

Actinides and Rare Earths Focus Topic

Room A215 - Session AC+LS+MI-MoM

Magnetism, Complexity, Superconductivity, and Electron Correlations in the Actinides and Rare Earths

Moderators: Krzysztof Gofryk, Idaho National Laboratory, Ladislav Havela, Charles University, Prague, Czech Republic

8:20am AC+LS+MI-MoM-1 Possible Structural Quantum Phase Transition in UCr₂Si₂ Accessed Through Cr → Ru Chemical Substitution, *Ryan Baumbach*, Florida State University **INVITED**

Materials with intertwined magnetic, electronic, and structural degrees of freedom often can be tuned (e.g., using pressure or chemical substitution) to induce novel behavior, including unconventional superconductivity. Examples include the cuprates, iron based superconductors, and lanthanide/actinide-based compounds, and despite their diversity of structure, chemistry and interaction mechanisms, their individual phase diagrams often conform to a semi-universal format that features a quantum phase transition. As a result, there have been prolonged efforts to develop new families of materials based on this paradigm. Even so, there still are few examples of f-electron intermetallics that combine both magnetic and structural quantum phase transitions. In this talk, we will present results from recent efforts to tune the ordered states of UCr₂Si₂, which is a Kondo lattice metal with antiferromagnetic ordering near $T_N \approx 24$ K and a structural phase transition near $T_S \approx 200$ K. In particular, we will focus on the influence of Cr to Ru chemical substitution, where we find that both T_N and T_S are rapidly suppressed towards separate quantum phase transitions. The impact of the quantum phase transitions on the structural, magnetic, and electronic properties will be examined in detail.

9:00am AC+LS+MI-MoM-3 Dynamic Spin Transport in Antiferromagnetic Insulators: Angular Dependent Spin Pumping in Y₃Fe₅O₁₂/NiO/Pt Trilayers, *Fengyuan Yang*, The Ohio State University **INVITED**

In recent years, pure spin transport driven by ferromagnetic resonance (FMR) spin pumping or a thermal gradient has attracted intense interest and become one of the most active frontiers in condensed matter and materials physics. Extensive research efforts have demonstrated pure spin currents in a broad range of materials, which enrich our understanding of dynamically-driven spin transport and open new paradigms for energy-efficient, spin-based technologies. Antiferromagnetic (AF) insulators possess various desired attributes, such as low loss and high speed up to THz frequencies, for future spintronic applications.

To probe the dynamic spin transport phenomena and the underlying mechanisms in AF insulators, we use high-quality Y₃Fe₅O₁₂ (YIG) epitaxial thin films excited by FMR as a source to inject spins into AF insulator NiO layers and detect the transmitted spin current using inverse spin Hall effect (ISHE) signals in YIG/NiO/Pt trilayers [1, 2]. We observed robust spin currents from YIG to Pt across AF insulators, which initially enhances the ISHE signals and can transmit spin currents up to 100 nm thickness, demonstrating highly efficient spin transport through an AF insulator carried by magnetic excitations. Recently, we studied the angular dependence of spin pumping in a series of YIG/NiO/Pt trilayers as the orientation of the applied magnetic field is rotated out of plane [3]. A simple sinusoidal angular dependence of V_{ISHE} has been viewed as a signature of spin pumping. Surprisingly, we observe an extensive plateau in the V_{ISHE} vs. ϑ_H plots with a pronounced peak feature at an out-of-plane angle of 45° to 60° when the measurement temperature is close to the Néel temperature (T_N) of NiO. This phenomenon can be understood as arising from the competition between the exchange coupling at the YIG/NiO interface, the easy-plane and in-plane easy-axis anisotropies of NiO, and the effect of the applied magnetic field. While insulating antiferromagnetic films can efficiently transmit spin currents and show promise for integration in spintronic devices, the underlying physics of spin ordering and dynamics is richer than currently understood.

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3. Y. Cheng, *et al.* *PRB* **99**, 060405(R) (2019)

9:40am AC+LS+MI-MoM-5 Pressure Studies of Strongly Correlated Phases in Rare Earth Compounds, *Rena Zieve*, University of California, Davis **INVITED**

Various strongly correlated materials have complex low-temperature phase diagrams, exhibiting magnetism and superconductivity as well as spin glass, non-Fermi liquid, and other behaviors. Since each material has its own quirks, determining the underlying universal influences has been challenging. Pressure is a key tool in these efforts, since pressure can tune the interactions within a material without changing its chemical composition or impurities. I will discuss how hydrostatic or uniaxial pressure can probe strongly correlated materials by changing valence, breaking crystal symmetry, or altering the dimensionality of the electron system. I will draw examples from various rare earth compounds. Finally, I will mention recent pressure application techniques that expand the range of possible characterization measurements.

10:40am AC+LS+MI-MoM-8 Fermi Surface Reconstructions and Transport Properties in Heavy-fermion Materials, *Gertrud Zwicknagl*, Institut f. Mathemat. Physics, TU Braunschweig, Germany

The search for new types of exotic topological orders has recently rekindled the interest in Fermi surface reconstructions. Of particular interest are Electronic Topological (Lifshitz) transitions where the number of FS sheets changes abruptly under the influence of external parameters like chemical doping, pressure, or magnetic field. Lifshitz transitions (LTs) are generally associated with the presence of critical points in the electronic band structure, i. e., maxima, minima, or saddle points whose presence follows directly from lattice periodicity. As their separation from the Fermi energy is of the order of the bandwidth the critical points usually do not affect the low temperature behavior. In heavy-fermion materials, however, magnetic fields can drive LTs which are reflected in pronounced anomalies in thermodynamic and transport properties. Here we demonstrate that the magnetic field-dependent anomalies in the Seebeck coefficient provide detailed information not only on the critical points, i. e., their character and position relative to the Fermi energy but also on the quasi-particle dispersion in the vicinity of the critical points, i. e., the effective mass tensor. For lanthanide-based HFS, the theoretical analysis is based on Renormalized Band (RB) structure calculations assuming that the heavy quasiparticles result from a Kondo effect. For U-based HFS, on the other hand, we adopt the "dual nature" model which allows for a microscopic description of the heavy bands. The calculated Lifshitz transitions reproduce the observed positions of anomalies in the Seebeck coefficients surprisingly well.

11:00am AC+LS+MI-MoM-9 Direct Measurement the 5 f_{5/2} and 5 f_{7/2} Unoccupied Density of States of UO₂, *James G. Tobin*, University of Wisconsin-Oshkosh; *S Nowak*, SLAC National Accelerator Laboratory; *C Booth*, Lawrence Berkeley National Laboratory; *E Bauer*, Los Alamos National Laboratory; *S Yu*, Lawrence Livermore National Laboratory; *R Alonso-Mori*, *T Kroll*, *D Nordlund*, *T Weng*, *D Sokaras*, SLAC National Accelerator Laboratory

In a world of ever increasing population and diminishing resources, the need for abundant and inexpensive energy remains critical. [1] Despite the problems associated with radioactive contamination/disposal and nuclear proliferation, electricity generated by nuclear power remains immensely important, [2] providing for 20% of the electrical grid of the USA and 50% or more for several European nations. [3-6] Uranium Dioxide (UO₂) is by far the widely used nuclear fuel for the generation of electricity. [7] Thus, a fundamental understanding of the electronic structure of UO₂ is crucial, if only to provide the best theoretical models for its disposal and storage. [7, 8]

Using High Energy Resolution Fluorescence Detection (HERFD) in a Resonant Inelastic Scattering (RIXS) experiment and electric dipole selection rules, the U 5f_{5/2} and U 5f_{7/2} Unoccupied Densities of States (UDOS) were determined. Significant changes were observed in going from UF₄ (localized, 2 5f electrons) to UCd₁₁ (localized, 3 5f electrons), consistent with the predictions of the Intermediate Coupling Model. The results for UO₂ were experimentally confirmed by direct comparison with the Bremsstrahlung Isochromat Spectroscopy for Uranium Dioxide.

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11:20am **AC+LS+MI-MoM-10 Optimizing the Magnetic Performance of Tetragonal $\text{ReFe}_{12-x}\text{M}_x$ Phases by First Principles Computational Simulations**, *Heike Christine Herper, O Vekilova, P Thunström, O Eriksson*, Uppsala University, Sweden

The increase of environmentally friendly energy production is coupled to an increasing demand for new magnetic materials. Especially, new Rare earth (Re) lean permanent magnets are highly sought after as possible replacement for high-performance magnets based on Nd-Fe-B and Dy to limit costs and supply risk. In this context the tetragonal 1:12 phase (TmMn_{12}) which contains 35% less Re than commercial Nd-Fe-B magnets are rediscovered. To stabilize this phase with light Re and Fe instead of Mn a nonmagnetic phase stabilizing element is needed but this degrades the magnetic performance.

To identify new 1:12 phases being suitable for permanent magnet applications materials design based on computational simulations has become an important tool. Here we focus on $\text{ReFe}_{12-x}\text{M}_x$ with Re = Y, Ce, Nd, Sm and M = Ti and V. We use state of the art density functional theory methods (VASP; full potential LMTO (RSPt)). The phase stability and the magnetic properties were calculated depending on the M concentration. Aiming to reduce the Re amount we monitor the performance depending on the Nd/Y ratio.

The key quantities are the magnetocrystalline anisotropy (MAE) and the magnetization. To capture the correct magnetic behavior, it is crucial to describe the localization of the 4f electron properly for each Re. While for Sm-based systems the spin-polarized core approximation is sufficient to describe the localized 4f electrons, it fails for Nd, e.g. the low temperature MAE of $\text{NdFe}_{11}\text{Ti}$ would be uniaxial instead of conic. Using a DFT+U approach with $U = 5$ eV, $J = 1.1$ eV for $\text{NdFe}_{11}\text{Ti}$ reproduces the experimentally observed behavior. Ce is special since the uniaxial MAE of $\text{CeFe}_{11}\text{Ti}$ is obtained independent from the treatment of the 4f electron. However, an analysis of the hybridization function analogue to [1] shows that a spin polarized core approximation is more appropriate for Ce-based 1:12 phases. For a deeper insight additional studies are carried out to examine the crystal field splitting.

With SmFe_{11}V system a new phase was found leading to an increase of the magnetization by 17% compared to the commonly used concentrations of V. In view of the MAE a replacement of Nd by Y turned out to be preferable over a reduction of Ti. MAE values of 1.3 MJ/m^3 ($(\text{NdY})\text{Fe}_{11}\text{Ti}$) and 1.7 MJ/m^3 (SmFe_{11}V) are predicted [2]. The latter could already be verified in recent experiments [2].

