

Direct Observation of Electrolyte Degradation Mechanisms in Li-Ion Batteries

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The rapidly growing field of new energy storage devices presents a need for non-invasive in-situ/in-operando characterization techniques, which can provide information about the fundamental processes that occur at the electrolyte/electrode interface during battery operation. The electrochemical stability of electrolytes in the new generation of high energy densities batteries is disturbed by both the oxidizing nature of the cathode and reducing nature of the anode, resulting often in the accumulation of insulating side products which leads to capacity fading. The stability of Li-ion electrolytes can be quantified by an electrochemical window that defines the specific voltage range and decomposition limits of each system. Development of *in-situ* liquid electrochemical stages for (scanning) transmission electron microscopes (*in-situ* liquid ec-(S)TEM) enables a real-time study of the electrochemical processes and provides a direct characterization of the degradation processes occurring within Li-ion battery electrolytes and at the electrolyte/electrode interface during charge/discharge cycles.

Here, we demonstrate the application of an *in-situ* liquid ec-(S)TEM stage to study electrolyte degradation mechanisms and new electrochemical windows for state-of-the-art Li-ion battery systems. The electrolyte breakdown is initiated by a localized interaction of the electron beam, and the resulting formation of decomposition products for five different electrolytes commonly used in Li-ion and Li-O₂ battery systems have been determined [1, 2]. Figure 1 shows two different degradation mechanisms of lithium hexafluoroarsenate (LiAsF₆) salt in 1,3-dioxolane, DOL (Figure 1a) and dimethyl carbonate, DMC (Figure 1b). The LiAsF₆ salt is known to undergo reduction during the electrochemical reaction at carbonaceous anodes, forming the LiF precipitants that are frequently observed at the electrode surfaces after battery cycling in electrolytes containing fluorinated salts (such as LiAsF₆ or LiPF₆ [3]). The presence of the liquid in the *in-situ* liquid ec-(S)TEM cell (i.e confirmation that it was a genuine liquid process) was verified by low-loss Electron Energy Loss Spectra (EELS), as shown in Figure 1c. These results demonstrate that the electron beam has the potential to mimic electrochemical reduction, and must be taken into account during in-situ ec-STEM measurements [4].

References:

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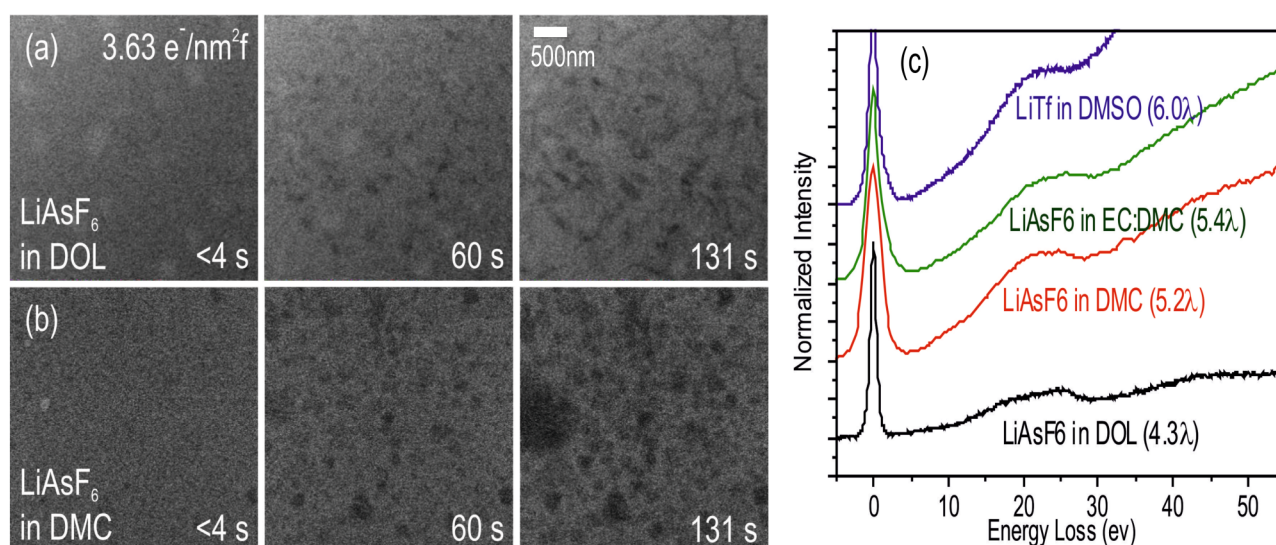


Figure 1. BF STEM images showing degradation in Li-ion battery electrolytes induced by the electron beam. The time evolution of degradation in 1 M LiAsF₆ salt for two different aprotic solvents; (a) DOL and (b) DMC with the dose values per image ($13.7 \text{ e}^-/\text{nm}^2\text{f}$) and exposure times of $t=3.2 \text{ s}$, 60 s , 131 s . (c) EEL spectra of 1M LiTf salt in DMSO electrolyte (purple) and 1M LiAsF₆ salt in EC:DMC (green), DMC (red) and DOL (black) electrolytes measured after the *in-situ* liquid STEM experiments with the thickness as a function of the mean free path (λ) in each spectrum.