

Li₄SiO₄ Prepared by Sol-gel Method as Potential Host for LISICON Structured Solid Electrolytes

Syed Bahari Ramadan Syed Adnan, Nor Sabirin Mohamed and Norwati K.A

Abstract—In this study, Li₄SiO₄ powder was successfully synthesized via sol gel method followed by drying at 150°C. Lithium oxide, Li₂O and silicon oxide, SiO₂ were used as the starting materials with citric acid as the chelating agent. The obtained powder was then sintered at various temperatures. Crystallographic phase analysis, morphology and ionic conductivity were investigated systematically employing X-ray diffraction, Fourier Transform Infrared, Scanning Electron Microscopy and AC impedance spectroscopy. XRD result showed the formation of pure monoclinic Li₄SiO₄ crystal structure with lattice parameters $a = 5.140 \text{ \AA}$, $b = 6.094 \text{ \AA}$, $c = 5.293 \text{ \AA}$, $\beta = 90^\circ$ in the sample sintered at 750°C. This observation was confirmed by FTIR analysis. The bulk conductivity of this sample at room temperature was $3.35 \times 10^{-6} \text{ S cm}^{-1}$ and the highest bulk conductivity of $1.16 \times 10^{-4} \text{ S cm}^{-1}$ was obtained at 100°C. The results indicated that, the Li₄SiO₄ compound has potential to be used as host for LISICON structured solid electrolyte for low temperature application.

Keywords— Conductivity, LISICON, Li₄SiO₄, Solid electrolyte, Structure.

I. INTRODUCTION

CRYSTALLINE as well as glassy Li₄SiO₄-based compounds have been investigated with regard to their use as solid electrolytes in secondary lithium batteries. The structure of Li₄SiO₄ has moderately good Li⁺ conductivity and is a versatile host structure for doping to form LISICON (Lithium Super Ionic) structure. Both Li⁺ interstitials and Li⁺ vacancies can be created resulting in high conductivities [1]. For example, when Si⁴⁺ ions are substituted by Al³⁺ ions, the Al³⁺ ions occupy Si⁴⁺ sites with Li⁺ ion entering interstitial sites, (Si⁴⁺ = Al³⁺ + Li⁺) to give a compound with a general formula, Li_{4+x}Al_xSi_{1-x}O₄ and when Si⁴⁺ ions are substituted by V⁵⁺ ions, Li⁺ vacancies are created, (Si⁴⁺ + Li⁺ = V⁵⁺) to give a compound with a general formula, Li_{4-x}V_xSi_{1-x}O₄ [2].

LISICON structured solid electrolytes based on Li₄SiO₄ have been reported to show high conductivity at high temperatures (200°C – 500°C) [3]. These compounds are commonly synthesized by conventional solid state reaction method. This method are lead to many problems such as its use of high firing temperature, contamination with impurities, volatilization, lack of control of the microstructure and composition and suffer to obtaining good ceramics free of grain boundary resistances.

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In order to overcome this problem, the sol gel method was used to prepare ion conductor materials. The sol gel technique has the advantages of lowering the synthesis temperature and can improving grain boundary conductivity and is a high purity process which leads to good homogeneity [4].

Recently Wu et al. reported the synthesis of Li₄SiO₄ employing sol gel technique [5-6]. In the former paper, the conductivity behavior of the compound was reported for the temperature range from 250 to 400°C. In the present study, Li₄SiO₄ compound was synthesized using a similar method. However, its conductivity behavior was studied at low temperatures ranging from 25 to 100°C in order to study the potential of this compound to be used as a host in LISICON structured solid electrolytes for low temperature electrochemical devices.

II. EXPERIMENTAL PROCEDURE

A. Synthesis of Li₄SiO₄

Li₄SiO₄ powder was prepared by sol gel method. Li₂O and SiO₂ were used as the starting materials and citric acid (C₆H₈O₇) was used as the chelating agent. The molar ratio of Li₂O: SiO₂ was fixed at 4:1. Li₂O was dissolved in distilled water before mixing with SiO₂ and citric acid. Citric acid was used to adjust the pH value of the solution to alkali (pH = 8.5). After that, the mixture was stirred under continuous reflux process for 1 hour until a colloidal solution was obtained. The colloidal solution was vaporized at 80°C and a gel was formed ultimately. The gel was dried at 150°C for 24 hours to remove H₂O particle, resistance organic group and also to avoid ceramic cracks. The flowchart of the synthesis procedure is shown in Figure 1. The obtained powder was palletized and the pallets formed were later sintered at temperatures from 600 – 750°C for four hours.

