

Thursday Morning, November 2, 2017

Applied Surface Science Division

Room: 13 - Session AS+BI+SA+SS-ThM

Spectroscopy of the Changing Surface

Moderators: Timothy Nunney, Thermo Fisher Scientific, UK, Tony Ohlhausen, Sandia National Laboratory

8:00am AS+BI+SA+SS-ThM1 In Situ Investigation of the Dynamic Transformations of Model Catalyst Surfaces using Ambient Pressure XPS, *Iradwikanari Waluyo*, Brookhaven National Laboratory **INVITED**

In heterogeneous catalysis, the interaction between reactant molecules and the surface of the catalyst often causes changes in the surface composition and chemical state of the catalyst, which may result in changes in the reactivity of the catalyst. Using ambient pressure x-ray photoelectron spectroscopy (AP-XPS), these changes can be monitored in situ under close-to-realistic conditions. Unlike conventional XPS, which requires UHV conditions, AP-XPS measurements can be performed in the presence of gases at pressures of up to 100 Torr through the use of differentially pumped analyzer, small analyzer entrance aperture, and x-ray transparent windows. Although AP-XPS measurements using lab x-ray sources are possible and becoming more common, experiments at modern synchrotron light sources have distinct and significant advantages including tunable photon energy, tightly focused beam, and better resolution. A general overview of the technique as well as recent experimental results will be presented. Examples shown include (1) the potassium-promoted reduction of $\text{Cu}_2\text{O}/\text{Cu}(111)$ by CO , in which the reduction of Cu^+ to Cu is accelerated by the presence of K through the formation of surface carbonate species, (2) the surface segregation of $\text{Pt}/\text{Cu}(111)$ model bimetallic catalyst in the presence of various reactant gases, and (3) the reduction of $\text{Cu}_2\text{O}/\text{Pt}/\text{Cu}(111)$ by H_2 .

8:40am AS+BI+SA+SS-ThM3 Observation of Oxygen Binding on PGM-free Electrocatalysts by Ambient Pressure XPS and XAS, *Kateryna Artyushkova*, University of New Mexico, *M.J. Dzara*, *S. Pylpenko*, Colorado School of Mines, *P. Atanassov*, University of New Mexico

The most promising class of PGM-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). They show promise as replacement of Pt in two different technological platforms - alkaline exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the *exact nature of the active sites* is still debated even after over 50 years of research. Understanding the specific roles of nitrogen and metal in the properties/activity/stability/durability of MNC-based catalytic materials is a prerequisite for the rational design of ORR electrocatalysts with improved performance.

The key component in elucidating the relationship between the chemistry of active sites and activity is a better understanding of the formation of adsorbates, intermediates, and products during reactions occurring within the fuel cell.

In situ monitoring reaction steps under realistic conditions in metal-free and metal-containing building blocks will shed light onto the reaction mechanism that is essential for developing active and durable PGM-free catalyst for ORR.

We will report on AP-XPS analysis for series of electrocatalysts belonging to Fe-N-carbon families based on sacrificial support method (SSM) and Metal-organic frameworks (MOF). The effect the nitrogen chemistry and the type of iron have on the oxygen binding was investigated by ambient pressure X-ray Photoelectron Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS) under an O_2 environment at operating temperature of the fuel cell. The effect of the relative abundance of different types of nitrogens, such as pyridinic, coordinated to iron and hydrogenated nitrogens (pyrrolic and hydrogenated pyridine) on the preference of oxygen binding is studied by high-resolution nitrogen photoelectron spectra. The role of metallic and atomically dispersed iron will be investigated by a combination of XAS and XPS. Linking differences in oxygen binding to the differences in the chemistry of the electrocatalysts are of ultimate importance for elucidating the oxygen reduction reaction mechanism.

1. Artyushkova, K., et al., *Oxygen Binding to Active Sites of Fe-N-C ORR Electrocatalysts Observed by Ambient-Pressure XPS*. The Journal of Physical Chemistry C, 2017. **121**(5): p. 2836-2843.

