Lithium Grain Attributes in Lithium Metal Anodes

Alexander Salter

EME Summer Research Internship Program 2022

Abstract

In an increasingly electric-dependent society, lithium batteries have emerged as the future of energy storage. While using a lithium metal anode promises the highest theoretical energy density and enables use of lithium-free or novel high-energy cathodes, the lithium metal anode suffers from poor morphological stability and Coulombic efficiency. In cycling, the non-uniformities in lithium deposition and stripping are found to correlate to grain attributes such as grain size and grain boundaries [1,2]. Image processing techniques were applied to lithium images in order to learn more about these attributes, improving our understanding of lithium metal morphology and taking one more step towards a highly effective battery.

Significance

From handheld devices, to electric vehicles, to storage for utility-scale renewable generation, lithium batteries have many applications for the progression of a society looking for cleaner energy sources. Being able to understand the nature of lithium grain boundaries, before and after cold rolling, tells us more information on the nature of lithium metal.

Process

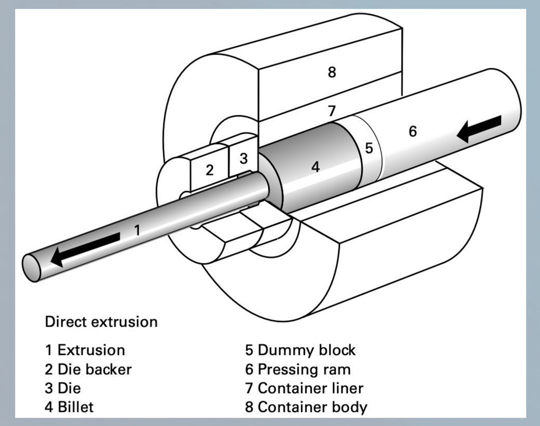

Figure 1. Direct extrusion process to produce 750 um Li [3]

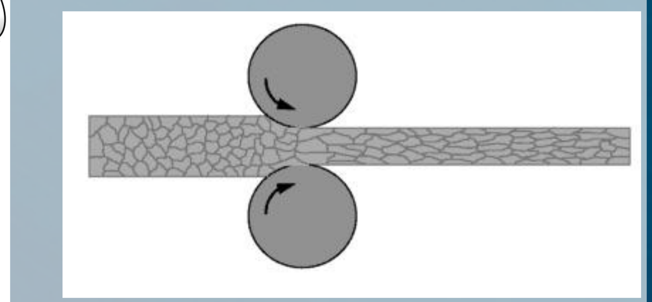

Figure 2. Cold-rolling process to produce 40 um Li [4]

The lithium metal was extruded to 750 um thickness, as seen in Figure 1. This was then cold-rolled to 40 um, as seen in Figure 2. Monitoring differences in the grains of each is the goal.

Image Processing

MATLAB software was used to identify grain attributes such as grain size and grain boundaries, so image pre-processing was a necessary step. Grain boundaries are more obvious to the human eye than a computer, so the grain boundaries had to be isolated from the rest of the image. Given an SEM (Scanning Electron Microscopy) image, there were several steps taken to isolate the grain boundaries. The original image went through contrast enhancement and color selection, further enhancing grain boundaries. Then, the grain boundaries were traced onto another layer, creating an image with only empty space (grains) and grain boundaries. Figure 3 shows the as received and fully traced image. Multiple images were stitched together in a 5x5 array. The MATLAB code then used line-intercept technique on this image in the 0° and 90° directions. These directions correlate to the rolling and transverse direction measurements from cold rolling.

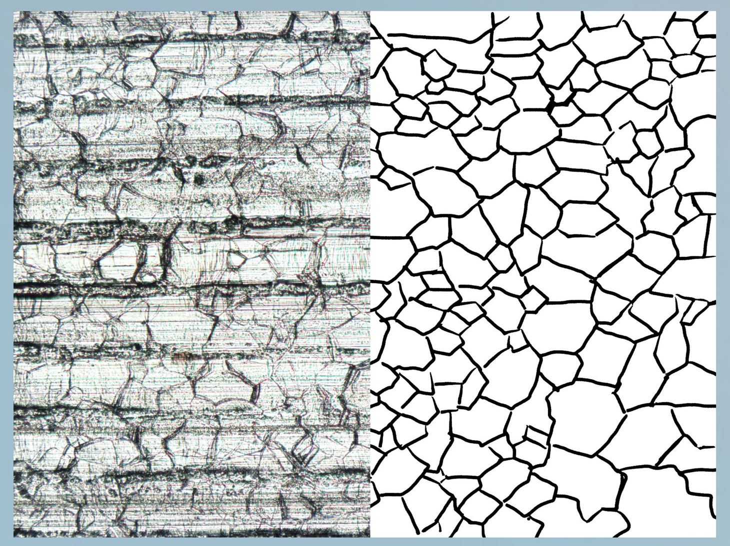

Figure 3. Before and after image pre-processing steps, before data collection.

