Thursday Morning, October 24, 2019

Surface Science Division
Room A220-221 - Session SS+AS+HC+TL-ThM
Surface Science of Energy Conversion and Storage

Moderators: Steven L. Tait, Indiana University, Francisco Zaera, University of California, Riverside

8:00am **SS+AS+HC+TL-ThM1 Chemical and Electrochemical Stability of Perovskite Oxide Surfaces in Energy Conversion: Mechanisms and Improvements***, **Bilge Yildiz,*** Massachusetts Institute of Technology **INVITED**

A broad range of highly active doped ternary oxides, including perovskites, are desirable materials in electrochemical energy conversion, catalysis and information processing applications. At elevated temperatures related to synthesis or operation, however, the structure and chemistry of their surfaces can deviate from the bulk. This can give rise to large variations in the kinetics of reactions taking place at their surfaces, including oxygen reduction, oxygen evolution, and splitting of H_2O and CO_2. In particular, aliovalent dopants introduced for improving the electronic and ionic conductivity enrich and phase separate at the surface perovskite oxides. This gives rise to detrimental effects on surface reaction kinetics in energy conversion devices such as fuel cells, electrolyzers and thermochemical H_2O and CO_2 splitting. This talk will have three parts. First, the mechanisms behind such near-surface chemical evolution will be discussed. Second, the dependence of surface chemistry on environmental conditions, including temperature, gas composition, electrochemical potential and crystal orientation will be described. Third, modifications of the surface chemistry that improve electrochemical stability and actvity, designed based on the governing mechanisms, will be presented. Guidelines for enabling high performance perovskite oxides in energy conversion technologies will be presented.

8:40am **SS+AS+HC+TL-ThM3 Mechanism of Oxygen Reduction Reaction on Nitrogen-doped Carbon Catalysts***, **Junji Nakamura,*** University of Tsukuba, Japan

Nitrogen-doped carbon materials are expected to be non-Pt catalysts for oxygen reduction reaction (ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) has been found to create ORR active sites in our previous work[1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Recently we have reported model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule and acridine (Ac)molecule)[2]. The DA molecules form a two-dimensional ordered structure along the direction of the HOPG substrate by self-organization. Adsorbed DA on the HOPG surface shows high ORR activity in terms of specific activity per pyridinic nitrogen and is comparable to that of pyridinic-nitrogen-doped carbon catalysts. We study the mechanism of ORR taking place on the DA/HOPG model catalyst. In acidic reaction conditions, pyridinic nitrogen is protonated to pyridinium nitrogen (NH+) species. It is suggested that the adsorption of oxygen take place on a carbon atom in a DA molecule upon reduction of the NH+ species. Generally, the reduction of NH+ is difficult to proceed thermodynamically at higher potentials above 0 V vs RHE. However, in the presence of oxygen, the reduction of NH+ is possible by an energy gain due to simultaneous adsorption of oxygen. The supplied electron goes to pai system as SOMO electron upon reduction, which is responsible for the adsorption of oxygen. That is, the role of pyridinic nitrogen is to provide SOMO electron upon reduction of NH+ species.

References

Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J, (2016). Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science*, 351, 361-365.

Shibuya R, Kondo T, Nakamura J, (2018). Bottom-up design of nitrogen-containing carbon catalysts for the oxygen reduction reaction. *ChemCatChem* doi.org/10.1002/cctc.201701928

9:00am **SS+AS+HC+TL-ThM4 Copper Corrosion Inhibition Investigated on the Molecular Scale Using APXPS***, **Bo-Hong Liu,*** Lawrence Berkeley National Laboratory*; O. Karslıoğlu,* Lawrence Berkeley Nationa lLaboratory*; M.B. Salmeron, S. Nemšák,* Lawrence Berkeley National Laboratory*; H. Bluhm,* Fritz Haber Institute of the Max Planck Society, Germany

