Short communication

Effect of interstitial Li\(^{+}\) ion and vacant site Li\(^{+}\) ion on the properties of novel Li\(_{2.05}\)ZnAl\(_{0.05}\)Si\(_{0.95}\)O\(_4\) and Li\(_{1.95}\)Zn\(_{0.95}\)Cr\(_{0.05}\)SiO\(_4\) ceramic electrolytes

S.B.R.S. Adnan\(^*\), F.M. Salleh, N.S. Mohamed

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

**A R T I C L E   I N F O**

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

Lisicon-type ceramic electrolytes, Li\(_{2.05}\)ZnAl\(_{0.05}\)Si\(_{0.95}\)O\(_4\) (interstitial Li-ion) and Li\(_{1.95}\)Zn\(_{0.95}\)Cr\(_{0.05}\)SiO\(_4\) (Li-ion vacant site) were synthesized by sol gel method. X-ray diffraction was applied to investigate the phase, structure and unit cell parameters of both solid electrolytes. Complex impedance spectroscopy was carried out in the 10 Hz–10 MHz frequency range and temperature range from 303–773 K to study the electrical properties of the electrolytes. Both compounds were indexed to the monoclinic unit cell in the space group \(P2_1/m\). Li\(_{2.05}\)ZnAl\(_{0.05}\)Si\(_{0.95}\)O\(_4\) compound gave slightly higher total conductivity values of \(3.39 \times 10^{-5}\) S cm\(^{-1}\) at ambient temperature and \(1.03 \times 10^{-4}\) S cm\(^{-1}\) at 773 K compared to Li\(_{1.95}\)Zn\(_{0.95}\)Cr\(_{0.05}\)SiO\(_4\) which showed total conductivity values of \(4.17 \times 10^{-6}\) S cm\(^{-1}\) at ambient temperature and \(4.01 \times 10^{-5}\) S cm\(^{-1}\) at 773 K. It is evident that, the Li\(_{2.05}\)ZnAl\(_{0.05}\)Si\(_{0.95}\)O\(_4\) yielded a compound containing a greater number of ions with higher mobility compared to the Li\(_{1.95}\)Zn\(_{0.95}\)Cr\(_{0.05}\)SiO\(_4\) compound. Linear sweep voltammetry results demonstrated that the Li\(_{1.95}\)Zn\(_{0.95}\)Cr\(_{0.05}\)SiO\(_4\) and Li\(_{2.05}\)ZnAl\(_{0.05}\)Si\(_{0.95}\)O\(_4\) ceramic electrolytes were electrochemically stable up to 2.7 V versus a Li/Li\(^{+}\).

© 2016 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

1. Introduction

Many types of solid electrolytes have been extensively researched for development of solid-state lithium ion secondary batteries. Ceramic electrolytes are considered to be effective in improving the safety of lithium ion batteries. Ceramic electrolytes are the only solid electrolytes that have ordered structure [1–5]. Generally, ceramic structures consist of lattice and unit cell which represent a crystal structure. Lattice is the collection of atoms or ions which are arranged in a periodic pattern. Basically, there are three types of lattice in a material’s structure which are face centered cubic, body centered cubic and hexagonal close package. Meanwhile, unit cell is the subdivision of the lattice which is the basic building block of the structure. The type of lattice will determine the number of sites per unit cell in the structure [6]. The ion diffusion is expected to occur through the tetrahedral site and octahedral site pathway. This indicates that the ion distribution between tetrahedral site and octahedral site is the key factor to create 3D pathway in the ceramic structure [7,8].

Li\(_{2}\)ZnSiO\(_4\) which is one of the promising ceramic electrolytes, is categorized into Lisicon (Lithium Super Ionic Conductor) type. This type of ceramic is based on \(\gamma\)-tetrahedral structure, Li\(_{2}\)M\(\text{X}\)O\(_4\) (M=Zn, Mg, Ca), (X=Ge, Si, Ti) which is isostructural with \(\gamma\)-Li\(_{2}\)PO\(_4\) [9–12]. The Li\(_2\)ZnSiO\(_4\) structure is monoclinic and composed of hexagonal close packed oxygen ion arrays. One-eighth of the tetrahedral vacancies in this packing are occupied by silicon cations and three-eighths of the vacancies are occupied by lithium and zinc. This means that half of the tetrahedral sites are occupied by the cations. The silicon, lithium and zinc ions are tetrahedrally co-ordinated to oxygen, MO\(_4\) (M=Si, Li, Zn) and are isolated but connected by sharing edges. The framework structure was formed by the MO\(_4\) tetrahedral and LiO\(_6\) octahedral to form a loose three-dimensional framework [4,13,14].

