

Problem Statement

“Until you get down to the microscopic and nanoscopic level...you can’t truly address those issues that come up.”

— Raymond Unocic, Oak Ridge National Laboratory

Lithium is an ideal metal for use in lithium-ion battery anodes due to its high energy density and high theoretical capacity. However, the two primary difficulties impeding the incorporation of Li anodes into secondary batteries are the formation of an unstable solid electrolyte interface (SEI) and the formation of dendrites which can cause the battery to short-circuit. These issues have plagued the development of Li-ion battery technology for decades. Consequently, an understanding of the nanoscale mechanism behind these processes is critical to overcoming these limitations.

Background

Li-ion batteries represent the standard cells used in portable electronics, such as cell phones and laptops. These batteries consist of a lithium based cathode, such as lithium cobalt oxide, and graphite as the anode. However, because of graphite’s limited storage

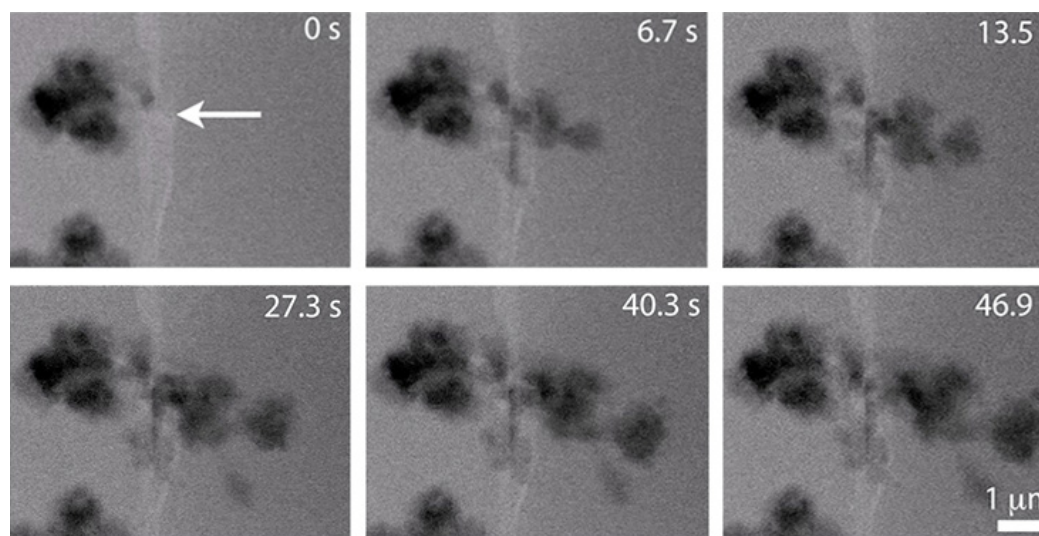
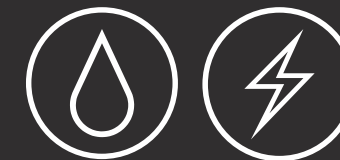


Figure 1: Series of ADF STEM images showing nucleation and growth of Li metal from GC electrode.

capacity, novel materials are needed to resolve the issues which current batteries face, in terms of greater cycle life, charge lifespan and energy density. Li metal is regarded as the ideal anode material, due to its high energy density and high theoretical capacity. However, for Li to be used as a cathode material, the underlying mechanism of dendrite and SEI formation needs to be thoroughly understood. Transmission electron microscopy has long been regarded as one of the most powerful tools available for the study of nanoscale processes. *In situ* TEM has been used

for years to study chemical and physical processes as they happen in real time, with unprecedented resolution. *In situ* liquid-cell TEM combines this nanoscale spatial resolution with the ability to simulate real life battery operations. As requirements for rechargeable batteries become greater, with regards to longer lifetimes and greater safety, *in situ* TEM will remain one of the most important techniques for understanding the chemical and physical processes that take place inside a battery during operation.



Methods

The Microscopy Group at Oak Ridge National Labs in Tennessee have used the latest advances in liquid cell fabrication and *in situ* TEM to study these two critical processes as they occurred. Led by Raymond R. Unocic, they used the Poseidon system along with a Cs aberration corrected FEI Titan operating at 300 kV. The Poseidon system enables the simultaneous use of quantitative STEM imaging and quantitative electrochemical measurements, allowing the team to study Li electrodeposition and SEI formation in great detail.

Conclusions

Site-specific reactions and structures were studied while performing controlled electrochemical sweep measurements, accurately representing the operation of a Li metal based Li-ion battery. Due to weak elastic scattering, it is difficult to study light elements such as Li using standard phase-contrast TEM imaging. However, ADF STEM imaging is very sensitive to light elements and so is an ideal technique for observing lithium deposition. Using the STEM image intensity, the team at Oak Ridge National Labs

determined that the SEI layer was twice as dense as the electrolyte. They also showed that image intensity could be used to estimate the mass and thickness of lithium deposits. Overall, they demonstrated that the Poseidon system *in situ* electrochemical holder could effectively combine detailed and quantitative electrochemical measurements with quantitative imaging in liquids. This makes *in situ* ec-S/TEM a potent method for studying electrochemical reactions, a vital prerequisite for future advancement of Li-ion batteries. Contact us to discuss the full range of capabilities of Poseidon Select. We can be reached at (919) 377-0800 or at contact@protochips.com.