Tuesday Morning, September 23, 2025

Applied Surface Science
Room 209 B W - Session AS-TuM

Surface Characterization of Energy Materials

Moderators: Jodi Grzeskowiak, TEL Technology Center, America, LLC, **Benjamen Reed**, National Physical Laboratory, UK

8:30am **AS-TuM-3 Solar Energy from a Big Picture Perspective to Nanoscale Insights via TOF-SIMS*, Steven P. Harvey,*** NREL **INVITED**

The world is rapidly changing the way that it gets energy due to rapid price declines in new energy sources and storage within the last ten years. We will briefly discuss solar energy trends as a whole, before diving into our recent contributions to the field using time-of-flight secondary-ion mass spectrometry (TOF-SIMS) at the National Renewable Energy Laboratory to improve the performance and reliability of solar cell and battery materials, and we will present some of our work that highlights the versatility of TOF-SIMS. This work includes: 1) Multi-scale, multi-technique investigations of photovoltaic module failure including TOF-SIMS to enable insights into the root-cause mechanisms of module degradation at the nanoscale that are observed at the length scale of meters 2) Investigations into the performance and stability of hybrid perovskite solar cell devices and our work to understand measurement artifacts in this materials class when profiling.

9:00am **AS-TuM-5 Introduction of Cryogenic X-Ray Photoelectron Spectroscopy for Chemical Analysis of Sensitive Battery Interfaces*, Sanzeeda Baig Shuchi,*** *Yi Cui, Stacey Bent,* Stanford University

Understanding the chemical environment of pristine interfaces is a long-sought goal in electrochemistry, materials science, and surface science. One such interface, the solid electrolyte interphase (SEI) in lithium battery anodes, is described as the nanometer-thick passivation layer between the lithium anode and electrolyte formed due to electrochemical and chemical decomposition of the electrolyte. For high performing electrolytes above ~95% Coulombic efficiency, SEI is considered the key performance modulator in next-generation lithium metal batteries.

Important understanding of the SEI is achieved using X-ray photoelectron spectroscopy (XPS). However, room temperature (RT) combined with the ultra-high vacuum (UHV) conditions of standard XPS can induce major SEI evolution from reactions and volatilization during measurement. Subsequently, a technique is necessary for SEI stabilization.

Here, for the first time, we develop cryogenic (cryo)-XPS with immediate plunge freezing and demonstrate SEI preservation. We show that cryogenic conditions can halt chemical reactions and freeze UHV-volatile species. Most chemical reactions are halted due to slow reaction kinetics at cryoT. We hypothesize that the true SEI thickness can also be retained, benefiting from the lower vapor pressure of different frozen SEI species at cryoT. Indeed, we discover completely different SEI composition and a thicker pristine SEI with cryo-XPS. While cryo-XPS ensures SEI preservation over an extended period under UHV, compositions derived from RT-XPS are dominated by stable species only. We confirm the SEI thickness preservation from Li 1s high-resolution spectra of the underlying metal substrate. We carefully analyze and decouple three major effects during SEI analysis: UHV effect, reaction effect, and beam effect. UHV and reaction are found to be the major drivers for SEI compositional changes under standard RT-XPS conditions.

While RT-XPS-based chemical descriptions fail to provide performance correlations, we show that pristine SEI composition achieved by cryo-XPS enables performance correlations across diverse electrolyte chemistries. We expect our research to inspire future studies of sensitive and reactive interface characterization under cryogenic conditions to ensure pristine state preservation.

9:15am **AS-TuM-6 Pulsed Laser Deposited-Ruthenium Dioxide Thin Films with Enhanced Electrocatalytic Performance for Energy Conversion Applications*, Ghanashyam Gyawali,*** North Carolina A&T State University

Ruthenium dioxide (RuO_2) is a promising material for advancing renewable energy solutions; however, its practical applications remain limited due to stability challenges and performance variations depending on the fabrication method. In this study, high-quality RuO_2 thin films were synthesized on crystalline sapphire substrates via the pulsed laser deposition (PLD) method. The orientation and crystallinity of the RuO_2 thin films were precisely controlled by adjusting the PLD growth temperature, and its impact on electrocatalytic performance was systematically investigated as the first part of this study. The structural and morphological properties of the films were characterized using high-resolution X-ray diffraction, X-ray reflectivity, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy, confirming epitaxial growth and high crystallinity. The second part of the study is focused on examining the effect of film thickness on the electrocatalytic activity and charge transfer behavior at the electrical double layer, enabling a comprehensive comparative analysis. Electrochemical characterization revealed a wide potential window with highly reversible redox reactions, indicating robust electrochemical activity. Furthermore, electrochemical impedance spectroscopy was conducted under varying applied potentials and different potassium hydroxide electrolyte concentrations to evaluate charge transfer dynamics. A comparative analysis of films with different thicknesses, controlled by varying the pulse number (4800 and 2100), demonstrated that thicker films with a higher pulse number exhibited superior electrocatalytic performance and enhanced stability. Notably, RuO_2 films grown at a pulse number of 4800 at 600 °C outperformed those fabricated at 2100, underscoring the significance of optimized deposition conditions. These findings highlight the potential of RuO_2 thin films as efficient and stable electrocatalysts, offering valuable insights for the advancement of energy conversion and storage technologies.