Copper has been used in a wide variety of applications. Though relatively inert, it corrodes when in contact with aqueous solutions/water vapor and corroding agents such as chlorine.[1] Benzotriazole (BTA) is a commonly used corrosion inhibitor to protect copper surfaces. A consensus regarding the mechanism of corrosion protection is that BTA complexes with surface copper atoms, resulting in a Cu(I)-BTA protective polymer layer.[2] UHV-based surface science studies clarified the structure of the BTA layer on copper single crystal surfaces at low dosage, as demonstrated by a very recent study combining DFT and spectroscopic techniques;[3] however, the effect of environmental factors could not be well addressed by this approach. Here, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) study of the influence of water vapor and chlorine on well-defined Cu surfaces. To capture the material complexity of the corrosion phenomenon, we study copper single crystals as well as polycrystalline foils of metallic copper, cuprous oxide and cupric oxide. In this presentation, we will show that the water uptake of copper surfaces under humid condition is strongly influenced by the presence of a BTA layer. Also, a BTA layer blocks chlorine uptake in some conditions. Based on these experimental results, factors that influence the BTA inhibitory effect on copper corrosion are identified.

1. Atlas, D.; Coombs, J.; Zajicek, O. T., THE CORROSION OF COPPER BY CHLORINATED DRINKING WATERS. *Water Research* **1982,***16* (5), 693-698.

2. Finsgar, M.; Milosev, I., Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. *Corrosion Science* **2010,***52* (9), 2737-2749.

3. Gattinoni, C.; Tsaousis, P.; Euaruksakul, C.; Price, R.; Duncan, D. A.; Pascal, T.; Prendergast, D.; Held, G.; Michaelides, A., Adsorption Behavior of Organic Molecules: A Study of Benzotriazole on Cu(111) with Spectroscopic and Theoretical Methods. *Langmuir* **2019,***35* (4), 882-893.

9:20am **SS+AS+HC+TL-ThM5 Analysis and Deliberate Modification of Electrochemical Interfaces***, **Esther Takeuchi**, K. Takeuchi, A. Marschilok,* Stony Brook University **INVITED**

Interfaces in electrochemical energy storage systems are critical in the transport of electrons and ions and are significant factors in electrochemical function, yet remain a challenge to fully understand. In lithium based systems, the interfaces or interphases often form spontaneously due to reactions of the active materials and the electrolytes. The interfaces formed due to these spontaneous reactions may prove beneficial as they provide needed protection inhibiting further and continuous reaction. However, the characteristics of the interface may also contribute to decreased ion transport and the accompanying increased effective resistance.

Conversion-type materials for next generation lithium ion systems are appealing due to the opportunity for multiple electron transfer within one metal center. However, implementation of conversion materials has been hindered by the phase transformations occurring during cycling as well as formation of a resistive solid electrolyte interphase (SEI). This presentation will explore the effective implementation of combinations of characterization techniques including the use of *ex-situ* and *operando* methods to provide insight into the formation, composition and deliberate modification of the SEI.

11:00am **SS+AS+HC+TL-ThM10 An Investigation on Active Sites of La_2O_3 Catalyst for OCM Reaction: A Combined Study of *in situ* XRD, XPS and Online MS***, **Yong Yang**, C. Guan, E.I. Vovk, Z. Liu, X. Zhou, J.P.H. Liu, Y. Pang,* ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C_2 products (ethane and ethylene). Previous results suggested that the bulk structure change of the La_2O_3 catalyst was related to the performance of the reaction. In this work, a designed *in situ* XRD-MS coupled characterization setup coupled with online MS instrument are used for measuring both the reaction products and the bulk structure of the catalyst in real time and under simulated industrial conditions. This allows for the more detailed study in order to relate information from of bulk structure change vs. CO_2 related treatment and quantitative analysis of the reaction products, thus for a further connection and understanding of the conversion rate of CH_4 and the selectivity of C_2. The work presented focused on online characterization of the OCM reaction on La_2O_3 catalyst, covering different parameters including: 1. La_2O_3 pretreatment under different CO_2 concentrations, 2.

