Monday Morning, November 6, 2023

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA1+AS+LS+NS+SS+VT-MoM

Modeling, AI, and Machine Learning Applied to Interfaces

Moderators: J. Trey Diulus, NIST, **Kateryna Artyushkova**, Physical Electronics

8:20am **CA1+AS+LS+NS+SS+VT-MoM-1 Topological and Geometric Descriptors of Complex Self-assembly at Liquid Interfaces***, **Aurora Clark**,* University of Utah **INVITED**

Amphiphilic surfactants at liquid/liquid interfaces can form complex self-assembled architectures that underpin interfacial reactivity and transport. This has been demonstrated by surface sensitive spectroscopies and molecular dynamics simulations within the domain of liquid/liquid extraction, which involves solute adsorption, complexation reactions and transport across the phase boundary. Being able to quantify surfactant organization is a significant challenge because the distribution of species is broad and highly heterogeneous. As such, in the analysis of molecular dynamics data, there is significant need to develop descriptors that allow statistical analysis of surface organization. This work presents recent developments based upon geometric measure theory and topological data analysis that are able to identify surface assemblies and their dynamic evolution. These methods are revealing intricate dependencies of surface assembly upon solution composition and the impact this has upon transport mechanisms.

References:

Kumar, N.; Clark, A. E. Persistent Homology Descriptors for Surface Image Analysis in Complex Chemical Systems, *Journal of Chemical Theory and Computation*, **2023**, *In Press.* ChemArXiv: https://doi.org/10.26434/chemrxiv-2023-vwrxj

Zarayeneh, N.; Kumar, N.; Kalyanaraman, A.; Clark, A. E. Dynamic Community Detection Decouples Hierarchical Timescale Behavior of Complex Chemical Systems, *Journal of Chemical Theory and Computation*, **2022**, *18,* 7043 – 7051. **DOI:**10.1021/acs.jctc.2c00454

Kumar, N.; Clark, A. E. Unexpected Inverse Correlations and Cooperativity in Ion-pair Phase Transfer, *Chemical Science,***2021**, *12,* 13930-13939.**DOI**: 10.1039/D1SC04004A

Liu, Z.; Clark, A. E. An Octanol Hinge Opens the Door to Water Transport,*Chemical Science*, **2021**, *12*, 2294 – 2303. **DOI**: 10.1039/D0SC04782A.

Alvarado, E.; Liu, Z.; Servis, M. J.; Krishnamoorthy, B.; Clark, A. E. A Geometric Measure Theory Approach to Identify Complex Structural Features on Soft Matter Surfaces, *Journal of Chemical Theory and Computation*, **2020**, *16,* 4579-4587.**DOI:** 10.1021/acs.jctc.0c00260,

9:00am **CA1+AS+LS+NS+SS+VT-MoM-3 Machine Learning and the Future of Surface Analysis***, J. Jones, M. Caouette,* ***Kateryna Artyushkova,*** Physical Electronics **INVITED**

Machine learning can potentially revolutionize all areas of material science and engineering, including surface analysis, by automating and accelerating data acquisition and analysis. The application of machine learning and artificial intelligence (ML/AI) has been actively evaluated and used in scanning probe microscopic methods[1-2], while the application of AI in surface analysis methods such as AES, XPS, and TOF-SIMS is in the very early stages.[3] In this talk, I will discuss the potential areas where AI will change how we do surface analysis.

With recent instrumental development yielding improvements in sensitivity and throughput, the data acquisition stage of surface analysis has become much faster than the experimental planning or data analysis stages, which bothrequire significant operator time and human-based decisions. Using a spectrometer still requires a human operator with instrument-specific knowledge and experience in how to operate it. More importantly, the operator uses physical and chemical knowledge to decide on what specific data must be obtained and from which locations on the sample, depending on the analytical question being addressed by the experiment. Experienced scientists make these decisions effortlessly during the experiment, but it is a very challenging task for ML algorithms that rely on training data with explicit descriptors.

Initial AI applications to analytical surface analysis will focus on instrument optimization and performance inherent in the analytical workflow. Unlike acquisition parameters based on chemical or material science requiring broader context, tuning, and standardizing the spectrometer can be easily cast into numerical terms processable by AI.

Machine learning can also be utilized as a live data integrity monitoring service during acquisition, recognizing and rejecting "bad data". Systemically erroneous data caused by charging or sample damage are often not discovered until the experiment is complete and the data analyzed by a human. Catching it automatically during the experiment saves valuable operator and instrument time. Here, I will present an initial application wherein ML was used to identify whether ToF-SIMS spectra were correctly calibrated.

1.S.V.Kalinin, *ACS Nano*2021, 15, 8, 12604–12627.

2. S.V.Kalinin, arXiv:2304.02048

3. G Drera *et al* 2020 *Mach. Learn.: Sci. Technol.*1 015008

9:40am **CA1+AS+LS+NS+SS+VT-MoM-5 Complexity to Clarity: Detecting, Identifying and Analyzing Complex Materials with Machine Learning***,* ***Paul Pigram****, W. Gardner, S. Bamford, D. Winkler, B. Muir, R. Sun, S. Wong,* La Trobe University, Australia

Our ability to analyze and understand any physical, chemical, or biological material relies on accurately determining its structure, characteristics, and responses. Contemporary analytical techniques produce large volumes of data from pointwise sample analyses (one dimensional (1D) data), maps of compositional distributions (two dimensional (2D) data), and depth profiles showing composition throughout a sample volume (three dimensional (3D) data).

Correlative analyses linking data from the same sample, obtained by different analytical techniques or different operating parameters, are becoming critically important. Different analytical perspectives on the same sample enhance the richness and depth of the conclusions that can be drawn from it.

Recent advances in analytical science have resulted in an overwhelming avalanche of data – the “big data” problem. In our lab a single time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiment might collect a map (512 x 512 pixels) with 2000 mass spectral peaks of significant intensity in 2 – 10 minutes. These half a billion data points all have differing degrees of significance.

In many cases, only a small number of peaks, 10 – 200, may be judged to be characteristic of a specific sample, and the rest of the data may be discarded. However, there are significant risks that such analyses are biased, and may miss important but subtle trends.

There is a very substantial knowledge gap in our ability to find and make full use of the information and knowledge contained in large scale data sets. This gap is driving rapid international progress in the application of materials informatics and machine learning to analytical surface science.

