

Effect of propylene carbonate on the ionic conductivity of polyacrylonitrile-based solid polymer electrolytes

Srinivasan Nithya,¹⁻³ Subramaniyan Selvasekarapandian,³ Shunmugavel Karthikeyan,⁴ Dharmalingam Vinoth Pandi⁵

¹Research and Development Centre, Bharathiar University, Coimbatore, Tamilnadu, India

²Department of Physics, Sri. S. Ramasamy Naidu Memorial College, Sattur Tamilnadu 626 023, India

³Materials Research Centre, Coimbatore, Tamilnadu 641 045, India

⁴Department of Physics, Madras Christian College, Tambaram, Chennai, Tamilnadu, India

⁵Coimbatore Institute of Technology, Coimbatore, Tamilnadu, India

Correspondence to: S. Selvasekarapandian (E-mail: sekarapandian@rediffmail.com)

ABSTRACT: Solid polymer electrolyte membranes consisting of polyacrylonitrile (PAN) as a host polymer, ammonium nitrate (NH_4NO_3) as a complexing salt, and propylene carbonate (PC) as a plasticizer were prepared by a solution casting technique. An increase in the amorphous nature of the polymer electrolytes was confirmed by X-ray diffraction analysis. A shift in the glass-transition temperature of the PAN/ NH_4NO_3 /PC electrolytes was observed in the differential scanning calorimetry thermograms; this indicated interactions between the polymer and the salt. The impedance spectroscopy technique was used to study the mode of ion conduction in the plasticized polymer electrolyte. The highest ionic conductivity was found to be 7.48×10^{-3} S/cm at 303 K for 80 mol % PAN, 20 mol % NH_4NO_3 , and 0.02 mol % PC. The activation energy of the plasticized polymer electrolyte (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC) was found to be 0.08 eV; this was considerably lower than that of the film without the plasticizers. The dielectric behavior of the electrolyte is discussed in this article. A literature survey indicated that the synthesis and characterization of ammonium-salt-doped, proton-conducting polymer electrolytes based on PAN has been rare. The use of the best composition membrane (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC) proton battery was constructed and evaluated. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41743.

KEYWORDS: amorphous; conducting polymers; dielectric properties; membranes; spectroscopy

Received 5 August 2014; accepted 6 November 2014

DOI: 10.1002/app.41743

INTRODUCTION

Batteries consists of three main components: anodes, cathodes, and electrolytes. The electrolyte is the key component of the battery. Among different electrolytes, solid polymer electrolytes have received a great deal of attention because of their potential large-scale application in the development of sensors, photovoltaic cells, electrochromic devices, smart electronics, and so on.¹ Recently, proton-conducting polymer electrolytes have been reported because of their suitability as a proton-conducting membrane in polymer electrolyte membrane fuel cells and other electrochromic devices.² The main aim of most research has been focused on the enhancement of ionic conductivity. Various techniques, such as the blending of polymers, crosslinking of polymers, and insertion of ceramic fillers and plasticizer in the polymer membrane, have been performed to enhance the ionic conductivity.³⁻⁶ Plasticization is an effective ways to improve the ionic conductivity.⁷ The addition of plasticizer to the polymer electrolyte decreases the glass-transition temperature

(T_g) of the polymer and softens the polymer backbone; this results in a higher segmental motion and thus increases the ionic conductivity. The plasticizer propylene carbonate (PC), with its low viscosity and high dielectric constant, was chosen as one of the plasticizers in this study. A variety of plasticized polymer electrolytes based on various host polymers⁸⁻¹⁰ have been developed for solid-state applications.

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been widely used because of its high strength and abrasion resistance and good insect resistance.¹¹ PAN is used to produce a large variety of products, including ultrafiltration membranes, hollow fibers for reverse osmosis, and fibers for textiles. However, the conductivity of PAN is less than 10^{-14} S/cm, and the static problem restricts its further application. PAN is usually synthesized with free-radical polymerization. Usually, it is a copolymer of acrylonitrile and methyl acrylate or acrylonitrile and methyl methacrylate. PAN has a melting point of about 319°C, and it also decomposes at this temperature. A

literature survey indicated that the study of proton-conducting polymer electrolytes based on PAN with ammonium salt has been rare. In this investigation, plasticized polymer electrolyte systems composed of PAN as a host polymer, ammonium nitrate (NH_4NO_3) as a salt, and PC as a plasticizer were prepared by a solution casting technique. Different techniques, such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), and alternating-current impedance spectroscopy, were used to characterize the prepared polymer electrolytes, and a proton battery was constructed and evaluated to determine the best composition membrane having the highest conductivity.

