

Requirements and Testing Protocols for Lithium Metal Secondary Batteries

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Abstract

The biggest single improvement in energy density and cost to today's lithium-ion batteries would be replacing the graphite host anode with a pure lithium metal anode. This has not yet been publicly demonstrated at automotive performance levels, including current density, cycle life, temperature, and reliability, despite decades of effort, due to the considerable challenge of preventing the formation of lithium dendrites that degrade performance and result in cell failure. We review prior efforts to cycle a lithium metal anode and a solid-state separator and outline the gaps between state-of-the-art results and the requirements of battery electric vehicles. We discuss measurement techniques and methods to clarify common presentations of results in literature.

1. Introduction

A key to reducing battery cost is increasing the specific energy (kWh/kg) of the battery, since the cost of raw materials and processing approximately scales with the mass of the battery. The biggest single improvement in energy density of a lithium ion battery would be to remove the carbon host anode material and use a lithium metal anode with no excess lithium. A lithium metal anode has not been successfully commercialized to-date due to the challenge of safely containing lithium metal, particularly at high current density. We present cell results demonstrating a separator and full cell capable of meeting automotive requirements with high reliability.

2. Cell & separator requirements

A next-generation automotive cell must demonstrate superiority relative to the current state-of-the-art lithium-ion cell in cost per range, power, and reliability. Specifically, regarding cost per range, a cell must improve energy density by having a) high mass-loading cathodes (≥ 4 mAh/cm²), b) no excess lithium buffer, and c) a thin separator made by a low-cost, scalable process. Regarding power, a cell must demonstrate a) continuous charge capability of at least 2C (≥ 8 mA/cm²), b) pulse charge rate of at least 4C, and c) low temperature discharge capability. Relative to reliability, a cell must a) demonstrate hundreds of cycles, b) demonstrate reliability, i.e. the worst performing cells must show hundreds of cycles, and c) be externally validated. The above nine requirements are all necessary conditions for commercialization – every one must be met simultaneously for a product to succeed.

To enable such a cell, a separator in a lithium metal cell must simultaneously meet four necessary conditions: 1) adequate bulk conductivity, 2) low interfacial resistance, 3) high coulombic efficiency (stability or passivation towards Li), and 4) safety and performance relative to the propensity of lithium to plate in mossy or dendritic structures.

Approaches aimed at addressing the challenge fall into three broad categories: 1) liquid systems with additives or innovative solvents, salts, and/or coating layers; 2) polymers with a shear modulus thought to be sufficient to resist deformation by lithium metal; or 3) solid separators that are hard enough to plastically deform lithium. A brief review of each approach will be given below. In summary, liquid systems have not been shown to meet the coulombic efficiency requirement due to the strongly reducing negative potential of lithium metal, while neither polymer nor ceramic systems have been shown to resist dendrite formation at high current densities [1].

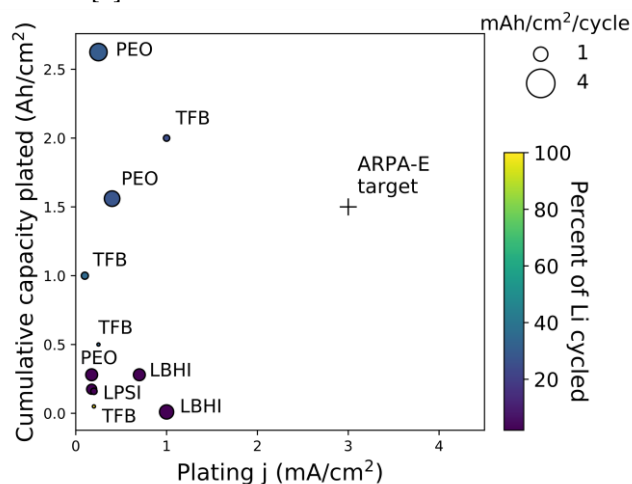


Fig. 1 Landscape of demonstrated cycling performance of lithium metal anodes with solid state separators. The axes are cumulative plated capacity versus plating current density. The size of each dot is the areal capacity plated per cycle, and the color of each dot is the percentage of the available lithium in the cell that is cycled each cycle. Also shown, the US ARPA-E target for cycling.

3. Advanced liquid Coulombic efficiency

Several groups have proposed enabling lithium metal cycling with either unique solvents, salts, additives, capping layers, or some combinations [2-3]. Aside from the exponential challenge of prevention of dendrites at higher current density [4], for long life at high reliability, limited Coulombic efficiency may prohibit commercialization of any liquid solution. Even allowing for the provision of 50% excess lithium,

which is likely cost-prohibitive and presents a potential safety risk, the Coulombic efficiency of an automotive battery that endures 200,000 miles of use (roughly 650 cycles if the pack size enables 300 mile range) is above 99.9%.

