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N00014-10-1-0572

*In-situ Optical Studies of Oxidation/Reduction Kinetics
on SOFC Cermet Anodes*

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Final Report

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Contract Information

Contract Number	N00014-10-1-0572
Title of Research	In-situ Optical Studies of Oxidation/Reduction Kinetics on SOFC Cermet Anodes
Principal Investigator	Robert Walker
Organization	Montana State University

Technical Section

Technical Accomplishments

As a result of unexpected costs for salaries and instrument maintenance, work supported by the Office of Naval Research under contract number N00014-08-WX-2-0679, additional support was requested in order to meet the project's original goals. This supplemental funding was requested in the form of a new, short-term proposal for the PI, Professor Rob Walker, at Montana State University. The new award (N00014-10-1-0572) amounted to \$44,856 and covered a period from March, 2010 through 30 September, 2010. These resources were used to accomplish two (3) primary goals:

(1) **Manuscript preparation** – The PI and his associates (two graduate students and one undergraduate) prepared and submitted four separate manuscripts for publication in peer reviewed journals. Two of these manuscripts have been published and one is accepted pending revision. A fourth is still awaiting the return of external reviews. In addition, the PI presented work supported by this award at the semi-annual meeting of the Electrochemical Society.

1. M. B. Pomfret, J. C. Owrutsky, and R. A. Walker "In situ Optical Studies of Solid Oxide Fuel Cells" *Ann. Rev. Anal. Chem.*, **3** 151-174 (2010).
2. B. C. Eigenbrodt¹, M. B. Pomfret, D. A. Steinhurst, J. C. Owrutsky and R. A. Walker "Direct, in situ optical studies of solid oxide fuel cells operating with methanol and methane" *J. Phys. Chem. C* **available online at ASAP**. (Content from this paper will also appear on the cover of Issue 6 of Volume 115 in February, 2011.)

3. B. C. Eigenbrodt¹ and R. A. Walker, "High Temperature Raman Mapping of Surface Electrolyte Oxide Concentration in Solid Oxide Fuel Cells" *submitted to Analytical Methods, accepted pending revisions.*
4. J. D. Kirtley, B. C. Eigenbrodt and R. A. Walker, "*In situ* optical studies of oxidation kinetics of Ni/YSZ cermet anodes" *submitted.*

(2) **Methods development** –The PI and his associates continued their comparative studies of a) SOFC performance with reformed fuels and b) mechanisms responsible for SOFC degradation and failure. These studies required continuing to develop new methods that coupled traditional electrochemical methods with spatially and temporally resolved *in situ* optical spectroscopy. As a result of these continued efforts, the experimental assembly used by the PI's research group can now measure vibrational spectra of molecules and materials at temperatures of 715°C with ~5 mm spatial resolution and ~3 sec temporal resolution. An example is shown below:

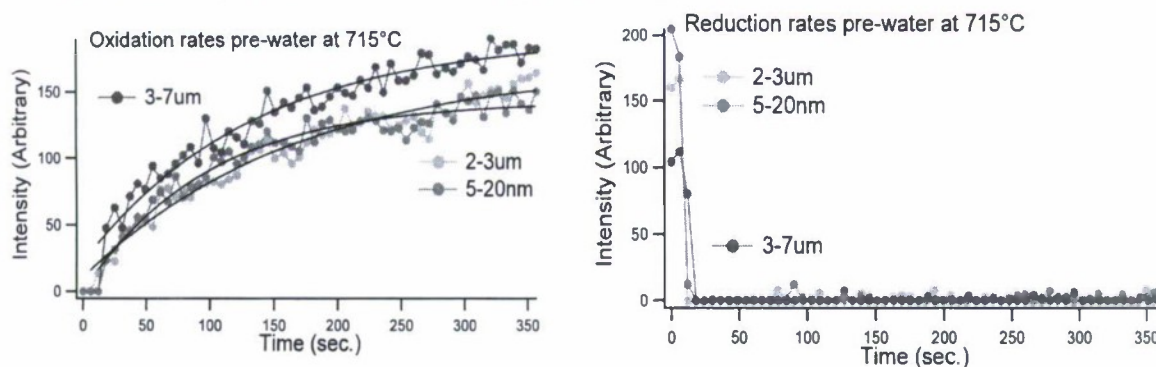


Figure 1. Kinetics of NiO formation/reduction for Ni/YSZ cermet samples where the Ni particles have different sizes. The data plot the intensity of the NiO vibrational band measured using *in situ* vibrational Raman scattering from cermet samples comprised of Ni particles having diameters of 3-7 μm (blue), 2-3 μm (green) and 5-20 nm (red). These experiments measure surface oxidation/reduction, not transformation of the complete particles. Oxidation is driven by an atmosphere of 20% O_2 in Ar, reduction by 5% H_2 in Ar. Reduction of NiO to form Ni is virtually instantaneous (on the timescale of seconds), while oxidation of Ni is much slower.

