BES018. High Performance Nano-Crystalline Oxide Fuel Cell Materials

Thomas O. Mason, Scott Barnett, Donald Ellis, Laurence Marks, Kenneth Poeppelmeier, Peter Voorhees

Northwestern University
Materials Science Department
2220 Campus Drive
Evanston, IL 60208
Phone: (847) 491-3198; Fax: (847) 491-7820
E-mail: t-mason@northwestern.edu

DOE Program Officer: Dr. Refik Kortan

Phone: (301) 903-3308
E-mail: Refik.Kortan@science.doe.gov

Subcontractors: None

Objectives

The proposed project aims to explore enhancements in the electronic and ionic transport properties of nano-scale oxides and surfaces, and to utilize these materials to enhance the performance of reduced-temperature solid oxide electrochemical cells (*i.e.,* fuel cells and electrolyzers). The project is focuses on electrode materials, and the use of nano-scale materials to enhance properties and surface areas to increase electrochemical reaction rates. Also, we are exploring the enhancement of electronic and oxide-ion transport properties, which help limit the reduced-temperature performance. Stability of nano-scale materials is also being explored.

Technical Barriers

Decreasing the operating temperature of solid oxide electrochemical cells is desirable from a number of perspectives including easing seals/interconnect materials issues, reducing balance of plant costs, and enabling applications in portable devices and transportation. However, reduced temperature significantly degrades performance, due to increased electrode polarization resistance and reduced electronic and ionic conductivities. The long-term stability of nano-scale materials needs to be investigated.

Abstract, Progress Report and Future Directions

The goal of this project is to utilize nano-structures, and any enhancements in electronic and ionic transport properties resulting from the nano-scale features sizes and/or high surface density, to address the electrode polarization and conductivity issues currently limiting low-temperature solid oxide fuel cell (SOFC) performance. In this update we highlight recent research results including nano-scale catalysts and effect of grain size on ionic conductivity.

Infiltrated Cathode Materials

On the cathode side, we have studied the effect of solution additives and processing techniques on the phase purity and performance of nano-composite cathodes produced via infiltration. In addition to achieving record low cathode performance from a single infiltration, simple models have been developed to predict the electrode polarization resistance.

$Sm_{0.5}Sr_{0.5}CoO_{3-x}$ (SSC) nano-particles with hemispherical radii of ~ 20 nm have been produced by nitrate infiltration $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) scaffolds. Polarization resistance, *Rp*, predictions were made using the modified Tanner, Fung, Virkar model.[1] The measured polarization resistances for SSC-GDC agreed well with the modified form of Tanner, Fung, Virkar model, as did those of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (LSCF)-infiltrated GDC cathodes. An exceedingly low polarization resistance of 0.1 Ωcm^2 at 600°C was achieved with a single infiltration. We expect that with multiple infiltrations, polarization resistances of this magnitude will be achievable at 500°C.

The coarsening behavior of infiltrated LSCF electrodes, and the associated changes in polarization resistance, have been studied. In order to accelerate changes to manageable time frames (normal cell life times are expected to be $> 40,000$ h), cathodes were maintained at temperatures higher than expected for operation (700-850°C). Field-emission scanning electron microscope (SEM) and polarization resistance measurements were used to detect changes. With time, LSCF nano-particles were observed to agglomerate together, coating less of the CGO scaffold and growing larger in size. Correspondingly, the polarization resistance increased substantially. The results are being fit to both standard coarsening power-law models and being used to constrain/validate phase-field modeling. The aim is to develop sufficiently detailed mechanistic models to allow accurate prediction of lifetimes at normal operating temperatures (500-700°C) for extended times.

Novel Anode Materials

The mixed conducting oxide, $LaSr_2Fe_2CrO_{9-x}$, (LSFCr) is a promising new anode. Ni cermets are the most commonly used SOFC anodes because of their excellent electrochemical performance in hydrogen fuel, but Ni is susceptible to sulfur poisoning and carbon

coking, which are detrimental to anode performance. Oxide anodes have potential for lower operating temperatures, while also being stable to higher impurity concentrations and active to different fuel compositions.

