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# Polyaniline (PANI) mediated cation trapping effect on ionic conductivity enhancement in poly(ethylene oxide) based solid polymer electrolytes with application in solid state dye sensitized solar cells

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## ABSTRACT

The ionic conductivity enhancement in solid polymer electrolytes due to introduction of polyaniline (PANI) conducting polymer is demonstrated using poly(ethylene oxide) (PEO) based solid polymer electrolyte comprising tertapropylamonium iodide ($Pr_4NI$) and iodine ($I_2$). The electrolyte with optimized composition has been characterized by ionic conductivity measurements, DC polarization test, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC). About eight-fold increase in the ionic conductivity from $9.33 \times 10^{-6}$ $Scm^{-1}$ to $8.61 \times 10^{-5}$ $Scm^{-1}$ at room temperature was obtained by the addition of 1.5 wt% of PANI to the PEO solid polymer host. FTIR measurements suggest that $Pr_4N^+$ cations are able to coordinate not only with oxygen atoms of PEO, but also with nitrogen atoms of the PANI polymer effectively immobilizing or "trapping" the bulky $Pr_4N^+$ cations and promoting ionic dissociation. DSC studies show that PANI, also acting as a plasticizer, reduces the crystallinity of PEO and lower it's melting temperature. The DC polarization tests confirmed the increased iodide ion conductivity evidently mediated by PANI due to the combined effect of cation trapping and plasticizing. Solid state dye sensitized solar cells fabricated with optimized electrolyte composition incorporating PANI exhibited the highest energy conversion efficiency of 5.01% compared to 3.52% for the DSSC without PANI.

## 1. Introduction

Developing new environmentally-friendly renewable energy technologies that power the world in the near future is critically important due to the fast depleting petroleum resources and environmental concerns. In this scenario, dye sensitized solar cells or DSSCs representing a low cost and clean energy technology that can harness solar energy efficiently are being intensively studied [1,2]. A typical DSSC is made of three major components, a dye-sensitized photoanode of nanocrystalline $TiO_2$, a redox electrolyte with iodide/triiodide couple and a platinum based counter electrode. The redox electrolyte medium fascilitate the efficient electron transfer between the sensitized photoanode and the counter electrode [3–5]. DSSCs based on liquid electrolytes and quasi-solid or gel electrolytes are more efficient compared to cells based on solid electrolytes due to their faster electron transfer dynamics, (but inherently possess some major drawbacks such as liquid leakage and evaporation, electrode corrosion and dye degradation. The use of solid state electrolytes, on the other hand, can circumvent most of these drawbacks enabling the real-world applications of DSSCs. In this context solid polymer electrolytes such as those based on poly(ethylene oxide) (PEO) have received a considerable attention [6,7]. However, the low ionic conductivities of PEO based polymer electrolytes at ambient temperatures limit their practical applications. In order to enhance the ionic conductivities of these electrolytes various methods, such as incorporating plasticizers (e.g. propylene carbonate (PC), ethylene carbonate (EC)) [7], doping with inorganic fillers (e.g. titania ($TiO_2$), alumina ($Al_2O_3$), silica ($SiO_2$)) [8,9], doping with ionic liquid [10] or introducing conducting polymers (polyaniline (PANI) and

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polythiophene (PT), etc.) [11,12] have been used.

Polyaniline or PANI has emerged as one the most important materials in the field of conducting polymers. PANI is an electronically conducting polymer with conjugate~~s~~ systems, showing interesting redox properties and known to have better thermodynamic stability and high conductivity than the other conducting polymers when it is doped with cations. In a DSSC comprised with $I^-$ ion containing solid polymer electrolytes, the contribution from the iodide and tri-iodide ion conductivity to the total ionic conductivity of the electrolyte is a major factor that determines the short circuit current density ($J_{sc}$) and hence the solar cell efficiency [12]. However, not much systematic studies has been reported on this subject particularly in relation to the effect of incorporating a conducting polymers. There are a few reports of the effects of PANI in DSSC electrolytes emphasizing the efficient electron transfer from the counter electrode to the redox species of the electrolyte ($I_3^-$) as well as on the catalytic behavior of PANI with the redox mediator of the electrolyte ($I^-/I_3^-$) [13,14]. However, to the best of our knowledge, a comprehensive study of the role of PANI on ionic conductivity of the DSSC electrolyte has not been reported so far. As far as we are aware, this is the first report of ionic conductivity enhancement in a solid polymer electrolyte due to PANI evidently caused by the combined effects of possible "*cation trapping*" and "*plasticizing*".

## 2. Experimental

### 2.1. Materials

Poly(ethylene Oxide) (PEO, Mw. $4 \times 10^6$), tetrapropylammonium iodide ($Pr_4NI$), plolyaniline (PANI emeraldine salt, Average Mw. > 15,000), iodine chips ($I_2$) and acetonitrile (anhydrous) were purchased from Merck. All the chemicals other than $I_2$ and acetonitrile were vacuum dried at 60 °C for 24 h prior to use.

### 2.2. Preparation of the PEO solid polymer electrolyte

For the preparation of polymer electrolytes, samples having different $P(EO)n.Pr_4NI$ compositions with $n = 6$, 8, 10, 12,14 and 20 (mole ratio of EO:$Pr_4NI$) were prepared by dissolving the appropriate materials in acetonitrile. As these electrolytes are intended for application in DSSCs, the addition of iodine to the above electrolytes was carried out by keeping the $Pr_4NI:I_2 = 10:1$ (mole ratio) constant for all the above compositions. Solid polymer electrolyte films were prepared by casting the well stirred solution mixtures on a Teflon sheet and allowing acetonitrile solvent to evaporate slowly at room temperature in air for overnight. These electrolyte films were then dried in a vacuum oven at 55 °C for different time periods until all the acetonitrile and moisture present in the samples were completely removed. It was observed from FTIR data (as discussed later) that 2.5 h of vacumme drying is sufficient to remove the residual acetonitrile and moisture in the electrolyte. Electrochemical impedance spectroscopic (EIS) measurements were carried out on the above visually uniform and buble free electrolyte films by using a Autolab Potentiostat/Galvanostat PGSTAT 128 N (Metrohm) covering the 1 MHz to 0.01 Hz frequency range. Since $n = 12$ composition exhibited the highest ionic conductivity another set of electrolytes were prepared by keeping EO:$Pr_4NI$ mole ratio of 12:1 but varing the amount of iodine in $PEO.(Pr_4NI)m.I_2$ compositions with $m = 7.0$,7.5,8.0,8.5,9.0,9.5,10.0,10.5 (mole ratio of $Pr_4NI:I_2$). This was done by considering the possible evaporation of added iodine during the vacuum drying proceses of the elecyrolytes. Therefore, in order to find the best iodide to iodine molar ratio which gives the highest conductivity even after the vacuum drying process to eliminate acetonitrile, above compositions were prepared and conductivity measurements were carried out. It was observed that the composition of $PEO.(Pr_4NI)m.I_2$ with $m = 8.0$ gave the highest ionic conductivity for the acetonitrile and moisture free solid polymer electrolytes. Finally, different weight percentages of polyaniline (PANI) were introduced by continuously stirring with the above optimized composition having $n = 12$ and $m = 8$. PANI weight percentages were selected relative to the PEO weight as 0.5%, 1.0%, 1.5%, 2.0% and 2.5%. Conductivity measurements were performed on the above samples after vacuum drying to remove acetonitrile and moisture.

### 2.3. FTIR measurements

In order to see the possible molecular interactions between salt-PEO, salt-PANI as well as between PANI and PEO, a set of identical polymer electrolyte samples with and without PANI were prepared and sandwiched in between two potassium bromide (KBr) pellets and dried in a vacuum oven at 55 °C for 2.5 h to remove acetonitrile and moisture. These samples were used for FTIR measurements using a Bruker Alpha FTIR spectrometer in the range from 400 to 4000 $cm^{-1}$.

### 2.4. Differential scanning calorimetry (DSC) measurements

DSC thermograms were obtained for samples using a Mettler Toledo DSC 30 differential scanning calorimeter. Each sample was scanned between −120 °C and 80 °C at a heating rate of 10 °C per minute. The sample weights used for DSC measurements were between 7 mg - 11 mg. All the experiments were performed under dry nitrogen gas flow.

### 2.5. Ionic conductivity measurements

Ionic conductivity of the solid polymer electrolyte films were determined by AC complex impedance spectroscopy using a computer controlled Metrohm Autolab (PGSTAT 128 N) impedance analyzer in the frequency range from 0.1 Hz to 1.0 MHz. Conductivity measurements were performed as a function of temperature in the range from 20 °C to 70 °C and the measurements were taken at 5 °C intervals after keeping the sample for about 20 min at each selected temperature for thermal equilibrium. The conductivity values at each temperature were determined from the impedance spectra.

