Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-MoM

Probing Surface and Interface Structure with X-ray Photoelectron Spectroscopy: In Memory of Charles Fadley

Moderators: Gregory Herman, Oregon State University, **Theva Thevuthasan**, Pacific Northwest National Laboratory

9:00am **AS+LS+RE+SS-MoM-3 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane**, ***Trevor Willey****, J. Lee,* Lawrence Livermore National Laboratory*; D. Brehmer, O. Paredes Mellone,* SLAC National Accelerator Laboratory*; L. Landt,* Lawrence Livermore National Laboratory*; P. Schreiner, A. Fokin, B. Tkachenko,* Institute of Organic Chemistry, Justus Liebig University, Germany*; A. de Meijere, S. Kozhushkov,* Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany*; T. van Buuren,* Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some fundamental saturated carbon cage compounds. Adamantane, C10H16, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C10H16 isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)12, and cubane, (CH)8, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C–C σ* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H σ* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octadedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)x. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C-C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

9:20am **AS+LS+RE+SS-MoM-4 Composition and Thermal Stability Analysis of Passive Films on NiCr and NiCrMo Alloys**, ***Keithen Orson****, A. Costine, E. Romanovskaia, J. Scully, P. Reinke,* University of Virginia

Ni-Cr based super-alloys are important because of their corrosion resistance, which derives mainly from a thin passive layer of chromia (Cr_2O_3). During aqueous corrosion, a complex surface layer containing $Ni(OH)_2$, $Cr(OH)_3$, and Cr_2O_3 forms whose chemistry and structure are still subject of discussion. Our work is designed to study how non-equilibrium growth of the passive layer during aqueous corrosion affects the properties of the passive layer. We apply a range of electrochemical conditions to two alloys - Ni22wt%Cr, and Ni22wt%Cr6%Mo. Alloys are processed in pH 4 aqueous chloride solution. The electrochemical reaction step uses high or low current density (100-0.1 nA/cm^2) to achieve fast and slow passive layer growth that is far or near equilibrium, respectively. The second step was a 10 ks potentiostatic hold at +0.2V. Electrochemical processing was followed Angle-Resolved X-Ray Photoelectron Spectroscopy (ARXPS) analysis to characterize the oxide and hydroxide chemistry of the passive layer and underlying alloy. Annealing to 400 °C served as a proxy to assess the passive layers stability, which we propose is related hydroxide network connectivity and pitting resistance. In as-prepared samples, Ni and Cr hydroxides are dominant in the passive layer, while chromia and $Cr(OH)_3$ are the dominant species at elevated temperatures. The underlying alloy tends to be moderately enriched in Cr. Under all conditions and temperatures, Cr is present as a mix of oxide and hydroxide with the oxide dominating at higher temperatures. In contrast, $Ni(OH)_2$ is detected at low temperatures, but no NiO is observed. For molybdenum-containing alloys, MoO_x and Cr_2O_3 coexist until MoO_x is reduced at T>300˚C. Continuous XPS spectra taken during annealing indicate smooth transitions between hydroxide and oxide visible in the O1s and C2p3/2 peak shape, while for Mo 3d3/2 and Ni2p3/2 peaks narrow transition regions for reduction are identified. Oxide thickness decreases with increasing temperature due to oxide loss from reduction and volatilization. The fast and slow growth on Mo-containing alloys without a subsequent potentiostatic hold produced a marked difference in oxide thickness. Molybdenum content affects multiple characteristics of the passive layer, including thickness, layering, and chromia content. Our work demonstrates how differing preparation conditions affect the chemistry and layering of NiCr and NiCrMo alloys. These results will be interpreted in the context of passive film performance and can ultimately be used to design alloys for optimal corrosion resistance.

9:40am **AS+LS+RE+SS-MoM-5 Reversible Changes in Surface Charging and Surface Oxide of $NiFe_2O_4$ Thin Films: A Temperature Dependent X-Ray Photoemission Study**, ***Arjun Subedi****, D. Yang, X. Xu, P. Dowben,* University of Nebraska-Lincoln

We have observed large binding energy shifts in temperature dependent X-ray photoelectron spectroscopy (XPS) of the $2p_{3/2}$ core levels of both Ni and Fe atoms in nickel ferrite ($NiFe_2O_4$) thin films grown on Al_2O_3. The binding energies of the core levels were found to be sensitive to photovoltaic charging. The apparent binding energies decreased by more than 5 eV for both core levels when the temperature was increased to 510 K from room temperature. This is evidence of large surface charging of the sample and indicative of insulating behavior at lower temperatures. The XPS spectra at higher temperatures were observed to be different from that at lower temperatures, suggesting a different surface oxide at higher temperatures. When temperature was lowered from 510 K to room temperature, the changes in surface charging and nature of the surface oxide were reversible. We conclude that the nature of the surface oxide is temperature dependent.

10:00am **AS+LS+RE+SS-MoM-6 The Reproducibility Crisis in Science as Manifested in X-Ray Photoelectron Spectroscopy (XPS). What's Been Done, and What's Being Done About It?**, ***Matthew Linford****,* Brigham Young University*; D. Baer,* PNNL*; G. Major,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. Conventional XPS probes 5 - 10 nm into surfaces, revealing both the atomic compositions and chemical states of the atoms at surfaces. During the past few decades, there has been a significant increase in the use of XPS worldwide, both in the number of papers published that show XPS data and in the number of new XPS systems being sold. However, the world appears to have created new XPS instruments faster than XPS experts. Indeed, a recent paper suggested that about 40% of the XPS peak fitting reported in the scientific literature is deeply flawed (see *J. Vac. Sci. Technol. A***2020**, *38*, 061204). An anecdotal report suggests that the XPS peak fitting in submitted manuscripts is even worse. In this talk, we discuss some of the efforts that are being made to address the reproducibility crisis in science vis-a-vis XPS and surface analysis in general. These efforts include a collection of guides on XPS that was recently published in JVST, a second set of guides to JVST that is currently accepting submissions, a set of guides being written to Applied Surface Science Advances that is also currently accepting submissions, and 'XPS Insight Notes' that will be accepted by Surface and Interface Analysis. These latest two sets of guides will accept papers on any surface analytical technique. It is hoped that by providing useful guidance on XPS and other surface analytical methods, these efforts will improve the quality of data collection and analysis that is appearing in the surface literature. This talk will also discuss common errors in XPS peak fitting in the literature and ways to fix them.

10:40am **AS+LS+RE+SS-MoM-8 Study of Surface Oxides on $Pt_3Ni(111)$ and $Pt_3Co(111)$ using Ambient Pressure XPS**, ***Bongjin Simon Mun****,* Gwangju Institute of Science and Technology, Republic of Korea **INVITED**

Utilizing AP-XPS, the surface chemical states of $Pt_3Ni(111)$ and $Pt_3Co(111)$ is examined under CO oxidation condition. Under elevated oxygen pressure, the presence of surface segregation of transition metals is clearly observed in AP-XPS. Also, with AP-STM, the formations of nanostructured transition-metal oxides are confirmed during the segregation. As CO oxidation occurs, the interfacial oxygens on the nanostructured metal oxides display unique chemical reactivity. Difference between Pt_3Ni and Pt_3Co alloys surface will be presented.

11:20am **AS+LS+RE+SS-MoM-10 Probing the Oxidation Chemistry of TRISO Nuclear Fuels Using Depth Profiled XPS and Ambient Pressure XPS***, **Jeff Terry,*** Illinois Institute of Technology

While the use of TRISO fuels has been long postulated within High Temperature Gas Reactors, an additional use is possible as an accident tolerant fuel in Light Water Reactors (LWRs). Before TRISO fuels can be used in LWRs, the corrosion properties of the different layers of TRISO fuels must be well understood. Photoelectron Spectroscopy (PES) has long been utilized to study the oxidation behavior of materials due to its sensitivity to both element and chemical state. The problem with (PES) has been that it has historically been an technique that required Ultrahigh Vacuum conditions for measurements. This made it difficult to study corrosion in situ. New instruments have expanded the capabilities of PES. It is now possible to measure photoemission spectra at ambient pressure. We have measured the in situ corrosion of a SiC layer grown as a TRISO simulant at a pressure of 1 mbar of H_2O at temperatures of 500 C using an ambient pressure photoemission system. In addition, we have grown multilayer SiC/ZrN/C systems designed to protect the environment from silver release. We will report on the corrosion chemistry of the SiC, ZrN, and C layers as measured using ambient pressure photoemission. Finally, We can also compare this to samples oxidized under high pressures of water and then measured with sputter-depth profiled conventional XPS measurements. These measurements help us to understand the potential failure modes of accident tolerant nuclear fuels.

11:40am **AS+LS+RE+SS-MoM-11 Environmental X-ray Photoelectron Spectroscopy Study of Catalyst-Ionomer Interactions in Polymer Electrolyte Membrane Fuel Cells***, **Jayson Foster**, S. Zaccarine, M. Dzara,* Colorado School of Mines, USA*; C. Baez-Cotto,* National Renewable Energy Laboratory*; S. Kim,* Colorado School of Mines, USA*; M. Batool, J. Jankovic,* University of Connecticut*; M. Ulsh, S. Mauger,* National Renewable Energy Laboratory*; S. Pylypenko,* Colorado School of Mines, USA

Proton exchange membrane fuel cells (PEMFCs) are an important technology providing on-demand energy without contributing to greenhouse gases. High demand for this technology requires scaled-up fabrication of PEMFC catalyst layers (CLs), thus motivating studies that relate catalyst chemistry and morphology to processing parameters and performance characteristics. Currently, interfacial interactions between catalyst and ionomer are not well understood fundamentally, including the evolution of this interface under humidified conditions.

Environmental X-ray photoelectron spectroscopy (EXPS) is a highly surface-sensitive technique primed to provide information into the surface properties of CLs and further improve understanding of interfacial interactions among the catalyst, support, and ionomer. Although Nafion ionomer is inherently susceptible to X-ray degradation, XPS can be used effectively through a modified acquisition strategy developed previously in our group. In this work, EXPS was used to probe CLs using a series of electrodes prepared by a Mayer rod coating method. The catalyst-ionomer interface was investigated as a function of carbon support material, loading of the Pt catalyst on the support, and ionomer content in the catalyst ink. Surface information was acquired using *ex situ* and *in situ* XPS to emphasize this technique's capabilities at probing ionomer interactions and their evolution in a humidified environment. Scanning transmission electron microscopy (STEM) was used to visualize distribution of Pt nanoparticles on support, relating catalyst and support properties to their surface behavior while integrated with ionomer. Furthermore, scanning electron microscopy (SEM) and STEM imaging in combination with energy-dispersive X-ray spectroscopy (EDS) mapping of electrode cross-sections were utilized to visualize distribution of ionomer and Pt in the CL to further assist with interpretation of EXPS data. Results from this dataset emphasize the strength of this technique to study complex interfaces in PEM catalyst layers motivating further work expanding to other catalysts and ionomers.

Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES*, David Cant,*** National Physical Laboratory, UK **INVITED**

‘Soft’ x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from ‘soft’ XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of ‘soft’ XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a ‘universal’ calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES*, Thierry Conard*,** *A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as TiN/HfO_2/SiO_2/Si as well as more complex stacks such as TaN/TiAl/TiN/HfO_2/SiO_2/Si or W/TiN/HfO_2/SiO_2/Si. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

References

[1]https://www.ulvac-phi.com/en/products/xps/quantes/

[2]https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument

[3]https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab

2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability**, *P. Dietrich,* ***Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

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 a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable**, *S. Coultas, J. Counsell,* Kratos Analytical Limited, UK; ***Christopher Moffitt,*** Kratos Analytical Inc.; *C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the “tool”. In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable

– delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***, Alberto Herrera-Gomez, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

[1] D. Cabrera-German, G.-B. Dulce-Maria, M. Mayorga-Garay, O. Cortazar-Martinez, J.-A. Torres-Ochoa, A. Carmona-Carmona, A. Herrera-Gomez, Peak and background parameters of the 2p core level of the pure first row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[2] D.-M. Guzman-Bucio, A. Carmona-Carmona, M.A. Gonzalez-Reyna, A. Herrera-Gomez, Peak and background parameters of the 3d core level of the pure second row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[3] A. Herrera-Gomez, D. Cabrera-German, A.D.A.D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, L. Gomez-Muñoz, L.G.M. Herrera-Gomez, Alberto., Dagoberto Cabrera-German., Anthony D. Dutoi., Milton Vazquez Lepe., Servando Aguirre-Tostado., Piero Pianetta., Dennis Nordlund., Orlando Cortazar-Martinez., Alejandro Torres-Ochoa., Oscar Ceballos-Sanchez., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. https://doi.org/10.1002/sia.6364.

[4] J.E. Castle, a. M. Salvi, Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 19 (2001) 1170. https://doi.org/10.1116/1.1378074.

4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide “fractional composition vs ion dose” profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the “fractional composition” profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***, **David Morgan**,* Cardiff University, UK

As XPS systems become ever more user-friendly, with “load-point-click-report” type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

[1] L. Edwards, P. Mack and D. J. Morgan, “Recent advances in dual mode charge compensation for XPS analysis”. Surface and Interface Analysis, 51 (2019) 925-933

[2] R. McLaren, G. Owen and D. J. Morgan, “Analysis Induced Reduction of a Polyelectrolyte”, Results in Surfaces and Interfaces, (2021) 100032

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4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed**,* National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene’s inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 “Surface Chemical Analysis”.

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Applied Surface Science Division
Room 320 - Session AS+LS+RE+SS-TuM

Synchrotron-Based Photoelectron Spectroscopy Studies of Technologically Important Materials: in Memory of David Shirley

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Eric L. Shirley**, National Institute of Standard and Technology

8:20am **AS+LS+RE+SS-TuM-2 Limitations in the Structural Determination of a Close-Packed Overlayer*, JG Tobin,*** U. Wisconsin-Oshkosh

The close-packed metal overlayer system c(10x2)Ag/Cu(001) has been the subject of extensive electronic structure studies. These include the examination of the two dimensional behavior at low coverages, the development from two- to three-dimensionality and the convergence to three-dimensional dispersion as in Ag(111). It would be of use to have a firmer picture of the placement of the first monolayer Ag atoms ($d_\perp$) versus the Cu(001) substrate. However, it will be demonstrated with FEFF that there are fundamental limitations to the extraction of that information with photon-induced electron diffraction. [1,2]

1. Part of the JVSTA Commemorative Volume of the Career of David A. Shirley

2**.** J. G. Tobin**,** "Limitations in the Structural Determination of a Close-Packed Overlayer,"J. Vac. Sci. Tech. A **39**, 063203 (2021), https://doi.org/10.1116/6.0001320.

8:40am **AS+LS+RE+SS-TuM-3 Sub-Micron Chemical Speciation Mapping of Uranium Dioxide Aged Under Humid Conditions*, David Shuh,*** *A. Ditter, J. Pacold,* Lawrence Berkeley National Laboratory (LBNL)*; Z. Dai, L. Davison,* Lawrence Livermore National Laboratory*; D. Vine,* Lawrence Berkeley National Laboratory (LBNL)*; S. Donald, B. Chung,* Lawrence Livermore National Laboratory **INVITED**

The oxidation of uranium is a critically important process across a variety of fields. It is a key component to understanding the nuclear fuel cycle, the fate and transport of uranium in the environment, and important signatures for nuclear forensics investigations. At room temperature, the humidity of the environment is more important to oxidation than the oxygen content of the atmosphere, so understanding the uranium oxidation can offer important insights into the provenance of a specimen. The scanning transmission X-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2 is an instrument capable of chemical speciation mapping below the micron scale. Uranium oxide powder was allowed to age and agglomerate at 98% relative humidity for 378 days, then a focused ion beam (FIB) was used to section a thin slice of this agglomeration for study at the ALS STXM. Results at the oxygen K-edge and uranium N_5-edge identify a bulk, UO_2 phase and an interfacial, schoepite phase, located in distinct regions of the sample. A modified non-negative matrix factorization (NMF) method was used to separate out the primary spectral components and identify these two phases, along with a surface phase which is suspected to be water adsorbed to the surface of the sample. Use of the STXM to identify uranium phases, particularly when coupled with FIB sectioning and NMF analysis is a promising method for uranium analysis going forward.

9:20am **AS+LS+RE+SS-TuM-5 On Photoelectron Spectroscopy and the Shirley Background*, Eric L. Shirley,*** NIST **INVITED**

Photoelectron spectroscopy and allied spectroscopies, electron-yield and Auger, provide rich information about occupied and unoccupied electron states in solids. Photoelectron spectroscopy and momentum-resolved photoemission allow one to probe band structure. However, photoemission is also plagued by inelastic losses, which occur because creation of additional excitations in the sample lowers a photoelectron's kinetic energy, usually manifested in the form of "satellite peaks." This can be a nuisance in some cases, because complicated interpretation is required when analyzing photoelectron spectra, but it also affords insight into the additional excitations. Background subtraction, such as is done using, say the "Shirley background," is one method used distill spectral features. Measuring electron-yield versus photon energy can be an excellent method for obtaining x-ray absorption spectra, and this can be accomplished using the same electron analyzers as for photoemission. Auger spectroscopy is also feasible using such analyzers, and the small angular acceptance of many current analyzers at hard-x-ray photoelectron spectroscopy (HAXPES) beamlines provides Auger spectroscopy with additional insight into unoccupied states, as will be shown. In this talk, we will survey theoretical treatments applied in connection with many of the above spectroscopies, discussing both insights gained and the treatments' limitations.

11:00am **AS+LS+RE+SS-TuM-10 Origin of the Complex Main and Satellite Features in Oxides*, Paul S. Bagus,*** University of North Texas*; C. Nelin, C. Brundle, B. Crist,* Consultant*; N. Lahiri, K. Rosso,* PNNL **INVITED**

The assignment of the complex XPS features of the cations in ionic compounds has been the subject of extensive theoretical work. However, there are strong disagreements, even for the origin of the main peaks, [1-2] and the agreement with experimental observations remains insufficient for unambiguous interpretation. In particular, previous cluster model treatments were not able to properly describe the satellite features for the cation XPS. Here we present a rigorous *ab inito* treatment of the main and satellite features in the cation 2p XPS of Fe_2O_3 and NiO which resolves this problem and provides a comparable treatment of both main and satellite features. This has been possible based on a new method for the selection of orbitals that are used to form the ionic wavefunctions. This method is a state averaging of the optimized orbitals over a mixture of normal and shake configurations. The normal configurations have only an electron removed from the cation 2p shell and the shake configurations include, in addition, an electron moved from orbitals of dominantly O(2p) character into the partly filled orbitals of dominantly cation 3d character. Previous cluster model XPS studies had used orbitals optimized only for the normal configuration. [1-2] Thus, for the first time, it is possible to have a set of orbitals that can describe, with comparable accuracy, both the normal and shake configurations. [3] This is especially important since, both in the states for the main and for the satellite XPS features, the normal and shake configurations can, and often do, mix. Thus, comparable accuracy is necessary to have proper descriptions of the ionic final states. It is also important that the character of the ionic states in terms of the occupations of the open shell core and valence orbitals and of the contributions of $2p_{1/2}$ and $2p_{3/2}$ ionization to the XPS intensities have been also determined. Thus, we are able to resolve the ongoing disagreement for the assignment of some regions of the spectra to normal configurations and other regions to shake, or charge transfer, configurations. This is possible because the theoretical treatment, based on cluster models of the oxides, allows us to obtain a detailed level of information about the character of the ionic configurations.

1. P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).

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3. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, Phys. Chem. Chem. Phys. **24**, 4562 (2022).

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis**, S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^3H) and lithium isotope (^6Li, ^7Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy***, A. Siebert, K. Goodman,* ***Monika Blum,*** LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020. [2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room 318 - Session LS1+2D+AS+EM+QS+SS-TuA

Operando Catalysis and Energy Systems

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **LS1+2D+AS+EM+QS+SS-TuA-1 In-situ/Real-time XPS Study of Electrochemical Reactions in All-solid-state Thin-film Lithium-Ion Batteries***,* ***Takuya Masuda,*** National Institute for Materials Science, Japan **INVITED**

All-solid-state lithium-ion batteries (ASSLIBs) are one of the most promising next generation rechargeable batteries because of their very high safety and reliability. Understanding of the mechanism of electrochemical reactions and related physicochemical phenomena is very important for improving cell performances and durability. Application of ex-situ techniques to multiple samples disassembled from cells after certain charge/discharge cycles often results in misinterpretation due to the variation of samples and undesired side effects during sample transfer between battery test environment and characterization apparatus. Thus, various in-situ techniques which can be applied to the same position of the same sample kept at a certain charge/discharge state have been developed for hierarchical understanding of a series of electrochemical events interplaying with each other. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the composition of reaction products, chemical state, and electronic structure of sample surfaces. By tuning the energy of incident x-rays, it also enables us to conduct the depth-resolved analysis of surfaces and interfaces including those buried with solid thin films. Recently, we developed an in-situ XPS apparatus equipped with a bias application system and a vacuum suitcase for sample transfer,[1] and applied it to the electrochemical lithiation/delithiation reactions of an amorphous Si thin film electrode sputter-deposited on a solid electrolyte sheet.[2] The chemical state of Si electrode changing during lithiation/delithiation processes was successfully tracked by sequential XPS measurements in the regions of Li 1s, C 1s, O 1s, and Si 2p. Not only lithium silicide (Li_xSi) which reversibly responds to the lithiation/delithiation but also irreversible species such as lithium oxides, lithium silicates and lithium carbonates were formed due to the lithiation of the Si electrode. Moreover, a rapid spectral change attributable to the phase transition of a crystalline Li_xSi to an amorphous phase was observed in the successive delithiation after preceding lithiation up to certain level. Based on the state of charge, Li content x in Li_xSi, and positions of XPS peaks, we summarized the lithiation/delithiation mechanism in Si electrodes. Further details will be presented.

[1] R. Endo, T. Ohnishi, K. Takada, T. Masuda, Journal of Physics Communications, 2021, 5, 015001.

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3:00pm **LS1+2D+AS+EM+QS+SS-TuA-3 Interaction of Molecular Nitrogen with Vanadium Oxide in the Absence and Presence of Water Vapor at Room Temperature: Near-Ambient Pressure XPS***, S. Nemsak,* Lawrence Berkeley National Laboratory*;* ***Kabirat Balogun****, P. Chukwunenye, T. Cundari, P. Bagus, J. Kelber,* Department of Chemistry, University of North Texas

Interactions of N_2 and H_2O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N_2/H_2O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N_2 partial pressures between 10^{-9} Torr and 10^{-1} Torr using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N_2-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N_2 and equal pressures of N_2 and H_2O vapor, up to a N_2 partial pressure of 10^{-1} Torr. In the absence of H_2O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10^{-9} Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of equilibrium with gas phase N_2. In the presence of equal pressures of N_2 and H_2O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10^{-1} Torr N_2 partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N_2-surface binding in the absence of N_2 overpressure are consistent with N_2 binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N_2/H_2O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to "shake" and normal transitions at 401 eV and 398.7 eV, respectively, for N_2 bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N_2 pi* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N_2 -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

Acknowledgement:

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No. DE-AC02-05CH11231. Work at UNT was supported in part by the NSF through grants DMR-2112864 (JAK, TRC), and via NSF support for the UNT CASCaM HPC cluster via Grant CHE-1531468. PSB was supported by the Geosciences Research Program, Office of Basic Energy Sciences, U.S. DOE through its Geosciences program at PNNL.

