Continuum-Scale Modeling of Lithium-Air Batteries

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A three-phase continuum-scale model is developed to explore the first discharge of a lithium-air battery. Constructed on the basis of porous-electrode theory and concentrated-solution theory,[1] the model accounts for transport, thermodynamic and dynamic processes occurring during discharge in all three phases in the porous cathode — the electrolyte phase, the insoluble discharge product phase, and the conductive matrix phase.

One challenge confronted in lithium-air battery modeling is that insoluble products deposit onto pore walls within the porous cathode during discharge, causing its microstructure to change.[2] Discharge-product growth shrinks (or even blocks) pores and pushes electrolyte out of the associated current collector, decreases the surface area available for charge transfer, and leads to interfacial resistances to charge and material exchange. Our model takes into account these effects of discharge-product growth by assuming that the electrode microstructure varies with depth of discharge. For instance, with cylindrical pores, cathode porosity ε and surface-to-volume ratio a_{v} are calculated as

$$\varepsilon = \frac{2\pi r^2}{\sqrt{3}r_{\mathrm{sep}}^2}, \; a_{\mathrm{v}} = \frac{4\pi r}{\sqrt{3}r_{\mathrm{sep}}^2}, \qquad (1)$$

where r_{sep}, is a characteristic pore separation distance; the instantaneous pore radius r depends on local charge state. Keeping track of the charge-state dependence of pore size and surface-to-volume allows general study of morphology evolution within the porous cathode. Treating the discharge-product phase explicitly in the model allows various transport mechanisms within the phase to be explored.[3]

In our present simulation, we assume neglibible separator thickness and an abundant oxygen supply at the cathode current collector. Figure 1 presents typical development of concentration profiles of lithium hexafluorophosphate ($LiPF_6$) and oxygen (O_2, dissolved in the electrolyte) in the cathode. As discharge continues, distribution of $LiPF_6$ remains more or less uniform and constant throughout the cathode, while oxygen is severely depleted in regions far away from the cathode current collector. The whole transport process in the cell is O_2 diffusion limited.

Figure 2 shows the evolving reaction distribution in the porous cathode. Initially, reaction takes place uniformly in the cathode. As time passes, the reaction zone, rather than being continuously evenly distributed throughout, moves toward the current collector edge of the cathode due to the abundance of O_2 supply there and the depletion of O_2 elsewhere. This observation indicates that O_2 diffusion limitation leads to only partial usage of the cathode, limiting the cell capacity.

Our model study aims to investigate a variety of factors that may limit cell capacity, and to provide design criteria that ensure complete cathode utilization.
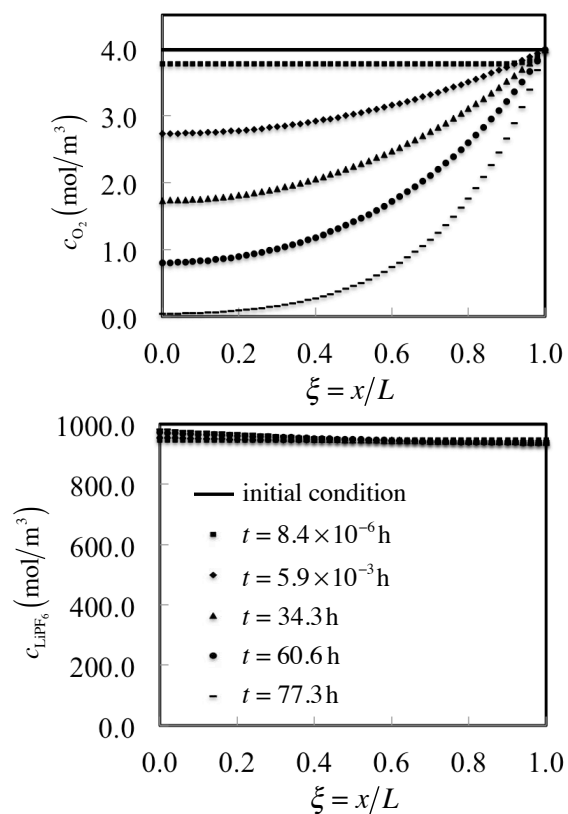

Figure 1. Concentration profiles of $LiPF_6$ and O_2 recorded at 6 different times during discharge. The simulation is implemented with properties of a 1000 mol/m³ $LiPF_6$ and 3.98 mol/m³ O_2 propylene carbonate (PC) solution. In the simulation, mass of $LiPF_6$ is conserved in the cell, and concentration of O_2 at the current collector $(\xi = 1)$ remains constant.
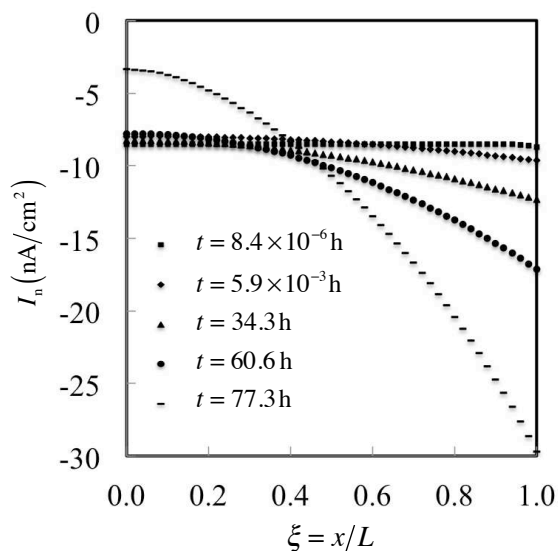

Figure 2. Distribution of reaction current exchanged between the electrolyte phase and the conductive matrix phase at 5 different times during discharge.

References
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3. P. Albertus *et al.*, *J. Electrochem. Soc.*, **158**, A343 (2011).