

Monday Afternoon, November 10, 2014

Novel Trends in Synchrotron and FEL-Based Analysis

Focus Topic

Room: 312 - Session SA-MoA

Synchrotron Studies of Processes in Energy Conversion, Electronic Devices and Other Materials II

Moderator: Charles Fadley, University of California, Davis

2:00pm **SA-MoA1 Synchrotron-based *In Situ* Study of PEMFC, SOFC, Battery and Supercapacitor Components, Benedetto Bozzini, Universita' del Salento - Italy** **INVITED**

Fuel cells and supercapacitors are electrochemical devices providing efficient and pollution-free production and transformation of electricity. Notwithstanding their environmental appeal, a host of materials-science problems – chiefly related to the limited durability of crucial functional components – are hindering the widespread application of these otherwise promising devices. Nanotechnology is foreseen to play a key role in the elimination of such drawbacks. Some nanotechnology solutions have already led to sensitive improvements of properties, functionality and performance of some components. However, the present knowledge is mostly at the macroscopic and empirical trial-and-error level and the answers to many questions require much deeper scientific understanding of the origin of degradation processes. In this regard, the development and implementation of appropriate methods for in-situ characterization of cell components at the functionally relevant length scales is highly required. Soft X-ray spectroscopies, namely X-ray absorption spectroscopy, X-ray emission (fluorescence) spectroscopy, resonant inelastic X-ray spectroscopy and X-ray photoelectron spectroscopy have been extensively employed for ex-situ characterization of materials used in electrochemical systems. Furthermore, adding spatial resolution capabilities by implementing proper optical solutions has opened unique opportunities for monitoring material changes and mass transport events occurring at submicron length scales. The input from these methods is providing correlative information about the status of the electrode surface and of the electrode/electrolyte interface and also of the processes occurring under operation conditions at the three phase boundary, namely the electrode-electrolyte-reactant interface¹⁻⁴. REFERENCES [1] B. Bozzini, A. Gianoncelli, P. Bocchetta, S. Dal Zilio, G. Kourousias, *Anal. Chem.* **86**, 664 (2014)

[2] B. Bozzini, M. Amati, L. Gregoratti, M. Kiskinova, *Sci. Rep.* **3**, 2848 (2013)

[3] B. Bozzini, A. Gianoncelli, C. Mele, M. Kiskinova, *Electrochim. Acta* **114**, 889 (2013)

[4] B. Bozzini, M. Kazemian Abyaneh, M. Amati, A. Gianoncelli, L. Gregoratti, B. Kaulich, Maya Kiskinova, *Chemistry – A European Journal* **18**, 10196 (2012)

2:40pm **SA-MoA3 Structure/Selectivity Studies of Promoted Rh/TiO₂ Catalysts under CO Hydrogenation Reaction Conditions, Robert Palomino, J. Magee, P. Carrillo Sanchez, Stony Brook University, M. White, Brookhaven National Laboratory and SUNY Stony Brook**

Rh-based catalysts are sought after for the conversion of syn gas (CO +H₂) to higher oxygenates due to their C-C coupling capabilities, but are highly selective to hydrocarbons. Through the addition of promoters (Fe, Mn, Mo), the selectivity can be altered to oxygenates by varying mechanisms.[1] Fe and Mo in particular have been known to enhance ethanol and other C₂₊-oxygenates through the suppression of methane. Unfortunately, little is known of the structure of these promoted catalysts under reaction conditions. This work focuses on the atomic structure determination of Fe- and Mo-promoted Rh/TiO₂ catalysts with varying promoter concentration. The atomic structure was monitored as a function of promoter concentration under reduced and CO hydrogenation conditions with synchrotron radiation at beamline X7B of the NSLS. X-ray diffraction (XRD) was utilized to elucidate the phase components in the catalysts, while Pair Distribution Function (PDF) analysis was used to determine the local atomic structure of the active components contained in the catalyst. By monitoring the evolution of phase and local atomic structure, we correlate the structure-selectivity relationship by direct comparison with selectivity measurements performed on the same catalysts.

1. Spivey, J.J. and A. Egbebi, *Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas*. *Chemical Society Reviews*, 2007. **36**(9): p. 1514-1528.

3:00pm **SA-MoA4 Synchrotron Infrared Nano-spectroscopy, Hans Bechtel, Lawrence Berkeley National Laboratory, E.A. Muller, R.L. Olmon, University of Colorado at Boulder, M.C. Martin, Lawrence Berkeley National Laboratory, M.B. Raschke, University of Colorado at Boulder**

By combining scattering-scanning near-field optical microscopy (s-SNOM) with mid-infrared synchrotron radiation, synchrotron infrared nano-spectroscopy (SINS) enables molecular and phonon vibrational spectroscopic imaging, with rapid spectral acquisition, spanning the full mid-infrared (500-5000 cm⁻¹) region with nanoscale spatial resolution. This highly powerful combination provides access to a qualitatively new form of nano-chemometric analysis with the investigation of nanoscale, mesoscale, and surface phenomena that were previously impossible to study with IR techniques. We have installed a SINS end-station at Beamline 5.4 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, making the s-SNOM technique widely available to non-experts, such that it can be broadly applied to biological, surface chemistry, materials, or environmental science problems. We demonstrate the performance of synchrotron infrared nano-spectroscopy (SINS) on semiconductor, biomineral and protein nanostructures, providing vibrational chemical imaging with sub-zeptomole sensitivity.

