

Thursday Afternoon, November 12, 2009

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference Room: C4 - Session IS+AS-ThA

In-Situ Microscopy and Spectroscopy: Surface Reactions Moderator: P. Nachimuthu, Pacific Northwest National Laboratory

2:00pm IS+AS-ThA1 Interface Science in Nanoparticles: An Electronic Structure View of Photon-in/Photon-out Soft-X-Ray Spectroscopy, *J.-H. Guo*, Lawrence Berkeley National Laboratory

Solar energy can be converted to electricity and chemical fuels for energy use and storage. However, the cost and conversion efficiency have been the biggest challenge for potential use of solar energy. There are the emerging technologies of using semiconductors for light harvesting assemblies; and charge transfer processes to solar cells. It could provide a significant contribution to our electrical and chemical resources if efficient and inexpensive systems utilizing readily available materials could be devised for the conversion process.

This presentation will shed some light on synchrotron radiation based soft-x-ray spectroscopy study of nanostructured materials. Soft-x-ray absorption probes the local *unoccupied* electronic structure (conduction band); soft-x-ray emission probes the *occupied* electronic structure (valence band); and the addition of resonant inelastic soft-x-ray scattering (Raman spectroscopy with soft x-rays) can tell the energy levels that reflect the chemical and physical properties of semiconductors. The experimental studies suggest that in-situ photon-in/photon-out soft-x-ray spectroscopy becomes an emerging tool for investigating the surface and interface science.

(1) The examples show quantum size effects on the exciton and band-gap energies of semiconductor nanocrystals (Hematite nanoarrays). Such finding strongly suggests that such designed nanomaterials could meet the bandgap requirement for the photocatalytic oxidation of water without an applied bias.

(2) The storage of hydrogen in a both safe and compact manner is of great importance for, for example, hydrogen powered vehicles. We have explored in-situ photon-in/photon-out soft-X-ray spectroscopy to study the molecular adsorption of H₂ on SWNTs under ambient pressures. The spectral changes with the increasing gas pressures provide the strong evidences for the tube-wall structure deformation and possibly a fraction of charge transfer due to the gas collision.

2:20pm IS+AS-ThA2 In Situ GIXAFS and HERFD-XAS Studies of Pt-modified Rh(111) and Rh(221) Electrodes, *D. Friebel, D.J. Miller, H. Ogasawara, T. Annyev, C.P. O'Grady, U. Bergmann, J. Bargar, A. Nilsson, Stanford Synchrotron Radiation Lightsource, K.T. Wikfeldt, L.G.M. Pettersson*, Stockholm University, Sweden

The oxygen reduction reaction at Pt electrodes has a high overpotential which drastically reduces the efficiency of fuel cells. The origin of the overpotential has been seen in the formation of stable Pt-O species at high potentials. Aiming at an unambiguous characterization of such Pt-O species, we use in situ grazing incidence x-ray absorption spectroscopy at the Pt L₃ edge to study the geometric and electronic structure of ultrathin Pt layers on Rh(111) and Rh(221) substrates as a function of the electrochemical potential. The use of Pt monolayers on a foreign metal substrate makes the bulk-penetrating hard x-ray probe surface sensitive and, furthermore, can be used for a variety of substrates to elucidate the influence of metal-metal interactions and interfacial strain on the catalytic activity of the Pt layer. The stepped Rh(221) surface serves as a well defined model substrate to study the influence of defects which are also expected to occur in nanoparticle catalysts.

We present our results from Pt L₃-edge grazing incidence x-ray absorption fine structure (GIXAFS) and high energy resolution fluorescence detection (HERFD) XAS measurements of an ultrathin Pt layer on Rh(111) in 0.01 M HClO₄ solution. The Pt layer was produced by UHV evaporation. In the HERFD-XAS experiment, we used a multi-crystal analyzer to reduce the core hole lifetime broadening. The high resolution spectra reveal additional spectral features of the near-edge region which can be theoretically modeled using the FEFF8 code and thus allow us to build an accurate structure model of the Pt/electrolyte interface.

2:40pm IS+AS-ThA3 Chemical Imaging of Catalytic Solids at the Micron- and Nanoscale, *B.M. Weckhuysen, E. de Smit*, Utrecht University, the Netherlands **INVITED**

Most characterization studies of catalytic solids focus on ensemble-averaged measurements, assuming that catalytic solids are spatially homogeneous materials when placed in a reactor. Structure-performance relationships can then be obtained by relating activity and selectivity with a multitude of spectroscopic signatures. However, these signatures are not necessarily identical across e.g. a catalyst grain or fixed bed reactor. Detailed knowledge on these spatial heterogeneities is required to better understand reaction and deactivation mechanism. This keynote lecture discusses the potential of spectroscopic methods for chemical imaging spatial heterogeneities within catalytic solids at the micron- and nanoscale. Special emphasis will be on the use of in situ Scanning Transmission X-ray microscopy (STXM), UV-Vis microscopy, synchrotron IR microscopy, Coherent Anti-Stokes Raman Scattering (CARS) microscopy and (confocal) fluorescence microscopy. Two showcases will be discussed, namely Fe-based Fischer-Tropsch Synthesis (FTS) and H-ZSM-5 zeolites, catalyzing the oligomerisation of styrene and methanol to hydrocarbons. For the latter showcase, large coffin-shaped H-ZSM-5 crystals have been studied.

