



Investigation of ionic conductivity and relaxation in plasticized PMMA-LiClO₄ solid polymer electrolytes

P. Pal, A. Ghosh*

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India



ARTICLE INFO

Keywords:

Broadband conductivity spectra
Ionic conductivity
Nearly constant loss
Electric modulus

ABSTRACT

We have studied ion conduction and relaxation in plasticized PMMA-LiClO₄ solid polymer electrolyte for different salt concentrations over a wide range of temperature. We have measured the complex conductivity spectra in a wide frequency range of 0.01 Hz–3 GHz and analyzed the experimental results using the random barrier model coupled with the contribution of electrode polarization in low frequency region. The temperature dependence of ionic conductivity and charge carrier relaxation time obtained from the analysis follows Vogel-Tammann-Fulcher behavior. The nearly constant loss response has been observed at low temperatures and/or at high frequency region. The temperature and frequency range of nearly constant loss response depends on the salt concentration in polymer matrix. The electric modulus spectra have been used to study charge carrier relaxation further. The stretched exponent, obtained from Kohlrausch-Williams-Watts (KWW) function, indicates highly non-exponential relaxation in the polymer electrolytes.

1. Introduction

Recently, solid polymer electrolytes (SPEs) have received much attention because of their potential technological applications in charge storage devices [1–4]. In spite of several studies related to charge carrier transport in SPEs, the understanding of the mechanism of charge carrier transport and relaxation still remains an open question [5–7]. Poly(methylmethacrylate) (PMMA) based electrolyte is a most widely studied system due to its amorphous nature and the presence of electron donating bulky ester functional group [O=C], which is highly active in coordinating with cations of alkali metal salts and thus easily dissociate the alkali salts [8–10]. But these PMMA based electrolytes are brittle and have low ionic conductivity at room temperature, which exclude them from technological applications. Many strategies have been adopted, such as plasticization to enhance the flexibility of PMMA chain [11,12], addition of nano filler to improve the ionic conductivity, mechanical strength and thermal stability [2,4,13–15], addition of ionic liquid which acts as a plasticizer as well as source of extra charge carrier [3,7], blending with other polymers [16], cross-linking [17], etc. In general, ion transport in SPEs takes place in the amorphous phase, where the ionic conductivity is controlled not only by local ion hopping, but also by local motion of the polymer chain segments [18]. Thus, ionic conductivity in SPEs is strongly coupled to the motion of the host polymer chain segments.

In general, various lithium salts such as LiClO₄, LiBF₄, LiPF₆, Li,

LiF₃SO₃, LiAsF₆, LiN(SO₂CF₃)₂, etc. are doped to introduce the charge carriers in polymer matrix [8–10]. Among these lithium salts, LiClO₄ is preferred because it is relatively stable at ambient moisture and less hygroscopic than the other salts. It has also low lattice energy, for which it has high solubility [8]. On the other hand, among various plasticizers, propylene carbonate (PC) is preferred due to its high dielectric constant ($\epsilon_r \approx 64.4$) and high molecular dipole moment (4.9 D) [19].

In this work, we have studied the ionic conductivity and relaxation of PMMA-LiClO₄ solid polymer electrolytes plasticized with propylene carbonate for different salt concentrations.

2. Experimental

2.1. Preparation of solid polymer electrolyte

Standard solution cast technique was used for the preparation of free standing polymer films. For the preparation of PMMA-LiClO₄ polymer electrolytes PMMA ($M_w = 120,000$, Sigma Aldrich) and appropriate amount of vacuum dried anhydrous LiClO₄ (Sigma Aldrich) were dissolved in tetrahydrofuran (THF) under stirring condition. The stoichiometric molar ratio of PMMA monomer unit carbonyl group (C=O) to the LiClO₄ cations (Li⁺) (i.e., MMA/Li⁺) were varied during preparation (It may be noted that increase in MMA/Li⁺ ratio indicates decrease in lithium salt concentration). A fixed amount (50 wt%) of

* Corresponding author.

