Aligning Lithium Metal Battery Research and Development Across Academia and Industry

Kelsey Hatzell[1,2]*, Wesley Chang[3]*, Wurigumula Bao[4], Mei Cai[5], Tobias Glossmann[6], Sergiy Kalnaus[7], Boryann Liaw[8], Ying Shirley Meng[9], Rana Mohtadi[10], Yujun Wang[11]

AUTHOR INFORMATION

[1] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08540 USA

[2] Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08540 USA

[3] Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, PA 19104 USA

[4] Department of NanoEngineering, University of California San Diego, La Jolla, CA 92093 USA

[5] General Motors R&D Center, Warren, MI 48090 USA

[6] Mercedes-Benz Research & Development North America, Farmington Hills, MI 48331 USA

[7] Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831 USA

[8] High Power Research Laboratory, LLC., Idaho Falls, ID 83404, USA

[9] Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637 USA

[10] Materials Research Department, Toyota Research Institute of North America, Ann Arbor, MI 48105 USA

[11] Cummins Inc., Columbus, IN 47201 USA

*Corresponding Authors: kelsey.b.hatzell@princeton.edu, weschang@drexel.edu,

All other authors are listed by last name alphabetically.

ABSTRACT

Successful integration of metallic lithium anodes into secondary batteries could enhance energy density and enable new forms of electrified transportation. However, the outlook for widespread lithium metal adoption in energy storage devices remains mixed. This comes in part from existing gaps in our understanding of the relationships connecting the initial state of lithium, its evolution with cycling, and end-of-life state. It remains important to develop standardized protocols for material and cell characterization, cycling performance, safety, and recycling procedures for lithium metal-based batteries. In February 2023 a cohort of scientists and engineers from academia, national laboratories and industry gathered to converge on a list of critical challenges and action items to provide better understanding of lithium metal evolution, and to enhance academic, government and industrial partnerships to address these challenges. Here we highlight the major discussion topics revolving around the manufacturing of lithium metal, its related metrology and integration into battery form factors, and best practices testing its electrochemical performance relevant to automotive applications. We introduce a power-controlled discharge testing protocol for research and development cells, in alignment between major automotive stakeholders, that may reveal lithium metal battery dynamics closer to practical driving behavior.

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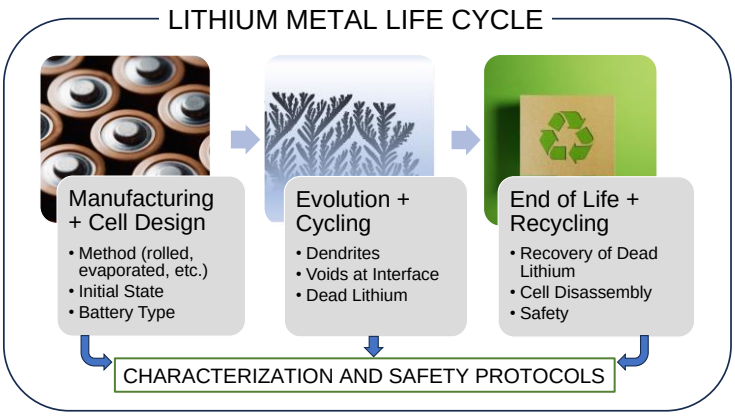

As lithium metal rechargeable batteries continue to be studied, their widespread adoption in electric vehicles remains around the corner. The growth of a rechargeable lithium metal battery market requires improved understanding of not only battery operation and failure, but also the evolution of lithium metal impacted by its initially manufactured state. Here, we summarize the thoughts, conversations, and discussion points from a group of lithium metal battery researchers from academia, industry, and government entities to outline the grand challenges associated with lithium metal. We detailed critical aspects that need to be understood, e.g., (i) the impact of manufacturing methods on lithium metal morphology, (ii) the origins of sample variations for as-prepared lithium metal, (iii) how physical properties of pristine lithium samples affect eventual degradation mechanisms and cycling irreversibility, and (iv) pre-treatment, protection, handling and storage, including related safety issues. We present the results of our discussions, which led to major automotive manufacturers, in agreement with battery manufacturing firms, national laboratory and academic researchers, to publish a recommended dynamic stress test cycling protocol. For research and development of new lithium metal battery chemistries, the usage of this test protocol is expected to generate results of high relevance to practical automotive applications. While not necessarily a mandated necessity for all studies, we believe this protocol can generate useful data for any study involving the behavior of a lithium metal electrolyte proven to work for rechargeability, but with dynamics not yet probed. For instance, how would sudden braking and acceleration, simulated by rapid power-controlled discharge steps, impact the lithium growth morphology over time?

