

Characterization and Predictions of Dual-Functioning Electrodes/Electrocatalysts for Rechargeable Lithium-Oxygen Batteries

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The lithium-oxygen couple, which is known for its intrinsic high capacity for energy storage, has many issues that prevent that capacity from being reversibly achieved in practice.¹ By exploring metal oxides that are known to form compounds with the ultimate discharge product, Li_2O , this work aims to address these issues and challenge the standard concept of lithium peroxide formation on highly porous carbon cathode surfaces.

Our approach is to predict, synthesize, and characterize the performance of materials that can store lithium oxide products in pores and on surfaces of an electrode/electrocatalyst material. Using ternary phase diagrams and density functional theory, promising candidates have been predicted and their voltage profiles calculated. Experimentally, $\alpha\text{-MnO}_2$ that can accommodate Li_2O within its tunnel structure has been characterized *in situ* during cell operation by X-ray absorption spectroscopy and high energy X-ray diffraction (HE-XRD), and *ex situ* with Raman spectroscopy and X-ray photoelectron spectroscopy. Interestingly, independent of the electrolyte used, crystalline lithium peroxide discharge products are not detected, yet cycling performance (gravimetric capacity and capacity retention) is on par with published results.² HE-XRD (Figure 1) and Raman (Figure 2) data suggest that there is a coupling of the discharge products with MnO_2 . In addition, we have preliminary evidence that lithium and oxygen can be electrochemically extracted from, and re-accommodated by, lithium-iron-oxide materials such as $\text{Li}_{15}\text{FeO}_4$ in reactions that occur above the voltage expected for the formation of pure Li_2O_2 and Li_2O .³ This presentation will discuss these results and their implications for exploiting $\text{Li}-\text{O}_2$ electrochemistry.

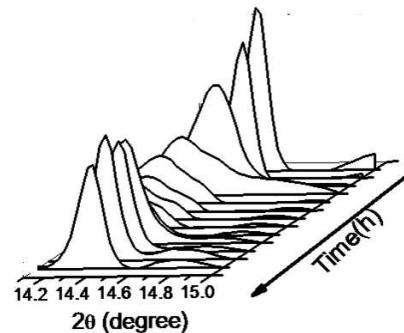


Figure 1. Evolution of MnO_2 HE-XRD peak during *in situ* cell discharge and recharge.

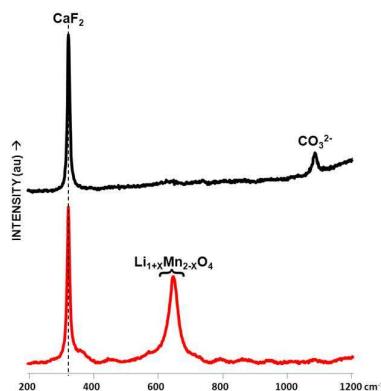


Figure 2. Raman (785 nm excitation) of a discharged, rinsed and dried MnO_2 electrode/electrocatalyst after reaction with lithium and oxygen in a PC-based electrolyte.

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