### 2.6. DC polarization measurements

DC polarization measurements were performed in order to estimate the ionic and electronic conductivity contributions to the total conductivity of the solid polymer electrolytes. Measurements were performed by sandwiching the electrolyte samples between two polished stainless steel (SS) blocking electrodes in the configuration of SS/electrolyte/SS and by applying a 0.5 V DC voltage across the sample and measuring the variation of current as a function of time. In order to determine the effect of PANI on iodide ion conductivity contribution and cationic contribution, a separate, independent DC polarization experiment was performed by replacing the $Pr_4NI$ salt in the polymer electrolyte by $MgI_2$ salt and the polarization tests were done for the two electrolyte samples, one with PANI and one without PANI. Each electrolyte sample was sandwiched between two highly polished Mg metal plates in the configuration Mg/electrolyte/Mg. The reason for selecting the $MgI_2$ salt, in place of $Pr_4NI$ for this test was purely due to the possibility of using non-blocking Mg electrodes in the polarization test in order to isolate and check the effect of PANI on iodide ion ($I^-$) conductivity in the polymer electrolyte. All DC polarization experiments were carried out at room temperature.

### 2.7. Polarized optical microscopic measurements

Polarized optical microscopy is one of the most effective techniques used to study the crystallization behavior of PEO and many other polymers. In the present work, polarized optical images of PANI-free and PANI-added PEO based polymer electrolyte samples were taken by using a polarized optical microscope (OLYMPUS BX 50) with the same

**x100** magnification to understand the changes in the crystalline nature of the solid polymer electrolyte films from their surface morphology. For these measurements, pure PEO as well as PEO:PANI solid polymer electrolyte samples were prepared by casting the electrolyte solution prepared by dissolving the polymers and the salt in acetonitrile on a glass slide and after solvent evaporation, keeping it at 70 °C for 15 min and then cooling down to room temperature.

## 3. Results and discussion

### 3.1. Ionic conductivity

The prestine PEO polymer at room temperature generally consists of a crystalline phase and an amorphous phase. The addition of the salt $Pr_4NI$ produces the $PEO:Pr_4NI$ polymer-salt complex and free cations and anions through ionic dissociation. At the same time it reduces the crystalline phase content and increases the amorphous phase content through the plasticizing effect, thereby increasing the ionic mobility and hence the ionic conductivity of the electrolyte.

In order to find the best $PEO:Pr_4NI$ salt ratio for the polymer electrolyte to be employed in dye sensitized solar cells, different compositions of PEO based polymer electrolytes were prepared and characterized as mentioned previously. Fig. 1 and Table 1 show the conductivity variation of the electrolyte with different amount of $Pr_4NI{\cdot}I_2$ as a function of $P(EO)n.Pr_4NI{\cdot}I_2$ at room temperature. Here the PEO content has been fixed at 0.264 g and the salt concentration has been varied to get different concentrations of $Pr_4N^+$ cations in the electrolyte. At the same time $I_2$ concentration in the electrolyte was calculated by keeping the $Pr_4NI:I_2 = 10:1$ (mole ratio) as this is the most widely used iodide to iodine molar ratio by the DSSC research community to achieve the highest cell efficiency.

As can be seen from Fig. 1(a) and Table 1, the conductivity of the polymer electrolyte film gradually increases with increasing amount of $Pr_4NI$ salt and reaches the highest value of $5.13 \times 10^{-5}$ S cm$^{-1}$ at room temperature for the mole ratio of $EO:Pr_4NI = 12:1$, composition containing salt ($I^-$) to $I_2$ molar ratio of 10:1. This conductivity increase with the addition of the ionic salt $Pr_4NI$ is clearly due to the increasing number of charge carriers resulting from ionic dissociation. The dissimilarity in the sizes of the $Pr_4N^+$ cation (0.46 nm) and the $I^-$ anion (214 pm) also promotes this salt dissociation. Due to their smaller size, iodide anions ($I^-$) are expected to make a major contribution to the ionic conductivity as their mobility by diffusion through the polymer matrix is relatively much higher compared to the contribution from bulky $Pr_4N^+$ cations as already explained. After reaching this maximum value at the $EO:Pr_4NI = 12:1$ mol ratio, the conductivity starts to decrease, evidently due to the decrease in the number of free ions due to the formation of ion pairs and higher ionic aggregates resulting from high salt concentration. The reduction of ionic mobility due to the stiffening of the polymer matrix caused by the presence of a large concentration of ion pairs and higher ionic aggregates also contribute to this conductivity decrease at higher salt concentrations [6].

In this study, it should be emphasized that due to the vacuum drying process to remove acetonitrile and moisture, some of the originally added $I_2$ (at salt:$I_2$ = 10:1 ratio) would have left from the electrolyte. Therefore, the remaining $I_2$ may not be sufficient to give the highest conductivity and the best solar cell performance [15,16]. Because of this, in order to determine the optimam $I_2$ composition of the solid electrolyte system, another set of solid electrolyte samples were prepared by changing the $I_2$ concentration for each sample as described under section 2.2. Finally, the system with $EO:Pr_4NI$ molar ratio of 12:1 and the added $I_2$ amount ($m$) in $[PEO.(Pr_4NI]m.I_2$ with $m = 8.0$ showed the highest ionic conductivity. Fig. 1(b) and Table 2 show the conductivity variation of $[PEO.(Pr_4NI]m.I_2$ as a function of $Pr_4NI:I_2$ molar ratio at room temperature. A comparison of Fig. 1 (Iodide:$I_2$ ratio = 10) and Fig. 2 (Iodide:$I_2$ ratio = 8) shows that the addition of more $I_2$ into the electrolyte has increased the conductivity of all the samples and the

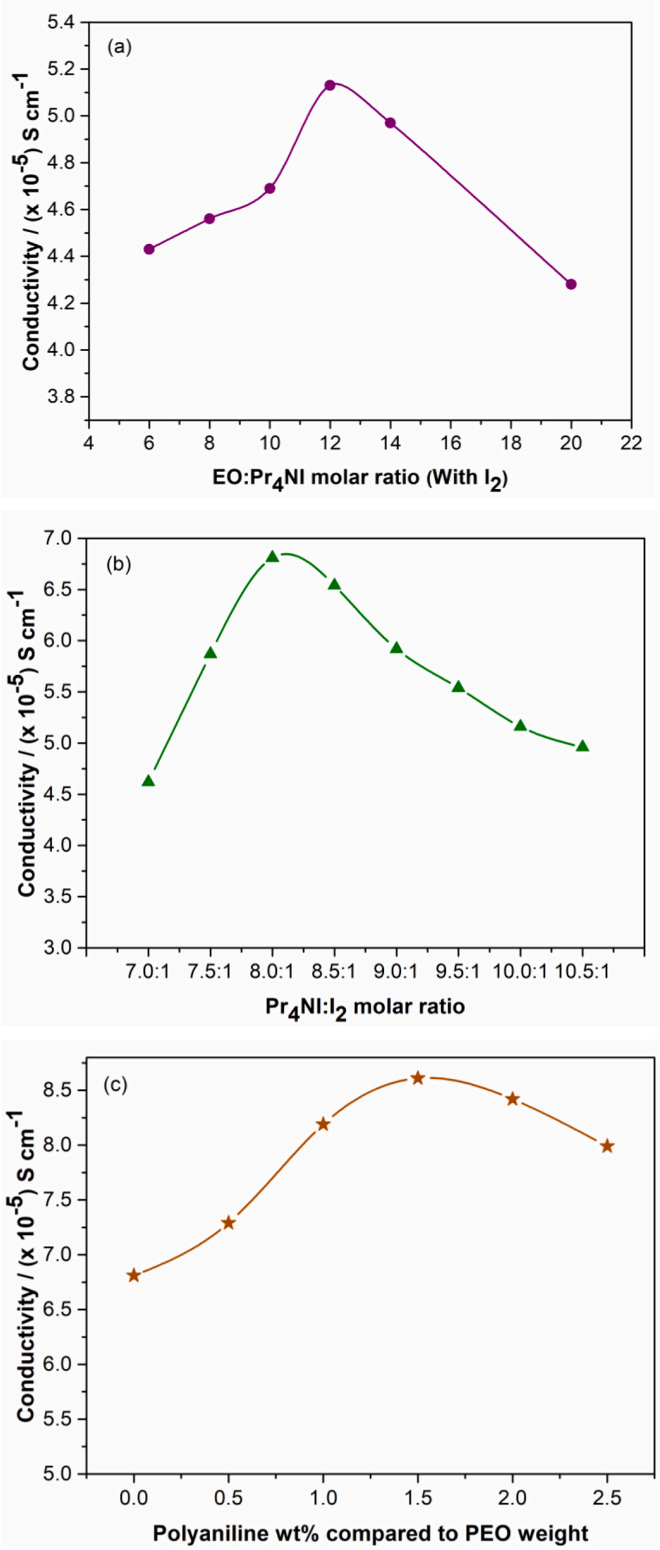


**Fig. 1.** (a) Room temperature conductivity of $P(EO)n.Pr_4NI{\cdot}I_2$ (iodine added electrolyte) as a function of $n$ with $Pr_4NI:I_2 = 10:1$ M ratio at room temperature, (b) Conductivity of $PEO.Pr_4NI:I_2$ as a function of $m$ ($m = Pr_4NI:I_2$ molar ratio) at room temperature, and (c) Variation of room temperature conductivity of $PEO:Pr_4NI:I_2:PANI$ solid polymer electrolyte with added PANI weight percentage.

