

Proton-conducting membranes: poly (*N*-vinyl pyrrolidone) complexes with various ammonium salts

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Received: 1 July 2007 / Revised: 23 January 2008 / Accepted: 6 February 2008 / Published online: 8 May 2008
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Abstract The present study focuses on the proton-conducting polymer electrolytes; poly (*N*-vinyl pyrrolidone)–ammonium thiocyanate and poly (*N*-vinyl pyrrolidone)–ammonium acetate prepared by solution casting technique. The XRD analysis indicates the amorphous nature of the polymer electrolytes. The Raman spectra of the C=O vibration of pure polymer PVP at $1,663\text{ cm}^{-1}$ has been appeared as doublet in the polymer electrolytes. The introduction of this new peak in the salt-doped polymer electrolytes may be due to interaction of the cation with the polymer. The room temperature ionic conductivity $\sigma_{303\text{K}}$ has been found to be high, $1.7 \times 10^{-4}\text{ S cm}^{-1}$ for 80 mol% PVP–20 mol% NH_4SCN and $1.5 \times 10^{-6}\text{ S cm}^{-1}$ for 75 mol% PVP–25 mol% $\text{CH}_3\text{COONH}_4$. The polymer electrolytes have been tested for their application in Zn–air battery.

Keywords Proton conductors · Poly (*N*-vinyl pyrrolidone) · Ammonium salts · Zinc–air cell

Introduction

Proton-conducting polymer electrolytes have so far been given much attention due to their possible applications in electrochemical devices such as batteries, fuel cells, humidity and gas sensors, capacitors, and electrochemical displays that work from sub ambient to moderately high

temperatures [1]. Some studies have focused on poly (vinyl alcohol) (PVA) [2], poly (vinyl acramide) (PAA) [3], and poly (*N*-vinyl pyrrolidone) (PVP) [4] based electrolytes for their possible application in these electrochemical devices. The ionic conduction in polymer electrolytes is dominated by the amorphous phase rather than crystalline phase. In order to enhance the conductivity, several approaches have been suggested [5]. The main goal of these studies is to obtain films with a high fraction of amorphous phase, which exhibits a much higher conductivity than the crystalline phase. Recently, we reported proton-conducting polymer electrolytes based on PVP– NH_4SCN with good thermal and electrical properties [6, 7]. As a continuation of our previous work, in this paper, we report a comparative vibrational and electrical properties of the polymer electrolytes based on poly (*N*-vinyl pyrrolidone)–ammonium thiocyanate (PVP– NH_4SCN) and poly (*N*-vinyl pyrrolidone)–ammonium acetate (PVP– $\text{CH}_3\text{COONH}_4$). A primary solid-state Zn–air cell with PVP– NH_4SCN polymer electrolyte has been assembled and characterized.

Experimental

Preparation of polymer electrolytes

The polymer electrolytes, PVP ($M_w=40,000$, SISCO) with NH_4SCN , and PVP ($M_w=40,000$, SISCO) with $\text{CH}_3\text{COONH}_4$ (SISCO) in the molar ratios (95:05), (90:10), (85:15), (80:20) and (75:25) were prepared by solution casting technique using distilled water as a solvent. In this method, solutions of pure polymer and the ionic dopant ($\text{NH}_4\text{SCN}/\text{CH}_3\text{COONH}_4$) are mixed together. The mixtures are then poured on a propylene Petri dishes and the solvent is evaporated slowly at 333 K.

Contribution to ICMAT 2007, Symposium K: Nanostructured and bulk materials for electrochemical power sources, July 1–6, 2007, Singapore

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Preparation of perovskite catalyst

The oxygen reduction perovskite catalyst $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ has been prepared by the sol–gel method. The nitrates of lanthanum ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, SISCO Research Laboratory), cobalt ($\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, MERCK) and calcium ($\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MERCK) are dissolved in distilled water in stoichiometric ratio. To this solution, citric acid was added such that the molar ratio of citric acid to metal ions is 1:1. The pH of the resultant metal citrate solution was adjusted to 6–7 by adding dilute ammonia drop by drop. The solution was slowly evaporated till it becomes a viscous solution. At this stage, the gelating reagent ethylene glycol was added such that the molar ratio of citric acid to ethylene glycol is 1:1.2. This mixture is heated on a hot plate stirrer at 100 °C for 2–3 h with constant stirring. When the solution starts solidifying and forms a gel like porous mass, the temperature was gradually increased to 160–180 °C till it becomes a solid mass. The resultant mixture is heated in the furnace from room temperature to 650 °C, kept at this temperature for 1 h. The sample was quenched suddenly. The resultant powder was crushed into fine powder and ground using mortar and pestle.

Electrodes used for the fabrication of the zinc–air cell

Anode: zinc was used as an anode.

Cathode: air electrodes with 80 mol% graphite (6–8 μm), 5 mol% MnO_2 and the perovskite catalyst $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ (15 mol%) were prepared using appropriate amount of IPA solvent.

