



P-ISSN2349-8528
 E-ISSN 2321-4902
 IJCS 2015; 3(3): 63-67
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 Received: 03-08-2015
 Accepted: 04-09-2015

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A comprehensive study of conductivity and dielectric behaviour of polyethylene oxide-lithium perchlorate solid polymer electrolyte films

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Abstract

Solid polymer electrolyte (SPE) are defined as a solvent-free salt solution in a polymer host material that conducts ions through the polymer chains. Compared to ISEs, SPEs are much easier to process, generally by solution casting, making them greatly compatible with large-scale manufacturing processes. Solid polymer electrolytes (SPEs) consisting of polyethylene oxide (PEO) complexes with lithium perchlorate (LiClO₄) have been synthesized by solution casting method. The ionic conductivity, dielectric response of the SPE system is studied within the frequency range of 100 Hz⁻¹ MHz and in the temperature range of 303-353 K. The room temperature ionic conductivity value of PEO-LiClO₄ electrolyte is found to be ~10⁻⁵ S cm⁻¹. The dielectric properties were studied using the complex dielectric permittivity spectra and complex electric modulus spectra of the SPE films. It is observed that magnitude of dielectric permittivity is high in the lower frequency region due to electrode polarization (EP) effect. The dielectric permittivity and loss were increased with increase of temperature. The AC conductivity follows universal power law with a small deviation in the EP dominated low frequency region.

Keywords: Solid polymer electrolytes, polyethylene oxide, lithium perchlorate and dielectric

1. Introduction

Solid polymer electrolytes (SPEs) are playing a vital role in the fabrication of rechargeable batteries, electrochemical cells, super capacitors, solar cells, and specific ion sensors [1-5]. Solid polymers have better mechanical strength than those of liquid and gel polymer electrolytes. SPE are synthesized using solution casting which facilitates fabrication in desired geometry. SPE also offers good contact between electrolyte and electrode [6-10]. The ion conducting polymer electrolytes are formed by the dissolution of alkali metal salts into the various polymer hosts. The polymer host and metallic salt play an important role in the preparation of SPE films. Among the polymer hosts, polyethylene oxide (PEO) is more important because, it is having larger sufficient high electron donor power to form co-ordination with cations. PEO forms more stable complexes with metallic salts and is having the higher solvating power of salt than other polymers [11]. The ionic conductivity of SPE is generally dependent on the wt% content of added salt. In the PEO-LiX polymer electrolyte system, ether O-atoms of the PEO chains co-ordinating with Li⁺ cations through Lewis acid-base interaction, thereby separating them from the X- counter anions (Scheme 1) identifying the ability of a polymer host material to dissolve salts [12]. The AC conductivity frequency relaxation spectroscopy gives valuable information regarding ion dynamics and segmental relaxation process. Recently, Sengwa and Choudhary [13], synthesized and studied dielectric properties and ac conductivity of PEO16lithium perchlorate (LiClO₄) (PEO M.W = 6 × 10⁵ g mol⁻¹) SPE thin films. The ionic conductivity of SPE system reported was of the order of 10⁻⁷ S cm⁻¹. However, in the present system, we could achieve conductivity few orders greater than reported.

The present study reports the work carried out on SPE composed of on PEO-LiClO₄ with wt% ratio (85:15). The systematic study of the impedance spectroscopy, dielectric, and modulus properties of SPE using complex impedance spectroscopy has been presented.

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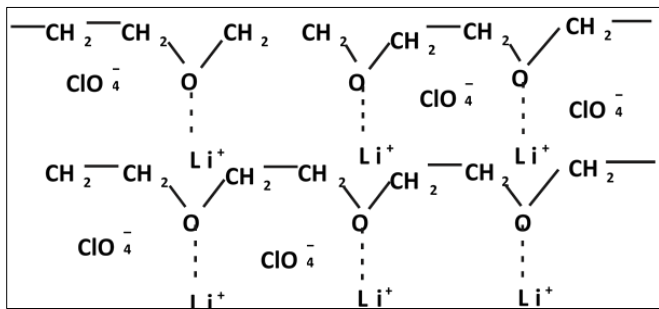


Fig 1: Probable geometry of complexation poly(ethylene oxide)

2. Experimental

2.1 Materials

PEO was procured from Sigma-Aldrich, USA with average molecular weight of 8×10^6 , LiClO_4 (ACS reagent, = 95.0%, Sigma-Aldrich, Japan), and methanol (HPLC grade, SD Fine) were used as starting materials to prepare SPEs.

