

Applied Surface Science Division Room A211 - Session AS+BI+CA+LS-TuA

Beyond Traditional Surface Analysis

Moderators: Michaeleen Pacholski, The Dow Chemical Company, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm AS+BI+CA+LS-TuA-1 Nanotechnology as a Driver for Going Beyond Traditional Surface Analysis, *Olivier Renault*, CEA-LETI, France **INVITED**

In the last 10 years, the progress of analytical methods has been more and more strongly connected to the pressing needs from materials and processing developments in the nanoelectronics industry. The field of materials analysis is now expanding as more and more complementary information are needed to tailor new materials for particular applications. Time-consuming techniques in the past (e.g. ARPES) are now accessible with increasing throughput, whereas the reliability of others, such as depth profiling, is improving. Finally, techniques like HAXPES implemented in the past only at synchrotron facilities, are now entering into laboratories.

In this talk I will illustrate by a series of examples in the field of device technology this evolution of surface analysis getting beyond traditional methods, driven by technological developments.

3:00pm AS+BI+CA+LS-TuA-3 Core Levels Sub-shell Photo-ionization Cross-sections of Au, Ag, Cu in the Hard X-ray Photon Energy Range of 7-26 keV, *Germán Rafael Castro*, *J Rubio Zuazo*, Spanish CRG BM25-Spline Beamline at the ESRF, France

Hard X-ray Photo-electron spectroscopy (HAXPES)^[1] has been developed in the last 10-15 years as a unique tool for retrieving accurate non-destructive^[2] compositional and electronic bulk property of materials in the tens of nano-meters depth-scale with nano-meter resolution. Furthermore, the ability to tune the excitation energy in the hard X-ray regime enables tuning the sampling depth, i.e. depth profile analysis, but also enables the discrimination between bulk and surface effects, especially if combined with variable incident and exit angle.

However, an important drawback is the lack of knowledge of the photo-ionization cross-section at the HAXPES photon energy and in special for now accessible deeper core levels. Recently theoretical data has been reported^[6] concerning the photo-ionization cross sections and parameters of the photo-electron angular distribution for atomic subshells but for binding energies lower than 1.5 keV of all elements with $1 \leq Z \leq 100$ in the photon energy range 1.5–10 keV. Unfortunately, these calculations do not contain information for deep orbitals accessible in HAXPES, even more there are scarce experimental results reported for both depth core levels and hard x-ray excitation energies.^[3,4]

In the present work we will show the experimentally obtained relative sub-shell photo-ionization cross sections for 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d core levels of gold (Au), 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d core levels of silver (Ag) and 1s, 2s, 2p, 3s, 3p, 3d core levels of Cooper (Cu) in the X-ray photon energy range of 7–26 keV. In the case of Au, cross sections have been corrected with experimental obtained angular anisotropy parameter. A comparison with theoretical sub-shell photo-ionization cross sections, and angular anisotropy photo-ionization parameters^[5,6] will be also presented.

References

1. J. Rubio-Zuazo, G.R. Castro, *Nucl. Instrum. Methods Phys. Res. A*, **547**, 64-72 (2005).
2. J. Rubio-Zuazo, P. Ferrer, G.R. Castro, *J. Electron Spectrosc. Relat. Phenom.*, **180**, 27-33 (2010).
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4. C. Kunz, S. Thiess, B. Cowie, T.-L. Lee, J. Zegenhagen, *Instrum. Methods Phys. Res. A*, **547**, 73-86 (2005).
5. J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8** 129–137 (1976).
6. M.B. Trzhaskovskaya, and V.G. Yarzhevsky, *At. Data and Nucl. Data Tables*, **119** (2018) 99–174

3:20pm AS+BI+CA+LS-TuA-4 Interfacial Photochemistry of Pyruvic Acid in Atmospheric Chemistry, *Yanjie Shen*, *Y Fu*, Pacific Northwest National Laboratory; *X Yao*, Ocean University of China; *Z Zhu*, Pacific Northwest National Laboratory; *X Yu*, Earth and Biological Sciences Directorate

Presentation Summary:

This presentation will show our latest results of pyruvic acid photochemical aging in dry and liquid surface analysis using time-of-flight secondary ion mass spectrometry.

Abstract

Pyruvic acid is widespread in fogs, aerosols, and clouds. The sunlight driven reaction pathways of pyruvic acid in the air-liquid interface are more elusive compared to its well-known gas and bulk phase chemistry in the atmosphere. We investigated photochemical aging products from pyruvic acid after different UV photolysis times up to 8 hours in dry and liquid samples using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Both ToF-SIMS spectral and spectral principal component analysis (PCA) were used to study the surface photochemical aging products among various photochemical aging samples. A number of aging products were observed in dry samples indicating the importance of interfacial reactions¹; however, the dry sample analysis cannot fully represent the air-liquid interfacial chemistry of pyruvic acid. Therefore, we used our unique liquid surface molecular imaging approach enabled by the SALVI microfluidic reactor to study the air-liquid interface. The *in situ* liquid SIMS observations show photochemical products of pyruvic acid at the air-liquid interface including oxidation products (i.e., acetic acid, oxalic acid, formic acid, lactic acid), oligomers (i.e., dimethyltartaric acid), and water clusters (i.e., $(\text{H}_2\text{O})_n\text{H}^+$, $(\text{H}_2\text{O})_n\text{OH}^-$) with submicrometer spatial resolution. In addition, SIMS three-dimensional chemical mapping provides visualization of the surface mixing state at the molecular level. For example, oligomers and oxidation products become more significant as illustrated in the chemical spatial mapping with increased photolysis time. Our study of the pyruvic acid aqueous surface provides new understanding of complex photochemical reactions as an important source of aqueous secondary organic aerosols (SOAs) in atmospheric chemistry.

Key Words: pyruvic acid, photochemical, dry SIMS, liquid SIMS, air-liquid interface, oligomer, water cluster, SOA.

References:

1. Fu, Y.; Zhang, Y.; Zhang, F.; Chen, J.; Zhu, Z.; Yu, X.-Y., Does interfacial photochemistry play a role in the photolysis of pyruvic acid in water? *Atmospheric Environment* **2018**, *191*, 36-45.

4:20pm AS+BI+CA+LS-TuA-7 Nanoscale Tomographic Mapping the Liquid-Solid Interface with Cryo-APT, *Daniel Perea*, *D Schreiber*, *J Evans*, *J Ryan*, Pacific Northwest National Laboratory **INVITED**

The liquid-solid interface plays an essential role in many phenomena encountered in biological, chemical, and physical processes relevant to both fundamental and applied science. However, study of the liquid/solid interface at the nanoscale is challenging as liquids are generally incompatible with many analytical techniques that require high to ultrahigh vacuum conditions. One strategy to probe the liquid-solid interface is to cryogenically freeze the liquid into solid form to preserve local ionic chemistry gradients and surface composition within a solid structure, making it more amenable to vacuum-based analyses such as Atom Probe Tomography (APT). However, the regular application of APT to hydrated materials is lacking due to challenges in preparing the necessary nanoscale needle-shaped specimens using a FIB-SEM and the subsequent environmentally-protected transfer of the frozen specimens to the APT instrument for analysis. In this presentation, I will discuss the development of a FIB-based site-specific liftout and attachment scheme of cryogenically cooled specimens involving a combination of redeposition and overcoating of organic and organometallic molecules. A modified commercially-available specimen suitcase shuttle device and an environmental transfer hub vacuum chamber at PNNL is used to facilitate environmentally-protected specimen transfer between the cryo FIB and the APT tool, allowing for the first time, APT analysis of a water/solid interface in 3D to reveal the complex nanoscale water-filled porous network of corroded glass. Application of this unique specimen preparation approach to biological specimens will also be discussed.

5:00pm AS+BI+CA+LS-TuA-9 Characterization of Electronic Materials using Low Energy Inverse Photoemission Spectroscopy, *Benjamin Schmidt*, *J Newman*, *J Mann*, *K Artyushkova*, *L Swartz*, Physical Electronics; *M Terashima*, *T Miyayama*, ULVAC-PHI Inc., Japan

The development of complex electronic materials in areas such as batteries, solar cells, and flexible display panels require a detailed knowledge of the electronic band structure in order to achieve desired performance. A few of the material properties of interest are electron affinity, work function, ionization potential, and bandgap. Photoemission spectroscopic techniques such as Ultraviolet Photoelectron Spectroscopy

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(UPS) and Inverse Photoemission Spectroscopy (IPES) have traditionally been used to measure these values.

Organic electronic materials are growing in popularity due to lower costs of production and the ability to create interesting mechanical structures. However, they are susceptible to chemical damage with prolonged exposure to high-energy electron beams during analyses, which can affect the measured properties.

Low Energy Inverse Photoemission Spectroscopy (LEIPS) is a variant of IPES but uses an incident electron beam at lower energy than traditional IPES (< 5 eV vs. ~10 eV, respectively), making it less damaging for organic materials. In this talk, the operating principles of LEIPS will be discussed. Several material system examples will be shown, including films of C60 and copper phthalocyanine (CuPc).

5:20pm **AS+BI+CA+LS-TuA-10 Deconvolution of Atom Probe Tomography on Nanomaterials for Renewable Energy**, *Margaret Fitzgerald, M Dzara, D Diercks*, Colorado School of Mines; *N Leick, S Christensen*, National Renewable Energy Laboratory; *T Gennett, S Pylypenko*, Colorado School of Mines

Technologies for hydrogen-based economy rely heavily on advancements in development of nano-structured materials. Nano-materials used in applications for energy conversion, storage and production have unique, desirable properties because of their intricate chemistries and morphologies, however this makes them difficult to characterize using traditional techniques. Of specific interest is elucidation of the surface properties and identification of differences between surface and bulk composition. This work features Atom Probe Tomography (APT) paired with other techniques that enable multi-scale characterization in 2D and 3D as a promising approach to create a more complete picture of the complexities of nano-structured materials.

APT is an incredibly powerful tool that has been used to render sub-nanometer-resolution, 3D reconstructions of metallic and, more recently, ceramic samples to enhance the understanding of local composition variations, such as around grain-boundaries and precipitates. This presentation outlines the procedures and considerations for expansion of APT towards analysis of nano-structured materials used for catalysis and hydrogen storage. Challenges related to both APT specimen preparation, APT analysis, and data reconstructions will be discussed. Specific considerations that will be addressed include sample pre-screening for mass spectrometry peak overlap, substrate and encapsulation material selection based on field evaporation compatibility, and prevention of sample damage for air- and beam-sensitive materials. In order to produce accurate 3D reconstructions of the APT data for these samples, initial assessment of a two-dimensional morphology of these materials is made using scanning transmission electron microscopy (STEM) and elemental distributions are acquired with energy dispersive x-ray spectroscopy (EDS). Surface chemistry of the sample is determined using X-ray Photoelectron Spectroscopy (XPS) in order to correlate surface chemistry between APT data and quantified XPS chemical ratios. This talk will provide evidence of cross-correlation across multiple techniques and integration of 2D and 3D data to provide a pathway for understanding these complex materials beyond traditional capabilities.

