Applied Surface Science Division
Room Ballroom A - Session AS-ThP

Applied Surface Science Poster Session

AS-ThP-1 Isolation of Pt Metal Atoms Using a Surface-Catalyzed Covalent Organic Framework, *David Wisman*, Indiana University Department of Chemistry; NAVSEA Crane; *Y. Bai, S. Tait,* Indiana University Department of Chemistry

Single-site metal centers in heterogeneous catalysts are highly desirable to improve reaction selectivity, due to the uniform active site geometry. It is often advantageous to have a predictable 2-D structure of single-site metal centers, making it necessary to integrate the single-site centers into an ordered array of receptor sites. One way to approach this challenge is through the formation of covalent organic frameworks (COFs). In the work reported here, we utilize a surface-assisted dehalogenation reaction of 1, 3, 5–tris(4-bromophenyl)benzene (**TBB**) to form a 2-D covalent organic framework on single-crystal metal surfaces. Following successful formation of the 2-D framework on the surface, favorable binding sites for metal catalysts (platinum) are formed by depositing 1, 10-phenanthraline-5, 6-dione (**PDO**) on the surface. **PDO** becomes confined within the porous COF and is then able to stabilize vapor deposited metal and single atom sites. X-ray photoelectron spectroscopy confirms the oxidation of the platinum metal when deposited with **PDO** molecules, while scanning tunneling microscopy confirms the confinement of **PDO** within the pores, and the absence of any external 1-D Pt:**PDO** chains. The highly predictable nature of the covalent organic framework chemistry makes this an exciting result for single-site metal center formation.

AS-ThP-2 In situ Spectroscopic Evaluation of the Aging Mechanisms of Molybdenum Disulfide, *Robert Chrostowski,* University of Texas at Austin; *J. Curry, M. Dugger,* Sandia National Lab; *F. Mangolini,* University of Texas at Austin

Molybdenum disulfide (MoS2) is a lamellar transition metal dichalcogenide extensively used as a solid lubricant in the aerospace industry due to its beneficial lubricating properties (i.e., low friction) in vacuum. Unfortunately, exposure to environmental contaminants, believed to be primarily oxygen and water, degrades the tribological performance of MoS2 in a process known as "aging". While aging of MoS2 coatings has been recognized as an important engineering problem occurring even in high-vacuum, the underpinning mechanisms are still poorly understood. Developing a fundamental understanding of chemical processes occurring in MoS2 and their kinetics upon exposure to different gases can provide guidance for developing novel approaches to prevent and/or reverse aging of MoS2 coatings.

Here, we employ an in situ surface-analytical approach, based on the combined use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS), to evaluate and quantify the surface chemical changes occurring upon aging MoS2 in aerobic conditions. Additionally, in situ annealing experiments of MoS2 samples inside the XPS chamber were carried out to evaluate the effect of annealing before and after aging on the surface chemical processes occurring inside and outside wear tracks upon aging. Finally, to identify the relative contribution of oxygen and water to the aging process, MoS2 samples were exposed to deuterium oxide (D2O) and oxygen-18 (18O) in the ToF-SIMS chamber. The subsequent ToF-SIMS analyses provided evidence for the high diffusivity of water in MoS2, and, especially, in tribologically-stressed regions.

The results of these investigations, providing novel insights into the relative contribution of oxygen and water to aging of MoS2 coatings and the effect of tribologically-induced structural variations on the transport of water in the near-surface regions of MoS2, add significantly to the understanding of the mechanisms underlying the aging process.

