Chemical Analysis and Imaging at Interfaces Focus Topic Room On Demand - Session CA-Contributed On Demand

Chemical Analysis and Imaging at Interfaces Contributed On Demand Session

CA-Contributed On Demand-1 Capturing Charge-Dynamics of Ionic-Liquid Electrolytes Within Energy Storage Devices With Operando X-Ray Photoelectron Spectroscopy*, E. Oz,* Bilkent University, Turkey*; M. Basaran,* Koc University, Turkey*; B. Ulgut,* Bilkent University, Turkey*; C. Kocabas,* Manchester University, UK*; A. Kocabas,* Koc University, Turkey*;* ***Sefik Suzer,*** Bilkent University, Turkey

Energy Supply and Storage Systems play pivotal role in current and future scientific and technological activities, and batteries are still on top of the list. However, batteries are slow, since they involve sluggish chemical reactions. Electrical-Double Layer Capacitors, or Super-Capacitors have recently been proposed as alternative, since they involve movement of ions only through liquid/solid interfaces.[1] Transport of the ions also controlls performance of these devices and need to be investigated during their operation. XPS is one of the most informative surface analyses techniques, which can deliver chemical as well as electrical properties of systems, when used in-Operando (o-XPS). Unfortunately, the technique requires Ultra-High-Vacuum environment, not very suitable for volatile liquids like water, but there are also several non-volatile liquids, like ionic liquids, which are also excellent electrolytes for battery and super-capacitor applications. Emergence of Ionic Liquids with several promising properties, including their low volatility, has rekindled the use of XPS.[2] Our recent efforts have also concentrated on ionic-liquids and their interfaces under **dc** and **ac** bias, and extended to monitoring electrochemical reactions, as well.[3-5] The common theme in our studies is the use of the bias dependent shifts in the positions of the core-levels as reflection of the electrical potentials, recorded in a non-invasive and chemically resolved fashion. We use both **the magnitude** and **the frequency** dependence of such potentials to extract pertinent information related to static, as well as dynamic chemical and/or electrochemical properties of the materials and their interfaces, configured as devices,[6-7] with particular emphases on the ionic liquids' certain chemical/physical parameters, like steric effects, ion size, diffusivity, etc.[9] Examples using ionic liquids, liquid poly-ethylene-glycol (PEG) and salts, as well as their mixtures, as electrolytes, will be presented and discussed.

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CA-Contributed On Demand-4 Operando Spatiotemporal Potential Mapping of Ionic Liquid Polarization in a Coplanar Electrochemical Device Using Xps and Sem Comparatively*,* ***Sefik Suzer,*** Bilkent University, Turkey*; E. Strelcov, A. Kolmakov,* National Institute of Standards and Technology (NIST)

Effects of the electrical potential developments along a co-planar capacitor, having an ionic liquid as the electrolyte, have been examined by a combination of two powerful analyses techniques, X-Ray Photoelectron Spectroscopy and Secondary Electron Microcopy for investigating the polarization dependent spatio-temporal response of the system, while imposing the device to external DC or AC (Square-Wave) biasing. The applied potential screening manifest as binding energy shifts using XPS and intensity variations using SEM. The magnitude of the developed electrical potential can be extracted under both DC (t = ∞) and AC (fast 1 kHz and slow 10 mHz) bias using both techniques to yield similar time-constants. This similarity is surprising, considering the differences in the underlying principles of the detected signals of the two techniques, but brings out the power of a synergistic combination of the two techniques with complementary capabilities, XPS with a higher chemical specificity but a lower spatial resolution, SEM with a higher spatial resolution and faster data accumulation speed.