9:30am **AS-TuM-7 Surface and Bulk Characterization of Organic Semiconductors Using XPS and UPS Techniques*, Jonathan Counsell,*** *Liam Soomary,* Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

Organic semiconductors have gained significant attention in recently due to their potential for flexible, lightweight, and low-cost electronic applications. These materials, enable charge transport via delocalized electronic states, a characteristic of their π-conjugated molecular structures. Their utility includes various organic electronic devices, including Organic Thin-Film Transistors (OTFTs), Organic Light-Emitting Diodes (OLEDs), Organic Photovoltaics (OPVs), and organic diodes. The selection and performance of these materials depends on the semiconductor properties such as charge carrier mobility, energy level alignment, and stability [1]. Among the widely studied molecules, DNTT and CuPc function as p-type semiconductors, facilitating hole transport, whereas $CuF_{16}Pc$ serves as an n-type semiconductor, supporting electron transport. Additionally, F4TCNQ, a strong electron acceptor, is commonly employed as a molecular dopant to enhance the conductivity of p-type materials. Understanding the surface properties and chemical interactions of these molecules is crucial for optimizing device performance and stability.

We will explain the utility of a combination of experimental methods using a modern X-ray Photoelectron Spectroscopy (XPS) spectrometer (both small-area spectroscopy and 2D XP imaging) to probe the surface and bulk properties of both blanket and printed structures. This approach allows for an in-depth analysis of how organic semiconductors interact with substrates and templating/electrode layers. Additionally, we will explore the effects of deposition processes and the evolution of electrical properties as a function of depth, employing Hard X-ray Photoelectron Spectroscopy (HAXPES) and ion milling techniques. Furthermore, Ultraviolet Photoelectron Spectroscopy (UPS) will be utilized to determine the work function of these materials, a critical parameter in optimizing charge injection and transport. A methodological approach to surface characterization will also be discussed, providing insights into the interfacial properties that govern device performance.

[1] Owen A. Melville, Benoît H. Lessard, and Timothy P. Bender, ACS Applied Materials & Interfaces 2015 7 (24), 13105-13118, DOI: 10.1021/acsami.5b01718

11:00am **AS-TuM-13 Investigations of the Solid-Electrolyte Interface in an All-Solid-State Battery Using ToF-SIMS*, Gabriel Parker,*** *Chanho Kim, Yaunshun Li, Guang Yang, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Abstract: All solid-state batteries are a rapidly expanding field with complex formations of both the anode and cathode materials. Solid-state lithium sulfur batteries provide increased energy storage and improved safety. In this presentation, we investigate the composition and formation of the solid electrolyte interface (SEI) for pristine and cycled sulfur-based solid-state batteries. We compare two sulfide solid state electrolyte, namely, Li_6PS_5Cl (LPSCL) and $Li_{10}GeP_2S_{12}$ (LGPS).The cathode material composition is $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ O_2 (NMC811). These nickel rich layered oxides provide contributions to energy storage and act as the active material offering high capacitance and voltage while the sulfide solid state electrolyte offers increased ionic conductivity. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to acquire surface spectra, depth profiles, 2D secondary electron (SE) images, and secondary ion 2D/3D images of the SEI. SIMS spectra and images were gathered using the 30 keV Bi_3^+ primary ion beam over a 500 × 500 μm^2 area for 60 scans. Depth profiles were obtained using the 2 keV Cs$^+$ sputter beam and 30 keV Bi$_3^+$ primary ion beam over a 100 × 100 µm^2 area for 250 scans. Sulfur clusters (S$_x$) were observed, which were attributed to the deformation of the cathode surface after cycling. The mass spectral analysis and 2D/3D results imaged the SEI with formation of sulfates, phosphates and fluorine compounds. Comparisons of the LPSCL and LGPS in spectral analysis and 2D/3D imaging illustrate that LPSCL has higher counts of SEI formation products as well as indication of bubbling on the surface. In contrast, LGPS has pitting.Our results show that ToF-SIMS can uncover the mechanistic differences in SEI formation of all solid-state batteries.

Keywords: Solid-state batteries, solid-electrolyte interface, ToF-SIMS, sulfide solid-state electrolyte, imaging.