EXPERIMENTAL

The raw materials used in this study were as follows:

1. PAN (molecular weight = 1,50,000, Sigma Aldrich).
2. NH_4NO_3 (molecular weight = 80, Sigma Aldrich).
3. PC (molecular weight = 102.09, Sigma Aldrich).

Plasticized polymer electrolytes with various compositions were prepared by a solution casting technique. In our earlier study,¹² we reported a polymer electrolyte with 80 mol % PAN and 20 mol % NH_4NO_3 had the highest conductivity of 2.74×10^{-6} S/cm. In this study, the plasticized polymer electrolytes were prepared by the addition of 0.01, 0.02, and 0.03 mol % of the plasticizer PC to the highest conductivity sample, 80 mol % PAN/20 mol % NH_4NO_3 . The mixtures were then stirred to get the homogeneous solution. The solutions were then dispersed in a polypropylene Petri dish and allowed to dry in vacuum at 50°C to get mechanically stable thin films with a thickness of 0.02 cm. The different compositions of plasticized polymer electrolytes investigated were as follows:

1. 80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC.
2. 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC.
3. 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC.

The prepared polymer electrolytes were subjected to various measurements. The XRD measurements were performed with a Philips X-ray diffractometer (model PW 3071) with $\text{Cu K}\alpha$ as the source. The Fourier transform infrared spectra for the pure PAN and the plasticized polymer-salt complexes were recorded at room temperature in transmission mode with a Shimadzu IR Affinity-1 spectrometer in the wave-number range 400–4000 cm^{-1} . The impedance measurement was carried out with a computer-controlled Hioki 3532-50 LCR Hi-Tester in the frequency range of 42 Hz to 5 MHz. The polymer films were sandwiched between the two aluminum blocking electrodes to take impedance measurements. A proton battery was constructed and studied with the highest conductivity polymer electrolyte (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC) as the electrode, $\text{PbO}_2/\text{V}_2\text{O}_5/\text{C}$ as the cathode, and a combination of zinc (metal) powder, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and graphite powder as the anode.

Preparation of the Cathode

The cathode was prepared by physical grinding to obtain a fine powder with $\text{PbO}_2/\text{V}_2\text{O}_5/\text{C}$ /polymer electrolyte (8:2:1:0.5), and graphite C was added to introduce electronic conductivity,

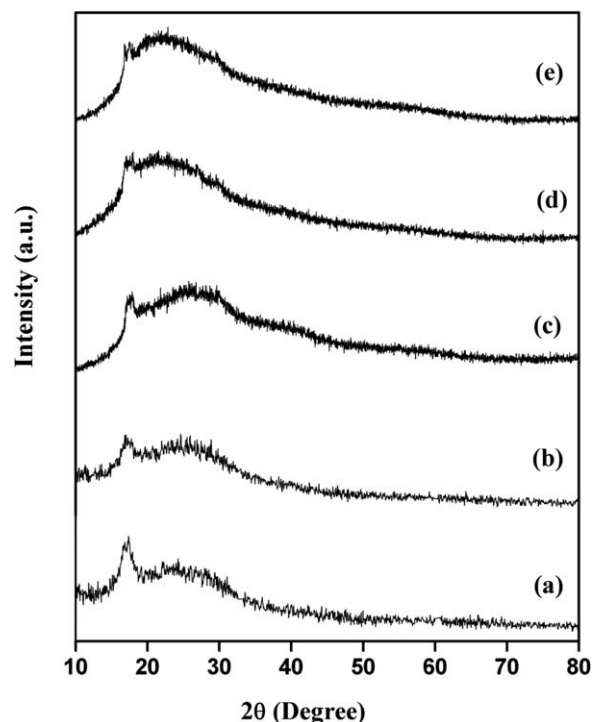


Figure 1. XRD pattern of the (a) pure PAN, (b) 80 mol % PAN/20 mol % NH_4NO_3 , (c) 80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, (d) 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and (e) 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC films.

whereas the addition of the polymer electrolyte helped to reduce the electrode polarization.¹³ The previous mixture was made into thin pellets. The thickness of the prepared pellet is was 1.04 mm.

Preparation of the Anode

Desired proportions (3:1:1) of zinc (metal) powder, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and graphite powder are taken and mixed together and finally ground well. Then, the mixture was pressed to form a thin pellet. The prepared pellet had a thickness of about 1.01 mm.

Cell Assembly

The polymer electrolyte was sandwiched between the anode and cathode pellets. This entire assembly was finally compacted in the sample holder. The current collectors were screwed tightly to ensure good contact between the layers of the battery components.

