Transport and Diffusion Properties in PEO-BaCl₂ Polymer Electrolytes for Battery Applications

Rohan N Sagar¹, V. Ravindrachary¹, Shreedatta Hegde¹, Guruswamy B¹

¹Department of Physics, Mangalore University, Mangalagangothri – 574199, India

*Corresponding author: vravi2000@yahoo.com

Abstract: Barium chloride (BaCl₂) doped polyethylene oxide (PEO) based solid polymer electrolyte (SPE) films are prepared using solution cast technique. Impedance analysis reveals that the ionic conductivity of pure PEO polymer enhances with frequency as well as BaCl₂ concentrations, the maximum ac - ionic conductivity (1.09 X 10⁻⁴ Scm⁻¹) is observed at 10 wt% BaCl₂ doped PEO polymer electrolyte films at high frequency. The temperature dependent conductivity studies were carried out for 10 wt% of BaCl₂ concentration, here the maximum dc - ionic conductivity achieved is 1.44 X 10⁻² Scm⁻¹ at 333K temperature. From transport properties, it is observed that the transference number of ions in the polymer electrolyte system is 0.98 and electronic transference number are 0.019. Hence ions are the majority charge carriers than the electrons in BaCl₂ doped PEO based solid polymer electrolytes. Diffusion coefficient study confirms the cations play a major role for the conduction mechanism with in the electrolyte system.

1. Introduction

Recent studies reveals that the usefulness of solid polymer electrolytes (SPE’s) in electrochemical/electrochromic device applications and to develop novel materials owing to the ever growing demand for high performing and high energy storage devices such as rechargeable batteries, super capacitors and electrochromic display devices. Generally solid polymer electrolyte (SPE’s) films consists multiphase combination comprising of crystalline and amorphous phases augmented from the uncomplexed polymer crystalline phase as well as polymer salt complexes. One of the most influential advantage of these SPE’s are of ease of fabrication and low cost to reach large scale demand in technological field. Precise attention is focused on the modifications in structural and ionic conductivity properties of PEO polymer due to doping. It is known that the ionic conduction in electrolyte films takes place in the amorphous phase of polymer matrix which can be affected through many factors, such as preparation methods, salt species and temperature as well as salt concentrations. Polymers contains free volumes also called cavities or holes which are of molecular dimensions arises due to the irregular molecular packing in amorphous phase of the polymers. These irregularities in polymer matrix will affects the electrical, thermal and mechanical properties, which can be altered by doping with organic/inorganic salts to the polymer, here dopant provides additional sites for mobile charge carriers to hop from one coordinating site to another. As the dopant concentration raised, the molecules begins to bridging the gap between the localised sites and reduces the potential barrier between those sites, which facilitates the maximum charge carriers to transfer between them. It is considered that the ionic conduction is mainly due to the hoping of ions between the coordinating sites and by polymer chain segmental motion. Hence the conductivity of a polymer can be tuned by adding proper ratio of dopants and by suited method of preparing solid polymer electrolytes [1]. PEO is a
semicrystalline polymer, having single helical structure which supports the ions transfer process actively within the polymer matrix and shows good complexation with most of the organic and inorganic salts, PEO constituted of ether oxygen atoms in its chains, which can abundantly coordinates with metal ions. PEO exhibits poor conductivity in its pristine form, hence it can be enhanced by doping with suitable dopants which results in the chemical modifications occurs between the polymer and dopants by inter/intramolecular interaction between dopant and the ether oxygen groups of PEO [2]. Barium chloride is an inorganic compound with molecular formulae BaCl₂, it has large Ba²⁺ ions (divalent) which may provide additional sites for ion migration, thus the enhancement in ionic conductivity within the electrolyte system is observed.

In the present study, the variation of ionic conductivity in BaCl₂ doped PEO solid polymer electrolyte is studied by using impedance analysis and ion transference number is estimated by Wagner’s polarization technique.