AS-ThP-4 Stm Investigations of Self-Assembly of Proline, *Benjamin Heiner, A. Pittsford, S. Kandel,* University of Notre Dame

Scanning tunneling microscopy, through the observation of molecular clusters and monolayers on surfaces, provides direct experimental evidence as to how intermolecular interactions result in the self-assembly of extended structures. A detailed understanding of the interplay of interactions will result in improved understanding and prediction of the behavior of self-assembling systems, with implications in a wide range of disciplines ranging from crystal engineering to supramolecular chemistry to protein secondary and tertiary structure. We present experimental results on the self-assembly of proline, as well as the results from computational modeling. Pulse deposition of d-proline on Au(111) reveals that it forms dimer or catamer chains and pentamer clusters. The dimer structures are chiral, as would be expected from an enantiopure adsorbate; however, the pentamers on the surface appear racemically mixed. Comparison of self-assembled structures to related molecules reveals similar behavior for proline, indole-2-carboxylic acid, and indoline-2-carboxylic acid, but substantial differences are observed for pyrrole-2-carboxylic acid.

AS-ThP-5 Efforts to Improve XPS Analysis Quality in an Era of Increasingly Diverse Uses and Users, *Don Baer,* Pacific Northwest National Laboratory; *J. Watts,* University of Surrey, U.K.; *A. Herrera-Gomez,* CINVESTAV-Unidad Queretaro, Mexico; *M. Linford, G. Major,* Brigham Young University

Use of XPS in publications continues to increase exponentially but anecdotal reports and systematic analyses show a growing presence of significantly flawed data and analyses. Examination of six months of XPS data in three journals found more than a quarter of the data presented to be highly flawed, often leading to incorrect conclusions. Recognition of this problem within the surface analysis community has increased with recognition that inexperienced users and increased use of XPS outside the surface analysis community contribute to the problem. Several efforts have been initiated to address the problem. This poster will identify some of the specific problems and describe some of the community efforts intended to address them. Challenges associated with reliable repeatable XPS measurements were recognized at the advent of commercial instrumentation and led to the formation of relevant ASTM and ISO standards committees. Recent efforts to address problems found in the literature include, review papers and tutorials including collection of papers on reproducibility with a focus on XPS in the Journal of Vacuum Science and Technology A (JVSTA), websites containing and summarizing useful information, implementation of expert systems to assist the collection and analysis, advanced software tools, and online forums that can enable community interactions to assist analysts. The poster focuses on evolving efforts to address three specific issues: i) incomplete data and analysis reporting, ii) the need for bite sized versions of important information for non-experts and iii) the high rate of peak fitting problems. Examination of XPS containing papers finds that information important for reproducible XPS results is often very incomplete. Approaches to develop, distribute, and encourage use of essential analysis information are being explored. To address the shorter attention spans of many in the age of online media and social networks papers to provide incremental bites of useful information are being developed for a series of paper to appear *Surface and Interface Analysis*. Multiple efforts are underway to address the high rate of problems associated with photoelectron peak fitting. These include guides to peak fitting, guides to peak identification and fitting for specific elements, and development of a peak fitting social network designed to connect new and experienced XPS users. In addition, development of a second JVSTA collection of Reproducibility Challenges and Solutions papers is under way.

AS-ThP-6 Metrology Developments in XPS and HAXPES, *David Cant, B. Reed, A. Shard,* National Physical Laboratory, UK

X-ray photoelectron spectroscopy (XPS) is a highly quantitative and surface sensitive technique for analysis of the chemical composition of a given sample. However, it is important that the data obtained during a photoemission experiment is interpreted correctly – both instrumental and sample-related factors must be accounted for to obtain a quantitative understanding of the sample composition. It is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument, as well as the *sample-dependent relative sensitivity factors* (RSFs) which account for the differences in emitted electron intensities for each peak.

In a recent VAMAS interlaboratory study, the huge variability of transmission functions between different laboratories and instruments has been demonstrated, underlining the need for an ISO standard on XPS intensity calibration which is now being developed under the auspices of ISO TC201 "Surface Chemical Analysis". Here we present instrument geometry-corrected reference spectra of low-density polyethylene (LDPE) for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Sensitivity factors are required to account for differences in the intensity of emitted electrons from different materials within a sample. Such differences arise

due to several factors, including the photoionisation cross-section; electron kinetic-energy-dependent variations in transport through a material; and the anisotropic emission of excited electrons. Theoretically determined sensitivity factors, such as the NPL AMRSFs for Al and Mg anode instruments,are commonly used.

