

## In-Situ TEM Characterization of Electrochemical Systems

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Transmission electron microscopy (TEM) is a powerful tool for characterizing materials with high temporal and spatial resolution. The development of various techniques to construct specimens that maintain special environments has broadened the application spectrum of TEM. In particular, the research of electrochemistry for energy applications in liquid environments is of great interest. As the technique is still in its early stages, fundamental investigations using model systems are also important. Two well-studied aqueous electrochemical systems [1-4] were investigated using this new technique, along with a preliminary observation of a fully packed lithium ion battery system.

A novel in-situ electrochemical wet cell comprising of two separate silver electrodes in aqueous  $\text{Ag}_2\text{SO}_4$  solution was used as a first model system, which demonstrated the considerations that must be made when utilizing this technique. The high-energy electron beam can both knock-out secondary electrons from a material and also inject free electrons to the system. This can lead to the ionization of the electrode as well as the reduction of cations from the electrolyte. The competition of each phenomenon will be influenced by the intensity of the electron beam along with the concentration of the electrolyte. The dynamic dissolution and deposition of the silver electrodes were observed in this system, and the extent of dissolution of the initial electrodes was found to be dependent on the concentration of the electrolyte as well as the strength of the beam. That is, the electrodes will largely dissolve in dilute solutions whereas they would maintain stability in saturated solutions. Also reaction rate was a function of beam current, with increased dissolution at higher beam currents. This indicates that the effect of the electron beam may also play an important role in the observation of certain systems and must be taken into account. These results were utilized to select an ideal electrolyte composition for characterizing electrochemical response, electrodeposition and electropolishing, in the system.

Electrodeposition and electropolishing of nickel was also observed, for comparison, using nickel electrodes within an aqueous  $\text{NiCl}_2$  solution (FIG. 1.). The investigation revealed a much more anisotropic electrodeposition rate in which spreading of the nickel film occurred much more rapidly than thickening. Electrodeposition in the system was driven much more by nucleation than crystal growth, leading to very anisotropic growth rates perpendicular and normal to the substrate. Electropolishing occurred much more uniformly.

Based on the successful observation of aqueous systems, a fully assembled battery comprising of a  $\text{LiCoO}_2$  thin film as the cathode and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanoparticles dispersed on a carbon film as the anode

with a standard organic lithium electrolyte as the electrolyte was also observed with TEM. Only the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanoparticles could be viewed in the specimen that was used (FIG. 2.). Preliminary results show promise of the capability to observe actual lithium ion battery systems in-situ via TEM [5].

### References

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- [5] The Authors would like to acknowledge the support from the National Science Foundation Division of Materials Research's Ceramics Program under contract DMR# 0906874. Microscopy was carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471.

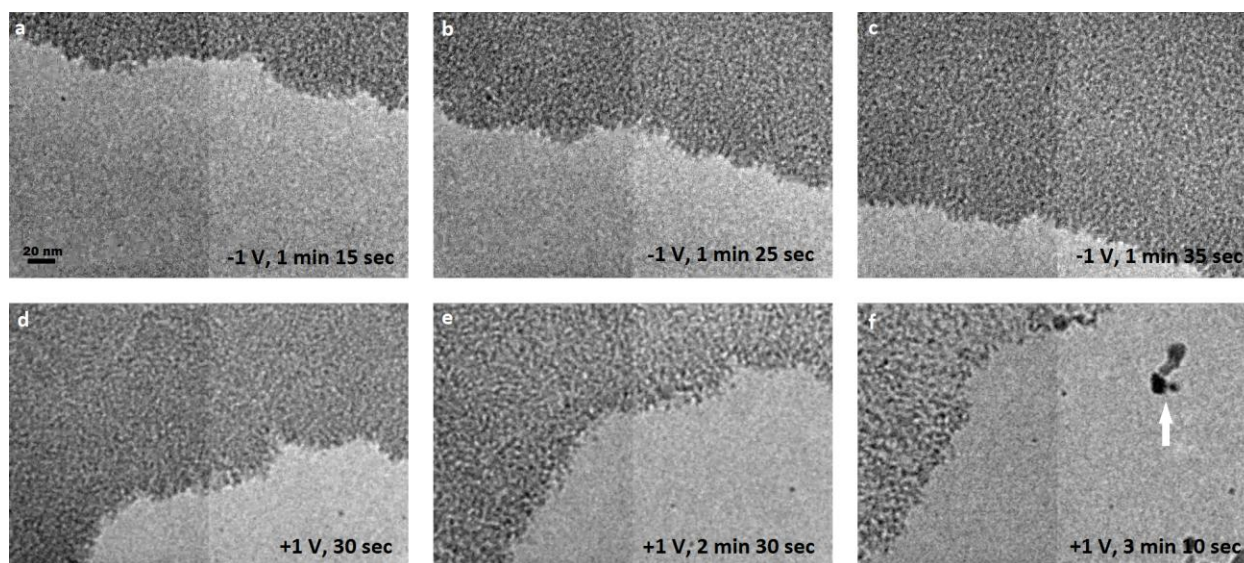


FIG. 1. In situ TEM observation ( $\times 100,000$ ) of nickel electrodeposition under  $-1$  V bias, at: (a) 1 min 15 sec; (b) 1 min 25 sec; (c) 1 min 35 sec; and electropolishing under  $+1$  V bias at: (d) 30 sec; (e) 2 min 30 sec; (f) 3 min 10 sec. The arrow in (f) indicates a particle migrating from the bottom toward the nickel electrode at the top.

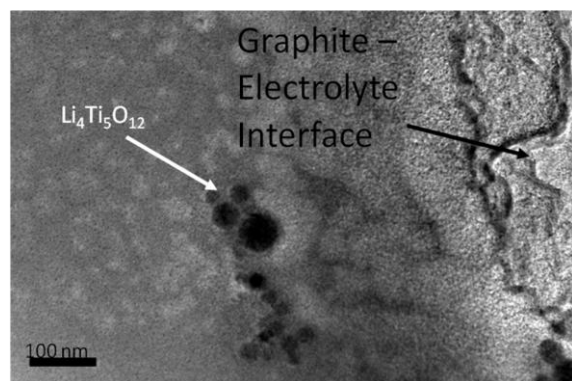


FIG. 2. TEM image of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanoparticles in a fully packed lithium ion battery.