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Key parameters governing the densification of cubic-$Li_7La_3Zr_2O_{12}$ Li^+ conductors

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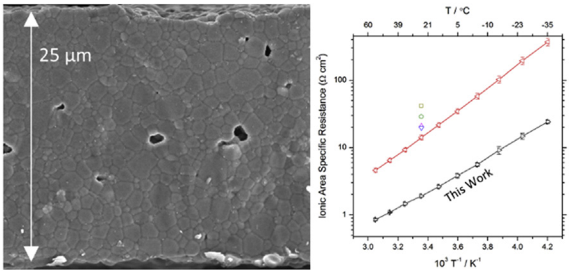
HIGHLIGHTS

- Ion (Li^+/H^+) exchange and densification of c-LLZO are correlated for the first time.
- Decomposed LLZO undergoes reaction driven densification at < 1000 °C.
- Flame made, fully decomposed nanopowders provide an ideal path to sintered films.
- Ga:LLZO thin films (25 μm) with high ionic conductivity (1.3 mS cm^{-1}) are produced.
- Record low ionic area specific resistance (2 Ω cm^2) is achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Cubic-$Li_7La_3Zr_2O_{12}$ (LLZO) is regarded as one of the most promising solid electrolytes for the construction of inherently safe, next generation all-solid-state Li batteries. Unfortunately, sintering these materials to full density with controlled grain sizes, mechanical and electrochemical properties relies on energy and equipment intensive processes. In this work, we elucidate key parameters dictating LLZO densification by tracing the compositional and structural changes during processing calcined and ball-milled Al^{3+} doped LLZO powders. We find that the powders undergo ion (Li^+/H^+) exchange during room temperature processing, such that on heating, the protonated LLZO lattice collapses and crystallizes to its constituent oxides, leading to reaction driven densification at < 1000 °C, prior to sintering of LLZO grains at higher temperatures. It is shown that small particle sizes and protonation cannot be decoupled, and actually aid densification. We conclude that using fully decomposed nanoparticle mixtures, as obtained by liquid-feed flame spray pyrolysis, provides an ideal approach to use high surface and reaction energy to drive densification, resulting in pressureless sintering of Ga^{3+} doped LLZO thin films (25 μm) at 1130 °C/0.3 h to ideal microstructures (95 ± 1% density, 1.2 ± 0.2 μm average grain size) normally accessible only by pressure-assisted sintering. Such films offer both high ionic conductivity (1.3 ± 0.1 mS cm^{-1}) and record low ionic area specific resistance (2 Ω cm^2).

1. Introduction

Pursuit of all-solid-state Li batteries that offer overall performance equal to or superior to current commercial batteries, especially with respect to safety, remains an important research

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objective [1,2]. Ceramic electrolytes that possess ionic conductivities similar to liquid counterparts yet with wider electrochemical and thermal stability windows are key to realizing such batteries [3,4]. Decades of study on doping and processing of ceramic electrolytes to identify Li^+ conduction channels and mechanisms provides target ceramic electrolytes for further study [3,5]. At present, cubic-$Li_7La_3Zr_2O_{12}$ (c-LLZO) is of utmost interest as it satisfies multiple performance metrics and also offers chemical stability to Li metal [3,6], an optimal anode material for its high theoretical capacity (3860 mAh g^{-1}) [7]. Although recent reports suggest c-LLZO suffers electrochemical instability to Li as the result of Li dendrite propagation during cycling [8,9], critical current densities can be improved by interface conditioning [10], surface microstructural control [11], or in-situ intermediate anode alloy layer formation [12,13]. Efforts are made to further understand and engineer c-LLZO/Li interfacial properties to raise permissible current densities to practical levels.

At a component level, the compositions and microstructures of c-LLZO with optimal electrochemical properties are well identified [3]. Al^{3+}, Ga^{3+}, Nb^{5+} and Ta^{5+} are commonly used high ionic conductivity cubic phase stabilizing dopants that provide ambient conductivities of 0.2–1.3 mS cm^{-1} when sintered to high densities ($\geq$ 94%) [3,14]. In contrast, un-doped LLZO presents a tetragonal crystal structure with ionic conductivities of 10^{-3} mS cm^{-1} [3]. Supervalent cations at selected concentrations are introduced to generate Li^+ vacancies which dramatically enhance ion conducting properties by promoting ion hopping [15,16]. Critical vacancy concentrations of 0.5 have been determined, where t-LLZO is fully converted to c-LLZO [17]. From a microstructural perspective, higher relative densities provide higher ionic conductivities [18], and small grains (20–40 μm) appear to offer improved cycling performance as well as lower c-LLZO/Li interfacial resistance compared to large grains (100–200 μm) [11]. This has been ascribed to distribution of Li^+ current along the LLZO grain boundaries at the c-LLZO/Li interface [11].