**Table 1**
Compositions of the $I_2$ added solid polymer electrolyte samples, P(*EO*)n.$Pr_4NI{\cdot}I_2$ and their room temperature conductivity values.

| *n* | PEO weight (g) | $Pr_4NI$ weight (g) | $I_2$ weight (g) | Conductivity (x $10^{-5}$ S $cm^{-1}$) |
|---|---|---|---|---|
| 20 | 0.264 | 0.0939 | 0.0094 | 4.28 |
| 14 | 0.264 | 0.1341 | 0.0134 | 4.97 |
| 12 | 0.264 | 0.1564 | 0.0156 | 5.13 |
| 10 | 0.264 | 0.1877 | 0.0187 | 4.69 |
| 8 | 0.264 | 0.2347 | 0.0234 | 4.56 |
| 6 | 0.264 | 0.3129 | 0.0313 | 4.43 |

**Table 2**
Variation of room temperature conductivity for the electrolyte compositions with EO:$Pr_4NI$ molar ratio of 12:1 (fixed) as a function of (*m*) representing added $I_2$ according to the equation $[PEO.(Pr_4NI]_m.I_2$.

| $I_2$ weight (g) | $Pr_4NI$:$I_2$ molar ratio(*m*) | PEO weight (g) | $Pr_4NI$ weight (g) | Conductivity (x $10^{-5}$ S $cm^{-1}$) |
|---|---|---|---|---|
| 0.0181 | 7.0:1 | 0.264 | 0.1564 | 4.62 |
| 0.0169 | 7.5:1 | 0.264 | 0.1564 | 5.87 |
| 0.0158 | 8.0:1 | 0.264 | 0.1564 | 6.81 |
| 0.0149 | 8.5:1 | 0.264 | 0.1564 | 6.54 |
| 0.0141 | 9.0:1 | 0.264 | 0.1564 | 5.92 |
| 0.0133 | 9.5:1 | 0.264 | 0.1564 | 5.54 |
| 0.0127 | 10.0:1 | 0.264 | 0.1564 | 5.16 |
| 0.0121 | 10.5:1 | 0.264 | 0.1564 | 4.96 |

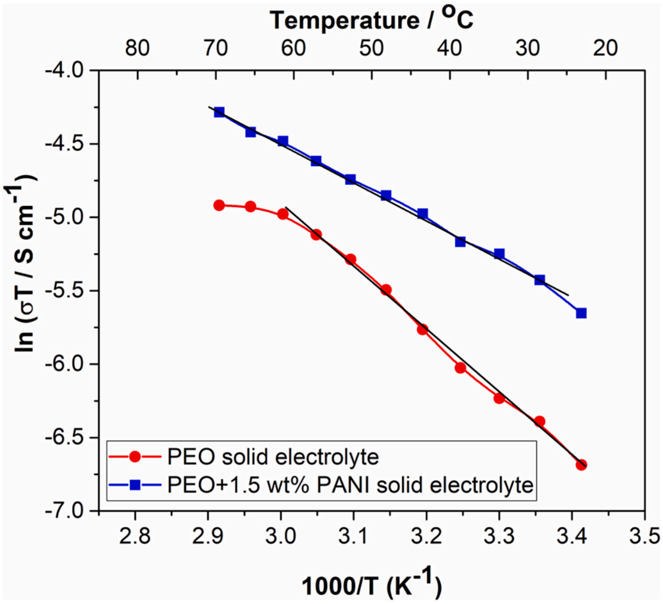


**Fig. 2.** ln(*σT*) vs 1000/*T* plots for PANI free PEO based solid polymer electrolyte and 1.5 wt% PANI added PEO based solid polymer electrolyte.

highest conductivity of 6.81 x $10^{-5}$ S $cm^{-1}$ was obtained for the mole ratios of EO:$Pr_4NI$ = 12:1 and $Pr_4NI$: $I_2$ = 8:1. Further increase of $I_2$ has decreased the conductivity very likely due to the conversion of more and more free $I^-$ ions in to $I_3^-$ ions and more bulky $I_5^-$ and higher iodide ionic aggregates resulting a lower mobility and hence a lower conductivity.

### 3.2. Effect of PANI on conductivity of the electrolyte

Fig. 1(c) shows the room temperature conductivity variation of the solid polymer electrolyte with optimized composition (EO:$Pr_4NI$ = 12:1 and $Pr_4NI$: $I_2$ = 8:1) as a function of different amounts of PANI (emeraldine salt) added to the electrolyte. Table 3 sumarizes the corresponding room temperature conductivity values.

**Table 3**
Amounts of polymer, salt, $I_2$ and PANI used in the PEO:$Pr_4NI$:$I_2$:PANI solid polymer electrolytes and corresponding conductivity values measured at room temperature.

| PANI wt% relative to PEO weight | PANI weight (g) | PEO weight (g) | $Pr_4NI$ weight (g) | $I_2$ weight (g) | Conductivity (x $10^{-5}$ S $cm^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0.0000 | 0.264 | 0.1564 | 0.0158 | 6.81 |
| 0.5 | 0.0013 | 0.264 | 0.1564 | 0.0158 | 7.29 |
| 1.0 | 0.0026 | 0.264 | 0.1564 | 0.0158 | 8.19 |
| 1.5 | 0.0040 | 0.264 | 0.1564 | 0.0158 | 8.61 |
| 2.0 | 0.0053 | 0.264 | 0.1564 | 0.0158 | 8.42 |
| 2.5 | 0.0066 | 0.264 | 0.1564 | 0.0158 | 7.99 |

According to Fig. 1(c) and Table 3, it can be seen that the conductivity of the PEO based solid polymer electrolyte initially increases with the addition of PANI up to 1.5 wt% and then starts to decrease with further addition of PANI. It is well established that conventional plasticizers like ethylene carbonate (EC) and propylene carbonate (PC) play an important role in inhibiting the formation of crystalline complexes and high ionic aggregations in PEO-based polymer-salt systems in addition to their ability to transform PEO from crystalline to amorphous state. Based on the evidence from this work (to be discussed later) PANI also appears to play a role similar to a conventional plasticizer in the present case.

Plasticizers with relatively high dielectric constants such as ethylene carbonate ($\varepsilon$ = 95) and propylene carbonate ($\varepsilon$ = 65.5) increase the ionic conductivity of polymer electrolytes due to the enhancement of the dissociation of ion pairs of the salt. The conducting polymer, PANI (emeraldine salt) we have chosen as an additive to the PEO based solid polymer electrolyte has a high room temperature dielectric constant ($\varepsilon$ ) of 394. Therefore, one of the most likely possibilities for the observed conductivity increase in the PANI added electrolyte is the ability of PANI to act as a plasticizer thereby changing the microstructure of the PEO based polymer electrolyte by increasing its amorphous phase content and enhancing the salt dissociation in the PEO:$Pr_4NI$,$I_2$ electrolyte and increasing the number of free $Pr_4N^+$ cations and $I^-$ anions. The conduction mechanism in the PANI added electrolyte depends also on the interactions of cations/anions of the $Pr_4NI$ iodide salt with PEO and PANI polymers. A novel and important finding emerging from this work based on our FTIR studies, to be discussed later, is that ion pair dissociation can be facilitated by the strong coordination of $Pr_4N^+$ cations with nitrogen sites in PANI in addition to their coordination with oxygen atoms in PEO. This suggests the possibility of "*cation trapping*" effectively "*immobilizing*" the $Pr_4N^+$ cations in the PEO-PANI matrix and making more free iodide (I) ions available for conductivity. More details of this mechanism supported by DC polarization tests, FTIR and DSC studies will be given later under relevant sctions. Due to the increase in ionic mobility caused by the plasticizing effect of PANI and due to the cation trapping effect of PANI which increases the number of mobile iodie ions, the iodide ion conductivity of the electrolyte and hence the short ciruit photocurrent density of the solar cell has increased. Experimental evidence for both these effects will be given and dicussed in detail in subsequent sections.

