Key parameters governing the densification of cubic- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Li^+ conductors

Eongyu Yi, Weimin Wang, John Kieffer and Richard M. Laine*

Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, USA

*Corresponding author. Tel.: +1 7347646203; fax: +1 7347634788.

E-mail address: talsdad@umich.edu (R. M. Laine).

Abstract

Cubic- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (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 change 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, 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 aids 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 $\pm$ 1 % density, 1.2 $\pm$ 0.2 μm average grain size) normally accessible only by pressure-assisted sintering. Such films offer both high ionic conductivity (1.3 $\pm$ 0.1 mS cm^{-1}) and record low ionic area specific resistance (2 $\Omega\cdot\text{cm}^2$).

Keywords : Solid electrolyte, Li conducting garnet, Thin film, Flame spray pyrolysis, Lithium ion battery

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 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- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (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 $0.2\text{--}1.3 \text{ mS cm}^{-1}$ when sintered to high densities ($\geq 94 \%$) [3,14]. In contrast, un-doped LLZO presents a tetragonal crystal structure with ionic conductivities of $10^{-3} \text{ mS cm}^{-1}$ [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 concentration of 0.5 has 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 ($20\text{--}40 \mu\text{m}$) appear to offer improved cycling performance as well as lower c-LLZO/Li interfacial resistance compared to large grains ($100\text{--}200 \mu\text{m}$) [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 $< 40 \mu\text{m}$, 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 $> 1100\text{ }^{\circ}\text{C}$ 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 have been made to reduce sintering times or temperatures such that 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 $\leq 1\text{ h}$ at $1000\text{-}1100\text{ }^{\circ}\text{C}$. 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 ($10^{-3}\text{ mS cm}^{-1}$) due to low relative densities and crystallinity imposed by the need to use sintering temperatures ($\leq 900\text{ }^{\circ}\text{C}$) 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 LLZO thin film membranes ($< 30\text{ }\mu\text{m}$) by pressureless sintering at $1090\text{ }^{\circ}\text{C}/1\text{ h}$, 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 [$\text{LiO}_2\text{CCH}_2\text{CH}_3$], lanthanum isobutyrate [$\{\text{La}[\text{O}_2\text{CCH}(\text{CH}_3)_2]_3\}$], zirconium isobutyrate [$\{\text{Zr}[\text{O}_2\text{CCH}(\text{CH}_3)_2]_2(\text{OH})_2\}$], and alumatrane [$\text{Al}(\text{OCH}_2\text{CH}_2)_3\text{N}$] were synthesized as described in our previous work [28]. Gallium-atrane [$\text{Ga}(\text{OCH}_2\text{CH}_2)_3\text{N}$] was synthesized by reacting gallium hydroxide [$\text{Ga}(\text{OH})_3$, 7 g, 0.06 mole] with triethanolamine [$(\text{HOCH}_2\text{CH}_2)_3\text{N}$, 10 g, 0.07 mole] using ethylene glycol [$\text{HOCH}_2\text{CH}_2\text{OH}$, 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 $\text{Li}_{6.25}\text{Ga}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga:LLZO) composition with 50 wt. % excess lithium. $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (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 ZrO₂ 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.

As-produced Ga:LLZO nanopowders were subject to the same cleaning process of dispersion, decantation, and drying. Suspensions were formulated per Table 1 by adding all components to a 20 ml vial and ball-milling with 3.0 mm diameter spherical ZrO₂ beads for 12-24 h to homogenize the suspension. Suspensions were cast using a wire wound rod coater (Automatic Film Applicator-1137, Sheen Instrument, Ltd.) to result in green films with thicknesses of 45±2 µm. Dried green films were manually peeled off the Mylar substrate, cut to selected sizes, and thermo-compressed at 80-100 °C with a pressure of 50-70 Mpa for 5-10 min using a heated bench top press (Carver, Inc.) to improve packing density.

Table 1. Suspension formulation.

	Role	Wt. ratio
LLZO powder	Ceramic	37
Polyvinyl Butyral	Binder	3
Benzyl Butyl Phthalate	Plasticizer	3
Polyacrylic Acid	Dispersant	1
Ethanol	Solvent	28
Acetone	Solvent	28

Green films of Ga:LLZO were heated to selected temperatures and dwell times in N₂ (100 ml min⁻¹), placed in between graphite foils to avoid possible contamination or reaction with common ceramic crucibles. Sintered films were subsequently heat treated to 700-800 °C for 1-4 h in O₂ to remove surface carbon deposits.

2.3. Characterization

X-ray diffraction measurements were carried out using a Rigaku Rotating Anode Goniometer (Rigaku Denki., LTD.). Scans were made from 10 to 70° 2θ, using Cu Kα radiation (1.541 Å) operating at 40 kV and 100 mA. The Jade program 2010 (Materials Data, Inc.) was used for analysis.

Specific surface areas (SSAs) were obtained using a Micromeritics ASAP 2020 sorption analyser. Samples (300 mg) were degassed at 150 °C/5 h. Each analysis was run at -196 °C (77 K) with N₂. The SSAs were determined by the BET multipoint method using ten data points at

relative pressures of 0.05–0.30. SSA was converted to average particle sizes (APS) using the equation $APS = 6/(SSA \times \rho)$. The net density (ρ) of the as-produced powder was approximated by rule of mixture.

