

Detailed Investigation of the Interfacial Electrode/Electrolyte Reactions and the Effect of Additives in Li-ion, Li-Sulfur and Li-Air Batteries by Operando *ec*-(S)TEM

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The high demand for new energy storage nanomaterials has created the need for novel experimental techniques that can provide *real-time* information on the dynamic structural changes and reactions that occur locally at the electrode/electrolyte interface inside the battery. The development of *in-situ* liquid electrochemical stages for (scanning) transmission electron microscopes (*ec*-(S)TEM) enables fabrication of a "*nano-battery*" to study the details of electrochemical processes under *operando* conditions. However, the high complexity of electrochemical processes during battery cycling requires careful calibration of the system to circumvent *e*⁻-beam damage and to control the side electrochemical reactions [1]. Here we demonstrate the application of this "*nano-battery*" approach to rechargeable Li-ion, Li-sulfur and Li-O₂ batteries. The full operation of these complex systems is yet not fully understood and typically involves multi-step electrochemical reduction/oxidation reactions, which often lead to lithium dendrite formation. There are many strategies to improve the interfacial stability of the Li anode and control/suppress Li dendrite growth, which is highly dependent on nature of electrolyte itself, such as mixture of different electrolyte solvents, salts and additives (e.g. HF, LiNO₃ etc). In one example, we investigate the role of electrolyte additives on the initial stages of Li deposition/stripping and the SEI layer formation. Under *operando ec*-(S)TEM conditions we can explore the role of the moisture that typically causes fast degradation of the electrolyte but here is used as a "catalyst" that controls the interfacial electrode/electrolyte reactions. With careful calibration of the water content, we obtain precise control of the interfacial reaction mechanism, which leads to suppression of the Li dendrite, increases Coulombic efficiency and to uniform Li grain growth (Figure 1) [2]. Similar mechanisms have been observed with LiNO₃ as an additive to control the mechanism of nucleation, growth and suppression of Li metal dendrites in Li-S batteries.

References:

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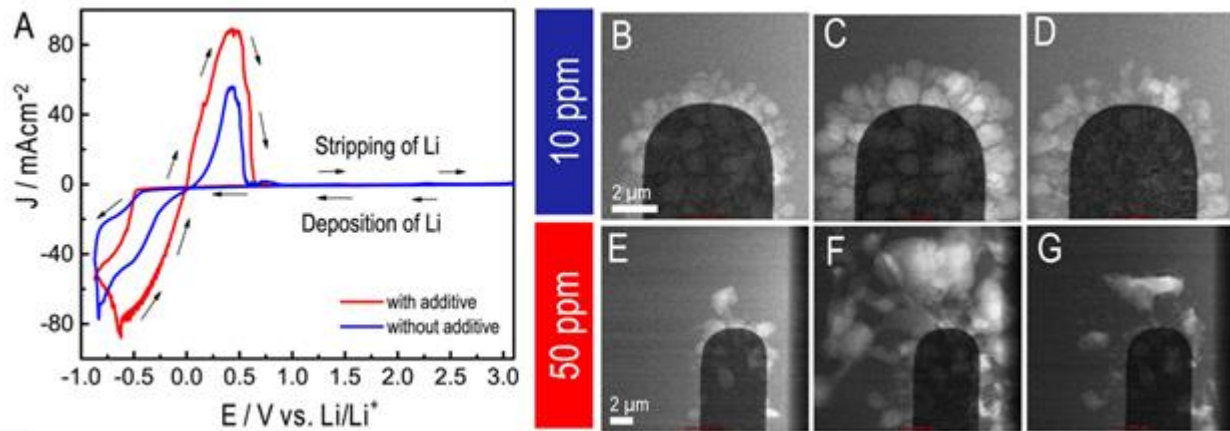


Figure 1. (A) Cyclic voltammograms obtained from the *operando ec*-(S)TEM cell showing the charge-discharge cycle for the electrolytes with 10 and 50 ppm additions of H₂O. Bright field (BF) images showing the deposition/stripping of Li for the electrolyte without additives (B) at the start of the deposition, (C) at the peak of the deposition and (D) after the discharge is complete. BF STEM images showing the same (E - G) for the electrolyte containing 50 ppm H₂O [2].