Fabrication of a zinc–air cell

Zn–air cell using the aforementioned electrodes were assembled. The configuration of the Zn air cell is as,

Current collector | Zinc anode | SPE |

(Graphite + MnO_2 + LCCO)cathode | current collector

where SPE=80 mol% PVP–20 mol% NH_4SCN polymer electrolyte LCCO= $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$.

Characterization techniques

X-ray diffraction patterns have been obtained from PANalytical X-ray generator in the 2θ range 10° to 60° using Cu-K α radiation. The Raman spectra have been performed using a Renishaw 1000 spectrometer in the range of 400–2,250 cm^{-1} for PVP– NH_4SCN polymer electrolytes and 400–2,000 cm^{-1} for PVP– $\text{CH}_3\text{COONH}_4$ polymer electro-

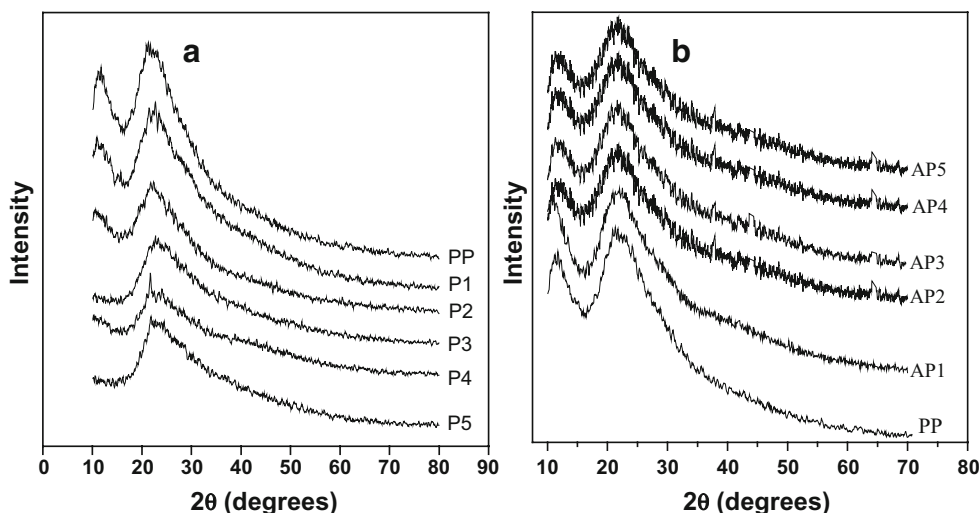
lytes. Curve-fitting analysis of the spectral data has been done using a commercial program, PEAK FIT to fit the Raman bands. The ionic conductivity of the polymeric electrolyte sandwiched between two aluminum-blocking electrodes has been measured using an LCR meter Hioki 3532 in the frequency range 42 Hz–5 MHz at 303 K. The conductivity measurements have been performed in a homemade vacuum setup so as to avoid the influence of the atmospheric water. In the present work, the charge/discharge cycles on the Zn–air cell has been performed at a current rate of 3 μA with a constant load of 4.7 M Ω in the potential range 1.4–0.6 V.

Results and discussion

XRD analysis

Figure 1 shows the XRD Spectra of (a) PVP & PVP– NH_4SCN and (b) PVP & PVP– $\text{CH}_3\text{COONH}_4$ polymer electrolytes. The broad peaks between 12°–15° and 19°–24° (Fig. 1) can be associated with the amorphous nature of pure PVP [8]. From the figure, it has been observed that the relative intensity of the broad peaks between 12°–15° and 19°–24° decreases with increase of NH_4SCN and $\text{CH}_3\text{COONH}_4$ concentration. The decrease in relative intensity with broadening of the apparent peak of the PVP– NH_4SCN and PVP– $\text{CH}_3\text{COONH}_4$ polymer electrolytes has been observed when compared with pure polymer. This result can be interpreted by considering the Hodge et al. [9] criterion, which establishes a correlation between the intensity of the peak and the degree of crystallinity. The interaction between the salt–polymer results in the lowering of crystallinity with rich amorphous phase which is manifested by the broad diffraction peak centered at $2\theta=12^\circ\text{--}15^\circ$ and $19^\circ\text{--}24^\circ$. The results observed from the XRD measurements strongly suggest that the crystallinity of the PVP has been destroyed by the addition of NH_4SCN and $\text{CH}_3\text{COONH}_4$. This change of intensity and broad nature of peaks in the polymer electrolytes suggests the amorphous nature of the polymer electrolytes. From Fig. 1a, the peaks $2\theta=24^\circ$ and 26° (JCPDS 23-0029) [10] corresponding to pure NH_4SCN have been found to be absent in the PVP– NH_4SCN polymer electrolytes indicating the complete dissociation of the salt in the polymer matrix. From Fig. 1b, the peaks $2\theta=18^\circ$, 21° and 22° (JCPDS 22-1035) [11] corresponding to pure $\text{CH}_3\text{COONH}_4$ have been found to be absent in the PVP– $\text{CH}_3\text{COONH}_4$ polymer electrolytes indicating the complete dissociation of the salt in the polymer matrix. The above results confirm the complex formation between polymer and dissociated salt in the PVP– NH_4SCN and PVP– $\text{CH}_3\text{COONH}_4$ polymer electrolytes.