Lithium metal foil properties are supplier-dependent. The processing route, shipping approach and storage method all impact the level of contamination, as observed by proprietary data shared by lithium metal suppliers. Molecular-scale contaminants in lithium metal are observed in the bulk as well as at exposed surfaces. For many lithium metal suppliers, the accurate detection and characterization of contamination remains an underdeveloped challenge and prevents direct comparisons between vendors and across research groups. Typically, exposure from a working environment is thought to be the origin of contamination (e.g.,

CO_2, nitrogen, moisture, corrosion products, etc.). Aside from contamination, processing routes can directly impact the microstructure (e.g., morphology, grain boundary, defect density, porosity) and morphology of the films.[1] Processing approaches such as extrusion, die calendaring, vapor deposition, electrolytic deposition, printing and pre-treatment strategies influence the foil properties. As it stands, developing comprehensive and fast metrology tools to produce controllable lithium metal foil remains a critical need for determining various physical properties of interest (**Table 1**).

Table 1 Important parameters for Li foil manufacturing control and related metrologies

Uniformity	**Metrology**	**Composition**	**Metrology**	**Microstructure**	**Metrology**	**Mech. Properties**	**Metrology**
Surface roughness, cracks and dents	Ultrasound, contact profilometry, AFM	Impurities, dopant concentration	ICP-OES, ICP-MS	Crystal orientation	PFIB+EBSD	Yield strength, creep	Tensile and compressive testing
Thickness	laser gauge, PFIB+SEM	Purities	TGC	Grain size	PFIB+SEM	Hardness	Hardness tester
Porosity (voids)	PFIB+SEM	Surface coatings	XPS			Adhesion	Tape test

From the perspective of the lithium metal supplier, there are a wide range of choices for processing and manufacturing methods and conditions for lithium metal foils, including extrusion, die calendaring from melt processing, vapor deposition, electrolytic deposition, printing methods, and processing from lithium metal powders.[2] The manufacturing or processing methods impact the sample size, processing speed, and relative control over microstructural properties. Calculation of the cell-level energy density as a function of lithium metal foil and current collector thickness shows how important precise control of thickness is to achieving high energy density. For instance, introduction of a current collector reduces the battery's energy density, as copper metal density (8.96 g/cm^3) is higher than that of lithium metal (0.534 g/cm^3). Conventional lithium metal foil manufacturing with an extrusion process produces foils with a minimum thickness of 100 μm.[2] A rolling process can further reduce the thickness to 20 to 50 μm but requires processing lubricants due to the high ductility and adhesive properties of lithium.[3] Thin lithium metal foil

(< 20 μm) may require vapor deposition-based techniques adopted from the semiconductor industry. With optimized conditions, 0.1 to 20 μm lithium metal foil can be produced, though substrate quality can influence the produced metal properties. There are several potential advantages to producing lithium foils from slurries or dry powder coating, such as low processing cost, high yield and easy adoption to existing high-speed, high-volume roll-to-roll production capability. However, slurry and dry coating methods are known to increase porosity in lithium foils that can lead to variability in samples. Melt processing involves melting of lithium ingots at elevated temperatures followed by extrusion into foils, which can also exhibit variable porosity.

