

Thursday Afternoon, October 31, 2013

In Situ Spectroscopy and Microscopy Focus Topic

Room: 203 B - Session IS+EN+SP+SS-ThA

In Situ Studies of Electrochemical Interfaces and Processes

Moderator: A. Kolmakov, Southern Illinois University Carbondale

2:00pm **IS+EN+SP+SS-ThA1 Direct In Situ Probe of Electrochemical Processes in Operating Fuel Cells, S.S. Nonnenmann, R. Kungas, J.M. Vohs, D.A. Bonnell**, University of Pennsylvania

Many strategies for advancing energy related processes involve high temperatures and reactive environments. Fuel cell operation, chemical catalysis, and certain approaches to energy harvesting are examples. Scanning probe microscopy boasts a versatile toolbox of local and often atomic resolution measurements of phenomena at a scale that enables understanding of complex processes involved in many systems. Applying these techniques to the realistic conditions under which these processes operate inherently poses significant experimental design challenges. To overcome this, we have developed a system allowing SPM at temperatures to 600°C in reactive gas environments. Here the characterization of an operating fuel cell serves as the first demonstration. Solid oxide fuel cells (SOFCs) offer the highest conversion efficiencies with operating temperatures ranging from 400°C - 1000°C and operate under variable gaseous fuel environments – H₂-based environments (anode side) and O₂-based environments (cathode side). Topography and the influence of the local ionic chemical potential on the surface potential are observed along the electrode/electrolyte interface while under operation. While not (yet) at atomic levels of spatial resolution, these probes are at the scale to examine local interface properties.

2:20pm **IS+EN+SP+SS-ThA2 Ex Situ Lift-Out of Specimens for In Situ TEM Studies, L.A. Giannuzzi, L.A. Giannuzzi & Associates LLC, Z. Yu, M.P. Harmer**, Lehigh University

In-situ transmission electron microscopy (TEM) of grain boundaries at elevated temperature requires accurate manipulation of electron transparent specimens to site-specific carbon films patterned on heating membranes measuring only ~5-10 micrometers in diameter. Ex-situ lift-out (EXLO) of focused ion beam (FIB) prepared or other electron transparent specimens (e.g., fibers, particles, platelet precipitates) is advantageous for accurate manipulation of specimens to these membranes because it is fast, reproducible, and avoids deleterious ion implantation into the specimens while FIB imaging during the in-situ lift-out method. The ex-situ lift-out technique for this application will be described and in-situ TEM results will be presented.

2:40pm **IS+EN+SP+SS-ThA3 In Situ Characterization of Thermal Degradation of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ Cathode Materials for Lithium Ion Batteries: Insights from Combined Synchrotron XRD, XAS and Environmental Microscopy Studies, E. Stach, S. Hwang, S.-M. Bak, K.-W. Nam, Brookhaven National Laboratory, W. Chang, Korean Institute of Science and Technology, X. Yu, E. Hu, K.-B. Kim, Brookhaven National Laboratory, K.-Y. Chung, Korean Institute for Science and Technology, X.-Q. Yang, Brookhaven National Laboratory** **INVITED**

Li-ion batteries have seen widespread application as secondary batteries in numerous applications in consumer electronics, and have attracted recent attention for various forms of electric vehicles. One particularly attractive material for the cathode is the Ni-rich system of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂. These materials are being explored as a replacement to LiCoO₂, as they offer several performance improvements, including higher energy density and lower cost. However, these materials have demonstrated a significant increase in impedance and capacity fade during aging, or upon cycling at elevated temperatures. Additionally, when in highly delithiated states, the reduction of Ni ions during thermal cycling releases oxygen from the crystal structure, which can lead to both thermal runaway and violent reactions with the flammable electrolyte.

We have utilized a variety of in-situ characterization methods to understand the mechanisms associated with the thermal degradation of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ materials, as a function of their delithiation / charge state. By combining time-resolved synchrotron x-ray diffraction and mass spectrometry, we have directly shown that these materials undergo a specific sequence of phase transformations - from layered to disordered spinel to rock salt - as a function of temperature, and directly correlate these phase transformations with the evolution of oxygen from the

microstructure. In-situ observations in an environmental transmission electron microscope confirm these global average measurements on the nanoscale, and allow us to kinetically track the evolution of oxygen from the surfaces of the nanoparticles into their bulk. In-situ spectroscopic results - from XAS and EELS - allow correlation between electronic structure changes and the resulting phase transformations. Finally by performing these same thermal treatments in-situ to the TEM and in the presence of excess oxygen, we show that it is possible to suppress these phase transformations to significantly higher temperatures, thereby suggesting that methods to protect the surfaces from oxygen evolution could lead to significant enhancements in the safety performance of these materials. Throughout the presentation, the insights gained from complementary in-situ techniques will be highlighted.

