

Tuesday Morning, October 19, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+SS-TuM

In Situ Spectroscopy – Interfacial Chemistry/Catalysis

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-TuM1 Oxidation and Reduction of Pd(100) and Supported Pd Nanoparticle Model Catalysts**, *R. Westerstrom, S. Blomberg, N. Martin, J. Gustafson, E. Lundgren, J.N. Andersen, M.E. Messing, K. Deppert*, Lund University, Sweden, *H. Bluhm*, Lawrence Berkeley National Laboratory, *O. Balmes, R. van Rijn*, ESRF Grenoble, France

Using *in situ* high pressure X-ray photoelectron spectroscopy, we study the oxidation and reduction by O₂ and CO in the mbar pressure regime of Pd(100) and Pd nanoparticles of 15 or 35 nm diameter supported on a SiO_x substrate. We find the oxidation behavior of these model catalysts to be qualitatively similar, with an ultra-thin surface oxide forming prior to the onset of bulk PdO formation. However, the Pd nano particles are observed to bulk oxidize at sample temperatures 40 degrees lower than Pd(100). For the PdO surface, we identify a core level shift of the Pd 3d and O 1s levels of -0.3 and -1.3 eV, respectively, relative to the corresponding levels in bulk PdO. In a CO atmosphere, the Pd 3d shift changes by +0.55 eV due to CO adsorption, and CO adsorbed on the oxide can be identified in the C1s. Also the reduction by CO is similar between the single crystal and the nanoparticle samples, but after the complete removal of the oxide, the nanoparticles incorporate carbon to form a Pd carbide. This is not observed for the single crystal sample.

8:20am **IS+SS-TuM2 In-situ XPS Studies of CO₂ Captured by Aqueous Monoethanolamine (MEA) Solutions**, *T. Lewis, A. Chaudhuri*, University of California, Irvine, *M. Faubel*, Max-Planck Institut fur Dynamik und Selbstorganisation, Germany, *B. Winter*, Helmholtz-Zentrum Berlin fur Materialien und Energie, Germany, *J.C. Hemminger*, University of California, Irvine

XPS on a micro liquid jet has been used to study solutions of monoethanolamine (MEA), which is commonly used in gas stream scrubbing for carbon dioxide capture. It is likely that interactions between CO₂ and the aqueous MEA solution at the gas/liquid interface are important to this process, yet there is little information available concerning the spatial distribution of species at the interface of such solutions. In the present work, aqueous solutions of MEA with a range of pH values as well as solutions of MEA reacted with CO₂ have been measured using tunable synchrotron radiation from the BESSY facility in Berlin, where the photoelectron kinetic energy can be varied to obtain depth dependent composition information. N1s photoemission spectra allow for the identification of protonated versus unprotonated MEA by the different binding energies of the two species, and likewise, C1s spectra allow for the determination of CO₂-reacted versus unreacted MEA. Depth profiling reveals that deprotonated MEA is more surface active than both protonated MEA and the CO₂-reacted species. The mechanism of the reaction of CO₂ with aqueous solutions of monoethanolamine will be discussed in light of our results.

8:40am **IS+SS-TuM3 Photoelectron Spectroscopy Under Humid Conditions**, *H. Bluhm*, Lawrence Berkeley National Laboratory **INVITED**

The interaction of water with surfaces plays a major role in many processes in the environment, atmosphere and technology. Weathering of rocks, adhesion between surfaces, and ionic conductance along surfaces are among many phenomena that are governed by the adsorption of molecularly thin water layers under ambient humidities. The properties of these thin water films, in particular their thickness, structure and hydrogen-bonding to the substrate as well as within the water film are up to now not very well understood. Ambient pressure photoelectron spectroscopy (APXPS) is a promising technique for the investigation of the properties of thin water films. We will discuss the basics of APXPS as well as the particular challenges that are posed by investigations in water vapor at Torr pressures, as well as show examples of the application of APXPS to the study of water films on metals and oxides.

