Preparation and characterization of PAN–KI complexed gel polymer electrolytes for solid-state battery applications

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Abstract. The free standing and dimensionally stable gel polymer electrolyte films of polyacrylonitrile (PAN): potassium iodide (KI) of different compositions, using ethylene carbonate as a plasticizer and dimethyl formamide as solvent, are prepared by adopting 'solution casting technique' and these films are examined for their conductivities. The structural, miscibility and the chemical rapport between PAN and KI are investigated using X-ray diffraction, Fourier transform infrared spectroscopy and differential scanning calorimetry methods. The conductivity is enhanced with the increase in KI concentration and temperature. The maximum conductivity at 30°C is found to be 2.089×10^{-5} S cm^{-1} for PAN:KI (70:30) wt%, which is nine orders greater than that of pure PAN ($<10^{-14}$ S cm^{-1}). The conductivity-temperature dependence of these polymer electrolyte films obeys Arrhenius behaviour with activation energy ranging from 0.358 to 0.478 eV. The conducting carriers of charge transport in these polymer electrolyte films are identified by Wagner's polarization technique and it is found that the charge transport is predominantly due to ions. The better conducting sample is used to fabricate the battery with configuration K/PAN + KI/I$_2$+ C + electrolyte and good discharge characteristics of battery are observed.

Keywords. Polyacrylonitrile; solution casting technique; differential scanning calorimetry; X-ray diffraction; electrical properties.

1. Introduction

Recently a lot of attention has been paid to the research activities of developing gel polymer electrolytes for solid-state battery applications with good conductivity. In view of the above fact that solid-state battery has many advantages, such as higher energy density, solvent-free condition, leak proof, easy process ability and light weight [1–5]. Several earlier studies in this field are focused upon polyethylene oxide (PEO), polyvinyl alcohol, polyvinyl pyrrolidone (PVP) and polyacrylonitrile (PAN) complexed with NaI, NaClO$_3$, NaYF$_4$, KYF$_4$ and LiCF$_3$SO$_3$ [6–12]. Although very few investigations are conducted on potassium complexed polymer electrolytes, still no attention is paid on potassium salt complexed PAN-based polymer electrolytes.

Lithium batteries have advantages such as high energy density and rechargeability, which make them commercially active. Despite their advantages, they experience the ill effects of operational limitations, for example, high cost, trouble in taking care of atmospheric conditions due to high reactivity. So, the research has been focused on potassium salts due to their several advantages over lithium counterparts. Potassium is less expensive and much more abundant than lithium.

The smoothness of this metal makes it easier for the components of the battery to have good contact to accomplish and keep contact with other components in the battery. Moreover, potassium is more moisture resistant than lithium [13].

Compared with the other polymers, PAN-based electrolytes have been extensively studied because of their good chemical, flame resistance and electrochemical stability [14–17]. PAN is one of the most important fibre-forming polymers and is widely used because of its high strength, abrasion resistance and good insect resistance [18]. It is used to produce a large variety of products, including ultrafiltration membranes, hollow fibres for reverse osmosis, fibres for textiles, oxidized flame retardant fibres like PANOX and carbon fibre. Although the conductivity of pristine PAN is less than 10^{-14} S cm^{-1}, this static problem confine its further applications.

PAN is usually synthesized using free radical polymerization. Generally it forms copolymers with acrylonitrile, methyl acrylate, acrylonitrile and methyl methacrylate. PAN has a glass transition point of about 107°C and melting point of about 319°C, and it decomposes at this temperature [19].

To enhance the conductivity of polymer electrolytes, several techniques are suggested in the literature, including the use of blend polymers, addition of a ceramic filler, plasticizers and radiation. Two plasticizing solvents ethylene carbonate (EC) and dimethyl formamide (DMF) are chosen as solvents in this study. EC has high dielectric constant and

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low viscosity, which weakens the columbic force between cation and anion of the salt. Consequently, salt separation takes place. Further, plasticizers decrease the glass transition temperature of the polymer electrolyte and accordingly enhance the segmental motion of the polymer backbone and create free volume. Therefore, the ions can migrate easily through the void, as a result ionic conductivity increases [20]. In the present work, we have developed and study the electrical properties of PAN-based KI complexed gel polymer electrolytes and verify their potential in solid-state battery applications.

2. Experimental

2.1 *Materials*

Polyacrylonitrile (PAN; MW = 1,50,000 g mol^{-1}), ethylene carbonate (EC) were from Sigma Aldrich and potassium iodide (KI), dimethyl formamide (DMF) were from Merck. All reagents were used, as received, without further purification.

