V.12 SECA Coal-Based Systems Core Research - University of Florida

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Objectives

- Apply computational approach to develop fundamental understanding of ionic transport and heterogeneous electrocatalysis in solid oxide fuel cells (SOFCs).
- Develop high resolution characterization techniques to quantify electrode microstructures.
- Combine heterogeneous catalysis, electrochemistry, and microstructure characterization techniques to deconvolute contributions to electrode polarization.

Accomplishments

- Utilized *ab initio* and molecular dynamic simulations to calculate defect and defect cluster formation energies and effect on ionic transport.
- Computationally and experimentally determining thermo-mechanical properties based on fundamental thermodynamic/bond-energy constants.
- Used atomic-level simulation methods to elucidate the effects of non-stoichiometry and temperature on the elastic properties of CeO_{2-x}.
- Determined adsorption and absorption energies for O on and in $LaFeO_3$ (110) using first principles, electronic structure calculations.
- Developed high resolution scanning electron microscopy (SEM) - focused ion beam (FIB) characterization technique and applied to SOFC cathodes to quantify 3D microstructure.
- Determined effect of sintering temperature on lanthanum strontium manganate (LSM) and lanthanum strontium cobalt ferrite (LSCF) cathode microstructures.
- Established first direct relationship between charge transfer and area normalized triple phase boundary length and between adsorption polarization resistance and volume normalized pore surface area.
- Developed a kinetic model that correctly predicts the relationship between experimentally obtained charge transfer polarization resistance and triple phase boundary length.
- Developing unique electrocatalytic techniques to determine fundamental oxygen exchange kinetics (k/D) on cathode surfaces based on O-isotope exchange as a function of applied voltage/current.
- Identified O_2 reduction mechanism steps on LSM and LSCF using O-isotope exchange.
- Demonstrated greater catalytic activity of LSCF versus LSM.

Introduction

To fully achieve the tremendous socio-economic benefits of electrochemical energy conversion and power generation, fundamental scientific breakthroughs in the transport of ionic species through electrolyte/membranes and reaction rates at electrode surfaces are necessary. Therefore, the mission of this project is to develop a fundamental understanding of ionic transport in, and electrocatalytic (electrochemical catalysis) phenomena on the surface of, ion conducting materials. The research spans the range from first-principles calculations and molecular dynamic simulations of ionic transport and gas-solid interactions of novel ion conducting materials and electrocatalysts to development of advanced technology devices for efficient energy utilization:

SOFCs – Increasing the ionic conductivity and electrode reaction rates results in higher power density cells at lower operating temperature. These higher power density cells will dramatically reduce the cost of fuel cell technology, thus, overcoming the final hurdle (cost) to widespread commercial deployment.

Membranes – Membrane reactors are a major component of the FutureGen Initiative. Improving the transport of ions through the membrane and reaction rates at the membrane surface will help achieve dramatic breakthroughs in industrial energy efficiency and cost of hydrogen production.

Sensors – By developing a fundamental understanding of the gas-solid reactions that occur on sensor electrodes we will be able to develop sensors that are highly sensitive and selective to specific gaseous pollutants. These sensors will allow more accurate control of combustion resulting in greater fuel economy and reduced air pollution.

Approach

Our computational research focuses first on gaining insight into mechanisms of ion transport and heterogeneous electrocatalysis, and then on applying this fundamental knowledge to the design of new materials. Using electronic structure calculations and large-scale atomic-level simulation on cluster parallel computers we are elucidating the fundamental processes of ion transport in various electrolyte and electrode materials. Among the effects being explored are the effect of defects and defect clustering on the mechanical behavior and on ionic transport. The effect of grain boundary interfaces is being determined from simulations of ionic transport in polycrystalline materials. The insights gained from these simulations will help guide the development of higher conductivity electrolyte and electrode materials.

In addition, we are using similar calculations to develop a fundamental understanding of heterogeneous electrocatalytic phenomena at the surface of ion conducting ceramics. Because cathode polarization limits the performance of SOFCs at low temperature, the insights gained from this study will lead to the development of lower polarization SOFC cathodes at lower temperatures. In addition, these computational methods will be used to determine the mechanisms responsible for the cathode performance degradation.