5:40pm **AS+BI+CA+LS-TuA-11 Mass Spectrometric Investigation of Ion Solvation in Liquids, a Comparison of *in situ* Liquid SIMS to Regular ESI-MS**, *Yanyan Zhang*, Institute of Chemistry, Chinese Academy of Sciences, China; *D Baer, Z Zhu*, Pacific Northwest National Laboratory

Ion solvation plays very important roles in many important biological and environmental processes. Mass spectrometry (MS)-based methods have been used to investigate this topic with molecular insights. To study ion solvation, ionization processes should be as soft as possible in order to retain solvation structures. An *in situ* liquid secondary ion MS (SIMS) approach developed in our group has been recently utilized in investigations of Li ion solvation in nonaqueous solution, and it detected a series of solvated Li ions.^[1] As traditionally SIMS has long been recognized as a hard ionization process with strong damage occurring at the sputtering interface, it is very interesting to study further how soft *in situ* liquid SIMS can be. In this work, we used halide ion hydration as a model system to compare the ionization performance of the *in situ* liquid SIMS approach with regular electrospray ionization MS (ESI-MS). Results show that, although ESI has been recognized as a soft ionization method, nearly no solvated halide ions were detected by regular ESI-MS analysis, and only strong signals of salt ion clusters were seen. As a comparison, in liquid SIMS spectra, a series of obvious hydrated halide ion compositions could be observed.^[2] Our findings demonstrated that the *in situ* liquid SIMS

approach is surprisingly soft, and it is expected to have very broad applications on investigation of various weak interactions and many other interesting chemical processes (e.g., the initial nucleation of nanoparticle formation) in liquid environment.

References:

[1] Zhang, Y.; Baer, D.; Zhu, Z.*, et al., "Investigation of Ion-Solvent Interactions in Non-Aqueous Electrolytes Using *in situ* Liquid SIMS", *Anal. Chem.*, **2018**, *90*, 3341–3348.

[2] Zhang, Y.; Zhu, Z.*, et al., "In Situ Liquid SIMS: A Surprisingly Soft Ionization Process for Investigation of Halide Ion Hydration", *Anal. Chem.* **2019**, published online, DOI: 10.1021/acs.analchem.8b05804.

6:00pm **AS+BI+CA+LS-TuA-12 Characterizing the Thickness and Physical Properties of Nearly Ideal Zirconium Oxide Surfaces Using Ellipsometry, ESCA, Profilometry and FIB**, *Edward Gillman*, Naval Nuclear Laboratory
Zirconium alloys are used in nuclear reactor cores due to their small neutron scattering cross-section and corrosion resistance. Corrosion of zirconium alloys results in the formation of a protective oxide layer that the corrosion species must travel through in order to continue the corrosion process. This oxide prevents further oxidation of the metal, slowing down the reaction rate. Characterizing this important oxide film on a metal is difficult. A number of analytical techniques are used to better understand the properties and growth of this oxide film. To insure that reliable information is reported, the thickness and physical properties of zirconium oxide deposited on a single-crystal silicon wafer by magnetron sputtering has been investigated. Data obtained from Electron Spectroscopy for Chemical Analysis (ESCA), profilometry, ellipsometry and Focused Ion Beam (FIB) experiments are all self-consistent with each other. This validates the utility of these measurements for the characterization of the oxide observed on metallic surfaces.

New Challenges to Reproducible Data and Analysis Focus Topic

Room A124-125 - Session RA+AS+CA+PS+TF-WeM

Reproducibility in Science and Engineering, including materials and energy systems

Moderators: Karen Gaskell, University of Maryland, College Park, Svitlana Pylypenko, Colorado School of Mines

8:00am **RA+AS+CA+PS+TF-WeM-1 Reproducibility and Replicability in Science and Engineering: a Report by the National Academies**, *T Winters*, National Academies of Sciences, Engineering, and Medicine; *Dianne Chong*, Boeing Research and Technology (Retired) **INVITED**

One of the pathways by which scientists confirm the validity of a new finding or discovery is by repeating the research that produced it. When a scientific effort fails to independently confirm the computations or results of a previous study, some argue that the observed inconsistency may be an important precursor to new discovery while others fear it may be a symptom of a lack of rigor in science. When a newly reported scientific study has far-reaching implications for science or a major, potential impact on the public, the question of its reliability takes on heightened importance. Concerns over reproducibility and replicability have been expressed in both scientific and popular media.

As these concerns increased in recent years, Congress directed the National Science Foundation to contract with the National Academies of Science, Engineering, and Medicine to undertake a study to assess reproducibility and replicability in scientific and engineering research and to provide findings and recommendations for improving rigor and transparency in research.

The committee appointed by the National Academies to carry out this task included individuals representing a wide range of expertise: methodology and statistics, philosophy of science, science communication, behavioral and social sciences, earth and life sciences, physical sciences, computational science, engineering, academic leadership, journal editors, and industry expertise in quality control. Individuals with expertise pertaining to reproducibility and replicability of research results across a variety of fields were included as well.

This presentation will discuss the committee's approach to the task and its findings, conclusions, and recommendations related to factors that influence reproducibility, sources of replicability, strategies for supporting reproducibility and replicability, and how reproducibility and replicability fit into the broader framework of scientific quality and rigor.

8:40am **RA+AS+CA+PS+TF-WeM-3 Directly Assessing Reproducibility in Materials Chemistry Research Using Literature Meta-analysis**, *David Sholl*, Georgia Institute of Technology **INVITED**

While it is widely agreed that making reported research more reproducible is a desirable goal, less is known about how reproducible current work in materials chemistry is. I will discuss using literature meta-analysis as a tool to obtain quantitative insight into the reproducibility of materials chemistry experiments. Case studies will be discussed involving measurements of gas adsorption in metal-organic frameworks and the synthesis of metal-organic framework materials. These are useful examples to study because comprehensive databases of information from the open literature are available, but they share features that are common in many areas of material chemistry. Insights from these case studies suggest possible paths towards improving data reproducibility for individual researchers, for academic departments and for professional organizations.

9:20am **RA+AS+CA+PS+TF-WeM-5 Reproducibility in Fundamental and Applied Science**, *George Crabtree*, Argonne National Laboratory, University of Illinois at Chicago **INVITED**

The scientific enterprise operates via a few basic features, including questions, insight, hypotheses, critique, reproducibility, elaboration and revision. All contribute to the process of discovery, none can be taken as the single signature of scientific truth. Discovery science is a dynamic process informed by new observations and continuous refinement of the precision, accuracy, principals and scope of our collective scientific knowledge. History has many examples of significant revisions of previously accepted dogma based on new observations (the earth is flat, matter is infinitely divisible, the stars are fixed). New insights lead to new fundamental principles (energy is conserved, nothing can go faster than light, germs cause disease) that open new opportunities for advancing the *Wednesday Morning, October 23, 2019*

scientific frontier and raising the quality of life. Examples of advances of the frontiers of energy science and their implications for reproducibility will be given.

11:00am **RA+AS+CA+PS+TF-WeM-10 Representativeness of a TEM image for Revealing New Phenomenon in Energy Storage Materials**, *Chongmin Wang*, Pacific Northwest National Laboratory; *D Baer*, Pacific Northwest National Laboratory

Transmission electron microscopy (TEM), as a imaging technique with high spatial resolution, appears to be a routine tool for showcasing, often viewed as an enlightening figure, the structural and chemical information of materials at multiscale of down to single atomic column. One of a very common questions that raised by the viewer, not necessarily suspicious, is the representativeness of the image to the real situation as considering the sampling scale of the TEM imaging method. This question is further elevated for the case of in-situ and operando observation as which naturally couples in another dimension of "time" in addition to the "spatial" scale. In addition, beam effect can be coupled in for artifacts. In this presentation, we will check into the reproducibility of TEM imaging of both in-situ and ex-situ for revealing new phenomenon in energy storage materials, while certain cautions may also be necessary for interpreting new observations based on TEM.

11:20am **RA+AS+CA+PS+TF-WeM-11 Reproducibility Issues when Developing Catalysts for Fuel Cell Applications**, *M Dzara*, *S Zaccarine*, Colorado School of Mines; *K Artyushkova*, Physical Electronics and University of New Mexico; *Svitlana Pylypenko*, Colorado School of Mines

This talk will discuss reproducibility issues encountered during the development of novel catalysts for low temperature fuel cell performance (PEMFC) as replacements of state-of-the-art catalysts that contain Pt-based nanoparticles supported on a high surface area carbon support. Examples across several catalytic systems will be shown, including low platinum-group metal (low-PGM) catalysts with extended surfaces derived from nanowire templates, and PGM-free catalysts based on N-doped carbon with an atomically dispersed transition metal.

Reproducibility issues related to the synthesis of these catalytic materials and their impact on the performance of these catalysts will be reported first following by discussion of challenges in characterization. Specifically, the need for complementary characterization will be highlighted along with issues that arise when materials are characterized by different groups using different techniques. Another set of reproducibility issues arises when conducting characterization of catalysts under in-situ and in-operando conditions.[1] The time constraints imposed by the availability of instrumentation result in datasets that have a limited number of samples, areas per samples and replicate measurements on the same sample.

(1) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas – Solid Interface with in Situ Spectroscopy : The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C* **2019**, *123* (14), 9074–9086.

11:40am **RA+AS+CA+PS+TF-WeM-12 Challenges in Multimodal Spectroscopic Analysis of Energy Storage Materials**, *Vijayakumar Murugesan*, Pacific Northwest National Laboratory; *K Mueller*, Joint Center for Energy Storage Research (JCESR) **INVITED**

Charge transfer across heterogeneous interfaces facilitated by redox reactions is the basis of energy storage technology. Capturing the interfacial processes over broad scales both spatially (ranging from angstroms up to 100 nm) and temporally (lasting from fs up to a few minutes) is a major challenge. This is one origin of the existing knowledge gaps in energy storage materials, which impede our ability to predict and control the emergent behaviors at electrochemical interfaces. As part of Joint Center for Energy Storage Research (JCESR) center, we developed a multi-modal in situ characterization tool set based on X-ray absorption, photoelectron and multinuclear NMR spectroscopy in combination with computational modelling that can access a range of the important complex processes. This multimodal approach helps us gain critical insights of the charge transfer process, but also presented unique challenges in data collection, analysis and reproducibility. The multitude of constituents and varying surface chemistry combined with external stimuli (applied potential and temperature) challenges the traditionally conceived time and spatial resolution limitations of the probes. For example, establishing reference systems and base line measurements for electrochemical process where combinatorial constituents react and depend on the charge state is a major challenge in spectroscopic studies and complicates subsequent corroboration with computational analysis. In this talk, we will discuss

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overcoming these challenges and apply the methods to critically analyzing solid-electrolyte interphase (SEI) evolution in Li-metal based batteries, multivalent ion transport across membranes and chemical stability of redox flow battery electrolytes.

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Operando Characterization Techniques for In situ Surface Analysis of Energy Devices

Moderator: Svitlana Pylypenko, Colorado School of Mines

2:20pm AS+CA+LS-WeA-1 Probing the Electronic Structure of Electrocatalysts and the Formation of Reaction Intermediates, *Kelsey Stoerzinger*, Oregon State University INVITED

Electrocatalysts are important constituents in numerous energy conversion and storage processes. Reactants adsorb onto the electrocatalyst surface, where the interplay of electronic states results in a lower activation barrier for the transfer of electronic and ionic species in the reaction pathway to product formation. Rational design of electrocatalysts with greater activity for higher efficiency devices requires an understanding of the material's electronic structure in situ, as well as the reaction intermediates involved.

Many surface science techniques, such as X-ray photoelectron spectroscopy (XPS), collect information from inherently surface-sensitive low-energy processes, requiring operation in ultrahigh vacuum. This constraint is lifted for ambient pressure XPS, which can probe the surface in equilibrium with the gas phase at pressures up to ~a few Torr, or with thin liquid layers using a higher incident photon energy. This presentation will discuss the insights obtained with this technique regarding the electronic structure of oxide electrocatalysts in an oxidizing or humid environment, as well as the reaction intermediates of relevance to electrocatalysis.¹ I will then extend the technique to probe electrocatalysts *in operando*,² driving current through a thin layer of liquid electrolyte and employing a tender X-ray source.

References:

[1] Stoerzinger, K.A. Wang, L. Ye, Y. Bowden, M. Crumlin, E.J. Du, Y. Chambers, S.A. "Linking surface chemistry to photovoltage in Sr-substituted LaFeO₃ for water oxidation". *Journal of Materials Chemistry A* 6 (2018) 22170-22178.