One of the workshop goals was to discuss standardization of metrics used to define "battery-grade" lithium foil. We all recognized that there is an urgent need to produce lithium foils with uniformity so that industry, academia, and government research facilities can reliably assess lithium metal battery technology. Creating reliable production methods may require best practices in handling, storing, and shipping lithium metal samples, whereas the foil quality can be validated by metrology tools for as-received samples. For instance, mechanical extrusion and vapor deposition may result in widely different surface roughness profiles. In-line gauges will help monitor and mitigate processing variability in thickness, especially for thin foils less than 30 μm. Complementary to thickness measurements, ultrasonic transmission and optical profilometry can be used to map out surface roughness.

Figure 1 Metrology tools for characterization of native lithium metal foil before electrochemical operation

Microstructure and phase information can be obtained from scanning electron microscopy (SEM) and X-ray diffraction (XRD) of selected samples. Plasma focused-ion beam scanning electron microscopy (PFIB-SEM) can image subsurface structures and is useful for detecting voids from processing. Adhesion between

the lithium metal foil or film and the underlying current collector can be measured via a standardized adhesion tape test. Inductively coupled plasma optical emission spectroscopy (ICP-OES) quantifies trace impurities (down to ppb resolution), which may be left behind from refined lithium salts or incorporated into the foil during processing. Titration gas chromatography (TGC) can be used for quantifying metallic lithium after cycling and cell disassembly. X-ray photoelectron spectroscopy (XPS) can be adopted to understand the surface chemistry including coatings and contamination during storage and shipping. While 100% purity may not be possible, it is also unclear whether ppb levels of contaminants, or even the incorporation of alloy compounds, have deleterious electrochemical effects. Regardless, these physical properties should be measured, understood, and reported by the research community, lithium metal suppliers and battery manufacturers alike.[4]

Once the supplied lithium foils are manufactured into cells and in contact with liquid or solid electrolytes, their morphological evolution during operation becomes highly dependent on electrolyte chemistry and operating conditions (**Figure 2**). The crystallographic orientation and morphology of the lithium anode will also impact cycling behavior.[5] Commercially available lithium foils are in BCC structure dominated by (110), (200), and (211) crystallographic features.[6] Aside from crystallographic texture, the surface features introduced by the processing of the lithium sheet also affect subsequent stripping and plating. Due to the low yield strength of less than 1 MPa, lithium foil surfaces often show severe plastic deformation in the form of slip lines, which occur when dislocations displace material across a slip plane, creating a reactive surface step measured to be around 500 nm in height.[7] Experimental evidence shows preferential stripping of lithium from grain boundaries and slip lines in liquid electrolytes and under high current densities.[7] Low applied current densities, however, result in the formation of pits that are not correlated with the microstructural features of the pristine lithium foil. Grain boundaries, due to their lower packing density, also promote faster atomic diffusion of lithium as well as solvent molecules of the electrolyte. This leads to formation of voids along the grain boundaries which may extend deep into the lithium.[7]

Even though rolled lithium foil is observed to contain orders of magnitude higher concentrations of impurities than evaporated lithium[8], the correlation between the impurity content and cycling performance of lithium anode has not been well established. Pressure distributions and geometric effects due to differences in form factors, pouch, prismatic and cylindrical, could influence patterning, local hotspots, and contact loss. In one case, slow charging (lithium plating) results in more compact lithium deposits,[9] whereas fast discharging after deposition[10] and asymmetric cycling protocols (slow charging and fast discharging)[11] can also improve battery cycle life. While the underlying mechanisms are not well understood, there are several proposed explanations based on electrolyte concentration gradients[11] and isolated lithium metal migration with polarized electric fields in the electrolyte.[10]

Figure 2 Lithium metal considerations which impact reversible operation and lifetime in next generation batteries.

Lastly, lithium metal battery safety was discussed as it is linked to operational performance. Lithium metal battery thermal runaway temperature was mentioned to be higher than for lithium-ion batteries, but this is likely chemistry dependent. For example, LiFSI salts with cathode decomposition products cause a particularly violent energy release, which was recently confirmed experimentally.[12] Another issue is the mechanical work performed by plating and stripping lithium, resulting in significant volume change.