Fig. 1 XRD pattern of **a** *PP* Pure PVP, *P1* 95 mol% PVP–05 mol% NH_4SCN , *P2* 90 mol% PVP–10 mol% NH_4SCN , *P3* 85 mol% PVP–15 mol% NH_4SCN , *P4* 80 mol% PVP–20 mol% NH_4SCN , *P5* 75 mol% PVP–25 mol% NH_4SCN **b** *PP* Pure PVP, *AP1* 95 mol% PVP–05 mol% $\text{CH}_3\text{COONH}_4$, *AP2* 90 mol% PVP–10 mol% $\text{CH}_3\text{COONH}_4$, *AP3* 85 mol% PVP–15 mol% $\text{CH}_3\text{COONH}_4$, *AP4* 80 mol% PVP–20 mol% $\text{CH}_3\text{COONH}_4$, *AP5* 75 mol% PVP–25 mol% $\text{CH}_3\text{COONH}_4$



Raman analysis

Figure 2 shows the Raman spectra of the host polymer, (a) PVP– NH_4SCN and (b) PVP– $\text{CH}_3\text{COONH}_4$ polymer electrolytes in the range $400\text{--}2,250\text{ cm}^{-1}$. The assignments of the bands in the Raman spectra of pure PVP and the ammonium salts-doped PVP polymer electrolytes have been presented in Table 1. From the figure, it has been observed that the intensity of the Raman band corresponding to C–C stretching vibration at 936 cm^{-1} in the pure PVP decreases with increase of NH_4X ($\text{X} = \text{SCN}^-/\text{CH}_3\text{COO}^-$) concentration. The significant changes in the C–C vibrational band can be related with the interaction of the salt with the polymer. The Raman bands in the region from $1,050\text{--}1,500\text{ cm}^{-1}$ can be attributed to a complex mixture of C–H bending and C–N stretching vibrations [12]. It has been observed that the bands related to $\nu(\text{C–N})$ stretching vibrations and $\nu(\text{C–H})$ bending vibrations gets broaden with the increase of salt concentration in both the polymer electrolytes. The band

broadening in Raman spectra is usually an indication of amorphous nature of the polymer electrolyte [13]. The above results have been found to be consistent with XRD analysis. Figure 3 shows the deconvoluted Raman spectrum of the carbonyl stretching region for pure PVP (PP), 95 mol% PVP–05 mol% NH_4SCN (P1) and 95 mol% PVP–05 mol% $\text{CH}_3\text{COONH}_4$ (AP1) polymer electrolytes. The characteristic vibrational band of C=O has been found to be at $1,663\text{ cm}^{-1}$ in pure PVP and this band shifts significantly in the salt-doped system. This band splits into two components, at $1,661\text{ cm}^{-1}$ and $1,674\text{ cm}^{-1}$ upon introducing NH_4SCN and at $\sim 1,664\text{ cm}^{-1}$ and $\sim 1,682\text{ cm}^{-1}$ upon introducing $\text{CH}_3\text{COONH}_4$. The introduction of a new peak in the salt-doped systems may be due to formation of (C–O H) vibrations. The hydrogen atom of the NH_4^+ group of the ammonium salt might be expected to interact with the C=O present in the pyrrolidone group of the polymer via hydrogen bonding. By the addition of NH_4SCN an additional band appears around $2,041\text{ cm}^{-1}$ which corresponds to the $\text{C}\equiv\text{N}$

Fig. 2 Raman spectra for **a** *PP* Pure PVP, *P1* 95 mol% PVP–05 mol% NH_4SCN , *P2* 90 mol% PVP–10 mol% NH_4SCN , *P3* 85 mol% PVP–15 mol% NH_4SCN , *P4* 80 mol% PVP–20 mol% NH_4SCN , *P5* 75 mol% PVP–25 mol% NH_4SCN **b** *PP* Pure PVP, *AP1* 95 mol% PVP–05 mol% $\text{CH}_3\text{COONH}_4$, *AP2* 90 mol% PVP–10 mol% $\text{CH}_3\text{COONH}_4$, *AP3* 85 mol% PVP–15 mol% $\text{CH}_3\text{COONH}_4$, *AP4* 80 mol% PVP–20 mol% $\text{CH}_3\text{COONH}_4$, *AP5* 75 mol% PVP–25 mol% $\text{CH}_3\text{COONH}_4$

