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Short communication

Demonstration of high current densities and extended cycling in the garnet $Li_7La_3Zr_2O_{12}$ solid electrolyte

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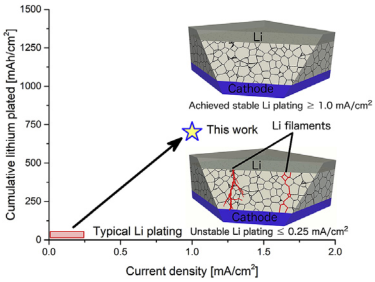
HIGHLIGHTS

- Critical current densities as high as 6.0 mA cm^{-2} were demonstrated at 60 °C.
- 702 mAh cm^{-2} total Li was plated at 60 °C with 3.0 mAh cm^{-2} per half cycle.
- $Li_7La_3Zr_2O_{12}$ is stable against Li during extended cycling.
- Ohmic behavior, EIS, and visual inspection verify short-free electrolyte.

GRAPHICAL ABSTRACT



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ABSTRACT

Replacing state-of-the-art graphite with metallic Li anodes could dramatically increase the energy density of Li-ion technology. However, efforts to achieve uniform Li plating and stripping in conventional liquid electrolytes have had limited success. An alternative approach is to use a solid electrolyte to stabilize the Li interface during cycling. One of the most promising solid electrolytes is $Li_7La_3Zr_2O_{12}$, which has high ionic conductivity at room temperature, high shear modulus and chemical and electrochemical stability against Li. Despite these properties, Li filament propagation has been observed through LLZO at current densities below what is practical. By combining recent achievements in reducing interface resistance and optimizing microstructure, we demonstrate Li cycling at current densities competitive with Li-ion. Li|LLZO|Li cells are capable of cycling at up to 0.9 ± 0.7 mA cm^{-2}, 3.8 ± 0.9 mA cm^{-2}, and 6.0 ± 0.7 mA cm^{-2} at room temperature, 40 and 60 °C, respectively. Extended stability is shown in Li plating/stripping tests that passed 3 mAh cm^{-2} charge per cycle for a cumulative capacity of 702 mAh cm^{-2} using a 1 mA cm^{-2} current density. These results demonstrate that solid-state batteries using metallic Li anodes can approach charge/discharge rates and cycling stability comparable to SOA Li-ion.

1. Introduction

Next generation electric vehicles and consumer electronics demand volumetric energy densities beyond that capable of state-of-the-art Li-ion technology [1,2]. All-solid-state-batteries (ASSBs) offer the potential for meeting these demands with energy densities > 1000 W h L^{-1} while improving safety [3]. These high energy densities are enabled through the use of a metallic Li anode, with a volumetric capacity of 2 A h cm^{-3}.

Metallic Li has long been explored for use as a negative electrode in secondary batteries but the well-known challenge of stabilizing the Li-electrolyte interface has impeded widespread implementation. Solid

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electrolytes offer a prospective solution by physically stabilizing the Li-electrolyte interface. The Monroe and Newman model predicts resistance to Li dendrite initiation if the shear modulus *G* of a solid electrolyte is greater than two times that of metallic Li (~4.5 GPa) [4]. This criterion has been extended to and is easily met by most solid electrolytes, provided they are homogeneous ionic conductors [5]. Yet, Li metal propagation occurs across nearly all known solid electrolytes in spite of their high shear moduli.

One of the most promising solid electrolytes is the garnet, LLZO ($Li_7La_3Zr_2O_{12}$). LLZO has high room temperature ionic conductivity (0.1–1.0 mS cm^{-1}), a wide electrochemical stability window (0–5 V vs Li/Li$^+$), and chemical stability towards metallic Li [6–8]. Despite having a shear modulus of G ~62 GPa, many have observed propagation of Li metal (filaments) through LLZO at low current densities when cycling, indicating the Monroe and Newman model may not be valid for polycrystalline electrolytes such as LLZO [9–11]. For example, Cheng et al. observed that Li metal can preferentially propagate along grain boundaries at high Li plating current densities [12]. In addition, Porz et al. found that flaws in the form of surface roughness act as nucleation sites for Li metal propagation and that failure due to short-circuiting in ceramic electrolytes is analogous to crack propagation [13].

While the mechanism that enables Li metal propagation in solid electrolytes is not well understood, understanding interface transport phenomena could guide approaches to increase the maximum tolerable current density. For example, Sharafi et al. determined that reduction of the Li-LLZO interfacial resistance increases the critical current density (CCD) [11]. The CCD is the current density at and above which Li metal propagates through the solid electrolyte upon plating, and below which stable cycling is achieved. Similarly, Sharafi et al. determined the CCD increases with increasing temperature in Li|LLZO|Li cells [11]. However, despite the recent progress, CCDs are highly variable and typically are ≤0.6 mA cm^{-2} [14–17]. To match the rate performance of state-of-the-art (SOA) Li-ion, the CCD must increase to the 1–3 mA cm^{-2} range [3]. Similarly, the quantity of charge or Li passed per cycle should match that of SOA Li-ion (e.g. ~ several mAh cm^{-2}). Currently, however, most published data fall far below these values and are typically in the 0.2–0.4 mAh cm^{-2} range [18,19]. Thus, to demonstrate performance comparable with SOA Li-ion, we believe a prospective solid electrolyte should follow the criteria such as those proposed by Albertus et al. [3]: i) plating/stripping of relevant areal charge densities of Li (e.g. > 3 mAh cm^{-2}) ii) plating and stripping at relevant current densities (e.g. ≥ 1 mA cm^{-2}), and iii) confirm that no short circuit or "soft short" occurred while cycling.

