

## Surface Science

### Room 120 - Session SS+CA+LS-TuM

#### Electrochemical Transformations on Surfaces

**Moderators:** Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, Zhuanghe Ren, University of Central Florida

8:00am **SS+CA+LS-TuM-1 Beyond Static Models: Chemical Dynamics in Energy Conversion Electrocatalysts**, *Beatriz Roldan Cuenya*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

Environmentally friendly technologies for green energy generation and storage in the form of chemical bonds are being urgently sought in order to minimize the future consequences of climate change. The latter includes developing more efficient and durable materials for green H<sub>2</sub> production from water splitting as well as for the re-utilization of CO<sub>2</sub> via its electrocatalytic reduction into value-added chemicals and fuels. Nonetheless, in order to tailor the performance of such energy conversion catalysts, fundamental insight must be gained on their evolving structure and surface composition under reaction conditions.

This talk will illustrate how morphologically and chemically well-defined pre-catalysts experience drastic modifications under operation. Examples for the electrocatalytic reduction of CO<sub>2</sub> as well as the oxygen evolution reaction in water splitting will be given. The model pre-catalysts studied range from size and shape-controlled nanoparticles (Co<sub>3</sub>O<sub>4</sub>, Fe/Co<sub>3</sub>O<sub>4</sub>, Fe/NiO, Cu<sub>2</sub>O, ZnO/Cu<sub>2</sub>O, Au/Cu<sub>2</sub>O), thin films (NiOx, CoFe<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>) to single crystals (differently-oriented Cu surfaces). The need of a synergistic multi-technique *operando* microscopy, spectroscopy and diffraction approach will be evidenced in order to follow the active state formation of complex catalytic materials. Correlations between the dynamically evolving structure and composition of the catalysts and their activity, selectivity and durability will be featured.

8:30am **SS+CA+LS-TuM-3 Sulfur-Doped Carbon Support Boosts CO<sub>2</sub>RR Activity of Ag Electrocatalysts**, *Xingyi Deng, D. Alfonso, T. Nguyen-Phan, D. Kauffman*, National Energy Technology Laboratory

In this work, we show that the activity of Ag electrocatalysts for electrochemical CO<sub>2</sub> to CO conversion is improved when supported on sulfur-doped (S-doped) carbon materials. S-doped carbon support was created by treating the heavily sputtered, highly oriented pyrolytic graphite (HOPG) in H<sub>2</sub>S at elevated temperatures, as confirmed by the S 2p X-ray photoelectron spectroscopy (XPS) peak. Scanning tunneling microscopy (STM) images indicated that Ag nanoparticles supported on S-doped HOPG had similar size distributions as those supported on sulfur-free (S-free) HOPG. While both catalysts reached > 90% CO Faradaic efficiency (FE<sub>CO</sub>) at E = -1.3 V vs. the reversible hydrogen electrode (RHE) in the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), Ag catalysts supported on S-doped HOPG demonstrated 70% higher CO turnover frequency (TOF<sub>CO</sub> = 3.4 CO/atom<sub>Ag</sub>/s) than those supported on S-free HOPG (TOF<sub>CO</sub> = 2.0 CO/atom<sub>Ag</sub>/s). Preliminary calculations based on density functional theory (DFT) indicated a more favorable energetic pathway of CO<sub>2</sub>-to-CO at the C-S-Ag interface, tentatively consistent with experiments. These results hint at a new approach to design active and selective electrocatalysts for CO<sub>2</sub> conversion.

8:45am **SS+CA+LS-TuM-4 Non-Metal Cations for Enhancing CO<sub>2</sub> Electroreduction on Bismuth Electrode**, *Theodoros Panagiotakopoulos, K. Shi, D. Le, X. Feng*, University of Central Florida; *T. Rahman*, University of Central Florida

In exploring the effectiveness of non-metal cations in CO<sub>2</sub> electroreduction, we have carried out a comparative examination of the mechanisms for CO<sub>2</sub> electroreduction to formate (HCOO<sup>-</sup>) and CO on the Bi(111) electrode in the presence of cations, Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, using grand canonical density functional theory. Our results reveal that the reduction of CO<sub>2</sub> to formate is driven by the direct hydrogenation of aqueous CO<sub>2</sub> with a hydrogen atom adsorbed on the electrode (H\*), i.e., CO<sub>2</sub>(aq) + H\* → HCOO<sup>-</sup>. The activation barrier for this process is found to be small, less than 100 meV, in the presence of both cations. Furthermore, our results show that the adsorbed intermediate COOH\* is formed via a proton shuttling process, i.e., H\* moves from the Bi(111) electrode to a H<sub>2</sub>O molecule and one of its H atoms is then transferred to a CO<sub>2</sub>\*. The activation energy barrier for this step was determined to be 0.77 eV and 0.75 eV in the presence of Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, respectively. CO is formed via the dissociation of COOH\* species with an activation energy barrier of 0.62 eV and 0.01 eV in the presence of Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, respectively. These findings lead to two important conclusions: 1) the non-metal cation NH<sub>4</sub><sup>+</sup> can be equally effective as the alkali metal cation Na<sup>+</sup>

in promoting the CO<sub>2</sub> electroreduction to formate; 2) NH<sub>4</sub><sup>+</sup> is actually more effective than Na<sup>+</sup> in promoting the CO<sub>2</sub> electroreduction to CO on the Bi(111) electrode, in excellent agreement with experimental observations [1].

[1]K. Shi, D. Le, T. Panagiotakopoulos, T. S. Rahman, and X. Feng, Effect of Quaternary Ammonium Cations on CO<sub>2</sub> Electroreduction (Submitted, 2024).

This work is supported in part by the U.S. Department of Energy under grant DE-SC0024083.

9:00am **SS+CA+LS-TuM-5 AVS Russell and Sigurd Varian Awardee Talk/SSD Morton S. Traum Award Finalist Talk: How do Cations Promote CO<sub>2</sub> Reduction at the Electrode-Electrolyte Interface**, *Kaige Shi<sup>1,2</sup>, D. Le, T. Panagiotakopoulos, T. Rahman, X. Feng*, University of Central Florida

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) can enable a promising path towards sustainable fuel production and closing the carbon cycle. Despite the reports of numerous electrocatalysts, the mechanism of CO<sub>2</sub>RR at the electrode-electrolyte interface remains to be elucidated, particularly on the role of electrolyte cations in the reaction. While most studies of CO<sub>2</sub>RR focused on alkali metal cations, we investigate CO<sub>2</sub>RR using quaternary ammonium cations, which provide unique tunability in size, shape, and charge distribution to elucidate the cation effect. For the CO<sub>2</sub>RR on a Bi catalyst that produces both CO and formate, we find that the cations are essential for both products. Furthermore, we observe a significant impact of the cation identity and concentration on CO production but a minor one on formate production. Our computational studies reveal that cations are required to stabilize adsorbed \*CO<sub>2</sub> on Bi surface via electrostatic interaction, and the quaternary ammonium cations have a more profound effect on the CO<sub>2</sub> adsorption characteristics and CO<sub>2</sub>RR activity than metal cations. The adsorbed \*CO<sub>2</sub> is an essential step for CO production, but not necessary for formate production due to the pathway with direct reaction of aqueous CO<sub>2</sub> with surface \*H species. Based on the understanding, we employ the substitute ammonium cations to enhance CO<sub>2</sub> electrolysis in a gas-diffusion-electrode (GDE) flow cell, which achieves multi-fold improvement of the activity for CO<sub>2</sub>RR to CO on Bi and other metal catalysts, as compared to that using alkali metal cations. Our work elucidates the critical effect of cations on the CO<sub>2</sub>RR at the electrode-electrolyte interface and demonstrates a strategy to enhance electrocatalysis by optimizing electrolyte composition. This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Catalysis Science program under Award Number DE-SC0024083.

9:15am **SS+CA+LS-TuM-6 Atomistic Simulations on the Triple-Phase Boundary in Proton-Exchange Membrane Fuel Cells**, *J. Jimenez, G. Soldano, E. Franceschini*, Facultad de Ciencias Químicas UNC, Argentina; *Marcelo Mariscal*, Universidad Nacional de Cordoba, Argentina **INVITED**

In this work, we use molecular dynamics simulations and electrochemical experiments on a Nafion/Pt/C system. We perform a systematic analysis, at an atomistic level, to evaluate the effect of several fundamental factors and their intercorrelation in the ECSA (electrochemical surface area) of the catalysts. Besides, we evaluate the diffusion and structuring processes of water at different system interfaces. Overall, this investigation allows us to rationalize how the catalyst utilization is affected, which is an important step in establishing the relationship between the environment and the effectiveness and durability of the PEMFC system. It is important to consider that when experimentally analyzing the changes originating from the different experimental parameters in the operation of a fuel cell, only the average effect of the catalyst, flow field and membrane as a whole can be measured, and it is not possible to separate the corresponding contributions, even less from a region as complex as the TPB. Thus, computational studies provide the appropriate tools for studying each of the parameters separately and in sufficient detail to understand the effects found experimentally.

Proton Exchange Membrane Fuel Cells (PEMFCs), are a well-developed technology aimed at providing cleaner and more sustainable energy solutions. They offer a promising alternative to traditional fossil fuel systems that produce harmful emissions. However, the success of these cells depends greatly on the Three-Phase Boundary (TPB), a critical region composed by the ionomer (liquid, usually Nafion), catalyst (solid, usually platinum) and fuel (H<sub>2</sub>gaseous) interact and is the most important region in a fuel cell, as it is where the electrochemical reaction occurs with the adsorption of the fuel (or oxygen) on the catalyst surface, electron transfer

<sup>1</sup> AVS National Student Awardee

<sup>2</sup> SSD Morton S. Traum Award Finalist

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to form  $H^+$  and subsequent conduction of the generated ions to the ionomer for transport across the membrane. This is because experimentally only a few very general parameters, such as temperature, humidity or fuel flow rate, can be modified, and each of these parameters affects all components of the fuel cell and not just the three-phase region so it is impossible to separate the contributions corresponding to the three-phase boundary from the effects occurring, for example, in the membrane or from the kinetic effects in catalysis. Therefore, understanding, characterizing, and optimizing the variety of factors that affect the TPB content in fuel cells provide excellent opportunities for performance enhancement.

9:45am **SS+CA+LS-TuM-8 Mechanism of Activity Decrease in Orr on Nitrogen-Doped Carbon Catalysts Based on Acid-Base Equilibrium, Kenji Hayashida**, R. Shimizu, Tsukuba University, Japan; J. Nakamura, M. Isegawa, Kyushu University, Japan; K. Takeyasu, Hokkaido University, Japan  
Fuel cells, which use the energy carrier hydrogen directly as a fuel, are important devices for achieving carbon neutrality. However, current fuel cell catalysts use a large amount of platinum, therefore a fuel cell catalyst that can replace platinum in the future is essential. A plausible candidate is nitrogen-doped carbon catalysts, which are durable and abundantly available. However, their activity is very low in acidic media, a practical condition, and this is the biggest challenge to overcome. In this study, we focused on the acid-base equilibrium of pyridinic nitrogen (pyri-N), the active site of nitrogen-doped carbon-based catalysts, to elucidate the reaction mechanism and clarify the mechanism of reduced activity in acidic media. Using a model catalyst with pyri-N-containing molecules adsorbed on a carbon support, we observed the change in electronic state upon immersion in electrolyte and application of potential, and analyzed the kinetics of the activities. It was found that the pyri-N, which is the active site, becomes protonated and hydration-stabilized in the acidic electrolyte, resulting in a decrease in activity. In particular, kinetic analysis showed that the 2 or 2+2 electron pathway via  $H_2O_2$  proceeds independently of the acid-base equilibrium. X-ray photoelectron spectroscopy revealed that the potential for the formation of pyri-NH, associated with oxygen adsorption, an important reaction intermediate, is 0.4 V lower in acidic than in basic conditions. This is due to the formation of pyri-NH<sup>+</sup>, in which pyri-N is protonated by acid-base equilibrium and its stabilization by hydration lowers the pyri-NH formation potential, resulting in lower activity in acidic conditions. Therefore, to improve catalytic activity in acidic conditions, it is important to increase the redox potential of this pyri-NH formation. A possible guideline is to decrease the  $pK_a$  and impart hydrophobicity.

11:00am **SS+CA+LS-TuM-13 Particle Size Effect of Ru Nanocatalyst for Nitrate Electroreduction, Zhen Meng**, K. Shi, Z. Ren, X. Feng, University of Central Florida

Electrochemical nitrate reduction reaction ( $NO_3RR$ ) shows great promise for the recycling of nitrate from wastewater sources for the denitrification of wastewater and sustainable  $NH_3$  production. Among various catalytic materials, Ru shows a high activity and selectivity for the  $NO_3RR$  to  $NH_3$ , while the effect of Ru atomic structure and active sites on the  $NO_3RR$  activity and selectivity remains ambiguous. Here, we prepare size-controlled Ru nanoparticles ranging from 2.2 to 7.1 nm and investigate the dependence of the  $NO_3RR$  on the Ru particle size. The activity (current density) decreases along with the increase of Ru particle size, mainly due to the more Ru surface area for the smaller particles, given the same Ru loading. In contrast, the specific (Ru-surface-area-normalized) activity for the  $NO_3RR$  exhibits a volcano-shaped dependence on the particle size, with 4.9-nm Ru nanoparticles showing the highest activity, which should reflect their intrinsic activity and active sites. On the other hand, the specific activity for the competing hydrogen evolution reaction (HER) increases with the particle size, so that an optimal selectivity for  $NO_3RR$  to  $NH_3$  is also reached on the 4.9-nm Ru nanoparticles. Looking into the size-dependent ratio of Ru surface sites, we find that the superior activity of 4.9-nm Ru nanoparticles correlates with the surface population of the  $D_5$  step site, which favors the adsorption of  $NO_3RR$  reaction intermediate as compared to other surface sites. This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

11:15am **SS+CA+LS-TuM-14 Probing Solvation with Liquid Jet Photoelectron Spectroscopy, Jared Bruce**, S. Faussett, R. Woods, University of Nevada, Las Vegas; K. Zhang, MIT; A. Haines, F. Furche, University of California Irvine; R. Seidel, Helmholtz Zentrum Berlin, Germany; B. Winter, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; J. Hemminger, University of California Irvine

The local chemical structure around solutes in aqueous solution is challenging to characterize on a molecular scale given the amount of hydrogen bonding interactions that occur in solution. Liquid jet photoelectron spectroscopy (LJ-XPS) can be a critical tool providing valuable chemical information both near the surface and in the bulk of the solution.

