

Laboratory-Based Ambient-Pressure X-ray Photoelectron Spectroscopy Focus Topic

Room Oregon Ballroom 203-204 - Session LX-TuP

Laboratory-Based AP-XPS: Poster Session

LX-TuP-1 Multimodal Liquid Cell for Lab-based APXPS: Investigating Ruthenium-based Organometallic Molecules in Various Environments, *Youngseok Yu, A. Vidal Muller*, Brookhaven National Laboratory; *Z. Xi*, Stony Brook University/Brookhaven National Laboratory; *M. Liu, E. Stavitski, J. Concepcion, A. Head*, Brookhaven National Laboratory

Dye-sensitized photo-electrosynthesis cells (DSPECs) hold great promise as sustainable and renewable energy sources. To enhance the adsorption efficiency, chromophores are anchored onto oxide surfaces to absorb visible light, as transition metal oxides typically possess band gaps within the range of 2-3 eV. In this research, we have developed a multimodal liquid cell for ambient-pressure X-ray photoelectron spectroscopy (APXPS) to investigate the solid/liquid interface of these systems. The cell design utilizes a graphene-covered holey SiNx membrane with deposited metal oxide and catalyst as the working electrode. Our study focuses on examining the electronic structure of a dye molecule, (bis-2,2'-bipyridine)[(4,4'-bis(diethyl phosphonate)-2,2'-bipyridine)]ruthenium(II) (or RuP), under various conditions, including being anchored on TiO₂, anchored on IrO₂, and in a 1mM NaOH solution. Our findings indicate that the electron density of the Ru metal center varies with its environment.

LX-TuP-2 Investigating Solvation with Liquid Jet Photoelectron Spectroscopy, *Jared Bruce*, University of Nevada, Las Vegas; *A. Haines, F. Furche*, University of California, Irvine; *R. Seidel*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; *B. Winter*, Fritz Haber Institute of the Max Planck Society, 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, we will explore the solvation of acetic acid in aqueous solution both near the interface and into the bulk of the solution. The difference in binding energy between the methyl and carboxyl carbons (ΔBE) was used to compare electronic structure calculations coupled with molecular dynamics simulations to the results from the LJ-XPS. Experiment and theory were found to overlap when a single water molecule was added to the first solvation shell of acetic acid calculation, whereas 20 water molecules were required to reproduce the experiment for acetate. Building on these results, liquid jet work at the synchrotron was used to explore the difference in solvation near the interface at lower probe depths compared to those in the bulk of the solution and in the lab-based experiments.

LX-TuP-4 Evaluation of AlCoCrFeNiMnTi High Entropy Alloys for CO₂ Hydrogenation, *Chiezugolum Odilinye, H. Kersell*, School of Chemical, Biological, and Environmental Engineering, Oregon State University; *X. Fan*, Department of Materials Science and Engineering, University of Tennessee, Knoxville; *Z. Lyu, P. Liaw*, Department of Materials Science and Engineering, University of Tennessee; *G. Herman*, School of Chemical, Biological, and Environmental Engineering, Oregon State University

Carbon dioxide (CO₂) hydrogenation is of considerable interest due to the ability to chemically recycle carbon dioxide with renewably generated hydrogen. A wide range of catalysts have been used for hydrogenation of CO₂ where methanation, Fischer-Tropsch, and methanol synthesis reactions are the most investigated. We are interested in evaluating high-entropy alloys (HEAs) for CO₂ hydrogenation, where we can take advantage of the multifunctional sites that exist at HEA surfaces. Indeed, certain HEAs recently showed promise for altering the selectivity and stability for CO₂ hydrogenation catalysts.^[1] In this study, we have used laboratory-based ambient pressure X-ray photoelectron spectroscopy (APXPS) to investigate the reaction of CO₂ and CO₂/H₂ mixtures with an AlCoCrFeNiMnTi HEA. For these experiments, the as-cast alloy was homogenized at 1100 °C, polished, and then sputter-cleaned in ultrahigh vacuum to remove adventitious carbon and native oxides. This clean surface was then exposed to 1 mTorr of CO₂, while we monitored the chemical state of the adsorbed carbon species, as well as the oxidation state of the surface metal atoms. We have

performed similar experiments with CO₂/H₂ mixtures and will contrast the observed surface chemistries with only CO₂. These studies demonstrate that APXPS is a powerful technique to monitor reactions on complex alloy surfaces.

Reference:

[1] K. Mori, N. Hashimoto, N. Kamiuchi, H. Yoshida, H. Kobayashi, and H. Yamashita, Hydrogen spillover-driven synthesis of high-entropy alloy nanoparticles as a robust catalyst for CO₂ hydrogenation, *Nat. Commun.*, 2021, 12, 3884

Author Index

Bold page numbers indicate presenter

— B —

Bruce, J.: LX-TuP-2, **1**

— C —

Concepcion, J.: LX-TuP-1, **1**

— F —

Fan, X.: LX-TuP-4, **1**

Furche, F.: LX-TuP-2, **1**

— H —

Haines, A.: LX-TuP-2, **1**

Head, A.: LX-TuP-1, **1**

Hemminger, J.: LX-TuP-2, **1**

Herman, G.: LX-TuP-4, **1**

— K —

Kersell, H.: LX-TuP-4, **1**

— L —

Liaw, P.: LX-TuP-4, **1**

Liu, M.: LX-TuP-1, **1**

Lyu, Z.: LX-TuP-4, **1**

— O —

Odilinye, C.: LX-TuP-4, **1**

— S —

Seidel, R.: LX-TuP-2, **1**

Stavitski, E.: LX-TuP-1, **1**

— V —

Vidal Muller, A.: LX-TuP-1, **1**

— W —

Winter, B.: LX-TuP-2, **1**

— X —

Xi, Z.: LX-TuP-1, **1**

— Y —

Yu, Y.: LX-TuP-1, **1**