In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS+HC-WeA

Ambient Pressure XPS Studies of Surface and Chemistry of Catalysts

Moderators: Franklin (Feng) Tao, University of Kansas, Anatoly Frenkel, Yeshiva University

2:20pm **IS+HC-WeA1 The Electronic Structure of Electrochemically Active Interfaces***, V. Pfeifer,* Fritz-Haber-Institut der Max-Planck-Gesellschaft and Helmholtz-Zentrum Berlin, Germany*; J.J. Velasco-Velez,* Max-Planck-Institut für Chemische Energiekonversion, Germany*; R. Arrigo,* Diamond Light Source Ltd., UK*; T.E. Jones,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; M. Hävecker,* Max-Planck-Institut für Chemische Energiekonversion, Germany*; E. Stotz,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; R. Schlögl,* Fritz-Haber-Institut der Max-Planck-Gesellschaft and Max-Planck-Institut für chemische Energiekonversion, Germany*;* ***Axel Knop-Gericke,*** Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

In this presentation I will describe the application of near ambient pressure photoelectron spectroscopy (NAPXPS) to the investigation of electrochemically active gas-solid and liquid-solid interfaces during electrochemical processes. Understanding the oxygen evolution reaction (OER) on a molecular level has become increasingly important over the last few years, beacuse energy storage of renewables is becoming more relevant now that CO_2 emission has been identified as a source of climate change.

Nafion membrane based NAPXPS experiments performed on Pt electrodes during the OER demonstrate that Pt oxides are detrimental for the OER. An oxygen induced species characterized by an Pt4f binding energy 0.6 eV above the metallic Pt4f peak was observed. However, these experiments were done in water vapor and the relevance of the results for the OER in liquid water is questionable [1]. Therefore a new approach to study the liquid-solid interface during an electrochemical process in liquid water was developed.

In this new process the electrode material is deposited on a bilayer of graphene that is stabilized by a silicon nitride window with a pinhole structure. The electrode is exposed to the aqueous electrolyte and is irradiated at the same time by synchrotron light through the bilayer graphene membrane. The emitted photoelectrons have to pass the graphene membrane before being detected in the photoelectron analyzer [2]. Recent progress in the study of the electronic structure of noble metal electrodes used in OER reaction will be discussed [3,4].

References:

1. R. Arrigo et al., In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, *Angew. Chem. Int. Ed.* **52**, 11660-11664 (2013)

2. J. J. Velasco-Velez et al., Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst, *Angew. Chem. Int. Ed.* **54**, 14554-14558 (2015)

3. V. Pfeifer et al., The electronic structure of iridium oxide electrodes active in water splitting, *PCCP*, **18**, 2292-2296 (2016)

4. V. Pfeifer et al., The electronic structure of iridium and its oxides, *Surf. Interface Anal.*, **48**, 261-273 (2016)

3:00pm **IS+HC-WeA3 In situ AP-XPS and NEXAFS Studies on CO Oxidation and CO_2 Dissociation on Copper Surfaces***, B. Eren,* ***Christian Heine,*** *G.A. Somorjai, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

This presentation contains three parts: 1- Surface science approach to CO oxidation reaction on the low-index Cu surfaces which shows at oxygen lean conditions where the Cu surface is not oxidized to Cu2O, (111) face of Cu is more active than more open (100) and (110) faces. This is due to high binding energy of atomic oxygen on Cu, i.e., poisoning of the lower coordinates sites of Cu. 2- Chemical state of the surface and subsurface, and adsorbate coverage on Cu(111) in steady state conditions. Here, we provide phase diagram of the surface under reaction conditions. Interestingly, no CuO phase occurs between 273K-413K when the CO:O2 ratio is chosen as 2:1 or above. Cu2O phase appears to be to more active phase, however it still unclean whether the reaction on Cu2O is a MvK or LH type. 3- Finally, we present the chemical state and the surface morphology of Cu during CO2 dissociation at ambient pressures, which appears to be different than in the presence of CO or O2 alone.

3:20pm **IS+HC-WeA4 Alcohol Adsorption and Reaction on $La_{0.7}Sr_{0.3}MnO_3$(100) by APXPS***,* ***David Mullins****, T.Z. Ward, S.H. Overbury,* Oak Ridge National Laboratory

Perovskite materials that are characterized by the composition ABO_3 can be formed by a wide variety of A and B cations. This enables the catalytic properties to be altered by selectively choosing the constituents while maintaining nominally the same structure. The adsorption and oxidation of simple alcohols such as methanol and ethanol have been identified as probe reactions to characterize and compare the catalytic properties of different oxide surfaces.

Methanol and ethanol oxidation on doped $La_{0.7}Sr_{0.3}MnO_3$(001) have been studied using ambient pressure x-ray photoelectron spectroscopy (APXPS). $La_{0.7}Sr_{0.3}MnO_3$(001) was grown on single crystal Nb-doped $SrTiO_3$(001) by pulse laser deposition. The growth of this film has been extensively characterized as a function of temperature, oxygen pressure and laser fluence in order to produce near ideal crystallinity and morphology in the film. The APXPS experiments were performed on the end station at the recently commissioned Beamline CSX-2 at NSLS II. In order to investigate the so-called “pressure gap” that may occur between reactions studied under vacuum conditions and at pressure approaching atmospheric pressure, experiments were conducted at nominally 10^{-5} torr and at 0.1 torr between 250° C and 350° C.

Methanol forms methoxy when adsorbed on the perovskite surface at 250° C. The surface coverage was four times greater at 0.1 torr compared to 10^{-5} torr. Methoxy was the only C-containing surface species observed at 10^{-5} torr with or without O_2. Methoxy was also the dominant surface species at 0.1 torr in the absence of O_2. However, small amounts of formate and atomic C were also evident. At the higher pressure the Mn 2p spectra indicated that the alcohol partially reduced Mn^{3+} to Mn^{2+}. There was also an indication in the O 1s spectra that O was removed from the surface.

When O was present at 0.1 torr formate became the dominant surface species with only trace amounts of methoxy and C also evident. Gas phase CO_2 and H_2O products were also detected in the C 1s and O 1s spectra.

Results using ethanol rather than methanol as the reactant were generally the same, i.e. only ethoxy on the surface at lower pressures, a mixture of ethoxy and acetate at higher pressure in the absence of O_2, and exclusively acetate on the surface when O_2 was present. The only significant difference between methanol and ethanol was a greater tendency for ethanol to form the carboxylate in the absence of O_2.

Operando experiments are planned to monitor the products with a mass spectrometer to determine whether the different pressures, and resulting surface species, lead to different products.

5:00pm **IS+HC-WeA9 *In situ* Spectroscopy for Catalyst Design***,* ***Rosa Arrigo,*** Diamond Light Source, Oxfordshire, UK **INVITED**

Observing structural dynamics of heterogeneous catalysts in action yields important mechanistic insights to guide the synthesis towards improved materials. Synchrotron-based ambient pressure X-ray photoemission spectroscopy (AP-XPS) has become very popular worldwide to serve this purpose.[1-3] One expanding field of application of this technique is electro-catalysis[2-3] due to its central role in a renewable energy scenario. In this contribution, I will present two examples of the application of this technique to study the gas/solid interface of electro-catalysts for a polymeric electrolyte membrane-based electrode assembly.[4] The first example is the oxygen evolution reaction (OER), which occurs at the anode side of an electrochemical cell for water electrolysis. Herein, the highly debated descriptions of the electronic structure of the oxygen evolving Pt[4] and Ir[5] surfaces are clarified. The second example is the CO_2 reduction reaction (CO_2RR) to fuel over Fe on N-functionalised carbon-based electro-catalysts. These catalysts proved to be active for the CO_2 reduction but the competing hydrogen evolution reaction (HER) from water reduction is favored. Results of this research will be presented which enable us to shine light onto the nature of the H evolving sites and CO_2 reducing sites on this type of catalyst.