This presentation will highlight our work on applying artificial neural network approaches to analysis of a variety of very large hyperspectral data sets to better understand complex materials and their interactions.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+NS+SS+VT-MoA

Environmental and Energy Interfaces

Moderators: Musahid Ahmed, LBNL, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

1:40pm **CA+AS+LS+NS+SS+VT-MoA-1 In situ Spectroscopies of Interfacial Reactions and Processes in Batteries***, **Feng Wang**,* Argonne National Laboratory **INVITED**

The performance and lifetime of batteries, whether they are traditional lithium-ion, solid-state, or other types, strongly depend on the effectiveness and stability of electrochemical interfaces within the devices. To design battery materials and interfaces with desired functionality, it is crucial to have a mechanistic understanding of the interfacial reactions and processes occurring during battery operation. This necessitates developing advanced techniques capable of characterizing local structures and capturing *non-equilibrium* dynamics at electrochemical interfaces, with the relevant spatial, time resolution and chemical sensitivity, both to light elements (H, Li, O) and heavy ones. Herein, we present the development and application of *in situ* spectroscopies specialized for probing interfacial reaction and processes in lithium-ion and solid-state batteries. With specific examples from our recent studies, we will show how to correlate the structure and function of electrochemical interfaces through *in situ* spectroscopy characterization, thereby gaining insights into the design and processing of battery materials, electrolytes and other components. Towards the end of this talk, we will discuss emerging opportunities in data-driven experimentation, analysis, and modeling for closed-loop battery development to accelerate the transition from lab discovery to commercial deployment.

2:20pm **CA+AS+LS+NS+SS+VT-MoA-3 Novel Strategies for the Characterization of the Next-Generation Energy Storage Materials by ToF-SIMS: From an in-Situ Exploration to an Operando Measurement***, **Tanguy Terlier**, Q. Ai, S. Sidhik, A. Mohite, J. Lou,* Rice University **INVITED**

Recently, advances in instrumentation and sample preparation have permitted a rapid development for characterizing a wide range of applications such as next-generation energy storage materials. Developing new materials is one of the most crucial topics for emerging technologies. However, the complexity of these materials in their structures makes them particularly challenging for numerous characterization and analytical techniques. Exploring chemical composition and the potential chemical reactions such as degradation, diffusion, or doping is crucial to understand advanced materials and to transfer the new technologies to the industry. Among the most suitable characterization tool, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a very sensitive surface analytical technique providing detailed elemental and molecular information about the surface, thin layers, interfaces, and full three-dimensional analysis of the samples.

Thanks to the advances in ToF-SIMS characterization, understanding of the chemical composition and the different components in the complex structures, permit a deeper exploration and a better knowledge in the next-generation energy storage materials such as batteries, perovskites, and 2D materials.

Firstly, we will focus on the characterization of batteries. Initially, we will discuss the sample preparation and our specific setup for transferring the specimens from the inert atmosphere in the glovebox to the ultra-high vacuum chamber of our instrument. We will illustrate the possibility to study the reversibility of the chemical composition between pristine, charged, and discharged batteries using surface mass spectrometry by ToF-SIMS in operando conditions. Then we will compare three methods of cross-sectioning used to identify the interfacial species in a composite cathode.

Secondly, we will show a study of an in-depth distribution of the 3D/2D heterostructures for perovskite solar cells where we have been able to identify individually the 3D and 2D heterostructures along with the depth of the film. Then, we will illustrate the characterization of interdiffusion in quasi-2D perovskite light-emitting diodes as a function of the organic ligand layer inserted into the perovskite crystals.

Finally, we will demonstrate how the retrospective analysis using ToF-SIMS can be very powerful and useful for exploring any single feature in 2D materials. Typically, ToF-SIMS acquisition is recording a full mass range spectrum per pixel (or voxel), which permits to isolate and to decorrelate specific regions of interest for resolving interfaces, diffusion, and doping in thin 2D structures. We will present how to treat a 3D volume image of a multilayer perovskite device for extracting useful information.

3:00pm **CA+AS+LS+NS+SS+VT-MoA-5 Advanced In-Situ and Ex-Situ S/TEM Probing of Interfacial Process in Rechargeable Batteries***, **Chongmin Wang**,* Pacific Northwest National Laboratory

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced battery performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of interfacial process in energy storage materials. Both ex-situ and In-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed. Most importantly, integration of different analytical tools appear to be the key for capturing complementary information.

3:20pm **CA+AS+LS+NS+SS+VT-MoA-6 Investigating sp^2 and sp^3 Carbon Ratios by XPS: A Study of the D-Parameter and a New Second Plasmon Loss (2PL) Parameter***, **Alvaro Lizarbe**, G. Major, B. Clark,* Brigham Young University*; D. Morgan,* Cardiff University, UK*; M. Linford,* Brigham Young University

The D-parameter provides a useful estimate of the ratio of the sp^2 and sp^3 carbon in a sample. It is the energy difference between the maximum and minimum of the derivative of the C KLL Auger peak. The D-parameter can be an important analytical resource for diamond samples, as the quality of diamond depends on the sp^3 to sp^2 carbon ratio and any lattice impurities. For example, the highly sought after type 2a diamonds, which are colorless and free from impurities, consist almost entirely of sp^3 carbon. According to the universal curve for XPS, electrons with different kinetic energies have different mean free paths. Thus, electrons with different kinetic energies sample materials at different depths. In the case of carbon, the KLL Auger peak comes shallower in a material compared to the C 1s signal, which is a result of electrons with much higher kinetic energies. That is, a limitation of the D-parameter is that it is based on the C KLL Auger peak, found at around 1220 eV, while it is often related to the C 1s peak located at approximately 284.8 eV. Thus, the D-parameter is much more sensitive to adventitious carbon contamination. In an effort to derive a parameter that will be more representative of the amounts of sp^2 and sp^3 carbon in a material, we have examined the plasmon loss peaks of the zero-loss C 1s peak of direct current chemical vapor deposition (DC-CVD) diamonds, carbon nanotubes, and graphitic materials such as HOPG. By analyzing the second plasmon loss signal of the C 1s narrow scan, we obtain a new parameter for analyzing carbonaceous materials: the 2PL parameter. The 2PL parameter is the difference in energy between the second plasmon loss signal and the C 1s peak. We compare the traditional D-parameter with the 2PL parameter for various materials. They correlate quite well. We have also investigated various mathematical methods of deriving the 2PL parameter, including via a weighted average of the second plasmon loss and C 1s signals. Ultimately, because the 2PL parameter involves signals that are closer to the C 1s photoemission binding energy, we believe it may be more representative of the full chemistry of carbonaceous materials.

