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Polyvinyl pyrrolidone/$Mg(ClO_4)_2$ solid polymer electrolyte: structural and electrical studies

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Abstract Polymer electrolytes comprising polyvinyl pyrrolidone (PVP) as host polymer and $Mg(ClO_4)_2$ as dopant salt have been prepared by solution casting technique using double-distilled water as solvent. The changes in the structural properties on the incorporation of dopant were investigated by XRD and FTIR analysis. The ionic conductivity and dielectric behavior were explored using AC impedance spectroscopy. The ionic conductivity increases with increasing dopant concentration. The conductivity enhancement with the increasing salt concentration is correlated with the increase in amorphous nature of the electrolytes. The frequency dependence of electrical conductivity obeys the universal Jonscher power law. The electrical modulus representation shows a loss feature in the imaginary component. The distribution of relaxation times was indicated by a deformed arc form of the Argand plot. The relative dielectric constant (ε_r) decreases with increase in frequency in the low frequency region whereas a frequency-independent behavior is observed in the high frequency region. The total ionic transference number studies have confirmed that the mobile charge carriers are ions. Results obtained by cyclic voltammetry on SS/60 mol% PVP/40 mol% $Mg(ClO_4)_2$ SPE/SS symmetrical cell show evidence for reversibility.

Keywords Ionic conductivity · Polymer electrolyte · Magnesium ion · XRD · FTIR

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Introduction

Over the past few decades, ion-conducting polymer electrolytes have continued to attract great interest from both scientific and industrial perspectives due to their potential application in all electrochemical devices such as rechargeable batteries, fuel cells, electrochromic displays, supercapacitors, and solar cells. Polymer electrolytes have good thermal, mechanical, and electrical stabilities besides its advantages like ease of fabrication, leak proof, less weight, improved safety, design flexibility, and good electrode/electrolyte contact. The mechanism of ion conduction in solid polymer electrolytes is still not well understood. However, it was widely believed that ionic conductivity occurred predominantly in the amorphous phase above the glass transition temperature T_g, driven by the local random Brownian motion of amorphous polymer chains [1].

Research on solid polymer electrolytes (SPEs) containing Mg^{2+} as the conducting species is scarce in literature when compared to Li^+/Na^+. SPEs containing Mg^{2+} as the conducting species are worthy to pursue on account of its advantages like (i) divalent charge, (ii) 2:1 anion to cation ratio, (iii) high abundance, (iv) low cost, and (v) possibility of using more stable magnesium metal as an electrode material [2, 3]. But the electrochemical deposition of Mg in non-aqueous media is difficult as magnesium metal is generally covered with a passive film, which may hinder the reversibility of Mg/Mg^{2+} electrochemical reaction. Therefore, much

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effort has been devoted to develop suitable electrolytes with high anodic stability as well as suitability for magnesium deposition or dissolution.

Among the polymers reported in literature, polyvinyl pyrrolidone (PVP) is a biocompatible, amorphous, and inexpensive polymer, possessing a high glass transition temperature. The rigid pyrrolidone group attached to the carbon chain backbone which can be a source of hydrogen bonding and hence assist the formation of polymer electrolytes [4]. PVP deserves special attention because of its good electrical properties, easy processability, and charge transport mechanism.

Materials and methods

Starting materials

Commercially available chemicals of PVP (molecular weight (MW) = 40,000 g/mol) and the electrolytic salt, namely, magnesium perchlorate ($Mg(ClO_4)_2$) (MW = 223 g/mol), were procured from HiMedia and used as received.

