



# Mg-ion conducting blend polymer electrolyte based on poly(vinyl alcohol)-poly (acrylonitrile) with magnesium perchlorate



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## ABSTRACT

Research on magnesium battery has gained momentum in recent years due to its high stability and hazardous free nature. For such batteries solid polymer electrolyte films have been prepared using blend polymer technique with the polymers polyvinyl alcohol (PVA) & polyacrylonitrile (PAN) (92.5PVA:7.5PAN) and  $\text{Mg}(\text{ClO}_4)_2$  of different molar mass percentage (m.m.%) as 0.05%, 0.1%, 0.15%, 0.2%, 0.25% and 0.3% by solution casting technique using DMF as solvent. The XRD results confirms that the incorporation of magnesium salt ( $\text{Mg}(\text{ClO}_4)_2$ ) which reduces the crystallinity of blend polymer (92.5PVA:7.5PAN). FTIR has been carried out to study the complex formation between the blend polymer and salt. AC impedance spectroscopy has been used to examine the ionic conductivity and dielectric behaviour of the blend polymer electrolyte (BPE). The maximum ionic conductivity of  $2.96 \times 10^{-4} \text{ S/cm}$  has been observed for the sample 92.5PVA:7.5PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  at room temperature for which the activation energy measured is minimum (0.21 eV). Electrochemical studies show that highest conducting BPE has the highest electrochemical stability. Transference number measurement confirms that the conducting species are  $\text{Mg}^{2+}$  ion. Primary magnesium battery has been constructed with maximum conducting electrolyte system and its discharge characteristics have been studied.

## 1. Introduction

Today's rapid development of portable electrochemical devices mainly mobile phones, laptops, tablets and notebook computers have been remarkable in the last decade, which increases the demand of high energy batteries. Due to high specific capacity and excellent cyclic stability lithium ion is incorporated in fabrication of commercially available batteries [1–3]. At the same time, lithium ion batteries are relatively expensive and suffer from safety limitations due to their explosive nature. Hence for future technological attention, we need rechargeable batteries with significant increase in energy density, cost effectiveness, low toxicity, ease of handling, and safer than lithium. This huge expectation in the battery industry leads to develop magnesium battery whose performance characteristic is closer to that of lithium counter parts [4–6]. Magnesium (Mg) is an ideal metal anode that has nearly double the volumetric capacity of lithium metal with many advantages such as (i) negative reduction potential of  $-2.37 \text{ Vs}$  standard hydrogen electrode (SHE) (ii) apparent lack of dendrite

formation during charging, which overcomes major safety and performance challenges encountered with lithium metal anodes [7] (iii) high melting point ( $649^\circ\text{C}$ ) (iv) low cost and (v) substantial abundance in nature. Despite the practical use of Mg batteries, development of rechargeable Mg batteries has been retarded by two problems (i) difficulties in the reversibility of the Mg negative electrode and (ii) lack of appropriate nonaqueous media that conduct  $\text{Mg}^{2+}$  species [8].

Over the past 40 years, the polymer electrolyte has been studied widely due to its high compliance, mouldability, processability, good electrode-electrolyte contact and high ambient temperature conductivity. These features permit the polymer electrolyte for the development of thin batteries with design flexibility for electrochemical devices. Various methods has been performed to improve the ionic conductivity and mechanical strength of the polymer electrolyte, which includes synthesizing new polymer [9]; Use of cross linking two polymers [10]; Blending of two polymers [11]; adding plasticizers to polymer electrolytes [12]; adding inorganic inert fillers [13] to make composite polymer electrolytes.

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In the present work, investigations have been focused primarily on polymer blends, which are the most promising and feasible approach because of easy for preparation and control the physical properties within the compositional regime. Blend polymer electrolytes (BPE) are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible to the molecular level. Through polymer blending properties of the final product can be tailored to the requirement of applications, which cannot be achieved alone by one polymer. However, the film properties depend on the miscibility of blend. The polymer–polymer miscibility may arise from any one of the interactions such as hydrogen bonding, dipole–dipole forces and charge transfer complexes for homopolymer mixtures [14–19]. Many researchers have reported on BPE systems such as PVA/PVP, PVA/PMMA, PAN/PEO, PVA/PAN with ammonium nitrate, lithium tetrafluoroborate, lithium triflate, lithium perchlorate respectively [20–23], etc., The literature review reveals that very little attention has been given to the polymer electrolytes based on PVA–PAN blend in which multivalent cations as the mobile species. Magnesium perchlorate  $\text{Mg}(\text{ClO}_4)_2$  is the fast conducting salt in a number of crystalline and amorphous materials, its incorporation in a polymeric system is expected to have more complexation with the polymer due to its large anions [24].

Polyvinyl alcohol (PVA) is a semicrystalline polymer, studied extensively because of its many interesting physical properties, such as high dielectric strength (1000 kV/mm), good charge storage capacity, dopant dependent electrical and optical properties which arise from the presence of OH groups and the hydrogen bond formation [20].

Polyacrylonitrile (PAN) is a synthetic organic polymer or copolymer of acrylonitrile which are mostly used to make fibers for fabrics. PAN has been extensively studied due to its semicrystalline nature, electrochemical stability, good chemical and flame resistance [25]. The choice of PAN as a host polymer has been first reported by Reich and Michelai [26]. Both polymers PVA and PAN are having a good charge storage capacity and dopant dependent electrical and optical properties. When these two polymers are mixed, the interactions between PVA and PAN are expected to occur through interchain hydrogen bonding. PVA–PAN is a potential material having good charge storage capacity and dopant dependent electrical and optical properties [27].

Siva devi et al., carried out a study on PVA–PAN based BPE and optimized the conductivity of 92.5PVA:7.5PAN as  $1.13 \times 10^{-7} \text{ Scm}^{-1}$  [28]. There have been some studies on this BPE based on ammonium and lithium salts [27,29–31]. As far as the knowledge of the author, literature survey reveals that in the electro chemical device applications, there has been minimum work on PVA/PAN BPE doped with magnesium salts. Hence the present work investigate the effect of  $\text{Mg}(\text{ClO}_4)_2$  of different ratios in the BPE system with the aim of obtaining improved ionic conductivities compared with pure blend (92.5PVA:7.5PAN). As in this research, the initial approach to suppress the high crystallinity is done by the dissociation of  $\text{Mg}(\text{ClO}_4)_2$  in 92.5PVA:7.5PAN matrix forming free ions, which could give high ionic conductivities to BPE films. These films have been characterized by means of various physical techniques, namely, X-ray diffraction, thermal analysis, infrared spectroscopy, complex impedance analysis, conductivity, linear sweep voltammetry and transport number measurements. The BPE is found to be a thermally and electrochemically stable material for application in power sources such as magnesium batteries.

## 2. Materials and methods

### 2.1. Materials

Polyvinyl alcohol (PVA) with an average molecular weight of 1,24,000 from Sd fine-chem Ltd., Polyacrylonitrile (PAN) with an average molecular weight of 1,50,000 from Sigma Aldrich and Magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ) of molecular weight 223.21 g/mol

from Himedia were used without any further purification to prepare the blend polymer electrolytes. Dimethyl formamide (DMF) with molecular weight 73.08 g/mol, density = 0.948–0.949  $\text{kg/m}^3$  from Merck specialties private Ltd., has been used as solvent.

### 2.2. Preparation of polymer electrolyte films

Blend polymer electrolyte (BPE) films were prepared using solution casting technique. BPE's of various salt concentration 0.05%, 0.1%, 0.15%, 0.2%, 0.25% and 0.3% molar mass percentage (m.m.%) have been prepared with optimized composition 92.5PVA:7.5PAN of the blend polymer. Initially PVA was added to the solvent at 60 °C and stirred continuously until the complete dissolution of the polymer. Then appropriate quantity of PAN was added to the solution and allowed to stir continuously to get a clear solution. Magnesium salt of various m.m.% (0.05%, 0.1%, 0.15%, 0.2%, 0.25% and 0.3%) was added to the solution. The resulting solution were poured over polypropylene petridishes separately and kept in vacuum oven at 60 °C for two days to remove excess solvent present in the sample. Free standing composite films of thickness 130 – 140  $\mu\text{m}$  were obtained.

