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Tape casting and sintering of $Li_7La_3Zr_{1.75}Nb_{0.25}Al_{0.1}O_{12}$ with Li_3BO_3 additions

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ABSTRACT

An approach for tape casting and sintering of $Li_7La_3Zr_{1.75}Nb_{0.25}Al_{0.1}O_{12}$ (LLZNbO) sheets suitable for use in solid-state battery development is described. The use of Li_3BO_3 as a sintering aid in both pellet and cast tape samples is examined. We find the optimal Li_3BO_3 content for ionic conductivity in pellets is between 1 and 2 wt% Li_3BO_3, much less than in prior reports. At this level, ionic conductivity is $\sim 2.5 \times 10^{-4}\,S\,cm^{-1}$ after sintering in an argon atmosphere at 1000 °C for 6 h. 150–175 micron thick LLZNbO + 0.5% Li_3BO_3 tapes sintered at 1000 °C for 6 h exhibit ionic conductivity values of $2\text{–}3 \times 10^{-4}\,S\,cm^{-1}$.

1. Introduction

Modern electronic devices and electrified vehicles rely heavily on the use of Li-ion batteries. As several accidents have shown, safer batteries are desirable, if not essential for more widespread application. A battery with a solid electrolyte would be a safer alternative to current Li-ion technologies utilizing organic liquid electrolytes. The ideal electrolyte for a solid-state Li-ion battery must have a high lithium ionic conductivity, a negligible electronic conductivity, be stable against elemental lithium and other electrode materials, and allow for operation across a wide electrochemical window. Also desirable is stability against air and water at room temperatures. The ready availability of high energy density bulk solid-state batteries (SSB's) would be a breakthrough advance for both battery safety and performance goals.

Investigations show that stuffed garnets may satisfy most of the criteria for a solid-state battery electrolyte [1]. In the cubic form, depending on the substitutions, it has conductivity ranging from 2 to $7 \times 10^{-4}\,S\,cm^{-1}$ [2]. In addition to its high conductivity, LLZO has also been shown to have high chemical and electrochemical stability with lithium metal [1,2].

LLZO pellets with conductivities $> 10^{-4}\,S\,cm^{-1}$ are routinely produced, but long sintering times at temperatures between 1100 and 1200 °C are typically required. Significant challenges are posed in trying to process dense bodies from Li-rich oxides because of Li losses that occur above ~900 °C in air. To counteract uncontrolled Li loss in pellets researchers typically add additional Li at various steps of grinding/calcination during solid-state processing. It is also common to surround pellets with the mother powder during sintering to further reduce losses from the pellet. Despite this, Li losses occur [3]. One often observes a shell of material on a pellet (e.g. $LaZrO_3$ rich) where there has been significant Li loss. These factors make it difficult to precisely control electrolyte stoichiometry.

Reduced sintering temperatures can decrease Li losses, but simply lowering the temperature risks reducing density too. The preferred way to reduce sintering temperature and still get acceptable densities is through the use of sintering aids, such as the introduction of low melting point phases. The use of sintering aids is well established for the processing of technologically important electrolytes, particularly in the SOFC arena [4]. Glasses often serve such a role in sintering of ceramics, but not all glasses are well suited, depending on factors including the reactivity with LLZO, the extent of grain boundary wetting, and the ionic conductivity. In typical liquid phase sintering systems, < 15 vol% liquid used in order to retain shape during sintering [5]. If too much liquid phase is used, or if complete particle wetting occurs, particles will be separated by the additive, and in a solid electrolyte, this means that current must pass through the liquid phase.

Most additives to LLZO give undesired reactions but Li_3BO_3 is a low melting point (~750 °C) compound that is compatible with LLZO [6–16]. Li_3BO_3 has been demonstrated to permit reduced sintering temperatures, thereby minimizing Li losses due to Li sublimation. Fig. S1 shows a section of the $Li_2O\text{-}B_2O_3$ phase diagram. Li_3BO_3 has a low melting point (773 °C), and is one component of a lower melting point eutectic (646 °C) at slightly higher B_2O_3 levels [17].