Preparation of the solid polymer electrolytes

Polymer electrolytes of different compositions of PVP/$Mg(ClO_4)_2$ have been prepared by a solution casting technique using double-distilled water as the solvent. PVP was initially added to the solvent and stirred continuously until the complete dissolution of the polymer in the solvent. Then, a required quantity of $Mg(ClO_4)_2$ was added and the resultant solution was stirred continuously until a clear homogeneous solution is obtained. The solution was then poured to polypropylene petri dishes and allowed to dry in air at room temperature for 7 days. Utmost care was taken to remove the residual traces of the water molecules by drying the films in an air oven at 80 °C for 72 h and then at 80 °C for 48 h in a vacuum oven. This procedure yields mechanically stable, free standing films of thickness between 190 and 200 μm. The obtained films were stored in vacuum desiccators to avoid moisture absorption until further use. X-ray diffraction scans were taken using a Philips X'Pert PRO diffractometer at room temperature. The diffraction peaks were recorded at Bragg's angle (2θ) in the range of 10° to 80°. The polymer electrolytes were subjected to FTIR study to investigate the complexation using a Shimadzu 8000 spectrophotometer in the wavenumber ranging 400–4000 cm^{-1}. The electrical conductivity of the polymer electrolytes was evaluated by impedance spectroscopy using a Hioki 3532 LCR impedance analyzer interfaced with a computer in the frequency range of 42 Hz–5 MHz from 303 to 353 K for all the samples with stainless steel (SS) as the blocking electrodes. Cyclic voltammograms (CVs) of the symmetrical cells were recorded using potentiostat/galvanostat (EG&G PARC Model VersaStat) at a scan rate of 1 mV s^{-1}.

Results and discussion

XRD analysis

Figure 1 shows the XRD pattern of $Mg(ClO_4)_2$, pure PVP, and PVP doped with different mole ratios of $Mg(ClO_4)_2$. The XRD pattern of pure PVP exhibits a broad peak at 2θ = 19° to 25° corresponding to the amorphous nature of PVP [4]. The reduction in the intensity with the broadening of this peak is observed for the increasing salt concentration. This result can be interpreted by considering the Hodge et al. [5] criterion, which establishes a correlation between the intensity of the peak and the degree of crystallinity. The change in the intensity and the broad nature of the peaks in the polymer electrolytes suggest the amorphous nature of the polymer electrolytes. This amorphous nature results in greater ionic diffusivity with high ionic conductivity. In the present work, 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ polymer electrolyte exhibits high

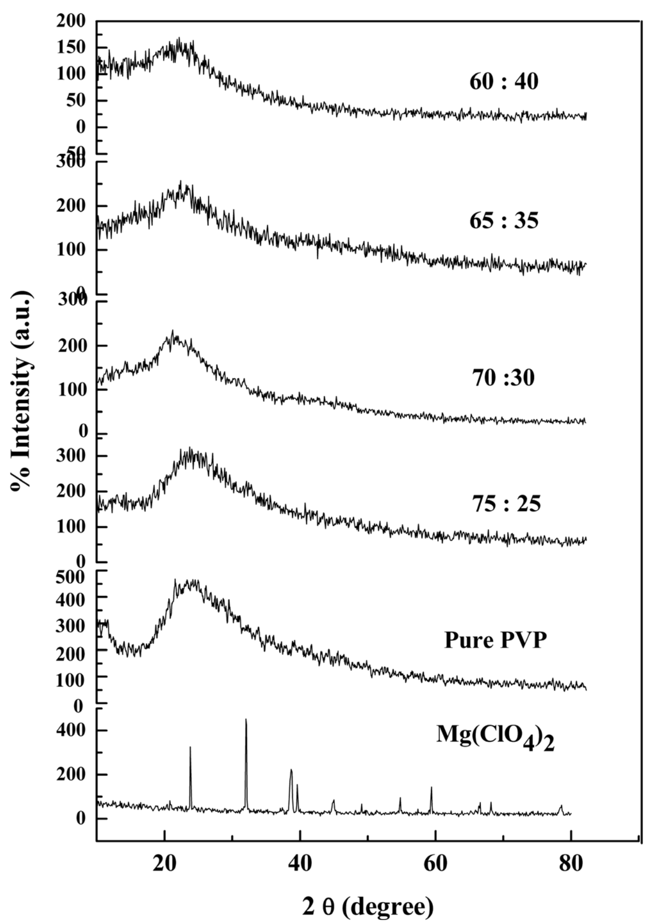

Fig. 1 XRD pattern of pure $Mg(ClO_4)_2$, pure PVP, and PVP–$Mg(ClO_4)_2$ SPE with different concentrations of the dopant

amorphicity when compared to other systems. Moreover, the peak corresponding to $Mg(ClO_4)_2$ is found to be absent in the polymer salt complexes indicating the complete dissolution of the salt in the polymer matrix.