B. Characterization Techniques.

Crystallographic phases present in the prepared samples were identified by XRD using Bruker AXS, with CuK α radiation. To confirm the formation of the phases, FTIR was done on the samples employing Perkin Elmer FTIR Spectrum RX1 Spectrometer. The FTIR spectra were recorded at a resolution of 1 cm⁻¹. The morphology of the samples was observed by the Energy Dispersive Xray (EDX) technique. The AC impedance measurements were carried out using impedance analyzer, SOLATRON 1260 with platinum as the blocking electrode in the temperature range from 25 to 300°C over a frequency range from 0.1 to 10⁶ Hz.

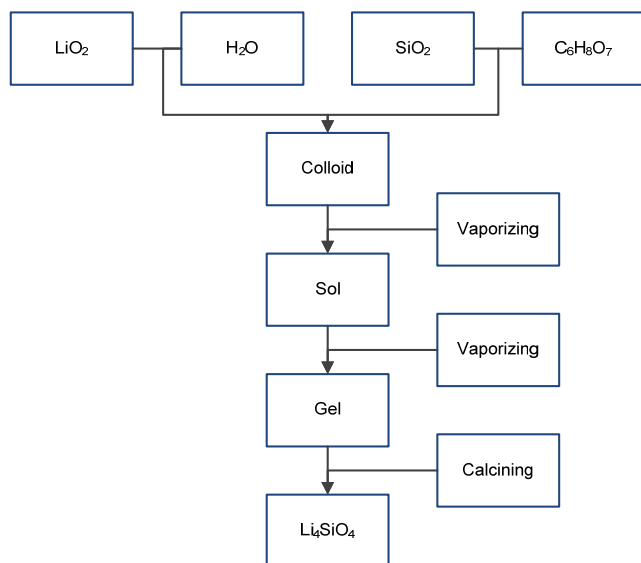


Fig. 1 Flow chart of sol gel procedure for the preparation of Li_4SiO_4 powder.

III. RESULT AND DISCUSSION

A. X-ray Diffraction.

Figure 2 shows XRD spectra of Li_4SiO_4 sintered at different temperatures for four hours. As can be seen in the figure, the samples sintered at 600-700°C exhibit sharp diffraction peaks attributed to Li_4SiO_4 and Li_2CO_3 indicated the presence of both Li_4SiO_4 and Li_2CO_3 in the samples. The XRD spectrum of the sample sintered at 750°C shows peaks attributed only to Li_4SiO_4 demonstrating that pure Li_4SiO_4 has been obtained. The crystal structure of Li_4SiO_4 is monoclinic with space group $P2_1/m$ and lattice parameters are $a = 5.140 \text{ \AA}$, $b = 6.094 \text{ \AA}$, $c = 5.293 \text{ \AA}$, $\beta = 90^\circ$ which are close to those of West et al.[7].

B. Fourier Transform Infrared

Figure 3 depicts the FTIR spectra of the Li_4SiO_4 sample, sintered at 700°C and 750°C. The sample sintered at 700°C show strong bands in the regions of $726\text{-}1071 \text{ cm}^{-1}$ and $1366\text{-}1588 \text{ cm}^{-1}$. This may be attributed to stretching and bending vibrational modes of Si-O (800 cm^{-1}) in SiO_4 tetrahedral [8-9], stretching and bending vibrational modes of C=O ($1550\text{-}1650 \text{ cm}^{-1}$) in CO_2 of Li_2CO_3 [10].

The Li_4SiO_4 sample sintered at 750°C does not show the bands between 1366 and 1588 cm^{-1} which is due to the disappearance of C=O from Li_2CO_3 . This observation is consistent with the result of XRD study and hence, confirms the formation of pure Li_4SiO_4 phase in the sample sintered at 750°C.

