



NASICON-type La^{3+} substituted $\text{LiZr}_2(\text{PO}_4)_3$ with improved ionic conductivity as solid electrolyte

Vishwanathan Ramar ^a, Sunil Kumar ^{a,b}, S.R. Sivakkumar ^a, Palani Balaya ^{a,*}

^a Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore, 117575, Singapore

^b Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Simrol, 453552, India



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ABSTRACT

NASICON-structured $\text{Li}_{1+x}\text{Zr}_{2-x}\text{La}_x(\text{PO}_4)_3$ ($x = 0-0.2$) solid electrolytes are prepared by sol-gel method. The influence of substitution of La^{3+} for Zr^{4+} on the ionic conductivity, morphology, and structure of the parent compound $\text{LiZr}_2(\text{PO}_4)_3$ (LZP) is investigated. Rietveld refinement of powder x-ray diffraction data reveals that the La^{3+} substitution stabilizes the LZP in the highly conducting rhombohedral $R\bar{3}c$ phase at room temperature. La^{3+} substituted LZP display enhanced ionic conductivity, showing the highest ionic conductivity of $0.72 \times 10^{-4} \text{ S/cm}$ at room temperature for the composition $\text{Li}_{1.1}\text{Zr}_{1.9}\text{La}_{0.1}(\text{PO}_4)_3$. The improvement in conductivity of LZP with another aliovalent substituent, Mg^{2+} , whose ionic radii is similar to Zr^{4+} (0.72 \AA) is also investigated. Further, the activation energy decreases from 0.53 eV for the parent LZP to 0.42 eV for $x = 0.1$ La^{3+} substituted LZP. Lithium-ion transference number obtained by direct current polarization for $\text{Li}_{1.1}\text{Zr}_{1.9}\text{La}_{0.1}(\text{PO}_4)_3$ is 0.99, confirming the high ionic conducting nature of the solid electrolyte. Cyclic voltammetry recorded for $\text{Li}_{1.1}\text{Zr}_{1.9}\text{La}_{0.1}(\text{PO}_4)_3$ shows electrochemical stability window up to $\sim 4.0 \text{ V}$ vs. Li. In particular, La^{3+} substituted NASICON-type LZP ($x = 0.1$) exhibits good chemical and structural stability after exposing to air, water, Li metal, acidic and basic solutions.

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1. Introduction

Next generation rechargeable lithium-ion batteries are being developed in the direction to realize superior energy & power densities, economical and enhanced safety than the existing battery technologies [1–3]. Under these directions, significant efforts are taken in developing rechargeable solid-state and hybrid Li-air batteries. High lithium-ion conductivity is a pre-requisite for the solid electrolyte used in solid-state Li-ion and hybrid Li-air batteries [3–5]. Although several groups have reported broad range of inorganic solid electrolytes, the development of solid electrolyte membranes with good ionic conductivity and chemical stability in aqueous solutions (as in the case of hybrid Li-air batteries) having wide pH range is challenging [6,7]. Of various inorganic solid electrolytes reported, NASICON structured $\text{LiM}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{Ge}, \text{and Zr}$) have drawn significant interest owing to their considerably high ionic conductivity. NASICON-type materials have rigid framework consisting of corner sharing PO_4 tetrahedra and MO_6 octahedra forming a 3D network with interstitial tunnels in which

Li-ions can hop easily [8,9]. Aliovalent substituted- $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{LiGe}_2(\text{PO}_4)_3$ solid electrolytes exhibit impressive ionic conductivity ($> 10^{-4} \text{ S/cm}$) [10,11]. However, the Ti^{4+} and Ge^{4+} ions in these materials are getting reduced against lithium metal or lithiated graphite anode, which limits their application in lithium batteries [12]. On the other hand, $\text{LiZr}_2(\text{PO}_4)_3$ (LZP) are stable against Li-metal and lithiated graphite due to highly stable Zr^{4+} . However, LZP displays relatively poor ionic conductivity ($10^{-5} - 10^{-8} \text{ S/cm}$) at room temperature (RT). LZP prepared at $1200 \text{ }^\circ\text{C}$ shows structural transition from Triclinic ($c\bar{1}$) to Rhombohedral ($R\bar{3}c$) phase above 310 K [13–18]. The Rhombohedral and Triclinic phases exhibit lithium ion conductivity of 10^{-5} and 10^{-8} S/cm at RT, respectively [13,19]. High ionic conductivity is the most important property for solid-electrolytes in rechargeable battery technologies. The ionic conductivity in the range of $\sim 10^{-5} \text{ S/cm}$ is sufficient for the solid electrolytes to be used thin film micro-batteries since the device current densities are very low [20]. On the other hand, solid electrolyte having relatively high ionic conductivity ($\sim 10^{-3} \text{ S/cm}$) is required in order to be employed in practical solid state lithium ion and hybrid lithium-air batteries. Ionic conductivities of LZP electrolytes are reported to be enhanced considerably by substitution of aliovalent cation [21–23]. Substitution of Zr^{4+} cations in LZP with

* Corresponding author.