FTIR analysis

The FTIR spectra of pure PVP and PVP doped with different concentrations of $Mg(ClO_4)_2$ are shown in Fig. 2. The band assignments of the polymer electrolytes are given in Table 1. The peak located at 2965 cm^{-1} in pure PVP is due to the stretching vibration of the CH_2 group, and its intensity is found to decrease in the polymer complexes indicating the complexation of the dopant with the polymer [6]. The peak observed around 1640 cm^{-1} in pure PVP corresponds to the C=O stretching and gets shifted to lower wavenumbers in the polymer complexes which implies the interaction of cations/anions with the carbonyl group of the host PVP. The absorption band observed around 1212 cm^{-1} corresponds to the CH_2 bending of pure PVP. The shifting of this peak to lower wavenumbers indicates the interaction of the dopant and the polymer. The vibrational peak appearing at 878 cm^{-1} assigned to the CH_2 rocking mode of PVP is found to be shifted in the polymer complexes. The bands at 931, 1294, and 1423 cm^{-1} are attributed to C–C stretching, C–N stretching, and C–H bending vibrations of pure PVP, respectively [7]. The shifting of the band positions in the FTIR spectra is a clear evidence for the complexation and interaction of the dopant with the host polymer.

Impedance analysis

The complex impedance plots for different molar ratios of PVP–$Mg(ClO_4)_2$ polymer electrolytes at room temperature (303 K) are shown in Fig. 3. The plot shows a high-frequency semicircular portion ascribed to the bulk effect of the electrolytes and a low-frequency inclined linear region due to the effect of the blocking electrodes [8]. The distinctly non-vertical spikes in the complex impedance plot suggest the surface roughness at the electrode–electrolyte interface. A slight decentralization of the semicircles has been observed for all the compositions indicating the non-Debye nature of the samples and the distribution of relaxation times. The bulk resistance (R_b) of the polymer electrolytes is calculated from the intercept of the high-frequency semicircle or the low-frequency spike on the real impedance (Z') axis. The ionic conductivity (σ) is calculated using the equation $\sigma = t/AR_b$ where t and A are the thickness and the area of the polymer electrolytes, respectively. The highest ionic conductivity at room temperature is found to be 5.6×10^{-4} Scm^{-1} for the 40 mol% salt doped system. The conductivity values of all the polymer electrolytes at room temperature are given in Table 2. The conductivity value is found to increase with increasing salt concentration which can be attributed to an increase in both mobility and charge carrier concentration.

Figure 4 shows the impedance plot for 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ polymer electrolytes at various temperatures. The ionic conductivity values were found to increase from 5.6×10^{-4} to 1.8×10^{-2} Scm^{-1} when the temperature increases from 303 to 353 K. From Fig. 4, it is obvious that as the temperature increases the diameter of the semicircle

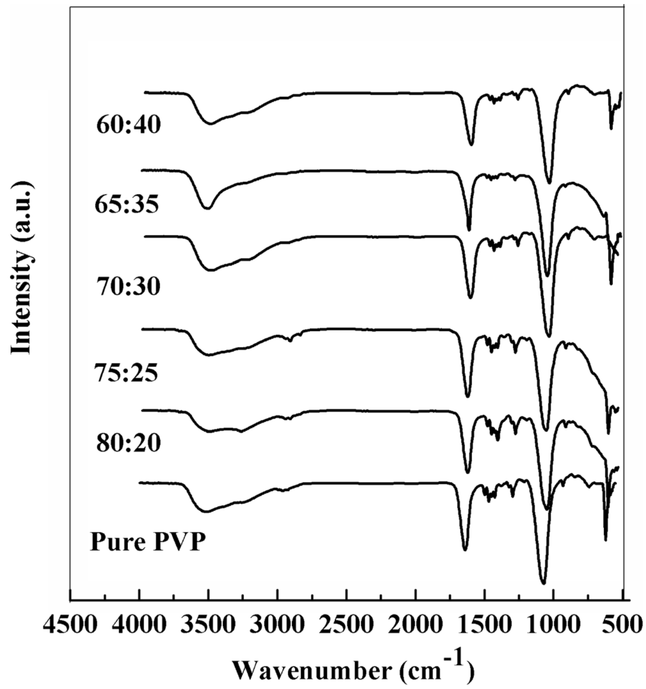

Fig. 2 FTIR pattern of pure PVP and PVP–$Mg(ClO_4)_2$ SPE with different concentrations of the dopant