3:20pm **LS1+2D+AS+EM+QS+SS-TuA-4 Catalysts Caught in the Act: an Operando Investigation of Copper during CO_2 Hydrogenation***,* ***Elizabeth Jones,*** University of Oxford, UK

Amongst the foremost challenges in mitigating global warming are replacing fossil fuels with renewable alternatives, and storing/using carbon captured from CO2-emitting processes. Methanol production by CO2 hydrogenation promises a possible solution to both of these issues, particularly if H2 can be obtained through water electrolysis. When the resulting methanol is used as a fuel an equivalent amount of CO2 is released making it a “net-zero” fuel alternative. CO2 hydrogenation is performed industrially using a CO2/H2 mix at 200-300oC, 50-100 bar with a Cu-based catalyst, and the addition of CO is known to increase the methanol yield. However, mechanistic understand of this reaction and the role played by CO remains limited. Soft X-ray spectroscopies can provide details on the chemical state of copper to uncover the chemistry behind this reaction, however the typical requirement for measurement under high vacuum constrains how realistic these studies can be. There has been much recent development on improving operando techniques to enable heterogeneous catalytic reactions to be studied under realistic pressure conditions (E. S. Jones et al., in Ambient Pressure Spectroscopy in Complex Chemical Environments, 2021, ACS Symposium Series, vol. 1396, ch. 8, 175-218). A promising approach is to use an environmental cell which encloses the desired gas and separates it from the high vacuum environment, using an X-ray transparent window (R. S. Weatherup, J. Phys. Chem. Lett., 2016, 7, 1622-1627).

Using a custom-designed high pressure environmental cell we have studied model Cu catalysts using operando NEXAFS in total electron yield mode up to pressures of 1 bar and temperatures of 200oC. A thin Cu film was deposited onto a Si3N-4 membrane which acted to seal the high pressure gas within the cell and as a transparent window for incident X-rays. The aim of the study was to investigate how the Cu oxidation states varied when exposed to H2 and CO2 in different sequential order and how the introduction of CO can further influence the chemical state of Cu. It was found that H2 can provide a protective barrier to oxidation from CO2 when dosed first, however if H2 was added after CO2 it is unable to return the surface to its metallic state where CO is then required for reduction. This offers an insight into why CO plays an important role in the industrial production of methanol. Additionally, advances in sealing of the environmental cell enabled high pressures to be achieved at elevated temperatures, allowing this approach to be extended to more industrially-relevant conditions.

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic

Room 318 - Session LS2+2D+AS+TF-TuA

Role of Defects in Materials

Moderator: Takuya Masuda, National Institute for Materials Science, Japan

4:20pm **LS2+2D+AS+TF-TuA-7 Visualizing Complex Many-Body Phenomena in 2D Materials Based Heterostructures and Devices***, **Jyoti Katoch**,* Carnegie Mellon University **INVITED**

Two-dimensional (2D) materials offer the freedom to create novel condensed matter systems, with unique properties, by mechanically assembling different (or same) 2D materials layer-by-layer to form atomically sharp vertical or lateral heterostructures. The van der Waals (vdW) heterostructures with small lattice mismatch and a relatively small twist angle between the constituent layers, have shown to exhibit coexisting complex phases of matter including Mott insulating state, superconductivity, bound quasiparticles, and topological states. The advent of the state-of-the-art angle-resolved photoemission spectroscopy with high spatial resolution (micro- and nano-ARPES) and the ability to perform these measurements on fully functional devices, has made it possible to directly probe many exotic physical phenomena in 2D based material systems. In this talk, I will discuss the utilization of the nanoARPES to investigate the highly tunable many-body effects in 2D based heterostructures and their devices.

5:00pm **LS2+2D+AS+TF-TuA-9 Dynamic Grating Development for Neutron Imaging Across Multiple Length Scales***, **Sarah M. Robinson**, R. Murphy, J. LaManna, C. Wolf,* National Institute of Standards and Technology (NIST)*; Y. Kim, M. Daugherty,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; M. Huber, P. Bajcsy, P. Kienzle, K. Weigandt, D. Hussey, N. Klimov,* National Institute of Standards and Technology (NIST)

Current neutron scattering techniques can provide sample structural information on the length scales of nano- to micrometers, but it is challenging to investigate the hierarchical structures found in non-homogeneous samples. We are developing a far-field grating interferometer (INFER) to nondestructively study the microstructures of samples averaged over a voxel size of 50 µm. In order to perform far-field neutron interferometry across multiple length scales, a large number of source grating periods are used to multiplex the signal and impart the required transverse quasi-coherence. To eliminate the need of fabricating, installing, and aligning a new static source grating for each period, we have developed a DynAmic ReconfIgUrable Source grating (DARIUS). DARIUS is a wafer-scale silicon microfluidic device that allows for the real-time adjustment of the grating period, ranging from 20 µm to 20,000 µm, with the potential to replace more than 500 static source gratings. In DARIUS, each of 5,000+ individual grating channels can be selectively infilled with a neutron and x-ray absorbing fluid to modulate the neutrons, creating an absorbing grating with an effective period based on the locations of the opaque fluid. A key part of DARIUS is a diffraction grating layer fabricated on a 100 mm Si wafer. In this layer, the grating channels are etched in silicon with period of 20 µm and depth of 125 µm, corresponding to a channel volume of enough fluid to locally attenuate the neutron beam. We have previously demonstrated that we can selectively fill 128 active channels with x-ray absorbing solution and, with that, modulate in real time an x-ray beam. Our next prototype, DARIUS-2.0, has an active area of 40.96 mm x 51.20 mm with 2,560 active channels on a single side of a 100 mm Si wafer. The channels are sealed by wafer-scale eutectic bonding to a capping wafer with vias for well and pumping port access. We will present results on initial testing of DARIUS-2.0 with x-ray imaging and progress on scaling up to a double-sided grating device to be incorporated in INFER to unlock the ability of analysis over a wider range of length scales.

5:20pm **LS2+2D+AS+TF-TuA-10 Dynamics, Stability and History-Dependence of Magnetic Skyrmions in the 2D van der Waals Magnets Fe$_x$GeTe$_2$***, **Kai Litzius**, M. Birch, L. Powalla, S. Wintz,* Max Plank Institute for Intelligent Systems, Germany*; M. Weigand,* 4Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany*; K. Kern, M. Burghard, G. Schutz,* Max Plank Institute for Intelligent Systems, Germany **INVITED**

Recently, the combination of 2-dimensional (2D) magnetism [1] with the field of spintronics, i.e. the manipulation of magnetic states with electric currents, has started to gain much traction in modern solid-state physics. The prospect of highly efficient low-dimensional devices, extreme ease to fabricate versatile heterostructures by stacking of separate individual layers, and the report of chiral topological magnetic solitons in 2D itinerant ferromagnets have further enhanced the field's interest in this fascinating class of materials. Requirements for technological implementation, however, are generally to realize both the fabrication of nanoscale devices and to understand different potential ways to tailor the material parameters and ferromagnetic ordering temperatures [2,3] in desirable ways.

In this work, we utilize real-space imaging of the magnetic texture in thin flakes of the van der Waals magnets Fe$_x$GeTe$_2$ to determine magnetic phase diagrams of various exfoliated films with varying compositions. We furthermore realize devices for local injection of skyrmions by means of vertical nanocontacts. Our findings show besides complex, history-dependent magnetization states also that changes in the composition and crystalline structure significantly alter the magnetic behavior and may be used to tune the stability of skyrmions or other magnetic textures in these novel magnetic systems. Ultimately, the choice of composition and nucleation mechanism result in a selective stabilization of a variety of (meta-) stable magnetic configurations. Especially individual skyrmions can then be injected by targeted current pulses through a nanocontact. Our findings open novel perspectives for designing van der Waal heterostructure-based devices incorporating topological spin textures.

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New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic
Room Ballroom A - Session LS-TuP

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Poster Session

LS-TuP-2 Synchrotron Hard X-Ray Scattering for Investigation of ALD Processes*, **Jeffrey Woodward**,* U.S. Naval Research Laboratory*; P. Myint, B. Jiang,* Boston University*; X. Zhang,* University of Vermont*; C. Wang, K. Ludwig,* Boston University*; R. Headrick,* University of Vermont*; S. Rosenberg,* U.S. Naval Research Laboratory*; K. Evans-Lutterodt, L. Wiegart, A. Fluerasu, R. Li, M. Fukuto,* Brookhaven National Laboratory*; C. Eddy,* U.S. Naval Research Laboratory

In recent years, synchrotron hard x-ray scattering has been increasingly utilized for *in situ* studies of atomic layer deposition (ALD) processes [1-3]. In addition to being non-destructive, sensitive to nanometer or sub-nanometer scale changes in topography or crystal structure, and providing statistical information averaged over large regions of the sample, hard x-rays are capable of penetrating the harsh process environments which preclude the use of techniques such as reflection high energy electron diffraction that are commonly used to monitor thin film growth by other methods. These advantages, combined with the high brilliance of synchrotron radiation available at modern light sources, enable the investigation of ALD growth kinetics and material properties as they evolve in real-time. This is particular useful for understanding plasma-enhanced ALD (PEALD) processes, as the plasma plays a complex role in providing both energy and reactive species through various reaction pathways, which can produce significant differences in growth behavior depending on the plasma properties.

We present an overview of various applications of synchrotron hard x-ray scattering which enable new fundamental insights into ALD processes. For each case, we highlight our studies of III-nitride semiconductor growth by PEALD conducted at National Synchrotron Lightsource II. We first discuss grazing incidence small-angle x-ray scattering (GISAXS), a highly surface sensitive technique for probing in-plane topography which is especially useful for monitoring the real-time evolution of surface islands. Next, we discuss x-ray photon correlation spectroscopy (XPCS) in a GISAXS geometry to investigate time-correlated local fluctuations about the average kinetics, or dynamics, which is made possible by utilizing a highly coherent x-ray beam. We then discuss scattering for greater incident angles, where intensity oscillations at the specular spot provide real-time information on layer thickness and surface roughness. Finally, we discuss *ex situ* grazing incidence wide-angle x-ray scattering (GIWAXS), which enables the rapid mapping of large regions of reciprocal space corresponding to interatomic distances, and is thus an extremely powerful characterization method for the myriad polycrystalline, phase change, and mixed-phase materials of interest to the ALD community.

