



Short communication

A direct current pulse technique to enhance conductivity of heterogeneous electrolytes

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ABSTRACT

A heterogeneous electrolyte comprised of PEG(6000):LiClO₄ (8:1)–MgO (20 wt.%) was prepared and characterized. The electrolyte was subjected to a DC potential of 10 mV and the effect of the potential on conductivity evolution was investigated. The DC potential enhanced the conductivity by a factor of 25. The enhancement in conductivity was due to the formation of space charge around MgO that resulted in the development of an internal field.

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1. Introduction

Polymer–ceramic composite electrolytes have received considerable attention in recent years because the incorporation of a ceramic phase in a polymer matrix leads to enhanced conductivity, cationic transport number and electrode–electrolyte interfacial stability [1,2]. Furthermore, the ceramic phase suppresses the crystallization of the polymer phase which is detrimental to the ionic transport. The nature of the interaction between the ions and the dielectric dopant was believed to be driven by the dielectric constant gradient [2]. Subsequent investigations [3,4] of composites involving a single lithium ion conductor and a dielectric phase have clearly demonstrated that the interaction involves immobilization of the charge carriers at or around the dielectric surfaces. The immobilized charge carriers act like sources of electric fields that radiate from the point charges. The electric field in turn accelerates transport of the conducting ions.

Two possible physical situations that can explain the conductivity data of polymer–ceramic composite electrolytes are—blocking and space charge effects. The influence of blocking entity is easier to understand as whenever mobile charge species move towards the dielectric dopant under the influence of the applied field, their forward motion is impeded and they are scattered in different paths in

the general direction of the field leading to an increased resistance and thus a decline of ionic conductivity of the solid. The second situation is the space charge formation originating from an immobilization of the charge carriers at the dielectric surfaces. The space charge has a major influence on the transport of conducting ions and enhances conductivity of ionic solids under appropriate conditions. Collectively, these factors determine whether or not a given dopant will have a positive space charge effect, i.e., an enhancement in conductivity with addition of the dopant.

The immobilized space charges can be destabilized by increasing temperature and in such a situation the beneficial effect on conductivity is destroyed. In a recent publication, the variables for conductivity measurement in heterogeneous electrolytes have been reported [5]. One of the variables is the temperature dependent formation and destruction of the space charge.

A heterogeneous solid electrolyte can be viewed as a solid in which there are free and immobilized ions. The concentration of these two types of ions greatly depends upon the temperature. Both of these types of ions can interact with an applied external DC field, which can destabilize and free the immobilized ions. After removal of the DC field, the free ions can again interact with the dielectric phase resulting in rearrangement of ions in the heterogeneous electrolyte which may be beneficial from the ionic conductivity point of view. This hypothesis forms the subject matter of this paper. In this investigation, the heterogeneous electrolyte comprised of poly(ethylene) glycol (PEG) is complexed with lithium perchlorate (LiClO₄) and nanosize MgO. The conductivity evolution of the elec-

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trolyte was measured as a function of temperature and applied external DC field.