Table 1 FTIR band assignments for pure PVP and the polymer complexes

Pure PVP	80:20	75:25	70:30	65:35	60:40	Band assignments
2965	2960	2956	2965	2951	2956	CH_2 asymmetric stretching
1640	1640	1637	1637	1626	1633	C=O stretching
1423	1425	1423	1423	1423	1422	C–H bending
1294	1294	1296	1297	1297	1296	C–N stretching
931	931	933	931	933	933	C–C stretching
878	852	844	844	850	840	C–H rocking

Table 2 Conductivity parameters of PVP/$Mg(ClO_4)_2$ polymer complexes

Sl. no.	PVP/$Mg(ClO_4)_2$ composition (mol%)	ac conductivity, Scm^{-1} (303 K)	t_{ion}	t_{ele}
1	70:30	1.2×10^{-6}	0.92	0.08
2	65:35	2.3×10^{-4}	0.93	0.07
3	60:40	5.6×10^{-4}	0.95	0.05

decreases which is a direct evidence for the decrease in bulk resistance (R_b) value and the increased charge carrier density. At higher temperatures, thermal movement of polymer chains and disassociation of salts into its counterparts would be improved, which increases ionic conductivity [9].

Transference number measurements

Figure 5 depicts the Wagner polarization curves for 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ SPE at room temperature [10]. The value of total ionic transference number was evaluated using the following equation:

$$t_{\text{ion}} = \frac{i_T - i_e}{i_T}$$

where i_T is the total current and i_e is the residual current. The polarization current was monitored as a function of time on the application of dc potential (0.7 V) across the cell in the SS/60 mol% PVP/40 mol% $Mg(ClO_4)_2$/SS configuration. It is observed from the plot that the sudden drop of current within the first 10 min hints that more contribution for conductivity is due to ions than electrons. This fall in current is considered to result from two processes: (i) growth at the electrodes of passivating layers, which occurs whether or not a current is flowing, and (ii) the establishment of a concentration gradient in the electrolyte which affects the motion of the ions. The total transport number calculated for the SPEs is listed in Table 2. The t_{ion} value was found to be in the range of 0.92–0.95 which concludes that the charge transport in these polymer electrolyte systems is predominantly due to ions.

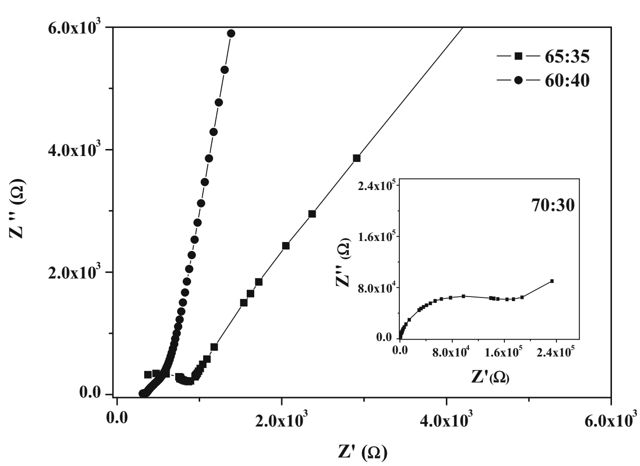

Fig. 3 Cole–Cole plot for the SPE with different concentrations of $Mg(ClO_4)_2$ at room temperature

Frequency-dependent conductivity analysis

The ac conductivity as a function of angular frequency for all the SPEs at room temperature is shown in Fig. 6. The plot consists of two regions within the measured frequency range, (i) the low-frequency dispersion region and (ii) the frequency-independent plateau region. The ac conductivity $\sigma(\omega)$ obeys the Jonscher power law [11], and it is found to vary with angular frequency ω.

$$\sigma(\omega) = \sigma_{\text{dc}} + A\omega^{n}$$

where σ_{dc} is the dc conductivity and A and n are temperature-dependent parameters.