11:15am **AS-TuM-14 Study of the Solid Electrolyte Interface Formation at Hard Carbon Electrodes in Sodium-Ion Batteries***, David Schaefer,* Justus Liebig University Giessen, Germany*; Sven Daboss, Christine Kranz,* Ulm University, Germany*; **Marcus Rohnke**,* Justus Liebig University Giessen, Germany

The performance and lifetime of sodium-ion batteries (SIBs) is determined by the interplay between material properties and solid electrolyte interphase (SEI) formation and evolution. The SEI enables electrochemical cells to function reliably and protects the cell from uncontrolled degradation.[1] It is formed primarily from electrolyte reduction products, with its main attributes targeted to be electric insulation, ionic conduction and stability against dissolution in the liquid electrolyte. Although the role of the SEI is recognized in the literature, its formation and evolution are not yet fully understood.[2]

This study focuses on the formation process and compositional evolution of the SEI on hard carbon composite anodes. The cells contain cyclic ester-based electrolytes including the additive fluoro ethylene carbonate and sodium metal counter electrodes. Morphological, chemical and electrochemical analyses were conducted at different sodiation potentials vs. Na$^+$/Na (unsodiated, 1.2 V, 0.9 V, 0.6 V, 0.2 V, 0.01 V) during the first half cycle, as well as during desodiation (0.3 V, 1.3 V, 2.0 V) until the end the first full cycle by scanning electron microscopy (SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electrochemical microscopy (SECM).

Starting from smooth particle surfaces in the pristine state, SEM revealed roughening during sodiation indicating SEI formation. Various visual representations of the SEI were obtained, showing a pox-, or bubble-like morphology. ToF-SIMS analysis revealed chemical differences at the surfaces between samples at different sodiation stages. An SEI consisting of the components Na$_2$O, NaOH, Na$_2$CO$_3$ and NaF with different compositions was observed by ToF-SIMS analyses of electrode surfaces, while oxidic components only seem to appear upon increased sodiation of the hard carbon composite electrode. Interestingly, the surface seems to have lost almost all oxidic residues after desodiation up to 2.0 V vs. Na$^+$/Na and regained sodium fluoride as the major residue salt component.

Information about changes in the electrochemical activity at the surfaces of the electrodes was obtained by SECM. Whereas pristine hard carbon particles are conductive and show a positive feedback signal this drastically changes upon formation of the SEI, hindering electron transport, which yields in a significant decrease in the electron transfer rate and a shift from positive to negative feedback response.

[1] J. Fondard, E. Irisarri, C. Courrèges, M. R. Palacin, A. Ponrouch, R. Dedryvère, *J. Electrochem. Soc.* **2020**, *167*, 070526.

[2] J. Sun, I. E. Gunathilaka, L. A. O’Dell, P. C. Howlett, M. Forsyth, *J. Power Sources* **2023**, *554*, 232298.

11:30am **AS-TuM-15 Surface Sensitive Chemical Imaging of Lithium Materials for Battery Applications by Auger Electron Spectroscopy***, **Juergen Scherer**,* Physical Electronics USA*; Masahiro Terashima, Kazutoshi Mamiya, Shin-ichi Iida,* ULVAC-PHI, Japan

Interest in all-solid-state batteries (ASSBs) has been increasing due to their higher safety, energy density, and longer lifespan compared to conventional lithium-ion batteries (LIBs). However, the internal resistance generated at the interface between the solid electrolyte (SE) and the electrode is a challenge for the practical use of ASSBs as it hinders fast charging and discharging. Several studies have been conducted to reduce the internal resistance through various surface modifications between the SE and cathode, which has led to a significant improvement in Li ion transport during charge and discharge. Despite the numerous studies on the SE/cathode interface of ASSBs, the mechanism behind the increase in interfacial impedance remains unclear.

In this study, we focus on lithium chemical mapping of the cross-section of the SE/cathode interface using Auger electron spectroscopy (AES). AES provides high spatial resolution information on chemical composition and state. The thickness of the anode, SE, and cathode layers in thin-film ASSBs is usually in the range of a few micrometers, making AES an ideal technique for obtaining chemical maps from solid-solid interfaces. Moreover, AES is more sensitive to changes in the lithium chemical state than X-ray photoelectron spectroscopy (XPS). However, it is well known that SEs are generally vulnerable to electron beam damage, and there are few reports on the application of AES in lithium mapping on SEIs.

We examine the electron beam damage on the surface of lithium phosphorus oxynitride (LiPON) as a model SE. The goal is to find the optimum conditions for AES lithium chemical mapping. To achieve this, the impact of electron beam damage on the LiPON surface was investigated. The results showed that the intensity of the LiPON peak was influenced by the beam energy, electron dose, and sample temperature. In conclusion, it was found that the optimal conditions for acquiring a lithium map are at room temperature using 3 keV electrons with a lower beam current.