2.2 *Preparation of the gel polymer electrolyte films*

Solution casting technique was used to prepare gel polymer electrolyte films. In this method, KI was first dissolved in the mixture of EC and DMF with continuous stirring at 60°C for 12 h. Then the polymer PAN was mixed with the prepared solution and the mixture was stirred up to 36 h to obtain a homogeneous solution. Subsequently, the prepared solution was poured into polypropylene Petri dishes and evaporated slowly at room temperature under vacuum until the gel film was formed. The polymer electrolyte samples were transferred into desiccators for further drying before the test. The films formed were mechanically stable, transparent and free standing with thickness range of 150 μm.

2.3 *Structural characterizations*

2.3a *X-ray diffraction*: To investigate the structure of the gel polymer electrolyte films, X-ray diffraction (XRD) spectra were carried out using an X'pert diffractometer (Philips PANalytical) with CuKα radiation (λ = 1.5403 Å), and the diffraction patterns were recorded for 2θ values between 10° and 90°.

2.3b *Fourier transform infrared spectroscopy*: Fourier transform infrared (FTIR) absorption spectra were recorded with the help of the Perkin Elmer FTIR spectrometer (Spectrum II USA) in the wavenumber range of 450–4000 cm^{-1} with spectral resolution of 2 cm^{-1}.

2.3c *Differential scanning calorimetry*: The glass transition temperature (T_g) and melting temperature (T_m) of the gel polymer electrolyte films were determined using an Auto Q20

DSC, TA Instruments, at a heating rate of 10°C min^{-1} under nitrogen atmosphere in the temperature range of 40–350°C.

2.4 *Electrical studies*

2.4a *Conductivity measurements*: For conductivity measurements, circular discs of diameter 2 cm were cut from the films. A disc sample was sandwiched between a pair of silver electrodes and spring loaded into a sample holder of lab-made conductivity setup [21]. Room temperature conductivities of films were measured using HIOKI 3532-50 LCR Hitester in 50 Hz to 5 MHz frequency range.

2.4b *Transport properties*: Wagner's polarization method was carried out at room temperature on disc-shaped samples, which were sandwiched between silver electrodes. Polarization current was measured with respect to time in response to an applied DC bias of 1.5 V. Ionic transport (t_{ion}) and electronic transport (t_{ele}) numbers were calculated using the graph of polarization current *vs.* time.

2.4c *Fabrication of polymer battery*: Potassium polymer battery was fabricated by sandwiching the salt complexed film as electrolyte between anode and cathode pellets with the arrangement [K (anode)/(PAN + KI) (polymer electrolyte)/(I$_2$ + C + electrolyte) (cathode)]. This entire assembly was finally covered in the sample holder. In this battery, potassium metal was used as the anode (negative electrode). For the preparation of cathode, an accurate mixture of iodine (I$_2$), graphite (C) and the electrolyte material in the wt% of 5:5:1, respectively, was obtained by mechanical grinding. It was pressed in the form of pellet at a pressure of 200 MPa after proper mixing of constituents. The battery parameters, short circuit current (SCC), open circuit voltage (OCV), current density, energy density, power density and discharge time were evaluated.

3. Results and discussion

3.1 *XRD analysis*

XRD measurements are performed on PAN-based KI complexed films to examine the crystallinity and the amorphous nature of the films. Figure 1 is a comparative study of the XRD patterns of pure PAN and PAN doped with different KI concentration regions. The comparative study shows that the intensity of the crystalline peak of PAN decreases gradually with the addition of KI salt (up to 30 wt%) to the polymer, significant decrease in the degree of crystallinity of the electrolyte films. It may be due to the disturbance in the semicrystalline structure of the film by an addition of KI salt. The XRD pattern of the pure PAN film shows a crystalline peak at 2θ = 17°, corresponding to orthorhombic PAN (110) reflection [22]. The XRD patterns show that the
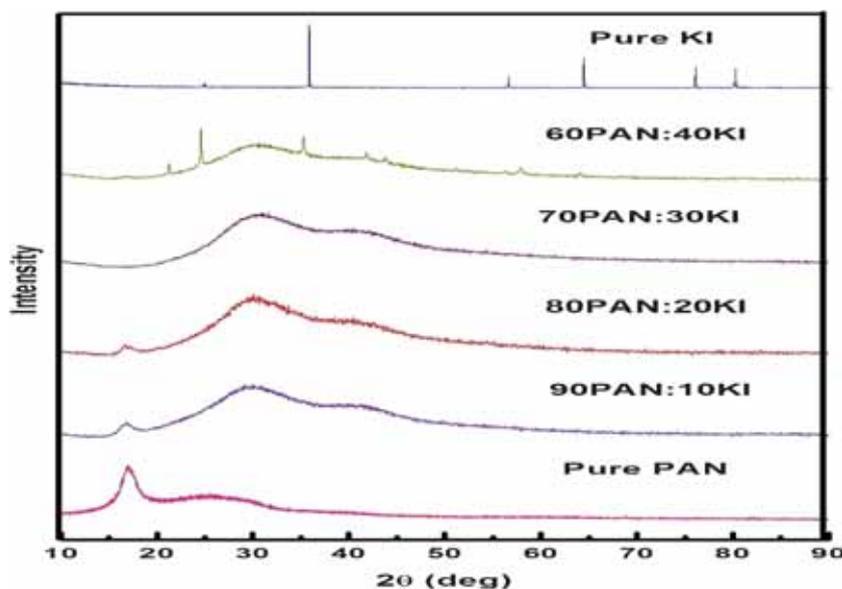
Figure 1. X-ray diffraction patterns of pure PAN, pure KI salt and PAN:KI complexed films.