E-mail address: mpepb@nus.edu.sg (P. Balaya).

ions of different radii and valence states tunes the hopping tunnel size for Li^+ ions, leading to enhanced Li ion mobility.

Herein, we report the influence of substitution of La^{3+} (ionic radii: 1.032 Å) for Zr^{4+} (ionic radii: 0.72 Å), in LZP on the lithium ion conductivity, morphology, structural aspects, and chemical stability.

2. Experimental

$\text{LiZr}_{2-x}\text{M}_x(\text{PO}_4)_3$ [$\text{M} = \text{La}^{3+}$ & Mg^{2+} for Zr^{4+} ; $x = 0, 0.05, 0.1$ and 0.2] compounds were synthesized via sol-gel method using Citric acid as a chelating agent. All precursors such as LiCOOCH_3 , $\text{La}_2\text{O}_3/\text{MgCOOCH}_3$, ZrO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were dispersed in an aqueous citric acid solution in stoichiometric ratio except LiCOOCH_3 (10% excess). To this solution, ethylene glycol having molar ratio of 1:1 to citric acid was added and stirred for 12 h at 80 °C. The premixed final solution was kept at 180 °C for 10 h for gelation. The gel obtained was then heat treated at 500 °C and 1000 °C for 6 h (heating/cooling rate: 5 °C/min) with intermediate grindings to obtain white powder. The white powders obtained were pressed at 200 MPa into cylindrical pellets with 2–3 mm thick and 10 mm diameter. Pellets buried in mother powder were then sintered at 1200–1400 °C for 18 h in air at a heating/cooling rate of 3 °C/min to obtain the solid electrolytes.

X-ray diffraction patterns for sintered pellets were obtained using Bruker-D8 advance eco diffractometer. Rietveld refinement using *Topas 3.0* software was carried out for the XRD analysis. The relative densities of the pellets were estimated from the pellet dimensions and weight. Field emission scanning electron microscope (FESEM, model JEOL JSM-6700F) was used to analysis the microstructure of the pellet. For conductivity measurements, the either side of pellet's surface was sputtered with gold. Electrochemical impedance spectroscopy (EIS) measurements for Au/pellet/Au symmetric cells were carried out using VMP3 (Bio-logic). The AC frequency used was in range of 1 MHz to 10 mHz and the AC amplitude was 500 mV. EIS measurements were performed between 30 °C and 120 °C \pm 1 °C. Prior to impedance measurements, the pellets were equilibrated at the designated temperatures for at least 15 min. Li/pellet/Au cells were used for cyclic voltammetry measurements. Solid electrolyte pellets coated with gold on either side of its surface was used for the determination of lithium-ion transference number by direct current polarization method. Chemical stability tests for the aliovalent ion substituted solid electrolytes were carried out against air, water, Li metal, acidic and basic solutions.

3. Results and discussion

Fig. 1(a) shows XRD patterns recorded for $\text{Li}_{1+x}\text{Zr}_{2-x}\text{La}_x(\text{PO}_4)_3$ ($x = 0, 0.05, 0.1, 0.2$). These materials were sintered at 1280 °C for 18 h. The diffractograms obtained confirms NASICON structured rhombohedral ($R\bar{3}c$) phase for all the materials. No additional Bragg peaks belong to triclinic phase is seen in the XRD diffractograms. However, when $x > 0.2$, impurity peaks due to unknown phase appeared. The unknown impurity peaks disappeared when the sample with $x = 0.3$ was sintered at a higher temperature of 1380 °C for 18 h and are not included in this study. This suggests that the pure rhombohedral phase formation temperature increases with increasing La^{3+} substitution to $x = 0.3$ ($x > 0.2$).

