

# Tuesday Evening Poster Sessions

## In-Situ Spectroscopy and Microscopy Focus Topic

Room: Hall 3 - Session IS-TuP

### In-Situ Spectroscopy and Microscopy Poster Session

**IS-TuP1 Investigations of Graphene Covered Metal Catalyst using Operando Ambient Pressure X-ray Photoelectron Spectroscopy.** *Qiang Liu*, Lawrence Berkeley National Laboratory (LBNL), *B.H. Mao*, Chinese Academy of Sciences, *E.J. Crumlin*, Lawrence Berkeley National Laboratory (LBNL), *Z. Liu*, Chinese Academy of Science

Carbonaceous deposition is always observed in carbon-containing catalysis reactions on metal catalysts. This carbon deposition layer blocks the active sites of the metal catalyst and, therefore, inhibits the catalytic reaction. Recent research revealed that by depositing a graphene overlayer on metal catalyst the detrimental interaction between reactant gases and the metal catalysts can be weakened, thus resulting in a lowering of the activation energy barrier for the desired catalytic reaction. In order to probe the fundamental charge transfer processes between the as-grown graphene layer and the metal catalyst we present our studies of this system using operando ambient pressure X-ray Photoelectron Spectroscopy (APXPS), with synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory. By intercalating gases (e.g. CO, O<sub>2</sub>) quasi-free-standing graphene can be prepared, which annulled the charge transfer between as the as-grown graphene and the metal. Using APXPS, we have studied the graphene-reactant and reactant-metal interactions under different temperature and pressure conditions. We will discuss the results from graphene-Cu and graphene-CuNi system under CO oxidation reaction and other reaction conditions.

**IS-TuP2 Probing the Electrode-Electrolyte Interfaces using In Situ Angle-resolved XPS.** *V. Shutthanandan*, *M.I. Nandasiri*, *A. Schwarz*, *T.C. Kaspar*, Pacific Northwest National Laboratory, *S.A. Thevuthasan*, Qatar Environment and Energy Research Institute, Qatar, *Murugesan Vijayakumar*, Pacific Northwest National Laboratory

The interaction between a charged surface (i.e. electrode) and an ionic solution (i.e. electrolyte) is the basic science that drives various systems ranging from biological membranes to energy storage and conversion devices. In a typical electrode-electrolyte interfacial region, ions from the electrolyte can form an electric-dipole with oppositely charged electrode and subsequently produce an electric double layer (EDL). This EDL formation is a highly reversible process that involves no chemical/phase changes and is widely used in modern devices such as chemical sensors, field-effect transistors and supercapacitors. However, a clear understating of the impact of the electrode surface chemistry and the nature of electrolyte ions on molecular structure-property relationship at modern interfaces is still lacking. One of the unique features of these interfaces is that they contain non-equilibrium ion concentration under biased conditions. A multilayer formation with alternative charges (i.e., cation/anion) is expected under charged conditions, which can subsequently result in gradient change in ion concentration depend on the applied potential. To clearly distinguish the role of each electrode/electrolyte parameter under charging conditions, an unique *in-situ* angle-resolved X-ray photoelectron spectroscopy (AR-XPS) setup was developed at the Environmental Molecular Sciences Laboratory (EMSL) in Pacific Northwest National Laboratory. The change in composition of Ionic liquid electrolyte and specifically cation/anion ratio at different charging conditions was analyzed as a function of depth using *in-situ* AR-XPS. Preliminary results obtained from a model system consisted of porous carbon electrode and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid electrolyte will be discussed here. In addition, the derived depth-profile information (such as surface adsorption and multilayer formation) will be compared with the number density profiles of cation/anions calculated from the optimized MD simulations.

**IS-TuP3 Bimetallic Nanoparticles Stability Investigated by In Situ XPS and TEM.** *Cecile Bonifacio*, University of Pittsburgh, *S.C. Carenco*, *M.B. Salmeron*, Lawrence Berkeley National Laboratory, *J.C. Yang*, University of Pittsburgh

Bimetallic Ni and Co nanoparticles (NPs) possess intriguing potential for industrial applications due their remarkable catalytic activity for methane production and selective CO<sub>2</sub> reduction. Synthesizing these NPs as a core-shell structure presents a cost-effective way to produce catalysts by using the less expensive metal in the core and the more expensive but active metal catalyst in the shell. The core-shell structure can also allow for the fine tuning of reactivity, aversion of sintering issues for the core material, and even enhancement of tolerance to high temperatures. Unfortunately, NPs

tend to be unstable at temperatures far below their bulk melting temperature. In this work, the structural stability of Ni-Co core-shell was studied using *in situ* techniques. The morphological, structural, and chemical changes involved in the core-shell reconfiguration were examined during *in situ* annealing through simultaneous imaging and acquisition of elemental maps in the transmission electron microscope (TEM), and acquisition of O 1s, Ni 3p, and Co 3p x-ray photoelectron spectra (XPS). By observing the structural rearrangements of the nanoparticles *in situ* as a function of temperature, we were able to determine the thermal conditions under which the as-synthesized structure is stable and the minimum temperature where significant elemental diffusion and aggregation occurs. The NPs were annealed *in situ* in the TEM and XPS from 80°C to 650°C under vacuum conditions. Energy-dispersive x-ray spectroscopy (EDS) maps were acquired after each annealing step, yielding the quantitative distribution of Ni and Co within the NPs. Our results show that core-shell reconfiguration occurred in a stepwise process of surface oxide removal and metal segregation. Removal of the stabilizing surface oxide occurred from 320°C to 440°C, initiating the core-shell reconfiguration. Above 440°C, Ni migration from the core to the shell disrupted the core-shell structure of the NP leading to the subsequent formation of a homogeneous Ni-Co mixed alloy at 600°C. This work impacts other fields besides catalysis – including metallurgy, magnetism, etc. – where nanoparticle stability under operating conditions is essential for their technical viability and long-term durability.

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