LSGM electrolyte supported fuel cells with $LaSr_2Fe_2CrO_{9-\delta}$ and $LaSr_2Fe_2CrO_{9-\delta}$/GDC composite anodes have been fabricated and tested. The $LaSr_2Fe_2CrO_{9-\delta}$ anode cells typically yielded peak power densities of 400-455 mW/cm^2 at 800°C with corresponding electrode polarization resistances of 0.27-0.40 Wcm^2. The $LaSr_2Fe_2CrO_{9-\delta}$/GDC (50:50 wt%) anode cells yielded similar performance as the pure $LaSr_2Fe_2CrO_{9-\delta}$ compounds with peak power densities 400-480 mW/cm^2 and polarization resistances of 0.25 - 0.40 Ωcm^2. The similar performance of the anodes with and with out GDC suggests that the $LaSr_2Fe_2CrO_{9-\delta}$ anodes are not limited by their oxygen ion conductivity. Currently, oxygen relaxation experiments are underway to determine the surface exchange rate and oxygen diffusivity of $LaSr_2Fe_2CrO_{9-\delta}$ under anodic conditions.

This group has also developed a novel class of anodes where nano-scale metal catalyst particles nucleate during cell operation. To investigate the precipitation of Ru nano-particles from (La,Sr)(Cr,Ru)O_3 (LSCrRu), fuel cells with LSCrRu/GDC anodes were operated in an environment of humidified H$_2$ condition at 800ºC for 120 hr. Focused ion beam (FIB) cross-sectional TEM revealed that the density of the Ru particles was non-uniform across the thickness of the anode and the particles were only found at the LSCrRu surface facing the electrolyte. It was observed that the average size and the area density of the formed Ru nano-particles was 2.9 nm and 5.1 x 10^4 particles/µm^2, respectively. It was also confirmed that the Ru nano-particles are crystalline, which is in good agreement with the results obtained from reduced LSCrRu powders. These results confirm that that the performance increases seen in LSCrRu/GDC anodes are, in fact, due to Ru nano-particle exsolution.

We have developed models to describe Ru exsolution from LSCrRu using phase field methods. The model indicates that as time evolves, the concentration of the Ru atoms in the LSCrRu decreases and the Ru nano-particles increase in size and form hemispherical shapes on the LSCrRu surface. While most of the growth is taking place through the bulk, the majority of the coarsening takes place via surface diffusion.

Transport In Nano-Scale Materials

Work in the Mason group has focused on continued application of the novel "nano-Grain Composite Model" (n-GCM) to characterize the local properties of fuel cell electrolytes as a function of grain size. As the n-GCM requires independently measured grain core dielectric constants as an input parameter, one side project in

the Mason group has been to characterize grain core (or single crystal dielectric constant) behavior over the temperature range of interest.

Using these grain core dielectric constant data, the n-GCM model was then applied to determine local properties of the four electrolyte systems: yttria stabilized zirconia (YSZ), tetragonal zirconia polycrystal (TZP), strontium- and magnesium-doped lanthanum gallate (LSGM), and gadolinia doped ceria (GDC). It was found that in each case, whereas grain core conductivities are not significantly different from that of the microcrystalline counterpart, the local grain boundary conductivities are significantly enhanced at the nano-scale, compared to conventional microcrystalline electrolytes. Despite the consistent increase in local grain boundary conductivity in the nano-grained samples, the total conductivity was seen to decrease monotonically with decreasing grain size in all four systems. This effect is due to the fact that grain boundaries remain barriers to transport (compared to grain cores) at the nano-scale, and there are many more grain boundaries in nano-crystalline samples.

The n-GCM also allows determination of electrical grain boundary widths, calculated from the volume fraction of grain cores. These values have been in excellent agreement with reported acceptor dopant segregation widths at grain boundaries. Furthermore, in collaboration with the Marks group we have shown that electrical grain boundary widths in our nano-YSZ samples agree with yttrium segregation widths measured on those same samples.

The Lattice Monte Carlo methodology has been used to study microstructure and thermodynamic properties of yttria stabilized zirconia, YSZ. Here a topological lattice representing the underlying crystal structure was described by a set of occupation numbers on two distinct sets of sites, defining (Y, Zr) and (O, vacancy) populations which were randomly sampled. A Cluster Expansion (CE) of energy at T=0 was developed as a polynomial in the occupation numbers, with coefficients determined variationally by fitting to a set of 'training configurations' whose energy was determined from fully self-consistent geometrically relaxed Density Functional (DF) calculations on supercells. Finite temperature free energy was developed by inclusion of vibrational entropy, in the harmonic approximation, using ensemble averages based upon the cluster expansions. The constant volume specific heat was developed directly as variation of internal energy with T, yielding results in good agreement with experiment. Two-body radial distribution functions were developed, again as ensemble averages at specified T, to display and help understand correlations between Zr-vacancy, vacancy-vacancy, Y-Y, etc site occupancy. The principal observations were that: (1) the oxygen coordination sphere around Zr is less populated than

that of Y, (2) vacancies tend to associate as 2nd neighbors with Y dopants, just as observed previously for vacancy-Zr association, (3) Y atoms tend to cluster together, and (4) vacancies repulse each other, as expected in terms of Coulomb interactions; however, a noticeable tendency toward vacancy ordering on the 3rd neighbor shells is predicted. Similar analyses for LSM, LSCrRu and LSCF are ongoing.