### 2.3. Characterizations

The amorphicity of blend polymer electrolyte (BPE) has been investigated using XRD. The XRD patterns of the films were recorded at room temperature by X'pert pro diffractometer system using the Cu-K $\alpha$  radiation in the range of  $2\theta = 10^\circ\text{--}80^\circ$ . The complex formation between the chemical constituents of the blend polymer (PVA–PAN) and the salt has been analyzed by using FTIR. FTIR spectrum of the films were recorded in the wavenumber range 3500–650  $\text{cm}^{-1}$  at room temperature using SNADZY-IR Affinity-1 spectrophotometer. The ionic conductivity of BPE membranes was measured by AC impedance spectroscopy analyser HIOKI 3532 in the range of 42 Hz–1 MHz with various temperatures from 303 K to 343 K. The thermal behaviors of the polymer electrolytes were examined by differential scanning calorimetry (DSC) using Perkin Elmer DSC 4000. The total ionic transport number  $t_{\text{ion}}$  was obtained by the d.c. polarization technique [32]. The  $\text{Mg}^{2+}$  ions transport number of maximum conducting electrolyte 92.5PVA:7.5-PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  was evaluated using a combination of AC impedance spectroscopy and DC polarization studies on a Mg/BPE/Mg cell as described by Evans et al. [33]. The electrochemical stability of the maximum conducting electrolyte was evaluated by means of linear sweep voltammetry using stainless steel as the working electrode and Mg disc as combined counter and the reference electrodes. Using the highest conducting BPE a magnesium battery has been constructed and their results are discussed.

## 3. Results and discussion

### 3.1. X-ray diffraction analysis

XRD is a significant tool to study the amorphous/crystalline nature of the polymer matrices. As the ions can freely move in amorphous phase due to low energy barriers, greater ionic diffusivity occurs and hence the conductivity increases [34]. The effect of complexation of  $\text{Mg}(\text{ClO}_4)_2$  with 92.5PVA:7.5PAN system has been investigated using XRD analysis. Fig. 1 represents the XRD pattern of undoped blend polymer electrolyte and doped blend polymer electrolyte with salt of different m.m.%. The broad peaks observed at  $2\theta = 20.3^\circ$  and  $40.8^\circ$  in the pure BPE is ascribed to pure PVA [27]. Addition of salt of different m.m.% decreases the intensity and makes the hump broader and flatter proving that the degree of amorphicity increases for blend polymer electrolytes. This could be due to the disruption of the long range ordering of PVA: PAN chains by  $\text{Mg}(\text{ClO}_4)_2$  salt. Hodge et al. [35] established a correlation between the intensity of the peak and the degree of crystallinity. The peak intensity was observed to be minimum for the

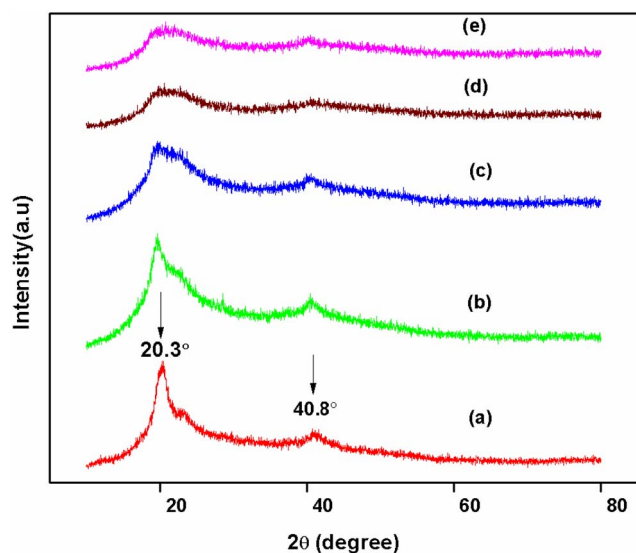


Fig. 1. XRD patterns of BPE (a) 92.5PVA:7.5PAN (b) 92.5PVA:7.5PAN:0.1 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN:0.2 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (d) 92.5PVA:7.5PAN:0.2 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> and (e) 92.5PVA:7.5PAN:0.3 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub>.

polymer complex 92.5PVA:7.5PAN:0.25 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub>, showing high degree of amorphicity which is in reliable with the conductivity result. From the XRD spectra it is evident that, when the salt concentration is > 0.25 m.m.% of Mg(ClO<sub>4</sub>)<sub>2</sub>, an increase in the intensity of the peak was observed at 20.3°. This suggests that the intercalated Mg<sup>2+</sup> ion swells the crystalline PVA-PAN [36]. Furthermore no separate peaks corresponding to Mg(ClO<sub>4</sub>)<sub>2</sub> were seen in the spectra indicating the better dissolution of Mg(ClO<sub>4</sub>)<sub>2</sub> in 92.5PVA:7.5PAN system and hence the complex formation between PVA-PAN and Mg(ClO<sub>4</sub>)<sub>2</sub>.

### 3.2. Fourier transform infrared analysis

FTIR analysis is a powerful tool to investigate the complex formation between the host polymer 92.5PVA:7.5PAN and the dopant Mg(ClO<sub>4</sub>)<sub>2</sub>. The interactions among atoms or ions in electrolyte system induce changes in the vibrational modes of the molecules. The FTIR spectra of pure 92.5PVA:7.5PAN along with the doped BPE's are shown in the Fig.2 and their spectral band assignments are listed in the

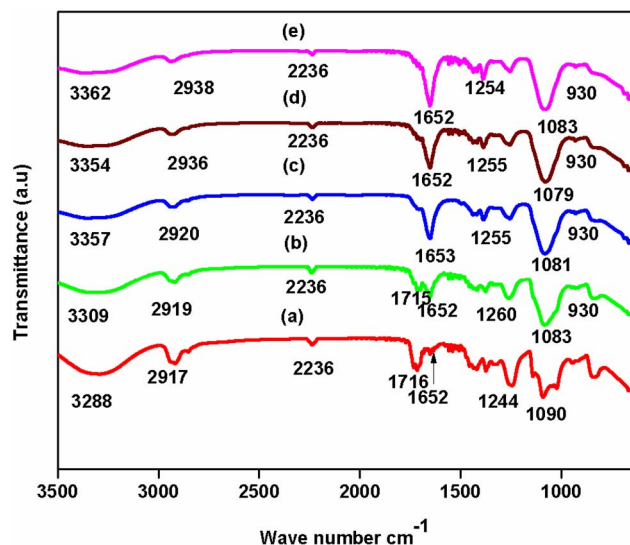


Fig. 2. FTIR spectra of BPE's (a) 92.5PVA:7.5PAN (b) 92.5PVA:7.5PAN:0.1 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN:0.2 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (d) 92.5PVA:7.5PAN:0.25 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> and (e) 92.5PVA:7.5PAN:0.3 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub>.

Table 1.

The peak at 3288 cm<sup>-1</sup> in pure 92.5PVA:7.5PAN blend is ascribed to hydroxyl group (O–H) stretching of pure PVA. Coates et al. and Awadhia and Agarwal et al., have mentioned that OH stretching occurs at 3615–3050 cm<sup>-1</sup> [37,38]. The absorption peak at 2917 cm<sup>-1</sup> in the blend polymer attributes to CH<sub>2</sub> asymmetric stretching of PVA [39]. The band at 2236 cm<sup>-1</sup> in the blend is assigned to the stretching vibration of nitrile (C≡N) group of PAN [40]. The band appearing at 1716 cm<sup>-1</sup> corresponds to C=O stretching in the BPE system [41]. The CH<sub>2</sub> bending, C–O–C symmetric and C–C asymmetric vibrations of the blend are observed at 1419 cm<sup>-1</sup>, 1244 cm<sup>-1</sup> and 1090 cm<sup>-1</sup> respectively [30]. The sharp band at 1652 cm<sup>-1</sup> in pure blend electrolyte is observed due to C=C stretching of PAN [42]. The observed FTIR peaks position and intensity (3288 cm<sup>-1</sup>, 2917 cm<sup>-1</sup>, 1716 cm<sup>-1</sup>, 1419 cm<sup>-1</sup>, 1244 cm<sup>-1</sup>, 1090 cm<sup>-1</sup> and 1652 cm<sup>-1</sup>) have been shifted due to the addition of 0.1, 0.2, 0.25 and 0.3 m.m.% of Mg(ClO<sub>4</sub>)<sub>2</sub>. The calculated vibrational frequencies for the pure BPE have been shifted due to the addition of Mg(ClO<sub>4</sub>)<sub>2</sub>, which indicates that the Mg(ClO<sub>4</sub>)<sub>2</sub> group affects the vibrational mode of PVA: PAN and confirms the complex formation between 92.5PVA:7.5PAN and Mg(ClO<sub>4</sub>)<sub>2</sub>.

