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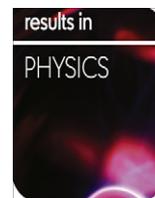
AC ionic conductivity and DC polarization method of lithium ion transport in PMMA–LiBF$_4$ gel polymer electrolytes

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ABSTRACT

Polymethylmethacrylate (PMMA)-based gel polymer electrolytes comprising ethylene carbonate–propylene carbonate (EC/PC) mixed solvent plasticizer and various concentrations of lithium tetrafluoroborate (LiBF$_4$) salt are prepared using a solvent casting technique. Electrical conductivity and transference number measurements were carried out to investigate conductivity and charge transport in the gel polymer electrolytes. The conductivity results show that the ionic conductivity of the samples increases when the amount of salt is increased, however decreases after reaching the optimum value. This result is consistent with the transference number measurements. The conductivity–frequency dependence plots show two distinct regions; i.e. at lower frequencies the conductivity increases with increasing frequency and the frequency independent plateau region at higher frequencies. The temperature-dependence conductivity of the films seems to obey the Arrhenius rule.

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Introduction

The development of electrochemical devices such as batteries, super capacitors, electro-chromic devices and sensors has increased rapidly in the past few decades [1,2]. Enormous interest has been shown in the development of rechargeable batteries, especially in acquiring a battery that combines long life, environmental safety, compact shape, low cost and high energy density [3–5]. Lithium ion batteries appear as one of the most promising power sources due to their high energy densities compared to lead-acid and nickel–cadmium batteries [6].

Previous research on batteries has focused on liquid and solid electrolytes, both of which have their advantages and disadvantages. A liquid electrolyte has very high conductivity, but it also bears the high risk of leakage and can cause corrosion during packaging [7,8]. A solid electrolyte, conversely, poses no problem with leakage or packaging, but possesses only low conductivity [9]. In order to overcome the problems related to solid and liquid electrolytes while also maintaining high ionic conductivity as well as good mechanical strength, gel polymer electrolytes (GPEs) have been proposed. The gel electrolyte comprises no problem for packaging and also maintains a reasonably high conductivity and better compatibility [10,11].

Many research efforts have been made to improve the gel polymer electrolytes' conductivity, including using different types of salts. The current electrolytes generally used in lithium-ion batteries are mainly composed of expensive low lattice energy lithium salts, such as lithium hexafluorophosphate (LiPF$_6$) [12]. The disadvantages of this salt are: (a) its high price, (b) its reactivity with water, (c) its thermal instability, and the associated rapid deterioration of cell performance at elevated temperatures, causing harmful effects [13–16]. Many salts have been used as alternatives for replacing LiPF$_6$; one of them is lithium tetrafluoroborate (LiBF$_4$). The advantages of LiBF$_4$ include a better thermal stability, a lower sensitivity towards environmental moisture, a low lattice energy and the fact that it provides a lower charge-transfer resistance, especially at lower temperatures [7,17,18].

In the present study, gel polymer electrolyte (GPE) samples consisting of PMMA, EC, PC and various concentrations of LiBF$_4$ were prepared. The ionic conductivity and ionic transport properties of the samples were studied by impedance spectroscopy and transference number measurements.

Experimental

Preparation of gel polymer electrolytes

Ethylene carbonate (EC), propylene carbonate (PC) and lithium tetrafluoroborate (LiBF$_4$), obtained from Aldrich, were used as received. Polymethylmethacrylate (PMMA) with a molecular weight of 9.96×10^5 g/mol (Aldrich) was dissolved in a homogeneous mixture of EC, PC and LiBF$_4$. The mass ratio of the sample was 2:2:1 for PMMA, EC and PC, while the concentrations of LiBF$_4$ were varied by weight percentage in the range of 5–30 wt.%. The mixtures were continuously stirred for several hours until

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homogeneous solutions were obtained. Then, the solutions were poured into petri dishes, and heated in an oven at 70 °C for 24 h. Finally, gel polymer electrolyte samples were obtained. The samples were then kept in a desiccator for further drying. The thickness of the samples was determined to be in the range of 0.9–1.3 mm.

Measurements

Impedance spectroscopy measurements were carried out to determine the conductivity of the GPE samples. The sample was cut into round shapes that fit the size of the electrodes. The samples were then sandwiched between two stainless steel blocking electrodes circular in shape with a diameter of 2 cm. A HIOKI 3532 LCR that interfaced with a computer was used to measure the impedance of GPE samples in the frequency range of 50 Hz to 1 MHz. From the Cole–Cole plot obtained, the bulk resistance, R_b, for each sample was determined and thus the conductivity (σ) of the sample could be calculated using,

$$\sigma = t/R_b A \tag{1}$$

where t is the thickness of the sample (cm), A is the area of the effective contact with the electrodes (cm^2) and R_b is the bulk resistance (Ω). Conductivity–temperature studies for the sample that exhibited the highest room temperature conductivity were carried out in the temperature range of 303–383 K.

