

Recent developments in garnet based solid state electrolytes for thin film batteries



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ABSTRACT

This paper reviews the current status of, and new progress in, the field of solid state electrolytes (SSE) for lithium ion batteries. In addition to a review of current technologies, we are also presenting our novel results on pulsed laser processing of garnet based SSEs, specifically $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO). LLZO powders with a tetragonal structure were prepared by a sol–gel technique, then a pulsed laser annealing process was employed to convert the powders to cubic LLZO without any loss of lithium. The tetragonal LLZO exhibited a Li ion conductivity of 1.8×10^{-7} S/cm, whereas the laser annealed cubic LLZO showed a Li ion conductivity of 1.0×10^{-4} S/cm at room temperature. A systematic study of the effect of pulsed laser annealing (PLA) on the crystal structure, morphology, composition, and ionic conductivity of LLZO was performed via X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS) measurements. These results demonstrate that PLA is a powerful processing technique for synthesizing the high ionic conductivity cubic phase of LLZO at relatively low temperatures, as compared to conventional methods.

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1. Introduction

Lithium ion batteries (LIB) are important for a wide variety of applications, spanning from portable electronics and hybrid automobiles to large-scale electrical power storage systems [1,2]. These batteries offer a number of advantages over other families of batteries, such as high energy density, long cycle lifetime, no memory effect and a wide range of operating temperatures. Currently the majority of LIBs are using liquid electrolytes due to their very high ionic conductivities, in the range of 10^{-3} S/cm. However, these liquid electrolytes suffer from very serious drawbacks such as flammability, leakages, and the formation of dendrites in the electrodes.

In this respect, solid state Li ion conductors have garnered interest as substitutes for the liquid electrolytes. Solid state Li ion electrolytes are expected to offer several advantages over the currently commercialized liquid electrolytes such as higher thermal stability, absence of leakage and pollution, and a large electrochemical stability window. In addition, the high elastic modulus in ceramics makes them suitable for the rigid thin film micro-batteries. Current solid-state Li ion conductors can be divided into four groups – NASICON type, perovskite type, LiPON type and garnet type. The following sections contain a brief introduction of each category.

1.1. NASICON structured Li ion conductors

The NASICON (Na super ionic conductor) type solid electrolytes are of increasing interest because of their potential to replace liquid electrolytes in LIBs. The general formula of a NASICON-type electrolyte is $\text{LiM}_2(\text{PO}_4)_3$, where M = Ti, Ge or Hf. NASICON consists of a covalent skeleton $\text{M}_2(\text{PO}_4)_3^-$ containing MO_6 octahedra and PO_4 tetrahedra, as shown in Fig. 1 [3]. The Li sites sit in the interstitials between the MO_6 octahedra and PO_4 tetrahedra [4]. The main factors that limit the use of NASICON type electrolytes are grain boundary effects, which behave as the scattering sites for ion transportation, thereby reducing the bulk ionic conductivity to 10^{-5} S/cm² [5].

It has been reported that in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{R}_x(\text{PO}_4)_3$, the lithium ion conductivity can be increased through the substitution of Ti^{4+} by other elements [6–10] (see Table 1). The substitution of the more stable Al^{3+} for the less stable Ti^{4+} increases the M–O bond strength and decreases the Li–O bond strength which results in the higher ionic conductivity [6,11–17]. Among the various doped NASICON electrolytes, an optimal ionic conductivity of 1.3×10^{-3} S/cm has been reported for the simultaneous doping of B and Al in $\text{LiTi}_2(\text{PO}_4)_3$ [18]. Despite this, the highest reported Li ion conductivity in a NASICON based micro-battery utilizing $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ thin film electrolyte is 2.7×10^{-6} S/cm (see Fig. 2) with only a 0.2% capacity loss per charging cycle [19–21]. Even though substitution provides an enhancement to the ionic conductivity,

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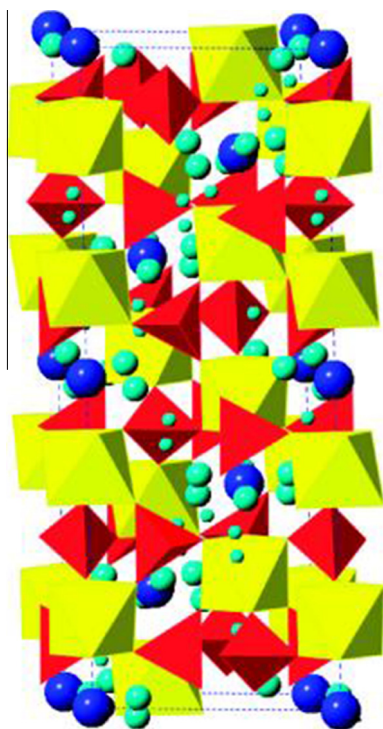


Fig. 1. $\text{LiTi}_2(\text{PO}_4)_3$ crystal structure where blue spheres represent Li atoms, yellow octahedra represent TiO_6 , and red tetrahedral represent PO_4 . Reprinted with permission from [4].