CA-Contributed On Demand-7 Selecting a Water-lean Solvent for CO_2 Capture Using Liquid ToF-SIMS*,* ***Jun Gao****, Y. Zhang, J. Son, Z. Zhu, D. Heldebrant, R. Rousseau, X. Yu,* Pacific Northwest National Laboratory

Water-lean solvents are considered a promising technology for carbon dioxide (CO_2) capture. Such solvent molecules include but not limited to N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), 3-methoxy-N-(pyridine-2-ylemthyl)propan-1-amine (MPMPA), and 1-((1,3-Dimethylimidazolidin-2-ylidene)amino)propan-2-ol (IPADM-2-BOL). To better apply these solvents for direct air capture of CO_2, it is necessary to understand the molecular structures, chemical compatibility with separation membranes, and CO_2 capture mechanisms. In this presentation, we will compare the three prominent water-lean solvents as CO_2 capture candidates.Non-CO_2 loaded and CO_2 loaded amine-based solvents were studied using static and *in situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS). Static SIMS is used to assure peak identification.We investigate the water-lean solvents using mass spectral imaging, namely time-of-flight secondary ion mass spectrometry (ToF-SIMS).Static SIMS was used to acquire high mass resolution reference spectra and support peak identification.In situ liquid SIMS imaging was performed to study liquid structural changes and select the optimal CO_2 capture solvent using the system for analysis at the liquid vacuum interface (SALVI) microreactor. Characteristic peaks indicative of 2-EEMPA were observed using in situ liquid SIMS, for example m/z^- 73 $C_4H_9O^-$, 86 $C_4H_8NO^-$ in the negative mode and m/z^+ 29 $C_2H_5^+$ and 128 $C_7H_{14}NO^+$ in the positive mode. The pseudo-molecular peaks, m/z^- 215 $C_{11}H_{23}N_2O_2^-$ deprotonated 2-EEMPA in the negative mode and m/z^+ 217 $C_{11}H_{25}N_2O_2^-$ protonated-2-EEMPA in the positive mode, were also observed, showing the power of molecular detection of liquid ToF-SIMS. In addition, ion pair peaks were observed including m/z^+ 261, 305, 349, and 393 corresponding to EEMPA···nCO_2, n=1-3, respectively, in the positive mode and the product peak of m/z^- 61 CHO_3^- in the negative mode, all suggesting complex solvent structural changes as a result of CO_2 capture in the water-lean solvents. These new in situ observations, mass spectral analysis, and liquid structural simulation facilitate the selection of a suitable candidate in direct air capture for follow-on applications.

CA-Contributed On Demand-10 Algorithms for Automatic Analysis of Image Based Process Control and Its Implementation from Lab to Fab*,* ***Julien Baderot****, H. Ozdoba, D. Misra, N. Clement, S. Martinez, J. Foucher,* POLLEN METROLOGY, France

The need for automatic tools for the metrology of semiconductor structures is more and more pressing as processes become more challenging. In addition to these tools for metrology, it is important to be able to easily transfer the process knowledge from the laboratory to the production chain. Current solutions in the semiconductor industry, mainly propose manual tools and transition from Lab to Fab is tedious and clumsy which results in slow yield ramp-up.

During R&D stages, there is a wide variability in the shape and size of objects before achieving the maturity of the recipe. For this reason, we developed a unique metrology software platform that allows users to perform automatic analysis of complex images, coming from TEM or SEM microscopes. Automation during R&D cycles is becoming a reality thanks to state of the art machine learning and deep learning approaches to overcome current traditional algorithm limitations. This metrology platform provides tools that allow users to define their structures of interest and the associated measurements. Once the structures are defined, users can analyse their images automatically and access their measurements, even with the inherited variability of R&D.

The machine learning pipeline, we present two linked strategies. The first focuses on object detection. It requires the user to annotate a rectangular box around their objects. The shape and aspect are covering any type of semiconductors structures including fuzzy boundaries such as fins, slanted structures or pillars. For the second strategy, we propose an instance segmentation method to extract precise boundaries of the defined structures.

Then, for the implementation of the algorithms library, we propose different tools that enable the use of the algorithms in a fab environment. The first one is the API (Application Programming Interface) which allows the automatic analysis of images through the Manufacturing Execution System (MES). The API will provide a report for each analysis to feed Statistical Process Control (SPC) tools.

Realtime demo of the software platform will be shown on several applications such as 3D Memory, Logic, AR/VR materials. Finally, key performance indicators will be presented and discussed.