With the optimum conditions, AES chemical mapping from the SE/cathode cross-section was conducted. Despite the challenges associated with lithium mapping using an electron beam, the study was successful in differentiating between the distributions of different chemical states of lithium in the form of LiPON and LiCoO$_2$. This was achieved through optimizing the beam energy, electron dose, and sample temperature. The results provide valuable insights into the lithium chemical distributions at the SE/electrode interface and contribute to a deeper understanding of the behavior of ASSBs at this interface.

11:45am **AS-TuM-16 Chemical and Elemental Analysis of Annealed Porous Transport Electrodes via X-ray Photoelectron Spectroscopy***, **Lonneke van Eijk**, Jayson Foster,* Colorado School of Mines*; Lei Ding, Weitian Wang, Feng Yuan Zhang,* University of Tennessee Knoxville*; Adam Paxson,* PlugPower*; Svitlana Pylypenko,* Colorado School of Mines

Optimization of proton exchange membrane water electrolyzers (PEMWEs) is crucial for ensuring commercially competitive green hydrogen generation and facilitating the societal transition toward increased green hydrogen adoption. Current efforts focus on improving catalyst activity and stability by optimizing Ir oxide-based catalysts and developing alternative materials. Additionally, research aims to enhance catalyst layer (CL) structures and integrate them effectively with the titanium-based porous transport layer (PTL), which often includes a protective platinum coating. This work focuses on development of porous transport electrodes (PTEs) that integratemixed iridium-ruthenium oxide (IrRuOx) catalysts with Pt-coated titanium PTL. The complexity of the PTEs requires a multi-technique characterization approach that combines electron microscopy methods with X-ray photoelectron spectroscopy (XPS) for surface analysis and time-of-flight secondary ion mass spectrometry (ToF-SIMS) for surface and interface characterization.

This presentation will discuss XPS analysis of porous transport electrodes (PTEs) featuring IrRuOx catalysts that were subjected to various post-treatments involving annealing in different environments. The aim is to investigate how these parameters influence the material's composition and structure, and their respective impact on electrochemical properties. Emphasis is placed on the complexities of characterizing Ir-based materials, with detailed attention to the Ir 4f, Ru 3d, and O1s spectral regions. Due to difficulty of analysis of Ir 4f spectra, various fitting methodologies for O1s spectra were evaluated. It was found that some cases require detailed fitting analysis, while in other cases, basic metrics like binding energy and full width at half maximum (FWHM) are effective in capturing trends that are directly related to catalytic activity and stability. Additionally, XPS-derived metrics were correlated with electrochemical performance using Principal Component Analysis (PCA), highlighting patterns within complex data. These results advance our understanding of XPS analysis of complex catalysts, emphasize the importance of thorough and careful analysis, and highlight opportunities for combining simple metrics with multivariate analysis for the development of energy materials.

12:00pm **AS-TuM-17 X-Ray Photoelectron Spectroscopy Challenges: Practical Solutions to Peak Overlap in Battery Electrodes and Catalysts***, **Lyndi Strange**,* Pacific Northwest National Laboratory*; Donald Baer, Mark Engelhard,* Pacific Northwest National Lab

X-ray photoelectron spectroscopy (XPS) is crucial for analyzing battery materials and catalytic systems. Several studies have indicated that XPS analyses in the literature exhibit significant analysis flaws. One sometimes subtle but remarkably significant issue occurs when a minor peak significant component in a sample overlaps with a peak of interest and importance from an element of interst. This is particularly true with the amount of chemical state of “active” elements at lower concentration are the desired information. This talk highlights peak overlap issues that have been observed in our laboratory. We have focused attention on an often-overlooked F Auger overlap in Ni 2p spectra, relevant to battery anodes. This overlap occurs in many battery electrodes which because of the materials involved have complex photoelectron structures, including simpler elements like Li and F but also a variety of transition metals. We discuss challenges in XPS analysis of Li and nickel–manganese–cobalt (NMC) battery electrodes. Lithium analysis faces preparation challenges and peak overlap with F. New XPS users often overlook the interference of the FKLL Auger signal with the Ni 2p spectrum generated by AlKα X-rays in NMC electrodes. Simulated spectra of F and NiO demonstrate the extent of F Auger contributions to the Ni 2p signal, depending on the F/Ni atom ratio. This suggests how significant these effects are on the resultant spectra. Our analysis shows that overlap issues are significant for real electrode materials. We will also note other examples of peak interferences in quantification including the overlap of Ru 3d and C 1s in catalysts materials and how photoelectron structure from a TiO_2 support influence Pt 4f quantification for catalytic and energy conversion materials.

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