[2] Stoerzinger, K.A. Wang, X.R. Hwang, J. Rao, R.R. Hong, W.T. Rouleau, C.M. Lee, D. Yu, Y. Crumlin, E.J. Shao-Horn, Y. "Speciation and electronic structure of La_{1-x}Sr_xCoO_{3-δ} during oxygen electrolysis". *Topics in Catalysis* 61 (2018) 2161-2174.

3:00pm AS+CA+LS-WeA-3 Surface Characterization of Battery Electrode/Electrolyte Materials Using XPS and ToF-SIMS, *Elisa Harrison*, S Peczonczyk, S Simko, Ford Motor Company; *K Wujcik*, Blue Current; *A Sharafi*, A Drews, Ford Motor Company

With a drive to develop hybrid electric and electric vehicles for improving fuel economy and lowering emissions, research of battery materials becomes necessary to increase the performance and durability of automotive batteries. Therefore, significant improvements in the energy capacity, stability, and safety of automotive batteries must be achieved. For the last two decades, traditional methods to characterize battery materials and interfaces have focused on the mechanical and electrochemical properties of the battery. There has been less emphasis on understanding chemical properties of the surface of the electrode and the chemistry that occurs at the electrode/electrolyte interface. Moving forward to develop new battery systems, gaining an understanding of the surface chemistry of battery materials is critical to improving performance.

The objective of this work is to highlight the need for surface analytical techniques and methodologies to fully characterize and improve battery materials. In this work, the surface chemistry of electrodes and electrolytes were analyzed using both X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These are powerful tools to identify slight changes to the surface chemistry of battery materials with respect to factors such as electrode and electrolyte formulation, cycling conditions, air exposure, contamination, and sample replication.

3:20pm AS+CA+LS-WeA-4 In Operando Molecular Imaging of Microbes as an Electrode, *Xiao-Ying Yu*, Pacific Northwest National Laboratory

Metal reducing bacteria, such as *Shewanella* and *Geobacter*, has attracted attention in recent years particularly for the potential as Genome Encoded Materials. They also can function as electrodes in microbial fuel cells (MFCs). Despite the surging interest and applications of various imaging tools to understand the microbial populations, little has been explored in

the *in vivo* study of MFCs using novel *in operando* electrochemical spectroscopy. We have invented a System for Analysis at the Liquid Vacuum Interface (SALVI) microfluidic cell that is suitable for culturing bacterial biofilms for *in vivo* molecular imaging. We have also illustrated that the electrochemical version of SALVI or the E-cell is viable for *in operando* study of the electrode-electrolyte interface. We have cultured *Shewanella* and *Geobacter sulfurreducens* biofilms in SALVI and published several papers recently. In this presentation, I will show most recent *in operando* molecular imaging results using E-cell and *in situ* liquid SIMS to investigate electron transport using *Shewanella* as a model MFC electrode.

4:20pm AS+CA+LS-WeA-7 Operando-XPS Investigation of Low-Volatile Liquids and Their Interfaces using Lab-Based Instruments, *Sefik Suzer*, Bilkent University, Turkey INVITED

X-Ray based Operando Investigations have traditionally been carried out in Synchrotron facilities, due to demanding instrumentation and expertise.^{1,2} However, although sporadic, several important lab-based XPS studies have also been reported.³ Emergence of Ionic Liquids with several promising properties, including their low volatility, has rekindled the use of XPS, especially for Operando types of measurements.⁴ Our initial investigations had also concentrated on ionic-liquids and their interfaces under **dc** and **ac** electrical bias, and extended to monitoring electrochemical reactions.^{5, 6} Recently, we have been investigating other low-volatile liquids and their drops on various substrates to tap into the Electrowetting phenomena.^{7,8} The common theme in all of our studies is the use of bias dependent shifts in the positions of the core-levels as reflection of the electrical potentials, recorded in a totally non-invasive and chemically resolved fashion. We use the magnitude and the frequency dependence of such potentials to extract pertinent information related to chemical and/or electrochemical properties of the materials and their interfaces. Several examples using ionic liquids, liquid poly-ethylene-glycol (PEG) and their mixtures will be presented and discussed.

References:

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[8] Gokturk; P.A., Ulgut; B., Suzer; S., *Langmuir* **35**, 3319-3326 (2019).

5:00pm AS+CA+LS-WeA-9 Decoupling Surface and Interface Evolution in Polymer Electrolyte Membrane Systems Through In Situ X-Ray Photoelectron Spectroscopy, *Michael Dzara*^{1,2}, Colorado School of Mines; *K Artyushkova*, Physical Electronics; *H Eskandari*, *K Karan*, University of Calgary, Canada; *K Neyerlin*, National Renewable Energy Laboratory; *S Pylypenko*, Colorado School of Mines

Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) enables surface sensitive study of gas-solid interfaces. The fundamental knowledge obtained from such measurements provides unparalleled insight into the physicochemical processes that drive electrocatalytic devices.¹ Studies featuring AP-XPS span a broad range of materials and reactions, with many focused on thin films or other well-defined materials. In such studies, there are often clear changes in the material upon transition from ultra-high vacuum to *in situ* conditions, or there are well-defined catalyst species that participate in the relevant process.

In this work, the differing evolution of the many interfaces in polymer electrolyte membrane (PEM) electrodes in the presence of water vapor is studied through detailed analysis of AP-XPS spectra. The complexity of analyzing these interfaces arises from the presence of both catalyst and

¹ ASSD Student Award Finalist

² National Student Award Finalist

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ionomer species in PEM electrodes, and the subtlety of the changes induced in AP-XPS spectra by interactions between the catalyst, ionomer, and gas. Adsorption of a gaseous reactant species onto a catalyst's surface results in a weak interaction and a small chemical shift in the adsorbent species, while ionomer may undergo re-orientation or degradation upon exposure to reactants, also altering the spectra. Therefore, spectral subtraction and highly-constrained curve fitting are applied to enable reliable identification of catalyst adsorbing sites and adsorption/desorption trends,² and ionomer changes in the presence of water vapor. Interactions between platinum-group metal-based catalysts and ionomer films with water vapor are first studied independently, and then simultaneously at the electrode scale. Such an approach allows changes in the electrode-water interface to be decoupled and assigned to either catalyst adsorption behavior, or ionomer response. This work lays the foundation for future study of different classes of electrocatalysts at the electrode scale, and *in operando* AP-XPS studies of electrocatalytic processes.

(1) Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H. Investigation of Solid/Vapor Interfaces Using Ambient Pressure X-Ray Photoelectron Spectroscopy. *Chem. Soc. Rev.* **2013**, *42*, 5833–5857.

(2) Dzara, M. J.; Artyushkova, K.; Shulda, S.; Strand, M. B.; Ngo, C.; Crumlin, E. J.; Gennett, T.; Pylypenko, S. Characterization of Complex Interactions at the Gas – Solid Interface with *In Situ* Spectroscopy: The Case of Nitrogen-Functionalized Carbon. *J. Phys. Chem. C* **2019**, *123* (14), 9074–9086.

5:20pm **AS+CA+LS-WeA-10 Low Temperature Scanning Tunneling Microscopy and Spectroscopy of Semiconductor Nanowire Device Surfaces**, *Yen-Po Liu, Y Liu, S Mousavi, L Sodergren, F Lindelöw, S Lehmann, K Dick Thelander, E Lind, R Timm, A Mikkelsen*, Lund University, Sweden

III-V semiconductor nanowires (NWs) show considerable promise as components in efficient and fast electronics as well as for quantum computing. In particular, the surfaces of the NWs play a significant role in their function due to the large surface to bulk ratio. Further, as the incorporation and activation of the nanowires in a device can affect their structure, it is relevant to study the surface structure and its influence on electronic properties in devices and during operation.

We use atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) to study InAs and GaAs NWs in planar device configurations. [1-3] We use atomic hydrogen cleaning at 400°C to obtain well-defined surfaces that can be scanned with STM while the complete device is still fully functioning. [2] We study both NWs grown directly in a planar configuration as well as wires harvested from a growth substrate and placed on top of predefined metal contacts with ~100nm precision using a micro/nano probe. In our new <10K closed-cycle STM we can identify the individual device NWs simultaneously as we can apply voltages across the devices using four additional electrical contacts in the low temperature STM. We initially investigate NW device geometric structure and morphology with high precision. Then we continue to perform atomic resolution and low temperature STS mapping on top of the NWs surfaces to investigate electronic structure and potential quantum confinement effects as well as the influence of defects. These measurements can be performed while the device is actively operating by external biases applied and the I(V) characteristic across the NW is obtained. The STM tip can also act as a role as a local gate for Scanning Gate Microscopy (SGM) [4], which we can precisely locate on the operating single NWs device for SGM on the areas as STM is performed.

[1] Persson, O. et al., (2015). *Nano Letters*, *15*(6), pp.3684-3691.

[2] Webb, J. et al., (2017). *Scientific Reports* *7*, 12790

[3] Hjort, M. et al., (2015). *ACS Nano*, *8*(12), pp.12346-12355

[4] Webb J.L. et al., (2014). *Nano Research* *7*, 877

5:40pm **AS+CA+LS-WeA-11 Work-function Estimation and In situ Measurement of Photoemission Spectroscopy of CuFeO₂ under Near Ambient Condition**, *Saumya Banerjee, P Sapkota*, University of Notre Dame; *A Cabrera*, Pontificia Universidad Católica de Chile, Chile; *S Ptasinska*, University of Notre Dame

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H₂O under operational conditions. Therefore,

knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. The work functions of pure and Ga-doped Delafossite p-type CuFeO₂ semiconductor crystals with different thicknesses were measured using near ambient pressure x-ray photoemission spectroscopy (NAP-XPS) in Ar ambient. The values differ with changing thickness as well as Ga doping. The effect of water and CO₂ on the samples was also studied using NAP-XPS to understand the interaction between atmospheric gases and CuFeO₂ which may be helpful for its practical application in solar cells. No significant changes were found in XPS result obtained from CuFeO₂ in water ambient with and without illumination whereas CO₂ induced changes in oxygen XPS peak positions.

6:00pm **AS+CA+LS-WeA-12 In-situ X-ray Photoelectron Spectroscopic Study of III-V Semiconductor/H₂O Interfaces under Light Illumination**, *Pitambar Sapkota, S Ptasinska*, University of Notre Dame

A number of studies on different semiconductor materials that can be used as a photoelectrode in photoelectron-chemical (PEC) cells for solar water splitting is continually growing in material sciences and solar energy communities. III-V based compounds have been the most promising candidates because of their efficient light and carrier management properties in addition to suitable band gap and band edge energies, which properly match the solar spectrum and water redox potentials, respectively. Although most of the highly efficient PEC water splitting cells are based on III-V semiconductor, these photoelectrode materials are unstable under operational conditions. Few studies suggest oxidation leading to corrosion as a major cause of the degradation of these photoelectrodes, but it is still not completely understood and little is known about the role of the oxides formed at the interfaces. Therefore, knowledge of the interfacial reactions in realistic situations and surface dynamics are necessary to advance our understanding of water splitting mechanism, as well as to build a stable and efficient PEC solar water splitting cell. In this study, we used state of the art spectroscopic technique, ambient pressure X-ray photoelectron spectroscopy, to characterize semiconductor (GaAs and GaP) surface and to study chemical reactions occurring at the water interface in presence of secondary light source. Core level photoemission spectra from Ga2p, As3d, P2p, and O1s were collected at different water pressures in presence of secondary light source to identify the newly formed surface species, particularly oxides, and to evaluate the interaction of GaAs and GaP with water under light illumination.

This research is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences under Award Number DE-FC02-04ER15533.