CA-Contributed On Demand-13 Factors Influencing Surface Carbon Contamination in Ambient-Pressure X-Ray Photoelectron Spectroscopy Experiments*, Nicolo' Comini,* *Z. Novotny, J. Diulus,* University of Zurich, Switzerland*; T. Huthwelker,* Paul Scherrer Institut, Switzerland*; J. Osterwalder,* University of Zurich, Switzerland

Carbon contamination is a notorious issue that has an enormous influence on surface science experiments, especially in near-atmospheric conditions.While it is often mentioned in publications when affecting the experimental results, its causes are rarely analyzed in detail. Usingambient-pressure X-ray photoelectron spectroscopy,we analyzed the build-up of carbon species(both inorganic and hydrocarbons) on a clean, well-orderedsurface using large-scale (50×10 mm^2) rutile TiO_2(110) single crystals when exposed to water vapor and liquid water[1].

Various factors and environmental conditions, such as beam illumination, residual gas pressure composition, as well as interaction with liquid water, are shown to play a role in the build-up of carbon. It became evident that beam-induced effects locally increase the amount of carbon in the irradiated area. At the same time, starting conditions independent of the light irradiation determine the initial overall contamination level. The introduction of molecular oxygen in the order of 10 mbar can be utilized for fast surface cleaning during X-ray illumination. The surface carbon can be completely removed when the oxygen partial pressure is comparable to the partial pressure of water. Our results support the hypothesis that progressive removal of carbon species from the chamber walls by competitive adsorption of water molecules following repeated exposure of the experimental chamber to water vapor.We believe that these findings will be useful for future studies of liquid-solid interfaces using tender X-rays, where carbon contamination plays a significant role.

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CA-Contributed On Demand-16 Effects of Electrolytes on the Oxidation and Corrosion of Iron Interfaces Using PM-IRRAS*, Kathryn Perrine,* Michigan Technological University

Corrosion is an expensive problem for materials degradation that involves reactions that occur at the gas/solid and liquid/solid interfaces. These complex reactions involve surface chemical and physical changes including ion adsorption, charge transfer, redox reactions, pitting, and film growth. Iron surfaces are the classic material that corrodes, in both gases and liquids, through spontaneous redox reactions. At the liquid/solid interface, iron is oxidized at the anode with oxygen and water reduced at the cathode. Complexity arises from the presence of ions, which catalyze the surface reaction, and gas adsorption, transforming the metal surface into oxides and minerals. Chloride ions initiate the corrosion by breaking down the oxide layer and pitting the surface. Inorganic scale is grown as a result of buildup on the surface. However, the role of cations is unknown in this surface reaction. Understanding these fundamental processes are critical to addressing materials infrastructure degradation, mineral cycling, and other natural processes on Earth and other planets. Minerals, soils, and atmospheric dust are composed of iron, whose surfaces undergo electrochemical and catalytic reactions in the water and mineral cycles. Our research is presented to investigate iron surface oxidation and corrosion at the gas/liquid/solid interface using a surface catalysis approach.

We developed a new method that uses polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS) with a liquid meniscus on a surface to measure the initial stages of surface oxidation and corrosion at the air/liquid/solid interface. This technique allows for observing the reaction of gradual atmospheric O_2 and CO_2 adsorption to the electrolyte/iron interface. In this presentation, the role of cations in chloride electrolytes was investigated on the oxidation and corrosion of iron interfaces. Iron surfaces were exposed to mono- and di-cation chloride electrolytes. We show how our PM-IRRAS method is used to observe the kinetics of oxidation and resulting formation of minerals at the air/electrolyte/iron interface. These results are corroborated with *ex situ* XPS and ATR-FTIR spectroscopy to measure the chemical changes of the interface. The physical changes of the surfaces were measured using *in situ* liquid AFM measurements during corrosion at the electrolyte/iron interface and after oxidation from O_2 and CO_2 at the air/iron interface. The findings of our studies suggest that cation partitioning at the air/electrolyte/iron interface catalyze and influence the mineral film formation in contrast to iron in the electrolyte, with no gradual adsorption of O_2 and CO_2. These results demonstrate how our PM-IRRAS method can be used to track other intermediate stages at gas/solid and liquid/solid interfaces for understanding electrochemical, catalytic, and environmental processes.