It has been reported that the ionic conductivity of Lisicon’s member can be increased by three orders of magnitude for Li\(_{2+x}\)Zn\(_{1-x}\)GeO\(_4\) [15,16] and Li\(_{2-x}\)CdGeO\(_4\) [17], compared with the two end members, Li\(_2\)ZnGeO\(_4\) and Li\(_2\)GeO\(_4\). The drastic increase in conductivity is believed to be caused by the increase in concentration of Li-ion vacant site in Li\(_{2-x}\)CdGeO\(_4\) and Li-ion interstitial in Li\(_{2+x}\)Zn\(_{1-x}\)GeO\(_4\) with the ionics defect acting as charge carriers. However, an understanding of the effect of Li-ion vacant site and interstitial Li-ion on the structure, electrical property and mobility of ions is still lacking; such details are important for developing strategies for optimizing the conductivity of the materials.

In this work, a simple citrate sol gel method was employed to
synthesize partially substituted Li₂ZnSiO₄ using Al³⁺ and Cr³⁺ ions to create Li-ion vacant sites in Li₁₋ₓZnxAlₓSiO₄ and interstitial Li-ions in Li₁₋ₓZnAlₓSiₓ₋₄O₄. Detailed study on the effects of the interstitial Li-ion and vacant sites was carried out.

2. Experimental procedure

2.1. Synthesis of Li₂.05ZnAl₀.05Si₀.95O₄ and Li₁.95Zn₀.95Cr₀.05SiO₄ samples

The Li₂.05ZnAl₀.05Si₀.95O₄ and Li₁.95Zn₀.95Cr₀.05SiO₄ ceramic samples were prepared via citrate sol gel method. For preparation of the samples, lithium acetate, zinc acetate, aluminum acetate (or chromium (III) acetate) and tetraethyl orthosilicate were first dissolved in deionized water with a molar ratio of Li:Zn:Al:Si fixed according to formula Li₂₋ₓZnxAlₓCrₓSiₓO₄ and Li₂₋ₓZnAlₓSiₓ₋₄O₄ (where x = 0.05). A solution of citric acid as the chelating agent was mixed together with the previously prepared solutions under magnetic stirring. Then, a solution of tetraethyl orthosilicate was later added to the homogeneous solutions. The solutions were transferred into reflux systems and continuously stirred for 12 h at 75 °C. The solutions were then taken out and vaporized for about 2 h under magnetic stirring at 75 °C. The resulting wet gels were dried in an oven at 150 °C for 24 h to remove water particles, resistance organic groups and also to avoid ceramic cracks. The powders obtained were sintered at 800 °C for 12 h. The powders obtained pressed using a Specac pellet press at 3 t pressure to form pellets with mass, diameter and thickness of 0.5 g, 13 mm and 2 mm respectively. Eventually the pallets sintered again at 800 °C for 1 h before characterization.

2.2. 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’pert³ with Cu-Kα radiation of wavelength of 1.5406 Å in 2θ range between 10° and 70° at a 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 [2,18],

\[
\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2 + k^2 \sin^2 \beta}{a^2} + \frac{l^2}{c^2} \right) - \frac{2h \cos \beta}{ac} \quad \text{and} \quad d = \frac{\lambda}{2 \sin \theta} \quad (1)
\]

where d is the distance between crystal planes of (hkl), λ is the X-ray wavelength, θ is the diffraction angle of crystal plane (hkl), hkl is the crystal index, a, b and c are the lattice parameters and β is the angle between a and c. The elemental compositions were analyzed by EDX which were carried out using Oxford Azteq x-Act EDX spectrometer attached to a Zeiss-Evo MA10 scanning electron microscope (SEM). 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 10⁶ Hz. An applied voltage was fixed at 200 mV. The conductivity which represents the direct current (dc) conductivity in the ceramic sample was calculated using the equation [2,19]:

\[
\sigma = \frac{d}{AR_T} \quad (2)
\]

In this equation, d is the sample thickness, A is the cross-sectional area of the sample and Rₜ is the total resistance. The mobility of ion, μ was determined using the equation [2,9,20–22]:

\[
\mu = \frac{\sigma}{ne} \quad (3)
\]

with n = e²στk⁻¹/C and C = σT/α₀p

where σ is the conductivity, e is the electron charge and n is the number density of mobile ions or charge carriers. n was calculated using Eq. (4) where α is the jump distance between two adjacent sites for the ions to hope which is assumed to be 3 Å for all samples, γ is the correlation factor which is equal to 1, k is the Boltzman’s constant, C is the lithium ion concentration, T is the temperature in Kelvin and α₀p is the ionic hopping rate obtained directly from logeα = vs log f spectra since it corresponds to σ(ω) = 2ν(0). The σ(0) is the dc conductivity of the sample. Meanwhile, the electrochemical stability was evaluated by linear sweep voltammetry using Wonatech ZIVE MP2 multichannel electrochemical workstation.

