Structural, electrical and electrochemical properties of novel Li$_{4+2x+y}$Zn$_x$M$_y$Si$_{1-x-y}$O$_4$ (where $x = 0.04$, $y = 0.03$; $M =$ Al, Cr) ceramic electrolytes

S.B.R.S. Adnan *, N.S. Mohamed

Centre for Foundation Studies in Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

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**A B S T R A C T**

Lisicon-type ceramic electrolytes, Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$, were synthesized by sol gel method. X-ray diffraction was applied to investigate the phase, structure and unit cell parameters of both solid electrolytes. The information of particles size distribution was obtained by laser particle sizer. Meanwhile, energy dispersive X-ray was used for elemental composition analysis. The complex impedance spectroscopy was carried out in the frequency range 10 Hz–10 MHz and temperature range 273 K to 773 K to study the electrical properties of the electrolytes. Both compounds were indexed to the monoclinic unit cell in the space group $P2_1/m$. The particle size in Cr substituted sample was smaller compared to that in the Al substituted sample. The EDX results showed that the chemical compositions for both compounds were very close to the designed compositions. The Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ compound gave slightly higher total conductivity values of $3.16 \times 10^{-5}$ S cm$^{-1}$ at ambient temperature and $1.78 \times 10^{-1}$ S cm$^{-1}$ at 773 K compared to Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ which showed total conductivity values of $1.16 \times 10^{-5}$ S cm$^{-1}$ at ambient temperature and $1.12 \times 10^{-3}$ S cm$^{-1}$ at 773 K. The conductivity-frequency spectra were used to estimate the hopping rate in the structure. The dielectric constant and dielectric loss were found to decrease with the increase of frequency but increased with the increase of temperature. Ionic transference number corresponding to Li$^+$ ion transport determined by means of Bruce and Vincent technique is 0.93 and 0.94 for Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ respectively. Linear sweep voltammetry results demonstrated that the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ ceramic electrolytes was electrochemically stable up to 4.10 V and 3.5 V versus a Li/Li$^+$ reference electrode respectively.

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1. Introduction

Li-ion batteries have received a large amount of attention due to their attractive properties such as high energy density, no memory effect and long cycle life. Hence, they are used in a plethora of household and portable applications [1]. In order to improve the performance of the batteries, substantial research is ongoing to develop new electrolyte materials. Ceramic electrolytes are considered effective in improving the safety of lithium ion batteries employing liquid electrolytes. This type of electrolytes also form an important class of materials due to their large electrochemical stability window, good thermal stability, absence of leakage and high resistance shock and vibrations [2]. Lithium orthosilicate, Li$_4$SiO$_4$ compound has been proven to be promising ceramic electrolyte material since it can be easily synthesized, less expensive to produce, safe and also stable in air. Besides, it does not react with lithium electrode, having low self-discharge, and can maintain constant conductivity with time. Its versatile structure allows non-stoichiometric materials to be produced by aliovalent or isovalent ions substitution [2–7]. In order to improve its ionic conductivity as well as its electrochemical activity, various modifications on Li$_4$SiO$_4$ compound have been explored. West et al. [8] improved the conductivity of Li$_4$SiO$_4$ compound by partial substituted of Si$^{4+}$ by Ti$^{4+}$. The best conductivity of $5 \times 10^{-4}$ S cm$^{-1}$ at 300 °C has been reported for the Li$_4$Ti$_2$Si$_2$O$_7$ system with $x = 0.4$. Khorassani et al. [9,10] modified the Li$_4$SiO$_4$ structure by partially substituted aliovalent ion such as Si$^{4+}$ with P$^{5+}$ to produce compounds with...
formula, Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$. The maximum conductivity obtained was $10^{-4}$ S cm$^{-1}$ at 100 °C for the compound with $x=0.4$. Similar effects have been observed by partial substitutions of Si$^{4+}$ by As$^{5+}$ and V$^{5+}$.