**Chemical Analysis and Imaging Interfaces Focus Topic
Room A120-121 - Session CA+NS+SS+VT-WeA**

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces I

Moderators: Juan Yao, Pacific Northwest National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-WeA-1 Chemical Analysis and Imaging of Environmental Interfaces**, *Vicki Grassian*, University of California at San Diego

INVITED

Environmental interfaces, defined as any surface in equilibrium with its surrounding environment, are ubiquitous. From this broad definition, there are a myriad of different types of environmental interfaces that include atmospheric aerosols, nanomaterials and indoor surfaces. This talk will focus on the use of different molecular probes including various spectroscopic and imaging techniques to investigate interfaces relevant to outdoor and indoor environments.

3:00pm **CA+NS+SS+VT-WeA-3 Liquid/Vapor Interfaces Investigated with Photoelectron Spectroscopy**, *Hendrik Bluhm*, Fritz Haber Institute of the MPG, Germany

INVITED

Aqueous solution/vapor interfaces govern important phenomena in the environment and atmosphere, including the uptake and release of trace gases by aerosols and CO₂ sequestration by the oceans.[1] A detailed understanding of these processes requires the investigation of liquid/vapor interfaces with chemical sensitivity and interface specificity under ambient conditions, *i.e.*, temperatures above 200 K and water vapour pressures in

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the millibar to tens of millibar pressure range. This talk will discuss opportunities and challenges for investigations of liquid/vapor interfaces using X-ray photoelectron spectroscopy and describe some recent experiments that have focused on the propensity of certain ions and the role of surfactants at the liquid/vapor interface.

[1] O. Björneholm et al., *Chem. Rev.* **116**, 7698 (2016).

4:20pm CA+NS+SS+VT-WeA-7 Methanol Hydration Studied by Liquid μ -jet XPS and DFT Simulations, Jordi Fraxedas, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *E Pellegrin, V Perez-Dieste, C Escudero*, CELLS-ALBA, Spain; *P Rejmak*, Institute of Physics PAS, Poland; *N Gonzalez, A Fontseré, J Prat, S Ferrer*, CELLS-ALBA, Spain

The advent of liquid μ -jet setups, in conjunction with X-ray Photoemission Spectroscopy (XPS), has opened up a plethora of experimental possibilities in the field of atomic and molecular physics [1]. Here, we present a combined experimental and theoretical study of the hydration of methanol at the aqueous solution/vapor interface. These are first experimental results obtained from the new liquid μ -jet setup at the Near Ambient Pressure Photoemission (NAPP) endstation of the CIRCE helical undulator beamline (100–2000 eV photon energy range) at the CELLS-ALBA synchrotron light source, using a differentially pumped SPECS PHOIBOS 150 hemispherical electron energy analyzer [2]. The experimental results are compared with simulations from density functional theory (DFT) regarding the electronic structure of single molecules and cluster configurations as well as with previous experimental studies.

Methanol is the simplest amphiphilic molecule capable of hydrogen bonding due to its apolar methyl and polar hydroxyl groups. The results obtained from pure water at 600 eV photon energy emphasize the short range tetrahedral distribution as previously observed for crystalline and amorphous ice. We also find indications for ordering phenomena in water/methanol mixtures by the reduced O1s XPS liquid line width (as compared to pure water), which could be ascribed to the amphiphilic character of the methanol molecule. Regarding the C1s XPS lines, the vapor/liquid peak ratios allow for a quantitative determination of the methanol volume concentrations in both the vapor as well as in the liquid phase, that are corroborated by an analogue analysis of the valence band (VB) spectra. A detailed quantitative analysis of the water/methanol liquid VB XPS spectrum accounting for the photon energy dependence of photoemission cross sections confirms the atomic/orbital characteristics of the methanol molecular orbitals involved in the transitions and their pertinent intensities. From the decomposition of the liquid VB spectrum of the water/methanol mixture together with finite XPS probing depth we derive a methanol volume fraction of 43% for the outer liquid layers as compared to the nominal bulk liquid value of 37.5%. Finally, from the different binding energy (BE) shifts of the water/methanol liquid VB spectrum with respect to that of pure methanol, we develop a $\text{CH}_3\text{OH}-(\text{H}_2\text{O})_3$ cluster-based model that relates these different BE shifts to the different MO hybridizations within that cluster.

[1] B. Winter, M. Faubel, *Chem. Rev.* **106** (2006) 1176.

[2] V. Pérez-Dieste, L. Aballe, S. Ferrer, J. Nicolàs, C. Escudero, A. Milán, E. Pellegrin, *J. Phys. Conf. Ser.* **425** (2013) 072023.

4:40pm CA+NS+SS+VT-WeA-8 Survey of Ionic Liquid Interfaces under Vacuum and Ambient Conditions: An XPS Perspective, Yehia Khalifa, Ohio State University; *A Broderick, J Newberg*, University of Delaware; *Y Zhang, E Maginn*, University of Notre Dame

Properties and behavior of Ionic Liquid interfaces tend to behave differently from their bulk counterparts. In this study the preferential enhancement of the lower molar concentration anion [TFSI] in a mixture of [C2MIM][OAc] and [C2MIM][TFSI] is shown in the top 17 Å via angle-resolved X-ray photoemission spectroscopy under ultra high vacuum conditions. This is supported by molecular simulations where a quantitative relationship is also established between the two techniques. This interfacial enhancement is not only unique to mixtures but is also displayed in a pure ionic liquid with a hydrophilic anion such as [HMIM][Cl] studied via ambient pressure X-ray photoemission spectroscopy. The surface of [HMIM][Cl] under vacuum and increasing pressures of water vapor was evaluated (maximum of 5 Torr, 27% relative humidity). Our quantitative results indicate a significantly larger mole fraction of water at the interface compared to the bulk with increasing pressures when compared to previously published tandem differential mobility analysis results on [HMIM][Cl] nanodroplets. Furthermore the reverse isotherms has shown that the water uptake on the interface is a reversible process. These results highlight the unique behavior of ionic liquid interfaces that can be exploited for smart materials design and application.

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5:00pm CA+NS+SS+VT-WeA-9 Ambient Pressure XPS Study of Gallium-Indium Eutectic (EGaln) Surface under Oxygen and Water Vapor, Meng Jia, *J Newberg*, University of Delaware

Liquid metals (LMs) have a combination of high thermal/electrical conductivity and excellent deformability. The application of LMs in the field of electronics has identified many opportunities for their use as stretchable electronics, self-healing conductors and interconnects. Gallium-Indium eutectic (EGaln) is one of the leading alternatives to toxic liquid mercury because of its low vapor pressure, low viscosity, low toxicity and high conductivity. A surface oxide layer is known to form when EGaln is exposed to ambient conditions. However, surface sensitive measurements of this chemistry occurring under ambient conditions are strongly lacking. Herein we present results from the interaction of oxygen and water vapor with the liquid-gas interface of an EGaln droplet deposited on an W foil using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). EGaln was examined up to a maximum of 1 Torr pressure at 550 K. Results reveal that under ambient conditions both oxygen and water vapor form a Ga(3+) oxide (Ga_2O_3) as an outer layer, while a thin layer of Ga(1+) oxide (Ga_2O) resides between metallic EGaln and the outer Ga(3+) oxide. Both gases were unreactive towards Indium under our experimental conditions. The oxidation kinetics in the presence of water vapor were much faster compared oxygen. Proposed reaction mechanisms will be discussed.

5:20pm CA+NS+SS+VT-WeA-10 Laboratory-based Hard X-ray Photoelectron System for the study of Interfaces, Susanna Eriksson, Scienta Omicron

Hard X-ray photoelectron spectroscopy (HAXPES) has traditionally found its application in the core topics of condensed matter physics, but the slowly growing number of beamlines worldwide has widened its appeal to other interest groups. HAXPES uses X-rays in the 2-10 keV range to excite photoelectrons, which are used to non-destructively study the chemical environment and electronic structure of materials.

In contrast to the very surface-sensitive XPS, HAXPES is much more bulk sensitive. This makes it applicable to bulk materials and structured samples, e.g. layered samples and heterostructures. In addition, its bulk sensitivity means that realistic samples can be investigated without the need of prior surface preparation. However, the number of existing HAXPES systems is very small and they are predominantly located at synchrotrons (approx. 20 beamlines worldwide) due to low photoionization cross sections necessitating high X-ray intensities, limiting their availability to users and applications.

This work presents a new laboratory-based instrument capable of delivering monochromated hard X-rays with an energy of 9.25 keV and a focused $30 \times 45 \mu\text{m}^2$ X-ray spot, giving excellent energy resolution of <0.5 eV. Systematic reference measurements are presented outlining the systems capability as well as the latest results from various application fields including energy related materials such as batteries.

Ultimately, this spectrometer presents an alternative to synchrotron-based endstations and will help to expand the number and range of HAXPES experiments performed in the future. HAXPES is a cutting edge characterisation method and the advancement of this technique will tremendously increase the potential to study an ever increasing range of inorganic materials and beyond.

Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic

Room B231-232 - Session HI+AS+CA-WeA

Advanced Ion Microscopy and Surface Analysis Applications

Moderators: Richard Livengood, Intel Corporation, Armin Götzhäuser, University of Bielefeld, Germany

2:20pm HI+AS+CA-WeA-1 Analytical Capabilities on FIB Instruments using SIMS: Applications, Current Developments and Prospects, Tom Wirtz, Luxembourg Institute of Science and Technology, Luxembourg; *J Audinot*, Luxembourg Institute of Science and Technology, Luxembourg, Luxembourg; *J Lovric, O De Castro*, Luxembourg Institute of Science and Technology, Luxembourg

INVITED

Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analyzing surfaces, owing in particular to its ability to detect all elements from H to U and to differentiate between isotopes, its excellent sensitivity and its high dynamic range. SIMS analyses can be

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performed in different analysis modes: acquisition of mass spectra, depth profiling, 2D and 3D imaging. Adding SIMS capability to FIB instruments offers a number of interesting possibilities, including highly sensitive analytics, in-situ process control during patterning and milling, highest resolution SIMS imaging (~10 nm), and direct correlation of SIMS data with data obtained with other analytical or imaging techniques on the same instrument, such as high resolution SE images or EDS spectra [1,2].

Past attempts of performing SIMS on FIB instruments were rather unsuccessful due to unattractive detection limits, which were due to (i) low ionization yields of sputtered particles, (ii) extraction optics with limited collection efficiency of secondary ions and (iii) mass spectrometers having low duty cycles and/or low transmission. In order to overcome these limitations, we have investigated the use of different primary ion species and of reactive gas flooding during FIB-SIMS and we have developed compact high-performance magnetic sector mass spectrometers operating in the DC mode with dedicated high-efficiency extraction optics. We installed such SIMS systems on different FIB based instruments, including the Helium Ion Microscope [3-5], a FIB-SEM DualBeam instrument and the npSCOPE instrument, which is an integrated Gas Field Ion Source enabled instrument combining SE, SIMS and STIM imaging with capabilities to analyse the sample under cryo-conditions.

Here, we will review the performance of the different instruments with a focus on new developments such as cryo-capabilities and new detectors allowing parallel detection of all masses, present a number of examples from various fields of applications (nanoparticles, battery materials, photovoltaics, micro-electronics, tissue and sub-cellular imaging in biology, geology,...) and give an outlook on new trends and prospects.

