TTITLE: **Characterization of Atomic and Electronic Structures of Electrochemically Active SOFC Cathode Surfaces**

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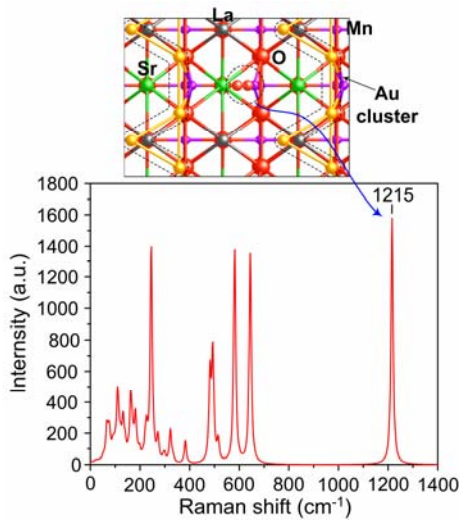
Objectives

The objective of this study is to characterize the details of oxygen reduction on the cathode of a solid oxide fuel cell using experimental and computational approaches. Experimentally, a dense $La_{0.85}Sr_{0.15}MnO_{3-\delta}$-$Ce_{0.9}Gd_{0.1}O_2$ **(**LSM-GDC) composite electrode is used to determine the electrochemical performance per unit length of triple-phase boundaries (TPBs) and surface catalytic properties of various cathode materials. Further, first-principles calculations are used to elucidate oxygen reduction mechanisms and predict surface catalytic properties.

Accomplishments to Date

Fabrication and Characterization of Dense LSM-GDC Composite Electrodes: Dense LSM-GDC composite electrodes have been developed to examine surface modification of cathodes. A dense LSM-GDC composite electrode is typically fabricated with a GDC electrolyte layer, forming a bi-layer structure using co-pressing and co-firing processes. To characterize the LSM and GDC grains in the composite, Energy Dispersive X-ray Analysis (EDX) was used. The specific TPB length per unit electrode surface area was systematically controlled by adjusting the LSM to GDC volume ratio of the composite from 40% to 70%, whereas the TPB length for each tested sample was determined through stereographic techniques and used to quantitatively correlate the cell performance and degradation with the specific TPB length per unit surface area. Additionally, percolation models employing overlapping spheres were used to estimate the amount of active TPB length in the samples. This method provides an unambiguous way to measure the performance of an electrode and allows for an accurate comparison between samples of varying TPB length.

Quantum-Chemical Calculations: In order to predict plausible adsorbed oxygen species with superoxo- and peroxo-like characteristics, a surface model for $La_{0.5}Sr_{0.5}MnO_3$ (LSM0.5) containing 19 ions (two La, two Sr, four Mn, and 11 O ions) and an oxygen vacancy was constructed. On the basis of the surface model, the oxygen reduction reaction was investigated using quantum chemical calculations and molecular dynamics (MD) simulations. It was demonstrated that quantum chemical calculations are a valuable tool in distinguishing active sites toward oxygen reduction at La and Mn cations on LSM-based cathodes which is inaccessible to experimental tools, implying that the computational framework may be able to provide important to rational design of more efficient electrode materials. Our quantum MD simulations showed that O_2 species preferentially adsorb on the Mn site rather than the La site according to the adsorption energy difference, supporting that B cations are more active than A cations for oxygen reduction on perovskite-type ABO_3 cathodes. The combination of minimum-energy path



(MEP) and MD calculations suggested a fast stepwise reaction mechanism on LSM0.5, along with charge transfer from the surface to the adsorbed oxygen species. The non-existence of reaction barriers for the oxygen reduction reaction ascertains a fast O_2 kinetics on LSM-based cathodes in SOFCs, and it will further affect oxygen ionic transport in the bulk phase. In addition to the mechanistic studies, we estimated vibrational frequencies of adsorbed oxygen species to interpret experimental results using Raman micro-spectroscopy, with and without surface enhancements. For example, the figure shows a typical predicted surface-enhanced Raman spectrum using Au nano-particles on LSM0.5 for an adsorbed superoxo-like species on the Mn ion with 1215 cm^{-1}.

Future Work

We plan to use the dense composite electrode as the platform for evaluating the surface catalytic properties of various cathode materials (sputtered film). For this testing, a variation of the current testing setup will be employed to increase precision between sample sets. Quantum-chemical calculations will focus on more detailed comparison of various surface configurations on perovskite-type cathode materials, which will be validated by experimental measurements.

LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS, AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Published Journal Articles

- Y. M. Choi, D. S. Mebane, M. C. Lin, M. Liu, "Oxygen Reduction on $LaMnO_3$-based Cathode Materials in Solid Oxide Fuel Cells," *Chemistry of Materials*, 19, 1690, 2007.
- D. S. Mebane, Y. Liu, M. Liu, "A Two-Dimensional Model and Numerical Treatment for Mixed-Conducting Thin Films: The Effect of Sheet Resistance," *J. Electrochem. Soc.*, 154, A421, 2007.
- R. Williams Jr., S. Zha, M. Liu, "Fabrication and Characterization of Dense $La_{0.85}Sr_{0.15}MnO_3$-$Ce_{0.9}Gd_{0.1}O_{1.95}$ Composite Electrodes," *Ceramic Engineering and Science Proceedings*, 2007.

Accepted and Submitted Journal Articles

- Y. M. Choi, M. C. Lin, M. Liu, "Computational Study of Catalytic Mechanism toward Oxygen Reduction on $La_{0.5}Sr_{0.5}MnO_3$(110) in Solid Oxide Fuel Cells," *Angewandte Chemie, International Edition*, in revision.
- Y. M. Choi, D. S. Mebane, J. H. Wang, M. Liu, "Continuum and Quantum-Chemical Modeling of Oxygen Reduction on the Cathode in a Solid Oxide Fuel Cell," *Catalysis Today (Invited)*, accepted.

Completed Presentations

- R. Williams Jr., S. Zha, M. Liu, "Fabrication and Characterization of Dense $La_{0.85}Sr_{0.15}MnO_3$-$Ce_{0.9}Gd_{0.1}O_{1.95}$ Composite Electrodes," 31st International Conference on Advanced Ceramics and Composites (ACerS), 2007.

Students Receiving Support from the Grant

- Robert Williams Jr., School of Materials Science & Engineering, Georgia Tech