Direct Observation of Li$_2$O$_2$ Nucleation and Growth with In-Situ Liquid ec-(S)TEM

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The rapidly growing field of high energy density rechargeable batteries for large-scale renewable energy applications has generated wide range of in-situ/operando experimental techniques that can provide significant insights into the battery operation [1, 2]. The recent development of the in-situ liquid electrochemical stages for (scanning) transmission electron microscopes (in-situ liquid ec-(S)TEM) enables fabrication of a “nano-battery” to study the details of electrochemical processes providing real-time information on the dynamic structural changes and processes that occur locally at the electrode/electrolyte interface during charge/discharge cycles. Here, we demonstrate application of an in-situ ec-(S)TEM cell to study the formation and decomposition mechanisms of lithium peroxide (Li$_2$O$_2$) in the rechargeable Li-O$_2$ battery system as an alternative to Li-ion batteries.

Li-O$_2$ batteries are currently considered for application in the next-generation electrochemical energy storage technologies and electric vehicles [3-5] due to their high theoretical energy densities, which are comparable to gasoline [6]. The principal operation of Li-O$_2$ battery is based on the mechanisms of reversible formation/oxidation of lithium peroxide (Li$_2$O$_2$) at the porous carbon-based cathode, the efficiency of which determines overall battery performance. However, Li-O$_2$ batteries exhibit a wide range of significant challenges that limit their practical application - 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 an in-situ ec-(S)TEM cell to investigate fundamental differences in the growth mechanism of Li$_2$O$_2$ nanoparticles and decomposition of the side products, which are strongly dependent on the current rate and significantly contribute to the cycling performance of Li-O$_2$ batteries. The quantitative analysis of the charge/discharge products in the standard coin-cell Li-O$_2$ battery show dynamic transition from predominant formation of Li$_2$O$_2$ nanoparticles to predominant formation of side products during the first few cycles as illustrated by in Figure 1 and Figure 2. We observe similar behavior while using the in-situ ec-(S)TEM cell approach with the Pt-single walled carbon nanotubes (SWCTs) microelectrode as a cathode and Pt-Li metal-anode submersed in aprotic electrolyte (1 M LiTf in tetraglyme). This Li-O$_2$ “nano-battery” design provides significant understanding to the origin of Li$_2$O$_2$ nanoparticles formation/oxidation, which leads to fundamental understanding of the long-term cycling stability of high capacity Li-O$_2$ batteries.

References:
Figure 1. SEM images of discharge cycles of Li-O$_2$ batteries. (a) Pristine carbone nanotubes modified with ruthenium nanoparticles (CNTs/Ru electrode); and discharge cycles of CNTs/Ru electrodes after the (b) 1$^{\text{st}}$, (c) 2$^{\text{nd}}$, (d) 3$^{\text{rd}}$, (e) 5$^{\text{th}}$, (f) 10$^{\text{th}}$, (g) 20$^{\text{th}}$ and (h) 50$^{\text{th}}$ cycles in the LiTf-Tetraglyme electrolyte. The significant transition of the Li$_2$O$_2$ particles occurs after the 1$^{\text{st}}$ discharge cycle leading to formation of the thick layer (c-h).

Figure 2. SEM images of discharge cycles of Li-O$_2$ batteries. (a) Pristine CNTs/Ru electrode and charging process of CNTs/Ru electrodes after the (b) 1$^{\text{st}}$, (c) 2$^{\text{nd}}$, (d) 3$^{\text{rd}}$, (e) 5$^{\text{th}}$, (f) 10$^{\text{th}}$, (g) 20$^{\text{th}}$ and (h) 50$^{\text{th}}$ cycles in the LiTf-Tetraglyme electrolyte. The inset shows structural changes at the CNTs/Ru surface after consecutive charging cycles.