[1] H. Bluhm, M. Hävecker, A. Knop-Gericke, M. Kiskinova, R. Schlögl, M. Salmeron, MRS Bulletin 32, 2007, 1022.

[2] J. J Velasco-Velez, V. Pfeifer, M. Hävecker, R. S Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl, A. Knop-Gericke, Angewandte Chemie International Edition 54, 2015, DOI: 10.1002/anie.201506044.

[3] Z. Liu, H. Bluhm, Hard X-ray Photoelectron Spectroscopy (HAXPES), 447-466. DOI: 10.1007/978-3-319-24043-5_17.

[4] R. Arrigo, M. Haevecker, M. E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schloegl, Angewandte Chemie International Edition, 52, 2013, 11660-11664.

[5] V. Pfeifer, T. Jones, J.-J. Velesco-Velez, M. Greiner, C. Massué, R. Arrigo, D. Teschner, F. Girgsdies, M. Scherzer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Haevecker, A. Knop-Gericke, R. Schlögl, Physical Chemistry Chemical Physics 18, 2015, DOI: 10.1039/C5CP06997A.

5:40pm **IS+HC-WeA11 *In Situ* and *Operando* Characterization of Model Metal Nanoparticle Catalysts: Size, Shape, and Chemical State Effects*, Beatriz Roldan Cuenya,*** Ruhr-University Bochum, Germany **INVITED**

In order to comprehend the properties affecting the catalytic performance of metal nanoparticles (NPs), their dynamic nature and response to the environment must be taken into consideration. The working state of a NP catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This talk provides examples of recent advances in the preparation and characterization of NP catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, and Cu catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), and *in situ* and *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering may be tuned through controlled synthesis.

Examples of catalytic processes which will be discussed include the gas-phase oxidation of alcohols (methanol, propanol, butanol), the oxidation and reduction of NO, the electrochemical oxidation of propanol and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the NP size, shape and chemical state in the activity and selectivity of the former reactions.

Thursday Morning, November 10, 2016

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS-ThM

In-situ and Operando Spectroscopy and Microscopy with Infrared Absorption Spectroscopy

Moderators: Franklin (Feng) Tao, University of Kansas, Judith Yang, University of Pittsburgh

8:00am **IS-ThM1 In-situ and Operando Characterization of Catalytic Reactions with Infrared Absorption Spectroscopy*, Francisco Zaera,*** University of California, Riverside **INVITED**

Infrared absorption spectroscopy has been used in our laboratory to study a number of catalytic systems, from model flat surfaces to catalysts with novel nanostructures, under in situ and operando conditions, and in both gas and liquid-solid interfaces. Examples of these applications will be discussed in this presentation, including adsorption on flat metal surfaces probed by reflection-absorption infrared spectroscopy (RAIRS) under ultrahigh vacuum, in operando conditions at atmospheric pressures, and in situ at liquid/solid interfaces. The liquid-solid interface has been characterized in total attenuated reflection (ATR) mode as well. In transmission mode, IR has been used to probe diffusion through different nanostructures, including dendrimers and silica and titania shells. Finally, diffuse-reflectance (DRIFT) IR absorption spectroscopy has been employed to follow reactions on yolk-shell nanocatalysts.

8:40am **IS-ThM3 Studying Birth, Life and Death of Catalytic Solids with In-situ and Operando Spectroscopy*, Bert Weckhuysen,*** Utrecht University, Netherlands **INVITED**

The search for new or more effective catalysts would benefit from a multiscale science approach bridging the molecular world with the macroscopic world. Recent breakthroughs in chemical imaging techniques, based on optical, electron and X-ray methods, demonstrate that such approach is within reach.

This lecture discusses the advances in spectro-microscopy of catalytic solids at different length scales, starting from single molecules and single atoms up to the level of individual catalyst particles. Special emphasis will be devoted to the exploration of mesoscale effects in heterogeneous catalysis.

9:20am **IS-ThM5 Direct Observation of CVD Graphene Growth and the Dynamics of Active Catalysts by *In situ* Scanning and Transmission Electron Microscopy***, Z-J. Wang, J. Cao, R. Farra, R. Schlögl,* ***Marc Georg Willinger,*** Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

During the last three years, we have modified the set-up of a conventional scanning electron microscope in order to enable the observation of catalyst surface dynamics under controlled atmosphere and temperature. Using this instrument, we investigate chemical vapor deposition (CVD) growth of graphene on different metal catalysts. Since the experiments are performed in the chamber of a microscope, it is possible to observe a complete CVD process from substrate annealing through graphene nucleation and growth and, finally, substrate cooling in real time at nanometer-scale resolution without the need of sample transfer. The nucleation and growth of single layer graphene can be investigated at temperatures of up to 1000°C, while at the same time, surface dynamics of the active metal catalyst can be imaged and directly related to the catalytic activity [1]. Due to the high sensitivity of the secondary electron signal to changes in the work function and charge transfer at the surface, we are able to visualize different degrees of graphene-substrate coupling [2] as well as the stacking sequence of few layer graphene. In addition, the *in situ* SEM images of edge misalignment between mutual layers and individual sheets provide real-time information on the evolution of the rotation angle between growing layers and formation of the stacking order. The growth behavior of graphene on nickel, copper and platinum substrates shows characteristic differences that are related to the catalytic activity and carbon solubility of the respective catalysts. In the case of Cu and Pt substrates, we observe grain orientation dependent growth dynamics. Real-time imaging during growth thus allows us to directly visualize and study the catalytic activity of differently oriented surfaces. ESEM observations during graphene growth highlight the dynamic nature of catalysts and reveal the sensitive response of the surface to changes in the chemical potential of the gas phase. *In situ* scanning electron microscopy furthermore covers the spatial resolution of complementary *in situ* techniques that provide spectroscopic information, such as ambient pressure X-ray and Raman spectroscopy. It completes the spectroscopic data with visual information and spatially resolved chemical dynamics. Finally, in combination with *in situ* TEM, it allows to correlate locally observed phenomena with collective dynamics of active catalysts.

References:

[1] Zhu-Jun Wang et al., ACS Nano, **2015**, 9 (2), 1506-1519

[2] Piran R. Kidambi et al., Nano Lett., **2013**, 13 (10), 4769-4778

11:00am **IS-ThM10 Characterizing Working Catalysts with Correlated Electron and Photon Probes*, Eric Stach,*** Brookhaven National Laboratory*; Y. Li,* Yeshiva University*; S. Zhao,* University of Illinois at Urbana Champaign*; A. Gamalski,* Brookhaven National Laboratory*; D. Liu, R. Nuzzo,* University of Illinois at Urbana Champaign*; J.G. Chen,* Columbia University/Brookhaven National Laboratory*; A.I. Frenkel,* Yeshiva University **INVITED**

Heterogeneous catalysts often undergo dramatic changes in their structure as the mediate a chemical reaction. Multiple experimental approaches have been developed to understand these changes, but each has its particular limitations. Electron microscopy can provide analytical characterization with exquisite spatial resolution, but generally requires that the sample be imaged both ex situ and ex post facto. Photon probes have superior depth penetration and thus can be used to characterize samples in operando (i.e when they are actively working). But they generally lack spatial resolution and thus give only ensemble average information.