For hard x-ray photoelectron spectroscopy (HAXPES), photoionisation cross-sections decrease significantly as photon energy increases, and anisotropy effects become more complex due to the increased contribution of non-dipolar effects. It is therefore increasingly important that a careful consideration be given to the estimation of RSFs. This is further complicated by the multiple photon energies and instrument geometries available in commercially available HAXPES instrumentation. Here we present a set of formulae, derived from fitting of theoretical database values, which allow the estimation of AMRSFs for instruments using any photon energy in the range 1.5 keV - 10 keV, with any instrument geometry. A few instrument geometries in which X-rays are polarised are insensitive to angular emission effects, and these are highlighted in this work.

AS-ThP-7 Advances in Automated XPS Analysis – from Data to Answers, *S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Inc*; K. Good, K. Macak,* **Christopher Blomfield,** Kratos Analytical Limited, UK

XPS has become a mainstay of the suite of analytical tools available for characterisation of new materials and processes.It would be fair to say that XPS instrumentation is now viewed as a "tool" by many users and the expectation is therefore that results are automatically produced.Here we discuss the latest improvements and advancements which provide not just data but results and answers.We look at improving peak identification from unknown samples and automatic region spectral acquisitions.In addition, we show how known samples can be quickly and efficiently acquired and processed to provide comparison results for QA or trend analysis.

AS-ThP-10 The Role of Artificial Intelligence in Minimizing Analysis Errors, Illustrated with EXAFS, Nanoindentation, and Core Level Photoemission*, Jeff Terry,* Illinois Institute of Technology

We have developed artificial intelligence based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS) measurements. This development will help to address the reproducibility problems that slow research progress and inhibit effective tech transfer and manufacturing innovation in these scientific disciplines. A machine learning approach was applied to the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy measurements collected using a synchrotron radiation facility. Specifically, a genetic algorithm was developed for fitting of the measured spectra to extract the relevant structural parameters. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. It requires the use of Larch and Feff for calculating the initial EXAFS paths. We have recently extended the code to make use of Feff8.5lite so it can calculate the paths needed for populating the analysis from within the EXAFS Neo package. The code base has been expanded for the analysis of nanoindentation data and simple x-ray photoelectron spectroscopy measurements. The publication describing the analysis package and where to obtain the software can be downloaded at: https://doi.org/10.1016/j.apsusc.2021.149059 or by contacting the speaker.

AS-ThP-11 X-ray Photoelectron Spectroscopy of Polymer Electrolyte Membrane Fuel Cell Components*, Maxim Shepherd, S. Pylypenko,* Colorado School of Mines

Development of sustainable technologies that produce energy are extremely important to reduce the environmental impacts of current technologies. Proton exchange membrane fuel cells (PEMFCs) generate clean energy using hydrogen and oxygen with water as the main byproduct. The state-of-the-art catalyst for the oxygen reduction reaction occurring at the cathode is based on Pt nanoparticles dispersed on carbon support (Pt/Carbon). The cathode catalyst layer has a major influence on the overall cost of a PEMFC due to the loading of platinum that is needed to achieve a reasonable power density. Optimization of the catalyst layers to achieve the most efficient distribution of the ionomer coating which directly effects the mass transport and device efficiency, is one of the current needs especially for catalysts layers produced using scalable routes. Furthermore, there is a general lack of understanding about how the catalyst support, catalyst, and ionomer interact with one another on a molecular scale. This work utilizes X-ray Photoelectron Spectroscopy (XPS), a highly surface sensitive technique to characterize elemental and chemical speciation of the catalyst layers. XPS is a very common technique to study catalyst but has not been widely applied to investigate catalyst layers.This poster will provide a general background on sample preparation, and data acquisition and analysis of catalysts and catalysts layers made with platinum on High Surface Area Carbon (HSC) catalyst, including findings related to Nafion ionomer degradation. Furthermore, this poster will present comparison of chemistry of the catalyst before and after incorporation into catalyst layer, and will discuss composition of catalyst layers as a function of ionomer loading.