semicrystalline structure is with the presence of mixed crystalline and amorphous phases. Hodge *et al* [23] studied a correlation between the intensity of the peak and the degree of crystallinity.

While KI salt dissolves in the PAN, the interaction between PAN and KI leads in the reduction of the inter-molecular interaction among the PAN polymer chains, which decreases the crystalline phases and therefore increases the amorphous regions. The sharp crystalline peaks corresponding to KI salt are observed at $2\theta = 24.9°$, $35.8°$, $56.6°$, $64.4°$, $76.1°$ and $80.1°$ (PCPDF file no. 780750), which are not present in the polymer electrolyte films up to 30 wt% salt. This indicates the complete dissolution of salt in the polymer matrix and no excess salt present in the polymer [24]. So, 70PAN:30KI gel polymer electrolyte film has more amorphous nature. The XRD pattern of 60PAN:40KI electrolyte film shows some crystalline peaks of KI. This indicates the existence of some undissolved salt in this composition, which raises the crystalline nature of the polymer electrolyte at higher concentration level of salt.

Further, in this work the percentage degree of crystallinity (χ) of pure PAN and KI complexed polymer electrolyte films are calculated from XRD patterns by using the following relation (1) [25]:

$$\chi = \frac{S}{S_0} \times 100, \tag{1}$$

where S is the sum of the areas of all the crystalline peaks and S_0 the total area under the diffractogram. The degree of crystallinity of the pure PAN is found to be 36%. For the composite films of PAN:KI, the degree of crystallinity is found to decrease to 29, 24 and 19% for films of composition (90:10), (80:20) and (70:30), respectively, but for the

(60:40) film the crystallinity increased to 24%. From these data it is confirmed that the maximum amorphousness is in the 70:30 composite film.

3.2 *FTIR studies*

FTIR is an effective tool to analyse the local structural changes in polymers. From the vibrational frequencies, the nature of bonding and different functional groups in the polymer complex can be identified [26]. Figure 2 represents the FTIR spectra of PAN, PAN:KI films in different wt% of PAN and KI as well as pure KI in the range between 450 and 4000 cm^{-1}. From the spectra, the absorption band observed at 2243 cm^{-1} can be assigned to the most characteristic band of nitrile group C≡N stretching of PAN [27]. The absorption band doublet frequencies observed at 1775 and 1800 cm^{-1} can be assigned to C=O stretching of EC and DMF. The position of these C≡N and C=O peaks are not changed with the addition of salt, but intensities have been decreased compared with that of pure PAN. It indicates that only a weak physical electrostatic interaction exists between the K$^+$ ion and C=O/C≡N.

The absorption bands at 2939, 1251, 1361 and 1455 cm^{-1} are assigned to C–H stretching, C–H wagging, C–H partial bending and C–H bending of pure PAN, respectively. It is observed from the spectra that there are no appreciable changes in the spectral position of these bands. The band at 865 cm^{-1} is assigned to C–H rocking of pure PAN. The position of this peak has been shifted to the higher wavelength side i.e., 878 cm^{-1} in the mixed films. The absorption peak at 1666 cm^{-1} can be assigned to C=C stretching in pure PAN. The position of this peak is shifted to 1627 cm^{-1} for complexed polymer electrolyte systems. The intensities of these peaks have been decreased and also broadened with the
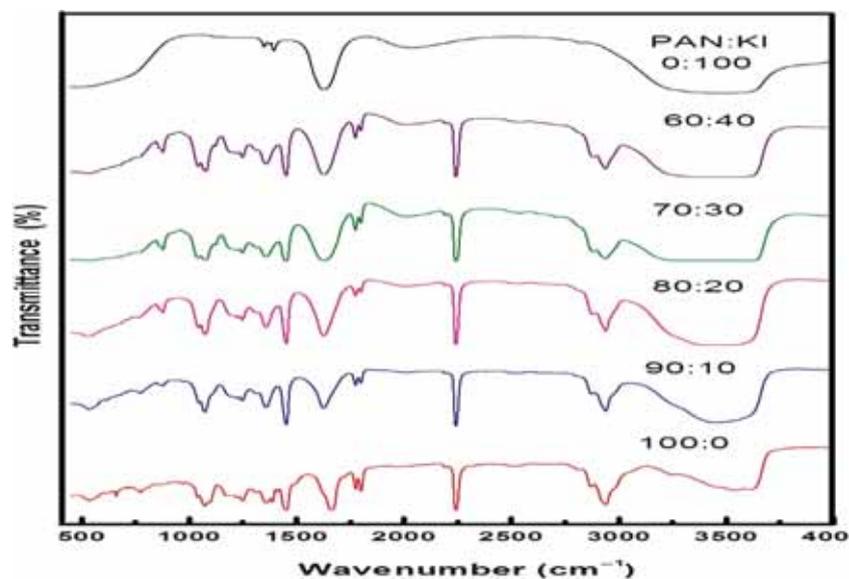
Figure 2. FTIR spectra of pure PAN, PAN complexed films for different wt% of KI and pure KI.

