Characterizing the Li-Li₇La₃Zr₂O₁₂ interface stability and kinetics as a function of temperature and current density

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Abstract

The stability and kinetics of the Li-Li₇La₃Zr₂O₁₂ (LLZO) interface were characterized as a function of temperature and current density. Polycrystalline LLZO was densified using a rapid hot-pressing technique achieving 97±1% relative density, and < 10% grain boundary resistance; effectively consisting of an ensemble of single LLZO crystals. It was determined that by heating to 175°C, the room temperature Li-LLZO interface resistance decreases dramatically from 5822 (as-assembled) to 514 Ω.cm²; a > 10-fold decrease. In characterizing the maximum sustainable current density (or critical current density – CCD) of the Li-LLZO interface, several signs of degradation were observed. In DC cycling tests, significant deviation from Ohmic behavior was observed. In post-cycling tests, regions of metallic Li were observed; propagating parallel to the ionic current. For the cells cycled at 30, 70, 100, 130 and 160°C, the CCD was determined to be 50, 200, 800, 3500, and 20000 μA.cm⁻², respectively. The relationships and phenomena observed

in this work can be used to better understand the Li-LLZO interface stability, enabling the use of batteries employing Li metal anodes.

Keywords: Solid state electrolyte, Li, current density, charge transfer

1. Introduction

Li-ion battery technology has advanced significantly in the last two decades [1-3]; however, future energy storage demands will require safer, cheaper and higher performance electrochemical energy storage. While the primary strategy for improving performance has focused on electrode materials [2], the development of new solid-state electrolytes (SSE) has been overlooked as a potential means to create a step change in energy storage performance and safety. Solid-state battery (SSB) employing Li metal anodes are an example of an advanced energy storage technology. Indeed the role that SSE will play in enabling SSB is clear, but relatively few have been identified as promising candidates. Recently, zirconium-based garnet electrolyte, with the formulation $\text{Li}_{6.28}\text{La}_3\text{Al}_{0.3}\text{Zr}_2\text{O}_{12}$ -(LLZO), was reported to have the unique combination of high room temperature Li-ion conductivity, stability against metallic Li, and moderate stability in air [4]. It is believed that lanthania and zirconia form a chemically stable atomic framework that is not decomposed upon contact with metallic Li [4,5]. The shear modulus is another important parameter that is used to predict the stability of the Li-SSE interface [6]. According to Monroe *et al.* the SSE must be approximately twice the shear modulus of metallic Li ($G_{\text{Li}} = 4.2$ GPa, [7]) to suppress Li dendrite initiation [6]. Ni *et al.* determined the shear modulus of LLZO to be 61 GPa using resonant ultrasound spectroscopy [8]. Likewise, according to the model developed by Monroe *et al.*, LLZO exhibits a more than adequate shear modulus to suppress Li dendrite initiation.

Recently, Ohta *et al.* [9] observed negligible capacity fade in an all solid state Li/LLZO/LiCoO₂ cell after 100 cycles. Kotobuki *et al.* also showed it is feasible to cycle a Li/LLZO/LiCoO₂ cell [10]. Conversely, Ishiguro *et al.* [11] observed abrupt swings and a sudden drop in voltage during direct current (DC) polarization tests at $\geq 0.5 \text{ mA.cm}^{-2}$ at room temperature. Moreover, it is believed that the current density is an external variable that affects the on-set of short-circuiting. Although it was not confirmed with post test materials characterization [11,12], it was suggested that the short-circuit could have resulted from Li dendrite formation and propagation.

Previously, Gibson *et al.* [13] characterized the Na-sodium beta alumina (Na-SBA) interface behavior as a function of temperature. It was determined that the interface-charge-transfer resistance decreased with increasing temperature. In addition, Virkar *et al.* [14] studied the effect of temperature on the maximum sustainable current density (or critical current density – CCD), associated with the initiation and propagation of Na metal dendrites, in Na-SBA and Na-NaSICON cells. It was determined that the CCD significantly decreased below the Na melting temperature. We believe the observations made by Gibson *et al.* and Virkar *et al.* in Na-SBA cells may also be observed in Li-LLZO cells, i.e. the Li-LLZO interface-charge-transfer resistance and stability should be strongly correlated to temperature. Thus, the purpose of this work was to investigate the effect of temperature and current density on the stability and kinetics of the Li-LLZO interface. Owing to the complications in fabricating and operating molten Li anode cells, the maximum cell temperature was kept below the Li melting point (180°C) [15]. Electrochemical impedance spectroscopy (EIS) was used to study the individual resistive elements that comprise the total Li/LLZO/Li cell resistance. DC cycling was used to determine the CCD as a function of temperature (30 – 175°C). Additionally, post test microscopy was used

to observe the LLZO surface after cycling. The goal of this work is to better understand the Li-SSE interfacial stability at current densities relevant to vehicle electrification ($> 1 \text{ mA.cm}^{-2}$).