4:00pm **CA+AS+LS+NS+SS+VT-MoA-8 Solid-Liquid Interfaces for Energy-efficient Chemical Separation of Critical Minerals and CO_2 Conversion***, **Manh-Thuong Nguyen**, V. Prabhakaran, D. Heldebrant, G. Johnson,* Pacific Northwest National Laboratory **INVITED**

Chemical separations consume around 15% of the energy used by industry today. It is thus critical to develop energy- and material-efficient approaches for large-scale separations. In the first part of this presentation, I will illustrate how we employ modified 2-dimensional materials and solvents to separate critical minerals including rare earth elements. Polar functional groups present at the interface of graphene oxide laminate membranes are demonstrated to improve the selectivity of metal cations separated by both adsorption and sieving. Hydrophobic ionic liquid molecules including 1-ethyl-3-methylimidazolium chloride, when used as a minor solvent component, are shown to increase the energy efficiency of the desolvation of aqueous lanthanide cations in electrochemical separations. In the second part, I will present studies exploring the use of functionalized hexagonal boron nitride (h-BN) membranes to separate CO_2

from multicomponent gas mixtures. Strategies for improving CO_2 separation selectivity and efficiency, such as chemical functionalization and engineering the dimensions of interlayer transport channels, will be discussed. Finally, I will present studies on the electrochemical conversion of CO_2 into value added chemical feedstocks such as methanol on membrane-supported catalysts. Insights into the effects of local structure modification and confinement on catalytic processes will be presented.

4:40pm **CA+AS+LS+NS+SS+VT-MoA-10 Buried Interfaces of Ir Photodetector Devices Analyzed with Lab-Based Xps/Haxpes***, **Roman Charvier**, M. Juhel,* STMicroelectronics, France*; O. Renault,* Univ. Grenoble-Alpes, CEA, Leti, France*; A. Valery, D. Guiheux, L. Mohgouk Zouknak,* STMicroelectronics, France*; B. Domenichini,* ICB UMR 6303 CNRS-Université de Bourgogne, France

The development of new IR photodetectors should respond to challenges in order to reach best performances. A major objective is to understand critical interfaces that play an important role in the final device properties. This work addresses to chemical analysis of molybdenum oxide (MoO_{3-x}) used as hole transport material which is deposited between a photosensitive material and top electrode often made of indium-tin oxide (ITO). Such critical interfaces are typically located under 20 to 50 nm under the surface.

In the case of MoO_{3-x}, the stoichiometry is generally controlled by X-ray photoelectron spectroscopy (XPS) which is well-known to obtain chemical data close to the material surface (analysis depth < 10 nm). Two methods can be used to analyse deeper buried layers: (i) the use of hard X-rays to perform Hard X-ray PhotoElectron Spectroscopy (HaXPES) and thus generate photoelectrons having a kinetic energy able to go through several tens of nm; (ii) the etching of the surface by means of an Ar^+ beam (having an energy from 0.5 to 3 keV) in order to remove the superficial layers giving access to the underlying layers. In the former case, the analyzed thickness remains far below 100 nm while in the latter case, the chemistry of the surface atoms are often modified by argon ion beam. It is then necessary to mix the two approaches to allow the chemical analysis of buried interfaces. This analysis way is used here to characterize the stoichiometry of MoO_{3-x} thin films buried under 50 nm of ITO using chromium Kα hard-X-ray from lab-based HaXPES.

5:00pm **CA+AS+LS+NS+SS+VT-MoA-11 Detection and Discrimination of Aquatic Toxins Targeting Voltage Gated Sodium Channels Using Static ToF-SIMS Imaging***, **Jiyoung Son**, K. Engbrecht, J. Mobberley,* PNNL

Neurotoxins from aquatic microorganisms, such as cyanobacteria and algae, have been a public health concern due to their harmful impacts on the nervous systems of animals, including humans. A subset of these neurotoxins, including saxitoxin and brevetoxin, bind to and alter the function of voltage-gated sodium channels, which are essential to generating the cell membrane action potential. Existing detection and categorization methods, such as PCR and antibody-based enzyme-linked immunosorbent assays, are too specific and they require live animals like the mouse bioassay. They also require time-consuming and expensive sample preparation for analysis using LC-MS/MS and HPLC. In this project, we developed a method to detect the activity of the aquatic sodium channel neurotoxins, brevetoxin and saxitoxin, using a cell-based process. We specifically examined the impact of these two neurotoxins on HEK-293 cells, a robust cell line that has been transfected with a voltage-gated sodium channel gene, SCN1A, in order to better study neurotoxins. We cultured a layer of cells onto disinfected silicon chips, exposed the cells to neurotoxins, performed chemical fixation, and then air-dried the chips. We also prepared mock exposed samples where the cells on the silicon chips were not exposed to neurotoxins, but just the solutions each neurotoxin was resuspended in, either a 3mM HCl solution (mock saxitoxin) or a 50:50 ACN: water solution (mock brevetoxin). Control samples, which just exposed cells to cell culture media only, gave us a baseline reference. Dried samples were analyzed with mass spectral imaging using time-of-flight secondary ion mass spectrometry (ToF-SIMS). After collecting a series of spectral data, we utilized an in-house MATLAB tool to run principal component analysis (PCA) as previously described (Yu et al., 2020). Our initial statistical analysis of SIMS spectral data using PCA shows a noticeable difference in peak trends between neurotoxin and mock-exposed cells as well as neurotoxin-exposed and control cells. Our approach utilizes chemical imaging to develop a threat-agnostic model system for detecting and classifying neurotoxin activity. The technology and protocols developed from this work could transition to other rapid cellular assays for pathogenic and chemical threats.