addition of salt. It indicates that the complexation has occurred between PAN and KI.

3.3 *DSC studies*

Thermal properties like glass transition temperature and melting temperature of polymer electrolytes are important parameters to assure adequate performance when it is operated at high temperatures and when safety is of concern. Figure 3 shows the differential scanning calorimetric thermograms of different compositions of gel polymer electrolytes in the temperature range of 40–350°C. T_g and T_m of pure PAN are 107 and 317°C [28]. The variations in the glass transition temperature and melting temperature are observed with variation of salt content to the pure PAN. From the differential scanning calorimetry (DSC) profile, low-intensity endothermic peak is observed around 71–90°C corresponding to the glass transition temperature and high-intensity exothermic peak is observed around 256–300°C corresponding to the melting temperature of the polymer electrolytes. It indicates that the miscibility of the polymer PAN, salt KI and plasticizers EC and DMF as the films exhibition of only single T_g and single T_m values.

From the DSC profile, the addition of plasticizing solvent DMF to the pure PAN decreases the T_g from 107 to 94°C and T_m from 317 to 304°C. The inclusion of plasticizer EC to the PAN + DMF again decreases the T_g from 94 to 90°C and T_m from 304 to 300°C. It indicates that the addition of plasticizers decreases the T_g and T_m values of polymer electrolytes due to increase in the distance between the PAN chains [29]. Besides, the T_g decreases from 90 to 71°C gradually with salt concentrations varying from 10 to 30 wt%, but T_g increases from 71 to 73°C for 40 wt% KI concentration film, which may be due to the presence of some undissociated salt in the
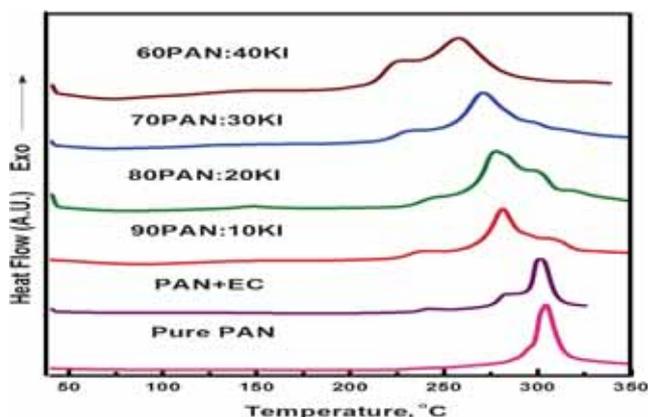

Figure 3. DSC thermograms for PAN complexed films for different wt% of KI from 40 to 350°C.

polymer matrix PAN. Similarly the T_m decreases from 300 to 256°C gradually with salt concentrations varying from 10 to 40 wt% due to the interaction between PAN and KI. It is also observed that the melting temperature peaks intensity decreases and is broadened with salt concentrations from 10 to 40 wt%. Therefore, the addition of KI decreases the T_g and T_m values [30,31]. The decrease in T_g signifies the increase in the amorphous nature of polymer electrolytes. This may be due to the plasticization effect of the electrolyte. In addition to plasticizers, salt is also found to enhance the segmental motion of the polymer electrolyte. Such segmental motion produces empty spaces, which enables the easy flow of ions in the material in the presence of electric field. The polymer electrolyte 70PAN:30KI exhibits low T_g value, indicating more amorphous nature and more flexibility compared with other polymer electrolytes, and this inference is also confirmed from XRD studies.