2. Experimental

The batch materials of heterogeneous electrolyte consisted of poly(ethylene glycol) [PEG, m.w. 6000, Alfa Aesar] and lithium perchlorate [LiClO_4 , Alfa Aesar, anhydrous 99%]. The PEG and LiClO_4 were dried at 55°C whereas MgO was dehydrated at 120°C . The PEG and LiClO_4 were mixed such that the $[\text{O}]:[\text{Li}^+]$ ratio was equal to 8:1 in an argon-filled dry box maintained at <100 ppm of oxygen. To this mixed batch of PEG and LiClO_4 , 20 wt.% of dried nanosize magnesium oxide [MgO , Inframat Advanced Materials, ~ 35 nm] was added and milled in an energy mill for 1 h. It is assumed that the energy milling of the PEG: LiClO_4 - MgO mixture distributes the MgO nanoparticles uniformly in the PEG: LiClO_4 complex even though an agglomeration of MgO remains a possibility. About 200 mg of milled batch was placed in a stainless steel die which was heated to 70°C and then pressed with a pressure of 392 MPa to obtain a disc of about $600\ \mu\text{m}$ thicknesses. The disc was sandwiched between two heated ($\sim 70^\circ\text{C}$) plates and pressed further with a load to yield a membrane thickness of about 200 – $250\ \mu\text{m}$. The membrane was cut into a circular disc of about $2.215\ \text{cm}^2$ area and placed in a fixture between two stainless steel (SS) electrodes. The fixture containing the SS/electrolyte/SS cell was subsequently placed and connected to electrical leads in a controlled atmosphere glass vessel. The glass vessel was then transferred to an environmental chamber and the electrical leads were connected to the impedance spectrometer (Solartron Instruments, Model 1260 with an electrochemical interface). Subsequently, the composite membrane of the assembled cell was heated to 64°C and held at this temperature for 14 h. Thereafter, the impedance of the electrolyte was measured while lowering the temperature from 64 to 18°C at intervals of 10°C . At each temperature, the specimen was equilibrated for an hour before the impedance measurement. The impedance measurements on the cell were carried out in the 0.1 – 10^6 Hz frequency range. The Z plot and Z view softwares were employed for the measurement and data analysis. The conductivity of the specimen was computed from the AC impedance spectra.

At ambient temperature, a DC potential of 10 mV (energy $\sim 1.6022 \times 10^{-23}$ J) for 10 min was applied to the specimen. Immediately after removing the DC potential, the impedance of the specimen was measured by the impedance spectrometer.

The thermal analysis of the polymer and polymer–ceramic composite electrolyte membranes was conducted by a differential scanning calorimeter (TA Instruments Model 2910). Specimens were scanned at the rate of $10^\circ\text{C}\ \text{min}^{-1}$ in a temperature range of 20 – 100°C under nitrogen atmosphere. Pure indium and tin were used for the temperature and enthalpy calibrations of the instrument. The 10 mg specimen was placed in an aluminum pan and an empty aluminum pan was used as a reference for the measurement.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC) studies

Fig. 1 shows the DSC results for the PEG(6000), PEG(6000): LiClO_4 (8:1) and PEG(6000): LiClO_4 (8:1)- MgO (20 wt.%) electrolyte specimens. The PEG(6000) and PEG(6000): LiClO_4 (8:1) specimens display a melting endotherm with a shoulder in the case of PEG(6000) at the lower temperature, which is ascribed to the melting of PEG(6000). The transition as depicted by the shoulder of the melting endotherm for PEG(6000) corresponds to the defolding of chains [6]. The temperature of the onset point corresponding

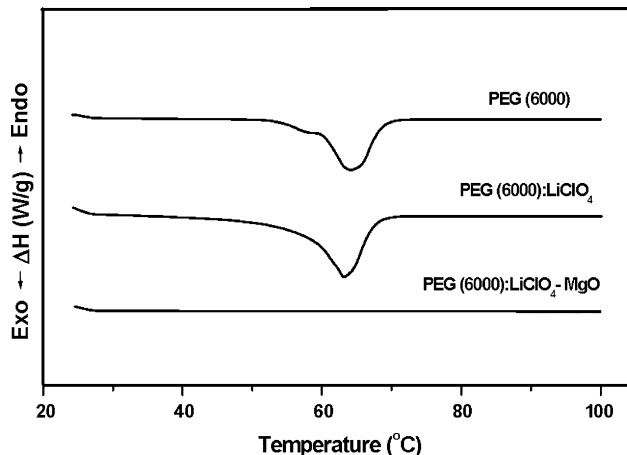


Fig. 1. Differential scanning calorimetry data of pure PEG(6000), PEG(6000): LiClO_4 (8:1) and PEG(6000): LiClO_4 (8:1)- MgO (20 wt.%) in the 20 – 100°C temperature range.