[1] T. Wirtz, P. Philipp, J.-N. Audinot, D. Dowsett, S. Eswara, *Nanotechnology* 26 (2015) 434001

[2] F. Vollnhals, J.-N. Audinot, T. Wirtz, M. Mercier-Bonin, I. Fourquaux, B. Schroepfel, U. Kraushaar, V. Lev-Ram, M. H. Ellisman, S. Eswara, *Anal. Chem.* 89 (2017) 10702

[3] D. Dowsett, T. Wirtz, *Anal. Chem.* 89 (2017) 8957

[4] T. Wirtz, D. Dowsett, P. Philipp, *Helium Ion Microscopy*, ed. by G. Hlawacek, A. Götzhäuser, Springer, 2017

[5] T. Wirtz, O. De Castro, J.-N. Audinot, P. Philipp, *Ann. Rev. Anal. Chem.* 12 (2019)

3:00pm HI+AS+CA-WeA-3 Correlated Materials Characterization via Multimodal Chemical Imaging using HIM-SIMS, A Belianinov, Oak Ridge National Laboratory; S Kim, Pusan National University, South Korea; A Trofimov, Olga S. Ovchinnikova, Oak Ridge National Laboratory

Multimodal chemical imaging simultaneously offers high resolution chemical and physical information with nanoscale, and in select cases atomic, resolution. By coupling modalities that collect physical and chemical information, we can address a new set of scientific problems in biological systems, battery and fuel cell research, catalysis, pharmaceuticals, photovoltaics, medicine and many others. The combined multimodal platforms enable local correlation of material properties with chemical makeup, making fundamental questions in how chemistry and structure drive functionality approachable. The goal of multimodal imaging is to transcend the existing analytical capabilities for nanometer scale spatially resolved material characterization at interfaces through a unique merger of advanced microscopy, mass spectrometry and optical spectroscopy. Combining helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) onto one platform has been demonstrated as a method for high resolution spot sampling and imaging of substrates. To advance this approach and to expand its capabilities I will present our results of multimodal chemical imaging using this technique on test substrates and show application of this approach for the multimodal analysis of perovskite (HOIPs) materials. I will discuss the performance metrics of the multimodal imaging system on conductive and non-conductive materials and discuss our results on understanding the chemical nature of ferroelastics twin domains in methylammonium lead triiodide (MAPbI₃) perovskite using HIM-SIMS.

3:20pm HI+AS+CA-WeA-4 Compositional Characterization of Biogenic Nanoparticles using the ORION NanoFab with SIMS, Christelle Guillermier, F Khanom, Carl Zeiss PCS, Inc.; D Medina, Northeastern University; J Audinot, Luxembourg Institute of Science and Technology, Luxembourg

Over the past several years, the use of both nanoparticles and nanostructured surfaces have emerged as an alternative's solution to antibiotic resistant bacteria as they effectively decrease bacterial survival without being highly toxic to mammalian cells. These nanoparticles whose

sizes span 10 nm to several hundred nm are composed of a variety of materials such as pure metals, metal oxides, and metalloids. Their chemical characterization however remains a challenge due to their small sizes. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) are the conventional analytical techniques of choice to determine the nanoparticles' morphology, size, and elemental composition. However, although sensitive enough to detect trace elements, SEM and EDX cannot provide elemental information for the smallest features on a bulk sample, or for the lightest elements.

The ORION NanoFab is an ion microscope that allows for high resolution secondary electron (SE) imaging with a He⁺ focused ion beam that can be focused to a 0.5 nm probe size. The same instrument offers a Ne⁺ ion beam with a focused probe size of 2 nm. Recently, this same platform has been configured with a custom-designed magnetic sector secondary ion mass spectrometer (SIMS). It allows for the detection of all periodic table elements including H and Li which EDS cannot easily detect. Importantly, SIMS with neon provides elemental imaging with spatial resolution smaller than 20 nm. The combination of high resolution He⁺ imaging (0.5 nm) with Ne⁺ SIMS elemental mapping yields a direct correlative technique particularly attractive for exploring nanoparticles and nanofeatures in general.

NanoFab-SIMS has already yielded information-rich images in diverse fields of applications. We will here illustrate its potential for the characterization of biogenic nanoparticles made by bacteria and plants.

4:20pm HI+AS+CA-WeA-7 Effects of Ion Irradiation on Two-Dimensional Targets: What is Different from Bulk Materials, Arkady V. Krasheninnikov, Helmholtz-Zentrum Dresden-Rossendorf, Germany

INVITED

Ion irradiation has successfully been used for introducing impurities and creating defects in two-dimensional (2D) materials in a controllable manner. Moreover, focused ion beams, especially when combined with in-situ or post-irradiation chemical treatments, can be employed for patterning and even cutting 2D systems with a high spatial resolution. The optimization of this process requires the complete microscopic understanding of the interaction of energetic ions with the low-dimensional targets.

In my presentation, I will dwell upon the multi-scale atomistic computer simulations of the impacts of ions onto free-standing (e.g., suspended on a TEM grid) and supported (deposited on various substrates) 2D materials, including graphene and transition metal dichalcogenides (TMDs), such as MoS₂ and WS₂. I will emphasize the differences between defect production under ion irradiation in 2D materials and bulk solids. The theoretical results will be augmented by the experimental data obtained by the coworkers. I will further present the results of multi-scale simulations of ion irradiation of free-standing [1] and supported [2] graphene and 2D TMDs, and demonstrate that depending on ion mass and energy, the defect production can be dominated by direct ion impacts, back scattered ions or atoms sputtered from the substrate [2]. Finally, I will touch upon the interaction of highly-charged [3] and swift heavy ions [4] with 2D systems and overview recent progress in modelling this using non-adiabatic approaches including time-dependent density functional theory and Ehrenfest dynamics [5].

1. M. Ghorbani-Asl, S. Kretschmer, D.E. Spearot, and A. V. Krasheninnikov, *2D Materials* 4 (2017) 025078.

2. S. Kretschmer, M. Maslov, S. Ghaderzadeh, M. Ghorbani-Asl, G. Hlawacek, and A. V. Krasheninnikov, *ACS Applied Materials & Interfaces* 10 (2018) 30827.

3. R. A. Wilhelm, E. Gruber, J. Schwestka, R. Kozubek, T.I. Madeira, J.P. Marques, J. Kobus, A. V. Krasheninnikov, M. Schleberger, and F. Aumayr, *Phys. Rev. Lett.* 119 (2017) 103401.

4. R. Kozubek, M. Tripathi, M. Ghorbani-Asl, S. Kretschmer, L. Madauß, E. Pollmann, M. O'Brien, N. McEvoy, U. Ludacka, T. Susi, G.S. Duesberg, R.A. Wilhelm, A. V. Krasheninnikov, J. Kotakoski, and M. Schleberger *J. Phys. Chem. Lett.* 10 (2019) 904.

5. A. Ojanperä, A. V. Krasheninnikov, and M. Puska, *Phys. Rev. B* 89 (2014) 035120.

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5:00pm **HI+AS+CA-WeA-9 Effects of He Ion Irradiation on Gold Nanoclusters: a Molecular Dynamics Study**, *Sadegh Ghaderzadeh, M Ghorbani-Asl, S Kretschmer, G Hlawacek*, Helmholtz-Zentrum Dresden Rossendorf, Germany; *A Krashennikov*, Helmholtz-Zentrum Dresden-Rossendorf, Germany

The interpretation of helium ion microscopy (HIM) images of crystalline metal clusters requires microscopic understanding of the effects of He ion irradiation on the system, including energy deposition and associated heating, as well as channeling patterns. While channeling in bulk metals has been studied at length, there is no quantitative data for small clusters. We carry out molecular dynamics simulations to investigate the behavior of gold nano-particles with diameters of 5-15 nm under 30 keV He ion irradiation. We show that impacts of the ions can give rise to substantial heating of the clusters through deposition of energy into electronic degrees of freedom, but it does not affect channeling, as clusters cool down between consecutive impact of the ions under typical imaging conditions. At the same time, high temperatures and small cluster sizes should give rise to fast annealing of defects so that the system remains crystalline. Our results show that ion-channeling occurs not only in the principal low-index, but also in the intermediate directions. The strengths of different channels are specified, and their correlations with sputtering-yield and damage production is discussed, along with size-dependence of these properties. The effects of planar defects, such as stacking faults on channeling were also investigated.

Finally, we discuss the implications of our results for the analysis of HIM images of metal clusters.

5:20pm **HI+AS+CA-WeA-10 Low Damage Imaging of Polymers with the Helium Ion Microscope**, *Doug Wei*, Carl Zeiss, RMS, Inc.; *J Notte*, Carl Zeiss PCS, Inc.; *A Stratulat*, Carl Zeiss Microscopy, Ltd., UK

Polymers present a combination of challenges for high magnification imaging with the conventional SEM or FIB. Because they are electrically insulating, polymers are susceptible to charge accumulation and can produce imaging artifacts. Or worse, the implanted charge and surface charge can generate fields large enough to induce catastrophic dielectric breakdown. The interaction of the primary beam with the chemical bonds can cause radiolysis, cross-linking, and chain scissions which alter their morphology and other properties. Ion beams of relatively heavy species (Ga and Xe) can cause appreciable sputtering especially at high magnifications. In some cases, the sputtering can be preferential for light atoms, causing disproportionate hydrogen loss. Further difficulties include heating effects, since the typical polymers are good thermal insulators. Compounding matters, they are often temperature sensitive and can be damaged at even modest temperature rises ~ 50 deg C.

However, some of the newly available light ion beams (H, He, Li) offer unique advantages that help to circumvent the problems traditionally encountered when imaging polymers. First, the charging effects are greatly diminished compared to the SEM. In part, this is because the incident ion is likely neutralized as it enters the sample, and remains in a mostly neutral state as it penetrates deeply. This leaves only a net surface charge, which is overall positive and made more so by the ejection of secondary electrons from the surface. This is easily resolved using a collection of low energy electrons provided by a flood gun. The light ion beams also have relatively low sputtering rates compared to the heavier ions. Their interactions are primarily with the electrons of the sample. So while they can affect bonding, they are much less likely to cause sputtering. The light ions will generally be implanted deeply, often hundreds of nanometers under the surface, and helium in particular is known to diffuse out over time. Thermal effects are also much reduced with the light ion beams compared to heavier ions or the SEM. The ion's initial kinetic energy is converted to random thermal energy over a relatively large volume. And much of the transferred energy goes to the electrons in the sample, and their relatively long mean free path helps to dissipate this energy into a larger volume.

Numerous imaging examples will be provided from a variety of polymers using the helium beam from the Zeiss ORION NanoFab. These serve as representative examples of the unique sample interaction of light ions and the advantages they offer for imaging polymers.

5:40pm **HI+AS+CA-WeA-11 Imaging of Biological Cells with Helium-Ion Microscopy**, *Natalie Frese, A Beyer, C Kaltschmidt, B Kaltschmidt*, Bielefeld University, Germany; *A Thomas*, Institute for Metallic Materials Dresden, Germany; *W Parak*, University of Hamburg, Germany; *A Götzhäuser*, Bielefeld University, Germany

Studies from the last decade have shown that helium-ion microscopy (HIM) is suitable for studying biological samples. In particular, cell membranes

can be imaged by HIM without metallic coatings, which could lead to disturbance of the surface. In this contribution, we give two examples of biological cells imaged by HIM: (i) mouse hippocampal neurons on patterned surfaces for neuronal networks and (ii) human cells treated with colloidal nanoparticles [1, 2]. Both examples benefit from the high resolution imaging of uncoated, biological materials by HIM, as for (i) the cell adherence to patterned surfaces could be imaged and for (ii) cell morphology images indicated harmful effects of colloidal nanoparticles to cells.

[1] M. Schürmann et al., PLoS ONE 13(2), e0192647 (2018)

[2] X. Ma et al., ACS Nano 11(8), 7807-7820 (2017)

6:00pm **HI+AS+CA-WeA-12 Channeling in the Helium Ion Microscope**, *Hussein Hijazi, L Feldman, R Thorpe, M Li, T Gustafsson*, Rutgers University; *D Barbacci, A Schultz*, Ionwerks

The helium ion microscope (HIM) has become a unique tool for modern materials science due to its high lateral resolution for imaging, high spatial resolution and nano-scale analysis. For crystalline materials, the incident beam may undergo ion channeling, which strongly modifies all of the basic ion-solid interactions associated with these HIM functions. Here, a 30 keV He⁺ beam was used for RBS channeling in a W(111) crystal using a novel time of flight (HIM/TOF) detector developed at Rutgers University to extract critical channeling parameters. Measurements of the minimum backscattering yield (χ_{min}), surface peak (SP), and critical angle, are compared to several theoretical estimates. The results illustrate the advantage of using channeling in a backscattering mode to characterize crystalline materials with the HIM, as the backscattering intensity modifications are far greater for scattered ions than for secondary electrons. This case of "ideal" channeling with the HIM now provides a basis for analysis of more complex materials such as polycrystalline materials and textured structures, and quantifies the role of HIM induced materials modification in crystalline materials.

Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+2D+AS+BI+NS-ThM

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II

Moderators: Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am CA+2D+AS+BI+NS-ThM-1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond, **Miquel B. Salmeron**, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas–solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am CA+2D+AS+BI+NS-ThM-3 Probing Solid-liquid Interfaces with Tender X-rays, **Zbynek Novotny**, *N Comini, B Tobler*, University of Zuerich, Switzerland; *D Aegerter, E Fabbri*, Paul Scherrer Institute, Switzerland; *U Maier*, Ferrovac GmbH, Switzerland; *L Artiglia, J Raabe, T Huthwelker*, Paul Scherrer Institute, Switzerland; *J Osterwalder*, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

[1] S. Axnanda, E. J. Crumlin et al., *Sci. Rep.* 5, 09788 (2014).

9:00am CA+2D+AS+BI+NS-ThM-4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogenous Liquid Electrolyte Interface, **Christopher Arble**, National Institute of Standards and Technology (NIST); *H Guo*, Southeast University, China; *E Strelcov, B Hoskins*, National Institute of Standards and Technology (NIST); *M Amati, P Zeller, L Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A Kolmakov*, National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications¹ that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.²⁻⁴ Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogenous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.⁵

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.⁶ We monitored the chemical speciation at the electrode- aqueous CuSO₄ electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confined irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

References:

1. Saveant, J., *Chemical Reviews* **2008**, 108, (7), 2348-2378
2. Siegbahn, H., *J. Phys. Chem.* **1985**, 89, (6), 897-909
3. Salmeron, M.; Schlögl, R., *Surf. Sci. Rep.* **2008**, 63, (4), 169-199
4. Starr, D.; et al., *Chem. Soc. Rev.* **2013**, 42, (13), 5833-5857
5. Kraus, J.; et al., *Nanoscale* **2014** 6, (23), 14394-14403
6. Yulaev, A.; et al., *ACS Appl. Mater. Interfaces* **2017**, 9, (31) 26492-26502

9:20am CA+2D+AS+BI+NS-ThM-5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces, **Roger Rousseau**, Pacific Northwest National Laboratory **INVITED**

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydro/lipophilicity of the support. In this talk. we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab initio molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in

the double layer as well as its orientation with respect to the electrode surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

References

1. Cantu DC, Wang YG, Yoon Y, Glezakou VA, Rousseau R, Weber RS. 2016, *Catalysis Today*, <http://dx.doi.org/10.1016/j.cattod.2016.08.025>
2. Perez Y, Fajardo M, Corma A. 2011, *Catalysis Communications*, 12, 1071-1074.
3. Padmaperuma AB, Cantu DC, Yoon Y, Nguyen MT, Wang YG, Glezakou VA, Rousseau R, Lliga MA. Manuscript in preparation, to be submitted.

11:00am **CA+2D+AS+BI+NS-ThM-10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices**, Y Liu, X Feng, *Jinghua Guo*, Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

References:

1. "Mg deposition observed by in situ electrochemical Mg K-edge X-ray absorption spectroscopy", T. S. Arthur, P.-A. Glans, M. Matsui, R. Zhang, B. Ma, J.-H. Guo, *Electrochem. Commun.* **24**, 43 (2012)
2. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy", J. J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J.-H. Guo, D. Prendergast and M. Salmeron, *Science* **346**, 831 (2014)
3. "Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery", M. Ling, L. Zhang, T. Zheng, J. Feng, J.-H. Guo, L. Mai, G. Liu, *Nano Energy* **38**, 82 (2017).
4. "Interfacial insights from operando sXAS/TEM for magnesium metal deposition with borohydride electrolytes", T. Arthur, P.-A. Glans, N. Singh, O. Tutusaus, K. Nie, Y.-S. Liu, F. Mizuno, J.-H. Guo, D. H. Asem, N. Salmon, R. Mohtadi, *Chem. Mater.* **29**, 7183 (2017).

"Revealing the Electrochemical Charging Mechanism of Nanosized Li₂S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, *Nano Lett.* **17**, 5084 (2017).

11:20am **CA+2D+AS+BI+NS-ThM-11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation**, *Olutoba Sanni*, University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al.* *Nature Biotech* 2012]. These novel poly (meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and

mammalian cell attachment. However, in protein-free media such as used by Hook *et al.*, this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlay coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+NS+SS+VT-ThA

Progress in Instrumentation and Methods for Spectro-microscopy of Interfaces

Moderators: Jinghua Guo, Lawrence Berkeley National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-ThA-1 Helium and Neon Ion Beams for the Imaging and Analysis of Interfaces**, *John A. Notte, C Guillemer, F Khanom, B Lewis*, Carl Zeiss PCS, Inc. **INVITED**

The recently developed ORION NanoFab instrument provides a single platform with He⁺, Ne⁺, and Ga⁺ focused ion beams. The gallium beam is a conventional FIB and offers high currents and high sputter yields for material removal applications such as sample preparation or exposing sub-surface features. The He and Ne ion beams originate from a sub-nanometer ionization volume of the gas field ion source (GFIS) and because of this, can be focused to remarkable small probe sizes, 0.5 nm and 1.9 nm respectively. The He beam is now well established for high resolution imaging with surface sensitivity, long depth of focus, and the ability to image insulating surfaces without a conductive overcoating. The helium beam has also been used successfully in a variety of nanofabrication tasks such as lithographic exposure of resist, fine sputtering, beam chemistry, and precision modification of materials. The neon beam with its intermediate mass provides a higher sputtering yield, and with that, the ability to perform SIMS analysis with an unprecedented small focused probe size. A newly integrated magnetic spectrometer enables analytical capabilities on this same platform, with a lateral resolution limited only by the collision cascade. Features smaller than 15 nm have been detected. Together these complementary imaging modes can be combined to provide insights of morphology and composition at the smallest length scales.

In this talk the underlying technology of the NanoFab-SIMS will be introduced, as will the physics of the beam-sample interactions. The bulk of the presentation will provide a survey of results, both published and new, demonstrating how this instrument can serve in a variety of applications related to interfaces.

3:00pm **CA+NS+SS+VT-ThA-3 Interfacial Studies using Ambient Pressure XPS**, *Paul Dietrich, A Thissen*, SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Over the last decades XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential in a wide variety of applications. Starting from operando studies of surface reactions in catalysis, the applications soon have been enhanced towards studies of processes at liquid surfaces, mainly using freezing/melting cycles, liquid jets or liquid films on rotation disks or wheels. Since more than 15 years, the need for basic studies of fundamental solid-liquid interface chemistry has attracted growing interest. Dip-and-pull experiments at synchrotron sources finally also demonstrated, that in-situ and operando XPS in electrochemical experiments can be realized, significantly contributing to the basic understanding of modern energy converting or storing devices, like batteries, fuel cells, etc.

The development of pure laboratory NAP-XPS systems with optimized sample environments, like special sample holders, Peltier coolers and operando liquid cells combined with full automation and process control provides possibilities for preparation and analysis of a multitude of liquid samples or solid-liquid interfaces on a reliable daily base.

Interfaces of semiconductors with organic solvents are important for production processes and device operation. The first example presented shows the simplicity of obtaining relevant results on Silicon in different organic solvents without the need of highly sophisticated set-ups or special excitation sources beyond Al K_α.

Another example shows an operando study of metal corrosion in acetic acid. Moreover a versatile set-up is presented, allowing for studies of solid-electrolyte interfaces for example in Lithium ion batteries as a simple laboratory experiment.

Finally an outlook is given on the future perspective of applications and scientific contributions of routine operando XPS.

4:00pm **CA+NS+SS+VT-ThA-6 Operando Spectroscopy and Microscopy of the Electrode-Electrolyte Interface in Batteries**, *Feng Wang*, Brookhaven National Laboratory **INVITED**

Real-time tracking structural/chemical changes of electrodes in batteries is crucial to understanding how they function and why they fail. However, in real battery systems electrochemical/chemical reaction occurs at varying length scales, leading to changes not only in the bulk but often locally at electrolyte/electrode interface. *In situ* X-ray techniques are typically employed for studying structural changes in the bulk electrodes and often limited by their poor spatial resolution in probing local changes at interface. Herein, we present our recent results from developing new *operando* spectroscopy and microscopy techniques, specialized for studying electrochemical/chemical reaction and structural modification of the solid-electrode surface and interface, *in the presence of the electrolyte and during battery operation*. Examples will be given to show how interfacial reaction during battery operation is visualized directly, allowing gaining insights into electrode/electrolyte design for practical use in batteries. New opportunities for combining *first principles* simulation and deep machine learning to complement and guide experiments will also be discussed.

4:40pm **CA+NS+SS+VT-ThA-8 Ultrasensitive Combined Tip- and Antenna-Enhanced Infrared Nanoscopy of Protein Complexes**, *B O'Callahan*, Pacific Northwest National Laboratory; *M Hentschel*, University of Stuttgart, Germany; *M Raschke*, University of Colorado Boulder; *P El-Khoury*, Pacific Northwest National Laboratory; *Scott Lea*, Pacific Northwest National Laboratory

Surface enhanced infrared absorption (SEIRA) using resonant plasmonic nanoantennas enables zeptomolar detection sensitivity of (bio)analytes, although with diffraction limited spatial resolution. In contrast, infrared scattering-scanning near-field optical microscopy (IR s-SNOM) allows simultaneous imaging and spectroscopy with nanometer spatial resolution through vibrational coupling to the antenna mode of a probe tip. In this presentation, we discuss our approach combining these two methods to image both continuous and sparse distributions of ferritin protein complexes adsorbed onto IR-resonant Au nanoantennas. The joint tip- and antenna-enhancement yields single protein complex sensitivity due to coupling with the vibrational modes of the bioanalytes. The coupling is revealed through IR s-SNOM spectra in the form of Fano lineshapes, which can be modelled using coupled harmonic oscillators. Through simulations of the recorded hyperspectral images, we extract the optical signatures of protein complex monolayers. This work paves the way for single protein identification and imaging through a combination of tip and antenna-enhanced IR nanoscopy.

5:00pm **CA+NS+SS+VT-ThA-9 Imaging and Processing in Liquid Gel Solutions with Focused Electron and X-ray Beams**, *T Gupta*, National Institute of Standards and Technology (NIST); *P Zeller, M Amati, L Gregoratti*, Elettra - Sincrotrone Trieste, Trieste, Italy; *Andrei Kolmakov*, National Institute of Standards and Technology (NIST)

Gels are porous polymeric scaffolds that can retain high volume fraction of liquids, can be easily functionalized for a specific need, can be made biocompatible and therefore, found numerous applications in drugs delivery, tissue engineering, soft robotics, sensorics, energy storage, etc. We have recently proposed a technique for micro-patterning and high-resolution additive fabrication of 3D gel structures in natural liquid solutions using electron and soft X-ray scanning microscopes [1]. The core of the technology is the employment of ultrathin electron (X-ray) transparent molecularly impermeable membranes that separate high vacuum of the microscopes from a high-pressure fluidic sample. In this communication, we report on effects of the beam and exposure conditions on to the degree of crosslinking of pristine and composite PEGDA hydrogels. We found that cross-linking occurs at very low irradiation doses. The size of the crosslinked area saturates with the dose and bond scission occurs at elevated radiation doses what has been supported with O 1s and C 1s XPS spectra evolution and prior research [2]. These chemically modified regions can be selectively etched what enables an additional partnering option for the gelled features with a spatial resolution of ca 20 nm. Finally, we defined the imaging conditions for guest particles in composite hydrogels in its liquid state during the crosslinking process. We were able to observe the electrophoretic migration of sub 100 nm Au nanoparticles inside the gel matrix.