3.4 *Conductivity studies*

Figure 4a shows the Cole–Cole plot for the highest conducting polymer electrolyte film 70PAN:30KI and figure 4b shows the plot of its real admittance *vs.* imaginary admittance at room temperature (303 K). The conductivity (σ) value of this polymer complex film is calculated from the bulk resistance (R_b) obtained from the intercept of the straight line on the real axis, area of the film (A) and thickness of the film (t), using the expression (2).

$$\sigma = t/R_b A. \tag{2}$$

The conductivity values of different complexes at room temperature (303 K) and at 373 K are listed in table 1. The intercept on the real impedance axis in the complex impedance plot is approximately the same as the reciprocal of the intercept on the real admittance axis in the complex admittance plot. The highest conductivity at ambient temperature is found to be 2.089×10^{-5} S cm^{-1} for PAN:KI (70:30) wt%. The effect of KI salt concentration on ionic conductivity of the PAN-based polymer electrolyte films at different temperatures is shown in figure 5. The conductivity of pure PAN is about 10^{-14} S cm^{-1} at room temperature [32,33]. When 30 wt% of KI is added, the ionic conductivity is observed to increase gradually up to 2.089×10^{-5} S cm^{-1} and beyond 30 wt%, the conductivity is decreased. With KI salt concentrations from 10 to 30 wt%, the increase in conductivity is assigned to increase more mobile ions. Plasticizing solvent EC also helps to increase the number of charge carriers by larger dissolution of the electrolyte salt, resulting in increased conductivity. In this concentration range, the rate of ion dissociation may be greater than the rate of ion
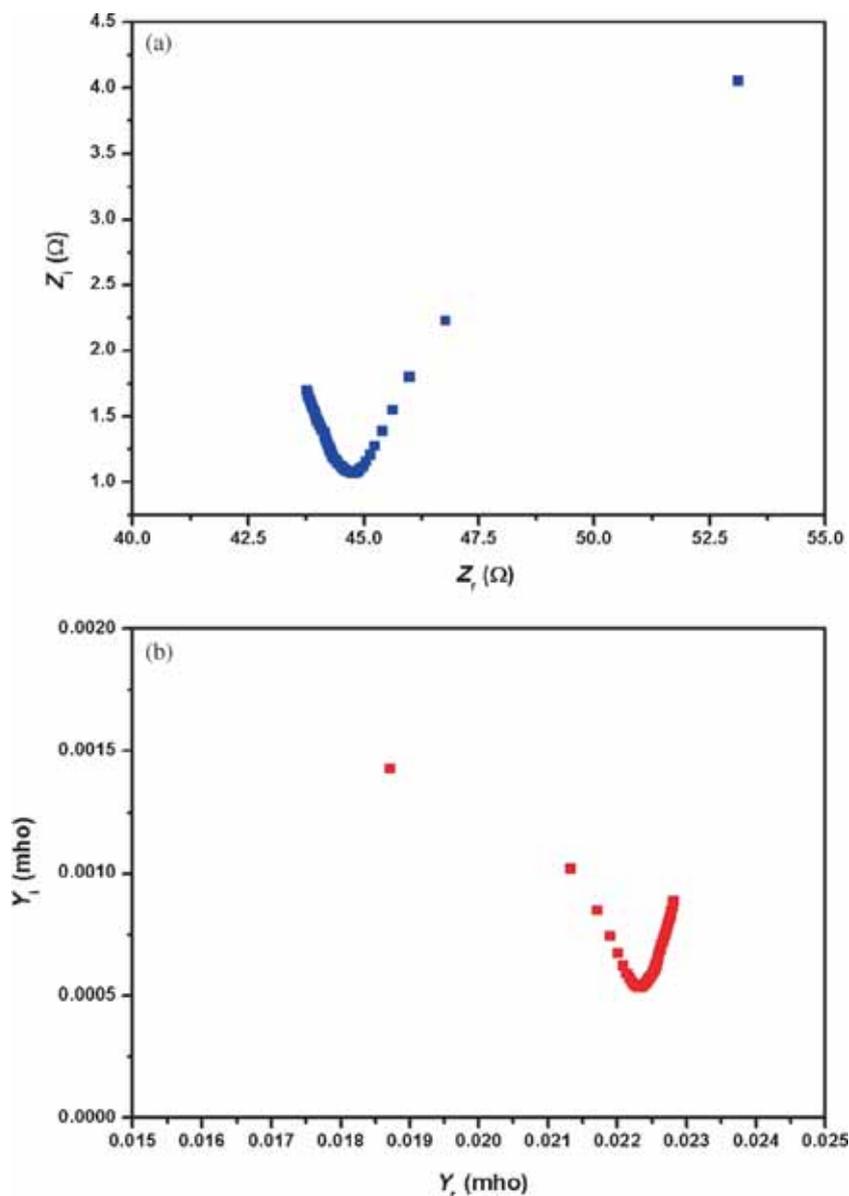

Figure 4. Complex (**a**) impedance and (**b**) admittance plots of the highest conducting film.