2.2 Preparation of SPE

The PEO- LiClO_4 SPE film was prepared in the wt% ratio (85:15) by solution cast technique using methanol as a solvent (Scheme 2). The solutions were magnetically stirred for 25-30 h at room temperature to get a viscous solution with high homogeneity. The viscous solution was poured into a petri dish and left to dry at room temperature for 3 days to allow the slow solvent evaporation. The prepared SPE films were then kept in desiccators. Bubble free regions of the films were employed for the characterization techniques.

2.3 Characterization Techniques

The complex impedance measurements were performed using computer controlled (HIOKI-3532-50) LCR HiTESTER in the frequency range 100 Hz to 1 MHz and in the temperature range 303-353 K.

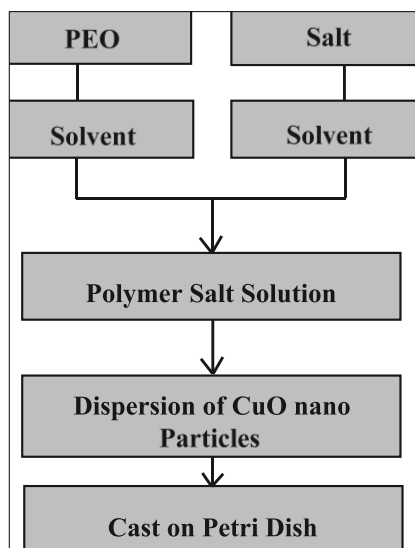


Fig 2: Flow Chart of Solution Cast Technique

2.4 Electrical Property Measurements

The capacitance (C), tan d and conductance (G) of the PEO- LiClO_4 solid electrolyte were measured in the above mentioned frequency range from 100 Hz to 1 MHz at different temperatures using the furnace interfaced LCR HiTESTER. The dielectric constant was evaluated from capacitance using the relation:

$$\epsilon' = \frac{tC_p}{A\epsilon_0} \quad (1)$$

Where, t is the thickness of the SPE film, A is the area of electrode contacting with SPE film, and ϵ_0 is the permittivity of free space $8.854 \times 10^{-12} \text{ Fm}^{-1}$.

$$\text{Loss factor } \epsilon'' = \epsilon' \tan \delta \quad (2)$$

The AC conductivity (δ_{ac}) values are calculated from the equation,

$$Gt \sigma = \frac{ac}{A} \quad (3)$$

The complex electric modulus M^* is given by,

$$M^* = 1/\epsilon^* = M' + jM'' \quad (4)$$

Where, M' and M'' are the real and imaginary part of the complex modulus,

$$M' = \frac{\epsilon'}{((\epsilon')^2 + (\epsilon'')^2)} \quad (5)$$

Where, ϵ' and ϵ'' are the real and loss parts of complex dielectric permittivity.

M^* is the inverse property of the complex dielectric permittivity ϵ^* .

3. Results and Discussion

3.1. Impedance Analysis

Impedance spectra of PEO- LiClO_4 SPE film at various temperatures are shown in Figure 1. The electrochemical characterization of ion conducting polymer electrolytes can be studied from these plots. From the impedance plots we can determine, bulk resistance (R_b), ionic conductivity, electrode electrolyte contact behavior, and type of charge carriers (ions or electrons) of polymer electrolytes [13, 14]. In impedance plots, a compressed semi-circular arc represents the bulk properties of the electrolyte film at the high frequency region. An inclined straight line in the low frequency region is due to the dominance of electrode polarization (EP) effect. The complete semi-circle is not observed in the high frequency region. This indicates that the applied frequency and temperature are insufficient for the complete circular arc. The bulk resistance intercept on X-axis is shifting toward the lower Z' region with increasing of temperatures. However, it is known that the region below the intercept represents the impedance due to EP effect while above the intercept gives the impedance due to bulk of the SPE [15].