3:40pm **SA-MoA6 Synchrotron-Based Spectroscopy Shedding Light on Solar Cells, Franz Himpel, University of Wisconsin-Madison** **INVITED**

After briefly discussing the role of photovoltaics in the current energy picture, this talk illustrates how spectroscopy with soft X-rays can assist the development of new types of solar cells with improved price/performance ratio. The starting point is the most general layout of a solar cell, which involves of a light absorber sandwiched between an electron donor and an electron acceptor. In contrast to the widely-used silicon solar cells, one can choose three different materials to optimize the four energy levels that are crucial for the performance of a solar cell. These are measured by a combination of X-ray absorption spectroscopy and photoelectron spectroscopy. Close coupling with first principles calculations makes it possible to discover and exploit systematic trends. Examples will be given, such as the combination of all three components in one molecule (donor- π -acceptor complexes [1],[2]). In addition to the energy levels one has to consider the lifetime of the photo-generated carriers. A future dream experiment will be discussed where the carriers are followed in real time on their way from the absorber to the contact electrodes, using pump-probe techniques at the latest generation of soft X-ray light sources. Such experiments have been performed in the UV/visible [3], but they would greatly benefit from the element- and bond-specific capabilities of X-ray absorption spectroscopy.

[1] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, Md. K. Nazeeruddin, E. W.-G. Diao, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **334**, 629 (2011).

[2] I. Zegkinoglou, M.-E. Ragoussi, C. D. Pemmaraju, P. S. Johnson, D. F. Pickup, J. E. Ortega, D. Prendergast, G. de la Torre, and F. J. Himpel, *J. Phys. Chem. C* **117**, 13357 (2013).

[3] G. Duvanel, J. Grilj, and E. Vauthey, *J. Phys. Chem. A* **117**, 918 (2013).

4:20pm **SA-MoA8 *In Situ* Soft X-Ray Absorption Spectroscopy for Investigation of Charge Storage and Actuation in Nanostructured Carbon Aerogels, J.R.I. Lee, M. Bagge-Hansen, B. Wood, T. Ogitsu, A. Wittstock, M. Worsley, Trevor Willey, M. Merrill, Lawrence Livermore National Laboratory, D. Prendergast, Lawrence Berkeley National Laboratory, I.C. Tran, M. Biener, T. Baumann, J. Biener, Lawrence Livermore National Laboratory, J.-H. Guo, Lawrence Berkeley National Laboratory, T.W. van Buuren, Lawrence Livermore National Laboratory**

Carbon aerogels (CAs) are a class of nanostructured, porous materials that have demonstrated applications in electrical energy storage (EES) due to their very high surface area, chemical and electrochemical stability, and relatively low cost. Tailoring these materials towards improved ESS performance can be significantly enhanced by a better understanding of nanostructured materials in aqueous environments under various potential gradients; therefore, we have pursued advanced in situ characterization techniques capable of probing the electronic structure and bonding of these electrode materials during charge-discharge cycling. We report the successful development of a cell for in situ soft x-ray absorption spectroscopy (XAS) studies of EES materials and the application of this cell to the investigation of CA supercapacitors. Our XAS measurements, combined with complementary ab initio modeling, reveal profound changes in the structure and bonding of the CAs in operando, which will be discussed in terms of their macroscopic physical properties. This work

performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

4:40pm **SA-MoA9 First-Principles Modeling of Near-Edge X-ray Spectroscopy for Lithium Compounds**, *John Vinson*, National Institute of Standards and Technology (NIST)

X-ray spectroscopy is a widely-used tool for probing local structural and chemical properties of materials. For devices such as batteries *operando* measurements are vital for understanding the structural changes that take place during the device's lifecycle. Computational modeling can assist experimental investigation by providing complementary data: pointing from proposed structure to observed spectra. The OCEAN spectroscopy package is capable of calculating K- and L-edge spectra of periodic or semi-disordered extended systems using a Bethe-Salpeter equation formalism. Here we present the OCEAN package and near-edge x-ray absorption calculations of lithium compounds. We showcase the effects of accounting for vibrational disorder as well as how a computational approach can be used to decouple the structural and charge-transfer effects on the x-ray spectra observed during (de)lithiation.

5:00pm **SA-MoA10 Soft X-ray Spectroscopy for Fundamental Understanding and Practical Optimization of Battery Materials**, *Wanli Yang*, Lawrence Berkeley National Laboratory **INVITED**

Improving the energy-density and safety of batteries remains a formidable and critical challenge for sustainable energy applications, especially for electric vehicles. The pressing demand calls for novel approaches based on modern material synthesis and advanced characterization tools. Synchrotron based soft x-ray spectroscopy is one of such incisive tools that probe the electronic states in the vicinity of the Fermi Level, which are directly related to battery operations.

This presentation will focus on the concepts of how the electronic structure revealed by soft x-ray spectroscopy could help the battery material research. The link between fundamental electron states and battery performance will first be explained in general^[1]. Several recent spectroscopic results will be discussed from both chemical and physical point of view: The chemical information delivered by soft x-ray indicates the complicated formation process of solid-electrolyte-interphases^[2]. The evolution of the transition-metal 3d states provides in-depth information of the phase transformation in positive electrodes^[3]. Key electronic states that could be directly detected by soft x-ray experiments provide clear guidelines for optimizing battery binder materials in negative electrodes^[4]. Additionally, *in-situ/operando* soft x-ray experiments reveal distinct charge dynamics in operating battery electrodes^[5]. Perspectives will be provided at the end on how to advance the battery material studies through novel instrumentation and methodology.

[1] Yang et al., JESRP 190, 64 (2013); [2] Qiao et al., Adv. Mater. Interf. 10.1002/admi.201300115 (2014); [3] Liu et al., JACS 134, 13708 (2012); [4] Liu et al., Adv. Mater. 23, 4679 (2011); [5] Liu et al., Nat. Commun. 4, 2568 (2013)

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