RESULTS AND DISCUSSION

XRD Analysis

The XRD patterns of the pure PAN, 80 mol % PAN/20 mol % NH_4NO_3 , 80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC, are shown in Figure 1(a–e). We observed that the addition of PC at different concentrations (0.01, 0.02, and 0.03 mol %) to the polymer electrolyte system with 80 mol % PAN/20 mol % NH_4NO_3 increased the amorphous nature of the polymer electrolyte. This was implied by the shifting of the peaks, the decrease in the peak intensity, and the broadening of peaks in the PAN/ NH_4NO_3 /PC polymer electrolyte system [Figure 1(c–e)]. The peak at 17.2° for the 80 mol % PAN/20 mol % NH_4NO_3 ,

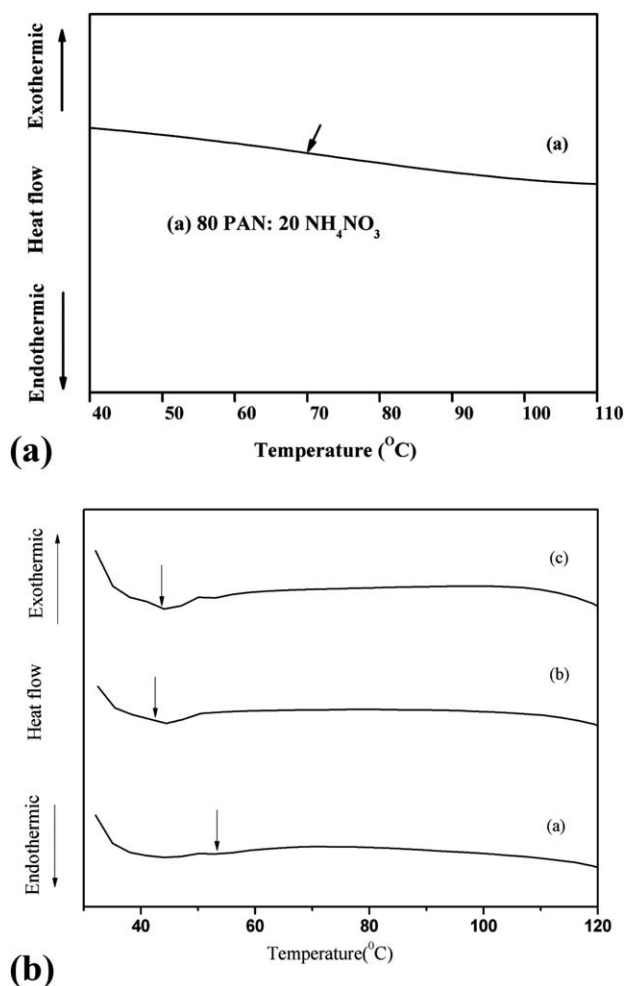


Figure 2. DSC thermograms of the (a) 80 mol % PAN/20 mol % NH_4NO_3 and (b) three different compositions of the plasticized polymer electrolyte.

system shown in Figure 1(b) shifted slightly to 17.90, 17.97, and 16.86° with the addition of 0.01, 0.02, and 0.03 mol % PC, respectively. Also, the peak intensity was found to be significantly lower compared to 80 mol % PAN/20 mol % NH_4NO_3 . Hence we observed that the amorphous nature of 80 mol % PAN/20 mol % NH_4NO_3 increased with the addition of the plasticizer PC. This increase in the amorphous nature caused a reduction in the energy barrier to the segmental motion of the polymer electrolyte.¹⁴

DSC

The DSC curve of 80 mol % PAN/20 mol % NH_4NO_3 and 80 mol % PAN/20 mol % NH_4NO_3 with different concentrations of the plasticizer (PC) is shown in Figure 2(a,b). T_g was measured at the midpoint of each transition. T_g for 80 mol % PAN/20 mol % NH_4NO_3 was observed at 65°C. The decrease in T_g with the addition of plasticizer indicated the increase in the polymer flexibility and implied that the amorphous phase was relatively high; this was also reflected in the XRD studies. The obtained T_g for the prepared plasticized polymer electrolytes are listed in Table I. The lowest T_g (42.6°C) was found for 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC. The decrease in

Table I. T_g Values of the PAN/ NH_4NO_3 /PC Polymer Electrolyte with Different Compositions

Polymer electrolyte (mol %)	T_g (°C)
80 mol % PAN/20 mol % NH_4NO_3 /0 mol % PC	65
80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC	53
80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC	42.6
80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC	46

the value of T_g with the addition of the plasticizer indicated the possibility of reduction in the internal viscosity of the films.^{15,16}

Impedance Spectral Analysis

Impedance spectroscopy measurements were carried out to establish the conduction mechanism of the plasticized polymer electrolytes.