Results

After taking a 750 um thick extruded lithium foil and cold rolling it down to 40 um thick, measurements were made using the 5x5 stitched images of each with the MATLAB code. Stitched images are pictured in Figure 4.

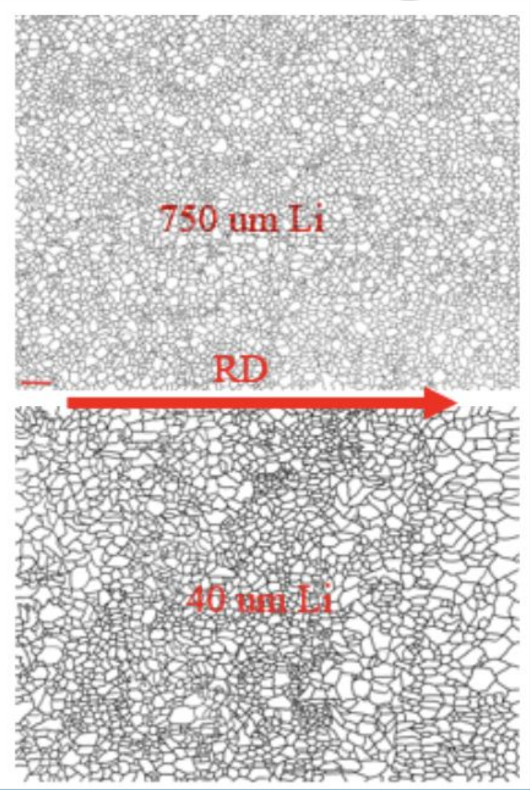

Figure 4. 5x5 stitched 750 um and 40 um thick Li, with rolling direction (RD) labeled