3. Result and discussion

Fig. 1 presents XRD patterns of Li₂.05ZnAl₀.05Si₀.95O₄ and Li₁.95Zn₀.95Cr₀.05SiO₄ ceramic electrolytes. Both samples were indexed to the monoclinic unit cell in the space group P2₁/m which are in good agreement with the X’pert HighScore file number 98-020-0357. There is no impurity peak observed in the Li₂.05ZnAl₀.05SiO₄ and Li₁.95Zn₀.95Cr₀.05SiO₄ compounds indicating the purity of the samples. To study the effect of Al³⁺ and Cr³⁺ substitution to the unit cell volume of the structure for both compounds, a, b and c lattice parameters were determined. The lattice parameters of both compounds calculated using Eq. (1) and unit cell volume, V = abc sin β where β = 90°, are listed in Table 1. As shown, the substitutions of Si⁴⁺ with Al³⁺ and Zn²⁺ with Cr³⁺ cause distortion of the hcp sublattices creating different values of lattice parameters compared to those of the Li₂ZnSiO₄ parent compound [9]. Meanwhile, the V of the Li₂.05ZnAl₀.05Si₀.95O₄ increases, but decreases of the Li₁.95Zn₀.95Cr₀.05SiO₄ compared to the parent compound. This may due to the difference in the ionic radius of Si⁴⁺ (0.41 Å) compared to Zn²⁺ (0.7 Å), Al³⁺ (0.54 Å) and Cr³⁺ (0.64 Å). Theoretical density (ρth) was also calculated from the mass and sample dimensions using following equations [23,24]:

\[
\rho_{th} = \frac{m}{nt^2} \quad (5)
\]
where \( m \) is the thickness, \( r \) is the radius and \( t \) is the thickness of the sample pallets. The density values of both Li_{2.05}ZnAl_{0.05}Si_{0.95}O_{4} and Li_{1.95}Zn_{0.95}Cr_{0.05}SiO_{4} compounds are also listed in Table 1. It is evidenced that \( \rho_{th} \) of Li_{1.95}Zn_{0.95}Cr_{0.05}SiO_{4} sample decreases while that of the Li_{2.05}ZnAl_{0.05}Si_{0.95}O_{4} sample increases. This is consistent with their lattice volume’s values discussed earlier. This is attributed to the fact that the atomic density of Li-ion interstitial’s compound, Li\(^{+}\) (0.53 g/cm\(^3\)) + Al\(^{3+}\) (2.70 g/cm\(^3\)) → Si\(^{4+}\) (2.33 g/cm\(^3\)) is higher than that of the parent compound. Meanwhile, the atomic density of Li-ion vacant compound (Zn\(^{2+}\) (7.14 g/cm\(^3\)) → Cr\(^{3+}\) (7.19 g/cm\(^3\)) → Li\(^{+}\) (0.53 g/cm\(^3\)) is lower than that of the parent compound. This confirms that the Li-ion interstitial/Li-ion vacant site affected the structures of the ceramic compounds.

Fig. 2 shows SEM micrographs of Li_{2.05}ZnAl_{0.05}Si_{0.95}O_{4} and Li_{1.95}Zn_{0.95}Cr_{0.05}SiO_{4} samples. Using these images, the average grain size was estimated to be 4.2 \( \mu \)m and 9.0 \( \mu \)m for Li_{2.05}ZnAl_{0.05}Si_{0.95}O_{4} and Li_{1.95}Zn_{0.95}Cr_{0.05}SiO_{4} respectively. These values are larger than that of the parent compound, Li_{2}ZnSiO_{4} (0.1 \( \mu \)m). This is attributed to the effect of Al\(^{3+}\) and Cr\(^{3+}\) substitutions on the grain growth.

Shown in Fig. 3 are the cole-cole plots of the studied samples at ambient temperature.
which consist of a semicircle at high frequency region and a spike in the low frequency region. In most cases, two semicircles are observed at high frequency region, which correspond to the bulk and grain boundary responses. However, only one semicircle can be seen for both studied samples because of overlapping of the bulk and grain boundary responses. It has been suggested that the resistance of a grain boundary is larger than the resistance of the bulk. The ionic conductivity values of both samples were calculated using Eq. (2) using the grain boundary resistance values obtained from Fig. 3.