The objective of this work was to integrate recent progress in understanding solid-state electrolyte interface resistance and microstructure control into one culminating effort to demonstrate up to now unprecedented cycling stability of metallic Li [18,20]. Owing to its stability against metallic Li and high ionic conductivity, LLZO was selected as the model solid electrolyte. Several processing aspects were integrated into this study to control the microstructure and interface resistance. First, to reduce the propensity for Li metal to propagate along grain boundaries, the area fraction of grain boundaries was reduced by densifying at 1225 °C [20]. Second, since it is known that CCD increases with decreasing interface resistance, the Li|LLZO interface resistance was reduced to < 10 Ω cm^2 by heat-treating [18]. Third, though not needed to reduce the nominal Li|LLZO interface resistance, a thin layer of Au was interposed between Li and LLZO. We believe a thin metal layer such as Au may help homogenize the charge distribution at the Li|LLZO interface to prevent hot spots. It is likely that numerous metallically conducting interlayers can achieve this, though Au is simple to deposit in thin and oxide-free form. The efficacy of this unique combination of advances in processing was tested in the cycling of prototypical Li|LLZO|Li all solid-state 100% liquid-free cells (ASSC). To highlight the dramatic increase in average value with rising temperature, CCDs were measured at 20, 40, and 60 °C. After demonstrating high CCD values, extended stable Li tests were conducted in symmetric Li|LLZO|Li cells with a current density of 1.0 mA cm^{-2} and 702 mAh cm^{-2} total Li plated per cell. To confirm that only Li$^+$, and not electrons, was the primary charge carrier during cycling, we propose a combination of analytical techniques consisting of electrochemical impedance spectroscopy (EIS), DC measurement, and simple visual inspection. The goal of this study was to demonstrate that the current density of a Li-solid electrolyte interface can approach that of SOA Li-ion. Because this is a communication, the scope is focused on the rapid dissemination of cycling results, rather than an in-depth study of the enabling mechanisms.

2. Results and discussion

$Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ powders were prepared by the solid-state reaction and densified using rapid induction hot-pressing as described in prior work to greater than 99% of theoretical [11,18]. X-ray diffraction of solid-state synthesized powders after hot pressing showed both $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ are cubic with low impurity levels (Fig. S1).

CCD measurements were performed on Li|$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$|Li symmetric cells at 25, 40, and 60 °C through galvanostatic cycling with increasing current in 0.1 mA cm^{-2} increments from 0.1 mA cm^{-2} until failure (Fig. 1). The method for determining CCD followed the protocol established by Sharafi et al.. [11,20] Typical DC cycling test to determine CCD at different temperatures are shown in Figs. S2, S3, and S4.

The average CCDs and their corresponding standard deviations for three cells were 0.9 ± 0.7 mA cm^{-2}, 3.8 ± 0.9 mA cm^{-2}, and 6.0 ± 0.7 mA cm^{-2} at room temperature, 40 and 60 °C, respectively. The average room temperature data is higher than previously reported, and the higher temperature values are far above published CCD values. We believe these values represent significant progress towards enabling realistic plating/stripping rates with metallic Li anodes. The Au interlayer used here appeared to reduce the standard deviation of CCDs versus uncoated samples but did not increase the absolute CCD values. Clearly, further experimentation on coating types and mechanism of action is necessary. As the relative standard deviation of CCD at room temperature is much higher than at 40 or 60 °C, 60 °C was chosen as the test temperature for long term stability. A current density of 1.0 mA cm^{-2} was chosen to represent realistic plating/stripping rates with high areal plating density.

Li|LLZO|Li symmetric cells were constructed and galvanostatically cycled at 60 °C at a current density of 1.0 mA cm^{-2} 3.0 mAh cm^{-2} (14.5 μm cm^{-2}) Li was plated per half cycle for 117 cycles for a cumulative total of 702 mAh cm^{-2}. This test was replicated using both $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$, with no difference observed in plating behavior with aliovalent dopant. A second condition, 700 mAh cm^{-2} plated at 0.2 mAh cm^{-2} per half cycle over 1750 cycles on a $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ cell, tested the effects of a high number of cycles. To show detail in the voltage vs time behavior, Fig. 2 highlights the first twenty and last twenty cycles of plating. The voltage plateaus during cycling do show polarization that follows Ohmic behavior during cycling (inset in Fig. 2), but the polarization is consistent across all cycles and does not indicate degradation of the solid electrolyte, which would manifest as a reduction to lower voltage under galvanostatic cycling. EIS measurements performed at 60 °C (Fig. S5) do not provide clearly identifiable features, but the total cell impedance averages 26.5 Ω, including uncompensated resistance. The dashed line in Fig. 2 corresponds to the expected Ohmic potential drop of 33 mV expected from the EIS total cell impedance (26.5 Ω × 0.00126 A = 0.033 V). These values closely match the voltage profiles during cycling, confirming the primary charge carrier through LLZO was Li$^+$ with no or negligible electronic conductivity that might result from Li metal propagation or electrolyte degradation (cation reduction in the electrolyte).

EIS was performed prior to and after cycling. Fig. 3a shows EIS