

Tuesday Morning, October 30, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+SS+EN-TuM

In Situ Spectroscopic Studies of Catalysis and Gas-Solid Reactions

Moderator: B. Roldan Cuenya, University of Central Florida

8:00am **IS+AS+SS+EN-TuM1 Ambient Pressure XPS for Alternative Energy Research and Environmental Science, H. Bluhm**, Lawrence Berkeley National Laboratory **INVITED**

Solid/vapor and liquid/vapor interfaces play a major role in many processes in the environment and technology. Examples include heterogeneous catalysis, fuel cell technology, aerosol chemistry, and weathering of minerals and rocks. The measurement of these interfaces under realistic conditions of gas pressure and temperature has gained increasing importance over the last decades. Ambient pressure photoelectron spectroscopy (APXPS) is a promising technique for the investigation of liquid and solid surfaces in the presence of gases at pressures in the Torr range. The heart of an APXPS instrument is a differentially pumped electrostatic lens system that separates the sample, which is in a gas atmosphere at pressures of up to 5 Torr, from the electron spectrometer, which is kept in vacuum. This talk will discuss the history and basics of APXPS and show examples of the application of APXPS to the study of aqueous solution, metal oxides, soot, and fuel cell electrodes under reaction conditions.

8:40am **IS+AS+SS+EN-TuM3 In Situ Soft X-ray Photon-in/Photon-out Spectroscopy of Photo-electrochemical Reactions of Hematite in Water Splitting, J.H. Guo**, Lawrence Berkeley National Laboratory, *A. Braun*, Empa, Swiss Federal Laboratories for Materials Science and Technology, *K. Sivula*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *D. Bora*, Lawrence Berkeley National Laboratory, *J.F. Zhu*, *L. Zhang*, University of Science and Technology of China, *M. Grätzel*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *E.C. Constable*, University of Basel, Switzerland

Hydrogen fuel generation by solar water splitting in photoelectrochemical cells (PEC) is one of the first steps in artificial photosynthesis and an essential part of the holy grail of solar energy conversion. Iron oxide, literally "rust", is an interesting PEC photoanode material because of its affordability, good stability, good spectral match of the solar spectrum, and yet controversial because of its poor electronic structure. At present, iron oxide is taking center stage as prospective PEC anode material.

PEC electrodes are typically semiconducting metal oxides to form electron-hole pairs when struck by light. In the photoanodes such as hematite, the generated holes must diffuse to the iron oxide surface where they can oxidize water to oxygen. However, the electronic structure of iron oxide is such that the photogenerated holes tend to recombine and annihilate with the electrons before reaching the surface and performing the required chemical work on water splitting. Currently, researchers worldwide try to understand the peculiarities of iron oxide so as to invent strategies to improve this material.

The Advanced Light Source produces soft X-rays which are optimally suited to study the electronic structure of electrode materials and which can detect electron holes. But the holes needed for solar water splitting by iron oxide require an anodic electric bias plus the illumination. Moreover, the holes are transitional and quite elusive. Also, soft X-rays cannot easily peek into a PEC cell. The unique design of the in-situ cell at the ALS has overcome the burden [1-3]. Recently the experiment has been performed for studying, under in-situ and operando conditions, the hole generation in a specifically designed photoelectrochemical cell. The oxygen valence band signature was recorded while tuning the PEC relevant parameters, two different types of holes in the valence band near the Fermi energy are discovered [4].

References:

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- [2] "Electronic Structure of Cobalt Nanocrystals Suspended in Liquid", H. Liu et al., *Nano Lett.* **7**, 1919 (2007).
- [3] "In situ soft X-ray absorption spectroscopy investigation of electrochemical corrosion of copper in aqueous NaHCO₃ solution", P. Jiang et al., *Electrochem. Comm.* **12**, 820 (2010).

[4] "Direct Observation of Two Electron Holes in a Hematite Photoanode during Photoelectrochemical Water Splitting", A. Braun et al., *J. Phys. Chem. C* **116**, 16870 (2012).

9:00am **IS+AS+SS+EN-TuM4 XANES and Ambient Pressure XPS (APXPS) Study: Investigations of the Local Structure and Final-State Effect in Partially Reduced SnO_x Nanoislands on Pt(111), S. Axnanda, Z. Liu, B. Mao**, Lawrence Berkeley National Laboratory

