

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic

Room B116 - Session LX+AS+HC+SS-MoM

Laboratory-Based AP-XPS: Advances in Instrumentation and Applications

Moderators: Sylwia Ptasińska, University of Notre Dame, Heath Kersell, Oregon State University

8:20am LX+AS+HC+SS-MoM-1 Instrumentation for Electron Microscopy and Spectroscopy in Plasma Environment, *Andrei Kolmakov*, NIST-Gaithersburg

Plasma-assisted processes are of principal importance for modern semiconductors microfabrication technology, catalysis, environmental remediation, medicine, etc. Understanding the chemical and morphological evolutions of the surfaces and interfaces under a plasma environment requires *operando* metrologies that have a high spatial, temporal, and spectroscopic resolution. Combining the APXPS system with ambient pressure scanning electron microscopy would, in principle, meet these needs. Here we review the status of the field and discuss the prospective designs as well as application examples of ambient pressure scanning electron microscopy and spectroscopy for *in situ* analysis and processing of the surfaces under plasma environments

9:00am LX+AS+HC+SS-MoM-3 Scienta Omicron HiPPLab - A Lab-based APXPS Instrument for Probing Surface Chemical Reactions, *Peter Amann*, Scienta Omicron, Germany

Investigating reaction intermediates, oxidation states, solid-liquid interfaces and buried interfaces under near ambient pressure conditions is highly desired in materials science applications. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful method to investigate the chemical nature of surfaces and interfaces and has undergone a tremendous improvement in the last years. The development of the HiPP analysers allowed to overcome the one bar pressure regime without using pressure separating membranes. [1] [2]

During the past decade, increased attention has been shown to laboratory based APXPS system solutions, which is motivated by the 24/7 access capability and possibility for highly customized sample environments. Drawing on extensive experience in the fields of photoelectron spectroscopy, UHV technology, and system design, Scienta Omicron has designed the HiPPLab as an easy-to-use system that encourages user creativity through flexibility, modularity and an innovate chamber design.[3] It combines a state-of-the-art HiPP analyser with a high flux, variable focus X-ray source. Multiple options complement the HiPPLab offer, including a gas reaction cell, a preparation chamber, laser heating, or options for mass-spectroscopy. Using automated gas-flow controllers, experiments can be conducted in a controlled way. Future upgrade possibilities are given.

The HiPP-3 analyser features a 2D detector allowing for spatial resolved measurements with customer proven results down to 2.8 μm resolution. The swift acceleration mode allows for high electron transmission without applying a sample bias. A sophisticated pre-lens design in which efficient pumping between two close-by apertures is implemented, allows dragging out corrosive gases or moisture, which would otherwise be detrimental to the instrument.

In this presentation, I will give an overview on our APXPS product portfolio focusing on laboratory based solutions and present application examples.

[1] Amann, et al. *Review of Scientific Instruments*, 2019 90(10)

[2] Takagi, et al. X-ray photoelectron spectroscopy under real ambient pressure conditions. *Applied Physics Express*, 2017, 10(7), 8–11.

[3] Scienta Omicron HiPPLab <https://scientaomicron.com/en>

9:20am LX+AS+HC+SS-MoM-4 Using Microheaters for Time-Resolved APXPS and Correlated ETEM, *Ashley Head*, Brookhaven National Laboratory; *B. Karagoz*, Diamond Light Source, UK; *J. Carpena-Nuñez*, Air Force Research Laboratory; *D. Zakharov*, Brookhaven National Laboratory; *B. Maruyuma*, Air Force Research Laboratory; *D. Stacchiola*, Brookhaven National Laboratory

With a rise in the number of lab-based APXPS systems, these instruments afford an opportunity to continue the development of multimodal and correlated capabilities for more comprehensive information of reactions at

surfaces. Here I will discuss the methods of using an ETEM commercial microheater for collecting APXPS data on the same sample under identical conditions. A specialized holder was fabricated to use commercial microheaters on MEMS chips in a lab-based APXPS instrument. The rapid heating of the microheater enables a time-zero for collecting APXPS data with a time resolution of 500 ms. Proof-of-principle measurements following the oxidation and reduction of a Pd film demonstrate correlative experiments with TEM. The specialized holder was fabricated with the possibility of dosing gases locally to the sample surface while confined by a graphene membrane. Using the gas lines, the Pd film was oxidized under a partial pressure of air (~0.4 mbar). Overall, using this microheater in APXPS offers chemical information complementary to structural changes seen in ETEM. The rapid heating enables new opportunities in time-resolution and increased pressure for APXPS experiments.

