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+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).

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

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).

Radiation Effects on Materials Focus Topic
Room 318 - Session RE+AS-FrM

Materials Analysis and Characterization with Radiation

Moderators: Scott Dubowsky, University of Illinois at Urbana-Champaign, **Camilo Jaramillo-Correa**, Pennsylvania State University

8:20am **RE+AS-FrM-1 Characterization of Materials and Surfaces with Various Types of Radiation*, Zachary Robinson,*** SUNY Brockport **INVITED**

In this talk, I will present an overview of various types of radiation that surface scientists use to characterize materials. In particular, I will focus on my recent work studying materials relevant for post-CMOS neuromorphic computational devices. These materials provide a potential path towards improved power and computational efficiency in a merged biomimetic and CMOS architecture. For this project, we characterized niobium oxides (NbO_2 and Nb_2O_5) using photons ranging from the infrared and visible for quantitative microscopy and spectroscopy through X-rays generated both at synchrotron sources and in benchtop instruments for diffraction and photoelectron spectroscopy. In particular, broad spectrum radiation allows us to study changes in composition and structure brought about in the as-deposited amorphous thin films upon annealing. The various sources of radiation inform our understanding of the material properties by providing information about the crystal structure, stoichiometry, impurities, crystallization percentage, and optical properties. Since undergraduate students were also an integral part of this work, I will describe our efforts in finding ways for them to be productive over a short (8-10 week) summer research internship when using relatively complicated instrumentation.

9:00am **RE+AS-FrM-3 High-Energy (MeV), Heavy Ion Irradiation of Chalcogenide Phase Change Thin Films*, David Adams,*** *E. Lang, T. Clark, C. Sobczak, E. Scott, J. Custer,* Sandia National Labs*; T. Beechem,* Purdue University*; K. Hattar, M. Kalaswad, M. Rodriguez,* Sandia National Labs

Phase change thin films continue to attract interest for applications such as non-volatile electronic memory, sensors, and nanophotonics, because the material can be rapidly switched between amorphous and crystalline states accompanied by large changes in electronic and optical properties. In particular, the germanium-antimony-tellurium system remains a benchmark for studies wherein $Ge_2Sb_2Te_5$ has received much attention. In this study, we have evaluated the response of various chalcogenide thin films to high energy, heavy ion irradiation in order to provide additional insight into phase stability. Crystalline $Ge_2Sb_2Te_5$ and $(Ge_2Sb_2Te_5)_xC_{1-x}$ thin films were irradiated with 2.8 MeV Au ions to different doses and characterized subsequently using Raman spectroscopy, X-ray diffraction, thermoreflectance, Transmission Electron Microscopy and 4-point probe methods. Irradiation experiments were specifically designed to induce disorder while avoiding substantial incorporation of projectile species into films therein preserving the as-deposited film chemistry. Specifically, the 2.8 MeV energy was chosen so that ion range > film thickness which leads to less than 0.01 mol.% of projectile species residing within 100 nm-thick chalcogenide films, according to SRIM estimates. Irradiation led to significant changes in both structure and properties. Pure $Ge_2Sb_2Te_5$ thin films were amorphized when irradiated above a threshold dose, ~1e12 cm^{-2}. Both the thermodynamically-stable trigonal and metastable cubic phases were disordered with concomitant changes in electrical resistivity and thermal conductivity observed. Various $(Ge_2Sb_2Te_5)_xC_{1-x}$ [$0 < 1-x < 0.12$] thin films were also amorphized when irradiated above threshold doses. As with pure $Ge_2Sb_2Te_5$, structural disordering was accompanied by increased electrical resistivity and decreased thermal conductivity. Further insight into collisional-induced disordering was revealed by In-situ Ion Irradiation Transmission Electron Microscopy (I^3TEM). In-situ transmission electron microscopy and electron diffraction mapped the phase-specific response of films confirming different threshold doses for cubic and trigonal phases. Additionally, I^3TEM has been used to study the effects of increasing carbon concentration on phase stability and ion radiation response.

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9:20am **RE+AS-FrM-4 Multiwavelength Raman Microscopy Used to Characterize Surfaces for Plasma-Wall Interaction Study in Tokamaks*, Cedric Pardanaud,*** *C. Martin, P. Roubin,* Aix-Marseille University / CNRS, France **INVITED**

Tokamaks aim to study the possibility to produce energy by exploiting hydrogen isotope nuclear reactions. The fusion plasma is confined magnetically, but a cold plasma is in interaction with the inner walls. This plasma-wall interaction, heterogeneous at the scale of the machine can lead to component melting, surface erosion, element migration inside the chamber, dust production, tritium retention, impurity contamination, mixed material formation… These walls were made of carbon in previous tokamaks (abandoned due to formation of thick hydrogenated rich deposits). Inner walls are now composed of tungsten and/or beryllium, presenting good thermal and chemical properties.