In this talk I will discuss how a combination of liquid jet photoelectron spectroscopy and electronic structure calculations were used to investigate the local chemical solvation of two systems –  $Fe^{2+}$  and acetic acid aqueous solutions. Each system has specific interfacial behavior that was investigated with liquid jet photoelectron spectroscopy. Fe showed coordination events with small anions like  $Cl^-$  alter the relative concentration of both species near the interface, whereas acetic acid shows alterations to its local solvation environment as a function of both the proximity to the interface and the pH of the bulk solution. Each will be discussed in detail and recent work from the lab at UNLV will be highlighted.

## Surface Science

### Room 120 - Session SS+CA+LS-TuA

#### Electrochemistry and Photocatalysis

**Moderators:** Jared Bruce, University of Nevada Las Vegas, Taku Suzuki, NIMS (National Institute for Materials Science), Japan

2:15pm **SS+CA+LS-TuA-1 Surface Sensitive Studies of the Electrolyte-Electrode Interface**, *Edvin Lundgren*, Lund University, Sweden **INVITED**  
The electrified electrode electrolyte interface is notoriously difficult to study during electrochemical (EC) reactions. Most traditional surface science techniques are disqualified due to the use of electrons, on the other hand, several new in-situ experimental methods have been developed recently. Examples are Electro Chemical X-ray Photoelectron Spectroscopy (ECXPS), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), High Energy Surface X-Ray Diffraction (HESXRD) [4] and EC-IRAS [5].

In the first part of the talk, the corrosion of an industrial Ni base Ni-Cr-Mo alloy will be addressed. A comprehensive investigation combining several synchrotron-based techniques are used to study the surface region of a Ni-Cr-Mo alloy in NaCl solutions in situ during electrochemical polarization. X-Ray Reflectivity (XRR) and ECXPS were used to investigate the thickness and chemistry of the passive film. Grazing Incidence X-ray Diffraction (GIXRD) was used to determine the change in the metal lattice underneath the passive film. X-Ray Fluorescence (XRF) was used to quantify the dissolution of alloying elements. X-ray Absorption Near Edge Structure (XANES) was used to determine the chemical state of the dissolved species in the electrolyte. Combining these techniques allowed us to study the corrosion process, detect the passivity breakdown in situ, and correlate it to the onset of the Oxygen Evolution Reaction (OER) [6].

In the second part, an alternative approach to study the development of a model electro catalyst surface is presented. By using a combination of Grazing Incidence X-ray Absorption Spectroscopy (GIXAS) [7], 2D Surface Optical Reflectance (2D-SOR) [8] and Cyclic Voltammetry (CV) and a Au(111) electrode model surface, direct surface information during real-time CV can be obtained.

- [1] S. Axnanda et al, *Sci. Rep.* **5** (2016) 9788.
- [2] A. A. Gewirth, B. K. Niece, *Chem. Rev.* **97** (1997) 1129.
- [3] K. Itaya, *Prog. Surf. Sci.* **58** (1998) 121.
- [4] M. Ruge et al, *J. Electrochem. Soc.* **164** (2017) 608.
- [5] T. Iwasita, F. C. Nart, *Prog. Surf. Sci.* **55** (1997) 271.
- [6] A. Larsson et al, *Adv. Mat.* (2023) 230462.
- [7] H. Abe, Y. Niwa, M. A. Kimura, *Phys. Chem. Chem. Phys.* **22** (2020) 24974.
- [8] S. Pfaff et al, *ACS Appl. Mater. Interfaces* **13** (2021) 19530.

2:45pm **SS+CA+LS-TuA-3 Operando Studies of CO<sub>2</sub>, CO and N<sub>2</sub> Catalytic Hydrogenation Reactions investigated with Ambient Pressure XPS**, *P. Amann*, Scienta Omicron, Germany; *Andrew Yost*, Scienta Omicron, USA  
Some of the most essential catalytic reactions for our energy society is to reduce CO<sub>2</sub> to hydrocarbons and alcohols to be used as fuels and base chemical for the chemical industry. Furthermore, the catalytic reduction of N<sub>2</sub> to ammonia has been considered as one of the most important discoveries during the 20<sup>th</sup> century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over. X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. Here we will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using a specially engineered XPS system built at Stockholm University (1) and permanently located at the PETRA III synchrotron in Hamburg. The instrument is commercially available at Scienta Omicron (BAR XPS) and can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive. Examples will be presented about the chemical state of Zn in Cu-Zn methanol (2) and of Fe in Fischer-Tropsch (3,4) and ammonia

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synthesis reactions (5) as well as the various adsorbates at different pressures and temperatures.

- (1) P. Amann et al. *Rev. Sci. Instrum.* **90**, 103102 (2019)
- (2) P. Amann et al. *Science* **376**, 603-608 (2022)
- (3) D. Degerman et al. *J. Phys. Chem. C* **128**, 13, 5542-5552 (2024)
- (4) M. Shipilin et al. *ACS Catalysis* **12**, 7609-7621 (2022)
- (5) C.M. Goodwin et al. *Nature*, **625**, 282-286 (2024)

3:00pm **SS+CA+LS-TuA-4 Understanding the Intrinsic Activity and Selectivity of Cu for Ammonia Electrosynthesis from Nitrate**, *Zhuanghe Ren, K. Shi, Z. Meng, X. Feng*, University of Central Florida

Electrocatalysis play a central role in the development of renewable energy technologies towards a sustainable future, such as the recycling of nitrate from wastewater sources. The concentration of nitrate (NO<sub>3</sub><sup>-</sup>) in ground water, rivers, and lakes has been increasing due to the excessive use of agricultural fertilizers and the discharge of industrial wastewater, which has caused severe environmental problems such as eutrophication. Electrochemical reduction of nitrate to ammonia has emerged as a promising route for the recycling of nitrate from wastewater and sustainable ammonia production when powered by renewable electricity. Here I present our recent study of Cu catalyst for nitrate electroreduction, with a focus on its intrinsic activity and selectivity. Using polycrystalline Cu foils for benchmarking, we elucidated the impact of often overlooked factors on nitrate reduction, including Cu facet exposure, nitrate concentration, and electrode surface area. We find that an electropolished Cu foil exhibits a higher activity and selectivity for nitrate reduction to ammonia than a wet-etched Cu foil, benefiting from a greater exposure of Cu(100) facets that are more favorable for the reaction. While the NH<sub>3</sub> selectivity shows no apparent dependence on the nitrate concentration, it increases with Cu electrode area, which is attributed to a promoted conversion of intermediately produced NO<sub>2</sub><sup>-</sup> to NH<sub>3</sub> on a larger electrode. Based on the understandings, we developed a modified Cu foil electrode with increased Cu(100) facets and surface area, which enhanced the NO<sub>3</sub>RR activity by ~50% with a NH<sub>3</sub> Faradaic efficiency of 91% at -0.2 V vs RHE.

This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

References:

- (1) Ren, Z.; Shi, K.; Feng, X. Elucidating the intrinsic activity and selectivity of Cu for nitrate electroreduction. *ACS Energy Lett.* **2023**, *8*, 3658-3665.

3:15pm **SS+CA+LS-TuA-5 Insights Into Photocatalytic Reduction Activities of Different Well-Defined Single Bulk Crystal TiO<sub>2</sub> Surfaces in Liquid**, *Olwale Ayode, W. Lu, H. Zhu, Z. Zhang*, Baylor University

Understanding the activity of TiO<sub>2</sub> photocatalysts is crucial for designing and optimizing efficient photocatalysts, requiring a fundamental understanding of the photooxidation and photoreduction activities of different TiO<sub>2</sub> crystal facets. Although photoreduction activities on several TiO<sub>2</sub> crystal facets have been extensively studied in reactor or ultra-high vacuum environments, studies of well-defined TiO<sub>2</sub> crystal facets in a liquid environment are still lacking. In this study, the photocatalytic reduction activities of resazurin (RZ) were investigated using well-defined bulk single-crystal anatase (001), anatase (101), rutile (001), and rutile (110) facets. The experiment used a liquid cell containing RZ solution and TiO<sub>2</sub> crystal. A lab-built Raman microscope monitored the photoluminescence (PL) spectra of RZ under UV irradiation. We observed an increase in peak intensity at 583 nm and a decrease at 630 nm in the PL spectra of the solution on the TiO<sub>2</sub> crystal facets upon UV illumination, suggesting a conversion from RZ to its product, resorufin (RS). Given that both RZ and RS have distinctive peaks, we used their ratios to estimate their concentrations. This enabled us to assess the conversion rate and reaction rate of the crystals. Our results show that rutile had significantly higher conversion rates and faster reaction rates than anatase for RZ reduction. Rutile (110) had conversion rates about four times greater, and rutile (001) about three times greater than anatase. Rutile (110) reaction rates were about 1.5 times faster than rutile (001) and significantly faster than anatase (101) & (001). Further evaluation of the photoreactivity was conducted using pseudo-order kinetics to determine the rate constant. The significant difference observed in rates between the rutile and anatase phases highlights the successful migration of electrons to the surface of the rutile crystal compared to the anatase surface, emphasizing the importance of crystal structure. The difference observed between rutile (001) and rutile (110) (as well as anatase facets 001 and 101) shows the effect of surface structure on photocatalytic activity. To advance the development of effective TiO<sub>2</sub>-based photoreduction

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materials, we explored plasmon-assisted photoreactions. We have studied the impact of Au nanoparticles on the reactivity of the aforementioned TiO<sub>2</sub> facets. This study will involve modulating hot electron generation and increasing electric fields to better understand their effects on photoreactivity.

## 4:00pm **SS+CA+LS-TuA-8 Selectivity Control by Ionic Liquid Layers: From Surface Science to the Electrified Interface**, *Joerg Libuda*, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Germany **INVITED**

Recently, the concept of "Supported Catalysts with Ionic Liquid Layer" (SCILL) has attracted much attention in heterogeneous catalysis and electrocatalysis. In the SCILL concept, a heterogeneous catalyst is impregnated with a thin layer of ionic liquid (IL) that serves as a catalytic modifier. In this presentation, we will give an overview of selected surface science and electrochemical surface studies on the origin of this selectivity control.

In the surface science studies, we investigated the growth, wetting behavior, structure formation and thermal behavior of various ILs on a wide range of model catalysts (Pt, Pd and Au single crystal surfaces and supported nanoparticles) using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRAS). We were able to show that most ILs form a strongly interacting wetting layer with a high degree of intrinsic structural flexibility. Depending on the conditions, 2D glassy or different crystalline wetting layers are formed, in which the molecular orientation is dynamic and allows the embedding of reactants and thus the modification of the reaction environment.

In our electrochemical surface science studies, we investigated the interaction of selected imidazolium-based ILs with reactive and non-reactive single-crystal electrodes (Au, Pt). Using electrochemical IRAS (EC-IRRAS), we monitored the potential-dependent adsorption of IL ions on the electrode and used electrochemical STM (EC-STM) to investigate the effects of the ILs on the electrode structure. We used the selective oxidation and reduction of hydrocarbon oxygenates as test reactions. For the selective electrooxidation of 2,3-butanediol (a very structure-sensitive reaction at Pt electrodes), we were able to show that small additions of specific ILs (e.g. [C<sub>1</sub>C<sub>2</sub>Im][OTf]) have a large effect on selectivity (e.g. on C-C bond cleavage and selectivity towards the two partial oxidation products acetoin and diacetyl). We attribute these effects to the possible adsorption of the IL anions on the Pt surfaces.

Our results rationalize the origin of selectivity control by IL coatings in heterogeneous catalysis and demonstrate the potential of ILs for selectivity control in electrocatalysis.