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11:40am **AC+LS+MI-MoM-11 Optical Excitation Effect on Magnetodielectric and Photodielectric Properties of Rare Earth doped $\text{ZnO}:\text{Na}$ Nanoparticles**, *W Jadwisieniczak, Mohammed Bsate, F Inbanathan*, Ohio University; *R Martinez*, University of Puerto Rico; *H Huhtinen*, University of Turku, Finland; *R Palai*, University of Puerto Rico

There have been ongoing efforts in developing rare earth (RE) ions doped semiconductors responsive to optical and magnetic stimuli for developing multifunctional devices. ZnO is considered as a promising semiconductor with wide range of applications in optoelectronics and spintronics due to its optical properties (i.e. direct band gap, high electron mobility, high thermal stability, strong absorption of UV), and at the same time being an attractive host for RE doping resulting in enhanced spin polarization in $\text{ZnO}:\text{RE}$ matrix [1]. In this project, undoped and RE ions (Er and Yb) doped and co-doped $\text{ZnO}:\text{Na}$ nanoparticles were studied with an aim to understand recently reported magnetodielectric and photodielectric effects stimulated by magnetic field and UV excitation stimuli [2]. After synthesizing well-defined Er and Yb-co-doped $\text{ZnO}:\text{Na}$ by sol-gel route, evaluation of structural, optical, magnetic and electrical characteristics of

synthesized nanoparticles was performed. Structure, morphology, and composition of the samples were analyzed by XRD and SEM showing high quality hexagonal crystal structure. The absence of secondary phases was confirmed by Raman spectroscopy and XPS analysis of all elements in $\text{ZnO}:\text{NaErYb}$ compound. Optical properties were investigated by optical reflectance spectroscopy, photoluminescence (PL), PL excitation, and PL kinetics with photons excitation energy corresponding to above and below bandgap energy. PL spectra were investigated under magnetic field of up to 2 Tesla in 7 K – 400 K temperature range. It was observed that PL spectra exhibit broad green-yellow defects emission band without NBE excitonic peak. PLE spectra revealed that both Er^{3+} and Yb^{3+} ions are optically active and involved in complex energy transfer between $\text{ZnO}:\text{Na}$ host and 4f-shell levels of RE^{3+} ions dopants. PL spectra show features related to intra-shell 4f-4f transitions of the Er^{3+} ion (at 522 nm) and Yb^{3+} ion (at 980 nm). It was observed that luminescence decay of the ZnO defect band is unexpectedly long ($>$ tens of 10^{-3} second), strongly affected by RE^{3+} ions doping and depends on the magnetic field strength when excited at 3.814 eV. In the presentation we will attempt to correlate reported magnetodielectric and photodielectric properties of the Er,Yb-co-doped $\text{ZnO}:\text{Na}$ [2] with observed optical characteristics.

References

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Actinides and Rare Earths Focus Topic

Room A215 - Session AC+AS+LS-TuM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: Melissa Denecke, University of Manchester, UK, James G. Tobin, University of Wisconsin-Oshkosh

8:00am AC+AS+LS-TuM-1 Study of the Early Actinide Oxides and Fluorides – Systematics of the Electronic Structure, Thomas Gouder, R Eloirdi, R Caciuffo, European Commission - Joint Research Centre, Germany INVITED Oxidation properties of uranium have a great influence on the stability of nuclear waste. U^{VI} has

a 1000 times higher solubility in water than U^{IV} , and so the dissolution of UO_2 based spent fuel nuclear waste strongly depends on the oxidation state of the surface. Oxygen incorporation into the surface of UO_2 first results in the formation of $U(V)$, found in UO_{2+x} and mixed valent oxides, and then formation of U^{VI} . But despite early reports on the existence of a pure $U(V)$ phase (U_2O_5) there are no spectroscopic data on pure $U(V)$. This may be due to its position between the highly stable UO_2 and UO_3 . Also, apparent mixed surface phases containing U^{IV} , U^V and U^{VI} may result from the strong redox gradient between the oxidizing environment and the reduced bulk, present in most corrosion experiments. Replacing bulk samples by thin films allows avoiding this problem, by confining the reaction to a thin region where final conditions are reached everywhere simultaneously, keeping the system homogeneous. This opened the path for a systematic study of the evolution of the electronic structure of uranium upon oxidation and follow the outer shell configuration from $5f^2$ (U^{IV}), to $5f^1$ (U^V) to $5f^0$ (U^{VI}).

We will present electron spectroscopy (XPS, UPS and BIS) and Electron Energy Loss (ELS) study of U_2O_5 compare results to the neighbouring oxides (UO_2 and UO_3). U_2O_5 has been produced by exposing UO_2 successively to atomic oxygen, leading to UO_3 , and to atomic hydrogen. Films have been deposited on polycrystalline gold foils (inert substrate). During gas exposure the samples were heated to 400°C to ensure fast diffusion and equilibrium conditions.

Determination of the U oxidation states was based on the characteristic U-4f core level satellites, separated from the main lines by 6, 8 and 10 eV for U^{IV} , U^V and U^{VI} , respectively. We managed producing films which showed exclusively a single 8 eV satellite, indicating the presence of pure U^V . The formation of U^V was confirmed by the intensity evolution of the $U5f$ valence emissions. Also the linewidth of the XPS $5f$ line decreases from UO_2 , with the $5f^2$ final state multiplet, to U_2O_5 , with a $5f^0$ final state singlet. The U-5d line also displays a multiplet structure due to interaction with the open $5f$ shell (U^{IV} and U^V). Evolution of the $O2p/O1s$ intensity ratio indicates increasing covalence of the U-O bond in higher oxides.

U oxide spectra will be compared to spectra of ThO_2 . Multiplet splitting and its dependence on the open shell was followed by comparing $5f^2$ (UO_2) and $5f^0$ (ThO_2) systems. Finally XPS/BIS of the valence region will be presented for various oxides (UO_2 , U_2O_5 , UO_3 and ThO_2) and fluorides (UF_4 and ThF_4).

8:40am AC+AS+LS-TuM-3 Broadening of the XPS Spectra of U Oxides, Paul S. Bagus, University of North Texas; C Nelin, Consultant INVITED

It is common to attempt to improve the energy resolution of XPS in order to obtain more information about the electronic structure. However, it may not be possible to improve the resolution because unresolved final states are present. When the energy separations of these states are less than or comparable to the lifetime of the core-hole, it will not be possible to resolve the states and there will only be a broadening, often quite significant, for the observed peak. The unresolved features may arise from closely spaced multiplets for the angular momentum coupling of the open shell electrons and from excitations to higher lying vibrational levels for the final ionic states; the later is especially important when bond distances for the core-ionized states are very different from those for the initial state; see, for example, Ref. [1]. Thus, for example, the $U(5f_{7/2})$ peak of UO_2 has a FWHM of 1.4 eV although the instrumental resolution was 0.3 eV. [2] Similar large FWHM have been observed for U in different oxidation states. [3-4] In order to be able to relate the widths of these broadened features to the chemical and physical interactions in the system, it is necessary to understand the separate contributions of the multiplet splittings and the vibrational excitations. It has been shown that, for $U(IV)$ 4f XPS in UO_2 , the contributions of the multiplet splitting and the vibrational excitations are comparable, each contributing ~0.5 eV to the FWHM. [2] In the present

work, the contributions of these mechanisms are examined for $U(IV)$, $U(V)$, and $U(VI)$ oxidation states. In addition, the broadening is examined for the XPS of different core levels where the relative importance of multiplet and vibrational broadening is different from that for the $U(4f)$ XPS. Furthermore, the importance of temperature for the vibrational broadening is also examined. The theoretical predictions for these different parameters can be validated [4] paving the way to extract chemical information from the measured FWHM. [5] The theoretical framework for these predictions is based on wavefunctions for embedded cluster models of the oxides which allows for a balanced treatment of spin-orbit, angular momentum coupling, and covalent bonding.

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5. P. S. Bagus, E. S. Ilton, and C. J. Nelin, *Catal. Lett.* 148, 1785 (2018).

9:20am AC+AS+LS-TuM-5 Multiscale Characterization of Lanthanide and Actinide Nanoparticles Embedded in Porous Materials, Stefan Minasian, S Alayoglu, S Aloni, Lawrence Berkeley National Laboratory; J Arnold, University of California at Berkeley; E Batista, Los Alamos National Laboratory; A Braun, C Booth, A Herve, Lawrence Berkeley National Laboratory; Y Liu, University of California at Berkeley; L Moreau, Lawrence Berkeley National Laboratory; T Lohrey, J Long, M Straub, S Robin, D Russo, University of California at Berkeley; D Shuh, Lawrence Berkeley National Laboratory; J Su, P Yang, X Zhang, Los Alamos National Laboratory INVITED Decades of synthetic work has shown that desirable physical properties can be obtained by tailoring the size and composition of main-group and transition metal nanoparticles. The origin of these phenomena can be traced to a variety of factors that are intrinsic to nanoparticles, including but not limited to (1) quantization of the electronic states and (2) increasing contributions from nanoparticle surfaces. Despite this progress, very few methods provide the level of synthetic control needed to prepare lanthanide and actinide nanoparticles with well-defined sizes and compositions. Furthermore, many conventional methods of characterization are unable to determine the relative roles of volume and surface chemistry on physical behavior involving the 4f- and 5f-electrons.

We established syntheses for lanthanide and actinide nanoparticles by adapting a conceptual approach employed previously by Fischer and Suh to form d-block transition metal and main-group element nanoparticles in metal organic frameworks (MOFs). Implantation of lanthanide and actinide precursor molecules in covalent organic frameworks (COFs) was achieved by sublimation, followed by decomposition to form nanoparticles via exposure to reactive gases and/or elevated temperatures. A multi-pronged imaging and spectroscopic strategy was developed to fully characterize the complex multi-component materials. The characterization techniques are complementary in that they provide atomic to micron-scale probes, element and bulk-level selectivity, and measurements that are individual and statistically significant (Figure 1). Transmission electron microscopy (TEM) showed that the COF-5 templates limited UO_2 nanoparticle growth to between 1-3 nm, which is similar to the COF-5 pore size (2.7 nm). In addition, small-angle X-ray scattering (SAXS) was used to determine the nanoparticle form factor (for size and polydispersity) in a globally-averaged manner. Scanning transmission X-ray microscopy (STXM) was used to probe micron-scale morphology and to evaluate composition with X-ray absorption spectroscopy at the B, C, and O K-edges. Finally, X-ray absorption fine structure (XAFS) spectroscopy was used to determine composition and structure because it does not require long-range crystallographic order, and because it is capable of probing the nanoparticles selectively despite the substantial background from the organic host. This presentation will also discuss our efforts to show how 4f and 5f-electron behavior changes with variations in size and composition at the nanometer level.