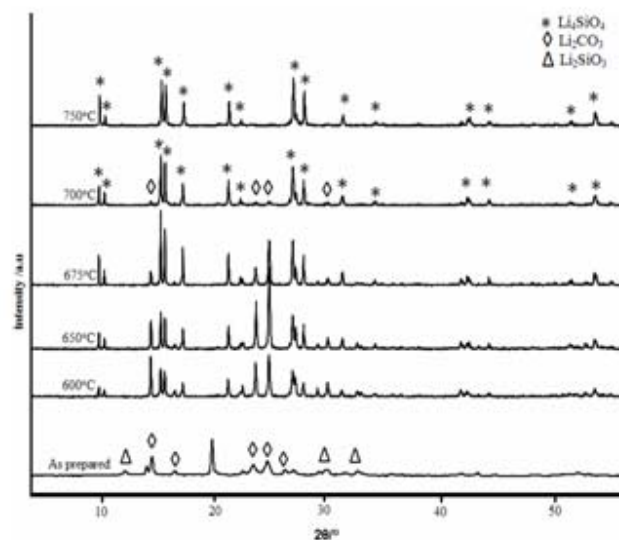


Fig. 2 XRD pattern of samples sintered at different temperatures.

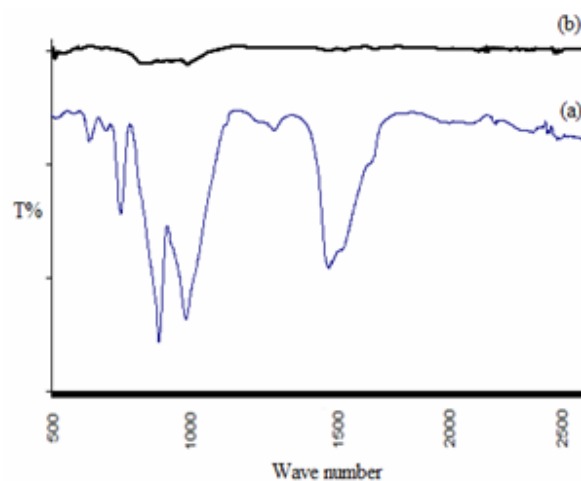


Fig. 3 FTIR spectra for Li_4SiO_4 sample sintered at (a) 700°C and (b) 750°C

C. SEM and EDX analysis

The SEM micrograph of the sample sintered at 750°C is shown in Figure 4 (a) and its EDX analysis is presented in Figure 4 (b). The atomic ratio of Si:O is determined to be 1:4. Since Li^+ ion is not detectable by EDX, the concept of charge neutrality is employed [11]. Using this concept it is found that the stoichiometry of EDX analysis is in good agreement with the designated stoichiometry. This observation is consistent with the result of XRD analysis. Carbon detected in this analysis may come from citric acid.

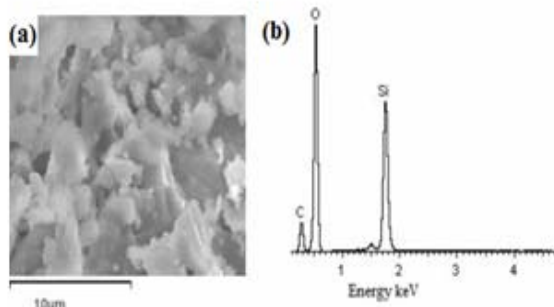


Fig. 4 a) SEM micrograph and (b) EDX analysis of Li_4SiO_4 sample sintered at 750°C

D. Ionic Conductivity

Figures 5(a) and 5(b) display impedance spectra of the sample sintered at 750°C recorded at 27°C and 100°C . The conductivity value of the bulk conductivity was calculated using (1):

$$\sigma_b = \frac{d}{AR_b} \quad (1)$$

where d is the sample thickness, A is the area of the electrode and R_b is the bulk resistance. The bulk conductivity of this sample at 27°C is found to be $3.35 \times 10^{-6} \text{ S cm}^{-1}$. The conductivity is observed to increase with increase in temperature. The increase in conductivity could be attributed to the greater movement of ionic point defect and the creation of greater ions movement due to an increase in thermal of energy [12]. The conductivity of the sample is determined to be $1.16 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C . The value is an order of magnitude higher compared to the $\text{Li}_{4-3x}\text{Ga}_x\text{SiO}_4$ (a modified Li_4SiO_4) system reported by Smith et al. measured at the same temperature [13].