We have taken advantage of the recent developments in closed-cell microscopy methods to develop an approach that allows us to successfully combine electron, x-ray and optical probes to characterize supported nanoparticle catalysts in operando. By measuring the reaction products at each stage of the reaction, we can directly correlate the information that can be obtained from each approach, and thus gain a deep insight into the structural dynamics of the system.

In this work, we will show how a combination of x-ray absorption near edge (XANES) and scanning transmission electron microscopy (STEM) can be used to characterize the changes that occur in a model NiPt bimetallic catalyst during oxidation and reduction. Bimetallics are of broad interest in heterogeneous catalysis as the provide the opportunity to selectively tune reactivity and selectivity. However, the characterization of their structure by averaged probes such as x-ray absorption spectroscopy is comprised by the heterogeneity that such systems may proscribe.

The presentation will focus on the development and application of experimental methods used to describe the morphological changes that occur in this model bimetallic system. These will include high temperature atmospheric pressure electron microscopy, the direct measurement of reaction products using gas chromatography-mass spectrometry and the ability of a newly developed electron microscope for operando microscopy (based on the FEI Talos platform) to characterize bimetallic nanoparticles through energy dispersive x-ray spectroscopy.

11:40am **IS-ThM12 Tracking Atoms and Charges in Metal Catalysts under Reaction Conditions*, Anatoly Frenkel,*** Yeshiva University

In the last decade, complexity of catalytic nanoparticles attracted much attention as a major factor in catalytic processes. Atomic and electronic structure and dynamics of particles, as well as their interactions with support and adsorbates, are important descriptors of their catalytic activity. The main challenge is how to investigate these factors in a working catalyst, at high temperature and pressure, and how to do so without breaking the correlations between components of this complex system. I will give a brief overview of new methods developed recently to enable such combined studies under realistic reaction conditions. Our approach is to single out electronic charge of metal atoms in a cluster as an “observable” quantity and develop methods to “observe” it experimentally under realistic reaction conditions, and model theoretically. In this framework, complex interactions between metal and adsorbates, metal and support, and support and adsorbates can be all accounted for in terms of their effects on the cluster charge. I will review recent results utilizing this approach for a prototypical catalyst, 1nm Pt nanoparticles supported on silica. Using high energy resolution methods of X-ray absorption and emission spectroscopies (HERFD and RIXS), as well as in situ IR spectroscopy (DRIFTS) and electron microscopy, aided with first-principles (DFT) modeling, we deduced that the structure of atoms and charges in the catalyst is strongly heterogeneous and that it changes dynamically with the change in temperature and pressure of adsorbates (H_2 or CO).

12:00pm **IS-ThM13 STEM Imaging of Catalysts to the Single-Atom Level, via Closed-Cell *In Situ* Gas Reaction Technology***, Lawrence Allard,* Oak Ridge National Laboratory*; S. Duan, J. Liu,* Arizona State University

In recent years, catalysis by single-atom species dispersed on supports has been shown to be an exciting and viable possibility, for catalytic reactions in many systems [e.g. ref. 1]. The stability of single metal atoms on a support during elevated temperatures typically seen in “real” reaction processes is a critical issue, and is necessary to characterize appropriately in order to develop robust single-atom catalysts (SACs). Imaging single heavy atoms on lower Z supports via aberration-corrected high-angle annular dark-field (HAADF) imaging techniques in modern electron microscopy has become routine over the past decade, and extending this imaging capability into the realm of *in situ* gas-reaction technology is a natural goal for the catalytic scientist to better understand dynamical movement and the anchoring of noble metal atoms on specific support sites. This understanding will allow the ability to synthesize SACs with significant loadings of catalytic species while maintaining the full dispersion at the single-atom level.

Novel *in situ* gas-reaction technologies that utilize MEMS-based heater devices retained in a “closed-cell” reactor specimen holder for use in aberration-corrected (S)TEM instruments have shown the remarkable ability for imaging atomic columns in a crystal structure even at elevated temperatures and at pressures up to a full atmosphere [e.g. ref 2]. The possibility to extend this imaging capability to SACs has been a goal of our work, and will be demonstrated in this talk. The effects of the electron beam on the sample, and the effects of electron scattering processes within the gas and window materials that comprise the gas-cell are problematical questions that are being addressed. An “ideal” SAC catalyst comprising Pt atoms on NiO nanocrystals has been used as the model sample for HAADF images to demonstrate cases from material on a standard TEM grid to material in the full geometry of the closed gas-cell reactor.

References:

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2. L.F. Allard, S.H. Overbury, W.C. Bigelow, M.B. Katz, D.P. Nackashi and John Damiano; “Novel MEMS-Based Gas-Cell/Heating Specimen Holder Provides Advanced Imaging Capabilities for *In Situ* Reaction Studies,” *Microsc. Microanal.***18**, 2012, pp. 656–666.

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS-ThA

Ambient Pressure Photoelectron Spectroscopy and Scanning Probe Techniques

Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **IS-ThA1 The Influence of Oxygen on the Catalytic Interaction between CO_2 and Copper studied by High Pressure X-ray Photoelectron Spectroscopy***, A. Regoutz, G. Kerherve, I. Villar-Garcia, C.K. Williams,* ***David Payne,*** Imperial College London, UK

CO_2 is a source for the production of carbon based fuels, such as methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of CO_2, as it is able to direct reactions through stable intermediates, e.g. CO. An important question concerns the influence of oxygen on the catalytic activity and whether oxides are formed on the surface. As this system is an excellent material for the reduction of CO_2 a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in the solid-state sciences but due to its nature as an ultra high vacuum technique (pressure 10^{-9} mbar) it is not possible to study gas-solid interfaces. High-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar. This work presents results on the interaction of CO_2 and CO_2/O_2 with the surface of polycrystalline Cu followed by HPXPS. Cu 2*p* core levels, as well as the Cu $L_3M_{4,5}M_{4,5}$ Auger line are used to investigate the state of the Cu surface. The C 1*s* and O 1*s* core levels are used to track the interaction between CO_2/O_2 and Cu and are compared to CO_2/O_2 gas phase measurements.

Ultimately, the presented results provide a starting point for the detailed understanding of these catalysts and lead to the identification of possible ways to further improve and develop their properties.

2:40pm **IS-ThA2 Graphene Membranes for Atmospheric Pressure Photoelectron Spectroscopy*, Robert Weatherup,*** *B. Eren, Y. Hao, H. Bluhm, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

Determining the chemical state of a catalyst under realistic reaction conditions is of crucial importance in designing catalytic systems with improved activity and selectivity towards sought after products, and a key step in developing or improving existing industrial processes. Ambient pressure X-ray photoelectron spectroscopy APXPS has has proved a powerful technique for providing quantitative and surface sensitive (within a few nm) information on the chemical composition of surfaces/interfaces, with commercial analyzers available that allow measurements at pressure in the tens of mbar regime.[1] However numerous reactions of interest occur at atmospheric pressures and above, and thus the behavior observed in existing APXPS systems may not be truly representative of such reactions.