2. Experimental

Cubic $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ (LLZO) was prepared using a solid-state synthetic technique [16,17]. The calcined powders were hot pressed using a rapid induction hot-press technique at 1100°C for 1 hour under constant uniaxial 62 MPa pressure [17]. The density of LLZO pellets were determined by dividing the mass by the measured volume and the relative density was defined from the ratio of the calculated density and the theoretical density (5.17 g.cm^{-3}). In this study, the LLZO pellets were $1.00 \pm 0.20 \text{ mm}$ thick and 12.7 mm in diameter. Powder X-ray diffraction (Bruker, D8 DaVinci diffractometer equipped with CuK_α X-ray radiation) was used to characterize the LLZO phase purity before and after hot pressing. Cross sectional analysis was performed on fracture surfaces using scanning electron microscopy (Carl Zeiss EVO LS25), to characterize microstructural features such as porosity, grain boundary integrity, and grain size.

To characterize the effect of temperature on Li/LLZO/Li cells, several procedures were developed to limit variability between cells. To maintain a consistent surface finish, all LLZO pellets were dry polished with 400 followed by 600 grit SiC sandpaper (Norton Abrasives) in an argon filled glovebox (0.1 ppm O_2 and $1 \text{ ppm H}_2\text{O}$). Solid-state symmetric cells were assembled by placing LLZO pellets between two Li foil (Alfa Aesar) disks. Li foil disks were scraped to remove the oxide layers on the surface. A custom load frame was built and instrumented with a load cell to apply and maintain 350 kPa of stack pressure. To prevent the Li anodes from short-circuiting along the LLZO pellet periphery while under pressure, $100 \text{ }\mu\text{m}$ thick polytetrafluoroethylene (PTFE) washers with 12.7 mm outer diameter and 7.8 mm inner diameter were used. The open area in the PTFE washers reduced the contact area between Li and

LLZO from 1.22 cm² to 0.48 cm² per face. The LLZO Ohmic and charge transfer resistances (the Li-LLZO interfacial resistance normalized per unit area) at the Li-LLZO interface were characterized using electrochemical impedance spectroscopy (EIS) between 1 Hz to 7 MHz using a potentiostat/galvanostat (Bio-logic SP200). The measurements were conducted at various temperatures between 30 and 175°C. In this study, 175°C (just 5°C below melting point of metallic Li [15]) was chosen as the maximum temperature because the use of molten Li would make the testing conditions more complex.

To characterize the effect of temperature on the critical current density, direct current (DC) cycling of Li/LLZO/Li symmetric cells was conducted between 30 and 160°C using the following procedure: (1) ten formation cycles (1hr per cycle) at +/- 10 $\mu\text{A}\cdot\text{cm}^{-2}$ at 175°C to ensure good contact between the Li electrode and the LLZO electrolyte, (2) reduce the temperature to various dwell temperatures ranging from 160°C down to room temperature (30°C) for galvanostatic cycling, and (3) galvanostatically cycle cells at various current densities (1 hour per cycle) with a rest period of 10 min between each current step.

X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific Model K-Alpha XPS instrument using a monochromated, micro-focused Al K $_{\alpha}$ X-ray source (1486.6 eV) with a variable spot size (50-400 μm). Areas for analysis included both pristine (white) areas and areas that were black or discolored. Because the discolored areas were small (10s of microns) an X-ray spot of 100 micron diameter was selected. Electron energy analyzer pass energies of 200 eV and 50 eV were used for survey spectra and core level spectra respectively. Core level spectra were used to determine chemical bond information. Ar-ion sputtering was done 1 keV ions rastered over an area of 1 x 2 mm. Charge compensation was performed with a flood gun using

a combination of low energy electrons and argon ions. Data were collected and processed using the Thermo Scientific Advantage XPS software package (v 4.61).

3. Results and discussion

The XRD patterns of the LLZO powder and pellet after hot pressing at 1100°C are shown in Figure 1a. After calcining and hot pressing, only single phase cubic LLZO was present. A representative microstructure of a LLZO fracture surface indicates the porosity was relatively low, which was consistent with the measured $97\pm1\%$ relative density (Figure 1b). It is observed that the fracture mode was mostly transgranular; evidence of relatively high grain boundary adhesion, which is typically correlated with relatively low grain boundary resistance ($< 10\%$ of the total resistance) [17].

