Effects of interstitial Li$^+$ ions on the properties of novel Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ ceramic electrolyte

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A R T I C L E   I N F O

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- Arhenius
- Ceramic electrolyte
- Conductivity
- Lithium orthosilicate
- Solid electrolyte

A B S T R A C T

The aim of this work was to investigate the effects of interstitial ions in the novel Li$_{4+x}$Zn$_{2x}$Si$_{1-x}$O$_4$ (x = 0.04) compound prepared via sol gel method. The compound was indexed to the monoclinic unit cell in the space group P2$_1$ m and the chemical composition of the compound was very close to the designed composition. The introduction of two interstitial Li$^+$ ions increased charge carrier concentration in the doped system resulting in an enhancement of conductivity by an order of magnitude as compared to that of the parent compound, Li$_4$SiO$_4$. The compound of Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ exhibited total conductivity values of 2.51 × 10$^{-5}$ S cm$^{-1}$ at ambient temperature and 3.01 × 10$^{-3}$ S cm$^{-1}$ at 500 °C. Ionic transference number corresponding to Li$^+$ ion transport was also found to be higher than the value obtained for the parent compound. This proved that interstitial Li$^+$ ions contributed to the total conductivity in the sample. Linear sweep voltammetry result showed that the Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ ceramic electrolyte was electrochemically stable up to 5.80 V versus a Li/Li$^+$ reference electrode.

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1. Introduction

Lithium orthosilicate, Li$_4$SiO$_4$ based compounds are among LISICON group members which have already been reported suitable for use as solid electrolytes in lithium ion battery [1]. These types of materials are easily synthesized, less expensive to produce and stable in air. The materials also show low self discharge and no reaction with lithium metal [2]. The Li$_4$SiO$_4$ has a versatile host structure that can form non-stoichiometric materials with extra vacancies or interstitial lithium ions. The structure has only half of the tetrahedral sites occupied by cations, and it allows additional cations to be accommodated at tetrahedral and octahedral co-ordination sites [1,3].

The partial substitutions using different cations can create more vacancies in the Li$_4$SiO$_4$ structure such as in Li$_{4+x}$Zn$_{2x}$Si$_{1-x}$O$_4$ (D =Zn$^{2+}$, Mg$^{2+}$) [4], Li$_4$Zn$_3$Ti$_x$O$_4$ (T = Al$^{3+}$, Ga$^{3+}$, In$^{3+}$) [4] and Li$_4$Zn$_3$M$_x$Si$_{1-x}$O$_4$ (M = V$^{5+}$, As$^{5+}$, P$^{5+}$) [4]. The void created through these partial substitutions can be accommodated by other lithium ion which is located in the intermediate vicinity. This leaves the previous site of the ion vacant and available to be a host for other ions. This helps to increase the mobility of the lithium ions and thus improves conductivity.

Meanwhile, partial substitutions can also create extra interstitial lithium ions in the Li$_4$SiO$_4$ structure such as in Li$_{4+x}$Zn$_{2x}$Si$_{1-x}$O$_4$ (T = B$^{3+}$, Al$^{3+}$, Ga$^{3+}$, Cr$^{3+}$, Fe$^{3+}$) [5–7]. The extra interstitial lithium ions are accommodated in the distorted tetrahedral or octahedral sites that leads to an increase of charge carrier concentration in the compound which in turn enhances conductivity. Partial substitution of Zn$^{2+}$ in the Li$_4$SiO$_4$ structure (Li$_{4-2x}$Zn$_{2x}$Si$_{1-x}$O$_4$) has been previously reported by the authors [4]. However, it only involved the partial substitution of Zn$^{2+}$ with Li$^+$ (Zn$^{2+}$ ↔ Li$^+$) which created two vacant sites in the structure. The partial substitution at the Si$^{4+}$ site in the Li$_4$SiO$_4$ compound using Zn$^{2+}$ (2Li$^+$ + Zn$^{2+}$ ↔ Si$^{4+}$) forming compounds with the formula Li$_{4-2x}$Zn$_{2x}$Si$_{1-x}$O$_4$ has never been reported in the literature. Other than enlarging the migration channel of the Li$_4$SiO$_4$ structure due to its larger ionic size, the substitution of Zn$^{2+}$ at the Si$^{4+}$ site is also expected to introduce two interstitial Li$^+$ ions. As such, in this study, Li$_{4+x}$Zn$_{2x}$Si$_{1-x}$O$_4$ (x = 0.04, 0.12 and 0.20) samples were synthesized by sol gel method and characterized. The effects of extra interstitial ions due to Zn$^{2+}$ substitutions on the structure, conductivity and electrochemical property of the Li$_4$SiO$_4$ were investigated using X-ray diffraction (XRD), Fourier transform infrared (FTIR), Scanning electron microscopy (SEM), Energy dispersive X-ray, impedance spectroscopy (IS), lithium transference number and linear sweep voltammetry (LSV).