Table 1. Conductivity, activation energies and transference numbers of polymer electrolyte films.

Polymer electrolyte	Conductivity (S cm^{-1})		Activation energy (eV)	Transference number	
	303 K	373 K		t_{ion}	t_{ele}
PAN + KI(90:10)	1.348×10^{-9}	0.525×10^{-7}	0.47	0.915	0.084
PAN + KI(80:20)	0.853×10^{-7}	0.199×10^{-5}	0.4	0.985	0.014
PAN + KI(70:30)	2.089×10^{-5}	2.57×10^{-4}	0.35	0.99	0.01
PAN + KI(60:40)	0.134×10^{-5}	2.04×10^{-5}	0.37	0.976	0.023
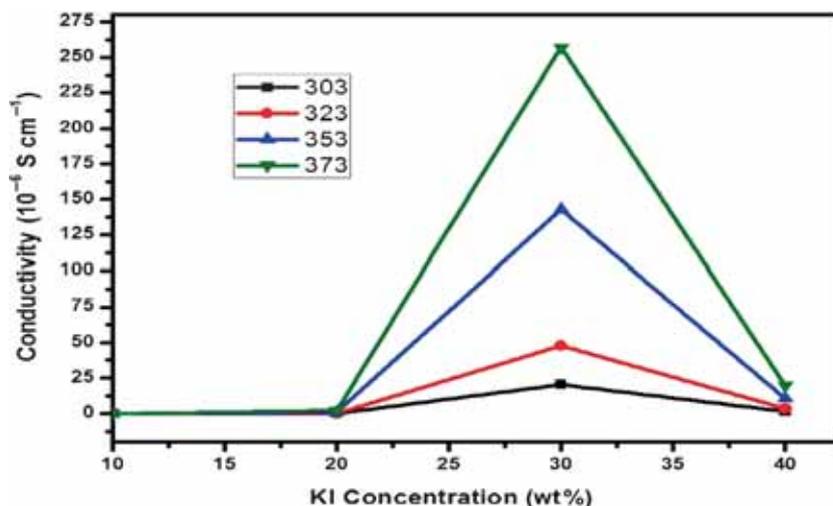
Figure 5. Ionic conductivity of polymer electrolyte films as a function of KI concentration at different temperatures.

association. While the concentration of KI salt is increased above 30 wt%, the conductivity is decreased, which may be due to the blocking of path for moving charges by the excess of salt deposited in the paths and further, at higher concentration, there will be aggregation of ions causing ions less facile to move when potential is applied [34]. Therefore, the number of mobile ions reaching the respective electrodes is decreased and this leads to the fall in conductivity. At high salt concentrations, the mobility of the ions can decrease due to the raise in salt concentration, which will raise the viscosity of the solution [35].

The variation of logarithm of ionic conductivity with inverse of absolute temperature for various concentrations of KI in PAN over a temperature range of 303–373 K is depicted in figure 6. From the graph, it is observed that the conductivity of the polymer electrolytes increases linearly with increasing temperature for all polymer electrolytes and does not show any abrupt jump in temperature. It indicates that there is no phase transition in PAN matrix due to the addition of KI in the temperature range studied [36,37]. The increase in conductivity with temperature may be due to the decrease in viscosity, and hence, increase in chain flexibility [38]. This can also be explained from the view point of free volume model and hopping of charge carriers between localized sites [39,40].

The polymer PAN and plasticizers EC and DMF dissociate the KI into K$^+$ ions and I$^-$ ions under the influence of applied electric field due to their polarity nature. The K$^+$ ions hop between the preferred nitrogen sites of PAN and oxygen sites of EC and DMF. In addition, the increasing temperature also enhances the vibrational energy of a segment which is sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and creates a small amount of space surrounding its own volume, in which vibrational motion can occur [31]. Therefore, the ions and polymer segments can move into the free volume around the polymer chain causing the mobility of ions and polymer segments, which will in turn enhance the ionic conductivity [41].

