TITLE:	**CHARACTERIZATION OF ATOMIC AND ELECTRONIC STRUCTURES OF ELECTROCHEMICALLY ACTIVE SOFC CATHODE SURFACES**

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GRANT NO.:	DE-FG26-06NT42735
PERIOD OF PERFORMANCE:	April 1, 2007 – March 31, 2008
DATE:	April 15

1. ABSTRACT

Program Introduction: Rationale and Objective

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, surface-enhanced Raman spectroscopy (SERS) is being used to probe oxygen species (intermediates for oxygen reduction) and new phases formed on electrode surfaces under practical operating conditions. Computationally, first-principles calculations are used to elucidate oxygen reduction mechanisms and to predict surface catalytic properties and bulk diffusion.

Accomplishments Achieved During the Current Period of Performance

Surface-enhanced Raman Spectroscopy. To generate a SERS signal from the surface of SOFC cathode materials, metal nanoparticles (typically silver or gold) need to be incorporated onto the electrode surface. We are exploring three methods to do so: (1) applying Ag/Au colloids dropwise to the electrode surface, (2) sputtering small islands (< 50 nm) of gold and silver onto the electrode, and (3) codepositing silver nanoparticles alongside nanoparticles of the cathode material using combustion chemical vapor deposition (CCVD). To this point, we have successfully generated SERS signals through the use colloids and CCVD. Figure 1 shows the effect on the Raman signal from the surface of $Sm_{0.5}Sr_{0.5}CoO_3$ electrode material with the addition of 20 nm silver colloid nanoparticles. The measured Raman signal intensity increased by up to three orders of magnitude and previously unseen peaks emerged. Our SERS measurements have also revealed the enhancements of lattice mode peaks from certain candidate perovskite-based cathode materials. This result is particularly interesting since these materials are normally only weakly Raman active. SERS can thus be used for structural analysis/identification of materials and species previously considered to be weak Raman scatterers.

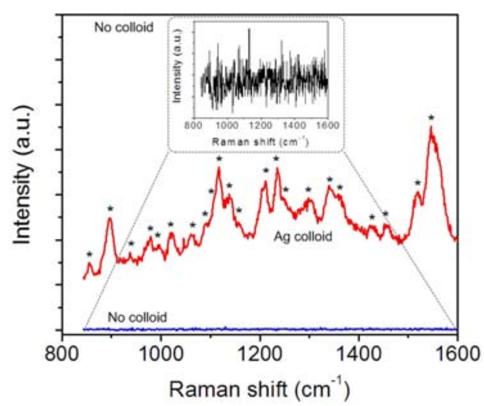

Figure 1. Raman signal from a dense pellet of $Sm_{0.5}Sr_{0.5}CoO_3$ with and without the presence of 20 nm silver colloid particles.

Rational design of MIEC cathodes using quantum chemical calculations. To rationally design high-efficiency MIEC cathode materials in SOFCs, quantum chemical calculations along with thermodynamic corrections and statistical-theory calculations have been applied. The thermodynamic-correction formalism along with first-principles calculations suggest that dissociated and molecularly adsorbed oxygen species on $LaMnO_3$ may be stable up to ~590 ^oC and ~1050 ^oC at pO_2= 0.2 atm, respectively, depending on adsorption energies, surface orientations, and surface coverages. In addition, the rate constants for the interactions between O_2 and $LaMnO_3$ or $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ (LSM50) were predicted based on potential energy profiles constructed using the nudged elastic band (NEB) method. Predicted rate constants for the dissociation of adsorbed oxygen species on $LaMnO_3$ (**lm**) and LSM50 (**lsm**) can be expressed: $k_{\mathbf{lm}} = 2.35\times10^{12}\exp[-0.50\ \text{eV/RT}]\ s^{-1}$ and $k_{\mathbf{lsm}} = 2.15\times10^{12}\exp[-0.23\ \text{eV/RT}]\ s^{-1}$, respectively, at a temperature in the range of 873 to 1273 K at 1 atm. We predicted surface and bulk diffusivities of oxygen on $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ (LSM50) and $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSC50) using transition state theory (TST). As shown in Figure 2, our TST predictions of surface diffusivities clearly support that LSC-based cathode materials have a much faster mobility than LSM-based ones, and oxygen ion conduction through LSC-based cathode materials is much faster than that through LSM-based ones.

