

## NEW SOLID-POLYMER-ELECTROLYTE MATERIAL FOR DYE-SENSITIZED SOLAR CELLS

### NOVI ELEKTROLITNI MATERIAL NA OSNOVI TRDNEGA POLIMERA ZA SONČNE CELICE, OBČUTLJIVE ZA SVETLOBO

**Vivek K. Singh, Bhaskar Bhattacharya, Shashank Shukla, Pramod K. Singh**

Material research laboratory, School of Basic Sciences & Research, Sharda University, G. Noida 201310, India  
vivekv445@gmail.com; singhpk71@gmail.com

*Prejem rokopisa – received: 2014-02-08; sprejem za objavo – accepted for publication: 2014-02-26*

A solid-polymer electrolyte consisting of polyvinylpyrrolidone (PVP) doped with ammonium iodide ( $\text{NH}_4\text{I}$ ) was developed and characterized for a possible application in a dye-sensitized solar cell. Complex impedance spectroscopy revealed an increase in the conductivity and the maximum conductivity was obtained at the  $w = 50\%$   $\text{NH}_4\text{I}$  mass concentration. Light photographs confirmed an enhancement in the amorphous nature of the host which was affirmed by XRD measurement. The composite nature of the polymer-electrolyte film was also confirmed with the FTIR spectrum. A dye-sensitized solar cell (DSSC) was fabricated using the most conductive film that showed an efficiency of  $0.025\%$  at the 1 sun condition.

Keywords: polymer electrolyte, conductivity, FTIR, XRD, dye-sensitized solar cell

Razvit in karakteriziran je bil trdni polimerni elektrolit, ki ga sestavlja polivinil pirolidon (PVP), dopiran z amonijevim jodidom ( $\text{NH}_4\text{I}$ ), za morebitno uporabo za sončne celice, občutljive za svetlobo. Kompleksna impedančna spektroskopija je odkrila povečano prevodnost z maksimumom pri masni koncentraciji  $w = 50\%$   $\text{NH}_4\text{I}$ . Posnetki s svetlobno mikroskopijo so odkrili povečanje deleža amorfnih osnov, kar so potrdile tudi XRD-meritve. Kompozitno naravo polimerne elektrolitne plasti je potrdil tudi FTIR-spekter. Sončne celice, občutljive za svetlobo (DSSC), so bile izdelane z uporabo najbolj prevodne plasti, ki je pokazala učinkovitost  $0,025\%$  v razmerah 1 sun.

Gljučne besede: polimerni elektrolit, prevodnost, FTIR, XRD, za svetlobo občutljive sončne celice

## 1 INTRODUCTION

Polymer electrolytes are promising candidates for electromechanical-device applications chiefly because they mechanically behave like solids but their internal structure and, consequently, the conductivity behavior closely resemble the liquid state.<sup>1</sup> The main advantages of polymeric electrolytes are satisfactory mechanical properties, easy fabrication of thin films and an ability to form a good electrode/electrolyte contact.<sup>2-5</sup>

Polyvinylpyrrolidone (PVP), also commonly called polyvidone or povidone, is a polymer made of N-vinylpyrrolidone monomer. PVP was first synthesized by Prof. Walter Reppe and a patent was filed in 1939. When dry it is a light flaky powder, which readily absorbs up to  $40\%$  of its weight in atmospheric water. PVP is soluble in water and other polar solvents. Since it has excellent wetting properties and readily forms films, it makes a good coating or an additive to coatings. PVP is used in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production. When added to iodine, PVP forms a complex called povidone-iodine exhibiting disinfectant properties and being beneficial for dye-sensitized solar-cell applications where iodide/polyiodide redox couple is frequently added to the electrolyte. Dye-sensitized solar cells (DSSCs) were first reported by O'Regan and Grätzel in 1991.<sup>6</sup>

Over the past decade, DSSCs have been intensely investigated as potential alternatives to the conventional

inorganic photovoltaic devices due to their low production cost and good efficiency for a conversion of solar energy into electricity. A typical cell consists of a nanocrystalline mesoporous titanium dioxide film sensitized with a monolayer dye, an electrolyte containing iodide/triiodide as the redox couple and a platinum counter electrode. Liquid electrolytes were replaced with solid-polymer electrolytes because the former lead to corrosion, evaporation and leakage. Thus, the solid-polymer electrolytes improved the long-term stability of DSSCs.

