

ALL-SOLID-STATE LITHIUM METAL BATTERIES FOR NEXT GENERATION ENERGY STORAGE

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ABSTRACT

Lithium metal dendrite growth in ultra-high capacity batteries continues to prevent the safe use of Li metal as the negative electrode. Solid-state materials demonstrate superior stability against lithium metal, however, our recent efforts to develop high energy density batteries based upon the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid phase electrolyte short-circuit at currents above about 1.5 mA due to dendrite formation between the electrodes. Preliminary results indicate that the solid phase electrolyte can support reversible, high current (> 1.5 mA) and high rate ($> C/10$) cycling at 100°C without short-circuiting, thus indicating that solid-state lithium metal batteries should be evaluated for elevated temperature applications.

KEYWORDS

Secondary battery, lithium metal, solid-state, glass-ceramic electrolyte

INTRODUCTION

For lithium (Li) ion batteries to find application in the next generation of technologies ranging from grid scale storage down to chip-level applications, a significant advance in energy storage capacity is necessary. Currently, the best commercial liquid electrolyte based batteries remain limited in specific energy density (about 200 Wh/kg), primarily due to inherent limitations in materials, cell architectures, and from the parasitic components including safety and temperature management packaging. In order to realize substantial gains energy storage, approaching a three-fold increase over state-of-the-art (SoA), new battery materials and architectures must be explored that go beyond conventional liquid and polymer based electrolyte cells. Foremost in this effort is the adoption of Li metal as the anode, given that Li has the highest specific capacity at 3876 mAh/g as compared to graphite (the conventional anode intercalation material) at about 372 mAh/g. However, it is quite well established that Li metal is very unstable in liquid electrolyte systems, thus necessitating the use of solid phase materials with its cell integration to improve stability, performance and safety.

In this paper, we detail our progress related to the development of ultra-high energy density, all-solid-state rechargeable batteries. All-solid-state battery architectures, built upon the use of glass-ceramic lithium-ion electrolytes, are not only poised to advance the SoA, but also provide the most straightforward path to miniaturization and integration for Microsystems applications. In addition to the all-solid, planar (thin film) architecture (Fig 1A), these batteries provide a number of key advantages including no thermal runaway resulting in a wide operating temperature range (from higher than 120°C to below 0°C), negligible leakage over the period

of years, and a robust chemistry that simplifies integration and packaging. Perhaps most important is the latter attribute, as it offers a direct route to the development of the Li metal secondary battery, where liquid cell technologies have until now failed.

This all-solid-state battery technology is built upon our development of two key sulfide-based solid phase chemistries for the rechargeable battery, a high capacity composite cathode and a glass ceramic electrolyte. The glass ceramic binary electrolyte, $\text{Li}_2\text{S-P}_2\text{S}_5$ [1], is similar to thio-LISICON [2], and provides exceptional ionic conductivity in excess of 1×10^{-3} S/cm (similar to liquid electrolytes) and chemical stability against Li metal. Being solid-state, the electrolyte layer not only provides pathways for ion conduction, but also serves as the mechanical separator between the electrodes, thus simplifying the overall battery cell architecture. Through composite cathode design including a high-rate TiS_2 chemistry (providing > 1200 W/kg), we have previously demonstrated the utility of this solid battery approach for high-power applications [3].

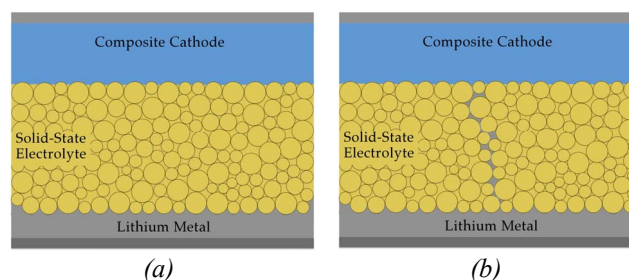


Figure 1. Schematics showing the side-view of (a) the all-solid-state composite cell architecture, and (b) the short-circuited cell after the Li metal dendrite grows within the electrolyte separator travelling via grain boundaries from the anode to the cathode.

The enabling characteristics of the all-solid-state architecture are only fully realized when an ultra-high capacity cathode chemistry is coupled with a Li metal anode, a configuration currently only achievable in the solid-state. To this end, we have recently developed a reversible composite cathode based upon an iron-sulfur chemistry that delivers in excess of 800 mAh/g at $30-60^\circ\text{C}$ and less than 3.0V [4], a six-fold improvement over SoA cathode chemistries. This electrode and cell level performance is realized through directed materials design coupled with composite engineering to maximize both the kinetics and realizable capacity. The result is a reversible Li metal battery chemistry that is predicted to provide an almost *three-fold increase* in packaged energy density when fully optimized (*ie.*, > 500 Wh/kg).