3:40pm **IS+EN+SP+SS-ThA6 In Situ Measurement and Control of Interaction Forces at Electrified Softmatter | Metal Interfaces, M. Valtiner, Max Planck Institut fur Eisenforschung GmbH, Germany, S.H. Donaldson, K. Kristiansen, M.A. Gebbie, J.N. Israelachvili**, University of California, Santa Barbara

Redox-active interfaces are ubiquitous in the realms of natural and technological systems. For instance, prevention of corrosive delamination at metal|oxide|paint interfaces, or bio-mimicry of adhesive bonding in natural systems (e.g. mussel glues) rely on a fundamental understanding of interaction forces at electrified and/ or redox-active solid|liquid|softmatter interfaces. Recently, we developed a newly designed electrochemical surface forces apparatus setup (EC-SFA) that allows control and measurement of both surface potentials and interfacial electrochemical reactions with simultaneous measurement of normal interaction forces and the absolute distances between (similar or dissimilar) apposing surfaces [1], [2].

To quantify both oxide growth and interaction forces between asymmetric apposing softmatter and metal surfaces we performed normal force measurements across atomically smooth polarized gold electrodes facing PEGolated lipid bilayers with different head-group chemistries. Switching electrochemical potentials allowed us to quantitatively and qualitatively identify, rationalize, and therefore control, which interaction forces dominated between the electrode surfaces and a surface coated with differently end-functionalized polyethylene glycol (PEG) polymers. In particular, the manipulation of *surface potentials and the oxidation of the gold have profound and very strong influences on the measured interaction forces*. Moreover, our measurements allowed us to *in-situ quantify the Au-oxide thickness with Angstrom accuracy*. Here, we will discuss in detail, how (1) electric double layer potentials, (2) change of surface chemistry (e.g. oxide growth, oxide thickness) as well as (3) polymer chemistry (functional groups and backbone chemistry) influence specific and non-specific interaction forces (electrostatic, hydrophobic and Van der Waals forces, see also [3]) across electrified softmatter|metal interfaces.

[1] Valtiner, M., Kristiansen, K., Greene, G. W. et al. in *Advanced Materials* 23, 2294 (2011).

[2] Valtiner, M., Banquy, X., Kristiansen et al. in *Langmuir* 28, 13080-13093 (2012).

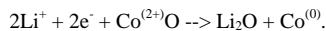
[3] Valtiner, M., Donaldson, S. H., Jr., Gebbie, M. A. et al. in *Journal of the American Chemical Society* 134, 1746-1753 (2012).

4:00pm **IS+EN+SP+SS-ThA7 In Situ Studies of Strain Evolution in Graphene on Ir(111) and Interplay with Magnetic Few Layer Cobalt Films, A. N'Diaye**, Lawrence Berkeley National Laboratory **INVITED**

Graphene's transport properties make it a promising component of spintronic applications and logic circuitry operating at gigahertz frequencies or as a support for nanocatalysts. Understanding graphene's interplay with the substrate is key to understanding and tailoring its properties. Here we show how thermal compression leads to few nanometer wide and micrometer long elongated wrinkles on single layer epitaxial graphene on Ir(111) to partially relieve compressive strain in the graphene layer. The strain relief process can be followed in-situ with spot profile analysis low energy electron diffraction (SPA-LEED) and low energy electron microscopy (LEEM). We show that micrometer wide regions of graphene slide over substrate and that the residual strain is spatially inhomogeneous. An other example for the interplay of graphene with its support is the enhancement of the perpendicular magnetic anisotropy in thin Cobalt films intercalated between graphene and Ir(111). We use spin-polarized LEEM (SPLEEM) to study the thickness induced spin reorientation transition in the graphene/Co/Ir(111) system and produce a phase diagram of an in-plane state, an out-of-plane state, and a partially canted state. This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-