I will demonstrate that multiwavelength Raman microscopy is a suitable technique for *post mortem* analyses of tokamak plasma facing components [1]. It delivers an information related to chemistry, which is complementary to the classically used Thermal Desorption Spectroscopy (TDS) and Ion Beam Analyses (IBA). I will focus on analyses of both laboratory made samples and samples collected inside some tokamaks.

I will illustrate my talk by presenting first how Raman, IBA and TDS of amorphous carbon deposits found inside the Tore Supra tokamak compare [2, 3]. Then, I will focus on the defective beryllium system in the JET tokamak [4- 6] and formation of beryllium hydrides [7]. I will finish by presenting some results about tungsten oxides [8, 9].

[1] C. Pardanaud, et al.

Raman spectroscopy and applications, chapter 1, edited by Khan Maaz, Intech (2017)

[2] C. Pardanaud, et al.

Diamond and Related Materials 34 (2013), 100-104

[3] C. Pardanaud et al.

Thin solid films 581 (2015), 92

[4] M.I. Rusu, et al.

Nuclear Fusion 57 (2017), 076035

[5] M. Kumar, et al.

Nuclear Materials and Energy 17 (2018) 295–301

[6] C. Pardanaud, et al.

Physica Scripta 96 (2021) 124031

[7] C. Pardanaud, et al.

Journal of Physics: Condensed Matter, 27 (2015) 475401

[8] Y Addab, et al.

Phys. Scr. T167 (2016), 014036

[9] C. Pardanaud, et al.

Nuclear fusion 60 (2020) 086004

10:00am **RE+AS-FrM-6 In Situ Optical Characterization of High Temperature Defect Kinetics in Mixed-Conducting Oxide Films*, Nicola Perry,*** University of Illinois, Urbana-Champaign **INVITED**

Thin films represent model platforms for the evaluation of new materials for intermediate-to-high temperature electrochemical devices, including electrolyzers and fuel cells. We focus on candidate perovskite-structured mixed- or triple-conducting electrode materials where the bulk mobile ions are oxide ions or protons, and the surface reactions of interest are oxygen reduction/evolution, hydration, and combinations of the two in the form of hydrogenation. Central to their performance is the dynamic defect behavior at temperatures from 300 – 700 °C, particularly the kinetics of defect transport (diffusivities, D) and interfacial reactions (surface exchange coefficients, k). Conventionally, electrochemical or electrical methods that place precious metal current collectors on the electrode surface are applied to evaluate the ion fluxes; however, we have demonstrated that the presence of such metals actually alters the measured parameters (e.g., k) aiming to quantify surface defect kinetics and bulk defect equilibria. Instead, we exploit the coupling between defect concentrations and UV-vis optical absorption to provide contact-free, continuous, and *in situ* evaluation of the films' defect kinetics via isothermal optical transmission relaxation (OTR) responses to step changes in gas-phase chemical potentials. This method has enabled us to observe the evolution of oxygen exchange kinetics during crystallization, where the onset of crystallization corresponds to the initiation of "breathing" by the films, and we demonstrate orders-of-magnitude enhancements in oxygen surface exchange kinetics in films grown by the low-temperature crystallization method vs. conventional high-temperature-grown films. We also have developed a two-dimensional OTR technique to observe defect kinetics across all regions of 1 x 1 cm^2 films simultaneously, of use in cases with spatially heterogeneous responses. We applied this 2D-OTR to model metal | perovskite heterointerfaces to further underline the catalytic effect of metal current collectors on mixed conductors for oxygen exchange and show the surprisingly large spatial extent of that effect away from the interface. Most recently we demonstrated the ability of the OTR method to evaluate hydrogenation kinetics in proton-conducting thin films for the first time, enabling quantitative comparison of candidate new triple-conductor electrodes. Origins and applications of the optical absorption-defect concentration relationship will be discussed.