The bulk resistance R_b of the polymer electrolyte at different temperatures was obtained directly from the common intercept of the arc and the inclined straight line with the Z' -axis. R_b values are given in Table 1. The ionic conductivity of the SPE is calculated using the relation [16],

$$\sigma_{ac} = \frac{t}{AR_b} \quad (6)$$

The R_b values of PEO- LiClO_4 SPE film decrease with increasing temperature. The ionic conductivity of the PEO-

LiClO₄ SPE system at different temperatures is summarized in Table 1.

3.2. Dielectric Analysis

The complex dielectric permittivity is defined as $\epsilon^*(\omega) = \epsilon' - j\epsilon''$, where ϵ' is the real part of the dielectric permittivity (dielectric constant) and ϵ'' is the imaginary part of the dielectric permittivity (dielectric loss). Figure 2 shows the complex permittivity spectra of the PEO-LiClO₄ SPE at different temperatures. From this, it is evident that a large ϵ' and ϵ'' values are observed at low frequencies. At these low frequencies, dipoles follows the field direction and the values of ϵ' and ϵ'' are found to be very high due to the EP phenomenon [15]. At moderate frequencies, dipoles begin to lag behind the field so the values of ϵ' and ϵ'' start to decrease. However, in the high frequency range dipoles cannot orient themselves in the applied electric field direction and hence the values of ϵ' and ϵ'' are constant and reach its minimum values [17]. It is also observed from Figure 2 that the values ϵ' and ϵ'' are gradually increase with temperature, which is attributed to migration and interfacial polarization of lithium ions. This type of trend is observed in the polar dielectrics in which orientation of dipoles facilitated with increasing temperature and thereby the values of ϵ' and ϵ'' are increased. In addition, the ϵ'' has shifted to a higher frequency region with increase of temperature, which confirms the thermally activated dynamical behavior of the PEO-LiClO₄ electrolyte system. The conductivity in PEO-LiClO₄ SPE is due to the migration of Li⁺ ions (Scheme 1).

Table 1: R_b, σ_{dc} and n values of PEO-LiClO₄.

Temperature (K)	R _b (Ω)	σ (Scm ⁻¹) dc	N 1	N 2
303	236.4	6.64×10 ⁻⁵	0.23	0.046
313	145.3	1.05×10 ⁻⁴	0.24	0.048
323	94.1	1.62×10 ⁻⁴	0.26	0.057
333	60	2.55×10 ⁻⁴	0.25	0.072
343	45.2	3.38×10 ⁻⁴	0.24	0.082
353	34.5	4.43×10 ⁻⁴	0.21	0.090

PEO=Polyethylene oxide, LiClO₄= Lithium perchlorate

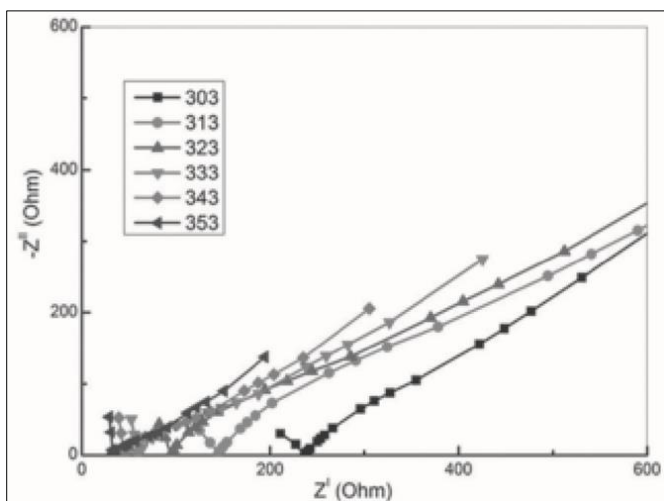


Fig 3: Impedance Spectra of Polyethylene Oxidelithium Perchlorate

3.3. Electric Modulus Analysis

Electric modulus spectra is a powerful tool to understand the conductivity relaxation process, ion hopping mechanism, transport process, and type of charge carriers present in an ionic conducting solid electrolytes.

This can be used as a restrain for the EP effect. The frequency dependence of real (M') and imaginary (M'') parts of electric modulus spectra of PEO-LiClO₄ SPE films at different temperatures are shown in Figure 3.