We are developing high-resolution, quantitative, microstructural characterization techniques based on a FIB/SEM. This includes development of mathematical techniques to create a 3D reconstruction of the entire porous electrode structure as well as quantify electrode microstructural features (e.g., triple phase boundary length, porosity and tortuosity). In addition, we are using the FIB/SEM to prepare samples for high resolution transmission electron microscope (HRTEM) analysis of specific interfaces for analysis of issues such as tertiary phase formation, cathode degradation, etc.

Finally, using heterogeneous catalysis techniques–temperature programmed desorption (TPD), reaction (TPR), and oxygen-isotope exchange–combined with electrochemistry techniques–impedance spectroscopy, I-V, and conductivity relaxation–and the microstructural characterization and computational approach (above), we are deconvoluting the various contributions to electrode polarization to obtain a more fundamental understanding and develop a methodology to design improved performance electrodes in the future.

Results

Computational – Previously, we showed that there is considerable elastic softening with increasing oxygen deficiency in CeO_{2-x}. By simulating a series of different systems, we have shown that this elastic softening arises mainly from the decreased electrostatic interactions in the system rather than from the free volume associated with the oxygen vacancies themselves. By comparing systems with corresponding expansions, we have determined that the chemical expansion has a much larger softening effect on the elastic properties than the corresponding expansion arising from thermal effects alone. We have also established that the lattice parameter and elastic moduli both depend essentially linearly on the ionic radii of aliovalent dopants and on their concentration. Simulations on the oxygen vacancy diffusion mechanism are underway.

In addition, we have used a combination of *ab initio* and thermodynamics to determine the surface energies of different low miller index planes of $LaFeO_3$ under varying oxygen partial pressure and temperature. Among the various low-miller index planes, weakly polar (010) and (101) planes have lower surface energies than the strongly polar (111), (110) and (011) planes. Guided by this result, we have continued our adsorption and absorption calculations of oxygen ions on the (010) plane of $LaFeO_3$ that has either LaO or FeO_2 terminations. In particular, we have considered several adsorption sites with and without oxygen vacancies. The LaO-terminated surface is predicted to have a lower oxygen-adsorption energy than the FeO_2-terminated surface. This is because the oxygen adatom preferentially bonds with the two La surface atoms on the LaO-terminated surface. In contrast, in the case of the FeO_2-terminated surface, the adatom is only able to bond with one Fe surface atom. These calculations are continuing now with oxygen molecules. Additionally, calculations on the $La_{1-x}Sr_xFeO_3$ and $LaCo_{1-x}Fe_xO_3$ surfaces are in progress to elucidate the effect of dopants on adsorption and absorption of oxygen ions and molecules.

Microstructural Characterization – Ongoing work involves a FEI Strata 235 dual beam FIB/SEM in reconstructing porous SOFC cathodes. Current studies are being conducted on LSCF and LSM of various isochronal sintering temperatures. FIB/SEM serial sectioning and imaging is conducted at ~20 nm intervals. The resulting two-dimensional (2D) images are stacked and aligned with the aid of fiducial marks. Amira Resolve RT software is then utilized to reconstruct a three-dimensional (3D) triangular mesh to represent the serially sectioned area of interest. The reconstruction's voxel (3D equivalent of pixel in 2D) dimensions are on the order of 3 nm X 4 nm X 20 nm thus making it possible to have ~100 nm particle resolution in the 3D reconstruction. This reconstruction is then used to quantify microstructural properties of the porous cathode such as average particle size, average pore size, closed porosity, open porosity, tortuosity, pore surface area, porosity grading, and triple phase boundary length (L_{TPB}).

Figure 1 shows an example of this technique for an LSCF cathode. First, a series of SEM images were obtained. Then they were integrated and reconstructed into a virtual 3D structure. Finally, that reconstructed 3D structure was analyzed to quantify microstructural features. In this case the phase fraction of yttria-stabilized zirconia (YSZ), LSCF, and pores were determined as a function of distance from the YSZ/LSCF interface.

Deconvolution of Electrode Polarization and Comparison of Microstructure with Electrochemical Performance – Symmetric LSM on YSZ samples were fabricated for electrochemical-microstructural comparison. Microstructural features (porosity, volume normalized pore surface area, L_{TPB}, and tortuosity) were modified by varying the sintering temperature and time used during fabrication. We evaluated the effects of sintering temperature on both electrochemical and microstructural characteristics of these LSM on YSZ symmetric cells. All microstructural quantities were influenced by sintering temperature with the most dynamic changes occurring at temperatures near and above 1,200°C.