Micrographs were taken using a FEI NOVA Nanolab system (FEI company). Powder samples were used as is, sintered films were fractured for imaging. All samples were sputter coated with gold using a SPI sputter coater (SPI Supplies, Inc.). For grain size measurements, sintered films were fractured and thermally etched at 930 °C for 0.2 h in N₂ prior to sputter coating. Lineal intercept method was used to calculate the average grain sizes.

Q600 simultaneous TGA/DSC (TA Instruments, Inc.) was used to observe thermal decomposition of as-produced powders and green films. Samples (15–25 mg) were loaded in alumina pans and ramped to 1000 °C at 10 °C min⁻¹ under constant air flow at 60 ml min⁻¹.

Dilatometry studies were conducting using a Dilatronic II single pushrod dilatometer (Theta Industries). Linear displacement was traced by a linear variable differential transformer (LVDT). Constant heating rate experiments were conducted from room temperature to 1050 °C at a ramp rate of 10 °C min⁻¹. Temperature was limited to 1050 °C to prevent excessive equipment damage from Li₂O volatilization.

AC impedance data were collected with broadband dielectric spectrometer (Novocontrol technologies) in a frequency range of 10 MHz to 0.1 Hz at -35 to 55 °C in increments of 10 °C. Concentric gold electrodes, 3 mm in diameter, were deposited using a SPI sputter coater on both surfaces of the films using a deposition mask. “EIS spectrum analyser” software was used for extracting total resistance. Equivalent circuit consisting of ($R_{total}Q_{total}$)($Q_{electrode}$) was used. R and Q denote resistance and constant phase element, respectively. SEM fracture surface images were taken to measure sample thicknesses.

Final sintered film densities were determined by Archimedes method using ethanol.

3. Results and discussion

3.1. Interplay of particle size, ion (Li^+/H^+) exchange, and densification

Solid state reaction is commonly used to produce LLZO powders which are subsequently ball-milled to reduce average particle sizes (APSs) prior to compaction [24,31,32]. Calcination and ball-milling conditions determine the final APSs which in turn strongly affect densification

behavior. In fact, Cheng et al., report an almost three fold higher densification rate with attrition milled, 1 μm LLZO particles compared to un-milled 10 μm counterparts [24]. However, it is likely that smaller particle sizes, that is, higher specific surface areas (SSAs), accelerate the protonation reaction during and/or after processing. It is common knowledge that LLZO readily reacts with H_2O , forming proton doped LLZO and LiOH , which soon converts to Li_2CO_3 [35,36]. This implies ball-milling introduces more processing variables, as discussed below, in addition to reduction in particle sizes. Reports on optimizing densification behavior and probing the role of hydration are available, yet the two aspects have never been coupled.

To simulate commonly used conditions yet access micron to sub-micron APSs, we calcined and ball-milled $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Al:LLZO) nanopowders with 15 wt. % excess Li ($\text{SSA} = 16 \text{ m}^2 \text{ g}^{-1}$) synthesized by liquid-feed flame spray pyrolysis (LF-FSP) method. Calcined powders (750 $^\circ\text{C}$ /20 h) were ball-milled in 2-propanol followed by air drying. Extended ball-milling of 40 and 80 h was selected to emphasize the degree as well as effect of protonation. Flame made nanoparticles were used because solid-state reaction derived powders generally require high-energy ball-milling to access sub-micron particles due to the higher temperatures required to calcine powders of target compositions [3,24,31].

Fig. 1 compares the morphologies, thermal stabilities and activities of the as-produced, calcined, and ball-milled Al:LLZO powders. As-produced nanopowders are a mixture of Li_2CO_3 and off-stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ ($\text{La}_3\text{Zr}_2\text{O}_{8.5}$) [28]. The rationale for producing fully decomposed LLZO is discussed just below. Calcination of these powders result in granules of 10-70 μm (Fig. 1b). After ball-milling, 0.5-1 μm primary particles decorated with nanoparticles < 50 nm result (Fig. 1c and 1d). No noticeable difference between 40 and 80 h ball-milled powders were observed by SEM. The surface nano-architecture is assumed to be Li_2CO_3 as it is impossible to mill micron size oxides to nanopowders (< 100 nm) by planetary ball-milling. In support of this statement, is the observation that ion (Li^+/H^+) exchange of LLZO results in Li_2CO_3 surface coatings [37]. XRD patterns of ball-milled powders also show diffraction peaks corresponding to Li_2CO_3 (Fig. 2b and 2c). SSAs of the 40 and 80 h ball-milled powders were 17 and 19 $\text{m}^2 \text{ g}^{-1}$, slightly higher than for as-produced nanopowders, 16 $\text{m}^2 \text{ g}^{-1}$. However, as evidenced in Fig. 1a, 1b, and 1c, this is likely due primarily to nanoscale surface roughness arising from Li_2CO_3 formation and does not imply smaller overall APSs.

Fig. 1. SEM of (a) LF-FSP synthesized Al:LLZO nanopowders, (b) calcined and crushed Al:LLZO powders, (c) and (d) 40 h ball-milled powders. (e) TGA and (f) DSC of as-produced and ball-milled (BM) powders. DSC curves are off-set for differentiation.