As addressed in recent review articles, the next phase of study should focus on processing LLZO in the correct form factor, films <40 μm, while replicating bulk form properties, using a low-cost mass-producible method [1,2,19]. To date, achieving high density c-LLZO at such fine thicknesses has been deemed extremely difficult. Typical LLZO sintering conditions involve heating powder compacts to temperatures >1100 °C for 10–40 h [20,21]. Ga^{3+} doped LLZO reaches high densities at shorter sintering times of 5–8 h as $LiGaO_2$ promotes sintering [22,23]. At this temperature, Li_2O volatilizes rapidly, and thus samples must be covered in the same powder to mitigate evaporation [21,24]. Yet, even the properties of the cover powder affect the final microstructure, complicating the process [24]. Therefore, efforts has been made to reduce sintering times or temperatures such that the fractional excess Li intentionally introduced in the starting powder can balance Li_2O loss without relying on a bed of powder. Successful approaches introduce a secondary driving force for densification; e.g. induction hot-pressing [17,18,25], field assisted [26] or spark plasma sintering [27]. Sintering times are shortened to $\leq$ 1 h at 1000–1100 °C. However, these methods are cost prohibitive for mass-production and as yet no examples of thin film formability have been forthcoming.

The majority of published sintering studies are limited to mm thick pellets whereas thin film processing work is scarce. The higher surface/volume ratios of thin films increase Li_2O loss rates, posing additional challenges [28,29]. For example, sol-gel coating efforts to produce LLZO thin films resulted in low ionic conductivities (10^{-3} mS cm^{-1}) due to low relative densities and crystallinity imposed by the need to use sintering temperatures ($\leq$ 900 °C) that restricted Li_2O loss [29,30]. Hence, a novel processing route that leads to consistent sintered bodies at fine thicknesses must still be developed.

Recently, we reported the very first examples of processing Al^{3+} doped, dense and flexible c-LLZO thin film membranes (< 30 μm) by pressureless sintering at 1090 °C/1 h, using flame made nanoparticles, overcoming the above listed challenges [28]. The origin of rapid densification observed in these studies requires further elucidation, as pinpointing the mechanisms extant allows one to control them to further improve processing conditions and final properties. The objectives of the work reported here are to determine the key variables affecting the densification of c-LLZO and to exploit the identified variables to demonstrate superior densification. In this work, flame made Al^{3+} doped LLZO powders were calcined and ball-milled using conditions similar to most commonly reported methods [24,31,32]. We monitored compositional and structural changes by TGA, DSC, XRD, BET, SEM, and dilatometry for the individual processing steps as well as on heating. Our findings are linked to a combination of events identified in the individual steps arising from these multiple different characterization methods. Using our improved understanding, Ga^{3+} doped LLZO powders were made by liquid-feed flame spray pyrolysis and processed to free standing thin films with superior control of compositional, microstructural, and electrochemical properties.

2. Experimental

2.1. Precursor synthesis and powder production

Lithium propionate [$LiO_2CCH_2CH_3$], lanthanum isobutyrate {$La[O_2CCH(CH_3)_2]_3$}, zirconium isobutyrate {$Zr[O_2CCH(CH_3)_2]_2(OH)_2$}, and alumatrane [$Al(OCH_2CH_2)_3N$] were synthesized as described in our previous work [28]. Gallium-atrane [$Ga(OCH_2CH_2)_3N$] was synthesized by reacting gallium hydroxide [$Ga(OH)_3$, 7 g, 0.06 mol] with triethanolamine [$(HOCH_2CH_2)_3N$, 10 g, 0.07 mol] using ethylene glycol [$HOCH_2CH_2OH$, 40 ml] as a solvent in a 250 ml round bottom flask equipped with a still head at 190 °C in N_2 atmosphere. Once transparent orange liquid was obtained, most of the ethylene glycol was distilled off, and the reactor was cooled down. Gallium hydroxide was prepared by adding aqueous ammonia to aqueous solution of gallium nitrate. Lithium propionate, lanthanum isobutyrate, zirconium isobutyrate, and gallium-atrane were dissolved in ethanol at a selected molar ratio to result in $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ (Ga:LLZO) composition with 50 wt% excess lithium. $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (Al:LLZO) with 15 wt% excess lithium was also produced by substituting gallium-atrane with alumatrane. The precursor solution with 3 wt% ceramic loading was aerosolized and combusted to generate nanoparticles using the liquid-feed flame spray pyrolysis (LF-FSP) apparatus [28]. Details of LF-FSP synthesis can be found in our previous work [28,33,34].

2.2. Powder and film processing

As-produced Al:LLZO nanopowders were dispersed in EtOH (200 proof, Decon Labs) with 2 wt% polyacrylic acid (M_n = 2000, Sigma-Aldrich) dispersant, using an ultrasonic horn (Vibra cell VC-505, Sonics and Materials, Inc.) at 100 W for 15 min. After 4 h of settlement to let larger particles to settle, supernatant was decanted and dried. Powders were then manually dry compacted to pellets and heated to 750 °C for 20 h. Resulting pellets were pulverized and subsequently ball-milled in 2-propanol for 40 and 80 h using 3.0 mm diameter spherical ZrO_2 beads, and then dried in air. Calcined and ball-milled powders were heated to 400, 600, and 800 °C for 1 h at a ramp rate of 10 °C min^{-1}.