

# Transport properties of a new Li<sup>+</sup> ion-conducting ormolyte: (SiO<sub>2</sub>-PEG)-LiCF<sub>3</sub>SO<sub>3</sub>

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The transport properties of a new fast Li<sup>+</sup> ion-conducting sol-gel-derived ormolyte, (SiO<sub>2</sub>-10 wt% PEG)-[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>, with [Li/O] = 0–0.1 (mol/mol), is reported. The composition with [Li/O] = 0.04 exhibited the highest conductivity ( $\sigma_{25\text{ }^\circ\text{C}} = 1 \times 10^{-4} \text{ S cm}^{-1}$ ), with an enhancement of  $10^3$  over the host matrix (SiO<sub>2</sub>-10 wt% PEG xerogel), and has been found to be the 'optimum conducting composition'. Direct determination of Li<sup>+</sup> ion mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) revealed that the enhancement was due to the increase in both  $\mu$  and  $n$ . Studies of the variation of  $\sigma$ ,  $\mu$ , and  $n$  versus temperature indicated that the system shows Arrhenius-type behavior. The activation energy and energies of migration and formation were evaluated from their respective Arrhenius plots. Measurement of the ion transference number ( $t_{\text{ion}}$ ) confirmed that the ions are the sole charge carriers in the system. These results are discussed in the light of existing theories.

## 1 Introduction

Li<sup>+</sup> ion-conducting polymer composite electrolytes have attracted widespread interest in recent years due to their potential industrial applications, namely, in solid-state rechargeable batteries, fuel cells, sensors, electrochromic display devices, and super capacitors. These solid electrolytes offer a variety of advantageous properties, *viz.*, high ionic conductivity ( $\sigma \approx 10^{-3} \text{ S cm}^{-1}$ ), light weight, transparency, flexibility, thin film formation, a wide electrochemical voltage window (0–4 V), *etc.*, although with poor mechanical properties. Inorganic fillers (also called dispersoids), such as SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, have been added during sample preparation to improve the mechanical properties, but with limited success (for reviews on the subject, see ref. 1–3). Ravaine *et al.* successfully eliminated this problem using the sol-gel method and reported room temperature ionic conductivity ( $\sigma \approx 7 \times 10^{-5} \text{ S cm}^{-1}$ ) with an enhancement of more than four orders of magnitude by incorporating a lithium salt, LiNO<sub>3</sub> or LiClO<sub>4</sub>, into the SiO<sub>2</sub>-poly(ethylene glycol) (PEG) xerogel.<sup>4</sup> The sol-gel method combines the properties of organic (*e.g.* PEG, PEO, PPG) and inorganic (SiO<sub>2</sub>) materials, which results in materials with superior properties, such as high room temperature conductivity, homogeneity, mechanical and thermal stability, optical transparency, ease of molding into a desired shape, *etc.*, due to its low temperature processing and high compositional flexibility *via* control of the processing variables.<sup>1</sup> Since then, a number of solid electrolytes have been investigated and exhibit ionic conductivities of  $10^{-6}$ – $10^{-4} \text{ S cm}^{-1}$ .<sup>5–16</sup> These solid electrolytes are now widely known as ormolytes (an abbreviation of *organically modified electrolytes*) and their properties strongly depend on the connectivity of the inorganic-organic phases and the mobility of both the structural network and the active species.<sup>6–14</sup>