9:20am **IS+SS-TuM5 Chemistry of Aminoacids at the Water – Metal Interfaces under UHV and AP Conditions**, *A. Shavorskiy*, Lawrence Berkeley National Laboratory, *T. Eralp*, The University of Reading, UK, *F. Aksoy, Z. Liu, H. Bluhm*, Lawrence Berkeley National Laboratory, *A. Cornish, D. Watson*, The University of Reading, UK, *K. Schulte, J.N. Andersen*, Lund University, Sweden, *G. Held*, The University of Reading, UK

Many important catalytic reactions take place at the interface between a solid catalyst and a solution, in particular aqueous solutions play a crucial role in all biological systems. The presence of the solvent at the solution-catalyst interface can dramatically change the chemical surface properties and, therefore, the entire catalytic process. Although surface science has been very successful in studying gas-surface reactions, most UHV-based surface science techniques cannot be applied to the co-adsorption of solvent and reactant molecules of important reaction systems because the solvent desorption temperature in UHV is too low to allow co-adsorption at realistic reaction temperatures. In order to keep significant amounts of water adsorbed near room temperature pressures of up to 1 mbar are needed for most metals. Recently, ambient pressure X-ray photoelectron spectroscopy (APPEs), has become available for studying these systems at close-to-real conditions [Bluh09].

For the experiments reported here we chose to study the influence of water on the adsorption of glycine and alanine on Pt[111] and Pt[110] in UHV and on Cu[110] at near-ambient pressure. The comparison between results obtained in UHV and at AP allows us to reveal importance of the reaction conditions (in particular reaction pressure and temperature) on the chemical composition and stability of the molecular adlayers on metals. It also bridges the pressure gap in studies of such kind of bio-related systems. Our results show an absence of any noticeable changes in the chemical composition of the aminoacids on Pt[111] and Pt[110] when co-adsorbed with water in UHV. On the other hand we observed clear decrease of the amino acid desorption temperature and a change of the desorption pathway (compared to UHV [Barl05]) on Cu[110] when the H₂O pressure is increased above 10⁻⁵ mbar. Two possible mechanisms of lowering the stability of the amino acids in the presence of water are discussed: (a) oxidation of the amino acid by OH or O or (b) hydrogenation of the anionic amino acid followed by desorption of the less stable intact form [Jone06].

[Bluh09] H. Bluhm, J. El. Spec. Rel. Phen., doi:10.1016/j.elspec.2009.08.006, 2009.

[Jone06] G. Jones et al Surf. Sci. 600 (2006) 1924.

[Barl05] S. M. Barlow et al Surf. Sci 590 (2005) 243.

[Ande07] K. Andersson et al. J. Phys. Chem. C 111 (2007) 14493.

9:40am **IS+SS-TuM6 In-situ Ambient Pressure XPS Observations of Reversible Charge Storage in Ni Electrodes**, *A.H. McDaniel, F. El Gabaly*, Sandia National Laboratories, *M. Grass, Z. Liu*, Lawrence Berkeley National Laboratory, *K.F. McCarty*, Sandia National Laboratories, *H. Bluhm*, Lawrence Berkeley National Laboratory

Electrochemical technologies will be increasingly used to supply energy to the world without contributing to climate change. These technologies can store and convert energy with unsurpassed efficiencies through, for example, the charging and discharging of batteries or the inter-conversion of electrical and chemical energy via fuel cell and electrolyzer. Perhaps the most important phenomena to understand in electrochemical energy storage/conversion is how electric charge is transferred across interfaces and subsequently stored in material phases and/or double layers. Currently, detailed knowledge is lacking of critical pathways such as which chemical reactions are responsible for charge transfer, what species are involved, and where charge transfer reactions occur in heterogeneous devices. These limitations arise in no small degree from the physical complexities of these devices, which consist of a variety of electrified materials undergoing chemical reactions. Lacking this knowledge, development proceeds largely using engineering approaches.

