

New Trends on Structural and Electronic Characterization of Materials, Interfaces, and Surfaces Using Synchrotron and FEL-Based Radiation Sources Focus Topic Room 318 - Session LS1+2D+AS+EM+QS+SS-TuA

Operando Catalysis and Energy Systems

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **LS1+2D+AS+EM+QS+SS-TuA-1 In-situ/Real-time XPS Study of Electrochemical Reactions in All-solid-state Thin-film Lithium-Ion Batteries, Takuya Masuda**, National Institute for Materials Science, Japan

INVITED

All-solid-state lithium-ion batteries (ASSLIBs) are one of the most promising next generation rechargeable batteries because of their very high safety and reliability. Understanding of the mechanism of electrochemical reactions and related physicochemical phenomena is very important for improving cell performances and durability. Application of ex-situ techniques to multiple samples disassembled from cells after certain charge/discharge cycles often results in misinterpretation due to the variation of samples and undesired side effects during sample transfer between battery test environment and characterization apparatus. Thus, various in-situ techniques which can be applied to the same position of the same sample kept at a certain charge/discharge state have been developed for hierarchical understanding of a series of electrochemical events interplaying with each other. X-ray photoelectron spectroscopy (XPS) is a powerful tool for analyzing the composition of reaction products, chemical state, and electronic structure of sample surfaces. By tuning the energy of incident x-rays, it also enables us to conduct the depth-resolved analysis of surfaces and interfaces including those buried with solid thin films. Recently, we developed an in-situ XPS apparatus equipped with a bias application system and a vacuum suitcase for sample transfer,[1] and applied it to the electrochemical lithiation/delithiation reactions of an amorphous Si thin film electrode sputter-deposited on a solid electrolyte sheet.[2] The chemical state of Si electrode changing during lithiation/delithiation processes was successfully tracked by sequential XPS measurements in the regions of Li 1s, C 1s, O 1s, and Si 2p. Not only lithium silicide (Li_xSi) which reversibly responds to the lithiation/delithiation but also irreversible species such as lithium oxides, lithium silicates and lithium carbonates were formed due to the lithiation of the Si electrode. Moreover, a rapid spectral change attributable to the phase transition of a crystalline Li_xSi to an amorphous phase was observed in the successive delithiation after preceding lithiation up to certain level. Based on the state of charge, Li content x in Li_xSi, and positions of XPS peaks, we summarized the lithiation/delithiation mechanism in Si electrodes. Further details will be presented.

[1] R. Endo, T. Ohnishi, K. Takada, T. Masuda, *Journal of Physics Communications*, 2021, 5, 015001.

[2] R. Endo, T. Ohnishi, K. Takada, and T. Masuda, *J. Phys. Chem. Lett.* 2020, 11, 6649–6654.

3:00pm **LS1+2D+AS+EM+QS+SS-TuA-3 Interaction of Molecular Nitrogen with Vanadium Oxide in the Absence and Presence of Water Vapor at Room Temperature: Near-Ambient Pressure XPS**, S. Nemsak, Lawrence Berkeley National Laboratory; Kabirat Balogun, P. Chukwunenye, T. Cundari, P. Bagus, J. Kelber, Department of Chemistry, University of North Texas

Interactions of N₂ and H₂O at transition metal oxide surfaces are of fundamental interest for gaining insight into electrocatalytic nitrogen reduction reaction (NRR) mechanisms. N₂/H₂O interactions at the polycrystalline vanadium oxide/vapor interface were monitored at room temperature and N₂ partial pressures between 10⁻⁹ Torr and 10⁻¹ Torr using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). The oxide film was predominantly V(IV), with significant V(III) and V(V) components. Such films have been previously demonstrated to be NRR active at pH 7. There is little understanding, however, of the detailed nature of N₂-surface interactions. XPS measurements were acquired at room temperature in environments of both pure N₂ and equal pressures of N₂ and H₂O vapor, up to a N₂ partial pressure of 10⁻¹ Torr. In the absence of H₂O, broad N 1s features were observed at binding energies of 401 eV and 398.7 eV with relative intensity ratios of ~ 3:1, respectively. These features remained upon subsequent pumpdown to 10⁻⁹ Torr, indicating that adsorbed nitrogen is stable at room temperature in the absence of