The results of breakout sessions to discuss the aforementioned topics led to an OEM-relevant battery test protocol proposed by automotive stakeholders. The idea behind the test protocol is to allow academia and startup companies to present data that would be meaningful to the automotive industry. This would make scientific publications on lithium metal batteries more valuable and help identify unresolved challenges of lithium metal battery technology. Specifically, a modified Cycle Life Dynamic Stress Test (DST) is proposed, based on the United States Advanced Battery Consortium's test manual (located in Section 3.9

Cycle Life Dynamic Stress Tests in the "Electric Vehicle Battery Test Procedures Manual" on the USCAR website: https://uscar.org/usabc/). The test procedure is publicly available and is normally scaled to a battery cell or system based on specific power. The cycle is power-controlled, rather than current-controlled, to be more realistic. For lithium metal testing we also recommend power control, except for early-stage half-cell setups for which current control is acceptable. We scale the power profile to the most critical parameter for lithium stripping and plating, which is current density (**Table 2**). The publicly available BatPac model (from Argonne National Laboratory) or any other model may be used to obtain a realistic current density, but a default value may be selected if target application information is not available.

After preparation of a power profile for the charge-depleting cycle, the full cycle life should be followed (**Figure 3**). There are two charge procedures, both of which are equally important. It is expected to extract from the results (1) how many charge cycles can be completed before the cell capacity drops to 80% of the capacity in the beginning-of-life (BOL), (2) how many DST cycles can be performed before the cell is depleted, (3) the maximum and average electrode charge and discharge current density at BOL and EOL at high and low SOCs, and (4) information about the evolution of cell capacity, direct current internal resistance (DCIR), columbic efficiency, stack pressure, stack thickness, and cell temperature. Due to power control, it is expected that the current density decreases with increasing impedance. We emphasize that this power-controlled discharge protocol only differs from standard R&D constant current testing by implementing a constant power discharge profile (while keeping the charge at constant current), to simulate electric vehicle driving behavior while ensuring a readily programmable and accessible test protocol for small-scale studies. As the results of such a test protocol for many emerging lithium metal battery chemistries are absent, any measurables would be informative and of high relevance for automotive OEMs. This is not a mandated absolute, but rather a suggested protocol by which automotive manufacturers would be interested in seeing.

Table 2 Cycle preparation procedure (prior to implementing the cycling protocol shown in **Figure 3**)

Step	Instruction	Default	Comment
1	Use BatPac or similar model to determine the electrode **current density** for a hypothetical cell for the target application required for a **3 h (C/3) to 5 h (C/5) discharge**. Faster average discharge rates are not realistic for automotive validation. If there is no specific application planned or it is a symmetric lithium cell setup, use **default** value.	1.0 mA/cm^2	Assuming reasonable areal capacity, for example, 4 mAh/cm^2, 6 mAh/cm^2 after demonstrating 4 mAh/cm^2. Current density to remain below 2 mA/cm^2.
2	Find peak discharge current density by selecting a value near a 1C rate.	4 mA/cm^2 match areal capacity	Avoid very high rates, which may mask lithium issues.
3	Determine nominal cell voltage $V_{nominal}$ by +0.1C/-0.33C at RT (measure the average voltage).	Chemistry dependent	Compare with USABC test manual.
4	Multiply $V_{nominal}$ with peak discharge current to obtain peak discharge power.		
5	Scale the DST profile by setting 100% power to peak discharge power.		For symmetric cells use current control instead of power.

Figure 3 Cycling procedures for A) slow charging and B) fast charging, both are important. C) Example power-controlled DST cycle. This cycle is to be repeated, as described in Table 2, until the cell hits the lower voltage discharge cutoff.