In addition to Li_3BO_3, lithium metaborate $LiBO_2$ (LB) and lithium tetraborate $Li_2B_4O_7$ (LB_2) are also highlighted in the diagram. These two compounds are often used together in combinations for fusion sample preparation. Lithium metaborate ($LiBO_2$) has a chain type metaborate (B-O-B) bond, which can be attacked by Li_2O [18]. Hence

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$LiBO_2$ extracts Li_2O from LLZO during sintering, resulting in the formation of $La_2Zr_2O_7$. Li_3BO_3 is composed of orthoborate (BO_3^{3-}) units, which do not react with Li_2O, so that Li_3BO_3 is relatively inert to LLZO. However, Li_3BO_3 is a poor lithium ion conductor (2×10^{-6} S cm^{-1}, 25 °C) compared to LLZO and thus composites are likely to have reduced conductivity compared to the pure phase [7]. As a result of these properties, Li_3BO_3 can act as a sintering aid, enabling LLZO sintering at temperatures > 900 °C, thereby reducing almost all Li loss [6,8].

Li_3BO_3 has also been shown to be compatible with a common cathode material, $LiCoO_2$ [7] [19]. Co-sintered electrolyte/electrode combinations using Li_3BO_3 additions in both LLZO and $LiCoO_2$ made by pressing composite layer pellets of LLZO + Li_3BO_3 and $LiCoO_2$ + Li_3BO_3 have been reported [8]. Such a process is not easily scalable to larger cross-sectional area cells.

Slight modifications to Li_3BO_3 have also been reported including a $53Li_2O$-$31B_2O_3$-$12SiO_2$-$2CaO$-$2Al_2O_3$ glass [12] and a $65Li_2O·27B_2O_3·8SiO_2$ glass [20]. Finally, some success was reported in lowering LLZO sintering temperatures by the addition of B_2O_3 alone, with LLZO-0.3 B_2O_3 pellets yielding 2.5×10^{-4} S cm^{-1} conductivity after sintering at 950 °C for 30 h [21].

In all of the above reports the LLZO-Li_3BO_3 composite was processed as a pellet. Thin electrolyte layers/sheets are desired for development of high-performance solid-state batteries. To date, in the majority of publications exploring the use of LLZO in batteries, the electrolyte has generally been sliced from a sintered pellet and then polished [8,22–30]. While this is suitable for producing small batteries in the lab, it is not an acceptable process for larger scale manufacturing, which requires inexpensive, scalable technology for electrolyte processing. This need can be met if tape casting can be applied to LLZO.

Tape casting is widely used in the manufacturing of electronic packaging and solid oxide fuel cells. It is an economical route to produce thin ceramic sheets, so is attractive for processing of solid-state batteries. Tape casting involves dispensing a slurry of powder onto a carrier film (e.g. silicone coated mylar). An adjustable doctor blade and the slurry viscosity determine the dispensed tape thickness height. The viscosity is adjusted by varying the amounts of organic additives (binder, plasticizers, and dispersants) in the slurry relative to the solids.

LLZO poses challenges for sintering of tape cast shapes because of the Li losses that occur above ~900 °C in air. Unfortunately, the problem of Li loss in LLZO is exacerbated in sintering of sheets, with their higher surface-volume ratio. A Li-deficient layer at a tape surface is undesired as a high impedance electrode/electrolyte interface will likely result.

To date, there have been few reports describing traditional tape casting of LLZO. The most success in fabricating tapes is the work of Laine and colleagues who synthesized flame pyrolyzed LLZO nanoparticles (90 nm in size), and formulated an organic solvent-based slip with a polyvinyl butyral binder. In order to minimize Li losses they sintered for only 1 h at 1090 °C in flowing N_2, but because of their small, uniform particle size they were still able to produce films < 30 μm thick that were 94% dense [31,32]. They did not use an additive like Li_3BO_3. They attributed the short time sintering success to a combination of uniform particle packing, the high surface energy of the nanoparticles, and liquid phase sintering promoted by molten Li_2CO_3. To account for Li loss they added 50 wt% excess Li in the starting LLZO formulation. In their case, they had an optimal film thickness of 40–50 μm. Films thicker than this were Li-rich while films thinner were Li-poor. In later studies they showed some of the rapid sintering in their samples can be attributed to decomposed LLZO that undergoes reaction driven densification at temperatures below 1000 °C [32]. Extended ball-milling leads to decomposition of the LLZO, with formation of Li_2CO_3 being important, as it melts at 720 °C, wets oxide particles, as acts as a transient liquid phase while reacting with oxide components and gradually forming LLZO.