CA-Contributed On Demand-19 *in situ* XPS for Catalysis; Up to and Above One Bar*, Christopher Goodwin,* Stockholm University, Sweden*; P. Loemker,* Deutsches Elektronen-Synchrotron, Germany*; M. Shipilin, D. Degerman, P. Amann, A. Nilsson,* Stockholm University, Sweden

The pressure gap is a well-known obstacle in the development of instrumentation and catalysis. We have developed a new instrument that can perform truly high-pressure X-ray photoelectron spectroscopy (XPS) measurements, up to and over 1 bar. With the new pressure regime opened, many reactions now become possible to study. We will present several ongoing projects, including CO oxidation, methanol synthesis, Haber-Bosch process, and Fischer–Tropsch catalysis. With the higher-pressure ranges that can now be reached, direct measurements of industrial systems can yield new levels of understanding at the atomic scale.

CA-Contributed On Demand-22 Electrically Detected Magnetic Resonance & Near-Zero Field Magnetoresistance in $^{28}Si/^{28}SiO_2$*, Elias Frantz,* Penn State University*; D. Michalak,* Intel Corp.*; N. Harmon,* University of Evansville*; E. Henry,* Intel Corp.*; M. Flatte,* University of Iowa*; S. King, J. Clarke,* Intel Corp.*; P. Lenahan,* Penn State University

We report low- and high-frequency electrically detected magnetic resonance (EDMR) and near-zero field magnetoresistance (NZFMR) measurements observed through spin-dependent trap-assisted-tunneling on unpassivated Si/SiO_2 metal-insulator-semiconductor (MIS) capacitors containing silicon of natural isotopic abundance and silicon depleted of ^{29}Si. This study explores the effects that electron-nuclear hyperfine interactions from nearby magnetic nuclei have on both the EDMR and NZFMR spectra. Although our measurements involve monitoring the spin-dependence of the trap-assisted-tunneling current responsible for leakage across the oxide, the high-frequency EDMR spectra resemble that of a combination of P_{b0} and P_{b1} silicon dangling bonds sites at the Si/SiO_2 interface. Additionally, we observed a half-field response in our low-frequency EDMR spectrum with the removal of ^{29}Si nuclei, indicating a small spin-spin separation distance. Capacitance versus voltage measurements also indicate a high interface trap density. These results suggest that the EDMR response is dominated by interface traps. We also observe a substantial narrowing of the NZFMR response with the removal of ^{29}Si nuclei. Since superhyperfine interactions between silicon dangling bonds at the Si/SiO_2 interface should be a full order of magnitude stronger than such interactions involving silicon dangling bonds defects (E′ center) within the oxide. Thus, the NZFMR results also strongly suggest a response dominated by Si/SiO_2 interface traps. These results collectively suggest very strongly that the leakage currents which we observe involve tunneling from Si/SiO_2 P_b dangling bonds to defects within the oxide, presumably oxide dangling bonds, that is E′ centers. Our results offer fundamental insight into technologically important phenomena involving oxide leakage currents in metal-oxide-semiconductor devices such as stress induced leakage currents and time dependent dielectric breakdown.

Acknowledgements

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This work was also partially supported by the Intel Global Supply Chain internship program.

CA-Contributed On Demand-25 Atomic-Scale Dynamics of Epitaxial Oxide Growth During Cu Oxidation Revealed by in Situ ETEM and DFT*, Meng Li,* *M. Curnan, S. House, W. Saidi, J. Yang,* University of Pittsburgh

The initial oxidation processes of metals and alloys are essential for a fundamental understanding of oxidation and play key roles in corrosion prediction, catalyst design, and oxide control. Instead of uniform oxide films, 3D oxide islands are observed in many metals and alloys during initial oxidation. However, the mechanisms for 3D oxide growth are still not clear, especially at the atomic scale. Using correlated in situ environmental transmission electron microscopy (ETEM), statistically-validated quantitative analysis, and density functional theory calculations, we show epitaxial Cu2O nano-island growth on Cu is layer-by-layer along $Cu_2O(110)$ planes, regardless of substrate orientation, contradicting classical models that predict multi-layer growth parallel to substrate surfaces. The mechanism for this unusual layer-by-layer growth is elucidated using correlated density functional theory calculations and statistically validated quantitative analysis. These results shed new light on the epitaxial oxide growth mechanism and provide a deeper understanding of the dynamic processes involved in initial oxidation, which will ultimately help to precisely predict, design, and control nanostructured oxide growth.