The temperature dependence of Li/LLZO/Li cell kinetics was determined using electrochemical impedance spectroscopy (EIS). The Li-LLZO charge transfer and total LLZO resistances were measured for each temperature (Figures 2a and 2b). **Figure 2a shows the Li-LLZO interface-charge-transfer resistance during heating and cooling. EIS analysis clearly indicates a reduction in Li-LLZO charge transfer with increasing temperature from 30 to 175°C. The lower values for charge transfer at each temperature during cooling in comparison with the values during heating shows the permanent reduction in charge-transfer-resistance. We believe the permanent reduction results from improved wetting and contact between Li and LLZO, which would agree with similar observations of the Na-sodium beta alumina electrolyte interface [13,14,19]. The minimum Li-LLZO charge-transfer-resistance ($2.7 \Omega\cdot\text{cm}^2$) was observed at 175°C. The reciprocal total LLZO resistance values were fitted using the Arrhenius equation (Eqn 1):**

$$R^{-1}T = A \exp (-E_a/k_bT) \quad \text{Eqn (1)}$$

where A is the pre-exponential factor, T is the absolute temperature, E_a is the activation energy, and k_B is Boltzmann's constant. The LLZO activation energy (total including grain and grain boundary resistances), was determined to be 0.28 eV, which is consistent with previously reported values [4,16,18]. Figure 2c shows representative Nyquist plots at 30°C before and after preconditioning at 175°C. The Nyquist plots consist of two distinct resistive components; one at relatively high frequencies (7 MHz - 500 kHz) and a second in the lower frequency region (500 kHz - 1 Hz). The high and low frequency semi-circles are attributed to Ohmic drop through the LLZO pellet, and Li-LLZO interface resistance, respectively. The EIS spectrums were modeled using an equivalent circuit to determine the separate resistive phenomena where, R and CPE refer to resistance and constant phase element, respectively. The calculated capacitance values refined from the equivalent circuit for the total (bulk and grain boundary) LLZO and charge transfer resistances range 10^{-12} to 10^{-8} F.cm⁻² and 10^{-7} to 10^{-5} F.cm⁻², respectively [21]. These values are within the range of the expected capacitance values for these physical processes [20,21], thus validating our assignment of the two semi-circles in Figure 2c. From Figure 2c, several observations can be made. First, it is apparent that the LLZO total resistance has remained constant (171 Ω.cm²) upon heating, preconditioning at 175°C, and cooling. This was expected since LLZO does not degrade in this temperature regime. Additionally, the total conductivity was calculated to be 0.46 mS.cm⁻¹ for LLZO, which is in good agreement with previous data for hot-pressed LLZO doped with Al [4,22]. Second, the charge transfer resistance irreversibly decreased after preconditioning and cooling the cell temperature to 30°C. Initially, the Li-LLZO charge transfer resistance was 5822 Ω.cm² at 30°C, but after heating to 175°C and preconditioning the charge transfer dramatically decreased to 514 Ω.cm² upon cooling to 30°C; a > 10-fold decrease. The charge transfer values were determined by dividing the low frequency

(larger) semicircle diameters by a factor of two since the cells employed two Li anodes of equal area. At room temperature, a charge transfer of $514 \Omega \cdot \text{cm}^2$ was measured, which matches the specified values for Li-LLZO interface ($530 \Omega \cdot \text{cm}^2$) as reported by Ohta *et al.* [23]. However, despite the dramatic reduction in charge transfer resistance, it remains relatively high compared to state-of-the-art (SOA) Li-ion technology that typically exhibits cell impedances in the tens of $\Omega \cdot \text{cm}^2$ [24]. Detailed studies are needed to further reduce the Li-LLZO charge transfer resistance.

The Li-LLZO interface stability was characterized as a function of current density and temperature using Li/LLZO/Li cells galvanostatically cycled between 30 and 160°C (Figure 3). From Figure 3, several observations can be made. First, for each temperature, Ohmic behavior was observed at lower current densities, followed by deviation from Ohmic behavior at higher current densities. Ohmic behavior refers to Ohm's Law (Eqn 2):