Electrochemical impedance spectroscopy (EIS), using a Solartron 1260 frequency response analyzer, was performed on the symmetrical samples prior to their analysis by the FIB/SEM. From the obtained impedance profiles charge transfer, dissociative adsorption, and gas diffusion related processes were identified. It was found that polarization resistance for both charge transfer and dissociative adsorption increase with sintering temperature. This corresponded to a decrease in specific microstructural features, L_{TPB} and pore surface area (normalized per unit volume - S_V), with increasing sintering temperature as quantified by the FIB/SEM.

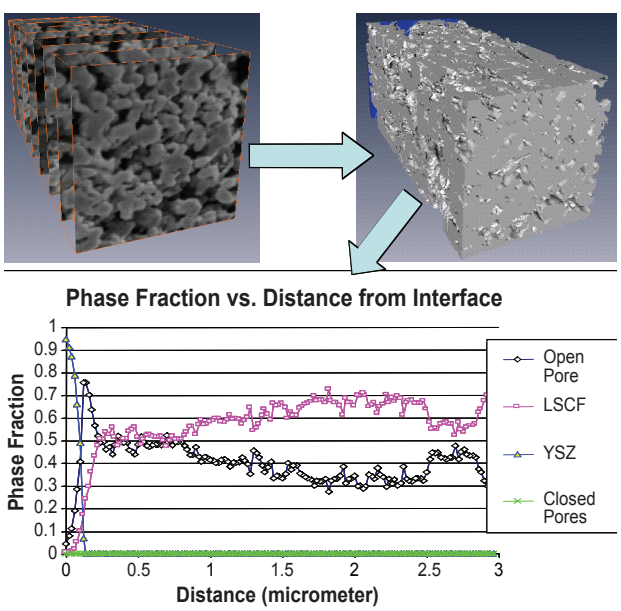

FIGURE 1. Progression from serially sectioned FIB/SEM images, reconstruction into a 3D representative structure; used to quantify the porous microstructure, in this case graded porosity.

Relating the microstructural and electrochemical results revealed that charge transfer polarization resistance (R_{CT}) decreased as L_{TPB} increased and polarization due to dissociative adsorption (R_{DA}) decreased as S_V increased. Excellent power law fits were obtained for both microstructural-polarization relationships (Figure 2):

$$R_{CT} = 2.93(L_{TPB})^{-3.5} \quad (1)$$

$$R_{DA} = 1025(S_V)^{-1.8} \quad (2)$$

These, first ever reported, direct relationships between microstructure and electrochemical performance can now start to be used to develop fundamental cathode polarization mechanisms.

The basic oxygen reduction reaction is

$$1/2O_2 + V_o^{\bullet\bullet} + 2e' \rightarrow O_o^x \quad (3)$$

We have shown that a power law dependence for R_{CT} on L_{TPB} can be obtained from this reaction (1).

$$R_{CT} = (RT/(nF)^2 k_f)([e'](\omega_{TPB}/A)_{e'})^{-m} ([O_2](\omega_{TPB}/A)_{O2})^{-n} ([V_o^{\bullet\bullet}](\omega_{TPB}/A)_{Vo\bullet\bullet})^{-p} \bullet (L_{TPB})^{-(n+m+p)} \quad (4)$$

In chemical reactions, the reaction order is given by the coefficients in the balanced chemical equation. Using the reaction order coefficients in Equation (3), the exponential quantity (n+m+p) is -3.5, resulting in $R_{CT} \propto L_{TPB}^{-3.5}$ which is exactly what we observed.

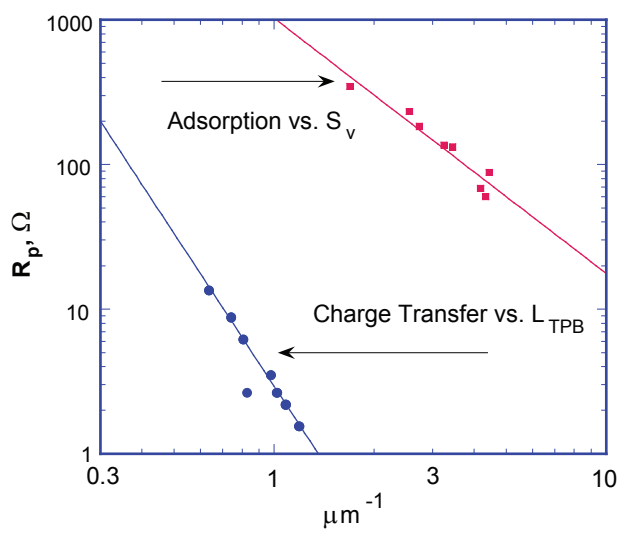

FIGURE 2. Effect of LSM microstructure on cathode polarization; dissociative adsorption as a function of pore surface area, and charge transfer polarization as a function of triple phase boundary length; at 800°C in air.

