



Correlating the interface resistance and surface adhesion of the Li metal-solid electrolyte interface

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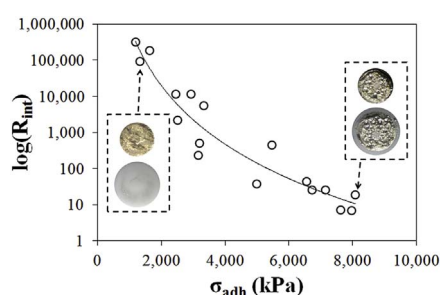
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HIGHLIGHTS

- Li-solid electrolyte interface strength is correlated with interfacial resistance.
- Low interfacial resistance is correlated with a strong Li-LLZO interface.
- The adhesion between Li-LLZO can exceed the ultimate tensile strength of Li.
- Presents a method of quantifying the wettability of Li on LLZO at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Solid electrolytes could enable stable cycling of metallic Li anodes, which can offer drastic increases to the capacity of Li-ion batteries. However, little is known about the mechanics of the Li-solid electrolyte interface. This study combines electrochemical and mechanical characterization to correlate interface kinetics with adhesive strength. Cubic garnet with the $\text{Li}_{6-25}\text{Al}_{0-25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) formulation was selected as a model solid electrolyte based on its high conductivity and stability against Li metal. Symmetric Li-LLZO cells were tested using electrochemical impedance spectroscopy to determine the interfacial resistance, R_{int} , and the adhesive strength of the Li-LLZO interface, σ_{adh} , was measured using a unique tensile test in an inert atmosphere. It was determined that the R_{int} is directly correlated to the adhesive strength of Li on LLZO. At the highest R_{int} in this study, $330 \text{ k}\cdot\text{cm}^2$ the σ_{adh} was 1.1 kPa and at the lowest R_{int} in this study, $7 \cdot\text{cm}^2$, σ_{adh} was 8 MPa. Furthermore, by optimizing the surface chemistry the wettability of LLZO was enhanced resulting in σ_{adh} exceeding the ultimate tensile strength of Li metal. The relationship demonstrated provides a deeper understanding of the mechanical properties of the Li-electrolyte interface, which will play an important role in the design of batteries employing metallic Li anodes.

1. Introduction

In recent years, solid state electrolytes have garnered interest as potential materials to enable the usage of Li metal anodes for high energy density batteries [1,2]. Unlike in conventional liquid electrolytes, solid state electrolytes not only offer the ability to conduct Li ions

but also act as a physical barrier to prevent dendrite penetration and parasitic SEI side reactions, which limit the use of Li metal in state-of-the-art cells [3,4]. The family of ceramic oxides with the garnet structure has shown promise as candidates for a solid electrolyte to use with Li metal. The cubic phase of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) in particular has shown potential due to its high ionic conductivity ($\sim 1 \text{ mS}/\text{cm}^2$) and

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stability against Li metal [5–8]. In order to successfully incorporate Li metal anodes into solid state batteries, it is imperative that the interface is sufficiently stable and the charge transfer kinetics are sufficiently fast for facile stripping and plating of Li metal. Currently there is a knowledge gap in the understanding of the mechanical behavior of Li metal, as well as the mechanics and properties at the LLZO-Li metal interface. Because of its instability in air, it is difficult to characterize Li metal using conventional techniques and even more difficult to characterize the mechanics of the metal-solid electrolyte interface since it is buried. Computational methods have been used to study the mechanical properties of Li metal [9], but few experiments have been able to verify these calculations. One study in particular was able to investigate the mechanical behavior of nanoscale Li pillars [10], however there have not been many other studies that have been able to determine the mechanical properties of Li metal. It is clear by the lack of experimental data on pure Li metal that there are many challenges in thoroughly studying the mechanics of the Li-electrolyte interface. However, in order to mature Li metal electrode technology, a deeper understanding of the relationship between electrochemical and mechanical properties of this metal-electrolyte interface is needed.

One of the biggest challenges in pairing most oxide electrolytes with metallic Li has been high interfacial resistance [11,12]. Recently, it was demonstrated that layers of Li_2CO_3 spontaneously form on the surface of the LLZO in humid air, which results in significant increases in the interfacial impedance [13]. Furthermore, a recent study compared the wettability of LLZO to the wettability of Li_2CO_3 and showed that the wettability of LLZO can be greatly improved by removing Li_2CO_3 contamination from the surface [14]. It is clear from these two studies that the degree of surface chemistry between Li metal and LLZO is not only related to the morphology of the LLZO surface features, but is also strongly related to the degree of contamination on the LLZO surface. However, currently there are no known methods of quantifying the wettability of a surface at room temperature. Since the wettability is typically measured for liquids or molten materials, the wettability of Li metal on a surface must be measured at temperatures above the melting point. This not only presents experimental challenges, but can also only provide information on the behavior of the liquid-solid interface and not a solid-solid interface, which is not representative of typical operating conditions. Since the wettability of Li on LLZO is an indication of chemistry at the interface, which not only correlates to low impedances, it should also correlate to a strong interfacial bond between the two surfaces. This leads to the hypothesis that the Li-LLZO interfacial resistance, R_{int} , should be intrinsically linked to the strength of the Li-LLZO adhesive bond, σ_{adh} . The goal of this work is to explore this relationship between the interfacial resistance and the mechanical strength of the interface to demonstrate intrinsic links between the electrochemical and physical properties of the Li-LLZO interface at room temperature.

