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.

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