- [1] R. Eschenbacher et al., *J. Chem. Phys. Lett.* **12**, 10079 (2021)
- [2] T. Yang et al., *Angew. Chem. Int. Ed.* **61**, e202202957 (2022)
- [3] M. Kastenmeier et al., *J. Phys. Chem. C* **127**, 22975 (2023)
- [4] H. Bühlmeier et al., *Chem. Eur. J.*, in press (2024), DOI10.1002/chem.202301328
- [5] Y. Yang et al., *J. Phys. Chem. C*, accepted for publication (2024)

## 4:30pm **SS+CA+LS-TuA-10 Area Selective Atomic Layer Deposition for Spatial Control of Reaction Selectivity on Model Photocatalysts**, *Wilson McNeary*, National Renewable Energy Laboratory; *W. Stinson*, Columbia University; *W. Zang*, *M. Waqar*, *X. Pan*, University of California Irvine; *D. Esposito*, Columbia University; *K. Hurst*, National Renewable Energy Laboratory

Photocatalytic water splitting holds great potential in the pursuit of the U.S. Department of Energy's Hydrogen Shot initiative to bring the cost of H<sub>2</sub> to \$1/kg by 2031. A key challenge in the development of photocatalysts is increasing their overall solar-to-hydrogen efficiency by enhancing charge separation yields and redox selectivity. In this work, we use area selective ALD of oxide films (e.g., TiO<sub>2</sub> and SiO<sub>2</sub>) to develop tunable interphase layers for selective oxidation and reduction reactions on a single substrate. This presentation details initial synthesis and characterization of monometallic Pt- and Au-based planar thin film electrodes in which Au regions were deactivated towards ALD growth through self-assembled thiol monolayers. The efficacy of thiols in suppressing ALD growth was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. A patterned planar sample comprised of interdigitated arrays of Au and Pt, used as a surrogate for a photocatalyst particle containing two different co-catalysts, was exposed to ALD growth and removal of the inhibitor species. Area selectivity of the ALD coatings on the patterned substrates was evaluated through cross-sectional scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS). Scanning electrochemical microscopy (SECM) was then used to probe the

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local activity of different regions of the patterned surface towards the hydrogen evolution reaction (HER) and iron oxidation and correlated with the ionic and e<sup>-</sup> blocking effects of the area selective ALD coating. We will also detail the application of these findings to the ongoing development of 3D, particle-based photocatalysts

## 4:45pm **SS+CA+LS-TuA-11 Titanium-Based Catalysts for CO<sub>2</sub> Activation: Experimental Modelling of Hybride (Photo-)Catalysts**, *N. Kruse*, *J. Klimek*, *C. Groothuis*, *Lars Mohrhusen*, University of Oldenburg, Germany

Conversion of greenhouse gases and especially CO<sub>2</sub> into useful hydrocarbons via a low-cost route is among the major challenges of the current energy transition. For this purpose, photocatalysis may be a relevant technology, as sunlight is a free and unlimited energy source, and photoreactions usually do not require high temperatures. Oxide-based photocatalysts usually consist of a semiconducting oxide support with nanostructured (noble) metal particles.<sup>1</sup> Unfortunately, these metals are often expensive and have limited lifetimes due to for example sintering, coking or poisoning with carbon monoxide. Thus, for several reasons, it is attractive to develop strategies to replace noble metal in such systems.<sup>2</sup>

Titanium is one of the few elements, that are attractive in terms of its natural availability and considering various economic and ecological aspects. Titanium dioxide (TiO<sub>2</sub>) for example offers a broad platform, as e.g. defects such as Ti<sup>3+</sup> interstitials can boost the photocatalytic activity towards oxygen containing molecules.<sup>3,4</sup> TiO<sub>2</sub> also readily forms hybrid systems with other oxides (e.g. WO<sub>3</sub> clusters)<sup>4</sup> or sulfides such as MoS<sub>2</sub>.<sup>5</sup> Thus, we investigate titanium-based hybrid photocatalytic systems using well-defined model catalysts under ultrahigh-vacuum conditions.

Herein, we present selected results from well-defined model catalysts en route to the desired Ti-based hybrid materials, for example, nanostructured combinations of TiS<sub>2</sub> and TiO<sub>2</sub>. TiS<sub>2</sub> has a broad light absorbance throughout the visible range, is easily reduceable and widely inert to CO poisoning, rendering it an attractive material. Our multi-method approach involves combinations of spectroscopy (esp. photoelectron spectroscopy (XPS)), microscopy (scanning tunneling microscopy (STM)) and reactivity studies (temperature-programmed desorption (TPD)). As one example, nanoparticles of TiS<sub>2</sub> as a classic 2D TMDC can be fabricated and studied on various substrates to derive an atomic-level understanding of structure-reactivity relationships.

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- [3] Mohrhusen, Al-Shamery *Catal. Lett.* **153**, 321-337 (2023).
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## 5:00pm **SS+CA+LS-TuA-12 Tracking the Ultrafast Dynamics of a Photoinduced Reaction at the Surface of a Reactive Semiconductor: CH<sub>3</sub>I Photoinduced Reaction on TiO<sub>2</sub> (110) Surface**, *A. Gupta*, University of Central Florida; *T. Wang*, University of Washington; *K. Blackman*, *C. Smith*, University of Central Florida; *X. Li*, University of Washington; *Mihai E. Vaida*, University of Central Florida

The detection of intermediate species during surface photoinduced reactions and the correlation of their dynamics with the properties of the surface is crucial to fully understand and control heterogeneous reactions. In this study, a technique that combines time-of-flight mass spectrometry with laser spectroscopy and fast surface preparation with molecules is employed to investigate the mechanism of photoinduced CH<sub>3</sub>I reactions on a TiO<sub>2</sub>(110) surface through the direct detection of intermediate species and final products. On a freshly prepared TiO<sub>2</sub>(110) surface, the photoinduced reaction dynamics of CH<sub>3</sub>I follows similar trends observed on other metal oxide surfaces.<sup>1,2</sup> Specifically, the pump laser pulse at 266 nm excites the CH<sub>3</sub>I molecule into the dissociative A-band, which leads to the formation of CH<sub>3</sub> and I intermediates that can further react to form I<sub>2</sub> and reform the CH<sub>3</sub>I molecule. Subsequently, the probe laser pulse ionizes the intermediate and final products, which are detected by a mass spectrometer as a function of the pump-probe time delay. The minimum dissociation time of CH<sub>3</sub> obtained by monitoring the CH<sub>3</sub><sup>+</sup> fragment, which is 110 fs, and the fast rise of the CH<sub>3</sub><sup>+</sup> signal, indicates that CH<sub>3</sub>I is adsorbed on pristine TiO<sub>2</sub>(110) with I atom facing the surface. A fraction of the I atoms produced on a freshly prepared TiO<sub>2</sub>(110) are trapped on the surface. On this TiO<sub>2</sub>(110) surface decorated with I atoms, the CH<sub>3</sub> fragment can react with CH<sub>3</sub>I to form CH<sub>3</sub>I-CH<sub>3</sub>, which leads to a completely different dynamics at the surface due to a change into the pump-probe schema. The

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evolution dynamics of  $\text{CH}_3^+$  and  $\text{CH}_3\text{I}^+$  after the  $\text{CH}_3\text{I}/\text{CH}_3$  photoexcitation will be discussed and compared with results obtained for  $\text{CH}_3\text{I}$  dosed on a freshly prepared  $\text{TiO}_2(110)$  surface.

1. M. A. K. Pathan, A. Gupta and M. E. Vaida, *J. Phys. Chem. Lett.*, 2022, **13**, 9759-9765.
2. M. E. Vaida and T. M. Bernhardt, in *Ultrafast Phenomena in Molecular Sciences: Femtosecond Physics and Chemistry*, eds. R. de Nalda and L. Bañares, Springer International Publishing, Cham 2014, pp. 231-261.

5:15pm **SS+CA+LS-TuA-13 Kinetic Theory of Mixed-Potential-Driven Catalysis and the Experimental Proof**, M. Yan, N. Namari, R. Arsyad, H. Suzuki, University of Tsukuba, Japan; J. Nakamura, Kyushu University, Japan; **Kotaro Takeyasu**, Hokkaido University, Japan

It has recently been suggested that thermal heterogeneous catalysis can also involve electrochemical processes, resulting in selectivity that is markedly different from that of conventional thermal catalysis. If the catalyst is conductive and a suitable electrolyte is present nearby, anodic and cathodic half-reactions may occur simultaneously on a single catalyst surface, forming a mixed potential. This reaction is characterized by the anode and cathode being exposed to the same reactant, unlike conventional fuel cells where different reactants are supplied to each electrode. Interestingly, mixed potentials have been reported to be involved in reactions with gas molecules, such as the formation of  $\text{H}_2\text{O}_2$  and the oxidation of alcohol. These reports suggest that electrochemical processes play a role in controlling catalytic activity and selectivity without external energy. Catalysts based on mixed potentials are a promising new category of catalysts for both basic research and industrial applications, but the principles that determine their activity and selectivity are not yet fully understood.

We first report the theoretical framework of mixed-potential-driven catalysis, including exchange currents, as a parameter of catalytic activity. The mixed potential and partitioning of the overpotential were determined from the exchange current by applying the Butler–Volmer equation at a steady state far from equilibrium [1].

To prove the theoretical framework, we measured the short-circuit current in a model reaction system without applying an external potential to demonstrate electron transfer for enzyme-like glucose oxidation. Specifically, glucose oxidation includes paired electrochemical anodic glucose oxidation and cathodic oxygen reduction, as evidenced by the consistency between the predicted and measured mixed potentials in identical reaction environments. Therefore, it can be categorized as a mixed-potential-driven catalysis. We further demonstrated that the Gibbs free energy drop, as the total driving force, was partitioned into overpotentials to promote each half-reaction in the mixed-potential-driven catalysis. This driving force partitioning, which is controlled by catalytic activity, is a powerful tool for guiding the design of mixed-potential-driven catalytic systems [2].

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[2] M. Yan, R. Arsyad, N. A. P. Namari, H. Suzuki, K. Takeyasu, *ChemCatChem*, accepted (2024).

## Chemical Analysis and Imaging of Interfaces Room 121 - Session CA-ThM

### In Situ and Operando Analysis of Energy and Environmental Interfaces I

**Moderators:** Sefik Suzer, Bilkent University, Turkey, Xiao-Ying Yu, Oak Ridge National Laboratory, USA

#### 8:00am CA-ThM-1 Rationally Engineering Interfaces to Improve Performances of Li Metal Batteries, *Bin Li*, Oak Ridge National Laboratory, USA

INVITED

Lithium (Li) metal batteries have attracted world-wide attention due to its low density (0.534 g/cm<sup>3</sup>), high theoretical capacity (3,860 mAh/g), and low electrochemical potential (-3.04 V vs. SHE), enabling their potential to double the cell-level energy of the state-of-the-art lithium-ion batteries. However, there are still key materials issues that inhibit lithium metal from being commercialized as an anode for rechargeable battery applications. The chemical and morphological (e.g., grain distribution, surface roughness, etc.) non-uniformity, coupled with the high reactivity of lithium drive heterogeneous solid-electrolyte interphase (SEI) formation, poor ionic flux distribution, active material consumption, and rapid dendrite growth. Currently, there are ex-situ and in-situ approaches to address the above issues. For example, one of approaches is to coat artificial SEI layers on Li metal anode surfaces. The component, distribution and structures of SEI layers should be designed and well controlled. The other approach is to exploit advanced electrolyte to in-situ form high-performance SEI layers. In this talk, we will present our recent work from the two aspects: a) novel closed-host bi-layer porous/dense artificial SEI layers were designed<sup>[1]</sup>; b) the microstructures of localized high-concentration electrolyte were deeply understood and thus new electrolytes with high-performance SEI layers being formed were discovered.<sup>[2]</sup>

References:

[1] Efav, Corey M., et al. "A closed-host bi-layer dense/porous solid electrolyte interphase for enhanced lithium-metal anode stability." *Materials Today* 49 (2021): 48-58.

[2] Efav, Corey M., et al. "Localized High-Concentration Electrolytes Get More Localized Through Micelle-Like Structures." *Nature Materials*, 2023.

#### 8:30am CA-ThM-3 Dynamic Molecular Investigation of the Solid-Electrolyte Interphase of an Anode-Free Lithium Metal Battery Using in situ Liquid SIMS and Cryo-TEM, *Zihua Zhu, Y. Xu, P. Gao, C. Wang*, Pacific Northwest National Laboratory

A fundamental factor that governs the performance of a lithium battery is the formation and stability of the solid-electrolyte interphase (SEI) layer on the anode surface. Despite a large body of literature documenting the structural and chemical nature of the SEI layer, essentially three levels of information regarding the SEI layer have never been fully understood: the formation dynamics, the molecular nature, and the spatial configuration. In this work, we use *in situ* liquid secondary ion mass spectroscopy, cryogenic transmission electron microscopy, and density functional theory calculation to delineate the molecular process in the formation of the SEI layer under the dynamic operating conditions. We discover that the onset potential for SEI layer formation and the thickness of the SEI show dependence on the solvation shell structure. On a Cu film anode, the SEI is noticed to start to form at around 2.0 V (nominal cell voltage) with a final thickness of about 40–50 nm in the 1.0 M LiPF<sub>6</sub>/EC-DMC electrolyte, while for the case of 1.0 M LiFSI/DME, the SEI starts to form at around 1.5 V with a final thickness of about 20 nm. Our observations clearly indicate the inner and outer SEI layer formation and dissipation upon charging and discharging, implying a continued evolution of electrolyte structure with extended cycling.

#### 8:45am CA-ThM-4 Understanding the Surface and Bulk Transitions of Functional Inorganic Materials for Energy Applications, *Ajay Karakoti*, Pacific Northwest National Laboratory; *K. Thangaraj*, Washington State University, US; *T. Bathena*, Oregon State University; *V. Shutthanandan*, Pacific Northwest National Laboratory; *S. Lee, K. Ramasamy, V. Murugesan*, Pacific Northwest National Lab

The research encompassing the discovery of novel materials has been the cornerstone for multiple major advancements in energy storage, utilization, and conversion. However, the design and selection of materials has become highly challenging owing to the complex requirements of energy applications that requires the desired properties of materials to be maintained under dynamic operational conditions. The independent

characterization and property measurement of such materials can shed light on the structure-property correlations of materials in static conditions however, in-situ and operando measurements allow the researchers to understand the evolution of materials properties during the application of external stimuli such as temperature, pressure, voltage, and environment.

