

# Electrical and electrochemical studies on magnesium ion-based polymer gel electrolytes

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**Abstract** The development of polymer gel electrolyte system with high ionic conductivity is the main objective of polymer research. Electrochemical devices based on lithium ion-conducting polymer electrolyte are not safe due to the explosive nature of lithium. An attempt has been made to synthesize magnesium ion-conducting polymeric gel electrolytes, poly (vinylidene fluoride-co-hexafluoropropylene)-propylene carbonate–magnesium perchlorate, PVdF(HFP)-PC–Mg(ClO<sub>4</sub>)<sub>2</sub> using standard solution-cast techniques. The maximum room temperature ionic conductivity of the synthesized electrolyte system has been observed to be  $5.0 \times 10^{-3}$  S cm<sup>-1</sup>, which is quite acceptable from a device fabrication point of view. The temperature-dependent conductivity and the dielectric behavior were also analyzed. The pattern of the temperature-dependent conductivity shows the Arrhenius behavior. The dielectric constant  $\epsilon_r$  and dielectric loss  $\epsilon_i$  increases with temperature in the low-frequency region but almost negligible in the high-frequency region. This behavior can be explained on the basis of electrode polarization effects. The real part  $M_r$  and imaginary part  $M_i$  versus frequency indicate that the systems are predominantly ionic conductors. Further, the synthesized electrolyte materials have been checked for its suitability in energy storage devices namely redox supercapacitor with conducting polymer polypyrrole as electrode materials, and finally, it was observed that it shows good capacitive behavior

in low-frequency region. Preliminary studies show that the overall capacitance of 22 mF cm<sup>-2</sup> which is equivalent to a single electrode specific capacitance of 117 F gm<sup>-1</sup> was observed for the above said supercapacitors.

**Keywords** Polymer gel electrolytes · PVdF(HFP) · Supercapacitor · Dielectric studies

## Introduction

Ion-conducting gel polymer electrolytes are of a major global interest to physicist, chemists, and engineers as they offer a better substitute to liquid electrolytes because of their potential application in various electrochemical devices particularly in batteries and supercapacitor [1–4]. It has been widely accepted that polymer gel electrolytes possess some distinct advantages over liquid electrolytes, such as reduced reactivity, reduced leakage, improved safety, and better shape flexibility and manufacturing integrity. Presently, worldwide attention has focused on the high performance and environment-friendly nature of the energy storage devices. Lithium ion is incorporated in most of the commercially available batteries for their fabrication due to its high specific capacity and excellent cyclic stability [5–7]. At the same time, lithium ion batteries are relatively expensive and suffer from safety limitations because of their explosive nature. Nowadays, magnesium ion-based rechargeable batteries are attracting more attention due to their performance characteristic which is closer to that of their lithium counterparts [5, 8–10]. Further, the magnesium-based electrochemical devices are more attractive from a device fabrication point of view due to their cost effectiveness, low toxicity, ease of handling, and safer than lithium. Magnesium ion-based gel polymer electrolytes have not been widely

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reported except for some recent studies [11–14]. Few rechargeable magnesium batteries were also reported by some workers using polymer gel electrolytes [10, 15, 16].

In the present study, polyvinylidene fluoride–hexafluoropropylene (PVdF–HFP)-based polymer gel electrolytes were prepared by incorporating propylene carbonate–magnesium perchlorate (PC)– $\text{Mg}(\text{ClO}_4)_2$  as the liquid electrolyte with magnesium ion as the doping salt. PVdF–HFP has been chosen because of its appealing properties. It has high dielectric constant,  $\epsilon$  of 8.4 as reported by Lee et al. [17], and occurred in two phases (amorphous and crystalline). Amorphous phase enhances higher ionic conduction in the system; meanwhile, crystalline phase provides strong mechanical support to the polymer electrolytes [18, 19]. PCs are used to improve the flexibility of polymer system.  $\text{Mg}(\text{ClO}_4)_2$  was used as the doping salt because it has smaller ionic radius, has smaller dissociation energy, and is highly soluble in most of the ionic solvents.