Throughout the workshop, the need for improved communication and transparency in sharing scientific results among academic research groups, national laboratories, lithium metal suppliers, cell manufacturers and electric vehicle manufacturers has been consistently emphasized as critical to accelerating the adoption of high energy density rechargeable lithium metal batteries in the marketplace. Workshop discussion topics ranged from the fundamental understanding of how crystallographic planes impact reversible operation, to new metrology tools that can hasten the characterization of manufactured lithium metal and cell-level

properties. For instance, the crystallography and metallurgy of lithium metal as a function of its processing parameters is still poorly understood. Does crystal size matter, and are there favorable dopants or defects that mitigate morphological variability and irreversibility? Lithium metal suppliers have shown that surface morphology, purity, electrochemical cycling performance may all vary depending on the processing method, and standardized metrics should be defined and accepted as a basis for comparison. The establishment of, and alignment on, a standardized power-controlled discharge cycling protocol amongst three large automotive manufacturers is expected to bring academic research in closer alignment with industry scaleup priorities.

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Declaration of Interests

The authors declare no competing interests.

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Figure 1

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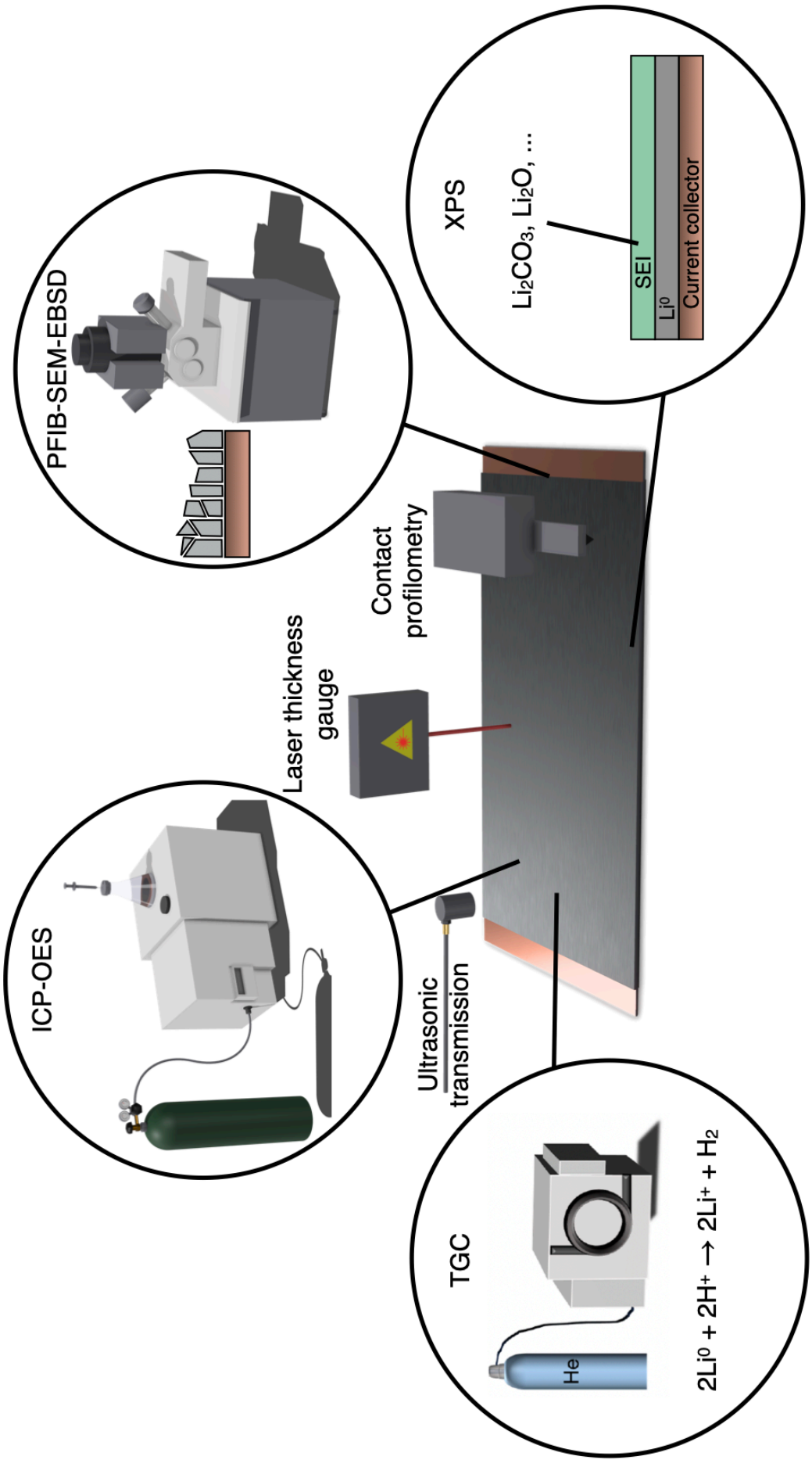