TGAs of ball-milled powders show mass losses at temperatures below the calcination temperature, suggesting H_2O and CO_2 uptake of LLZO during processing (Fig. 1e). Mass loss at $< 400^\circ\text{C}$ is attributed to H_2O , whereas $> 400^\circ\text{C}$ is due to CO_2 evolution [35,36]. In addition to the Li_2CO_3 melting endotherm at 720°C , two distinct thermal processes, exotherms at $250\text{--}350^\circ\text{C}$ and near 610°C , are observed on heating (Fig. 1f). The origins of these exotherms were identified by XRD of powders heated to selected temperatures.

Fig. 2 shows XRDs of calcined, ball-milled, and heated Al:LLZO powders. A mixture of t-LLZO and c-LLZO are observed in the as-calcined state due to excess Li, known to stabilize t-LLZO even when c-LLZO stabilizing dopants are present (Fig. 2a) [25]. Traces of Li_2ZrO_3 and LaAlO_3 intermediate phases were also present but disappear on heating to higher temperatures. On ball-milling, t-LLZO disappears and peaks corresponding to c-LLZO and Li_2CO_3 are observed (Fig. 2b and 2c). The presence of Li_2CO_3 suggests that LiOH forms due to protonation during and/or after ball-milling. Similar results have been previously reported [36]. Compared to the highly crystalline, as ball-milled XRD patterns, an amorphous hump appears at $400^\circ\text{C}/1\text{ h}$ (Fig. 2b and 2c). The high noise level also implies a high fraction of amorphous phase. Hence, the initial DSC exotherm is attributed to the collapse of the protonated LLZO lattices (Fig. 1f).

This has never been reported as little attention is given to ball-milled powders heated to low temperatures as the final target of most studies is to reach high densities by sintering. Furthermore, larger particle sizes of solid state reaction derived ball-milled powders likely have less proton doped LLZO due to lower SSAs, making it difficult to notice. XRD patterns of powders heated to 600 °C/1 h show c-LLZO with broad peaks corresponding to $\text{La}_2\text{Zr}_2\text{O}_7$ (Fig. 2b and 2c). La_2O_3 is also likely present based on the molar ratio but is unidentifiable due to peak overlap. This suggests the second DSC exotherm originates from crystallization of the amorphous phase (Fig. 1f). Ion exchange (Li^+/H^+) has been reported to commonly occur for Li garnets with more than three Li ions per formula unit [38]. In particular, Galvenet al. also reports decomposition of protonated $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ (LLSO) Li garnet to Li_2SnO_3 , $\text{La}_2\text{Sn}_2\text{O}_7$, and La_2O_3 on heating, while no XRD data is presented [39]. In their study, decomposed mixtures are Li short compared to LLSO as the ion exchange reaction was conducted in benzoic acid/ethanol solution where Li^+ likely dissolved. On heating to 800 °C/1 h, a mixture of t-LLZO and c-LLZO is recovered (Fig. 2d).

Fig. 2. XRD patterns of the samples along the processing flow chart at selected stages. Initial and final stages show the same pattern yet intermediate temperatures show different phase fractions based on degree of protonation which leads to lattice collapse followed by crystallization. In Fig. 2b and 2c, unlabeled peaks are from c-LLZO.

Based on lower ceramic yields, stronger initial exotherm, and stronger $\text{La}_2\text{Zr}_2\text{O}_7$ relative peak intensities, 80 h ball-milled powders seem to have a higher degree of protonation (Fig. 1e, 1f, 2b, and 2c). Higher SSAs also suggests more Li_2CO_3 decorates the primary particle surfaces. It can

be concluded that ball-milling times, that is, APSs, dictate degree of protonation which leads to different degrees of decomposition on heating, in turn affecting densification as discussed below.

Fig. 3. Comparison of the linear shrinkage of the as-produced and ball-milled powders. Maximum temperature was limited to 1050 °C to prevent excessive equipment damage from Li₂O volatilization.

Dilatometry studies were conducted to observe the effect of decomposition on densification behavior. Fig. 3 compares linear shrinkages of powder compacts on heating. Densification takes place in two distinct stages in the observed temperature range. We assign the first steep linear shrinkage near the Li₂CO₃ melting point (720 °C) to liquid phase wetting the solid oxide particles thereby exerting compressive capillary force, one of the densification mechanisms prevalent in the liquid phase sintering [40]. The shrinkage rate of the first stage also indirectly supports longer ball-milling time leading to higher degrees of protonation as evidenced by greater shrinkage of the 80 h vs 40 h ball-milled powder compacts. As-produced powder shows the highest first stage shrinkage rate as it is fully decomposed, possessing the highest fraction of Li₂CO₃. The second, slower densification is likely from reaction of molten Li₂CO₃ and oxide components, gradually forming LLZO (Fig. 2d). Reaction driven densification is completed the fastest for the as-produced powder due to mixing at finer length scales (Fig. 1a). We conclude LLZO decomposition gives rise to reaction driven densification at lower temperatures which provides a superior platform for further densification of LLZO at higher temperatures.

Ion (Li^+/H^+) exchange, contrary to having negative effects on sintered LLZO [41,42], acts advantageously in processing terms by introducing additional densification mechanisms. It appears others who performed calcination and ball-milling of LLZO powders benefitted from this phenomena without noticing [21,24,31,43].

As a representative example, Cheng et al. also reports densification near the Li_2CO_3 melting point followed by densification of LLZO grains at higher temperatures when heating attrition milled 1 μm LLZO powder compacts using dilatometry [24]. They claim ball-milling only affected the particle sizes based on XRD. However, reaction driven densification near and slightly above the Li_2CO_3 melting point is evident in their study. The corresponding densification rate is $\sim 5\%$, indicating lower degree of protonation, making it difficult to detect Li_2CO_3 solely by XRD due to low relative intensity ratios.