To correlate R_{int} with σ_{adh} , all solid-state Li-LLZO-Li cells were fabricated and characterized using conventional electrochemical techniques and a mechanical testing apparatus. R_{int} was measured using electrochemical impedance spectroscopy (EIS) as a function of surface treatment, which affected the surface chemistry. σ_{adh} was measured with a unique tensile tester in an inert gas atmosphere. The observed correlation agrees with the hypothesized relationship between the interfacial resistance and interfacial strength and may provide further insight into the interactions between Li metal and oxide electrolytes.

2. Experimental

2.1. Material synthesis and processing

Al-stabilized cubic LLZO with nominal composition $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ was prepared by a solid state synthetic method. The starting precursors, Li_2CO_3 (1 μm , Alfa Aesar, Ward Hill, MA), $\text{La}(\text{OH})_3$ (1 μm , Alfa Aesar, Ward Hill, MA), Al_2O_3 (0.05 μm , Mager

Scientific Inc. Dexter, MI), and ZrO_2 (30–60 nm, Inframat, Advanced Materials, Manchester, CT) were weighed with the appropriate stoichiometry and were milled in ethanol on a roller mill for 20 h s. A 5 wt % excess amount of Li_2CO_3 was added to the precursors to account for volatilization during the calcination process. The powders were dried, cold-pressed, and calcined at 1000 °C for 4 h s in dry air. The resulting pellets were ground into powders and then hot-pressed at 1100 °C under 47 MPa for one hour, using a rapid-induction hot-pressing technique as described by Rangasamy et al. [15]. The resulting pellet was then cut into 1.5 ± 0.2 mm thick samples using a diamond saw and polished with sandpapers and diamond pastes of varying degree, ranging between a final polish of 1200grit to a 1 μm polish. In order to minimize the exposure to air, the LLZO specimens were stored in an Ar-filled glovebox. Before testing, some LLZO samples were heat treated at 400 °C temperature for 3 h s inside the glovebox in order to remove the Li_2CO_3 surface layers.

2.2. Solid-state cell assembly

Symmetric Li-LLZO-Li cells were fabricated using the same procedure reported by Sharafi et al. [11]. Li foils (Alfa Aesar), 750 μm thick, were scraped to remove any oxide layers from the surface and then pressed onto each side of the LLZO disc. To fabricate cells with high R_{int} , the Li foil was simply pressed onto the LLZO by hand at room temperature and then tested. To fabricate cells with lower R_{int} , the Li foil was pressed onto the LLZO and then preconditioned at ~ 170 °C under a load of ~ 1 MPa for 4 h s. To fabricate cells with the lowest R_{int} achievable, the LLZO was heat-treated at 400 °C for 3 h s in an inert atmosphere before attaching the Li foil and preconditioning at ~ 170 °C with a load of ~ 1 MPa for 4 h s.

2.3. Electrochemical testing

The interfacial resistance of the cell was measured with electrochemical impedance spectroscopy (EIS) using a Biologic VMP-300 galvanostat/potentiostat. EIS was performed after the samples had cooled to room temperature and was conducted from 1 Hz to 7 MHz with a perturbation of 100 mV. The obtained spectra were fit to a modified version of the model proposed by Huggins [16]. In the Huggins model, three parallel elements, representing the bulk, grain boundary, and interfacial impedances, are connected in series, with each element containing a resistor and capacitor in parallel. In the model used, the capacitors are replaced with constant phase elements to account for variations in the time constants. It is well known that the interfacial impedance corresponds to the lower frequencies in the EIS spectra and corresponds to Q values of $\sim 10^{-6}$ F. These impedances corresponding to Q values close to 10^{-6} F were taken to be the total interfacial impedance and were multiplied by the area of the Li foil to obtain the R_{int} .

2.4. Mechanical testing

For measuring the adhesive strength of the Li-LLZO interface, σ_{adh} , an Instron 5944 tension/compression testing unit was integrated inside a custom designed Ar-filled glovebox. Measuring the shear strength of the interface was initially considered, but minor misalignments in the test set-up led to dramatic variability in the results. After preconditioning, the cells were cooled to room temperature and one side of the cell was attached to a steel pin using an acrylic based adhesive (Loctite Super Glue Gel). The pin was mounted in one of the tension fixtures of the Instron, while another pin was mounted in the opposite fixture. The two pins were aligned in the tension grips and then the other side of the cell was adhered to the other pin. This method of alignment minimized the loads applied by the Instron grips, perpendicular to the tensile axis. Fig. 1 shows a schematic of the experimental setup. The strength of the Li-LLZO interface was measured using a

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