Consecutive OCM reactions, comparing the behavior of a clean surface La_2O_3 catalyst with a La_2O_3 catalyst after OCM, 3. OCM performed after La_2O_3 has undergone pretreatment with pure CO_2. Results indicate that carbonates formation on La2O3 is two step, surface carbonates formation at below 500°C and bulk formation at 500-700°C. *In situ* TPD performed in a high pressure gas cell (HPGC) and XPS measurement results confirm the above.

The results showed that bulk CO_3^{2-} formation under CO_2 exposure, results in higher light-off temperature of CO_2 and C_2 than the clean surface during OCM reaction. There is carbonate formation on commercial La_2O_3 during OCM reaction and CO_2 desorption after OCM reaction by in situ XRD-MS, and it influences the light-off temperature of CO_2 and C_2 up to 65°C higher than the clean surface. It is proposed that CO_3^{2-} may perform as a catalyst poison in this reaction. This result provides an important insight of the active site for OCM reaction. Based on this result, a brief XPS study of the carbonate free sample surface, which may be only preppared from the HPGC vacuum connected further reveals an oxide feature related with methane activation. Additional DFT calculations based upon the experimental data indicates a carbonation mechanism which occurs in the subsurface, which in turn could be related to La_2O_3 activity.

11:20am **SS+AS+HC+TL-ThM11 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers***, J.A. Phillips, K.P. Boyd, I. Baljak, L.K. Harville,* ***Erin Iski,*** University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an applied external potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Furthermore, by shifting from a nonpolar to polar side chain, island area also increased. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

11:40am **SS+AS+HC+TL-ThM12 Deposition and Structure of MoO_3 Clusters on Anatase TiO_2 (101)***,* ***Nassar Doudin****, Z. Dohnálek,* Pacific Northwest National Laboratory

Oxide clusters supported on metal oxide substrates are of great interest due to their importance in heterogeneous catalysis [1]. The nature and strength of the interactions between the metal oxide clusters and the support materials not only govern their structure and stability but also control the energetics of elementary steps that are critical for the overall activity [1]. Understanding the nature of the interactions is therefore important to tailor the supported metal oxide cluster systems to achieve the desired reactivity and selectivity. Here, we present a scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study of the monodispersed MoO_3 clusters deposited by the sublimation of MoO_3 powder on anatase $TiO_2(101)$ surface at 300 K. After the deposition, the STM images of the lowest concentration of MoO_3 show that the clusters initially migrate over the surface and preferentially anchor at step edges before they start to aggregate on the terraces. Interestingly, the aggregates are mostly composed of three adjacent clusters, with a small concentration of monomers and dimers. Further exposures to MoO_3 increase the cluster coverage until a fully saturated over-layer is created with each clusters being are centered on top of the Ti sites. The adsorbed clusters appear as bright protrusions, with an apparent cluster height of approximately 1.5 Å and diameter of about 8.5 Å. Since the cyclic $(MoO_3)_3$ trimers are known to be a dominant gas phase species resulting from the sublimation of MoO_3 [1], we propose that each cluster on the surface is a trimer. Annealing to 550 K results in a better-order of the $(MoO_3)_3$ layer, but further annealing to 650 K leads to three-dimensional clusters. The XPS results indicate that the $Mo(3d_{5/2})$ binding energy in as-deposited $(MoO_3)_3$ is characteristic of Mo^{6+}, and the oxidation state of Mo remains (+6) upon heating to 600 K. As such, this system may offers great promise as an ideal platform for reactivity studies on well-defined supported model transition-metal oxide catalysts.

[1] Zdenek Dohnálek et al. Royal Society of Chemistry 43, 7664−7680 (2014).

Author Index

Bold page numbers indicate presenter