9:40am LX+AS+HC+SS-MoM-5 NAP-XPS Instrumentation Came a Long Way - Where Will Applications Lead Us from Here?, *P. Dietrich*, *F. Mirabella*, *K. Kunze*, *O. Schaff*, *Andreas Thissen*, SPECS Surface Nano Analysis GmbH, Germany

INVITED

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into the most important standard surface analytical method in many laboratories for surface and materials characterization.

For the last fifteen years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention. Although invented as a laboratory method it initially started to grow at synchrotrons. The development of more efficient and sensitive electron analyzers and high-brilliance monochromated laboratory X-ray and UV sources running at pressures of up to 100 mbar finally brought it back to the individual laboratories. The reasons are the availability of individual infrastructure for sample preparation and handling, safety regulations and easier access to measurement time on a daily basis. Nowadays the vast majority of instruments worldwide are laboratory-based.

It opened the method XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces and many more. The development of instrumentation followed the important applications and besides the "active" components, mainly excitation sources and electron analyzers, a lot of developments have been done in the fields of sample environments, sample handling, system setup and automation and combination with other techniques and even in quantification of data. There are only a few applications left where experiments at synchrotron based beamlines and end stations offer the only solution.

The market driving applications nowadays are catalysis, electrochemistry, behaviour of liquid phases, biological samples and surface chemistry. Along these applications this presentation will show the existing instrumentation, discuss its limits and the perspective for near future developments to further increase the user base of laboratory based NAP-XPS systems to turn it into an integral part of the large routine analysis community.

10:40am LX+AS+HC+SS-MoM-8 Evolution of Metal-Organic Frameworks in the Presence of a Plasma by AP-XPS and IRRAS, *J. Anibal Boscoboinik*, Brookhaven National Laboratory and State University of New York at Stony Brook; *M. Ahmad*, Stony Brook University/Brookhaven National Laboratory; *M. Dorneles de Mello*, Brookhaven National Laboratory; *D. Lee*, Johns Hopkins University; *P. Dimitrakellis*, University of Delaware; *Y. Miao*, Johns Hopkins University; *W. Zheng*, University of Delaware; *D. Nykpanchuk*, Brookhaven National Laboratory; *D. Vlachos*, University of Delaware; *M. Tsapatsis*, Johns Hopkins University

INVITED

Zeolitic imidazolate frameworks (ZIF), a class of metal-organic frameworks, are promising materials for various applications, including the separation and trapping of molecules and catalysis. Recent work has shown that exposure to plasma can result in the functionalization of the framework for tailored applications. This talk will report in-situ plasma studies of ZIF-8 as a model system. We will study the framework's evolution in the presence of N_2 , O_2 , and H_2 plasmas by combining lab-based ambient pressure XPS and infrared reflection absorption spectroscopy.

11:20am LX+AS+HC+SS-MoM-10 Surface Degradation and Passivation in Perovskite Solar Cells, *Wendy Flavell*, The University of Manchester, UK

INVITED

There is an urgent requirement to make better use of the 120,000 TW of power provided by the Sun, by using it to generate power, or by using its energy directly to make useful chemical feedstocks. Around the world,

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there is an explosion of research activity in new systems for harvesting solar energy, including solar cells based organometal halide perovskites. Issues of key importance are the interfacial energy level line-up of the cell components, and the influence of the surface properties of these materials on charge separation in the devices. Indeed, the deployment of perovskites in solar cells is currently limited by their high reactivity and rate of surface oxidation. Thus, a key problem is to develop an understanding of the interface chemistry of solar heterojunctions in order to develop passivation strategies. I show how a combination of techniques including near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and hard X-ray photoelectron spectroscopy (HAXPES) may be used to investigate surface ageing and the surface degradation reactions[1-7], chemical composition as a function of depth[4,5], and to develop passivation strategies for perovskite solar cell heterojunctions[2,3,5-7].