E-mail address: spag@iacs.res.in (A. Ghosh).

propylene carbonate (PC, Sigma Aldrich) was then added to above (PMMA-LiClO₄) solution under stirring condition for plasticization. The solution became thick and homogeneous after stirring for 10–12 h due to solvent evaporation at room temperature. Finally, the solution was cast onto polytetrafluoroethylene (PTFE) container to get free standing films by slow evaporation of the solvent in ambient condition. These films were further dried in vacuum oven under a 0.01 mbar vacuum at 328 K for ~48 h to remove the residual solvent traces. The polymer electrolyte films were obtained for MMA/Li⁺ = 4, 6, 8, and 10.

2.2. Conductivity measurements

A conductivity cell containing two stainless steel blocking electrodes was used for the ac electrical measurements. The measurements of the capacitance and the conductance of the films of thickness in the range of 200–300 μm and the diameter of about 10 mm were carried out at various temperatures in an anhydrous environment using an LCR (HIOKI, model 3522–50 LCR Hi-tester) in the frequency range of 0.01 Hz to 100 kHz and an LCR meter (Quad Tech, model 7600 plus) in frequency range of 10 Hz–2 MHz. All measurements were done by placing the sample cell in a cryostat in vacuum (0.01 mbar) with stability of temperature of ~0.10 K. The measurements of capacitance and conductance in the frequency range from 1 MHz to 3 GHz were carried out in a broadband dielectric spectrometer (Agilent, model E4991A) employing the coaxial reflectometry technique (Novocontrol Technologies GmbH).

3. Results and discussion

3.1. Broadband conductivity spectra

Fig. 1(a) and (b) show respectively the frequency dependence of the real (σ') and imaginary (σ'') parts of the complex conductivity $\sigma^*(\omega)$ at different temperatures for the salt concentration MMA/Li⁺ = 4. The frequency dependence of σ' in Fig. 1(a) shows three distinct regions associated with different phenomena: (i) in the low frequency region, σ' spectra show a rapid drop due to accumulation of charge carriers at metal electrode, forming a space charge layer, known as electrode polarization which depends upon the nature of the electrode-polymer interface and thickness of the sample [5], (ii) a frequency independent region (σ_{dc}) represents long range charge carrier diffusion via hopping and (iii) high frequency dispersion region, where σ' increases with increase in frequency. It is noted in Fig. 1(b) that the electrode polarization starts at a certain frequency ω_{on} corresponding to a minimum in σ'' , while the full development of the electrode polarization occurs at a lower frequency ($\omega \sim \omega_{max}$) corresponding to a peak in σ'' . It is further noted that the conductivity increases and dispersive region shifts toward higher frequencies with the increase in temperature. The cross-over from frequency independent region σ_{dc} to dispersive region implies the onset of the conductivity relaxation related to macroscopic charge-transport. In the high frequency region, both real (σ') and imaginary (σ'') part of the complex conductivity increase with increasing frequency due to the contribution of dielectric relaxation of the PMMA dipoles primarily. The frequency dependent real and imaginary conductivity for different salt concentrations at $T = 303$ K are also shown in Fig. 2(a) and (b) respectively. The real (σ') and imaginary (σ'') parts of complex conductivity spectra at different temperatures in three different frequency ranges (a) 0.01 Hz–100 kHz, (b) 10 Hz–2 MHz and (c) 1 MHz–3 GHz for plasticized PMMA-LiClO₄ polymer electrolyte for the salt concentration MMA/Li⁺ = 4 are shown in Fig. S1 and Fig. S2 respectively. The frequency and temperature dependence of real and imaginary parts of complex conductivity spectra for different concentrations shows similar behavior.