AS-ThP-12 Nanoscale Surface Sensitive Chemical Imaging of Additive Manufacturing Materials*, Ashley Maloney, K. Artyushkova,* Physical Electronics USA*; O. Renault, E. De Vito,* CEA/LETI-University Grenoble Alpes, France

Additive manufacturing is an ever-growing area of research interest that depends upon the high quality of precursor materials in order to achieve a robust final printed product. In this work, an alloy powder material of CuCrZr used in the laser-powder bed diffusion process of 3D printing will be analyzed for grain boundary diffusion and for chemical variation among different particle sizes. Recent advances in Auger Electron Spectroscopy, including *in situ* FIB capabilities, put AES at the forefront of surface analysis techniques with respect to characterization of such defects on the nanoscale. The quantitative elemental information AES provides from solid surfaces combined with FIB tomography allows for *in situ* cross-sectioning and subsequent elemental characterization of the CuCrZr powder particles. The variation of chemistry across different sized particles will also be assessed via quantitative chemical analysis using XPS.

In this work, CuCrZr alloy powder particles were cross-sectioned and analyzed using a PHI 710 scanning Auger nanoprobe equipped with a 25kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). We demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site-specific imaging of grain boundary diffusion within the alloy.

AS-ThP-13 Data Reporting in XPS: A Consistent Lack of Information*, Max Clark, G. Major, M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is widely used to probe the top 10 nm of materials. It is based on the photoelectric effect. Spectra acquired in XPS typically require peak fitting. To properly peak fit, various mathematical functions, including the background and peak shapes, are used. Additionally, different experimental conditions typically change the types of peaks that are required for a fit. We have surveyed the XPS reporting from 2021 papers in three major journals. About 900 papers were surveyed. Only 70% listed the XPS instrument that was used. Among publications with fitted XPS data, over 90% did not indicate the line shape(s) used and over 35% did not indicate the background used. In this presentation, we provide information on other aspects of reporting as well. To improve the reporting in the literature, which should improve the reproducibility of studies, we recommend that (at a minimum) the following be reported:

1. The manufacturer and model number of the photoelectron spectrometer
2. The X-ray anode and energy (for example, in conventional XPS, Mg Kα or Al Kα with energies of 1253.6 or 1486.6 eV, respectively)
3. The type of source: non-monochromatic or monochromatized
4. The X-ray power and spot size
5. The photon energy used in the measurement, along with energy resolution
6. The vacuum level during the analysis Additionally, information about the line shape(s), fitting program, peak positions, and background should also be included if fitting data.

AS-ThP-14 Electrochemical Flow Cell for Surface and Interface Analysis Cluster, *Soniya Gahlawat,* CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria*; M. Valtiner,* TU Wien/IAP, CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria

Electrochemistry plays a pivotal role in scientific and technological advancements. In order to achieve the circular carbon neutral economy goals, we need to advance our infrastructure to study electrochemical processes such as hydrogen production, batteries, fuel cells, recycling, and corrosion. The common feature in all these processes are interface reactions and the key to further development is improving the understanding of these phenomena.

In fundamental research, we have seen increasing use of classical Ultra-High Vacuum (UHV) analysis techniques at higher pressures, although the pressure range is still well below atmospheric conditions and even more so below operating conditions of any real-world electrochemical device.[1] Therefore, we decided to mimic the real operating conditions for electrochemical devices and combined with UHV surface and interface analysis techniques. We integrate the electrochemistry into a UHV system for quasi-operando analysis to explore the energy storage and conversion research areas at nanoscale.