$$V = IR \quad \text{Eqn (2)}$$

Where the applied current (I) results in a stable Li/LLZO/Li cell voltage (V) based on the cell resistance (R). When cycling at 30 and 70°C , deviation from Ohmic behavior was marked by a subtle linear decrease in cell voltage followed by a sudden drop to $\sim 0 \text{ V}$ (Figures 3a, b). For the cells cycled at 30 and 70°C , the sudden drop to 0 V occurred at 50 and $200 \mu\text{A} \cdot \text{cm}^{-2}$, respectively. In comparison, when cycling at 100, 130 and 160°C the deviation in Ohmic behavior was marked by a non-linear increase in cell potential, followed by a sudden drop in potential (Figures 3c-e). For the cells cycled at 100, 130 and 160°C , the sudden drop to 0 V occurred at 800, 3500, and $20000 \mu\text{A} \cdot \text{cm}^{-2}$, respectively. Correlation between the two different mechanisms that deviate from Ohmic behavior is not known at this time; however, future work will investigate this phenomenon. Regardless, a drop to 0 V in all Li/LLZO/Li cells was apparent in the respective current ranges tested between 30 and 160°C . In this study, "critical current density" (CCD) is

defined as the current density at which the cell voltage dropped to 0 V. Second, regardless of the type of deviation from Ohmic behavior, the CCD significantly increased with increasing temperature. The CCD is plotted as a function of temperature in Figure 3f. We believe that increasing the temperature improved wetting and contact between Li and LLZO, thus reducing interface-charge-transfer resistance. Reducing the interface-charge-transfer resistance likely resulted in more uniform current density, thus increasing the CCD. Similar observations were made in Na-sodium beta alumina cells cycled by Virkar *et al.* [14,25].

Figure 4a shows the EIS behavior of a Li/LLZO/Li cell before and after the cycling at 30°C, where the CCD was exceeded. The EIS data before DC cycling shows two distinctive semicircles between 7 MHz - 500 kHz and 500 kHz - 1 Hz, similar to Figure 2c. In contrast, the EIS data are more or less clustered near the origin after the CCD was exceeded, indicating an electronic short circuit had occurred. XPS analysis suggests that the dark linear spots or regions have a more metallic Li character compared to the white or normal LLZO areas in the cycled pellet. These spots are initiated and propagated from the Li plating face to the counter Li electrode. Detailed XPS analyses are underway for a better understanding of the relative composition of the dark spots and correlate with Li deposition process at various current densities. The Figure 4b insets show the distinct linear morphology (LLZO pellet face) and that the trajectory of the Li spots (LLZO cross-sectional fracture surface) follows the Li-ion current path between Li electrodes.

4. Conclusions

In this study, we demonstrated that temperature and current density significantly affect the Li-LLZO interface kinetics and stability between 30 – 175°C. First, it was shown that the Li-LLZO interface resistance decreased with increasing temperature reaching a minimum value of 2.7

$\Omega\cdot\text{cm}^2$ at 175°C ; just below the melting point of Li (180°C). Second, the room temperature Li-LLZO interface resistance decreases dramatically from 5822 (as-assembled) to $514 \Omega\cdot\text{cm}^2$ by heating Li/LLZO/Li cells to 175°C and cooling to room temperature. We believe heating, under constant pressure (350 kPa) improved contact between Li and LLZO to reduce the interfacial resistance. Third, it was shown that the maximum sustainable current density (or critical current density – CCD) increases significantly with increasing temperature. The CCD values as a function of temperature were 50, 200, 800, 3500 and $20000 \mu\text{A}\cdot\text{cm}^{-2}$ at 30, 70, 100, 130, and 160°C , respectively. Furthermore, the formation of metallic Li spots were observed when the CCD was exceeded. Overall, we believe the results of this study will help better understand the Li-LLZO interface stability to enable the use of batteries employing Li metal anodes.

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Figure 1. a) XRD patterns of the LLZO calcined powder and hot pressed pellet at 1100°C, JCPDS 45-109 is a reference for cubic garnet, b) secondary electron SEM image of LLZO pellet fracture surface.

Figure 2. a) The Resistance of the Li-LLZO interface ($R_{\text{Li-LLZO}}$) as a function of temperature during heating ($\circ$) and cooling ($\bullet$), b) the logarithm of the total LLZO resistance as a function of inverse temperature during heating ($\circ$) and cooling ($\bullet$), c) representative Nyquist plots for Li/LLZO/Li cells at room temperature before ($\circ$), and after ($\bullet$) preconditioning at 175°C. Markers indicate experimental data and dotted lines represented the equivalent circuit modeling data for the Li/LLZO/Li cells.

Figure 3. Galvanostatic cycling of Li/LLZO/Li cells at a) room temperature (30°C), b) 70°C, c) 100°C, d) 130°C, and e) 160°C. The critical current density vs temperature for Li/LLZO/Li cells (f).

Figure 4. a) EIS data of a Li/LLZO/Li cell cycled at room temperature: before ($\circ$) and after the CCD was exceeded ($\blacktriangle$); b) optical images of the dark spots that appeared in the cycled LLZO pellet: top face (top right), and cross-sectional fracture (bottom right) surfaces.