Here we demonstrate atmospheric pressure XPS using single-layer graphene membranes as photoelectron-transparent barriers that sustain pressure differences in excess of 6 orders of magnitude.[2] The graphene-based membranes are produced by transferring graphene grown by chemical vapor deposition,[3] onto metal (Au or Al) coated silicon nitride grids using a polymer-free transfer technique. The graphene serves as a support for catalyst nanoparticles under atmospheric pressure reaction conditions (up to 1.5 bar), where XPS allows the oxidation state of Cu nanoparticles and gas phase species to be simultaneously probed. We thereby observe that the Cu^{2+} oxidation state is stable in O_2 (1 bar) but is spontaneously reduced under vacuum. We further demonstrate the detection of various gas-phase species (Ar, CO, CO_2, N_2, O_2) in the pressure range 10–1500 mbar including species with low photoionization cross sections (He, H_2). Pressure-dependent changes in the apparent binding energies of gas-phase species are observed, attributable to changes in work function of the metal-coated grids supporting the graphene. We expect atmospheric pressure XPS based on this graphene membrane approach to be a valuable tool for studying nanoparticle catalysis.

[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] Weatherup, R. S.; Eren, B.; Hao, Y.; Bluhm, H.; Salmeron, M. B. Graphene Membranes for Atmospheric Pressure Photoelectron Spectroscopy. *J. Phys. Chem. Lett.***2016**, *7*, 1622–1627.

[3] Hofmann, S.; Braeuninger-Weimer, P.; Weatherup, R. S. CVD-Enabled Graphene Manufacture and Technology. *J. Phys. Chem. Lett.***2015**, *6*, 2714–2721.

3:00pm **IS-ThA3 Development of Graphene Environmental Cells for Atmospheric Pressure Photoelectron Spectroscopy and Microscopy*, Andrei Kolmakov,*** Center for Nanoscale Science and Technology, NIST **INVITED**

Atmospheric pressure electron spectroscopy and microscopy are fast growing branches of the chemical and morphological analysis of the practically important interfaces relevant to catalysis, energy storage, harvesting and conversion as well as biomedical research. A great progress in this area achieved so far is largely due to meticulously engineered differentially pumped electron energy analyzers installed now at many laboratories and at synchrotron radiation facilities. Very recently a new approach for truly atmospheric pressure XPS, SEM, and TEM was demonstrated, which radically reduces the requirements to analytic instrumentation and, in principle, makes it possible high-pressure research using the standard laboratory electron spectrometers and microscopes. The core of this method are electron transparent membranes made of novel 2D materials, which separate high-pressure liquid (or gas) sample compartment from the UHV conditions of the spectrometer or microscope. In this report, we survey different designs and application practices of the graphene liquid cells and demonstrate their potential using X-ray Photoelectron Spectroscopy, X-ray Absorption Spectroscopy, Auger Electron Spectroscopy, Photoemission and Scanning Electron Microscopies of liquid interfaces.

4:00pm **IS-ThA6 Probing Surface Structural and Chemical Evolutions at Atomic Scale in Bi-metallic Catalysts using *In Situ* STEM*, Miaofang Chi,*** Oak Ridge National Laboratory*; C. Wang,* Johns Hopkins University*; K. More,* Oak Ridge National Laboratory*; Y. Xia,* Georgia Institute of Technology **INVITED**

The catalytic performance of nanocatalysts in terms of activity, selectivity, and durability, is primarily determined by the precise nature of the surface and near-surface atomic configurations. The surface atomic arrangements of nanoparticles (NPs), both in structure and chemistry, however, are highly dynamic during synthesis treatments and reaction conditions. Precisely understanding the complete evolution of NPs as a function of synthesis and reaction environments is imperative towards the rational design of nanocatalysts with optimized performance. With the ability of chemical-sensitive imaging at atomic resolution and the simultaneous acquisitions of electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX) analysis, *in situ* scanning transmission electron microscopy (STEM) plays an important role in such studies. In this presentation, we will demonstrate how atomic-scale surface arrangements respond dynamically to *in situ* thermal annealing and gas reaction conditions in bi-metallic nanocatalysts. In particular, by tracking the *same individual* NPsduring *in situ* annealing, the influence of post-synthesis treatments on Pt_3Co NPs will be discussed. Five distinct stages of surface elemental rearrangements are discerned at the atomic scale: initial random (alloy) elemental distribution; surface Pt-skin-layer formation; nucleation of structurally ordered domains; ordered framework development; and finally, initiation of amorphization. Furthermore, the responses of surface atomic configurations in alloyed Pd-Au NPs to different reactive environments, including both reducing and oxidizing gases, will be discussed. In both cases, comprehensive interplays among phase evolution, surface faceting, and elemental inter-diffusion are revealed.

Acknowledgements: This work was supported by the Center for Nanophase Materials Sciences, which is U. S. Department of Energy Office of Science User Facility.

4:40pm **IS-ThA8 Calculations of Electron Inelastic Mean Free Paths for Liquid Water at Energies from 50 eV to 30 keV***, H. Shinotsuka, B. Da, S. Tanuma, H. Yoshikawa,* National Institute for Materials Science (NIMS), Japan*;* ***Cedric Powell,*** *DR. Penn,* National Institute of Standards and Technology

We calculated electron inelastic mean free paths (IMFPs) for liquid water from its optical energy-loss function (ELF) for electron energies from 50 eV to 30 keV. These calculations were made with the relativistic full Penn algorithm (FPA) that has been used for previous IMFP and electron stopping-power calculations for many elemental solids [1]. We also calculated IMFPs of water with three additional algorithms: the relativistic single-pole approximation (SPA), the relativistic simplified SPA, and the relativistic extended Mermin method. These calculations were made using the same optical ELF in order to assess any differences of the IMFPs arising from choice of the algorithm. We found good agreement among the IMFPs from the four algorithms for energies over 300 eV. For energies less than 100 eV, however, large differences became apparent. IMFPs from the relativistic TPP-2M equation for predicting IMFPs were in good agreement with IMFPs from the four algorithms for energies between 300 eV and 30 keV but there was poorer agreement for lower energies. We made comparisons of our IMFPs with earlier calculations from authors who had used different algorithms and different ELF data sets. IMFP differences could then be analyzed in terms of the algorithms and the data sets. Finally, we compared our IMFPs with measurements of IMFPs and of a related quantity, the effective attenuation length (EAL). There were large variations in the measured IMFPs and EALs (as well as their dependence on electron energy). Further measurements are therefore required to establish consistent data sets and for more detailed comparisons with calculated IMFPs.

[1] H. Shinotsuka, S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 47, 871 (2015).

5:00pm **IS-ThA9 Structural Response of Compact Copper Surfaces to CO Adsorption and its Effects of Reactivity***, **Baran Eren**, G.A. Somorjai, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

The most compact and stable surfaces of copper, namely the (111), (100), and (110) faces undergo massive reconstructions in the presence of carbon monoxide at room temperature at pressures in the Torr range. They decompose into two-dimensional nanoclusters. This is a double effect of of low cohesive energy of copper compared to other active metals and the high gain in adsorption energy at under-coordinated sites. With atomically resolved STM images and DFT calculations we provide a rationale for this behavior. Finally, we show that the surfaces which are broken up into clusters are more active for water dissociation, a key step in the water gas shift reaction.

5:20pm **IS-ThA10 Using a Novel In-situ/Operando Chemical Cell to investigate Surface Reactions such as the Reduction of Oxygen and Surface Oxides***, **Philipp Kerger**, D. Vogel, M. Rohwerder,* Max-Planck-Institut fuer Eisenforschung, Germany

A novel in-situ/operando electrochemical cell for doing Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) studies was developed. The cell allows treating the electrode surface with various preparation techniques such as sputtering and deposition as well as analyse it by XPS and other complementary characterisation methods. The electrode is covered under full electrochemical control by a nanoscopic electrolyte layer. This allows in-situ/operando investigations of electrochemical reactions such as oxygen reduction or oxide reduction by ambient pressure XPS. Examples will be presented and discussed in detail.