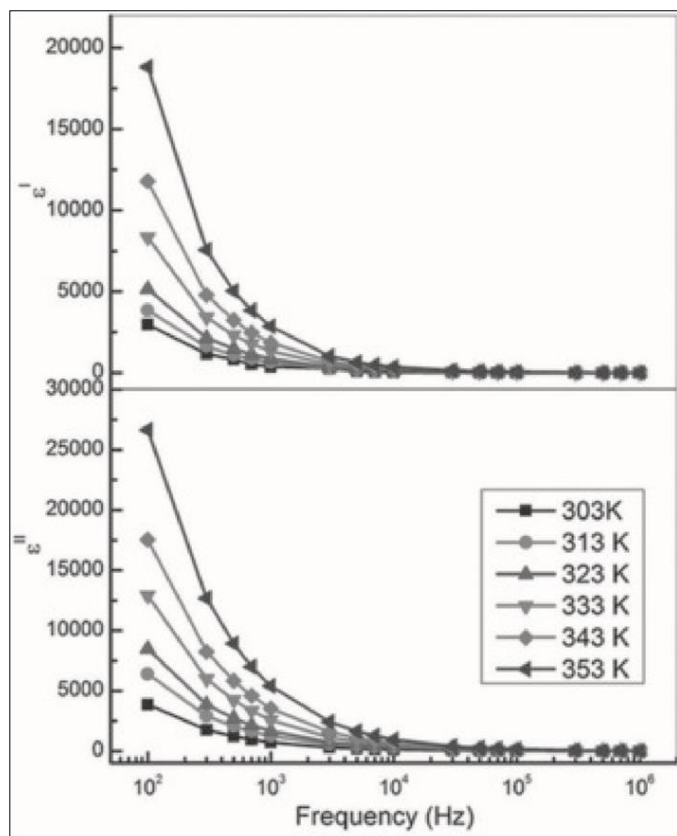


Fig 4: Frequency Dependent Spectra of Real Part (ϵ') and Loss (ϵ'') of Dielectric

Permittivity of Polyethylene Oxide-lithium Perchlorate System at Different Temperatures

From Figure 3, the dispersion in SPE films was identified at high frequency region. At low frequency region, SPE films are not showing any dispersion. In the low frequency region, the EP effect is dominated and hence M' and M'' values are found close to zero which is because of the product $M^*(\omega)$. $\epsilon^*(\omega) = 1$. The small value of M' in the low frequency region represents the ion migration type of conduction.

In general, the imaginary modulus spectra of the ion conducting electrolyte show a peak in the high frequency region corresponding to the ionic conductivity relaxation process [18]. However, in the case of a PEO-LiClO₄ electrolyte system, the peaks in the M' spectra does not appear in the measured upper limit of the frequency range. With an increase of temperature of the SPE, the M' and M'' dispersion have shifted toward higher frequency side, which tells that the ionic conduction relaxation is thermally activated with the hopping of charge carriers.

3.4. AC Conductivity Analysis

AC ionic conductivity (σ_{ac}) of PEO-LiClO₄ SPE film at a different temperature is shown in Figure 4.

The σ_{ac} values indicate a progressive rise in ac conductivity with increase in frequency up to a certain frequency and then it remains almost steady. In the high frequency region, the PEO-LiClO₄ electrolytes follow the Jonscher's universal power law [19].