equilibrium with gas phase N₂. In the presence of equal pressures of N₂ and H₂O vapor, the 401 eV N 1s feature was reduced in intensity by ~ 50% at 10⁻¹ Torr N₂ partial pressure, with the feature at 398.7 eV binding energy barely observable. DFT calculations show that the above NAP-XPS data demonstrating stable N₂-surface binding in the absence of N₂ overpressure are consistent with N₂ binding at V(IV) or V(III) sites, but not at V(V) sites, and further show that N₂/H₂O binding is competitive. SCF-HF calculations suggest that the two N 1s XPS features correspond to "shake" and normal transitions at 401 eV and 398.7 eV, respectively, for N₂ bonded end-on to the surface. The shake feature involves a charge transfer from V 3d to N₂ π* in addition to N 1s ionization. The difference in binding energies of the two features, ~ 2.3 eV, strongly suggests N₂ -V(III) binding. The data presented demonstrate the ability of NAP-XPS, in concert with theory, to provide atomic-level insight concerning interfacial reactions relevant to electrocatalysis.

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3:20pm **LS1+2D+AS+EM+QS+SS-TuA-4 Catalysts Caught in the Act: an Operando Investigation of Copper during CO₂ Hydrogenation, Elizabeth Jones**, University of Oxford, UK

Amongst the foremost challenges in mitigating global warming are replacing fossil fuels with renewable alternatives, and storing/using carbon captured from CO₂-emitting processes. Methanol production by CO₂ hydrogenation promises a possible solution to both of these issues, particularly if H₂ can be obtained through water electrolysis. When the resulting methanol is used as a fuel an equivalent amount of CO₂ is released making it a "net-zero" fuel alternative. CO₂ hydrogenation is performed industrially using a CO₂/H₂ mix at 200-300°C, 50-100 bar with a Cu-based catalyst, and the addition of CO is known to increase the methanol yield. However, mechanistic understanding of this reaction and the role played by CO remains limited. Soft X-ray spectroscopies can provide details on the chemical state of copper to uncover the chemistry behind this reaction, however the typical requirement for measurement under high vacuum constrains how realistic these studies can be. There has been much recent development on improving operando techniques to enable heterogeneous catalytic reactions to be studied under realistic pressure conditions (E. S. Jones et al., in *Ambient Pressure Spectroscopy in Complex Chemical Environments*, 2021, ACS Symposium Series, vol. 1396, ch. 8, 175-218). A promising approach is to use an environmental cell which encloses the desired gas and separates it from the high vacuum environment, using an X-ray transparent window (R. S. Weatherup, *J. Phys. Chem. Lett.*, 2016, 7, 1622-1627).

Using a custom-designed high pressure environmental cell we have studied model Cu catalysts using operando NEXAFS in total electron yield mode up to pressures of 1 bar and temperatures of 200°C. A thin Cu film was deposited onto a Si₃N₄ membrane which acted to seal the high pressure gas within the cell and as a transparent window for incident X-rays. The aim of the study was to investigate how the Cu oxidation states varied when exposed to H₂ and CO₂ in different sequential order and how the introduction of CO can further influence the chemical state of Cu. It was found that H₂ can provide a protective barrier to oxidation from CO₂ when dosed first, however if H₂ was added after CO₂ it is unable to return the surface to its metallic state where CO is then required for reduction. This offers an insight into why CO plays an important role in the industrial production of methanol. Additionally, advances in sealing of the environmental cell enabled high pressures to be achieved at elevated temperatures, allowing this approach to be extended to more industrially-relevant conditions.

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