References

1. J C-R Ke, A S Walton, A G Thomas, D J Lewis, *et al.*, *Chem Commun* **53**, 5231 (2017).
2. J C-R Ke, D J Lewis, A S Walton, B F Spencer, *et al.*, *J Mater Chem A*, **6**, 11205 (2018).
3. C-R Ke, D J Lewis, A S Walton, Q Chen, *et al.*, *ACS Applied Energy Materials* **2**, 6012 (2019).
4. B F Spencer, S Maniyarasu, B P Reed, D J H Cant *et al.*, *Applied Surface Science* **541**, 148635 (2021).
5. S Maniyarasu, J C-R Ke, B F Spencer, A S Walton *et al.*, *ACS Applied Energy Materials* **13**, 43573 (2021).
6. S Maniyarasu, B F Spencer, H Mo, A S Walton *et al.*, *J Mater Chem A*, **10**, 18206 (2022).
7. D Zhao, T A Flavell, F Aljuaid, S Edmondson *et al.*, *ACS Applied Materials and Interfaces*, submitted.

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic

Room B116 - Session LX+AS+BI+HC+SS+TH-MoA

Laboratory-Based AP-XPS:Surface Chemistry and Biological/Pharmaceutical Interfaces

Moderators: **Gregory Herman**, Argonne National Laboratory, **Ashley Head**, Brookhaven National Laboratory

1:40pm **LX+AS+BI+HC+SS+TH-MoA-1 The Role of Co-Adsorbed Water in Decomposition of Oxygenates**, *H. Nguyen, K. Chuckwu, Líney Árnadóttir*, Oregon State University **INVITED**

The decomposition of oxygenates in the presence of water finds various applications in chemical processes, such as biomass conversion. The presence of co-adsorbates and solvents affects both the reaction rate and selectivity. In this study, we used NAP-XPS and DFT to investigate the decomposition of acetic acid on Pd(111) as a model system for the decomposition of small oxygenates in the absence and presence of water. The decomposition of acetic acid occurs through two main reaction pathways, decarboxylation, and decarbonylation, forming CO₂ or CO, respectively. Our DFT calculations indicate that the two pathways have similar barriers without water. However, in the presence of water, the decarboxylation path becomes. Similarly, our AP-XPS experiments show an increase in the CO₂/CO ratio as well as a decrease in the CO/acetate-acetic acid and acetic acid/acetate ratios when water is present. The shift in selectivity is not due to a single reaction step, but rather the decreasing barrier in general for OH scissoring and the increasing barrier for C-O scissoring. This shift favors the formation of CO₂, as demonstrated by our microkinetic model.

2:20pm **LX+AS+BI+HC+SS+TH-MoA-3 Integrating First-principles Modeling and AP-XPS for Understanding Evolving Complex Surface Oxides in Materials for Hydrogen Production and Storage**, *B. Wood, Tuan Anh Pham*, Lawrence Livermore Laboratory **INVITED**

Chemical processes occurring at solid-gas, solid-liquid, and solid-solid interfaces critically determine the performance and durability of hydrogen production and storage technologies. While directly probing behavior of these interfaces under actual operating conditions remains challenging, modern surface science approaches such as ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) can provide insight into the evolution of surface chemistry in approximate environments. However, interpretation of these spectra can be complicated: standards for complex surface chemical moieties are often unavailable, and bulk standards can be unreliable. First-principles computations are emerging as an important companion approach, offering the ability to directly compute spectroscopic fingerprints. This has the advantage of aiding interpretation of the experiments, while simultaneously using the experiment-theory comparison to inform construction of more accurate interface models. In this talk, I will show how computation has been combined with laboratory-based AP-XPS measurements to understand the evolving chemistry of complex native surface oxides. Two examples will be drawn from activities within the U.S. Department of Energy HydroGEN and HyMARC consortia, which focus on renewable hydrogen production and materials-based hydrogen storage, respectively. First, I will discuss the application to surface oxidation of III-V semiconductors for photoelectrochemical hydrogen production, which demonstrates transitions between kinetically and thermodynamically controlled oxidation regimes with implications for device performance. Second, I will also show how the same approach has been applied to understand the rate-determining role of surface oxides in the dehydrogenation performance of NaAlH₄ for solid-state hydrogen storage.