to the main peak of pure PEG(6000) is 65.3°C and the fusion enthalpy, ΔH is $137.3\ \text{J}\ \text{g}^{-1}$, while the temperature of the onset point corresponding to the main peak of PEG(6000): LiClO_4 (8:1) is 63.1°C and the corresponding fusion enthalpy, ΔH is $193.2\ \text{J}\ \text{g}^{-1}$. The T_m decreases and the endothermic heat ΔH increases with the addition of LiClO_4 in pure PEG(6000). This phenomenon indicates that the crystalline structure of PEG(6000) with Li^+ doping is clearly not disrupted. The MgO addition eliminated crystallinity of PEG(6000) as shown in Fig. 1. According to the literature [7,8], the coordination of Li^+ ions with the ether oxygen of PEG not only arrests the local motion of the polymer segments but also causes physical cross-linking, increasing the T_m of the PEG segments. The PEG(6000): LiClO_4 (8:1) complex transformed into an amorphous form with the addition of MgO . It demonstrates that the PEG(6000): LiClO_4 (8:1) polymer complex and ceramic phases in the system interact to provide an amorphous phase.

3.2. Ionic conductivity

The Arrhenius plots of conductivity of PEG: LiClO_4 (8:1) and PEG: LiClO_4 (8:1)- MgO (20 wt.%) electrolyte membranes in the temperature range of 18 – 64°C are shown in Fig. 2. The 20% MgO doping in this study was practiced because in an earlier work the highest conductivity was obtained for the 20% doping level in the PEO: LiBF_4 - MgO system [9]. The conductivity of PEG: LiClO_4 are lower than the conductivity of PEG: LiClO_4 - MgO (20 wt.%) across the entire temperature range. The conductivity of PEG: LiClO_4 - MgO (20 wt.%) increases from $1 \times 10^{-6}\ \text{S}\ \text{cm}^{-1}$ at 18°C to $1 \times 10^{-3}\ \text{S}\ \text{cm}^{-1}$ at 64°C . The ambient temperature conductivity value of the specimen is $5.16 \times 10^{-6}\ \text{S}\ \text{cm}^{-1}$. The conductivity of the PEG: LiClO_4 - MgO (20 wt.%) specimen is greater than the PEG: LiClO_4 specimen by approximately a factor of 2 (100%). The enhancement in conductivity is significant because only a 5% experimental error in measured values has been observed. As shown in Fig. 2, a nonlinearity in Arrhenius plot for the PEG: LiClO_4 at around 52°C is noted. Similar feature has been reported for even in high molecular weight polymer electrolyte systems [10,11]. Interestingly, the doping of the MgO into the polymer system has removed the nonlinearity in the Arrhenius plot. It should be noted that there is a time dependent component of conductivity in composite electrolytes [9] which will be further elaborated in the next section. Therefore, the conductivity data of the PEG: LiClO_4 (8:1)- MgO (20 wt.%) should be interpreted in that context.

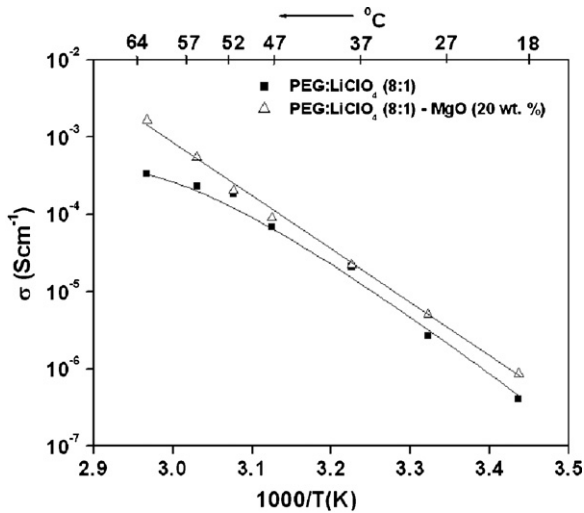


Fig. 2. Arrhenius plots of the conductivity of PEG(6000):LiClO₄ and PEG(6000):LiClO₄-MgO (20 wt.%) electrolyte membranes heat treated at 64 °C overnight. The conductivity of the specimens was measured while cooling to 18 °C.