## Experimental sections

### Sample preparation

The gel polymer electrolyte PVdF (HFP)–PC– $\text{Mg}(\text{ClO}_4)_2$  was prepared by using the standard “solution-cast” technique. PVdF–HFP (mol. wt. = 400,000, Aldrich) as polymer,  $\text{Mg}(\text{ClO}_4)_2$  (Aldrich) as salt, and PC (Loba Chemie) and tetrahydrofuran (THF) (Merck) as solvent were used as received without further treatment. The mixture of polymers and doping salt in suitable amounts were mixed in common solvent THF and stirred continuously by a magnetic stirrer for 6 h at 50°C until homogenous solutions were obtained. The solutions were poured into a glass petri dish and left to dry at room temperature. Finally, mechanically stable, free-standing and flexible thin films were obtained. The films were kept in desiccators for further drying.

Polypyrrole (pPy) films were electrochemically polymerized on indium tin oxide (ITO)-coated conducting glass substrate (Balzers, sheet resistance 80  $\Omega \text{ cm}^2$ ). The monomer pyrrole (Aldrich) was distilled in a vacuum before use. The electrodeposition of pPy was carried out in the cell containing 0.1 M pyrrole and 0.2 M  $\text{LiClO}_4$  solution in acetonitrile at a constant current of 2 mA for 3 min. in a single-compartment three-electrode cell with platinum foil as counter electrode and saturated calomel electrode as reference electrode. The solutions were purged with dry nitrogen during electrosynthesis to eliminate the oxygen content.

### Conductivity analysis

To study the conductivity behavior of the polymer electrolytes, impedance spectroscopy was performed using LCR

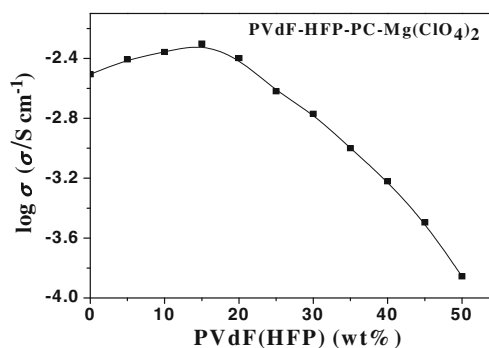
HiTESTER (3522-50, Hioki, Japan). The samples were cut into proper size and sandwiched between two stainless steel electrodes. The conductivity ( $\sigma$ ) was calculated using the equation  $\sigma = t / R_b A$  where,  $t$  is thickness of the electrolyte,  $A$  is electrolytes' contact area, and  $R_b$  is the bulk resistance obtained from the plots of real impedance  $Z_r$  against imaginary impedance  $Z_i$ .

Electrochemical measurements of capacitor cell were carried out by impedance spectroscopic technique using a computer-controlled LCR HiTESTER (3522-50, Hioki, Japan) in the frequency range from 1 mHz to 100 kHz. The signal level was kept at 10 mV. Overall capacitance  $C$  of the capacitor cell was evaluated using the relation  $C = -1 / (\omega Z'')$  where,  $\omega$  is the angular frequency and  $Z''$  is the imaginary part of total complex impedance. Single-electrode specific capacitance was evaluated by multiplying the overall capacitance by a factor of two and dividing the mass of a single electrode.

## Result and discussion

### Polymer concentration dependence conductivity

Polymer gel electrolyte PVdF(HFP)–PC– $\text{Mg}(\text{ClO}_4)_2$  system was initially optimized in order to get both highly conducting and mechanically stable and flexible films for checking its suitability as electrolyte materials in the fabrication of solid-state redox supercapacitors. In the process, first of all, liquid electrolyte is prepared by the addition of different molar concentrations of salt,  $\text{Mg}(\text{ClO}_4)_2$ , in the solvent PC. The optimized conductivity of liquid electrolyte is found to be  $3.63 \times 10^{-3} \text{ S cm}^{-1}$  for the composition of PC– $\text{Mg}(\text{ClO}_4)_2$  (0.3 M). Different weight percents (0–50 wt%) of the polymer PVdF(HFP) were then added in the optimized liquid electrolytes for the gel formation. Figure 1 shows the variation of ionic conductivity of [PVdF(HFP)–PC– $\text{Mg}(\text{ClO}_4)_2$  (0.3 M)] gel polymer electrolyte system. In