This talk will focus on the characterization of materials used in energy storage and catalysis under different stimuli such as high temperature and gaseous environment using multi-modal analytical capabilities. Specifically, we will demonstrate the temperature dependent phase transition of lead dioxide, critical to its application as an active electrode material in lead-acid batteries, using in-situ X-ray photoelectron spectroscopy (XPS) combined with residual gas analysis. We will follow this with the demonstration of high temperature X-ray diffraction (XRD) measurements of copper hydroxy chloride (CHC) along with thermogravimetric analysis for understanding its potential as a material for thermochemical energy storage (TCES) applications. We will demonstrate that CHC could be used for TCES based on its hydration and dehydration characteristics however, the hydration-dehydration reversibility is limited by the decomposition of CHC at higher temperatures. We also show that the decomposition of CHC at higher temperatures proceeds with loss of chlorine accompanied by the formation of copper oxide and that its application as a TCES material hinge on preventing its decomposition reducing the chlorine loss. Finally, we will conclude by demonstrating the use of in-situ XPS for understanding the changes in the oxidation states of bismuth and molybdenum in bismuth molybdate catalyst during its redox cycling. We show that the bismuth molybdate catalyst undergo surface oxidation state and stoichiometry changes during initial 3-5 redox cycles, which are also reflected in the dynamic phase changes observed by the X-ray Diffraction, before stabilizing into a temperature dependent equilibrium composition.

#### 9:00am CA-ThM-5 In situ Imaging and Spectroscopy of Boehmite Particles in Liquid, *Xiao-Ying Yu*, Oak Ridge National Laboratory

This work presents in situ imaging of boehmite ( $\gamma$ -AlOOH) particles, suspended in liquid, in a vacuum compatible microfluidic sample holder using a suite of tools including scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), highlighting the advantage of multiscale analysis in material sciences. Boehmite particles are known to exist in high-level radioactive wastes at the Hanford site. These particles are difficult to dissolve and cause rheological problems for processing in the nuclear waste treatment plant. Therefore, it is important to understand how boehmite particles form aggregates in waste tanks. Of particular interest is the pH effect on the boehmite aggregation and morphological change simulating tank waste relevant conditions. Polydisperse boehmite particles under different pH conditions in deionized (DI) water were studied using in situ SEM and liquid SIMS imaging in high vacuum, enabled via a transferrable and vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI) [1, 2]. In situ liquid SEM provides descriptions of particle size, shape, morphology enhanced with elemental mapping [3]. When comparing particle morphology and shape changes under different pH conditions, more aggregates are seen. In situ liquid SIMS is used to study particle molecular structure and composition. In situ SIMS provides detailed submicron molecular mapping of the particle and its surrounding water cluster environments as well as molecular identification of small molecules in liquid. These new results demonstrate advancements of in situ correlative imaging of liquid surfaces and solid-liquid interfaces using a universal microfluidic interface [4].

References:

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# Thursday Morning, November 7, 2024

9:15am **CA-ThM-6 Square Wave Modulated Xps Enables Capturing Dynamics of Local-Electrical Potential Variations of Solid-Liquid Interfaces**, *E. Kutbay*, Bilkent University, Ankara, Turkey; *P. Aydogan-Gokturk*, Koc University, Istanbul, Turkey; *S. Ergoktas*, *C. Kocabas*, Manchester University, UK; *Sefik Suzer*, Bilkent University, Chemistry Department, 06800 Ankara, Turkey

X-Ray Photoelectron Spectroscopy (XPS) has been utilized to extract local electrical potential profiles by recording core level binding energy shifts upon application of a DC and/or AC [Square Wave (SQW)] bias with different frequencies. In this work, to carry out these measurements on a co-planar capacitor with a polyethylene membrane (PEM) coated with a 1:1 by volume mixture of Ionic Liquids (ILs) N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) and N,N-Diethyl-2-methoxy-N-methylthamaminium tetrafluoroborate (DEME-BF<sub>4</sub>). Analyses were carried out in-operando; such that XPS measurements were carried out simultaneously with current measurements. ILs have complex charging/discharging processes and they induce formation of the Electrical Double Layer (EDL) at the interface of the electrode. Certain properties of this process can be extracted via AC modulation under appropriate time windows. Here, two frequencies, 10 kHz and 0.1 Hz, were selected to investigate the effects of the fast polarization and the slow migratory currents, respectively. Local electrical potential developments were extracted at different locations of the device, from the variations in binding energies before and after adding two equivalent resistors in series to the device. This simple modification of the circuit allows us to quantify the AC currents passing through the device as well as the system's resistance and capacitance under specific conditions. Moreover, we were able to detect differences in the time-behavior of the two anionic (BF<sub>4</sub><sup>-</sup> and TFSI<sup>-</sup>) moieties. With this relatively non-invasive methodology, XPS becomes a useful tool for extracting localized electrochemical information and may be of great importance in better understanding of energy harvesting and storage systems.

9:30am **CA-ThM-7 Infrared Spectro-Microscopy of Solid-Liquid Interfaces**, *Xiao Zhao*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Nanoscale properties and dynamical processes at solid-liquid interface are critical for many natural phenomenon and industrial applications, including catalysis, energy storage and self-assembly. However, fundamental study of those processes is often challenged by radiation damage from electron or X-ray probe, which may drive the structure and chemical states of interface away from its original state. Besides, most imaging techniques offer morphological information at the interfaces, while the chemical and structural information is lacking. Herein we demonstrate a new non-destructive platform that enables nanoscale interfacial sensitive Infrared (IR) spectroscopy for solid-liquid interface by combining a graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). With that we investigated the nanoscale dynamic structural evolution of protein assemblies to external environments as well as dynamic interaction between nanoparticles with electrolyte and ligand capping layer for CO<sub>2</sub> electroreduction. The protein substructure and ordering, specific adsorption configuration of ligand on nanoparticles and interfacial water structure are monitored by their characteristic IR vibrational bands at nanometer scale under realistic condition, which provides complimentary information to other operando imaging techniques. Our platform opens broad opportunities for *operando* chemical imaging of soft materials or nanostructures (membrane protein, virus and nanoparticle) in their realistic condition and under external stimuli.

9:45am **CA-ThM-8 Scanning Photoelectron Spectro-Microscopy – Opportunities and Possibilities of Operando Micro-Imaging and Chemical Analysis**, *Zygmunt Milosz*, *M. Amati*, *L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy

Due to the short escape depth of electrons X-ray Photoelectron Spectroscopy (XPS) is the best surface sensitive analytical techniques for probing surface and interface chemical composition. The Scanning PhotoEmission Microscope (SPEM) uses a direct approach to add the spatial resolution and characterize materials at the submicron scale i.e. the x-ray photon beam is downsized to a submicron spot and the sample surface is mapped by scanning the sample with respect to the focused beam. With the SPEM hosted at the Escamicroscopy beamline (Elettra-Sincrotrone Trieste) the beam can be downsized, by using Zone Plates, to a diameter of up to 150 nm with overall energy resolution better than 200 meV [1].

Investigation of complex systems in electrochemistry and catalysis often requires Near Ambient Pressure (NAP) conditions. Due to samples

inhomogeneity in submicron scale conventional XPS systems did not allow to examine them in proper way. We present an alternative way for operando XPS measurements based on a special NAP cell [2] (SI fig. 1) with working pressure up to 2x10<sup>-1</sup> mbar and temperature range from room temperature (RT) up to 550°C. The NAP cell combined with focused synchrotron beam allows for continuous operando chemical characterization of the systems and imaging the surface within scanning areas of 450 μm<sup>2</sup> [1]. It opens new opportunities for operando measurements on the systems in micro- and nanometric scale.

Fuel cells are electrochemical devices providing efficient and environmentally-friendly production of electricity directly converting the electrons exchanged in a redox reaction (such as a combustion) into electric current. One of the still unresolved issues that impedes their widespread applications is related to the limited durability of crucial components and mass transport events that deteriorate the performance.

Recent achievements in the chemical and electronic characterization of fuel cell components will be presented providing an overview of the capabilities of The NAP cell technique. For example the in situ characterization of novel non-noble metal catalysts for the Oxygen Reduction Reaction (ORR) and the characterization of a Self-Driven Single Chamber SOFC in operando condition will be shown [3].

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[2] H. Sezen et al. *ChemCatChem*, Vol. 7 - 22, pp. 3665-3673 (2015)

[3] B. Bozzini et al. *Scientific Report* 3, 2848, 2013

11:00am **CA-ThM-13 The Dynamics of Encapsulated Clusters Under the Microscope**, *Barbara A.J. Lechner*, Technical University of Munich, Germany

**INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure scanning tunneling microscopy (NAP-STM) and X-ray photoelectron spectroscopy (NAP-XPS) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a TiO<sub>2</sub>(110) support, different sintering and encapsulation dynamics are observed in O<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> environments, respectively, and we show that the degree of support reduction plays an important role. We also compare the encapsulation of nanoparticles, which is well established, with that of small clusters, where no satisfying atomistic model exists to date. On Fe<sub>3</sub>O<sub>4</sub>(001), encapsulation stabilizes small Pt clusters against sintering [1]. Moreover, the cluster size and the cluster footprint on the support affect its diffusivity and can therefore be used to tune the sintering mechanism. Interestingly, small clusters of up to 10 atoms even still diffuse intact after encapsulation, and we can observe and track this diffusion in real time using our FastSTM [2].

[1] S. Kaiser et al., *ACS Catalysis* 13, 6203-6213 (2023).

[2] C. Dri et al., *Ultramicroscopy* 205, 49-56 (2019).

11:30am **CA-ThM-15 Scanning Tunneling Microscopy for High Entropy Materials**, *TeYu Chien*, University of Wyoming

High entropy materials, including high entropy alloys (HEAs), high entropy Van der Waals materials, and high entropy oxides, have drawn the attention of scientists and engineers for their various functionalities and properties. While a wide variety of properties are being studied in these materials, microscopic understanding is still challenging. In this talk, I will talk about our recent efforts in using scanning tunneling microscopy (STM) based techniques to study this intriguing material system. Including synchrotron X-ray STM (SX-STM) in which combining the atomic scale spatially resolving STM with the elemental resolving X-ray absorption spectroscopy (XAS) to achieve distinguishing elements at sub-nm scale on the surface of HEA; revealing short-range order and local lattice distortion; and revealing gap features in high entropy alloys and compounds, which might originate from strong correlation physics in the high entropy materials.

11:45am **CA-ThM-16 in-Situ Observation of Chemical and Morphological Transformations by Multi-Modal X-Ray Characterization**, *Slavomir Nemsak*, Lawrence Berkeley National Laboratory

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) in both soft and tender/hard X-ray regime has

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established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 of the Advanced Light Source [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) and the beamline will be also discussed.

## References

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[4] H. Kersell, S. Dhuey, D. Kumar, S. Nemsak, *Synchr. Rad. News* **35**, 61-66(2022).

12:00pm **CA-ThM-17 NO Adsorption on Pd(111): A Relationship between Coverage and Spectral Shift**, *Sayantani Sikder*, Stony Brook University; *E. Fornero*, Universidad Nacional del Litoral (UNL), Argentina; *A. Boscoboinik*, Center for Functional Nanomaterials, BNL

Understanding the adsorption of nitric oxide (NO) on catalytic surfaces like Pd (111) is crucial for environmental and health reasons. Despite previous research, there is a gap in understanding spectral changes across different coverage ranges. Addressing this, we investigate the relationship between spectral shifts, integrated intensity, and coverage of NO on Pd (111) in IRRAS (Infra-red reflection Adsorption Spectroscopy). We conducted experiments at 200 K under ultra-high vacuum conditions to high doses of NO ~ 5L, to ensure precise control over NO exposure and adsorption. A mathematical expression was developed for the relationship of coverage & dose. We observed that as we approach the saturation coverage, the coverage/dose correlation changes from linear (0.3 to 0.6 ML), when NO adsorbs in three-fold and bridge sites, to a more complex correlation above 0.6 ML, when the adsorption is a combination of atop and bridge sites. The IRRAS peak positions are useful in providing insights toward this conclusion. In short, our research provides valuable insights into NO adsorption dynamics on Pd (111), advancing our comprehension of surface adsorption phenomena with implications for catalytic converter design and environmental mitigation strategies.



## Chemical Analysis and Imaging of Interfaces

### Room 121 - Session CA-ThA

#### In Situ and Operando Analysis of Energy and Environmental Interfaces II

**Moderators:** Ashley Head, Brookhaven National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:15pm **CA-ThA-1 Understanding the Molecular Rearrangement at Interface by Atomic Modeling, Difan Zhang, D. Heldebrant**, Pacific Northwest National Laboratory; V. Glezakou, R. Rousseau, Oak Ridge National Laboratory

**INVITED**

A fundamental knowledge of the molecular rearrangement at surfaces, gas/liquid, and solid/liquid interfaces is crucial for many applications. The atomic modeling provides an important tool to quantify the structural variation and corresponding property changes at interfaces. In this presentation, I will highlight our recent studies that combined experimental characterization and computational modeling to reveal how molecules rearrange at different interfaces and how such nanostructure changes impact the interfacial properties. For example, the interfacial interactions between the carbon capture solvent and polymer membrane create unique channels that allow for faster diffusion of carbon oxide gas, enhancing the overall performance of the membrane/solvent device. Interestingly, the addition of a small fraction of water molecules further enhances the transport of carbon oxide gas through the membrane/solvent interface. In a different case, atomic modeling also demonstrates the improved selectivity of a graphene-oxide-modified polymer membrane for the separation of organics and water. Overall, these atomic simulations illustrate the effectiveness of modifying interfacial nanostructures to fine-tune interfacial transport and selectivity in complementary to experimental measurements.