3:40pm IS+AS-ThA6 Using Synchrotron Based in situ X-ray Techniques and TEM to Study Electrode Materials for Lithium Batteries, *X.Q. Yang*, Brookhaven National Laboratory **INVITED**

Recently, we have developed techniques using the combination of a high intensity synchrotron x-ray beam and fast detectors (image plate or position sensitive detectors) to do in-situ X-ray diffraction (XRD) during charge-discharge cycling and time resolved X-ray diffraction during the thermal decomposition of charged cathode materials. We have also developed synchrotron based in-situ X-ray absorption (XAS) techniques to study the changes of oxidation states and coordination of the transition metal elements during cycling. The in-situ and ex-situ soft x-ray absorption spectroscopy techniques we have developed allow us to distinguish the structural differences between the surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors simultaneously. In this presentation, we will report our studies on the structural changes of various cathode materials such as layered LiMO₂ (M=Co, Mn, Ni) and olivine structured LiMPO₄ (M=Fe, Mn, Co, Ni) with and without surface coating, during charge-discharge cycling as well as during thermal decompositions. The results of these studies provide very important information for synthesizing new cathode materials with improved properties. Preliminary results of studies using in-situ transmission electron microscopy and high-resolution analyses will also be reported. **ACKNOWLEDGMENT** This work done at Brookhaven National Lab. was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. DOE under Contract No. DE-AC02-98CH10886

4:20pm IS+AS-ThA8 Direct Observation of Interfacial Layer Formation in Li-Ion Battery using In-Situ TEM and EELS, *C.M. Wang, W. Xu, L. Saraf, B. Arey, J. Liu, Z. Yang, J.G. Zhang, S. Thevuthasan, D.R. Baer*, Pacific Northwest National Laboratory

One of the fundamental challenges facing the Li-ion battery development is the understanding of the fading mechanism of the active electrode materials during the repeated charging and discharging. In-situ methods based on x-rays have provided some information regarding the structural evolution of the electrode materials during the operation of a battery. However, in-situ work using x-ray only gives the average results, yielding no spatial resolution. Furthermore, it has been generally realized that the microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration play a vital role on the performance as well as the overall life-cycle of the battery. In-situ transmission electron microscopy (TEM) and spectroscopy will be ideal tools for probing the structural evolution of the electrode materials during battery operation. However, related to the high vacuum operation of a TEM as well as the requirement of electron transmission through the sample, a prototype battery must be sealed with thin membrane that enables the electron transmission at the interested region. It is known that electrolytes based on ionic liquid have a low vapor pressure. Therefore, it is generally expected that using ionic liquid as electrolyte, the prototype battery may be operated in vacuum without sealing the whole system using a thin membrane. In this work, we report our exploratory work on developing in-situ TEM devices that will eventually enable direct and high spatial resolution observation of the structural evolution of the interface between the electrolyte and the electrode materials. In a model experiment, a prototype Li-ion battery was developed in the system of using SnO₂

nanowire as anode, an air stable salt LiTFSI in a hydrophobic ionic liquid as electrolyte, and LiCoO₂ as cathode. Focused ion beam (FIB) manipulation of a single nanowire enables the assembling of a prototype battery. Furthermore, due to the low vapor pressure of the ionic liquid, the whole system can be directly loaded into a TEM without sealing. The interface across the solid-ionic liquid was studied during charging and discharging using TEM imaging and electron energy loss-spectroscopy (EELS). By comparing these results with those obtained from batteries based on coin cell design, several challenges were identified. These results will be discussed along with the future research directions.

4:40pm **IS+AS-ThA9 Characterizing Solid Oxide Fuel Cells during Electrochemical Operation Using Ambient Pressure XPS**, *F. El Gabaly, A.H. McDaniel*, Sandia National Laboratories, *M. Grass, Z. Liu, H. Bluhm, Z. Hussain*, Lawrence Berkeley National Laboratory, *G.S. Jackson, C. Zhang, S.C. Decaluwe*, University of Maryland, College Park, *K.F. McCarty, M.A. Linne, R.L. Farrow*, Sandia National Laboratories

Electrochemical systems for energy applications are hampered by lack of fundamental measurements and understanding of ion transport and interfacial charge transfer mechanisms. Electrochemical devices based on the conduction of O²⁻ anions through a solid electrolyte, such as a solid oxide fuel cell (SOFC) or electrolyzer (SOEC), have great potential for both clean, efficient power generation and efficient production of fuels such as hydrogen or synthesis gas. The essential physical phenomena that govern reaction and charge transfer across material interfaces are poorly understood. The ability to directly observe changes in chemical composition and elemental oxidation state at surfaces and interfaces under electrochemically active conditions will provide insight into such processes. Here, we report in situ measurements of Ni and Pt patterned thin films (300nm) electrodes in solid-oxide electrochemical cells using ambient pressure X-ray photoelectron spectroscopy[1] (APXPS, Beamline 11.0.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory). This novel setup provides quantitative information about the elemental surface composition, local surface potential in the yttria-stabilized zirconia electrolyte, and changes in elemental oxidation state as a result of electrochemical and thermochemical activity occurring under relevant operating conditions: typically 0.25 Torr of hydrogen and 0.25 Torr of water, T=1023K, and under applied bias potential. Chemical changes on the fuel cell electrodes under different electrochemical operation will be discussed, as well as the existence of transient species that could help reveal where and how the charge-transfer mechanism is occurring.

References

[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, *Rev. Sci. Instrum.* 73 (2002) 3872.

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