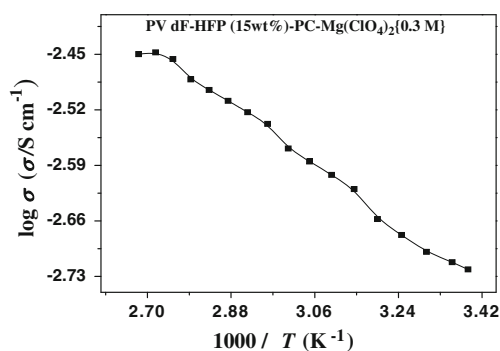


**Fig. 1** Variation of ionic conductivity of gel polymer electrolyte as a function of different weight percents of polymer [PVdF(HFP)] concentration

the present studies, one important observation has been recorded. It can be seen that initially, the electrical conductivity of polymer gel electrolyte is slightly higher than that of the liquid electrolytes [PC–Mg(ClO<sub>4</sub>)<sub>2</sub>(0.3 M)] by the addition of polymer content. It reaches a maximum value of  $5.0 \times 10^{-3} \text{ S cm}^{-1}$  at a concentration of 15 wt% of the polymer (PVdF–HFP) content, and thereafter, conductivity decreases by further addition of the polymer at room temperature (25°C). Similar types of observation have been reported earlier by few workers [20, 21]. This observation is found to be in good agreement with the “breathing chain model” proposed by Chandra and co-workers [21, 22]. According to this model, polymeric gels are considered to be consist of dissociated ions (free ions), ion pairs, undissociated salts, solvents, and polymeric chains existing either in folded or partially/fully unfolded form. At lower concentration of polymer, the system behaves like liquid electrolytes as a result of dissociation of salts. With an increase in polymeric contents beyond 15 wt%, the viscosity of the electrolyte solutions increases, and it tends to decrease the mobility of free ions which further leads to the decrease in the conductivity of the gel electrolytes. In low-concentration region below 15 wt% of the polymer content, it is assumed that at microscopic level, the polymer chain “breathes” when it opens or folds by occupying different volumes at different time spans. Hence, folding and unfolding of the polymeric chain lead to localized pressure fluctuations in the surrounding volumes, and this localized turbulent pressure leads to further dissociation of ion pairs, hence enhancing the mobility and conductivity of the system. Due to this reason, the higher conductivity of polymer gel electrolyte as compared to pure liquid electrolyte is observed at lower concentration of polymer. Further, it is observed that [PVdF(HFP) (15 wt%)–PC–Mg(ClO<sub>4</sub>)<sub>2</sub> (0.3 M)] composition of gel polymer electrolytes under present investigations, having free-standing film, exhibits maximum ionic conductivity of  $5.0 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature, which is appreciably higher than the values reported by different workers in the literature [5–16]. Since the order of conductivity of gel electrolytes as obtained in the present studies ( $5.0 \times 10^{-3} \text{ S cm}^{-1}$ ) shows better performance as compared to the reported one and these are acceptable values from a device fabrication point of view, finally, this composition of gel polymer electrolytes is chosen for further investigations and has been tested successfully for its application in supercapacitor as an electrolyte material.

#### Temperature dependence conductivity

Measurement of ionic conductivity over a wide range of temperature is a good indicator of the thermal stability of the gel polymer electrolytes. Figure 2 shows the ionic conductivity of gel electrolyte system under the present



**Fig. 2** Variation of ionic conductivity of optimized gel polymer electrolyte PVdF(HFP) (15 wt%)–(0.3 M) Mg (ClO<sub>4</sub>)<sub>2</sub> as a function of temperature

investigation at different temperatures. From the plot, it is evident that as the temperature increases, the ionic conductivity also increases for the electrolyte systems. The increase in conductivity with temperature may be due to the decrease in viscosity and hence increased chain flexibility [23]. The  $\sigma$  versus  $1/T$  curves for gel polymer electrolyte system shows a linear pattern, suggesting Arrhenius behavior and thermally activated processes, which can be expressed as  $\sigma = \sigma_0 \exp(-E_a/kT)$  where,  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy, and  $T$  is the absolute temperature in Kelvin scale [24]. The activation energy is found to be in the order of 0.036 eV in polymer electrolyte system which has been calculated by fitting the curve in lower temperature region up to 70°C. The variation in conductivity with temperature has been explained in terms of segmental motion that results in an increase in free volume of the sample and hence the motion of ionic charge. The amorphous nature of composite blend provides a greater free volume of the system upon increasing the temperature [25]. Thus, the segmental motion either permits the ions from one site to another or provides the pathway for ions to move. This inter-chain or intra-chain ion movements are responsible for the high ionic conductivity in the electrolyte system. It is a well-established fact that for the application in devices operating over a wide range of temperature, it is desirable to have electrolytes with uniform conductivity and low activation energies [26, 27]. The magnesium-ion based gel polymer electrolytes chosen in the present studies show uniform conductivity over a wide temperature range as can be seen from Fig. 2, having activation energy in the order of 0.036 eV, which is appreciably lower than that of the lithium ion-based polymer electrolyte as reported in the literature by different workers [28, 29]. Hence, synthesized polymer gel under present investigation may be treated as promising materials for its application in supercapacitor devices over a wide temperature range.