9:00am AS+BI+SA+SS-ThM4 In situ Monitoring of Electrochemically Generated Carbene by XPS, *Pinar Aydogan Gokturk**, *S.E. Donmez*, *Y.E. Turkmen*, *B. Ulgut*, *S. Suzer*, Bilkent University, Turkey

Ionic liquids provide a platform for fundamental electrochemical studies in vacuum. In this present work, we report an in-situ X-ray photoelectron spectroscopic (XPS) investigation of N-heterocyclic carbene(NHC) generation from the electrochemical reduction of imidazolium based ionic liquids (ILs) through changes in oxidation state of nitrogen atoms. The IL serves as an electroactive material as well as the electrolyte in the cell between a Si substrate which is connected to the instrument ground and a gold wire connected to the sample holder for electrical connection. Through the course of the electrochemical reaction, the positive charge on imidazolium cation is neutralized to give free NHC as reflected by the distinct shifts in the N 1s and C 1s binding energies. The observations are further supported by colorful adduct formation of carbenes with CS_2 , reversible redox peaks in the voltammogram and the density functional theory calculations. The presented structure and XPS measurements can lead on understanding of the mechanism for various electrochemical reactions.

9:20am AS+BI+SA+SS-ThM5 The Influence of Water on the Ionic Liquid-Vapor Interface, *John Newberg*, University of Delaware, *M.B. Shiflett*, University of Kansas, *A. Broderick*, *Y. Khalifa*, University of Delaware

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions and it is important we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction and electrochemical window. In this talk we will highlight our recent efforts examining the IL-water vapor interface utilizing ambient pressure X-ray photoelectron spectroscopy (APXPS). APXPS allows for a molecular level assessment of the IL-vapor interface including a quantitative assessment of interfacial water concentration, moiety specific electronic environment changes, structural changes and obtaining adsorbate energetics.

9:40am AS+BI+SA+SS-ThM6 Ambient Pressure XPS Studies of Model N-C and Fe-N-C Catalysts Under Oxygen Environment, *Michael Dzara*, Colorado School of Mines, *K. Artyushkova*, University of New Mexico, *C. Ngo*, *M.B. Strand*, *J. Hagen*, *S. Pylpenko*, Colorado School of Mines

Producing inexpensive polymer electrolyte membrane fuel cells requires significant reduction in the amount of platinum group metal (PGM) oxygen reduction reaction (ORR) catalyst used. High surface area iron- and nitrogen-functionalized carbon (Fe-N-C) materials are a promising PGM-free replacement. These catalysts are very heterogeneous, leading to difficulties in discerning contributions from various potential active sites and identifying the most active species.¹ Techniques such as scanning transmission electron microscopy (STEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS) provide structural and chemical information that can be correlated to ORR activity measured with electrochemical methods. Ambient pressure XPS (AP-XPS) and x-ray absorption spectroscopy (XAS) conducted in a humidified O_2 environment, at an elevated temperature, and with applied potential offer opportunities to study materials under *in situ* conditions to determine adsorbates, intermediates, and products during ORR steps.^{2,3}

In this work, model Fe-N-C catalysts are studied along with reference nitrogen-doped carbon (N-C) materials. Development of model catalyst materials with controlled morphology and speciation can simplify the elucidation of active sites. Micro-porous N-C nanospheres with high graphitic content were synthesized by a solvothermal treatment of resorcinol, formaldehyde, and ethylenediamine, and a subsequent pyrolysis in N_2 .⁴ Incorporation of Fe into the N-C nanospheres was carried out by wet-impregnation of various Fe precursors followed by a second N_2 pyrolysis. By varying synthetic parameters, a set of N-C and Fe-N-C nanospheres with diverse compositions and properties were produced. Differences in composition and structure were evaluated using STEM-EDS and XPS, demonstrating control over N and Fe quantity and speciation. Select N-C and Fe-N-C nanospheres were then characterized with *in situ* AP-XPS, and in the case of Fe-N-C nanospheres, *in situ* XAS. By understanding the ORR on

* ASSD Student Award Finalist

these model Fe-N-C nanospheres, synthesis-property-performance conclusions are drawn, guiding the development of highly active Fe-N-C catalysts.