As seen from Table 3, the conductivity increase up to the addition of 1.5 wt% PANI is evidently caused by the increase in the concentration of free iodide ions due to enhanced ionic dissociation as mentioned above, combined with the increased mobility caused by the enhanced plasticizing effect and increased amorphous nature of the PEO based solid polymer electrolyte. This is in general agreement with similar results reported by Joshi Purushottham et al. [14] for the PEO:$NaCF_3SO_3$:PANI polymer salt complex. In the present system, when more and more PANI beyond the maximum conductivity composition is added, the aggregation tendency of PANI particles reduces the available

PANI sites for coordination and "trapping" $Pr_4N^+$ ions and obstructs the availability of more free $I^-$ ions for ionic transport. This will reduce the overall conducivity of the electrolyte due to further addition of PANI (Fig. 1(c)).

Fig. 2 shows the temperature dependence of ionic conductivity in the PEO solid electrolyte with and without PANI. The PANI added electrolyte shows significantly higher conductivities throughout the measured temperature range. The slightly lower activation energy, as seen from the smaller gradient of the upper straight line is consistent with the increased amorphous nature of the electrolyte due to plasticizing effect caused by PANI addition. According to Fig. 2, as expected, the conductivities have increased with increasing temperature for both systems in the measured temperature range from 20 °C to 70 °C largely due to the increase in the amorphous phase content of the PEO host which enhances the ionic mobility through reduced viscosity in the medium as well as due to the increased number of charge carriers resulting from increased ionic dissociation [18].

The variation of ionic conductivity of the PEO based solid polymer electrolytes with temperature follows the Arrhenius equation,

$$\sigma T = Bexp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where $E_a$ is the activation energy, $B$ is the pre-exponential factor, $k$ is the Boltzmann constant and $T$ is absolute temperature. As described earlier, the ionic species involved are free $Pr_4N^+$ cations and $I^-$ and $I_3^-$ anions and possibly some ionic aggregates. Because of the bulky size of the $Pr_4N^+$ cation, the dominant contribution to the ionic conductivity is expected from the iodide ($I^-$) and tri-iodide ($I_3^-$) ions, which migrate by diffusion assisted by the segmental flexibility of the PEO chains. This is a thermally activated process as seen from the linear behavior of the ln $\sigma T$ vs $1/T$ variation for both electrolytes. Activation energy ($E_a$) values were obtained from the linear fits to conductivity data in Fig. 1(d) in the 20 °C to 70 °C temperature range. The $E_a$ value for the 1.5 wt% PANI added electrolyte is 0.24 eV (22.9 kJ $mol^{-1}$) which is significantly lower compared to the $E_a$ value of 0.37 eV (35.3 kJ $mol^{-1}$) for the PANI free electrolyte. Lower activation energy suggests that ionic migration become easier in the PANI incorporated system evidently due to the strong plasticizing effect and increased amorphous phase content in the electrolye medium due to PANI as already discussed. The role played by PANI in enhancing the ionic conductivity of PEO based solid polymer electrolytes is yet to be properly understood. In a recent paper, Duan et al. have reported the lowest activation energy of 39.7 kJ $mol^{-1}$ for PEO:1.0 wt% PANI electrolyte containing LiI as the salt, but the explanation given by these authors states that as a conducting polymer, PANI can form conducting channels through the PEO matrix and provide conducting pathways for electron migration [13]. This explanation given for the conductivity enhancement due to PANI by these authors is entirely different from the mechanism proposed by us here. In this context, supported by results of our FTIR and DSC measurements to be discussed in more detail later, we propose that the presence of PANI can enhance the ionic conductivity by the combined effect of "*cation trapping effect*" and plasticizing effect due to the presence of PANI electronic conductor with high high dielectric constant.

### 3.3. Polarized optical microscopy

Figs. 3(a) and 3(b) show the polarized optical microscopic photographs of thin, free standing films of PANI free and PANI added PEO based solid polymer electrolyte films respectively. As seen from these photographs, after introducing PANI the PEO electrolyte film becomes dark brown in colour. Further, after the solvent evaporation and vacuum drying process, the electrolyte films become thin, flexible solid films. As confirmed by FTIR measurements, these films are free from traces of acetonitrile and moisture. Figs. 3(c) and 3(d) show their optical microscopy images taken with the same magnification.

PEO polymer electrolytes consist of both crystalline and amorphous regions, as well as intermediate regions at the crystalline/amorphous interphase. When a PEO electrolyte sample is heated to around 60 °C and cooled sown slowly, spherulites consisting of the crystalline phase are formed. The crystalline phase limits its ionic conductivity. The suppression of the degree of crystallinity of the polymer chains leads to an increase in its amorphous phase content and improves the ionic mobility, thereby leading to better ionic conduction. The number of sperullites present per unit area of the electrolyte membrane is therefore a measure of the degree of crystallinity of the polymer electrolyte.

Fig. 3(c) exhibits the polarized micrograph of the pure PEO solid film, demonstrating its crystalline nature of the spherulitic texture usually observed for pure PEO [19–21]. For pure PEO (Fig. 3(c)), only few large spherulites exhibiting a typical compact spherulitic morphology can be seen, similar to those reported by Lioa et al. [20]. Here, during cooling, the crystal growth of pure PEO proceeds without any disturbance. The spherulitic texture in the polymer film shows its typical lamellar crystalline nature. The polarizing optical microscopy images shown in Fig. 3 clearly show the decrease in PEO crystallinity (by reduced spherullite size) and hence the increase in amorphous phase content which facilitate the iodide ion mobility in the PANI added electrolyte. This is also well supported by DSC results.

Fig. 3(d) shows the polarized micrograph of PEO/PANI complexed polymer film after the addition of 1.5 wt% of PANI. When PEO is complexed with PANI, the size of the spherulites have reduced significantly while their number observed within the same area of observation has increased. The dark areas in Fig. 3(d) representing the amorphous phase of PEO have also increased compared to Fig. 2(c). These results clearly suggest that PANI in the composite PEO electrolyte acts as a plasticizer reducing the spherulite size (or crystallinity) and increasing the amorphous phase content.

Fig. 3(e) shows the polarized micrograph of PEO/$Pr_4NI$ salt added complexed electrolyte film. Surface morphology of similar nature is reported in other PEO based electrolytes such as PEO:Li systems [21–23], PEO: Na systems [19,24] and PEO:Mg system [25]. This shows that the decrease in crystallinity and increase in amorphous content of the PEO-salt complex due to the presence of the salt, as indicated also in DSC studies, described later. Fig. 3(f) shows the PEO polymer electrolyte complexed with both PANI and $Pr_4NI$ salt. On the addition of both PANI and the salt, further change in the spherulitic texture is observed in Fig. 3(f). The spherulite sizes are much smaller than the ones seen in Fig. 3 (c) and (d) for pure PEO and PANI added PEO respectively. This is evidently due to the formation of polymer-salt complexes. Moreover, in this system (Fig. 3(f)) the increase in amorphous phase content due to the addition of PANI is clearly visible from the appearance of more dark regions in the micrograph. The introduction of PANI has clearly reduced the crystallinity of the PEO-salt system further. This reduction of crystallinity due to plasticization effect is also confirmed by the DSC results. Similar results are reported by several groups for blend polymer systems with PEO and another polymer such as methylcellulose [23], poly(3-hydroxybutyrate) [26] and poly(2-vinyl pyridine)-b-(ethylene oxide) [27].

### 3.4. DC polarization measurements with PEO:$Pr_4NI$:PANI and PEO:$MgI_2$ electrolytes

DC polarization technique has long been in use as an important and widely used simple method to understand the ion transport mechanism in solid electrolyte systems and to estimate the ration of ionic/electronic contributions to the total ionic conductivity [28]. Results of DC polarization tests carried out for PEO:$Pr_4NI$ and EO:$Pr_4NI$:PANI (1.5 wt %) electrolyte films using Stainless Steel (SS) blocking electrodes in the configuration SS/electrolyte/SS are shown in Fig. 4.

