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Stability of garnet-type Li ion conductors: An overview

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ABSTRACT

Garnet-type lithium ion conductor is a promising candidate of solid electrolyte on the way towards all-solid-state lithium ion batteries. This short review presents the latest efforts on the stability of lithium garnet against ambient air, lithium metal, cathodes, and liquid electrolytes. The discussion on the air stability includes the reaction mechanisms as well as the effects of material properties and environmental parameters. The interface stability with Li metal and cathode materials covers both thermodynamic computation and experimental results. The Strategies to reduce the garnet/Li interfacial impedance and to subsequently suppress the Li dendrite formation are highlighted. The last section on "hybrid electrolyte" discusses the stability of lithium garnets in liquid electrolytes, namely aprotic and aqueous electrolytes.

1. Introduction

As one major success in modern electrochemistry, lithium ion battery (LIB) has been developed into one of the most popular types of rechargeable batteries for portable electronics, and is believed to play an important role for electric vehicles, aerospace and large-scale energy storage applications. Although present LIBs can provide considerable volumetric and gravimetric energy densities up to 770 Wh/L and 260 Wh/kg, respectively, the demand for batteries with even higher energy and power densities is more than ever. To this end, the conception of all-solid-state lithium ion batteries (ASSLIBs) based on solid electrolytes has been proposed and has been attracting increasing attention due to its intrinsic safety, high energy density and potentially long cycle life in that it may make battery configuration more efficient, and may enable metallic Li anode and high-voltage cathode.

Solid electrolyte, or lithium ion conductor, is the key component in ASSLIBs. Ideal electrolyte materials should have high Li^+ conductivity (e.g., $> 10^{-4}$ S/cm) at room temperature, negligible electronic conductivity, wide electrochemical window (e.g., > 6 V vs Li^+/Li), stability against both electrodes and moisture, environmental friendliness, low cost and easiness to prepare. Among various solid electrolyte materials, garnet-type oxide, $Li_7La_3Zr_2O_{12}$ (LLZO) in particular, has drawn increasing interest since it was first reported by Murugan and coworkers in 2007 [1]. Now after one decade of intensive research, much effort has been devoted to material synthesis, cation doping, structure characterization, Li^+ transport mechanism, and conductivity improvement of LLZO. Several excellent review papers have been published discussing these aspects [2–6].

Table 1 lists several typical synthesis methods and the relevant material properties. Room-temperature ionic conductivity as high as 1.6 mS/cm has been reported for LLZO pellets, approaching that of conventional carbonate-based liquid electrolyte. However, compared to Li^+ conductivity itself, the improvement of stability of LLZO, especially stability against different environmental conditions and electrode materials may be of more importance, as specifically reviewed in this article. Section 2 of this article covers the stability of LLZO in ambient air; Sections 3 and 4 discuss the interface stability with Li metal and cathode materials, respectively; Section 5 highlights the concept of "hybrid electrolyte" and focuses on the stability of LLZO in liquid electrolytes, namely aprotic and aqueous electrolytes.

2. Stability of lithium garnet in ambient air

Garnet-type solid-state electrolyte was initially believed to be chemically stable in ambient air. However, subsequent experimental and computational research demonstrated that the air stability of LLZO is susceptible to moisture and CO_2 in the air, which leads to Li_2CO_3 formation and ionic conductivity degradation. Since lithium garnet will inevitably be exposed to ambient air during the preparation process and the subsequent cell-assembly process, it is imperative to fully understand the air stability of lithium garnet and figure out ways to improve it.

2.1. Structure stability and reaction mechanisms

Moisture in the air plays a main role in degrading the structural

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Table 1
The synthesis methods, relative density, total Li conductivity and activation energy of typical lithium garnets.

Composition	Synthesis method	Relative density (%)	RT ionic conductivity (mS/cm)	Activation energy (eV)	Ref.
$Li_7La_3Zr_2O_{12}$	Solid state reaction, 1230 °C, 36 h, in air	92	0.774	0.30	[7]
$Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$	Solid state reaction, 1100 °C, 24 h, in air	94.1	1.46	0.25	[8]
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$	Hot pressing, 1150 °C, 1 h, 20 MPa in Ar	99.6	1.6	0.26	[9]
$Li_6La_3Zr_2O_{11.5}$	Sol-gel, 1180 °C, 36 h	–	0.139	–	[10]
$Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$	Flame spray pyrolysis, 1130 °C, 0.3 h	95 ± 1	1.3	0.28 ± 0.01	[11]
Ta- and Al-LLZO	Radio frequency magnetron sputtering (RF-MS)	–	0.12	0.47	[12]

stability of lithium garnet in ambient environment. Nyman et al. reported the replacement of Li^+ in garnet lattice by H^+ from water when powder samples of $Li_5La_3Nb_2O_{12}$ or $Li_5La_3Ta_2O_{12}$ were dispersed in water and a rise in the pH value of the aqueous media was observed [13]. Similar observation of the Li^+/H^+ exchange reaction was reported by Galven et al. for single crystal $Li_7La_3Sn_2O_{12}$ in ambient air [14]. By using powder neutron diffraction, solid-state nuclear magnetic resonance, and chemical analysis, Galven et al. further showed that the Li^+/H^+ exchange feasibility is directly connected to the lithium stoichiometry- only when more than three Li^+ per formular is the garnet sensitive to humidity [15]. More recently, Ma et al. used the scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analysis to graphically illustrate that the Li^+/H^+ exchange reaction of LLZO in water was reversible and did not change the garnet structure even under a high exchange rate of 63.6% [16].

