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In-situ, non-destructive acoustic characterization of solid state electrolyte cells

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HIGHLIGHTS

- Dendrite penetration in solid state electrolytes causes short-circuiting.
- Acoustic pulse-echo technique monitors changes in microstructural integrity in-situ.
- Can observe dendrite propagation by reduction in stiffness.

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ABSTRACT

Solid-state electrolytes such as cubic $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZO) can enable solid-state batteries, metallic lithium anodes and higher voltage cathodes. However, the stability of cubic LLZO is affected by current density. In beta alumina solid electrolyte, microstructural failure was caused by Na dendrite penetration, and was shown to be a function of the fracture toughness, K_{IC}. The relationship between dendrite penetration and K_{IC} indicates electronic failure is related to creation of microstructural damage, and the microstructural damage may be used as an indicator of imminent electronic failure. To monitor microstructural damage during cycling, we developed a non-invasive, in-situ cell monitoring apparatus to help to correlate mechanical stability with Li-ion current density in LLZO. A pulse-echo transducer was integrated into all solid-state Li-LLZO-Li cells. The capability enables the characterization of microscopic inhomogeneities through the careful measurement of changes to the elastic moduli. The elastic moduli and fracture toughness have been previously reported for dense (>99%) specimens, but monitoring of the relative change in moduli during cycling has not been explored. In this study, an acoustic monitoring method is presented to monitor LLZO specimens during cycling.

1. Introduction

An approach to improve the performance and safety of batteries is replace state-of-the-art liquid electrolytes with solid-state ceramic electrolytes [1–3]. Myriad solid-state electrolytes are currently under development, including polymers [4] and ceramics such as sulfides, oxides, and phosphates [1,2].

Garnet of nominal formulation $Al_{0.25}Li_{(6.25)}La_3Zr_2O_{12}$ (LLZO), is a promising candidate electrolyte and is believed to be stable against metallic Li and has adequate room temperature ionic conductivity to replace liquid electrolytes [1,2,5]. While these attributes are important in the context of technology maturation, the maximum current tolerable ionic current density (or critical current density – CCD) must approach ~1 mA cm^{-2} or values comparable to liquid-based electrolytes.

Recent studies [6–8] indicated that the CCD of LLZO may be < 1 mA cm^{-2} at room temperature when employing symmetric Li anode cells. It is believed that Li metal dendrites initiate and propagate between cell electrodes, thus causing short-circuiting. Little is known about the Li metal initiation and propagation in LLZO as a function of current density. The most relevant work was conducted decades ago where the initiation and propagation of Na metal through sodium beta-alumina (SBA) solid electrolyte was studied [9]. The majority of the investigations involved DC cycling of molten Na at elevated temperature (300 °C) [10–12]. Several models were established to describe the phenomenon; some were based on experimental data indicating the mechanical properties, such as the fracture toughness and elastic modulus, had a profound effect on governing the maximum tolerable current density

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[10–12]. Above the critical current density, Na metal propagated as dendrites or filaments through the SBA microstructure [12]. Thus, based on this previous work, we believe that a characterization approach that measures changes in mechanical properties resulting from the introduction of microstructural defects could elucidate the metal propagation through solid electrolytes. Hence, the goal of this study is to establish a novel, in situ, non-invasive technique to characterize the mechanical and microstructural properties of LLZO before, during, and after the CCD has been exceeded. To this end, an acoustic technique was employed to enable the measurement of acoustic wave speed orthogonal to Li-ion current in Li-LLZO-Li symmetric cells. As Li dendrites propagate, the introduction of flaws or cracks filled with a relatively low elastic modulus phase (E_{Li} = 13.0 GPa) compared to the LLZO parent phase (E_{LLZO} = ~150 GPa) results in a measurable decrease in acoustic wave speed. Thus, correlation with a reduction in wavespeed or elastic modulus upon Li dendrite propagation through LLZO will shed light on the phenomena that govern the CCD. We also believe this technique is applicable to other solid electrolytes and maybe useful in characterizing the mechanical integrity of ceramic electrolyte-ceramic electrode interfaces during cycling.

2. Experimental procedure

2.1. Specimen preparation

Cubic $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZO) was calcined from starter powders of Al_2O_3 (99.9%, AP-212, Mager Scientific, Dexter MI), Li_2CO_3 (99.0%, 36225, Alfa Aesar, Ward Hill MA), $La(OH)_3$ (99.95%, 43123, Alfa Aesar), and ZrO_2 nanopowder (99.9%, 40N-0801, Inframat Advanced Materials, Manchester CT). A 5 at% excess lithium precursor was added to the stoichiometric quantities of precursors to allow for lithium loss during calcination. The doping concentration of alumina was chosen to maximize the Li-ion conductivity [9]. A precursor powder batch of 80 g was milled in a 500 mL agate lined jar (01.462.0225, Retsch GmbH, Haan, Germany) with 50 g of 10 mm agate spherical media (Retsch GmbH, Haan, Germany) at 350 RPM for 8 h in a planetary ball mill (PM100, Retsch GmbH), with 5 min intervals of milling followed by 5 min rest and reversal of rotation direction. The mixed powders were removed from the jar with a stainless steel spatula and passed through a 425 μm sieve (0488110R, Fisher Scientific) to break up the larger agglomerates.

