

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

Novel Applications and Approaches in Interfacial Analysis

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

8:20am **CA+AS+NS+SE+SS-FrM1 Chemical Reactions on Bimetal Surfaces with Operando Surface Techniques, Jeong Young Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea INVITED**

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

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

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

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

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

9:00am **CA+AS+NS+SE+SS-FrM3 Principal Component Analysis to Reveal Camouflaged Information in Spectromicroscopy of (complex) Oxides, David Mueller, M. Giesen, Forschungszentrum Juelich GmbH, Germany; D. Stadler, University of Cologne, Germany; T. Duchon, F. Gunkel, V. Feyer, Forschungszentrum Juelich GmbH, Germany; S. Mathur, University of Cologne, Germany; C.M. Schneider, Forschungszentrum Juelich GmbH, Germany**

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

Two cases where PCA revealed information that might have been missed otherwise are presented here: Firstly, iron oxide thin films grown by CVD showed a considerable influence of an external magnetic field on chemistry and crystallinity. Combination of O-K- and Fe-L-Edge X-PEEM unambiguously identified different iron oxide polymorphs (Fe₃O₄ and α -Fe₂O₃) depending on field strength during deposition. The former XAS Edge showed subtle spatial variations in the EXAFS regime that could be

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

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

9:20am **CA+AS+NS+SE+SS-FrM4 In situ Electron Microscopy of Catalysts with Atomic Resolution under Atmospheric Pressure, Xiaoqing Pan, University of California Irvine INVITED**

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

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

10:00am **CA+AS+NS+SE+SS-FrM6 Exposing Buried Interfaces in Thin Film Photovoltaics through Thermo-mechanical Cleaving, Deborah McGott, Colorado School of Mines; C.L. Perkins, W.K. Metzger, National Renewable Energy Laboratory; C.A. Wolden, Colorado School of Mines; M.O. Reese, National Renewable Energy Laboratory**

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

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

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

10:20am CA+AS+NS+SE+SS-FrM7 Switchable Dopants on Percolation Networks of 2D Materials for Chemiresistive Sensing Applications in Aqueous Environments, Peter Kruse, McMaster University, Canada

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

10:40am CA+AS+NS+SE+SS-FrM8 Analysis Of Radioactive Materials In Liquid Using In Situ Sem And Tof-Sims, Jennifer Yao, X.-Y. Yu, Z.H. Zhu, E.C. Buck, Pacific Northwest National Laboratory

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of UO_2 spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of UO_2 materials is possible using SALVI. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high level nuclear waste.

11:00am CA+AS+NS+SE+SS-FrM9 Interactions between Synthetic Bilgewater Emulsion and Biofilms, Jiyoung Son, Earth and Biological Sciences Directorate; J. Yao, Earth & Biological Sciences Directorate; X.-Y. Yu, Pacific Northwest National Laboratory

Presentation Summary:

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

Abstract

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

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

Reference

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

11:40am CA+AS+NS+SE+SS-FrM11 Artificial Intelligence—An Autonomous TEM for In-situ Studies, Huolin Xin, University of California Irvine INVITED

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

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