Combining the findings of Cheng et al. where they report higher sintered densities of Al:LLZO pellets at shorter sintering times when attrition milled powders were used, with results shown above as well as our recent success in pressureless sintering Al:LLZO using flame made fully decomposed LLZO nanopowders at heating schedules similar to when hot-pressed, we conclude decomposed LLZO with small APSs is an ideal starting point to minimize required external energy for reaching high densities. Therefore, aerosol combustion synthesis is well-suited for this purpose as it continuously produces fully decomposed LLZO nanoparticles.

Calcined and ball-milled powders may also lead to results similar to flame made nanoparticles when sintered. However, no further efforts were made to convert the ball-milled powders to films as excess Li content has to be adjusted to accommodate higher surface/volume ratios [28]. Furthermore, flame made nanopowders readily reach high density sintered bodies without additional intermediate processing, making calcination and ball-milling processes unnecessary.

3.2. Achieving thin film membranes with properties equal to bulk

First examples of continuous production of fully decomposed LLZO powders were demonstrated by Djenadic et al. using spray pyrolysis (SP) in which metal nitrate precursors dissolved in deionized water were sprayed into a hot tube ($900\text{ }^\circ\text{C}$) [44]. In SP, droplets undergo solvent evaporation, metal salt decomposition, and oxide formation typically producing aggregated large particles [45,46]. As-produced powders were a mixture of Li_2CO_3 , $\text{La}_2\text{Zr}_2\text{O}_7$,

and La_2O_3 . The particles showed a broad size distribution ranging from nano to several microns with several morphologies; nano-aggregates, spheres, and broken shell, hollow spheres. The non-uniform size distribution and morphologies of the as-synthesized powders are attributed to the non-uniformity of the initially sprayed precursor solution droplets, one of the key parameters affecting the final particle morphologies in SP synthesis [45,46]. Based on the phase composition, reaction driven densification must have taken place, yet the final densities reached were just 56 %. This can be ascribed to the poor morphological features of the starting powder interrupting uniform packing. On another note, La_2O_3 is hygroscopic, requiring storage of SP synthesized powders in a dry atmosphere.

Liquid-feed flame spray pyrolysis (LF-FSP) can be used to overcome the shortcomings found with SP derived powders. In LF-FSP, precursor droplets gasify on combustion generating a cloud of ions that subsequently undergo nucleation, growth, and quenching, resulting in unaggregated nanoparticles of kinetic phases [33,45]. Uniform particles are obtained in LF-FSP as the precursors are gasified on combustion, and hence the aerosolized droplet size does not affect the final particle characteristics. Furthermore, La_2O_3 can be incorporated into $\text{La}_2\text{Zr}_2\text{O}_7$ phase, forming La rich pyrochlore, providing air stable starting powders. Details are discussed below.

Fig. 4. (a) SEM image of the as-produced Ga:LLZO nanopowder. (b) TGA-DSC curve of the as-produced nanopowder and green film. DSC curves are off-set for differentiation.

Fig. 4 shows nanopowders of $\text{Li}_{6.25}\text{Ga}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga:LLZO) composition with 50 wt. % excess lithium produced by LF-FSP. As-produced nanopowders show spherical morphologies with a narrow size distribution with SSAs of $15 \text{ m}^2\text{g}^{-1}$, corresponding to APSs $\approx 100 \text{ nm}$ (Fig.

4a). XRD confirms the as-produced nanopowders are a mixture of Li_2CO_3 and off-stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ ($\text{La}_3\text{Zr}_2\text{O}_{8.5}$), not LLZO, due to the instability of LLZO in the LF-FSP synthesis atmosphere (Fig. 5a-1). Ga_2O_3 is non-detectable due to small fraction. The primary byproducts of combustion, H_2O and CO_2 , coupled with high flame temperatures ($>1500^\circ\text{C}$) make formation of LLZO nanopowders unfavorable [39]. However, such materials provide excellent starting points for reasons discussed above.

The Ga^{3+} dopant stabilizes the high conductivity cubic phase and the excess lithium balances its loss during sintering. Excess lithium content is also a design parameter that may be optimized as residual excess lithium after sintering results in partial stabilization of low conductivity t-LLZO [25]. However, given that t-LLZO can be annealed to result in c-LLZO when cubic stabilizing dopants are present, no special care was given, see below.

TGA of the as-produced nanopowder shows an endotherm due to Li_2CO_3 melting (720°C), with concomitant CO_2 mass loss as Li_2CO_3 and constituent oxides react to form LLZO. Off-stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$ phase in the composition of $\text{La}_3\text{Zr}_2\text{O}_{8.5}$ is formed, as confirmed by XRD peak shifts using $\alpha\text{-Al}_2\text{O}_3$ internal standard, instead of a mixture of $\text{La}_2\text{Zr}_2\text{O}_7$ and La_2O_3 , contrary to what one might expect based on the $\text{La}_2\text{O}_3\text{-ZrO}_2$ binary phase diagram. This is due to quenching from the high flame temperatures, resulting in kinetics phases. That is, phases normally stable only at high temperatures can be accessed with LF-FSP [47]. In comparison, in Djenadic et al.'s work, since the particle formation temperature equals that of the hot tube (900°C), a mixture of Li_2CO_3 , stoichiometric $\text{La}_2\text{Zr}_2\text{O}_7$, and La_2O_3 are formed. As a reference, the La rich $\text{La}_2\text{Zr}_2\text{O}_7$ phase is stable at temperatures above 1550°C [48].