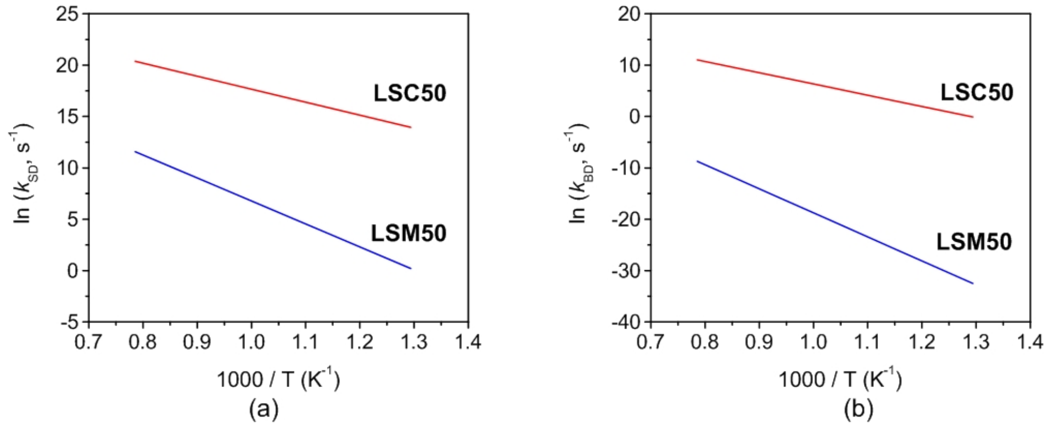

Figure 2. (a) Predicted surface diffusivities (k_{SD}) of adsorbed oxygen species on **LSM50** and **LSC50**. (b) Predicted bulk diffusivities (k_{BD}) of oxygen ions in **LSM50** and **LSC50**.

Plans for the Remaining Period of Performance

- Refine the procedures for generating consistent SERS measurements and test the upper temperature limits possible for maintaining a SERS signal in order to define the operating conditions under which SERS measurements are possible.
- Predict the concentrations of oxygen vacancies, electrons and electron holes as well as the rate-constants for O_2 adsorption, desorption and dissociation on SOFC materials such as $La_{1-x}Sr_xCoO_{3-\delta}$, $La_{1-x}Sr_xFeO_{3-\delta}$, $La_{1-x}Sr_xMnO_{3-\delta}$, and $La_{1-x}Sr_xCrO_{3-\delta}$ in relation to the interpretation of experimental oxygen surface exchange coefficients.
- Apply the predicted diffusivities for continuum modeling to examine electrochemical properties of SOFCs since these values are directly applicable to our continuum models that examine transport/kinetics inside and on the surface of MIECs

2. 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, and M. Liu, "Oxygen Reduction on $LaMnO_3$-based Cathode Materials in Solid Oxide Fuel Cells," *Chemistry of Materials*, 19, 1690-1699, 2007.
- Y. M. Choi, M. C. Lin, and M. Liu, "Computational Study on the Catalytic Mechanism toward Oxygen Reduction on $La_{0.5}Sr_{0.5}MnO_3$(110) in Solid Oxide Fuel Cells," *Angewandte Chemie, Inter.Edition*, 46, 7214-7219, 2007.
- Y. M. Choi, D. S. Mebane, J. H. Wang, and M. Liu, "Continuum and Quantum-Chemical Modeling of Oxygen Reduction on the Cathode in a Solid Oxide Fuel Cell," *Topics in Catalysis (Invited)*, 46(3-4), 386-401, 2007.
- D. S. Mebane, Y. J. Liu, and M. Liu, "Refinement of the Bulk Defect Model for $La_xSr_{1-x}MnO_{3\pm\delta}$," *Solid State Ionics*, 178(39-40), 1950-1957, 2008.

Completed Presentations

- H. Abernathy, Z. Cheng, X. Lou, and M. Liu, "Probing and mapping SOFC anode reactions using *in situ* Raman spectroscopy," 233rd ACS National Meeting, IL, 2007.

Student Supported Under this Grant

- Harry Abernathy, School of Materials Science & Engineering, Georgia Institute of Technology.