However, ultra-high capacity Li metal battery cycle life remains a major research challenge for the battery community at large, because the transport of significant

Li^+ across the cell, even in the solid-state, inevitably results in cell short-circuiting and failure by dendrite formation during the charge cycle (Fig 1B). In fact, dendritic growth in the all-solid-state battery came as a surprise to our research team, since it was anticipated that the solid electrolyte layer would act as a physical barrier to the dendrite. While no discussion of dendrite formation is found in the solid-state literature, extensive work has been done in liquid electrolyte cells to understand the formation and growth patterns of Li metal dendrites, and to engineer solutions to the problem. For example, stability enhancement of the Li metal anode, which ultimately leads to improved cyclability, can be attained through utilization of the alloy effect [5] which has historically been used to control macroscopic electrodeposition processes. Co-depositing a small amount of sodium with Li metal has been shown to increase the stability of the anode, but at slightly reduced coulombic efficiency, near 91% [6]. Additionally, other work has shown that implementing solid-state electrolytes with a shear modulus in excess of 10 GPa (1.45 Msi) will provide substantial mechanical resistance to the formation and growth of dendrites on the surface of the Li metal anode [7].

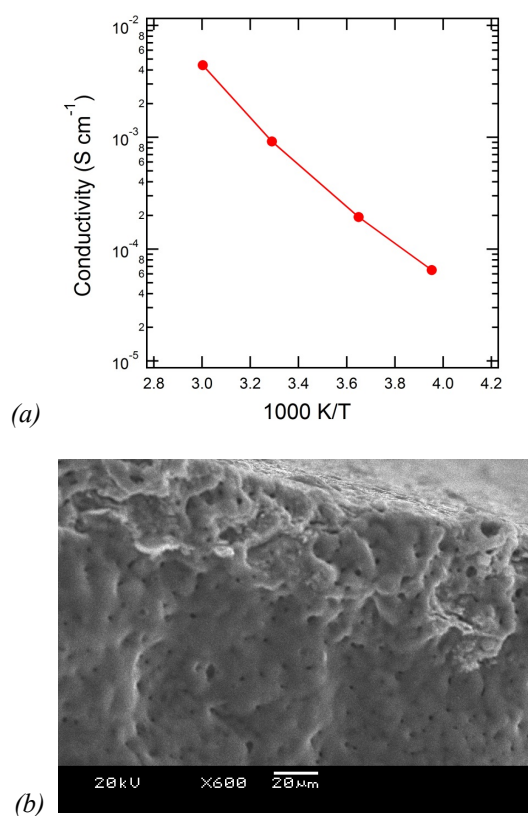


Figure 2. (a) Ionic conductivity of the 77.5Li₂S-22.5P₂S₅ solid electrolyte plotted versus inverse temperature. (b) SEM image showing the morphology of the as ball-milled electrolyte.

At this stage however, dendrite formation in solid phase electrolytes, whether occurring by inter- or trans-granular growth, remains uninvestigated by the battery

community. The physico-chemical properties of solid phase electrolytes, as opposed to their liquid counterparts, offer a wider range of engineering possibilities for controlling, and possibly solving, the dendrite problem. To this end, we describe our ongoing efforts to treat this problem through electrolyte materials engineering, with the goal of demonstrating a cyclable all-solid-state Li metal battery that utilizes our iron-sulfur cathode chemistry and the Li₂S-P₂S₅ electrolyte.

FABRICATION

In short, the Li₂S-P₂S₅ electrolyte used in this work is prepared by ball milling of the Li₂S and P₂S₅ precursors for up to 24 hours in a ratio of 77.5 to 22.5, respectively, creating a partially crystalline powder product with an average particle size between 1 and 5 micrometers and an optimal composition of 77.5Li₂S-22.5P₂S₅ [1]. In order to form the solid electrolyte separator layer, the ball milled powder is cold-pressed at 3-5 tons to form a solid pellet with porosities ranging from 2-8%, depending upon processing conditions. Battery cell manufacture, including composite cathode preparation, is further detailed in references 3 and 4.