Due to the addition of Mg(ClO<sub>4</sub>)<sub>2</sub> from 0.1 to 0.3 m.m.%, the intensity of the band at 2236 cm<sup>-1</sup> assigned to the stretching vibration of nitrile (C≡N) has been reduced to 80% compared to undoped 92.5PVA:7.5PAN electrolyte. It is the most characteristic band of pure PAN [43,44]. The peak absorbed at 930 cm<sup>-1</sup> in all the BPE's is ascribed to the symmetric stretching of the free anion ClO<sub>4</sub><sup>-</sup> ion which remains the same in all the compositions. This result indicates the coordination of ClO<sub>4</sub><sup>-</sup> ion with the polar group present in the polymer of the polymer complexes [45]. When the salt Mg(ClO<sub>4</sub>)<sub>2</sub> of different concentrations are doped with the pure 92.5PVA:7.5PAN blend the hydroxyl band peaks at 3288 cm<sup>-1</sup> gets broaden and shifted towards higher wave number in the complexes as shown in Fig. 2. It gives strong indication of interaction of Mg(ClO<sub>4</sub>)<sub>2</sub> and host polymer PVA in the polymer electrolytes. The addition of Mg(ClO<sub>4</sub>)<sub>2</sub> to the sample 92.5PVA:7.5PAN shifts the carbonyl group (C=O) stretching vibration, which implies that strong intermolecular interaction is between magnesium ion from doping salts and oxygen atoms resulting in polymer salt complexes. The oxygen atoms from PVA are expected to act as electron donor atoms and they form co-ordinate bond with magnesium ion from doping salts [46]. The shift in stretching modes of the carbonyl bonds has been seen for the sample with 0.1 m.m.% of salt and disappearance of the peak is seen for rest of the electrolytes which indicates complexation of the polymer.

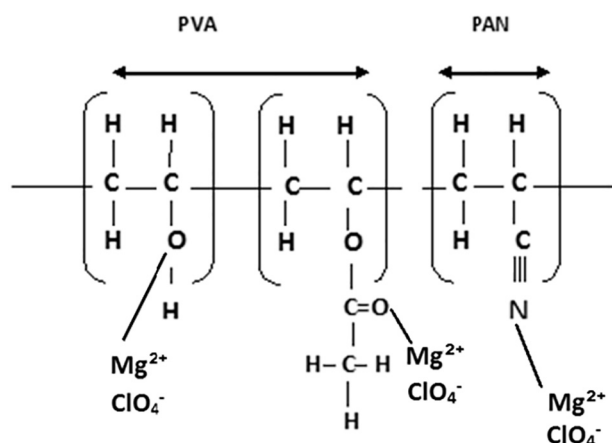
Fig. 3 shows the conduction mechanism of 92.5PVA:7.5PAN/Mg(ClO<sub>4</sub>)<sub>2</sub> complex in magnesium ion battery. The hydroxyl group, carbonyl group, nitrile group and perchlorate interactions between pure BPE and Mg(ClO<sub>4</sub>)<sub>2</sub> implies that the ions are mobile in the system. Ion mobility is important in an electrolyte system as high mobility will favour to high ionic conductivity. This suggests that Mg(ClO<sub>4</sub>)<sub>2</sub> has the potential to function as the charge carrier in the system. A conduction pathway has been proposed to be formed as there will be a weakly bound of Mg<sup>2+</sup> ion, which can be easily dissociated under the influence of electric field. This Mg<sup>2+</sup> ion can hop through the coordinating site of O–H, C=O and C≡N of host polymer and the conduction takes place [47]. Thus, the spectral analysis confirms the complexation and interaction between PVA, PAN and magnesium salt Mg(ClO<sub>4</sub>)<sub>2</sub>.

### 3.3. Differential scanning calorimetry

The Fig. 4 shows the DSC thermograms for BPE's of different salt concentrations 0.15, 0.25, 0.3 m.m.% of Mg(ClO<sub>4</sub>)<sub>2</sub> and the glass transition temperature (T<sub>g</sub>) values are given in the Table 2. The glass transition temperature (T<sub>g</sub>) of the blend polymer 92.5PVA:7.5PAN electrolyte is 136.4 °C [27]. It has been observed that the T<sub>g</sub> of polymer electrolytes with 0.15 and 0.25 m.m.% of salt decreases with the increase in concentration of Mg(ClO<sub>4</sub>)<sub>2</sub>. The decrease in T<sub>g</sub> indicates

**Table 1**  
Vibrational peaks and assignments observed in 92.5PVA-7.5PAN and Mg(ClO<sub>4</sub>)<sub>2</sub> blend polymer electrolyte films.

92.5PVA:7.5PAN	92.5PVA:7.5PAN + 0.1 m.m. % Mg(ClO <sub>4</sub> ) <sub>2</sub>	92.5PVA:7.5PAN + 0.2 m.m. % Mg(ClO <sub>4</sub> ) <sub>2</sub>	92.5PVA:7.5PAN + 0.25 m.m. % Mg(ClO <sub>4</sub> ) <sub>2</sub>	92.5PVA:7.5PAN + 0.3 m.m. % Mg(ClO <sub>4</sub> ) <sub>2</sub>	Assignments
3288	3309	3357	3354	3362	O–H stretching
2917	2919	2920	2936	2938	CH <sub>2</sub> asymmetric stretching
2236	2236	2236	2236	2236	C≡N stretching
1716	1715	–	–	–	C=O stretching
1652	1652	1653	1652	1652	C=C stretching
1419	1419	1437	1436	1437	CH <sub>2</sub> bending
1244	1260	1255	1255	1254	C–O–C stretching
1090	1083	1081	1079	1083	C–C asymmetric stretching vibrations of ClO <sub>4</sub> <sup>–</sup>
	930	930	930	930	



**Fig. 3.** Possible interaction between blend polymer (PVA: PAN) and Mg(ClO<sub>4</sub>)<sub>2</sub>.

increase in mobility of polymer chains [48]. This may be due to plasticization effect of the electrolyte with the addition of salt. The complexation of the electrolyte with 0.25 m.m.% of salt has been found to have a low  $T_g$  of 46.96 °C. The low glass transition temperature causes the higher segmental motion of the polymer electrolyte [49]. However, for 92.5PVA:7.5PAN:0.3 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> the  $T_g$  has been found to increase which may be due to the decrease in amorphous nature of the host polymer matrices. This observed shift in  $T_g$  values of the polymer electrolytes in DSC thermograms indicates the interaction between the polymer and the salt. Polu et al., has reported similar results for 30 m.m.% Mg(NO<sub>3</sub>)<sub>2</sub> doped PVA system. The low values of  $T_g$  attributes to the softening of the complexation by the guest salt which facilitates the magnesium ion transport [50].

### 3.4. AC impedance analysis

#### 3.4.1. Cole - Cole

The ionic conductivity of the polymer electrolyte depends upon many factors such as ionic species concentration, cationic or anionic type carriers, the mobility of charge carriers and the temperature. AC impedance spectroscopy is a significant tool to characterize the electrical properties of a material.

Sivadevi et al., has initially optimized the conductivity value as  $1.2 \times 10^{-7}$  S/cm for the BPE 92.5PVA:7.5PAN [28]. The Fig. 5 represent Cole-Cole plot for the prepared BPE's at room temperature (303 K) along with the equivalent circuit. The plot consist of a high-frequency depressed semicircle represented by a frequency-dependent capacitor  $C_g$  which is mainly due to immobile polymer chains, parallel to a bulk resistor ( $R_b$ ) due to the mobile ions inside the polymer matrix [51]. The low-frequency spike is due to the effect of electrode and electrolyte interface which can be represented by a constant phase element (CPE). As the salt concentration increases the semicircle has

been found to be absent suggesting that only the resistive component of the polymer electrolytes prevails [52].

Electrochemical Impedance Spectroscopy (EIS) parameter of the polymer membrane has been determined from the Cole-Cole plot using EQ software developed by B.A. Boukamp [53,54]. The EIS parameters obtained for the prepared polymer membranes have been tabulated in the Table 3.