5:40pm **IS-ThA11 Monitoring of Electrochemical Reactions on Metal Surfaces with Sub-monolayer Sensitivity by Means of Polarization Optical Spectroscopy and EC-STM***, **Christoph Cobet**, M.-H. Chien, R. Sharif, V. Solokha, Gh. Barati, K. Hingerl,* Johannes Kepler University, Austria

We combine spectroscopic ellipsometry (SE), reflection anisotropy spectroscopy (RAS), and a homemade electrochemical scanning tunneling microscope (EC-STM) to study the surface of electrodes on the atomic level in liquids i.e. electrochemical environments. This combination of in-situ methods provides complementary information in comparison to conventional cyclic voltammetry (CV). While in CV the integrated charge and ion-exchange is measured, EC-STM provides direct snapshots of the surface morphology and electron corrugation. Polarization optical spectroscopy, on the other hand, is known for high surface/interface sensitivity regarding chemical modifications, sub-monolayer film formation and morphology transformations. The optical information can be additional recorded with almost the same time resolution like in conventional CV and allows the study of reaction kinetics. Thus it is finally possible to relate measured Faraday-currents to different surface processes.

Here, we report on the results on Cu single crystal surfaces of different orientation in halide solutions. The observed processes include halide adsorption, Cu(I) and Cu(II) dissolution, hydrogen evolution, as well as the initial formation of CuO. These studies are motivated by questions concerning e.g. the corrosion behavior and the catalytic functionality of Cu surfaces. The adsorption of Cl on Cu(110) at anodic potentials for example minimizes the surface energy by a formation of monoatomic steps parallel to the [001]-direction which finally ends up in a faceting of the surface. It turns out that some of the characteristic redox peaks in CV correlate with the surface transformation while others relate to a Cu(I) dissolution. The observed morphology transformations compares in parts with the oxide/chloride induced surface structures as measured UHV. This behavior is only observed at the more “open” and instable (110) surface. The (111) surface, in contrast, retains a smooth surface upon halide adsorption but with a distinct surface reconstruction. At more cathodic potentials we could monitor the hydrogen absorption and the hydrogen gas evolution at Cu surface by RAS and SE, respectively.

6:00pm **IS-ThA12 A Liquid-Jet AP-XPS Study of TiO_2 Nanoparticles in an Aqueous Electrolyte Solution***, **Randima Galhenage**, M.J. Makowski, J.M. Langford, J.C. Hemminger,* University of California, Irvine

To our knowledge, this is the first attempt to understand a true colloidal titania nanoparticle/water interface using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS). Titania has attracted a significant amount of research interest due to its broad catalytic applications, many of which involve titania nanoparticles in aqueous solution. Therefore, understanding the titania nanoparticle/water interface is critical for the rational development of such systems. Here, we have employed liquid-jet Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) to investigate the solid/liquid interface of 20 nm diameter TiO_2 nanoparticles in 0.1M aqueous nitric acid solution. Liquid-jet AP-XPS experiments were conducted at beamline 11.0.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The temperature controlled liquid jet system generates a 25 um diameter liquid beam at a constant flow rate. The jet is irradiated by x-rays of variable photon energies which, therefore, enables us to probe different depths of the solution. Ejected electrons travel through a small aperture and are analyzed by a deferentially pumped electrostatic analyzer. A combination of the Ti2p line shape and the absolute binding energies of Ti2p and O1s reflect a stoichiometric titania lattice and no indication of oxygen vacancies (Ti^{3+}). Further, by increasing the x-ray excitation energy, the difference in O1s binding energies between that of liquid water ($O1s_{liq}$) and the titania lattice ($O1s_{lat}$) oxygen was measured over an increasing experimental probe depth into the particle. The titania lattice, $O1s_{lat}$, binding energy decreases by 250 meV when probing from the surface into the bulk of the particle. This binding energy difference cannot be accounted for by any other interfacial species as they should have a larger binding energy shifts with respect to the lattice oxygen. Moreover, due to the lack of characteristic Ti^{3+} signal, it is clear that further dissociation of water does not occur on the colloidal particles during the course of our XPS study. The observed change in binding energy is interpreted as downward band bending at the surface, resulting from accumulated charge on the surface of the titania nanoparticle.

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room Hall D - Session IS-ThP

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Poster Session

IS-ThP3 Challenges and Current Progress in Characterizing the Solid Electrolyte Interface in Lithium-Sulfur Batteries*, **Manjula Nandasiri**, A.M. Schwarz, V. Shutthanandan,* Pacific Northwest National Laboratory*; P. Kandasamy,* Pusan National University, Republic of Korea*; S.A. Thevuthasan,* Qatar Environment and Energy Research Institute*; V. Murugesan,* Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) battery is a promising candidate to replace Li-ion battery due to their high theoretical specific capacity and energy density. However, there are some challenges to overcome to realize the practical applications of Li-S batteries. One of the most critical challenges to overcome is the shuttling of long chain lithium polysulfides (LiPS), which results in the formation of solid-electrolyte interface (SEI) layer on the electrodes and fading of the battery capacity. The constituents and properties of the SEI layers are dependent on the electrolyte and not very well-understood. It was suggested that the application of *in-situ* or *in-operando* techniques can capture the dynamic changes in the SEI layer during the battery cycling. Thus, our aim was to study the fundamental properties of SEI layer of various electrode-electrolyte systems in their working environment using *in-situ* XPS and imaging XPS. In order to do that, we developed an in-situ XPS capability at Environmental Molecular Sciences Laboratory located in Pacific Northwest National Laboratory.

Analyzing the SEI layers *in-situ* using XPS techniques is very challenging task due to the nature of the electrolytes and their behavior in vacuum systems. Therefore, a vacuum friendly ionic liquid (1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide) was selected as the electrolyte along with Li and graphite electrodes for the in-situ XPS characterization of SEI layers. Using this *in-situ* configuration, we were able to determine the composition of SEI layers formed on Li anode and graphite cathode in Li/ionic liquid/graphite battery system. These XPS results show the gradual formation of LiPS compounds and the decomposition of electrolyte on Li anode with the formation of LiF during the charging and discharging process.Moreover, the elemental and chemical state distributions of SEI layer were mapped using *in-situ* imaging XPS. In addition, we continued the SEI layer characterization of electrodes cycled in the electrolytes which cannot be handled in vacuum using a glove box attached to the XPS system. The XPS and imaging XPS results of these studies will be extensively discussed.

IS-ThP4 Traceable Calibration of High-Quality Pitch Standards Based on an Atomic Force Microscopy System Combined with a Piezo-Actuated Flexure Stage*, **Chien-ying Su**, N.N. Chu, M.H. Shiao, C.N. Hsiao, F.Z. Chen, J.A. Yeh,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

A high-precision atomic force microscope (AFM) metrology system has been established for traceable calibration of transfer standards based on a commercial AFM system and a piezo-actuated flexure stage. By adopting a DSP-based controller, this system is capable of providing high-level nanomotion control. The piezo-actuated flexure stage includes capacitive position sensors in all three axes for highly linear motions over 110 mm scan size and as low as one nanomenter out-of-plane motion. And the capability of subnanometer resolution with linearity error as less as 0.05% is achievable. For measuring periodical structures such as pitch standards, two operation modes are applicable: (a) Combined scanning mode, where the position of the closed-loop displacement stage is controlled point by point while the AFM scanner head measures and records the height variations simultaneously; (b) Direct scanning mode, where the closed-loop displacement stage actuates three axes offsets which are multiples of the pitch length according to the feedback signal of the AFM scanner head in order to locate edge profiles.

