



Nanomechanical measurements shed light on solid-state battery degradation

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Lithium-ion batteries have enabled the widespread use of portable electronic devices and are propelling the growing electric vehicle market, but new battery technologies with improved performance are necessary for emerging applications such as electric aircraft. The solid-state battery is one such technology that could exhibit enhanced safety and higher energy density compared to conventional lithium-ion batteries. The use of a pure lithium metal anode within solid-state batteries is key for higher energy density (**Figure 1a**), and it is thought that using solid-state electrolytes instead of conventional liquids could increase the chemical and structural stability of lithium metal.¹ Despite continued progress in the development of new inorganic solid-state electrolyte materials, however, a persistent problem has emerged: lithium metal tends to grow as filaments during charging instead of as a flat film, and these filaments can penetrate and fracture the stiff solid-state electrolyte to short circuit the cell (**Figure 1b**).^{2–4} To prevent this chemo-mechanical degradation process and enable filament-free charging, it is critical to understand the mechanical properties of lithium metal, which have been elusive because of the highly reactive nature of lithium.

Citrin et al. report an important advance in measuring the mechanical properties of nanoscale lithium filaments grown directly from solid-state batteries.⁵ They find that the strength of lithium is strongly dependent on filament size, which could help explain why nanoscale lithium filaments can penetrate stiff inorganic electrolytes, causing solid-state batteries to fail.

Observations of fracture in solid-state electrolytes driven by lithium filament penetration have become commonplace in the development of solid-state batteries.^{3,4} While the governing mechanisms are not entirely understood, recent work has suggested that lithium electrodeposition into flaws at the lithium/solid electrolyte interface could cause stress accumulation and crack growth.⁶ Thus, understanding the size-dependent mechanical properties of lithium is a key piece of the puzzle, but this has proven challenging with conventional methods because of to the presence of surface contamination layers on lithium that can affect mechanical deformation. Experiments on bulk polycrystalline lithium under inert environments have shown sub-MPa yield stress and deformation that is largely

governed by creep.^{7,8} Nanoindentation experiments probing much smaller micron-scale regions of films have shown significantly higher yield stresses than the bulk,⁹ and recent *in situ* transmission electron microscopy (TEM) experiments on Li₂CO₃-coated lithium filaments also showed high yield stress.¹⁰ Although these studies have provided important information, it has remained a challenge to measure the properties of filaments with the size, structure, and surface properties found in actual solid-state batteries.

To overcome these issues, Citrin et al.⁵ use a clever experimental setup to directly grow lithium filaments from a solid-state battery cell within a scanning electron microscope (SEM), followed by *in situ* nano-compression experiments in the same SEM. This enables the authors to visualize the nucleation and growth behavior of lithium particles and filaments, and then directly measure the mechanical properties of individual filaments. The lithium itself is likely of high purity and similar to that found in actual solid-state batteries. With these techniques, the authors find that small lithium filaments with diameters between ~300 and ~800 nm have more than an order of magnitude higher yield stress than bulk lithium, indicating that the deformation and flow behavior of lithium varies substantially with the size of the structure of interest.

This quantification of the strength of lithium filaments has important implications for the stability of solid-state batteries. Lithium metal must withstand relatively large stresses to drive crack growth in ceramic solid-state electrolytes, and the previously measured low yield stress of bulk lithium made it difficult to understand how such a material could drive crack propagation. This discrepancy could be explained if the small-scale lithium filaments are stronger than bulk lithium, as shown by Citrin et al.⁵ Furthermore, short circuit-induced failure only requires a single filament to propagate across the cell stack (**Figure 1b**), and the relatively wide distribution of yield stress values measured in this study suggests that the defect character within individual filaments could vary substantially, resulting in different mechanical behavior. This result indicates that certain filaments with particularly high strength are perhaps more prone to causing chemo-mechanical degradation.