Table 3 gives the resistance value of 92.5PVA:7.5PAN as  $2.3011 \times 10^5 \Omega$  whereas for the BPE's with 0.05–0.3 m.m.% of salt, the value of resistance decreases from  $4.698 \times 10^4 \Omega$  to  $9.8 \times 10^1 \Omega$ . The CPE for pure blend was obtained as  $9.5811 \times 10^{-10}$  F whereas for BPE's with 0.05–0.3 m.m.% of salt the CPE value lies in the range of  $7.909 \times 10^{-10}$  F to  $7.1061 \times 10^{-6}$  F. The highest conductivity BPE 92.5PVA:7.5PAN:0.25 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> has  $R_b = 23.757 \Omega$  and  $CPE = 4.4401 \times 10^{-6}$  F.

The ionic conductivity is calculated using the equation

$$\sigma = l/R_b A, \text{ S/cm} \quad (1)$$

where 'L' is the thickness,  $R_b$  is the bulk resistance and 'A' is the surface area of the polymer electrolyte film. The Table 3 indicates the calculated ionic conductivity for BPE's with different salt concentrations at different temperatures. The value shows that the ionic conductivity increases with increase in salt concentration and attains a maximum value of  $2.94 \times 10^{-4}$  S/cm at room temperature for 92.5PVA:7.5PAN:0.25 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub>, which has greater ionic conductivity than that of 92.5PVA:7.5PAN ( $1.30 \times 10^{-8}$  S/cm). This variation of the ionic conductivity and activation energy as a function of Mg(ClO<sub>4</sub>)<sub>2</sub> concentration expressed in m.m.% at room temperature is also shown in Fig. 6. An apparent increase in the conductivity might be due to the combination of high ionic mobility and dissociation constant of the salt. Salts with low lattice energies are easier to dissociate into cations and anions thus enhancing the conductivity [55]. However, the conductivity decreased when > 0.25 m.m.% of salt was added to the 92.5PVA:7.5PAN system. This is most likely due to the aggregation of the ions, leading to the formation of ion clusters which reduces the number of mobile charge carriers [56,57].

#### 3.4.2. Conductance spectra analysis

The logarithmic plots of the conductivity as a function of angular frequency for BPE's with different salt concentration are shown in the Fig. 7. Generally the conductance spectra can be divided into three regions (i) the low-frequency dispersion region which represents the space charge polarization at the blocking electrodes (ii) the frequency-independent plateau region which is on the log  $\sigma$  (y-axis) gives dc conductivity ( $\sigma_{dc}$ ) of polymer complex (iii) the high frequency region which corresponds to the bulk relaxation phenomenon, which is due to the coulombic interaction of charge carrier and disorder within the structure [58]. By extrapolating the plateau region on the log  $\sigma$  axis the dc conductivity values of the BPE's obtained agrees well with values obtained from cole-cole plot. As the frequency decreases, more and

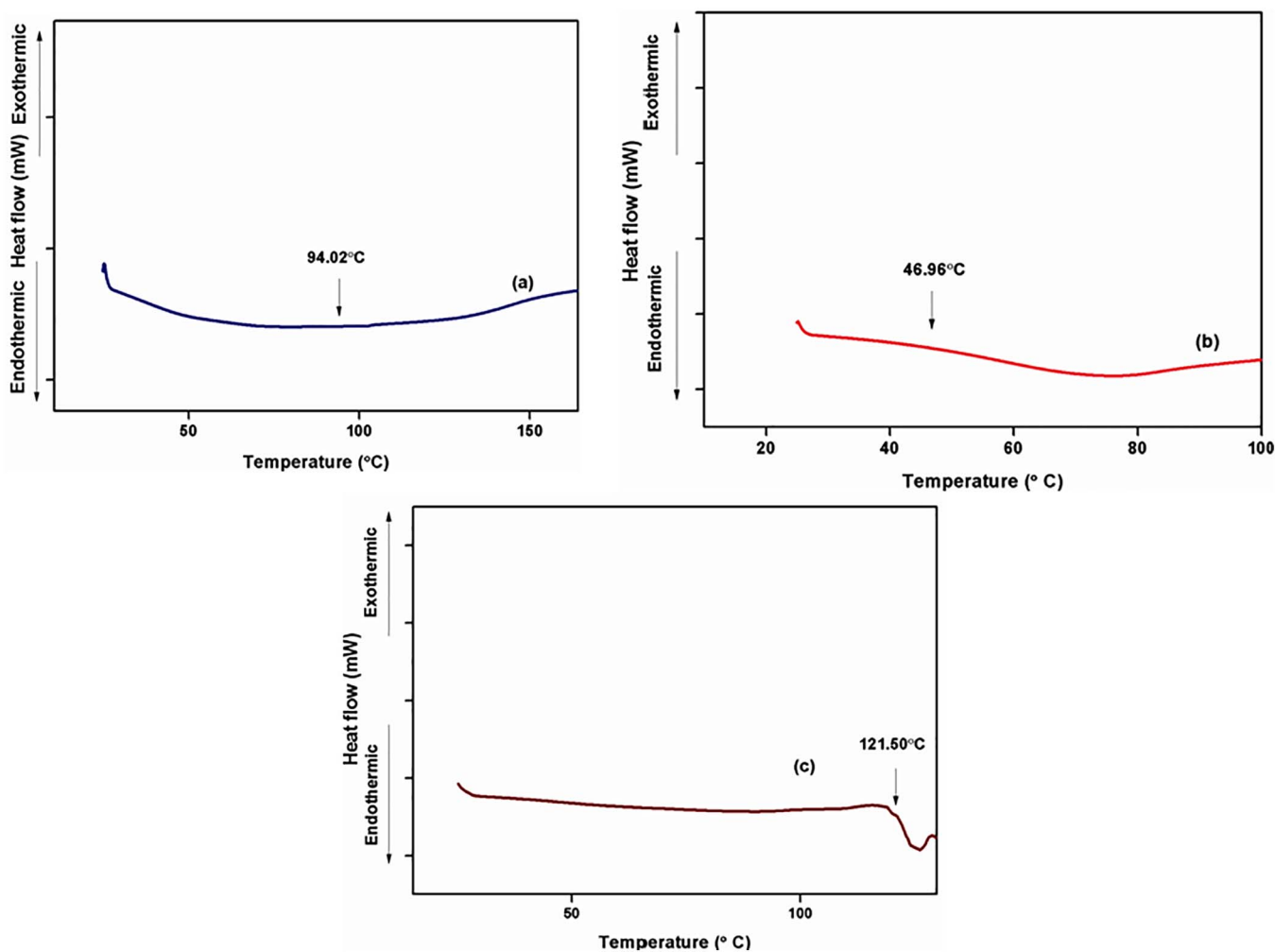


Fig. 4. DSC plot for BPE's (a) 92.5PVA:7.5PAN:0.15 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  (b) 92.5PVA:7.5PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  and (c) 92.5PVA:7.5PAN:0.3 m.m.%  $\text{Mg}(\text{ClO}_4)_2$ .

Table 2

Glass transition temperature ( $T_g$ ) values of 92.5PVA:7.5PAN and  $\text{Mg}(\text{ClO}_4)_2$  polymer electrolyte with different salt concentrations.

Composition 92.5PVA:7.5PAN: x m.m.% $\text{Mg}(\text{ClO}_4)_2$	Glass transition temperature ( $^{\circ}\text{C}$ )
0	136.4° [27]
0.15	94.02
0.25	46.96
0.3	121.50

more charge accumulation occurs at the electrode–electrolyte interface which leads to decrease in number of mobile ions and eventually to a drop in conductivity at low frequency. In high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency [59].