3:00pm **CA-ThA-4 Advances in Electron Microscopy for Imaging Surfaces, Saumya Mukherjee, S. Böttcher**, SPECS Surface Nano Analysis GmbH, Germany; K. Kunze, SPECS Surface Nano Analysis GmbH, Germany, Gibraltar; O. Schaff, SPECS Surface Nano Analysis GmbH, Germany

Electron beam-based microscopy faced the challenge of limited accessibility to surface sensitive information and damaging samples owing to the high-kinetic-energy-electron dependent working principle. This led to the development of alternative imaging techniques using low-energy and photo-emitted electrons [1,2]. Photoelectron emission microscopy (PEEM) and Low energy electron microscopy (LEEM) provides the ideal tool to probe surfaces without damaging the sample. Recent advancement in collaboration with Rudolf M. Tromp at IBM, this technique is pushed to produce energy filtered images highlighting its ability for Spectromicroscopy. A lateral resolution below few nanometers is achievable and allowed to measure a wide variety of surfaces. By usage of aperture combinations photoelectrons can be selected within element specific energy range. This provides contrast in images and allows to study delicate biological samples such as imaging of neurons in cells as shown by Boergens et. al [3]. In the present talk, I will discuss in further details the development in surface imaging and complement with results to illustrate the strength of LEEM-PEEM and attract attention of broader imaging community to use this tool beyond conventional electron microscopy on wide variety of sample surfaces.

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3:15pm **CA-ThA-5 The NanoMi Open-source Electron Microscope: Electronics Builds and SEM/STEM Image Generation, Darren Homeniuk**, National Research Council, Canada; M. Kamal, University of Alberta Edmonton, Canada; M. Malac, M. Schreiber, M. Salomons, National Research Council of Canada; S. Ruttiman, National Research Council, Canada; X. Wang, University of Alberta, Canada; K. Kwan, National Research Council of Canada; O. Adkin-Kaya, J. Calzada, University of Alberta, Canada; P. Price, M. Cloutier, M. Hayashida, National Research Council of Canada; R. Egerton, University of Alberta, Canada; K. Harada, RIKEN, Japan; Y. Takahashi, Hitachi, Ltd., Japan

We are developing a public license electron microscopy platform that we refer to as NanoMi [1,2]. Our goal is for others to be able to build their own version of the platform with minimal money and time invested. The NanoMi platform features modularity in its mechanical and electrical design for adaptability. Further information is available at nanomi.org.

The focus here is to present the electronics builds that support the mechanical hardware. Custom printed circuit boards have been designed, built and tested for the deflectors, beam-shaping stigmators, and piezoelectric movers. The designs were made to be modular, flexible, and cost effective. Through the use of a field-programmable gate array, image generation electronics referred to as a STEM scanner was also created. A first prototype of a custom-built STEM scanner is now complete which provides USB communications to a computer, generation of output X/Y scan signals in 16-bit resolution, simultaneous read-in of 8 14-bit resolution detection signals from the microscope, and an on-board RAM that stores image data until it is ready for transmission. Clock speeds for scanning are 25MHz, which allows the system to acquire samples from the microscope every 40 nanoseconds. A python user interface has been created which allows for settings changes and displays resulting images while allowing the user access to image analysis tools.

Figure 1 shows early results of a 200 mesh copper grid from the new STEM scanner and a comparison image from a simple data acquisition unit, while Figure 2 shows the user interface (UI) during acquisition. Figure 3 shows an image of the board while acquiring Figure 1.

**Acknowledgment:**Support for the project was provided by NRC-NANO and by NSERC RGPIN-2021-02539

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3:30pm **CA-ThA-6 Advancing Carbon Dioxide Removal Technologies with Microscopic Insights Gained Using in-Situ and Operando Transmission Electron Microscopy, Wei-Chang David Yang**, National Institute of Standards and Technology (NIST)

**INVITED**

Carbon dioxide removal is crucial for achieving net-zero emissions and mitigating climate change. Still, technological challenges like inconsistent sorbent performance and catalyst degradation hinder the deployment of carbon dioxide capture and conversion to value-added products [1,2]. Transition metals (Ni, Co, Fe), which catalyze CO<sub>2</sub> conversion into hydrocarbon fuels, face deactivation (coking) due to carbon deposition on the catalyst surface [3]. Burning off the carbon deposit coarsens the catalyst and deteriorates performance, highlighting the need for a nonthermal regeneration process. Meanwhile, many mesoporous sorbents impregnated with amine-based polymers for direct air capture show inconsistent performance in the literature [4], requiring high-spatial-resolution multimodal characterization for benchmarking from single pores to overall performance.

This talk covers how in-situ and operando methods developed for an environmental transmission electron microscope (ETEM) address the above issues. Firstly, we used an electron beam to excite and characterize localized surface plasmon (LSP) resonance on aluminum nanoparticles in the presence of CO<sub>2</sub> using in-situ electron energy-loss spectroscopy (EELS). LSP field enhancement in the ultraviolet (UV) spectral range boosted the reverse Boudouard reaction (RBR), consuming carbon deposits and reactivating transition metal catalysts without heating.[5] We also coupled a TEM gas cell holder to gas chromatography-mass spectrometry (GC-MS) for operando detection of CO produced during the reaction, which can be

# Thursday Afternoon, November 7, 2024

reused for hydrocarbon fuel production. The findings offer a new solution for regenerating catalysts in CDR technology.

The second part of the talk focuses on developing in-situ cryogenic EELS imaging to characterize the adsorption ability of individual mesopores. The energy-loss near-edge structure (ELNES) obtained at cryogenic conditions showed the carbonyl core to  $\pi^*_{C=O}$  transition ( $\approx 289$  eV) in ammonium carbamate [6], indicating the formation of chemisorbed species when exposed to dry  $CO_2$ . This is the first direct observation of  $CO_2$  chemisorption on amine-impregnated mesoporous silicas at the single pore level. Ongoing studies aim to elucidate the amine chemistry and kinetics exposed to  $CO_2$  within the mesopores.

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4:00pm **CA-ThA-8 In situ Photoelectron and Infrared Spectroscopic Studies of Materials Under Various Plasmas**, *Ashley Head*, Brookhaven National Laboratory; *T. Hu*, Brookhaven National Laboratory and State University of New York at Stony Brook; *A. Boscoboinik*, *D. Stacchiola*, Brookhaven National Laboratory

Non-thermal plasma has been used to functionalize materials, to enhance the deposition of films, and as a reactant in catalysis. Depending on how plasma is made, there can be a range of gaseous species. Tools are needed for in situ studies in plasmas environments to understand the interactions with materials.<sup>1,2</sup> The application of infrared reflection absorption spectroscopy (IRRAS) and ambient pressure X-ray photoelectron spectroscopy to plasma environments will be discussed. As an example system, the functionalization and reduction of HKUST-1, a Cu-based metal-organic framework, has been studied with these techniques. IRRAS follows the framework stability while APXPS follows the Cu oxidation state changes. This correlative methodology is being baselined for future studies of plasma-enhanced catalysis of MOFs and metal oxides.

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4:15pm **CA-ThA-9 Chemical and Morphological Stability of Diamond Device Interfaces Under Operando Plasma-XPS**, *J. Trey Diulus*, NIST-Gaithersburg; *A. Head*, *J. Boscoboinik*, Center for Functional Nanomaterials, BNL; *A. Kolmakov*, NIST-Gaithersburg

Device fabrication of field effect transistors (FET)s and other electronics are still largely dependent on Si, which has been the core semiconductor material for over seven decades. Alternatively, diamond is a promising semiconductor material, with its ultra-wide bandgap (5.5 eV), unmatched thermal conductivity, breakdown voltage, and high charge carrier mobility in the range of  $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , while offering improved chemical stability compared to other wide-bandgap alternatives, like SiC and GaN. However, surface hydrogenation via  $H_2$  plasma is necessary to fabricate high-mobility diamond FETs, and the resulting surface is sensitive to ambient adsorbates that deteriorate the stability of surface conductivity with modern manufacturing processes. Alternatively, introducing the hydrogenation step later in the manufacturing process, i.e. after deposition of metal contacts or the gate dielectric, could allow for improved control of the diamond/metal or diamond/metal-oxide interfaces. Recently, high resolution x-ray photoelectron spectroscopy (XPS) collected under plasma conditions has been reported, allowing for *operando* chemical stability measurements. Herein, we prepared un-doped diamond and B-doped diamond samples with the standard contact metal stack (Ti/Pt/Au) deposited on half of the samples for plasma-XPS in  $H_2$  and  $O_2$  plasmas, respectively. Interestingly, a significant shift of  $\sim 50$  eV to higher binding energy is seen in the XPS spectra of the un-doped diamond when a plasma is ignited at 13 Pa partial pressure of  $H_2$  that is not seen in the spectra for the metalized part in the same environment. Additionally, the B-doped diamond exposed to the same pressure of an  $O_2$  plasma also does not exhibit a shift of the same magnitude as the un-doped diamond in  $H_2$ . The insulating nature of un-doped diamond creates this significant charging effect seen by XPS, which varies with the surface conductivity of diamond, suggesting a potential route to estimate the conductance state of diamond. Furthermore, with *ex*

*situ* scanning electron microscopy, we see significant erosion in the Au coated surface that is exposed to  $H_2$  plasma, likely due to a sputtering effect from ion impingement. Evidence of parasitic reactions from chamber wall exposure is also seen from residual gas analysis. This stresses the importance of designing a plasma that minimizes ions but maximizes neutrals, while also utilizing a well-cleaned chamber with minimal surface area to avoid scrubbing the chamber during plasma exposure. Overall, our efforts aim to better understand the interaction of plasma with diamond to provide researchers with a streamlined route towards diamond device manufacturing.

## Chemical Analysis and Imaging of Interfaces

Room Central Hall - Session CA-ThP

### Chemical Analysis and Imaging of Interfaces Poster Session

**CA-ThP-1 Multimodal in-Situ Characterization of Fe Anode for Aqueous Battery, Xiao Zhao**, Lawrence Berkeley National Laboratory; *E. Carlson, A. Burgos, W. Chueh*, Stanford University

Metallic iron is an attractive anode material for aqueous batteries, particularly if the full 3-electron redox between Fe and Fe (III) can be accessed reversibly. However, oxidation of Fe (II) to Fe (III) causes drastic morphology change and irreversible formation of highly resistive phases. Yet, it remains unclear how these phases form at the nanoscale and, crucially, how they might be avoided. To achieve fully reversible Fe anodes, it is critical to obtain a mechanistic understanding of nanoscale morphology and phase evolution during electrode cycling. Here we investigated the electrochemical transformation pathways between Fe (0)/Fe (II) and Fe (III) oxides using various in-situ spectroscopic and microscopic techniques, including Raman, Electrochemical Atomic Force Microscopy (ECAFM), soft X-ray Absorption Near Edge Structure (XANES), Infrared Nanospectroscopy (nano-FTIR) and Scanning Transmission X-ray Microscopy (STXM). Correlating the morphological evolution during this transformation to local (and surface) Fe oxidation state, phase and conductivity offers fundamental insight into Fe (0/II)/(III) conversion and inspire novel engineering of the Fe anode to achieve higher capacity and cyclability.

**CA-ThP-2 Off-axis EELS Bandgap Measurements at Complex Oxide Interfaces, Kory Burns**, University of Virginia, USA; *J. Hachtel, J. Poplawsky*, Oak Ridge National Laboratory, USA

Complex oxide interfaces have captivated the research community in the last 15 years due to the potential emergent nanoscale phenomena, owing to the strong interaction among charge, spin, orbital, and structural degrees of freedom. Studying these interfaces across a few unit cells is challenging with conventional methods, as optical probes tend to be around 1  $\mu\text{m}$  in diameter. This makes it's impossible to study an individual interface of a vertically stacked transition metal oxide from a cross-sectional sample as the optical probe collects an averaged signal from each layer. In this talk, electron probes are used to overcome the diffraction-limit set by optical probes. This is done by converging electrons to a focused beam to collect spectroscopic signal from an oxide-interface with electron energy loss spectroscopy (EELS). A monochromated aberration corrected scanning transmission electron microscopy (MAC-STEM) is used to couple unprecedented energy resolution and spatial resolution to do vibrational spectroscopy at atomic resolution. When the EELS aperture is in conventional settings, where the bright field disc is perfectly aligned with the entrance aperture, the EELS signal is delocalized and dominated by optical selection rules. Accordingly, the bright field disc is electrostatically shifted by the projector lens so that the dark field disc is highlighted, which describes a technique known as off-axis EELS. We use this to create a localized signal dominated by impact scattering so that the long-range contributions are suppressed, and band edges can be resolved without plasmon interference. Ultimately, we aim to introduce a novel technique to determine the structure-property relationship of complex oxides to bring oxide-electronics to new heights.