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

3:00pm **LX+AS+BI+HC+SS+TH-MoA-5 Particle Encapsulation on Reducible Oxides Under Near-Ambient Pressures**, *F. Kraushofer, M. Krinninger, P. Petzoldt, M. Eder, S. Kaiser, J. Planksky, T. Kratky, S. Günther, M. Tschurl, U. Heiz, F. Esch, Barbara A. J. Lechner*, TUM, Germany **INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and

reducing treatments at elevated pressures on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a TiO₂(110) support, we can either selectively oxidize the support or both the support and the Pt particles by tuning the O₂ pressure.^[1] We find that the growth of the encapsulating oxide overlayer is inhibited when Pt is in an oxidic state. Our experiments show that the Pt particles remain embedded in the support once encapsulation has occurred. On Fe₃O₄(001), the encapsulation stabilizes small Pt clusters against sintering.^[2] Moreover, the cluster size and thus footprint lead to a change in diffusivity and can therefore be used to tune the sintering mechanism. Very small clusters of up to 10 atoms even still diffuse intact after encapsulation.

[1] P. Petzoldt, P., M. Eder, S. Mackewicz, M. Blum, T. Kratky, S. Günther, M. Tschurl, U. Heiz, B.A.J. Lechner, Tuning Strong Metal-Support Interaction Kinetics on Pt-Loaded TiO₂ (110) by Choosing the Pressure: A Combined Ultrahigh Vacuum/Near-Ambient Pressure XPS Study, *J. Phys. Chem. C* 126, 16127-16139 (2022).

[2] S. Kaiser, J. Planksky, M. Krinninger, A. Shavorskiy, S. Zhu, U. Heiz, F. Esch, B.A.J. Lechner, Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on Fe₃O₄(001) by SMSI, *ACS Catalysis* 13, 6203-6213 (2023).

4:00pm **LX+AS+BI+HC+SS+TH-MoA-8 Applications of NAP XPS in Pharmaceutical Manufacturing: Surface Analysis, Hydrogen Bonds, and Solute-Solvent Interactions**, *Sven Schroeder*, University of Leeds, UK **INVITED**

The availability of laboratory-based NAP XPS creates novel interface research opportunities for scientific disciplines and technology areas that deal with materials incompatible with traditional ultra-high vacuum XPS. This is, for example, the case for many organic and/or pharmaceutical materials and formulations, whose characterization by XPS has hitherto been restricted by their vapour pressures. NAP XPS permits for the first time systematic and detailed analysis of the light element photoemission lines (especially C/N/O 1s) in these materials. In conjunction with elemental analysis by survey XP spectra they provide quantitative information on composition and speciation both in the bulk and at the surfaces of pure organic solids, in their formulations with other components and in solutions. Especially of interest are studies of the solid/liquid interface with water, which is of high relevance for understanding and controlling drug release profiles from tablets. To illustrate these points I will present various examples of research on pharmaceutical materials. Moreover, near-ambient pressure core level spectroscopy turns out to be an extremely powerful probe for the structure and dynamics of hydrogen bonding and proton transfer in materials, both in the solid state and in solutions. NAP XPS measurements provide unique insight into proton dynamics in noncrystalline solids and liquids, where traditional characterisation by crystallography and nuclear magnetic resonance fails or provides ambiguous information on proton locations.

