

## 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-ThM-1 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<sub>2</sub>O and CO<sub>2</sub>. 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<sub>2</sub>O and CO<sub>2</sub> 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 activity, 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-ThM-3 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<sup>1</sup>. 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)<sup>2</sup>. 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<sup>+</sup>) species. It is suggested that the adsorption of oxygen take place on a carbon atom in a DA molecule upon reduction of the NH<sup>+</sup> species. Generally, the reduction of NH<sup>+</sup> is difficult to proceed thermodynamically at higher potentials above 0 V vs RHE. However, in the presence of oxygen, the reduction of NH<sup>+</sup> is possible by an energy gain due to simultaneous adsorption of oxygen. The supplied electron goes to pi 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<sup>+</sup> 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-ThM-4 Copper Corrosion Inhibition Investigated on the Molecular Scale Using APXPS, *Bo-Hong Liu*, Lawrence Berkeley National Laboratory; *O Karstoğlu*, Lawrence Berkeley National Laboratory; *M Salmeron*, *S Nemšák*, Lawrence Berkeley National Laboratory; *H Blumh*, 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.<sup>1</sup> 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.<sup>2</sup> 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;<sup>3</sup> 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-ThM-5 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-ThM-10 An Investigation on Active Sites of La<sub>2</sub>O<sub>3</sub> Catalyst for OCM Reaction: A Combined Study of *in situ* XRD, XPS and Online MS, *Yong Yang*, *C Guan*, *E Vovk*, *Z Liu*, *X Zhou*, *J Liu*, *Y Pang*, ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C<sub>2</sub> products (ethane and ethylene). Previous results suggested that the bulk structure change of the La<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> related treatment and quantitative analysis of the reaction products, thus for a further connection and understanding of the conversion rate of CH<sub>4</sub> and the selectivity of C<sub>2</sub>. The work presented focused on online characterization of the OCM reaction on La<sub>2</sub>O<sub>3</sub> catalyst, covering different parameters including: 1. La<sub>2</sub>O<sub>3</sub> pretreatment under different CO<sub>2</sub> concentrations, 2.

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Consecutive OCM reactions, comparing the behavior of a clean surface  $\text{La}_2\text{O}_3$  catalyst with a  $\text{La}_2\text{O}_3$  catalyst after OCM, 3. OCM performed after  $\text{La}_2\text{O}_3$  has undergone pretreatment with pure  $\text{CO}_2$ . Results indicate that carbonates formation on  $\text{La}_2\text{O}_3$  is two step, surface carbonates formation at below  $500^\circ\text{C}$  and bulk formation at  $500\text{--}700^\circ\text{C}$ . *In situ* TPD performed in a high pressure gas cell (HPGC) and XPS measurement results confirm the above.

The results showed that bulk  $\text{CO}_3^{2-}$  formation under  $\text{CO}_2$  exposure, results in higher light-off temperature of  $\text{CO}_2$  and  $\text{C}_2$  than the clean surface during OCM reaction. There is carbonate formation on commercial  $\text{La}_2\text{O}_3$  during OCM reaction and  $\text{CO}_2$  desorption after OCM reaction by *in situ* XRD-MS, and it influences the light-off temperature of  $\text{CO}_2$  and  $\text{C}_2$  up to  $65^\circ\text{C}$  higher than the clean surface. It is proposed that  $\text{CO}_3^{2-}$  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 prepared 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  $\text{La}_2\text{O}_3$  activity.

11:20am **SS+AS+HC+TL-ThM-11 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers**, *J Phillips, K Boyd, I Baljak, L 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-ThM-12 Deposition and Structure of  $\text{MoO}_3$  Clusters on Anatase  $\text{TiO}_2$  (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  $\text{MoO}_3$  clusters deposited by the sublimation of  $\text{MoO}_3$  powder on anatase  $\text{TiO}_2(101)$  surface at 300 K. After the deposition, the STM images of the lowest concentration of  $\text{MoO}_3$  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  $\text{MoO}_3$  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  $1.5 \text{ \AA}$

and diameter of about  $8.5 \text{ \AA}$ . Since the cyclic  $(\text{MoO}_3)_3$  trimers are known to be a dominant gas phase species resulting from the sublimation of  $\text{MoO}_3$  [1], we propose that each cluster on the surface is a trimer. Annealing to 550 K results in a better-order of the  $(\text{MoO}_3)_3$  layer, but further annealing to 650 K leads to three-dimensional clusters. The XPS results indicate that the  $\text{Mo}(3d_{5/2})$  binding energy in as-deposited  $(\text{MoO}_3)_3$  is characteristic of  $\text{Mo}^{6+}$ , 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).

12:00pm **SS+AS+HC+TL-ThM-13 Ionic Conducting Nanostructures Tailored on Porous Mixed Conduction Composite Electrodes for Enhancement of Oxygen Reduction Reaction**, *Jong-Eun Hong, D Joh, S Kim, H Ishfaq*, Korea Institute of Energy Research, Republic of Korea; *C Jung, J Park*, DGIST, Republic of Korea; *S Lee, H Kim, T Lim, S Park, R Song*, Korea Institute of Energy Research, Republic of Korea; *K Lee*, DGIST, Republic of Korea

With decrease in the operation temperature of solid oxide fuel cells, the oxygen reduction reaction (ORR) in the cathodes, which is sluggish, plays an important role in improving the electrochemical performance. Much effort has given to facilitate the ORR by the applications of cathode surface modification using active catalysts, nano-particle cathodes, and advanced cathode materials. In particular, the cathode surface modification with a reactive electro-catalyst has been appeared to increase the electrode reactivity and thus to decrease the polarization resistance to the oxygen reduction reaction. Infiltration of electro-catalysts has been widely utilized to tailor the cathode microstructures as it is a facile method. In this study, one-step infiltration using an *in-situ* sol-gel process was applied to modify porous mixed conducting composite cathodes, and the impact of surface microstructure tailoring on the electrochemical performances was investigated. The precursors of Sm- and Nd-doped ceria (SNDC), whose ionic conductivity is even higher than that of Gd-doped  $\text{CeO}_2$  (GDC), were infiltrated into the cathode by using an ultrasonic spray nozzle to produce fine and uniform droplets. The infiltrated samples then experienced an *in-situ* heat-treatment after repeating the ultrasonic spraying and drying processes and were submitted for electrochemical measurements. The detailed results on the microstructure evolution and electrochemical properties of the specimens prepared using the ultrasonic spraying infiltration are presented, and the elucidation of the results are discussed.

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