By exploring the frequency-dependent electrical response of polymeric-based electrolyte system, we may get a better understanding about the nature of ionic transport mechanism

in the given system. Due to this reason, the complex impedance of electrolyte system is analyzed by the formalisms of complex permittivity ( $\epsilon$ ), electrical modulus ( $M$ ), and conductivity  $\sigma$  ( $\omega$ ) studies.

### Dielectric analysis

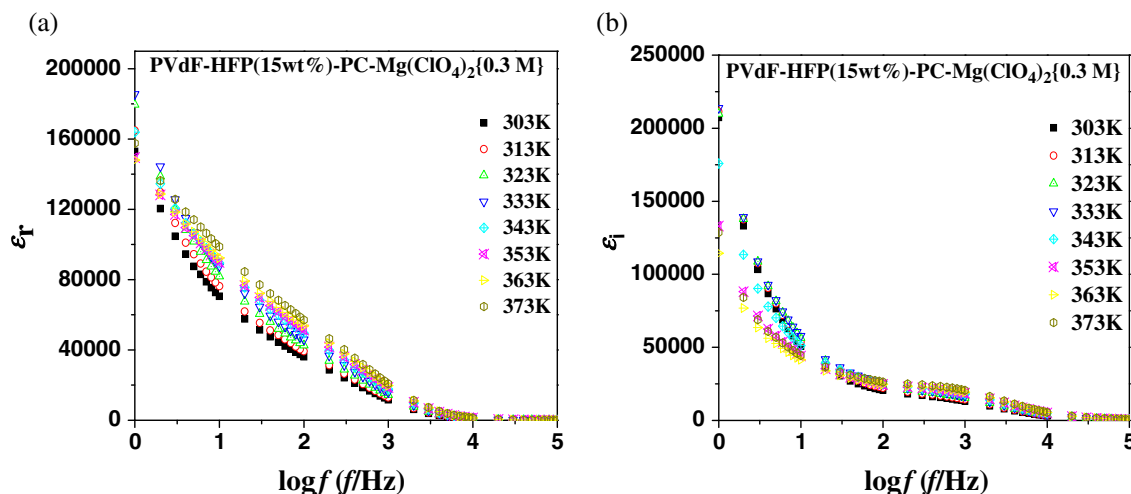
In order to better understand the ionic transport phenomenon of any polymer electrolyte system, its dielectric relaxation was further studied [30]. The complex permittivity ( $\epsilon^*$ ) or dielectric constant of a material is defined as  $\epsilon^* = \epsilon_r - j\epsilon_i$  where,  $\epsilon_r$  is the real part of dielectric constant and  $\epsilon_i$  is its imaginary component which basically represents the storage and loss of energy in every cycle of the applied electric field, respectively [31]. Figure 3a, b shows the dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\epsilon_i$ ) as a function of frequency at various temperatures for gel polymer electrolyte system [PVdF(HFP) (15 wt%)-PC-Mg(ClO<sub>4</sub>)<sub>2</sub> (0.3 M)]. From Fig. 3a, it can be seen that the values of  $\epsilon_r$  is rising very sharply towards low-frequency region, which can be explained on the basis of electrode polarization effect [32]. This low-frequency dispersion region is basically attributed to the high contribution of charge accumulation at the electrode–electrolyte interfaces [33–35]. In high-frequency region, it is found that the value of  $\epsilon_r$  is almost constant with frequency. It happens because the periodic reversal of the electric field occurs so fast that the charge carriers will not get sufficient time to orient themselves in the field direction. Hence, there is no excess ion diffusion in the direction of the field and it further leads to the decrease in the values of dielectric constant [36]. Again, from Fig. 3b, it can be seen that the dielectric loss ( $\epsilon_i$ ) becomes very large ( $\sim 10^5$ ) towards low-frequency region. It is due to the motion of free charge carriers within the material [37]. These values of dielectric loss do not correspond to the bulk dielectric