11:00am AC+AS+LS-TuM-10 Multiple Forms of Uranium Hydrides and their Electronic Properties, Ladislav Havela, V Buturlim, E Chitrova, O Koloskova, P Minarik, M Cieslar, M Dopita, L Horak, M Divis, I Turek, Charles University, Prague, Czech Republic; D Legut, VSB-Technical University of Ostrava, Czech Republic; T Gouder, European Commission - Joint Research Centre, Germany

Although the published U-H binary phase diagram contains only the UH_3 phase, a recent progress in sputter deposition synthesis led to the

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discovery of UH_2 , which is with its CaF_2 structure type analogous to e.g. PuH_2 or YH_2 [1]. In addition, a high pressure synthesis yielded several U hyper-hydrides (as UH_3), which are predicted to be a high-temperature superconductors [2]. As both UH_3 (appearing in two structure modifications, α - and β - UH_3) and UH_2 allow alloying with selected transition metals, we have a whole spectrum of U-H hydrides and certain general features can be deduced, which have a serious implications for our understanding of actinides in general.

The striking fact that both UH_3 phases have, despite very different crystal structure, practically identical size of U moments and magnetic ordering temperature $T_C \approx 165$ K, which do not change even in the nanostructured state (grain size several nm) is underlined by the fact that both parameters only weakly depend on substantial alloying with Mo and other d -metals. UH_2 with substantially larger U-U spacing is a ferromagnet, as well, its $T_C \approx 125$ K. Structure of all those forms contains identical building blocks, H atoms inside U tetrahedra of invariable size, which are only set up into different patterns. The U-H bonding seems to be therefore an ingredient, which is more important than the conventional U-U spacing. The nature of the bonds is revealed by ab-initio calculations. One general feature is the U- $6d$ hybridization with the H-1s states, which leads to an electron transfer towards H. However, unlike rare-earth trihydrides, UH_3 remains metallic, UH_2 naturally, too. The $5f$ states largely released from the $5f-6d$ hybridization can therefore develop a strong ferromagnetism despite low U-U spacings. The transfer could be traced even in the real space using the Bader analysis.

The ab-initio techniques, which are successful in capturing the equilibrium volumes and U magnetic moments, are so far less successful in description of photoelectron spectra close to the Fermi level, which indicates importance of electron-electron correlations.

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11:20am **AC+AS+LS-TuM-11 Hafnium L-Edge X-ray Absorption Near Edge Structure Spectra Reveals Crystal Field Splitting**, *David Shuh*, D Caulder, Lawrence Berkeley National Laboratory; *L Davis*, Pacific Northwest National Laboratory; *M Mara*, University of California at Berkeley; *C Booth*, Lawrence Berkeley National Laboratory; *J Darab*, *J Icenhower*, *D Strachan*, Pacific Northwest National Laboratory

One method for the safe disposal of actinides currently under consideration by the U.S. Department of Energy is immobilization of radionuclides in a glass or ceramic wastefrom that will subsequently be stored in a geological repository. To develop successful, stable wasteforms, it is necessary to acquire an understanding of the fundamental chemistry of the actinides (U, Pu, etc.) and neutron absorbers (B, Gd, Hf) that will be incorporated into the glass or ceramic matrix. The X-ray absorption near edge structure (XANES) at the hafnium L_3 and L_1 absorption edges has been investigated to elucidate the local structure of Hf in wastefrom glasses that are currently being considered as candidates for the immobilization of radionuclides. During our investigations of the structure of Hf, a neutron absorber and potential Pu(IV) surrogate, we noted an unusual feature at the white line maximum at the L_3 absorption edge: The examination of a variety of Hf model compounds demonstrates that the second derivative of the Hf L_3 XANES displays structure characteristic of crystal field splitting of the empty d -manifold. The peralkaline glasses studied exhibit L_3 XANES spectra typical of Hf in an octahedral crystal field. The L_1 XANES data corroborate these results, as the L_1 spectra of the glasses also resemble that of an octahedral Hf siloxane model compound, distinct from spectra of other standards measured.

11:40am **AC+AS+LS-TuM-12 Electrical Resistivity in Uranium-based Thin Films**, *Evgeniya Tereshina-Chitrova*, *L Havela*, *M Paukov*, *M Dopita*, *L Horak*, *M Cieslar*, Charles University, Prague, Czech Republic; *Z Soban*, Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic; *T Gouder*, *F Huber*, *A Seibert*, Joint Research Center, European Commission, Germany

Metallic $5f$ materials have a very strong coupling of magnetic moments and electrons mediating electrical conduction. It is caused by strong spin-orbit interaction together with involvement of the $5f$ states in metallic bonding. In this work we investigate the electrical resistivity $\rho(T)$ of various uranium-based thin films using the Van der Pauw method. Thin film samples of U-Mo and their hydrides were prepared by reactive sputter deposition [1]. The basic in-situ diagnostics was performed using a photoelectron

spectroscopy (XPS). The films were further characterized using x-ray diffraction (XRD) methods and Transmission Electron Microscopy (TEM). The $\rho(T)$ of the films studied correspond to known bulk systems of equivalent composition but provide much more variability of concentrations and geometries.

We studied superconductivity in the U-Mo films by measuring low-temperature resistivity down to 0.4 K. The 100 nm-thick $\text{U}_{0.79}\text{Mo}_{0.21}$ film shows a transition to the superconducting state at 0.55 K. The transition is wide and extends to 0.4 K. The upper critical field for the thin U-Mo film is ~ 1 T, i.e. much lower than for the bulk U-Mo obtained by splat cooling [2].

The hydrides of the U-Mo films had to be prepared using a cooled substrate (≈ 177 K). The study of the $(\text{UH}_3)_{0.74}\text{Mo}_{0.26}$ of estimated thickness 210 nm showed that it is a ferromagnet with the Curie temperature of ≈ 165 K, i.e. equivalent to bulk UH_3 , which underlines the general insensitivity of U hydrides to structure modifications. Overall temperature dependence is very weak and the absolute value of 2 m Ω cm, estimated from the nominal thickness, is very high for a metallic system.

The net negative resistivity slope in the U-Mo films and hydrides can be attributed to the randomness on atomic scale, yielding very strong scattering of electrons and weak localization. In the hydrides it is supported also by random anisotropy, randomizing local directions of U moments.

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[1] Gouder, R. Eloirdi, F. Wastin, E. Colineau, J. Rebizant, D. Kolberg, F. Huber, Phys.Rev. B **70**, 235108 (2004).

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Actinides and Rare Earths Focus Topic

Room A215 - Session AC+AS+LS-TuA

Forensics, Science and Processing for Nuclear Energy

Moderators: Paul S. Bagus, University of North Texas, Tomasz Durakiewicz, National Science Foundation, David Geeson, AWE

2:20pm **AC+AS+LS-TuA-1 Helium Implantation Studies in Metals and Ceramics for Nuclear Energy Applications, Microstructure and Properties, Peter Hosemann, M Baloach, S Stevenson, A Scott, University of California, Berkeley; Y Yang, Lawrence Berkeley Lab, University of California, Berkeley**

INVITED

Helium damage in materials is a concern for fission and fusion materials. The development of Helium bubbles in a solid can lead to fundamental property changes ranging from embrittlement to surface blistering. Especially shallow ion beam implantation is of interest to the fusion community since the surface degradation of materials is one of the main materials degradation mechanism. This work features a rapid Helium implantation and screening method based on nanometer precise helium implantation using the helium ion beam microscope (HIM). This tool allows multiple doses in the same grain with subsequent rapid materials examination. We evaluate single and polycrystalline SiC, W, Cu, and Ti in this work and find interesting channelling phenomena which have been fit to modelling results from the literature. Further we evaluate mechanical and microstructural property changes using TEM, nanoindentation, AFM and micropillar compression testing on these alloys.

3:00pm **AC+AS+LS-TuA-3 Origin of Element Selectivity during Solvent Extraction of Rare Earths: Studies of Model Interfaces using Synchrotron Radiation, M Miller, Y Liang, H Li, M Chu, S Yoo, Northwestern University; W Bu, University of Chicago; M Olvera de la Cruz, Pulak Dutta, Northwestern University**

INVITED

Solvent extraction, commonly used to remove lanthanides from aqueous solutions, is known to preferentially extract heavier lanthanides. To understand the underlying nanoscale mechanisms, we studied a model system: extractant monolayers floating on an aqueous solution containing lanthanide ions. X-ray fluorescence near Total Reflection (XFNTR) was used to detect interfacial cations, using synchrotron radiation at the ChemMatCARS facility, Advanced Photon Source.

We found that the interfacial density of adsorbed cations increases very sharply as the solution concentration is increased, reminiscent of a first-order phase transition. The threshold concentration is an order of magnitude lower for erbium ($Z=68$) compared to neodymium ($Z=60$). When the solution contains both ions equally, only erbium is found at the extractant interface, and the bulk erbium concentration must be decreased by one order of magnitude relative to neodymium before both species appear equally at the interface.

These results indicate that element selectivity during liquid-liquid extraction occurs at the extractant-laden interface. Electrostatic effects arising from the dielectric mismatch, ionic correlations, and the sizes of the cations can be used to theoretically model the observed behaviors.

4:20pm **AC+AS+LS-TuA-7 Analysis of Aged of Uranium Particles via X-ray Xpctromicroscopy, Andrew Duffin, J Ward, Pacific Northwest National Laboratory**

INVITED

Uranyl fluoride (UO_2F_2) particles are a common by-product when uranium hexafluoride (UF_6), a volatile form of uranium used in industry, is released into air. Uranyl fluoride particles continue to react in the environment, eventually moving towards uranium oxide. Understanding the chemical changes uranyl fluoride takes is important as the chemical state affects how this contaminant is transported in the environment. We employed scanning transmission X-ray microscopy (STXM) to map the chemical changes that occur in single particles of uranyl fluoride, aged under controlled conditions. We have shown that ligand K-edge X-ray absorption spectroscopy can fingerprint uranium chemical species at the nm spatial scale and we have used this specificity to gain insight into the transformation of uranyl fluoride to uranium oxide.

