

Modeling Lithium Plasticity in Lithium-metal Batteries  
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Lithium-metal batteries are of great interest to the field of battery technology due to their high energy density and specific energy. Much effort has been devoted to the development of separators and protective layers to inhibit dendrite growth, the major cause of failure in lithium-metal batteries. This research addresses the problems that could occur even if the propagation of dendrites is controlled, namely large-scale shape change of the lithium/separator interface. The focus of this talk is on the plastic deformation of the lithium caused by stresses induced by the resistance of the separator to the movement of the underlying lithium.

Previous electrochemical modeling was done using COMSOL Multiphysics, which uses a finite-element approach.<sup>1</sup> This model incorporates electrode tabbing (figure 1) where, during discharge, the current is drawn from the top of the positive tab and inserted into the bottom of the negative tab. Also modeled is a moving boundary at the negative electrode/separator interface, a  $\text{CoO}_2$  intercalation positive electrode, and a lithium-metal negative electrode. A polymer separator strong enough to prevent dendrite propagation (as predicted by Monroe and Newman<sup>2</sup>) was used. Finally, the negative electrode in this model is stoichiometrically twice the thickness required, to avoid the need for a separate negative current collector.

The model shows that, even without dendrites, there is significant large-scale movement of lithium both during each half cycle and after a full cycle of a discharge followed by a charge (dashed line in figure 2). Specifically, more lithium is depleted near the negative tab while discharging the cell, yet after a full cycle of a discharge followed by a charge, there is a net migration of lithium towards the negative tab. The model shows that this migration is caused by three separate phenomena: the cell geometry, the slope of the open-circuit-potential function of the positive electrode, and concentration gradients in both the solid and liquid phases in the cell.<sup>1</sup>

In order to inhibit dendrite growth, the polymer separator employed is required to have a shear modulus about twice that of lithium. This equates to a separator which is substantially stiffer than that of lithium. The outcome of this is that even modest changes in the

thickness of the lithium results in pressures above the yield strength of lithium ( $0.655 \text{ MPa}$ )<sup>3</sup> where the lithium could deform both elastically and plastically.

Using the constitutive laws of plasticity, a mechanical model of the lithium negative electrode has been created. This model approximates the separator as a perfectly elastic material and allows the lithium to deform both elastically and plastically. The stress profile computed from the electrochemical model previously described is used at the initial condition for the mechanical model and the resulting deformation is computed.

From the solid line in figure 2, it can be seen that both elastic and plastic deformation has occurred. The flat regions of the height profile are where the lithium has been deformed plastically, with compressive deformation on the left and tensile deformation on the right. While elastic deformation has occurred throughout, it is most visible in the center of the plot, between  $x$  values of 0.25 and 0.5, where the stresses on the lithium were insufficient to deform the lithium plastically.

Furthermore, through an integration of the plastic deformation of the lithium, it is seen that there is a plastic flow of lithium toward the region in tension (the right side of the plot). This means that there is a non electrochemical movement of the lithium which is not matched in the positive electrode. To explain this further, without any plasticity being considered, the accumulation of lithium on the left side of the negative electrode (dashed line in figure 2) is matched in the positive electrode by a decrease in the local concentration of lithium on the left side of the cell. However, if the plasticity of the lithium is considered, a flow of the lithium at the negative electrode back to the right is seen while the local concentration of lithium in the positive electrode remains the same. We can also vary the mechanical parameters of the separator to see its effect on the flow of lithium.

1) A. Ferrese, P. Albertus, J. Christensen, and J. Newman. Lithium Redistribution in Lithium-Metal Batteries, *JES* 159 (10), A1615 (2012).

2) C. W. Monroe, Dendrite Initiation and Growth in Lithium/Polymer Systems, Dissertation, University of California, Berkeley, 2004.

3) R. Schultz. Lithium: Measurement of Young's Modulus and Yield Strength, Fermilab TN 2191, 2002.

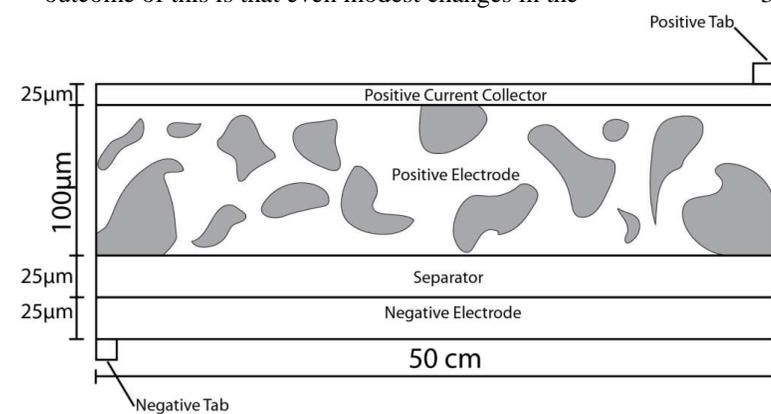


Fig. 1. (Top) Two-dimensional model geometry of a lithium-metal battery, consisting of a lithium metal negative current collector, a lithium metal negative electrode, a liquid electrolyte separator, composite cathode, and aluminum positive current collector.

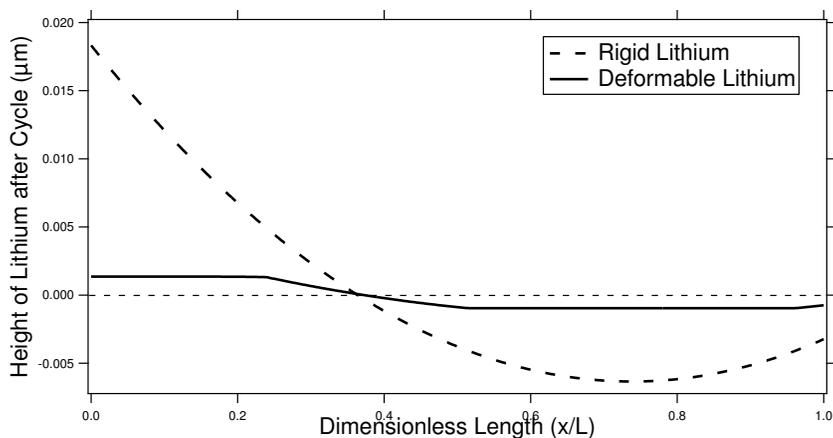


Fig. 2. (Bottom) Height of the lithium negative electrode after a discharge followed by a charge if the lithium is considered rigid (dashed line) and if it is allowed to deform elastically and plastically (solid line).