

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

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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[2] Lichterman, M. F., Hu, S., Richter, M. H., Crumlin, E. J., Axnanda, S., Favaro, M., Drisdell, W., Hussain, Z., Mayer, T., Brunshwig, B. S., Lewis, N. S., Liu, Z. & Lewerenz, H.-J. *Energy & Environmental Science* **8**, 2409-2416 (2015).

[3] Foelske-Schmitz; A., Ruch; P.W., Kötze; R., J. *Electron Spectrosc. Relat. Phenom.* **182**, 57-62 (2010).

[4] Lovelock, K. R. J., Villar-Garcia, I. J., Maier, F., Steinrück, H.-P. & Licence, P., *Chemical Reviews* **110**, 5158-5190, (2010).

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[6] Camci, M. T.; Ulgut, B.; Kocabas, C.; Suzer, S., *ACS Omega* **2**, 478-486 (2017).

[7] Gokturk; P.A., Ulgut; B., Suzer; S., *Langmuir* **34**, 7301-7308 (2018).

[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-XP 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.

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(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.

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[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.

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