5:00pm **AC+AS+LS-TuA-9 Heat Transfer and Phase Stability of Early Actinides and Actinide Compounds, Dominik Legut, L Kyvala, U Wdowik, G Jaglo, P Piekarz, Technical University of Ostrava, Ostrava, Czechia; L Havela, Charles University, Prague, Czechia**

INVITED

Actinides and especially their carbides as prospective nuclear fuel materials for the generation IV reactors were investigated using the density
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functional theory. We demonstrate that their electronic, magnetic, elastic, and thermal properties can be at present well described if the spin-orbit interaction and partial delocalization 5f electrons is properly included in the computational approaches. One can well reproduce not only basic electronic structure but also elastic constants, phonon dispersions, and their density of states, provided by XPS, UPS, BIS, and inelastic neutron scattering data [1-4]. The localization of the 5f electrons could be captured using a moderate value of the on-site Coulomb interaction parameter. The case studies include a realistic description of the ground-state properties of elemental metals as Th, U and their monocarbides ThC and UC. The realistic description of the electronic structure and lattice dynamics (phonons) explains much higher thermal expansion and heat capacity in pure actinides (as Th) comparing with respective actinide monocarbides. The modelling also gives an insight up to which temperature the heat transport depends on lattice vibrations and where the electron transport starts to dominate. We can identify the vibration modes influencing the heat transport most. Carbides are compared with actinide oxides, where the major role is played by optical phonon branches [3]. The phase stability and elastic properties have been explored in a cascade of uranium hydrides [5], for which the requirement to reproduce the ferromagnetic moments gives an important feedback for the choice of on-site Coulomb U and Hund's exchange J.

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5:40pm **AC+AS+LS-TuA-11 Reactivity of Potential TRISO Fuel Barrier Layers (SiC and ZrN) with H₂O Probed with Ambient Pressure Photoelectron Spectroscopy, Jeff Terry, M Warren, Illinois Institute of Technology; R Addou, G Herman, Oregon State University**

While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, another potential use for the TRISO fuels is as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with PES has been that it has historically been a technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H₂O at temperatures up to 500 C using an ambient pressure photoemission system. We see no oxidation of the SiC layer by water at temperatures up to 350 C. Above 350 C, the SiC begins to oxidize with the formation of SiO₂. In contrast, ZrN reacts at a pressure of 1 mbar of H₂O at room temperature. As the temperature increases, the ZrN layer is completely converted to ZrO₂. In the TRISO fuel, the barrier layer is surrounded by pyrolytic carbon. We model the protective ability of the outer carbon layer by making multilayers SiC/C and ZrN/C and measuring these under the same conditions. We find that a 2 nm carbon layer prevents the underlying barrier layers from reacting with water.

Applied Surface Science Division

Room A211 - Session AS+BI+CA+LS-TuA

Beyond Traditional Surface Analysis

Moderators: Michaelen Pacholski, The Dow Chemical Company, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **AS+BI+CA+LS-TuA-1 Nanotechnology as a Driver for Going Beyond Traditional Surface Analysis, Olivier Renault, CEA-LETI, France** **INVITED**
In the last 10 years, the progress of analytical methods has been more and more strongly connected to the pressing needs from materials and processing developments in the nanoelectronics industry. The field of materials analysis is now expanding as more and more complementary

information are needed to tailor new materials for particular applications. Time-consuming techniques in the past (e.g. ARPES) are now accessible with increasing throughput, whereas the reliability of others, such as depth profiling, is improving. Finally, techniques like HAXPES implemented in the past only at synchrotron facilities, are now entering into laboratories.

In this talk I will illustrate by a series of examples in the field of device technology this evolution of surface analysis getting beyond traditional methods, driven by technological developments.

3:00pm AS+BI+CA+LS-TuA-3 Core Levels Sub-shell Photo-ionization Cross-sections of Au, Ag, Cu in the Hard X-ray Photon Energy Range of 7-26 keV, Germán Rafael Castro, J Rubio Zuazo, Spanish CRG BM25-Spline Beamline at the ESRF, France

Hard X-ray Photo-electron spectroscopy (HAXPES)^[1] has been developed in the last 10-15 years as a unique tool for retrieving accurate non-destructive^[2] compositional and electronic bulk property of materials in the tens of nano-meters depth-scale with nano-meter resolution. Furthermore, the ability to tune the excitation energy in the hard X-ray regime enables tuning the sampling depth, i.e. depth profile analysis, but also enables the discrimination between bulk and surface effects, especially if combined with variable incident and exit angle.

However, an important drawback is the lack of knowledge of the photo-ionization cross-section at the HAXPES photon energy and in special for now accessible deeper core levels. Recently theoretical data has been reported^[6] concerning the photo-ionization cross sections and parameters of the photo-electron angular distribution for atomic subshells but for binding energies lower than 1.5 keV of all elements with $1 \leq Z \leq 100$ in the photon energy range 1.5–10 keV. Unfortunately, these calculations do not contain information for deep orbitals accessible in HAXPES, even more there are scarce experimental results reported for both depth core levels and hard x-ray excitation energies.^[3,4]

In the present work we will show the experimentally obtained relative sub-shell photo-ionization cross sections for 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d core levels of gold (Au), 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d core levels of silver (Ag) and 1s, 2s, 2p, 3s, 3p, 3d core levels of Cooper (Cu) in the X-ray photon energy range of 7–26 keV. In the case of Au, cross sections have been corrected with experimental obtained angular anisotropy parameter. A comparison with theoretical sub-shell photo-ionization cross sections, and angular anisotropy photo-ionization parameters^[5,6] will be also presented.

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3:20pm AS+BI+CA+LS-TuA-4 Interfacial Photochemistry of Pyruvic Acid in Atmospheric Chemistry, Yanjie Shen, Y Fu, Pacific Northwest National Laboratory; X Yao, Ocean University of China; Z Zhu, Pacific Northwest National Laboratory; X Yu, Earth and Biological Sciences Directorate

Presentation Summary:

This presentation will show our latest results of pyruvic acid photochemical aging in dry and liquid surface analysis using time-of-flight secondary ion mass spectrometry.

Abstract

Pyruvic acid is widespread in fogs, aerosols, and clouds. The sunlight driven reaction pathways of pyruvic acid in the air-liquid interface are more elusive compared to its well-known gas and bulk phase chemistry in the atmosphere. We investigated photochemical aging products from pyruvic acid after different UV photolysis times up to 8 hours in dry and liquid samples using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Both ToF-SIMS spectral and spectral principal component analysis (PCA) were used to study the surface photochemical aging products among various photochemical aging samples. A number of aging products were observed in dry samples indicating the importance of interfacial reactions¹;

however, the dry sample analysis cannot fully represent the air-liquid interfacial chemistry of pyruvic acid. Therefore, we used our unique liquid surface molecular imaging approach enabled by the SALVI microfluidic reactor to study the air-liquid interface. The *in situ* liquid SIMS observations show photochemical products of pyruvic acid at the air-liquid interface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(\text{H}_2\text{O})_n\text{H}^+$, $(\text{H}_2\text{O})_n\text{OH}^-$) with submicrometer spatial resolution. In addition, SIMS three-dimensional chemical mapping provides visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant as illustrated in the chemical spatial mapping with increased photolysis time. Our study of the pyruvic acid aqueous surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosols (SOAs) in atmospheric chemistry.

Key Words: pyruvic acid, photochemical, dry SIMS, liquid SIMS, air-liquid interface, oligomer, water cluster, SOA.

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4:20pm AS+BI+CA+LS-TuA-7 Nanoscale Tomographic Mapping the Liquid-Solid Interface with Cryo-APT, Daniel Perea, D Schreiber, J Evans, J Ryan, Pacific Northwest National Laboratory

INVITED

The liquid-solid interface plays an essential role in many phenomena encountered in biological, chemical, and physical processes relevant to both fundamental and applied science. However, study of the liquid/solid interface at the nanoscale is challenging as liquids are generally incompatible with many analytical techniques that require high to ultrahigh vacuum conditions. One strategy to probe the liquid-solid interface is to cryogenically freeze the liquid into solid form to preserve local ionic chemistry gradients and surface composition within a solid structure, making it more amenable to vacuum-based analyses such as Atom Probe Tomography (APT). However, the regular application of APT to hydrated materials is lacking due to challenges in preparing the necessary nanoscale needle-shaped specimens using a FIB-SEM and the subsequent environmentally-protected transfer of the frozen specimens to the APT instrument for analysis. In this presentation, I will discuss the development of a FIB-based site-specific liftout and attachment scheme of cryogenically cooled specimens involving a combination of redeposition and overcoating of organic and organometallic molecules. A modified commercially-available specimen suitcase shuttle device and an environmental transfer hub vacuum chamber at PNNL is used to facilitate environmentally-protected specimen transfer between the cryo FIB and the APT tool, allowing for the first time, APT analysis of a water/solid interface in 3D to reveal the complex nanoscale water-filled porous network of corroded glass. Application of this unique specimen preparation approach to biological specimens will also be discussed.

5:00pm AS+BI+CA+LS-TuA-9 Characterization of Electronic Materials using Low Energy Inverse Photoemission Spectroscopy, Benjamin Schmidt, J Newman, J Mann, K Artyushkova, L Swartz, Physical Electronics; M Terashima, T Miyayama, ULVAC-PHI Inc., Japan

The development of complex electronic materials in areas such as batteries, solar cells, and flexible display panels require a detailed knowledge of the electronic band structure in order to achieve desired performance. A few of the material properties of interest are electron affinity, work function, ionization potential, and bandgap. Photoemission spectroscopic techniques such as Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Photoemission Spectroscopy (IPES) have traditionally been used to measure these values.

Organic electronic materials are growing in popularity due to lower costs of production and the ability to create interesting mechanical structures. However, they are susceptible to chemical damage with prolonged exposure to high-energy electron beams during analyses, which can affect the measured properties.

Low Energy Inverse Photoemission Spectroscopy (LEIPS) is a variant of IPES but uses an incident electron beam at lower energy than traditional IPES (< 5 eV vs. ~10 eV, respectively), making it less damaging for organic materials. In this talk, the operating principles of LEIPS will be discussed. Several material system examples will be shown, including films of C60 and copper phthalocyanine (CuPc).

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5:20pm **AS+BI+CA+LS-TuA-10 Deconvolution of Atom Probe Tomography on Nanomaterials for Renewable Energy**, *Margaret Fitzgerald*, *M Dzara*, *D Diercks*, Colorado School of Mines; *N Leick*, *S Christensen*, National Renewable Energy Laboratory; *T Gennett*, *S Pylypenko*, Colorado School of Mines

Technologies for hydrogen-based economy rely heavily on advancements in development of nano-structured materials. Nano-materials used in applications for energy conversion, storage and production have unique, desirable properties because of their intricate chemistries and morphologies, however this makes them difficult to characterize using traditional techniques. Of specific interest is elucidation of the surface properties and identification of differences between surface and bulk composition. This work features Atom Probe Tomography (APT) paired with other techniques that enable multi-scale characterization in 2D and 3D as a promising approach to create a more complete picture of the complexities of nano-structured materials.

