

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+HC+SS-ThA

IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.**, *Klaus Attenkofer, E. Stavitski, M. Liu, D. Lu, M. Topsakal, D.J. Stacchiola, M.S. Hybertsen*, Brookhaven National Laboratory

INVITED

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a "field of view" in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistically relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA3 Soft X-ray Spectroscopy for High Pressure Liquid**, *Ruimin Qiao, J.-H. Guo, W. Chao*, Lawrence Berkeley National Laboratory

INVITED

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid (up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation**, *Zongfang Wu, H. Kühlenbeck, W. Schöllkopf, H.J. Freund*, Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions

regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the $V_2O_3(0001)/Au(111)$ (~10 nm thick) and a $TiO_2(110)$ single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 μm) IR radiation. For $V_2O_3(0001)/Au(111)$ the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the $TiO_2(110)$ single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA7 Spectroscopic Insight into Resistive Switching Processes in Oxides**, *C. Baeumer, C. Schmitz*, Forschungszentrum Juelich GmbH, Germany; *A. Kindsmüller*, RWTH Aachen University, Germany; *N. Raab, V. Feyer, D.N. Mueller, J. Hackl, S. Nemsak*, Forschungszentrum Juelich GmbH, Germany; *O.T. Mentès, A. Locatelli*, Elettra-Sincrotrone Trieste, Italy; *R. Waser, R. Dittmann, Claus Michael Schneider*, Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3(STO)$ and ZrO_2 with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

[1] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser and R. Dittmann, Nat Commun **7** (2016) 12398.

[2] A. Kindsmüller, C. Schmitz, C. Wiemann, K. Skaja, D. J. Wouters, R. Waser, C. M. Schneider and R. Dittmann, APL Materials **6** (2018) 046106.

[3] C. Baeumer, R. Valenta, C. Schmitz, A. Locatelli, T. O. Mentès, S. P. Rogers, A. Sala, N. Raab, S. Nemsak, M. Shim, C. M. Schneider, S. Menzel, R. Waser and R. Dittmann, ACS Nano **11** (2017) 692.

4:40pm **SA+AS+HC+SS-ThA8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy**, *Yulin Chen*, Oxford University, UK

INVITED

The electronic structure of matter is critical information that determines its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

Thursday Afternoon, October 25, 2018

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

[1] Science, 325, 178 (2009), Science, 329, 659 (2010), Nature Nanotechnology, 6, 705 (2011), Nature Chemistry, 4, 281 (2012), Nature Physics, 9, 704 (2013), Science, 343, 864 (2014), Nature Materials, 13, 677 (2014), Nature Physics, 11, 728 (2015), Nature Materials, 15, 27(2016), Nature Communications 7, 12924 (2016), Nature Communications, 8, 13973 (2017).

5:20pm **SA+AS+HC+SS-ThA10 Electronic Structure of FeO, γ -Fe₂O₃ and Fe₃O₄ Epitaxial Films using High-energy Spectroscopies**, *German Rafael Castro*, Spanish CRG BM25-SpLine Beamline at the ESRF, France; *J. Rubio Zuazo*, Spanish CRG BM25-SpLine at the ESRF, France; *A. Chainani*, Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China; *M. Taguchi*, RIKEN SPring-8 centre, Japan; *D. Malterre*, Institut Jean Lamour, Université de Lorraine, France; *A. Serrano Rubio*, Spanish CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ -Fe₂O₃ (maghemite) and Fe₃O₄ (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ -Fe₂O₃ and Fe₃O₄ films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO₆ cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd} , the charge-transfer energy Δ , and the metal-ligand hybridization strength V . The results also provide estimates for the ground state and final state contributions in terms of the d^n , $d^{n+1}L1$ and $d^{n+2}L2$ configurations. Both FeO and γ -Fe₂O₃ can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO₆ cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ -Fe₂O₃ and Fe₃O₄. Based on simplified calculations using an M₂O₇ cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ -Fe₂O₃ and Fe₃O₄.

5:40pm **SA+AS+HC+SS-ThA11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation**, *M.H. Nielsen, J.A. Hammons, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgkin, K. Champley, W. Shaw*, Lawrence Livermore National Laboratory; *N. Sinclair*, Washington State University; **Trevor Willey**, Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutch is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector

at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

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