The major challenge with operando and in-situ clusters is to have an ideal electrochemical flow cell suitable for studying the solid/liquid interface dynamics. Most of the cells with easy transfer of working electrode have poor electrode geometries, which results in high ohmic resistance. Additionally, it is pertinent to prevent the presence of organic impurities in the cell as they may get adsorb at the surface and obstruct the surface-interface analysis. We have initiated the development of our experimental setup based on a cell designed by Olaf Brummel[2] and tried to overcome the above-mentioned limitations. To avoid the glass corrosion, the lower part of cell is designed with Teflon and further the geometry of the cell is modified in a unique way. I will present my initial results in this direction as well as an overview of electrochemical surface and interface analysis cluster being developed at TU Wien.

References:

1.   A. Foelske-Schmitz, *X-Ray Photoelectron Spectroscopy in Electrochemistry Research*, In: Wandelt, K., (Ed.) Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry, Elsevier Inc. (2018), vol. 1, 591–606.
2.   M. Bertram et. al, Cobalt Oxide-Supported Pt Electrocatalysts: Intimate Correlation between Particle Size, Electronic Metal–Support Interaction and Stability, J. Phys. Chem. Lett.2020, 11, 19, 8365–8371.

AS-ThP-15 Optical Measurements of Temperature Driven Phase Change in Doped Niobium Oxides for Neuromorphic Computing Applications, *James Michels,* Z. Robinson, V. Daviero, State University of New York College at Brockport*; K. Beckmann, N. Cady,* SUNY Polytechnic Institute, Albany

Significant research has focused on low-power stochastic devices built from memristive materials. These devices foster 'neuromorphic' approaches to computational efficiency enhancement in merged biomimetic and CMOS architectures. Niobium dioxide has volatile memristive properties that include a phase change from an insulating to a conductive state at temperatures above around 800C. This phase change makes it an ideal candidate for future neuromorphic electronics. An ultra-high vacuum technique for measuring the effect of dopants on the phase change has been built, and relies on *in situ* infrared spectroscopy to assess the effect of the phase change on optical reflection and transmission. Further, changes in the macroscopic optical absorption properties of titanium doped NbO_2 are presented as a function of temperature and optical wavelength. The results reveal an interesting optical transmission behavior in a localized temperature range in contrast to its overall decrease with increasing temperature. The latter may provide modulation capabilities for memristive devices.

AS-ThP-16 Laser Surface Melting to Mitigate Intergranular Corrosion of Sensitized AA 5083, *Md Sojib Hossain,* University of Virginia, USA, Bangladesh*; J. Skelton,* University of Virginia*; W. Moffat, A. Wang, G. Lu, J. Fitz-Gerald,* University of Virginia, USA

The precipitation of an anodic Mg-rich phase in 5xxx series aluminum alloys causes them to become sensitized and highly susceptible to corrosion, especially when used in marine-based applications. Heat treatments (>240°C) can dissolve the secondary phases back into the matrix but are unrealistic for service components. In this study, laser surface melting (LSM) is used to reverse the sensitization at the alloy's surface. An excimer ns-pulsed laser was employed at a fluence of 1.5 J/cm 2 to rapidly melt and solidify the surface of highly sensitized AA5083 samples. Characterization of the composition, roughness, and corrosion resistance of these samples were performed to achieve a holistic understanding of how the alloy surface changes after laser melting. Results show that laser processing decreased the open circuit potential from -780 mV to -980 mV (vs. SCE) due to surface homogenization and dissolution of secondary phases, which contribute to micro-galvanic corrosion. A reduction in the corrosion rate was attributed to the dissolution of anodic precipitates into the solid aluminum solution within the melted region, approximately 7 um deep beneath the surface. This work illustrates the efficacy of using LSM to reverse the sensitization of Al-Mg alloys, leading the way toward a method of restoring the original corrosion resistance of sensitized in-service material