RESULTS AND DISCUSSION

As opposed to conventional liquid electrolyte systems, the solid phase electrolyte shows improved ionic conductivity with increasing temperature, as expected for ion transport in crystalline solids. In Fig 2A, the Arrhenius behavior for the ionic conduction of 77.5Li₂S-22.5P₂S₅ is shown. The activation barrier for Li⁺ diffusion is estimated to be about 0.38 eV, which compares favorably to many conventional systems including the LiPF₆ based liquid electrolytes [8]. Interestingly, solid phase electrolytes such as the Li₂S-P₂S₅ system show consistent behavior over a much wider range of working temperatures, whereas liquid electrolytes tend to lose conductivity much more rapidly at lower temperature due to a phase change. Shown in Fig 2B, the typical morphology of the electrolyte after ball milling is determined by scanning electron microscopy (SEM). Extensive nanoporosity and surface roughness of the material is seen, which is supported by BET surface area measurements typically on the order of 700 m²/g for the electrolyte powder. The observed morphology is non-ideal for a solid electrolyte electrode separator, since interfacial defects such as those observed in Fig 2B are mechanically weak and will provide unwanted pathways for dendrite growth, as discussed next. Improving the morphology and mechanical properties of the electrolyte remains an outstanding requirement, and is currently underway in our laboratories.

Empirical evidence from our ongoing work indicates that Li metal battery cells utilizing the iron-sulfur cathode chemistry short circuit and fail within the first 1-3 cycles due to the dendrite phenomenon when the cell current is above about 1.5 mA. The corresponding cell operating temperatures lie between 30 and 60°C, with active material loading in the composite cathode typically at 30%. Of note here is that cell short-circuiting does not

precede thermal runaway as in liquid cells, thus demonstrating the improved safety of the all-solid-state cell architecture. In Fig 3, representative cell cycle data is presented for an iron-sulfide composite Li metal battery. The underlying discharge/charge electrochemistry in this battery system is described in detail elsewhere [4]. The discharge/charge profile for the third cycle (solid line) was obtained at a C/10 rate. For the subsequent cycle (dashed line), the rate was increased to C/2. The cell current at C/10 was 1.4 mA, while the increased rate corresponded to a current of 7.0 mA. As evidenced in Fig 3, the dramatic increase in current short-circuited the cell at C/2 rate during the charging portion of the cycle.

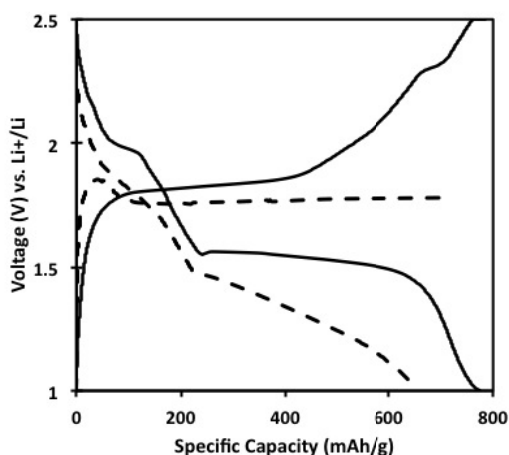


Figure 3. The third (solid lines) and fourth (dashed lines) cycles shown for an iron-sulfur all-solid-state Li metal battery. Upon increasing the cell current after the third cycle, the cell short-circuits due to dendrite formation in the next charge cycle.

Initial evidence indicates that dendrite growth occurs in our $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte system via intergranular pathways. Given the porous nature of our cold-pressed electrolyte pellets (Fig 2B), such a mechanism is not surprising. This mechanism was confirmed in our electrolyte by cross-sectioning a pellet and imaging with field emission SEM (FE-SEM) and energy dispersive X-ray spectroscopy. Shown in Fig 4A, a cold-pressed $77.5\text{Li}_2\text{S}-22.5\text{P}_2\text{S}_5$ electrolyte pellet is imaged after cross-sectioning. Preliminary results indicate that Li metal dendrites grow along grain boundaries within the electrolyte pellet, however, further work is required to confirm this result. To date, the effect of sintering the pellet to improve the mechanical strength at the grain boundaries has not been fully explored as a means to preventing dendrite formation.

Given the wide temperature range over which the solid phase electrolytes can be utilized [1, 5], our current efforts are directed towards identifying a minimum operating temperature above which dendrite formation becomes unlikely. This premise is built upon the longstanding model for dendrite formation that first begins with a roughening of the anode interface during discharge where Li^+ is transported from the anode to the cathode [5-7]. Upon charging, Li^+ returns through the

electrolyte separator to the anode. In a conventional lithium metal anode architecture as shown in Fig 1A, the Li metal forms a two dimensional (planar) interface with the solid-state electrolyte. As the energy density of composite cathode increases (e.g., by thickening the cathode), the current density at the anode interface increases accordingly. Although Li metal is regarded as a nonpolarizing electrode, it can still develop quite large overpotential at a high current since its charge transfer resistance at the interface cannot be zero. In addition to this polarization issue, a high current density will initiate dendritic growth of lithium metal during charge cycle of at the roughened interface, eventually causing a short circuiting of the battery as Li^+ are progressively reduced at the dendrite front.