Table 1
List of properties for trivalent ion doped $\text{Li}_{1+x}\text{Ti}_{2-x}\text{R}_x(\text{PO}_4)_3$ compound.

R	Li ionic conductivity at room temperature (S/cm)	Activation energy (eV)
Al [6]	6×10^{-4}	0.28
Sn [8]	1×10^{-4}	0.32
B [7]	2×10^{-4}	0.48
Al, Si [9]	3.8×10^{-4}	N/A
Ge, B [10]	6×10^{-4}	0.33

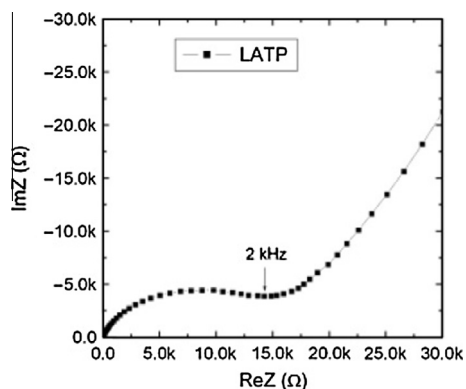


Fig. 2. Nyquist plot for $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ thin film at room temperature. Reprinted with permission from [21].

NASICON still possess many drawbacks, including the fact that they are not stable when in contact with lithium metal because of the rapid Ti^{4+} reduction [22–24], which greatly hinders their potential in LIBs.

1.2. Perovskite structured Li ion conductors

Another class of promising Li ion conductors are the perovskite (ABO_3) type oxides (see Fig. 3). The ionic conductivity of these oxides is very sensitive to both the lithium content and the concentration of A-site vacancies [25–30]. A-site vacancies allow the lithium ions to hop by a vacancy mechanism through a planar bottle neck formed by four neighboring oxygen ions. The optimal lithium vacancy concentration has been found to be in the range of 0.44–0.45 [31]. The highest Li ion conductivity of a perovskite structured $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) thin film electrolyte was reported to be 5.25×10^{-5} S/cm, see Fig. 4 [32].

The main factors that limit the perovskite electrolytes in Li ion batteries are: the large amount of Li intercalation that occurs when in contact with the Li electrode and the coexistence of Ti^{4+} and Ti^{3+} that leads to an increased electronic conductivity [22]. This facile Ti^{4+} reduction makes perovskite solid electrolytes unstable with Li metal. In addition, lithium deficiencies have been observed during the high temperature sintering process, which makes it difficult to control the lithium content and therefore the ionic conductivity [33,34].

1.3. LiPON structured Li ion conductors

Lithium phosphorous oxy-nitride (LiPON) electrolytes with the composition $\text{Li}_x\text{PO}_y\text{N}_z$, where $x = 2y + 3z - 5$, have a moderate Li ion conductivity ($\sim 10^{-6}$ S/cm) and are stable in contact with metallic lithium up to a potential of 5.5 volts [35–38]. Fig. 5 shows a typical Nyquist plot of a LiPON thin film [39]. It consists of a high

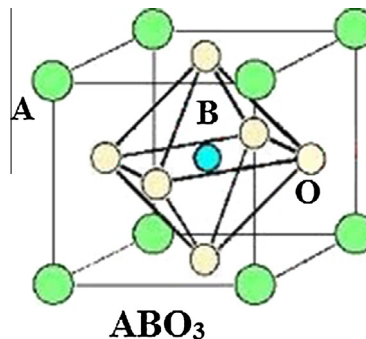


Fig. 3. Crystal structure of perovskite (ABO_3) type oxides.

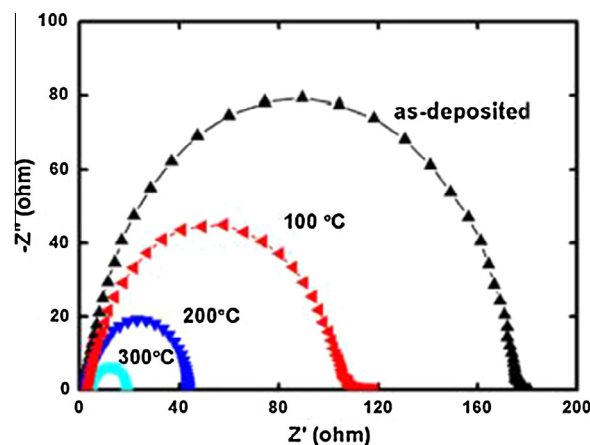


Fig. 4. Nyquist plots for LLTO thin film with various post annealing temperatures. Reprinted with permission from [32].

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