In the present paper, we report on new solid-polymer electrolyte films of a polyvinylpyrrolidone (PVP) complex with ammonium iodide ( $\text{NH}_4\text{I}$ ) and a DSSC that was fabricated using the film with the maximum electrical conductivity.

## 2 MATERIALS AND METHOD

Polyvinylpyrrolidone (PVP,  $M_w = 130,000$ ), ammonium iodide ( $\text{NH}_4\text{I}$ ) and iodine ( $\text{I}_2$ ) were purchased from Sigma-Aldrich, USA while methanol was purchased from Qualikems Fine Chem. Pvt. Ltd., Vadodara, India.

The following approach was taken to prepare the electrolytes. PVP (500 mg) was dissolved in about 4 mL of methanol under continuous magnetic stirring ( $\approx 30$  min) or until complete dissolution at room temperature. Then an appropriate quantity of  $\text{NH}_4\text{I}$  salts was added to

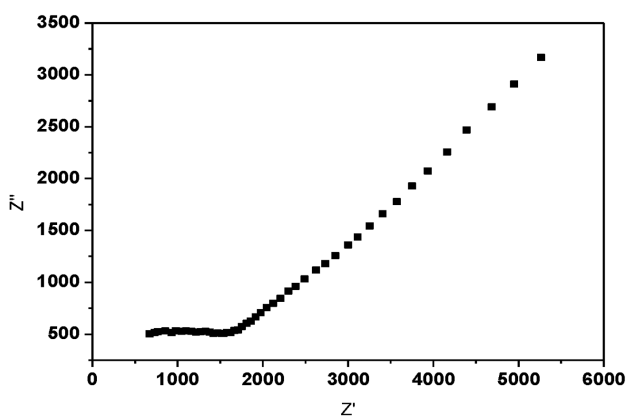
the PVP methanolic solution and stirred continuously. After the solvent evaporation the polymer-salt complex was poured into polypropylene Petri dishes. Free-standing films of different PVP compositions –  $w(\text{NH}_4\text{I})/\%$  (where  $w = (10, 20, 30, 40, 50, 60, 70) \%$ ) – were obtained and further characterized using various characterization tools.

A dye-sensitized solar cell with an active area of  $0.72 \text{ cm}^2$  was fabricated with the procedure reported elsewhere.<sup>7</sup> With the common procedure the  $\text{TiO}_2$  paste was applied on the fluorine-doped  $\text{SnO}_2$  substrate (FTO) using the doctor-blade method. The adhesive scotch tape was used to control the thickness of the as-coated  $\text{TiO}_2$  film with a thickness of  $\approx 50 \mu\text{m}$ , followed by a heat treatment at  $500 \text{ }^\circ\text{C}$  for 30 min. The porous  $\text{TiO}_2$  film formed on the FTO substrate was  $10 \mu\text{m}$  thick and a pore had a diameter of  $10\text{--}15 \text{ nm}$ .<sup>8–13</sup> The porous  $\text{TiO}_2$  film on the FTO substrate was then immersed in a ruthenium sensitizer dye solution (0.5 mmol N-719, Solaronix, in ethanol) and left overnight to allow a sufficient dye adsorption. This  $\text{TiO}_2$  working electrode with the dye was then rinsed off with distilled water and ethanol solution. A Pt-thin-film-coated counter electrode was prepared separately by spin-coating the  $\text{H}_2\text{PtCl}_6$  solution onto the FTO substrate. The viscous polymer-electrolyte solution ( $\approx 400 \mu\text{L}$ ) containing PVP: $\text{NH}_4\text{I} + \text{I}_2$  (the maximum  $\sigma$ ) was finally cast on the working electrode (a two-step casting) and sandwiched between the platinized counter electrode and the  $\text{TiO}_2$  working electrode.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Conductivity measurement

Ionic conductivity of the polyvinylpyrrolidone-based polymer-electrolyte film was measured using a CH Instruments workstation (model 604D, USA) over a frequency range of  $100\text{--}10^5 \text{ Hz}$ .