2. Experimental Procedure

2.1. Synthesis of Samples

Lithium acetate, zinc acetate and tetraethyl orthosilicate were used as the starting materials while citric acid was used as the chelating agent. Lithium acetate and zinc acetate were first dissolved in distilled water and then mixed with citric acid under magnetic stirring until a homogeneous solution was formed. Solution of tetraethyl orthosilicate...
was later added to this homogeneous solution. The solution was transferred into a reflux system and continuously stirred for 12 h at 75 °C. The solution was taken out and then vaporized for about 2 h under magnetic stirring at 75 °C. The resulting wet gel was dried in an oven at 150 °C for 24 h to remove water particles and also to avoid ceramic cracks. The resulting powder samples was sintered at different temperatures of 750 °C, 800 °C and 850 °C for 12 h and later pressed using a Specac hydraulic press to form pellets with diameter and thickness of 13 mm and 2 mm respectively. Eventually, the pellets were then sintered at the same temperatures for 2 h to increase the contact between grains.

2.2. Characterization Techniques

XRD patterns of the powder samples were obtained using X-ray diffraction spectrometer (PANalytical-X’pert™) with Cu-Kα radiation of wavelength of 1.5406 Å in 2θ range from 10° to 70° at the rate of 0.016° in step width and analyzed using high score plus software. FTIR was carried out to confirm the structure of the studied ceramic materials. Infrared spectra were recorded at room temperature using a Perkin Elmer Frontier Spectrometer with resolution 1 cm⁻¹. The ceramic electrical properties were determined by ac impedance spectroscopy using Solartron 1260 impedance analyzer over a frequency range from 1 to 10⁶ Hz. An applied voltage was fixed at 200 mV.

Lithium transference number measurement was carried out using Bruce and Vincent method in order to determine the actual type of charge carriers. This method requires characterization of cell before and after polarization (after reaching the steady state) by using a combination of IS and DC polarization technique. For this measurement, the samples were sandwiched between lithium metal non-blocking electrolyte and after polarization (after reaching the steady state) by using a commercial cell (Nafion). The cell was connected to a multichannel electrochemical workstation.

3. Result and Discussion

Presented in Fig. 1 are XRD spectra of the Li₄₋ₓZnₓSi₁₋ₓO₄ compounds with x = 0.20, 0.12 and 0.04 sintered at different temperatures for 12 h. The XRD spectra of all samples can be indexed to monoclinic structure of Li₄SiO₄. The initial resistance of the passive layer (before polarization), Rₒ is the resistance of the passive layer (after polarization) and ΔV is the applied voltage bias (ΔV = 0.5 V). The electrochemical stability window was evaluated by linear sweep voltammetry using a Wonatech ZIVE MP2 multichannel electrochemical workstation.

### 3.1. Impedance Spectroscopy

The impedance spectrum taken at 303 K reveals overlapped semicircles due to bulk resistance, Rₒ and grain boundary resistance, Rₒgb respectively. However, at 773 K, the Rₒ value is approximately equal to 0 to give Rₒ = Rₒgb. This is because of the high ionic mobility in the sample which minimizes the resistance from grain boundary. The total conductivities were determined using the equation [16]:

\[
\sigma = \frac{1}{\sigma_b} + \frac{1}{\sigma_{gb}}
\]

where \(\sigma_b\) and \(\sigma_{gb}\) represent the bulk and grain boundary conductivity, respectively. In these equations, d is the sample thickness, A is the cross-sectional area of sample, \(\sigma_b\) is the bulk resistance and \(\sigma_{gb}\) is the grain boundary resistance. As the temperature increases, the total resistance, \(R = (R_b + R_{gb})\) value shifts towards lower values indicating conductivity enhancement.