3.3. Time dependence of conductivity

After stabilizing the PEG:LiClO₄-MgO (20 wt.%) specimen at 27 °C, the AC impedance of the specimen was measured as a function of time. Computed conductivity as a function of time is shown in Fig. 3. The conductivity increased from 5.16×10^{-6} to 4.17×10^{-5} S cm⁻¹ after 91 h at room temperature. The increase in conductivity is almost linear up to 50 h and then it increases exponentially. The increase in conductivity over the 91 h is over a factor of 8. The time dependence of conductivity has been reported in earlier publications [12,9] and is a characteristic of heterogeneous electrolytes. Even at room temperature, the mobile charge carriers (Li⁺ and ClO₄⁻) interact with MgO, resulting in space charge-induced enhancement of conductivity.

The interaction of a dielectric phase and an ionic species is schematically illustrated in Fig. 4. An ionic species such as lithium or perchlorate ion is shown by an arrow whereas the dielectric phase, MgO, is depicted by open circles. The interaction of MgO and lithium ion leads to the immobilization of the conducting species. Once immobilized, the lithium ion (Fig. 4 shows only immobi-

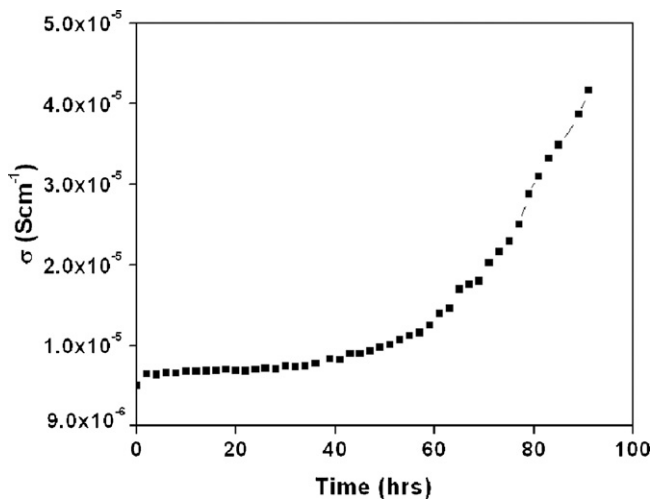


Fig. 3. Conductivity of PEG(6000):LiClO₄-MgO (20 wt.%) heterogeneous electrolyte membrane as a function of time.

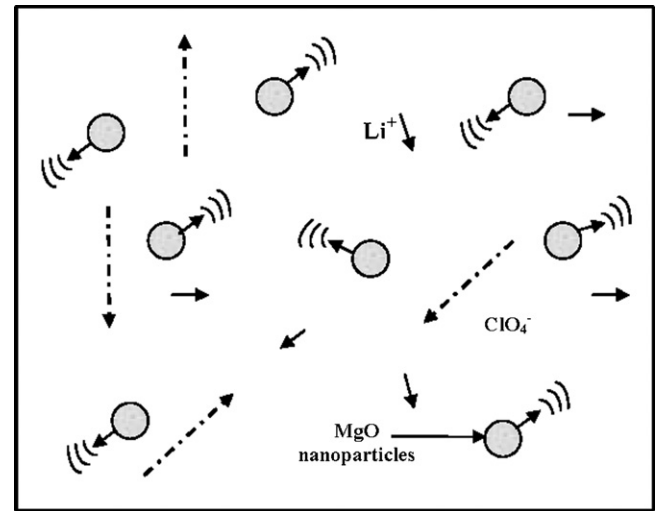


Fig. 4. Schematic of interaction of lithium and chlorate ions with MgO nanoparticles in PEG(6000) matrix.

lized lithium ions but it could be ClO₄⁻ ions as well) becomes a source of an electric field, as shown by arcs in Fig. 4. The localized electric field assists in the transport of the conducting ions and therefore the conductivity increases with time. The MgO-Li⁺ interaction energy is estimated to be around 4.8065×10^{-22} J [3]. The low interaction energy suggests that the immobilized ions can be destabilized by using either thermal or electrical energy. The destabilization by the use of thermal energy has been demonstrated in an earlier publication [3]. The destabilization due to electrical energy and its resulting effects will be presented in the remainder of this paper.