Reference

M. Li, M. T. Curnan, M. A. Gresh-Sill, S. D. House, W. A. Saidi, J. C. Yang, Unusual layer-by-layer growth of epitaxial oxide islands during Cu oxidation. *Nat. Commun.***12**, 2781 (2021).

Acknowledgment

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CA-Contributed On Demand-28 Observing Plasma Assisted Processes *in situ* using SEM*, Andrei Kolmakov,* NIST

Multiple processes related to semiconductor microfabrication, aerospace industries, environmental remediation, and biomedical technology rely on plasma processing. Therefore, there exists a great need for *in situ* nanoscale imaging of surfaces under the plasma environment. This, however, is a challenging task for commonly used electron beam or scanning probe-based microscopies due to pressure gaps, signal interferences, strong spatial potential gradients and, etc [1]. Recently, we proposed a microflow discharge reactor equipped with a few-10s nm-thick SiN membrane as a tool to image surfaces with near-field scanning-probe-based microwave microscope immediately (a few seconds) after plasma processing with a sub-100 nm spatial resolution [2]. These SiN membranes are also largely transparent to a few keV electrons and isolate high vacuum SEM column from plasma environment around the sample, and thus enables real-time SEM imaging of a surface of interest under plasma conditions. In this communication, using CVD graphene as a model system, we report on true operando SEM imaging of the plasma-assisted etching process. In particular, signal strength, frame rate, spatial resolution, probing depth, and beam-induced effects were evaluated. We observe that graphene degrades significantly after a few seconds of ca. 200 mW oxygen plasma treatment. Under optimal conditions, a spatial resolution below 10 nm and a frame rate on the order of 1 Hz can be achieved. We also found that the contrast formation in SEM is due to the local difference in the electron emission yields of the sample and the supporting SiN membrane and it can be affected by the presence of static charges in the SiN membrane. The plasma etching of the graphene often results in the formation of highly conductive filamentary structures - a phenomenon that requires further studies.

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CA-Contributed On Demand-31 Graphene Encapsulation Platform for Multi-Technique Spectromicroscopy of Biological Cells and Hydrated Objects*, C. Arble,* NIST-Gaithersburg*; H. Guo,* Southeast University, Nanjing, China*; A. Matruglio,* University College London, UK*; L. Vaccari,* Elettra-Sincrotrone Trieste, Italy*; **Andrei Kolmakov,*** NIST-Gaithersburg

Label-free methods of spectroscopy and microscopy of live cells offer the capability to examine the cellular functions and structure in-vivo thus providing valuable insight into biomolecular components of cells [1]. However, live cells require aqueous media to be in equilibrium with interstitial fluid to survive. This requirement is inherently incompatible with the vacuum-based analytical techniques that use soft x-rays and electrons and impedes electron or soft x-ray imaging and spectroscopic studies under physiological conditions. The recent development of ultrathin molecularly impermeable X-ray (electron) transparent membranes, i.e. graphene, makes it possible to isolate the hydrated sample environment from UHV conditions and thus apply powerful spectromicroscopy tools that previously have been only used with vacuum compatible samples [2]. This approach can now be extended to (bio-) medical samples and interfaces. Herein we report the design and fabrication of graphene encapsulated liquid cell platform for in-vivo studies of hydrated biological samples with a photon (Vis, IR, and soft X-rays) and electron-based spectromicroscopies that operate both under ambient condition and high vacuum environment. The platform consists of an array of microfabricated 50 nm thick SiN windows allowing for combinatorial batch samples analysis both in transmission and reflection signal acquisition geometry. The samples are immobilized on top of the SiN windows and wet-encapsulated conformally with graphene. The encapsulation allows the sample to be isolated from the ambient and yet have its nutrition media preserved and sufficient to be studied with conventional analytical techniques [3]. This approach minimizes the volume of liquid retained along the optical axis, reducing the parasitic absorption and scattering while still providing cells with nutrients via peripheral cites [4]. Combining the sample immobilization with an onboard biocompatible hydrogel feeding media allows for extended cellular lifetimes during the measurement. Preliminary results on the viability of graphene encapsulation for biological samples were conducted with fluorescence optical, fluorescence, SEM, and synchrotron radiation bases XRF and FTIR spectromicroscopies.

