Lithium Dendrite Growth through Polymer Electrolytes

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Lithium metal batteries have the highest energy density of any battery technology and are, therefore, being considered for electric vehicles.[1] The Department of Energy has established that battery energy density needs to double to enable large-scale commercialization of electric vehicles.[2] Replacing the typical graphite based anode with lithium metal will increase its energy density by an order of magnitude. [1,3] However, this technology has a failure mode that prevents its widespread use. Namely, lithium metal changes its shape under cycling, resulting in the growth of lithium metal dendrites through the electrolyte that eventually short-circuit the cell.

Imaging lithium dendrite growth is difficult because lithium is highly reactive and ductile. [4] As such, the microstructure of the lithium is easily altered upon handling. Nonetheless, several techniques including nuclear magnetic resonance (NMR)[5], magnetic resonance imaging (MRI)[6], and scanning electron microscopy (SEM) have been used to study lithium dendrite growth. However, these techniques are indirect and give an incomplete view of dendrite growth. [7,8]

Hard X-ray microtomography has the unique capability to non-destructively monitor the formation and growth of lithium dendrites.[9] The technique yields information about the surface of the lithium dendrite in addition to showing the morphology of the full, three-dimensional structure and how it interfaces with the electrode. Because of this, we have learned that the dendritic structure extends deeply into the lithium electrode. An image of a dendrite is shown in Figure 1. Furthermore, in situ imaging of dendrite growth gives an uncharted view into the initiation and growth of these lithium microstructures in cycling cells. Finally, the relationship between cycling parameters and the morphology of the dendrite can be directly monitored.

References

1 Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. Nature **414**, 359-367 (2001).

2 DOE. Multi-Year Program Plan 2011 - 2015: Vehicle Technologies Program. (2010).

3 Whittingham, M. S. Lithium batteries and cathode materials. Chem Rev **104**, 4271-4301, doi:Doi 10.1021/Cr020731c (2004).

4 Yaws, C. L. Yaws' Handbook of Properties of the Chemical Elements. (Knovel).

5 Bhattacharyya, R. et al. In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries. Nat Mater **9**, 504-510, doi:Doi 10.1038/Nmat2764 (2010).

6 Chandrashekar, S. et al. Li-7 MRI of Li batteries reveals location of microstructural lithium. Nat Mater **11**, 311-315, doi:Doi 10.1038/Nmat3246 (2012).

7 Stone, G. M. et al. Resolution of the Modulus versus Adhesion Dilemma in Solid Polymer Electrolytes for Rechargeable Lithium Metal Batteries. J Electrochem Soc **159**, A222-A227, doi:Doi 10.1149/2.030203jes (2012).

8 Rosso, M. et al. Dendrite short-circuit and fuse effect on Li/polymer/Li cells. Electrochim Acta **51**, 5334-5340, doi:DOI 10.1016/j.electacta.2006.02.004 (2006).

9 F. R. N. C. Maia, A. M., S. Marchesini, H. A. Padmore, D. Y. Parkinson, J. Pien, A. Schirotzek, C. Yang. in SPIE 7800.

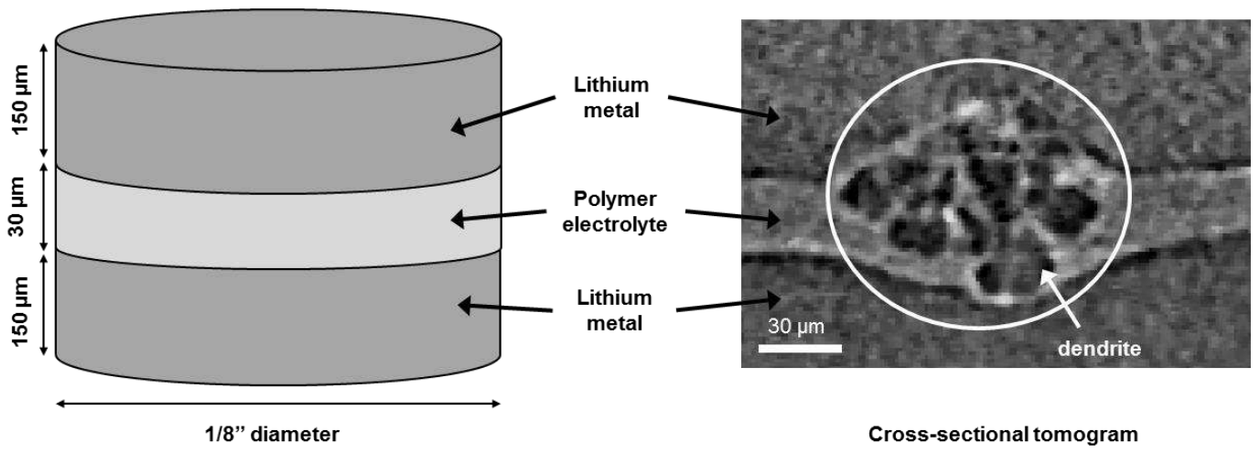

Figure 1. X-ray microtomography was used to make a three-dimensional reconstruction of a shorted, lithium – polymer electrolyte – lithium cell. The image on the right shows a cross-sectional slice through a dendrite that penetrated through the polymer electrolyte. The electrolyte was polystyrene block polyethylene oxide mixed with LiTFSI salt. The symmetric cell was cycled at a temperature of 90℃ and a current of 0.17 mA/cm^2 until it shorted.