The impedance [$Z^*(\omega)$] is given by

$$Z^*(\omega) = |Z| \exp(-i\phi)$$

$$Z^*(\omega) = |Z| \cos \phi - i|Z| \sin \phi$$

$$Z^*(\omega) = Z'(\omega) - iZ''(\omega)$$

where i is the $\sqrt{-1}$, ϕ is the phase angle and Z' and Z'' are the real and imaginary parts of the complex impedance, respectively.

The complex impedance (Cole–Cole) plots for the electrolyte system of 80 mol % PAN doped with 20 mol % NH_4NO_3 (unplasticized) and the systems plasticized by PC at 0.01, 0.02 and 0.03 mol % concentrations are shown in Figure 3(a,b).

The plot [Figure 3(a)] consisted of a high-frequency semicircle and a low-frequency spike. The semicircle may have been due to the bulk effect of the electrolyte, and the spike may have been due to the effect of the blocking electrodes. The intercept of the semicircle or spike with the real axis provided the bulk electrical resistance (R_b) of the polymer electrolyte.

The conductivity (σ) of the plasticized polymer electrolyte was calculated with eq. (1):

$$\sigma = l/AR_b \quad (1)$$

where l is the thickness of the polymer electrolyte and A is the surface area of the polymer electrolyte.

The disappearance of the semicircle with the addition of plasticizer led to the conclusion that the charge carriers were ions, and hence, the total ionic conductivity was due to ion conduction.¹⁷ The highest ionic conductivity at ambient temperature was found to be 7.48×10^{-3} S/cm for the 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC polymer electrolyte. Figure 3(c) shows the complex impedance plot of the highest conductivity sample at different temperatures. The ionic conductivity values for the unplasticized polymer film (80 mol % PAN/20 mol % NH_4NO_3) and for the plasticized polymer systems with different concentrations of PC at different temperatures are shown in Table II.

Conductance Spectra

The logarithm plots of the conductivity variation as a function of the frequency for different compositions of plasticized

polymer electrolytes (80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC) at room temperature are shown in Figure 4(a), and those of the highest conductivity plasticized polymer electrolyte (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC) at different temperatures are shown in Figure 4(b).

The curve consisted of two distinct regions with in the measured frequency range. The low-frequency region described the electrode–electrolyte interfacial phenomena, which were ascribed to the space charge polarization at the blocking electrodes;¹⁸ this was followed by the frequency-independent plateau region, which corresponded to ionic conductivity (σ_{dc}) of the complexed polymer electrolyte. Hence, the σ_{dc} values were obtained by the extrapolation of the plateau region to the y axis.

As the temperature increased, the low-frequency dispersion region became prominent and shifted to a higher frequency region, and the frequency-independent plateau region decreased. Hence, the polarization effect became dominant as the temperature increased. The variation of the conductivity value with temperature obtained from the conductance spectra was in accordance with those obtained from the Cole–Cole plot.

Temperature-Dependent Conductivity

Temperature-dependent ionic conductivity measurements are carried out to analyze the mechanism of ionic conduction in the polymer electrolyte membranes. We observed that the temperature dependence of the conductivity obeyed the following Arrhenius relationship:¹⁹

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

where E_a is the activation energy, K is the Boltzmann constant, and σ_0 is the pre-exponential factor. The σ values of the plasticized polymer electrolyte 80 mol % PAN/20 mol % NH_4NO_3 /PC were used to plot $\log \sigma$ versus $1000/\text{absolute temperature } (T)$, as shown in Figure 5. The plot showed that the conductivity increased with increasing temperature. The nature of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and, hence, increase the conductivity to a higher value.²⁰ It is also understood that the increase in the conductivity with temperature can be linked to a decrease in the viscosity and, hence, an increase in the chain flexibility.²¹ The low activation energy for the highest conductivity polymer electrolyte (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, $\sigma = 7.48 \times 10^{-3}$ S/cm) suggested that the ion transport was due to the increase in the amorphous nature of the polymer electrolytes, which facilitated the fast ion motion in the polymer network.

Dielectric Spectral Analysis

The complex permittivity (ϵ^*) or dielectric constant of the system was defined by

$$\epsilon^* = \epsilon'(\omega) - i\epsilon''(\omega) \quad (3)$$

where $\epsilon'(\omega)$ is the real part of the dielectric constant and $\epsilon''(\omega)$ is the imaginary part of the dielectric constant of the material.