### 3.4.3. Temperature dependant conductivity

The linear variation of ionic conductivity with inverse of absolute temperature gives the Arrhenius type thermally activated process which is governed by the relation

$$\sigma T = \sigma_0 \exp(-E_a/KT) \quad (2)$$

where  $\sigma$ ,  $\sigma_0$ ,  $E_a$ ,  $K$  and  $T$  are the ionic conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature respectively. The Fig. 8 reveals the Arrhenius plot for the BPE

92.5PVA:7.5PAN with 0.05–0.3 wt% of salt  $\text{Mg}(\text{ClO}_4)_2$  from room temperature to 70  $^{\circ}\text{C}$ . The regression values of linear fit of the plots which are close to unity shows that the temperature dependent ionic conductivity for all the BPE's obey the Arrhenius rule. Similar behaviour has been reported in PEO-LiAsF<sub>6</sub> solid polymer electrolytes [60]. Systems with low values of activation energies are desirable to have uniform conductivity which are suitable for the devices operating over a wide temperature range [61]. The activation energy,  $E_a$  is calculated for all the prepared BPE by linear fit of the Arrhenius plot and is listed in the Table 3. The activation energy which is the combination of the energy of defect formation and the energy of migration for the sample 92.5PVA:7.5PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  was found to decrease from 0.76 to 0.21 eV with an increase in salt content. The low activation energy for the magnesium ion transport is due to the complete amorphous nature which provides a bigger free volume of the polymer electrolytes. As the amorphous region increases, the polymer chain acquires faster internal modes in which bond rotation produces segmental motion to favour inter and intra-chain ion hopping and thus the conductivity becomes high [62]. Hence it is observed that the sample 92.5PVA:7.5PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$  has a higher ionic conductivity ( $7.51 \times 10^{-4} \text{ Scm}^{-1}$  at 343 K) and lower activation energy (0.21 eV) compared to other compositions.

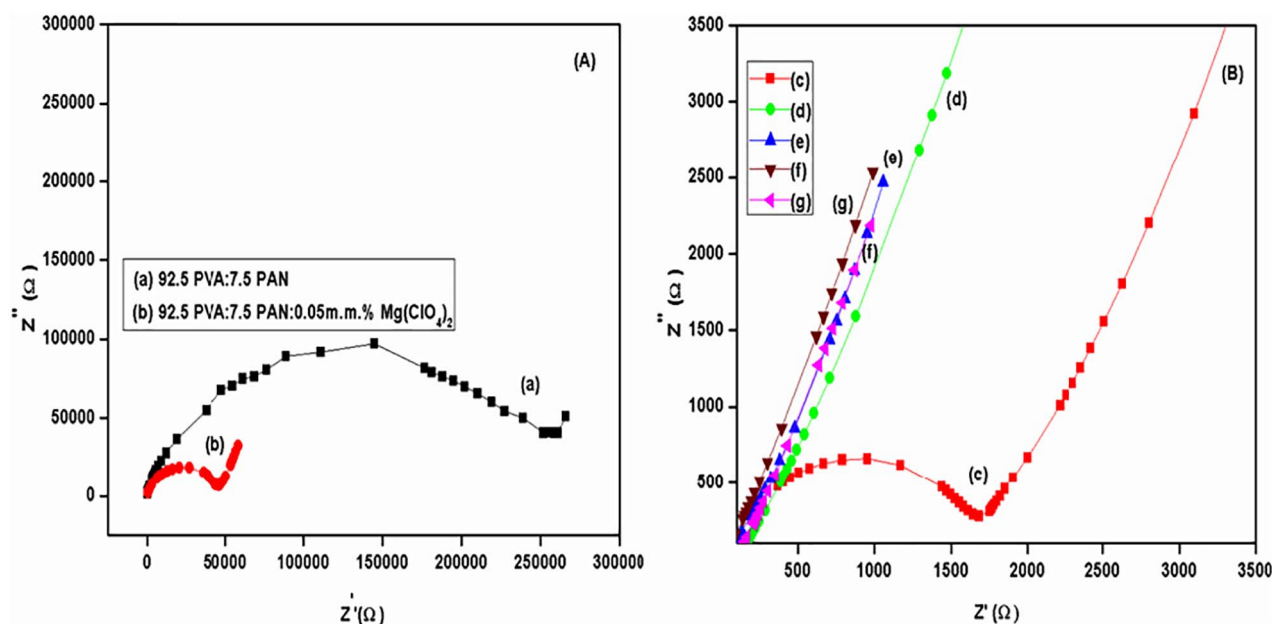


Fig. 5. (A) Cole-Cole plot (B) Cole-Cole plot for various compositions of BPE's at 303 K (c) 92.5PVA:7.5PAN:0.1 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (d) 92.5PVA:7.5PAN:0.15 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (e) 92.5PVA:7.5PAN:0.2 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (f) 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> and (g) 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>.

### 3.5. Dielectric spectra

#### 3.5.1. Dielectric constant

Dielectric constant is a representative of stored charge in a material while dielectric loss is a measure of energy losses to move ions when the polarity of electric field reverses rapidly [63]. Using the relation

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon' - j(\sigma'/\omega\epsilon_0) \tag{3}$$

The real and imaginary parts of the complex permittivity from the measured impedance data were calculated. Real  $\epsilon'$  & imaginary  $\epsilon''$  components are the storage and loss of energy in each cycle of the applied electric field [64]. The Fig. 9 represents the frequency dependence of  $\epsilon'$  with  $\log \omega$  for the pure 92.5PVA:7.5PAN along with the doped Mg(ClO<sub>4</sub>)<sub>2</sub> BPE's with different concentrations (0.2,0.25,0.3 m.m.%). The increase in the dielectric constant represents a fractional increase in charges within the polymer electrolyte. The dependence of charge carrier concentration upon the dissociation energy, U and dielectric constant  $\epsilon'$  can be explained by the following equation [65]

$$n = n_0 \exp(U/\epsilon kT) \tag{4}$$

where k is the Boltzmann constant and T, the absolute temperature.

The dielectric constant  $\epsilon'$  has been experimentally found to increase for the sample 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> and this constant indicates that there is an increase in charge carrier concentration

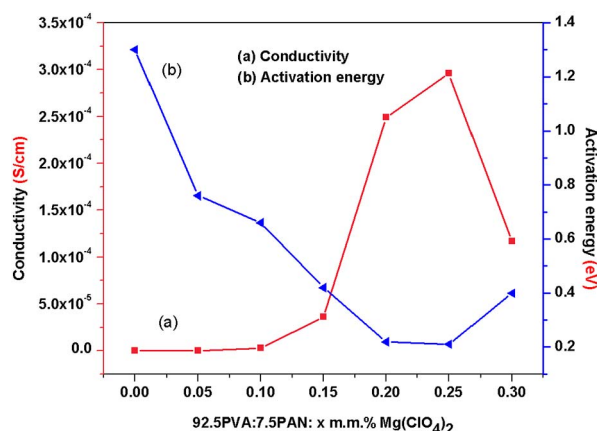


Fig. 6. Variation of conductivity and activation energy as a function of salt concentration.

and hence the conductivity [66]. Further addition of salt decreases the dielectric constant which causes a fall in mobility of charge carriers and cause a significant fall in ionic conductivity in accordance with equation

$$\sigma = n \times q \times \mu \tag{5}$$

The variation of dielectric constant for 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> electrolyte at different temperatures is indicated in the

Table 3  
Ionic conductivity at different temperatures and activation energy values for the prepared blend polymer electrolytes.

Polymer composition 92.5PVA:7.5PAN: x m.m.% Mg(ClO <sub>4</sub> ) <sub>2</sub> X	Ionic conductivity (S/cm)					R,Ω	CPE,μF	n	Activation energy at room temperature (eV)
	303 K	313 K	323 K	333 K	343 K				
0	1.30 × 10 <sup>-8</sup>	1.56 × 10 <sup>-7</sup>	5.03 × 10 <sup>-7</sup>	3.28 × 10 <sup>-6</sup>	4.65 × 10 <sup>-6</sup>	2.3011 × 10 <sup>5</sup>	9.5811 × 10 <sup>-10</sup>	0.8591	1.33
0.05	8.93 × 10 <sup>-8</sup>	1.79 × 10 <sup>-7</sup>	4.3 × 10 <sup>-7</sup>	1.07 × 10 <sup>-6</sup>	2.67 × 10 <sup>-6</sup>	4.698 × 10 <sup>4</sup>	7.909 × 10 <sup>-10</sup>	0.853	0.76
0.1	2.88 × 10 <sup>-6</sup>	5.08 × 10 <sup>-6</sup>	1.09 × 10 <sup>-5</sup>	2.58 × 10 <sup>-5</sup>	5.26 × 10 <sup>-5</sup>	1.848 × 10 <sup>3</sup>	5.732 × 10 <sup>-9</sup>	0.791	0.66
0.15	3.6 × 10 <sup>-5</sup>	7.04 × 10 <sup>-5</sup>	1.11 × 10 <sup>-4</sup>	1.71 × 10 <sup>-4</sup>	2.39 × 10 <sup>-4</sup>	1.284 × 10 <sup>2</sup>	2.397 × 10 <sup>-6</sup>	0.742	0.42
0.2	2.48 × 10 <sup>-4</sup>	2.94 × 10 <sup>-4</sup>	4.04 × 10 <sup>-4</sup>	5.09 × 10 <sup>-4</sup>	6.12 × 10 <sup>-4</sup>	3.945 × 10 <sup>1</sup>	4.865 × 10 <sup>-6</sup>	0.725	0.22
0.25	2.94 × 10 <sup>-4</sup>	3.56 × 10 <sup>-4</sup>	4.80 × 10 <sup>-4</sup>	6.20 × 10 <sup>-4</sup>	7.51 × 10 <sup>-4</sup>	2.375 × 10 <sup>1</sup>	4.44 × 10 <sup>-6</sup>	0.756	0.21
0.3	8.71 × 10 <sup>-5</sup>	2.34 × 10 <sup>-4</sup>	4.10 × 10 <sup>-4</sup>	6.39 × 10 <sup>-4</sup>	8.18 × 10 <sup>-4</sup>	9.847 × 10 <sup>1</sup>	7.106 × 10 <sup>-6</sup>	0.751	0.49