At low frequencies, the charge carriers accumulate at the electrode–electrolyte interface, reducing the number of mobile ions responsible for conductivity. As the frequency increases, the space charge built up at the electrode–electrolyte interface is minimized and the mobile ions contribute to the high value of conductivity [12, 13]. It is observed that the conductivity increases with the increase in dopant concentration indicating the increase in the available charge carriers.

Dielectric analysis

The dielectric permittivity (ε') vs. log ω spectra for different compositions of PVP–$Mg(ClO_4)_2$ SPEs at room temperature is given in Fig. 7. A high value of

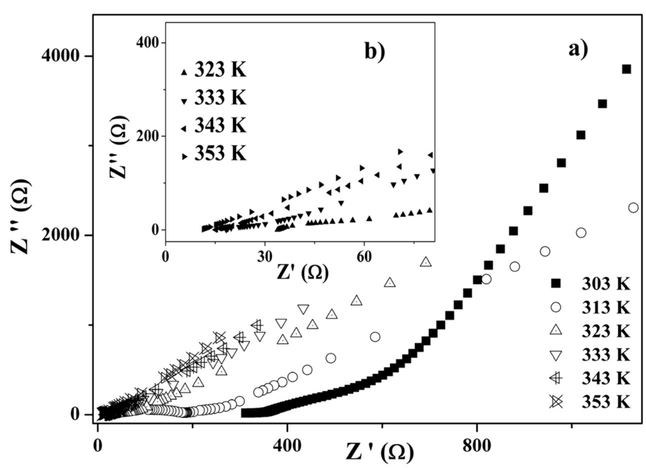

Fig. 4 **a** Typical impedance plot for 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ SPE at various temperatures. **b** *Inset* showing the enlarged view of the impedance plot for 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ at 323, 333, 343, and 353 K

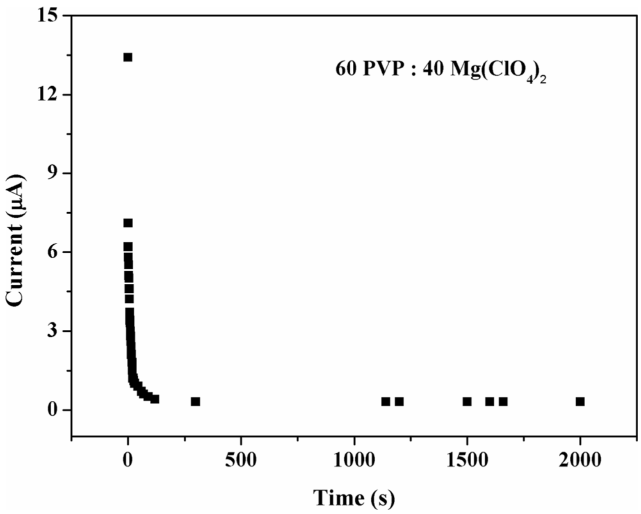

Fig. 5 Current vs. time plot of 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ polymer electrolytes at room temperature

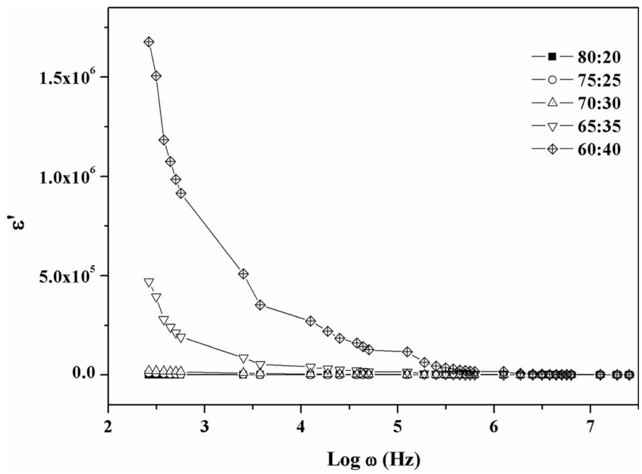

Fig. 7 Plot of log ε′ vs. log *f* for SPE with different concentrations of $Mg(ClO_4)_2$ at room temperature