Heterogeneous catalysts consisting of small particles having a high concentration of structural defects and under-coordinated sites make up the majority of the catalytic processes in industrial chemistry. One important recent example of interest shows that the interface-confined coordinatively unsaturated ferrous (CUF) sites together with the metal supports (FeO_x/Pt(111)) are active for dioxygen activation which causes the ensemble to be highly efficient for CO oxidation at low temperature under typical operating conditions of a proton-exchange membrane fuel cell.[1-2] In this work, we report another spectroscopic evidence to further confirm an enhanced reactivity at the edges of small catalyst particles. The system of interest is partially oxidized SnO_x (Sn²⁺) nanoislands supported on Pt(111) for ethanol oxidation reaction (EOR), an electrode material in a direct alcohol fuel cell (DAFC). Our findings suggested that SnO_x/Pt(111) inverse catalysts have improved activity for EOR in acidic media as compared to a bare Pt(111) surface.[3] We also found that the most active surface had a small coverage of SnO_x (0.3- 0.4 ML). Water activation at low potentials is currently attributed to be the promoting effect of SnO_x nanoparticles, since this enhances the oxidation of chemisorbed CO formed on Pt sites during the EOR.[4] To better understand this increased activity, we performed study with the goal to indicate the actual state of Sn in SnO_x nanoislands before and after the SnO_x /Pt(111) is used in EOR showing the increased activity: purely oxide Sn or mixed Sn alloy and Sn oxide, using a combination of APXPS and XANES techniques. BE shift in the XPS core-line spectra of Sn and O, soft X-ray XANES spectra (Sn M_{4,5}-edge, O K-edge) will be collected and compared to the corresponding XPS spectra (Sn 3d, O 1s) to explain the actual state of Sn before and after the SnO_x/Pt(111) is used in the EOR.

1. Fu, Q., et al., Interface-Confined Ferrous Centers for Catalytic Oxidation. *Science*, 2010. 328: p. 1141.
2. Deng, X., et al., Reactivity Differences of Nanocrystals and Continuous Films of α -Fe₂O₃ on Au(111) Studied with In Situ X-ray Photoelectron Spectroscopy. *J. Phys. Chem. C*, 2010. 114: p. 22619.
3. Zhou, W.P., et al., Enhancement in Ethanol Electro-Oxidation by SnO_x Nanoislands Grown on Pt(111): Effect of Metal Oxide-Metal Interface Sites. *Journal of Physical Chemistry C*, 2011. 115: p. 16247.
4. Axnanda, S., W.P. Zhou, and M.G. White, CO Oxidation on Nanostructured SnO_x/Pt(111) surfaces: Unique Properties of Reduced SnO_x. *Phys. Chem. Chem. Phys.*, 2012. Submitted.

9:20am **IS+AS+SS+EN-TuM5 Epitaxial Strontium Substituted Lanthanum Cobalt Oxides Investigated using In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Near Operating Conditions Under Applied Potentials, E. Crumlin, E. Mutoro**, Massachusetts Institute of Tech., *Z. Liu*, Lawrence Berkeley National Lab, *M.D. Biegalski*, Oak Ridge National Lab, *W.T. Hong*, Massachusetts Institute of Tech., *H.M. Christen*, Oak Ridge National Lab, *H. Bluhm*, Lawrence Berkeley National Lab, *Y. Shao-Horn*, Massachusetts Institute of Tech.

Operating conditions for solid oxide fuel cell (SOFC) are typically at high temperatures (~500 – 1000 °C) and ambient pressures (~1 atm). We have to understand how the physical and chemical properties of SOFC materials, particularly the cathode which is responsible for a majority of the fuel cells area specific resistance, change under operating conditions. Such data can provide insights into the mechanism of the oxygen reduction reaction (ORR) which may lead to material development strategies to improve the cathode performance. However, these operating conditions are far away from conventional characterization techniques that are often applied at room temperature or even in ultrahigh vacuum (UHV). Our recent work using *in situ* ambient pressure X-ray photoelectron spectroscopy (APXPS) has shown that (001) oriented epitaxial films of La_{0.8}Sr_{0.2}CoO_{3- δ} (LSC₁₁₃) can exhibit Sr enrichment in the near-surface perovskite lattice structure ("lattice") as temperatures were raised from 220 °C to 520 °C in a p (O₂) of 1×10⁻³ atm. In contrast under the same conditions, a bulk pellet of LSC demonstrated no changes in Sr content within the "lattice" region. The Sr enrichment is believed to play a key role in the observed one order of magnitude enhancement in ORR activity (as measured by the surface exchange coefficient, k^s) of the (001) epitaxial films relative to bulk LSC₁₁₃. In this work, we continue the previous investigations of the chemical properties of (001) epitaxial LSC₁₁₃ as a function of temperature cycling

between 220 °C and 520 °C at a $p(\text{O}_2)$ of 1×10^{-3} atm. Additionally, the comparison of LSC₁₁₃, (La_{0.5}Sr_{0.5})₂CoO_{4±δ} (LSC₂₁₄), and LSC₂₁₄-decorated LSC₁₁₃ (LSC_{113/214}) at $p(\text{O}_2)$ of 1×10^{-3} atm as a function of temperature and under applied cathodic potentials will be presented in order to provide insights into the physical origin responsible for the observed ~3 orders of magnitude ORR activity enhancement of LSC_{113/214} relative to (001) epitaxial LSC₁₁₃.

