Tracking Displacement Reactions in Cu\textsubscript{x}V\textsubscript{2}O\textsubscript{5} Cathodes by in-situ TEM

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In order to meet the growing demand of the rapidly-miniaturized electronics and high-power mobile devices (i.e. hybrid electric vehicles), a lot of new electrode materials are studied to replace the traditional LiCoO\textsubscript{2} (cathode) and graphite (anode). Cu-V-O compounds with high capacity (~250-500 mAh.g\textsuperscript{-1}) have emerged as one of the most promising cathode materials for next-generation lithium ion batteries. However, for these applications one of the issues is the poor cycle life, namely capacity decay with cycling. In these compounds, the reduction/oxidation of Cu between 2+ and 0, which results in local formation/consuming of metallic Cu nanostructures, leads to significant changes in both crystal structure and morphology [1]. Whether the structure/morphology can be fully reversed or not during cycling significantly influences its electrochemical performance, e.g., capacity, cycling stability, therefore it’s crucial to understand these structural and morphological evolutions in Cu-V-O cathode material during cycling.

To track physical and chemical changes in the live electrodes of batteries, various in situ techniques have been developed. However, most of these techniques, such as those based on X-ray scattering, are suited for studying bulk electrodes but has no adequate spatial resolution to probe physical and chemical evolutions at the scale of nanometer. In contrast, in situ TEM, with access to local reactions down to nanometer scale, has become a unique tool to determine where and how new phases nucleate and propagate within single nanostructure. Here, we designed two different electrochemical cells for use in the TEM by employing solid and liquid electrolyte respectively to study the electrochemical reaction of Cu\textsubscript{x}V\textsubscript{2}O\textsubscript{5} nanostructures with lithium. A solid in-situ cell consists of a mobile lithium probe and thin lithium oxide layer on the lithium surface acting as solid electrolyte [2] and individual Cu\textsubscript{x}V\textsubscript{2}O\textsubscript{5} nanorods coated with carbon as cathodes. During lithiation, fine particles with bright contrast in scanning TEM (STEM) high angle annular dark field (HAADF) image appear gradually as shown in Figure 1a. They are metallic Cu, as further verified by high-resolution TEM and electron energy loss spectroscopy (not shown here). The extrusion of Cu preferentially nucleates from specific facets rather than uniformly from the entire surface. For example, large amount of Cu extruded from the top facet to form a large metallic cluster (highlighted by yellow arrows in Figure 1a), implying the barrier to migration of Cu ions along this channel is much lower than that of others. Even on the same facet extrusion of Cu is very often non-uniform, which may be due to the local structural defects (highlighted by red arrows in Figure 1a). Upon de-lithiation, some of created Cu particles are not consumed completely, which may account for the capacity decay of Cu\textsubscript{x}V\textsubscript{2}O\textsubscript{5} electrodes (Figure 1b).

These results based on a solid electrolyte cell inside TEM give insightful information on structural and chemical evolution of electrodes with high resolution, but some of fundamental electrochemical phenomena in real batteries with common LiPF\textsubscript{6}-based organic carbonate electrolyte are not accessible from this configuration of battery cells. A fully sealed and compact liquid cell was assembled with liquid electrolyte, Cu\textsubscript{x}V2O5 electrode and lithium metal counter electrode for in situ TEM studies. Although the spatial resolution is sacrificed, the in situ TEM measurements using liquid battery cell can provide more precise information of how the battery works under real electrochemical conditions. Such
experiments are ongoing and more results will be presented, for comparison to the in-situ TEM observation using solid cells.[3]

References:

[3] The authors gratefully acknowledge the financial support through LDRD.

Figure 1. (a) Time-lapse high angle annular dark field (HAADF) images of Cu₃V₂O₅ nanorods upon lithiation, showing gradual formation of metallic Cu particles (highlighted by arrows). (b) Representative STEM-HAADF images of Cu₃V₂O₅ nanorods from in-situ measurement for the first cycle, showing that some of the extruded Cu nanostructures cannot be inserted back.