

## Direct Observation of $\text{Li}_2\text{O}_2$ 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 ( $\text{Li}_2\text{O}_2$ ) in the rechargeable Li-O<sub>2</sub> battery system as an alternative to Li-ion batteries.

Li-O<sub>2</sub> 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<sub>2</sub> battery is based on the mechanisms of reversible formation/oxidation of lithium peroxide ( $\text{Li}_2\text{O}_2$ ) at the porous carbon-based cathode, the efficiency of which determines overall battery performance. However, Li-O<sub>2</sub> 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  $\text{Li}_2\text{O}_2$  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<sub>2</sub> batteries. The quantitative analysis of the charge/discharge products in the standard coin-cell Li-O<sub>2</sub> battery show dynamic transition from predominant formation of  $\text{Li}_2\text{O}_2$  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 (SWCNTs) microelectrode as a cathode and Pt-Li metal-anode submersed in aprotic electrolyte (1 M LiTf in tetraglyme). This Li-O<sub>2</sub> “nano-battery” design provides significant understanding to the origin of  $\text{Li}_2\text{O}_2$  nanoparticles formation/oxidation, which leads to fundamental understanding of the long-term cycling stability of high capacity Li-O<sub>2</sub> batteries.

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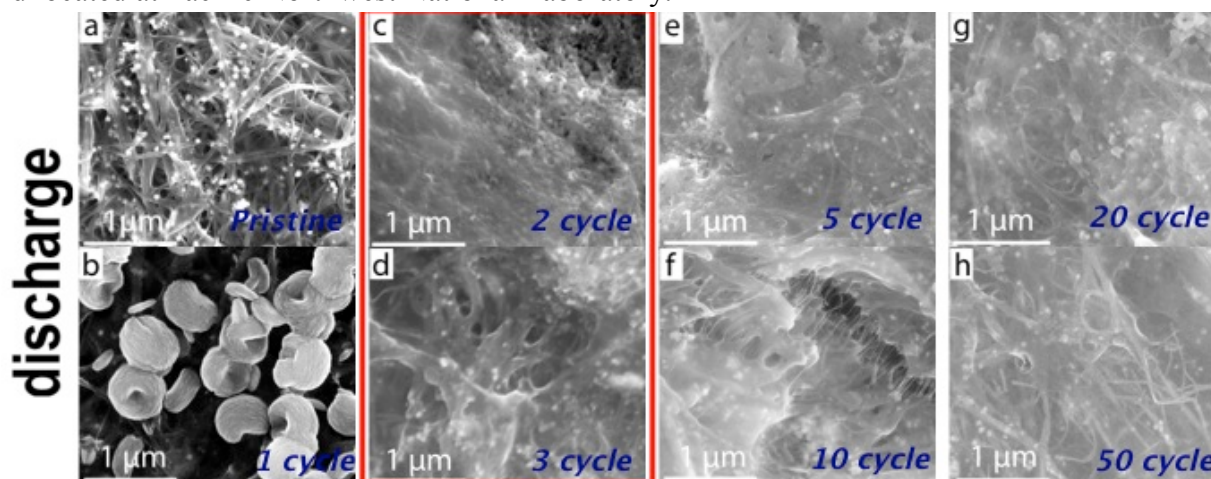
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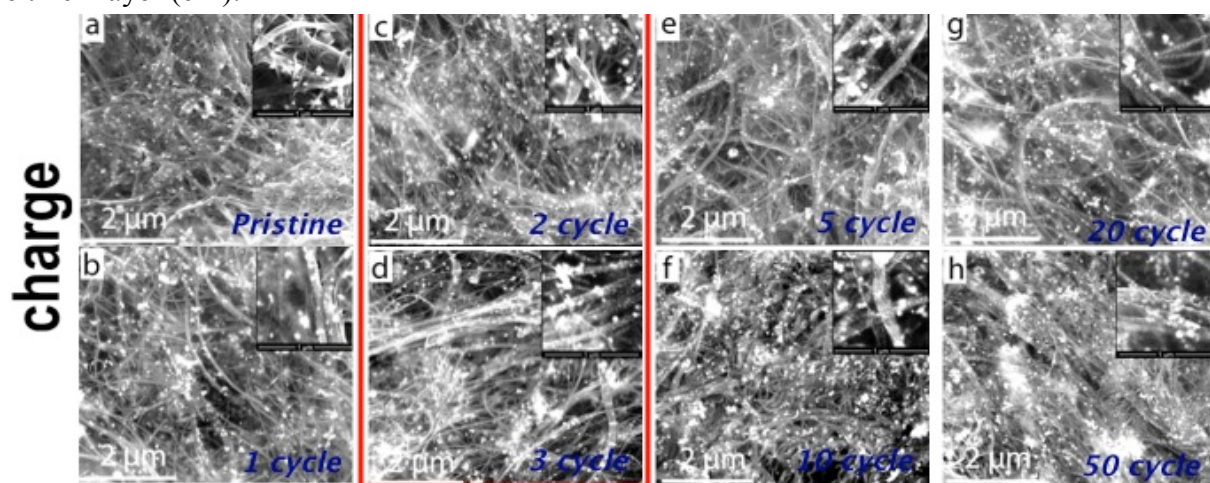
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**Figure 1.** SEM images of discharge cycles of Li-O<sub>2</sub> batteries. (a) Pristine carbon nanotubes modified with ruthenium nanoparticles (CNTs/Ru electrode); and discharge cycles of CNTs/Ru electrodes after the (b) 1<sup>st</sup>, (c) 2<sup>nd</sup>, (d) 3<sup>rd</sup>, (e) 5<sup>th</sup>, (f) 10<sup>th</sup>, (g) 20<sup>th</sup> and (h) 50<sup>th</sup> cycles in the LiTf-Tetraglyme electrolyte. The significant transition of the Li<sub>2</sub>O<sub>2</sub> particles occurs after the 1<sup>st</sup> discharge cycle leading to formation of the thick layer (c-h).



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