dielectric permittivity is observed at low frequencies, and as the frequency increases, the dielectric permittivity value decreases. The high dielectric permittivity observed at low frequencies is due to the accumulation of charge carriers at the electrode–electrolyte interface, which indicates the non-Debye type of behavior [14, 15]. As the frequency increases, the polarity reversal of the field occurs very quickly, and hence, the dipoles cannot orient themselves along the field direction and no excess ion diffusion takes place, resulting in a decrease in the dielectric permittivity value at high frequencies. A high positive dielectric permittivity is obtained for the polymer electrolyte with 40 mol% $Mg(ClO_4)_2$ indicating the increase in the mobile charge carriers and, hence, increase in conductivity which is in good agreement with the impedance analysis.

Modulus analysis

The dielectric modulus analysis is used to study the dielectric properties of the polymer electrolytes by suppressing the polarization effect of the electrode. The imaginary part of the dielectric moduli as a function of frequency for some selected SPEs is shown in Fig. 8. The long tail observed in the low-frequency regime implies the large capacitance value associated with the electrode polarization effects. The broad and asymmetric nature of the peak observed for the polymer electrolyte with 30 mol% $Mg(ClO_4)_2$ signifies the distribution of relaxation times [16]. The reduction in the values of M″ at higher salt concentration is due to the increased charge carrier density. The disappearance of M″ peaks in the spectra at higher salt concentration is due to the experimental frequency limitation.

In order to investigate the type of relaxation occurring in the SPEs, an Argand plot at different temperatures for the highest conducting sample (60 mol% PVP/40 mol%

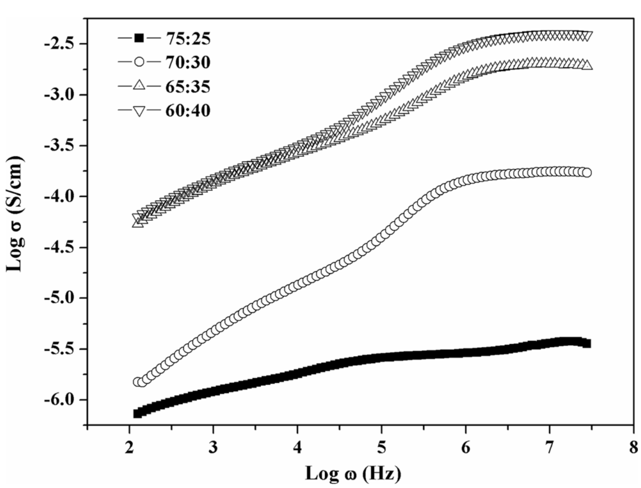

Fig. 6 Conductance spectra of SPE with different concentrations of $Mg(ClO_4)_2$ at room temperature

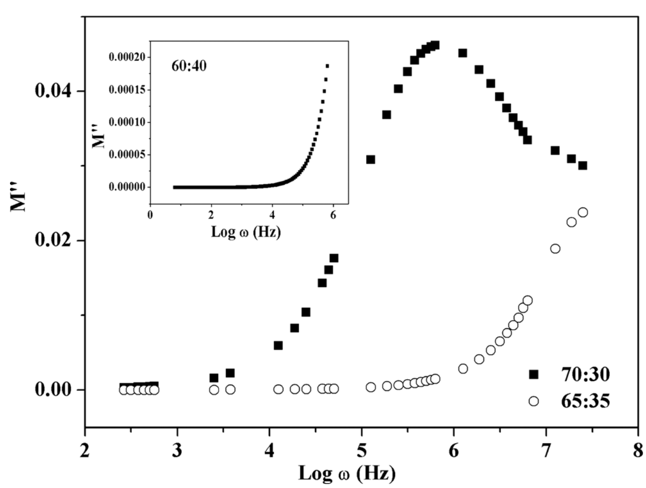

Fig. 8 Variation of imaginary parts of the modulus (M″) with frequency for SPE with different concentrations of $Mg(ClO_4)_2$ at room temperature