According to the DC polarization test results, both PEO:PANI and PEO:PANI:$Pr_4NI$:$I_2$ electrolytes are predominantly ionic conductors with negligible electronic conductivity. However, the electronic

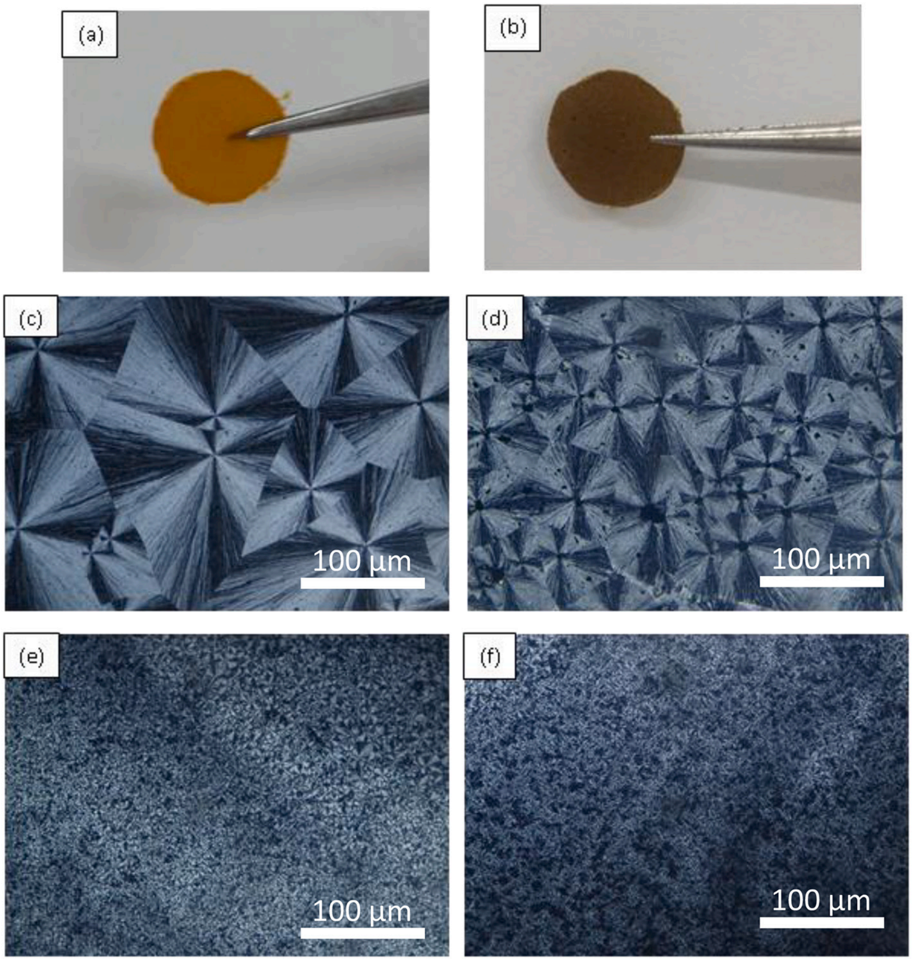


**Fig. 3.** Polarizing microscopy photographs of PEO based free standing solid electrolyte film, (a) without PANI additive, (b) with PANI additive. Cross-polarized optical micrographs of (c) pure PEO, (d) PEO/PANI mixed polymer film, (e) PEO/$Pr_4NI$ (EO:$Pr_4NI$ molar = 12:1) polymer electrolyte film without PANI additive and (f) PEO/$Pr_4NI$ (EO:$Pr_4NI$ molar = 12:1) polymer electrolyte film containing 1.5 wt% PANI. Same x100 magnification was used for all four images.

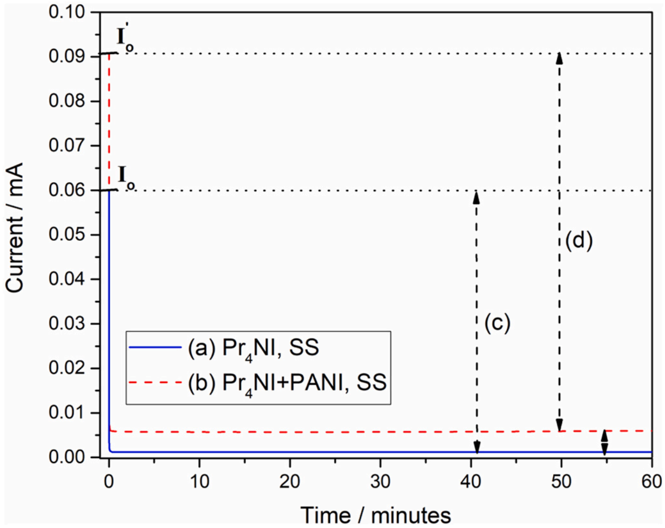


**Fig. 4.** Current vs time plots for solid polymer electrolyte samples obtained by DC polarization test with stainless-steel blocking electrodes. The values of the initial ($t$ = 0) currents are 0.06 mA for the PEO:$Pr_4NI$ electrolyte and 0.09 mA for the PEO:$Pr_4NI$:PANI (1.5 wt%) electrolyte. The vertical distances (c) and (d) represent ionic conductivity parts for the two electrolytes.

conductivity of the PANI added system is higher compared to the PANI free system, indicating the effect of increased electronic conductivity due to PANI which by nature is an electronically conducting polymer. The ionic conductivity of the PANI added system is significantly higher compared to the PANI free electrolyte which is also consistent with the conductivity vs temperature data presented in Fig. 2. Using plots of $I_t/I_o$ vs time (not shown) for these two electrolytes the ionic transference numbers $t_{ion}$ were calculated and the values obtained are, $t_{ion}$ = 0.96 for the PANI free system and $t_{ion}$ = 0.99 for the PANI added system. These results along with results from Fig. 2 clearly shows that the ionic conductivity in the PEO based solid polymer electrolyte has increased significantly due to the incorporation of 1.5 wt% PANI.

In order to estimate exclusively the difference in iodide conductivity contributions with and without PANI in the PEO based electrolytes we have conducted an independent and simple DC polarization experiment using PEO complexed with $MgI_2$ iodide salt as Mg metal can easily be used in a Mg/electrolyte/Mg symmetrical symmetrical cell arrangement to estimate the cationic ($Mg^{++}$) and anionic ($I^-$) conductivity contributions separately. In this experiment, DC polarization measurements were performed using PEO:$MgI_2$ and PEO:$MgI_2$:PANI as the electrolytes. This enabled us to use Mg metal as $Mg^{++}$ ion transparent electrodes. DC polarization curves taken initially for the SS/Electrolyte/SS symmetrical cell with electrolyte samples with and without PANI sandwiched between two stainless-steel electrodes are shown in Fig. 5. Curves (a) and (b) correspond to samples without and with PANI respectively. For these two samples, the rapid decay of currents with time finally approaching almost zero in 60 min implies the predominantly

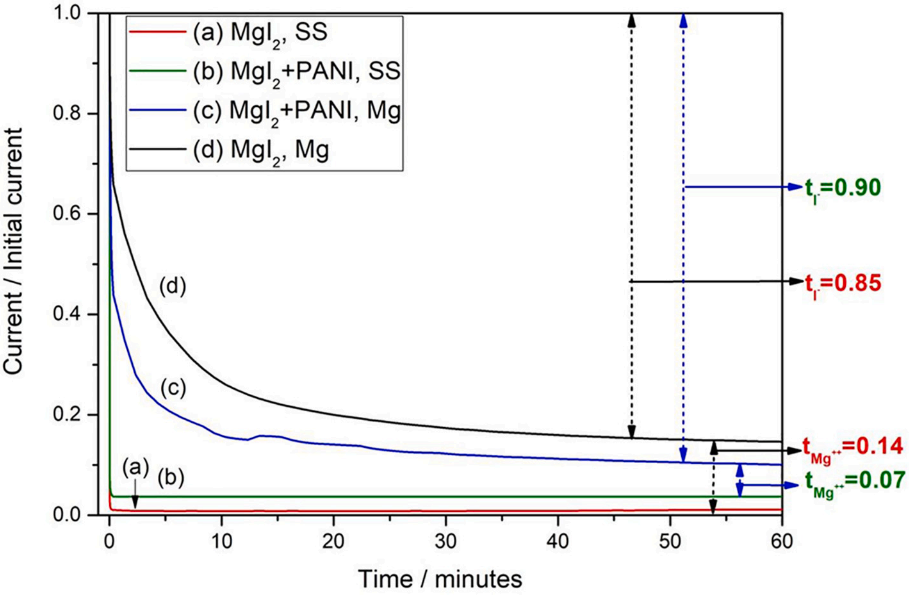


**Fig. 5.** Current/initial current vs time plots for PEO:MgI$_2$ solid electrolyte samples with and without PANI obtained by DC polarization test with Mg non-blocking electrodes and stainless-steel (SS) blocking electrodes.

ionic nature of the electrolytes. It is important to note that the PANI added PEO:MgI$_2$ electrolyte (curve (b)) shows slightly enhanced electronic conductivity as expected, as PANI emeraldine salt used is a good electronic conductor.