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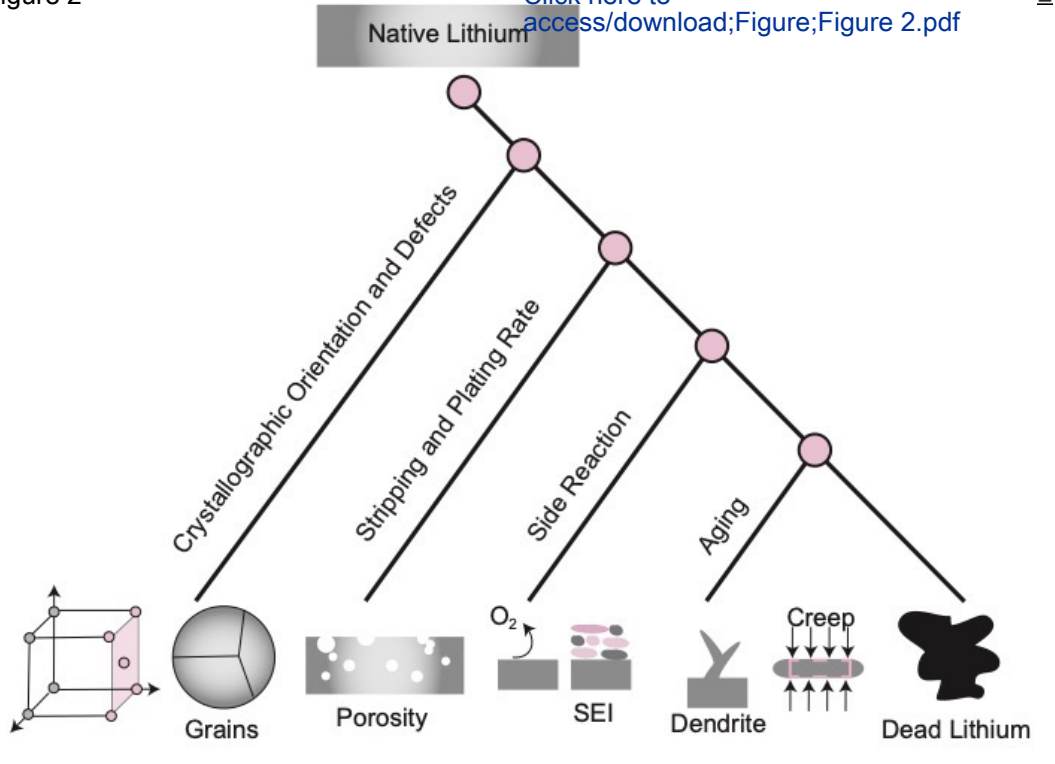