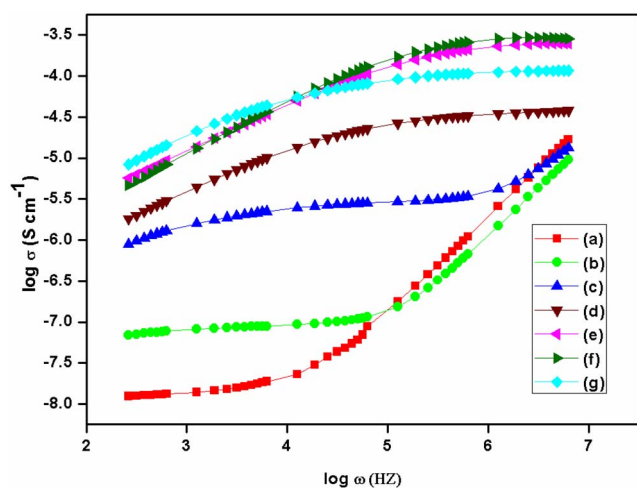


Fig. 7. Conductance spectra for various compositions of BPE's at 303 K (a) 92.5PVA:7.5PAN (b) 92.5PVA:7.5PAN:0.05 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN:0.1 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (d) 92.5PVA:7.5PAN:0.15 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (e) 92.5PVA:7.5PAN:0.2 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (f) 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (g) 92.5PVA:7.5PAN:0.3 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>.

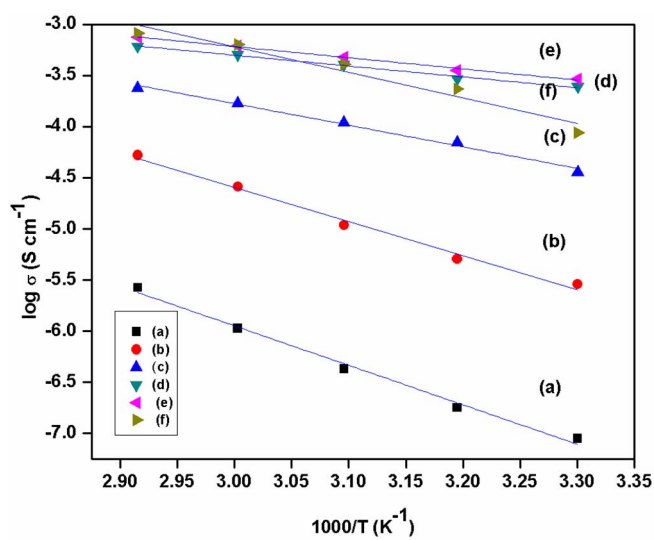


Fig. 8. Arrhenius plot for (a) 92.5PVA:7.5PAN: 0.05 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (b) 92.5PVA:7.5PAN: 0.01 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN: 0.15 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (d) 92.5PVA:7.5PAN: 0.2 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (e) 92.5PVA:7.5PAN: 0.25 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> and (f) 92.5PVA:7.5PAN: 0.3 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub>.

Fig. 10. The observed variation in  $\epsilon''$  with frequency could be attributed to the formation of a space charge region at the electrode and electrolyte interface, which is familiarly known as the non-Debye (Debye) type of behaviour, where the space charge regions with respect to the frequency are explained in terms of ion diffusion [67]. At low frequencies the dielectric constant is high due to the accumulation of the charge carriers near the electrodes [68,69]. At high frequencies there is a decrease in dielectric constant due to the high periodic reversal of the applied field which able the charge carriers to orient themselves in the field direction resulting in decrease of dielectric constant [70].

### 3.5.2. Dielectric loss

The dielectric loss curves for 92.5PVA:7.5PAN:x m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> (x = 0, 0.2, 0.25 and 0.3) BPE's at room temperature and 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> electrolyte for different temperatures is shown in the Figs. 11 and 12. It reveals two prominent relaxation processes: the low frequency  $\alpha$ -relaxation peak; pronounced at higher temperatures, may be caused by the movement of main

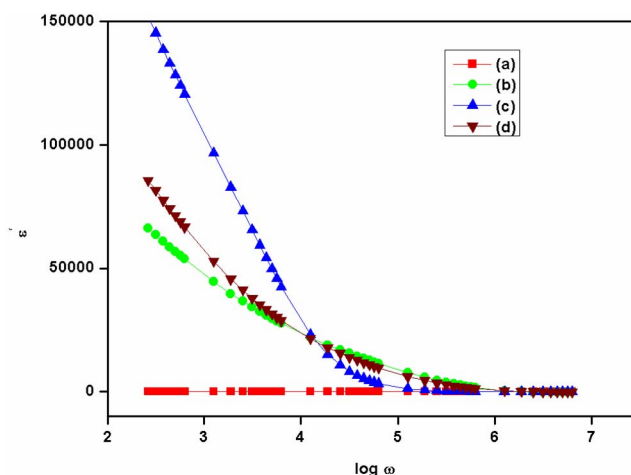


Fig. 9. Plot for  $\log \omega$  vs  $\epsilon'$  for BPE's (a) 92.5PVA:7.5PAN (b) 92.5PVA:7.5PAN:0.2 m.m.% Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> and (d) 92.5PVA:7.5PAN:0.3 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>.

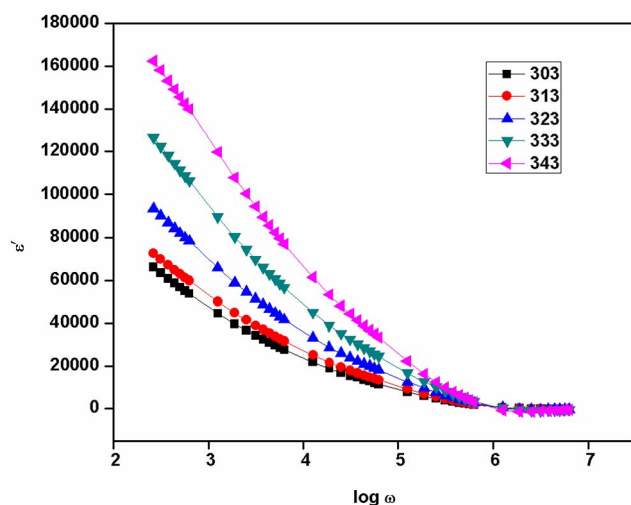


Fig. 10. Plot for  $\log \omega$  vs  $\epsilon''$  for BPE 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> at different temperatures.

segments and the other at high frequency side, the so-called  $\beta$ -relaxation may be caused by side group dipoles and the nearest part of the backbone [71]. The relaxation peaks appear to be broad due to different mechanisms associated with local molecular motions [72].

The relationship between the conductivity and the dielectric loss factor can be given by

$$\epsilon'' = \sigma / \omega \epsilon_0 \quad (6)$$

Since  $\sigma$  is strongly dependent on temperature, the dielectric loss is strongly dependent on temperature and hence the increase in  $\epsilon''$  value with increase of temperature.