In addition, inductively coupled plasma reactive ion etching (ICP-RIE) process has been applied for high-quality pitch standard fabrication. System details, characteristics and results for pitch standard calibrations are presented. System calibrations through transfer standards such as 99.999 nm pitch standard with expanded uncertainties of 0.014 nm establish traceability to the national metrology institute Physikalisch-Technische Bundesanstalt (PTB). The estimated combined uncertainties of this system for pitch standard calibration are in accordance with the Guide to the Expression of Uncertainty in Measurement (ISO GUM).

Keywords: high-precision, transfer standards, nanomotion, flexure stage, feedback, ICP-RIE, combined uncertainties, metrology

IS-ThP5 XPS Enables Visualization of Charge Screening in Metal-ionic Liquid Interfaces with Temporal- and Lateral-resolution*, M.T. Camci,* Mrs, Turkey*; P. Aydogan, B. Ulgut, C. Kocabas, **Sefik Suzer**,* Bilkent University, Turkey

X-ray photoelectron spectroscopic (XPS) investigation of charge screening across two gold electrodes fabricated on a porous polymer surface which is impregnated with an ionic liquid (IL) will be presented. The IL provides a sheet of conducting layer to the insulating polymer film, and allows monitoring charging and screening dynamics at the polymer + IL / vacuum interface in a laterally resolved fashion across the electrodes. Time-resolved measurements are also implemented by recording F1s peak of the IL, while imposing 10 mHz square-wave-pulses (SQW) across the two electrodes in source-drain geometry. Variations in the F1s binding energy reflects directly the transient local electrical potential, and allow us visualize screening of the otherwise built-in local voltage drop on and across the metal electrodes in the range of millimeters. Accordingly, the device is partitioned into two oppositely polarized regions, each following polarization of one electrode through the IL medium. On the other extreme, upon imposing a relatively fast 1 kHz square-wave pulses the charge screening is prevented and the device is brought to assume a simple resistor role. The presented structure and variants of XPS measurements, enabling to record voltage transients in unexpectedly large lateral distances away from the interface(s), can impact on understanding of various electrochemical concepts.

IS-ThP6 Ambient Pressure Photoemission Instrumental Development and Applications within the Field of Energy Related Research*, **John Åhlund**,* Scienta Omicron, Sweden

Ambient pressure photoelectron spectroscopy (APPES) is a rapidly developing technique, suitable for studies in the field of energy harvesting, e.g. solar cells and energy storage, e.g. batteries. We have developed two analysers, capable of measuring samples with a surrounding gas pressure in the mbar range.

Here we present the design and performance of these two new hemispherical electron energy analyzers, the Scienta Omicron HiPP-2 analyser, designed for energies ranging from x-ray photoelectron spectroscopy (XPS) to hard x-ray photoelectron spectroscopy (HAXPES) and the Scienta Omicron HiPP-3 analyser, designed for XPS energies. Where the latter also having imaging capabilities.

For laboratories both analyzers can be equipped with an Al Kα X-ray anode, as demonstrated in Eriksson et al RSI 85(2014)075119 and Edwards et al, NIMA, 785(2015)191. Firstly the performance of the analysers in combination with Al Kα X-rays is demonstrated using standard test samples and procedures, including a demonstration of the HiPP-3 spatial performance under ambient pressure conditions. Secondly the performance is linked to a general discussion about sample to first aperture distance (Kahk et al, JEPEC, 205(2015)57).

Finally we will demonstrate the performance of the HiPP-2 analyzer with applications examples from a dye-sensitized solar cell interacting with water (Eriksson et al Top. Cal. 59(2016)583) and a method to study the battery solid/liquid interface. For the first time the presence of a liquid electrolyte was realized during photoemission measurements (Maibach et al RSI 86(2015)044101).

IS-ThP7 Highly Sensitive Ion Trap Mass Spectrometer for Inline Process Control*, G. Fedosenko, H.-Y. Chung, M. Aliman, A. Laue, R. Reuter, V. Derpmann, M. Antoni, L. Gorkhover, **Tina Graber**,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Most of the real-time process gas analysis was carried out with differentially pumped Residual Gas Analyzer (RGA) which are based on a linear quadrupole mass filtering technique. To generate a complete mass spectrum, a RGA usually needs a few minutes which is often too slow for real-time inline process control. A new process control mass spectrometer, based on Fourier-Transform 3D-Quadrupole Ion Trap technology, is more appropriate for real-time inline process and will be presented in this work.

The 3D-Quadrupole Ion Trap mass spectrometer (*iTrap®*) by ZEISS is installed in a vacuum chamber (120mm x 120mm x ~ 500mm) with an ALD valve for pulsed gas sample injection (pulse duration ~ 50ms). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically without using any separate particle detector. The mass spectrum is finally obtained by a Fourier Transform of the recorded electrode current signal in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap®* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap®*. This result is extremely useful for the process control of Plasma processes and inline real-time contaminations control for high-end applications such as the EUV Lithography manufacturing.

MOCVD process for GaN growth was also investigated with *iTrap®*. The result shows that gas species related to wafer holder contamination, gas phase reaction products and dopant memory effects due to Cp2Mg could be observed clearly. These information will help the user to recognize process drift and/or minimize chamber cleaning intervals.

The new mass spectrometer of ZEISS (*iTrap®*) has successfully detected real-time SnH4 signal in the hydrogen plasma cleaning process. Inline measurement at a MOCVD chamber showed that *iTrap®* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap®* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

IS-ThP8 Real-time State-resolved Reactivity Measurements as a Probe of Carbon Dissolution Kinetics on Ni(111), *Eric Dombrowski*, *E.H. High, A.L. Utz,* Tufts University

The steam reforming of methane to produce hydrogen occurs on an industrial scale at catalyst temperatures exceeding 1000 K, but most of the published sticking data on the methane / nickel system focuses on low surface coverages and surface temperatures, T_s, below 650K. At higher T_s, the carbon products of methane dissociation dissolve into the nickel bulk, which prevents post-dose measurements of reactivity.

To address this limitation, we couple King & Wells molecular beam reflectivity measurements with modulated infrared laser excitation to quantify methane's dissociative chemisorption probability, S,over a wide range of incident fluxes and T_s. This new method simultaneously measures ground state and eigenstate resolved reactivities in real time. Each dose produces upwards of 20 independent reactivity measurements, increasing our precision greatly. Our ability to quantify S in real time reveals the coverage-dependent reaction probability, $S(q,T_s)$. Measuring the full adsorption isotherm further constrains our measured value of the initial sticking probability, S_0.

We measure $S(\Theta,T_s)$ for methane on Ni(111) over a wide range of T_s (500 - 1000 K) and reactive flux (from 0.004 to 0.40 ML/s). Under these conditions, methane initially dissociates into H and methyl fragments. The surface-bound methyls then dehydrogenate to C + 3H, and recombinative desorption of H at these surface temperatures is prompt. Initial measurements of $S(\Theta=0,\ T_s)$ show how elevated surface temperatures promote methane dissociation. As the dose proceeds, we observe coverage-dependent changes in $S(\Theta,T_s)$ that arise from the accumulation of C on and beneath the surface. These effects reveal the kinetics of carbon dissolution into bulk nickel starting with the initial CH bond cleavage event. We observe a sharp transition for the onset of observed site blocking. At all investigated reactive fluxes no site blocking occurs above T_s = 900 K. Below 900K, we observed a reactive flux dependent induction period as the carbon dissolution kinetics approach steady state. Observing how these kinetics change with reactive flux shows how the presence of surface and subsurface C can enhance or inhibit methane activation under the high temperature conditions present in a steam reforming reactor.