Trivalent cations such as B$^{3+}$, Al$^{3+}$, Ga$^{3+}$, In$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$ can also be partially substituted into Li$_4$SiO$_4$ structure to create interstitial Li$^+$ with general formula of Li$_{4+x}$T$_x$Si$_{1-x}$O$_4$ (T = trivalent ion) [11]. Masquelier et al. [12] have succeeded in synthesizing B$^{3+}$ and Al$^{3+}$ substituted Li$_4$SiO$_4$ compounds which exhibited conductivity values of $8.48 \times 10^{-6}$ and $7.28 \times 10^{-3}$ S cm$^{-1}$ at 100 °C respectively. Chavarria et al. [13] have reported the solid solutions of Li$_{4-x}$Al$_x$SiO$_4$ with conductivity value of $6 \times 10^{-5}$, Li$_{4-x}$Ga$_x$SiO$_4$ with conductivity of $6 \times 10^{-6}$ and Li$_{4-x}$In$_x$SiO$_4$ with conductivity of $6 \times 10^{-8}$ S cm$^{-1}$.

The conventional solid state reaction technique is the most common method used to synthesize Li$_4$SiO$_4$ and modified Li$_4$SiO$_4$ compounds. However, the synthesis using sol gel method has been reported can enhance the conductivity compared to the conventional solid state reaction. Furthermore, this technique has other advantages such as lowering the synthesis temperature, improving the linkage between grain boundary and molecular-level homogeneity. This method is also simple and therefore suitable for both small and large scale productions [3,4,14].

The scope of the present work is to study the structural, electrical and electrochemical properties of novel double partial substituting using dopants Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$ in the Si$^{4+}$ site of Li$_4$SiO$_4$ using citrate sol gel method. Apart from its larger size than Si$^{4+}$, which is expected to increase the size of migration channel, the substitutions of Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$ into the Li$_4$SiO$_4$ structure are expected to introduce extra lithium interstitial ions leading to an increase of lithium ion concentration in the compound. To the best of our knowledge, limited studies have been carried out using Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$ as the property enhancing agent in the Li$_4$SiO$_4$ structure. In this paper, for the first time, detailed electrical and electrochemical properties of Li$_{4-2x+y}$Zn$_x$M$_y$Si$_{1-x}$O$_4$ (M = Al, Cr) with $x=0.04$; $y=0.03$ are reported.

1.1. Experimental Procedure

1.1.1. Synthesis of Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr)

For this study, the Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) ceramic electrolytes were prepared via citrate sol gel method. For

Fig. 1. XRD patterns of (a) Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ and (b) Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$.

Fig. 2. XRD peaks of the Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) compounds at different planes at room temperature (dotted line indicated the peaks from the parent compound[2]).
preparation of samples, lithium acetate, zinc acetate, aluminum acetate (or chromium(III) acetate) and tetaethyl orthosilicate were first dissolved in deionized water with molar ratio of Li: Zn: Al/Cr: Si fixed according to formula Li_{x+2y}Zn_{M-x}M_{y}Si_{1-y}O_{4} where $x=0.04$, $y=0.03$; $M=\text{Al, Cr}$. Solution of citric acid as the chelating agent was mixed together to the previously prepared solutions under magnetic stirring. Solution of tetaethyl orthosilicate was later added to the homogeneous solutions. The solutions were transferred into reflux systems and continuously stirred for 12 hours at 75 °C. The solutions were then taken out and vaporized for about 2 hours under magnetic stirring at 75 °C. The resulting wet gels were dried in an oven at 150 °C for 24 hours to remove water particles, resistance organic groups and also to avoid ceramic cracks. The powders obtained were sintered at 800 °C for 12 hours and later pressed using a Specac pellet press to form pellets with diameter and thickness of 13 mm and ~2 mm.

