

# Wednesday Morning, October 22, 2008

**In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference**  
**Room: 310 - Session IS+SY+SS-WeM**

**In Situ Spectroscopy – Interfacial Science and Catalysis**  
**Moderator: D.R. Baer, Pacific Northwest National Laboratory**

8:00am **IS+SY+SS-WeM1 Probing the Electrochemistry of Ceria in Solid-Oxide Fuel Cell Anodes under Operation using Ambient-Pressure XPS**, *H. Blumh, J.T. Newberg, Z. Liu, Z. Hussain*, Lawrence Berkeley National Laboratory, *S.C. DeCaluwe, C. Zhang, G.S. Jackson*, University of Maryland, College Park, *F. El Gabaly, R.L. Farrow, K.F. McCarty, M.A. Linne, A.H. McDaniel*, Sandia National Laboratories

Solid-oxide fuel cells (SOFCs) are an important technology for converting chemical energy to electrical energy. A compelling advantage of SOFCs is the ability to utilize fuels such as hydrogen, synthesis gas, and hydrocarbons. In a conventional SOFC, selective catalytic and charge transfer processes produce  $O^{2-}$  ions at the cathode/electrolyte interface, which then diffuse through a dense electrolyte to an anode/electrolyte interface where adsorbed fuel species are oxidized. Ceria ( $CeO_2$ ), a mixed conductor capable of transporting both  $O^{2-}$  ions and electrons, is being considered as a coke-resistant anode catalyst to improve SOFC performance. A key unknown about ceria-catalyzed anodes is the cerium (Ce) oxidation state during fuel cell operation. Cell performance is critically affected by the Ce oxidation state because  $Ce^{3+}$  and  $Ce^{4+}$  states coexist in  $CeO_2$ , and both electronic and ionic conductivities are determined by the abundance of  $Ce^{3+}$ . To exploit the potential of ambient-pressure XPS to characterize functioning electrochemical devices, we have fielded an SOFC experiment on beamline 11.0.2 at the Advanced Light Source. A single chamber cell was created by patterning working and counter electrodes from ceria and platinum atop single crystal yttria-stabilized zirconia (YSZ) electrolyte. The cell was characterized in atmospheres of  $H_2/H_2O$  and  $H_2/O_2/H_2O$  under forward and reverse polarization at approximately 973 K and 0.5 Torr. Standard chronoamperometric and impedance measurements were conducted simultaneously with ambient-pressure XPS. A focused x-ray beam (diameter < 0.1 mm) was used to spatially resolve changes in the Ce oxidation state as a function of position between counter and working electrodes under positive and negative bias. Electrochemically induced changes in the Ce oxidation state were directly observed and were dependent upon electrode polarization and proximity to electrochemically active regions. In addition, the oxidation state and surface potential of the YSZ electrolyte were also characterized. Implications of our findings on understanding the electrochemical mechanisms of SOFC operation with ceria anodes will be discussed.

This research was supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000 (Sandia) and DE-AC02-05CH11231 (LBNL). UMD participants were supported by the Office of Naval Research under Contract No: N000140510711.

8:20am **IS+SY+SS-WeM2 In-situ Dynamics of CO Oxidation on Pt(110) with Ambient Pressure XPS**, *Z. Yang, F. Aksoy, Z. Liu*, Lawrence Berkeley National Laboratory, *H. Kondoh*, Keio University, Japan, *P. Ross*, Lawrence Berkeley National Laboratory, *B. Mun*, Hanyang University, Korea

Considering the recent increasing demands of improved catalytic materials in energy industry, the understanding clear mechanism of catalytic reactions at an atomic scale level has become more critical. Especially, the formations of oxide on transition metal surface have been actively studied due to its importance in fundamental understanding of heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxide on Pt [110] received much attention due to its unique surface reconstruction under high pressure reaction conditions. Previously, with the combinations of high pressure STM and in-situ x-ray diffraction, the formation of surface Pt oxide is observed when the reaction rate is enhanced, and showed the surface oxide formed is stable with carbonate species.<sup>1,2</sup> In this work, using the ambient pressure XPS (AP XPS) and mass spectrometer, the in-situ dynamics of CO oxidation on Pt [110] surface are discussed under close to the realistic condition. Under the reaction conditions ( $T=420K$ ) with the pressure of CO and O gases at 450 mTorr in the AP XPS chamber, our results show that a) the chemisorbed oxygen is not stable under the reaction conditions, b) there is no formation of surface oxide on Pt surface under our reaction conditions.

