A crystallographic aspect of Li metal anodes: Understanding the functionality of lithium-ion all-solid-state batteries

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Background
Enabling the use of Li metal as an anode in all-solid-state batteries (ASSB) promises higher energy density and safer operation when compared to current Li-ion batteries due to the integration of nonflammable solid-state electrolyte. Increasing demand for safe electrical energy storage, especially in the transportation sector, has resulted in rapid and continuous growth of ASSB research [1].

It is undeniable that both cathode and anode microstructure have a direct impact on battery cell performance. The coulombic output, charge and discharge rates, and life cycle depend on grain size, boundary characteristics, and crystal orientation (texture). The small grain size tends to increase electrical resistivity, which degrades battery performance. High-angle grain boundaries are the most resistive due to corresponding strain fields, which are the result of high dislocation densities. Crystal orientation can promote intercalation, prohibit intercalation, or increase instability [2]. For example, closely packed crystallographic planes (grain facets) are favorable for higher ion mobility. Considering the many microstructural parameters and relationships between them, it is critical to evaluate the best candidate for Li metal anode before battery fabrication.

However, there is little work reported on the microstructural characterization, which allows for the evaluation and comparison of various lithium metal sources.
Li is highly sensitive to oxygen, nitrogen, water, and carbon dioxide, which makes sample preparation for microstructural characterization impossible in ambient atmosphere. Lithium is also a very soft material, and its crystallographic structure can be easily damaged by mechanical interaction. The inherent characteristics of lithium metal demand a controlled environment workflow from sample preparation to structural investigation in a scanning electron microscope (SEM). In the past few years, considerable effort has been devoted to developing accurate sample transfer technology [3].

We demonstrate a workflow that allows the evaluation and comparison of different lithium anode sources. The workflow consists of cryogenic broad Ar ion beam milling sample preparation, cryogenic sample transfer to the SEM, and microstructural characterizations. We will discuss the challenges of cryogenic observations in the SEM. All results are supported by energy dispersive X-ray spectroscopy (EDS) and backscatter electron diffraction (EBSD) measurements.

Methods
All samples [pure Li metal ribbons, Sigma-Aldrich] were prepared using a broad Ar ion beam milling system [TrionMill, Fischione Instruments]. The samples were transferred from the ion mill to a Ga FIB system [Scios DualBeam, Thermo Fisher Scientific] using cryo transfer [Actively Cooled Transfer device, Quorum Technologies Ltd. / Fischione Instruments]. The Scios DualBeam is equipped with a PP3004 airlock and PP3005 SEM/FIB cryo stage [Quorum Technologies Ltd.] All SEM analytical measurements were done using an X-Max 150 mm2 EDS detector coupled with Aztec software [Oxford Instruments] and e-FlashFS EBSD detector combined with Esprit software [Bruker Nano Analytics].

Results and conclusions

Three lithium sheets (Li-1, Li-2, and Li-3) were compared. Figure 1 shows the inverse pole figure (IPF) color-coded EBSD maps for the three samples. The average grain size is 100 µm, 150 µm, and 1150 µm (Li-1, Li-2, and Li-3, respectively). Figure 2 represents corresponding pole figures. Note that multiple maps acquired from different sample regions were used for average grain size and texture determination for each sample. Sample L1-1 is characterized by {110}<001> texture, sample L1-2 has strong rotated cube texture {100}<011> in the rolling (RD), transverse (TD), and normal (ND) reference directions, while sample Li-3 represents random texture. If one of these materials was integrated as an anode material to ASSB, the normal direction would be aligned with the Li+ mobility direction between the anode and cathode.

The {110} crystal facets have the lowest surface energy and the closely packed atom arrangement for body-centered cubic lithium structure; these characteristics contribute to high Li diffusivity, which improves cycling stability and battery lifetime [4]. Large grains are more desirable for high coulombic output, while small grains are not [5]. Therefore, larger grain sizes combined with a {110}<001> texture would be the best choice for a Li metal anode because it is likely to provide the best battery performance.

Accurately evaluating lithium anode microstructure is critically important to developing superior battery performance.

Graphic:

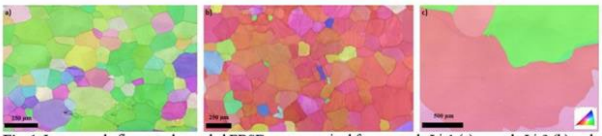

Fig. 1. Inverse pole figure, color-coded EBSD maps acquired from sample Li-1 (a), sample Li-2 (b) and Li-3 (c).

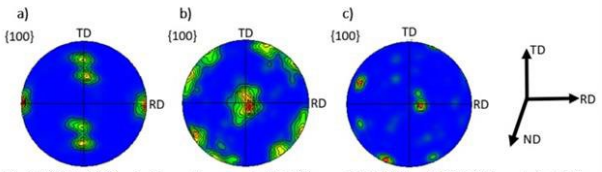

Fig. 2. EBSD {100} pole figures from sample Li-1 (a), sample Li-2 (b) and Li-3 (c). Presented statistics were calculated over at least four maps per each sample acquired from different sample regions.

Keywords:

Li-ion battery, texture, microstructure, BIB

Reference:

1. B. Stéphanie, et al., International Energy Agency, http://iea.li/nzeroadmap (accessed on Jan 31, 2023).
2. A. Quinn, et al., Cell Reports Physical Science, 1, 8 (2020).
3. N. Stephant, et al., Micron, 110 (2018).
4. R. Hendriks, et al., ACS Applied Energy Materials, 1, 12 (2018)
5. B.L. Mehdi, et al., Scientific Reports, 6, 1 (2016).