2. Experimental
Polyethylene oxide (PEO) (mw: 600,000 g/mol) was obtained from M/s. Sigma Aldrich, Bangalore, Barium Chloride (BaCl₂) (mw: 244.28 g/mol) from Glaxo, Mumbai. Pure and BaCl₂ doped PEO polymer electrolyte films were prepared using solution cast technique using Methanol as solvent. The impedance analysis and AC – ionic conductivity measurements were performed using Agilent 4294A Precision Impedance Analyser with the frequency range 40 Hz-5 MHz for the prepared electrolyte films by configuring Ag/PEO-BaCl₂/Ag. The transport properties in BaCl₂ doped PEO polymer electrolyte films were carried out using Keithley-236 source measuring unit.

3. Results and Discussion

3.1 Impedance Analysis

![Figure 1: a) Nyquist plot of pure PEO and PEO-BaCl₂ (1, 3, 5, 7 and 10%) polymer electrolyte films, b) Temperature dependant Niquist plot for 10 wt% of BaCl₂.](image-url)

The real and imaginary part of complex impedance (Nyquist plot) plots for pure and BaCl₂ doped PEO polymer are shown in figure 1(a). From the figure it is clear that a semicircle observed at high frequency region is due to the bulk response of electrolyte films. Here the ionic movement takes place through free volumes of amorphous phase which can be resembles the resistive part and the static polymer chains become polarized which resembles the capacitive part of the electrolyte in the presence of alternating field. The parallel combination of the ionic motion and the bulk polarization gives the broadened semicircle and
the tail at low frequency region is due to accumulated double layer charge carriers at electrode and electrolyte interface. The intercept of semicircle and the spike line gives the bulk resistance ($R_b$); using the measured surface area ($A$) and thickness of the sample ($d$), dc – ionic conductivity of polymer electrolyte films were calculated applying the equation,

$$\sigma = \frac{d}{R_b A}$$

From the figure 1(a) it is observed that the semicircle decreases gradually with increase in dopant concentration and at 5 wt% BaCl$_2$ concentration the observed spike line is less than 90$^\circ$. This behaviour indicates that the capacitive part of electrolyte increases due to inhomogeneity in electrode/electrolyte interface. This feature is mainly attributed to the random distribution of dopant and hence the dipoles within the polymer, as a result resistive part is dominating at this composition which leads to the decrease in ionic mobility within the electrolyte system. After 5 wt% of BaCl$_2$ (10 wt%) concentration semicircle is vanishes indicating the resistive component is decreases and the capacitive part is small enough to hop ions from one conducting site to another. Apart from this in the presence of applied electric field, created dipoles are orient themselves within the polymer chains which leads to the increase in flexibility of polymer backbone chains.

As a result, the ionic mobility through polymer chain segmental motion increases and hence the ionic conductivity increases at higher dopant concentration. The maximum conductivity achieved for higher BaCl$_2$ concentration (10 wt%) is $\sigma = 8.07 \times 10^{-3}$ Scm$^{-1}$ at ambient temperature. To understand the ionic mobility within the electrolyte films temperature dependent conductivity study has been conducted for 10 wt% BaCl$_2$ concentration and observed results are given in figure 1(b). Here the figure shows the 10 wt% dopant concentration for 303 K (inset), here the observed $R_b$ value is 520.44 $\Omega$ and its value decreases with increase in temperature. Finally it is observed that the semicircle disappears at 333 K and $R_b$ value reduced to 101.05 $\Omega$. The observed spike bending towards imaginary axis shows that the electrolyte is less resistive at high temperature and the total conductivity in polymer electrolyte is mainly due to the ions. The ionic conductivity is mainly due to the ionic mobility that takes place through the polymer chains in the free volumes which leads to the enhancement of conductivity in the electrolyte system [2] and the maximum dc – ionic conductivity achieved is 4.7 $\times 10^{-2}$ Scm$^{-1}$ at 333 K.