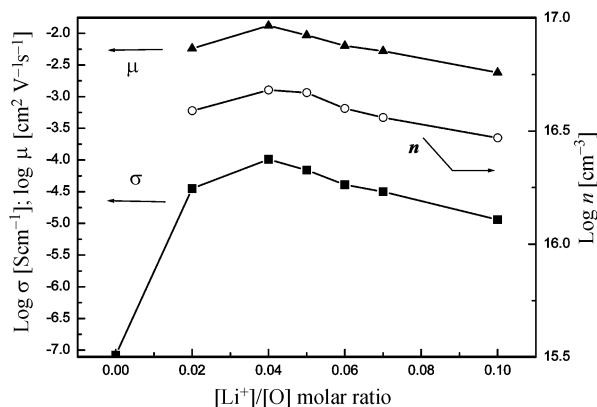
This paper reports the transport properties of a new Li<sup>+</sup> ion-conducting sol-gel-derived ormolyte, (SiO<sub>2</sub>-10 wt% PEG)-[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>. The SiO<sub>2</sub>-10 wt% PEG xerogel has recently been investigated in this laboratory<sup>17,18</sup> and exhibits superior physical, mechanical, optical, and thermal properties, confirming its potential as a host matrix for incorporating lithium salts. Furthermore, LiCF<sub>3</sub>SO<sub>3</sub> (lithium trifluoromethanesulfonate) is also quite thermally and electrochemically stable, as well as

being weakly coordinated, and therefore does not tend to form ion pairs.<sup>10</sup> The aim of the present work is to: (1) identify the 'optimum conducting composition' of the ormolyte for device applications from a study of  $\sigma_{25\text{ }^\circ\text{C}}$  versus [Li/O] ratio, (2) explore the reasons for the conductivity enhancement by direct determination of the ionic mobility ( $\mu$ ) and, hence, the mobile ion concentration ( $n$ ), as a function of the [Li/O] ratio, (3) determine the phase and thermal stability *via* X-ray diffraction (XRD) studies and thermal differential analysis-thermal gravimetric analysis (DTA-TGA), respectively, (4) explain the ion transport mechanism by evaluating the temperature dependence of  $\sigma$ ,  $\mu$ , and  $n$ , and finally, (5) identify the nature of charge carriers by ionic transference number ( $t_{\text{ion}}$ ) measurement. These results are then discussed in the light of existing theories.

## 2 Experimental

Highly pure Aldrich chemicals ( $\geq 99\%$ ) were used in preparing the ormolyte (SiO<sub>2</sub>-10 wt% PEG)-[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>. A mixture of tetraethoxysilane (TEOS), PEG (MW: 400 g mol<sup>-1</sup>), and LiCF<sub>3</sub>SO<sub>3</sub> with composition {1 mol TEOS:10 wt% PEG with respect to TEOS:[Li/O] mole ratio with respect to PEG ethereal oxygens} was stirred at room temperature for 15 min, then mixed with a solution of composition 0.01 HCl: 4 H<sub>2</sub>O:3.8 ethanol (all mol/mol with respect to TEOS; the total volume of solution was  $\sim 25$  ml). Subsequently, the hydrolysis-condensation reactions was performed under reflux at  $75 \pm 3\text{ }^\circ\text{C}$  for 1 h, resulting in a clear solution. The sol was left to cool for a few minutes at room temperature, then poured into a polypropylene-based container and covered with paraffin film with small holes in it in order to control the evaporation rate. Gelation occurred after about 48 h. The wet gel was further aged at 50 °C for a week and then dried at 90 °C for a further week. The finished products were quite transparent bulk samples, with diameters of around 2 cm and thicknesses of 2–3 mm. The sample preparation was carried out in a Labconco glove box filled with dry N<sub>2</sub> gas (RH < 15%).

Before performing the experimental studies, the samples were kept at *ca.* 90 °C for 12 h in a vacuum oven to eliminate moisture effects. A Rigaku D/Max 2500/K X-ray diffractometer

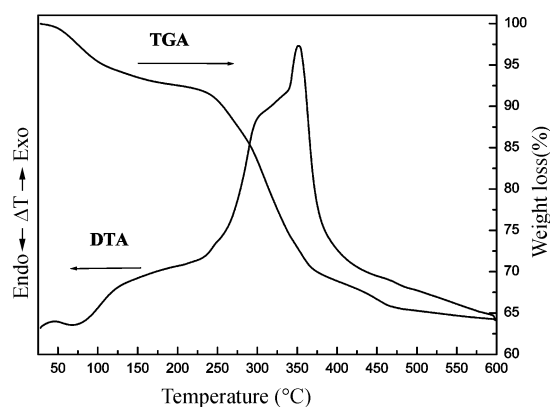


**Fig. 1** Compositional variation of room temperature conductivity ( $\sigma$ ), ion mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) for the ormolyte system (SiO<sub>2</sub>-10 wt% PEG)-[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>.