The ionic transference number, $t_{ion}$ was estimated using the equation

$$t_{ion} = 1 - {}^{I_i}\!/_{I_f} \tag{2}$$

where, $I_i$ is the initial current and $I_f$ is the final residual current. This gives, $t_{\text{ion}} = 0.99$ for the electrolyte without PANI and $t_{\text{ion}} = 0.97$ for the electrolyte with PANI, showing that the electronic contribution has increased from 0.01% to 0.03% due to the presence of 1.5 wt% of PANI in the PEO:MgI$_2$ electrolyte.

In each of the above two samples, using the two polarization curves (c) and (d) close to 60 min, the cationic ($Mg^{++}$) and anionic ($I^-$) contributions can be separately estimated and the values obtained are.

$t_{Mg++} = 0.14$ and $t_{I^-} = 0.85$ for the PANI free electrolyte sample (from curves (a) and (d) and.

$t_{Mg++} = 0.07$ and $t_{I^-} = 0.90$ for the PANI added electrolyte sample (from curves (b) and (c).

The electronic conductivity contribution is therefore, 1% for the PANI free electrolyte sample and 3% for the PANI added electrolyte sample.These estimates clearly show that the PANI added PEO:MgI$_2$ electrolyte exhibits a higher iodide ion transference number and therefore, a higher iodide ion conductivity compared to the electrolyte without PANI. In addition to the plasticizing effect, the dominant role of PANI appears to be to "*tra*p" $Mg^{++}$ ions and reduce cationic conductivity while allowing more free $I^-$ ions to be available for iodide ion conductivity in the PANI added electrolyte. Such a "*trapping effect*" on some $Mg^{++}$ ions can be expected from the electron transport in doped conducting polymers such as PANI which involves electrons transported to the conducting polymer backbone while counter-*cations* become immobilized and are thus *trapped* inside the polymer structure [29]. The above results are further suported by other observations made under FTIR, DSC and EIS measurements on PEO:Pr$_4$NI electrolytes to be discussed later.

We presume that a similar reasoning as above can be extended for the PEO:Pr$_4$NI:PANI system as well where $Pr_4N^+$ ions can be expected to be "*trapped*" by PANI while leaving out more free odide ions available for conductivity. In the case of $Pr_4N^+$ cations, the decrease in cationic conductivity due to PANI by the proposed "*trapping effect*" is expected to be much greater than for the MgI system as the $Pr_4N^+$ cation is more bulkier and less mobile compared to the $Mg^{++}$ cation. A mechanism similar to the above can be used to explain the decrease in cationic conductivity and increase in iodide ion conductivity and electronic conductivity in the PANI added PEO:Pr$_4$NI polymer electrolytes. A conductivity increase due to the presence of PANI in PEO-salt complexes have been reported by Purushottam et al. and by Kunteppa et al. for PEO/PANI system but using higher wt% of PANI and the explanation given for the conductivity increase in quite different to what we propose here [17,30].

### 3.5. FTIR analysis

In a PEO-ionic salt system, there are four characteristic regions corresponding to four types of vibration bands: CH$_2$ rocking vibrations, C–O–C stretching vibrations, CH$_2$ twisting vibrations and CH$_2$ bending vibrations. Conformational changes when PEO-salt complexes are formed would be expected to affect the dynamics of $Pr_4N^+$ cation coordination to the PEO backbone facilitating ionic dissociation producing free iodide ($I^-$) ions, which determines the iodide ion conductivity and short circuit photocurrent in DSSCs.

In this work, the molecular interactions between PEO and PANI in the PEO based electrolytes were studied by FTIR spectroscopy. FTIR spectra taken in the region 500–4000 cm$^{-1}$ are compared in Fig. 6. Curve marked by (a) shows the FTIR spectrum of pure PEO and details are summarized in Table 4, column 1. These observations are consistent with the data reported in literature [17,30,31]. In Figs. 6 curve (b) shows the FTIR spectrum of pure PANI. The presence of PANI is confirmed from the predominant peaks at the wave number of 1603 cm$^{-1}$ corresponding to C=C stretching of the quinine ring, 1494 cm$^{-1}$ for C=C stretching of benzenoid ring, 1296 cm$^{-1}$ for C–N stretching, 1126 cm$^{-1}$ due to C-O-C stretching and 819 cm$^{-1}$ due to C–H vibration of benzonoid benzene rings. Similar FTIR results for PANI have been reported by Kunteppa et al. [30] and Mihali et al. [32].

In Figs. 6, curve (c) shows the FTIR spectra of PEO:Pr$_4$NI polymer-salt complex with EO:Pr$_4$NI = 12:1 mol ratio. In the FTIR transmission spectrum of pure Pr$_4$NI, there is a strong peak at 2980 cm$^{-1}$ [23]. The shifts of major peak positions summarized in Table 4, column 1 are clearly due to the interactions between PEO and Pr$_4$NI. The peaks have

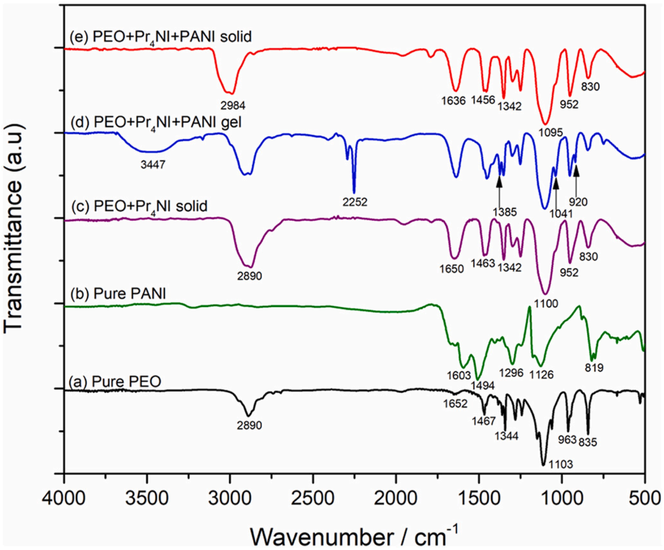


**Fig. 6.** FTIR spectra of (a) Pure PEO, (b) Pure PANI, (c) PEO + $Pr_4NI$ solid electrolyte, (d) PEO+ $Pr_4NI$ + 1.5 wt% PANI gel electrolyte prior to vacuum drying and (e) PEO+ $Pr_4NI$ + 1.5 wt% PANI solid electrolyte in the region 500–4000 cm$^{-1}$.

shifted to the lower wave numbers evidently due to the formation of coordinating bonds between oxygen atoms in PEO and bulky tetrapropylammonium ion ($Pr_4N^+$). The shift to the lower frequency values upon to complexation of polymer-salt system has been reported by other authors also [30,31].

The FTIR spectrum of the PEO:$Pr_4NI$:1.5 wt% PANI electrolyte is shown in Fig. 6 (curve, d) before vacuum drying (in gel state) and Fig. 6 (curve, e) after vacuum drying (in the solid state). Fig. 6 (curve, e), confirms the complete absence of traces of acetonitrile and moisture in the solid polymer electrolyte samples due to vacuum drying for 2.5 h at 55 °C.

With the presence of PANI (Fig. 6, curve (e) and Table 4), it is seen that the C—H stretching band of PEO appearing at 2890 cm$^{-1}$ is shifted to higher frequency at 2984 cm$^{-1}$ clearly indicating that there is also a significant polymer-polymer interaction between PANI and PEO possibly mediated via the salt. This indicates that the $Pr_4N^+$ cations are able to coordinate not only with oxygen atoms of PEO, but also with nitrogen atoms of the PANI polymer effectively immobilizing or "*trapping*" the bulky $Pr_4N^+$ cations. This supports the results obtained from conductivity measurements and DC polarization measurements which indicates enhanced iodide ($I^-$) ion conductivity due to incorporation of PANI. Also, the C-O-C stretching band of PEO is shifted further to 1095 cm$^{-1}$ due to the presence of PANI. Based on these FTIR results, we can conclude that the nitrogen sites of PANI together with oxygen atoms of PEO, contribute towards making a strong interaction with the $Pr_4N^+$ cations of the salt and essentially "*immobilizi*ng" the cation and thereby enhancing the anionic conductivity in the electrolyte.