To help answer these questions we have spectroscopically characterized electrochemical charge-transfer and storage as it occurs. This is accomplished by primarily using a new diagnostic based on synchrotron X-ray spectroscopies that we have been developing at the Advanced Light Source (ALS, LBNL, Berkeley, CA). Photoelectrons are used as a contactless probe for the direct measurement of the electric inner potential everywhere in a Ni-YSZ based electrochemical cell operating at near ambient pressure. This information, in addition to space-resolved chemical characterization of the surface species showing phase changes relevant to Ni-metal-hydride batteries, will be discussed. The experimental configuration consists of a thin-film Ni electrode that is electrochemically modified by injection of O₂⁻ ions. During an applied bias, charge is stored

in the electrode by the conversion of the Ni to NiOOH. This leads to dramatic changes in the XPS spectra as well as the existence of a constant discharge potential plateau resulting from the equilibrium of NiOOH with two other phases, Ni and H₂O. Thus, our approach has the ability to identify the phases that store charge, which are only stable under electrical bias. This rich data will provide new understanding on how electrochemically driven phases form.

10:40am **IS+SS-TuM9 Hard X-ray Photoelectron Spectroscopy: an Effective Probe for Electronic Structure in Materials Science, W. Drube**, Deutsches Elektronen-Synchrotron DESY, Germany **INVITED**

The use of hard X-ray excitation in the range from about 2 to 15 keV for photoelectron spectroscopy (HAXPES) is a rapidly emerging technique at synchrotron sources worldwide since it significantly widens the range of applications, in particular in the study of complex materials and buried nano-structures or interfaces. Due to the increased electron inelastic mean free paths, it becomes possible to probe chemical composition and electronic structure in the bulk of materials with considerable sensitivity, down to typically 10-20 nm at 10 keV kinetic energy. This not only is essential in the study of complex correlated materials which often exhibit a modified surface electronic structure but also is very relevant for technologically interesting multi-layered materials with buried interfaces. As an additional benefit, "as-grown" materials can be measured without need for prior surface treatment.

A drawback is the rapidly decreasing photoelectric cross section in the hard X-ray range, especially for shallow core levels and valence states, and - until recently - the limited availability of suitable high-voltage electron spectrometers. The latter are available meanwhile and the high X-ray flux at undulator beamlines has been shown to effectively compensate the cross section decrease. In addition, the X-ray tunability over a large energy range not only allows to significantly vary the electron probing depths and the photoelectric cross sections, but also enables the study of resonance phenomena at deep inner-shell thresholds. Further, the excitation of X-ray standing wave fields within single crystals or multi-layered structures can be effectively used to correlate geometric and electronic structure information.

In the past five years, HAXPES activities at synchrotron laboratories worldwide have increased dramatically and the trend continues as new instruments are currently being built and planned. A brief overview is given on the current activities worldwide, both on instrumental developments and results obtained. At DESY, HAXPES experiments routinely use a dedicated spectrometer at an X-ray wiggler with moderate energy resolution (~0.5 eV), well suited for many core level studies. Very recently, high-resolution studies also became possible at DESY with the availability of PETRA III, a new storage ring source providing the highest X-ray brilliance.

11:20am **IS+SS-TuM11 Novel Applications in Surface Science – In situ Sample Analysis in Extreme Environments, A. Thissen**, SPECS Surface Nano Analysis GmbH, Germany

Modern devices are often only functional in environments far away from ultrahigh vacuum, still being the standard operation conditions for all Surface Science techniques. In parallel the importance of surfaces for the correct device operation is continuously increasing due to miniaturization down to the nanoscale. To contribute to advanced materials analysis in future means using Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Also extremely low or high temperatures might be necessary. In past all standard Surface Science Techniques did not work under these *extreme* environments. This work summarizes and presents existing solutions nowadays and future development routes to new instruments and materials analysis methods being functional under these working conditions. Opportunities and limits will be discussed, from the perspective of a supplier of scientific instruments. Finally applications, examples and results from existing *In situ* methods like high pressure treatments cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy Systems (NAP-PES or HP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in highest or lowest temperatures, high magnetic fields and static or dynamic potentials will be demonstrated.

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