The transference number of the samples was measured by using the direct current (dc) polarization method. The electronic and ionic transference numbers can be determined by using the following equations:

$$t_e = \sigma_e/\sigma_t = i_e/i_t \tag{2}$$

and

$$t_i = 1 - i_e/i_t = 1 - t_e \tag{3}$$

where t_e and t_i are the electronic and ionic transference numbers, respectively. i_e and i_T are the electronic and total currents, respectively, while σ_e and σ_T refer to the electronic and total conductivities, respectively [19,20].

Results and discussion

Room temperature conductivity studies

Fig. 1 shows the Cole–Cole plots for the GPE samples containing 5, 20 and 30 wt.% of LiBF$_4$. The inset figure shows the Cole–Cole plot for a GPE sample without salt. The R_b value of the sample was calculated from the Cole–Cole plot in the intercept of the higher frequency region on the Z_r axis and was used to calculate the conductivity, σ from Eq.(1). The Cole–Cole plot for the GPE sample without salt exhibits a semicircle at the high frequency region while in the Cole–Cole plots for the GPE samples containing salt the semicircle at the high frequency region apparently disappeared. This is due to the increase in the salt concentration, and the total conductivity is mainly the result of the ionic conduction [21].

Fig. 2 shows the plot of conductivity versus the weight percentage of LiBF$_4$ in the gel polymer electrolytes. It can be observed that the conductivity of the gel polymer electrolyte samples without salt is increased to ~3 orders of magnitude when 5 wt.% of LiBF$_4$ was added. The conductivity continued to increase until it reached the highest value of 2.24×10^{-3} S cm^{-1} at 20 wt.% of LiBF$_4$ salt. Therefore, 20 wt.% LiBF$_4$ salt is the conductivity optimizing concentration. It is well known that the conductivity of polymer electrolytes can be described by the relationship [22]:

$$\sigma = \sum \mu_i n_i q_i \tag{4}$$

where μ_i, n_i, and q_i represent the mobility of the i species, the concentration of carriers of the i species and the charge of the i species, respectively. Hence, the increase in the conductivity with increasing salt concentration could be attributed to the increase in the number of charge carriers and the mobility of the charge carriers. When the amount of LiBF$_4$ salt added is higher than 20 wt.%, a saturation in the gel polymer electrolytes samples occurs and this leads to the reduction of free space in the samples; thus the ionic conductivity is decreased [23]. This is probably due to the formation of ion aggregates; and thus the number of charge carriers is decreased [24]. Morita et al. [25] also confirmed the formation of ion aggregates using Raman spectroscopy for the system PEO-PMMA/LiCF$_3$SO$_3$–LaCF$_3$SO$_3$. They reported a decrease in ionic conductivity for the
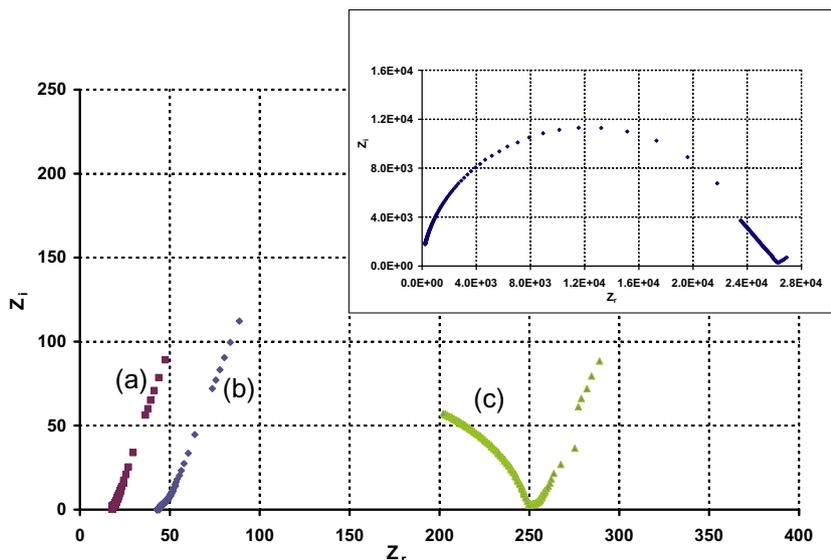