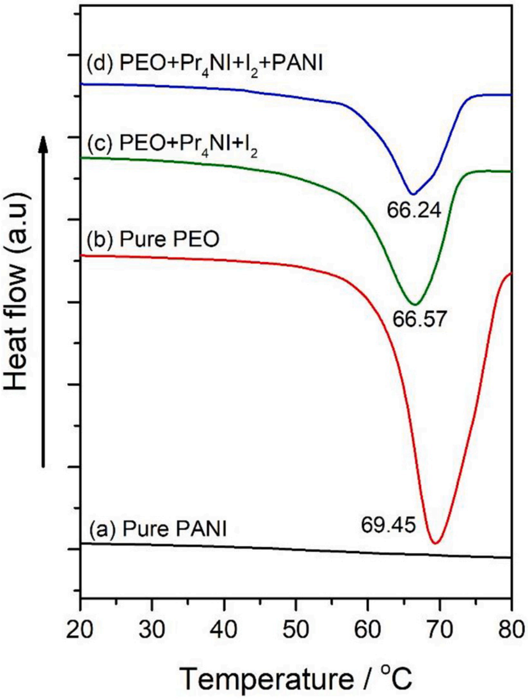


**Fig. 7.** DSC spectra of (a) pure PANI, (b) pure PEO, (c) PEO with optimum $Pr_4NI$ salt and $I_2$ and (d) PEO + $Pr_4NI$ + $I_2$ + 1.5 wt% PANI solid polymer electrolytes in the region 20 °C to 80 °C.

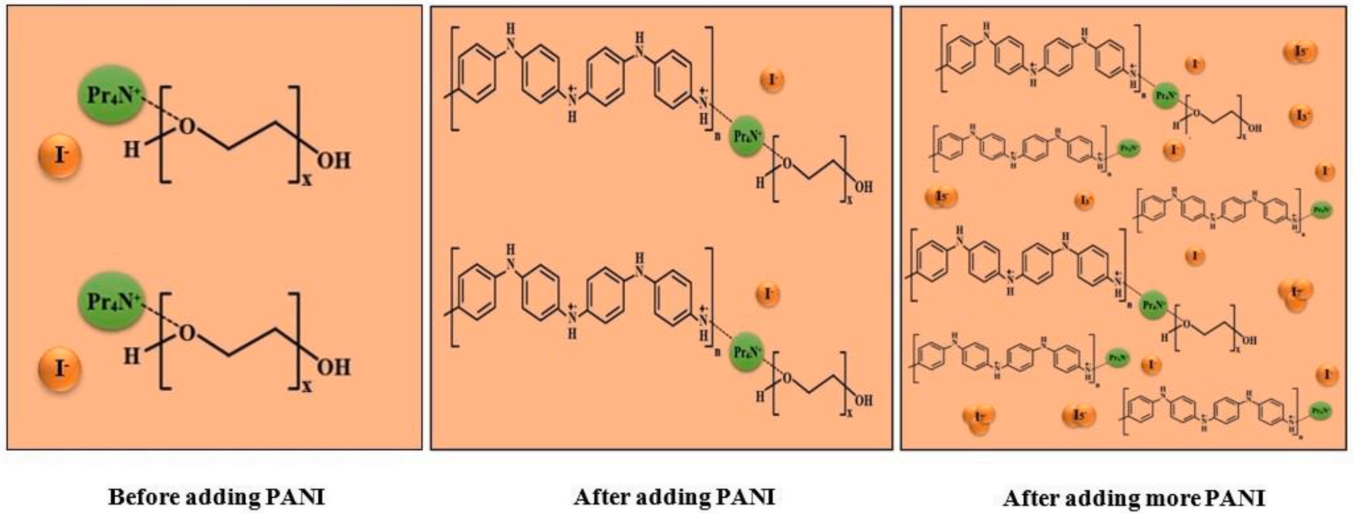
When an ionic salt is incorporated to the PEO polymer, the main absorption band of PEO in the polymer-salt complex gets shifted from 1103 cm$^{-1}$ to a lower value 1100 cm$^{-1}$ suggesting a strong co-ordination of cations with ether oxygens in PEO. The addition of 1.5 wt % of PANI has shifted this peak to a still lower value of 1095 cm$^{-1}$ suggesting PANI-$Pr_4NI$ salt interactions. The peak at the 1059 cm$^{-1}$ position associated with the crystalline structure in pristine PEO has largely disappeared, indicating a decrease of crystallinity in the salt added system. These FTIR results indicate possible PEO-salt interactions, PANI-salt interactions and polymer-polymer interactions between PANI (C—N) and PEO (C–O–C) through H-bonds [13].

### 3.6. DSC analysis

Fig. 7 shows the DSC thermograms of (a) pure PANI, (b) pure PEO, (c) PEO with optimum $Pr_4NI$ salt concentration and $I_2$ and (d) PEO + $Pr_4NI$ + $I_2$ + 1.5 wt% PANI solid electrolytes in the temperature range from 20 °C to 80 °C. A sharp endothermic peak

**Table 4**
Comparison of FTIR peaks in PEO, PEO:$Pr_4NI$ and PEO:$Pr_4NI$:PANI systems.

| PEO | PEO:Pr4NI | PEO:Pr4NI:PANI |
|---|---|---|
| 2890 $CH_2$ stretching | 2890, but broadened and higher intensity evidently due to the PEO:Salt interaction.<br>Salt has the strongest peak at 2980. | Shifted to 2984 due to PEO-PANI interaction causing cation immobilization facilitating salt dissociation at low salt concentrations. |
| 1652C=O stretching | Shifted to 1650, strong broad and intense peak due to slat-polymer interaction. | Shifted to lower energy at 1636 due to PANI-salt interaction. |
| 1467 asymmetric $CH_2$ bending | Shifted to 1463 due to salt-polymer interaction | Shifted to 1456 (to lower energy) due to PANI-salt interaction. |
| 1344 symmetric $CH_2$ wagging | 1342 shifted slightly to lower energy; Intense;<br>Due to salt-polymer interaction | 1342 peak has not changed. |
| 1103C-O-C stretching | 1100 Lower energy; Intense, broad peak; Polymer-salt interaction | 1095 lower energy;<br>PANI-salt interaction. |
| 963 asymmetric $CH_2$ rocking | 952 Lower energy; Polymer-salt interaction | 952 no further shift |
| 835C-O stretching | 830 Lower energy; Polymer-salt interaction | 830 no further shift |



Before adding PANI

After adding PANI

After adding more PANI

**Fig. 8.** Schematic diagram of the PEO:$Pr_4NI$:PANI solid polymer electrolyte showing the "*cation trapping effect*" due to interactions between $Pr_4N^+$ cations and PANI/PEO polymers allowing more iodide ions to be available for iodide ion conduction.

corresponding to the crystallite melting temperature $T_m$ in pure PEO is seen at 69.45 °C and value is reasonably close to the value reported by Johan et al. [33]. After the addition of the $Pr_4NI$ salt and $I_2$, the $T_m$ has decreased from 69.45 °C to 66.57 °C. This is clearly due to the plasticizing effect of the salt as reported by others for PEO:LiX polymer salt complexes [22,34–38]. After the addition of 1.5 wt% of PANI, the $T_m$ has reduced further to 66.24 °C again confirming the increased plasticizing effect by PANI already seen from FTIR and optical microscopy results. (See Fig. 8.)

In order to analyze these thermograms more quantitatively, the relative percentage of crystallinity ($X_c$) was calculated for each sample, based on the following eq. (3),

$$X_c = \frac{\Delta H_m}{\Delta H_m^o} \times 100\% \qquad (3)$$

where, $\Delta H_m{}^o$ is the standard enthalpy of fusion of pure PEO and $\Delta H_m{}^o$ is the enthalpy of fusion of the solid polymer electrolyte calculated using the peak areas of melting. The values, $T_m$, melting peak area, $\Delta H_m$ and $X_c$ of solid polymer electrolytes are summarized in Table 5.