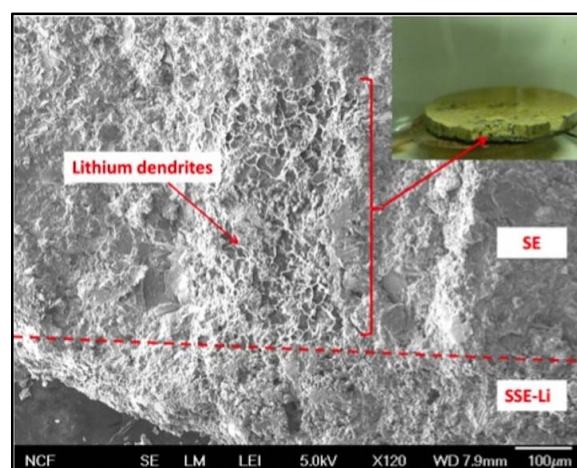


Figure 4. FE-SEM image of the cross-section of a cold-pressed $77.5\text{Li}_2\text{S}-22.5\text{P}_2\text{S}_5$ electrolyte pellet removed from a short-circuited battery. The cross-sectioned electrolyte pellet is shown in the upper-right inset.

Anodic roughening can be mitigated by increasing the operating temperature of the battery, thus increasing Li^0 atom diffusion rates and the kinetic smoothing the anode interface. Preliminary work to this end has identified a temperature window between 75-85°C for the $77.5\text{Li}_2\text{S}-22.5\text{P}_2\text{S}_5$ electrolyte where the typical 1.5 mA cell short-circuits at rates between C/10-C/2. The measurements were performed by fabricating $\text{Li}/\text{Li}_2\text{S}-\text{P}_2\text{S}_5//\text{Li}$ cells and cycling the Li^+ back and forth between the two Li metal electrodes. In this way, electrolyte conductivity and susceptibility to short-circuiting could be evaluated as a function of temperature and rate. In Fig 5, the electrolyte test cell is cycled at 100°C, a temperature above which dendrite growth should be inhibited. The solid line represents the applied voltage, while the dashed line is the cell current. Stable cycling is observed over the entire test, where the first 4.5 cycles are used to condition the cell at a C/2 rate (giving about 0.75 mA) and the following 5.5 cycles are performed at a rate of 1C (giving about 1.5 mA). The latter test condition at 1C and 1.5 mA reliably yields short-circuiting in similar test cells at 30, 60 and 80°C (not shown) upon the first charge cycle, however, at 100°C the cell does not fail after 6 cycles.

These initial data are encouraging, as it indicates that the solid phase electrolyte can be utilized in a Li metal battery architecture that operates at or above 100°C without the risk of short-circuiting. Further work is ongoing in our laboratories to confirm this hypothesis and to determine the effects of elevated temperature on the iron-sulfur electrochemistry of the composite cathode.

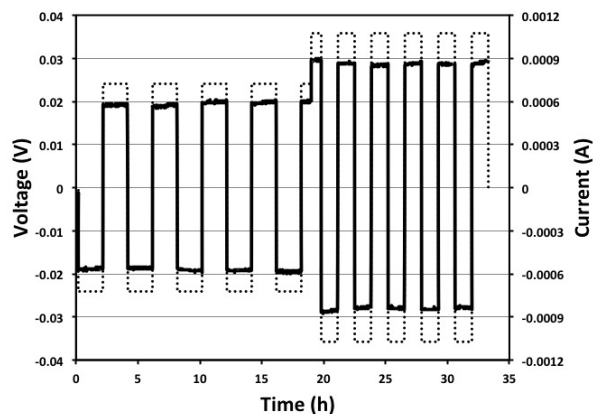


Figure 5. Cycling behavior for a Li//77.5Li₂S-22.5P₂S₅//Li test cell operated at 100°C and rates between C/2 and 1C without short-circuiting. Identical cells tested at or below 80°C consistently short-circuit due to dendritic growth on the first charge cycle.

CONCLUSIONS

Dendrite formation and short-circuiting in secondary batteries continues to plague the battery community and ultimately prevents the adoption of Li metal as the negative electrode. As a consequence, standard paths to increased energy storage will fall far short of the almost three-fold increase promised by Li metal technology. All-solid-state batteries, on the other hand, have the potential to utilize Li metal in a reliable and safe way, thus paving the way to a dramatic increase in achievable energy density. In this paper, the Li₂S-P₂S₅ solid electrolyte enables Li⁺ cycling at elevated temperature without short-circuiting. Further electrolyte engineering is necessitated to solve the dendrite problem, and to enable the inclusion of ultra-high capacity cathodes into the secondary battery architecture without risk of failure due to dendritic growth at lower temperatures. However, this research work indicates that elevated temperature operation may be able to circumvent the dendrite problem, presenting a potential solution that is uniquely enabled by the solid phase electrolyte.

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