APT is an incredibly powerful tool that has been used to render sub-nanometer-resolution, 3D reconstructions of metallic and, more recently, ceramic samples to enhance the understanding of local composition variations, such as around grain-boundaries and precipitates. This presentation outlines the procedures and considerations for expansion of APT towards analysis of nano-structured materials used for catalysis and hydrogen storage. Challenges related to both APT specimen preparation, APT analysis, and data reconstructions will be discussed. Specific considerations that will be addressed include sample pre-screening for mass spectrometry peak overlap, substrate and encapsulation material selection based on field evaporation compatibility, and prevention of sample damage for air- and beam-sensitive materials. In order to produce accurate 3D reconstructions of the APT data for these samples, initial assessment of a two-dimensional morphology of these materials is made using scanning transmission electron microscopy (STEM) and elemental distributions are acquired with energy dispersive x-ray spectroscopy (EDS). Surface chemistry of the sample is determined using X-ray Photoelectron Spectroscopy (XPS) in order to correlate surface chemistry between APT data and quantified XPS chemical ratios. This talk will provide evidence of cross-correlation across multiple techniques and integration of 2D and 3D data to provide a pathway for understanding these complex materials beyond traditional capabilities.

5:40pm **AS+BI+CA+LS-TuA-11 Mass Spectrometric Investigation of Ion Solvation in Liquids, a Comparison of *in situ* Liquid SIMS to Regular ESI-MS**, *Yanyan Zhang*, Institute of Chemistry, Chinese Academy of Sciences, China; *D Baer*, *Z Zhu*, Pacific Northwest National Laboratory

Ion solvation plays very important roles in many important biological and environmental processes. Mass spectrometry (MS)-based methods have been used to investigate this topic with molecular insights. To study ion solvation, ionization processes should be as soft as possible in order to retain solvation structures. An *in situ* liquid secondary ion MS (SIMS) approach developed in our group has been recently utilized in investigations of Li ion solvation in nonaqueous solution, and it detected a series of solvated Li ions.^[1] As traditionally SIMS has long been recognized as a hard ionization process with strong damage occurring at the sputtering interface, it is very interesting to study further how soft *in situ* liquid SIMS can be. In this work, we used halide ion hydration as a model system to compare the ionization performance of the *in situ* liquid SIMS approach with regular electrospray ionization MS (ESI-MS). Results show that, although ESI has been recognized as a soft ionization method, nearly no solvated halide ions were detected by regular ESI-MS analysis, and only strong signals of salt ion clusters were seen. As a comparison, in liquid SIMS spectra, a series of obvious hydrated halide ion compositions could be observed.^[2] Our findings demonstrated that the *in situ* liquid SIMS approach is surprisingly soft, and it is expected to have very broad applications on investigation of various weak interactions and many other interesting chemical processes (e.g., the initial nucleation of nanoparticle formation) in liquid environment.

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6:00pm **AS+BI+CA+LS-TuA-12 Characterizing the Thickness and Physical Properties of Nearly Ideal Zirconium Oxide Surfaces Using Ellipsometry, ESCA, Profilometry and FIB**, *Edward Gillman*, Naval Nuclear Laboratory

Zirconium alloys are used in nuclear reactor cores due to their small neutron scattering cross-section and corrosion resistance. Corrosion of zirconium alloys results in the formation of a protective oxide layer that the corrosion species must travel through in order to continue the corrosion process. This oxide prevents further oxidation of the metal, slowing down the reaction rate. Characterizing this important oxide film on a metal is difficult. A number of analytical techniques are used to better understand the properties and growth of this oxide film. To insure that reliable information is reported, the thickness and physical properties of zirconium oxide deposited on a single-crystal silicon wafer by magnetron sputtering has been investigated. Data obtained from Electron Spectroscopy for Chemical Analysis (ESCA), profilometry, ellipsometry and Focused Ion Beam (FIB) experiments are all self-consistent with each other. This validates the utility of these measurements for the characterization of the oxide observed on metallic surfaces.

Applied Surface Science Division Room A211 - Session AS+CA+LS-WeA

Operando Characterization Techniques for In situ Surface Analysis of Energy Devices

Moderator: Svitlana Pylypenko, Colorado School of Mines

2:20pm AS+CA+LS-WeA-1 Probing the Electronic Structure of Electrocatalysts and the Formation of Reaction Intermediates, *Kelsey Stoerzinger*, Oregon State University **INVITED**

Electrocatalysts are important constituents in numerous energy conversion and storage processes. Reactants adsorb onto the electrocatalyst surface, where the interplay of electronic states results in a lower activation barrier for the transfer of electronic and ionic species in the reaction pathway to product formation. Rational design of electrocatalysts with greater activity for higher efficiency devices requires an understanding of the material's electronic structure in situ, as well as the reaction intermediates involved.

Many surface science techniques, such as X-ray photoelectron spectroscopy (XPS), collect information from inherently surface-sensitive low-energy processes, requiring operation in ultrahigh vacuum. This constraint is lifted for ambient pressure XPS, which can probe the surface in equilibrium with the gas phase at pressures up to ~a few Torr, or with thin liquid layers using a higher incident photon energy. This presentation will discuss the insights obtained with this technique regarding the electronic structure of oxide electrocatalysts in an oxidizing or humid environment, as well as the reaction intermediates of relevance to electrocatalysis.¹ I will then extend the technique to probe electrocatalysts *in operando*,² driving current through a thin layer of liquid electrolyte and employing a tender X-ray source.

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3:00pm AS+CA+LS-WeA-3 Surface Characterization of Battery Electrode/Electrolyte Materials Using XPS and ToF-SIMS, *Elisa Harrison, S Peczonczyk, S Simko*, Ford Motor Company; *K Wujcik*, Blue Current; *A Sharafi*, A Drews, Ford Motor Company

With a drive to develop hybrid electric and electric vehicles for improving fuel economy and lowering emissions, research of battery materials becomes necessary to increase the performance and durability of automotive batteries. Therefore, significant improvements in the energy capacity, stability, and safety of automotive batteries must be achieved. For the last two decades, traditional methods to characterize battery materials and interfaces have focused on the mechanical and electrochemical properties of the battery. There has been less emphasis on understanding chemical properties of the surface of the electrode and the chemistry that occurs at the electrode/electrolyte interface. Moving forward to develop new battery systems, gaining an understanding of the surface chemistry of battery materials is critical to improving performance.

The objective of this work is to highlight the need for surface analytical techniques and methodologies to fully characterize and improve battery materials. In this work, the surface chemistry of electrodes and electrolytes were analyzed using both X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These are powerful tools to identify slight changes to the surface chemistry of battery materials with respect to factors such as electrode and electrolyte formulation, cycling conditions, air exposure, contamination, and sample replication.

3:20pm AS+CA+LS-WeA-4 In Operando Molecular Imaging of Microbes as an Electrode, *Xiao-Ying Yu*, Pacific Northwest National Laboratory

Metal reducing bacteria, such as *Shewanella* and *Geobacter*, has attracted attention in recent years particularly for the potential as Genome Encoded Materials. They also can function as electrodes in microbial fuel cells (MFCs). Despite the surging interest and applications of various imaging tools to understand the microbial populations, little has been explored in

the *in vivo* study of MFCs using novel *in operando* electrochemical spectroscopy. We have invented a System for Analysis at the Liquid Vacuum Interface (SALVI) microfluidic cell that is suitable for culturing bacterial biofilms for *in vivo* molecular imaging. We have also illustrated that the electrochemical version of SALVI or the E-cell is viable for *in operando* study of the electrode-electrolyte interface. We have cultured *Shewanella* and *Geobacter sulfurreducens* biofilms in SALVI and published several papers recently. In this presentation, I will show most recent *in operando* molecular imaging results using E-cell and *in situ* liquid SIMS to investigate electron transport using *Shewanella* as a model MFC electrode.

4:20pm AS+CA+LS-WeA-7 Operando-XPS Investigation of Low-Volatile Liquids and Their Interfaces using Lab-Based Instruments, *Sefik Suzer*, Bilkent University, Turkey **INVITED**

X-Ray based Operando Investigations have traditionally been carried out in Synchrotron facilities, due to demanding instrumentation and expertise.^{1,2} However, although sporadic, several important lab-based XPS studies have also been reported.³ Emergence of Ionic Liquids with several promising properties, including their low volatility, has rekindled the use of XPS, especially for Operando types of measurements.⁴ Our initial investigations had also concentrated on ionic-liquids and their interfaces under **dc** and **ac** electrical bias, and extended to monitoring electrochemical reactions.^{5,6} Recently, we have been investigating other low-volatile liquids and their drops on various substrates to tap into the Electrowetting phenomena.^{7,8} The common theme in all of our studies is the use of bias dependent shifts in the positions of the core-levels as reflection of the electrical potentials, recorded in a totally non-invasive and chemically resolved fashion. We use the magnitude and the frequency dependence of such potentials to extract pertinent information related to chemical and/or electrochemical properties of the materials and their interfaces. Several examples using ionic liquids, liquid poly-ethylene-glycol (PEG) and their mixtures will be presented and discussed.

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5:00pm AS+CA+LS-WeA-9 Decoupling Surface and Interface Evolution in Polymer Electrolyte Membrane Systems Through In Situ X-Ray Photoelectron Spectroscopy, *Michael Dzara*^{1,2}, Colorado School of Mines; *K Artyushkova*, Physical Electronics; *H Eskandari*, *K Karan*, University of Calgary, Canada; *K Neyerlin*, National Renewable Energy Laboratory; *S Pylypenko*, Colorado School of Mines

Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) enables surface sensitive study of gas-solid interfaces. The fundamental knowledge obtained from such measurements provides unparalleled insight into the physicochemical processes that drive electrocatalytic devices.¹ Studies featuring AP-XPS span a broad range of materials and reactions, with many focused on thin films or other well-defined materials. In such studies, there are often clear changes in the material upon transition from ultra-high vacuum to *in situ* conditions, or there are well-defined catalyst species that participate in the relevant process.

In this work, the differing evolution of the many interfaces in polymer electrolyte membrane (PEM) electrodes in the presence of water vapor is studied through detailed analysis of AP-XP spectra. The complexity of analyzing these interfaces arises from the presence of both catalyst and

¹ ASSD Student Award Finalist

² National Student Award Finalist

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ionomer species in PEM electrodes, and the subtlety of the changes induced in AP-XPS spectra by interactions between the catalyst, ionomer, and gas. Adsorption of a gaseous reactant species onto a catalyst's surface results in a weak interaction and a small chemical shift in the adsorbent species, while ionomer may undergo re-orientation or degradation upon exposure to reactants, also altering the spectra. Therefore, spectral subtraction and highly-constrained curve fitting are applied to enable reliable identification of catalyst adsorbing sites and adsorption/desorption trends,² and ionomer changes in the presence of water vapor. Interactions between platinum-group metal-based catalysts and ionomer films with water vapor are first studied independently, and then simultaneously at the electrode scale. Such an approach allows changes in the electrode-water interface to be decoupled and assigned to either catalyst adsorption behavior, or ionomer response. This work lays the foundation for future study of different classes of electrocatalysts at the electrode scale, and *in operando* AP-XPS studies of electrocatalytic processes.