1.2. Characterization techniques.

X-ray diffraction (XRD) was done in order to elucidate structural information of the synthesized ceramic samples. XRD patterns of the powder samples were obtained using X-ray Diffraction spectrometer PANalytical-X’pert$^\text{3}$ with Cu-K$_{\alpha}$ radiation of wavelength of 1.5406 Å in 2θ range between 10° to 70° at the rate of 0.016° in step width. The data obtained were analyzed using High score plus software. The lattice parameters of the monoclinic compound were calculated using equation as follows [15],

\[ \frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) - 2hl \cos \beta \cos \gamma \]  

where $d$ is the distance between crystal planes of $(hkl)$, $\lambda$ is the X-ray wavelength, $\theta$ is the diffraction angle of crystal plane $(hkl)$, $hkl$ is the crystal index, $a$, $b$ and $c$ are the lattice parameters and $\beta$ and $\gamma$ are the angles between a and c. The elemental compositions were analysed by EDX which were carried out using Oxford AzteXX-MA10 scanning electron microscope (SEM). The particle size information was obtained using FRITSCH- Analysette 22 NanoTec laser particle sizer. The ceramic electrical properties were determined by ac impedance spectroscopy which was performed using Solatron 1260 impedance analyzer over a frequency range from 10 to $10^7$ Hz. An applied voltage was fixed at 200 mV. The total conductivity, $\sigma_t$ (bulk conductivity, $\sigma_b$ + grain boundary conductivity, $\sigma_{gb}$) which represents the direct current (dc) conductivity in the ceramic sample was calculated using the equation [2, 5, 16],

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

where $\sigma_b = \frac{d}{A_{gb}}$ and $\sigma_{gb} = \frac{d}{A_{gb}}$

In these equations, $d$ is the sample thickness, $A$ is the cross-sectional area of sample, $R_b$ is the bulk resistance and $R_{gb}$ is the
granular boundary resistance. The ac conductivity has been evaluated from dielectric data in accordance with the relation:

\[ \sigma_{dc} = \omega \varepsilon_{r} \varepsilon_{0} \tan \delta \]  

(3)

where \( \varepsilon_{r} \) is the permittivity of the free space \( (8.854 \times 10^{-14} \text{ F cm}^{-1}) \), \( \tan \delta \) is the tangent loss factor, \( \varepsilon' \) is the dielectric loss. Lithium transference number measurement was carried out using Bruce and Vincent method [17,18] in order to determine the actual type of charge carriers. The samples were sandwiched between lithium metal electrodes which served as non-blocking electrodes that only allowed Li\(^+\) ions to flow. The lithium transference number \( (\tau_{Li^+}) \) was calculated using the equation:

\[ \tau_{Li^+} = \frac{I_{S} (\Delta V - I_{0} R_{0})}{I_{0} (\Delta V - I_{S} R_{0})} \]  

(4)

In equation (4), \( I_0 \) is the initial current \( (t=0) \), \( I_S \) is the steady state current, \( R_0 \) and \( R_S \) are the initial resistances of the passive layer, before polarization and after polarization respectively. \( \Delta V \) is the applied voltage bias \( (\Delta V = 0.5 \text{ V}) \). The electrochemical stability window was evaluated by linear sweep voltammetry using a Wonatech ZIVE MP2 multichannel electrochemical workstation.