The TGA-DSC curve of the green film shows mass loss with a corresponding exotherm at intermediate temperatures ($200\text{-}400^\circ\text{C}$) due to oxidative removal of polymeric additives including dispersant, plasticizer, and binder (Fig. 4b). A Li_2CO_3 melting endotherm is noted at 720°C with concomitant mass loss, consistent with that of as-produced powder. This suggests that there were no reactions during ball-milling and the original powder composition is maintained as the powder is fully decomposed to begin with.

Despite the known benefits of colloidal processing **such as excellent shape formability, access to agglomerate free green bodies, and facile mass-producibility [49-51]**, only recently, we have demonstrated the first examples of c-LLZO film processing based on casting-sintering of flame made nanoparticles. The exceptional challenge in obtaining high density c-LLZO sintered

bodies based on previously reported methods likely prohibited colloidal processing of such materials at low thicknesses.

Fig. 5. (a) XRD patterns of (a-1) as-produced Ga:LLZO nanopowders, and green films sintered to (a-2) 800 °C/1 h, and (a-3) 1000 °C/1 h. (b) XRD patterns of green films sintered to (b-1) 1130 °C/0.3 h, (b-2) 1140 °C/0.3 h, and (b-3) 1130 °C/0.3 h followed by 900 °C/2 h annealing.

Green films heated to 800 °C/1 h show t-LLZO as the main crystalline phase with traces of Li_5GaO_4 (Fig. 5a-2). Extra lithium filling the interstitial sites of LLZO likely distorts the crystal structure, stabilizing the tetragonal phase. Li_5GaO_4 also suggests the presence of excess lithium as both Li^+ and Ga^{3+} occupy the same crystallographic sites [52]. At 1000 °C/1 h, a mixture of c-LLZO and t-LLZO are present as Li_2O is partially lost (Fig. 5a-3). Li_2O loss has been reported at temperatures as low as 900 °C [29]. A new peak ascribed to c-LLZO in between two t-LLZO peaks as shown in the inset (27-29° 2θ) appears (Fig. 5a-3). The overall broad base for all peaks indicates the presence of t-LLZO as tetragonal peaks split around the cubic phase peaks on lattice distortion appearing as shoulders.

Unlike common sintering of refractory ceramics, where higher temperatures and longer duration generally result in higher relative densities, the same approach cannot be applied to LLZO sintering due to rapid Li_2O loss at high temperatures. Furthermore, densification must be complete before all excess Li is lost calling for fine control of all processing parameters. Through iterative sintering studies modifying the dwell temperatures and dwell times, we find these films to sinter to high densities at 1130 °C/0.3 h (Fig. 5b-1, and 6a), an extremely short

dwel compared to solid state reaction derived approaches (10-40 h) [3,20,21]. However, XRD shows these films are a mixture of c-LLZO and t-LLZO (Fig. 5b-1).

Fig. 6. (a) SEM fracture surface image of Ga:LLZO films sintered to 1130 °C/0.3 h. (b) and (c) SEM fracture surface image of films sintered to 1130 °C/0.3 h → 900 °C/2 h. (d) Thermally etched fracture surface of films sintered to 1130 °C/0.3 h → 900 °C/2 h.

Twin boundary fringes inherent to t-LLZO are also observed in the SEM fracture surface image (Fig. 6a) [53]. Extending the dwell time results in $\text{La}_2\text{Zr}_2\text{O}_7$ and La_2O_3 secondary phase formation (Fig. 5b-2). Note that t-LLZO co-exists with secondary phases when heated to 1140 °C/0.3 h, as it is odd Li deficient phases form when the Li rich phase is present (Fig. 5b-2). We assume the Li_2O loss at the surface is faster than re-distribution of Li^+ within the bulk. Given the former is gasification whereas the latter is diffusion within a crystalline solid, they must happen at different rates. Hence, the temperatures were lowered to < 1000 °C where the two rates could balance empirically. By annealing the 1130 °C/0.3 h sintered films at 900 °C/2 h, c-LLZO was obtained with traces of La_2O_3 (Fig. 5b-3). Microstructural features due to twin boundaries also disappeared (Fig. 6b and 6c). Fig. 6c shows the surface smoothness and thickness uniformity of the sintered films. It appears 50 % excess Li is overkill, and processing studies of Ga:LLZO with lower excess Li content are underway. The smallest ever reported average grain sizes of $1.2 \pm 0.2 \mu\text{m}$ in the LLZO family is obtained which translates to films 20-27 grain thick, providing superior mechanical properties compared to larger AGS films (Fig. 6d). As a comparison Al:LLZO films in our previous work are 10-15 grains thick due to larger AGS

(2.4 μm) [28]. It is possible to achieve such fine, final grain sizes because we start with nanopowders.