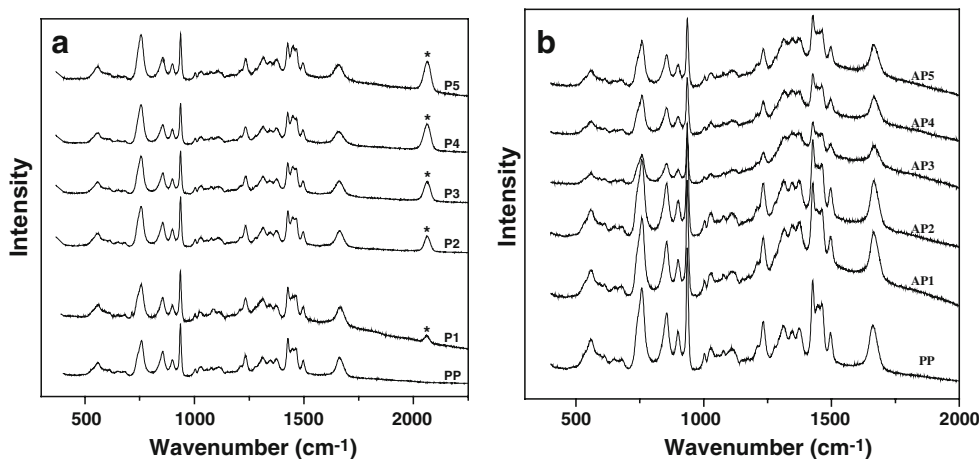


Table 1 Raman band Frequencies and their Assignments for Pure PVP, PVP–NH₄SCN and PVP–CH₃COONH₄ polymer electrolytes

Wave number (cm ⁻¹)			Assignment
Pure PVP	PVP: NH ₄ SCN	PVP: CH ₃ COONH ₄	
738	736	735	C–N
–	744	–	C–S stretching
758	757	758	C–N
899	898	901	CH ₂ rocking
935	936	935	C–C stretching
1,028	1,029	1,027	CH ₂ symmetric stretching
1,232	1,234	1,232	C–N stretching
1,426	1,425	1,426	C–H bending
1,663	1,661	1,663	C=O
–	1,674	1,680	C–O–H
–	2,044	–	Free ion
–	2,061	–	Contact ion pair
–	2,074	–	Aggregates

stretching region of the anion, (indicated as * in Fig. 2). Figure 4 shows the deconvoluted Raman spectra in the C≡N stretching region for different PVP–NH₄SCN polymer electrolytes. The deconvolution [7] of this band for 5 mol% doped polymer electrolyte leads to two bands, fitted by Lorentzian line shapes at 2,042 cm⁻¹ and 2,061 cm⁻¹ which are ascribed to free SCN⁻ ion contact ion pair (NH₄⁺...SCN⁻), respectively. It has been observed that the fraction of free ions and contact ion pairs increases as the salt concentration increases. For 10 mol% salt added polymer electrolyte a new peak around 2,074 cm⁻¹ has been observed corresponding to the formation of ion

aggregates and the area under this peak increases with increase of NH₄SCN concentration.

The area under each peak as a function of salt concentration has been shown in Fig. 5. The area of these peaks is proportional to the relative concentration of these kinds of ionic species. The concentration of the free ions increases gradually from 5 mol% to 20 mol% of salt concentration. The ion aggregates increases gradually from 10 mol% to 20 mol%. For the 25 mol% salt-doped polymer electrolytes the concentration of the ion aggregates increases rapidly. By the deconvolution of the Raman spectrum of 25 mol% salt-doped system, the intensity of the 2,041 cm⁻¹ band decreases at the expense of 2,061 cm⁻¹ and 2,074 cm⁻¹. The decrease in intensity of the 2,041 cm⁻¹ peak indicates that the number of ion aggregates is larger than the free ions. The formation of ion aggregates lowers the number of mobile charge carriers which accounts for the decrease of conductivity.

Conductivity analysis

Figures 6 and 7 show the complex impedance plot for the PVP–NH₄SCN and PVP–CH₃COONH₄ polymer electrolytes, respectively. A high frequency semicircle and a low frequency spike for 5–15 mol% NH₄SCN and 20–25 mol% CH₃COONH₄ polymer electrolytes. The semicircle can be represented by a parallel combination of a capacitor, which is due to the immobile polymer chain and a resistor due to the resistance offered by a polymer matrix to mobile ion. The low frequency spike can be attributed to the effect of blocking electrodes. The low frequency response appearing as an inclined spike is distinctly non-vertical. The spikes

Fig. 3 Deconvoluted Raman spectra for C=O stretching mode for pure (PP), 95 mol% PVP–05 mol% NH₄SCN (P1) and 75 mol% PVP–25 mol% CH₃COONH₄ (AP1) polymer electrolytes