¹ A. Serov, K. Artyushkova, E. Niangar, C. Wang, N. Dale, F. Jaouen, M.-T. Sougrati, Q. Jia, S. Mukerjee, and P. Atanassov, *Nano Energy* **16**, 293 (2015).

² K. Artyushkova, I. Matanovic, B. Halevi, and P. Atanassov, *J. Phys. Chem. C* **121**, 2836 (2017).

³ Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E.F. Holby, P. Zelenay, and S. Mukerjee, *ACS Nano* **9**, 12496 (2015).

⁴ N.P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, and M. Jaroniec, *Chem. Mater.* **26**, 2820 (2014).

11:00am **AS+BI+SA+SS-ThM10 Real-time Photoelectron Spectroscopy Observation of Oxidation and Reduction Kinetics of Ni(111) Surface, Ryo Taga, S. Ogawa, Y. Takakuwa**, Tohoku University, Japan

Nitrogen contained in the air is oxidized and then harmful nitrogen oxide (NO_x) is formed in the combustion chamber of engine. Accordingly, the exhaust gas which contains NO_x is purified by catalysts. However, platinum group metals, whose prices are likely to rise by the depletion of resources in the future, are used as the catalysts, so the reduction of the amount used is an important matter for industrial and environmental fields. On the other hand, it has been already known that Ni has an effect to NO_x reduction, but its catalytic ability disappears when the Ni surface is oxidized. If O atoms on the Ni surface can be efficiently desorbed, Ni is expected as a catalyst for NO reduction. In the previous studies, some of researches have studied about reduction of oxidized Ni surfaces, but the relation between oxide reduction kinetics and behavior of O atoms has not yet been clarified. In this study, the oxidation and reduction kinetics on Ni(111) surfaces was investigated by real-time ultraviolet photoelectron spectroscopy (UPS). To investigate the amount of O atom adsorption and the changes of work function.

The experiments were performed using UPS apparatus with base pressure of $\sim 3 \times 10^{-8}$ Pa. The Ni(111) surface was firstly cleaned by the Ar⁺ ion bombardment, and the annealed at 600°C. O₂ gas (1×10^{-5} Pa) was directly introduced to UPS apparatus at the sample temperature of 100°C. After the end of the introduction of O₂ gas, the sample heated up to and H₂ gas (1×10^{-5} Pa) was introduced in order to investigate the Ni oxide reduction process. The photoelectron spectra were measured repeatedly each 72 s during oxidation and reduction.

From the time evolution of O 2p photoelectron spectra, we obtained the O 2p uptake curve and the change in work function. When O₂ gas was introduced, O 2p intensity increases linearly, so it turned out that the oxidation of Ni(111) surfaces was a zero order reaction. After introduction of H₂ gas, O 2p intensity decreases gently for about 500 s and then decreased rapidly. On the other hand, the work function slightly increased and then rapidly decreased. The work function reaches the same value on the clean Ni(111) surface. Therefore, Ni oxide can be reduced completely using H₂ gas.

These changes after introduction of H₂ gas can be divided into two areas. In the first area, O atoms are drawing from subsurface because of slight increase of work function. In the second area, then, it is suggested that the reduction progresses and the clean Ni surface area enlarges as like to island growth. In the symposium, we will discuss the reduction process of the oxidized Ni surface by NO gas.