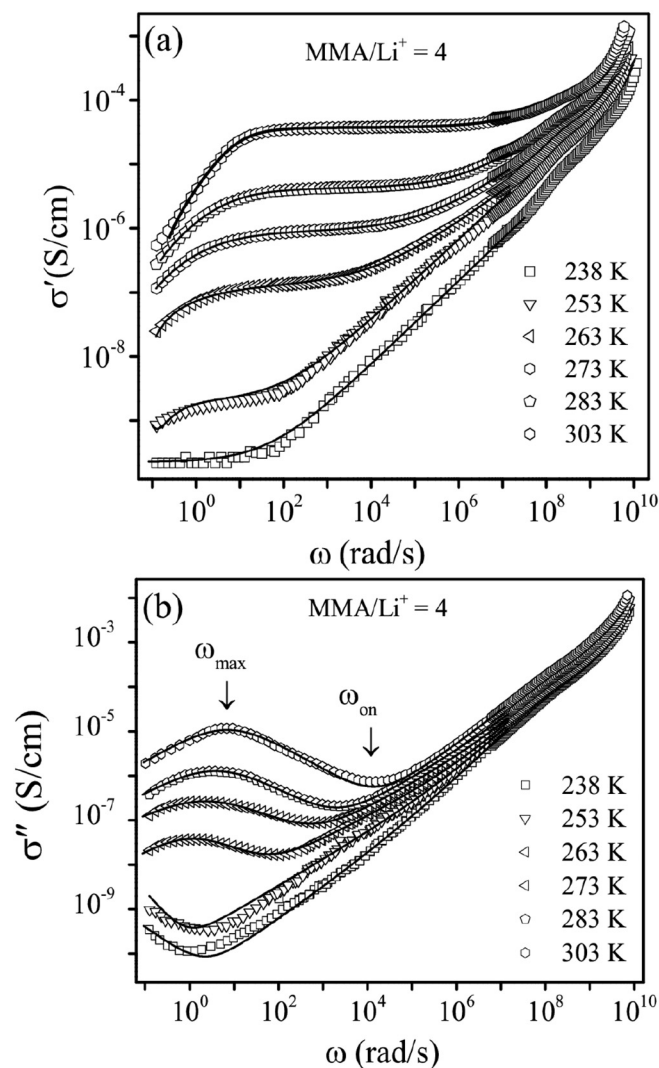


Fig. 1. (a) Real and (b) imaginary parts of complex conductivity spectra at different temperatures in the frequency range 0.01 Hz–3 GHz for plasticized PMMA-LiClO₄ polymer electrolyte for the salt concentration MMA/Li⁺ = 4. Solid lines are the best fits to Eqs. (1) and (2).

3.2. Analysis of broadband conductivity spectra

The frequency dependence of complex conductivity has been analyzed using random barrier model (RBM) [20]. In this model, charge transport takes place via hopping of charge carrier in conducting materials, which are subjected to spatially random energy landscapes. According to RBM, the complex conductivity $\sigma_1^*(\omega)$ is given by [20]

$$\sigma_1^*(\omega) = \sigma_{dc} \left[\frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)} \right], \quad (1)$$

where σ_{dc} is the dc conductivity and $\tau_e = 1/\omega_e$, where ω_e is the attempt frequency to overcome the free-energy barrier determining the dc conductivity. Several authors [21,22] have calculated the contribution of electrode polarization observed in the low frequency region and at relatively high temperatures by considering the fractal nature of the electrode-polymer interface and obtained the complex conductivity $\sigma_2^*(\omega)$ at low frequency region:

$$\sigma_2^*(\omega) = \sigma_0 + \frac{\sigma_{dc} - \sigma_0}{1 + (i\omega\tau_f)^{-\alpha}}, \quad (2)$$

where σ_0 takes into account contribution of the conductivity at constant electric field and the value of σ_0 does not coincide with the value of σ_{dc}

Download English Version:

<https://daneshyari.com/en/article/7744447>

Download Persian Version:

<https://daneshyari.com/article/7744447>

[Daneshyari.com](https://daneshyari.com)