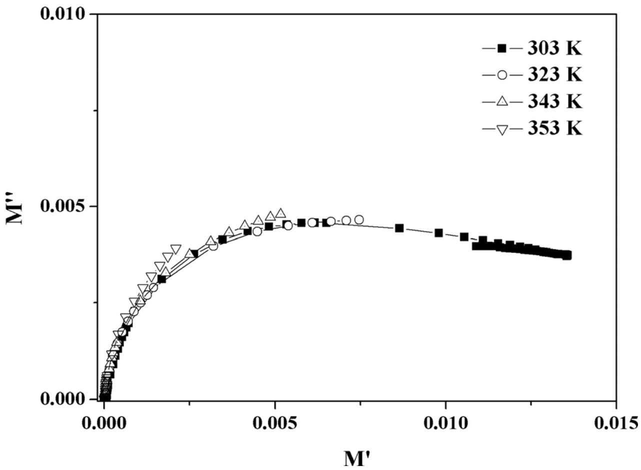

Fig. 9 Argand plot for 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ SPE at various temperatures

$Mg(ClO_4)_2$) is shown in Fig. 9. The incomplete half semicircles in the Argand plot suggest non-Debye relaxation in the polymer electrolytes. This may be due to the presence of polar side groups, hopping, and inhomogeneities. It is obvious from the plot that with increasing temperature, the Argand curves shift towards the origin which may be due to the increase in conductivity with temperature [17].

Cyclic voltammogram studies

The establishment of reversibility of Mg/Mg^{2+} in the solid polymer medium is an important characteristic of a polymeric system for its possible application in solid-state rechargeable batteries. Mg/SPE/Mg symmetrical cell consisting of SPE with highest conductivity was subjected to cyclic voltammetry between −4.5 and 4.5 V at a scan rate of 1 mVs^{-1}, and it is shown in Fig. 10. The voltammogram shows two distinct oxidation and reduction peaks in the voltage range studied. This suggests the occurrence of the anodic oxidation and cathodic reduction at the electrode–electrolyte interface. However, the peak potential separation is higher than 0.03 V because the experiments were carried out with a two-electrode geometry without the reference electrode [18, 19]. The above observation confirms the existence of an electrochemical equilibrium between the Mg metal and Mg^{2+} ions in the polymer electrolyte.

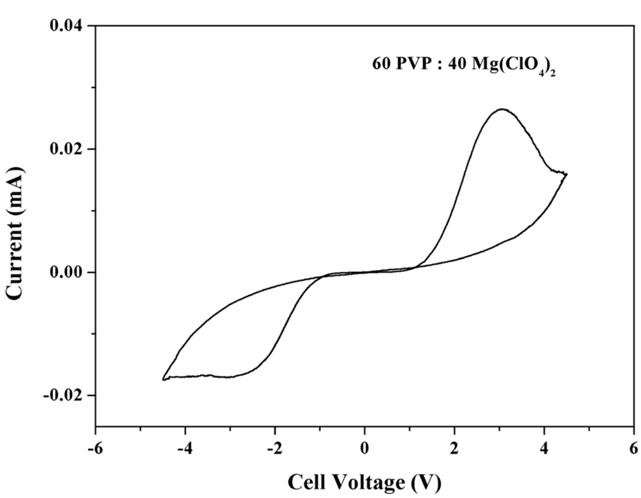

Fig. 10 Cyclic voltammogram of (SS)Mg/60 mol% PVP/40 mol% $Mg(ClO_4)_2$/Mg(SS) SPE at room temperature at a scan rate of 1 mVs^{-1}

Conclusion

The polymer electrolytes containing Mg^{2+} as the conducting species have been prepared by a solution casting method. The complexation of the dopant with the polymer host has been confirmed by XRD and FTIR analyses. From the electrical conductivity studies, the highest room temperature conductivity was found to be 5.6×10^{-4} S/cm for the polymer electrolyte with the 60 mol% PVP/40 mol% $Mg(ClO_4)_2$ composition. The modulus spectra and the dielectric studies show the non-Debye nature of the electrolyte membranes. The CV measurement suggests that the cathodic deposition and anodic oxidation of Mg are facile at the Mg electrode and the solid polymer electrolyte interface.

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