The growing need for high energy density rechargeable batteries used in large-scale energy applications has spawned a wide range of in-situ/operando experimental techniques to provide insights into their operation [1, 2]. The recent development of the in-situ liquid electrochemical stages for (S)TEM (in-situ liquid ec-(S)TEM) has enabled the fabrication of a “nanobattery” to study the details of the electrochemical process by providing real-time information on the dynamic structural changes that occur at the electrode/electrolyte interface during charge/discharge cycles. Here, we demonstrate the application of this cell to study fundamental operational mechanisms such as the formation and decomposition of lithium peroxide (Li$_2$O$_2$) in rechargeable Li-O$_2$ batteries, Li-ion battery electrolyte degradation processes and dendrite formation mechanisms and kinetics at Li and Mg anodes.

Li-O$_2$ batteries are being developed for electric vehicles [3,4] due to their high theoretical energy densities - which are comparable to gasoline. The operation of a Li-O$_2$ battery involves the reversible formation/oxidation of lithium peroxide (Li$_2$O$_2$) at the cathode, the efficiency of which determines the overall battery performance. However, Li-O$_2$ batteries exhibit significant challenges - such as low rate capability, limited charge-discharge cycles resulting from decomposition of both the electrolyte and the electrode material during oxygen reduction and evolution. This leads to accumulation of insulating side products, which causes a high overpotential and fast capacity fading during cycling. Here, we use the in-situ ec-(S)TEM cell to investigate the differences in the growth mechanism of Li$_2$O$_2$ nanoparticles and the decomposition of the side products.

Another example of the in-situ ec-(S)TEM cell is to study electrolyte degradation mechanisms and new electrochemical windows for state-of-the-art Li and Mg batteries. The electrolyte breakdown can be initiated by the localized interaction of the electron beam and provide significant understanding of the reduction/degradation products formed during battery operation, which significantly decreases the time of postmodem analysis. The resulting formation of decomposition products and an example the results obtained for 5 electrolytes commonly used in Li-ion and Li-O$_2$ battery systems is demonstrated in Figure 1 [6].

References:

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Fig. 1: STEM images of e-beam induced degradation mechanisms in LiAsF$_6$ in (a) DOL, (b) DMC, (c) EC/DMC, (d) LiPF$_6$ in EC/DMC, (e) highly stable LiTf in DMSO and (f) EC/DMC for the same electron dose and exposure times. (g) post mortem analysis LiAsF$_6$ in DMC and the formation of LiF nanocrystals.