and a TA Instruments SDT 2960 DTA-TGA unit were used for phase identification and thermal characterization, respectively, of the powder samples. The electrical conductivity ( $\sigma$ ) was measured by impedance spectroscopy (IS) using a computer-controlled HP 4192A impedance analyser in the frequency range 10 Hz–10 MHz. Colloidal graphite was painted on both sides of the pellets as blocking electrodes for this measurement. Ionic mobility ( $\mu$ ) and ionic transference number ( $t_{\text{ion}}$ ) were measured by transient ionic current (TIC) and dc polarization techniques, respectively.<sup>19–22</sup> A computer-controlled Radiant Precision Pro source-current meter was used to monitor the current as a function of time.

### 3 Results and discussion

Fig. 1 shows the room temperature electrical conductivity ( $\sigma$ ) as a function of [Li/O] ratio for the ormolyte system (SiO<sub>2</sub>-10 wt% PEG)-[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>. The log  $\sigma$ -[Li/O] plots follow the usual pattern exhibited by the majority of ormolyte and two-phase composite electrolyte systems,<sup>3–16</sup> that is,  $\sigma$  initially increases rapidly with increasing [Li/O] ratio, before attaining a peak value and then decreasing. The composition with [Li/O] = 0.04 exhibited the highest conductivity ( $\sigma_{25\text{ }^\circ\text{C}} = 1 \times 10^{-4}$  S cm<sup>-1</sup>), with an enhancement of 10<sup>3</sup> over the host matrix, and is referred to as the ‘optimum conducting composition’ (OCC). In polymer electrolytes having etheral groups, Li<sup>+</sup> ion conduction occurs within the amorphous phase of the material *via* a liquid-like migration of Li<sup>+</sup> ions assisted by segmental motion of neighboring polymer chains.<sup>5–10,23–26</sup> Recently, using NMR and FT-IR spectroscopy and glass transition temperature ( $T_g$ ) studies, Nishio and co-workers proposed a comb-shaped structure for SiO<sub>2</sub>-PEG-LiClO<sub>4</sub>/LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> ormolytes.<sup>13,14</sup> According to them, the free end groups of the comb structure transport the Li<sup>+</sup> ions. An increase in the number of end groups decreases the  $T_g$ , resulting in a liquid-like structure of the host matrix. Increasing the lithium salt concentration up to 0.05 gives rise to a structure with a quasi-liquid phase in which the movements of segments of PEG carry many Li<sup>+</sup> ions. Further increases in the lithium salt concentration increases  $T_g$ , thus decreasing the segment activity, which leads to decreased ionic conductivity and mobility.<sup>13,14</sup> The number of mobile ions was also found to be an important factor, affecting the Coulomb interactions responsible for the formation of ion pairs, polymer (solvent) separated pairs, ionic multiplets, and even salt aggregation, as observed by Raman and Brillouin scattering studies on several PEO/PPO-LiCF<sub>3</sub>SO<sub>3</sub>/LiClO<sub>4</sub> systems with increasing [Li/O] ratio and temperature.<sup>9,10,23–26</sup> Hence, similar reasoning can also be applied to explain the compositional variation of conductivity. The increase in the conductivity with increasing salt concentration up to [Li/O] = 0.04