4:40pm **LX+AS+BI+HC+SS+TH-MoA-10 The Change of DNA and Protein Radiation Damage Upon Hydration: In-Situ Observations by Near-Ambient-Pressure XPS**, *Marc Benjamin Hahn*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany **INVITED**

X-ray photoelectron-spectroscopy (XPS) allows simultaneous irradiation and damage monitoring. Although water radiolysis is essential for radiation damage, all previous XPS studies were performed in vacuum. [1] Here we present near-ambient-pressure XPS experiments to directly measure DNA damage under water atmosphere. They permit in-situ monitoring of the effects of radicals on fully hydrated double-stranded DNA. Our results allow us to distinguish direct damage, by photons and secondary low-energy electrons (LEE), from damage by hydroxyl radicals or hydration induced modifications of damage pathways. The exposure of dry DNA to x-rays leads to strand-breaks at the sugar-phosphate backbone, while deoxyribose and nucleobases are less affected. In contrast, a strong increase of DNA damage is observed in water, where OH-radicals are produced. In consequence, base damage and base release become predominant, even though the number of strand-breaks increases further. Furthermore, first data about the degradation of single-stranded DNA binding-proteins (GSP / GV5 and hmtSSB) under vacuum and NAP-XPS conditions are presented.

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[1] Hahn, M.B., Dietrich, P.M. & Radnik, J. In situ monitoring of the influence of water on DNA radiation damage by near-ambient pressure X-ray photoelectron spectroscopy. *Commun Chem* 4, 50, 1-8 (2021). <https://doi.org/10.1038/s42004-021-00487-1>

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. Goluński, 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-static¹. The analyzed surfaces were bombarded at the rate of ~ 1000 impacts/sec with $1-6 \times 10^6$ 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" model². 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 graphene³.

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.

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

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

³D.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 led 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^{+} 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

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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].

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

²Lida, 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)

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic

Room Oregon Ballroom 203-204 - Session LX-TuP

Laboratory-Based AP-XPS: Poster Session

LX-TuP-1 Multimodal Liquid Cell for Lab-based APXPS: Investigating Ruthenium-based Organometallic Molecules in Various Environments, *Youngeok Yu, A. Vidal Muller*, Brookhaven National Laboratory; *Z. Xi*, Stony Brook University/Brookhaven National Laboratory; *M. Liu, E. Stavitski, J. Concepcion, A. Head*, Brookhaven National Laboratory

Dye-sensitized photo-electrosynthesis cells (DSPECs) hold great promise as sustainable and renewable energy sources. To enhance the adsorption efficiency, chromophores are anchored onto oxide surfaces to absorb visible light, as transition metal oxides typically possess band gaps within the range of 2-3 eV. In this research, we have developed a multimodal liquid cell for ambient-pressure X-ray photoelectron spectroscopy (APXPS) to investigate the solid/liquid interface of these systems. The cell design utilizes a graphene-covered holey SiNx membrane with deposited metal oxide and catalyst as the working electrode. Our study focuses on examining the electronic structure of a dye molecule, (bis-2,2'-bipyridine)[(4,4'-bis(diethyl phosphonate)-2,2'-bipyridine)]ruthenium(II) (or RuP), under various conditions, including being anchored on TiO₂, anchored on IrO₂, and in a 1mM NaOH solution. Our findings indicate that the electron density of the Ru metal center varies with its environment.

LX-TuP-2 Investigating Solvation with Liquid Jet Photoelectron Spectroscopy, *Jared Bruce*, University of Nevada, Las Vegas; *A. Haines, F. Furche*, University of California, Irvine; *R. Seidel*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; *B. Winter*, Fritz Haber Institute of the Max Planck Society, Germany; *J. Hemminger*, University of California, Irvine

The local chemical structure around solutes in aqueous solution is challenging to characterize on a molecular scale given the amount of hydrogen bonding interactions that occur in solution. Liquid jet photoelectron spectroscopy (LJ-XPS) can be a critical tool providing valuable chemical information both near the surface and in the bulk of the solution.