1.3. Result and Discussion

1.3.1. Structural studies

Presented in Fig. 1 are XRD patterns of Li\(_{4.11}Zn\(_{0.04}M_{0.03}Si_{0.93}O_{4}\) \( (M = Al, Cr) \) compounds. The diffraction positions for both compounds can be indexed to the monoclinic unit cell in the space group \( P2_1/m \) which composed of hexagonal close packed (hcp) oxygen ion arrays without evidence of any impurity phase. To see the effects of double substitutions of Si\(^{4+}\) with Zn\(^{2+}/Al^{3+}\) and Si\(^{4+}\) with Zn\(^{2+}/Cr^{3+}\) in the Li\(_4\)SiO\(_4\) unit cells, the peaks at (100), (020) and (001) planes which represent lattice parameters of \( a \), \( b \) and \( c \) respectively were carefully analyzed. Fig. 2 shows the XRD peaks of Li\(_{4.11}Zn\(_{0.04}M_{0.03}Si_{0.93}O_{4}\) \( (M = Al, Cr) \) at different planes. From the figures, all peaks at different planes which were contributed by the double substitutions Si\(^{4+}\) with Zn\(^{2+}/Al^{3+}\) and Si\(^{4+}\) with Zn\(^{2+}/Cr^{3+}\) shift to high diffraction angles compared to the unsubstituted Li\(_4\)SiO\(_4\) [2,8]. This suggests that there are more ions accommodated in the lattice structure. The lattice parameters, unit cell volumes and relative densities for both compounds are listed in Table 1. The relative densities are in the range of 92.5–93.2\% compared to the theoretical density of parent compound, Li\(_4\)SiO\(_4\) (2.40 g cm\(^{-3}\)) [19]. The relative densities of the substituted compound increase compare to that than of the non-substituted sample. This may due to the extra Li\(^+\) interstitial ions in the sample. The substitutions of Si\(^{4+}\) by Zn\(^{2+}\) and Al\(^{3+}/Cr^{3+}\) *cause distortion of the hcp sublattices generating tetrahedral packed array due to the difference in the ionic radius of Si\(^{4+}\) (0.41 Å) compare to Zn\(^{2+}\) (0.74 Å), Al\(^{3+}\) (0.54 Å) and Cr\(^{3+}\) (0.64 Å). The mechanism allows additional cations to be accommodated in the tetrahedral sites. This is especially advantageous for lithium ions which owing to their small size can be readily accommodated in the distorted tetrahedrally and octahedrally co-ordinated. The unit cell volume of both Li\(_{4.11}Zn\(_{0.04}M_{0.03}Si_{0.93}O_{4}\) \( (M = Al, Cr) \) also increases. This is attributed to the extra lithium ion content in the structure. Meanwhile, the large ionic radii of Al\(^{3+}\) and Cr\(^{3+}\) than

![Fig. 4. SEM micrograph of (a) Li\(_{4.11}Zn\(_{0.04}Al_{0.03}Si_{0.93}O_{4}\) and (b) Li\(_{4.11}Zn_{0.04}Cr_{0.03}Si_{0.93}O_{4}\) samples.](image)

![Fig. 5. Particle size distribution of Li\(_{4.11}Zn\(_{0.04}M_{0.03}Si_{0.93}O_{4}\) \( (M = Al, Cr) \) at ambient temperature.](image)
Fig. 6. Particle size distribution of Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ ($M$ = Al, Cr) with different sintering temperature.

Fig. 7. EDX analyse of (a) Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and (b) Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$. 
that of Si$^{4+}$ also caused expansions of tetrahedron in the Li$_4$SiO$_4$ structure. Fig. 3 (a) and (b) shows the XRD peaks for both compounds at different planes and at different sintering temperatures (303 K–673 K) for one hour. As can be seen in this figure, all of the peaks are unshifted suggesting that there was no phase transition occurred in both compounds. This also indicates that the samples are stable to temperature change. The stability of the compounds is important as the electrolytes have the possibility to be exposed to high temperature which could change the phase and conductivity values as well.

1.4. SEM, Particle size distribution and EDX studies

The morphology of the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ samples was observed by SEM (Fig. 4) while particle size distributions for both samples are displayed in Fig. 5. From the figures, it is clear that the particles in Cr$^{3+}$ doped sample are smaller compared to those in the Al$^{3+}$ substituted sample. The average particle sizes for Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ are 3.27 and 3.98 μm respectively. The small particle size in Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ is favorable as this may improve contact with electrode materials when it is used for device fabrication. Fig. 6 illustrated the particle size distribution with sintering temperature. The figure shows that, the particle size for both samples increases when the sintering temperature increases. This is attributed to the grain growth process occurred in both samples due to a force generated by thermal energy drives the grain boundaries to grow [20].

EDX analysis was also carried out to examine the elemental compositions of both samples and the results are shown in Fig. 7. The atomic ratios of Zn: Al: Si: O and Zn: Cr: Si: O are 0.038: 0.031: 0.935: 4.00 and 0.041: 0.028: 0.928: 4.00 respectively. As

![Figure 8](image_url)  
Fig. 8. Impedance spectra for Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) at room temperature.