3.4. Effect of applied DC potential

A DC potential of 10 mV ($\sim 1.6022 \times 10^{-23}$ J) across the PEG:LiClO₄ (8:1)-MgO (20 wt.%) electrolyte specimen was applied for 10 min and subsequently the field was removed. The effect of the applied DC potential is shown in Fig. 5. The conductivity vs. time data of Fig. 5 shows an initial decrease in the conductivity. Subsequently, the conductivity shows a linear increase with time up to about 90 h, after which the conductivity stabilizes or perhaps decreases slightly. The conductivity increase by over a factor

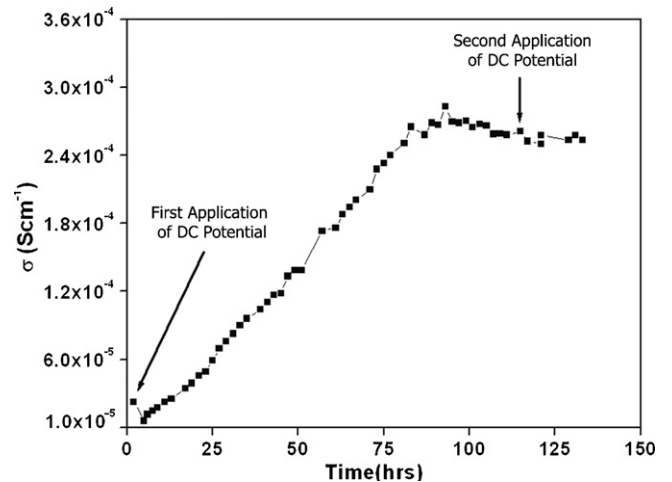


Fig. 5. The effect of an applied DC potential of 10 mV for 10 min on conductivity of PEG(6000):LiClO₄-MgO (20 wt.%) heterogeneous electrolyte membrane at 27 °C.

Table 1

Conductivity data of PEG(6000):LiClO₄ (8:1)–MgO (20 wt.%) membrane with respect to time before and after application of external DC potential of 10 mV for 10 min across the membrane at 27 °C.

At 27 °C	
Time (h)	σ (S cm ⁻¹)
Before application of DC potential	
0	5.03×10^{-6}
45	8.99×10^{-6}
91	4.17×10^{-5}
After application of DC potential of 10 mV for 10 min	
0	1.0×10^{-5}
51	1.3×10^{-4}
121	2.5×10^{-4}

of 25 is a significant accomplishment and is believed to be related to the reformation of space charge regions around the dielectric MgO and polymer interface. A second application of the 10 mV for 10 min towards the later part of the experiment showed no beneficial effect.

Immediately after the DC potential was removed, the conductivity decreased slightly, as shown in Fig. 5. Such an observation of the effect of an electric field on conductivity of heterogeneous electrolytes has also been reported earlier [13]. This observation has been explained by experimental evidence [3] that an interaction involving dielectric phase and conducting ions occurs in heterogeneous electrolytes. The interaction for the PEG:LiClO₄ (8:1)–MgO (20 wt.%) electrolyte is expressed by the following equation:



The reversible nature of the equation has been established by the conductivity measurement and reported earlier for the LATP–Al₂O₃ heterogeneous electrolytes [3]. The MgO:Li⁺ complex can be destabilized by an energy $>4.8065 \times 10^{-22}$ J. The application of 10 mV ($\sim 1.6022 \times 10^{-23}$ J) DC field led Eq. (1) to proceed from right to left, thereby diminishing the space charge effect which resulted in a negative influence on the conductivity.

After the initial decay, the conductivity increases up to 90 h. The diffusion coefficients of the ions (Li⁺ and ClO₄⁻) in these heterogeneous electrolytes are low— 2.70×10^{-8} cm² s⁻¹ for lithium and much lower expected value for ClO₄⁻ ion at the room temperature [14]. The diffusion of these ions is significant enough to interact with MgO. It may be argued that they possess enough mobility to re-interact with MgO and Eq. (1) proceeds towards the right and generates the space charge effect to make a positive contribution for the conductivity enhancement. The conductivity increase by a factor of 25 is a major contribution and it appears that the DC field has helped homogenize the creation of the space charge effect within the bulk structure of the heterogeneous electrolyte.

Table 2

Conductivity, carrier concentration and mobility of PEG(6000):LiClO₄ (8:1) and PEG(6000):LiClO₄ (8:1)–MgO (20 wt.%) electrolytes membranes.

