Pore-Scale Transport Resolved Model of Li₂O₂ Formation in Li-Air Batteries

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The widespread electrification of transportation cannot be realized without the development of a rechargeable high-capacity, portable battery technology. The lithium-air battery, shown schematically in Fig. 1, boasts an energy density of 11680 Wh/kg, which is close to the gravimetric energy density of gasoline [1]. However, a major hurdle facing the development of Li-air systems is their poor round-trip efficiency owing to the formation of electrically insulating lithium peroxide (Li_2O_2) at the solid cathode surface. Although it is known that Li_2O_2 inhibits the reduction process during cell charging, exactly how the deposition morphology of Li_2O_2 affects the cell performance is poorly understood.

Computational simulation will be an indispensible tool in bridging this divide and facilitating the fabrication of better electrodes. Ex-situ imaging has shown that the Li-air electrodes have highly intricate structures and the deposition of Li_2O_2 is equally complex [2]. However, all existing simulations thus far treat the electrode/Li_2O_2 matrix as a homogenous continuum and utilize simply-shaped electrode morphologies, such as spheres and rods, to construct volume-averaged expressions for porosity and surface area [3, 4]. The formation of Li_2O_2 is then modeled as growing uniformly about these simplified electrodes, and manifests merely as a change in bulk porosity. Such assumptions are insufficient in characterizing the precise effect of the complex electrode/ Li_2O_2 microstructure on cell performance.

We present in this work a physics-based model of the Li-air battery that fully accounts for the distinct 3-phase microstructure of the electrode matrix (electrolyte, electrode, and Li_2O_2). This approach requires no empirical correlations regarding the electrode morphology. Additionally, the growth of Li_2O_2 will be modeled locally and no longer requires the assumption of uniform deposition. This pore-scale model will allow us to directly capture the effect of the realistic electrode microstructure. The comparison between volume-averaged and pore-scale models is shown in Fig. 2.

We have already utilized our pore-scale model to predict discharge behavior under a variety of electrode/Li_2O_2 morphologies, as seen in Fig. 3. With an increase in the electrically insulating peroxide, the cell performance can be clearly seen decreasing. Further investigations into the characterization of the electrode/Li_2O_2 microstructure will be presented.

References:
[1] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Wilcke, "Lithium−Air Battery: Promise and Challenges," *The Journal of Physical Chemistry Letters,* vol. 1, pp. 2193-2203, 2010/07/15 2010.
[2] J. Read, "Characterization of the Lithium/Oxygen Organic Electrolyte Battery," *Journal of The Electrochemical Society,* vol. 149, pp. A1190-A1195, 2002.
[3] P. Andrei, J. P. Zheng, M. Hendrickson, and E. J. Plichta, "Some Possible Approaches for Improving the Energy Density of Li-Air Batteries," *Journal of The Electrochemical Society,* vol. 157, pp. A1287-A1295, 2010.
[4] Y. Wang, "Modeling discharge deposit formation and its effect on lithium-air battery performance," *Electrochimica Acta,* vol. 75, pp. 239-246, 2012.

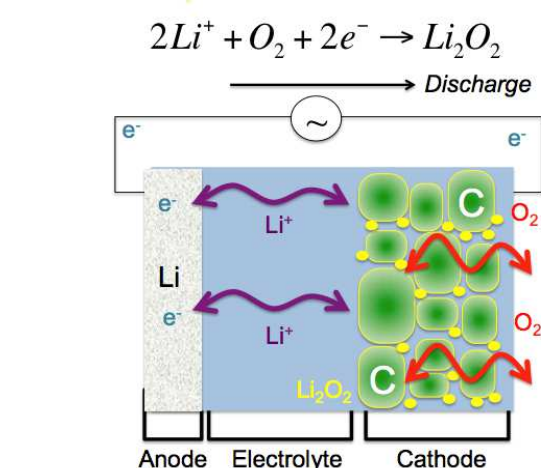$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$$

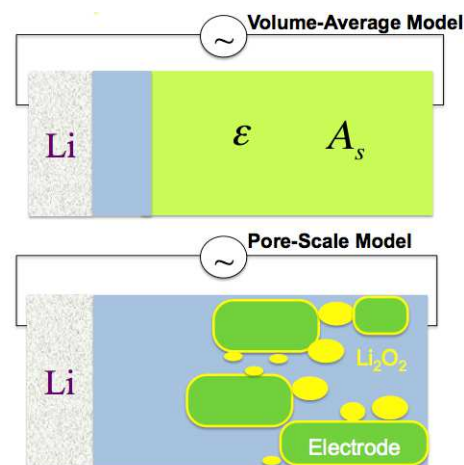Fig. 1: Schematic of air-breathing Li-air battery.

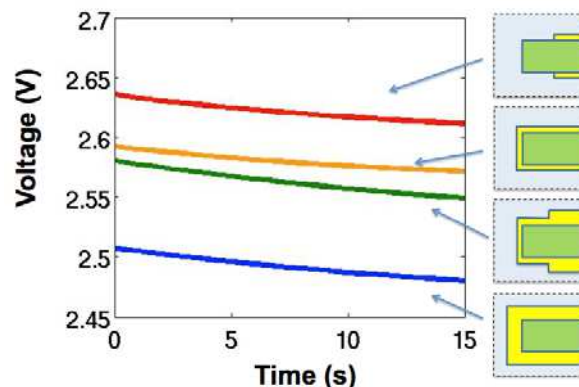Fig. 2: Illustration of volume-averaged and pore-scale models.

Fig. 3: Voltage curve shown for four different electrode (green) / Li_2O_2 (yellow) morphologies. The degradation of voltage with increasing Li_2O_2 is obvious.