Review Article

Nanostructured Garnet-type $Li_7La_3Zr_2O_{12}$: Synthesis, Properties, and Opportunities as Electrolytes for Li-ion Batteries

Candace K. Chan[*], Ting Yang, J. Mark Weller

Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, 501 E Tyler Mall, ECG 301, Tempe, AZ 85287-6106, USA

ABSTRACT

The garnet-type Li^+ ion conductor $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising candidate as a solid electrolyte for all-solid-state Li-ion batteries. Significant progress towards understanding the structure and properties of LLZO, conventionally synthesized using solid state reaction methods, has already been made in the last decade. The aim of this review is to summarize recent efforts on the synthesis of nanostructured LLZO, with a focus on electrospinning, cellulose templating, and low-temperature ($< 900\,°C$) sol-gel based methods, as well as to highlight the unique properties of nano-sized LLZO. Further research is still needed to fully understand the potential benefits of using nanostructured LLZO in pellet-type, ceramic electrolytes, but a natural opportunity for nanostructured LLZO is in the role of ceramic filler within solid composite polymer electrolytes (CPEs). The current status of CPEs embedded with LLZO ceramic fillers is summarized, including the elucidation of Li^+ transport pathways using nuclear magnetic resonance (NMR) spectroscopy.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Because Li-ion batteries contain the highest energy density of commercially available rechargeable energy storage systems, they are attractive for supplying power in portable and vehicular applications. However, Li-ion batteries can fail, catch fire, and/or explode due to abuse from high temperature exposure [1,2], overcharging [3,4], or short-circuiting from lithium dendrite formation [5,6]. One important component of this problem is the flammability and low flashpoints ($< 30\,°C$) of the organic carbonate-based solvents comprising the electrolyte [7,8]. This issue has motivated research on the development of Li^+ conducting electrolytes based on polymers, ionic liquids, glasses, or crystalline ceramics to replace the liquid electrolyte and improve the safety characteristics of Li-ion batteries through the implementation of all-solid-state devices [9–12]. Additionally, solid electrolytes have the potential to increase the safety characteristics of Li metal batteries [13], mitigate the problem of polysulfide dissolution from the cathode in Li/sulfur batteries [14], and circumvent the organic electrolyte oxidation problem in Li/oxygen (or Li/air) batteries [15].

Since inorganic materials display superior mechanical properties and thermal stability compared to polymers [10], a great deal of research has been devoted to the study of ceramic solid electrolytes. To be a suitable solid electrolyte, the ceramic must: 1) display high ionic conductivities, 2) display chemical stability to Li-ion battery cathodes and anodes, 3) be cost-effective to synthesize, and 4) be easily integrated with the cathode and anode [8]. The first criterion has been a major challenge, as the ionic conductivity of the commonly used electrolyte (1 M $LiPF_6$ in ethylene carbonate/diethylene carbonate solvent) is 10^{-2} S cm^{-1} [16], while the conductivities of solid electrolytes are lower, in the range of 10^{-7}–10^{-3} S cm^{-1} [9,12]. However, if a dense thin film (*e.g.*, $< 100\,\mu m$) of the solid electrolyte can be prepared, materials with ionic conductivities between 10^{-4}–10^{-3} S cm^{-1} can be used in practical applications [14,17]. Many solid electrolytes have also failed the second criterion, a well-known example being the perovskite lithium lanthanum titanate, $(Li,La)TiO_3$, which exhibits a high bulk conductivity of $\sim10^{-3}$ S cm^{-1} [18] but becomes reduced by lithium metal [19,20].

In 2003, Thangadurai *et al.* reported that garnet-type Li^+ conductors with a cubic structure based on $Li_5La_3M_2O_{12}$ (M = Nb, Ta) were stable against reaction with molten lithium, but only displayed a bulk ionic conductivity of $\sim10^{-6}$ S cm^{-1} at room temperature [21]. The 2007 discovery [22] of the cubic garnet $Li_7La_3Zr_2O_{12}$ (LLZO) with relatively high ionic conductivity of $\sim10^{-4}$ S cm^{-1}, non-reactivity with lithium, and wide voltage stability window (> 5 V vs. Li/Li$^+$) generated a great deal of further interest

* Corresponding author.
  E-mail address: candace.chan@asu.edu (C.K. Chan).

in garnets. Since then, there have been many studies, as summarized in several recent reviews [23–25] exploring the properties of LLZO and its doped derivatives. As a result, LLZO has emerged as one of the most promising solid electrolyte materials for all-solid-state Li-ion batteries.

LLZO is conventionally synthesized using a solid state reaction (e.g., from LiOH or Li_2CO_3, La_2O_3, and ZrO_2) requiring high temperatures (>1180 °C) and long calcination times (e.g. 36 h) [22]. LLZO adopts two polymorphs with Li^+ ionic conductivities that differ by 2 – 3 orders of magnitude. LLZO with a tetragonal structure (t-LLZO, space group $I4_1/acd$), which is the thermodynamically stable phase at room temperature [26], typically exhibits a total ionic conductivity of 10^{-7} – 10^{-6} S cm^{-1} [27,28]. The higher ionic conductivity on the order of 10^{-4} S cm^{-1} is correlated to LLZO with a cubic structure (c-LLZO, space group Ia-$3d$), which in earlier studies was formed inadvertently by doping of Al^{3+} into the Li^+ sites through contamination from the alumina crucibles used during the solid state synthesis [29]. Since then, many syntheses include intentional incorporation of Al^{3+} as an extrinsic dopant to stabilize the c-LLZO phase at room temperature. Aluminum doping, however, comes with its own issues, including a greater activation energy for Li^+ conduction, likely due to the electrostatic repulsion of the Al^{+3} ions in Li^+ sites, which can limit the lithium ion mobility [30]. The substitution of Zr^{+4} with Ta^{+5} [31] is another popular approach for stabilizing the cubic structure, while using Ga^{3+} dopants can lead to ionic conductivities $\sim 10^{-3}$ S cm^{-1} [32,33]. In the absence of extrinsic dopants, the t-LLZO to c-LLZO phase transition has been reported to occur between 600 – 650 °C [30,34,35].

