

# Modeling Discharge Pathways in Li-O<sub>2</sub> Batteries to Optimize Capacity

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Li-O<sub>2</sub> batteries offer the possibility of storing twice the gravimetric energy density of Li-ion batteries. Li-O<sub>2</sub> batteries operate by reacting oxygen with lithium ions in a non-aqueous solvent to form Li<sub>2</sub>O<sub>2</sub> on a conductive cathode material. However, Li<sub>2</sub>O<sub>2</sub> has poor electronic conductivity and passivates the electrode area. Achieving high capacity requires careful attention to Li-O<sub>2</sub> discharge mechanisms in order to optimize cathode void space filling by Li<sub>2</sub>O<sub>2</sub>.

Li-O<sub>2</sub> discharge occurs by two competing mechanistic pathways which are responsible for two possible morphologies of Li<sub>2</sub>O<sub>2</sub> discharge product. The surface pathway involves two consecutive electron transfers to form a ~10 nm thin film of Li<sub>2</sub>O<sub>2</sub>. The solvent pathway involves the solvation of the reaction intermediate Li<sup>+</sup>-O<sub>2</sub><sup>-</sup>, which then reacts in solution to form ~100 nm in diameter toroids of Li<sub>2</sub>O<sub>2</sub>. Since toroids allow for greater volumes of Li<sub>2</sub>O<sub>2</sub> to form with less electrode area coverage, toroids are preferable to maximize capacity. However, the exact dependence of each pathway on different discharge conditions and solvent properties to promote toroid formation is not fully understood.

To understand these pathway trends, rotating ring-disk electrode (RRDE) experiments were performed. A rotating rod creates convection currents that sweep reactants to the central disk electrode (Figure 1). Li<sub>2</sub>O<sub>2</sub> film and soluble Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> are formed at the disk. Soluble Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> is swept to the ring electrode and oxidized, providing a measure of the relative size of the solvent pathway. By comparing ring and disk currents, the separate contribution of each discharge pathway can be determined.

We then developed a model based on nucleation and growth of the Li<sub>2</sub>O<sub>2</sub> film to explain potentiostatic discharge curves collected from RRDE experiments under different discharge conditions, such as varying solvent water content (Figure 2). The model demonstrates that high Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> solvent solubility inhibits the surface pathway and that this effect is primarily responsible for toroid promotion.

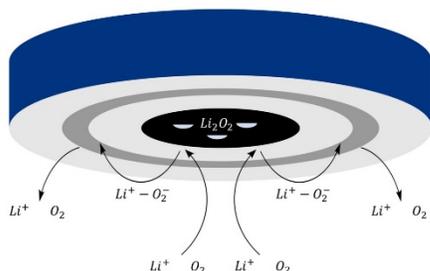


Figure 1: Schematic of RRDE setup. Disk electrode in black; ring electrode in dark gray. Li<sub>2</sub>O<sub>2</sub> film deposits on the disk. Toroid precursor Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> oxidizes at the ring.

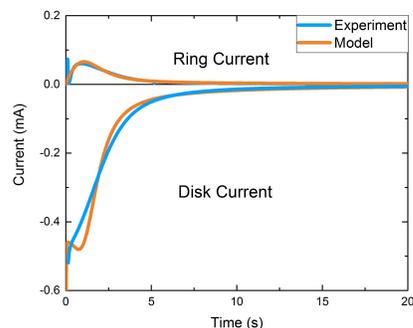


Figure 2: Model fit (orange) of experimental disk and ring currents (blue) collected at 2.4 V vs Li<sup>+</sup>/Li at 1600 rpm in 0.1M LiClO<sub>4</sub> DMSO.

## Further Reading

- R.R. Mitchel, B.M. Gallant, Y. Shao-Horn, and C.V. Thompson, "Mechanisms of Morphological Evolution of Li<sub>2</sub>O<sub>2</sub> Particles during Electrochemical Growth," *Journal of Physical Chemistry Letters*, vol. 4, no. 7, p. 1060, Mar. 2013.
- D. G. Kwabi, M. Tulodziecki, N. Pour, D. M. Itkis, C.V. Thompson, Y. Shao-Horn, "Controlling Solution-Mediated Reaction Mechanisms of Oxygen Reduction Using Potential and Solvent for Aprotic Lithium-Oxygen Batteries," *The Journal of Physical Chemistry Letters*, vol. 7, no. 7, pp. 1204–1212, Mar. 2016.