

Energy Harvesting & Storage Room Lehua - Session EH-TuE

Battery/Supercapacitor Coatings, egs., Li⁺ Batteries & Thermo-/Piezo-electrics

Moderator: Takuya Masuda, NIMS (National Institute for Materials Science), Japan

6:00pm EH-TuE2 Electrochemistry at Well-defined Interfaces in Organic Environments, *Nenad Markovic*, Argonne National Laboratory, USA

In recent years, improvements in the fundamental understanding of electrochemical interfaces and their role in electrocatalytic processes have started to revolutionize the development of alternative energy systems for clean energy production, storage and conversion. In many respects the subject of surface electrochemistry in aqueous environments is more advanced than the corresponding understanding of interfaces in organic solvents. This is due to a long-standing difficulty associated with developing in-situ methods that are capable of characterizing interfaces at atomic-/molecular levels in organic solvents. This intrinsic disparity in understanding, however, has a tendency to mask the inherently close ties that exist between interfacial phenomena in aqueous and organic environments [1]. In this presentation, by building a bridge between these two artificially differentiated types of interfaces will allow for us to define the landscape of parameters that control the coupled roles of surface structure, chemical identity, electrostatic field, solvation and other related factors that determine the functional links between activity, selectivity and stability of any electrochemical interface. Selected example will be discussed, ranging from oxygen electrochemistry to metal deposition of Mg all the way down to intercalation processes on well-defined single crystal oxide materials. We identify the profound impact of trace levels of H₂O (<3ppm) on the kinetics of Mg deposition as well Mg intercalation in a layered V₂O₅ compound. Two types of water has been found; a "bad water", that via the formation of MgO and Mg(OH)₂ passive films inhibits Mg deposition as well as a "good water" that helps intercalation of Mg²⁺ into V₂O₅ structures [2]. We conclude that understanding the complexity of electrochemical interfaces would open new avenues for design and deployment of alternative storage systems.

References:

1. V.R. Stamenkovic, D. Strmcnik, P. Lopes, and N.M. Markovic, *Nature Materials* (2016), in press.
2. S. Tepavcevic, C. Johnson, N.M. Markovic and T. Rajh, *ACS Nano* 9 (2015) 8194.

6:20pm EH-TuE3 Coupling in-situ TEM and Ex-Situ Analysis to Understand Heterogeneous Sodiation of Antimony, *David Mitlin*, Clarkson University, USA

We employed an in-situ electrochemical cell in the transmission electron microscope (TEM) together with ex-situ time-of-flight, secondary-ion mass spectrometry (TOF-SIMS) depth profiling, and FIB - helium ion scanning microscope (HIM) imaging to detail the structural and compositional changes associated with Na/Na⁺ charging/discharging of 50 and 100 nm thin films of Sb. TOF-SIMS on a partially sodiated 100 nm Sb film gives a Na signal that progressively decreases towards the current collector, indicating that sodiation does not proceed uniformly. This heterogeneity will lead to local volumetric expansion gradients that would in turn serve as a major source of intrinsic stress in the microstructure. In-situ TEM shows time-dependent buckling and localized separation of the sodiated films from their TiN-Ge nanowire support, which is a mechanism of stress-relaxation. Localized horizontal fracture does not occur directly at the interface, but rather at a short distance away within the bulk of the Sb. HIM images of FIB cross-sections taken from sodiated half-cells, electrically disconnected and aged at room temperature, demonstrate non-uniform film swelling and the onset of analogous through-bulk separation. TOF-SIMS highlights time-dependent segregation of Na within the structure, both to the film-current collector interface and to the film surface where a solid electrolyte interphase (SEI) exists, agreeing with the electrochemical impedance results that show time-dependent increase of the films' charge transfer resistance. We propose that Na segregation serves as a secondary source of stress relief, which occurs over somewhat longer time scales.