Fig. 1(b) displays the effect of lanthanum content on the lattice constants of $\text{Li}_{1+x}\text{Zr}_{2-x}\text{La}_x(\text{PO}_4)_3$ (LZLaP). A gradual increment in the lattice constants (a & c) and cell volume (V) with increase in x is seen. The difference in ionic radii between Zr^{4+} (0.72 Å) and La^{3+} (1.032 Å) cations is attributed to the increase in lattice parameters.

This corroborates with the literature report stating that substitution of Zr^{4+} by larger cation in the NASICON structure would result in an expansion of unit cells [24]. Rietveld refinement patterns for compositions $\text{Li}_{1+x}\text{Zr}_{2-x}\text{La}_x(\text{PO}_4)_3$; $x = 0$ & 0.1 are presented in Fig. 2. During structural refinement, the occupancy of La^{3+} and Zr^{4+} were presumed to take up random positions in the octahedral site. Nominal compositions of La^{3+} and Zr^{4+} were used for fixing their occupancies.

Analyses of Rietveld refinement of XRD data show that all the four compounds ($x = 0$ –0.2) possess pure rhombohedral structure and no traces of triclinic phase. Further, the extended 2θ region of the compositions $x = 0$ and 0.1 of Fig. 2(b) and (d) confirms that there are no Bragg peaks which belongs triclinic phase. It is reported that the rhombohedral phase is stable above 60 °C [16]. However, the Rietveld refinement of XRD pattern of pristine LZP ($x = 0$) reveals that the rhombohedral phase is stable at RT without aliovalent substitution which is consistent with some of the earlier reports [14,25]. Further, the structural phase transition in LZP is owing to the dislocation of Li1 and Li2 from tetrahedral. Replacing the smaller cation Zr^{4+} (0.72 Å) by larger aliovalent cation La^{3+} (1.032 Å) could facilitate in increasing Li^+ for charge compensation as well as the distribution of Li1 in symmetry-equivalent M' site by the level of distortion of MO_6 octahedra [16,17].

There have been many papers where synthesis of the pure rhombohedral phase of $\text{LiZr}_2(\text{PO}_4)_3$ (LZP) is reported to be unsuccessful [18,21,26]. For instance, Xie et al. [21] mention instability of NASICON-type phase formation for pure LZP even after heating at 1200 °C for 38 h. Our own earlier attempts of synthesizing LZP via a sol-gel route invariably resulted in some amount of triclinic phase even after heating the sample at 1250 °C [18]. However, recently El-Shinawi et al. [25] reported the formation of a pure rhombohedral phase of LZP via a sol-gel process upon heating at 1200 °C for 6 h. It was also reported that using the phosphorus precursor 5% less than the nominal stoichiometry resulted in higher purity of rhombohedral LZP phase [25]. In the present work, we have achieved similar results by utilizing $\text{NH}_4\text{H}_2\text{PO}_4$. One tentative explanation could be related to the degree of disorder in the LZP system prepared via different precursors. It is well known that LZP synthesized at high temperature undergoes a triclinic to rhombohedral phase transition at \sim 60 °C. Preparation of a given compound through different synthesis methods and using different precursors could result in drastically different defects arrangement (usually via nature of intermediate phases during synthesis, shape and size effects). In the case of LZP, increase in such disorder could shift the phase transition temperature below room temperature as well as make the phase transition more diffused; and thus, favoring appearance of the higher symmetry rhombohedral phase at room temperature. However, we really don't have a conclusive proof of such changes in defect structure and it is beyond the focus of the present investigation.

A cross-sectional FESEM image for sintered pellets of La-substituted LZP (LZLaP) for various values of x is presented in Fig. 3. Morphology with noticeable pores is seen in Fig. 3(a) for LZP. This pellet was sintered at 1280 °C (dwelling time: 18 h) and estimated to have a density of \sim 86%. There is a considerable degree of increment in average grain size as well as decrease in pores thereby significant improvement in the relative density was observed upon substitution of La^{3+} for Zr^{4+} . FESEM images of $\text{Li}_{1.1}\text{Zr}_{1.9}\text{La}_{0.1}(\text{PO}_4)_3$ pellet shows highly interfused grains without any tangible pores. For $\text{Li}_{1.2}\text{Zr}_{1.8}\text{La}_{0.2}(\text{PO}_4)_3$ sintered at 1280 °C (dwelling time: 18 h), the grain boundaries are significantly evident (marked with red colored arrow) than the other samples though which is not apparent in XRD pattern. The relative density of pellet initially increases from 86% to 95% on doping (for the $x = 0$ to 1), but decreases

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