The stability of $Li_7La_3M_2O_{12}$ (M = Zr, Sn, Hf) in environments containing gaseous H_2O and CO_2 was analyzed by Kang and Sholl based on the density functional theory (DFT) calculations [17]. The lithium garnets exposed to humid air thermodynamically tend to form hydroxides and carbonates according to the following reactions:

$$2Li_7La_3M_2O_{12} + 7H_2O \leftrightarrow 14LiOH + 3La_2O_3 + 4MO_2$$

$$2Li_7La_3M_2O_{12} + 7CO_2 \leftrightarrow 7Li_2CO_3 + 3La_2O_3 + 4MO_2$$

The calculation results showed that among these three garnets, $Li_7La_3Sn_2O_{12}$ showed higher chemical stability than the other two; all three materials are more stable with respect to H_2O than to CO_2. However, it is worth noting that the DFT calculations are based solely on thermodynamics, and cannot provide information on the potential role of reaction kinetics in practical applications.

Indeed as for the reaction mechanism, Xia et al., [18] based on experimental observations and literature, recently summarized a reaction mechanism as shown in Fig. 1.Wherein, once the garnet pellets are exposed to humid air, water vapor from the air will be adsorbed on the pellet surface and Li^+/H^+ exchange occurs to form a layer of $LiOH{\cdot}H_2O$. The $LiOH{\cdot}H_2O$ is a necessary intermediate and required precursor to react with CO_2 to form Li_2CO_3. The top layer of Li_2CO_3 serves as protective barrier for the underneath LLZO and prevents Li^+ from diffusing through the Li_2CO_3 layer for further reaction. The surface Li_2CO_3 layer is also directly correlated to the air specific resistance and/or interfacial resistance between lithium garnets and Li metal.

2.2. Factors affecting air stability

The material properties as well as the environmental conditions play an important role in influencing air stability of lithium garnets. For example, Jin and McGinn [19] reported that grain boundaries are more susceptible to moisture than grains due to their higher interfacial energy. This is consistent with the observation by Xia et al. [20], where LLZO pellets were prepared in both Al_2O_3 and Pt crucibles. The pellets sintered in Pt crucibles have higher relative density, larger grains and less grain boundaries than in alumina crucibles, which leads to better air stability. On the other hand, Cheng et al. [21,22] claimed that the air stability for the small-grained (grain size of ~20 μm) samples was better than that for the large-grained (grain size of 150–200 μm) ones, and attributed this difference to the variation in the Al and Li distribution at sample surfaces. As shown in Fig. 2, in large-grained samples, Al tends to segregate at grain boundaries resulting in an Al depleted surface; Al is restrained within the grains of the small-grained samples resulting in an Al rich surface. The latter has limited reaction during air exposure and produces less Li_2CO_3 impurity on the LLZO surface. Regarding environmental conditions, Xia et al. [18] stored Ta doped LLZO in dry air (humidity ~5%) and humid air (humidity ~80%) for 6 weeks and found that the room-temperature ionic conductivity decreased from 6.45×10^{-4} S/cm to 3.61×10^{-4} S/cm in humid air, whereas it barely dropped in dry air. Clearly, humidity is one critical factor affecting air stability.

2.3. Air stability improvement

Surface polishing can effectively remove the top Li_2CO_3 layer on the

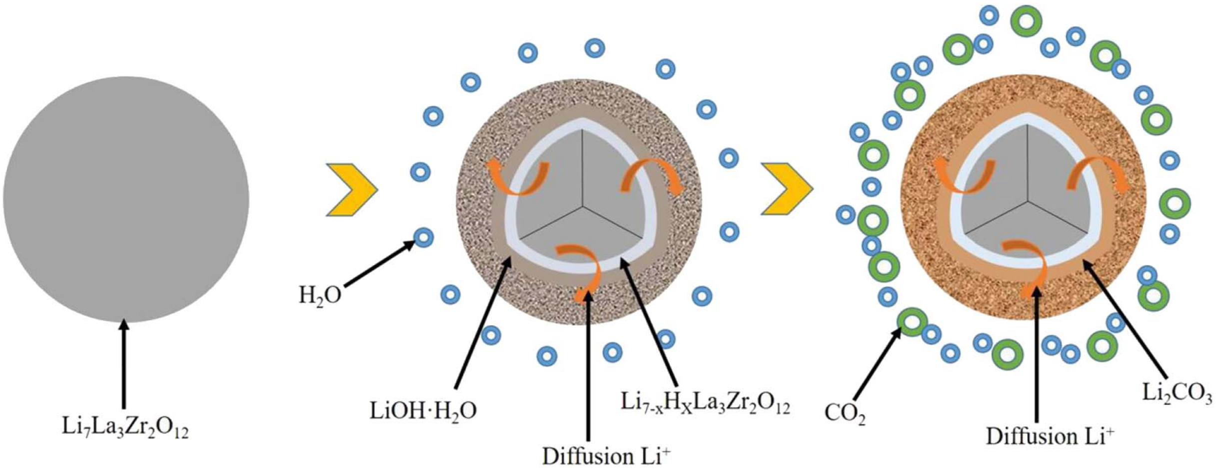

Fig. 1. A schematic model illustrating the Li_2CO_3 formation process on the surface of lithium garnets, after Ref. [18].