Reference

Yu, J., Zhou, Y., Engelhard, M. *et al.In situ* molecular imaging of adsorbed protein films in water indicating hydrophobicity and hydrophilicity. *Sci Rep***10**, 3695 (2020). https://doi.org/10.1038/s41598-020-60428-1

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+LX+MN+SE+SS-TuM

Novel Developments and Applications of Interfacial Analysis

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+AS+LS+LX+MN+SE+SS-TuM-1 Hypervelocity Nanoprojectile Impacts on Graphene, Graphene-Solid/Liquid Interphases: From Mechanisms of Interaction/Ejection to Practical Applications*, Dmitriy Verkhoturov,*** Texas A&M University*; S. Lee,* Mayo Clinic*; M. Eller,* California State University Northridge*; M. Gołuński, S. Hrabar,* Jagiellonian University, Poland*; S. Verkhoturov,* Texas A&M University*; Z. Postawa,* Jagiellonian University, Poland*; A. Kolmakov,* National Institute for Science and Technology (NIST)*; A. Revzin,* Mayo Clinic*; E. Schweikert,* Texas A&M University **INVITED**

Presented here are the experiment and theory on processes accompanying the impacts of C_{60} and Au_{400} projectiles (~1 keV/atom) on graphene/matter interphases. A variety of targets were used: a) free standing graphene, b) molecules and extracellular vesicles (EVs) deposited on free standing graphene, c) interphases graphene-solids/liquids, d) EVs deposited on functionalized monocrystals.

Two custom-built Cluster ToF secondary ion mass spectrometry (SIMS) devices with similar parameters were used. The experiments were run in the event-by-event bombardment/detection mode where the regime of bombardment is super-static[1]. The analyzed surfaces were bombarded at the rate of ~1000 impacts/sec with $1\text{-}6\times10^6$ impacts collected on a surface area of 50-500 µm in diameter. This regime allows acquisition of individual mass spectra for each impact, thus allowing the comparison of experimental data with MD simulations at the level of single projectile impacts. The method allows detection of ejecta in reflection (3D case) and transmission (2D case) directions.

The mechanisms of ejection from 2D and 3D materials (including graphene-solid/liquid interphase) are different. For example, in the case of C_{60} impacts on a molecular layer deposited on graphene (2D case) the mechanism of ejection is described with the "trampoline" model[2]. For the 3D case of graphene-solid/liquid interphase, graphene suppresses the ejection of molecules. The compression of matter in the excitation volume around the impact is not sufficient to destroy the graphene[3].

Our method allows to test individual nano-objects. A biological example is EVs. There were anchored on functionalized Si and graphene substrates, with the EVs labeled with antibodies carrying lanthanide tags (Ab@Ln) for normal hepatic and liver cancer markers. Up to four Ab@Ln tags could be detected simultaneously, enabling analysis of population heterogeneity with single EV resolution and to distinguish between normal and cancer EVs based on surface marker expression. Using co-localization of cancer biomarkers, it is possible to find small subpopulation of EVs originating from cancerous cells potentially allowing for early cancer detection. The sensitivity of the method can be increased several folds via transmission configuration where ejecta are emitted and detected in the forward direction. In this case nano-objects, such as EVs, are anchored on graphene oxide, a 2D material.

[1] S.V. Verkhoturov et al. J. Chem. Phys. 150 (2019)

[2] R.D. Rickman et al. Phys. Rev. Lett. 92, 047601 (2004)

[3] D.S. Verkhoturov et al. Biointerphases 11, 02A324 (2016)

Acknowledgements: NSF Grant CHE-1308312, NIH Grant R01 GM123757-01,

Polish National Science Center 2019/33/B/ST4/01778, PLGrid Infrastructure Grant

8:40am **CA+AS+LS+LX+MN+SE+SS-TuM-3 Applying *in Situ* Bias During TOF-SIMS Analysis to Investigate Ion Migration in Perovskite Devices*, Steven Harvey,*** National Renewable Energy Laboratory*; I. Gould,* University of Colorado, Boulder*; D. Morales, M. McGehee,* University of Colorado Boulder*; A. Palmstrom,* National Renewable Energy Laboratory

Metal Halide Perovskite Photovoltaics have the potential to be a game-changing technology in photovoltaics, with low cost solution processing inherent to the technology and a rapid progress in device efficiency and stability. Understanding ion migration in these materials has lead to improvements in both efficiency and reliability, and further understanding of these phenomena is of great importance.

Time of flight secondary ion mass spectrometry is well suited to provide unique insight for this class of materials, as it can reveal the distribution of both the organic and inorganic components of a device stack (both through the depth as well as laterally with 2-D and 3-D imaging). We will briefly cover our past work on technique development for this class of materials, before presenting new work where an *in situ* electrical bias was placed on a perovskite device while under investigation with TOF-SIMS. This was completed with simple commercial off the shelf components in an ION-TOF TOF-SIMS V instrument and could be easily implemented on other instruments. A device stack of glass / ITO / Me-4PACz / DMA0.1FA0.6Cs0.3Pb(I0.8Br0.2)3 / LiF (1 nm) / C60 (30 nm) / SnOx (15 nm)/Au (20 nm) was used for this study. An electrical bias was applied between the top gold contact and the bottom ITO contact during TOF-SIMS measurements. By applying a +0.75V and -0.75V forward and reverse bias to the device, a driving force for negatively charged halide ions is created to migrate towards the back or front of the device, respectively. The *in-situ* data shows the halide ion migration towards the back ITO contact after the forward bias is applied. The negative bias was then applied and the halide ions migrate back towards the front of the device and return to the original unbiased state. In both cases the formamidinium and lead traces do not show similar migration, showing only the charged species in the device are affected by the bias. The results show a framework that can be used for further study. Potential complications with the analysis of this type of data will be discussed.

9:00am **CA+AS+LS+LX+MN+SE+SS-TuM-4 Oxidation of a Single Fe Nanoparticle at the Nanoscale and Real-Time by Operando Atom Probe*, Sten V. Lambeets,*** Pacific Northwest National Laboratory*; N. Cardwell, I. Onyango,* Washington State University*; T. Visart de Bocarmé,* Université libre de Bruxelles, Belgium*; J. McEwen,* Washington State University*; D. Perea,* Pacific Northwest National Laboratory

Physics governing surface chemical reactions and interfaces involved in heterogeneous catalysts fundamentally depends on the synergistic interactions between reactive gases and specific surface structures. Surface science techniques are continuously evolving to help bridge knowledge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O_2/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP).

APM techniques are capable of imaging the apex of sharp needles with nanometric lateral resolution, which can be seen as model nanoparticles. FIM is used to image such needles with atomic resolution and to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. The resulting FIM image corresponds to a stereographical projection of the apex and allows the identification of the crystal orientations with atomic resolution. Regular APT, from which the OAP derives, relies on the thermally assisted field evaporation of positively charged ions from a needle shaped specimen. In regular use, the APT is performed in an Ultra High Vacuum ($<10^{-11}$ mbar) while the sample is cooled at 50K. The OAP modification consists of performing the atom probe analysis in the presence of reactive gas at 300 K.