Looking to the future, it is critical to understand how the interplay among defect character, filament size, and

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surface chemistry of lithium affects mechanical properties and deformation behavior. Furthermore, since the vast majority of solid-state electrolytes are chemically unstable in contact with lithium metal, the chemo-mechanical properties of interphase regions must also be measured,² and their effect on crack propagation and lithium growth should be understood. Finally, while recent work has revealed important information about the dynamic processes by which lithium filaments drive crack growth,^{3,6} new *in situ* and *operando* imaging techniques need to be developed to probe these mechanisms at shorter length scales. With a comprehensive understanding of the size-dependent chemo-mechanical behavior of lithium, our community will make more rapid progress toward batteries that can power the next generation of electric vehicles and sustainable technologies.

References

1. K.B. Hatzell, X.C. Chen, C.L. Cobb, N.P. Dasgupta, M.B. Dixit, L.E. Marbella, M.T. McDowell, P.P. Mukherjee, A. Verma, V. Viswanathan, A.S. Westover, W.G. Zeier, *ACS Energy Lett.* **5** (3), 922 (2020).
2. J.A. Lewis, J. Tippens, F.J.Q. Cortes, M.T. McDowell, *Trends Chem.* **1** (9), 845 (2019).

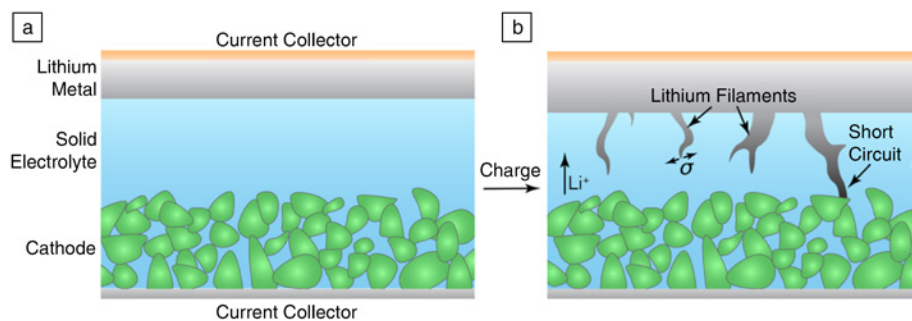


Figure 1. Schematic of a solid-state battery (a) in the pristine state and (b) after charging causes lithium filaments to grow and induce fracture in the solid-state electrolyte because of stress σ at the crack tip.

3. E. Kazyak, R. Garcia-Mendez, W.S. LePage, A. Sharafi, A.L. Davis, A.J. Sanchez, K.-H. Chen, C. Haslam, J. Sakamoto, N.P. Dasgupta, *Matter* **2** (4), 1025 (2020).
4. E. J. Cheng, A. Sharafi, J. Sakamoto, *Electrochim. Acta* **223**, 85-91 (2017).
5. M.A. Citrin, H. Yang, S.K. Nieh, J. Berry, W. Gao, X. Pan, D.J. Srolovitz, J.R. Greer, *MRS Bull. Impact* (2020), forthcoming.
6. L. Porz, T. Swamy, B.W. Sheldon, D. Rettenwander, T. Frömling, H.L. Thaman, S. Berendts, R. Uecker, W.C. Carter, Y.-M. Chiang, *Adv. Energy Mater.* **7** (20), 1701003 (2017).
7. A. Masias, N. Felten, R. Garcia-Mendez, J. Wolfenstine, J. Sakamoto, *J. Mater. Sci.* **54** (3), 2585 (2019).
8. W.S. LePage, Y. Chen, E. Kazyak, K.-H. Chen, A.J. Sanchez, A. Poli, E.M. Arruda, M.D. Thouless, N.P. Dasgupta, *J. Electrochem. Soc.* **166** (2), A89 (2019).
9. E.G. Herbert, S.A. Hackney, V. Thole, N.J. Dudney, P.S. Phani, *J. Mater. Res.* **33** (10), 1347 (2018).
10. L. Zhang, T. Yang, C. Du, Q. Liu, Y. Tang, J. Zhao, B. Wang, T. Chen, Y. Sun, P. Jia, H. Li, L. Geng, J. Chen, H. Ye, Z. Wang, Y. Li, H. Sun, X. Li, Q. Dai, Y. Tang, Q. Peng, T. Shen, S. Zhang, T. Zhu, J. Huang, *Nat. Nanotechnol.* **15** (2), 94 (2020). □