11:20am **AS+BI+SA+SS-ThM11 Comparison of Initial Oxidation Kinetics between p- and n-type Si(001) Surfaces Studied by Real-time Photoelectron Spectroscopy, Yuki Sekihata, S. Ogawa**, Tohoku University, Japan, A. Yoshigoe, JAEA, Japan, R. Taga, Tohoku University, Japan, S. Ishidzuka, National Institute of Technology, Akita College, Japan, Y. Takakuwa, Tohoku University, Japan

An oxidation reaction is the "trade" of electrons between oxygen and other materials, therefore it is thought that there is a difference in the oxidation kinetics on between p-type and n-type Si substrates. In the previous researches about the kinetics of the thermal oxidation of Si, the oxidation rate have not taken account of the difference of conduction type because the thermal oxidation was performed in high temperature region above 600°C named intrinsic region where the intrinsic carrier concentration becomes comparable to the donor or acceptor concentration. On the other hand, oxidation temperature becomes lower to form thin oxide films below 1nm. Therefore, we believe that the difference of conductivity affects an oxidation kinetics on the Si(001) surfaces, but there is no oxidation reaction models that takes into account the difference of conductivity. In this study, we investigated the oxidation reaction kinetics on p- and n-type Si surfaces using real-time ultraviolet photoelectron spectroscopy.

The samples for oxidation were p-Si(001) and n-Si(001) surfaces. The dopants were Boron and arsenic for p- and n-type substrates, respectively. Their density of dopants were approximately 10^{18} atoms/cm³ so extrinsic region can be kept in the high temperature region even below 700°C. These

samples were oxidized using O₂ gas at the pressure of 1.0×10^{-5} Pa. During the oxidation reaction, the photoelectron spectra were measured repeatedly, therefore time evolution of the amount of oxygen adsorption, work function, and band bending can be investigated.

In the room temperature oxidation, it is found that oxidation reaction coefficient on n-Si(001) is larger than that on p-Si(001). To clarify the reasons, we focus to the changes of work function due to the formation of dipole layer. The work function of the n-Si(001) surface shows negative value but p-Si(001) is positive value. From this result, we can estimate the adsorption positions of O atoms. O atoms have a negative charge in the bond of Si-O, so it can be assumed that oxygen is placed on the n-Si(001) surfaces, but it is subsurface in case of the p-Si(001) surface. In case of n-Si(001) substrates, the doped electrons spill out into the surface because many electrons exist in the substrate. As the result, oxidation reaction is promoted in the n-Si(001) surface. From these results, we found that there is a difference of oxidation kinetics depending on the conductivity. In the presentation, we will show also the difference of oxide states between them.

11:40am **AS+BI+SA+SS-ThM12 Co-Pyrphyrin on Cu₂O(111) and TiO₂(110): Properties and Stability under Near Operando Conditions, Zbynek Novotny, W.-D. Zabka, M. Hotz, D. Leuenberger**, University of Zurich, Switzerland, L. Artiglia, F. Orlando, M. Ammann, Paul Scherrer Institut (PSI), Switzerland, J. Osterwalder, University of Zürich, Switzerland

The pyridine-based macrocycle Co-pyrphyrin (Co-Pyr) is a promising molecular water reduction catalyst recently synthesized at the University of Zurich [1]. We investigated Cu₂O(111) and TiO₂(110) substrates covered with a complete monolayer of Co-Pyr at pressures spanning from ultra-high vacuum (UHV) up to near ambient pressures of 1 mbar of water vapor. To study the surface photovoltage (SPV) effect, samples were illuminated with UV laser light through the electron spectrometer lens system. Both under UHV and water pressures up to 1 mbar, SPV-induced shifts of the order of $\Delta E_k = +120$ meV were observed in case of Cu₂O(111), while for TiO₂(110), much smaller SPV shifts of -0.12 meV were observed. X-ray absorption spectroscopy (XAS) of the Co L3-edge in dependence of illumination and water exposure was used to monitor the electronic structure of the Co metal center of Co-Pyr molecules. Comparison to simulated XAS spectra reveals that on the TiO₂(110), the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on the Cu₂O(111), the Co remains in the +2 oxidation state irrespective of the water exposure. Our measurements provide insights into the stability and behavior of the Co-Pyr molecules studied under near operando conditions, further stimulating the use of these molecular catalysts in the next-generation of solar fuel cells.

[1] Joliat, E et al., *Dalton Transactions* **2016**,45 (4), 1737-1745.

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