[1] J.M. Woodward *et al*., J. Vac. Sci. Technol. A **37**, 030901 (2019)
[2] N. Nepal *et al*., J. Vac. Sci. Technol. A **37**, 020910 (2019)
[3] J. Dendooven *et al*., Nat. Commun. **8**, 1074 (2017)

LS-TuP-3 High Energy X-Ray Photoelectron Spectroscopy of COTS Electronics Interfacial Failure Modes*, **Samantha G. Rosenberg**, M. Meyerson, M. Kottwitz,* Sandia National Laboratories*; R. Rajendran,* Georgia Institute of Technology*; M. Reingold, B. Young,* Sandia National Laboratories*; P. Singh, J. Kacher,* Georgia Institute of Technology*; J. Fowler,* Sandia National Laboratories

The increasing complexity and miniaturization of electronics have driven demands to lean heavily on commercial off the shelf (COTS) electronics parts. COTS part defects are typically stochastic, making root cause identification challenging when failures occur. This study aims to identify a novel characterization scheme which can uncover fundamental relationships between interfacial material defects and chemical and physical phenomena which drive ultimate failure of COTS parts in relevant field environments. We first apply accelerated stress testing in corrosive environments using salt-fog chambers and environmental chambers to identify marginal or defective parts and then characterize these parts to identify corresponding (electro)chemical phenomena. Characterization includes studying the local electric field around the parts with scanning vibrational electrode technique (SVET) and examining latent and emerging defects in the COTS parts using in-situ liquid cell transmission electron microscopy (in-situ TEM) to correlate and predict interfacial material properties with electrochemical phenomena in relevant field environments. HAXPES will then allow for identification of subsurface chemistry related to metal migration, metal precipitate, and corrosion product formation due to exposure in various accelerated aging experiments performed before beamtime exposure using the aforementioned techniques.

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LS-TuP-4 Insitu AFM Imaging of the Structural and Morphological Evolution of Epitaxial $LiCoO_2$ Films during Charge and Overcharge*, **Yingge Du**,* Pacific Northwest National Laboratory*; W. Samarakoon,* Oregon State University*; J. Hu, L. Wang,* Pacific Northwest National Laboratory*; Z. Feng,* Oregon State University*; J. Tao,* Pacific Northwest National Laboratory

Capacity decay of layered cathodes in high voltage applications underscores the need to utilize accurate and precise techniques to understand the underlying mechanisms. Here, we use well-defined epitaxial $LiCoO_2$ (LCO) films on $SrRuO_3/SrTiO_3$ (SRO/STO) with controlled orientations and defect structures along with *in situ* electrochemical atomic force microscopy to probe the structural and morphological evolutions during the charge and overcharge processes. We quantitatively show the morphological changes in both reversible delithiation regime and irreversible over-delithiation regime, and correlate the overall electrochemical behaviors to atomic scale defect evolutions in the films. We also observe a significantly lower charging capacity for LCO/SRO/STO(111) compared to that of LCO/SRO/STO(001) films of the same thickness, which is ascribed to the different types of atomic scale defects formed during the film growth process.

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+LS+MI-WeM

Magnetism, Electron Correlation, and Superconductivity in the Actinides/Rare Earths

Moderators: James G. Tobin, University of Wisconsin-Oshkosh, **Ladislav Havela**, Charles University, Czech Republic, **Gertrud Zwicknagl**, Technical University Brauschweig, Germany

8:00am **AC+LS+MI-WeM-1 The Relation between Crystal Chemistry and Superconductivity in Actinide-Based Superconductors***, **Eteri Svanidze,*** Max Plank Institute, Dresden, Germany **INVITED**

Crystallographic features play an important role in the physical and chemical properties of a given solid-state material. In particular, actinide-based systems exhibit a wide range of properties – from unconventional superconductivity to peculiar magnetic orders. In this talk, I will highlight some of the old and new actinide-based superconductors, in which a delicate interplay between chemistry and physics is observed. A comprehensive characterization of properties of UBe_{13} has revealed a deep interrelation between the physical and chemical features. Notably, single crystals of this material tend of include many defects which have a dramatic effect on superconducting state [1]. Motivated by this issue, an alternative method of studying intrinsic properties is investigated [2-4]. By creating a micro-scale device, it is possible to measure intrinsic superconductivity of UBe_{13}, whichhas so far remained out of reach [4]. The properties of UBe_{13} are compare to those of other actinide-based superconductors – UTe_2 [5] and $Th_4Be_{33}Pt_{16}$ [6] – in which a strong coupling of lattice and superconducting properties is observed. By studying these systems, it is possible to expand the understanding of crystal chemistry of solid-state materials, while simultaneously providing an insight into which crystallographic parameters impact the physical properties of a given solid-state material.

[1] A. Amon *et al.*, “Tracking aluminium impurities in single crystals of the heavy-fermion superconductor UBe_{13},”*Sci. Rep.***8**, 10654 (2018)

[2] E. Svanidze *et al.*, “Revealing intrinsic properties of UBe_{13}”, *in preparation* (2022)

[3] A. Amon *et al.*, "Interplay of atomic interactions in the intermetallic semiconductor Be_5Pt", *Angew. Chem. Int. Ed.***58**, 2 (2019).

[4] I. Antonyshyn *et al.*, "Micro-scale device - an alternative route for studying the intrinsic properties of solid-state materials: case of semiconducting TaGeIr", *Angew. Chem. Int. Ed.***59**, 2 (2020)

[5] E. Svanidze *et al.*, “Intrinsic crystal structure of UTe_2”, *in preparation* (2022)

[6] P. Kozelj *et al.*, “A noncentrosymmetric cage superconductor $Th_4Be_{33}Pt_{16}$”, *Sci. Rep.***11**, 22352 (2021)

8:40am **AC+LS+MI-WeM-3 Revealing The Beauty of Uranium Compounds:the UMB_4 (M=V, Cr, Fe, Co, Mo, W, Re, Os) and UFe_xSb_2 Cases***, **Antonio Pereira Gonçalves,*** Instituto Superior Técnico, Univ. Lisboa, Portugal **INVITED**

Uranium-based phases with d-metals show a vast and rich variety of physical properties, some of them unique, which are mainly driven by the large 5*f* spin-orbit coupling and the degree of delocalization of the 5*f* states. The understanding of such behaviors is critical for the advance of Solid State Sciences and can lead to the discovery of new phenomena and ground states. In this talk, examples of uranium compounds with unusual properties are presented, the focus being on UMB_4 materials and UFe_xSb_2 alloys.

UMB_4 (M=V, Cr, Fe, Co, Mo, W, Re, Os) compounds are quite notable, crystallizing in the $YCrB_4$-type (for V, Cr, Fe, Co) and $ThMoB_4$ type (for Mo, W, Re, Os) polymorphs. Both structures are closely related, containing the same number of atoms in the unit cell and similar coordination polyhedral, which allows the comparison of their properties as a function of the d-metal. Their electronic structure is influenced by a strong hybridization between the B-2*p* states and both the *d*-metals *d*-states and the uranium (5*f*) valence band states. This avoids the formation of narrow bands with high density of states at the Fermi level, even if the 5*f*-*d* hybridization is weak, i.e. for late d-metals. Hence, the explored UMB_4 compounds are weak Pauli paramagnets, with a density of states at Fermi level of only ~4 times higher than for α-U. Those crystalizing in the $ThMoB_4$ structure show anomalous lattice vibrations, in particular the presence of low-energy Einstein modes, which can lead to superconducting ground states.

UFe_xSb_2 alloys crystallize in the $HfCuSi_2$ type structure and present a remarkable ground state evolution with Fe concentration. $UFe_{0.5}Sb_2$ shows a non-Fermi liquid behavior, with a change from metallic to semiconductor-upon applying magnetic field. In contrast, $UFe_{0.7}Sb_2$ (and, in a minor scale, $UFeSb_2$), shows an increase in electrical resistivity with decreasing temperature under zero magnetic field, but for high magnetic fields a metallic behavior is established. First principles calculations indicated that in $UFeSb_2$ some bands cross the Fermi level, but they are relatively steep and, as a result, the density of states at Fermi level is low, which supports the semi-metallic character of this composition. In the case of $UFe_{0.5}Sb_2$, a higher concentration of bands at the Fermi level, some of them relatively flat, exist, which cause a sudden step-shaped drop of density of states just above Fermi level. The magnetic field application can raise the Fermi level into the pseudo-gap, which is probably the reason for the change from a metallic-like to a semiconductor-like behavior.

11:00am **AC+LS+MI-WeM-10 Uranium Hydrides Revisited***, **Ladislav Havela,*** Charles University, Faculty of Mathematics and Physics, Czechia*; D. Legut,* VSB Technical University Ostrava, Czechia*; J. Kolorenc,* Institute of Physics, Czech Academy of Sciences, Czechia

Uranium hydrides are not only materials important for understanding of fundamental aspects of actinides. They are also relevant for nuclear technologies as well as for specific hydrogen storage tasks, as e.g. storing of tritium in nuclear fusion devices. Electronic structure of uranium hydrides (α- and β-UH_3, UH_2) reflects two contradictory tendencies. One is a charge transfer from U towards H, the other is a stability of the *f* shell. The latter is illustrated also on the case of rare earth hydrides with anomalous rare earth elements, such as Yb or Eu, which surprisingly retain their lower valence state, i.e. with a higher *f*-occupancy. The transfer is thus realized in U by the 6*d* and 7*s* electrons, which become noticeably depleted, but the 5*f* occupancies remain high. The concomitant reduction of the 5*f*-6*d* hybridization contributes, together with the volume expansion, to pronounced ferromagnetism of the U hydrides with Curie temperatures far above 100 K. We compare individual hydrides described by the GGA+*U* calculations, yielding numbers on the charge transfer or spin and orbital moments, with relevant experimental data. Interesting feature obtained from calculations is that the two different U sites in β-UH_3 have the respective magnetizations non-collinear. The same calculations yield also phonon dispersion relations, which are used to determine the temperature dependence of phonon contribution to heat capacity. The agreement in the paramagnetic range is so good that it allows to determine both the magnetic entropy and changes of the Sommerfeld coefficient between the ground state and paramagnetic state, the latter being twice higher. The position of the U hydrides on the map of localization-delocalization dichotomy will be discussed.

The work was supported by the Czech Science Foundation under the grant No. 21-09766S.

11:20am **AC+LS+MI-WeM-11 Towards a Better Understanding of the Rkky Interaction in Ce- and Yb-Based Compounds: Anisotropies from Cef Effects and Fermi Surfaces***, **Gertrud Zwicknagel,*** Institut für Mathematische Physik, Germany*; V. Zevin,* The Racah Institute of Physics, Israel

We calculate the influence of Crystalline Electric Field (CEF) effects and the Fermi surface topology on the indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange interaction between local 4f moments in Ce- and Yb-compounds. Starting from a periodic Anderson model, we show that the anisotropy of the CEF ground state manifests itself in the anisotropy of the effective exchange coupling constant J(R,R’) between two moments at sites R and R’. If spin-orbit effects among the conduction states can be neglected, the interaction between two Kramers doublets is isotropic in pseudo-spin space. Adopting the Stationary Phase approach, we derive the asymptotic form of the exchange constant for arbitrary Fermi surfaces. We evaluate the anisotropy of the RKKY interaction in tetragonal Ce- and Yb-122 compounds for realistic model bands. The influence of spin-orbit interaction among the conduction electrons is discussed.

11:40am **AC+LS+MI-WeM-12 Mechanically Forced Tuning of Interactions in Tetragonal 221 Intermetallics**, ***Petr Král**, J. Prchal,* Charles University, Czech Republic*; J. Kaštil,* Czech Academy of Sciences, Czech Republic*; D. Daisenberger,* Diamond Light Source, UK*; D. Staško,* Charles University, Czech Republic

Family of R_2T_2X intermetallics adopting the tetragonal Mo_2FeB_2-type crystal structure represents the group of anisotropic systems with potential to exhibit geometrical frustration effects due to the Shastry-Sutherland-like arrangement of *R*-atoms in the aa-planes alternated by usually non-magnetic *T-X* planes along the crystallographic *c*-axis. Crucial for resulting magnetic behavior are the interatomic distances affecting the exchange interactions between individual ions. Especially interesting may be the compounds close to the empirical boundary of crystal structure stability since, based on available data, the lowest observed unit-cell volume among Mo_2FeB_2-type materials is about $V_{\text{f.u.,crit}} = 200$ Å^3.