(1) Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H. Investigation of Solid/Vapor Interfaces Using Ambient Pressure X-Ray Photoelectron Spectroscopy. *Chem. Soc. Rev.* **2013**, *42*, 5833–5857.

(2) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas – Solid Interface with In Situ Spectroscopy: The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C* **2019**, *123* (14), 9074–9086.

5:20pm **AS+CA+LS-WeA-10 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of Semiconductor Nanowire Device Surfaces**, *Yen-Po Liu, Y Liu, S Mousavi, L Sodergren, F Lindelöw, S Lehmann, K Dick Thelander, E Lind, R Timm, A Mikkelsen*, Lund University, Sweden

III-V semiconductor nanowires (NWs) show considerable promise as components in efficient and fast electronics as well as for quantum computing. In particular, the surfaces of the NWs play a significant role in their function due to the large surface to bulk ratio. Further, as the incorporation and activation of the nanowires in a device can affect their structure, it is relevant to study the surface structure and its influence on electronic properties in devices and during operation.

We use atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) to study InAs and GaAs NWs in planar device configurations. [1-3] We use atomic hydrogen cleaning at 400°C to obtain well-defined surfaces that can be scanned with STM while the complete device is still fully functioning. [2] We study both NWs grown directly in a planar configuration as well as wires harvested from a growth substrate and placed on top of predefined metal contacts with ~100nm precision using a micro/nano probe. In our new <10K closed-cycle STM we can identify the individual device NWs simultaneously as we can apply voltages across the devices using four additional electrical contacts in the low temperature STM. We initially investigate NW device geometric structure and morphology with high precision. Then we continue to perform atomic resolution and low temperature STS mapping on top of the NWs surfaces to investigate electronic structure and potential quantum confinement effects as well as the influence of defects. These measurements can be performed while the device is actively operating by external biases applied and the I(V) characteristic across the NW is obtained. The STM tip can also act as a role as a local gate for Scanning Gate Microscopy (SGM) [4], which we can precisely locate on the operating single NWs device for SGM on the areas as STM is performed.

[1] Persson, O. et al., (2015). *Nano Letters*, *15*(6), pp.3684-3691.

[2] Webb, J. et al., (2017). *Scientific Reports* *7*, 12790

[3] Hjort, M. et al., (2015). *ACS Nano*, *8*(12), pp.12346-12355

[4] Webb J.L. et al., (2014). *Nano Research* *7*, 877

5:40pm **AS+CA+LS-WeA-11 Work-function Estimation and In situ Measurement of Photoemission Spectroscopy of CuFeO₂ under Near Ambient Condition**, *Saumya Banerjee, P Sapkota*, University of Notre Dame; *A Cabrera*, Pontificia Universidad Católica de Chile, Chile; *S Ptasinska*, University of Notre Dame

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H₂O under operational conditions. Therefore,

knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. The work functions of pure and Ga-doped Delafossite p-type CuFeO₂ semiconductor crystals with different thicknesses were measured using near ambient pressure x-ray photoemission spectroscopy (NAP-XPS) in Ar ambient. The values differ with changing thickness as well as Ga doping. The effect of water and CO₂ on the samples was also studied using NAP-XPS to understand the interaction between atmospheric gases and CuFeO₂ which may be helpful for its practical application in solar cells. No significant changes were found in XPS result obtained from CuFeO₂ in water ambient with and without illumination whereas CO₂ induced changes in oxygen XPS peak positions.

6:00pm **AS+CA+LS-WeA-12 In-situ X-ray Photoelectron Spectroscopic Study of III-V Semiconductor/H₂O Interfaces under Light Illumination**, *Pitambar Sapkota, S Ptasinska*, University of Notre Dame

A number of studies on different semiconductor materials that can be used as a photoelectrode in photoelectron-chemical (PEC) cells for solar water splitting is continually growing in material sciences and solar energy communities. III-V based compounds have been the most promising candidates because of their efficient light and carrier management properties in addition to suitable band gap and band edge energies, which properly match the solar spectrum and water redox potentials, respectively. Although most of the highly efficient PEC water splitting cells are based on III-V semiconductor, these photoelectrode materials are unstable under operational conditions. Few studies suggest oxidation leading to corrosion as a major cause of the degradation of these photoelectrodes, but it is still not completely understood and little is known about the role of the oxides formed at the interfaces. Therefore, knowledge of the interfacial reactions in realistic situations and surface dynamics are necessary to advance our understanding of water splitting mechanism, as well as to build a stable and efficient PEC solar water splitting cell. In this study, we used state of the art spectroscopic technique, ambient pressure X-ray photoelectron spectroscopy, to characterize semiconductor (GaAs and GaP) surface and to study chemical reactions occurring at the water interface in presence of secondary light source. Core level photoemission spectra from Ga2p, As3d, P2p, and O1s were collected at different water pressures in presence of secondary light source to identify the newly formed surface species, particularly oxides, and to evaluate the interaction of GaAs and GaP with water under light illumination.

This research is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences under Award Number DE-FC02-04ER15533.

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic Room A124-125 - Session LS+AS+SS-ThM

Operando Methods for Unraveling Fundamental Mechanisms in Devices Towards Renewable Energies

Moderator: Olivier Renault, CEA-University Grenoble Alps, France

8:00am **LS+AS+SS-ThM-1 X-Ray Insight into Fuel Cell Catalysis: Operando Studies of Model Surfaces and Working Devices**, *Jakub Drnec*, *I Martens*, European Synchrotron Radiation Facility, France; *T Fuchs*, University of Kiel, Germany; *T Wiegmann*, European Synchrotron Radiation Facility, Germany; *A Vamvakeros*, Finden Ltd., UK; *R Chattot*, European Synchrotron Radiation Facility, France; *O Magnussen*, University of Kiel, Germany

INVITED

Complete physico-chemical operando characterization of electrochemical devices in whole, or its constituent materials separately, is necessary to guide the development and to improve the performance. High brilliance synchrotron X-ray sources play a crucial role in this respect as they act as a probe with relatively high penetration power and low damage potential. In this contribution the new possibilities of using high energy, high intensity X-rays to probe model fuel cell catalysts and energy conversion devices will be presented.

HESXRD (High Energy Surface X-ray Diffraction) [1] and TDS (Transmission Surface Diffraction) [2] provide ideal tools to study structural changes during reaction conditions on single crystal model electrodes. The main advantage of both techniques is the possibility to follow the structural changes precisely with atomic resolution. While HESXRD is ideally used to determine exact atomic position, the TSD is easier to use and allows studies with high spatial resolution. For example, HESXRD can be used to follow the atomic movement of Pt atoms during electrochemical oxidation and dissolution with very high precision, explaining the different catalyst degradation behaviors and suggesting possible routes to improve its durability [3-4]. The TSD is an excellent tool to study advanced 2D catalysts.

To study fuel cells or batteries as a whole, elastic scattering techniques, such as WAXS and SAXS, can be employed as they can provide important complementary information to more standard X-ray imaging and tomography. The advantage is that the chemical contrast and sensitivity at atomic and nm scales is superior. Coupling these technique with the tomographic reconstruction (XRD-CT and SAXS-CT) is much less common as it requires bright synchrotron sources and advanced instrumentation, but allows 3D imaging of operational devices with unprecedented chemical sensitivity. This can be demonstrated on imaging of standard 5 cm² fuel cells during operation. The change in morphology and atomic arrangement of the catalysts, PEM hydration and water distribution can be followed in one experiment as a function of operating conditions. Furthermore, the fundamental processes leading to the catalyst aging can be assessed with high temporal and spatial resolution. These advanced scattering techniques open a door to holistic investigations of operational devices, which are needed to successfully incorporate new materials at the device level.

[1] J. Gustafson et al., *Science* 343, 758 (2014)

[2] F. Reikowski et al., *J. Phys. Chem. Lett.*, 5, 1067-1071 (2017)

[3] J. Drnec et al, *Electrochim. Acta*, 224 (2017),

[4] Chattot et al., *Nature Materials*, 17(2018)

8:40am **LS+AS+SS-ThM-3 Multi-scale Operando X-ray Tomography of Solid-state Li Battery Electrolytes at Elevated Temperatures and Pressures**, *Natalie Seitzman*, Colorado School of Mines; *J Nelson Weker*, SLAC National Accelerator Laboratory; *M Al-Jassim*, National Renewable Energy Laboratory; *S Pylypenko*, Colorado School of Mines

Solid state Li ion conductors are next-generation battery technologies that reap the capacitive benefits of Li metal anodes while mechanically resisting the Li interface evolution and thus prolonging lifetime. Additionally, they are not flammable, offering greater safety than liquid counterparts. However, interface evolution and Li protrusions are observed in solid state batteries despite the mechanical resistance.^{1,2} There is debate as to whether these protrusions nucleate at the Li anode or within the ceramic electrolyte, and there are several factors that affect these protrusions including electrolyte density, pre-existing defects, anode/electrolyte interfacial contact, and imperfect electronic insulation within the electrolyte.³ Understanding the influence of these variables is greatly

enhanced by directly imaging the interior of the ceramic at multiple scales in conjunction with electrochemical experiments.

This talk addresses the contribution of electrolyte density and defects, interfacial contact, and conductivity to structural changes in β -Li₃PS₄ (LPS) ceramic electrolyte in operating cells via 3D X-ray imaging with sub-micron resolution. Cells of Li, LPS, and a blocking contact are constructed and studied *in operando* at 200 psi and 70°C. Because electrolyte density and initial defects depend on the composition and synthesis of the ceramic conductor, two syntheses of LPS with different particle sizes are compared. Also, pressure is a key parameter in the quality and stability of interfacial contact while temperature affects both the ionic and electronic conductivity of the ceramic.

Synchrotron micro-tomography is combined with synchrotron transmission x-ray microscopy to study the cells with spatial resolution in the hundreds of nanometers and tens of nanometers. Image analysis of these data has identified sites of Li microstructure growth⁴ and now isolates variable-dependent trends such as pressure-dependent void formation in the Li anode. Linking structural changes observed *in operando* to these factors that contribute to Li evolution will guide the design of robust ceramic electrolytes with improved performance and safety.

