Lithium "dendrite" morphology in transparent single crystal lithium ion conductors

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Lithium is both the most electropositive and lightest metal, making it the ideal anode material. Non-flammable ceramic electrolytes paired with Li metal anodes could potentially result in safe, energy dense batteries surpassing state-of-the-art lithium ion batteries. Oxide solid electrolytes typically have high shear moduli, far beyond that of Li metal, which one criterion [1] suggests should suppress lithium metal dendrites. However, our group has recently shown that fracture of the solid electrolyte initiating at surface defects can create pathways for dendritic growth of metallic Li that short-circuit the device. [2]

In this work, *in-situ* optical microscopy has been conducted to characterize the propagation of Li dendrites through single crystal solid electrolytes under a variety of electrochemical conditions. The complete absence of grain boundaries excludes that class of internal defects as paths for propagation. A unique morphological structure of the lithium dendrite observed within the single crystal support a Griffith flaw based fracture model, and in addition, suggest a local field-intensification mechanism of dendrite growth within the solid. Results for the single crystals compared to those from polycrystalline solid electrolytes, in literature and from our own work.

Additionally, it is shown that the initiation of Li propagation through single crystals may be affected by the electrode geometry. Under certain circumstances, Li infiltration is observed to initiate at the perimeter of the electronic conductor contact with the electrolyte – especially at corners with high local curvature. This behavior suggests that localized field and current concentration is also important, and may compete with surface flaws as the sites for initiation of Li metal propagation during electrodeposition.

References:

[1] Monroe, C. & Newman, J. The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces. J. Electrochem. Soc. 152, 396–404 (2005).
[2] Porz, L. et al. Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes. Adv. Energy Mater. 1701003, 1–12 (2017).