3.2 Ionic Conductivity Studies

![Figure 2](image_url)

**Figure 2:** a) log $\sigma$ vs log$f$ of PEO-BaCl$_2$(0,1,3,5,7 and 10 wt%)polymer electrolyte films, b) variation of ac conductivity of 10 wt% BaCl$_2$-PEO polymer electrolyte films at different temperature, c) log $\sigma_{dc}$ vs 1000/T (K$^{-1}$)
Using the measured value of dielectric parameters conductivity of the sample is estimated using the equation

\[ \sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta \]  \hspace{1cm} (2)

where \( f \) – the applied frequency, \( \varepsilon_r \) – permittivity of free space, \( \varepsilon_r \) – dielectric constant and \( \tan \delta \) – dielectric loss. Figure 2(a) shows the ac-conductivity as a function of angular frequency for pure and BaCl\(_2\) doped PEO polymer electrolyte films. The observed ac–conductivity spectra reveals two distinct regions: a low frequency dispersion region (frequency independent) corresponding to dc – conductivity, arises due to the space charge polarization at blocking electrodes. The high frequency plateau region (frequency dependent) occurs due to the hopping of ions between the nearest coordinating sites. From the conductivity plot it is observed that the conductivity varies with frequency, the change in conductivity is due to the interatomic interaction between the polar groups of PEO and BaCl\(_2\) through hydrogen bonding. The return results in the structural modifications including microcrystalline domains occurs within the polymeric network and forms charge transfer complexes (CTC’s). The formed CTC increases the charge carrier concentrations as the dopant concentration increases, which are evident with the FTIR and XRD results as explaind in literature [3], hence the enhancement in conductivity is observed in BaCl\(_2\) doped PEO polymer electrolyte. As the frequency raises, the bonds present in the polymer starts rotating with applied frequency. Thus the polymeric chain becomes more flexible, as a result rapid motion of ions takes place through the amorphous phase of the electrolyte system. Hence the conductivity of electrolyte system increases with frequency, the maximum ac - ionic conductivity observed is 1.09 X 10\(^{-4}\) Scm\(^{-1}\) at 10 wt% BaCl\(_2\) doped PEO polymer electrolyte system. The high conducting polymer electrolyte sample is further studied with different temperatures as a function of frequency, which is depicted in figure 2(b). The variation of ionic conductivity as a function of frequency at different temperatures follows Jonscher’s universal power law.

\[ \sigma_{ac} = \sigma_{dc} + A\omega^s \]  \hspace{1cm} (3)

Where \( \sigma_{dc} \) – DC conductivity and is obtained by extrapolating the low frequency region to y-axis (log \( \sigma_{ac} \)), \( A \) – pre-exponential factor and \( s \) – frequency exponent factor ranging from 0 to 1. From the conductance plot it is observed that the conductivity increases with increase in temperature as well as frequency [4]. The increase in ionic conductivity with temperature is interpreted in terms of hoping mechanism, polymer chain segmental motion and local structural relaxation. As the temperature increases the complex sites within the electrolyte system increase, this enables Ba\(^+\) ions to jump from one conducting site to another. Hence the conductivity enhances with temperature and the highest dc - conductivity is observed at 333K, i.e. \( \sigma = 1.44 \times 10^{-2}\) Scm\(^{-1}\). Figure 2(c) shows the Arrhenius plot (dc – conductivity vs temperature inverse) of BaCl\(_2\) (10 wt%) doped PEO polymer electrolyte system. From the plot it is noticeable that the dc conductive conductivity is found to be enhances with temperature. After 313 K, a sudden increase in conductivity is observed, which is attributed to transition of polymer crystalline/semicrystalline phase to amorphous phase upon doping [5]. As a result active ionic motion (interchain hoping mechanism) takes place through the free volumes of amorphous phase, thus the high dc – ionic conductivity is observed at 333 K. The enhancement of ionic mobility (active ionic motion) within the electrolyte system can be further comprehended in transport mechanism.

3.3 Transport Properties
To understand the ion transport phenomenon within the SPE’s, a fixed dc-voltage (1V) is applied across the electrodes embedded within and the dc polarization current is monitored as the function of time. The transport mechanism depends on many factors such as dopant species, ionic mobility and salt segregation with in the polymer matrix. The transference number in 10 wt% BaCl\(_2\) doped PEO polymer electrolyte film is evaluated using Wagner’s polarization technique, the corresponding ionic (t\(_i\)) and electronic (t\(_e\)) transport numbers are calculated using the equation,
\[ t^- = I_i - I_f / I_i \quad \text{and} \quad t^+ = I_f / I_i \] (4)

Where \( I_i \) - initial current and \( I_f \) - final residual current. Figure 3 shows the plot of polarization current as a function of time for 10 wt% BaCl₂ doped PEO polymer electrolyte. From the plot it is observed that, as time initiates the current decreases and after few minutes it attains a linear steady state, this is because when a constant voltage is applied the ions get migrated towards respective electrodes. Once the ions get polarized completely, then the observed current conduction is due to electrons only. The total ion transference number in BaCl₂ doped PEO polymer electrolyte system is 0.98 and total electron transference number is 0.019. These observed results suggest that the ions are the majority charge carriers for the conduction process and electronic contribution is negligible in the BaCl₂ doped PEO solid polymer electrolyte system.