In addition to exploring the defect chemistry and effect of dopants on the properties of LLZO, there have been substantial efforts focusing on the development of low-temperature synthesis methods for LLZO. Part of the motivation for doing so is to avoid the high calcination temperatures required in solid state synthesis, which can also lead to Li^+ loss through volatilization. Since the lithium content in LLZO has been shown to also play a role in the preferred phase that is adopted [26,35,36], better control of the LLZO composition can be important for obtaining materials with the desired ionic conductivity. Low-temperature synthesis methods, such as sol-gel approaches, can also enable the preparation of nanostructured materials, which may display additional advantageous properties, such as improved sintering and densification behavior.

One observation that has appeared in numerous low-temperature syntheses is that the cubic phase can be stabilized at room temperature in nanostructured forms of LLZO. This will be discussed in more detail in the following sections. The mechanism for the phase stability of c-LLZO at room temperature in nanostructured LLZO is still not completely understood. Other metal oxides with multiple polymorphs (e.g., titania, zirconia) also display similar size dependent phase stabilization due to differences in surface energy and crossovers in polymorphic stability as the surface area of the materials increases [37–40]. It is plausible that a similar phenomenon could account for cubic stabilization of LLZO below a critical size parameter. However, the properties of nanostructured LLZO have still not been fully investigated, and other factors such as surface reactions with H_2O and CO_2 from the ambient atmosphere could also be playing a role on the phase stability of LLZO [30,34,35,41,42]. To better understand size-dependent properties, well-controlled synthetic routes are needed. The development of nanostructured LLZO with shape-controlled morphologies, however, is still far from mature, with electrospinning as one of the most promising methods that has been established so far for preparing LLZO with a one-dimensional nanowire or nanofiber morphology [43,44].

Although a decade has passed since LLZO was first reported, the application of LLZO as a ceramic electrolyte in all-solid-state batteries is still met with several practical challenges [17]. For example, LLZO does not form good contacts or interfaces with electrodes [45–47], although this can be addressed through careful engineering of the interfaces to avoid large contact resistances [48–52]. Further, co-sintering with cathode layers has been found to result in inter-diffusion of metal cations at the LLZO/cathode interface, which leads to poor cyclability [53–55]. Intriguingly, lithium metal dendrites have also been observed growing within voids or along grain boundaries of LLZO, despite pellet densities > 97% [48,56–58].

As a result, it is not surprising that since the properties of conventional bulk LLZO are still under investigation, understanding how the properties of LLZO differ when prepared as a nanostructured material compared to the bulk form is still limited. Indeed, the grain size dependence of LLZO on its properties is still not fully established, even at the micron-scale. Cheng et al. conducted comparison studies on large grained (100 – 200 μm) and smaller grained (20 – 40 μm) LLZO and found that small grained LLZO may be more air-stable and resistant to reaction with ambient CO_2 and water vapor [59], while also displaying lower interfacial resistance, higher densification rates, and better cycling behavior than large grained LLZO [60]. However, similar studies extrapolated to nanoscaled grain sizes still need to be performed in a systematic way. Pellets prepared from c-LLZO derived from solid-state reaction [36] compared to one prepared from sol-gel derived LLZO [61] showed that the two pellets, both with similar Li and Al contents and prepared using hot-pressing, displayed similar total ionic conductivities at room temperature. The pellet prepared from sol-gel derived LLZO (average grain size of 260 nm) had higher total conductivity at higher temperatures compared to the pellet made from the solid state reaction derived LLZO (average grain size of 3.3 microns); however, the activation energy for the sol-gel LLZO was 0.41 eV, which is higher than the one observed in the solid-state reaction LLZO of 0.26 eV, the origin of which is still not understood. Nonetheless, the properties of nanostructured ceramics, such as densification at milder sintering conditions [62,63], decreased impurity segregation to grain boundaries [64], and superplasticity [65] may lead to improved properties in pellets derived from nanostructured LLZO.

While further research is still needed to fully understand the potential benefits of nanostructured LLZO in pellet-type, ceramic electrolytes, a natural opportunity for nanostructured LLZO is in the role of ceramic filler in solid composite polymer electrolytes (CPEs). The application of nano-sized particles as ceramic fillers has already been demonstrated to be effective for enhancing the mechanical stability and ionic conductivity of polymer-based solid electrolytes, but these fillers have mostly comprised of spherical particles of inert or "passive" components without intrinsic Li^+ conductivity. Several recent studies using LLZO-embedded into polymer films have revealed different degrees of effectiveness, indicating that more careful design of the CPEs, including the optimization of the LLZO fillers and more detailed mechanistic study of the Li^+ transport pathways, may be needed for the development of CPEs with high ionic conductivity.

The aim of this review is to summarize recent efforts on the synthesis of nanostructured LLZO, with a focus on the electrospinning and cellulose templating methods investigated in our group. Other low-temperature (< 900 °C) sol-gel based methods will be reviewed, and recent progress on the utilization of LLZO as a ceramic filler in composite polymer electrolytes will be summarized. Finally, future outlooks and opportunities will be provided.