(3) **Personnel development** - A consequence of these two technical accomplishments came in the form of personnel development. The senior graduate student on this project, Bryan Eigenbrodt, is analyzing and preparing for publication his final series of experiments and he expects to defend his Ph.D. dissertation in February or March, 2011. He has applied for several post-doctoral fellowships (including an NRC Fellowship at the Air Force Laboratory in Dayton, OH). John Kirtley, a second year graduate student in Chemistry, spent the summer shadowing Bryan and learning the protocols and methods required for fabricating membrane electrode assemblies, constructing SOFC devices, and studying their performance using both electrochemical techniques and *in situ* vibrational Raman scattering. Our group also had the opportunity to mentor an American Indian high school student (from the Gros Ventre Tribe, Fort Belknap, MT), Mr. JoDarryl Gone, who spent 2 months at MSU during Summer '10 on a fellowship offered by the Montana Apprenticeship Program (MAP). JoDarryl assisted John studying the kinetics associated with ceria oxidation and reduction as a function of temperature and gas phase composition. JoDarryl's responsibilities included learning how to use the Raman microscope in conjunction with our thermal heating stage (with an upper limit of 600°C) and data processing (using routines developed in house for Igor Pro). JoDarryl returned to

Havre High School to finish his senior year and is considering both Montana State and the University of Montana, for his undergraduate studies.

Current activity

Despite our advances in applying vibrational Raman scattering to questions about electrochemical oxidation mechanisms in SOFCs, the experimental assembly developed by our research program suffers from two limitations: spatial resolution and assembly sensitivity. We have continued to advance our ability to use *in situ* vibrational Raman scattering to study chemistry occurring across SOFC anodes. Doing so will involve designing next generation, optically-accessible SOFC rigs that can be supported on a computer-controlled, 2-dimensional xy stage. With support from the Murdock Charitable Trust we will soon be enhancing our capabilities to include new Raman microscope using ultraviolet, 244 nm excitation.

Because the intensity of the Raman scattered signal depends upon the incident frequency raised to the 4th power $((\omega_0 - \omega_{\text{vib}})^4)$, where ω_0 is the excitation frequency and ω_{vib} is the frequency of the vibration being excited), using UV excitation rather than visible excitation will improve our instrument's sensitivity by more than a factor of 20. Furthermore, using a UV excitation source will eliminate almost all blackbody emission background from the detected Raman signal. For samples at 715°C, the background emission at ~244 nm is *12 orders of magnitude* less than the background emission near the 488 nm excitation wavelength now in use. Finally, a shorter wavelength excitation source will improve spatial resolution allowing us to better identify where chemistry occurs across SOFC MEAs.

We intend to exploit this new sensitivity in several ways: first, we will expand the search for chemical intermediates formed on SOFC anodes during electrochemical oxidation. Our findings to this point have been instructive in terms of identifying general behaviors of carbon containing fuels used in SOFCs, but most of the data have focused on the presence (or absence) of graphite *and* changes in the relative intensities of different metal oxide vibrational bands. Efforts to observe -CO and -CH containing intermediates have proven mostly unsuccessful. With the shorter excitation wavelength and correspondingly enhanced sensitivity, we will be better equipped to identify reactive intermediates thought to form during the electrochemical oxidation of carbon containing fuels.

In situ optical studies are also being used to assess of the role of reforming on SOFC performance. Experiments take advantage of the newly developed capabilities and are beginning to quantify relative amounts of surface intermediates formed by methane that has been allowed to reform with varying levels of humidity in the fuel feed. Motivating this project is an extensive debate over the importance of fuel reforming for SOFC operation and durability. Methane is relatively unreactive as a fuel, but combining methane with water or small amounts of O₂ creates gas phase mixtures consisting of variable amounts of H₂, CO, and CO₂ as well as unreacted CH₄ and H₂O. While these heterogeneous mixtures undergo more efficient electrochemical oxidation, the molecular origins of this enhanced reactivity are largely speculative. Using *in situ* Raman and IR measurements, we are beginning to monitor the relative amounts of adsorbed -CO and -CH₂ that form as a function of cell polarization. The degree of reforming will be controlled externally by varying the humidity and residence times in high temperature regions prior to fuels reaching the SOFC anode. Our studies will also map where these species form relative to the fuel inlet, current collector and electrode/electrolyte boundary. With spatial resolution of only ~1 μm, these experiments will not be able to differentiate with nanometer accuracy chemical reactivity across the very short lengthscales assumed to represent electrochemically relevant three phase boundaries, but XPS and oxide mapping experiments described above show definitively that the effects of cell polarization can extend tens of microns away from the edge of a SOFC electrode.

The work described above continues with support from a recent award from the Office of Naval Research (Award number: N000141010954). This renewal continues to support our efforts to expand our repertoire of optical methods capable of probing electrocatalytic activity and degradation in functioning

SOFCs. In addition, these methods will be used to quantify and spatially resolve electrochemical oxidation kinetics *in situ*. This combination of methods development and scientific discovery will serve two purposes. First, studies of electrochemical oxidation, reduction and material transformation will provide quantitative information that can feed directly into models used to predict SOFC performance and provide systems control feedback. Second, new, stand-off methods will be used to benchmark new sensing diagnostics destined for inline device monitoring. Our efforts correlate closely with complementary studies being performed at the University of Maryland, College Park and the Naval Research Laboratories. These collaborations will continue into the foreseeable future through combined scientific investigations and cooperative efforts to educate the community about the ability of *in situ* optical methods to identify mechanisms responsible for SOFC operation and degradation.



December 28, 2010

Defense Technical Information Center
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Ref: N00014-10-1-0572
Final Technical Report with SF 298

To Whom It May Concern:

Accompanying this letter, please find the Final Technical Report with SF 298 for the above referenced agreement.

Should you require any additional information, please contact me at 406-994-2381 or tracim@montana.edu.

Sincerely,

Traci Miyakawa, CRA
Senior Fiscal Manager

cc: W3027

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