9:40am **IS+AS+SS+EN-TuM6 Probing Nitrogen and Metal Speciation in Non-Platinum Electrocatalysts by Ambient Pressure X-ray Photoelectron Spectroscopies and DFT Calculations.** *K. Artyushkova, B. Halevi, A. Serov, The University of New Mexico, B. Kiefer, New Mexico State University, P. Atanassov, The University of New Mexico*

X-ray Photoelectron Spectroscopy (XPS) has been the main surface analysis method for determining the chemical environment and coordination of nitrogen and transition metal (TM) in the non-precious group metal oxygen reduction reaction (ORR) electrocatalysts. Even though there is an agreement that Me-N_x serve as one of the possible active sites in ORR, the distribution of Me-N₂ vs Me-N₄ centers and their specific role still remains unresolved. XPS which heavily relies on use of reference spectra in accurate identification of species cannot address this issue directly as no reference compounds with Me-N₂ moieties are available. The assignment of peaks and nitrogen coordination is not straightforward due to overlapping peaks that appear within a narrow energy window of 2.5-eV and the full width half maximum (fwhm) for individual species is on the order of 1.2-1.5-eV. Being able to calculate binding energy shifts based on molecular structure can be very important tool for assisting in this task. We will report on BE shifts that have been calculated at the DFT level and their comparison to experimentally obtained values for metal-less and metal-containing porphyrins. Information obtained from the DFT calculations will be used as input into curve-fitting XPS spectra for various model N-Me containing compounds as well as from electrocatalyst. We will compare chemical information derived from conventional XPS as well as in-situ ambient-pressure XPS using variable energy synchrotron source.

10:40am **IS+AS+SS+EN-TuM9 Resolving Growth of Palladium Nanocatalysts Using In Situ FT-IR, XAS and PDF under Practical Atomic Layer Deposition Conditions.** *Y. Lei, J. Lu, B. Liu, H. Zhao, J. Greeley, P. Chupas, J. Miller, J.W. Elam, Argonne National Laboratory*

Nanostructured Pd catalysts prepared by ALD have been demonstrated highly active for alkene hydrogenation, methanol decomposition reaction, and alcohol oxidation for fuel cells. Development of supported Pd nanoparticles with Controlled size/structure relies on the fundamental understanding of the two half reactions with high precision during Pd ALD. However, evolution of Pd surface species, as well as the subsequent nucleation and growth of palladium nanoparticles during Pd ALD is still not clear.

Mechanism of assembly of highly dispersed Pd nanoparticles on TiO₂ surfaces from palladium hexafluoroacetylacetonate (Pd(hfac)₂) were investigated by means of *in situ* Infrared (IR) spectroscopy, X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) under practical atomic layer deposition condition simultaneously. Density function theory simulation was applied to understanding the reaction mechanism. On chlorine-containing TiO₂ surface, Pd(hfac)₂ primarily adsorbed on TiO₂ surface as Pd(hfac)Cl₂* species, confirmed by both XAS and DFT calculations. *In-situ* FT-IR results reveal that deligation of Pd(hfac)Cl₂* species began at as low as 100 °C with the present of formalin. Further on, *in-situ* XAS results indicated that cleavage of Pd-O bond occurred first, followed by cleavage of Pd-Cl bond. Sequentially, Pd atoms started to gain mobility and agglomerate to small nanoparticles. The hfac ligands spilled to TiO₂ surface as site blockers for ALD. The surface poisons were eventually removed at 225 °C. Nano-size palladium-carbon phase was also found after long exposure of formalin. Atomic resolution aberration-corrected STEM image showed one nanometer size crystalline Pd particles were synthesized using ALD. The catalytic performance of these Pd nanocatalysts was further demonstrated in several applications.

In summary, dynamic growth of Pd nanocatalysts was obtained utilizing a combination of *in-situ* techniques.

11:00am **IS+AS+SS+EN-TuM10 Catalyst Characterization using In Situ XAS and XPS: From Nanoparticles Synthesis to Evolution of Structural/Electronic Properties under Reaction Conditions.** *A.M. Karim, Pacific Northwest National Laboratory* **INVITED**

Catalysts are used to facilitate the important industrial chemical processes, leading to products valued in the trillions of dollars annually just in the U.S and most catalysts used in large-scale processes are solids. To maximize the number of sites available for reaction, catalysts are typically comprised of metallic/metal oxide nanoparticles dispersed on high surface area supports.