IS-ThP9 Design and Performance of Large Surface Area Graphene Liquid Cell for in Situ Electron Spectroscopy and Microscopy, *Hongxuan Guo,* National Institute of Standards and Technology (NIST)*; A. Yulaev, A. Kolmakov,* National Institute of Standards and Technology

For applications such as electrochemistry, environmental science or (photo-) catalysis it is important to characterize materials and interfaces in reactive liquid or aquatic environments. However, interface sensitive characterization techniques, such as X-ray photoelectron spectroscopy (XPS), XAS, Auger electron spectroscopy (AES), SEM, electron microscopies require high or ultrahigh vacuum environments for their operation. To circumvent these pressure gap challenges, the graphene membrane based environmental cells have been recently developed [1, 2, 3] Graphene is the strongest materials with one molecularly impermeable atomic layer thick and it is transparent to electrons and x-rays in a wide energy range. Therefore, it is the best separating membrane material so far for fabrication of liquid cell for the*in-situ* studies of liquid samples in high or ultra-high vacuum environments.

We report on high yield fabrication of double layer graphene capped multichannel matrix which can be impregnated with a large variety of liquids and electrolytes for in-situ SEM, EDS, SAM, XPS. The liquid life time inside a cell can reach many hours and is limited by the defects density in the graphene and interfacial diffusion between the graphene membrane and MCA matrix. Using SEM, in combination with EDS and XAS spectroscopies we analyzed the electronic structure and dynamics of water-graphene interface. Auger spectroscopy was used to analyzed the attenuation of the water generated Auger electrons by double layer graphene. Electrochemical graphene liquid cells have been fabricated via Pt electrodes atomic layer deposition deep in to the MCA matrix. , We performed first feasibility tests via electroplating and stripping of Cu on the surface of double layer graphene from $CuSO_4$ solution. This new sample platform provides a new experimental ground for characterization of liquid materials for energy, catalysis, biomedical and environmental research.

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In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS-FrM

In situ Characterization of Nanomaterials

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:20am **IS-FrM1 In-situ High-Energy X-ray Scattering for Probing Colloidal Nanoparticles in Solution***, **Yugang Sun**,* Temple University **INVITED**

Growth and transformation of colloidal nanoparticles are important for synthesizing functional nanoparticles with tailored properties that represent the foundation for enabling nanotechnology. However, the involving chemical and physical processes are very complicated and barely understood, which limits the precise control over the properties of the nanoparticles. In this presentation, high-energy x-ray scattering techniques will be discussed to serve as unique in-situ approach to monitor these processes in real time. High-energy x-rays have strong penetration in reaction solutions, enabling the possibility to probe the solid colloidal nanoparticles with small volume fractions. In addition, the weak absorption of high-energy x-rays in materials can eliminate the possible side reactions. Reaction systems including the synthesis of colloidal silver nanocubes and microwave synthesis of silver nanoparticles have been successfully studied with the high-energy x-ray scattering at the beamline 1ID of Advanced Photon Source (APS)

9:00am **IS-FrM3 Microfluidics Applied to Ultrafast Spectroscopy***, **Adrien Chauvet**,* University of Sheffield, UK **INVITED**

The use of ultrafast laser technologies became essential in the characterization of molecular complexes, as these techniques have opened new doors for the study of fundamental photo-chemical and photo-physical behaviour. However the application of laser-based spectroscopy for the study of biological samples came along with technical challenges: On one hand, purified biological samples are sensitive to their environment (e.g. oxygen) and are only available in small (sub-millilitres) quantities. On the other hand, the use of ultrafast laser systems primarily demands that the sample is refreshed at each laser shot, at a few kHz repetition rate. Consequently, there exists a pressing need to apply microfluidics systems in the field of ultrafast spectroscopy.

After a brief introduction on laser spectroscopy, I will describe some of the most common solutions that are currently in use in order respond to the constraints of both, the sample and the analytical system. I will then present our newly developed microfluidic flow cell: the cell, while it is convenient to set-up and to use, is suitable to most laser systems up to ~10 kHz repetition rate, and requires a minimal sample amount of ~ 250 microL. The benefits of such a microfluidic system will be illustrated through the analysis of multi-hemes cytochromes.

9:40am **IS-FrM5 Adsorbate-Induced Structural Changes Precious Metal Nano Catalysts***, **Zheng Lu**, Y. Lei,* University of Alabama in Huntsville

Metal nanoparticles can exhibit dramatically different catalytic properties compared to their bulk counterparts. The structure of the supported metal nanoparticles can change dynamically under reaction condition such as when molecules adsorb on the surface. A fundamental understanding of the structure of supported nano catalysts under reaction conditions is an important step towards achieving precise structure-reactivity relationship in catalysis and will ultimately lead to better catalysts.

In this work, we combined X-ray absorption spectroscopy (XAS), pair distribution function (PDF) and small angle X-ray scattering (SAXS) measurements to reveal the lattice contraction and expansion of supported small platinum, palladium and Au nanoparticles as a function of the particle size and the adsorbates. X-ray absorption spectroscopy measurements were performed at the sector 10 beamline at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Scattering data of PDF were collected at beamline 11-ID-B at the APS. High energy X-rays (58 keV) were used in combination with a large area detector. SAXS experiments were performed at the APS 12-ID-B station. The 2D SAXS data were collected on an area detector, a q range of 0.006−0.7 Å-1 with an incident energy of 12 keV.

The support precious metal nano catalysts were studied under selective oxidation reaction conditions.These findings will help us to understand adsorbate-induced structural and chemical changes in precious metal nano catalysts and be useful for improving catalytic activity.

10:00am **IS-FrM6 Understanding the Role of Atmospheric Surface Adsorbates on the Chemical Reactivity of Zirconium Hydroxide Nanopowders using *Operando* Vibrational Spectroscopy***, **Robert Balow**,* NRC/NRL Postdoctoral Fellow*; W. Gordon,* Edgewood Chemical Biological Center*; D.E. Barlow,* Naval Research Laboratory*; I. Iordanov, C. Knox,* Edgewood Chemical Biological Center*; V. Bermudez, J. Lundin, J. Wynne,* Naval Research Laboratory*; G.W. Peterson, C. Karwacki,* Edgewood Chemical Biological Center*; P.E. Pehrsson,* Naval Research Laboratory

Much effort has been focused on developing materials and sorbents for decontamination of chemical warfare agents (CWAs); however, CWAs can have different reactivity and decomposition pathways, making it difficult to find an all-in-one decontamination solution. Zirconium hydroxide (Zr(OH)$_4$) has excellent sorption properties and wide-ranging reactivity towards numerous types of CWA and simulants.[1] This reactivity has been attributed to a combination of diverse surface hydroxyl species (terminal, bridging, etc.) and under-coordinated Zr defects. Unfortunately, these promising preliminary results were often obtained under pristine and unrealistic operating conditions in which the potential impact of atmospheric components (e.g. H$_2$O and CO$_2$) and trace contaminants (e.g. NO$_x$, SO$_2$, H$_2$S and various hydrocarbons) was not a factor.

A more complete picture of the reactivity under *operando* conditions is necessary to evaluate the potential field use of Zr(OH)$_4$ for CWA decontamination. We couple insights from theory with a suite of *operando* infrared spectroscopy techniques to probe the Zr(OH)$_4$ surface, at ambient pressure, under atmospheric components such as humidity and CO$_2$. Contaminated surfaces are then exposed to a sarin CWA simulant, dimethyl methylphosphonate, to evaluate the impact of these adsorbed surface contaminants on the decomposition performance of Zr(OH)$_4$.