**CA-ThP-3 ToF-SIMS Analysis of Biofilms after Overlayer Removal by fs-Laser Ablation, Gabriel Parker**, A. Karaginnakis, R. Shavandi, University of Illinois - Chicago; *X. Yu*, ORNL; *L. Hanley*, University of Illinois - Chicago

The biological secretions from bacterial biofilms contain fatty acids, metabolites, and other components of the extracellular polymeric substances (EPS). These secretions can result in corrosion of hard surfaces. Fatty acids produced by *Paenibacillus* sp. 300A, *Acidovorax* JHL-9, and *Shewanella ondenensis* MR-1 are thought to degrade glasses, polymers, and other materials. Observation of these fatty acids and other metabolites like quinolones, flavonoids, and quorum sensing molecules help reveal the metabolic process that can contribute to material degradation. The depth profiling capabilities of ToF-SIMS are particularly useful for distinguishing processes at the air-biofilm interface from those at the biofilm-material interface. However, ToF-SIMS depth profiling by gaseous cluster ion beams is only reliable for elucidating biofilm composition and structures down to a depth of a few micrometers and biofilms can grow to thicknesses surpassing a millimeter [1]. Ablation with 800 nm, ~75 fs laser pulses (fs-LA) has used for layer removal and depth profiling at much greater depths and without damage to the underlying biofilm [2, 3]. Femtosecond-LA

combined with X-ray photoelectron spectroscopy has also been demonstrated for depth profiling in polymers [1]. Stand-alone fs-LA is used here to expose buried regions of biofilms of *Paenibacillus* sp. 300A biofilms cultured on Si wafers and other substrates for analysis using ToF-SIMS. Comparison of the mass spectra of ablated vs. non-ablated regions shows an absence of laser-induced changes in their respective chemical compositions, demonstrating the feasibility of fs-LA for probing buried regions of biofilms that are not readily accessible to gaseous cluster ion beams.

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**CA-ThP-4 Breakdown Failure Analysis of Diamond Lateral Schottky Barrier Diode Device Using EBIC-Based Metrology, Andrei Kolmakov**, NIST-Gaithersburg; *Z. Han, J. Lee*, UIUC; *K. Cheung, E. Strelcov, O. Ridzel, J. Villarrubia, G. Holland*, NIST-Gaithersburg; *C. Bayram*, UIUC

Diamond ca 5.5 eV wide band gap, high (> 20 W /cm K) thermal conductivity, carrier mobility (>2000 cm<sup>2</sup> /V s) and critical electric field (> 10 MV/cm) make it an ideal material for emerging high-power electronics. For these applications, the development of the diodes with highest breakdown voltage is a requirement. The analysis of the breakdown mechanism and leakage channels in diamond devices however remains to be an experimental challenge. Electron beam induced current microscopy (EBIC) is often used to characterize the imbedded/induced electric field distributions at the surface as well as buried interfaces and obtain the current maps in semiconductor devices. In this report, the combined electrical and EBIC measurements were applied to the same p-type lateral Schottky barrier diamond diode before and after its soft breakdown. This allowed to univocally identify the development of the device leakage channels and relate them with device fabrication defects.

**CA-ThP-5 Oxide Layer Characterization of Superconducting Two-layer Tin Films: Al/Nb and Al/Nb-Ti-N on Silicon, G. Bhandari, V. Dewasurendra, F. Akinrinola, J. Metzger, A. Sheppard**, West Virginia University, USA; *T. Stevenson, E. Barrentine, L. Hess*, NASA Goddard Space Flight Center; *M. Johnson, Micky Holcomb*, West Virginia University, USA

Superconducting devices are important for the detection of microwave to x-ray radiation. Identifying the factors affecting oxide thickness, uniformity, and chemical composition will lead to the development of more reliable and lower noise detectors. We compare x-ray absorption spectroscopy (XAS) measurements and depth-dependent x-ray photoemission spectroscopy (XPS). We have studied two types of superconducting thin films: Al/Nb and Al /Nb-Ti-N. Depth-dependent niobium oxide (Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> and NbO) formation has been evaluated. We explore the impact of different etching and oxide cleaning treatments to the presence of these oxides. This research is supported by NASA EPSCoR Award# 80NSSC22M0173. We acknowledge the use of the research facilities at the Lawrence Berkeley National Laboratory and West Virginia University Shared Research Facilities.

**CA-ThP-6 Deep Probing of Buried Layers with HAXPES - Chemical Analysis with Bias Applied Operando Setup for Electronic Devices, Marcus Lundwall**, T. Sloboda, Scienta Omicron, Sweden; *D. Beaton*, Scienta Omicron; *M. Machida*, Scienta Omicron, Japan

Introduction

Buried interfaces in electronic devices such as batteries, solar cells, transistors etc. are highly chemically sensitive and reliable instrumentation is necessary for material development. While X-ray photoelectron spectroscopy (XPS) is a powerful method to investigate the chemical nature of surfaces, buried interfaces in device electronics are more difficult to investigate due to scattering. Hard X-rays giving increased information depth, have therefore been increasingly used in the photoelectron spectroscopy field.

HAXPES and XPS applications

Having access to XPS and HAXPES X-ray sources enables measurements of core levels with different resulting kinetic energy of the photoelectrons. With a soft X-ray XPS source, the kinetic energy is low and thus the obtained information is very surface sensitive. With Hard X-rays it is possible to be both surface and bulk sensitive, as electrons stemming from deep core levels will have lower kinetic energy and contain more surface sensitive information. Similarly, electrons stemming from shallow "XPS" core levels will have higher kinetic energy and contain more bulk sensitive information. This is especially valuable when detecting artefacts formed by sample exposure to different environments (e.g. air, moisture, heat, cold

etc.) or by preparation steps known to induce chemical changes on the surface (e.g. sputtering). Scienta Omicron's HAXPES Lab uses both an XPS Al K $\alpha$  source and a monochromatic Ga K $\alpha$  MetalJet HAXPES source with excitation energy of 9.25 keV, therefore enabling artefact-free investigations with superior information depth, which clearly extends beyond limits of conventional XPS surface analysis. This unlocks a comprehensive and effective characterisation of layered materials. Combined with a hemispherical electron analyzer with a  $\pm 30$  degree acceptance angle, investigation of buried interfaces, operando devices and real-world samples becomes achievable. (Fig.1). Over the years it has proven invaluable in research of semiconductor materials in thin film electronic devices including the operando characterization of bias induced changes in chemical composition of material interfaces. Other applications include polymer materials, metal surfaces and coatings. This presentation will give an overview of HAXPES applications with focus on buried interfaces in electronic devices such as passivation of luminescent quantum dots studied through a 35 nm overlayer, and semiconductor device band alignment by operando measurement with the Si substrate signal as reference detected through 20 nm TiN + 4 nm ZrO stack without sputtering and risk of artifacts.

## CA-ThP-7 Stability and Dielectric Strength of Model Metal/Al<sub>2</sub>O<sub>3</sub>/Diamond Interfaces Under Harsh Environments, J. Trey Diulus, A. Biacchi, E. Bittle, A. Kolmakov, NIST-Gaithersburg

Recent progress towards innovation in power electronics has largely been through implementation of new wide-bandgap (WBG) semiconductor materials, like SiC or GaN. Alternatively, diamond is another WBG material with a high theoretical hole mobility (1300 cm<sup>2</sup>\*V<sup>-1</sup>\*s<sup>-1</sup>), thermal conductivity, and breakdown voltage that rivals SiC and GaN, while also offering improved chemical and thermal stability over its WBG counterparts. Recently, diamond electronic devices have been fabricated displaying impressive electrical performance and thermal management, however little has been investigated for these model devices at high temperatures in combination with heavily oxidizing or reducing ("harsh") environments. In this work, we fabricated model diamond devices that possess metal/Al<sub>2</sub>O<sub>3</sub>/metal/diamond, and metal/Al<sub>2</sub>O<sub>3</sub>/diamond interfaces by depositing the standard metal contact stack (Ti/Pt/Au) or pure Pt on undoped and non-hydrogenated diamond followed by growth of a 40-50 nm Al<sub>2</sub>O<sub>3</sub> film via ALD as a gate dielectric. We then investigated the dielectric properties of this un-gated device by conducting I-V and capacitance measurements prior to any exposure. Next, the sample surface chemistry and morphology are investigated with x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The device is then annealed to 600 °C, followed by exposures to H<sub>2</sub> and O<sub>2</sub> partial pressures of up to 10 kPa also at elevated temperature, where XPS, SEM, and 2-point I-V are all collected at each intermediate step *in situ* without breaking vacuum. Overall, we defined the stability range of a model diamond interfaces at high temperature and reactive environments.

## CA-ThP-9 Differential Ion Movement is Captured by XPS under Voltage-Bias through a Multi-Layered-Graphene Electrode in contact with a Mixed Ionic Liquid Medium, E. Kutbay, Bilkent University, Chemistry Department, 06800 Ankara, Turkey; F. Krebs, O. Hoeffft, F. Endres, Clausthal University of Technology, Germany; Sefik Suzer, Bilkent University, Chemistry Department, 06800 Ankara, Turkey

Under application of a voltage bias, asymmetric ion-movement of a mixed ionic liquid (IL), having the same anion [bis(trifluoromethylsulfonyl)imide / TFSI] but two different cations [1-butyl-1-methylpyrrolidinium / BMP<sup>+</sup> and Rb<sup>+</sup>] through a multi-layered graphene (MLG) electrode, has been detected by x-ray photoelectron spectroscopy (XPS), via recording the intensities of the C1s, N1s, F1s and Rb3d core level peaks. Accordingly, upon increasing the bias gradually from 1 to 3.5 V, we have observed up to 3-fold increase in the Rb3d peaks signal, accompanied with parallel F1s and N1s peak intensity changes, albeit to a lesser degree. The C1s peak of the graphene layer was observed to decrease, clearly indicating the increase in the surface composition of the IL. Moreover, a discernable differential change in the N1s peaks of the anion (N<sup>-</sup>) and the cation (N<sup>+</sup>) was also observed. Additionally, bias dependent binding energy shifts, extracted through the changes in the positions of F1s, N1s and C1s and Rb3d peaks of the IL mixture and the C1s of the graphene electrode indicate that multi-faceted and distinct solid-liquid interfaces develop throughout the entire intercalation process with an additional and pertinent evidence for finite potential drops. Details of the experimental set-up, and dynamics of bias-induced ion movement will be presented and discussed.

## CA-ThP-10 ToF-SIMS Analysis of Two-Dimensional Metal Carbide Catalysts, Tobias Misicko, Oak Ridge National Laboratory, Louisiana Tech University; G. Parker, Oak Ridge National Laboratory; Y. Xiao, Louisiana Tech University; X. Yu, Oak Ridge National Laboratory, USA

MXene is a class of two-dimensional metal carbides with an empirical formula of M<sub>n+1</sub>X<sub>n</sub>T<sub>x</sub>, where M is an early transition metal, X is a carbon or nitrogen, and T is a surface functional group (such as F<sup>-</sup> or OH<sup>-</sup>). In our recent studies<sup>[1,2]</sup>, incipient wetness impregnation was used to load platinum (Pt) onto Mo<sub>2</sub>TiC<sub>2</sub> MXene to synthesize a 0.5% (wt.) Pt/Mo<sub>2</sub>TiC<sub>2</sub> MXene catalyst. The catalyst containing Pt nanolayers exhibited excellent catalytic activity in alkane dehydrogenation with turnover frequencies (TOFs, converted molecules per surface Pt atom) of 0.4~1.2 s<sup>-1</sup> for converting methane<sup>[1]</sup> and ethane<sup>[2]</sup>, respectively. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements, including surface spectra, mass spectral imaging, secondary electron imaging, and depth profiling, were used to investigate the surface and subsequent monolayer structures of both unsupported Mo<sub>2</sub>TiC<sub>2</sub> MXene and 0.5% Pt/Mo<sub>2</sub>TiC<sub>2</sub> MXene catalysts. These analyses were used to derive the structure-activity relationship between Pt/Mo<sub>2</sub>TiC<sub>2</sub> catalysts and their catalytic dehydrogenation performance in this work.

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**Keywords:** ToF-SIMS, MXene, Catalyst, Alkane Dehydrogenation, Methane Activation

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## CA-ThP-11 Surface Chemistry and Film Growth at Complex Air/Solution/Iron Interfaces, Kathryn Perrine, Michigan Technological University

Complex interfaces are prevalent in the natural and industrial environments, including water pipelines, batteries, geochemical transformations, and environmental processes. Surface chemistry occurs through adsorption, reduction-oxidation, and catalysis at the air/liquid or liquid/solid interface. Uncovering these reactions are essential for addressing environmental challenges, such as rising CO<sub>2</sub> levels. Mitigating CO<sub>2</sub> levels are addressed by geological sequestration, through capture and conversion to carbonates. Iron is an earth abundant catalyst that is found in soils and dust as iron oxides. In the environment, iron interfaces interact with ions, particularly chloride, thus initiating corrosion, altering the physical structure. Here we show how surface corrosion, spontaneous reduction-oxidation, and deposition lead to film formation on iron interfaces for CO<sub>2</sub> capture mechanisms.

This poster will summarize our group's research on our advanced method to measure surface vibrational signatures of CO<sub>2</sub> adsorption and conversion to carbonate films. Polarized modulated – infrared reflection absorption spectroscopy (PM-IRRAS) was used to probe through an ultra-thin liquid layer to observe *in situ* reactions at the air/solution/iron interface. We observe iron surface oxidation and mineral formation, using the vibrational modes to track air adsorption and mineral film growth. The results are corroborated with XPS and ATR-FTIR spectroscopy to show the films produce signatures of different natural carbonates. *In situ* liquid AFM was used to verify the corrosion rate and resulting morphologies after air oxidation.