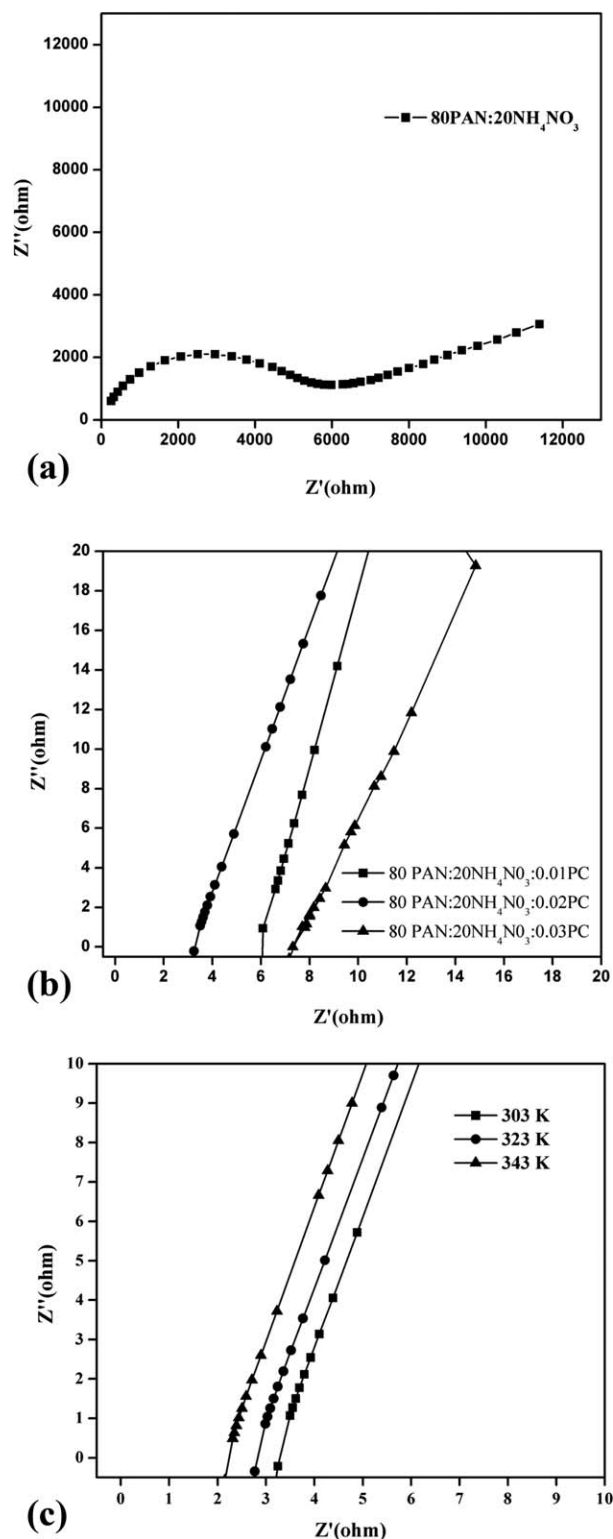


Figure 3. Complex impedance plot for the (a) 80 mol % PAN/20 mol % NH_4NO_3 polymer electrolyte system at ambient temperature (303 K), (b) plasticized polymer electrolyte systems (80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC) at ambient temperature (303 K), and (c) 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC polymer electrolyte at different temperatures.

Table II. Ionic Conductivity and Activation Energy Values for the Polymer Electrolytes

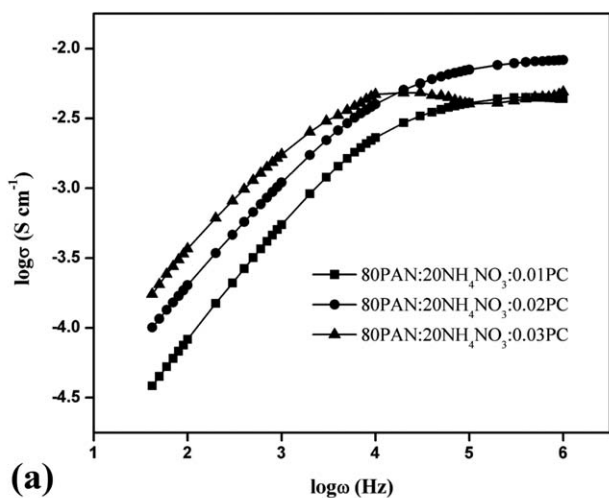
Polymer electrolyte (mol %)	σ (S/cm)			E_a (eV)
	303 K	323 K	343 K	
80 mol % PAN/20 mol % NH_4NO_3 /0 mol % PC	2.74×10^{-6}	7.05×10^{-6}	2.11×10^{-5}	0.58
80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC	4.38×10^{-3}	5.10×10^{-3}	7.28×10^{-3}	0.11
80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC	7.48×10^{-3}	8.60×10^{-3}	1.10×10^{-2}	0.08
80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC	4.03×10^{-3}	4.42×10^{-3}	4.85×10^{-3}	0.09