Once the FIM characterization is complete the sample is maintained at 300K before starting APT analysis and introducing 1.1×10^{-7}mbar of pure O_2. As soon as the O_2 is introduced, we can measure the surface formation of Fe oxides by monitoring the local concentration of Fe_2O^{n+} ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. We observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation. The combination of the different concentrations allows us to reconstruct the full movie of the surface oxidation in real-time. However, since the measurements are performed in the presence of very strong electric fields (>10 V/nm), it is necessary to discuss the potential influences of it on the system as well.

9:20am **CA+AS+LS+LX+MN+SE+SS-TuM-5 Reporting Interfaces: Unconventional Excitation of Interfaces Enables Exquisite Gas Sensing Toward Our Sustainable Future***, **Radislav Potyrailo**,* GE Research **INVITED**

As our society is developing solutions for more sustainable types of energy, the need for reliable, yet affordable tools for monitoring of emissions of greenhouse and other gases in urban and industrial environments is a substantial undertaking for two main reasons. First, to achieve a desired accuracy, existing gas monitoring solutions in complex backgrounds utilize traditional analytical instruments. While their mathematical design principles provide needed independent response outputs, their hardware design principles do not allow cost-effective ubiquitous implementations. Second, all gas sensors based on interface-driven interactions between gases of interest and sensing materials are single-output devices. By their original design principles from early last century, these sensors operate well only when levels of interfering gases are low. Once levels of interfering gases increase, existing sensors lose their accuracy because of competing interactions between the sensor interface and numerous interfering gases versus a gas of interest.

In this talk, we will present gas sensors that we built following mathematics of traditional analytical instruments but with our own different types of independent variables for detection of multiple gases with enhanced accuracy and stability. These sensors are multivariable gas sensors where independent response outputs are provided by our unconventional methodologies of excitation of interfaces between a sensing material and different ambient gases. We will show that our approach results in a reliable differentiation of one or more analyte gases in complex backgrounds of interfering gases with an individual multivariable gas sensor. This exquisite (i.e., accurate and reliable) gas sensing provides an affordable technical solution for monitoring of emissions of greenhouse and other gases in urban and industrial environments. Such technical solution is mathematically not feasible using conventional single-output sensor designs. We will also show that such multivariable gas sensors have the ability for self-correction for sensor drift. Our approach for the multi-gas detection and drift self-correction should allow implementations of gas sensors in diverse applications that cannot afford weekly, monthly, or quarterly periodic maintenance, typical of traditional analytical instruments.

11:00am **CA+AS+LS+LX+MN+SE+SS-TuM-10 A "Simple" Approach to Combine Electrochemistry and Operando Near Ambient Pressure XPS Studies***, F. Mirabella, **Paul Dietrich**, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant, first-row transition metal-based catalysts, Ni and Fe oxides have shown promising performances as effective and low-cost catalysts of the oxygen evolution reaction (OER) in alkaline media. Notably, their structure evolves under oxygen evolution operating conditions with respect to the as-prepared catalysts but these changes and consequently the active sites have not been identified yet due to the difficulties associated with surface analysis measurement under working conditions (*operando*).

In this presentation, we will demonstrate the enormous potential of laboratory NAP-XPS for investigations of solid-liquid interfaces in electrochemical systems at elevated pressures (≤ 25 mbar), also illustrating the ease of use of this specific setup. We will show a versatile three-electrodes electrochemical setup that allows for operando studies of solid-electrolyte interfaces, i.e., of nickel oxide foils as cathode for OER in alkaline environment as a simple laboratory NAP XPS experiment.

11:40am **CA+AS+LS+LX+MN+SE+SS-TuM-12 Recent Developments in Probing Buried Interfaces Using Standing-Wave Photoelectron Spectroscopy***, **Slavomir Nemsak**,* Lawrence Berkeley Lab

Standing-wave photoelectron spectroscopy of multi-layer structures proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5].These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce novel tools and approaches for standing-wave experiments and I will highlight some of the recent applications [8,9,10].

[1] S. Nemsak et al., *Physical Review B* **93** (24), 245103 (2016).

[2] H. P. Martins et al., *arXiv preprint arXiv:2012.07993.*

[3] S. Nemsak et al., *Nature Communications* **5**, 5441 (2014).

[4] O. Karslioglu et al., *Faraday Discussions* **180**, 35 (2015).

[5] C. Baeumer et al., *Nature Materials* **20**, 674 (2021).

[6] S.-H. Yang et al., *Journal of Applied Physics* **113**, 073513 (2013).

[7] O. Karslioglu et al., *Journal of Electron Spectroscopy and Related Phenomena* **230**, 10 (2019).

[8] M Scardamaglia, et al., *Journal of Electron Spectroscopy and Related Phenomena* **262**, 147281 (2023).

[9] G. Conti et al., *Journal of Micro/Nanopatterning, Materials, and Metrology* **20**, 034603 (2021).

[10] H.P. Martins et al., *Journal of Physics D: Applied Physics* **56**, 464002 (2021).

12:00pm **CA+AS+LS+LX+MN+SE+SS-TuM-13 The Influence of Surface Structure and Electrostatics on Measuring Unoccupied Electronic States via Low Energy Inverse Photoemission Spectroscopy (LEIPS)***, **James Johns**,* Physical Electronics USA

A material's energetic distribution of electronic states near the fermi level is a key physical property for determining how it behaves in electronic, chemical, and optical applications.Photoemission has long been the gold standard for measuring the occupied electronic states below the Fermi level and is one of the most common surface science techniques worldwide.Inverse photoemission (IPES), the related process whereby an electron is absorbed at the surface and a photon is emitted, is similarly a very powerful tool for measuring the unoccupied electronic states. Unfortunately, the intrinsically lower rate for IPES and technical hurdles related to relevant photodetectors has historically necessitated the use of electron sources with sufficient energy to damage all but the most chemically robust surfaces.

The availability of narrow bandpass optical filters at UV photon energies between 3.5 and 6 eV over the past decade have enabled the development and commercialization of Low Energy Inverse Photoemission Spectroscopy (LEIPS)[1,2].Efficient detection of low energy UV photons (lower than traditional IPES at 9-10 eV) enables the use of low energy electrons (below 5 eV) which avoid damaging sensitive materials including organics.This key innovation has revitalized interest in IPES because the technique can now be applied to molecular materials and interfaces relevant to wide range of applications *e.g.* batteries, photovoltaics, organic semiconductors and OLEDs, chemical sensors.Furthermore, optical UV filters also improve the energy resolution, further enhancing the appeal of LEIPS over traditional IPES.