The temperature dependence of D.C. conductivity of Li₄₋ₓZnₓSi₁₋ₓO₄ is shown in Fig. 7. The activation energy for the thermally activated hopping process was obtained by fitting the D.C. conductivity data with Arrhenius equation:

\[
\sigma_T = A(T) \exp \left(\frac{-E_a}{RT}\right)
\]

where \(A\) is the pre-exponential factor, \(E_a\) is the activation energy for conduction and \(k\) is the Boltzmann constant. The conductivity of the samples increases with temperature. The D.C. conductivity value at ambient temperature is 2.51 × 10⁻⁹ S cm⁻¹ while at 500 °C, the conductivity is 3.01 × 10⁻⁹ S cm⁻¹. The higher conductivity obtained in this study compare to parent compound [17] is due to the introduction of extra interstitial ions that increases lithium ions’ concentration in the sample. The conductivity value at ambient temperature is also
comparable to those of other ceramic electrolyte systems such as Thio Lisicon-type system, Li$_{4-2x}$Zn$_x$GeS$_4$ (6.5 × 10$^{-5}$ S cm$^{-1}$) reported by Kanno et al. [18], NASICON-type system, Li$_3$Sc$_2$(PO$_4$)$_3$ (3.0 × 10$^{-6}$ S cm$^{-1}$) reported by Amatucci et al. [19], Garnet-type system, Li$_6$BaLa$_2$Ta$_2$O$_{12}$ (4.05 × 10$^{-5}$ S cm$^{-1}$) reported by Thangadurai and Weppner [20], and Perovskites-type system, Li$_{0.34}$La$_{0.51}$TiO$_{2.94}$ (2.0 × 10$^{-6}$ S cm$^{-1}$) reported by Amatucci et al. [19], Garnet-type system, Li$_6$BaLa$_2$Ta$_2$O$_{12}$ (4.05 × 10$^{-5}$ S cm$^{-1}$) reported by Thangadurai and Weppner [20], and Perovskites-type system, Li$_{0.34}$La$_{0.51}$TiO$_{2.94}$ (2.0 × 10$^{-6}$ S cm$^{-1}$) reported by Amatucci et al. [19], Garnet-type system, Li$_6$BaLa$_2$Ta$_2$O$_{12}$ (4.05 × 10$^{-5}$ S cm$^{-1}$) reported by Thangadurai and Weppner [20], and Perovskites-type system, Li$_{0.34}$La$_{0.51}$TiO$_{2.94}$ (2.0 × 10$^{-6}$ S cm$^{-1}$).

Fig. 1. XRD pattern of (a) $x = 0.20$, (b) $x = 0.12$ and (c) $x = 0.04$ at different sintering temperatures of (i) 750 °C, (ii) 800 °C and (iii) 850 °C for 12 h.

Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a$ ± 0.005 (Å)</th>
<th>$b$ ± 0.016(Å)</th>
<th>$c$ ± 0.014 (Å)</th>
<th>$\beta$ ± 0.04</th>
<th>$V$ (Å$^3$)</th>
<th>$d$ (g/cm$^3$)</th>
</tr>
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<tbody>
<tr>
<td>$x = 0.00$ [10]</td>
<td>5.147</td>
<td>6.094</td>
<td>5.293</td>
<td>90.25</td>
<td>166.01</td>
<td>2.40</td>
</tr>
<tr>
<td>$x = 0.04$</td>
<td>5.167</td>
<td>6.063</td>
<td>5.320</td>
<td>90.33</td>
<td>166.66</td>
<td>2.43</td>
</tr>
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</table>
$10^{-5}$ S cm$^{-1}$) reported by Inaguma et al. [21]. However, the conductivity of the system at 500 °C is low compared to those of other ceramic electrolyte systems. But, the system may be useful for devices that operate at temperature at least 500 °C. Further studies on this material still need be done to improve its conductivity or to investigate the behavior of this material at higher temperatures.