Films sintered under optimal conditions provide Nyquist plots showing semi-circles at high frequencies and spikes at low frequencies, due to ion conduction and blocking effects, respectively (Fig. 7a inset). The right intercept of the semi-circle with the real axis reduces with temperature suggesting faster conduction as Li^+ diffusion is thermally activated. No secondary arc arising from grain boundary resistance is noticeable due to high relative densities and superior grain boundary contact as revealed by low porosity, trans-granular fracture surfaces (Fig. 6b and 6c). Samples with lower relative densities with the inter-granular fracture mode have been reported to show two semi-circles arising from grain and grain boundary resistance [28]. An Arrhenius trend is found as Li^+ conduction is a diffusional process where Li^+ migrates through hopping between interstitial sites (Fig. 7a) [15,16]. Ionic conductivities range from 0.1 to 3 mS cm^{-1} in the measured temperature span (-35 to 55 $^{\circ}\text{C}$), with $1.3 \pm 0.1 \text{ mS cm}^{-1}$ room temperature conductivity. Activation energy (E_a) of $0.28 \pm 0.01 \text{ eV}$ is obtained from the Arrhenius plot, similar to what is reported for Ga^{3+} doped LLZO pellets [23]. E_a is lower compared to Al^{3+} doped LLZO films processed in our previous studies, 0.35 eV, suggesting less energy is needed for the hopping, and hence faster Li^+ conduction.

Fig. 7. (a) Arrhenius plot of Ga:LLZO sintered to optimal conditions. Inset shows Nyquist plots at selected temperatures. Note the electrode area and sample thickness are factored in (unit : $\text{k}\Omega\cdot\text{cm}$) (b)

Comparison of reported ionic area specific resistance of LLZO electrolytes. Detailed information of the labels are in Table 2.

Table 2. Reported properties of LLZO membranes produced by methods suitable for mass production.

	Dopant(s)	Method	d (μm)	$\sigma_{\text{tot.}}$ (mS cm^{-1})	IASR ($\Omega\cdot\text{cm}^2$)	Ref.
(1)	Al^{3+}	sol-gel dip coating	1	0.0024	42	29
(2)	Al^{3+}	compact/sinter	150	0.52	29	24
(3)	Al^{3+}	sol-gel spin coating	0.39	0.0019	21	30
(4)	$\text{Al}^{3+}/\text{Ta}^{5+}$	compact/sinter/saw cut	200	1.02	20	54
(5)	Al^{3+}	cast/sinter	28	0.2	14	28
(6)	Ga^{3+}	cast/sinter	25	1.3	2	This work

Several properties of the LLZO films produced by methods applicable to mass-production are compared in Table 2. Sol-gel coating can access thicknesses $\leq 1 \mu\text{m}$ but suffer from low ionic conductivities ($\sim 10^{-3} \text{ mS cm}^{-1}$) due to low relative densities and crystallinity, resulting in high ionic area specific resistance (IASR) [29,30]. Low relative densities also suggest open porosities where Li dendrites can easily propagate through over cycle. Compaction derived routes generally result in high densities but are limited to high thicknesses leading to high IASR. Such samples may be diamond saw cut but still cannot access thicknesses $< 40 \mu\text{m}$ [54]. IASR can be minimized by decreasing the ion conduction layer thickness and increasing the ionic conductivity ($\text{IASR} = d/\sigma_{\text{tot.}}$).

We demonstrate that through careful processing of flame-made nanoparticles, c-LLZO films at thicknesses $< 30 \mu\text{m}$ that show same conducting properties with thick pellet counterparts can be produced, at a short sintering time and at smaller grain sizes. Record low IASR of $2 \Omega\cdot\text{cm}^2$ is reached in this study.

4. Conclusions

In summary, we show that ion (Li^+/H^+) exchange cannot be decoupled with small particle sized LLZO, and it actually acts as an advantage in processing terms by introducing additional densification mechanisms. Reaction driven densification at intermediate temperatures (700-900 °C) as a result of Li_2CO_3 melting and its reaction with constituent oxide components provide

a superior platform for further sintering of LLZO grains at higher temperatures. Based on earlier observations and what is reported here, we conclude that fully decomposed LLZO nanoparticles are an ideal starting point in processing LLZO films. Indeed, using flame made nanopowders of fully decomposed Ga:LLZO as an example, we achieve extremely short sintering times (1130 °C/0.3 h) and low final film thicknesses (25 μm), while replicating the bulk form properties ($1.3 \pm 0.1 \text{ mS cm}^{-1}$, $95 \pm 1\%$ density) via simple pressureless sintering. The resulting ionic area specific resistance is the lowest ever reported in the garnet family ($2 \text{ } \Omega \cdot \text{cm}^2$).

Acknowledgements

We thank the support of a significant portion of this work by NSF through DMR 1105361 and DMR 116058. We also thank the University of Michigan Energy Institute (UMEI) and Michigan Translational Research and Commercialization (MTRAC) program for support to purchase chemicals, solvents, furnace and LF-FSP reactor components.

References

- [1] B. Wu, S. Wang, W. J. Evans Iv, D. Z. Deng, J. Yang, J. Xiao, *J. Mater. Chem.* A4 (2016) 15266-15280.
- [2] R. Chen, W. Qu, X. Guo, L. Li, F. Wu, *Mater. Horiz.* 3(2016) 487-516.
- [3] V. Thangadurai, S. Narayanan, D. Pinzaru, *Chem. Soc. Rev.* 43 (2014) 4714-4727.
- [4] Y. Ren, K. Chen, R. Chen, T. Liu, Y. Zhang, C.-W. Nan, B. Vyas, *J. Am. Ceram. Soc.* 98 (2015) 3603-3623.
- [5] J. C. Bachman, S. Muy, A. Grimaud, H. H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, *Chem. Rev.* 116 (2016) 140-162.
- [6] M. Kotobuki, K. Kanamura, Y. Sato, T. Yoshida, *J. Power Sources* 196 (2011) 7750-7754.
- [7] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, *Energy Environ. Sci.* 7 (2014) 513-537.
- [8] R. Sudo, Y. Nakata, K. Ishiguro, M. Matsui, A. Hirano, Y. Takeda, O. Yamamoto, N. Imanishi, *Solid State Ionics* 262 (2014) 151-154.
- [9] Y. Ren, Y. Shen, Y. Lin, C.-W. Nan, *Electrochem. Commun.* 57 (2015) 27-30.