1. L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, and Y.-M. Chiang, *Adv. Energy Mater.*, 7, 1701003 (2017).

2. E. J. Cheng, A. Sharafi, and J. Sakamoto, *Electrochim. Acta*, 223, 85–91 (2017).

3. F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang, and C. Wang, *Nat. Energy* (2019).

4. N. Seitzman, H. Guthrey, D. B. Sulas, H. A. S. Platt, M. Al-Jassim, and S. Pylypenko, *J. Electrochem. Soc.*, 165, 3732–3737 (2018).

9:00am **LS+AS+SS-ThM-4 Correlating the Atomic and Electronic Structure in the Formation 2DEGs in Complex Oxides**, *Jessica McChesney*, *X Yan*, *F Wrobel*, *H Hong*, *D Fong*, Argonne National Laboratory

Using a multimodal approach, we investigate the interplay of the atomic and electronic structure of the formation of 2-D electron gas (2DEG) in complex oxide systems. Using hybrid molecular beam epitaxy for synthesis and in-situ synchrotron x-ray scattering atomic precision of the growth is obtained. The electronic structure then characterized via a combination of resonant soft x-ray angle-resolved photoemission and core level spectroscopy and compared with transport measurements.

9:20am **LS+AS+SS-ThM-5 Uncover the Mystery of Oxygen Chemistry in Batteries through High-Efficiency mRIXS and Theory**, *Wanli Yang*, Lawrence Berkeley National Laboratory

INVITED

Energy storage through electrochemical devices (batteries) is under pressure to be greatly improved for today's sustainable energy applications, especially the electric vehicles and power grid using renewable energy sources. A battery utilizes transition-metal (TM) oxides as one of the critical electrodes, the positive electrode, which is often the bottleneck of the energy density. In general, the operation of battery cycling is based on reduction and oxidation (Redox) reactions of TMs and a recently proposed oxygen, which involve the changes on the electron occupation numbers in TM-3d and O-2p states, as well as the evolution of the electronic configuration. However, technical challenges are formidable on probing these states directly, especially for the unconventional oxygen redox states.

This presentation will start with a brief introduction of several needs and grand challenges of battery devices related with oxygen states, which is followed by soft X-ray spectroscopic experiments for providing relevant information. The focus of this presentation is on an active debate of the oxygen states in charged electrodes. We will explain the limitations on conventional soft X-ray absorption spectroscopy (sXAS) for characterizing the important oxygen states, then showcases the power of full energy-range mapping of resonant inelastic X-ray scattering (mRIXS) for clarifying the oxygen redox behaviors in batteries.

We show that mRIXS provides the ultimate probe of the intrinsic oxygen redox reactions in the lattice of battery electrodes [1], which is associated with transition-metal configurations [2]. These spectroscopic results could be quantified to decipher the electrochemical capacity [3], providing both the rationality of the device performance and evidences for understanding the fundamental mechanism of electrochemical materials for energy applications. Furthermore, the mRIXS results indicate a universal driving force of the oxygen redox reactions [4], which could be tackled through

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combined studies of mRIXS and theoretical calculations [5]. We show that such a spectroscopic and theoretical collaboration could deliver unprecedented information for both fundamental understanding and practical optimization on grand challenges in developing high-performance battery devices.

[1] Gent et al., *Nat Comm* 8, 2091 (2017)

[2] Xu et al., *Nat Comm* 9, 947 (2018)

[3] Dai et al., *Joule* 3, 518 (2019)

[4] Yang & Devereaux, *J. Power Sources* 389, 188 (2018)

[5] Zhuo et al., *JPLCL* 9, 6378 (2018)

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic Room A124-125 - Session LS+HC+SS-ThM

Frontiers of Time-resolved Techniques for Energy & Catalysis Highlight Session

Moderator: Jessica McChesney, Argonne National Laboratory

11:00am **LS+HC+SS-ThM-10 How to Probe Solid/Liquid Interfaces using Standing-wave Photoemission?**, *Slavomir Nemsak*, Lawrence Berkeley National Laboratory; *H Bluhm*, Fritz Haber Institute, Germany; *C Fadley*, University of California, Davis

A great efforts have been made in the development of *in-situ* and *operando* experimental methods in the last two decades, with ambient pressure photoelectron spectroscopy being one of the most profound examples [1]. In combination with advanced techniques, such as standing wave excitation, an unprecedented depth resolution across operating interfaces can be obtained, providing valuable information on processes governing interfacial behavior.

With the excellent depth selectivity and sensitivity to chemistry and electrostatic gradients, standing wave ambient pressure photoelectron spectroscopy is exploited to probe two different solid/liquid interfaces relevant to energy research, electrochemistry, and atmospheric and environmental science [2,3]. Liquid layers are prepared either by water adsorption in a saturated vapor ambience or using a so-called meniscus method, in which the sample is pulled out of a liquid reservoir leaving a thin liquid film on the sample's surface. The latter experimental configuration allows also for the *operando* electrochemistry [4]. The outlook and future developments of the technique will be also discussed.

[1] D.E. Starr et al., *Chem. Soc. Rev.* **42**, 5833 (2013).

[2] S. Nemšák et al., *Nat. Comm.* **5**, 5441 (2014).

[3] O. Karslıoğlu et al., *Faraday Discuss.* **180**, 35 (2015).

[4] S. Axnanda et al., *Sci. Rep.* **5**, 9788 (2015).

11:20am **LS+HC+SS-ThM-11 In situ Spectroscopy of Synthesis of Next-Generation Cathodes for Batteries**, *Feng Wang*, Brookhaven National Laboratory

There has been considerable interest in developing low-cost, high-energy electrodes for batteries. However, synthesizing materials with the desired phases and properties has proven difficult due to the complexity of the reactions involved in chemical synthesis. Additional challenge comes from the fact that synthesis is often undertaken under conditions and, hence, the process is hard to be predicted by theoretical computations. Probing of synthesis reactions allows for identification of intermediates and determination of thermodynamic/kinetic parameters governing kinetic reaction pathways, thereby enabling synthetic design of materials with desired structure and properties. In this presentation, we will report our recent results from technique development and application to *in situ* probing and synthetic control of local structural ordering and stoichiometry during synthesis of next-generation cathode materials for lithium-ion batteries. Findings from this study, along with its implication to designing viable cathodes for practical use in batteries, will be discussed.

ACKNOWLEDGMENT. This work was supported by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office, Contract No. DE-SC0012704.

11:40am **LS+HC+SS-ThM-12 Structural Heterogeneity and Dynamics of 2D Materials Studied by Full-field X-ray Diffraction Microscopy and Ultrafast Surface X-ray Diffraction**, *Haidan Wen*, Argonne National Laboratory
INVITED

Transition metal dichalcogenides (TMD) at the two-dimensional (2D) limit have sparked great interests in both fundamental physics and devices applications. Surfaces and interfaces play an important role in the most common setting, i.e., a monolayer crystal on a substrate, for studying 2D phenomena and device applications. However, the structural characterization with atomic accuracy in this form has been a challenge because the crystal size is usually small and transmission electron microscopy is difficult to apply. In this talk, we show microscopic insights of structural properties can be obtained in the space or time domain using newly developed multimodal full-field x-ray imaging and ultrafast surface x-ray scattering. In the first example, we demonstrate full-field x-ray diffraction imaging of a monolayer 2D material at the Advanced Photon Source. The structural variation across a TMD monolayer or heterostructure is spatially correlated with the electronic properties characterized by the *in-situ* photoluminescence measurements. The correlation reveals mesoscale structure-property relationship in TMDs. In the second example, we report the first femtosecond surface X-ray diffraction using the free-electron laser at Linac Coherent Light Source to quantify the ultrafast structural dynamics of monolayer WSe₂ crystals supported on a substrate. We found the absorbed optical photon energy is preferably coupled to the in-plane lattice vibrations within one picosecond whereas the out-of-plane lattice vibration amplitude remains unchanged during the first ten picoseconds. The observed nonequilibrium anisotropic structural dynamics agrees with first-principles modeling in both real and momentum space, marking the distinct structural dynamics of monolayer crystals from their bulk counterparts.

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Emerging Methods with New Coherent Light Sources

Moderator: Germán Rafael Castro, Spanich CRG BM25-SpLine Beamline at the ESRF

4:00pm **LS+AC+HC+SS-ThA-6 Resolving X-ray Based Spectroscopies in the Sub-nanometer Regime: Enabling Atomic Scale Insights into CO Adsorption on Thin Film Surfaces, Heath Kersell, B Eren, C Wu,** Lawrence Berkeley National Laboratory; *I Waluyo, A Hunt,* Brookhaven National Laboratory; *G Somorjai, M Salmeron,* Lawrence Berkeley National Laboratory

X-ray based spectroscopies routinely yield detailed elemental, chemical, electronic, and magnetic information on a wide array of physically and chemically diverse samples. However, the spatial resolution of these techniques is limited, frequently by the size of the X-ray spot. Conversely, certain structural probes readily resolve sample topography with nanoscale- or even atomic-resolution. The union of X-ray based spectroscopies with nanoscale structural probes enables the acquisition of spectroscopic information at unprecedented length scales. We will demonstrate the combination of X-ray based spectroscopies (e.g. X-ray photoelectron spectroscopy {XPS}) with scanning tunneling microscopy (STM), and its application to CO adsorption and oxidation on model catalyst surfaces.

CO adsorption on various crystal surfaces plays a critical role in numerous chemical processes, including for example CO oxidation, the water gas shift reaction, and methanol oxidation. CO oxidation is widely used as a prototype reaction for studies of fundamental catalytic phenomena and is crucial in exhaust gas processing for automobiles and stationary CO sources. Recent studies demonstrate strikingly high activity for CO oxidation by Pt nanoparticles supported on cobalt oxide (CoO_x) as compared to either of the constituent materials. In the further development of these catalysts, a deeper understanding of the active sites and their deactivation is crucial. Using a combination of *operando* high pressure STM (HP-STM) and ambient pressure XPS (AP-XPS), we investigate the nature of catalytically active sites for CO oxidation on CoO-Pt catalysts at CO and O₂ pressures up to 130 mTorr. Our experiments showed very different behavior for the lattice oxygen (O_{lat}...) in CoO between fully oxidized and sub-stoichiometric cobalt oxides. At RT, fully oxidized Co films adsorbed CO in the form of stable surface carbonate species, poisoning the reaction until reaching higher temperatures where they decomposed. On sub-stoichiometric CoO_x the CO oxidation reaction proceeded at RT, reducing the oxide to the metallic state. We discuss these results in the context of structural transformations observed *in-situ*- via HP-STM, and demonstrate the behavior of surface sites under relevant gas mixtures.