The unique tool allowing to act directly on the interatomic distances without changes of chemical composition is mechanical pressure. Employing the high-pressure techniques, it is possible to influence all lattice-related physical properties including e.g. the magnetic interactions and electronic structure. Especially in the strongly anisotropic compounds, the hydrostatic pressure effect depends on the compressibility of individual lattice parameters. This is the case, when the uniaxial pressure may represent the opportunity to act selectively in chosen crystallographic directions and thus to provide the insight into the layout of interactions within the crystal lattice.

Herewith, we are presenting the results of systematical study of pressure impact on the R_2T_2X compounds. Special attention is paid to Ce_2Pd_2In considered to be one of the most interesting systems among R_2T_2X family. It represents the rare example of Ce-based ferromagnet, however the ground state is reached through the antiferromagnetic interphase. High sensitivity of magnetic behavior to hydrostatic pressure has been revealed showing the preference of antiferromagnetic phase at lower pressures followed by the Kondo-like anomaly formation and suppression of magnetic ordering at pressures around 4 GPa. Based on the results of high-pressure XRD experiment, the hydrostatic pressure acts more significantly within the basal plane. Indeed, different response to the uniaxial pressure applied along the *c*-axis was observed.

Compounds with the unit-cell volume closest to $V_{\text{f.u.,crit}}$ belongs to the series R_2Cu_2In. Among them the ferromagnets Dy_2Cu_2In (exhibiting the signs of spin-reorientation at lower temperatures) and Tm_2Cu_2In (with signs of spin-glass behavior) were investigated. Concerning the later one, the pressure was found to support the frustration effects responsible for the spin-glass properties as the unit-cell volume tends to reach the $V_{\text{f.u.,crit}}$.

12:00pm **AC+LS+MI-WeM-13 Effects of O_2 Growth Pressure on the Magnetization of $LaMnO_3$-$SrTiO_3$ Thin Films**, ***Ghadendra Bhandari,*** West Virginia University*; R. Trappen,* University of Waterloo*; N. Mottaghi, M. Holcomb,* West Virginia University

Magnetic properties of epitaxial $LaMnO_3$ thin films grown on $SrTiO_3$ substrate have been studied. Thin films are grown at various oxygen pressure using pulsed laser deposition and deposition has been monitored by reflection high energy electron diffraction (RHEED) to verify layer-by-layer growth. Bulk stoichiometric $LaMnO_3$ exhibits A-type antiferromagnetic order, whereas thin films show a ferromagnetic FM phase. Structure and magnetic properties have been characterized by X-ray diffractometry (XRD), X-ray reflectivity (XRR) and vibration sample magnetometry (VSM). The thin films are showing ferromagnetic (FM) phase. Depth dependent magnetization studied by polarized neutron beam reflectivity found that magnetization is higher near interfacial region and a magnetically dead region lies at the surface. We have observed c-lattice correlated magnetization, which is minimized at 30mTorr O_2 pressure.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM

Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples**, ***Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode**, *Y. Wang,* University of Maryland College Park*;* ***Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 $mAcm^{-2}$) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko,*** Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov,*** Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao,** M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+HC+LS+VT-WeM
Multiphase Interfacial Analysis and Imaging

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

8:00am **CA+HC+LS+VT-WeM-1 Probing the Impact of Nanoscale Defect Sites in Perovskite Photovoltaic Films with Time-Resolved Photoemission Electron Microscopy***, **Keshav Dani,*** 1919-1 Tancha, Kunigami-kun, Japan **INVITED**

Hybrid perovskite photovoltaic devices have rapidly emerged as promising contenders for next generation, low-cost solar cell technology. Yet, the presence of defect states critically impacts device operation, including device efficiency and potentially long-term stability. Understanding the nature of these defects, and their role in photocarrier trapping, requires techniques that are capable of probing ultrafast photocarrier dynamics at the nanoscale.

In this talk, I will discuss the development of time-resolved photoemission electron microscopy (TR PEEM) techniques in my lab [1, 2], applied to hybrid perovskite solar materials. Thereby, we directly visualize the presence of the performance limiting nanoscale defect clusters and elucidate the role of diffusion in the charge carrier trapping process [3]. By correlating PEEM measurements with other spatially resolved microscopies, we identify different types of defects that form, and study how passivation strategies may have a varied impact on them [4]. Finally, we show that these defect can act as seeds for degradation [5].

[1] M. K. L. Man, *et al.* Imaging the motion of electrons across semiconductor heterojunctions. *Nature Nanotech.***12**, 36 (2017).

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[3] T. A. S. Doherty*, A. J. Winchester*, et al.Performance-limiting trap clusters at grin junction in halide perovskites. *Nature***580**, 360 (2020). *equal authors

[4] S. Kosar, et al. Unraveling the varied nature and roles of defects in hybrid halide perovskites with time-resolved photoemission electron microscopy. *Energy Environ Sci*. 14, 6320 (2021)

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8:40am **CA+HC+LS+VT-WeM-3 Correlating Structure and Chemistry Using Ambient Pressure Photoemission and X-Ray Scattering***, **Slavomir Nemsak,*** Lawrence Berkeley Laboratory Advanced Light Source **INVITED**

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

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9:20am **CA+HC+LS+VT-WeM-5 Gating of the 2D Hole Transport in Diamond by Subsurface Charges***, E. Strelcov, **Andrei Kolmakov,*** NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based FETs one of the most prospective devices for high-frequency power electronics. Transfer doping of hydrogenated diamond is a common process to form 2D conducting channels in diamond FET. The electron /hole transport of such a device is sensitively dependent on near-surface scatters including charged traps.

Here, using SEM (EBIC) and AFM Kelvin probe force (KPFM) microscopies we report on imaging of the hole transport in narrow conducting channels as a function of the density and depth of near-surface charges. We demonstrate the gating effect induced by trapped charges and discuss the methods to minimize these effects.

9:40am **CA+HC+LS+VT-WeM-6 Development of 0–D Argon Collisional Radiative Model conjoined with Optical Emission Spectroscopy between 1 mTorr to 760 Torr***, **Tag Choi,** N. Abuyazid, D. Patel,* University of Illinois at Urbana-Champaign*; D. Jacobson,* LytEn. Inc*; S. Keniley, S. Dubowsky, D. Barlaz, D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

Optical emission spectroscopy (OES) is a non-invasive plasma diagnostic, which can be utilized with 0-dimensional argon collisional radiative model (Ar CRM) to understand dynamics of excited and charged argon species and determine plasma parameters in the system. This work aims to study rate coefficients of excited and charged argon species, calculate their densities over time and verify the theoretical results with experimental optical spectra in a wide range of pressure regimes. The model considers various types of collisions such as electron and atom excitation/ionization, photon emission, diffusion, penning ionization, and excimer formation. A merit function is used to obtain a better correlation between the theoretical and experimental densities of the various argon species. This allows the model to get a more accurate estimate of the electron temperature and the densities. Various plasma sources are used such as a low pressure inductively coupled plasma (ICP) source, dielectric barrier discharge (DBD), and microwave discharges, to produce different types of plasmas at pressure ranges of 10 – 50 mTorr and 1 – 760 Torr. The optical emission spectra and Langmuir probe measurements are collected for verifications on a low pressure ICP source and DBD discharge. For the verification of atmospheric microwave discharge, OES data is collected for temperature calculations from Specair and the model. Different plasma sources produce different electron temperatures and densities. The ICP source, DBD and microwave discharge have electron temperatures (T_e) of 2 – 5 eV, 1 – 3 eV, and 0.4 – 0.6 eV and electron density (n_e) of 1E16 to 1E18 m^3, 1E18 to 1E21 m^3, and 1E19 to 1E22 m^3 respectively. A methane and argon gas mixture are introduced to the microwave discharge to understand how plasma parameters differ from a pure argon environment.

11:00am **CA+HC+LS+VT-WeM-10 Atomic-Scale Modeling of Bismuth and Argon Clusters Sputtering of Water/Vacuum Interfaces***, **Zbigniew Postawa,** M. Kański, C. Chang, S. Hrabar,* Jagiellonian University, Poland **INVITED**

Modeling of water/vacuum interfaces should consider the high vacuum pressure of water. First, there is continuous evaporation of the liquid into the vacuum chamber, which must be considered. This phenomenon poses a significant challenge for conventional experimental techniques. Yang *et al.* presented a way to reduce the impact of this phenomenon by using a microfluidic channel [1]. This approach uses an ion beam to drill a 2-3 µm window in the channel wall, exposing the liquid flowing below. Such an arrangement allows for maintaining a low base pressure (~10^{-7} mbar) in the measuring chamber. This technique has already been used to study photochemical reactions, biofilms, and liquid-liquid interfaces by secondary ion mass spectrometry or secondary electron microscopy [2]. Recently, another approach minimizing the effect of high vacuum pressure of water that uses a graphene cell encapsulating a liquid was proposed in studies with transmission electron microscopy [3].

Recently, we have developed a new ReaxFF potential parameterization for modeling C/H/O systems designed directly for sputtering simulations [4]. This parametrization is up to 3 times faster than standard ReaxFF. New force-field allowed us to perform molecular dynamics computer simulations of water and graphene-covered water systems sputtered by bismuth and argon clusters. The mechanism of molecular emission from these two systems is investigated. The effect of the projectile size and the influence of the protecting graphene sheet on the emission process is discussed.

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Acknowledgments

The work has been supported by Polish National Science Center Grant 2019/33/B/ST4/01778 and the PLGrid Infrastructure.

11:40am **CA+HC+LS+VT-WeM-12 Finite-Elements Modeling of Solid-Electrolyte Interfaces in Through-Membranes Imaging and in-Liquid Scanning Probe Experiments***, **Alexander Tselev,*** Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal **INVITED**

Studies of the physicochemical processes at the interfaces between solids and electrolytes interfaces require *operando* multi-parametric measurements with chemical and electric potential sensitivity, in-depth selectivity, as well as with a high lateral resolution. A number of experimental techniques were implemented for this purpose. In this talk, we will describe applications of finite-elements (FE) modeling to elucidate and interpret microscopic imaging and measurements with liquids ranging from non-polar ones to decimole electrolyte solutions. This includes probing through graphene membranes with the use of microscopy and spectroscopy tools based on high-energy beams—X-rays and electron beams, as well as low-energy probing with the use of scanning probe techniques. Scanning probe techniques can be implemented both with probes in liquids and with probes separated from the electrolytes by membranes. We will discuss liquid-solid interface probing by the Kelvin probe force microscopy (KPFM) through graphene membranes as well as by near-field microwave microscopy through dielectric membranes. Furthermore, models for piezoresponse force microscopy and KPFM with probes immersed in electrolytes will be presented. Support of this work by the project CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC (Portugal) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement is acknowledged.