Figure 6(a) shows the variation of dielectric constant (ϵ') as a function of the frequency for the 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC polymer electrolyte at 303 K. Figure 6(b) shows the variation of dielectric loss (ϵ'') as a function of the frequency for the highest conductivity system with 0.02 mol % of PC at different temperatures. The values of ϵ' were very

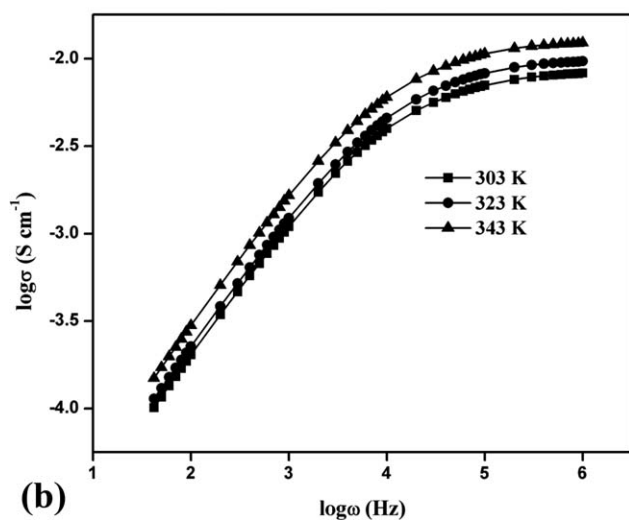
high at low frequency and relatively constant at higher frequencies. Such a high value of ϵ' may have been due to space charge effects, which were contributed by the accumulation of charge carriers near the electrodes.^{22,23}

At higher frequencies, the periodic reversal of the electric field occurred so fast, and there was no excess ion diffusion in the direction of the applied field. The polarization was due to the charge accumulation at the electrode decreasing; this led to a decrease in the value of ϵ' .²⁴

The frequency dependence of ϵ'' for the highest conductivity plasticized polymer electrolyte (80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC) at different temperatures clearly showed the high-frequency β -relaxation peak, which was pronounced at higher temperatures. This may have been caused by the movement of the side-group dipoles²⁵ of the polymer electrolytes. We also observed that the dielectric constant and dielectric loss increased with increasing temperature. This was because as the temperature increased, the degree of salt dissociation and redissociation of ion aggregates increased, and this resulted in an increase in the number of free ions or the charge carrier density.



(a)



(b)

Figure 4. Conductance spectra of the (a) plasticized polymer electrolyte systems (80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC) at ambient temperature (303 K) and (b) 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC polymer electrolyte at different temperatures. ω , hopping frequency.

Swelling Ratio of the Polymer Electrolyte

Dried 80 mol % PAN/20 mol % NH_4NO_3 , 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/