The next step in deconvolution of the cathode polarization is to determine the fundamental oxygen reduction mechanisms and rate constants of LSM and LSCF. In order to do this, we used the heterogeneous catalysis techniques of TPD and TPR, as well as oxygen-isotope exchange.

Oxygen Exchange Kinetics – Temperature programmed isotope exchange on SOFC cathode materials can elucidate the surface exchange mechanisms as well as characterize reactivity towards the oxygen reduction reaction. For these experiments, ~3,000 ppm $^{18}O_2$ balanced in He is flowed over a small amount of cathode powder, the temperature is ramped 30˚C/min, and the reactor effluent recorded by mass spectrometry. Since the oxide is made of ^{16}O, and $^{18}O_2$ is only found in the gas phase, we can determine what happens to the oxygen. If it goes into the lattice, a decrease in the mass 36 signal is seen. If dissociation occurs and there is a buildup of surface intermediates, the scrambled product $^{16}O^{18}O$ (mass 34) will be detected. Oxygen coming out of the lattice in large quantities will be seen as $^{16}O_2$, or mass 32. From these experiments, the mechanisms and kinetics of oxygen incorporation are being studied *in situ*.

As seen from the surface-area normalized (0.26 m^2) plots in Figure 3, LSM20 (Nextech) shows very little activity compared with LSCF6428 (Praxair) for the same given temperature. Surface exchange, producing $^{16}O^{18}O$, does not occur until about 350˚C for LSM but begins as early as 150˚C for LSCF. This indicates LSCF is a better catalyst for oxygen dissociation and would be better than LSM as an intermediate temperature SOFC cathode material. At higher temperatures, the $^{18}O_2$ and $^{16}O^{18}O$ signal completely disappears from the LSCF spectrum, indicating that the incorporation step is much faster than the dissociation step. Looking at the $^{16}O_2$ signal at higher temperature (400-600˚C) shows the material becomes oxygen deficient. The kinetics of the desorption process is much faster than that of incorporation. Additional isothermal experiments will be performed to study the effect of temperature and oxygen partial pressure on the rate law that governs oxygen exchange on these cathode materials.

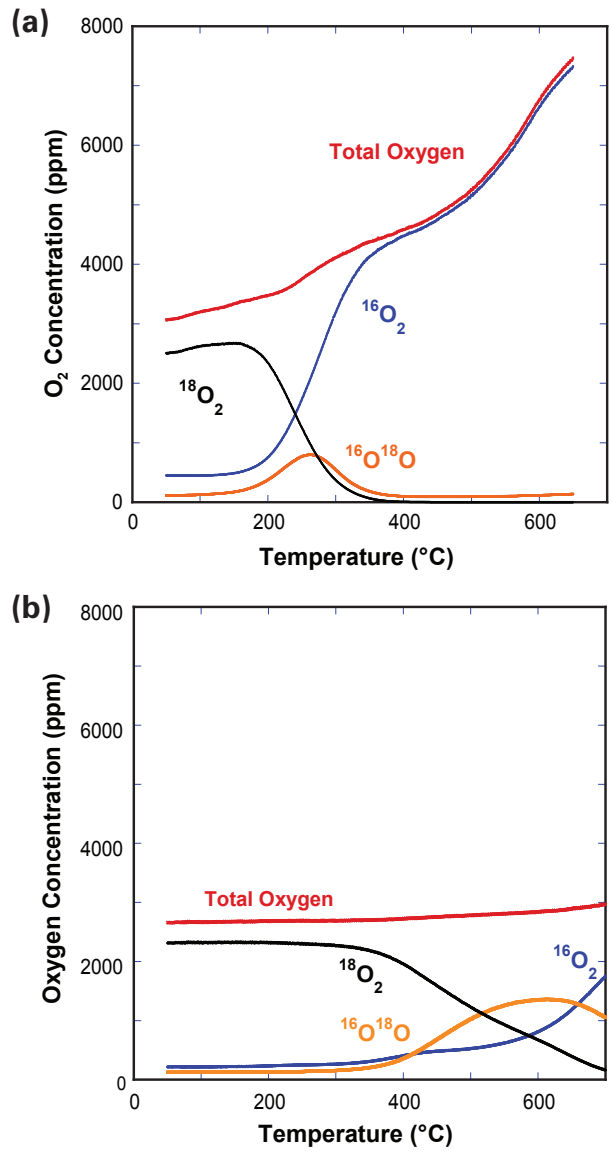

FIGURE 3. Oxygen Isotope Exchange of (a) LSCF and (b) LSM.