**Fig. 2** DTA-TGA curves for the ormolyte system OCC, (SiO<sub>2</sub>-10 wt% PEG)-0.04 LiCF<sub>3</sub>SO<sub>3</sub>.

can be ascribed to the increase in the number of cations having long range Coulomb interactions,<sup>5–9,24–26</sup> as well as ionic mobility<sup>10,13,14,24–26</sup>. The decrease of  $\sigma$  at higher [Li/O] ratio, as suggested,<sup>5–16,23</sup> is a consequence of the immobilization of the polymer chains due to the formation of O-Li<sup>+</sup>-O cross-links between oxygen atoms of different polymer chains. Several theoretical models, such as space charge,<sup>27</sup> percolation,<sup>28</sup> adsorption-desorption,<sup>29</sup> morphological,<sup>30</sup> effective medium theory,<sup>31</sup> and mobility enhancement,<sup>32</sup> originally proposed to explain the mechanism of conductivity enhancements in two-phase composite electrolyte systems, also support these arguments. According to these models (1) space-charge regions exist at the interface of the host matrix and ion-conducting salt, which increases the mobile ion concentration and (2) highly conducting pathways exist between space-charge regions, resulting in increased ionic mobility. Further details can be found in the original papers and a review article.<sup>3</sup> Hence, just to cross-check the explanations mentioned above, the ionic mobility ( $\mu$ ) has been measured directly using the transient ionic current (TIC) technique,<sup>19–21</sup> as mentioned earlier in section 2. In this method, the bulk sample was sandwiched between the blocking electrodes and completely polarized by applying a fixed dc potential ( $V$ ) of 1 V across the sample. Its polarity was then reversed and, subsequently, current was recorded as a function of time. The occurrence of a peak in the current *versus* time plot gave the time ( $t$ ) taken by the mobile ion cloud to cross the thickness ( $d$ ) of the sample. The ionic mobility was then evaluated using the expression

$$\mu = d^2/Vt \text{ [cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{]}$$

The mobile ion concentration ( $n$ ) was calculated by substituting the  $\sigma$  and  $\mu$  data into the well-known equation  $\sigma = nq\mu$ . The measured values of  $\mu$  and  $n$  are shown along with  $\sigma$  in Fig. 1 as log plots for direct visualization. It is obvious from the figure that  $\sigma$ ,  $\mu$ , and  $n$  vary analogously with increasing [Li/O] ratio, indicating that the enhancement in the room temperature conductivity is due to the increase in the ionic mobility ( $\mu$ ) and mobile ion concentration ( $n$ ), which supports the findings of other research groups,<sup>4–16,23–26</sup> as well as the theoretical models.<sup>3,27–32</sup> The room temperature values of  $\mu$  and  $n$  for the OCC are  $1.3 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $4.8 \times 10^{16}$  cm<sup>-3</sup>, respectively.

To identify the phase of the OCC, (SiO<sub>2</sub>-10 wt% PEG)-0.04 LiCF<sub>3</sub>SO<sub>3</sub>, an XRD study was performed, including the host matrix, SiO<sub>2</sub>-10 wt% PEG xerogel (data not shown). A characteristic amorphous broad hump at  $2\theta = 20\text{--}25^\circ$  was observed, most probably due to the coherent diffraction domains of the silica backbone, indicating the amorphous nature of the system.<sup>10,16</sup> Fig. 2 shows the DTA-TGA curves of the ormolyte OCC. These curves are similar to those obtained

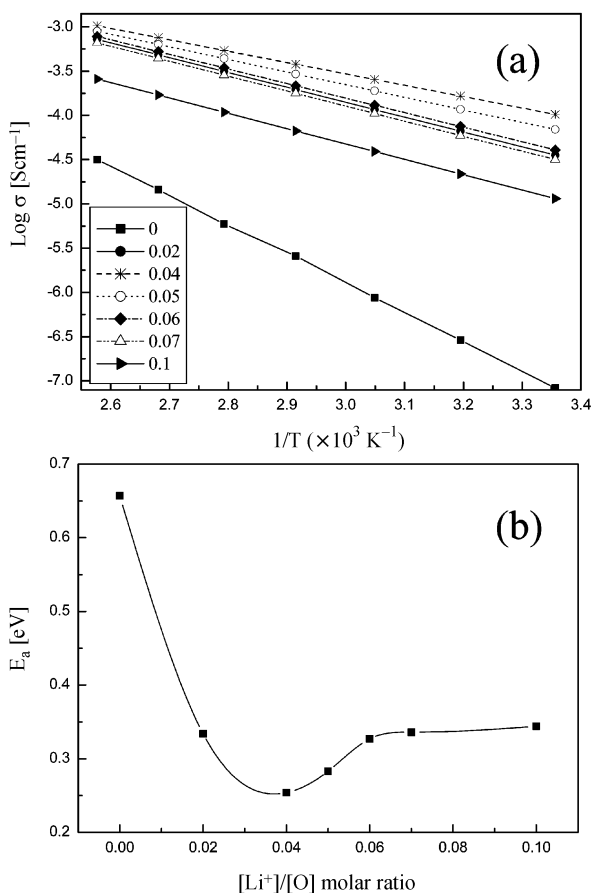
for the host matrix xerogel and, hence, can be assigned using previous arguments.<sup>4,17,33</sup> The broad endothermic peak appearing at  $\sim 75$  °C is probably due to the loss of adsorbed water, which often observed in sol-gel-derived materials. The strong and broad exothermic peak in the range 230–400 °C, accompanied by rapid weight loss, can be ascribed to the decomposition of organic siloxane and/or PEG. This study indicated that the sample is thermally stable up to  $\sim 230$  °C.