At 27 °C			
Time (h)	σ (S cm ⁻¹)	n_i	μ_i
PEG(6000):LiClO ₄ (8:1)			
0	2.24×10^{-7}	1.30×10^{13}	1.08×10^{-1}
45	2.58×10^{-7}	1.18×10^{13}	1.36×10^{-1}
91	2.47×10^{-7}	2.35×10^{13}	6.56×10^{-2}
Applied step DC potential of 10 mV for 10 min	1.20×10^{-7}	1.16×10^{13}	6.46×10^{-2}
PEG(6000):LiClO ₄ (8:1)–MgO (20 wt.%)			
0	8.63×10^{-6}	2.27×10^{13}	2.37
45	1.06×10^{-5}	2.36×10^{13}	2.80
91	4.09×10^{-5}	2.74×10^{13}	9.32

The conductivity data as a function of time before and after application of the 10 mV DC potential are also presented in Table 1. The data in Table 1 suggests that the ionic conductivity of heterogeneous electrolytes has inherent tendency to increase around ambient temperature even without the application of a DC field. This observation is consistent with earlier publications [12,9] and points out that Eq. (1) is proceeding in the right direction at the ambient temperature. If the base conductivity value is taken at the 0 h before the application of the DC field and compared with the conductivity value obtained at 121 h after application of the DC field, the conductivity is enhanced by a factor of 50.

3.5. Mobility and number of charge carriers measurements

The conductivity, σ , is often expressed by Eq. (2). The z and e are the valence and electronic charge, respectively, and are constants.

$$\sigma = \mu_i(n_i z e) \quad (2)$$

where μ_i is the mobility of charge carriers and n_i is the number of charge carriers.

Therefore, the conductivity data can be explained in terms of μ_i and n_i . The n_i should be constant in a given volume of a heterogeneous electrolyte. Therefore, the question arises as to the mechanism of conductivity enhancement resulting from the aging before and after the application of the DC field. To answer the question, the number of charge carriers, n_i and mobility, μ_i were measured by a technique described in prior publications [15,16]. The technique involves polarizing the specimen using a DC field for a given period of time and subsequently monitoring the decay of current resulting from the polarized charges. Such a specimen acts like an electrochemical cell whose potential drops to zero after a certain period of time.

Table 2 presents σ , n_i and μ_i of the PEG:LiClO₄ (8:1) and PEG:LiClO₄(8:1)–MgO (20 wt.%) specimens at 27 °C. In the case of PEG:LiClO₄ (8:1) specimen, the conductivity remains relatively constant as a function of time. The differences in n_i and μ_i values are attributed to error in the experimental measurement. After an application of 10 mV, the conductivity decreases to about 50% which could be attributed to polarization of conducting ions. The reduced conductivity is also reflected by decreased n_i and μ_i . The PEG:LiClO₄ (8:1)–MgO (20 wt.%) specimen shows an entirely different trend as compared to PEG:LiClO₄ (8:1) specimen. The conductivity increases by a factor of 5 in 91 h. The number of charge carriers, n_i remains fairly constant whereas the mobility, μ_i increases by almost a factor of 4. The increased mobility is attributed to the creation of space charge or internal field due to the interaction of MgO and conducting ions Li⁺ and ClO₄⁻.

4. Summary and conclusions

This paper covered the ionic conductivity of PEG(6000):LiClO₄ and PEG(6000):LiClO₄-MgO (20 wt.%) electrolytes. The ionic conductivity of the heterogeneous PEG(6000):LiClO₄-MgO (20 wt.%) electrolyte was higher than the ionic conductivity of PEG(6000):LiClO₄ polymer electrolyte in the temperature range of 18–64 °C. The electrolytes were subjected to a DC potential of 10 mV and the effect of the potential on conductivity evolution was determined. Initially, the conductivity decreases after removal of the DC potential; however, the conductivity increases under isothermal condition with increasing time by a factor of 25. The enhancement in conductivity is attributed to the formation of space charge due to an interaction of the dielectric phase MgO and ionic species Li⁺/ClO₄⁻. The space charge subsequently creates internal field which accelerates transport of conducting ions.

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