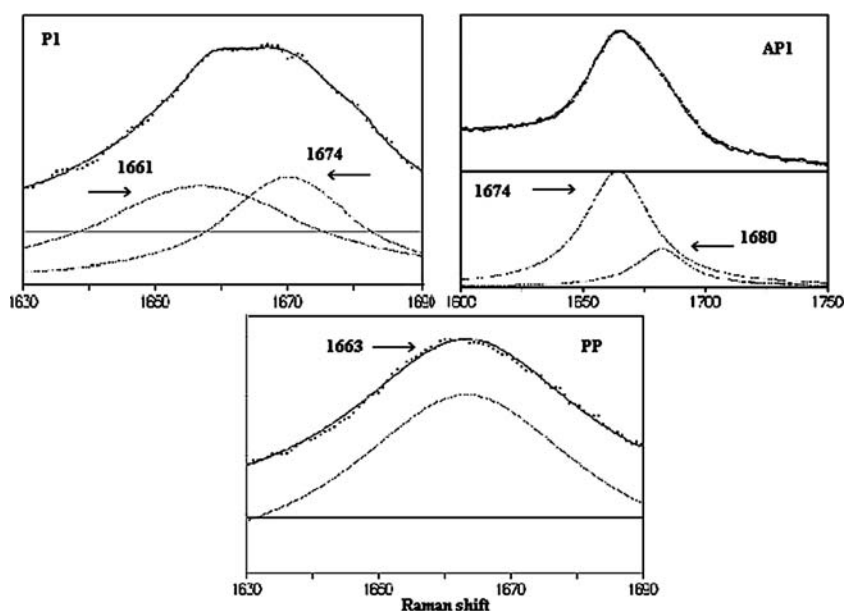
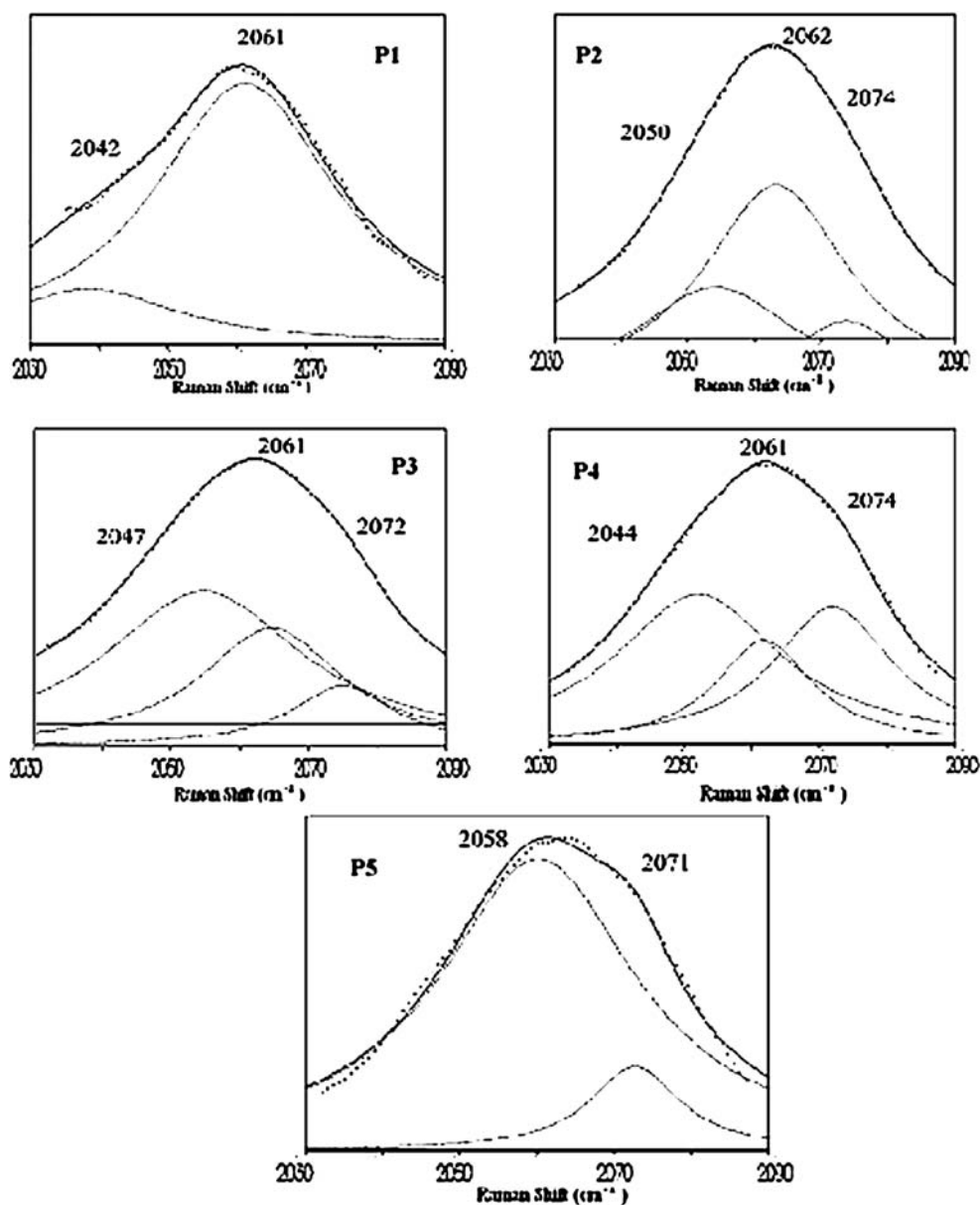