Like any surface science technique, the quality of LEIPS data depends on both the instrumentation and sample preparation. Here, I will discuss the material requirements and limitations for successful LEIPS measurements, several of which differ from more common techniques such as XPS, SPM, or electron microscopy.I will also present LEIPS data from taken at the interface between two metals and explain those results using calculated trajectories of the electron beam.Finally, I will illustrate a key difference between LEIPS, which probes the true unoccupied electronic density of states, and optical methods, such as optical spectroscopy or EELS which measure the joint density of states, by presenting LEIPS spectra of an excitonic 2D material.

[1] Yoshida, H; "Near-ultraviolet inverse photoemission spectroscopy using ultra-low energy electrons" *Chem. Phys. Lett.* **539-540**, 180-185, (2012)

[2] Lida, S.; Terashima, M; Mamiya, K; Chang, H. Y.; Sasaki, S; Ono, A; Kimoto, T; Miyayama, T; "Characterization of cathode-electrolyte interface in all-solid-state batteries using TOF-SIMS, XPS, and UPS/LEIPS" *J. Vac. Sci. & Tech. B*, **39**, 044001, (2021)

Light Sources Science Mini-Symposium
Room C124 - Session LS+AC+LX+MI+TH-ThM

Tender X-ray Science and Time Resolved Studies

Moderators: Alison Pugmire, LANL, **David Shuh**, Lawrence Berkeley National Laboratory, **James G. Tobin**, University of Wisconsin-Oshkosh

8:00am **LS+AC+LX+MI+TH-ThM-1 Developments of High Resolution X-Ray Spectroscopic Tools for Probing Structural Properties of Actinide System from the Metal and Ligand Perspective*, Tonya Vitova,*** Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Germany **INVITED**

High energy resolution X-ray absorption and emission spectroscopic techniques became indispensable methods in actinide and radionuclide research.[1-5] One important motivation is studies concerning the mobilization and retention of long-lived actinides and fission products in geochemical processes relevant for safety studies of a potential deep geological nuclear waste repository.[3-4] In-depth insights into the actinide-ligand binding properties is a main application of these novel experimental techniques too.[6] Development at the ACT experimental station of the CAT-ACT wiggler beamline at the Karlsruhe Institute of Technology (KIT) Light Source will be discussed. One experimental technique especially powerful to differentiate oxidation states of actinides (An) is the An $M_{4,5}$-edge high-energy resolution X-ray absorption near-edge structure (HR-XANES).[4] This presentation highlights the latest technological developments at the ACT station enabling the HR-XANES spectroscopic technique for samples with low radionuclide loading down to 1 ppm in combination with a cryogenic sample environment reducing beam-induced sample alterations.[7-8] It paves the way for the examination of coupled redox/solid-liquid interface reactions.[8] Examples of applications of An $M_{4,5}$ edge core-to-core and valence band resonant inelastic X-ray scattering (CC-RIXS and VB-RIXS) for probing the electronic structure and binding properties of the actinide elements will be illustrated.[6] First results obtained using a newly developed versatile chamber for soft X-ray spectroscopy at the X-SPEC beamline at the KIT Light Source will be discussed.

This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 847593. We also acknowledge funding from the ERC Consolidator Grant 2020 under the European Union's Horizon 2020 research and innovation program (grant agreement No. 101003292).

References

1. Vitova, T. et al., *Inorganic Chemistry* **2020,***59* (1), 8-22.
2. Vitova, T. et al., *Chem Commun* **2018,***54* (91), 12824-12827.
3. Vitova, T. et al., *Nature Communications* **2017,***8*, 16053.
4. Pidchenko, I. et al., *Environ Sci Technol* **2017,***51* (4), 2217-2225.
5. Bagus, P. S. et al., *Inorganic Chemistry* **2021,***60* (21), 16090-16102.
6. Vitova, T. et al., *Chem Sci* **2022,***13* (37), 11038-11047.
7. Schacherl, B. et al., *J Synchrotron Radiat* **2022,***29* (1), 80-88.
8. Schacherl, B. et al., *Anal Chim Acta* **2022,***1202*, 339636.

8:40am **LS+AC+LX+MI+TH-ThM-3 High-Energy-Resolution X-Ray Spectroscopy and Actinides Research at SLAC*, Dimosthenis Sokaras,*** SLAC National Accelerator Laboratory **INVITED**

Nowadays, high-energy-resolution x-ray spectroscopy is a well-established and powerful tool available in state-of-the art synchrotron facilities. The suppression of the core-hole lifetime contribution within the conventionally broad spectroscopic features of actinide series has revitalized the role of x-ray spectroscopy in the study of actinide complexes and intermetallics. Numerous studies have leveraged the fine structure of M or L absorption edge resonances to sensitively probe and quantify the oxidation state, 5f delocalization, and ligation of the actinides species. The increasing availability of large solid angle instruments coupled with high flux beamlines is quickly enabling such advanced studies for dilute samples or samples under special sample environments. In this presentation we will summarize the high-resolution tender and hard x-ray spectroscopy advances at SLAC and the actinides research program that these capabilities have enabled during the last decade.

9:20am **LS+AC+LX+MI+TH-ThM-5 New Insight Into Excited-State Chemical Dynamics Using Ultrafast X-Rays:Recent Highlights, Future Opportunities & Development Plans at LCLS*, Robert Schoenlein,*** Linac Coherent Light Source - SLAC National Accelerator Laboratory **INVITED**

Ultrafast X-rays from free-electron lasers (XFELs) are driving a qualitative advance in our understanding of condensed-phase chemical dynamics and catalysis. Ultrafast soft X-rays provide element-specific mapping of chemical bonds, charge distributions, oxidation states and frontier orbitals. Ultrafast hard X-ray pulses reveal the atomic scale structural dynamics of excited-state dynamics – revealing relaxation pathways, and the coupling of atomic structure, electronic structure, and solvent dynamics. This talk will highlight recent results from the Linac Coherent Light source (LCLS) using advanced ultrafast X-ray methods to track excited-state charge-transfer and relaxation pathways, and reveal the influence of molecular structural dynamics, and solvent coupling. Notably, multi-modal methods combining time-resolved X-ray scattering and spectroscopy represent a powerful approach for linking X-ray experimental observables with theory to achieve a deeper understanding of excited-state dynamics to advance the development of design principles for creating molecules, complexes, and assemblies with desired functions.