processes but are due to the free charges that are built up at the interface between the materials of electrolyte and electrode. When the values of frequency are very low, charge carriers get sufficient time to build up at the electrode–electrolyte interfaces before the field changes its direction, and this contributes to the large values of dielectric loss. This phenomenon is called “conductivity relaxation” [38]. The increase in the values of dielectric constant and dielectric loss at higher temperature has been observed which can be attributed to the increase in charge carrier density due to the increase in dissociation of ion aggregates. A further analysis of dielectric behavior for the polymer gel electrolyte system has been achieved successfully using dielectric modulus analysis, which suppresses the effect of electrode polarization [39].

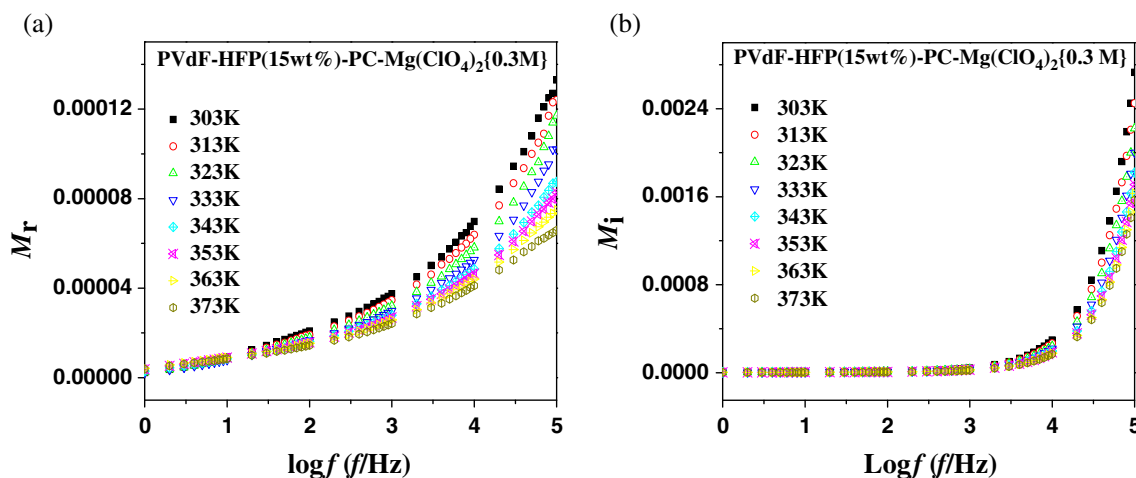
### Modulus spectra

Analysis of modulus spectroscopy reveals the bulk properties of the materials, and it is complementary to impedance spectroscopy which basically highlights electrode and grain boundaries effect. Electrical modulus  $M^*$  may be defined as the reciprocal of the complex relative permittivity  $\epsilon^*$  as  $M^* = 1/\epsilon^* = M_r + jM_i$ .

Figure 4a, b shows the real part ( $M_r$ ) and imaginary part ( $M_i$ ) of electrical modulus as a function of frequency at various temperatures for gel polymer electrolytes. Both  $M_i$  and  $M_r$  are observed to increase in the high-frequency region and to give a long tail at lower frequencies. The peaks in the modulus formalism at high frequencies show that the polymer electrolyte films are predominantly ionic conductors [40]. The peak curve at higher frequencies may be due to bulk effect. It is observed from the plots that  $M_r$  and  $M_i$  decrease towards low frequencies. This is due to the electrode polarization phenomenon which makes a negligible



**Fig. 3** Variation of **a** dielectric constant and **b** dielectric loss of optimized gel polymer electrolyte system PVdF(HFP) (15 wt%)-(0.3 M) Mg(ClO<sub>4</sub>)<sub>2</sub> as a function of frequencies at various temperatures