Based on DSC measurements, the enthalpy of fusion and relative crystallinity of pure PEO are 196.25 $Jg^{-1}$ and 91.83%, respectively. At the optimum salt added electrolyte composition, $X_c$ reduces to 49.39% and after adding 1.5 wt% of PANI, it reduces further down to 18.67%. This is an impressive 79.7% crystallinity drop compared to that of pure PEO. The role of PANI in reducing the crystallinity phase content of the polymer-salt complex is quite evident from these DSC results, further confirming the conclusions drawn from FTIR and polarizing optical microscopic studies. The decrease of both the $T_m$ as well as $X_c$ due to PANI incorporation to PEO matrix have evidently increased the amorphous phase content of the PEO electrolyte. The net result is the enhancement of iodide ion mobility and iodide ion conductivity which would lead to performance enhancement in dye sensitized solar cells made from PANI incorporated PEO based solid polymer electrolyte.

**Table 5**
The melting point, $T_m$, the melting enthalpy $\boldsymbol{\Delta H_m}$ and relative percentage of crystallinity $\boldsymbol{X_c}$ **%** of pure PEO and PEO based solid polymer electrolyte films.

| Electrolyte composition | $T_m$ (°C) | Peak Area / mJ | Weight / mg | $\Delta H_m$/ $Jg^{-1}$ | $X_c$ % |
|---|---|---|---|---|---|
| PEO | 69.45 | 1560.24 | 7.95 | 196.25 | 91.83 |
| PEO+ $Pr_4NI$ + $I_2$ | 66.57 | 706.14 | 6.69 | 105.55 | 49.39 |
| PEO + $Pr_4NI^+$ $I_2$ + 1.5% PANI | 66.24 | 325.62 | 8.16 | 39.90 | 18.67 |

### 3.6.1. Dye sensitized solar cell performance

The photocurrent density-voltage (*J-V*) curves for the DSSCs fabricated with PEO + $Pr_4NI^+$, $I_2$ and PEO + $Pr_4NI^+$,$I_2$ + 1.5% PANI solid polymer electrolytes are shown in Fig. 9. The values of short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (*FF*) and power conversion efficiency ($\eta$) obtained from these curves are summarized in Table 6. It is clearly seen that the DSSC made with the solid polymer electrolyte without PANI showed an efficiency of 3.52% and with the addition of 1.5 wt% of PANI to the electrolyte the efficiency has increased up to an impressive 5.01%. This is a remarkable efficiency enhancement of 42% which is among the highest for solid polymer electrolyte based DSSCs reported in the literature [4,11,22]. It is clear that the addition of 1.5 wt% PANI to the PEO polymer electrolyte has enhanced the $J_{sc}$ and overall solar cell efficiency evidently due to the increased iodide ion conductivity caused by the reduced crystallinity of the PEO-salt complex due to the plasticizing effect of PANI as well as increased ionic dissociation due to the *cation trapping effect* of PANI. These results substantiate the results of DC polarization, FTIR, optical microscopy and DSC measurements supporting the role played by PANI. The presence of more amorphous regions in the PANI incorporated electrolyte also improves the contact interface area between the $TiO_2$ photoanode and the electrolyte of the DSSC, thereby contributing to the increase in the short circuit photocurrent, $J_{sc}$. Fig. 9. depicts a schematic diagram of the DSSC showing the "cation trapping effect" by salt-PANI and salt-PEO interactions in the solid polymer electrolyte medium allowing more iodide ions to be available for iodide ion conductivity.

In summary, we describe below the role played by PANI in enhancing the iodide ion contribution in the PEO:$Pr_4NI$:PANI electrolyte.

(a) The polarizing optical microscopy images shown in Fig. 3 clearly show the decrease in PEO crystallinity (by reduced spherullite size) and hence the increase in amorphous phase content which facilitate the iodide ion mobility in the PANI added electrolyte. This is also well supported by DSC thermogram results.

(b) As seen from Fig. 4, the DC polarization test, the ionic conductivity of the PANI added system is significantly higher compared to the PANI free electrolyte which is also consistent with the conductivity vs temperature data presented in Fig. 2. The "*indirect*" experiment on PANI added PEO:MgI electrolyte provide evidence of increase in iodide ion conductivity due to the presence of PANI.

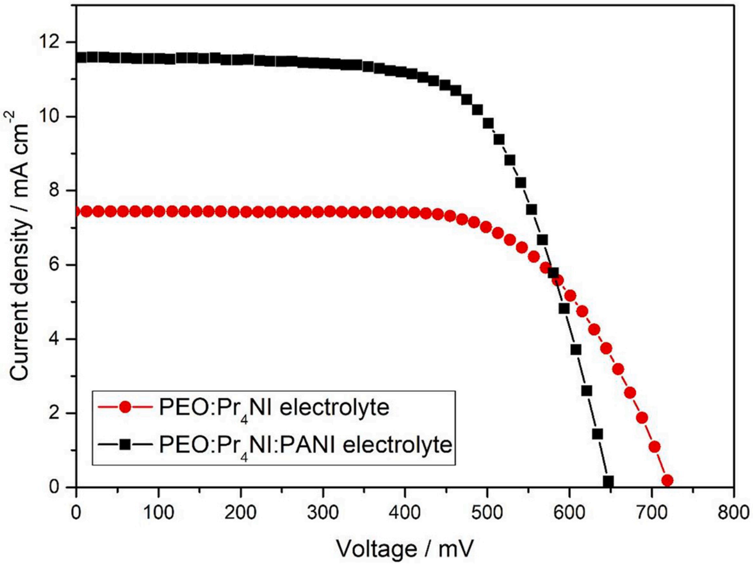


**Fig. 9.** Photocurrent density-voltage curves for DSSCs based on PEO + $Pr_4NI$ (circles) and PEO + $Pr_4NI$ + 1.5 wt% PANI (squares) solid polymer electrolytes.

**Table 6**
Photovoltaic parameters of the DSSCs fabricated with PEO + $Pr_4NI$ and PEO + $Pr_4NI$ + 1.5 wt% PANI solid polymer electrolytes.

| Composition | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$(mV) | FF % | $\eta$ % |
|---|---|---|---|---|
| PEO + $Pr_4NI$ + $I_2$ | 7.44 | 720.2 | 75.3 | 3.52 |
| PEO + $Pr_4NI$ + $I_2$ + PANI | 11.57 | 648.5 | 66.2 | 5.01 |

(c) The analysis of FTIR results shown in Fig. 6 and Table 4 clearly indicates that the $Pr_4N^+$ cations are able to coordinate not only with oxygen atoms of PEO, but also with nitrogen atoms of the PANI polymer effectively immobilizing or “*trapping*” the bulky $Pr_4N^+$ cations. This facilitates ionic dissociation of $Pr_4NI$ salt and release more “free” iodide ions for conductivity. This is consistent with the results obtained from conductivity measurements and DC polarization measurements which indicate enhanced iodide ($I^-$) ion conductivity due to incorporation of PANI.

All these factors taken together provide strong evidence for the role played by PANI in enhancing the iodide ion conductivity and thereby increasing the short circuit photocurrent density of the solar cells (due to both, increased iodide ion mobility and increased number of iodide ions).

## 4. Conclusions

Solid polymer electrolytes based on PEO and $Pr_4NI$ iodide salt were fabricated with different EO:$Pr_4NI$ and $Pr_4NI$:$I_2$ molar ratios to find the best electrolyte composition. The optimum polymer electrolyte composition with the highest conductivity at room temperature was for EO:$Pr_4NI$ = 12:1 mol ratio and for $Pr_4NI$:$I_2$ = 8:1 mol ratio. Addition of 1.5 wt% of PANI to this electrolyte further enhanced the total ionic conductivity. Temperature dependent conductivity measurements confirmed that the 1.5 wt% PANI added electrolyte had the highest conductivity at all temperatures. FTIR spectrum and DC polarization test confirmed that the enhanced iodide ion conductivity very likely due to the “*cation trapping*” effect caused by the strong cation-PANI and cation-PEO salt polymer interactions. The associated decrease in relative percentage of crystallinity in the PANI added electrolyte was observed from polarizing optical microscopy and DSC thermograms. The enhancement in conductivity is also promoted by the decrease in the crystalline phase content and the increase in the amorphous phase content of the PEO based solid polymer electrolyte evidently due to the strong plasticizing effect of PANI. The variation of ionic conductivity with temperature of the polymer electrolytes obeyed the Arrhenius law and the low activation energy of the PANI added system agrees with the increased amorphous nature of the electrolyte. Dye sensitized solar cells fabricated with optimized electrolyte composition incorporating PANI exhibited the highest energy conversion efficiency of 5.01% in comparison with 3.52% for the DSSC without PANI. The results obtained from all the characterizations of the electrolytes as well as the DSSCs made with PANI free and PANI added electrolytes suggest that the PEO/PANI solid polymer electrolyte is a suitable electrolyte for fabrication of high efficiency, solid state polymer electrolyte based DSSCs.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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