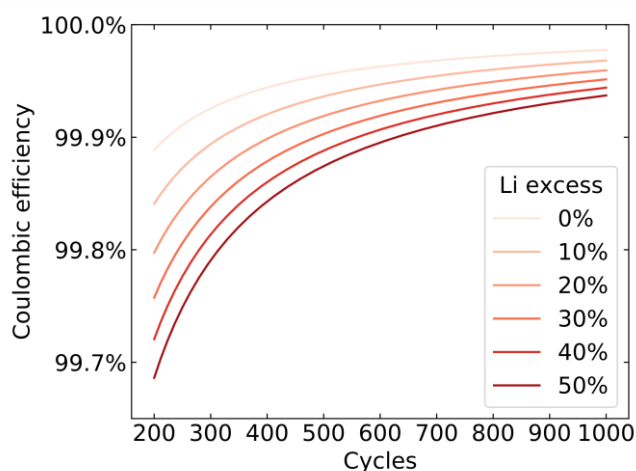


Fig. 2 Lower bound on Coulombic efficiency required versus cycle count for various lithium excess quantities. The figures presented are a lower bound in the sense that Coulombic inefficiency is the only considered fade mechanism.

The strongly reducing nature of lithium introduces tremendous difficulty in designing around the Coulombic efficiency limitation. Interfacial coatings would have to insulate the liquid from lithium potential and remain robust during large volume expansion and contraction during each cycle. Alternately, a solvent or combination of solvents would have to be found that is stable to lithium potential and meet all of the other requirements to deliver high conductivity.

4. Polymer and ceramic dendrite resistance

Solid polymers in the PEO family are the only commercialized lithium metal technology for automotive use, however they are limited to high temperature, low energy, and low power applications. Polymer/inorganic composites have not been demonstrated to pass appreciable current densities before failure.

Thin film batteries (TFB) using LiPON are the other commercialized lithium metal secondary battery chemistry, but the low conductivity and high cost relegates them to niche markets. Borohydrides (LBHI), phosphates, perovskites, and antiperovskites likely cannot meet the voltage stability requirement for a separator. Garnet materials have not yet been demonstrated to survive more than minutes at 0.5 mA/cm² at room temperature [5] although they may survive hours at 15 mA/cm² at temperatures as high as 160 °C [6]. Sulfides span a large range of materials and performance attributes, with some promising but early indications in materials such as LPSI [7].

5. Measurement techniques

Two particularly challenging areas for separator materials highlighted above are voltage stability and dendrite stability. A common measurement technique to assess voltage stability

is the cyclic voltammetry (CV) test, and a common measurement of dendrite stability is a test of current density in a lithium-lithium symmetric cell. We propose improvements to each test to provide a more accurate assessment of real-world performance.

Researchers often infer a misleadingly wide voltage stability window from CV measurements for three reasons: 1) limited electrode contact area, 2) limited dynamic range, 3) limited measurement time. First, cathodes in high energy batteries must be thick, as noted above, and therefore have high surface area in contact with the catholyte; in contrast, a typical CV measurement is performed with a planar electrode, we estimate a factor of 10¹-10²× lower surface area. Second, the current range of the measurement would need to span approximately six orders of magnitude to capture both the high rate capability of desirable reactions and the low rate undesirable side reactions, while typical test equipment can span at most four orders of magnitude of current. Third, an automotive battery must be guaranteed for at least six years, whereas the typical CV measurement lasts hours at most, not allowing sufficient time to observe the progression of side reactions. To properly measure voltage stability, we suggest a full cell measurement with high surface area electrodes, accelerated by high temperature and overcharge, for at least a period of 6 weeks.

Second, a lithium-lithium measurement is an aggressive test of separator dendrite tolerance, however, it may be misinterpreted since a good cell exhibits behavior that is nearly identical to a failed cell (low and steady impedance). We suggest that after the test, either or both of the following tests are performed to verify that the cell is not shorted. 1) EIS sweep versus temperature to demonstrate the expected activation energy. 2) Strip all the lithium from one side of the cell and show that the voltage rises smoothly after the expected amount of charge is passed.

6. Conclusions

Automotive requirements present stringent demands on batteries; all of the requirements must be met simultaneously. Two test methods, namely full strip of Li-Li symmetric cells and full cell voltage stability measurements, highlight two areas where the community could adopt measurements to gain a realistic assessment of how close various materials and processes are to commercial requirements.

Acknowledgements

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