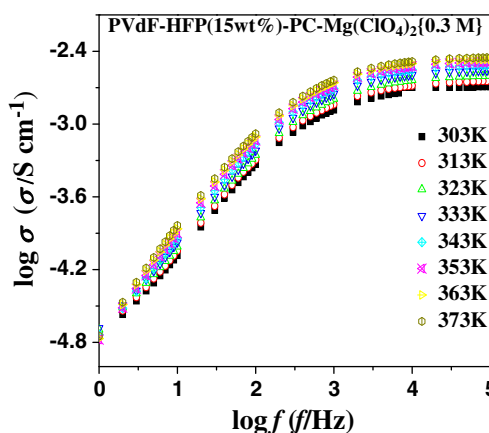
**Fig. 4** Variation of **a** real part and **b** imaginary part of electrical modules at different frequencies for PVdF(HFP) (15 wt%)-(0.3 M) Mg(ClO<sub>4</sub>)<sub>2</sub>-based gel polymer electrolyte system

contribution, and its effect seems to be clearly vanishing towards low-frequency domain. The presence of this long tails in the low-frequency regions is probably due to their large capacitance values associated with the electrodes [41]. The increasing peak of Fig. 4b can be assumed to be related to the translational ion dynamics and mirrors the conductivity relaxation of the mobile ions. The shapes of all the plots are identical for all temperatures and show a single relaxation peak in the range of temperature and frequency determined under present studies. The angular frequency  $\omega_c$  at which the maximum  $M_i$  occurs represents the relaxation time  $\tau_c$  by the mathematical relation  $\tau_c \omega_c = 1$  [42]. Further, it is observed that  $M_i$  shows a slightly asymmetric peak at each temperature. The peak shifts towards higher frequency sides with increasing temperature. The broad nature of the peaks can be understood as being the results of distributions of relaxation time. These peaks are broader than the Debye peak, which is treated as an ideal ionic conductor represented by a single parallel RC element [43]. The broad and asymmetrical shape of electrical modulus plot is generally explained by the non-exponential decay function of the electric field using the mathematical relation  $\varphi(t) = \exp[-(t/\tau)^\beta]$  where,  $\tau$  is the relaxation time, and  $\beta$  is the well-known Kohlrausch parameter which decreases with an increase in the relaxation time distribution and its values lies between 0 and 1 for practical solid electrolyte system, which is indicative of departure from the Debye relaxation ( $\beta=1$ ) [44].

Conductance spectra

The conductance spectra for [PVdF(HFP) (15 wt%)-PC-Mg(ClO<sub>4</sub>)<sub>2</sub> (0.3 M)] gel polymer electrolytes with different temperature are shown in Fig. 5. The spectra consist of two regions; a low-frequency dispersive region due to electrode-electrolyte interfacial phenomena and the plateau representing

the dc conductivity. As the frequency decreases, more and more charge accumulation occurs at the electrode-electrolyte interface which leads to the 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 [41]. It has been observed that the dc conductivity increases with temperature, which suggests that the free volume around the polymer chain causes the mobility of ions and polymer segments. The phenomenon of the conductivity dispersion is generally represented by Jonscher's law [45]. Mathematically, it can be written as  $\sigma(\omega) = \sigma_{dc} + A\omega^n$  where,  $\sigma_{dc}$  is the dc conductivity of the sample,  $A$  is a constant for a particular temperature, and  $n$  is the frequency exponent lying in between the range of  $0 < n < 1$ . The values of  $n$  basically represent the degree of interaction between the mobile ions and the environments surrounding them. For ionic



**Fig. 5** Variation of ionic conductivity as a function of frequency for gel polymer electrolyte system PVdF(HFP) (15 wt%)-(0.3 M) Mg(ClO<sub>4</sub>)<sub>2</sub>

conductors, this value lies between 0.5 and 1, indicating the ideal long range pathway diffusion of the ions and can be best explained by hopping models [45]. When the value of  $n=0$ , the motion is completely random and the independent Debye-like ion hops. The transport mechanism of ionic conductor in general can be explained by the thermally activated hopping process between two different sites separated by energy barriers. In order to explain the frequency dispersion behavior of the ionic conductors, a physical model namely “jump relaxation model” has been proposed [46]. According to this model, at very low frequencies when  $\omega \rightarrow 0$ , ions available on one site can easily jump to its neighboring vacant sites successfully, contributing to the dc conductivity. At higher frequencies, the probability of ions to return back to its initial site increases due to the availability of very short time periods. The high probability of forward–backward hopping at higher frequencies together with the relaxation of the dynamic cage potential is mainly responsible for the observation of high-frequency dispersion in its conductivity.