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+LS+MI-WeA

Chemistry and Physics of the Actinides/Rare Earths

Moderator: Krzysztof Gofryk, Idaho National Laboratory

2:20pm **AC+LS+MI-WeA-1** ***Novel Preorganized Ligands for Selective and Efficient Separation of f-Elements , Santa Jansone-Popova,*** Oak Ridge National Laboratory **INVITED**

Selective separation of f-elements (lanthanides and actinides) is challenging to realize due to their very similar properties. For example, lanthanides exist predominantly in 3+ oxidation state and their ionic radii decrease across the lanthanide series on average by only 0.01 Angstrom per unit increase in atomic number. Organic molecules (ligands) capable of magnifying these effects and selectively recognizing one element over another are extensively sought after. Implementation of such ligands in separating f-elements would result in substantial cost and energy savings. The neutral organic molecules decorated with at least four donor atoms (oxygens and/or nitrogens), designed to complex with metal ions and that do not undergo conformational change in the process, demonstrate exceptional size selectivity.[1-3] The innate rigidity and size of the cavity in addition to the electronic structure of ligands provide the means to control the selectivity across the trivalent f-element series by design. On the contrary, organic molecules with donor groups that are connected to freely rotating single bonds show high affinity for metal ions that are more Lewis acidic.[4] Superior performance of preorganized ligands in two immiscible solvent system in selectively separating adjacent lanthanides or lanthanides from actinides will be discussed in detail. More specifically, the chemistry of hydrophobic and hydrophilic bis-lactam-1,10-phenanthroline-based ligands having four donor atoms will be presented, focusing on the separation of adjacent lanthanides (e.g., Nd-Pr, Tb-Gd, Ho-Dy) and Americium-Europium pair separation. Additionally, the contrasting performance of rigid ligands decorated with two to four donor atoms will be shown and compared to their non-preorganized counterparts.

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3:00pm **AC+LS+MI-WeA-3 Impact of Noncovalent Interactions on Actinide Structural Chemistry*, Karah E. Knope,*** Georgetown University*; J. Wacker,* Lawrence Berkeley National Lab*; M. Shore,* Georgetown University **INVITED**

Noncovalent interactions (NCIs) have received significant attention over the past several years. This interest is fueled by recent examples that have shown that these interactions, which exist beyond the first coordination sphere of a metal ion, can be used to isolate novel structural units, push chemical equilibria, and tune redox behavior. As illustrated by these examples, it has become clear that consideration of NCIs is important for understanding the overall chemical behavior of a metal ion. Taken together with our group's interest in the factors that govern actinide speciation and reactivity, our recent work has thus focused on the solution and solid-state structural chemistry of actinide complexes and clusters that form from acidic aqueous solution in the presence of heterocycles capable of N-H hydrogen bonding interactions. Specifically, we have examined the identity (i.e. composition, charge, coordination number) of actinide structural units that precipitate from monoanionic ligands systems including Br^{1-}, Cl^{1-}, and NO_3^{1-} with N-heterocycles ranging from pyridinium to terpyridinium. While bromide, chloride, and nitrate all form weak relatively weak complexes with the actinides (Th-Pu), clear effects of NCIs are present only in the chloride ligand system with chloride rich (e.g. $[Th(H_2O)_2Cl_6]^{2-}$) to chloride poor (e.g. $[Th(H_2O)_7Cl_2]^{2+}$) complexes having been observed. By contrast, speciation is much more limited in the Br^{1-} and NO_3^{1-} ligand systems. Presented here will be an overview of our experimental and computational efforts to understand the effects of NCIs on phase formation.

4:20pm **AC+LS+MI-WeA-7 XPS Characterization of a Pu-7at.%-Ga Alloy*, Paul Roussel,*** AWE, UK*; K. Graham, S. Hernandez, J. Joyce, T. Venhaus,* Los Alamos National Laboratory

Gallium is often used in small concentrations (<10 at. %) as an alloying element with plutonium to stabilize the face centred cubic phase.Most XPS analyses of these plutonium materials have focused on low concentration alloys (< 4 at. %) where it is difficult to measure the signal and effects of gallium.Here we report the analysis of a higher alloy concentration of $Pu_{0.93}Ga_{0.07}$ in the as received state, during sputter depth profiling and following oxidation either from the addition of Langmuir quantities of oxygen or the in situ environment of the ultra high vacuum system.Quantification of the spectra has been undertaken by comparison of the elastic peak intensity and this has allowed us to test the recently reported relative sensitivity factors for plutonium [1]. The higher alloying concentration has permitted quantification of gallium in both the metal and oxides and, for the first time, the gallium chemical state plot for both alloy and oxide has been determined along with those of plutonium and oxygen.In addition to this we highlight a novel method to quantify the C1s peak which overlaps with the $Pu5p_{1/2}$ photoemission line and demonstrate the effect of gallium on the in situ oxidation rate of this alloy.

1) P. Roussel, A. J. Nelson, Quantitative XPS of plutonium: Evaluation of the Pu4f peak shape, Relative Sensitivity Factors and estimated detection limits, Surf. Interface Anal. https://doi.org/10.1002/sia.7083.

4:40pm **AC+LS+MI-WeA-8 Nanoscale Uranium Oxide: Correlating Colloidal Synthesis Pathways with Structure at the Atomic and Nanometer Length Scale*, Liane Moreau,*** Washington State University

Nanoscale uranium oxide is of interest for the development of advanced nuclear fuels and its importance in the corrosion of conventional fuel pellets and trends in uranium mobility within environmental systems. Knowledge of nanoscale properties of uranium oxide, however, are limited due to 1) a lack of synthetic methods capable of forming monodisperse actinide oxide nanoparticles and 2) the challenges associated with characterization of complex interfaces. Organic-phase colloidal approaches prove promising towards the synthesis of actinide oxide nanoparticles due to precedence for formation of highly monodisperse transition metal oxide nanoparticles, and the capability to synthesize particles in rigorously air- and water-free environments. Three systems will be discussed which exploit colloidal uranium oxide synthesis. The first explores oxidation kinetics in UO_2 nanoparticles. Synthesis is paired with X-ray diffraction and X-ray spectroscopy to compare nanoparticle oxidation trends with those observed in bulk counterparts under controlled oxidative environments. The second traces the formation mechanism of UO_2 nanoflowers and demonstrates the role of solvent interactions in anisotropic growth. The established growth patterns are particularly interesting as anisotropic growth in transition metal counterparts have traditionally depended on surface binding species and trace impurities rather than solvent chemistry. The third system investigates the deposition of uranium oxide onto iron nanoparticle cores, which serves as an analogue to environmental systems where uranium and plutonium have shown to preferentially bind to Fe-based minerals. The high-surface area particles provide a means to investigate the interface in atomistic detail. In describing the aforementioned systems, X-ray focused approaches and characterization method development will be discussed, which prove critical to resolving structural attributes and making connections between synthetic parameters and resulting atomic and nanoscale structure.

5:00pm **AC+LS+MI-WeA-9 Chemical Speciation Mapping of Spent Nuclear Fuel Using Soft X-Ray Spectromicroscopy at the Advanced Light Source*, Alexander Ditter,*** *D. Smiles, D. Lussier,* Lawrence Berkeley National Laboratory (LBNL)*; A. Altman,* Northwestern University*; M. Bachhav, L. He,* Idaho National Laboratory*; M. Mara,* Northwestern University*; S. Minasian,* Lawrence Berkeley National Laboratory (LBNL)*; C. Degueldre,* Lancaster, UK*; D. Shuh,* Lawrence Berkeley National Laboratory (LBNL)

A nuclear reactor is a complex environment, with high temperatures, large temperature gradients and a multitude of fission products in various states. Spent nuclear fuel offers a key window into this environment, but is an important object of study in its own right, particularly with regards to the release of radioisotopes into the environment. The oxidation of spent nuclear fuel is especially important as this can govern the transport and solubility of fission products. To study this process, a focused ion beam (FIB) was used to make thin sections of a low burnup spent fuel pellet at Idaho National Laboratory. These FIB sections were then measured at the O K-edge, U $N_{4,5}$-edges and Ce $M_{4,5}$-edges at the scanning transmission x-ray microscope (STXM) at Advanced Light Source (ALS) Beamline 11.0.2. O K-edge results were analyzed by a modified form of non-negative matrix factorization and revealed two main components, the bulk of the sample which is made up primarily of UO_2, and a thin (est. 8 nm) layer of UO_{2+x} on the surface of the FIB section. This oxidation occurred after FIB sectioning as a thin layer over the entire sample. Cerium measurements showed that the Ce (~ 0.4 wt. %) is at least predominantly in the 3+ oxidation state, though a small contribution of tetravalent cerium cannot be ruled out, representing the first known measurements of Ce oxidation state in spent nuclear fuel. This work lays the foundations for future STXM measurements of FIB sections of spent nuclear fuel which can be expanded to mixed-oxide, uranium nitride, or other advanced fuels.

5:20pm **AC+LS+MI-WeA-10 Structural, Thermodynamics, and the Electronic Properties of Al, Ga, In, and Tl Stabilized δ-Pu***, **Sajib Barman**, S. Hernandez,* Los Alamos National Laboratory

The 5*f* electrons in plutonium show mystifying character contrary to other elements in the periodic table, where there are six solid state phases of plutonium that undergo five solid-state phase transformations in a relatively short temperature range. The low temperature α-phase is brittle and has a monoclinic structure where the high temperature δ-phase is ductile and has an FCC structure. From a metallurgical point of view, the ductile δ-Pu is mostly important due to its favorable elasticity compared to the brittle α-Pu. Therefore, stabilizing δ-Pu at room temperature can be done by alloying with Group IIIA elements (X = Al, Ga, In, and Tl). Nevertheless, the alloyed δ-Pu stability zones highly depend on the alloying content, where the stability zone decreases with increasing atomic number of the Group IIIA elements. In this work, we will present a systematic density functional theory investigation of the thermodynamic stability of alloyed δ-Pu with Group IIIA elements as a function of alloying content (3.125, 6.25, and 9.375 at. %). We have calculated that the δ-Pu-Ga alloys have the highest thermodynamic stability compared to the other Group IIIA alloys, where the stability trend follows Pu-Ga > Pu-Al > Pu-In > Pu-Tl at 0K. After volume optimization, the volume contracts for Pu-Ga and Pu-Al alloys, while the volume expands for Pu-In and Pu-Tl alloys with increasing alloy content. Finally, we will show the electronic structure analysis to discuss the electronic interaction between Pu and the Group IIIA elements within the δ-matrix.

This work was carried out under Los Alamos National Laboratory's LDRD-DR project #20210001DR.

Applied Surface Science Division
Room 320 - Session AS+CA+HC+LS-WeA

Shining a Light on Surface Chemical Metrology: In Memory of Martin Seah

Moderators: Donald Baer, Pacific Northwest National Laboratory, **Alexander Shard**, National Physical Laboratory, UK

2:20pm **AS+CA+HC+LS-WeA-1 Metrology Lights the Way for Advances in Metabolic Imaging at the Single-cell Scale***, **Ian Gilmore**,* National Physical Laboratory, UK **INVITED**

The international community recently paid homage to Martin Seah in a Special Issue of Surface Interface Analysis [1] with reminiscences, biographical accounts of his considerable achievements, reviews and research articles. The collection takes its title “Shining a light on surface chemical analysis” from Martin’s research career of over 5 decades dedicated to guiding the community to make better measurements in traditional and emerging areas of surface chemical analysis. Where there was darkness, he brought light. Here, we begin with a retrospective look at Martin’s considerable achievements in XPS, AES, SIMS, AFM and leadership in International Standardisation.

Martin was never one for too much retrospection though and was always full of energy and enthusiasm to tackle the issues of tomorrow. We therefore show how by using Martin’s methodology that metrology is lighting the way for metabolic imaging at the single-cell scale, which is of critical importance in the development of new pharmaceuticals, understanding tumour heterogeneity and fundamental biological studies to understand metabolic rewiring in diseases.