### 3.6. Transference number measurement

#### 3.6.1. Wagner's polarization technique

Transference number measurement (TNM) is a dimensionless parameter which informs about the contribution of the particular charged species whether ions or electrons present in the BPEs system. The total ionic transport number ( $t_{ion}$ ) which determines the nature of species responsible for the conductivity in the present electrolyte system was evaluated by the dc polarization technique [32]. In this technique, the SS/92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>/SS cell was polarized by applying a step potential 1.0 V and the resulting potentiostatic current was monitored as a function of time for

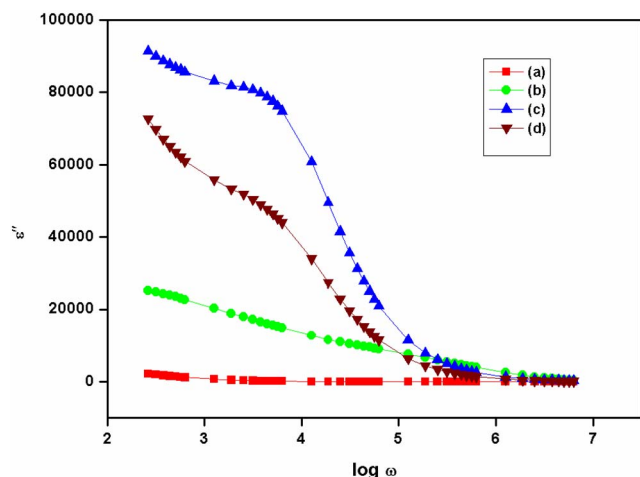


Fig. 11. Plot for  $\log \omega$  vs  $\epsilon''$  for BPE's (a) 92.5PVA:7.5PAN (b) 92.5PVA:7.5PAN:0.2 m.m. %Mg(ClO<sub>4</sub>)<sub>2</sub> (c) 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> and (d) 92.5PVA:7.5PAN:0.3 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>.

92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> system. The stainless steel (SS) is used as blocking electrodes. The value of  $t_{ion}$  was determined using the formula:

$$t_{ion} = \frac{i_T - i_e}{i_T} \quad (7)$$

where  $i_T$  and  $i_e$  are total and residual current respectively. The value of  $t_{ion}$  is determined using Eq. (1) and found to be > 0.99 for all the BPE's. This shows that the overall conductivity of the BPE's is predominantly ionic.

### 3.6.2. Evans polarization technique

The cationic transport number measurement is an important study to determine the performance of the BPE film from its application point of view, i.e. magnesium rechargeable batteries. An effort has been made to evaluate the transport number ( $t^+$ ) of Mg<sup>2+</sup> ions in the solid polymer electrolyte using a combination of AC and DC techniques on a Mg|BPE|Mg cell, as proposed by Evans et al. [33]. In this technique, the Mg|BPE|Mg cells were polarized potentiostatically by applying a voltage,  $V = 0.5$  V and the initial and final currents were recorded. As a part of the technique, the cells were subjected to AC impedance measurements prior to and after the polarization. Values of the electrode–electrolyte contact resistances were obtained from the impedance

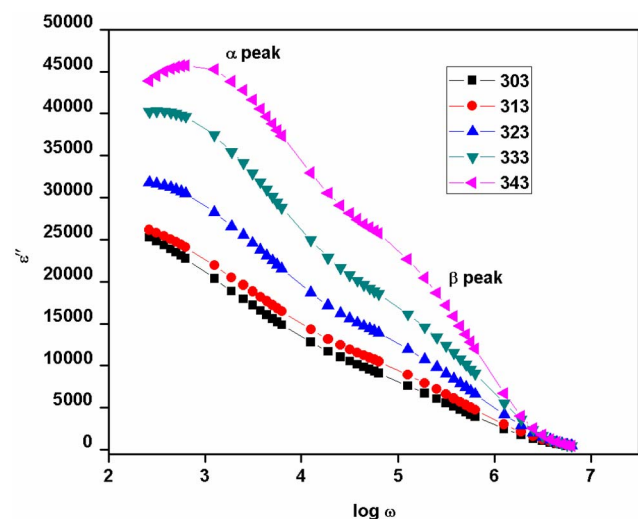


Fig. 12. Plot for  $\log \omega$  vs  $\epsilon''$  for BPE 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> at different temperatures.

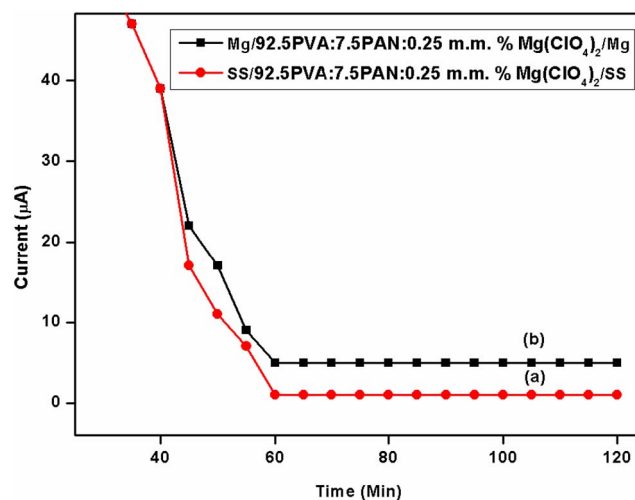


Fig. 13. DC polarization curve of BPE.

plots.

The  $t_+$  values were calculated using the expression:

$$t^+ = I_s(\Delta V - R_o I_o) / I_o(\Delta V - R_s I_s) \quad (8)$$

where  $I_o$  and  $I_s$  are the initial and final currents;  $R_o$  and  $R_s$  are the cell resistances before and after the polarization respectively. The d.c. polarization curve of the maximum conducting BPE film containing 0.25 wt% of Mg(ClO<sub>4</sub>)<sub>2</sub> salt is shown in Fig. 13. The value of Mg<sup>2+</sup> ions transport number has been calculated using Eq. (6) and the value has been found to be 0.27. This value is same as reported by Pandey et al. [73] for Mg(Tf)2/EMITf/PVdF-HFP gel polymer electrolyte.

### 3.7. Linear sweep voltammetry

The electrochemical stability of BPE is an important parameter to be evaluated for its application in energy storage devices. The electrochemical stability of the highest conducting BPE 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> film has been measured using linear sweep voltammetry (LSV) and recorded on the SS|BPE|Mg cell as shown in Fig. 14. The voltage is swept from 0 V towards positive values with a scan rate of 5 mV s<sup>-1</sup> until a large current is obtained at certain potential, which is due to the electrolyte decomposition at the inert electrode interface. The anodic decomposition limit of the polymer electrolyte is considered as the voltage at which the current flows through the cells [74]. It is found that the BPE film is stable up to

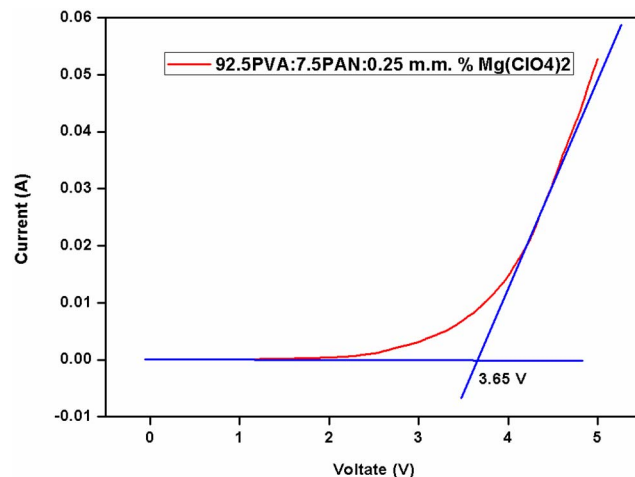


Fig. 14. Linear sweep voltammetry recorded at a scan rate of 5 mVs<sup>-1</sup> at room temperature.



