
High Performance Nano-Crystalline Oxide Fuel Cell Materials: Defects, Structures, Interfaces, Transport, and Electrochemistry

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Objectives

The main aim of this project is to investigate nano-scale materials of interest for low-temperature solid oxide fuel cell (SOFC) applications, integrating fundamental studies done from the atomic scale (point defects) to extended defects (interfaces, grain boundaries, and surfaces) to the morphological scale (typically 50 – 1000 nm in SOFC electrodes). A major focus will be on transport and oxygen exchange properties of nano-scale materials needed to make fuel cell membrane/electrolytes that can operate effectively over a wider range of conditions, including temperatures $\leq 500^\circ\text{C}$. Another major focus will be on relating quantitative 3D nano/microstructure and materials properties to electrochemical properties. Overall, this work aims to provide a scientific basis for engineering high efficiency nano-composite materials for SOFC applications.

Technical Barriers

Solid oxide fuel cells (SOFCs) will become an increasingly important technology as their operating flexibility is improved; of particular interest is the reduction of operating temperature. However, reducing operating temperatures generally increases electrode polarization resistance and electrolyte oxygen transport resistance. Thus, approaching operating temperatures of 500°C will require novel new materials and well-designed nano-structures with enhanced transport properties. SOFC materials with improved functionality, *e.g.* improved stability, ability to operate under a range of operating conditions or cyclically varying conditions, and tolerance to impurities, are also needed.

Abstract, Progress Report and Future Directions

This talk will describe our group's investigations of nano-scale oxide materials with potential for enhancing fuel cell performance, particularly for reduced temperature operation. Several related research thrusts are actively being pursued. A new method for forming nanometer-sized catalyst particles, that substantially improves the performance of solid oxide fuel cell (SOFC) anodes, will be described. Studies of the production of nano-phases within cathode materials via infiltration, and their stability under fuel cell operating conditions, will be discussed. New mixed-conducting oxide phases that are stable in highly reducing conditions, and thereby suitable for use in oxide anodes, will be described. Theoretical approaches to understanding the anomalously high ionic conductivity of nano-structured oxides such as yttria-stabilized zirconia will be discussed. We will describe fabrication of nano-scale lanthanum gallate materials that have potential as high-conductivity electrolyte/membrane materials.

Nanostructured oxide materials have been shown to provide substantial increases in ionic conductivity, making them attractive potential candidates for reduced-temperature electrolyte materials. This has been demonstrated in nano-crystalline materials and also in nano-layered structures containing Samaria-doped Ceria ionic conductor with various levels of doping.¹ Optimizing this approach as well as understanding the mechanisms underlying the increased ionic conductivity requires a detailed understanding of interfacial properties in this system. We have carried out *ab initio* calculations of the equilibrium composition profile (of dopants and vacancies) across a coherent {100} interface mimicking the experimentally synthesized Samaria-doped Ceria superlattices. We find that the coherent interfaces between the layers significantly alter the equilibrium vacancy concentration up to distances of the order of 50 nm. Since the nano-layers have a period of the order of 50 nm as well, it is clear that vacancy concentration is affected by the interfaces throughout most of the volume of the material, thus suggesting a very plausible explanation for the observed significant ionic conductivity improvements. Moreover, the equilibrium profile in a superlattice structure is such that it allows the system to reach close to the optimal dopant concentration over wide regions, even though this optimal doping level lies in the middle of a miscibility gap. Future work in this area will be to more quantitatively link the predictions with experimentally-measured conductivities.

Experimental work is underway to synthesize novel nano-crystalline phases of lanthanum gallate, a relatively new oxygen-ion electrolyte material of interest for SOFCs. Since lanthanum gallate has one of the highest conductivities amongst electrolyte materials, enhancing its conductivity via nano-structuring could allow SOFCs with very low operating temperatures. However, LaGaO_3 is a line compound that readily forms “impurity” phases if prepared outside of its single-phase range. Sol-gel methods have been explored to produce LaGaO_3 ; while higher calcining temperatures are useful for forming the single-phase perovskite, they also grow the grains beyond the desired ~ 10 nm range. Work continues on this challenging synthesis problem, and we will also add the dopants Sr and Mg in order to produce the high conductivity composition. On another front, we have acquired a hot press (with separate funding) that will allow us to form thin dense layers of nano-crystalline electrolyte materials, including doped lanthanum gallate, for detailed testing and use in SOFCs.