Fig. 1. The Cole–Cole plots for GPE samples containing (a) 20 wt.%, (b) 5 wt.% and (c) 30 wt.%. Inset: Cole–Cole plot for GPE sample without salt.
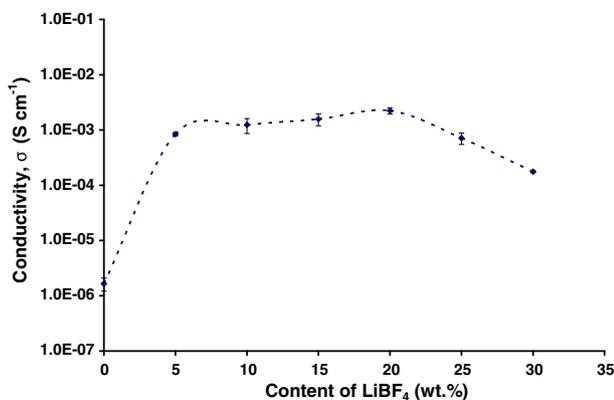
Fig. 2. Conductivity versus weight percentage of LiBF$_4$ salt in GPE samples.

Fig. 4. Normalized current versus time for GPE samples containing (a) 20 wt.%, (b) 5 wt.% and (c) 30 wt.% of LiBF$_4$ salt.

higher concentrations of LaCF$_3$SO$_3$ due to the formation of aggregates when added to the system PEO-PMMA/LiCF$_3$SO$_3$.

Fig. 3 represents the variation of conductivity with frequency for different salt concentrations in the GPE samples. A general pattern in the frequency dependence of conductivity is observed for all GPE samples. The plots consist of two distinct regions: at the lower frequencies, <10 kHz, the conductivity is found to increase with increasing frequency, describing the electrodes polarization phenomena [26], and is followed by the frequency independent plateau region at higher frequencies, >40 kHz. The frequency independent conductivity is correlated with the dc conductivity, σ_{dc} [27] . The σ_{dc} of the prepared GPE samples has been determined by extrapolating the plateau region on the σ-axis. The calculated σ_{dc} values from the conductivity–frequency dependence plots are in good agreement with those obtained from the Cole–Cole plot [28]. The pattern of conductivity–frequency dependence obtained in this study is very similar to the one reported from previous work that focused on ionically conducting polymers, glasses and doped crystalline solids [29–31]. This is believed to be reflected in the mechanism of charge transport behavior of charge carriers.

Transference number measurements

The ionic transference numbers (t_i) for the GPE samples containing 5, 20 and 30 wt.% of LiBF$_4$ were estimated using the dc polarization technique, and the result can be seen in Fig. 4. The values of t_i for samples containing 5, 20 and 30 wt.% are calculated using the Eq. (3) and were found to be 0.81, 0.89 and 0.80, respectively. These results are consistent with the conductivity results,
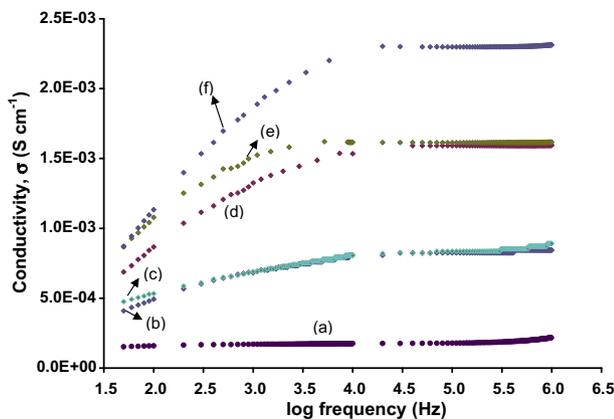
implying that the increase in charge carriers plays a vital role in the conductivity enhancement. This also shows that the charge carriers in these gel polymer electrolyte samples are predominantly ions [32].

Conductivity–temperature dependence studies

Fig. 5 shows the plot of log conductivity ($\log \sigma$) versus reciprocal temperature ($1000/T$) for the highest room temperature conductivity sample. The plot illustrates a linear line, implying that it follows the Arrhenius type as in equation;

$$\sigma = \sigma_o \exp(E_a/kT) \tag{5}$$

where σ_o is the conductivity pre-exponential factor, E_a is the activation energy for conduction, k is the Boltzmann constant and T is the temperature in Kelvin. In the present work, the experimental data indicate that the ionic conductivity has been enhanced with increasing temperature. This indicates that the sample has been thermally activated [33]. As the conductivity temperature-dependence data follow the Arrhenius relationship, the result can be explained in the way that the ions 'jump' into the neighboring vacant sites and cause the conductivity to increase [34]. The activation energy, E_a, which is a combination of energy of defect formation and energy of defect migration, can be observed from the slope of the plot [35]. The calculated value of activation energy of the sample was determined to be 0.19 eV. It is found that the values of conductivity and activation energy obtained in this work are within the range reported by others, as tabulated in Table 1. The low activation energy, E_a, for the lithium ion transport is caused by the completely amorphous nature of the polymer electrolytes that ease the fast Li$^+$