Fig. 4 Deconvoluted Raman spectra in the C≡N stretching region for different PVP–NH₄SCN polymer electrolytes



inclined at an angle of less than 90° to the real axis indicate the inhomogeneous nature of the electrode–electrolyte interface. For 20, 25 mol% NH₄SCN, the semicircle has been found to be absent in the complex impedance plots indicates the prevailing of the resistive component of the polymer electrolytes [6]. The bulk resistance *R_b* decreases with increase in salt concentration. This may be due to increase in the mobile charge carriers by the addition of ionic dopant. The bulk resistance has been found to be low for 80 mol% PVP–20 mol% NH₄SCN and 75 mol% PVP–25 mol% CH₃COONH₄ polymer electrolytes and has been found to be 1.7×10² Ω and 2.5×10⁴ Ω at 303 K, respectively. The room temperature conductivity values

for all PVP–NH₄SCN and PVP–CH₃COONH₄ polymer electrolytes have been tabulated in Table 2.

Charge discharge tests

From the detailed analysis of the PVP–NH₄SCN and PVP–CH₃COONH₄ polymer electrolytes, the 80 mol% PVP–20 mol% NH₄SCN polymer electrolyte has been found to be suitable electrolyte having good electrical properties for the fabrication of Zn–air cell fabrication. The Zn–air cell having Zn anode, 80 mol% PVP–20 mol% NH₄SCN polymer electrolyte and a cathode having Graphite, MnO₂ and the catalyst La_{0.6}Ca_{0.4}CoO₃ has been fabricated. A

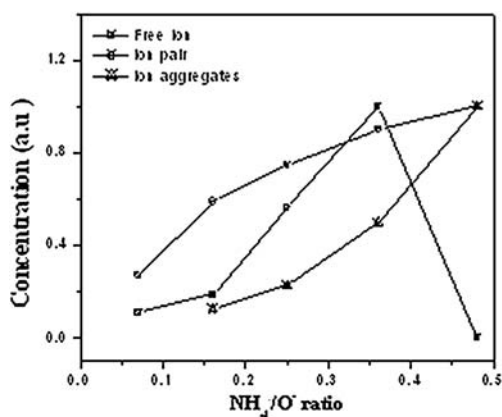


Fig. 5 Variation of concentration of various states of ions as a function of ammonium thiocyanate concentration

typical charge/discharge curve for the fabricated cell has been shown in Fig. 8. Since the cell is assembled in charged condition, it is first subjected to discharge at 3 μA in the potential range 1.4–0.6 V. The discharge capacity obtained is about 24 $\mu\text{Ah/g}$ between the cutoff voltages of 1.2–0.6 V. The initial discharge capacity of the cell having 24 $\mu\text{Ah/g}$ decreases with an irreversible capacity loss of 17 $\mu\text{Ah/g}$ during the first cycle. With an increase in cycle number, however, it has been found that the discharge curve exhibits a voltage dip, which may be due to the formation of the ZnO layer and, hence, the capacity loss.