While nano-scale materials can be stable at SOFC operating temperatures that are typically $\leq 800^\circ\text{C}$,² and may be as low as 500°C ,³ they typically coarsen into larger particles at the relatively high firing temperatures (up to $1,400^\circ\text{C}$) used to process SOFCs. One example of this is in the area of oxide anodes,⁴ materials that are interesting because of their potential to work with hydrocarbon fuels, their good stability during redox cycling, and reduced sensitivity to sulfur-containing fuel impurities.⁴ We have demonstrated a method for forming electrocatalytic nanoparticles on lanthanum chromite anode surfaces after the high-temperature firing and without additional processing steps. Ru was used since it is less susceptible than Ni to sintering and coking⁵. Instead of adding the Ru as a separate phase, it was dissolved in the lanthanum chromite phase. The Ru nanoparticles precipitated from the lanthanum chromite phase upon heating in hydrogen at the start of SOFC operation, accompanied by a dramatic reduction in anode polarization resistance. Transmission electron microscope and x-ray photoelectron spectroscopy observations showed that Ru nano-clusters precipitated onto $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.82}\text{Ru}_{0.18}\text{O}_{3-\Delta}$ surfaces after exposure to hydrogen at 800°C , with Ru cluster size stabilizing at ≤ 5 nm for the longest times tested, ~ 300 h. Solid oxide fuel cell tests were done in humidified hydrogen at 800°C with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.82}\text{Ru}_{0.18}\text{O}_{3-\Delta}$ - GDC (GDC = Gd-doped ceria) anodes on LSGM electrolyte-supported cells. Cell power density increased over the first ~ 50 h of cell operation from ~ 200 to 400 mW cm^{-2} due to an anode polarization resistance decrease from ~ 0.6 to < 0.2 Ωcm^2 . Future work in this area will be to better characterize and understand the Ru precipitation process as well as the stability of the nano-clusters.

Nano-particle formation and stability in SOFCs is being modeled using continuum methods that account for transport and phase transitions. This is being applied

to the metal nano-cluster work described above, where a key aim is to understand the excellent observed stability of Ru nano-clusters. We are also studying a nitrate infiltration process that produces nano-scale phases in SOFC cathodes.⁶ The work to date has focused on $(\text{La,Sr})(\text{Fe,Co})\text{O}_3$ infiltration into micron-scale porous Gd-doped Ceria structures, producing a combined nano/microstructure. Initial results show a substantial reduction in polarization resistance compared to conventional cathode microstructures. The structure of these materials will be studied in detail, and the changes in structure and electrochemical characteristics over time studied. This will allow us to study and model the coarsening of nano-scale cathode particles, and then to correlate this with changes in electrochemical performance.

Finally, we have begun studying the properties of a new perovskite phase, $\text{LaSr}_2\text{Cr}_2\text{FeO}_{\delta+x}$, that exhibits mixed conductivity and is sufficiently stable under reducing conditions for use in anodes. Mixed conductivity is potentially useful for extending the electrochemical reaction zone beyond triple-phase boundaries to the entire perovskite surface. Preliminary tests incorporating this material into composite anodes (with a Gd-doped Ceria second phase) in SOFCs with Gd-doped ceria electrolytes showed very promising results, with an anode polarization resistance of ~ 0.2 Ωcm^2 at 800°C , low enough to be consistent with 1 W/ cm^2 (the total cell area-specific resistance should be ≈ 0.3 Ωcm^2 to yield a power output of 1 W/ cm^2). More detailed studies of the basic properties of this material will be carried out and further SOFC testing will be done to determine the effect of anode composition and structure on electrochemistry.

Publications (including patents) acknowledging the grant or contract

1. Madsen, B., Kobsiriphat, M., Wang, Y., Marks, L.D., Barnett, S.A., Nucleation of Nanometer-Scale Electrocatalyst Particles In Solid Oxide Fuel Cell Anodes. *Journal of Power Sources*, in press (2007). Available online at: <http://www.sciencedirect.com/science/article/B6TH1-4MV0M9B-G/2/77e097c702e8f20a11c044ceb733bbd2>
2. B.D. Madsen, S.A. Barnett, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.98}\text{V}_{0.02}\text{O}_3$ - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ - Ni Anodes for Solid Oxide Fuel Cells: Effect of Microstructure and Ni Content, *Journal of the Electrochemical Society* (2007), in press.
3. B.D. Madsen, W. Kobsiriphat, Y. Wang, L.D. Marks, S.A. Barnett, SOFC Anode Performance Enhancement Through Precipitation of Nanoscale Catalysts, *Electrochemical Society Transactions* (SOFC X Symposium Proceedings, 2007), in press.
4. Patent application: Formation of a Nano-Scale Catalyst Phase in SOFC Anodes Via Controlled Precipitation, B.D. Madsen, W. Kobsiriphat, Y. Wang, L.D. Marks, S.A. Barnett

References

1. I. Kosacki, C. M. Rouleau, P. F. Becher, J. Bentley, and D. H. Lowndes, *Solid State Ionics* **176**, 1319 (2005).
2. A. J. McEvoy, *Solid State Ionics*, **132** (3-4) (2000). 159-165.
3. Z. Shao, Z. Zhan, S. M. Haile, J. Ahn, P. D. Ronney, S. A. Barnett, *Nature*, **435** (2005). 795-798.
4. A. Atkinson, S. A. Barnett, R. J. Gorte, J. T. S. Irvine, A. J. McEvoy, M. Mogenson, S. C. Singhal, J. Vohs, *Nat. Mater.*, **3** (2004). 17-27.
5. A.-L. Sauvet, J. Fouletier, F. Gaillard, M. Prime, *J. Catalysis*, **209** (2002). 25-34.
6. K. Yamahara, C. P. Jacobson, S. J. Visco, and L. C. De Jonghe, *Solid State Ionics* **176**, 451-456 (2005).