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Understanding Li-O_2 Battery Cathode Product Formation via Liquid Cell Electron Microscopy

Saran Pidaparthy[1], Chang Liu[1], Ryan Stephens[2], Qian Chen[1] and Jian-Min Zuo[1]

[1]University of Illinois at Urbana-Champaign, Urbana, Illinois, United States, [2]Shell International Exploration and Production Inc., Houston, Texas, United States

The lithium-oxygen (Li-O_2) battery is a beyond lithium-ion (Li-ion) technology that can provide a theoretical energy density of 3500 Wh/kg, which is ~10 times greater than what state-of-the-art Li-ion batteries can deliver [1]. Despite the energy benefit of Li-O_2 batteries, there are significant scientific challenges to overcome to enable this technology. In particular, we need a deeper understanding of the cathode product evolution during battery cycling and its impact on the performance of the battery [1]–[3]. While there have been many efforts in elucidating Li-O_2 cathode product evolution during battery cycling, there is still disagreement on the growth mechanisms responsible limiting the battery efficiency. With the advent of liquid cell electron microscopy and electrochemical biasing sample holders, such transient battery phenomena can be measured at high spatial and temporal resolution. When this technique is adapted to a Li-O_2 system, we have a method to resolve the growth mechanism by capturing the discharge product growth processes on a Li-O_2 cathode in real-time during battery cycling.

Here, we report direct observation of Li-O_2 battery cathode discharge product formation via in-situ liquid cell electron microscopy. The experiments were carried out using a Hitachi 9500 environmental TEM with a LaB_6 emitter (Hitachi High-Technologies Corp.) operated at 200 kV combined with a liquid-flow, electrochemical-biasing TEM holder (Hummingbird Scientific). To mitigate the electron beam effect, the dose rate was maintained at $< 0.7\ e^-/Å^2s$. Adapted from prior literature [4]–[6], the Li-O_2 micro battery was assembled using commercial electrochemical biasing chips (Hummingbird Scientific) with a gold working electrode and lithium iron phosphate ($LiFePO_4$) counter electrode. During image acquisition, we flowed an oxygen-saturated electrolyte of 1.0 M lithium perchlorate ($LiClO_4$) in dimethyl sulfoxide (DMSO) through the holder's liquid channels and simultaneously performed galvanostatic discharging at 1000 nA.

During discharging, we observe surface growth of discharge products on the working electrode in real-time (see Figure 1). Following an initial incubation period, which is likely due to a nucleation overpotential, these particles grow via kinetic roughening on the working electrode surface [7]. The discharge products appear as round deposits across the entire surface with an average radius of 50 nm – 70 nm. At higher magnifications, the surface of these particles appears as dense, fractal deposits. Post-mortem SEM also shows evidence of toroidal morphology, which is consistent electrochemically formed crystalline Li_2O_2 [1], [8]. From electron diffraction, the discharge products were identified as a nanocrystalline combination of both lithium peroxide (Li_2O_2) and lithium hydroxide (LiOH) phases. We further benchmarked these results against a lab-scale Li-O_2 cell with a similar configuration as the liquid cell setup. We characterized the lab-scale cathode after discharging via SEM, XRD, and TEM, and found similar product morphology, phases, and microstructure [9].

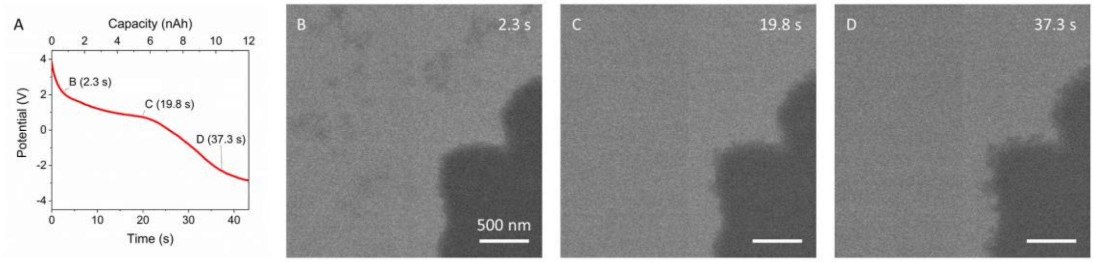

Figure 1. A correlation of galvanostatic discharging data with a time-series of product growth on the Li-O2 micro battery working electrode. (A) Shows the acquired discharging curve with highlighted time stamps at (B) 2.3 s, (C) 19.8 s, and (D) 37.3 s. (B)-(D) Shows the corresponding frames from a time-series image sequence of the growth of electrochemically formed discharge products on the working electrode surface. Scale bar: 500 nm.

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