Conclusions and Future Directions

- Demonstrated with computational simulations that the mechanical properties of CeO_{2-x} are dominated by the electrostatic interactions between the ions.
- Computationally determined adsorption and absorption energies for O on/in $LaFeO_3$ (110) cathodes, and established with electronic structure calculations that oxygen preferentially adsorbs on the LaO-terminated surface of $LaFeO_3$ rather than the FeO_2-terminated surface.
- Developed high resolution SEM/FIB characterization technique and applied to SOFC cathodes. Demonstrated that results can be used to produce 3D reconstructions. Quantified LSM and LSCF cathode microstructures as a function of sintering.
- Combined microstructural characterization of LSM cathodes with impedance spectroscopy results to deconvolute polarization mechanisms and quantify effect of microstructure on electrode polarization.
- Determined direct relationship between charge transfer resistance and triple phase boundary length ($R_{CT} \sim L_{TPB}^{-3.5}$) in LSM cathodes. These experiments will continue and will be applied to LSCF cathodes for comparison.

- Demonstrated ability of O-isotope exchange to elucidate oxygen reduction mechanism and further demonstrated greater catalytic activity of LSCF than LSM using this approach.
- Additional isotope experiments will be conducted to fully investigate the mechanism of oxygen surface exchange. Steady-state isotopic-transient kinetic analysis (SSITKA) will be used to study *in situ* oxygen surface exchange kinetics and intermediates. This method is based on the isothermal switching of the feed stream between lines containing oxygen isotope $^{16}O_2$ and $^{18}O_2$. This switch introduces a traceable isotopic step without perturbing the steady state oxygen concentration, pressure and flow rate. Monitoring changes in the various isotope concentrations with time will yield valuable information towards understanding the surface exchange mechanism and the effective rate constant for surface exchange. By understanding which surface step(s) limit performance in intermediate temperature SOFCs, better cathodes can be engineered to counteract the natural loss in performance at lower temperatures.
- These kinetic experiments should result in specific rate constants and P_{O2} dependencies of the basic cathode materials, LSM and LSCF. When combined with deconvoluted impedance data and quantified LSM and LSCF cathode microstructures, a fundamental and quantifiable understanding of cathode performance should finally be achieved.

FY 2007 Publications/Presentations

1. "Evaluation of the Relationship Between Cathode Microstructure and Electrochemical Behavior for SOFCs," J.R. Smith, A. Chen, D. Gostovic, D. Hickey, D. Kundinger, K.L. Duncan, R.T. DeHoff, K.S. Jones and E.D. Wachsman, Solid State Ionics, submitted.

2. "3D Reconstruction of LSCF Cathodes," D. Gostovic, J.R. Smith, K.S. Jones and E.D. Wachsman, Electrochemical and Solid State Letters, submitted.

3. "Deconvolution of SOFC Cathode Polarization," E.D. Wachsman, *Solid Oxide Fuel Cells X, ECS Transactions*, K. Eguchi, S.C. Singhal, H. Yokokawa, and J. Mizusaki, Ed, **7-1**, 1051 – 1054 (2007).

4. "Oxygen Diffusion Mechanism in δ-Bi_2O_3 Using Molecular Dynamics Simulations", D. S. Aidhy, S. B. Sinnott, E. D. Wachsman and S. R. Phillpot, 31st International Cocoa Beach Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, 21–26 January, 2007.

5. "Mechanical Properties of Ceria by Molecular Dynamics Simulation", H. Xu, R. K. Behera, Y. Wang, F. Ebrahimi, E. D. Wachsman, S. B. Sinnott and S. R. Phillpot, 31st International Cocoa Beach Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, 21–26 January, 2007.

6. "Chemical Properties of $LaFeO_3$ from First Principles Calculations: Implications for Use as SOFC Cathodes", C. Lee, E. D. Wachsman, S. R. Phillpot and S. B. Sinnott, 31st International Cocoa Beach Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, 21–26 January, 2007.