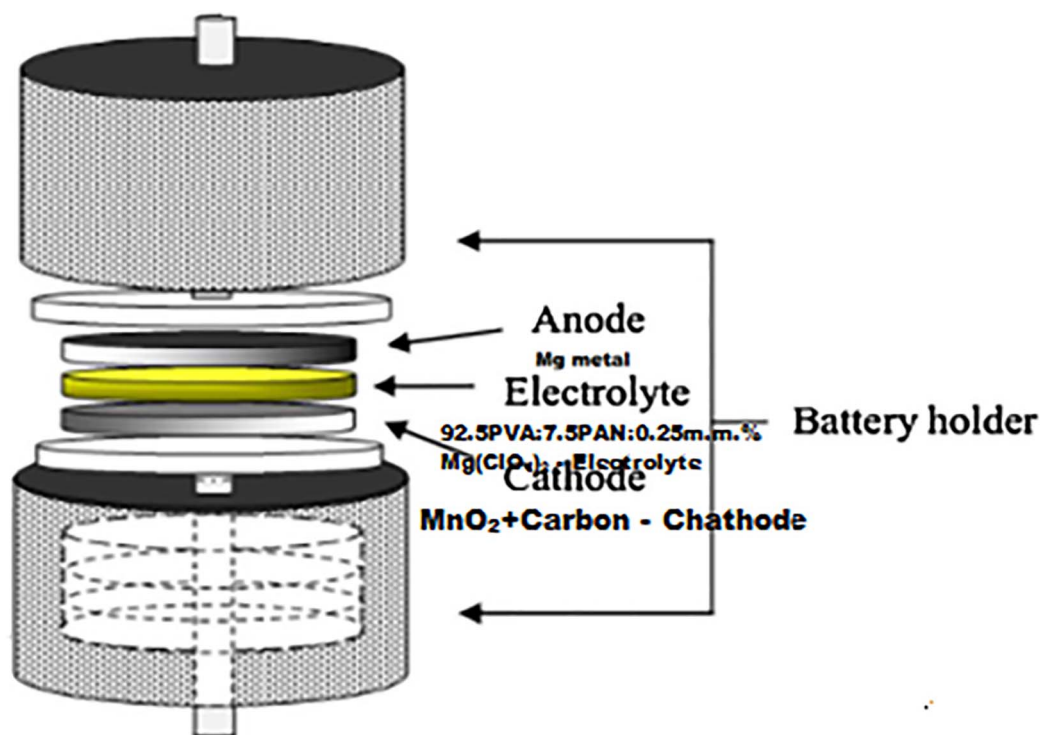


Fig. 15. Battery configuration.

3.65 V which is a sufficient range for electrochemical applications, particularly for Mg batteries [75]. Pandey et al., has reported the electrochemical stability value of  $\text{Mg}(\text{Tf})_2/\text{EMITf}/\text{PVdF-HFP}$  gel polymer electrolyte as 3.5 V [73].

#### 4. Fabrication and characterization of primary magnesium battery

The results reported in the preceding sections reveal that the BPE 92.5PVA:7.5PAN:0.25 m.m.% $\text{Mg}(\text{ClO}_4)_2$  possesses reasonable conductivity for primary magnesium battery application at ambient temperature. In order to demonstrate the application of the BPE,  $\text{Mg}/92.5\text{PVA}:7.5\text{PAN}:0.25 \text{ m.m.}\% \text{Mg}(\text{ClO}_4)_2/\text{MnO}_2$  cells were assembled and their performance was evaluated. This highest conducting system was used as an electrolyte and Mg-metal in pellet form was used as anode. Preparation of the cathode powder  $\text{MnO}_2$  was taken and grind well for 2 h and made into thin pellet. The polymer electrolyte was sandwiched between the anode and cathode pellets as given in the Fig. 15. The open circuit voltage (OCV) of the fabricated cell has been observed to be  $\sim 2.06 \text{ V}$  and has been found to slightly reduced to  $\sim 1.85 \text{ V}$  in two days. The cell is allowed to equilibrate under the value of 1.85 V in open circuit condition for 1 month 10 days (1000h) is shown in Fig. 16. The intermediated drop in the voltage of the cell after fabrication has been due to the cell formation reaction at the electrodes. Similar OCV of 1.95 V was reported for PVdF-HFP with 10% of MgO [76]. The OCV of a magnesium cell is described as the difference between the equilibrium potentials at each electrode, with the positive and negative electrode potentials. The use of solid polymer electrolyte shows good electrochemical performance that leads to a low cost, renewable and environment friendly electrolyte than lithium ion batteries.

The oxidation reaction occurs in the anode is,



The reduction reaction occurs in cathode is,



Overall reaction,

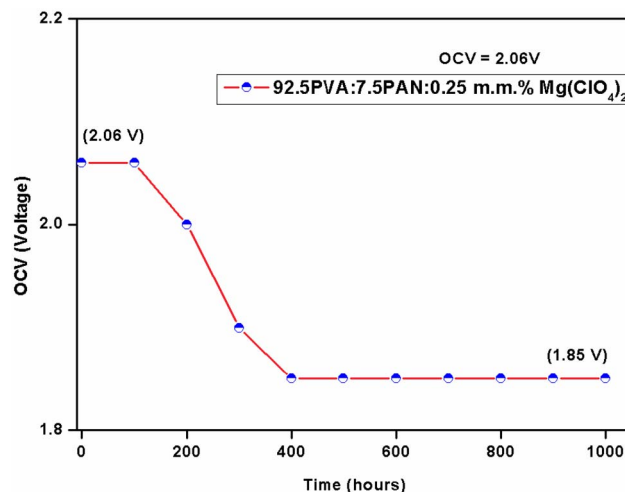
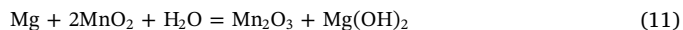


Fig. 16. Open circuit voltage as a function of time for BPE 92.5PVA:7.5PAN:0.25 m.m.%  $\text{Mg}(\text{ClO}_4)_2$ .



The discharge characteristic of fabricated magnesium battery for 92.5PVA:7.5PAN:0.25 m.m.% $\text{Mg}(\text{ClO}_4)_2$  at room temperature, by connecting it to an external load  $1 \text{ M}\Omega$  are shown in Fig. 17. In BPE system, the initial sharp decrease in voltage of this cell may be due to the activation polarization. The activation polarization occurred because the rate of an electrochemical reaction at an electrode surface is controlled by sluggish electrode kinetics [77]. While discharging through  $1 \text{ M}\Omega$  load, the cell voltage has been remained constant at 0.86 V for 200 h. The region in which the cell potential reaches flat discharge rate is called “Plateau region”. The cell potential then decreases after this region. The OCV and discharge time for plateau region and other cell parameters are listed in Table 4.

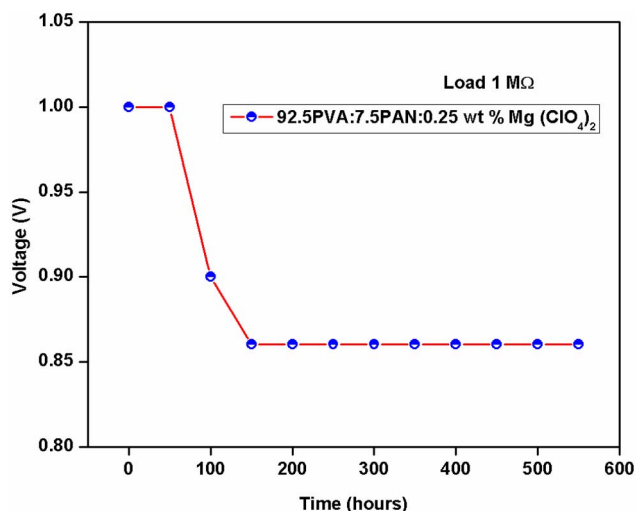


Fig. 17. Discharge curve of the cell using 1 MΩ for BPE 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub>.

Table 4  
Cell parameters.

Cell parameters	Measured values of discharge through 1 MΩ
Cell area (cm <sup>2</sup> )	1.1304
Cell weight (g)	1.2
Effective cell diameter (cm)	1
Cell thickness (cm)	0.427
Open circuit voltage (V)	2.06
Discharge time for plateau region (h)	200

## 5. Conclusion

Blend polymer electrolytes based on PVA-PAN and Mg(ClO<sub>4</sub>)<sub>2</sub> has been successfully prepared using solution-casting technique. The XRD spectrum confirms the amorphous nature of the polymer electrolytes. The strong interaction between the blend polymer and the salt has been observed from FTIR spectra. The maximum ionic conductivity of  $2.9 \times 10^{-4}$  S/cm at room temperature for the system 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> which has been confirmed through EIS analysis. The temperature dependent ionic conductivity of this highest conducting BPE obeys the Arrhenius relationship with low activation energy. Measurement of ionic transference number ( $t_+$ ) reveals that the conducting species are predominantly magnesium ions. The electrochemical stability for 92.5PVA:7.5PAN:0.25 m.m.%Mg(ClO<sub>4</sub>)<sub>2</sub> proved that the BPE is suitable to be applied in electrochemical devices. The primary magnesium conducting battery has been fabricated and the open circuit voltage has been observed to be 1.85 V for 1 month 10 days and their main parameters have been reported. Efforts for further improvement in discharge capacity of the Mg batteries are continued.

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