<sup>1</sup> B.L.M. Hendrikson and J.W.M. Frenken, *Phys.Rev. Lett.* 89, 046101(2002)

<sup>2</sup> M.D. Ackermann et al., *Phys.Rev. Lett.* 95, 255505(2005).

8:40am **IS+SY+SS-WeM3 Medard W. Welch Award Lecture: Novel X-ray Photoelectron Spectroscopy Techniques for In Situ Studies of Surfaces in Equilibrium with Gases in the Torr Pressure Regime: Application to Catalysis and Environmental Sciences**, *M. Salmeron\**, Lawrence Berkeley National Laboratory

**INVITED**

X-ray photoelectron spectroscopy (XPS) ideally suited to investigate the chemical nature of surfaces. Due to the scattering of electrons by gas molecules XPS is in generally performed under high vacuum conditions. However, because of thermodynamic and/or kinetic limitations, the surface chemical state observed under vacuum is not necessarily the one under the pressures that are relevant to catalysis and the environment (Torr to atmosphere). We developed a electrostatic lens system combined with differentially-pumped chambers that permits operation at pressures of up to 10 Torr. I will describe this ambient pressure XPS apparatus and show recent applications to studies of oxidation and heterogeneous catalytic reactions. I will also show how the technique can solve and advance our fundamental knowledge of surfaces in environmental science studies, particularly in the presence of water vapor.

9:20am **IS+SY+SS-WeM5 Nano Scale X-ray Absorption Spectroscopy of In Situ Modified Samples using Scanning Transmission X-ray Microscope**, *T. Tyliszczak*, Lawrence Berkeley National Laboratory

**INVITED**

Observation and spectroscopy of in situ chemical reactions on nanoscale is important but not easy task. It is important in many fields, especially in research of heterogeneous catalysts. Typically, transmission electron microscopy has been used under in situ conditions, but the strict low pressure requirements for this technique prevent it from being carried out under catalytically relevant conditions. Recently however, by using a specially designed microreactor, promising TEM experiments have been performed under 1 bar conditions but with a limitation of gases which could be used.<sup>1</sup> Other techniques include STM, fluorescence and optical microscopy. Most of these techniques allow imaging of intermediate steps of reactions with limited information about reaction chemistry. Scanning Transmission X-ray Microscopy (STXM) with relatively good spatial resolution of 20-30 nm, high chemical sensitivity and much lower restriction on the environment of a sample is promising to provide new insights into the catalytic reactions. By using soft X-rays (130 -2000 eV) as a microprobe, it is possible to study both the active phase of the catalyst, through absorption edges of the inorganic species, and the organic, reactant phase of the catalyst through the absorption edges of carbon, oxygen and nitrogen. While the maximum spatial resolution of STXM is still significantly worse than for example STEM-EELS, there are important advantages in application STXM, most notably the superior spectral resolution and the reduced radiation damage in the study of softer core hole edges (C, N, O K-edges) and hydrated samples. Bell et al.<sup>2</sup> first demonstrated the use of STXM for the study of a catalytic material under in situ conditions. Their cell design allowed sample treatments in gases up to 260 °C. E. de Smit et al.<sup>3</sup> used modified ETEM cell to in situ studies of a complex iron oxide based Fischer-Tropsch catalyst. They were able to heat the sample up to 500oC at gas pressure up to 1.2 bar opening a way to study real catalyst normal conditions. The cell, manufactured as a microelectromechanical system (MEMS), basically consists of a 500 \* 500 mm reactor chamber connected by micrometer-sized gas-flow channels. Two amorphous Si3N4 optical windows, etched down to a thickness of 10 nm in certain places, separate the reactor from the outside environment. The thickness of the reactor, thus gas path length, is only about 50 mm, and therefore ensures minimum attenuation of the X-ray light by the gas phase molecules. Spacers, placed between the windows prevent the windows from sticking together. The sample is loaded by flowing a powder suspended in a solvent (e.g. ethanol) through the reactor and subsequent drying. After drying, the sample is supported on the SiNx windows. E. de Smit et al were able to track reaction steps measuring changes in chemical state of iron and oxygen. They also investigated a role of carbon in the reaction. Progress in technical development of reaction cell and increasing resolution of the x-ray microscope provide opportunity to investigate gas - solids or liquid - solids in situ, in relevant conditions on nanometer scale.