The activation energy values have been calculated, shown in figure 6, using the Arrhenius relation (3)

$$\sigma = \sigma_0 \exp(-E_a/kT), \qquad (3)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The activation energy values of the polymer electrolytes are given in table 1. From table 1, it is observed that as the KI concentration increases, the activation energy value decreases up to the composition 70PAN:30KI and again increases after that. It means that the highest conducting sample
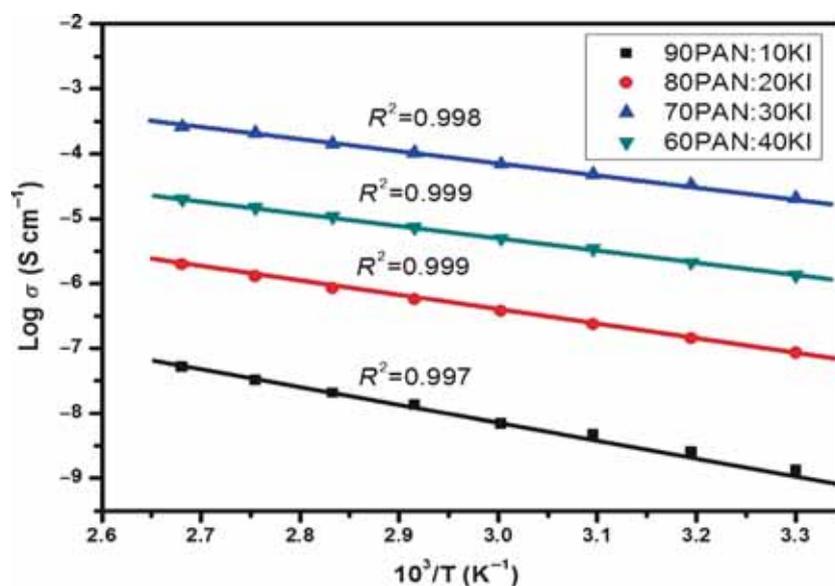
Figure 6. Plots of log σ *vs.* 1000/T for PAN complexed films for different wt% ratios of KI.
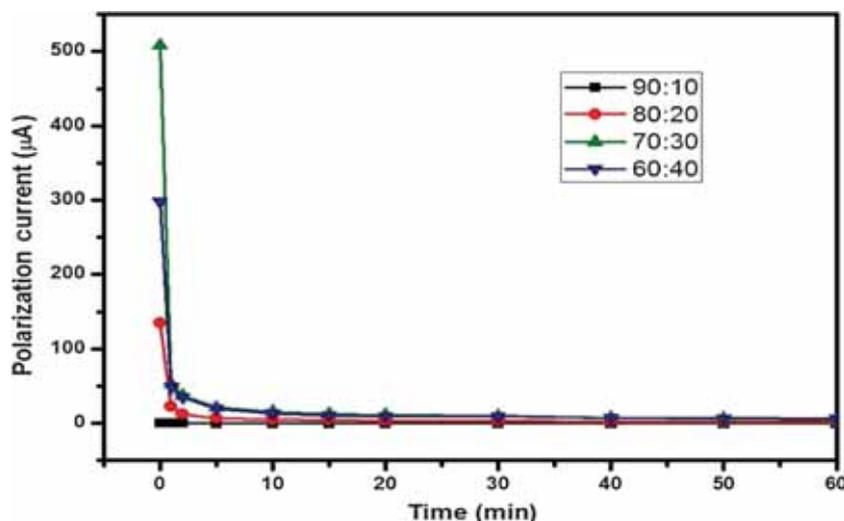

Figure 7. Transference number measurements of PAN complexed polymer electrolyte films for different wt% ratios of KI.

gives the lowest activation energy. It may be due to the amorphous nature of the polymer electrolyte which makes easy for the ionic motion in the polymer.

3.5 *Transport properties*

For estimating the nature of types responsible for conductivity in the present electrolyte system, the transport numbers have been calculated using Wagner's polarization technique, i.e., by applying a constant DC potential of 1.5 V across the cell in the configuration (Ag/PAN + KI/Ag) at room temperature. The polarization current versus time plot at room temperature is shown in figure 7. From figure, in the beginning of polarization the initial current rises up only to decay

immediately and asymptotically approaches steady state after a long time of polarization, before stabilizing at a much lower level. The transference numbers (t_{ion}, t_{ele}) are calculated using the equations (4) and (5),

$$t_{ion} = 1 - I_f/I_i, \tag{4}$$

$$t_{ele} = I_f/I_i, \tag{5}$$

where I_i is the initial current and I_f the final current.