![Figure 9](image_url)  
Fig. 9. Equivalent circuit of the samples on the basis of impedance analysis.
such, the elemental compositions of the prepared ceramic electrolyte samples can be identified as Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$, which are very close to the designed compositions. The presence of lithium could not be detected by the EDX because of its light weight.

### 1.5. Effects of temperature and frequency on total conductivity

Illustrated in Fig. 8 are typical impedance spectra obtained for Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) at room temperature. The spectra consist of two depressed semicircles in high and intermediate frequency region followed by a spike in the low frequency region. The depressed semicircles at high frequency and intermediate frequency are due to bulk resistance ($R_b$) and grain boundary resistance ($R_{gb}$) of the compound. Meanwhile, the spike in the low frequency is due to the processes occurring at the electrode and electrolyte interface [21]. The semicircles observed in the graphs also can be represented by the equivalent circuit using combination of resistance $R_p$ and capacitance, $C_p$ with constant phase element (CPE) behavior. A CPE is equivalent to a distribution of capacitor in parallel where were calculated from the observed impedance spectra using the circuit shown in Fig. 9. The general expression of the CPE is [22]:

$$Z = \frac{1}{C(j\omega)^n}$$

(5)

Here, $C$ indicates ideal capacitance where $n = 1$, $j = (-1)^{1/2}$ and $\omega$ shows the angular frequency.

### Table 1

Lattice parameters and unit cells volume for different compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a$ ± 0.047 (Å)</th>
<th>$b$ ± 0.011 (Å)</th>
<th>$c$ ± 0.033 (Å)</th>
<th>$\beta$ ± 0.03</th>
<th>$V$ (Å$^3$)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$SiO$_4$ [2]</td>
<td>5.147</td>
<td>6.094</td>
<td>5.293</td>
<td>90.33</td>
<td>166.01</td>
<td>92.5</td>
</tr>
<tr>
<td>Li$<em>{4.11}$Zn$</em>{0.04}$Al$<em>{0.03}$Si$</em>{0.93}$O$_4$</td>
<td>5.243</td>
<td>6.070</td>
<td>5.299</td>
<td>90.25</td>
<td>168.64</td>
<td>92.9</td>
</tr>
<tr>
<td>Li$<em>{4.11}$Zn$</em>{0.04}$Cr$<em>{0.03}$Si$</em>{0.93}$O$_4$</td>
<td>5.261</td>
<td>6.096</td>
<td>5.290</td>
<td>90.25</td>
<td>169.65</td>
<td>93.2</td>
</tr>
</tbody>
</table>

*Theoretical density of Li$_4$SiO$_4$ is 2.40 g/cm$^3$.*

### Table 2

The values of $\omega_p$, C, $n$ and $\mu$ for Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) samples at various temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T$ (K)</th>
<th>$\omega_p$ (MHz)</th>
<th>$C$ (S cm$^{-1}$ K Hz$^{-1}$)</th>
<th>$n$ (cm$^{-1}$)</th>
<th>$\mu$ (cm$^2$V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{4.11}$Zn$</em>{0.04}$Cr$<em>{0.03}$Si$</em>{0.93}$O$_4$</td>
<td>303</td>
<td>0.021</td>
<td>$4.54 \times 10^{-7}$</td>
<td>$2.71 \times 10^{27}$</td>
<td>$7.29 \times 10^{-14}$</td>
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<td></td>
<td>373</td>
<td>0.033</td>
<td>$4.53 \times 10^{-7}$</td>
<td>$2.70 \times 10^{27}$</td>
<td>$9.19 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>0.066</td>
<td>$4.54 \times 10^{-7}$</td>
<td>$2.71 \times 10^{27}$</td>
<td>$1.45 \times 10^{-13}$</td>
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<tr>
<td></td>
<td>573</td>
<td>0.321</td>
<td>$4.55 \times 10^{-7}$</td>
<td>$2.72 \times 10^{27}$</td>
<td>$5.77 \times 10^{-13}$</td>
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<td></td>
<td>673</td>
<td>1.054</td>
<td>$4.54 \times 10^{-7}$</td>
<td>$2.71 \times 10^{27}$</td>
<td>$1.62 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>3.034</td>
<td>$4.54 \times 10^{-7}$</td>
<td>$2.71 \times 10^{27}$</td>
<td>$4.09 \times 10^{-12}$</td>
</tr>
<tr>
<td>Li$<em>{4.11}$Zn$</em>{0.04}$Al$<em>{0.03}$Si$</em>{0.93}$O$_4$</td>
<td>303</td>
<td>0.016</td>
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<td>373</td>
<td>0.042</td>
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<td>$1.31 \times 10^{27}$</td>
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<td>673</td>
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<td>$1.31 \times 10^{27}$</td>
<td>$2.70 \times 10^{-12}$</td>
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<tr>
<td></td>
<td>773</td>
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<td>$2.17 \times 10^{-7}$</td>
<td>$1.31 \times 10^{27}$</td>
<td>$3.38 \times 10^{-12}$</td>
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</table>
Fig. 11. The characteristic frequency dependencies of real part of $\sigma'$ of (a) Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and (b) Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ compounds at different temperatures.