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The electrolyte (from alkali and alkaline chlorides) is found to influence the type and rate of film grown at the air/electrolyte/iron interface. The divalent cations (from  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{FeCl}_2$ ) are compared with the monovalent cations (from  $\text{KCl}$ ,  $\text{NaCl}$ ) as well as electrolytes of various pH's ( $\text{HCl}$ ,  $\text{NaOH}$ ). The  $\text{Cl}$  ions are found to initiate the corrosion, pitting through the native oxide layer, thus producing nucleation sites for film growth. The adsorption of atmospheric  $\text{CO}_2$ , and  $\text{O}_2$ , results in carbonate film growth, resulting in a specific-cation effect. The  $\text{Fe}^{2+}$  that dissolves during corrosion competes for adsorption with the other cations suggesting other surface-solution mediated mechanisms exist. These findings are relevant for understanding surface chemistry impacting mechanisms of  $\text{CO}_2$  capture, geochemical formations, and other processes at complex air/liquid/solid interfaces.

## Chemical Analysis and Imaging of Interfaces

### Room 121 - Session CA-FrM

#### Materials, Interfaces and Metrologies for Electronics

**Moderators:** Alex Belianinov, Sandia National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

8:15am **CA-FrM-1 Surface Transfer - Modulation Doping at the Diamond-Dielectric Interface**, A. Deshmukh, Y. Yang, F. Koeck, R. Nemanich, Kevin Hatch, Arizona State University **INVITED**

Great progress in diamond wafer technology and diamond epitaxy have inspired new concepts for diamond electronics particularly for power conversion and RF applications. However, the high activation energy of substitutional p- and n-type dopants in diamond has limited the development of field effect transistors (FET). An alternative approach of charge transfer doping at a diamond-dielectric interface, which results in the formation of a hole accumulation layer, is not limited by thermal activation [1]. However, the hole transport shows a mobility that is much lower than predicted. It is widely accepted that the low mobility is due to scattering from the near interface negative charges transferred into the dielectric layer.

Following the concept of modulation doping at heterostructure interfaces, we have proposed and demonstrated a dielectric layer configuration that results in a nearly ten-fold mobility increase for the accumulated holes at the diamond interface [2]. In this approach MoO<sub>3</sub> is used as the charge transfer dielectric, and Al<sub>2</sub>O<sub>3</sub> is employed as the modulation doping spacer layer. The charge transfer is driven by the energy difference between the diamond valence band and the charge transfer states in the MoO<sub>3</sub>. The thickness of the spacer layer also affects the hole accumulation layer charge density.

In this study photoemission spectroscopy is employed to measure the band alignment and band bending throughout the multi-layer structure. The relative distribution of the charge near the interface is deduced from the band diagram. These experiments and the model of Surface Transfer - Modulation Doping demonstrates a new approach to FET channel doping for diamond field effect transistors.

This research was supported by a grant from MIT-Lincoln Laboratories and the NSF through Grant Nos. DMR-1710551 and DMR-2003567.

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8:45am **CA-FrM-3 Probing the Nanoscale: The Synergy of XPS and LEIS Analyses**, Joshua W. Pinder, J. Crossman, Brigham Young University; S. Prusa, T. Sikola, Brno Institute of Technology, Czechia; M. Linford, Brigham Young University

Over the past few decades, with the development of novel, advanced materials, the significance and need for surface characterization techniques has increased dramatically. These advanced materials appear in diverse sectors of the economy including in semiconductors, thin films, catalysts, batteries, fuel cells, adhesion, and for material durability. An understanding of surface and material composition often leads to improvements in material properties. In this talk, we discuss the synergy and usefulness of two important surface techniques: X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS).

XPS is a mature and well-developed technique, providing both elemental and chemical state information about surfaces. However, XPS spectra do not always unambiguously identify the depths of atoms at surfaces. It is not always clear whether an atom is exposed at a surface or slightly below it. Whether an atom is exposed or not has profound implications in various fields, including in catalysis. Accordingly, LEIS, which is sensitive to the outermost atomic layer of surfaces, ideally complements XPS. Both techniques are, for the most part and for many surfaces, non-destructive.

As examples of the combined use of XPS and LEIS, we present the analyses of hydrogen-terminated, single-crystal diamond and various copper samples. First, hydrogen-terminated, single-crystal diamond is a low free energy material that can be easily cleaned. We show the reaction of hydrogen-terminated diamond with atomic oxygen and follow that oxidation by XPS and LEIS. We then reduce this surface with atomic

hydrogen, again following this process with XPS and LEIS. The different functional groups that are created by oxidation and then removed by hydrogen reduction are identified and quantified by both techniques. Second, the analysis of copper highlights the extraordinary surface sensitivity of LEIS. Quantities of surface oxygen that minimally affect the XPS spectra (compared to the spectrum of the pure, unoxidized metal), very strongly alter the LEIS spectra. For example, copper metal itself is very inefficient at reionizing helium projectiles, while oxygen at the copper surface is. This difference leads to a dramatic difference in the reionization backgrounds of copper metal and oxidized copper.

For the reasons discussed in this talk, we believe that the combination of XPS and LEIS will play an increasingly important role in surface analysis.

9:00am **CA-FrM-4 Capacitively and Electrically Detected Magnetic Resonance in 4H SiC MOSFET**, Artur Solodovnyk, P. Lenahan, The Pennsylvania State University

Silicon carbide MOSFETs show great potential in high-power, high-temperature applications. However, electrically active interface traps, which have a substantial impact on the device's channel-carrier mobility and threshold voltage stability are still not completely understood [1]. Several spectroscopic techniques can help identify the physical and chemical nature of such defects, among them, electrically detected magnetic resonance (EDMR)[2] and as we show in this work, capacitively detected magnetic resonance (CDMR). To the best of our knowledge, CDMR was first demonstrated in Si-based MOS devices by Brandt and coworkers [3-4]. In this work, we show that such capacitive measurements are also possible in SiC-based devices. Furthermore, we compare EDMR and CDMR measurements on the same devices at very different fields and frequencies. The line-widths and g-tensors are approximately the same for both cases. We report on EDMR and CDMR studies on 4H SiC MOSFET in capacitor configuration (gate-body). The relatively narrow line with  $g_{\perp} = 2.0023(\pm 0.0005)$  and  $g_{\parallel} = 2.0010(\pm 0.0005)$  with the respect to the device's SiC/SiO<sub>2</sub> interface has been observed in both EDMR and CDMR. We observe close similarities at low (500 MHz, Fig. 1) and high frequency (9.784 GHz, Fig. 2) with negative bias of 3 V for both measurements. The line-width at both measured frequencies is about 6.8(±0.3) G. The measurements were carried out at room temperature.

It should be noted, that these measurements were made on devices with quite high interface trap density [5]. Thus, we feel the significance of this work, is mainly to point out the potential utility of CDMR in studies of SiC MOSFETs.

This work was supported by the Air Force Office of Scientific Research under Award No. FA9550-22-1-0308. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the United States Air Force.

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9:15am **CA-FrM-5 Photoluminescence Mapping of Gallium Oxide Surfaces and Epilayers**, Matthew McCluskey, Washington State University

Photoluminescence (PL) spectroscopy is an important method to characterize dopants and defects in gallium oxide. Features in the PL spectrum include the intrinsic UV band, blue and green bands that involve donor-acceptor pairs, and red emission due to Cr<sup>3+</sup> impurities. PL mapping with excitation wavelengths as short as 266 nm reveals the spatial distribution of these features with submicron resolution. In addition to defects in the bulk, PL microscopy has revealed several specific defects on the surface. Some of these localized centers are very bright UV emitters. Raman scans of these bright emitters revealed hydrocarbon peaks, which may point toward the origin of the light emission. Homoepitaxial layers grown by metalorganic chemical vapor deposition (MOCVD) show defects that are observed via the shifts in the PL band, likely due to the strain field around a dislocation core. Damage due to high-intensity, sub-bandgap laser pulses results in a drop in the intensity of the UV band. A ring or "halo" around the damaged region is observed under 532 nm excitation, attributed to color center defects.

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9:30am **CA-FrM-6 Focused Ion Beam Low Energy Implantation**, *M. Titze, C. Smyth*, Sandia National Laboratory; *J. Poplawsky*, Oak Ridge National Laboratory; *B. Doyle, E. Bielejec, Alex Belianinov*, Sandia National Laboratory

**INVITED**

Ion implantation is a key capability for the semiconductor industry. As devices shrink, novel materials enter the manufacturing line, and quantum technologies transition to being more mainstream, traditional implantation methods fall short in terms of energy, ion species, and positional precision. However, lowering the implantation energy while maintaining nanometer scale spot size is a technological challenge. This presentation will show an overview of techniques at Sandia National Laboratories Ion Beam Facility that allow focused ion implants 10-200 keV range for quantum relevant applications.

Additionally new developments in sub-1 keV focused ion implants into Si and 2D devices, using a focused ion beam system, validated by atom probe tomography will be shown. We illustrate that identical results for low energy ion implants can be achieved by either lowering the column voltage, or decelerating ions using bias – while maintaining good spatial resolution. Furthermore, our data reveal that standard implant modeling approaches overestimates experimental depth by a significant margin. Finally, we discuss how our results pave a way to much lower implantation energies, while maintaining high spatial resolution.

10:00am **CA-FrM-8 NIST Nanocalorimetry for In-Plasma Process Metrology Relevant to Semiconductor Fabrication**, *Andrei Kolmakov, J. Diulus, F. Yi, D. LaVan*, NIST-Gaithersburg

Plasma processing is among the most widely used technologies in semiconductor fabrication industry. In particular, plasma is employed for (reactive-) plasma etching, wafers cleaning, plasma-assisted chemical/physical vapor depositions and etc. However, despite variety of existing plasma diagnostics methods, there is a shortage of metrologies for *in situ* sensitive monitoring/control of the interfacial interactions relevant to semiconductor fabrication. This is particularly valid for plasma processing that relies on neutral reactive radicals and/or pulsed radicals' exposures, which are hard to detect. The current state of the art method for radicals detection in research lab settings are based on catalytically activated thermocouples or quartz microbalance based etch sensors which are often too slow or not sensitive enough.

On the other hand, modern microfabricated nanocalorimeters can operate at kHz frequency domain range and can detect fast physical and chemical (endo-)exothermal surface reactions with high sensitivity on the order of a nJ/K, including adsorption-desorption processes, interfacial reactions, chemical etching reactions all relevant to fabrication of semiconductor devices. Nanocalorimeters are small to be easily integrated to any microfabrication chambers and cheap enough to be readily modified to meet a specific process requirement.

Here we report the pilot tests of NIST microfabricated nanocalorimeters to detect reactive radicals generated by low power (ca 20-70 W) remote (ca 10 Pa) hydrogen plasma. The setup consists of two otherwise identical sensors but one of them having Au layer exposed to vacuum. Au layer serves as a catalyst with known hydrogen recombination coefficient and the difference in heat of the recombination reactions is detected comparatively by activated and inert nanocalorimeters. The second non-activated sensor is also used to discriminate against parasitic signals such as UV-Vis radiation, ions and electrons fluxes. The setup was successfully tested and major parameters such as sensitivity and response time have been estimated and compared with existing plasma diagnostic tools.

## Surface Science

Room 120 - Session **SS+AMS+AS+CA+LS-FrM**

### Advanced Surface Characterization Techniques & Mort Trau Presentation

Moderator: **Charles Sykes**, Tufts University

8:15am **SS+AMS+AS+CA+LS-FrM-1 Infrared Spectroscopy as a Surface Science Technique**, *Michael Trenary*, University of Illinois - Chicago **INVITED**  
Infrared spectroscopy is widely used to probe the vibrational properties of molecules in the gas, liquid, and solid phases. On the other hand, precise information on the structure and chemistry of solid surfaces, and of molecular adsorbates on solid surfaces, is best gained through use of surface science methods. These methods generally entail the use of single

crystals, ultrahigh vacuum conditions, and surface sensitive techniques. Reflection absorption infrared spectroscopy (RAIRS) is a surface sensitive technique that can be used in ultrahigh vacuum to study molecular adsorption on well characterized metal single crystal samples. Unlike many other surface science methods, it can also be used under elevated gas pressures. The spectra obtained display features that are quite distinct from those of other phases of matter. For example, in the gas phase, rotational fine structure greatly complicates the appearance of the spectra but is absent in the spectra of adsorbed molecules. In the liquid phase, spectra are broadened by both static and dynamic effects often making it difficult to resolve vibrational peaks due to different chemical species. In polycrystalline molecular solids, molecules are randomly oriented relative to the electric field directions of the infrared radiation, limiting the value of the spectra as a structural probe. In contrast, when molecules adsorb on metal surfaces, they often adopt a definite orientation with respect to the surface normal. This orientation can be deduced through the surface dipole selection rule, which states that only normal modes with a component of the dynamic dipole moment oriented along the surface normal will be allowed. While IR spectroscopy in several forms has long been used to study molecular adsorption on supported transition metal catalysts, the high degree of heterogeneity of the catalyst surfaces leads to very broad peaks, with full width at half maxima (FWHM) of 10-50  $\text{cm}^{-1}$ . In contrast, the FWHM of peaks measured with RAIRS on well-ordered metal surfaces can be quite narrow, in some cases even less than 1  $\text{cm}^{-1}$ . When a polyatomic molecule exhibits sharp peaks throughout the mid-IR range, the advantages of performing RAIRS with a Fourier transform infrared spectrometer are most pronounced. This talk will cover the speaker's forty years of research using the technique of RAIRS to study molecular adsorbates on metal surfaces.