The calculated transference values are given in table 1. It is observed from the table that the ionic transport number of present polymer electrolyte systems is in the range of 0.915–0.99 and electronic transport number is in the range
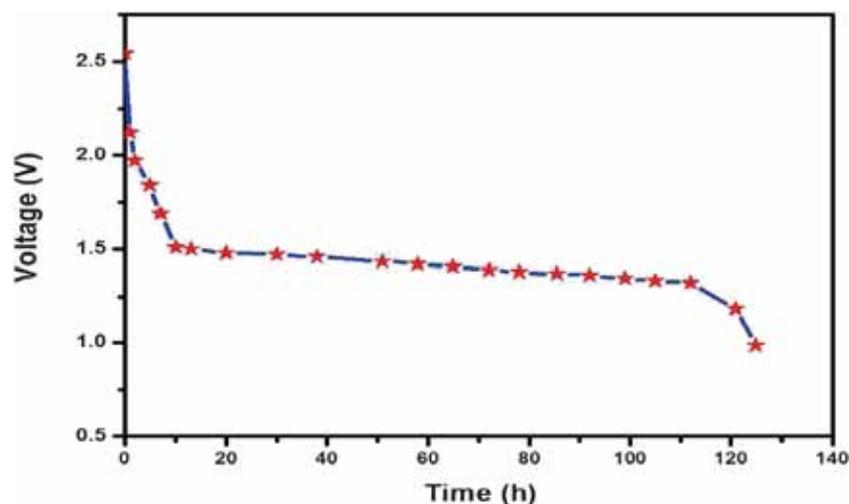
Figure 8. Discharge characteristics of 70PAN:30KI polymer electrolyte solid-state battery (at load = 100 kΩ).

Table 2. Cell parameters of PAN:KI polymer electrolyte battery.

Cell parameters	K/PAN:KI (70:30)/ (I_2 + C + electrolyte)
Open circuit voltage	2.54 V
Short circuit current	1.2 mA
Effective area of the cell	1.32 cm^2
Weight of the cell	1.5 g
Discharge time for plateau region	101 h
Current density	0.909 mA cm^{-2}
Power density	2.032 W kg^{-1}
Energy density	205.2 W h kg^{-1}
Discharge capacity	121.2 mA h

of 0.084–0.01. It indicates that the charge transport in these polymer electrolyte systems is predominantly ionic with a negligible contribution from electrons. The ionic transport number increases with the increase of salt concentration, which is due to the enrichment of ionic concentration that results in high initial current. The ionic transport number reached a high value of 0.99 for 70PAN:30KI polymer electrolyte system, which may be sufficient to meet the requirements of solid-state electrochemical cells [42–44].

3.6 *Discharge characteristics of an electrochemical cells*

The discharge characteristics of electrochemical cells with the configuration (K/electrolyte/I_2 + C + electrolyte) for highest conducting polymer electrolyte 70PAN + 30KI system at room temperature for constant load of 100 kΩ are shown in figure 8. The half cell reactions for this configuration can be written as follows:
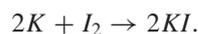
At the anode:

$$K \rightarrow K^+ + e^-$$

and at the cathode:

$$I_2 + 2e^- \rightarrow 2I^-.$$
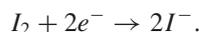
The overall reaction can be written as follows

$$2K + I_2 \rightarrow 2KI.$$

As shown in figure, during discharge, the cell voltage decreases initially and then remains constant for a particular duration (time of stable performance of the cell) and after that, voltage declines. The initial sharp decrease in the voltage may be due to the activation polarization and/or to the formation of thin layer on potassium at electrode–electrolyte interface [45]. The cell parameters, such as OCV, SCC, current density, energy density, power density, plateau region (the region in which cell voltage remains constant) and discharge capacity etc., have been evaluated for the above electrochemical cell and the obtained data are listed in table 2. From table 2, it is clear that the cell with the composition 70PAN:30KI exhibits better performance and stability than PEO + KYF$_4$, PVP + KYF$_4$ and PEO + KBrO$_3$ complexed polymer electrolyte systems [13,45]. Hence the cell developed in this research offers interesting alternatives for room temperature solid-state batteries.

4. Conclusions

Polyacrylonitrile-based potassium iodide complexed polymer electrolyte films are prepared by using solution casting technique. These films are characterized using XRD, FTIR and DSC techniques. The XRD and FTIR spectral studies have proved the complexation of PAN with KI. FTIR studies have confirmed that only a weak physical electrostatic interaction exists between the K$^+$ ion and C=O/C≡N. DSC studies have confirmed that the addition of plasticizers and KI increase the flexibility of the polymer electrolytes due to decrease in T_g and T_m values of polymer electrolytes. In the

present study, the polymer electrolyte system 70PAN:30KI has been found to have more ionic conductivity. The ionic conductivity increases with increase of the temperature as well as in the KI concentration. The temperature dependence of ionic conductivity has exhibited an Arrhenius type thermally activated process. The charge transport in these polymer electrolyte systems is predominantly ionic with a negligible contribution from electrons. Using 70PAN:30KI gel polymer electrolyte system solid-state battery 'K/PAN + KI/I_2 + C + electrolyte' has been fabricated and their discharge characteristics are studied, and these results are found to be better than the existing potassium battery results.

Acknowledgements

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