Fig. 6 Complex impedance plot of PVP–NH₄SCN polymer electrolytes at 303 K

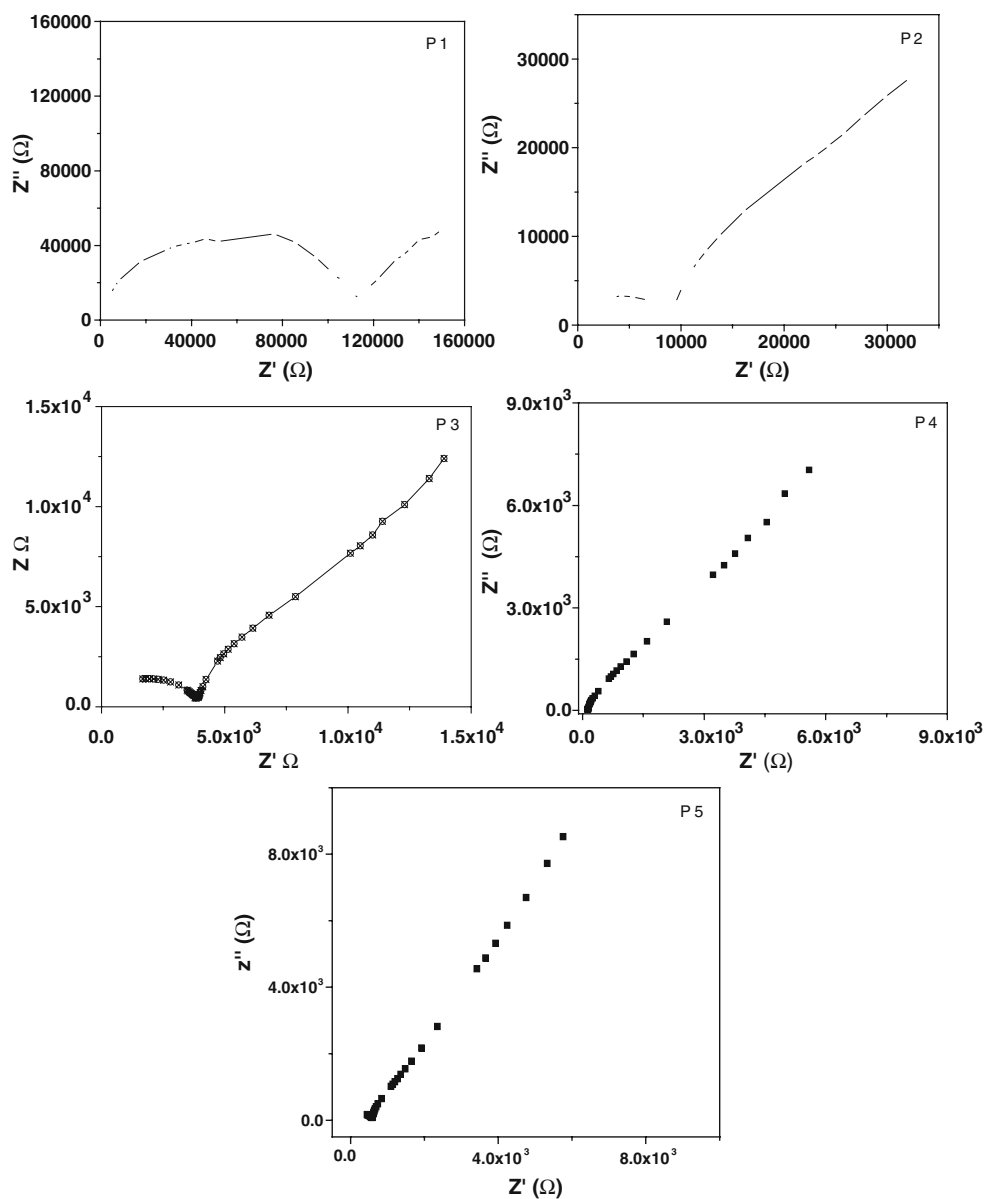


Fig. 7 Complex impedance plot of PVP–CH₃COONH₄ polymer electrolytes at 303 K

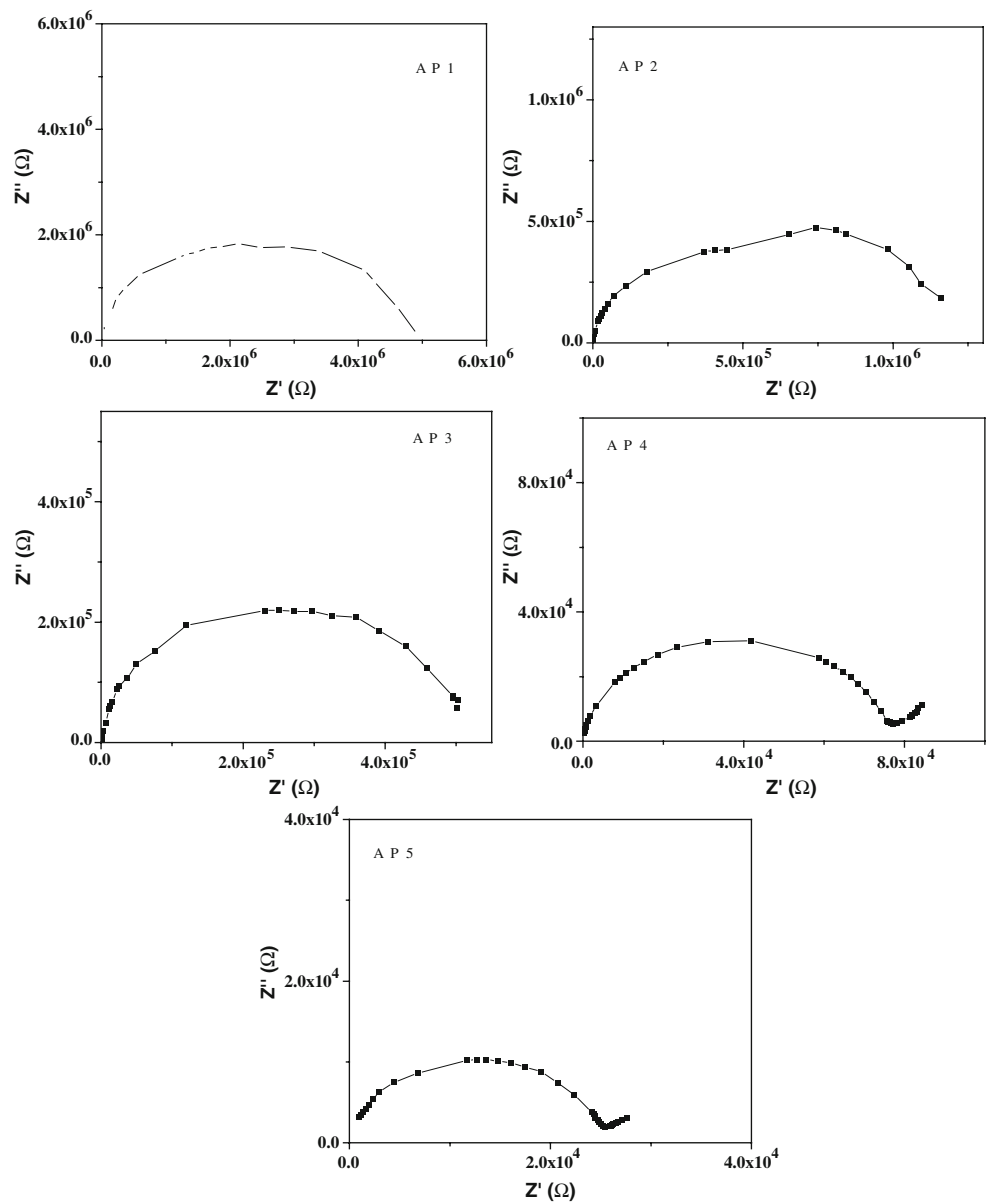


Table 2 Conductivity data for PVP–NH₄SCN and PVP–CH₃COONH₄ polymer electrolytes at 303 K

Ammonium thiocyanate/ ammonium acetate concentration (mol %)	Conductivity (PVP–NH ₄ SCN) σ 303 K (S cm ⁻¹)	Conductivity (PVP– CH ₃ COONH ₄) σ 303 K (S cm ⁻¹)
05	4.8×10^{-7}	5.6×10^{-9}
10	6.5×10^{-6}	2.9×10^{-7}
15	2.0×10^{-5}	5.4×10^{-7}
20	1.7×10^{-4}	6.1×10^{-7}
25	3.7×10^{-5}	1.5×10^{-6}

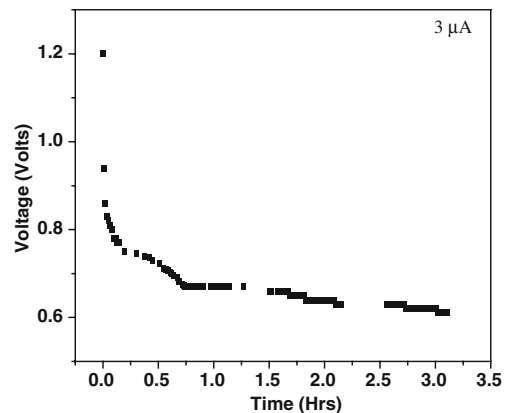


Fig. 8 Discharge profile of a Zn anode/SPE/air cathode cell with a current of 3 μ A

Conclusion

The proton-conducting polymer electrolytes based on PVP and ammonium thiocyanate (NH_4SCN); PVP and ammonium acetate ($\text{CH}_3\text{COONH}_4$) with different molar ratios have been prepared by solution casting technique. The XRD spectra of both the polymer electrolytes indicate the increase in amorphous nature of polymer with the increase of salt concentration. The Raman analysis confirms the interaction of the ammonium proton of NH_4SCN and $\text{CH}_3\text{COONH}_4$ with the carbonyl group of the polymer, PVP. The band broadening in Raman spectra is usually an indication of amorphous nature of the polymer electrolyte. The indication of the increase of amorphousness from the Raman results has been found to be consistent with X-ray diffraction results. The conductivity has been found to be high for 80 mol% PVP–20 mol% NH_4SCN and 75 mol% PVP–25 mol% $\text{CH}_3\text{COONH}_4$ polymer electrolytes and has been found to be $1.7 \times 10^{-4} \text{ S cm}^{-1}$ and $1.5 \times 10^{-6} \text{ S cm}^{-1}$ at 303 K, respectively. The analysis of the anionic peak in PVP– NH_4SCN polymer electrolytes ($\sim 2,041 \text{ cm}^{-1}$) supports for the decrease in ionic conductivity at 25 mol% NH_4SCN polymer electrolyte which indicates the decrease in the number of free ions at higher salt concentrations. From the detailed analysis, PVP– NH_4SCN polymer electrolytes has been found to have good electrical properties when compared to PVP– $\text{CH}_3\text{COONH}_4$. Hence, 80 mol% PVP–20 mol%

NH_4SCN polymer electrolyte has been used to fabricate a Zn–air cell and its performance has been studied.

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