Fig. 3(a) shows the variation of  $\log \sigma$  against  $1/T$  for (SiO<sub>2</sub>–10 wt% PEG)–[Li/O] LiCF<sub>3</sub>SO<sub>3</sub>, with [Li/O] = 0–0.1. The conductivity ( $\sigma$ ) increases linearly with increasing temperature, exhibiting Arrhenius-type behavior, which is well known for ormolyte and two-phase composite electrolyte systems.<sup>3–16</sup> Arrhenius-type conductivity behavior can be expressed as

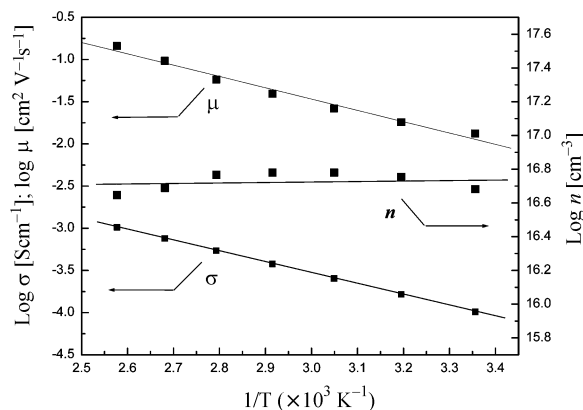
$$\sigma = \sigma_0 \exp(-E_a/kT) \text{ [S cm}^{-1}\text{]}$$

where  $\sigma_0$  is the pre-exponential factor and the other notations have their usual meanings. The values of the activation energy ( $E_a$ ), calculated from the straight lines of the above equation with different [Li/O] values, are shown in Fig. 3(b). The minimum value of  $E_a$  ( $\sim 0.254$  eV) was obtained for the OCC, indicating the ease of ion transport at this composition and supporting the conclusions from the compositional dependence study of  $\sigma$ ,  $\mu$  and  $n$ .

Fig. 4 shows the  $\log \mu$ – $1/T$  and  $\log n$ – $1/T$  plots for the ormolyte OCC. The  $\log \sigma$ – $1/T$  plot for the OCC from Fig. 3 is also shown for direct comparison. It can be seen that  $\mu$  increases linearly with increasing temperature, while  $n$  decreases slightly with increasing temperature. Hence, similarly to the Arrhenius equation for the conductivity, the variation of  $\log \mu$ – $1/T$  and  $\log n$ – $1/T$  can also be expressed by the following thermally activated equations<sup>3,20,21</sup>



**Fig. 3** (a)  $\log \sigma$  vs.  $1/T$  plots for the ormolyte system (SiO<sub>2</sub>–10 wt% PEG)–[Li/O] LiCF<sub>3</sub>SO<sub>3</sub> with [Li/O] = 0–0.1. (b)  $E_a$ –[Li/O] plot.