The $\sigma$-1000/T plot in Fig. 7 also shows a discontinuity at ~300 °C (1000/T = 1.745 K$^{-1}$). The change in slope of log $\sigma$-1000/T plot could be due to the transformation from extrinsic to intrinsic regime which changes the ion arrangement caused by an order–disorder process transition of $2\text{Li}^+ + \text{Zn}^{2+} \rightarrow \text{Si}^{4+}$ [1,10,22,23] since there was no phase transition occurring in the sample upon heating up to 500 °C as reported in [4,23]. In the extrinsic regime, the conductivity depends only on the mobility of lithium ions due to extrinsic defect with less thermal energy contribution. Upon reaching the intrinsic regime, the mobility of lithium ions increases dramatically due to the increase of intrinsic defect concentration (Schottky and Frankel) and thermal energy that help more ions hopping through migration channel. The activation energy values of the sample for both regimes were extracted from the slope of the Arrhenius graph and are also given in Fig. 7. The activation energy in the intrinsic regime shows a higher value compared to that of the extrinsic regime. This is ascribed to both the activation energy for ion to jump and the enthalpy of the formation of intrinsic defect (Schottky and Frankel).

Fig. 8 presents the plot of current versus time of the Li/Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$/Li for the lithium transference number determination in the solid electrolyte. The values of $I_0$, $I_{\infty}$, $R_a$ and $R_\infty$ obtained from this measurement are also shown in Fig. 8. The calculated lithium transference number value is found to be 0.92. This value is higher than that obtained for the parent compound (0.79) [10]. This confirms the
which increases lithium ion contribution to the total conductivity.

References

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Table 2

<table>
<thead>
<tr>
<th>Vibrational bands of $\nu_3$ (SiO$_4$)</th>
<th>$\nu_3$ (SiO$_4$) (cm$^{-1}$)</th>
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<td>$\nu_3$ (SiO$_4$) (cm$^{-1}$)</td>
<td>$\nu_3$ (SiO$_4$) (cm$^{-1}$)</td>
</tr>
<tr>
<td>952.95</td>
<td>949.74</td>
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<td>959.90</td>
<td>959.74</td>
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<td>968.85</td>
<td>968.74</td>
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<tr>
<td>926.25</td>
<td>926.46</td>
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<td>979.85</td>
<td>979.50</td>
</tr>
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4. Conclusions

The effects of interstitial Li$^+$ ions on the properties of novel Li$_4$Zn$_{0.04}$Si$_{0.96}$O$_4$ were successfully reported. The compound showed enhanced conductivity (an order of magnitude higher compared to the parent compound) due to the presence of interstitial Li$^+$ ions. Its greater values of lithium ion transference number indicated that the interstitial ions contributed to total conductivity. The conductivity—temperature study illustrated that the compound obeyed the Arrenhius law. The higher conductivity value at intrinsic regime was attributed to the Arrhenius mechanism of interstitial-type Li$^+$ conductor, Li$_{4+x}$Zn$_x$Si$_{1-x}$O$_4$ ($0 < x < 0.7$), Solid State Ionics 47 (1991) 149–154.

Acknowledgments

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References

[1] S.B.R.S. Adnan, N.S. Mohamed, Characterization of novel Li$_4$Zn$_{0.04}$Si$_{0.96}$O$_4$ and Li$_4$Cr$_{0.02}$Zn$_{0.06}$Si$_{0.94}$O$_4$ ceramic electrolyte, Solid State Ionics 40/41 (1990) 34–37.

Fig. 9 shows linear sweep voltammogram of the Li$_4$Zn$_{0.04}$Si$_{0.96}$O$_4$ ceramic electrolyte. The Li$_4$Zn$_{0.04}$Si$_{0.96}$O$_4$ ceramic electrolyte exhibits an electrochemical stability up to 5.80 V at room temperature indicating that it is suitable for application in lithium battery. This value is higher than the value reported for the parent compound, Li$_4$SiO$_4$ [10]. This suggests that the compound is electrochemically stable in a wider voltage window.

Fig. 5. EDX analysis of Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ sample.

Fig. 6. Impedance spectra of Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ at 303 K and 707 K.

Fig. 7. Arrhenius plot of total conductivity for Li$_{4.08}$Zn$_{0.04}$Si$_{0.96}$O$_4$ sample.
Fig. 8. Current versus time plot for Li₄ₓZn₀.₀₄Si₀.₉₆O₄ sample. Impedance responses of the sample before and after polarization are shown in inset.

Fig. 9. Linear sweep voltammogram of Li₄ₓZn₀.₀₄Si₀.₉₆O₄ sample.