References

1. Shah, M., Nicholas, J.D. & Barnett, S.A. Prediction of infiltrated solid oxide fuel cell cathode polarization resistance. *Electrochemistry Communications* **11**, 2-5 (2008).

2. Nicholas, J.D. & DeJonghe, L.C. Prediction and Evaluation of Sintering Aids for Cerium Gadolinium Oxide. *Solid State Ionics* **178**, 1187-1194 (2007).

3. Avila-Paredes, H.J. & Kim, S. The Effect of Segregated Transition Metal Ions on the Grain Boundary Resistivity of Gadolinium Doped Ceria: Alteration of the Space Charge Potential. *Solid State Ionics* **177**, 3075-3080 (2006).

Publications acknowledging the grant

1. N.H. Perry, T.C. Yeh, and T.O. Mason, "Temperature Dependence of Effective Grain Core/ Single Crystal Dielectric Constants for Acceptor-Doped Oxygen Ion Conductors," Journal of the American Ceramic Society (2010), in final revision.

2. M Gong; DM Bierschenk; J. Haag; KR Poeppelmeier; SA Barnett; C Xu; JW Zondlo; X Liu, "Degradation of $LaSr_2Fe_2CrO_{9-\Delta}$ SOFC anodes in phosphine-containing fuels," J. Power Sources, in press.

3. W. Kobsiriphat, B.D. Madsen, Y. Wang, M. Shah, L.D. Marks and S.A. Barnett, "Ni- and Ru-Doped Lanthanum Chromite Anodes: Effects of Nanoscale Metal Precipitation on Solid Oxide Fuel Cell Performance," *J. Electrochemical Society* **157** (2010) B279-B284.

4. Nicholas, J.D. and Barnett, S. A., "Measurements and Modeling of $Sm_{0.5}Sr_{0.5}CoO_{3-x}$ -$Ce_{0.9}Gd_{0.1}O_{1.95}$ SOFC Cathodes Produced Using Infiltrate Solution Additives," J. Electrochemical Society, (2010), 157, B536.

5. N.H. Perry and T.O. Mason, "Grain core and grain boundary electrical/dielectric properties of yttria-doped tetragonal zirconia polycrystal (TZP) nanoceramics," Solid State Ionics 181 (2010) 276-284.

6. JD Nicholas and SA Barnett, "Effect of Infiltrate Solution Additives on $Sm_{0.5}Sr_{0.5}CoO_{3-x}$ -$Ce_{0.9}Gd_{0.1}O_{1.95}$ Nano-Composite SOFC Cathodes", ECS Transactions - Vienna, Austria Volume 25, Solid Oxide Fuel Cells 11 (SOFC-XI).

7. Nicholas, J.D. and Barnett, S.A. Finite-Element Modeling of Idealized Infiltrated Composite Solid Oxide Fuel Cell Cathodes. *J. Electrochemical Society*, 2009, 156, B458-B464.

8. Shah, M., Nicholas, J.D. and Barnett, S. Prediction of Infiltrated Solid Oxide Fuel Cell Cathode Polarization Resistance. *Electrochemistry Comunications*, 2009, 11, 2-5.

9. Kobsiriphat, W., Madsen, B., Wang, Y., Marks, L.D. and Barnett, S.A. $La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_3$ - $Gd_{0.1}Ce_{0.9}O_{1.95}$ Solid Oxide Fuel Cell Anodes: Ru Precipitation and Electrochemical Performance. *Solid State Ionics*, 2009, 180, 252-256.

10. Shah, M. and Barnett, S.A. Solid oxide fuel cell cathodes by infiltration of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ into Gd-Doped Ceria. *Solid State Ionics*, 2008, 179, 2059-2064.

11. Haag, J.M., Madsen, B.D., Barnett, S.A. and Poeppelmeier, K.R. Application of $LaSr_2Fe_2CrO_{9-x}$ in Solid Oxide Fuel Cell Anodes. *Electr Solid State Lett*, 2008, 11, B51-B53.

12. Kidner, N.J., Perry, N.H. and Mason, T.O. The Brick-Layer Model Revisited: Introducing the Nano-Grain Composite Model. *Journal of the Americal Ceramics Society*, 2008, 91, 1733-1746.

13. Perry, N.H., Kim, S. and Mason, T.O. Local Electrical and Dielectric Properties of Nanocrystalline Yttria-Stablized Zirconia. *Journal of Materials Science*, 2008, 43, 4684-4692.