**Fig. 4**  $\log \sigma$ – $1/T$ ,  $\log \mu$ – $1/T$ , and  $\log n$ – $1/T$  plots for the ormolyte system OCC, (SiO<sub>2</sub>–10 wt% PEG)–0.04 LiCF<sub>3</sub>SO<sub>3</sub>.

$$\mu = 3.6 \times 10^2 \exp(-0.267/kT) \text{ [cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{]}$$

$$n = 3.7 \times 10^{16} \exp(+0.012/kT) \text{ [cm}^{-3}\text{]}$$

where the energies of migration ( $E_m$ ) and formation ( $E_f$ ) are 0.267 and  $-0.012$  eV, respectively.  $E_m$  and  $E_f$  are involved in the above thermally activated processes and can be related to the activation energy ( $E_a$ ) of the OCC by<sup>3,20,21</sup>

$$E_a = E_m + E_f$$

The  $+/-$  signs in the arguments of the exponential represents the negative/positive slope of the straight line or, in other words, a decrease/increase in the factor on the left hand side of the above equation with increasing temperature.

The temperature dependence of  $\sigma$ ,  $\mu$ , and  $n$  can be explained by considering the ion conduction in the polymer electrolyte, which takes place *via* segmental motion of neighboring polymer chains carrying many Li<sup>+</sup> ions.<sup>5–16,23–26</sup> The increase in temperature leads to an increase in the chain flexibility, there by increasing the ionic mobility and conductivity of the system.<sup>23–26</sup> The mobility-dominated behavior is qualitatively in accordance with the expectations of the free-volume or configurational entropy theories of the ionic migration mechanism.<sup>3,23–26</sup> The small decrease in mobile ion concentration ( $n$ ) with increasing temperature is most probably due to the ion pairing, as observed previously for other polymer electrolyte systems.<sup>23–26</sup>

In order to ascertain the extent of the electronic and ionic contributions to the total conductivity, the transference number of the ormolyte system has been measured using the dc polarization method,<sup>22</sup> as discussed earlier in section 2, which is similar to the TIC technique used for ionic mobility measurements.<sup>19–21</sup> In this method, the sample was sandwiched between blocking electrodes. A fixed dc potential ( $\sim 1$  V) was applied across the sample and electrical current was monitored as a function of time. The residual current ( $I_{e,h}$ ) observed after a long time ( $\sim 1$  h) in the current *versus* time plot corresponds to the electronic contribution to the total current ( $I_T$ ). The ionic transference number ( $t_{ion}$ ) was calculated using the well-known expression  $t_{ion} = 1 - (I_{e,h}/I_T)$ . The value of  $I_{e,h}$  for the OCC was negligibly small ( $\sim 12$  nA) as compared with the total current ( $I_T \approx 1.5$   $\mu$ A), indicating that the ions are the sole carriers of the system. This result is quite similar to that reported by Nishio and co-workers.<sup>13,14</sup>

## 4 Conclusion

A new fast Li<sup>+</sup> ion-conducting ormolyte, (SiO<sub>2</sub>–10 wt% PEG)–[Li/O] LiCF<sub>3</sub>SO<sub>3</sub> was synthesized by the traditional sol-gel

method with  $[Li/O] = 0-0.1$ . The composition with  $[Li/O] = 0.04$  [the 'optimum conducting composition' (OCC)] exhibited the highest room temperature ionic conductivity ( $\sigma \approx 10^{-4} \text{ S cm}^{-1}$ ) with an enhancement of  $10^3$  over the host matrix,  $\text{SiO}_2-10 \text{ wt\% PEG}$  xerogel. The direct determination of  $\text{Li}^+$  ion mobility ( $\mu$ ) and mobile ion concentration ( $n$ ) indicated that the conductivity enhancement is due to an increase in both  $\mu$  and  $n$ . Temperature dependence studies on  $\sigma$ ,  $\mu$ , and  $n$  were carried out for the OCC samples and the energies involved in different thermally activated processes were evaluated from their respective Arrhenius-type plots. Measurements of the ion transference number ( $t_{\text{ion}}$ ) implied that the ions are the sole charge carriers in the ormolyte system.

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