- [10] A. Sharafi, H. M. Meyer, J. Nanda, J. Wolfenstine, J. Sakamoto, *J. Power Sources* 302 (2016) 135-139.
- [11] L. Cheng, W. Chen, M. Kunz, K. Persson, N. Tamura, G. Chen, M. Doeff, *ACS Appl. Mater. Interfaces* 7 (2015) 2073-2081.
- [12] W. Luo, Y. Gong, Y. Zhu, K. K. Fu, J. Dai, S. D. Lacey, C. Wang, B. Liu, X. Han, Y. Mo, E. D. Wachsman, L. Hu, *J. Am. Chem. Soc.* 138 (2016) 12258-12262.
- [13] C. L. Tsai, V. Roddatis, C. V. Chandran, Q. Ma, S. Uhlenbruck, M. Bram, P. Heitjans, O. Guillon, *ACS Appl. Mater. Interfaces* 8 (2016) 10617-10626.
- [14] D. Rettenwander, G. Redhammer, F. Preishuber-Pflugl, L. Cheng, L. Miara, R. Wagner, A. Welzl, E. Suard, M. M. Doeff, M. Wilkening, J. Fleig, G. Amthauer, *Chem. Mater.* 28 (2016) 2384-2392.
- [15] R. Jalem, Y. Yamamoto, H. Shiiba, M. Nakayama, H. Munakata, T. Kasuga, K. Kanamura, *Chem. Mater.* 25 (2013) 425-430.
- [16] K. Meier, T. Laino, A. Curioni, *J. Phys. Chem. C* 118 (2014) 6668-6679.
- [17] T. Thompson, A. Sharafi, M. D. Johannes, A. Huq, J. L. Allen, J. Wolfenstine, J. Sakamoto, *Adv. Energy Mater.* 5 (2015) 1500096.
- [18] Y. Kim, H. Jo, J. L. Allen, H. Choe, J. Wolfenstine, J. Sakamoto, G. Pharr, *J. Am. Ceram. Soc.* 99 (2016) 1367-1374.
- [19] B. D. McCloskey, *J. Phys. Chem. Lett.* 6 (2015) 4581-4588.
- [20] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* 46 (2007) 7778-7781.
- [21] H. Imagawa, S. Ohta, Y. Kihira, T. Asaoka, *Solid State Ionics* 262 (2014) 609-612.
- [22] H. El Shinawi, J. Janek, *J. Power Sources* 225 (2013) 13-19.
- [23] C. Bernuy-Lopez, W. Manalastas, J. M. Lopez del Amo, A. Aguadero, F. Aguesse, J. A. Kilner, *Chem. Mater.* 26 (2014) 3610-3617.
- [24] L. Cheng, J. S. Park, H. Hou, V. Zorba, G. Chen, T. Richardson, J. Cabana, R. Russo, M. Doeff, *J. Mater. Chem. A* 2 (2014) 172-181.
- [25] E. Rangasamy, J. Wolfenstine, J. Sakamoto, *Solid State Ionics* 206 (2012) 28-32.
- [26] Y. Zhang, F. Chen, R. Tu, Q. Shen, L. Zhang, *J. Power Sources* 268 (2014) 960-964.
- [27] S.-W. Baek, J.-M. Lee, T. Y. Kim, M.-S. Song, Y. Park, *J. Power Sources* 249 (2014) 197-206.
- [28] E. Yi, W. Wang, J. Kieffer, R. M. Laine, *J. Mater. Chem. A* 4 (2016) 12947-12954.