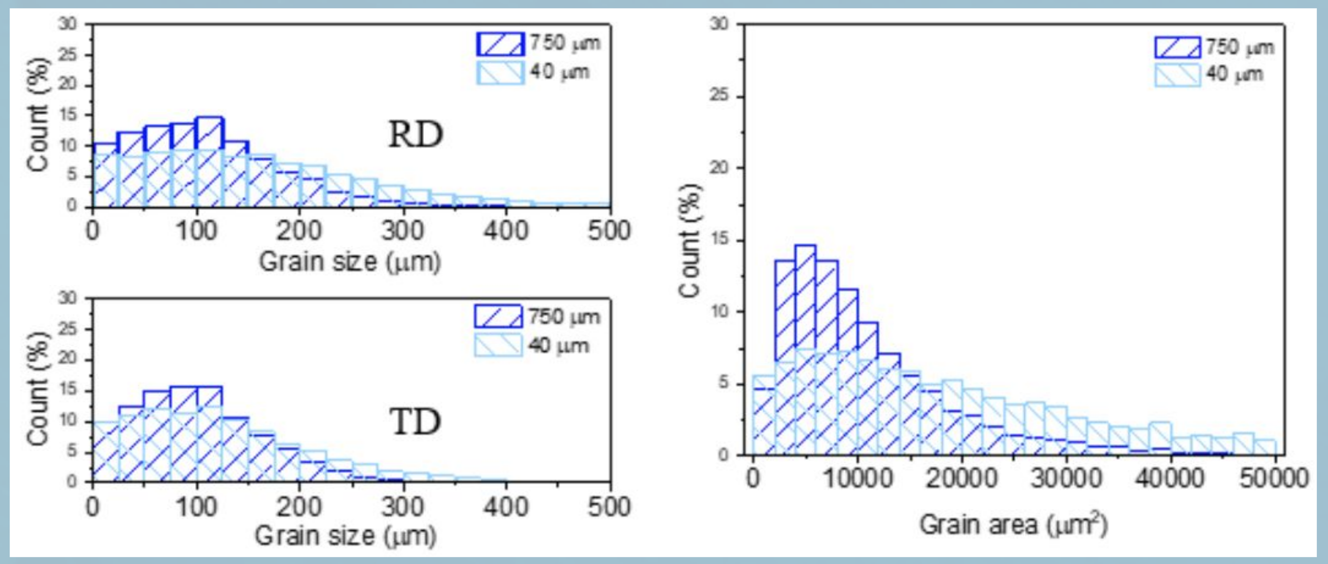

Figure 5. Results of lithium grain size distribution in rolling direction (RD) and transverse direction (TD) in um, as well as grain area distribution in um^2, for 750 and 40 um thick lithium.

The same area was measured for both the thick and thin lithium, and the distribution of grain size and area is displayed in Figure 5. The lighter blue bars represent the 40 um Li foil and the darker blue bars represent the 750 um Li foil.

As can be seen both in Figure 5 above and Table 1 to the right, there are some clear differences in the makeup of the 750 um and 40 um Li foils.

sample	Grain number	Grain size along RD	Grain size along TD	Grain area
750 5x5	8155	114.24 um	107.29 um	10955 um2
40 5x5	2664	192.88 um	137.71 um	26703 um2

Table 1. Statistics regarding grain number, average grain size (in RD and TD, and average grain area, for 750 and 40 um thick lithium.

In Table 1 above, the averages for multiple statistics regarding the 750 and 40 um foils are shown. In the same amount of area, the 40 um foil has less grains and hence, a larger average grain area. Also, it is seen that the 40 um foil has a larger difference between the measurement in the rolling direction (RD) and than in the transverse direction (TD).

In Table 2, on the right, there is a grain boundary density effect from cold rolling, showing a higher GB density for the 750 um Li.

	750 um Li	40 um Li
Grain boundary density	1.60 m / cm^2	0.98 m / cm^2

Table 2. Grain boundary density, in m/cm^2, for both 750 and 40 um thick lithium.

Results and Consistency with Literature

The elongation of grains during cold rolling in the rolling direction is consistent with the literature, and displays no grain recrystallization [5].

As shown in Figure 2, the grains elongate due to cold rolling, hence increasing grain size.

An increase in grain size due to cold rolling means a decrease in grain boundary density as well. This tracks, as the grains take up more space within the measured area, leaving less space for grain boundaries.

To sum up everything, Lithium was extruded to 750 um thickness as a baseline and then cold-rolled to 40 um thickness. The effects of this cold rolling were elongated grains in the rolling direction, leaving stretched grains of larger area. This decreased grain boundary density and will play a role in the deposition interactions of lithium onto the lithium anode.

Citations

1. Sanchez, A. J., Kazyak, E., Chen, Y., Chen, K. H., Pattison, E. R., & Dasgupta, N. P. (2020). Plan-View Operando Video Microscopy of Li Metal Anodes: Identifying the Coupled Relationships among Nucleation, Morphology, and Reversibility. ACS Energy Letters, 5(3), 994–1004. https://doi.org/10.1021/acsenergylett.0c00215
2. Shi, F., Pei, A., Boyle, D. T., Xie, J., Yu, X., Zhang, X., & Cui, Y. (2018). Lithium metal stripping beneath the solid electrolyte interphase. Proceedings of the National Academy of Sciences of the United States of America, 115(34), 8529–8534. https://doi.org/10.1073/pnas.1806878115
3. Black, J. T., & Kosher, R. A. (2012). Extrusion. DeGarmo's Materials and Process, 11, 418–419.
4. "Grain Structure." The Warren, The Warren School, https://www.the-warren.org/ALevelRevision/engineering/grainstructure.htm.
5. Nikolic, V., Wurster, S., Firneis, D., & Pippan, R. (2016). Improved fracture behavior and microstructural characterization of thin tungsten foils. Nuclear Materials and Energy, 9, 181–188. https://doi.org/10.1016/j.nme.2016.06.003

Acknowledgements

I would like to thank Dr. Feifei Shi and Hanrui Zheng for their continued support, guidance, and encouragement throughout the research process. I would also like to thank the John and Willie Leone Family Department of Energy and Mineral Engineering for the opportunity to learn and conduct research this summer.

PennState College of Earth and Mineral Sciences

John and Willie Leone Family Department of Energy and Mineral Engineering