The equivalent circuit consists of a series of array of parallel $RC$ elements attached with a series resistor, $R_s$. Series resistance corresponds to bulk resistance whereas grain boundary resistance is represented by a resistance which is attached in parallel to a capacitor [23].

The plots of temperature dependence of $\sigma'$ for both Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ ($M = Al, Cr$) ceramic electrolytes are shown in Fig. 10. The conductivity plots of the samples are linear and fit the Arrhenius equation as expressed by:

$$
\sigma'(T) = A(T) \exp \left( -\frac{E_t}{kT} \right)
$$

(6)

where $A$ is the pre-exponential factor, $E_t$ is the activation energy for total conductivity and $k$ is the Boltzmann constant. The conductivity of both samples shows an increasing trend with the increase in temperature. The Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ exhibits total conductivity values of $3.16 \times 10^{-3}$ S cm$^{-1}$ at ambient temperature and $1.78 \times 10^{-3}$ S cm$^{-1}$ at 773 K. Meanwhile, the Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ shows total conductivity values of $1.16 \times 10^{-3}$ S cm$^{-1}$ at ambient temperature and $1.12 \times 10^{-3}$ S cm$^{-1}$ at 773 K. Both $\sigma$-1000/T plots show a discontinuity at $\sim 473$ K ($1/T = 0.0021$ K$^{-1}$). This temperature is lower than that observed for the parent compound Li$_4$SiO$_4$ ($\sim 573$ K) [2] but is in agreement with the result obtained for Li$_{4+x}$Si$_{1-x}$O$_4$ ($M = B^{3+}, A^{3+}$) reported earlier by Masquelier et al. [12]. The change in the slope of $\sigma$-1000/T plots could be attributed to the change from extrinsic to intrinsic regime which caused the ion (Li$^+$) rearrangements in the structure. This occurred due to order–disorder process of transition between Si$^{4+}$ with Zr$^{4+}$/Cr$^{3+}$ and Si$^{4+}$ with Zr$^{4+}$/Al$^{3+}$ [5]. 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 [24]. The values of activation energies, $E_r$,s were determined from the slopes of the Arrhenius plots and are also shown in Fig. 10. The low values of $E_r$ allow more ions to jump from one site to another site. This situation resulted in high mobility of ions thereby increases the conductivity of the compound.