In this talk, we will explore the solvation of acetic acid in aqueous solution both near the interface and into the bulk of the solution. The difference in binding energy between the methyl and carboxyl carbons (ΔBE) was used to compare electronic structure calculations coupled with molecular dynamics simulations to the results from the LJ-XPS. Experiment and theory were found to overlap when a single water molecule was added to the first solvation shell of acetic acid calculation, whereas 20 water molecules were required to reproduce the experiment for acetate. Building on these results, liquid jet work at the synchrotron was used to explore the difference in solvation near the interface at lower probe depths compared to those in the bulk of the solution and in the lab-based experiments.

LX-TuP-4 Evaluation of AlCoCrFeNiMnTi High Entropy Alloys for CO₂ Hydrogenation, *Chiezugolum Odilinye, H. Kersell*, School of Chemical, Biological, and Environmental Engineering, Oregon State University; *X. Fan*, Department of Materials Science and Engineering, University of Tennessee, Knoxville; *Z. Lyu, P. Liaw*, Department of Materials Science and Engineering, University of Tennessee; *G. Herman*, School of Chemical, Biological, and Environmental Engineering, Oregon State University

Carbon dioxide (CO₂) hydrogenation is of considerable interest due to the ability to chemically recycle carbon dioxide with renewably generated hydrogen. A wide range of catalysts have been used for hydrogenation of CO₂ where methanation, Fischer-Tropsch, and methanol synthesis reactions are the most investigated. We are interested in evaluating high-entropy alloys (HEAs) for CO₂ hydrogenation, where we can take advantage of the multifunctional sites that exist at HEA surfaces. Indeed, certain HEAs recently showed promise for altering the selectivity and stability for CO₂ hydrogenation catalysts.^[1] In this study, we have used laboratory-based ambient pressure X-ray photoelectron spectroscopy (APXPS) to investigate the reaction of CO₂ and CO₂/H₂ mixtures with an AlCoCrFeNiMnTi HEA. For these experiments, the as-cast alloy was homogenized at 1100 °C, polished, and then sputter-cleaned in ultrahigh vacuum to remove adventitious carbon and native oxides. This clean surface was then exposed to 1 mTorr of CO₂, while we monitored the chemical state of the adsorbed carbon species, as well as the oxidation state of the surface metal atoms. We have

performed similar experiments with CO₂/H₂ mixtures and will contrast the observed surface chemistries with only CO₂. These studies demonstrate that APXPS is a powerful technique to monitor reactions on complex alloy surfaces.

Reference:

[1] K. Mori, N. Hashimoto, N. Kamiuchi, H. Yoshida, H. Kobayashi, and H. Yamashita, Hydrogen spillover-driven synthesis of high-entropy alloy nanoparticles as a robust catalyst for CO₂ hydrogenation, *Nat. Commun.*, 2021, 12, 3884

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).

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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.
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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), 3d 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 4d 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 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.

Thursday Morning, November 9, 2023

11:40am **LS+AC+LX+MI+TH-ThM-12 First Real-Time Tracking of Oxidation States During Fast Redox of UO₂ 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 UO₂ 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 UO₂ 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 M₄-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 UO₂. The spectra obtained also provided insight into the electronic structure of U(VI) in the UO₂ alteration process. This successful international scientific collaboration showcases the potential of a PAMEC for in-situ and operando experiments with UO₂ and highlights its promising broad application for characterization of spent nuclear fuel systems.

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(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% ²³⁵U 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.

Thursday Afternoon, November 9, 2023

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 Braunschweig

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 nanoprobe, 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 nanoprobe, 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 will 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 Actinide 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.

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 Liu, M.: LX-TuP-1, 7
 Lussier, D.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Lyu, Z.: LX-TuP-4, 7

— M —

Mara, M.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Maruyama, B.: LX+AS+HC+SS-MoM-4, 1
 McEwen, J.: CA+AS+LS+LX+MN+SE+SS-TuM-4, 5
 McGehee, M.: CA+AS+LS+LX+MN+SE+SS-TuM-3, 5
 McNamara, B.: LS+AC+LX+MI+TH-ThM-12, 9
 Miao, Y.: LX+AS+HC+SS-MoM-8, 1
 Minasian, S.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Mirabella, F.: CA+AS+LS+LX+MN+SE+SS-TuM-10, 6; LX+AS+HC+SS-MoM-5, 1
 Morales, D.: CA+AS+LS+LX+MN+SE+SS-TuM-3, 5