The temperature dependence of the bulk conductivity is illustrated in Fig. 6 is found to be linear and well fits the Arrhenius equation (2),

$$\sigma_b T = A \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where A is the pre-exponential factor, E_a the activation energy for conduction and k the gas constant. This indicates that there are no structure and phase changes in the sample for the studied temperature range

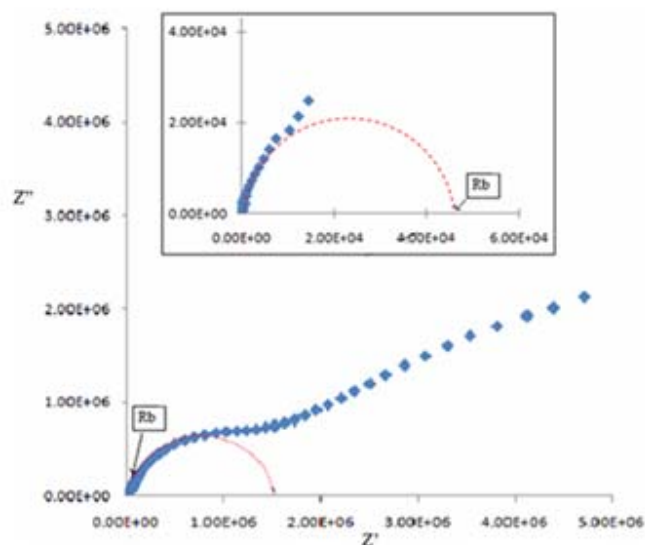


Fig. 5(a): Impedance plot of Li_4SiO_4 at room temperature ($R_b =$ bulk resistance). The figure in insert focuses on low impedance region.

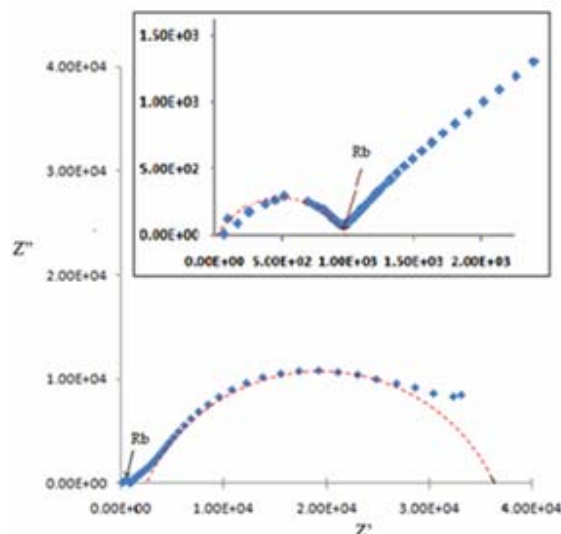


Fig. 5(b): The conductivity of Li_4SiO_4 at 100°C ($R_b =$ bulk resistance). The figure in insert focuses on the low impedance region.

Activation energy normally includes energy for formation and migration of ions. The Li_4SiO_4 structure is in the extrinsic regime below 200°C [14]. In this extrinsic regime, the activation energy is dominated by the migration energy. In this case, the activation energy can be represented by the migration energy for the doped oxide ionic conductors [15]. The activation energy; E_a determined from Figure 6 is 0.19 eV. The low value of activation energy is evidence for high mobility of ions in the sample.

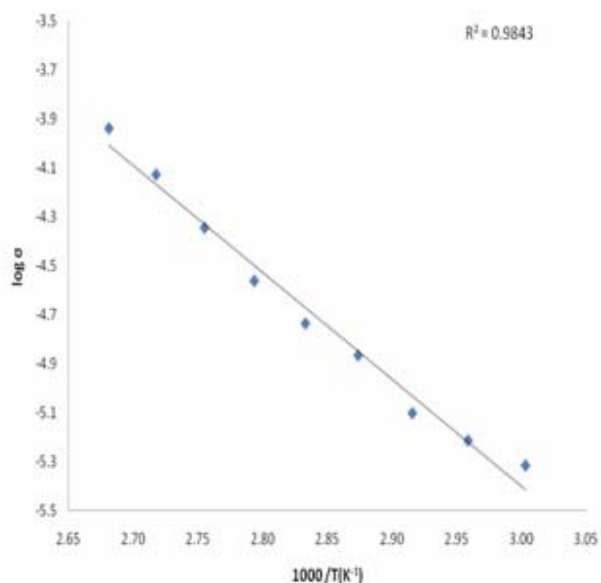


Fig. 6 Arrhenius plot of the bulk conductivity for Li_4SiO_4 sample sintered at 750°C

IV. CONCLUSIONS

A pure Li_4SiO_4 sample was successfully prepared by sol gel method followed by sintering at 750°C . The conductivity of the Li_4SiO_4 compound obtained in this study showed conductivity in the order of $10^{-4} \text{ S cm}^{-1}$ at 100°C and is higher compared to the modified Li_4SiO_4 compound reported by other researchers. This gives an indication of its potential to be used as a host for low temperature LISICON structured solid electrolytes.

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