3.4 Diffusion Coefficient

The total ionic mobility in solid polymer electrolyte system can be divided into cationic and anionic mobility. It is difficult to determine the exact mobility of charge carriers in the polymer electrolyte system, because most of them are bounded to ion pairs. These can be estimated by using following equations, the diffusion coefficient and mobility of ions in polymer electrolyte are calculated using,

\[ D = kT\sigma / ne^2 \] (5), \[ \mu = \sigma / ne \] (6)

Where, \( k \) – Boltzmann constant, \( T \) – temperature, \( \sigma \) – ionic conductivity, \( n \) – number molecules present in cm⁻³ and \( e \) – charge of electron. The total calculated ionic mobility is \( 6.33 \times 10^{-7} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1} \), the diffusion coefficients (\( D^+ \) and \( D^- \)), cationic (\( \mu^+ \)) and anionic (\( \mu^- \)) mobility for PEO-BaCl₂ polymer electrolyte system are determined using equations described in literature [6] and are listed in table 1,

Table 1: Transference number, ionic mobility and diffusion coefficient of 10 wt% BaCl₂ doped PEO polymer electrolyte.

| Weight ratio | \( t^- \) | \( t^+ \) | \( \mu^+ \) (cm² v⁻¹ s⁻¹) | \( \mu^- \) (cm² v⁻¹ s⁻¹) | \( D^+ \) (cm² s⁻¹) | \( D^- \) (cm² s⁻¹) |
|--------------|----------|----------|-----------------------------|-----------------------------|----------------|----------------|
| 10 wt% BaCl₂ | 0.98     | 0.019    | 6.203 \times 10^{-7}       | 0.127 \times 10^{-7}       | 1.617 \times 10^{-9} | 0.033 \times 10^{-9} |
If the mobility of ions increased then the ionic conductivity of electrolyte system also increases, similar behaviour is observed in cationic diffusion coefficient \((D^+\)) From Table 1, it is observed that the ions are the majority charge carriers within the electrolyte system. The increased cationic mobility \((\mu^+)\) and cationic diffusion coefficient \((D^-)\) reveals that the ionic conductivity is strongly influenced by cationic motion and diffusion coefficient of cations within electrolyte system. Hence the ionic conduction in BaCl\(_2\) doped PEO polymer electrolyte is strongly due to cations.

**Acknowledgement**
Authors are grateful to Microtron centre, Mangalore University for providing electrical conductivity studies.

**References**
[1] E. M. Fahmi, A. Ahmad, N. N. M. Nazeri, H. Hamzah, H. Razali, M. Y. A. Rahman, Int. J. Electrochem. Sci 7 (2012)5798-5804.
[2] K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V. V. R. Narasimha Rao, Physics B 406 (2011)1706-1712.
[3] Rohan N Sagar, V. Ravindrachary, B. Guruswamy, Shreedatta Hegde, S. D. Praveena, Res. J. Physical Sci 5(2) (2017)5-7.
[4] N. Rajeshwari, S. Selvasekarapandian, S. Karthikeyan, H. Nithya, C. Sanjeeviraja, Int. Journal of polymeric materials 61 (2012)1164-1175.
[5] Nadimicherla Reddappa, A. K. Sharma, V.V.R. Narasimha Rao, Wen Chen, Measurement 47(2014)33-41.
[6] Kingslin Mary Genova Francis, Selvasekarapandian Subramanian, Karthikeyan Shunmugavel, Vijaya Naranappa, Sivadevi Soundra Murugesan Pandian, SanjeevirajaChinnappanadar, Polymer-Plastics Technology and Engineering 55 (2016) 25-35.