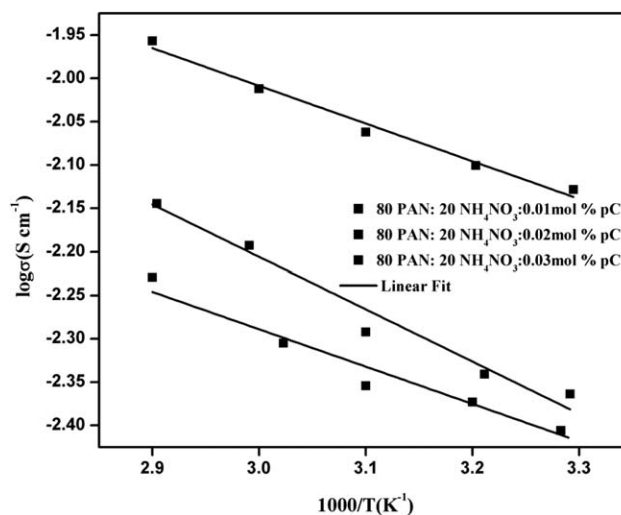
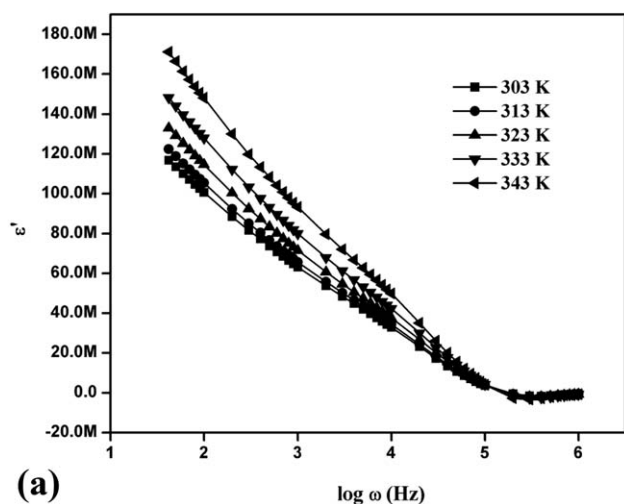
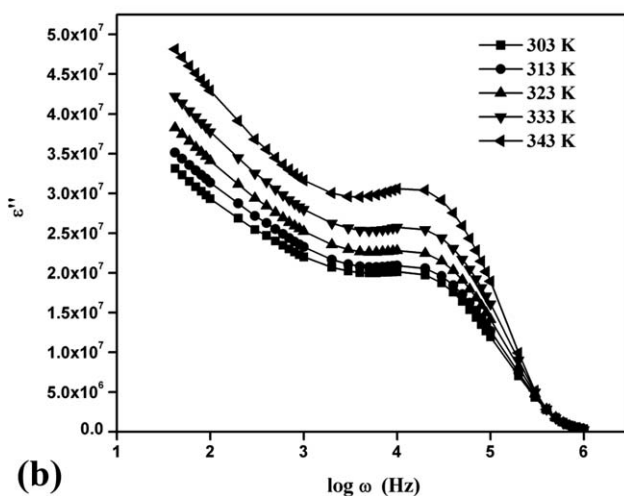


Figure 5. Temperature dependence of the conductivity of the plasticized polymer electrolytes (80 mol % PAN/20 mol % NH_4NO_3 /0.01 mol % PC, 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC, and 80 mol % PAN/20 mol % NH_4NO_3 /0.03 mol % PC).



(a)



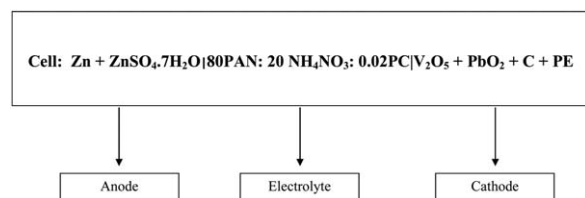
(b)

Figure 6. (a) Variation of ϵ' with the frequency for 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC at different temperatures. (b) Variation of ϵ'' with the frequency for 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC at different temperatures.

20 mol % NH_4NO_3 /0.03 mol % PC polymer electrolytes were immersed in distilled water at room temperature. We observed that there was no change in weight for the polymer electrolytes. There was no absorption of water by the membrane when they were immersed in water for 24 h.

Cell Configuration

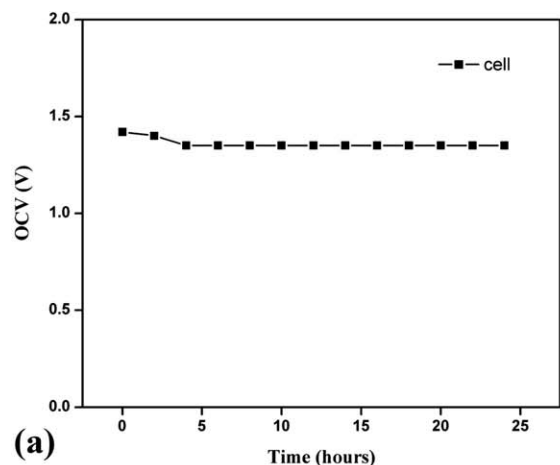
Among the prepared polymer electrolytes under study 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC possessed the highest conductivity. Hence, the cell was constructed with 80 mol % PAN/20 mol % NH_4NO_3 /0.02 mol % PC polymer electrolyte. The cell, so obtained, had the following configuration.



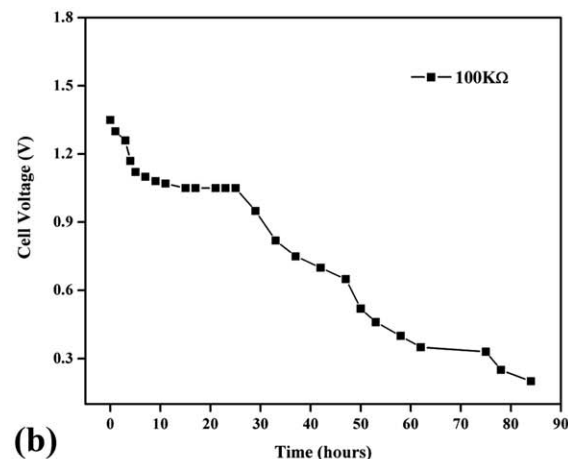
Discharge Characteristics

The open-circuit voltage (OCV) value of the cell was about 1.42 V. The cell was allowed to stabilize for a certain duration to attain a constant voltage.