4:40pm **IS+EN+SP+SS-ThA9 The Lithium-Induced Conversion Reaction of CoO Thin Film Battery Materials in Ultra-High Vacuum.**
R. Thorpe, S. Rangan, M. Sina, F. Cosandey, R.A. Bartynski, Rutgers University

Lithium-ion conversion batteries can store 2-3 times more charge than intercalation batteries by utilizing the full range of oxidation states of their constituent divalent or trivalent transition metal compounds during discharge. A prototypical conversion compound is CoO, which follows the reaction



Cobalt oxide and other transition metal oxides are attractive for use as Li-ion anodes in portable electronics due to their high charge storage capacity and moderate voltage versus Li^+/Li^0 . However, the cycling stability of conversion electrodes is poor, and capacity losses have thus far prevented their implementation.

In order to understand phase progression during the conversion reaction of CoO, high-purity CoO thin films grown in UHV were sequentially exposed to atomic lithium. The electronic structure of the pristine films and of the products of lithiation was studied using x-ray photoemission spectroscopy (XPS), UV photoemission spectroscopy, and inverse photoemission spectroscopy. The crystal structure and film reorganization were probed in parallel with transmission electron microscopy (TEM) and scanning tunneling microscopy.

The amount of CoO reduction for a given Li dose was observed to be highly dependent upon the temperature at which lithiation was performed. At 150°C, Li mobility in the active material was sufficient to allow full reduction of the CoO film as confirmed by XPS. Consistent with electrochemically lithiated CoO electrodes, precipitation of Co nanoparticles in a Li_2O matrix was observed in TEM images. However, at room temperature, the Li-rich overlayers that formed on the CoO film after initial lithiations inhibited further Li diffusion. This could be due to the intrinsically poor kinetic properties of Li_2O or to the formation of Li_2O_2 and/or LiOH passivating films.

The reactivity of CoO films was also found to depend on the orientation of the film. CoO(100) films exhibited a higher degree of conversion for a given Li exposure than polycrystalline films. STM and angle-resolved XPS of these films have been used to investigate the differences between these two film morphologies upon exposure to Li.

Authors Index

Bold page numbers indicate the presenter

— B —

Bak, S.-M.: IS+EN+SP+SS-ThA3, 1
Bartynski, R.A.: IS+EN+SP+SS-ThA9, 2
Bonnell, D.A.: IS+EN+SP+SS-ThA1, 1

— C —

Chang, W.: IS+EN+SP+SS-ThA3, 1
Chung, K.-Y.: IS+EN+SP+SS-ThA3, 1
Cosandey, F.: IS+EN+SP+SS-ThA9, 2

— D —

Donaldson, S.H.: IS+EN+SP+SS-ThA6, 1

— G —

Gebbie, M.A.: IS+EN+SP+SS-ThA6, 1
Giannuzzi, L.A.: IS+EN+SP+SS-ThA2, **1**

— H —

Harmer, M.P.: IS+EN+SP+SS-ThA2, 1
Hu, E.: IS+EN+SP+SS-ThA3, 1
Hwang, S.: IS+EN+SP+SS-ThA3, 1

— I —

Israelachvili, J.N.: IS+EN+SP+SS-ThA6, 1

— K —

Kim, K.-B.: IS+EN+SP+SS-ThA3, 1
Kristiansen, K.: IS+EN+SP+SS-ThA6, 1
Kungas, R.: IS+EN+SP+SS-ThA1, 1

— N —

Nam, K.-W.: IS+EN+SP+SS-ThA3, 1
N'Diaye, A.: IS+EN+SP+SS-ThA7, **1**
Nonnenmann, S.S.: IS+EN+SP+SS-ThA1, **1**

— R —

Rangan, S.: IS+EN+SP+SS-ThA9, 2

— S —

Sina, M.: IS+EN+SP+SS-ThA9, 2
Stach, E.: IS+EN+SP+SS-ThA3, **1**

— T —

Thorpe, R.: IS+EN+SP+SS-ThA9, **2**

— V —

Valtiner, M.: IS+EN+SP+SS-ThA6, **1**
Vohs, J.M.: IS+EN+SP+SS-ThA1, 1

— Y —

Yang, X.-Q.: IS+EN+SP+SS-ThA3, 1
Yu, X.: IS+EN+SP+SS-ThA3, 1
Yu, Z.: IS+EN+SP+SS-ThA2, 1