References

Thursday Afternoon, October 24, 2019

[1] T. Gupta *et al.*, "Focused Electron and X-ray Beam Crosslinking in Liquids for Nanoscale Hydrogels 3D Printing and Encapsulation," *arXiv preprint arXiv:1904.01652*, 2019.

[2] N. Meyerbröker and M. Zharnikov, "Modification and Patterning of Nanometer-Thin Poly (ethylene glycol) Films by Electron Irradiation," *ACS applied materials & interfaces*, vol. 5, no. 11, pp. 5129-5138, 2013.

5:20pm **CA+NS+SS+VT-ThA-10 In Situ TEM Visualization of Solution-based Nanofabrication Processes: Chemical Wet-etching and Capillary Forces, Utkur Mirsaidov**, National University of Singapore, Singapore **INVITED**

Controlled fabrication of 3D nanoscale materials from semiconductors is important for many technologies. For example, scaling up the density of the transistors per chip requires the fabrication of smaller and smaller vertical nanowires as channel materials [1]. Two key processes essential to the fabrication of these devices is a precise etching of the nanostructures and the damage-free solution based cleaning (damage occurs during post-clean drying due to capillary forces). However, very little is known about both of these processes because it is extremely challenging to visualize etching and cleaning with solutions directly at the nanoscale. Here, using in situ liquid phase dynamic TEM imaging [2-4], we first describe the detailed mechanisms of etching of vertical Si nanopillars in alkaline solutions [5]. Our design of liquid cells includes a periodic array of patterned nanopillars at a density of $1.2 \times 10^{10} \text{ cm}^{-2}$. We show that the nanoscale chemical wet-etch of Si occurs in three stages: 1) intermediates generated during alkaline wet etching aggregate as nanoclusters on the Si surface, 2) then the intermediates detach from the surface before 3) dissolving in the etchant.

Next, we describe the capillary damage of these high-aspect-ratio Si nanopillars during drying after the solution-phase cleaning. Our results reveal that drying induced damage to nanopillars occurs in three distinct steps. First, as water evaporates from the surface patterned with nanopillars, water film thins down non-uniformly leaving small water nanodroplets trapped between the nanopillars. Second, the capillary forces induced by these droplets bend and bring the nanopillars into contact with each other at which point they bond together. Third, droplets trapped between the nanopillars evaporate leaving the nanopillars bonded to each other. We show that even after the nanodroplets finally evaporate, interfacial water covering the nanopillars act as a glue and holds the pillars together.

Our findings highlight the importance of being able to visualize the processes relevant to nanofabrication in order to resolve the failure modes that will occur more frequently as the device sizes get even smaller in the future.

[1] C. Thelander *et al*, *Mater. Today* 9 (2006), 28–35.

[2] M. J. Williamson *et al*, *Nature Materials* 2 (2003), p. 532.

[3] H. Zheng *et al*, *Science* 324 (2009), p. 1309.

[4] U. Mirsaidov *et al*, *Proc. Natl. Acad. Sci. U.S.A.* 109 (2012), p. 7187.

[5] Z. Aabdin *et al*, *Nano Letters* 17 (2017), p.2953.

[6] This work was supported by Singapore National Research (NRF-CRP16-2015-05).

Thursday Evening Poster Sessions, October 24, 2019

Chemical Analysis and Imaging Interfaces Focus Topic Room Union Station AB - Session CA-ThP

Chemical Analysis and Imaging at Interfaces Poster Session

CA-ThP-1 Probing Solid-liquid Interfaces with Tender X-rays, Nicolò Comini, Z Novotny, B Tobler, University of Zuerich, Switzerland; D Aegeerter, E Fabbri, Paul Sherrer Institute, Switzerland; U Maier, Ferrovac GmbH, Switzerland; L Artiglia, J Raabe, T Huthwelker, Paul Sherrer Institute, Switzerland; J Osterwalder, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid. Despite its importance, it is very difficult to collect meaningful signals from this buried interface. We recently built a new instrument at the Swiss Light Source that combines ambient-pressure X-ray photoelectron spectroscopy with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid film by a dip&pull method [1] and using tender X-rays, we can probe the solid-liquid interface while having potential control over the electrolyte film. We will present results from the first commissioning beamtime and outline the future direction we are going to pursue.

[1] S. Axnanda, E. J. Crumlin et al., *Sci. Rep.* 5, 09788 (2014).

CA-ThP-2 Using AES, EDS, and FIB to Detect, Identify, and Image Buried

Metallic Particles, Ashley Ellsworth, D Paul, J Newman, Physical Electronics
Auger Electron Spectroscopy (AES) is a powerful analytical tool that provides quantitative elemental information from surfaces of solid materials. The average depth of analysis for an AES measurement is approximately 5 nm with lateral spatial resolution as small as 8 nm. The information AES provides about surface layers or thin film structures is important for many industrial and research applications where surface or thin film composition plays a critical role in performance including: nanomaterials, photovoltaics, catalysis, corrosion, adhesion, semiconductor devices and packaging, magnetic media, display technology, and thin film coatings used for numerous applications.

In this work, we demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site specific imaging of microscale features beneath a sample surface. The combination of the two techniques allows for high spatial resolution analysis of buried particles and defects. This information can be very useful in helping to determine important parameters such as the origin of defects, corrosion mechanisms, coating problems, etc. We will highlight the advantages of FIB milling compared to traditional depth profiling. Energy dispersive x-ray spectroscopy (EDS) is also a powerful complementary technique to Auger analysis as it provides information from much deeper in the sample surface (few μm). With the combination of AES, FIB, and EDS, we show that buried metal particles can be first located and characterized with EDS, followed by the subsequent FIB milling and high spatial resolution Auger spectroscopy and imaging of the particles.

CA-ThP-3 Secondary Ion Mass Spectrometry Designed for Ultra-sensitive

Molecular Analysis of Solids and Liquids, Stanislav Verkhoturov, D

Verkhoturov, E Schweikert, Texas A&M University
SIMS is a method of choice for elemental and molecular surface thin layer analysis. We present here significant enhancements in SIMS capability with regards to a) detection sensitivity, and b) applicability to liquid samples.

Detection of atto to zeptomole amounts of analyte is demonstrated with deposits of fractional monolayers of organics on double layer graphene. Three innovations make ultrasensitive analysis possible. The graphene support minimizes interference between analyte and substrate signals. Secondly, the analysis is run in a unique experimental setup. The sample on graphene is bombarded with 50 keV C_{60}^+ in transmission mode, i.e. the ejecta are mostly in the forward direction where they are collected in a time-of-flight mass spectrometer, ToF MS. Thirdly, the bombardment is reduced to a series of single C_{60} impacts, each coupled with ToF measurement. This event-by-event bombardment-detection mode allows the selection of specific impacts on analyte at the exclusion of signals from supporting materials. In this approach, unusually high ionization of analyte molecules (e.g. $\sim 10\%$) was observed. A distinct ejection-ionization mechanism operates here. The molecules "trampoline" off the graphene following a C_{60} impact. The mass spectra contain abundant peaks of molecular ions. The proposed mechanism of ionization involves tunneling of electrons from the vibrationally excited area around the hole to the

molecules. Another proposed mechanism is a direct proton transfer exchange.

Liquid samples are inherently incompatible with SIMS, which operates under vacuum. We demonstrate the feasibility of storing liquids in carbon nanotube, CNT, sponges. We found that within a practical experimental time of 30 min, liquids with vapor pressure of < 1 torr can be analyzed. The CNT sponge (97% porosity) was made from multiwall carbon nanotubes (CNT cross-section ~ 6 layers). Hydrophilic and hydrophobic sponges were examined. For the hydrophobic case, we examined the lubricant fluids (vapor pressure ~ 100 millitorr). The mass spectra of pure fluids were used as a blank for comparison with mass spectra of wear tracks on metals. For the hydrophilic case, pure glycerol and the glycerol-water mixture have been examined. Glycerol evaporates slowly from the sponge. The method allows to investigate the organic molecules dissolved in glycerol and glycerol water mixture. Thus, the event-by-event technique applied on CNT sponges is a promising method for analysis of liquid and soft materials by Cluster SIMS.

Work supported by NSF grant CHE-130832

Chemical Analysis and Imaging Interfaces Focus Topic Room A226 - Session CA+AS+NS+SE+SS-FrM

Novel Applications and Approaches in Interfacial Analysis

Moderators: Paul Dietrich, SPECS Surface Nano Analysis GmbH, Germany, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

8:20am **CA+AS+NS+SE+SS-FrM-1 Chemical Reactions on Bimetal Surfaces with Operando Surface Techniques, Jeong Young Park**, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea **INVITED**

The origin of the synergistic catalytic effect between metal catalysts and reducible oxide has been debated for decades. Clarification of this effect, namely the strong metal-support interaction (SMSI), requires an understanding of the geometric and electronic structures of metal-metal oxide interfaces under operando conditions.[1] A bimetallic platinum (Pt) alloy catalyst is an excellent platform to uncover the contentious role of the metal-metal oxide interface because the alloyed transition metal can coexist with the Pt surface layer in the form of an oxidized species on the bimetal surface during catalytic reactions.

In this talk, I present in-situ observation results of structural modulation on Pt-Ni metastable and Ni (111) surfaces at 0.1 Torr pressure of CO, O₂, and CO oxidation conditions with ambient-pressure scanning tunneling microscopy (AP-STM) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).[2] We show that the stable Pt-skin covered Pt₃Ni(111) surface is broken by segregation of dissociative oxygen-induced Ni oxides under elevated oxygen pressure environment, which evolved clusters could have a crucial relation with enhanced catalytic activity. We show that NiO_{1-x}/Pt-Ni nanostructures are on the Pt₃Ni(111) surface under CO oxidation and these metal-oxide interfaces provide more efficient reaction path for CO oxidation [2]. Furthermore, I will show the research efforts for understand the catalytic behavior of bimetal PtCo and PtNi nanocatalysts using in-situ surface techniques including catalytic nanodiode and transmission electron microscopy. The catalytic nanodiode that consists of metal catalyst film, semiconductor layers, and Ohmic contact pads revealed the strong correlation between the hot electron flux (chemicurrent) and catalytic activity under CO oxidation and hydrogen oxidation. Using this approach, the catalytic activity and hot electron generation on PtCo bimetal nanoparticles were investigated. In-situ transmission electron microscopy reveals the formation of metal oxide layers on bimetal nanoparticle surfaces under oxygen conditions. We show that formation of interface between Pt and CoO enhances both of catalytic activity and chemicurrent yield [3].

[1] J. Y. Park et al. Chemical Reviews 115, 2781-2817 (2015)

[2] J. Kim et al. Science Advances 4, eaat3151 (2018).

[3] H. Lee et al. Nature Communications 9, 2235 (2018).