Displayed in Fig. 4 are Arrhenius plots of the ionic conductivity for both ceramic electrolytes. Both electrolytes show a linear plot, suggesting that there are no structural and phase changes in the samples for the studied temperature ranges. A similar behavior was reported for the parent compound, Li₂ZnSiO₄ [9]. The conductivity of Li₂.05ZnAl₀.05Si₀.95O₄ is 3.38 × 10⁻⁵ S cm⁻¹ at ambient temperature and 2.36 × 10⁻³ S cm⁻¹ at 773 K. Meanwhile, the Li₁.95Zn₀.05Cr₀.05SiO₄ compound showed total conductivity values of 4.26 × 10⁻⁶ S cm⁻¹ at ambient temperature and 1.01 × 10⁻⁵ S cm⁻¹ at 773 K.

The mobility of ions in the both samples calculated using Eq. (3) and the data extracted from log ω vs log ω graphs (Fig. 5) are tabulated in Table 2. From the table, the mobile ion concentration, C and the number density of the mobile ions, n for Li₂.05ZnAl₀.05Si₀.95O₄ are higher than Li₁.95Zn₀.05Cr₀.05SiO₄. Meanwhile, the mobility of ions, μ for Li₂.05ZnAl₀.05Si₀.95O₄ is also higher than Li₁.95Zn₀.05Cr₀.05SiO₄. This shows that, the interstitial Li-ion gives more favorable effect to mobility of ions compared to the Li-ion vacant site.

Fig. 5 shows the linear sweep voltammograms for both compounds. As shown in the figure, the values of electrochemical stability voltage for both compounds were close to each other (2.7 V) showing that the voltage stability of the ceramic compounds does not depend on the conductivity but may depend only on the frame of ceramic structures.

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>σ (Scm⁻¹)</th>
<th>ωp (kHz)</th>
<th>C (Scm⁻² kHz⁻¹)</th>
<th>n (cm⁻²)×10²⁵</th>
<th>μ (cm²V⁻¹s⁻¹)×10⁻¹¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂.05ZnAl₀.05Si₀.95O₄</td>
<td>303</td>
<td>3.39×10⁻⁵</td>
<td>6.13×10⁴</td>
<td>1.29×10⁻⁸</td>
<td>4.84</td>
<td>4.38</td>
</tr>
<tr>
<td>Li₁.95Zn₀.05Cr₀.05SiO₄</td>
<td>303</td>
<td>4.17×10⁻⁶</td>
<td>1.58×10⁴</td>
<td>4.00×10⁻⁹</td>
<td>1.49</td>
<td>1.47</td>
</tr>
</tbody>
</table>
4. Conclusion

Both Li$_{2.05}$ZnAl$_{0.05}$Si$_{0.95}$O$_4$ and Li$_{1.95}$Zn$_{0.95}$Cr$_{0.05}$SiO$_4$ ceramic electrolytes successfully synthesized by sol gel method were indexed to the monoclinic unit cell in space group P2$_1$/m. The conductivity of Li$_{2.05}$ZnAl$_{0.05}$Si$_{0.95}$O$_4$ compound was higher than that of Li$_{1.95}$Zn$_{0.95}$Cr$_{0.05}$SiO$_4$ due to higher concentration and mobility of ions. The stability voltage for ceramic compound did not depend on the conductivity but depend on the frame of ceramic structures.

Acknowledgment

Financial support by University of Malaya grants (BK049–2014 and PG032–2015A) are gratefully acknowledged.

References


[2] S.B.R.S. Adnan, N.S. Mohamed, Structural, electrical and electrochemical properties of novel Li$_{4-x}$Zn$_x$M$_{3-x}$Si$_x$O$_{4}$ (where x = 0.04, y = 0.03; M = Al, Cr) ceramic electrolytes, Electrochim. Acta 146 (2014) 598–610.


[4] S.B.R.S. Adnan, N.S. Mohamed, Characterization of novel Li$_{4-x}$Zn$_x$Si$_{2}$O$_{4}$ and Li$_{4-x}$Mg$_{2}$Zn$_x$Si$_{3}$O$_{4}$ ceramic electrolytes for lithium cells, Ceram. Int. 40 (2014), 6473–6379.


[21] S.B.R.S. Adnan, N.S. Mohamed, Effect of Cr$^{3+}$ substitutions on conductivity of Li$_{4-z}$Zn$_z$Cr$_{3}Si$_{2-z}$O$_{4}$ (0.01 ≤ y ≤ 0.03) ceramic electrolytes at high temperature, Int. J. Electrochem. Sci. 10 (2015) 795–804.