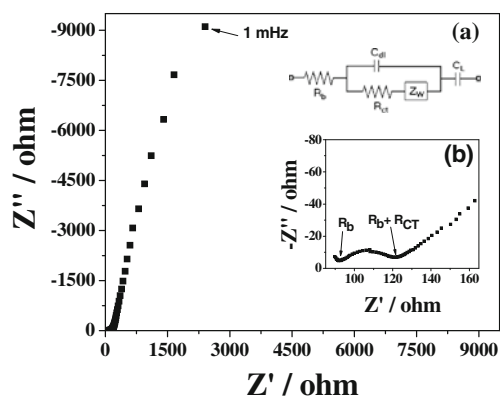
#### Characteristics of supercapacitor cell

In order to check the suitability of magnesium ion-based polymer gel electrolyte having an optimized conductivity of  $5.0 \times 10^{-3} \text{ S cm}^{-1}$  for its application in energy storage devices particularly redox supercapacitor, an impedance spectroscopic method has been adapted. Capacitor cell has been constructed using pPy as an electrode material with optimized polymer gel electrolyte having the following configuration:

cell A : pPy|[PVdF(HFP)(15wt%) – PC – Mg(ClO<sub>4</sub>)<sub>2</sub>(0.3M)]|pPy.

The complex impedance plot of the above said capacitor cell is shown in Fig. 6. Impedance spectroscopy is considered to be a very powerful technique to characterize any electrochemical cell, particularly supercapacitors. With the help of this technique, various electrical parameters which

are associated with the bulk properties of the electrolyte, electrode–electrolyte interfaces, equivalent series resistance (ESR) of the overall capacitors, potential dependent faradic resistances, low-frequency capacitance values, etc. can be evaluated separately in different frequency ranges [47]. It should be noted that the impedance response of ideal capacitor is a straight line parallel to the imaginary axis of the complex impedance plots. However, in the real capacitor, the steep rising capacitive impedance response is observed in low-frequency region accompanied with high-frequency semicircular features owing to the bulk and interfacial properties. The impedance response of a capacitor cell shows a small semicircular spur in the higher frequency region (expanded portion of Fig. 6b in inset) followed by a steep rising portion in the lower frequency region up to 1 mHz. This steep rising behavior indicates the capacitive character of the cell in lower frequency region, whereas the high-frequency semicircle spur shows the bulk properties of the electrolytes and the interfacial charge transfer processes. In addition to these impedance features, a straight line making a phase angle of  $\sim 45^\circ$  with respect to the real axis ( $Z'$ ) has also been observed for the capacitor cell in the middle frequency range (Fig. 6b inset). This dispersion feature of impedance plots represents diffusion/migration due to concentration gradients in the electrolyte [48, 49] or charging of deep pores of electrodes [50] or as a minor effect, resulting from thermal and stochastic effects [51]. This response is associated mainly with the interfacial characteristics having a specific porous structure of the electrode material in contact with the highly flexible and mechanically stable magnesium ion-based polymeric gel electrolytes. The impedance response of various possible geometries for the porous structure of the electrode material has been described theoretically by some workers [47, 50]. A comparison with the impedance response observed in the present case indicates that the electrochemically deposited pPy on ITO conducting glass possesses almost cylindrical geometry of the pores accessible to the gel electrolytes. Such overall impedance response of the solid-state redox supercapacitor indicates that the equivalent circuit should be represented by a modified Randles circuit [52] as shown in Fig. 6a as an inset. The semicircle, which is observed to be slightly suppressed towards the real axis, is attributed to the parallel combination of a double layer capacitance  $C_{dl}$  and charge transfer resistance  $R_{ct}$  in series with Warburg impedance. The Warburg impedance is related with the diffusional process of ions at the porous electrode–electrolyte interface, which corresponds to the transmission line type RC equivalent circuit [47]. Various electrical parameters such as bulk resistance  $R_b$  ( $58 \Omega \text{ cm}^2$ ) and interfacial charge transfer resistance  $R_{ct}$  ( $17 \Omega \text{ cm}^2$ ) have been evaluated from the intercepts on the real axis of the complex impedance response. A few parameters associated with Warburg



