

Recent Li Ion battery research: where we are and where we need to be.

Effect of Cobalt Incorporation and Lithium Enrichment in Lithium Nickel Manganese Oxides H. Deng, I. Belharouak, H. Wu, D. Dambournet, and K. Amine Journal of The Electrochemical Society, 157, 7, A776-A781 (2010)

MLi₂Ti₆O₁₄ (M = Sr, Ba, 2Na) Lithium Insertion Titanate Materials: A Comparative Study Damien Dambournet, Ilias Belharouak, and Khalil Amine Inorg. Chem. 2010, 49, 2822–2826

Lithium Tetrafluoro Oxalato Phosphate as Electrolyte Additive for Lithium-Ion Cells Yan Qin, Zonghai Chen, Jun Liu, and Khalil Amine Electrochemical and Solid-State Letters, 13, 2, A11-A14 (2010)

Nanostructured Lithium Nickel Manganese Oxides for Lithium-Ion Batteries Haixia Deng, Ilias Belharouak, Russel E. Cook, Huiming Wu, Yang-Kook Sun, and Khalil Amine, Journal of The Electrochemical Society, 157, 4, A447-A452 (2010).

Olivine electrode engineering impact on the electrochemical performance of lithium-ion batteries Wenquan Lu, Andrew Jansen, Dennis Dees, and Gary Henriksen J. Mater. Res., 25, 8 (2010)

Recommended and with a commentary by Albert Migliori, Los Alamos National Laboratory.

Energy storage in all its forms is continually evolving but in the 21st century the need has become urgent for electrical energy storage science. Today, electrochemical storage uses highly engineered systems of supports, catalysts, and electrolytes to control processes that are intrinsically nanoscale. However, as we see with the papers cited above, modern science approaches do not lead to general engineering principles because they are primarily phenomenological, continuum, macroscopic, and empirical. Needed is a combination of physics and chemistry to take the clues provided by these and many other works and craft from them a fundamental scientific understanding. This is not an easy task.

Among other things, there are two global processes that govern the science that determines energy losses above the thermodynamic minimum in batteries and fuel cells. One is the dissociation of the input chemical at the surface of an electrode. The adsorptive dissociation of the reactant is affected by the electronic density of states of the catalyst, the surface electronic and physical structure, the work function, and the electrolyte. The other is the irreducible single-ion viscous drag as a single reactant is dragged away from the electrode through regions of extreme electric fields (this region is the charged double-layer or Debye screening region). These losses are affected by the gradients of the electric fields, composition of all components, the distance through which a charged species must move before reaching a region of low electric field, and the viscosity itself.

In examining several recent papers on Li-Ion batteries, we find several hints of fundamental science needs. These papers describe high quality phenomenological studies of Li-ion-based chemistry processes in storing and recovering electrical energy. Among these selections, work on the electrolyte, the electrodes, the nanostructure, and more are described. The experimental tools brought to bear include electron microscopy [1,2,3,4,5], differential scanning calorimetry (DSC)[1], x-ray diffraction (XRD)[1,2,4], electrochemical impedance spectroscopy[1,3,5] (EIS) below 100kHz, simple battery capacity [1,2,3,4,5], cyclic voltammetry (this is what chemists call an I-V curve) [2]. The major conclusions that point toward fundamental processes and the need for more microscopic studies are outlined below.

Ref [1] compares some macroscopic properties of Li_(1+x)Ni_{0.25}Co_{0.15}Mn_{0.6}O_(2.175+x/2) electrodes to a cobalt-free optimized sample. In these systems, extensively studied, it is conjectured that the layered structure and transition-metal ions are important. But we really do not know the how and why. Noting that the charged double layer where all the electrochemical action occurs is of order a nanometer thick, the only probe brought to bear in this work that has a real microscopic component is EIS. This is because the primary component of the electrical impedance of a battery using this material arises from action in the Debye screening layer. In this region, the concept of continuum dielectric constant fails, the electric fields are so high that electrostrictive

forces produce very substantial pressures, and the surface structure can be modified easily by the thermodynamics. EIS measures charge transport and polarization in this microscopic region of extreme conditions. But there is little in the way of theory to understand just what is going on so that it can be connected to electrode chemistry and structure. Interestingly, XRD produces unexpected line broadening. Is this a result of pressure and electric fields in the Debye screening region? Can a microscopic analysis be had? Without a theory backup to these excellent measurements, the search for improvements in performance can be dauntingly broad.

In Ref [2], the $MLi_2Ti_6O_{14}$ ($M = Sr, Ba, 2Na$) titanates that exhibit open channels mediate reversible insertion of lithium ions when made into electrodes for batteries, something very desirable. The striking crystallographic studies show these channels. Their tunable electrochemical properties make them stable at the intermediate voltages needed for the common electrolytes used. The I-V characteristics however, show some sort of initial conditioning. Why is this? What is trapping Li? Can we generate a microscopic model of transport? The problem is that there are insufficient microscopic data to work with. Reference [3] measures the effect of Lithium Tetrafluoro Oxalato Phosphate (LTFOP) electrolyte additive as a protective passivation generator. The chemistry is well studied, but the solid-electrolyte interface (where the action is) leaves important open questions that remain unresolved as to why charge transport through this layer is so good. The EIS study shows a complicated impedance (real and imaginary) versus frequency, a potentially microscopic datum, but no microscopic theory or explanation for its details. Thus a useful measurement raises an important set of questions that battery engineers could use answers to, but without a microscopic attack, there is little hope.

The XRD patterns of these important positive-electrode materials, nanostructured lithium nickel manganese oxides, [4] do not fit the expected description of a one-layer structure. The materials, in nanoscale particles, exhibit both layer and spinel phases. This complex structure introduces possibly geometric effects on local electric fields in the Debye screening region. That is, do electric field enhancements and gradients arising from morphology introduce important drivers for chemical reactions? In this study, the authors conclude that the primary effects are from geometry but we lack what amounts to a nanoscale electrostatics approach, and the tools to measure electric fields at the length scale over which chemistry occurs. However, hints abound. Does the observed unusual broadening of XRD peaks mean that the local environment is unusual? What is driving the move away from layers into the spinel phase? Is it thermodynamics at small length scales? Do the mysterious changes in unit cell volume from those expected indicate electrostrictive forces etc?

The composite electrode of $LiFePO_4$ active material [5] was studied with an eye to understanding electrode porosity. However, only EIS could get a window on the observed performance changes. Can electrostatics at nanometer length scales help? What probes should be used? With the structures investigated here, viscosity is an obvious target, but there is a dearth of insight into the effects of high electric fields and nanometer length scales on the viscosity. We see then, that microscopic probes are critically needed to provide the foundation for predictive theories. NMR, Raman, scattering probes, wet electron microscopy and tunneling microscopy, and more could help.