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10:20am **IS-FrM7 *In Situ* Molecular Characterization of the Solid-Electrolyte Interface on Lithium Metal Anode***, Y. Zhou, **Xiaofei Yu**, R. Cao, W. Xu, M. Su, Z. Xu, D.R. Baer, C. Wang, Z. Zhu,* Pacific Northwest National Laboratory

Currently, the main stream anode material in Li ion battery industry is graphite. Though it has been a great commercial success, the energy density of graphite-based Li-ion batteries will reach their limit soon. Li metal is an ideal anode material for next generation rechargeable Li batteries because of its extremely high theoretical specific capacity and very low negative electrochemical potential. It has been over 40 years since the first attempt of using Li metal as an anode; however, large-scale commercial applications are still not achieved due to a few challenges, such as dendritic Li growth and limited Columbic efficiency. Recent years, it has been reported that highly concentrated electrolytes, such as 4.0 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME), can result in the dendrite-free plating of Li metal and with high Columbic efficiency. However, the detailed mechanism is not clear. In this research, in situ liquid SIMS was used to molecularly characterize the structure of the Solid-Electrolyte Interfaces (SEI) formed in 1.0 M and 4.0 M LiFSI in DME. The thickness of the SEI in 4.0 M electrolyte is thinner than that in 1.0 M electrolyte. More importantly, less solvent molecules (DME) and Li metal residuals were found in the SEI layer formed in 4.0 M electrolyte. In addition, more F$^-$ was found in the SEI layer formed in 4.0 M electrolyte, indicating that more LiF stays in the SEI layer formed in 4.0 M electrolyte. Our data suggest that the residual solvent molecules (DME) in the SEI layer may play an important role in formation of dendrite and decreasing of Columbic efficiency.

10:40am **IS-FrM8 *In Situ* DRIFTS of TiO$_2$ Nanoparticles***, **Michelle Foster**,* University of Massachusetts, Boston

This project describes recent work focused on the surface chemistry of TiO$_2$ nanoparticles. These materials are commonly used in photocatalytic systems, where light induced reactions take place at the interface between the nanoparticle and an adsorbed sensitizing molecule. There are two primary classes of photocatalytic reactions: an adsorbate is excited by the light and interacts with the substrate, or the substrate is excited by the light and transfers an electron to the molecule. In both types of catalysis, it is the interaction of the adsorbate with the nanoparticle that truly drives the entire system. To optimize these catalytic processes, a better understanding of the interactions between the nanoparticles and the adsorbate is needed. *In situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is well suited for analyzing the surface reactions on

TiO_2 nanoparticles. These powders are mostly transparent to the infrared and the multi-bounce nature of the diffuse reflectance helps to increase the signal from these low coverage reactions. This project explores, on a molecular level, the reactions between acetic acid and TiO_2 nanoparticles using *in situ* DRIFTS as a function of both temperature and relative humidity. To better understand the reactivity, different crystal structures of TiO_2, including anatase, rutile, and the commercially available P25 are investigated. Using DRIFTS and a high-temperature reaction chamber, we monitor surface changes when the TiO_2 is exposed to water and acetic acid. It is important to first understand how water alone reacts with the surface, creating a surface hydroxyl layer. After the reactivity between water and TiO_2 nanoparticles is clarified, the reaction of acetic acid with the surface of TiO_2 nanoparticles is investigated under a variety of different water coverages to better understand the role surface hydroxyls play in the reaction between acetic acid and TiO_2 nanoparticles.

11:00am **IS-FrM9 In situ Characterization of Green Rust Synthesized in Ionic Liquids by Liquid ToF-SIMS and SALVI***, **Juan Yao**, X. Sui, D. Lao, J. Weisenfeld, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

Ionic liquids as green solvents have wide applications in material synthesis, catalysis, and separation. A model switchable ionic liquids (SWILs) consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with carbon dioxide (CO_2) gas was chosen to synthesize nanocrystalline green rust. Under anoxic conditions, a nanoparticulate green rust with carbonate (nano GR) was synthesized by the addition of methanol to the degassed switchable ionic liquid (SWIL) solution consisting of 1-hexanol, DBU, CO_2 and iron (II) acetate ($Fe(C_2H_3O_2)_2$). The structure and oxidation state of nanocrystalline green rust were confirmed using SEM, TEM and Mössbauer spectroscopy. More importantly, the molecular structure change of the ionic liquid leading to green rust formation was characterized using in situ liquid using time-of-flight secondary ion mass spectrometry (ToF-SIMS) coupled with a vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface). Principal component analysis (PCA) was conducted to identify the key components of the solvated iron acetate in methanol and the green rust synthesized in the SWILs. Our results show that liquid SIMS can be a useful tool to study complex liquids at the molecular level providing insights in predicative synthesis of nanomaterials using environmentally friendly solvents.

11:20am **IS-FrM10 Direct Observation of the Growth and Dissolution Process of SnO_2 Nanowires***, **Bethany Hudak**, Y.-J. Chang,* University of Kentucky*; L.F. Allard,* Oak Ridge National Laboratory*; B.S. Guiton,* University of Kentucky

The vapor-liquid-solid (VLS) nanowire growth mechanism is a widely used synthesis technique known to produce high-quality, single crystalline nanowires. This method was first developed by Wagner and Ellis to grow silicon nanowires, and has evolved to utilize many different catalyst materials with facile control over nanowire length, diameter, and dopant concentrations. While this method is prevalent for the growth of inorganic nanowires, the growth kinetics of the VLS mechanism are not well understood, especially for binary and ternary crystal systems. Theoretical predictions suggest that the VLS growth mechanism is governed by steady-state kinetics, and that the crystal chemistry of the reverse process may be different from that which governs nanowire growth. The use of *in situ* microscopy techniques has advanced the understanding of the VLS growth process and nanowire growth kinetics. Through the use of *in situ* heating and atmosphere control in the transmission electron microscope (TEM), we have developed a method to study the forward and reverse growth mechanism of Au-catalyzed SnO_2 nanowires, the reverse process being dubbed solid-liquid-vapor (SLV) nanowire dissolution. By controlling the total pressure of the sample environment, the forward and reverse growth mechanisms can be directed. This method of observing the growth and dissolution of SnO_2 nanowires should provide an experimental platform to explore features relevant to the VLS growth mechanism, such as saturation concentration of a reactant within a VLS catalyst droplet and the use of VLS catalyst metals for controlled etching of semiconducting materials.

11:40am **IS-FrM11 Probing Glyoxal Aqueous Surface Chemistry by In Situ Molecular Imaging***, **Fei Zhang**, Y. Zhou, X. Sui,* Pacific Northwest National Laboratory*; J. Chen,* Shandong University*; Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

Aqueous surfaces after photochemical and dark reactions of glyoxal and hydrogen peroxide (H_2O_2) have been studied by a microfluidic reactor coupled with in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach made it possible to observe glyoxal hydrolysis (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid), oligomers, and water clusters (i.e., $(H_2O)_nH^+$, $(H_2O)_nOH^-$) with sub-micrometer spatial resolution. Spectral principal component analysis was used to determine similarities and differences among various photochemical aging and dark reaction samples and controls. Observations of oxidation products give the physical foundation to deduce new reaction pathways at the aqueous surface. The first chemical mapping of water cluster changes between dark and photochemical aging provides the direct physical evidence that glyoxal oxidation affects the hydrophobicity and water microenvironment at the surface. SIMS three-dimensional chemical mapping enables visualization of the surface mixing state at the molecular level. We potentially provide a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

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