- [29] K. Tadanaga, H. Egawa, A. Hayashi, M. Tatsumisago, J. Mosa, M. Aparicio, A. Duran, *J. Power Sources* 273 (2015) 844-847.
- [30] R.-J. Chen, M. Huang, W.-Z. Huang, Y. Shen, Y.-H. Lin, C.-W. Nan, *J. Mater. Chem. A* 2 (2014) 13277-13282.
- [31] N. Janani, S. Ramakumar, S. Kannan, R. Murugan, B. Dunn, *J. Am. Ceram. Soc.* 98 (2015) 2039-2046.
- [32] M. Kotobuki, H. Munakata, K. Kanamura, Y. Sato, T. Yoshida, *J. Electrochem. Soc.* 157 (2010) A1076-A1079.
- [33] C. R. Bickmore, K. F. Waldner, R. Baranwal, T. Hinklin, D. R. Treadwell, R. M. Laine, *J. Eur. Ceram. Soc.* 18 (1998) 287-297.
- [34] E. Yi, W. Wang, S. Mohanty, J. Kieffer, R. Tamaki, R. M. Laine, *J. Power Sources* 269 (2014) 577-588.
- [35] G. Larraz, A. Orera, M. L. Sanjuan, *J. Mater. Chem. A* 1 (2013) 11419-11428.
- [36] Y. Wang, L. Wei, *J. Power Sources* 275 (2015) 612-620.
- [37] L. Cheng, C. H. Wu, A. Jarry, W. Chen, Y. Ye, J. Zhu, R. Kostecki, K. Persson, J. Guo, M. Salmeron, G. Chen, M. Doeff, *ACS Appl. Mater. Interfaces* 7 (2015) 17649-17655.
- [38] C. Galven, J. Dittmer, E. Suard, F. Le Berre, M.-P. Crosnier-Lopez, *Chem. Mater.* 24 (2012) 3335-3345.
- [39] C. Galven, J.-L. Fourquet, M.-P. Crosnier-Lopez, F. Le Berre, *Chem. Mater.* 23 (2011) 1892-1900.
- [40] W. D. Kingery, *J. Appl. Phys.* 30 (1959) 301-306.
- [41] L. Cheng, E. J. Crumlin, W. Chen, R. Qiao, H. Hou, S. Franz Lux, V. Zorba, R. Russo, R. Kostecki, Z. Liu, K. Persson, W. Yang, J. Cabana, T. Richardson, G. Chen, M. Doeff, *Phys. Chem. Chem. Phys.* 16 (2014) 18294-18300.
- [42] Y. Jin, P. J. McGinn, *J. Power Sources* 239 (2013) 326-331.
- [43] Y. Ren, H. Deng, R. Chen, Y. Shen, Y. Lin, C.-W. Nan, *J. Eur. Ceram. Soc.* 35 (2015) 561-572.
- [44] R. Djenadic, M. Botros, C. Benel, O. Clemens, S. Indris, A. Choudhary, T. Bergfeldt, H. Hahn, *Solid State Ionics* 263 (2014) 49-56.
- [45] S. Li, Y. Ren, P. Biswas, S. D. Tse, *Prog. Energy Combust.* 55 (2016) 1-59.
- [46] G. L. Messing, S.-C. Zhang, G. V. Jayanthi, *J. Am. Ceram. Soc.* 76 (1993) 2707-2726.

- [47] T. R. Hinklin, J. Azurdia, M. Kim, J. C. Marchal, S. Kumar, R. M. Laine, *Adv. Mater.*20 (2008) 1373-1375.
- [48] R. S. Roth, *J. Res. Natl. Bur. Stand.*, 56 (1956) 17-25.
- [49] G. N. Howatt, R. G. Breckenridge, J. M. Brownlow, *J. Am. Ceram. Soc.*30 (1947) 237-242.
- [50] D. Hotza, P. Greil, *Mater. Sci. Eng.*, A202 (1995) 206-217.
- [51] K. P. Plucknett, C. H. Caceres, C. Hughes, D. S. Wilkinson, *J. Am. Ceram. Soc.*77 (1994) 2145-2153.
- [52] R. Wagner, G. J. Redhammer, D. Rettenwander, A. Senyshyn, W. Schmidt, M. Wilkening, G. Amthauer, *Chem. Mater.*28 (2016) 1861-1871.
- [53] J. Wolfenstine, E. Rangasamy, J. L. Allen, J. Sakamoto, *J. Power Sources*208 (2012) 193-196.
- [54] K. Liu, C.-A. Wang, *Electrochem. Commun.*48 (2014) 147-150.

Figure caption

Fig. 1. SEM of (a) LF-FSP synthesized Al:LLZO nanopowders, (b) calcined and crushed Al:LLZO powders, (c) and (d) 40 h ball-milled powders. (e) TGA and (f) DSC of as-produced and ball-milled (BM) powders. DSC curves are off-set for differentiation.

Fig. 2. XRD patterns of the samples along the processing flow chart at selected stages. Initial and final stages show the same pattern yet intermediate temperatures show different phase fractions based on degree of protonation which leads to lattice collapse followed by crystallization. In Fig. 2b and 2c, unlabelled peaks are from c-LLZO.

Fig. 3. Comparison of the linear shrinkage of the as-produced and ball-milled powders. Maximum temperature was limited to 1050 °C to prevent excessive equipment damage from Li₂O volatilization.

Fig. 4. (a) SEM image of the as-produced Ga:LLZO nanopowder. (b) TGA-DSC curve of the as-produced nanopowder and green film. DSC curves are off-set for differentiation.

Fig. 5. (a) XRD patterns of (a-1) as-produced Ga:LLZO nanopowders, and green films sintered to (a-2) 800 °C/1 h, and (a-3) 1000 °C/1 h. (b) XRD patterns of green films sintered to (b-1) 1130 °C/0.3 h, (b-2) 1140 °C/0.3 h, and (b-3) 1130 °C/0.3 h followed by 900 °C/2 h annealing.

Fig. 6. (a) SEM fracture surface image of Ga:LLZO films sintered to 1130 °C/0.3 h. (b) and (c) SEM fracture surface image of films sintered to 1130 °C/0.3 h → 900 °C/2 h. (d) Thermally etched fracture surface of films sintered to 1130 °C/0.3 h → 900 °C/2 h.

Fig. 7. (a) Arrhenius plot of Ga:LLZO sintered to optimal conditions. Inset shows Nyquist plots at selected temperatures. Note the electrode area and sample thickness are factored in (unit : kΩ·cm) (b) Comparison of reported ionic area specific resistance of LLZO electrolytes. Detailed information of the labels are in Table 2.