AS-ThP-17 Chemistry and Mechanism of Two-Dimensional Transition Metal Carbide and Nitride Mxene Synthesis, *Mark Anayee, R. Wang, Y. Gogotsi,* Drexel University

MXenes comprise a family of two-dimensional carbides and nitrides that has grown to encompass numerous structures and compositions − >30 single transition metal MXenes with a near infinite number of solid solutions ranging in thickness depending on the number of atomic layers, from 5-11. MXenes are promising for a variety of applications ranging from electrodes for energy storage to wireless communication, optoelectronics, and medicine because of their high electrical conductivity, redox-active surfaces, plasmonic behavior, and other attractive properties. MXenes are typically derived *via* topochemical etching of atomically thick layers from precursor layered MAX phases using corrosive halogenated aqueous or vapor etchants. Knowledge of the reaction mechanism and process kinetics are of fundamental importance for the synthesis and property control of MXenes. Prediction of the optimal synthesis approaches will facilitate new MXene composition discovery and prediction of optimal processing time as a function of various parameters will also facilitate scaling up the wet chemical synthesis of MXenes for industrial use. Despite their importance, such studies have been challenging because of the atomic thickness of the A-element layers being etched and the aggressive etchants that hinder in situ studies. Herein, we investigate the defects in the metal and carbon site in the parent MAX phase using ex situ photoemission spectroscopy and mass spectrometry to understand how MXenes develop from MAX phases. Moreover, we investigate the effect of such defects and MAX structure and chemistry influence the etching reaction mechanism through in situ optical profilometry and Raman spectroscopy of single MAX particles to monitor the structural and chemical transformation. Through these methods, we gain fundamental understandings of atomic etching mechanism and kinetics for layered materials and how the reaction starts, proceeds, and finishes.

AS-ThP-19 Multilayer Method Modification for the Quantitative Chemical Composition Analysis on Initial Oxidation of Nickel, *D. Guzmán Bucio, G. Gómez Sosa, D. Cabrera German , M. Bravo Sánchez, J. Torres Ochoa, O. Cortazar Martínez , A. Carmona Carmona,* **Alberto Herrera Gómez**, *M. Mayorga-Garay,* CINVESTAV-Unidad Queretaro, Mexico

Peak-fitting of the Ni 2p core-level from metallic nickel and its oxides is challenging due to the high asymmetry of the main peak, the complex multiplet structure, and the intense Shirley-type background. This work presents X-ray photoelectron spectra acquired from a clean metallic Ni film (sublimated on Si [001]). These are analyzed with two approaches that account for the apparent asymmetry of the main photoemission line: one being the use of the double Lorentzian asymmetric line shape; the other, a set of symmetric peaks. Both approaches lead to excellent fits with undistinguishable peak envelopes and backgrounds; however, they lead to different sets of previously unreported low-intensity satellites. The application of the Block Approach to the analysis of the partially oxidized Ni spectra allowed for the robust identification of five doublets corresponding to the oxide. It is remarkable that the sum of these oxide peaks closely reproduces the Ni^{3+} spectra, which is consistent with the assessed composition ($Ni_2O_{3.1\pm0.3}$). The strong overlap and shape similarity of the $Ni0$ $L_3M_{45}M_{45}$ Auger structure with that of the Ni^{3+} strongly suggests that the Auger Parameter modified does not provide additional information to that provided by the binding energy shift of the 2p core level. The latter is in contrast to the claims made by other specialists. The angular dependence of the peak intensities is not consistent with a simple layer oxidation mechanism but with the formation of oxide regions protruding deeper into

the film. The existence of regions with protrusions might depend on the grain orientation. For the first time in the history of X-Ray Photoelectron Spectroscopy, in the analysis of the surface chemical composition and the morphology, the uncertainty propagation methods were applied considering the covariance between the parameters of the depth profile parameters and those of the chemical composition.

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