The characteristic frequency dependencies of real part of $\sigma^r (\omega_{dc})$ of Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) at different temperatures are depicted in Fig. 11. At low frequencies, a plateau characterizes the dc conductivity which is in good agreement with the value shown in Fig. 10. At high frequencies, the $\sigma^r$ increases according to the universal power law and can thus be represented by the expression as follows:

$$\sigma^r (\omega) = \sigma (0) + A\omega^\alpha$$

where $\sigma(0)$ is the dc conductivity of the sample, $A$ is a temperature dependant parameter and $\alpha$ is the power law exponent which represents the degree of interaction between the mobile ion and is less than 1. When temperature increases, the dispersion region shifts towards higher frequency indicating that conductivity of the sample is thermally activated. The ionic hopping rate, $\omega_p$, can be obtained directly from $\sigma^r$ spectra data since it corresponds to $\sigma^r (\omega) = 2\sigma (0)$ [4,6,7,14,25,26]. On the other hand, the lithium ion concentration, $C$ can be calculated from the total conductivity of the ion conducting material which is given by [4,6,7,14,27]:

$$C = \frac{\sigma T}{\omega_p} = C = ne^2a^2\gamma k^{-1}$$

where $e$ is the electron charge, $\gamma$ is the correlation factor which is set equal to 1, $a$ is the jump distance between two adjacent sites for the ions to hop which is assumed to be 3 Å for all materials, $n$ is concentration of mobile lithium which can be calculated using Eq. 8 and $k$ is Boltzmann constant. The ionic mobility, $\mu$ can be determined using the equation:

$$\mu = \frac{\sigma T}{n e^2}$$

The values of $\omega_p$, $C$, $n$ and $\mu$ for Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) samples at various temperatures are tabulated in Table 2. The table reveals that the lithium ion concentration, $C$ in the both samples is constant over the selected temperature range. This implies that all the lithium ions which are responsible for the conductivity are in mobile state and thus can be best represented by the strong electrolyte model [4,6,7,14,26–28]. The higher conductivity observed for Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ is due to its higher mobile lithium ion concentration ($2.71 \times 10^{27}$) compared to that of the Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ ($1.31 \times 10^{27}$) sample. Meanwhile, the
mobility of ions, $\mu$ increases with increasing temperature in both samples. This means that the increase in conductivity with increasing temperature in the samples is attributable to the increase in ionic mobility since the charge carrier concentration is constant over the whole temperature range.

1.6. Frequency dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$)

Presented in Fig. 12 and Fig. 13 are frequency dependencies of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at different temperatures for both $\text{Li}_{4.11}\text{Zn}_{0.04}\text{M}_{0.03}\text{Si}_{0.93}\text{O}_4$ ($\text{M} = \text{Al}, \text{Cr}$) ceramic electrolytes. It is clear from the figures that $\varepsilon'$ and $\varepsilon''$ for both electrolytes decrease with increasing frequency. This behaviour is similar to that obtained for $\text{Li}_4\text{SiO}_4$ and other modified $\text{Li}_4\text{SiO}_4$ compounds [3,7]. The $\text{Li}_{4.11}\text{Zn}_{0.04}\text{Cr}_{0.03}\text{Si}_{0.93}\text{O}_4$ exhibits higher $\varepsilon'$ and $\varepsilon''$ at low frequencies compared to the $\text{Li}_{4.11}\text{Zn}_{0.04}\text{Al}_{0.03}\text{Si}_{0.93}\text{O}_4$. The higher $\varepsilon'$ value is due to larger amount of lithium ion accumulation at the interface of electrode. Meanwhile the higher value of $\varepsilon''$ in $\text{Li}_{4.11}\text{Zn}_{0.04}\text{Cr}_{0.03}\text{Si}_{0.93}\text{O}_4$ is ascribed to higher migration rate of lithium ions which causes greater loss of energy to the lattice as heat [3,4,6,7,14,29,33].

The $\varepsilon'$ for both ceramic electrolytes also increases with temperature. This can be attributed to the fact that at low temperature, most of the charge carriers cannot orient themselves with respect to the direction of the applied field giving a weak contribution to the polarization and $\varepsilon'$. When temperature increases, the charge carriers acquire sufficient excitation thermal energy and are able to rotate more easily to obey the change in external field which in turn increases their contribution to the polarization leading to an increase in $\varepsilon'$[3,4,6,7,14,29–33]. Meanwhile, the $\varepsilon''$ in both ceramic electrolytes also increases with temperature as can be seen in Fig. 11. The increase in $\varepsilon''$ with temperature is attributed to an increase of ion migration rate [3,4,6,7,14,29–33]. This is can be ascribed to an increase mobility of lithium ions as shown in Table 2.