8:45am **SS+AMS+AS+CA+LS-FrM-3 Modeling Pipeline Surface Chemistry: Reaction of Monochloramine on Iron Surfaces**, *Kathryn Perrine, S. Pandey, O. Agbelusi*, Michigan Technological University

Monochloramine ( $\text{NH}_2\text{Cl}$ ), a secondary disinfectant, is utilized to treat pathogens in the municipal water system, producing fewer halogenated disinfection by-products and lasting longer than free chlorine (hypochlorite). Although a weaker oxidant,  $\text{NH}_2\text{Cl}$  has the potential to corrode the surface of pipeline materials resulting in the dissolution of unwanted species. Copper and lead pipelines have been shown to corrode in chloramine solutions, however on iron materials the surface chemistry is unexplored. Complex chemistry occurs on the surface of pipelines at solution/metal interfaces, thus providing catalytic sites for dissociation, decomposition, and degradation. Iron comprises distribution pipelines and also exists as oxides in soils in the natural environment. Redox reactions occur on the surface of iron materials, thus initiating surface corrosion. Here, various active sites on iron are produced and known for high reactivity with nitrogen compounds. Our group employs a surface science approach to uncovering mechanisms at complex interfaces.

In this study, the reaction of monochloramine ( $\text{NH}_2\text{Cl}$ ) was investigated on single crystal Fe(111) in ultra-high vacuum at the gas/solid interface using *in situ* infrared reflection absorption spectroscopy and Auger electron spectroscopy. At -160 °C,  $\text{NH}_2\text{Cl}$  molecularly adsorbs to the surface while the annealing leads to the loss of key vibrational modes, suggesting that either molecular desorption or dissociation occurs. These observations are contrasted with our findings at the solution/iron interface, where polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS), ATR-FTIR, XPS, and XRD were used to assess the various regions after corrosion and their film growth. In solution, localized heterogeneous corrosion products were observed and identified, suggesting different reaction pathways exist in strongly oxidizing solutions. These findings are important for understanding the mechanism of chloramines and water disinfectants on iron interfaces relevant for water quality, material degradation, and other complex environmental processes.

9:00am **SS+AMS+AS+CA+LS-FrM-4 Development of Tip-Enhanced Raman Spectroscopy for Solid-Liquid Interfaces**, *Naihao Chiang*, University of Houston

Tip-enhanced Raman spectroscopy (TERS) combines the spatial resolution of scanning probe microscopy (SPM) with the chemical sensitivity of Raman spectroscopy. TERS with sub-nanometer resolution has been demonstrated under ultrahigh vacuum conditions. We aim to extend this unprecedented chemical mapping capability to interfacial studies under the solution phase. Specifically, we have developed a scanning ion-conductance microscope for TERS (SICM-TERS) capable of interrogating soft samples. In this presentation, the instrumental design will be discussed first. SICM-TERS

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probe fabrication and evaluation will be followed. Then, a distance-dependent SICM-TERS measurement on two-dimensional MoS<sub>2</sub> sheets will be used to assess the strain created by the SICM probe in close proximity. Our results demonstrate the potential of combining TERS with SICM for obtaining chemical information at interfaces, thus setting the stage for future investigation into soft materials in electrolytic environments.

**9:15am SS+AMS+AS+CA+LS-FrM-5 Ion Based Pump-Probe: Probing the Dynamics Following an Ion Impact, Lars Breuer, L. Kalkhoff, A. Meyer, N. Junker, L. Lasnik, Universität Duisburg-Essen, Germany; Y. Yao, A. Schleife, University of Illinois at Urbana Champaign; K. Sokolowski-Tinten, A. Wucher, M. Schleberger, Universität Duisburg-Essen, Germany**

The study of ion-surface interactions is crucial for understanding material properties and their atomic-level dynamic responses. The transient nature of these interactions, occurring on ultrafast time scales, has so far limited direct experimental observation and has left the field reliant on computer simulations. Existing experimental methods, such as pump-probe techniques, have faced challenges in generating and precisely timing short, monoenergetic ion pulses essential for capturing these ultrafast phenomena.

Our group has pioneered a novel approach that overcomes these limitations by generating the world's shortest monoenergetic ion pulses in the keV regime, with a current duration of approximately 5 ps. These pulses are produced using femtosecond photoionization of a geometrically cooled gas jet, coupled with miniaturization of the ionization section.

In our experiments, we conduct ion-based pump-probe experiments observing the emission of hot electrons post-ion impact, similar to processes studied in two-photon photoemission (2PPE) experiments. Our findings not only demonstrate the feasibility of our approach and provide direct measurements of the ion pulse characteristics but also offer insights into the non-equilibrium dynamics of electronic excitation in solids following an ion impact. We can track the electronic excitation and determine the temporal evolution of a pseudo electron temperature.

This research opens new avenues for understanding the fundamental processes underlying ion-solid interactions, with significant implications for semiconductor manufacturing and materials science. Our work sets a new standard for temporal resolution in the study of ion-induced phenomena and lays the groundwork for future innovations in the field.

**9:30am SS+AMS+AS+CA+LS-FrM-6 How Hot Plasmonic Heating Can Be: Phase Transition and Melting of P25 TiO<sub>2</sub> from Plasmonic Heating of Au Nanoparticles, W. Lu, R. Kayastha, B. Birmingham, B. Zechmann, Zhenrong Zhang, Baylor University**

Plasmonic heating has been utilized in many applications including photocatalysis, photothermal therapy, and photocuring. However, how high the temperature can be reached for the surrounding media due to the collective heating of the plasmonic nanoparticles (NPs) and the impact of the heat dissipation on the surrounding media is not clear. Herein we studied the impact of plasmonic heat generated by resonantly excited gold (Au) NPs on P25 TiO<sub>2</sub> nanoparticle film. Under 532 nm continuous laser irradiation at the surface of the Au-TiO<sub>2</sub>, the surface evaporation of Au nanoparticles and phase transition of TiO<sub>2</sub> were observed at moderate laser power. More importantly, as high as the melting point of TiO<sub>2</sub> of 1830°C is confirmed from the molten TiO<sub>2</sub> rutile phase. When Au/TiO<sub>2</sub> was irradiated with an off-resonance laser at 638 nm, no phase transformation or melting of TiO<sub>2</sub> was observed. The temperature calculation shows that the heating generated by Au nanoparticles is not localized. The collective heating from an ensemble of Au nanoparticles in the irradiated area produces a global temperature rise that melts TiO<sub>2</sub>. Our results suggest that the photothermal effect could be a major mechanism in the plasmon-assisted photocatalytic reactions. The experimental observation of the high temperature of the supporting media suggests new applications for utilizing plasmonic heating, for example, additive manufacturing.

**9:45am SS+AMS+AS+CA+LS-FrM-7 Kinetics and Dynamics of Recombinative Desorption of Oxygen from Silver and Rhodium Surfaces, Dan Killelea, Loyola University Chicago**

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

I will discuss our observations of subsurface oxygen emerging from beneath Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, it was recently discovered that decomposition of

oxygenaceous surface phases on Ag(111) also exhibit pronounced shifts in the energetics of the desorbing oxygen molecules. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

**10:00am SS+AMS+AS+CA+LS-FrM-8 Mort Traum Award Announcement,**

**10:30am SS+AMS+AS+CA+LS-FrM-10 Unveiling Surface Mysteries with XPS Lab from Scienta Omicron, T. Sloboda, Scienta Omicron, Sweden; P. Amann, Scienta Omicron, Germany; B. Gerace, F. Henn, Andrew Yost, X. Zhang, Scienta Omicron; M. Lundwall, Scienta Omicron, Sweden**

Surface analysis is paramount for understanding material properties, and Scienta Omicron's XPS Lab system excels in this realm. Featuring a compression unit for superior count rates and sensitivity, it offers unparalleled quantitative XPS enabled by a true counting multi-anode detector inside the Argus CU analyser. This unique detector employs 128 individual counters connected to a striped-anode array. With a linear response extending to the highest count rates and an exceptional dynamic range, it ensures high resolution precise measurements across various sample types.

The versatility of XPS Lab is evident through its scanning, imaging, snapshot, and dynamic measurement modes (see Figure 1), enabling researchers to tailor their experiments to specific needs. The chemical state mapping capability of the XPS Lab provides comprehensive insights into surface chemistry, empowering researchers to unravel complex phenomena.

Illustrating its prowess, case studies span catalysis, energy storage, semiconductor technology, and biomaterials, showcasing its ability to address diverse research challenges. Recent enhancements further strengthen its capabilities, solidifying XPS Lab as the premier choice for XPS analysis.

In summary, Scienta Omicron's XPS Lab system offers unmatched precision, sensitivity, and versatility, driving advancements in surface science and materials research.

**10:45am SS+AMS+AS+CA+LS-FrM-11 Investigation of Stannane (SnH<sub>4</sub>) Decomposition and Sticking Coefficient on Varied Metal Surfaces in EUV Lithography Environments, Emily Greene, N. Barlett, D. Qerimi, D. Ruzic, University of Illinois at Urbana-Champaign**

In the context of extreme ultraviolet (EUV) lithography, the evaporation of tin droplets frequently leads to the deposition of tin on various chamber surfaces, including collector mirrors. A prevalent method to remove this tin deposition involves hydrogen plasma etching, which transforms the deposited tin into stannane (SnH<sub>4</sub>). This compound, existing in a gaseous state under operational conditions, can be evacuated from the chamber using a vacuum pump. However, stannane is characterized by its instability, tending to decompose and adhere to various surfaces within the chamber.

To systematically study the decomposition behavior of stannane, a specialized experimental chamber has been designed. This chamber integrates a load-lock mechanism for inserting a test tube containing liquid stannane into a loading section, which is isolated from the main vacuum chamber by a valve. Within the main chamber, a quartz crystal microbalance (QCM), regulated by a cartridge heater, measures the mass of stannane deposits. The QCM will be set to temperatures between 30-300 °C. Upon opening the valve, the stannane vaporizes and interacts with the temperature-controlled QCM, facilitating the quantitative determination of the sticking coefficient as a function of both the surface material and the temperature.

Stannane is synthesized through the reaction of LiAlH<sub>4</sub>, SnCl<sub>4</sub>, C<sub>8</sub>H<sub>18</sub>O, and C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>. The four chemicals are mixed in a 3-neck flask while under vacuum. The reaction produces SnH<sub>4</sub> which flows through three U-tubes traps. The first trap is held at -96 °C to trap precursors, the second two traps are held at -196 °C and trap the stannane. The stannane is increasingly pure the more traps are used.

This investigation aims to understand and quantify the mechanisms of stannane deposition and decomposition, enhancing the maintenance and efficiency of EUV lithographic systems by optimizing the cleaning protocols for tin contamination.



# Friday Morning, November 8, 2024

11:00am **SS+AMS+AS+CA+LS-FrM-12 First Principles Methods for Predicting Surface Reaction Mechanisms for Chemical Functionalization of Semiconductor Surfaces**, *Roberto Longo, S. Sridhar, P. Ventzek*, Tokyo Electron America Inc.,

The density of semiconductor devices continues to increase, accompanied by the subsequent scaling down of the critical dimension (CD) size, which is now on the order of a few nanometers. This results in device structure changes, from two-dimensional (2D) to three-dimensional (3D) structures, because the CD size has reached its limit of reduction. To accomplish this, precise chemical modification of the required surfaces with atomic scale precision is key to obtain the desired geometric control. Precise modification implies being able to leverage knowledge of individual plasma born species and surface interactions. Unfortunately, species specific chemical interaction mechanisms in the context of reactive ions and chemical etching are still poorly understood for the full range of chemical environments at play. Once dissociated in plasma radicals, there might be a wide array of compositions. For similar atomic compositions, variations in the molecular structure of the chemical precursor can also result in significant differences as to the surface modifications and subsequent etching characteristics. The chemical nature of the surface including coverage and chemical activity add significant dimensionality to the problem of controlling plasma surface interactions in general. We divide the problem of elucidating plasma surface interactions into two major categories for practical purposes: hydrofluorocarbon driven for oxide etch and halogen driven for silicon etch. We present here semiconductor surface modeling with general characteristics and investigate the reaction mechanisms undergone by a large variety of hydrofluorocarbon molecular precursors using density-functional theory (DFT), with a focus on reactive halogen adsorption. Given the large parameter space of this problem, we describe computational approaches that efficiently and accurately generate fundamental data. Physical and chemical surface reactions and the corresponding byproducts are identified, obtaining self-limitation thresholds for each specific functionalizing chemistry. Therefore, our computational results provide valuable insights on the complex physical, chemical, and dynamic molecular and ion interactions with functionalized semiconductor surfaces, paving the road for designing tailored strategies with the desired outcome for each specific system.

11:15am **SS+AMS+AS+CA+LS-FrM-13 A Model Interstellar Medium Reactivity Study: Low Energy Electron Induced Chemistry of CH<sub>3</sub>OH@H<sub>2</sub>O**, *Ahmad Nawaz, M. Asscher*, The Hebrew University of Jerusalem, Israel

The desorption kinetics for MeOH@H<sub>2</sub>O sandwich films from Ru(0001) surfaces are investigated using temperature-programmed desorption (TPD) at ultrahigh vacuum, with a base pressure of  $2 \times 10^{-10}$  Torr and temperature 25K. The TPD spectra of all the prominent stable molecular products were well detected by an in-situ quadrupole mass spectrometer (QMS). However, variation of the QMS signals were observed to be lower at different exposure to the negative charges in different time interval. Further, the MeOH parent molecules decompose, upon exposure to electrons at energies of 100 eV and 6.4 eV. Molecules at m/z of 2, 28 and 44, assigned to H<sub>2</sub>, CO and CO<sub>2</sub>, were the most abundant products. The typical mass spectra of the parent molecules within the sandwich layer (16 ML) are shown in Figure 1. Here, the MeOH peaks appears at ~140K while the water desorption peak is at ~160K.

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