<sup>1</sup> J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro and H. W. Zandbergen, *Ultramicroscopy*, In Press, Accepted Manuscript.

<sup>2</sup> I. J. Drake, T. C. N. Liu, M. Gilles, T. Tyliszczak, A. L. D. Kilcoyne, D. K. Shuh, R. A. Mathies and A. T. Bell, *Review of Scientific Instruments*, 2004, 75, 3242-3247.

<sup>3</sup> E. de Smit, I. Swart, J. F. Creemer, G. H. Hoveling, M. K. Gilles, T. Tyliszczak, C. Morina, P. J. Kooyman, H. W. Zandbergen, B. M. Weckhuysen and Frank M.F. de Groot, *Nature*, submitted manuscript.

\* Medard W. Welch Award Winner

10:40am **IS+SY+SS-WeM9 In Situ Synchrotron X-ray Study of the Synthetic Processes for Inorganic Solid Oxide Nanomaterials**, *Y. Mao, J. Dorman, J.P. Chang*, University of California at Los Angeles

Nanostructured crystalline inorganic solid oxides show various intriguing properties and process many important technological applications. To better control the property and device performance of materials, growth kinetic and mechanistic information of structure changes should be pursued to provide feedback for the development of new “designer” materials to meet the challenges of the future. Time-resolved in situ experimentation represents the most likely means, especially with the synchrotron radiation as the x-ray source due to its high energy flux. In this study, we focus on advanced luminescent nanomaterials, since they have practical applications in nearly all devices involving the artificial production of light and are applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent investigation by in-situ time-resolved synchrotron x-ray diffraction (XRD) and absorption spectroscopy (XAS) on the synthesis of rare-earth doped metal oxide nanostructures, including Er:Y<sub>2</sub>O<sub>3</sub> nanotubes and nanoparticles and Er: La<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> nanoparticles, by hydrothermal and molten-salt syntheses.<sup>1,2,3</sup> Our results demonstrate that in situ XRD and XAS data support each other. For the hydrothermal synthesis of Er:Y(OH)<sub>3</sub> nanotubes, the hydroxide phase starts to form immediately and continues to grow. For the dehydration process from Er:Y(OH)<sub>3</sub> nanotubes to Er:Y<sub>2</sub>O<sub>3</sub> nanotubes, the dehydration starts at ~250°C and completes at 450°C and an intermediate oxyhydroxide phase was found for the first time. Furthermore, the in situ XRD study provided guidance on the selection of proper annealing temperature for the molten salt synthesis of Er:Y<sub>2</sub>O<sub>3</sub> and Er: La<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> nanoparticles. Their growth kinetics will be obtained from further investigation of these processes under different ramp rates and reaction temperatures.

<sup>1</sup> Mao, et al. Synthesis and luminescence properties of erbium-doped Y<sub>2</sub>O<sub>3</sub> nanotubes, *J. Phys. Chem. C*, 112, 2278 (2008).

<sup>2</sup> Mao, et al. Molten salt synthesis of highly luminescent erbium-doped yttrium oxide nanoparticles, submitted (2008).

<sup>3</sup> Mao, et al. La<sub>2</sub>Zr<sub>x</sub>O<sub>7</sub> and La<sub>2</sub>Hf<sub>x</sub>O<sub>7</sub> nanoparticles from single-source complex precursors: kinetically modified synthesis and luminescent properties, submitted (2008).