In addition, new science opportunities enabled by the nearly-completed upgrade of LCLS (LCLS-II) coupled with advanced instrumentation and methods will be discussed. LCLS-II will provide tunable soft X-ray pulses (0.25 to 5.0 keV) at high repetition rate (up to 1 MHz) and hard X-rays up to 25 keV (at 120 Hz). This unprecedented capability will support powerful new methods such as time-resolved resonant inelastic X-ray scattering (RIXS). The new ChemRIXS instrument is optimized for studying solvated complexes with C, N, O (K-edges), 3*d* transition metals (L-edges), and rare-earth elements (M-edges) – where 2D RIXS maps of excited-state dynamics coupled with quantum chemical calculations will reveal the evolution of frontier orbitals. The Tender X-ray Instrument (TXI, 2.1-5.0 keV), now under development for LCLS-II, will support time-resolved tender X-ray spectroscopy (spanning the 4*d* transition metal L-edges and key functional ligands including P, S, and Cl), coherent scattering, and novel nonlinear X-ray pump / X-ray probe methods - combining X-rays from two independently tunable XFEL sources.

11:00am **LS+AC+LX+MI+TH-ThM-10 Attosecond Studies of Radiolysis at XFELs*, Linda Young,*** Argonne National Laboratory **INVITED**

We report the first attosecond x-ray pump/x-ray probe transient absorption study in condensed phases using a pure liquid water target. With tunable two-color attosecond x-ray pulses, the pump ionizes the valence band of water and the probe scans the oxygen K-edge absorption region. Theory establishes the nature of the detected transient absorption and models the observed signal for sub-femtosecond delay times.

Acknowledgements: This work supported in part by by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under award # DEAC02-06CH11357. Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

critical importance for fields ranging from cancer therapy to the longevity of nuclear reactors to space travel. In these applications, radiolysis is initiated by a high-energy particle that leads to the ejection of energetic primary electrons followed by inelastic and non-adiabatic processes that produce damaging low energy electrons and reactive radical species. A microscopic understanding of reaction mechanisms, especially in complex systems, is missing as typical techniques used to detect prominent species, EPR and UV spectroscopies, lack either time resolution or spectral clarity. Tunable ultrafast x rays can dissect the radiolysis process. That is, x-ray pump/x-ray probe studies can systematically either peel electrons from valence, or, eject them from core orbitals and follow the ensuing dynamics on a site-specific basis.

11:40am **LS+AC+LX+MI+TH-ThM-12 First Real-Time Tracking of Oxidation States During Fast Redox of UO_2 Using a Microfluidic Electrochemical Cell and HR-XANES**, ***Jennifer Yao,*** Pacific Northwest National Laboratory*; B. Schacherl,* Karlsruhe Institute of Technology (KIT), Germany*; B. McNamara,* Pacific Northwest National Laboratory*; C. Vollmer,* Karlsruhe Institute of Technology (KIT), Germany*; N. Lahiri, E. Ilton, E. Buck,* Pacific Northwest National Laboratory*; T. Vitova,* Karlsruhe Institute of Technology (KIT), Germany

Real-time tracking of the oxidation states of a UO_2 electrode during electrochemical oxidation and reduction was achieved using operando high-resolution X-ray absorption near-edge structure (HR-XANES) spectroscopy at the ACT station of the CAT-ACT beamline at the KIT Light Source, Karlsruhe, Germany. This was made possible by utilizing a particle-attached microfluidic electrochemical cell (PAMEC) developed at PNNL, and employing KIT's advanced actinide M-edge HR-XANES technique.[1-2] The PAMEC is a three-electrode system consisting of a working electrode (WE) made of the materials of interest a platinum (Pt) reference electrode, and a Pt counter electrode.[3] The electrochemical analyzer connected to the PAMEC device controlled the redox process, e.g., applying constant potential on the UO_2 WE to reduce (-1.1 V vs Pt) or oxidize it (0.5 V vs Pt), while HR-XANES simultaneously scanned its surface chemistry. The U M_4-edge HR-XANES spectra revealed the evolution of U from U(IV) to U(V) and finally to U(VI) during the oxidation process. We were able to demonstrate the reversibility of this process by reducing the same electrode back to pure U(IV), as confirmed by HR-XANES. To our knowledge, this study reports the first in-situ and operando measurement of real-time oxidation state changes of UO_2. The spectra obtained also provided insight into the electronic structure of U(VI) in the UO_2 alteration process. This successful international scientific collaboration showcases the potential of a PAMEC for in-situ and operando experiments with UO_2 and highlights its promising broad application for characterization of spent nuclear fuel systems.

References:

(1) Vitova, T.; Pidchenko, I.; Fellhauer, D.; Bagus, P. S.; Joly, Y.; Pruessmann, T.; Bahl, S.; Gonzalez-Robles, E.; Rothe, J.; Altmaier, M.; Denecke, M. A.; Geckeis, H., The role of the 5f valence orbitals of early actinides in chemical bonding. *Nature Communications* **2017,***8*, 16053. 10.1038/ncomms16053

(2) Schacherl, B.; Prüssmann, T.; Dardenne, K.; Hardock, K.; Krepper, V.; Rothe, J.; Vitova, T.; Geckeis, H., Implementation of cryogenic tender X-ray HR-XANES spectroscopy at the ACT station of the CAT-ACT beamline at the KIT Light Source. *Journal of synchrotron radiation* **2022,***29*, 80-88. 10.1107/s1600577521012650

(3) Yao, J.; Lahiri, N.; Tripathi, S.; Riechers, S. L.; Ilton, E. S.; Chatterjee, S.; Buck, E. C., A microfluidic electrochemical cell for studying the corrosion of uranium dioxide (UO2). *RSC Advances* **2022,***12*, 19350-19358. 10.1039/D2RA02501A

12:00pm **LS+AC+LX+MI+TH-ThM-13 Use of Artificial Intelligence Techniques To Analyze Materials Characterization Data From Actinide Containing Materials**, ***Jeff Terry,*** Illinois Institute of Technology

We have developed artificial intelligence (AI) based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS), Nanoindentation, and core level photoemission. Specifically, we use a genetic algorithm to extract the relevant structural parameters through fitting of the measured spectra. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. I will illustrate the use of this package with fits of actinide species in the barrier layer of Tristructural-isotropic (TRISO) encapsulated nuclear fuel particles. The current particle design consists of a two-phase uranium-oxide/uranium-carbide kernel of 19.74% ^{235}U enrichment, a porous carbon buffer layer, and consecutive layers of pyrolytic carbon, silicon carbide (SiC) and pyrolytic carbon. The SiC layer provides the main barrier to fission product release. Much work has gone towards studying metallic fission product interaction in the SiC containment layer due to the propensity of metallic fission product release as a function of high temperature (safety) testing. Here, I will show how the interaction dynamics of plutonium and uranium within this layer have been determined through EXAFS measurements that have been fit with AI. One of the major benefits of using this technology is that actinide containing materials often have edges from higher Z-elements that limit the usable range of the spectrum. Our method fits momentum space data which does not suffer from transformation artifacts of real space over a small momentum range.