— N —

Nemsak, S.: CA+AS+LS+LX+MN+SE+SS-TuM-12, 6
 Nguyen, H.: LX+AS+BI+HC+SS+TH-MoA-1, 3
 Nykpanchuk, D.: LX+AS+HC+SS-MoM-8, 1
 — O —
 Odilinye, C.: LX-TuP-4, 7
 Onyango, I.: CA+AS+LS+LX+MN+SE+SS-TuM-4, 5

— P —

Pacold, J.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Palmstrom, A.: CA+AS+LS+LX+MN+SE+SS-TuM-3, 5
 Perea, D.: CA+AS+LS+LX+MN+SE+SS-TuM-4, 5

Petzoldt, P.: LX+AS+BI+HC+SS+TH-MoA-5, 3
 Pham, T.: LX+AS+BI+HC+SS+TH-MoA-3, 3
 Planksy, J.: LX+AS+BI+HC+SS+TH-MoA-5, 3
 Postawa, Z.: CA+AS+LS+LX+MN+SE+SS-TuM-1, 5
 Potyrailo, R.: CA+AS+LS+LX+MN+SE+SS-TuM-5, 6

— R —

Revzin, A.: CA+AS+LS+LX+MN+SE+SS-TuM-1, 5

— S —

Schacherl, B.: LS+AC+LX+MI+TH-ThM-12, 9
 Schaff, O.: LX+AS+HC+SS-MoM-5, 1
 Schoenlein, R.: LS+AC+LX+MI+TH-ThM-5, 8
 Scholl, A.: LS+AC+AS+LX+MI+TH-ThA-1, 10
 Schroeder, S.: LX+AS+BI+HC+SS+TH-MoA-8, 3
 Schweikert, E.: CA+AS+LS+LX+MN+SE+SS-TuM-1, 5
 Seidel, R.: LX-TuP-2, 7
 Shuh, D.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Smiles, D.: LS+AC+AS+LX+MI+TH-ThA-5, 10
 Sokaras, D.: LS+AC+LX+MI+TH-ThM-3, 8
 Stacchiola, D.: LX+AS+HC+SS-MoM-4, 1
 Stavitski, E.: LX-TuP-1, 7

— T —

Terry, J.: LS+AC+LX+MI+TH-ThM-13, 9
 Thissen, A.: CA+AS+LS+LX+MN+SE+SS-TuM-10, 6; LX+AS+HC+SS-MoM-5, 1
 Tsapatsis, M.: LX+AS+HC+SS-MoM-8, 1
 Tschurl, M.: LX+AS+BI+HC+SS+TH-MoA-5, 3

— V —

Verkhoturov, D.: CA+AS+LS+LX+MN+SE+SS-TuM-1, 5
 Verkhoturov, S.: CA+AS+LS+LX+MN+SE+SS-TuM-1, 5
 Vidal Muller, A.: LX-TuP-1, 7

Visart de Bocarmé, T.:

CA+AS+LS+LX+MN+SE+SS-TuM-4, 5
 Vitova, T.: LS+AC+LX+MI+TH-ThM-1, 8;
 LS+AC+LX+MI+TH-ThM-12, 9
 Vlachos, D.: LX+AS+HC+SS-MoM-8, 1
 Vollmer, C.: LS+AC+LX+MI+TH-ThM-12, 9

— W —

Winter, B.: LX-TuP-2, 7
 Wood, B.: LX+AS+BI+HC+SS+TH-MoA-3, 3

— X —

Xi, Z.: LX-TuP-1, 7

— Y —

Yao, J.: LS+AC+LX+MI+TH-ThM-12, 9
 Young, L.: LS+AC+LX+MI+TH-ThM-10, 8
 Yu, Y.: LX-TuP-1, 7

— Z —

Zakharov, D.: LX+AS+HC+SS-MoM-4, 1
 Zheng, W.: LX+AS+HC+SS-MoM-8, 1