Fig. 3. Conductivity–frequency dependence for GPE samples containing (a) 30 wt.%, (b) 5 wt.%, (c) 25 wt.%, (d) 10 wt.%, (e) 15 wt.% and (f) 20 wt.% of LiBF$_4$ salt.
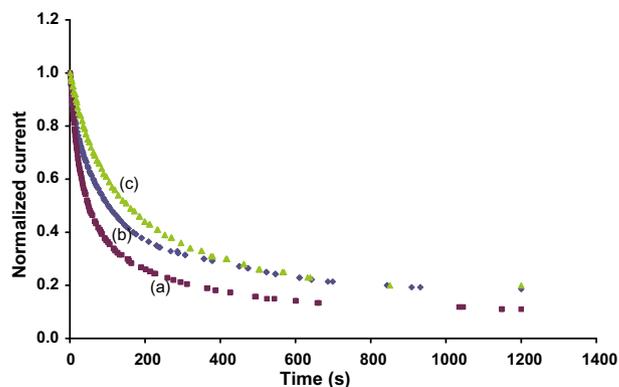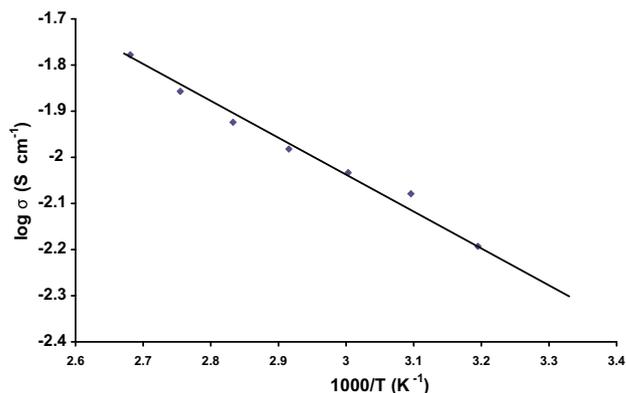

Fig. 5. Log σ versus $1000/T$ plot for the GPE sample containing 20 wt.% LiBF$_4$.

Table 1
The conductivity and activation energy values of various GPE systems.

GPE system	Conductivity (S cm^{-1})	E_a (eV)	Reference
PMMA + PC + XClO$_4$			
X = Na	4.33×10^{-2}	0.16	[37,38]
X = Li	2.06×10^{-2}	0.20	
X = Zn	4.16×10^{-2}	0.17	
X = Mg	1.59×10^{-2}	0.20	
PMMA + PC + XClO$_4$			
X = Li	1.28×10^{-4}	0.20	[39]
X = Na	6.67×10^{-4}	0.16	
X = Mg	2.38×10^{-4}	0.21	
X = Cd	2.86×10^{-4}	0.15	
X = Zn	3.07×10^{-4}	0.17	
PMMA + PC + EC + Mg(CF$_3$SO$_3$)$_2$	4.20×10^{-4}	0.04	[40]
PMMA + EC + PC + NaClO$_4$ + SiO$_2$	3.70×10^{1}	0.25	[41]
PVDF–HFP + g-PMMA + LiPF$_6$ + EC + PC	2.00×10^{-2}	0.22	[42]
PMMA–PVC–LiTFSI + liquid ionic	1.64×10^{-4}	0.26	[43]
Gelatin + LiBF$_4$	1.45×10^{-4}	0.45	[44]

ion movement in the polymer. The completely amorphous nature also gives a larger free volume in the gel polymer electrolyte sample when the temperature is increased [36].

Conclusions

The ionic conductivity and transport behavior of gel polymer electrolytes containing PMMA, EC, PC and LiBF$_4$ were studied. The highest room temperature conductivity was 2.24×10^{-3} S cm^{-1} and was obtained from the sample containing 20 wt.% of LiBF$_4$. The increase in the conductivity with increasing salt concentration could be attributed to the increase in the number and mobility of the charge carriers. The decrease in the conductivity is due to the saturation of the salt, hence the number of charge carriers is decreased. The conductivity–frequency dependence plots show two distinct regions: at lower frequencies, the conductivity increases with increasing frequency and is then followed by the frequency independent plateau region at higher frequencies. The ionic transference number shows that the conducting species in the gel polymer electrolyte samples are predominantly ions. The conductivity–temperature dependence follows the Arrhenius rule in the temperature range of 303–373 K.

Acknowledgements

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