Light Sources Science Mini-Symposium
Room C124 - Session LS+AC+AS+LX+MI+TH-ThA

Facility Upgrades and Recent Capability Development

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **James G. Tobin**, University of Wisconsin-Oshkosh, **Gertrud Zwicknagl**, Technical University Brauschweig

2:20pm **LS+AC+AS+LX+MI+TH-ThA-1 The Impact of Upgraded High-Brightness Synchrotron Lightsources on the Chemical Speciation of Nanoscale Heterogeneous Aggregates and Transformations***, **Andreas Scholl**,* Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

ALS-U is an ongoing upgrade of the Advanced Light Source (ALS) at Berkeley Lab that will endow the ALS with revolutionary x-ray capabilities. The new storage ring will enable the production of highly focused beams of soft x-ray light that are at least 100 times brighter than those of the existing ALS. Applying this technology at the ALS will help us better understand and develop new materials and chemical systems needed to advance our research needs in energy science, environmental systems research, and biosciences in the 21st century. This will create a world-leading platform for next-generation soft x-ray and tender x-ray instrumentation.

Four beamlines with new and upgraded capabilities will become available after the upgrade. The FLEXON beamline (FLuctuation and EXcitation of Orders in the Nanoscale), a high-brightness coherent soft x-ray beamline, will provide x-ray photon correlation spectroscopy and diffraction imaging techniques to study electronic, chemical, and magnetic fluctuations in quantum materials with nanosecond temporal and nanometer spatial resolution. A new ALS-U developed tender x-ray beamline is designed to address challenges at the frontiers of diverse scientific areas, ranging from soft condensed matter and biomaterials to energy science and Earth and environmental sciences. It will offer state-of-the-art nanometer-resolved chemical imaging and resonant scattering nanoprobes, enabling operando and in situ studies of materials of K-edges of elements (Na through Ca) and the M and L edges of lanthanides and actinides. These two beamlines will be complemented by two upgraded beamlines for nanometer 3D chemical tomography based on ptychography of light elements and first-row transition metals and for high-resolution ARPES.

The high coherent flux of the upgraded ALS will drastically improve the speed, sensitivity, and spatial resolution of nanoprobes, enabling the speciation and forensic study of nanoscale constituents and contaminants via x-ray absorption spectroscopy and fluorescence detection. Chemical signatures can be correlated with morphology and compared with chemical standards. Operando experiments, for example, of liquid phase systems and studies under ambient conditions, will be enabled by specially designed sample holders and liquid cells using the high penetration of tender x-rays.

3:00pm **LS+AC+AS+LX+MI+TH-ThA-3 The Advanced Photon Source Upgrade: A transformative tool for understanding material structure.***, **Jonathan Lang**, J. Lang,* Argonne National Laboratory **INVITED**

The APS is currently undergoing a major upgrade of the facility that will increase the brightness of the x-ray beams by factors of up to 500. This upgrade will provide transformational capabilities for examining the nanoscale structure and electronic configuration of materials and their evolution with external stimuli. This presentation with provide an update on the current status of the APS-U project, and discuss the new opportunities for imaging actinide and rare-earth compounds with this new source

3:40pm **LS+AC+AS+LX+MI+TH-ThA-5 Combining Focused Ion Beam Sectioning, Soft X-ray Spectromicroscopy, and Non-Negative Matrix Factorization to Reveal Acrtinide Chemical Speciation at the Nanoscale***, **Alexander Ditter**, D. Smiles, J. Pacold, D. Lussier,* Lawrence Berkeley National Laboratory*; Z. Dai,* Lawrence Livermore National Laboratory*; A. Altman,* Lawrence Berkeley National Laboratory*; M. Bachhav,* Idaho National Laboratory*; B. Chung,* Lawrence Livermore National Laboratory*; C. Degueldre,* Lancaster University, UK*; S. Donald,* Lawrence Livermore National Laboratory*; L. He,* Idaho National Laboratory*; M. Mara, S. Minasian, D. Shuh,* Lawrence Berkeley National Laboratory **INVITED**

Spectromicroscopy methods, combining the chemical insight of spectroscopy with microscopy imaging, can give a unique and informative view of a sample of interest. Scanning Transmission X-ray Microscope (STXM) spectromicroscopy is one such method, utilizing synchrotron radiation to probe electronic structure with a spatial resolution in the tens of nanometers. Specialized methods like ptychography can push the spatial resolution even lower into the single nanometer range.

Discussed here, STXM spectromicroscopy is applied to two actinide samples: spent nuclear fuel, which offers a unique insight into the complex environment of nuclear fuel undergoing burnup, and uranium oxide allowed to age in a humid environment, which serves as a demonstration of the power of this technique for nuclear forensics investigations. These samples are created by focused ion beam (FIB) sectioning to generate cross-sections of ideal thickness for soft x-ray measurements (100-200 nm). The FIB method of sample preparation also allows for the measurement of highly radioactive spent fuel without containment due to the extremely small amount of material present.

Data analysis is a key component to the understanding of spectromicroscopy results for varied samples like these. Non-negative matrix factorization (NMF) is employed to identify key components and recent efforts to improve NMF to work with noisy individual STXM spectra are outlined here. Reproducibility of the analysis is a concern (as with similar methods like multivariate curve regression) and methods to enhance both reproducibility and interpretability of the results are discussed.

Combining STXM spectromicroscopy, FIB sectioning, and NMF analysis has allowed for unique insights into actinide materials. Potential future developments utilizing this method for other samples and with advanced techniques like ptychography are also discussed.

Author Index

Bold page numbers indicate presenter