Funding Source: DOE BES Grant # DE-SC-0018963

10:40am **RE+AS-FrM-8 Exploring the Effects of Radiation on Planetary Surfaces through the Analysis of Experimental Analogs and Returned Samples from the Moon and Asteroids***, Michelle Thompson,* Purdue University **INVITED**

Materials on the surfaces of airless bodies are continually exposed to the harsh environment of interplanetary space through a process known as space weathering. Space weathering alters the microstructure, chemistry, and optical properties of grains on the surfaces of bodies like the Moon and asteroids. This process is driven by two primary mechanisms: hypervelocity dust impacts, and the interaction of surface material with energetic particles from the solar wind. We can investigate the effects of these processes by performing laboratory experiments and by analyzing materials collected by sample return missions. Samples returned from the Moon via the Apollo missions and from near-Earth asteroids Itokawa and Ryugu by the Hayabusa and Hayabusa2 missions, respectively, have demonstrated that the microstructural and chemical characteristics resulting from solar wind irradiation are complex. Solar wind ions work to vesiculate and amorphize the outer rims (<100 nm) of grains on the surfaces of these bodies, and the depth and degree of this amorphization (e.g., presence and distribution of nanocrystalline domains) varies significantly in relation to the grain composition and its exposure timescale to interplanetary space. Similarly, solar wind radiation can cause preferential sputtering and redeposition, radiation-enhanced diffusion, and/or recoil mixing which can develop atomic-scale chemical heterogeneities on grain rims. We observe such multilayer rims with segregated cation/anion structures in solar wind irradiated silicate minerals from both the Moon and asteroids. In addition, high-energy Fe-group nuclei from solar flares create trails of ionization damage called solar flare tracks. The concentration of these tracks can be used as a proxy for the exposure timescale a grain has experienced on an airless planetary surface. We can further understand these microstructural and chemical characteristics by conducting experiments in the laboratory using ions and energies appropriate for the solar wind. This work has revealed fundamental discrepancies between experimental and natural space weathering, including the rate at which samples amorphize and the development of vesiculated textures. Such results suggest that ion flux, grain composition, and microstructure play a significant role in the development of atomic-scale irradiation characteristics in returned samples. A combined approach of sample analysis and experiments enables us to investigate how solar wind irradiation alters materials throughout the solar system which is critical for building an understanding of the evolution of planetary surfaces through time.

11:20am **RE+AS-FrM-10 Ground-Based Space Environmental Testing of Materials and Components for Spacecraft Mission Assurance***, Sven Bilén, J. McTernan, C. Zawaski,* The Pennsylvania State University **INVITED**

Space presents an extreme environment for spacecraft materials and systems. For example, in the low-Earth-orbit (LEO) space environment, materials and structures are exposed to high vacuum (10^{-4}–10^{-5} Pa), thermal cycling (−150 to 150 °C), ultraviolet light (100–200 nm), space radiation, potential surface impact from micrometeorites and orbital debris (MM/OD), and atomic oxygen (AO). Materials showing promise for future use in space must be assessed and evaluated for their reaction to exposure to the space environment before being baselined for inclusion into critical space infrastructure. Such evaluation can occur via *in-situ* experiments on space vehicles, but such testing is costly, of limited throughput, experiences significant time lags, and provides less specific information to identify points of failure. Ground-based testing of materials and systems under simulated space environmental conditions can address these limitations. Indeed, space hardware, depending on mission assurance requirements, goes through a battery of testing in space-simulation facilities, such as thermal–vacuum, vibration, acoustic, EMI, etc.

Penn State has facilities for full-scale testing of small spacecraft (e.g., 3-U CubeSats) in a LEO–type environment, individual components and materials, spacecraft charging mitigation schemes, and spacecraft–plasma interactions. This facility is comprised of a vacuum chamber capable of thermal cycling through a range of realistic temperatures, a plasma source capable of producing streaming ions (1–4 eV) and low-energy electrons (~0.1 eV), shake tables, anechoic chambers (for EMI testing), outgassing assessment, and radiation (via its Radiation Science and Engineering Center and Breazeale Reactor). This facility is also capable of testing individual components, whose operation is dependent on the plasma environment (e.g., thermionic cathodes, field emitters, plasma diagnostic tools, *in-situ* diagnostics such as Langmuir probes, etc.). System-wide tests that combine multiple tests are beneficial as results can be interdependent. For example, thermal cycling under vacuum that causes outgassing could contaminate sensors or other diagnostic tools such as Langmuir probes. We are working to add atomic-oxygen exposure, increased thermal range, high-energy electron exposure, UV exposure, and simulated MM/OD damage (via short, focused laser pulses) to our capabilities.

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