As an outlook, we will discuss various *in-situ* multi-modal approaches which enhance the spatial resolution of X-ray based spectroscopies toward the nano- or even single atom scales. Such a union of spectroscopic and structural probes will provide a more accurate and complete picture of operating devices in the near future.

4:20pm **LS+AC+HC+SS-ThA-7 Imaging with XPS: Advanced Characterization for Advanced Materials and Devices, Tatyana Bendikova, H Kaslasi, E Sanders, E Joselevich, D Cahen,** Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS), as a surface sensitive technique with the sensitivity down to single atomic layer, provides unique information about elemental composition and chemical and electronic states of elements in the material. For some research goals, however, this knowledge is not sufficient as it does not provide the entire information required for a comprehensive characterization of the investigated system. In addition to the basic functions of standard XPS, our instrument is equipped with advanced capabilities such as XPS imaging, which is particularly valuable in the analysis of patterned or inhomogeneous specimens. Following image acquisition, specific areas can thus be chosen and small spot XP spectra acquired at sites of particular interest. This information is useful in the characterization of patterned surfaces or inhomogeneous samples with surface features between several to hundreds of micrometers.

We present here two examples where XPS imaging is successfully used providing crucial information for understanding the investigated systems.

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In the first example bunches of GaN nanowires (50-100 nm each) randomly spread on Si substrate were monitored with XPS imaging. Then, focusing on the GaN bunch itself, small area XP spectra were obtained. This allowed to get precise top surface composition of the bunches significantly consuming the analysis time.

In the second example variations in chemical composition though dimensions of the $\text{Cs}_x\text{Ma}_{1-x}\text{PbBr}_3$ (MA = CH_3NH_3)

crystal were studied using XPS imaging. Significant changes in the N/Cs ratio, depending on the distance from the crystal edge/center, were observed on the top surface. Variations in the N/Cs and Pb/(N+Cs) ratios were also observed along the crystal bulk.

4:40pm **LS+AC+HC+SS-ThA-8 Time-Resolved Photoemission with Free-Electron Lasers, Kai Rossnagel,** CAU Kiel / DESY, Germany **INVITED**

Photoelectron spectroscopy is an essential analytical tool for learning about the properties and workings of quantum materials and functional interfaces, in which electrons are the main actors. In practice, photoelectron spectroscopy is a toolbox comprising three major techniques, where the momentum selectivity and atomic-site specificity of valence and core electron emissions are exploited, respectively: Angle-resolved photoelectron spectroscopy (ARPES) is the most powerful imaging technique for the energy-momentum space of the active electrons near the Fermi level, while x-ray photoelectron spectroscopy (XPS) is a universal tool for chemical analysis and x-ray photoelectron diffraction (XPD) an established surface structural probe. A dream is to combine all three techniques into a single experiment, make it complete by adding spin and femtosecond time resolution, and thus be able to shoot femtostroboscopic movies of intertwined electronic, magnetic, chemical, and geometric structure dynamics and gain previously unachievable, direct "in operando" insight into dynamic structure-function relationships of materials and interfaces. Here, we aim to realize this dream by combining the soft x-ray SASE3 free-electron-laser (FEL) beam at the European XFEL with the most advanced photoelectron detection scheme currently available: the time-of-flight momentum microscope with efficient 3D energy-momentum detection and 2D spin filtering. The status of the project and of FEL-based photoelectron spectroscopy in general will be presented.

5:20pm **LS+AC+HC+SS-ThA-10 Ultrafast Magnetization Dynamics on the Nanoscale, Bastian Pfau,** Max Born Institute, Germany **INVITED**

Nanometer-scale spin configurations are attractive as information entities for spintronic applications to realize nonvolatile and energy-efficient data storage and processing. In recent years, this research field was stimulated by the discovery that the spin can be effectively manipulated using ultra-short light pulses exciting suitably designed magnetic materials. Scattering and imaging methods based on sources delivering ultra-short x-ray pulses are particularly successful in revealing the magnetization dynamics on the relevant time and length scales. I will present research results on optically induced demagnetization and formation of nanoscale magnetic domains and skyrmions in Co-based multilayer systems. We investigate these processes using small-angle scattering signals or direct imaging via holography with femtosecond x-ray pulses delivered by free-electron laser sources. These methods additionally allow to address the influence of lateral nanoscale inhomogeneity and to work with laterally localized or structured excitation.

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic Room A210 - Session LS+AC+NS-ThA

Photon Science for Imaging Materials from the Meso- to the Nanoscale

Moderator: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy

2:20pm **LS+AC+NS-ThA-1 Triplet Dynamics in Photovoltaic Materials Measured with Time Resolved X-Ray Spectroscopies, R Costantini,** University of Trieste; *R Faber,* Technical University of Denmark; *A Cossaro, A Verdini, L Floreano,* CNR - Istituto Officine Materiali; *C Haettig,* Ruhr-University Bochum, Germany; *A Morgante,* University of Trieste, Italy; *S Coriani,* Technical University of Denmark; *Martina Dell'Angela,* CNR - Istituto Officine Materiali, Italy **INVITED**

Singlet exciton fission (SF) is a multiexciton generation process in organic molecules, where an optically excited singlet exciton is converted into two triplet excitons. The exploitation of this mechanism has been shown

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capable of boosting the efficiency of solar energy conversion, and it has been proposed as a mean for exceeding the Shockley-Queisser limit of efficiency of solar cells. In the last decade, several studies have investigated different chromophores to identify the ones suitable to produce high yield SF and long living triplets. Such studies spanned from the fundamental to the applicative approach, also dealing with the optimization of the interfaces with the other materials in the device in order to achieve an overall increased efficiency of the charge transport. In particular, the study of the dynamics of the triplet states, when formed and transported across all the interfaces, is crucial for modelling the charge transport properties in a working device. Here we present a new experimental approach to measure the triplet dynamics at the picosecond timescale, that uses the advantage of chemical sensitivity with respect to conventional optical techniques, thus offering the possibility of tracking the dynamics of the triplet states across different materials. We exploit the chemical selectivity of X-ray absorption spectroscopy (XAS) in an optical pump/X-ray probe experiment at a pump-probe setup that we developed at the Elettra synchrotron and with the support of novel implemented calculation methodologies. We studied triplet dynamics in pentacene thin films (the prototypical singlet fission material) with lifetime of about 300ps.

3:00pm **LS+AC+NS-ThA-3 Synchrotron X-Ray Tomography to Understand Structure and Physical Transformations in Solid State Batteries, Kelsy Hatzell, M Dixit, Vanderbilt University** **INVITED**

The increasing demand for portable electronics, stationary storage, and electric vehicles is driving innovation in high-energy density batteries. Solid electrolytes that are strong enough to impede lithium dendrite growth may enable energy dense lithium metal anodes. Currently, the power densities of all-solid state batteries is limited because of ineffective ion transport and chemical and physical decomposition at solid|solid interfaces. The nature of ionic transport at intrinsic and extrinsic interfaces is important for mitigating chemical and structural instabilities. Extrinsic interface instabilities are responsible for high interfacial resistances. In order to displace liquid electrolytes, new materials and engineering strategies need to be developed to negate these degradation pathways. New insight into the governing physics that occurs at these interfaces are critical for developing engineering strategies for the next generation of energy dense batteries [1,2]. However, buried solid|solid interfaces are notoriously difficult to observe with traditional bench-top and lab-scale experiments. In this talk I discuss opportunities for tracking phenomena and mechanisms in all solid state batteries *in-situ* using advanced synchrotron techniques. Synchrotron techniques that combine reciprocal and real space techniques are best equipped to track relevant phenomena with adequate spatial and temporal resolutions.

Thursday Evening Poster Sessions, October 24, 2019

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic

Room Union Station AB - Session LS-ThP

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Poster Session

LS-ThP-1 Bringing Synchrotron Capabilities to a Local X-ray Facility: the Lyncean Compact Light Source, Benjamin Hornberger, J Kasahara, M Gifford, Lyncean Technologies, Inc.

Synchrotron facilities around the globe are the supercomputers of X-ray science, contributing to many areas of materials science. There are more than fifty synchrotrons worldwide serving more than ten thousand researchers. The light generated by these sources is typically high flux, monochromatic, energy-tunable and, in some cases, coherent. They serve a myriad of applications and thousands of researchers, but they come at a high construction and operating cost and generally require government support. Furthermore, these facilities are oversubscribed by an ever-expanding user base.

Consequently, there is an increasing need for small, locally owned and operated, multi-discipline, X-ray facilities that provide the flux and energy tunability that is required for experiments such as diffraction, spectroscopy, or dynamic imaging.

The Lyncean Compact Light Source (CLS) is the cornerstone of this kind of modern, multi-discipline, and high-performance laboratory. The Lyncean CLS is the first commercially developed X-ray source in its class; it was specifically created to deliver a true home laboratory alternative to many experiments performed today at the large synchrotrons. X-rays are produced in the CLS via inverse Compton scattering through the interaction of low energy electrons (25 to 45 MeV) in a miniature storage ring with a micrometer-period, high powered laser pulse (laser-undulator). Tunable, monochromatic, and high flux undulator synchrotron radiation is generated in the CLS "mini-synchrotron" as a result of the high repetition rate (~65MHz) of this interaction. Characteristics of the CLS X-ray beam are similar to those of a bending magnet synchrotron in terms of flux and coherence, and as such, similar synchrotron quality applications can be performed: imaging/tomography, diffraction, scattering, and spectroscopy.

In this presentation we describe the technology behind the Lyncean Compact Light Source and provide examples of the various measurements that are possible with the system. The broad range of applications served by the Lyncean Compact Light Source illustrates our vision for a new kind of multi-discipline X-ray facility.

LS-ThP-2 Observing Formation of Detonation Nanodiamond at Sub-Microsecond Timescales at the Advanced Photon Source, Trevor Willey, J Hammons, M Bagge-Hansen, M Nielsen, L Lauderbach, R Hodgkin, W Shaw, W Bassett, E Stavrou, S Bastea, L Fried, L Leininger, Lawrence Livermore National Laboratory

Over the past few years, we have developed a capability to perform small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) during high explosive detonation. We can acquire a SAXS or WAXS pattern from individual 80 ps x-ray pulses, which at the APS in 24-bunch mode, arrive every 153.4 ns. We can acquire up to eight frames, from sequential pulses, per event. Various morphologies of carbon condensates appear during detonation, dependent upon the pressure and temperature attained, and liquid, diamond, and graphitic phases can be inferred from the SAXS and WAXS. Transmission electron microscopy of recovered nanoparticles confirms these phases. Nanoparticles, including detonation nanodiamond, form over a few hundred nanoseconds. Here, we present an overview of the capability and a few select results.

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