Tape casting of Al-substituted $Li_7La_3Zr_2O_{12}$ (LLZO) - poly(ethylene oxide) (P(EO)20-$LiClO_4$) composites has been reported [33]. However such tapes are used as-cast, and are not sintered after drying. Hanc, et al., tape cast 500 μm thick LLZO tapes with ZnO as a sintering aid [34]. Tapes were sintered at 1250 °C for 5 h while covered with the mother powder. Covering the tapes with powder is undesirable for practical manufacturing. Their tapes achieved conductivity of 8×10^{-5} S cm^{-1}. Rather than a free-standing tape, a $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) membrane supported on porous alumina was reported by Liu, et al. [35]. A slurry was prepared from LLZTO powder, ethylene glycol monoethyl ether solvent, a small amount of polyvinyl butyral binder, and glycerol trioleate dispersant. The slurry was coated on an Al_2O_3 honeycomb, dried and sintered at 1140 °C for 5 h in a covered alumina crucible. Additional Li_2CO_3 powder was placed in the closed crucible to limit Li losses from the LLZTO. The result was a thin (~70 μm) LLZTO membrane bonded to the porous Al_2O_3.

Tape casting of a $La_{2/3-x}Li_{3x}TiO_3/Al_2O_3$ composite was reported by Zhang, et al. [36]. They sintered at 1200 °C but did not provide any details about their tape cast formulation. They did document the occurrence of Li-loss during sintering. Ohta, et al., described the fabrication of a solid-state battery where the $LiCoO_2$ active cathode compound is bonded to the Nb-doped LLZO electrolyte by employing Li_3BO_3 glass in the cathode [7]. In this case the Li_3BO_3 + $LiCoO_2$ (25:75 wt%) composite material was screen printed as a paste onto the Nb-LLZO. The paste was prepared by mixing $LiCoO_2$ and Li_3BO_3 powders and ethyl cellulose binder in a solvent. After drying, the paste was annealed at 700 °C for 1 h, melting the Li_3BO_3. Li, et al. reported on the effect of B_2O_3 additions on the aqueous tape cast Li_2O–Nb_2O_5–TiO_2 compounds [37]. They found that as the B_2O_3 concentration increased, the slurry viscosity dramatically increased. This was attributed to formation of $B(OH)_4^-$, which results from dissolution of B_2O_3 in the aqueous solution.

In this work, we describe the application of tape casting to the fabrication of LLZNbO sheets suitable for use in solid-state battery development. First, dilatometry studies are presented to help define the effect of Li_3BO_3 additions on LLZO pellet densification. Then challenges posed by the wetting behavior of Li_3BO_3 with various substrates by Li3BO3 are described. Finally observations on how Li_3BO_3 additions affect the sintering of LLZNbO in, both pellet and cast tape forms are presented.

2. Experimental methods

$Li_7La_3Zr_{1.75}Nb_{0.25}Al_{0.1}O_{12}$ (LLZNbO) is produced via a solid-state reaction of $LiOH·H_2O$, La_2O_3, ZrO_2, Nb_2O_5 and Al_2O_3. This composition was chosen since it was reported as optimal in published work [38]. 7.5% excess $LiOH·H_2O$ is added by weight. The La_2O_3 is dried overnight at 900 °C before weighing. The precursors are ball milled together with ZrO_2 media for ~24 h in ethanol. After drying the mixture is reacted twice at 1100 °C for 6 h, with an intermediate mortar and pestle grinding. The resulting calcined powder is milled again in ethanol for 48 h. The final dry powder is annealed at 650 °C for 2 h to drive off any residual organics and promote uniform surface hydration.

Li_3BO_3 is produced from stoichiometric amounts of $LiOH·H_2O$ and H_3BO_3. The precursors are mixed by hand with mortar and pestle and then reacted at 600 °C for 2 h in air. X-ray diffraction shows complete conversion to Li_3BO_3.·The reacted powder is then milled in a zirconia jar in a Spex high energy mill for 15 min.

Pellets for dilatometry studies were 5 mm in diameter and approximately 5 mm tall as pressed. The pellets were pressed at 340 MPa. A Linseis Model L75 dilatometer was used for the studies. The pellets were positioned between two Al_2O_3 supports. Samples were typically heated at 10 °C/min to 700–1000 °C. In some cases, intermediate hold temperatures were employed as is discussed below. The theoretical density of LLZO-Li_3BO_3 mixtures were calculated by following the rule of mixtures and using the theoretical density values for LLZO (5.1 g/cm^3) and Li_3BO_3 (2.16 g/cm^3). The