**Fig. 6** Typical impedance plot of capacitor cell pPy|PVdF–HFP–PC–Mg(ClO<sub>4</sub>)<sub>2</sub>|pPy recorded at room temperature in the frequency range of 100 kHz to 1 mHz

impedance could not be evaluated due to lack of facilities. The capacitance values observed for a capacitor cell at 1 mHz is found to be  $22 \text{ mF cm}^{-2}$  which is equivalent to a single-electrode specific capacitance of  $117 \text{ F g}^{-1}$  for magnesium ion-based gel polymer electrolyte with pPy electrodes. This value of capacitance is relatively better than that of the earlier system which uses lithium, sodium, and tetraethylammonium tetrafluoroborate-based polymer gel electrolytes with the same pPy electrodes as reported by Tripathi et al. [53]. Further, the value of the capacitance of the cell comprising liquid electrolyte is expected to be quite larger as compared with that of the polymer/gel electrolyte-based capacitor. This difference is possibly due to inaccessibility of the solid-like gel electrolyte to form the complete interfacial contact with the active electrode materials like pPy. An attractive aspect of the present studies is that it offers relatively smaller values of its charge transfer resistance,  $R_{ct}$  ( $17 \Omega \text{ cm}^2$ ) and bulk resistance  $R_b$  ( $58 \Omega \text{ cm}^2$ ). These lower resistances mainly contribute to the ESR, which further leads to the relatively higher power densities of the solid-like redox supercapacitors. This indicates substantially proper contact between pPy electrodes and highly flexible and conducting magnesium ion-based polymeric gel electrolytes.

## Conclusion

Combining all the above experimental studies, the following important conclusions can be drawn:

- (a) The magnesium ion-based gel polymer electrolytes [PVdF(HFP)–PC–Mg(ClO<sub>4</sub>)<sub>2</sub>] with different compositions have been prepared by “solution-cast” technique. The highest conductivity  $\sigma = 5.0 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature is obtained for [PVdF(HFP) (15 wt%)–PC–Mg(ClO<sub>4</sub>)<sub>2</sub> (0.3 M)] gel polymer electrolyte.
- (b) The polymer gel electrolyte film is flexible and free standing with good mechanical strength.
- (c) The low-frequency dispersion of dielectric constant reveals the space charge effects arising from the electrodes. It also indicates that ionic and polymer segmental motion is strongly coupled.
- (d) The modulus spectrum and dielectric studies show the non-Debye nature of the electrolyte materials which corresponds to long-time slow polarization and relaxation of hopping charges.
- (e) The temperature variation of the conductivity plot shows the Arrhenius behavior of the electrolyte system. The activation energy of the electrolyte system is found to be in the order of 0.036 eV.
- (f) Preliminary studies on supercapacitor have been carried out for electrochemically deposited pPy-based redox supercapacitor with optimized polymer gel electrolyte [PVdF(HFP) (15 wt%)–PC–Mg(ClO<sub>4</sub>)<sub>2</sub> (0.3 M)] using ac impedance analysis.
- (g) The overall capacitance values have been observed to be  $22 \text{ mF cm}^{-2}$ , which is equivalent to a single-electrode specific capacitance of  $117 \text{ F g}^{-1}$  of pPy electrode owing to the flexible nature of magnesium ion-based polymer gel electrolyte.
- (h) An attractive aspect of the present studies is that the values of its charge transfer resistance  $R_{ct}$  is in the order of  $17 \Omega \text{ cm}^2$  and bulk resistance  $R_b$  is  $58 \Omega \text{ cm}^2$  which is relatively smaller than that of the solid-state supercapacitor cells based on conventional solid polymer electrolyte system.
- (i) From the above said results on supercapacitor, one may conclude that magnesium ion-based gel polymer electrolyte is a promising electrolyte material suitable for the fabrication of electrochemical redox supercapacitor with pPy as conducting polymer electrodes.
- (j) Capacitance values as well as its internal resistance “ESR” show that either of these values is comparable or better than the values obtained for lithium- or sodium ion-based polymeric systems. Further, magnesium ion-based electrolytes are environment-friendly as well as cheaper than lithium ion-based electrolytes. Hence, magnesium ion-based electrochemical devices may be treated as the alternative substitute for commercially available lithium ion-based devices.

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