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_2 production from water splitting as well as for the re-utilization of CO_2 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_2 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_3O_4, Fe/Co_3O_4, Fe/NiO, Cu_2O, ZnO/Cu_2O, Au/Cu_2O), thin films (NiOx, $CoFe_2O_4$, Co_3O_4, Fe_3O_4) 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 CO2RR 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_2 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_2S 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_{CO}) at E = -1.3 V vs. the reversible hydrogen electrode (RHE) in the CO_2 reduction reaction (CO_2RR), Ag catalysts supported on S-doped HOPG demonstrated 70% higher CO turnover frequency (TOF_{CO} = 3.4 CO/$atom_{Ag}$/s) than those supported on S-free HOPG (TOF_{CO} = 2.0 CO/$atom_{Ag}$/s). Preliminary calculations based on density functional theory (DFT) indicated a more favorable energetic pathway of CO_2-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_2 conversion.

8:45am **SS+CA+LS-TuM-4 Non-Metal Cations for Enhancing CO_2 Electroreduction on Bismuth Electrode*, Theodoros Panagiotakopoulos*,** *K. Shi, D. Le, X. Feng,* University of Central Fllorida*; T. Rahman,* University of Central Florida

In exploring the effectiveness of non-metal cations in CO_2 electroreduction, we have carried out a comparative examination of the mechanisms for CO_2 electroreduction to formate (HCOO–) and CO on the Bi(111) electrode in the presence of cations, Na+ and NH_4^+, using grand canonical density functional theory. Our results reveal that the reduction of CO2 to formate is driven by the direct hydrogenation of aqueous CO_2 with a hydrogen atom adsorbed on the electrode (H*), i.e., $CO_2(aq) + H^* \rightarrow HCOO^-$. 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_2O molecule and one of its H atoms is then transferred to a CO2*. The activation energy barrier for this step was determined to be 0.77 eV and 0.75 eV in the presence of Na^+ and NH_4^+, 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^+ and NH_4^+, respectively. These findings lead to two important conclusions: 1) the non-metal cation NH_4^+ can be equally effective as the alkali metal cation Na^+ in promoting the CO_2 electroreduction to formate; 2) NH_4^+ is actually more effective than Na^+ in promoting the CO_2 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_2 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_2 Reduction at the Electrode-Electrolyte Interface*, Kaige Shi*[1,2]**, *D. Le, T. Panagiotakopoulos, T. Rahman, X. Feng,* University of Central Florida

Electrochemical CO2 reduction reaction (CO2RR) can enable a promising path towards sustainable fuel production and closing the carbon cycle. Despite the reports of numerous electrocatalysts, the mechanism of CO2RR at the electrode-electrolyte interface remains to be elucidated, particularly on the role of electrolyte cations in the reaction. While most studies of CO2RR focused on alkali metal cations, we investigate CO2RR using quaternary ammonium cations, which provide unique tunability in size, shape, and charge distribution to elucidate the cation effect. For the CO2RR 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 *CO2 on Bi surface via electrostatic interaction, and the quaternary ammonium cations have a more profound effect on the CO2 adsorption characteristics and CO2RR activity than metal cations. The adsorbed *CO2 is an essential step for CO production, but not necessary for formate production due to the pathway with direct reaction of aqueous CO2 with surface *H species. Based on the understanding, we employ the substitute ammonium cations to enhance CO2 electrolysis in a gas-diffusion-electrode (GDE) flow cell, which achieves multi-fold improvement of the activity for CO2RR 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 CO2RR 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. Francesichini,* Facultad de Ciencias Quimicas 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 critial region composed by the ionomer (liquid, usually Nafion), catalyst (solid, usually platinum) and fuel (H_2 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

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[1] **AVS National Student Awardee**

[2] **SSD Morton S. Traum Award Finalist**

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$^+$, 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.

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