Prior to calcination, the mixed powders were pressed into 25.4 mm diameter pucks of 10 g each with 9000 N force for 2 min. Three 10 g pucks per batch were placed on a MgO boat and calcined in a tube furnace (STF 15/180, Carbolite LTD, Derbyshire, United Kingdom) with a 50 mm diameter alumina tube (EQ-TA-50D-M1000-LD and EQ-FL-50, MTI Corporation, Richmond CA) and 2 L min^{-1} flowing dry air, heated to 1000 °C at 100 °C h^{-1}, held at 1000 °C for 4 h, and cooled to room temperature at 240 °C h^{-1}. The resulting calcined pucks, each between 7.71 g and 7.76 g, exhibited a core yolk of pale yellow material extending to the surface. The yellow material and the immediate surrounding material was manually removed, approximately 25% of the mass of each puck, and the remaining white cubic LLZO material of the pucks were ground and sieved through a 75 μm sieve (0488110BB, Fisher Scientific). The ground and sieved cubic LLZO powder was milled for 30 min in an 80 mL agate line jar (01.462.0197, Retsch GmbH) with 6 × 10 mm agate spherical media at 350 RPM, with 5 min intervals of milling followed by 5 min rest and reversal of rotation direction.

Each specimen was hot pressed from 8 to 10 g of milled LLZO powder from a single calcination batch in a graphite foil (99.8%, 42953, Alfa Aesar) lined die. The powder was cold pressed at 62 MPa or 16 MPa for 30 min, then sintered at 1100 °C and the same 62 MPa or 16 MPa for 1 h by rapid induction hot press (IH15A, Across International, Livingston NJ). The sintered specimens were each sanded with 1500-grit paper to remove the graphite foil from the surface.

After removal of graphite foil, the sides of the specimen were secured with mounting wax (MWH135 South Bay Technology, San Clemente, CA) and the cylinder edges were cut by slow speed diamond saw (11-2180, Buehler, Lake Bluff, IL) at 100 RPM to create a rectangular cross section of approximately 8–9 mm per side. Each of the 6 faces of the parallelepiped specimen was polished with 15 μm diamond paste and glycol-based diamond extender on a technotron polishing cloth (diamond paste 810-915, extender 811-004, cloth 812-452, Leco Corp., St. Joseph, MI) using an automatic polishing wheel (LP 900A machine and 150 fixture, South Bay Technology).

2.2. Materials characterization

A sample of the white calcined powder from each calcination batch and each of the densified specimens were examined by X-ray diffraction (Rotating Anode X-Ray Diffractometer, Rigaku, Tokyo, Japan) with a copper anode and graphite monochromater at 40 kV and 100 mA to determine phase purity, as compared to cubic LLZO in the literature, $Li_{6.5}La_3(Ta_{0.55}Zr_{1.45})O_{12}$ (ISCD 183686) [13].

Fractured or cut and polished surfaces of the LLZO specimens were imaged by SEM (Quanta 200, FEI, Hillsboro, Oregon) at 15 kV and 0.31 nA.

2.3. Cycling experiment

Cycling was performed within an argon glovebox with less than 0.25 ppm oxygen content. The LLZO specimen consists of a rectangular parallelepiped shaped solid electrolyte with a height taller than that the face of an ultrasonic transducer and cross section of approximately 9 mm × 9 mm. Prior to cycling, each of the approximately 9 mm × 9 mm faces that were to be in contact with lithium metal were sanded with a sheet of 1500-grit sandpaper inside the glovebox immediately before assembling. The lithium metal (10769, Alfa Aesar) was scraped with a stainless steel spatula to expose a fresh metallic surface, then a piece was cut to fit onto each sanded specimen surface. A piece of nickel-based foil (ASTM A753 Type 4) was placed on the outside of the lithium as an electrical connection. The entire stack (Ni-Li-LLZO-Li-Ni) was placed inside a Teflon sleeve with a cutout window, and compressed between two 12.7 mm nickel rods with manual force (Fig. 1a). Proper contact between the LLZO and the Li metal, with reasonable bulk and contact resistance, was confirmed by electrochemical impedance spectroscopy (EIS) from 7 MHz to 1 Hz (VMP-300 hardware and EC-Lab V10.40 software, Bio-Logic SAS, France).

The stack was heated to 170 °C and preconditioned by cycling at ± 0.01 mA cm^{-2} for 30 min in each direction, repeating for a total of 10 full cycles to reduce the contact resistance [6]. After cooling to room temperature, a change in contact resistance was measured by EIS.

Cycling was performed at room temperature in steps of 0.05, 0.1, 0.2, 0.3 and 0.4 mA cm^{-2}. Each cycle was performed for 30 min forward and 30 min in reverse polarization, followed by a 5 min or 10 min pause between cycles with no potential. Cycling was continued until a short circuit was observed, identified by a sudden drop in cell potential to near 0 V.

During cycling, changes in the LLZO acoustic properties were monitored by measuring the acoustic wavespeed using a longitudinal transducer (pulser-receiver 5073 PR-15-U, transducer V110-RM, couplant SWC, Olympus NDT Inc., Walham MA), (Fig. 1b and c). The transducer was secured onto the side of the specimen in a pulse-echo configuration with a rubber band. Pulse time through