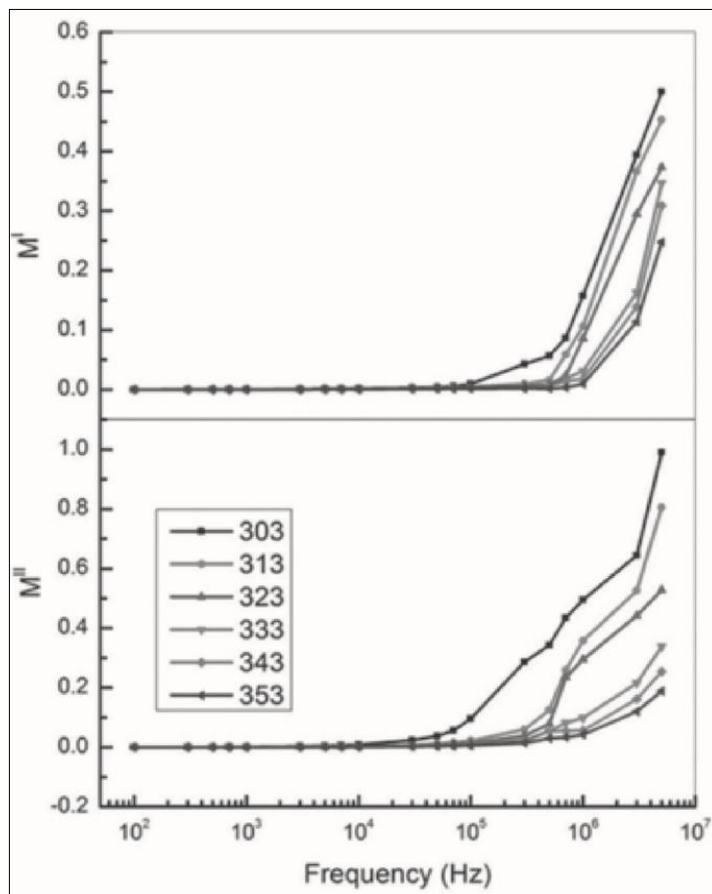


Fig 5: Frequency Dependent Spectra of Real Part (M') and loss (M'') of Complex Electric

Modulus of Polyethylene Oxide-Lithium Perchlorate System at Different Temperatures

$$\sigma(\omega) = \sigma_{dc} + A \omega^{n_1} + B \omega^{n_2} \quad (8)_{ac}$$

Where, A is pre-exponential function and n is the fractional exponent which varies between 0 and 1. In the present study, it is noticed that there are two linear regions with frequency. The low frequency region (Region I) up to 30 KHz with the exponent values represented by n1. While the high frequency region is denoted as Region II described by the second exponent n2. The two slopes indicate that the conduction takes

place due to two different hopping frequencies. Choudhary and Sengwa [14] have reported that hopping conduction is universal. The n value physically represents the strength of ion-ion and ion-dipolar interactions [20].

The calculated exponents n1 and n2 in low and higher frequency regions are tabulated in Table 1. At high frequency region, the n values of electrolyte film increase with temperature. This weakens ion-ion and ion-dipolar interactions and increases polymer segmental motion of SPE films. The n values of the electrolytes are observed to be less than one suggesting the ion transportation is happening through hopping mechanism [18].

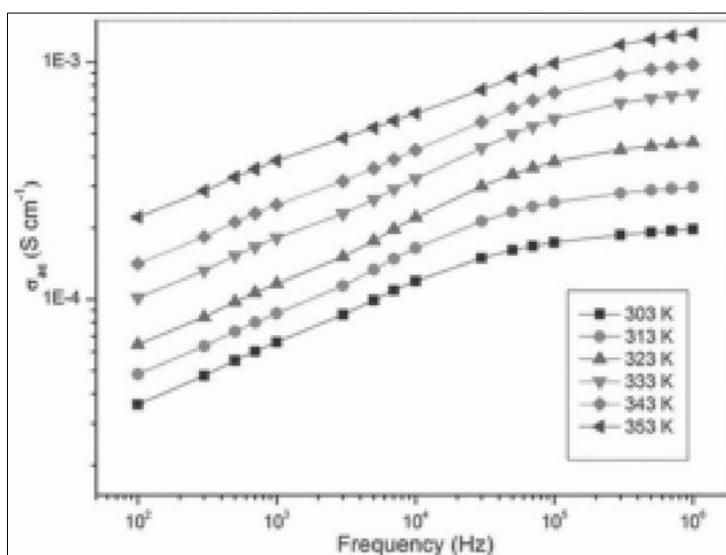


Fig 6: Variation of ac Conductivity with Frequency of Polyethylene Oxide-Lithium Perchlorate at Different Temperatures

4. Conclusions

The polymer electrolyte based on PEO-LiClO₄ has been prepared by solution casting method. The magnitude of ionic conductivity increased with the increase of temperature. The decrease in dielectric permittivity with frequency is described to polar nature of the sample. Large magnitudes of ϵ' and ϵ'' values are observed in the low frequency region is due to EP effect. From a study of electric modulus spectra, ionic conduction relaxation is thermally activated with the hopping of charge carriers. The ac conductivity follows Jonscher's universal power law in the higher frequency region with a small deviation in the EP dominated low frequency region.

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