6:40pm EH-TuE4 Polymer-based Piezoelectric Nanogenerators for Energy Harvesting Applications, *Sohini Kar-Narayan*, University of Cambridge, UK INVITED

Harvesting energy from ambient sources in our environment has generated tremendous interest as it offers a fundamental energy solution for 'small power' applications, including, but not limited to, ubiquitous wireless sensor nodes; portable, flexible and wearable electronics; biomedical implants and structural/environmental monitoring devices. Energy harvesting from ambient vibrations is particularly attractive as these are ever present and easily accessible, originating from sources such as moving parts of machines, fluid flow and even body movements. In this context, piezoelectric materials offer the simplest means of directly converting mechanical vibrations into electrical power and are well suited for microscale device applications, thus offering a means of superseding traditional power sources such as batteries that require constant replacing/recharging and that do not scale easily with size. In particular, nanoscale piezoelectric energy harvesters, or *nanogenerators*, are capable of converting small ambient vibrations into electrical energy, thus paving the way for the realisation of the next generation of self-powered devices. A recent review article from our group [1] highlighted the fact that nanogenerator research to date has mainly focused on traditional piezoelectric materials in the form of ceramics, but these are stiff and prone to mechanical failure. On the other hand, piezoelectric polymers [1-3], although less well studied, have several advantages over ceramics such as being flexible, robust, lightweight, easy and cheap to fabricate, lead free and bio compatible. However, they do suffer from inferior piezoelectric properties in comparison to ceramics. The field thus faces orthogonal difficulties associated with these two classes of materials. In this talk, I will discuss work from our group aimed at developing novel hybrid polymer-ceramic nanocomposites [2,4,5] combining the best of both materials, while developing scalable nanofabrication techniques for flexible, low-cost and highly efficient polymer-based nanogenerators and sensors.

[1] S. Crossley, R.A. Whiter & S. Kar-Narayan, *Materials Science and Technology* 30, 1613 (2014).

[2] R.A. Whiter, V. Narayan & S. Kar-Narayan, *Advanced Energy Materials* DOI: 10.1002/aenm.201400519 (2014)

[3] S. Crossley & S. Kar-Narayan, *Nanotechnology* 26, 344001 (2015).

[4] C. Ou, P. E. Sanchez-Jimenez, A. Datta, F. L. Boughey, R. A. Whiter, S.-L. Sahonta & S. Kar-Narayan, *ACS Applied Materials & Interfaces* DOI: 10.1021/acsami.6b04041 (2016)

[5] F. L. Boughey, T. Davies, A. Datta, R. A. Whiter, S.-L. Sahonta, S. Kar-Narayan, *Nanotechnology (Letters)* 27, 28LT02 (2016).

7:40pm EH-TuE7 High-Resolution Observation of Electronic Properties of a Cathode Material in a Li-ion Battery, *Ryuma Osaka*, Kansai University, Japan

Li-ion batteries are widely used in many portable electronic devices and are recognized to be energy storage devices for mass-produced electric vehicles. However, to improve of power density, durability and safety, it is crucial to optimize the structure of the electrode as well as exploring new materials because the kinetics of the electrode reaction depends on the structure of the composite electrode.

The main elements are positive electrodes, negative electrodes, separators, and electrolytes. The electrolyte is typically a nonaqueous mixture of organic carbonates containing complexes of Li ions, which are noncoordinating anion salts such as Li hexafluorophosphate (LiPF₆). The separator is, for example, monolayer polypropylene. The electrode materials hold the key to determine the performance of the batteries. They are generally intercalated lithium compounds. Depending on the materials, the voltages, capacities, and lifetimes of the batteries greatly change. Therefore, they have been actively investigated.

The cathode material is also an oxide such as lithium cobalt oxide (LiCoO₂). Concerning the cathode materials, some materials, Li₂MnO₃, Li_{1.2}Mn_{0.4}Fe_{0.4}O₂, LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂, etc., have been proposed, developed, and investigated. Redox of the transition metal oxides or valence fluctuation of transition metals play important roles of charge neutral. Therefore, not only ionic conductivity but also electronic conductivity is important for battery operation. However, electric conductivity varies with valence fluctuation of the transition metals due to extraction or insertion of Li ions. We present results on a change in band structure of LiCoO₂ corresponding to the Li-ion concentrations, which were obtained via a scanning probe microscope.

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