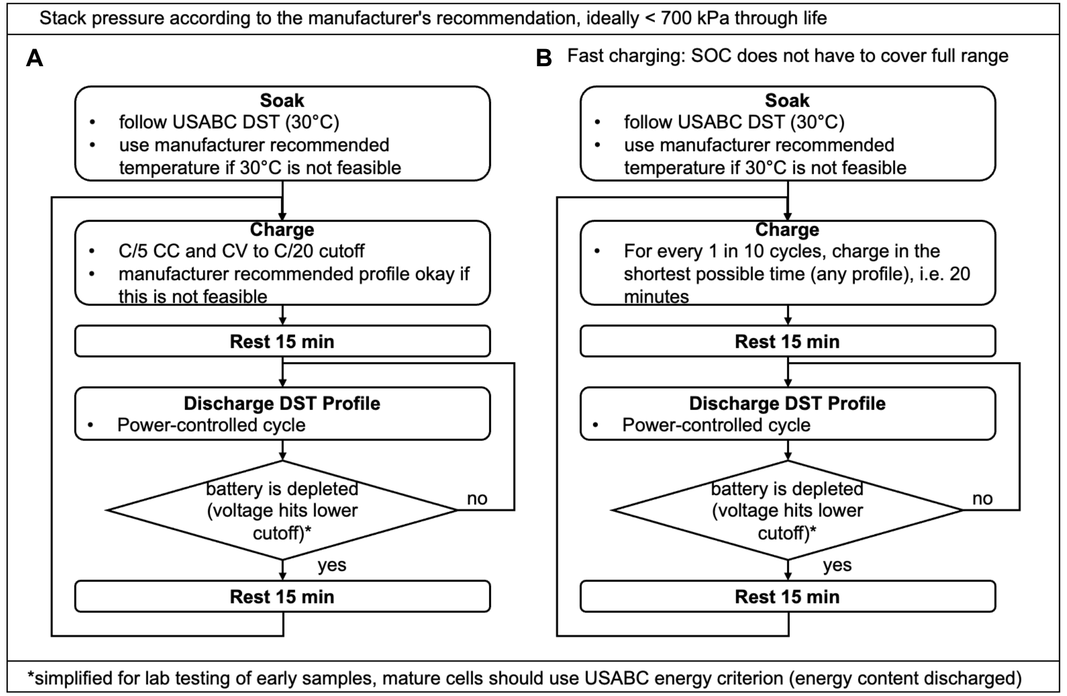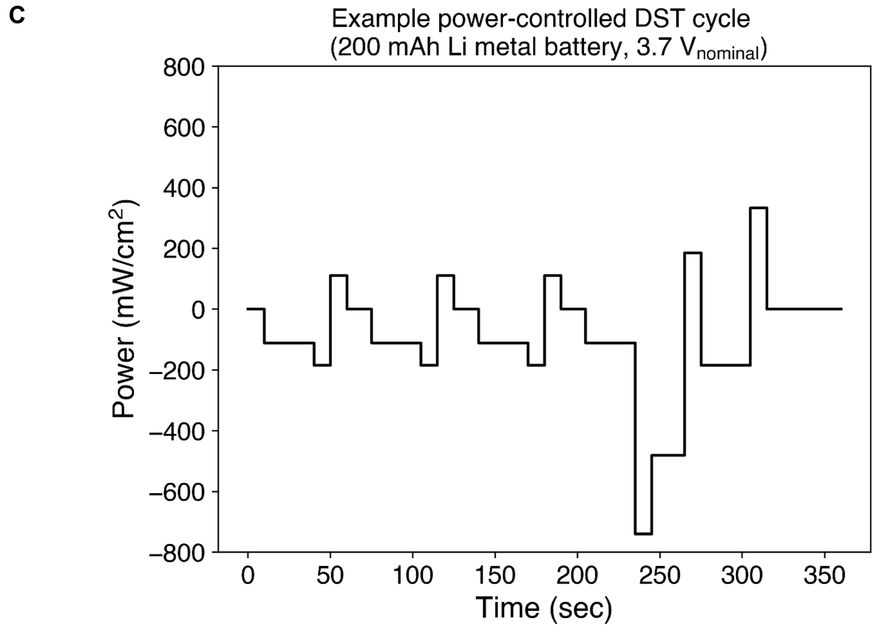
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