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3:00pm **AS+CA+HC+LS-WeA-3 Two-Point Calibration Method for Quantifying Organic Binary Mixtures Using SIMS in the Presence of Matrix Effects***, **Alexander Shard**,* National Physical Laboratory, U.K.*; A. Miisho,* Kobelco, Japan*; J. Vorng, R. Havelund, I. Gilmore,* National Physical Laboratory, U.K.*; S. Aoyagi,* Seikei University, Japan

Quantification of composition for organic mixtures is required in the analyses of technological materials from organic electronics to drug delivery systems. The molecular specificity of secondary ion mass spectrometry provides an unparalleled ability to distinguish organic materials, however it is difficult to use for quantitative analysis. In a few cases, there is a linear dependence between the composition, expressed as a ratio of component volumes, and the secondary ion intensities, expressed as a ratio of intensities of ions from each component. However, this ideal relationship fails in the presence of matrix effects and linearity is observed only over small compositional ranges, particularly in the dilute limits. We present an empirical method which introduces a power law dependence between the intensity ratio and the volume fraction ratio. A physical model of the organic matrix effect is employed to test the limits of the method and a mixed system of 3,3’-bis(9-carbazolyl) biphenyl and tris(2-phenylpyridinato)iridium(III) is used to demonstrate the method. In practice, we describe a two-point calibration, which determines both the exponent in the power law and the sensitivity factor for the conversion of ion intensity ratio into volume fraction ratio. We demonstrate that the two-point method significantly improves the accuracy of quantification compared to a one-point, linear calibration and is valid over a wide compositional range. Since the method enables the use of clearly identifiable secondary ions for quantitative purposes and mitigates commonly observed matrix effects in organic materials, the two-point calibration method could be of significant benefit to SIMS analysts.

3:20pm **AS+CA+HC+LS-WeA-4 OrbiSIMS Metrology: Optimization of Inorganic Depth Profiling using Ge and Sb Delta-layer Samples***, Y. Zhou,* National Physical Laboratory, UK*; A. Franquet, V. Spampinato,* IMEC, Belgium*; A. Pirkl,* IONTOF GmbH, Germany*; W. Vandervorst, P. Van Der Heide,* IMEC, Belgium*; **Ian Gilmore**,* National Physical Laboratory, UK

In 2017, NPL introduced the 3D OrbiSIMS instrument [1] for sub-cellular resolution molecular imaging with high-mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). Since then, IONTOF installed multiple Hybrid SIMS systems around the world with a growing range of applications, largely in, but not limited to, the life-sciences.[2,3] The dual ToF-MS and Orbitrap-MS analyzers combined with Bi liquid metal, gas cluster, and low energy $O_2^+$and Cs^+ ion beams provide a highly versatile platform for materials science studies.

Since the Orbitrap-MS is designed to operate with a continuous ion source, the instrument is well configured to take advantage of single ion beam depth profiling approaches. For example, Sul et al[4] recently demonstrated the ability to sputter depth profile a blue phosphorescent OLED device using GCIB sputtering with Orbitrap-MS. Similarly, Spampinato used the high-mass resolving power of the Orbitrap-MS to study thin EUV photoresist films where ToF-SIMS suffered from severe molecular interferences. [5] Moreover, there is growing interest in the application of the OrbiSIMS to inorganic semiconductors. Franquet et al[6] recently showed how the high mass resolution of the Orbitrap-MS analyzer combined with 2 keV Cs^+ sputtering enabled the composition of SiGe architectures down to < 20 nm to be determined with improved accuracy using the Self Focusing SIMS methodology.[6]

In this study, we use a sample consisting of 8 Ge delta-layers with a spacing of 4.8 nm in a silicon matrix. The thickness of each delta-layer is ~0.2 nm with a concentration of below 1 atom%. A second sample consisting of 5 Sb delta-layers with a spacing of 10 nm in a silicon matrix was also used. A sputter gun using either O_2^+or Cs^+ between 1 keV and 2 keV was used for both sputtering and analysis with Orbitrap-MS detection. The optimization of instrument parameters including sputter rate, injection time and sputter beam energy on the depth resolution ($\lambda_{g,}$ λ_d and Gaussian broadening)[7]will be discussed.

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7. M.G. Dowsett, et al, P.N. Allen, J. Vac. Sci. Technol. B 12 (1994)186.

4:20pm **AS+CA+HC+LS-WeA-7 Complementary Perspectives on the Impacts of Martin Seah on Surface Analysis*, Don Baer,*** Pacific Northwest National Laboratory **INVITED**

Throughout his more than four decade career Dr. Martin Seah had a major impact on quantitative surface analysis and the surface analysis community. There were many facets to his activities, interactions, and leadership and most of those who interacted with him knew only a portion of his many contributions. This talk will describe ways that he impacted my career and some of the activities that may have been less visible to many in the surface analysis community. Accurate quantitative surface analysis was a theme throughout his career. My introduction to his work was associated with measurements of the segregation of trace elements to the grain boundaries of metals and metal alloys.In the 1970s understanding of the challenges to quantitative analysis of electron spectroscopy was evolving and results were often inconsistent and sometimes a source controversy. Work by Seah and Hondros was important to put these measurements on a sound foundation. An important trait of Martin's work was his ability to identify needs or information gaps and to proceed to fill them.There are many examples of this, including application of XPS to measure very thin oxide films on silicon wafers, simple models of electron mean free path lengths, models for understanding sputtering rates of cluster ion sources and the development of consistent terminology for surface methods and analysis. Martin made significant and enjoyable efforts to communicate information to the community and offered encouragement to other researchers in a variety of ways.Although his presentations seemed to be spontaneous and often full of humor, they were always well thought out and delivered clear and important messages. In viewing one of my presentations the year of his death, he made many complementary remarks in email correspondence, but chided me for having too much information on my closing slide.He said that it was important to have a simple clear final message for each talk. A portion of his influence and success was due to many delightful professional and informal social interactions.When he liked a presentation, he would offer a simple "well done" and I very much valued such comments when I received them.At an American Chemical Society Meeting in New York City we went to the half price theatre ticket booth and chose to attend not a Broadway musical but a delightful Arthur Miller play with almost no audience.

5:00pm **AS+CA+HC+LS-WeA-9 The 'Crypto-Electron' Question: XPS of Tribo-electrified Insulators*, Hagai Cohen,*** Perlman bdg., The Weizmann Institute, Israel

Recent experiments on tribo-electrification have raised fundamental questions on the role of electrostatic charge in chemical and physical surface activity. Cryptolectrons were claimed to be created and, subsequently, be exploited to establish 'single-electrode electrochemistry'. However, our XPS study of this problem reveals methodological issues that were not taken into account. I will show that XPS proposes an interesting template for studies of various processes under controlled surface charge conditions, with which limiting factors on the magnitude of electrostatic surface fields can be extracted. How would a cryptoelectron, if existing, look like and can XPS imitate this creature to some extent – these questions and related ones will be discussed.

5:20pm **AS+CA+HC+LS-WeA-10 Effects, in XPS, on Composition Determination Using Different Background Removal Procedures: Single Crystal Fe_2O_3 as an Example*, Christopher R. Brundle,*** C R Brundle and Associates*; B. Crist,* xpsdata*; P. Bagus,* University of North Texas

Precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult, even for homogenous materials. Normalizations for σ and λ are required, but the procedures are by now well understood. The accuracy of removing a background to establish the intrinsic spectrum is on less secure ground. There are several approaches, and implementation requires adjustment of parameters either manually, or automatically by the software used. The situation is at its most unsure when an XPS core level "peak" consists of overlapping structure spread over a wide (up to several 10's ev) BE range, such as with Fe 2p (multiplet splitting; shake structure) and O1s (shake) in Fe_2O_3 (1). The situation is similar for many other transition metal compounds. We examine, for a hematite single crystal, Tougaard and Shirley based background removals. Our conclusion is that the high BE endpoint, ie. where the person taking, or analyzing, the data sets the background to meet the experimental spectrum (implying there is no further intrinsic signal beyond that BE) is critical for high composition accuracy. Obviously, theory input on where intrinsic substructure ends helps to establish what is a reasonable endpoint (1). It is quite possible to adjust endpoints (Fe2p and O1s) to return the "expected" answer, 40% atomic Fe, but this is arbitrary, and, of course, assumes 100% accuracy of the relative σ and relative λ in addition to assuming a) that the Transmission Function, TF, of the instrument has been accurately calibrated, and b) that a small signal from surface OH is properly accounted for. So, in this presentation we are more concerned with the *range in composition* returned by each method (and variations within each method), rather than absolute values, when different, but plausible, endpoints are used. We also find that results differ using high energy resolution and low resolution. The two effects together amount to a ~4% variation in determined Fe %age for Tougaard and ~6% for Shirley. We stress that this work represents a practical approach, using the particular versions of the Tougaard and Shirley software available with the instrument involved, and no sample treatment within the instrument, which we believe is the way most practical XPS analyses are actually performed. Finally, we discuss the reasons for the differences observed and examine other possible procedures.

1) Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3, Paul S. Bagus, Connie J. Nelin, C. R. Brundle, B. Vincent Crist, N. Lahiri, and Kevin M. Rosso, PCCP 2022 and references therein.

5:40pm **AS+CA+HC+LS-WeA-11 XPSOasis.org: the XPS Peak-Fitting Network*, Alberto Herrera-Gomez,*** CINVESTAV, Mexico*; D. Herrera-Rendon, E. Aguilar-Diaz,* RDATAA, Mexico

The XPSOasis Web platform aims to make available to the XPS community, free of charge, tools that facilitate communication between XPS users; this includes discussion forums, peak-fitting databases (one for each core-level), dynamic communication between users, and free data analysis software. The web platform allows users of different fitting software to easily upload posts to ask questions with images of the fitting that concern them. To answer the questions, the posts contain the data, allowing knowledgeable users to download and work on the recommendations.Novice users can consult expert users in direct conversations. Technical discussions on the analysis of XPS data can also be held.

To hook expert (and non-expert) users, the participation is rewarded with *Spicer* points, which are accumulated through *likes* in their posts (given by other users) and when one of their posts reaches the peak-fitting data base (which is a decision of the corresponding moderator).Categories are defined in terms of the points.User belonging to certain categories can compete to become moderators of a certain core-level forum and database.They could also offer courses.Another advantage of having posts in the database is that they become the norm and could be cited.

The usefulness of XPSOasis.org is a function on the availability of peak-fitting parameters for each core-level for each element under a variety of chemical environments.Since it is a user-based platform, it becomes more useful as the number of users posts increases.This is a possible solution (which will, in fact, be provided by the XPS community itself) for the erroneous XPS analyses all too common in the scientific literature.

6:00pm **AS+CA+HC+LS-WeA-12 ASSD Peter Sherwood Mid-Career Award Talk: Advancing X-ray Photoelectron Spectroscopy (XPS) Methodologies for Materials Research*, Mark Biesinger*[1]*,*** Surface Science Western, Canada **INVITED**

Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard

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[1] **ASSD Peter Sherwood Award**

samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems [1,2,3]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots [4,5]. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [5], have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications.

An overview of these curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.A recent assessment of available charge corrections procedures for insulating samples will also be shown [6].

