pederson LR, Williams MC, Coffey GW, Meinhardt KD, Nguyen CD, and Thomsen EC. "Electrode Performance in Reversible Solid Oxide Fuel Cells.” *J. Electrochem. Soc.*, 154 (5): B452–B459 2007.
4. McCarthy BP, Pederson LR, Anderson HU, Zhou XD, Singh P, Coffey GW, and Thomsen EC. "Enhanced Shrinkage of Lanthanum Strontium Manganite ($\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_{3+\delta}$) Resulting from Thermal and Oxygen Partial Pressure Cycling.” *J. ACerS* 2007 (*in press*).
5. Zhou XD and Pederson LR. "Solid State Materials for Energy Conversion.” Presented by Xiao-Dong Zhou (Invited Speaker) at 53rd Midwest Solid State Physics Conference, Kansas City, Missouri, October 6–8, 2006.
6. McCarthy BP, Pederson LR, Anderson HU, Zhou XD, and Coffey GW. "Anomalous Shrinkage of Strontium Doped Lanthanum Manganite.” Presented at Materials Science & Technology Conference, Cincinnati, OH, October 15–19, 2006.
7. Zhou XD, Thomsen EC, Nie Z, Coffey GW, and Pederson LR. "Oxide Thermoelectric Materials and Devices.” Presented at Materials Science & Technology Conference, Cincinnati, OH, October 15–19, 2006.
8. Zhou XD, Thomsen EC, McCarthy BP, Nie Z, Senor DJ, Coffey GW, Simner SP, and Pederson LR. "Processing and characterization of Calcium Cobaltates.” Presented at Materials Science & Technology Conference, Cincinnati, OH, October 15–19, 2006.
9. Zhou XD, Xia GG, Yang Y, Thomsen EC, Coffey GW, Stevenson JW, and Pederson LR. "High Temperature thermoelectric power and electrical conductivity in perovskites and spinels.” Presented at Materials Science & Technology Conference, Cincinnati, OH, October 15–19, 2006.
10. Marina OA, Pederson LR, Thomsen EC, Simner SP, Templeton JW, and Andersen M. "Performance of Single Cell Reversible SOFCs under Various Operating Conditions.” Presented at 4th International Symposium on Solid Oxide Fuel Cells (SOFC), Daytona Beach, FL on January 23, 2007.
11. Zhou XD and Pederson LR. "Oxides for Direct Thermal-to-Electric Energy Conversion.” Presented at Materials Research Society Spring Meeting, San Francisco, CA, April 9–13, 2007.
12. Pederson LR, Singh P, and Zhou XD. "Application of Vacuum Deposition Methods to Solid Oxide Fuel Cells.” Presented at International Conference on Metallurgical Coatings and Thin Films, San Diego, CA on April 24, 2007 (invited).
13. Zhou XD and Pederson LR. "Size Dependence of Electrical and Thermal Transport Properties in Oxides.” US-Korea Nanotechnology Forum, Honolulu, HI, April 26–27, 2007.

References

1. Tremblay JP, Gemmen RS, Bayless RJ. "The effect of IGFC warm gas cleanup system conditions on the gas-solid partitioning and form of trace species in coal syngas and their interactions with SOFC anodes.” *J. Power Sources* 163,986(2007).