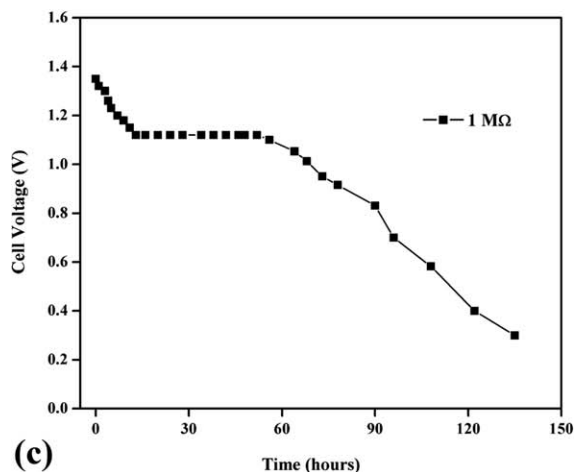
The variation in the OCV of the cell was monitored for 24 h and is shown in Figure 7(a). The cell did not show much decline in the OCV, and this revealed the lower self-discharging of the cell.



(a)



(b)



(c)

Figure 7. (a) OCV as a function of the time. (b) Discharge curve of the cell for 100 K. (c) Discharge curve of the cell for 1 MΩ.

Table III. Important Cell Parameters

Cell parameter	Zn + ZnSO ₄ · 7H ₂ O/80 mol % PAN/20 mol % NH ₄ NO ₃ /0.02 mol % PC/PbO ₂ + V ₂ O ₅	
	1 MΩ	100 KΩ
Cell area (cm ²)	1.12	1.12
Cell weight (g)	0.950	0.920
Effective cell diameter (cm)	1.2	1.2
Cell thickness (cm)	0.30	0.28
OCV (V)	1.42	1.42
Discharge time for plateau region (h)	38	12

The stabilized voltage of 1.35 V was observed for the cell. After the attainment of the stabilized voltage, the cell was discharged through 100-KΩ and 1-MΩ loads at room temperature.

Typical discharge curves for the fabricated cell are shown in Figure 7(b,c). The figure shows the cell-potential variation as a function of time for the 100-KΩ and 1-MΩ load resistances, respectively. During discharge, the cell voltage decreased initially and then remained constant for a particular time, after which there was a decrease in the voltage. The initial decrease in the cell voltage may have been due to the activation polarization.²⁶ When discharged with a low load resistance (i.e., 100 KΩ), the time of stable performance of the cell was a relatively quick discharge compared to the discharge with a high load resistance (1 MΩ).

While discharging through 1-MΩ and 100-KΩ loads, the voltage values of the cell remained constant at 1.12 and 1.05 V for about 38 and 12 h, respectively. The region in which the cell voltage remained constant is called the *plateau region*. Beyond the plateau region, again there was a drop in the voltage value of the cell. When the load was greater (1 MΩ), the cell voltage remained constant for a long time. Table III shows the lists of a few important cell parameters.

CONCLUSIONS

PAN-based, ion-conducting polymer electrolytes containing NH₄NO₃ and PC were prepared by a solution casting technique. The amorphous nature of the polymer electrolyte was confirmed by XRD analysis. The thermal transition of the polymer electrolyte was studied by DSC. It was depicted in the impedance spectroscopic analysis that the maximum conductivity value 7.48×10^{-3} S/cm at 303 K was observed for the 80 mol % PAN/20 mol % NH₄NO₃/0.02 mol % PC electrolyte system. The increase in the conductivity was related to the donor number and the viscosity of the plasticizer and not with the dielectric constant. The temperature dependence of the ionic conductivity of the plasticized polymer electrolyte system obeyed an Arrhenius-type relation. The dielectric loss spectrum of the polymer electrolyte plasticized with 0.02 mol % PC exhibited β relaxation. The optimized polymer electrolyte, with a high conductivity and low activation energy, 80 mol % PAN/20 mol % NH₄NO₃/0.02 mol % PC, was applied as a proton battery. The discharge character-

istics of the cell revealed that the cell performance was fairly good when it was discharged through a 1-MΩ load compared to when it was discharged through a 100-KΩ load.

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