References:

1. M.C. Biesinger, et al., *Surf. Interface Anal.***41** (2009) 324.

2. M.C. Biesinger, et al., *Appl. Surf. Sci.***257** (2010) 887.

3. M.C. Biesinger, et al., *Appl. Surf. Sci.***257** (2011) 2717.

4. J.L. Bourque, M.C. Biesinger, K.M. Baines, *Dalton Transactions***45** (2016) 7678.

5. M.C. Biesinger, *Surf. Interface Anal.***49** (2017) 1325.

6. M.C. Biesinger*, Appl. Surf. Sci*. **597** (2022) 15381.

Actinides and Rare Earths Focus Topic
Room 318 - Session AC+AS+LS-ThM

Emerging Topics and Methods in Actinide/Rare Earth Science

Moderators: David Shuh, Lawrence Berkeley National Laboratory, **Alison Pugmire**, LANL, **Paul Roussel**, AWE, UK

8:00am **AC+AS+LS-ThM-1 Nuclear Forensics 2020:A Strategic Inflection Point*, David Willingham,*** Lawrence Livermore Laboratory **INVITED**

The terrorist attacks of 9/11/01 greatly increased the visibility of nuclear forensics, as policy makers became increasingly concerned about the possibility of well-organized terrorist groups obtaining a nuclear weapon or dirty bomb.The Departments of Defense (DOD), Energy (DOE), Homeland Security (DHS), and State (DOS), as well as the Federal Bureau of Investigation (FBI) and the intelligence community, all play key roles in nuclear forensics. DHS, for example, was founded in November 2002 and included, from the start, a formal nuclear forensics program in its Science & Technology Branch.An August 2007 presidential decision directive established the specific roles these agencies would play and formally established the National Technical Nuclear Forensics Center (NTNFC) within DHS to coordinate planning, integration, assessment, and stewardship of the U.S. government's nuclear forensics capabilities. In 2010, the Nuclear Forensics & Attribution Act established a National Nuclear Forensics Expertise Development Program (NNFEDP) within the NTNFC aimed at "developing and maintaining a vibrant and enduring academic pathway from undergraduate to post-doctorate study in nuclear and geochemical science specialties directly relevant to technical nuclear forensics."National laboratories like LLNL have particularly benefitted from the establishment of postdoctoral fellowships.

In 2021, primary responsibility for nuclear forensics within the US Government transferred from DHS to the National Nuclear Security Administration (NNSA) within DOE with the issuance of National Security Presidential Memorandum 35, National Technical Nuclear Forensics. However, the Nuclear Forensics & Attribution Act of 2007 is still in force, which defines certain roles for DHS, particularly for stewardship of the nuclear forensics' workforce. Starting with the FY21 budget, there have been substantial increases in funding for NNSA for both nuclear forensic operations and R&D. However, the exact configuration of the nuclear forensics expertise development program(s) going forward is still being determined."

This talk will highlight some of the outstanding research conducted by our DHS postdoctoral fellows, including:

1. Development of RIMS as a tool for in situ analyses for nuclear forensics.
2. Improved determination of half-lives and branching ratios important for U rad-chem
3. Exploration of the use of isochrons for age dating of impure samples.
4. Development of new stable isotopic systems as new sources of signatures for nuclear forensics.
5. Development of rapid methods for dissolving solid samples

8:40am **AC+AS+LS-ThM-3 The Non-Integer Occupancy Ground State Hypothesis*, Miles Beaux,*** Los Alamos National Laboratory **INVITED**

A deeply ingrained and long-standing practice exists for identifying integer orbital occupancy ground state electronic configurations for neutral atoms of the elements. For certain elements, the identification of the electron occupancies of the orbitals in a neutral atom can be a controversial topic, instigating heated debate among scientists. The pedagogy of how atomic structure and the periodic table are initially taught might serve as a driver for this practice. For example, the octet rule is often used to explain the most energetically favorable ionic states, similarities in properties of like-group elements, and the most stable compounds formed by the transfer and sharing of electrons. However, the octet rule is also insufficient to explain the existence, structure, and properties of transition metal elements, including the lanthanides and actinides.

A more fundamental quantum-based understanding of electronic structure provides a firm basis for the overall structure of the periodic table. Specifically, the octet rule is understood as the stability of completely filled *s*-, and *p*-orbitals each having electron capacities of two (l=0; m_l=0; m_s=±½) and six (l=1; m_l=-1,0,+1; m_s=±½), respectively, with each Period, n, having n_s and n_p orbitals (except for Period 1, for which no 1*p* orbital exists). Extrapolation of this quantum mechanical underpinning of the Periodic Table explains the existence of the *d*- and *f*-blocks. The filling patterns of the orbitals for elements in the Period Table reveals relative energies of the various orbitals. Deviations from the filling pattern are often explained to varying degrees of satisfaction by the interplay between Hund's rule and the Aufbau principle for near-degenerate states; the stability of empty, half-filled, and completely filled orbitals; and core level screening. As the energy landscape for electron orbitals becomes more crowded for higher Period elements, the potential for near energy degenerate states increases. The potential for quantum superposition of electrons in these near energy states leading to effective non-integer orbital occupancies will be discussed in the context of observed instabilities in actinide and rare earth elements. Experimental and theoretical efforts to investigate this hypothesis for a series of Np, Pu, and Am compounds will also be described.

9:20am **AC+AS+LS-ThM-5 Legacy Plutonium at the Hanford Site*, Edgar Buck*,** *D. Reilly, G. Hall, K. Kruska, L. Liu, S. Triphathi, B. McNamara, A. Casella, D. Meier,* Pacific Northwest National Laboratory **INVITED**

The morphological characteristics of plutonium materials may provide information on the processes that were used to create the material; however, understanding of the detailed thermodynamic and kinetic processes needed to predict the evolution of its particle size distribution, crystal habit, and agglomerated state is still evolving. There has been an effort to fill this technical gap using an integrated experimental and modeling approach for formation of plutonium phases, including oxides and oxalates. Several different types of plutonium phases have been observed in wastes at the Hanford site, such as the Z9 crib near the former plutonium finishing plant and plutonium solids found in the SY102 and TX118 tanks. Laboratory experiments have been conducted to probe the formation mechanisms for these materials. By examining the preciptiating plutonium solids using a combination of in-situ optical microscopy (OM), scanning electron microscopy (SEM), cryo-electron microscopy (CryoEM) and in-situ transmission electron microscopy (TEM)., we have been able to demonstrate the occurrence of non-classical crystalline pathways for plutonium particle growth in some instances.

Understanding crystallization pathways in plutonium materials depends on the ability to unravel relationships between the intermediates and final crystalline products at the nanoscale, which is a particular challenge with radioactive materials. However, these powerful new tools of in-situ and cryoEM are providing new insights into the plutonium chemical system. The experimental data is helping to parameterize the computational modeling with the potential to lead to the development of predictive tools for identification.

11:00am **AC+AS+LS-ThM-10 Focused Ion Beam for Spatially Resolved Morphological Analysis of Nuclear Materials*, Brandon Chung*,** *S. Donald , D. Rosas, S. Sen-Britain, V. Som, N. Teslich, A. Baker,* Lawrence Livermore National Laboratory*; A. Ditter, D. Shuh,* Lawrence Berkeley National Laboratory

Nuclear forensics requires accurate identification of distinguishing material characteristics of interdicted nuclear materials. Local morphological and chemical variations in nuclear materials are nearly ubiquitous due to the varying provenance, process, and pathways. Conventional analysis using bulk nuclear material provides an overall analytical value, but a typical nuclear material is heterogeneous, requiring highly spatially resolved characterization. Consequently, averaging material characteristics may obscure critical forensic signatures resulting from local chemical and structural variations. We will describe our efforts to strengthen operational and scientific methodologies to employ the focused ion beam-scanning electron microscopy (FIB-SEM) on uranium (U) and plutonium (Pu) materials for direct three-dimensional (3D) morphological analysis or to prepare site-specific material features to obtain spatially resolved characterizations using transmission electron microscopy (TEM) and X-ray synchrotron spectromicroscopy. Our work shows the internal morphological and chemical variations in host nuclear materials provide valuable information about the material's production processes and recent environmental exposures. We identified that internal microscopic features entrapped within bulk nuclear materials contain trace elements or chemical that are attributable to their origin, processing, and environmental exposures.

Prepared by LLNL under Contract DE-AC52-07NA27344. This work was supported by the Office of Defense Nuclear Nonproliferation Research and Development within the U.S. Department of Energy's National Nuclear Security Administration. This support does not constitute an express or implied endorsement on the part of the Government. LLNL-ABS-835643

11:20am **AC+AS+LS-ThM-11 Studying Combined Influence of Alpha Irradiation and Dissolved Hydrogen on UO-$_2$ Corrosion Using a Microfluidic Electrochemical Cell***, **Jennifer Yao**, B. McNamara, M. O'Hara,* Pacific Northwest National Laboratory*; N. Lahiri,* Pacific Northwest National Lab*; E. Ilton, C. Wang, E. Buck,* Pacific Northwest National Laboratory

It is well accepted concept that α-decay is the most important source of radiation in the spent nuclear fuel (SNF) after 1,000 years [1]. The influence of α-irradiation in the presence of dissolved H_2 on the corrosion of UO_2 can provide important information to assess the impact of the long-term SNF to the storage environment. However, experiments with bulk amount of SNF are expensive owing to the need for shielded hot cell facilities to protect researchers from the intense radiation field. To address this challenge, we employed a novel invention, particle-attached microfluidic electrochemical cell (PAMEC), to investigate UO_2 corrosion under different conditions (e.g., α-irradiation and H_2) at the microscale. Less than 10 µg of UO_2 (containing 1% to 10% $^{233}UO_2$) powder was mixed with polyvinylidene fluoride (PVDF) and carbon black to form the working electrode and included into PAMEC, which ^{233}U was used as alpha source to simulate the"aged" spent fuel [2]. The response of the corrosion potential of a ^{233}U contained UO_2 working electrode to dissolved H_2 in 0.1 M $NaClO_4$ (pH=9.5) will be presented. In addition, the 50nm thick Si_3N_4 detection window on PAMEC allows in situ imaging of the corrosion process using the high-resolution imaging technique, such as scanning electron microscope (SEM) coupled withEnergy-dispersive X-ray spectroscopy (EDS). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the UO_2 electrode that was exposed to alpha radiation and dissolved H_2. Our work demonstrates the study of combined influences on UO_2 corrosion under the conditions that are known to be present in the long-term SNF environment by employing a microfluidic electrochemical cell. We vision this approach can be widely applied to study the influences of conditions that resemble the practical repository environment on SNF, while with greatly reduced hazardous risk when performing such experiments.

References:

(1) Ewing, R. C., Long-term storage of spent nuclear fuel. *Nature Materials* **2015,***14*, 252-257. 10.1038/nmat4226

(2) Carbol, P.; Cobos, J.; Glatz, J.-P.; Ronchi, C.; Rondinella, V.; Wegen, D. H.; Wiss, T.; Loida, A.; Metz, V.; Kienzler, B.; Spahiu, K.; Grambow, B.; Quinones, J.; Martínez Esparza, A., *The effect of dissolved hydrogen on the dissolution of 233 U doped UO 2 (s), high burn-up spent fuel and MOX fuel*. 2005; p 140.

11:40am **AC+AS+LS-ThM-12 A Model to Extract the Size-Dependent Surface Structure of Actinide Oxide Nanoparticles***, **Shinhyo Bang**, L. Moreau,* Washington State University

Characterization of actinide oxides at the nanoscale presents unique challenges due to their radioactivity, high surface area, and inherent diffraction broadening due to small grain size. Extended x-ray absorption spectroscopy (EXAFS) is an analytical method to investigate atomic-scale structural properties that enables their encapsulation and does not rely on long-range order. There is a limitation that EXAFS only gives the averaged structural information of heterogeneous samples. We aimed to deconvolute EXAFS results to extract the surface coordination environment of UO_2 NPs by proper modeling, and investigate how it evolves with varying sizes (1.4, 4.7, 8 nm). The termination effect was used to quantify the surface terminating species of UO_2 NPs. A higher degree of oxygenation on the surface was observed for 8 nm NPs. EXAFS simulation was implemented to backtrack the surface structure of these NPs. It was observed that the bond contraction due to the surface relaxation effect was localized in a few outermost layers of NPs and the surface disorder of 1.4 and 4.7 nm NPs was significantly enhanced from that of bulk.

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