1.7. Lithium Transference Number

Fig. 14 (a) and 14 (b) present plots of current versus time for the $\text{Li}/\text{Li}_{4.11}\text{Zn}_{0.04}\text{Cr}_{0.03}\text{Si}_{0.93}\text{O}_4/\text{Li}$ and $\text{Li}/\text{Li}_{4.11}\text{Zn}_{0.04}\text{Al}_{0.03}\text{Si}_{0.93}\text{O}_4/\text{Li}$
cells used for lithium transference number determination. Under a dc polarization of 0.5 V, the current in the both cells exhibits only a small decay with time. The initial and final steady current for the Li/Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) compounds.

The impedance responses of the cells prior and after polarization for the Li/Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$/Li cell are $R_\infty = 8000 \Omega$ and $R_{ss} = 5000 \Omega$ respectively. On the other hand, for the Li/Li$_{4}$Cr$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$/Li cell, the impedance responses prior and after polarization are $R_\infty = 3900 \Omega$ and $R_{ss} = 4000 \Omega$ respectively.

The Li$^+$ transference number was determined using Eq. 4. The lithium transference number value is 0.94 for the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ and 0.93 for the Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$. These values show that double partial substitution of Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$ on the Si sites increases the Li$^+$ ions transport number compared to the Li$_4$SiO$_4$ parent compound (0.79) [2]. This is due to the introduction of extra interstitial ions that increases lithium ions concentration in the sample.

1.8. Linear Sweep Voltammetry

The electrochemical stability window of the ceramic electrolytes was also investigated. The stability was evaluated by linear sweep voltammetry. Fig. 15 shows linear sweep voltammograms of the Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) ceramic electrolytes. From the figure, the anodic and cathodic limit potential are at -3.0 V and 3.0 for the Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ and -4.1 V and 4.1 V versus Li/Li$^+$ for the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ respectively. The current starts to increase at potentials beyond this limit due to decomposition of the electrolyte. The potential limit of the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ is higher than Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$. This is due to higher electronegativity value of Cr (1.66) than Al (1.61) resulting in stronger bond between Cr and O than that of Al and O. Meanwhile, this analysis also shows that the double
partial substitutions of Si$^{4+}$ using Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$ increase the electrochemical stability windows as compared to Li$_4$SiO$_4$ parent compound [2].

2. Conclusion

The Li$_{4.11}$Zn$_{0.04}$M$_{0.03}$Si$_{0.93}$O$_4$ (M = Al, Cr) ceramic electrolytes were successfully synthesized by sol gel method. Both compounds can be indexed to the monoclinic unit cell in space group $P2_1/m$. Temperature dependencies of the total conductivity illustrated that both electrolytes obey the Arrhenius law. The conductivity of Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ compound was higher than that of Li$_{4.11}$Zn$_{0.04}$Al$_{0.03}$Si$_{0.93}$O$_4$ compound due to higher lithium ion concentration. The conductivity parameters such as lithium concentration, hopping frequencies and mobility of lithium ion also have been calculated by fitting the conductance spectra to power law variation. These parameters proved that the higher conductivity of the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ ceramic electrolytes was due to higher mobile lithium ion concentration and mobility. This is further supported by its higher dielectric constant and dielectric loss that could be clearly observed at low frequencies. The conductivity parameters also suggested that the increase in conductivity with temperature also due to increase in number of mobile lithium ions with temperature. This was in agreement with the increase in dielectric constant and dielectric loss values in both samples with temperature. The value of lithium transference number increased by double substitutions of Si$^{4+}$ using Zn$^{2+}$ and Cr$^{3+}$/Al$^{3+}$. However, the Li$_{4.11}$Zn$_{0.04}$Cr$_{0.03}$Si$_{0.93}$O$_4$ exhibited a higher stable voltage window up to 4.10 V versus Li/Li$^+$ reference electrode.

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