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CA-Contributed On Demand-34 Ultrathin Free-Standing Oxide Membranes for Environmental Spectroscopic Study of Solid-Gas and Solid-Liquid Interface*, X. Zhao,* Lawrence Berkeley National Laboratory (LBNL), China*; Y. Lu,* Lawrence Berkeley National Laboratory (LBNL), Taiwan*; C. Carlos,* Lawrence Berkeley National Laboratory (LBNL), Spain*; M. van Spronsen,* Diamond Light Source, UK, Netherlands*; **Miquel Salmeron**,* Lawrence Berkeley National Laboratory (LBNL)

Many surface-sensitive techniques have been improved recently to narrow the gap between measuring environmental conditions from vacuum to practical gas and liquid environments. To extend the pressure range and to enable measurements of the liquid phase, thin film membranes acting as windows in environmental cells have been fabricated. Herein, we present a new generation of ultrathin (2-3nm) free-standing oxide membranes made with oxide films (Al_2O_3, TiO_2, etc.). The films, synthesized using Plasma Enhanced Atomic Layer Deposition (PE-ALD), are mechanically robust and transparent to electrons and photons. Their applicability for various environmental spectroscopies, such as X-ray Photoelectron Spectroscopy (XPS, 1bar) and Fourier Transform Infrared Nanospectroscopy (nano-FTIR, solid-liquid interface) is demonstrated. The remarkable properties of such ultra-thin oxide membranes open up broad opportunities for atomic/molecular level studies of interfacial phenomena (corrosion, catalysis, electrochemical reactions, energy storage, geochemistry, and biology) in a broad range of environmental conditions.

Chemical Analysis and Imaging at Interfaces Focus Topic Room On Demand - Session CA-Invited On Demand

Chemical Analysis and Imaging at Interfaces Invited On Demand Session

CA-Invited On Demand-7 Measuring the Depth Profiles of Surfactants, Ions, and Solvent at the Angstrom Scale*, X. Zhao,* University of Wisconsin - Madison*; G. Andersson,* Flinders University, Australia*; **Gilbert Nathanson**,* University of Wisconsin - Madison **INVITED**

We use neutral impact ion scattering spectroscsopy (NICISS) to measure the depth profiles of ionic surfactants, their counterions and co-ions, and solvent molecules in liquid glycerol. The experiments yield an Angstrom-scale picture of how these species populate the interfacial region. The chosen surfactants are tetrahexylammonium bromide and sodium dodecyl sulfate in the absence and presence of additional sodium bromide. NICISS determines the depth profiles of the elements C, O, Na, S, and Br through the loss in energy of He^+ ions that travel into and out of the liquid, which is then converted into depth. In the absence of NaBr, we find that THA^+ and its Br^- counterion segregate together because of charge attraction, forming a narrow double layer that is 10 Å wide and 150 times more concentrated than in the bulk.With the addition of NaBr, THA$^+$ is “salted out” to the surface, increasing the interfacial THA$^+$ and Br$^-$ concentration and spreading the ions over a ~30 Å depth. Added NaBr similarly increases the interfacial concentration of DS$^-$ ions and broadens their positions. However, the dissolved Br$^-$ ions are strongly repelled from surface DS$^-$ because of charge repulsion. These different interfacial Br$^-$ propensities correlate with previously measured gas-liquid reactivities: gaseous Cl$_2$ readily reacts with Br$^-$ ions in the presence of THA$^+$ but drops 70-fold in the presence of DS$^-$, demonstrating that surfactant headgroup charge controls the reactivity of Br$^-$ ions through changes in its depth profile.

CA-Invited On Demand-13 In-Situ/Operando Soft X-Ray Spectroscopy Characterization of Chemical Interfaces

Y. Liu, X. Feng, Lawrence Berkeley National Laboratory (LBNL)*;* ***Jinghua Guo,*** Lawrence Berkeley National Laboratory **INVITED**

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Soft x-ray spectroscopy characterization 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 have a great influence on performances of energy conversion and energy storage materials, chemical and catalytic processes. However, it is challenging to reveal the real mechanism of the chemical processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical speciation at the solid/gas and solid/liquid interfaces in real time.