The activity and selectivity of metallic nanoparticles strongly depend on their size, shape and composition [1-8]. In order to design more active and selective catalysts, it is essential to identify the catalytically active sites and understanding their geometric and electronic properties which requires: (1) synthesis of well-defined catalyst structures and (2) the ability to correlate individual reaction pathway(s) with the type of active site(s) available on the catalyst surface under reaction conditions.

This talk is going to cover our work on *in situ* characterization of nanoparticles from the synthesis stage to the evolution of their structural/electronic properties under reaction conditions using X-ray photoelectron and X-ray absorption spectroscopies. The catalyst systems that will be covered include:

Pd nanoparticles synthesis in solution: Understanding the nucleation and growth mechanisms.

Supported Pt, PtRe and PtNi nanoparticles under aqueous phase reaction condition: Correlating the structural and electronic properties with the catalytic activity and selectivity.

References:

- [1] Boudart, M. *Adv. Catal.* 1969, 20, 153.
- [2] Boudart, M. *Journal of Molecular Catalysis* 1985, 30, 27.
- [3] Ichikawa, S.; Poppa, H.; Boudart, M. *Journal of Catalysis* 1985, 91, 1.
- [4] Somorjai, G. A.; Carrazza, J. *Industrial & Engineering Chemistry Fundamentals* 1986, 25, 63 [5] Liu, Z.; Hu, J. E.; Wang, Q.; Gaskell, K.; Frenkel, A. I.; Jackson, G. S.; Eichhorn, B. *Journal of the American Chemical Society* 2009, 131, 6924.
- [6] Alayoglu, S.; Nilekar, A. U.; Mavrikakis, M.; Eichhorn, B. *Nature Materials* 2008, 7, 333.
- [7] Sinfelt, J. H. *Journal of Catalysis* 1973, 29, 308.
- [8] Sinfelt, J. H. *Accounts of Chemical Research* 1977, 10, 15.

11:40am **IS+AS+SS+EN-TuM12 In Situ Study of the Oxidation of CO over Ir(111).** *J. Knudsen, Lund University, Sweden, Y. Monya, Keio University, Japan, J. Schnadt, M.A. Arman, E. Grånäs, Lund University, Sweden, H. Kondoh, Keio University, Japan, J.N. Andersen, Lund University, Sweden*

The platinum group metals are known to be excellent catalysts for the oxidation of carbon monoxide, and the reaction mechanisms over the surfaces of these metals have been studied for a long time. Nevertheless, only during recent years a new picture has emerged which suggests that the catalytically active phase often is formed first under reaction conditions – which implies realistic pressures rather than ultrahigh vacuum (UHV) – and that it is different from the adsorption structures known from UHV experiments. In the case of the Pt(111) surface a very oxygen-rich chemisorbed phase has been suggested as the catalytically active phase [1], whereas a surface oxide have been suggested for the Ru(0001) surface [2]. Thus, for each different surface different phases and mechanisms might be at play, and, moreover, the phase might depend quite strongly on the conditions (pressure and temperature) used.

With this in mind we have studied the CO oxidation reaction over the Ir(111) surface and the related adsorption systems of CO and oxygen on Ir(111) using a combination of *in situ* Ambient pressure x-ray photoelectron spectroscopy (APXPS) – carried out at the new APXPS instrument at the Swedish synchrotron radiation facility MAX IV Laboratory – and *ex situ* Scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) measurements performed in UHV.

A recent surface x-ray diffraction study reports different oxygen phases for the Ir(111) surface at oxygen pressures from 10⁻⁶ to 100 mbar – chemisorbed oxygen, a trilayer, a multilayer oxide, and a bulklike oxide [3]. Concentrating on pressures at around 1 mbar, we find a variety of oxygen-rich structures. The corresponding CO adsorption phase formed at 1 mbar CO pressure is an assembly of separated CO₁₆ clusters with the CO molecules sitting in on-top sites [4].

The reactivity at 1 mbar total pressure (O₂:CO ratio 9:1) and at different temperatures was studied by APXPS and simultaneous monitoring of the gas composition. We find that the phase with the highest activity for the oxidation of CO is a surface phase which contains both CO and oxygen. By comparing with the measured adsorption structures of oxygen we find that the oxygen structure is quite similar to the p(2x1)-O structure formed on Ir(111) under UHV conditions. This contrasts with what is found for other platinum group metals such as the Pt(111) surface [2], for which CO oxidation is favoured over oxygen rich phases.

- [1] A. L. Gerrard, J. F. Weaver, *J. Chem. Phys.* **123** (2005) 224703.
- [2] H. Over et al., *Science* **287** (2000) 1474.
- [3] Y. B. He et al., *J. Phys. Chem.* **112** (2008) 11946.
- [4] L.-M. Yang, S.-L. Yau, *J. Phys. Chem. B.* **104** (2000) 1769.

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