9:00am **CA+AS+NS+SE+SS-FrM-3 Principal Component Analysis to Reveal Camouflaged Information in Spectromicroscopy of (complex) Oxides, David Mueller, M Giesen**, Forschungszentrum Juelich GmbH, Germany; *D Stadler*, University of Cologne, Germany; *T Duchon, F Gunkel, V Feyer*, Forschungszentrum Juelich GmbH, Germany; *S Mathur*, University of Cologne, Germany; *C Schneider*, Forschungszentrum Juelich GmbH, Germany

Spectroscopic imaging techniques are becoming more and more accurate and available, which results in an increase of data to handle and analyze. Near Edge X-Ray absorption spectroscopy, especially in the soft X-Ray regime, has the ability to identify inhomogeneities in chemistry and electronic structure, which is mostly done by fingerprinting or using internal standards. In a spectromicroscopic image, each pixel contains such a spectrum, and by the lack of rigorous fitting routines that are for example present in XPS, reduction and preevaluation of data is needed. Principal Component Analysis (PCA) of X-PEEM data affords this in an unambiguous and unbiased way by identifying and highlighting spectroscopic features which contribute to a spectrum.¹

Two cases where PCA revealed information that might have been missed otherwise are presented here: Firstly, iron oxide thin films grown by CVD showed a considerable influence of an external magnetic field on chemistry and crystallinity. Combination of O-K- and Fe-L-Edge X-PEEM unambiguously identified different iron oxide polymorphs (Fe₂O₃ and α -Fe₂O₃) depending on field strength during deposition. The former XAS Edge showed subtle spatial variations in the EXAFS regime that could be

identified as the breakdown of long-range ordering, pointing to incomplete crystallization when films are deposited without magnetic field assistance.²

The second example is the surface decomposition of Pr_{0.5}Ba_{0.5}CoO_{3- δ} (PBCO), a promising material for the use as water splitting catalyst and solid oxide electrochemical cell electrode. Using spatially resolved O-K-, Co-L-, and Ba- and Pr-M-Edge XAS, changes in surface chemical composition upon annealing and its impact on the electronic structure were observed. Laterally resolved by X-PEEM, PCA could reveal that exposing thin films of the material to technologically relevant conditions (1073 K, 20 mbar of O₂) leads to a more complex decomposition pathway than simple spinodal unmixing to the end members BaCoO₃ and PrCoO₃ as the spectromicroscopic dataset could only be described satisfactory by a linear combination of three components.

9:20am **CA+AS+NS+SE+SS-FrM-4 In situ Electron Microscopy of Catalysts with Atomic Resolution under Atmospheric Pressure, Xiaoqing Pan**, University of California Irvine **INVITED**

Understanding the atomic structures of catalysts under realistic conditions with atomic precision is crucial to design better materials for challenging transformations. For example, under reducing conditions, certain reducible supports migrate onto supported metallic particles and create strong metal-support states that drastically change the reactivity of the systems. The details of this process are still unclear and preclude its thorough exploitation. In the past decade, most of atomic-scale transmission electron microscopy (TEM) studies involving gas-solid interactions were conducted in an environmental TEM, where the gas pressure is typically limited to less than 1/100 of atmosphere. Recently, it has become possible to overcome this limitation through a MEMS-based, electron-transparent closed cell with a heating stage.

In this talk, I will present our recent results using this device (the Protochips Atmosphere™ system) in selected catalyst systems. In a palladium/titania (Pd/TiO₂) catalyst, we directly observed the formation of the oxide overlayers on the supported Pd particles with atomic resolution under atmospheric pressure and high temperature. It shows that an amorphous reduced titania layer is formed at low temperatures, and that crystallization of the layer into either mono- or bilayer structures is dictated by the reaction environment. This transition occurs in combination with a dramatic reshaping of the metallic surface facets. *In-situ* TEM observations of a modular Pd-ceria core-shell nanostructured catalyst (Pd@CeO₂) showed that an unexpected structural transformation occurs upon heating at high temperatures. The system reaches to a stable state with the mixture of nanoparticles with two different sizes, which accounts for the exceptional catalytic properties that have been reported. Using the similar techniques, we also studied the core-shell platinum-metal (Pt-M) nanoparticles which show a catalytic performance in the oxygen reduction reaction (ORR) superior to that of pure Pt nanoparticles. To understand the formation mechanism of the Pt shell, we studied thermally activated core-shell formation in Pt₃Co nanoparticles via *in-situ* electron microscopy with the gas cell. The disordered Pt₃Co nanoparticle was found to transform into an ordered intermetallic structure after annealing at high temperature (725°C) in 760 Torr O₂, followed by layer-by-layer Pt shell growth on (100) surfaces at low temperature (300°C). The apparent 'anti-oxidation' phenomenon promoted by the ordered Pt₃Co phase is favorable to the ORR catalyst, which operates in an oxidizing environment.

10:00am **CA+AS+NS+SE+SS-FrM-6 Exposing Buried Interfaces in Thin Film Photovoltaics through Thermo-mechanical Cleaving, Deborah McGott**, Colorado School of Mines; *C Perkins, W Metzger*, National Renewable Energy Laboratory; *C Wolden*, Colorado School of Mines; *M Reese*, National Renewable Energy Laboratory

Thin film solar cells, such as cadmium telluride (CdTe) and Cu(In,Ga)Se₂ (CIGS), contain buried interfaces that are critical to carrier transport, recombination, and device performance, yet are poorly understood due to their inaccessibility within the device stack. In particular, accessing the interface in a way that preserves the chemical structure has historically been extremely difficult. Here, we describe an innovative technique to expose buried interfaces through a two-step thermo-mechanical cleaving process. First, a stressor layer (typically an epoxy or commercially available polymeric backsheets) is applied to the solar cell. Then, the stack is submerged in a cold bath (T \leq -30°C) to thermally shock the system. This causes the stressor to contract quickly and pull the polycrystalline film cleanly off of its substrate at an interface that is weakened by a monolayer accumulation of 2-D material (CdCl₂ in CdTe and MoS₂ in CIGS).

Focusing on CdTe solar cells, we then use X-ray photoelectron spectroscopy to probe the oxidation states at the newly exposed SnO₂ interface. We

show that the tin oxide front electrode promotes the formation of nanometer-scale oxides of tellurium and sulfur. Most oxidation occurs during CdCl_2/O_2 activation. Surprisingly, we show that relatively low-temperature anneals (180–260°C) used to diffuse and activate copper acceptors in a doping/back contact process also cause significant changes in oxidation at the front of the cell, providing a heretofore missing aspect of how back contact processes can modify device transport, recombination, and performance. Device performance is shown to correlate with the extent of tellurium and sulfur oxidation within this nanometer-scale region. Mechanisms responsible for these beneficial effects are proposed.

10:20am CA+AS+NS+SE+SS-FrM-7 Switchable Dopants on Percolation Networks of 2D Materials for Chemiresistive Sensing Applications in Aqueous Environments, Peter Kruse, McMaster University, Canada

Permanent doping of semiconductors and low-dimensional structures to modulate their electronic properties is a well-established concept. Even in cases where doping of thin films by analytes (e.g. carbon nanotubes by ammonia) is applied in sensors, it is only reversed by physical removal of dopant molecules, e.g. heating. We have introduced the concept of molecular switches as chemical dopants for thin nanocarbon (or other 2D-materials) films. These molecules can be switched between doping and non-doping states in the presence or absence of a particular analyte. They impart selectivity not only due to their change in doping behavior, but also by physically blocking other potential dopants in the analyte solution from interacting with the conductive film. The resulting structures can act as chemiresistive films. Chemiresistive sensors are a well-established technology for gas-phase sensing applications. They are simple and economical to manufacture, and can operate reagent-free and with low or no maintenance. Unlike electrochemical sensors they do not require reference electrodes. While in principle they can be made compatible with aqueous environments, only a few such examples have been demonstrated. Challenges include the need to prevent electrical shorts through the aqueous medium and the need to keep the sensing voltage low enough to avoid electrochemical reactions at the sensor. We have built a chemiresistive sensing platform for aqueous media. The active sensor element consists of a percolation network of low-dimensional materials particles that form a conducting film, e.g. from carbon nanotubes, pencil trace, exfoliated graphene or MoS_2 . The first member of that platform was a free chlorine sensor. We are currently working to expand the applicability of our platform to other relevant species, in particular anions and cations that are commonly present as pollutants in surface and drinking water. Our sensors can be incorporated into a variety of systems and will also be suitable for online monitoring in remote and resource-poor locations.

10:40am CA+AS+NS+SE+SS-FrM-8 Analysis Of Radioactive Materials In Liquid Using In Situ Sem And ToF-Sims, Jennifer Yao, X Yu, Z Zhu, E Buck, Pacific Northwest National Laboratory

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of UO₂ spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of UO₂ materials is possible using SALVI. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high level nuclear waste.

11:00am CA+AS+NS+SE+SS-FrM-9 Interactions between Synthetic Bilgewater Emulsion and Biofilms, Jiyoung Son, Earth and Biological Sciences Directorate; J Yao, Earth & Biological Sciences Directorate; X Yu, Pacific Northwest National Laboratory

Presentation Summary:

This presentation will showcase our latest results of the interaction between biofilms and synthetic bilgewater using a surface chemical imaging technique.

Abstract

Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. It is hypothesized that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. Three strains were selected *Pseudomonas*, *Arthrobacter*, and *Cobetia marina*. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1]. Biofilms were cultured in a microchannel to allow healthy culture [2]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

Key words: bilgewater emulsion, oil-in-water, microfluidics, biofilm, EPS, surfactant

Reference

1. Church, J., D.M. Paynter, and W.H. Lee, *In Situ Characterization of Oil-in-Water Emulsions Stabilized by Surfactant and Salt Using Microsensors*. Langmuir, 2017. **33**(38): p. 9731-9739.
2. Yao, J., et al., *In Situ Characterization of Boehmite Particles in Water Using Liquid SEM*. J Vis Exp, 2017(127).

11:20am CA+AS+NS+SE+SS-FrM-10 Mechanistic Insights into the Study of γ -Al₂O₃ Surface and its Interface with Pt, Kofi Oware Sarfo, A Clauser, M Santala, L Árnadóttir, Oregon State University

Metal/metal oxide interfaces occur in heterogeneous catalysis where metal catalyst nanoparticles are dispersed on highly porous metal oxide supports to increase the surface area for reactions. The interactions between catalyst nanoparticles and the catalyst support has previously been shown to affect the extent of dispersion of the active metal catalyst, particle sintering and the electronic properties of the catalyst. The capability to describe and predict the structure of the catalyst, the catalyst support and the interface between the two is therefore a critical step towards understanding the catalyst-support interactions. γ -Al₂O₃, a polymorph of Al₂O₃ is a commonly used catalyst support due to its durability at operation conditions and high surface area. Here we combine theoretical and experimental methods to investigate and predict the structure and thermodynamic stability of the interface between γ -Al₂O₃ and Pt nanoparticles. The experimental approach involves the fabrication of the embedded Pt nanoparticles and the use of high resolution transmission electron microscopy (HRTEM) to image the atomic structure for the embedded interfaces. The theoretical approach utilizes density functional theory (DFT) and thermodynamic models to calculate surface energies of γ -Al₂O₃ (111) and interfacial energies between Pt(111) and γ -Al₂O₃ (111) to describe the stabilities of the surfaces and interfaces. Of the three interfacial terminations, Pt atoms interacting with oxygen terminated γ -Al₂O₃ (111) are the most stable interfaces at atmospheric conditions. The stability of this interface is based on the strong electrostatic interaction between the Pt atoms and the oxygen atoms at the oxygen terminated interface. This work therefore, provides the complement to experimental study of the atomic structure of the interface between γ -Al₂O₃ and Pt nanoparticles.

11:40am CA+AS+NS+SE+SS-FrM-11 Artificial Intelligence—An Autonomous TEM for In-situ Studies, Huolin Xin, University of California Irvine INVITED

Deep learning schemes have already impacted areas such as cognitive game theory (e.g., computer chess and the game of Go), pattern (e.g., facial or fingerprint) recognition, event forecasting, and bioinformatics. They are beginning to make major inroads within materials science and hold considerable promise for materials research and discovery. In this talk, I will introduce deep convolutional neural networks and how they can be applied to the computer vision problems in transmission electron microscopy. I will also discuss the development and application of liquid TEM to the study of solid/liquid interfaces at the nanoscale.

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