Three-Dimensional Measurements of Li Ion Battery Electrodes Using FIB-SEM
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In collaboration with Dr. Stephen J Harris of General Motors, we have carried out three-dimensional microstructure measurements of Li ion battery positive electrodes with the aim of studying battery degradation mechanisms. The ISEN funding has allowed us to establish a presence in the Li-ion battery field based on our unique capabilities for 3D microstructure measurements. The ISEN-funded work has led to this topic becoming a central theme in the first real energy IRG in the MRSEC proposal. Work is also underway on a DoE BES proposal on this topic.

The ISEN funding has allowed for early work applying focused ion beam – scanning electron microscopy (FIB-SEM) to determining the three-dimensional microstructure of Li-ion battery positive electrodes. The FIB-SEM measurements can provide 3D structural information that is typically lacking for battery electrodes, such as surface area density, average Li intercalation path lengths, and volume percentage of electronically isolated electrode. Such data could provide a basis for developing more-detailed models for battery performance.

Five commercial laptop computer battery samples were used in this study: an unused and a cycled (~20% capacity loss) LiCoO₂ electrode, as well as an unused, a moderately cycled, and a heavily cycled Li(Co₃Mn₁/₃Ni₁/₃)O₂ / LiCoO₂ composite electrode. The samples were then serial-sectioned with a FIB-SEM in order to achieve quantitative electrode structural data. Figure 1 shows a typical cross-sectional micrograph of the composite electrode, with 3D image renderings of individual particles of each electrode composition displayed at the top. In addition to the individual particles shown, complete 3D reconstructions of the bulk volume of the electrodes were achieved, as shown in Figure 2 for the uncycled LiCoO₂ electrode, in order to calculate macroscopic structural properties with confidence.

Figure 1. Two 3D image renderings showing respective LiCoO₂ and Li(Co₁/₃Mn₃/₃Ni₁/₃)O₂ particles of a composite positive electrode. A cross-sectional micrograph at the bottom illustrates each type of particle.
It was observed that most of the LiCoO₂ particles have internal cracks that extend to the particle exteriors, such that there are additional electrolyte/oxide interfaces where Li can enter/leave the particles. The anisotropic particle shape and presence of internal cracks leads to surfaces areas 50 – 100% larger than obtained if one assumes spherical particles with the same volume. This can impact both interfacial kinetics and the average Li bulk diffusion distance. For example, in one case it was found that 23% of the volume of a LiCoO₂ particle was closer to the internal surface of cracks, compared to the shortest distance to the outer surface. While the Li(Co₃Mn₁/₃Ni₁/₃)O₂ particles also had internal porosity, the pore networks were isolated within the particle and were inactive for electrode-electrolyte charge transfer. It is possible the porosity is an artifact of the particle processing, or is a natural result of the volume expansion and contraction that occurs upon lithium insertion and removal.

It was also observed that many of the LiCoO₂ particles and all of the Li(Co₃Mn₁/₃Ni₁/₃)O₂ particles consisted of multiple grains. Figure 3 shows EBSD data for the LiCoO₂ electrode, emphasizing a multi-grained particle that also was starting to form cracks along the grain boundaries. In the case of the Li(Co₃Mn₁/₃Ni₁/₃)O₂ particles, the grain boundaries extended radially from the center of the particle, perhaps enhancing the surface area and thus the electrochemical performance.
the Li intercalation through direct grain-boundary diffusion.

The 3D measurements may also provide new insights into electrode degradation. Initial results on the electrode structure before and after cycling were analyzed. In both types of electrodes it was observed that the LiCoO$_2$ particles showed slight decreases in surface area, suggesting a mechanism for coarsening, perhaps through Co diffusion in the electrolyte. Further work is underway to better understand these observed changes. Another effect of interest is whether there is any change in connectivity which would result in electrically isolated particles. This calculation is challenging due to the fact that once the pore structure has been infiltrated with epoxy, the binder and conductive carbon present in the electrode can no longer be distinguished. Further efforts to identify these phases are currently being conducted.

**Publications:**

**Presentations:**

S. Harris, P. Shearing, N. Brandon, L. Howard, P. Jorgensen, J. Wilson, J. Cronin and S. Barnett, "3-Dimensional Characterization of Li-Ion Battery Electrodes" 217th ECS Meeting, April, 2010, Vancouver, BC, Canada