I will give some basics on in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices, and how to use the powerful in-situ/operando characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS) to investigate the real electrochemical mechanism during the operation. A number of electrochemical liquid cells will be presented with success in revealing the catalytic and electrochemical reaction at real time.

CA-Invited On Demand-19 Direct-Write Electron Beam Processing of Topologically Complex Functional Nanomaterials using Thermo-Electrically Energized Multiphase Precursor Jets

Andrei Fedorov, Georgia Institute of Technology **INVITED**

Focused Electron Beam Induced Processing (FEBIP) is a powerful method for atom-by-atom fabrication of topologically complex nanostructures from a variety of materials. It provides a complete processing environment for emerging electronic and quantum devices based on 2D materials.[1] Energized micro/nano-jets of thermally or electro-kinetically energized precursors in both gas [2-4] and liquid [5] phase provide unique capabilities for localized delivery of precursor molecules to the substrate, thus establishing locally controlled deposition/etching site for FEBIP. This enhances the growth rate and purity by selectively tuning of precursor and contaminant sticking and surface diffusion coefficients as well as adsorption/desorption activation energies.[6] Expanding on gas-phase jet delivery of precursors, we recently demonstrated a new approach to FEBIP using liquid phase precursors delivered via a nanoelectrospray jetting process into a vacuum environment.[5] This enabled (1) dramatically increasing the growth rate of deposition/etching, (2) enabling deposition of composite materials and alloys with tailored electromechanical properties, and (3) fabrication of new, truly 3D topologies of nanostructures that are fundamentally out of reach of current gas-phase FEBID techniques. These unique new capabilities of NESA-FEBIP are matched by the complexity of the underlying physics and chemistry of ion transport and electrochemical reaction interactions, which need to be understood on the most fundamental level in order to take full advantage of and further develop new FEBIP modes and applications to emerging electronic and quantum devices based on 2D materials. I will highlight development and demonstration of a complete set of processing capabilities using FEBIP to fabricate devices from monolayer graphene, including high resolution, high speed etching [4], dynamic patterning and n-p-n junction formation [7,8], low resistance, Ohmic contact at the metal-graphene junctions [9], and “direct-write” reduction of graphene oxide, forming high electronic mobility conductive line patterns on the substrate. [10]

DOE BES Grant Support (DE-SC0010729) in acknowledged.

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CA-Invited On Demand-25 From Bulk to Constriction: Scaling Analysis of Ionic Transport Through Nanopores and Channels

Michael Zwolak, NIST*; S. Sahu,* University of Colorado at Boulder **INVITED**

Single pores through 2D materials, such as graphene and MoS$_2$, provide new opportunities for biochemical analysis and probing fundamental transport mechanisms of ions and molecules through confined environments [1]. For these “atomically thin” membranes, ion transport depends on dynamics both inside and outside the geometric volume of the pore due to several commensurate length scales, such as the effective membrane thickness, radii of the first and the second hydration layers, pore radius, and Debye length. We will demonstrate that a novel scaling analysis [2] and associated golden aspect ratio [3] enable all-atom molecular dynamics and other simulations to capture the transition between pore- and access-dominated ionic conductance as the pore radius increases beyond the effective membrane thickness (around 1 nm). In the pore-dominated regime, the physics of ion transport subdivides into mechanisms controlled by the free-energy landscape and diffusion. The latter again depends strongly on the flow of ions from bulk to the pore, just as in the access-dominated regime but now due to diffusive limitations and giving rise to sub-ohmic transport. A small strain applied to the 2D membrane can tune transport between these two mechanisms by modulating the balance of dehydration and electrostatic interactions via picometer changes in atomic positions and giving rise to optimal transport (and selectivity) regimes [4]. Overall, these concepts tie transport in nanoscale synthetic pores to transport in biological ion channels, as well as provide several tools for the rigorous simulation and modeling of biological and synthetic pores alike.

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