11:00am **IS+SY+SS-WeM10 Surface Chemistry of Model Solid Oxide Fuel Cells Studied In-Situ by Synchrotron Based Photoemission Microscopy and Spectroscopy**, *K. Adib, M. Backhaus-Ricoult, T.P. St. Clair*, Corning Incorporated, *B. Luerksen*, Justus Liebig Universitaet, Germany, *L. Gregoratti, A. Barinov*, Sincrotrone Elettra, Italy

We have used synchrotron based X-ray photoemission spectroscopy (XPS) and scanning photoemission microscopy (SPEM) to study the surface compositions of model solid oxide fuel cells containing La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>3</sub> (LSM) cathode and yttrium-stabilized zirconia (YSZ) electrolyte under various oxygen pumping conditions at approximately 650°C and an oxygen partial pressure of 5×10<sup>-7</sup> mbar. SPEM in the vicinity of the LSM/YSZ interface indicates depletion of Mn atoms from the LSM surface and their accumulation on the YSZ surface with increasing cathodic bias. XPS indicates that the accumulation of Mn on the YSZ is accompanied by reduction in the oxidation state of Mn. Within a wide range of applied voltage these changes are reversible. XPS of oxygen core levels also indicates that under cathodic bias, during which oxygen is incorporated from the surrounding gas into the cathode and pumped through the electrolyte, an additional oxygen species is present on the surface of LSM. The concentration of this species increases with increasing cathodic bias and we tentatively assign this species to surface oxygen as distinct from lattice oxygen. On the YSZ surface, no such change in the concentration of the surface oxides with cathodic bias was detected emphasizing the role of LSM in enhanced adsorption of oxygen.

11:20am **IS+SY+SS-WeM11 Organic Solar Cells and Microgels: Examples of In Situ Applications of Soft X-ray Microscopy**, *H. Ade*, North Carolina State University

**INVITED**

Soft x-ray microscopy has achieved a spatial resolution of ~ 30-40 nm. At the same time, soft x-rays are penetrating enough to investigate samples sandwiched between thin silicon nitride membranes or thin metal layers. This allows the investigation of wet samples or samples sandwiched between thin electrodes. When coupled with Near Edge X-ray absorption Fine Structure (NEXAFS) spectroscopy, unique characterization capabilities results that range from compositional mapping, to charge state determination and induced current measurements. This presentation will review the state-of-the-art of NEXAFS microscopy. The focus will be on a range of in-situ applications and most extensively on the characterization of microgels and organic solar cells.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Ade, H.: IS+SY+SS-WeM11, **2**  
Adib, K.: IS+SY+SS-WeM10, **2**  
Aksoy, F.: IS+SY+SS-WeM2, 1

## — B —

Backhaus-Ricoult, M.: IS+SY+SS-WeM10, **2**  
Barinov, A.: IS+SY+SS-WeM10, **2**  
Bluhm, H.: IS+SY+SS-WeM1, **1**

## — C —

Chang, J.P.: IS+SY+SS-WeM9, **2**

## — D —

DeCaluwe, S.C.: IS+SY+SS-WeM1, 1  
Dorman, J.: IS+SY+SS-WeM9, **2**

## — E —

El Gabaly, F.: IS+SY+SS-WeM1, 1

## — F —

Farrow, R.L.: IS+SY+SS-WeM1, 1

## — G —

Gregoratti, L.: IS+SY+SS-WeM10, **2**

## — H —

Hussain, Z.: IS+SY+SS-WeM1, 1

## — J —

Jackson, G.S.: IS+SY+SS-WeM1, 1

## — K —

Kondoh, H.: IS+SY+SS-WeM2, 1

## — L —

Linne, M.A.: IS+SY+SS-WeM1, 1  
Liu, Z.: IS+SY+SS-WeM1, 1; IS+SY+SS-WeM2,  
1  
Luerssen, B.: IS+SY+SS-WeM10, **2**

## — M —

Mao, Y.: IS+SY+SS-WeM9, **2**  
McCarty, K.F.: IS+SY+SS-WeM1, 1  
McDaniel, A.H.: IS+SY+SS-WeM1, 1

Mun, B.: IS+SY+SS-WeM2, **1**

## — N —

Newberg, J.T.: IS+SY+SS-WeM1, 1

## — R —

Ross, P.: IS+SY+SS-WeM2, 1

## — S —

Salmeron, M.: IS+SY+SS-WeM3, **1**  
St. Clair, T.P.: IS+SY+SS-WeM10, **2**

## — T —

Tyliszczak, T.: IS+SY+SS-WeM5, **1**

## — Y —

Yang, Z.: IS+SY+SS-WeM2, 1

## — Z —

Zhang, C.: IS+SY+SS-WeM1, 1