**Figure 1:** Cole-cole plot of the PVP +  $w(\text{NH}_4\text{I})$  50 % polymer-electrolyte system

**Slika 1:** Cole-cole-diagram polimernega elektrolitnega sistema PVP +  $w(\text{NH}_4\text{I})$  50 %

We used steel electrodes as contacts to measure the ionic conductivity ( $\sigma$ ) and we calculated ionic-conductivity values using the following formula:

$$\sigma = G \cdot l/A \quad (1)$$

where  $\sigma$  is the ionic conductivity,  $G$  is the conductance (in the case of  $1/R_b$ ,  $R_b$  is the bulk resistance where the Nyquist plot intercepts with the real axis),  $l$  is the thickness of the sample and  $A$  is the area of the given sample.

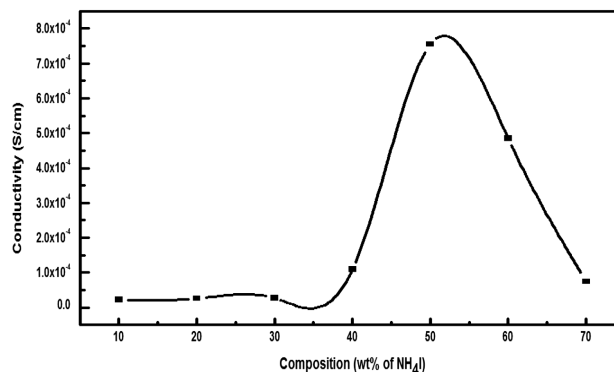
The cole-cole plot (complex impedance plot) of a typical sample of the PVP +  $w(\text{NH}_4\text{I})$  50 % polymer electrolyte is shown in **Figure 1**. The room-temperature ionic conductivity (deduced from different cole-cole plots) of polymer electrolytes as a function of the  $\text{NH}_4\text{I}$  concentration is shown in **Figure 2** and its values are listed in **Table 1**.

**Table 1:** Room-temperature ionic conductivity of the PVP: $\text{NH}_4\text{I}$  polymer electrolyte system

**Tabela 1:** Ionska prevodnost PVP: $\text{NH}_4\text{I}$  polimernega elektrolitskega sistema pri sobni temperaturi

Composition ( $w(\text{NH}_4\text{I})/\%$ )	Conductivity ( $\text{S cm}^{-1}$ )
10	$2.24 \times 10^{-5}$
20	$2.57 \times 10^{-5}$
30	$2.63 \times 10^{-5}$
40	$1.09 \times 10^{-4}$
50	$7.55 \times 10^{-4}$
60	$4.85 \times 10^{-4}$
70	$7.45 \times 10^{-5}$

As observed in **Figure 2** and **Table 1**, the ionic conductivity ( $\sigma$ ) increases with the increase in the  $\text{NH}_4\text{I}$  concentration and reaches its maximum at the  $w(\text{NH}_4\text{I}) = 50 \%$  ( $\sigma = 7.55 \times 10^{-4} \text{ S/cm}$ ) concentration and then it decreases. The increase in the ionic conductivity with the increasing  $\text{NH}_4\text{I}$  concentration can be related to the increase in the number of mobile charge carriers, while the possible decrease in the ionic conductivity at a  $\text{NH}_4\text{I}$  mass concentration greater than 50 % can be attributed to the formation of ion multiples.



**Figure 2:** Effect of the  $\text{NH}_4\text{I}$  amount on the conductivity of the polymer electrolyte (PVP: $\text{NH}_4\text{I}$ ) measured at room temperature

**Slika 2:** Vpliv vsebnosti  $\text{NH}_4\text{I}$  na prevodnost polimernega elektrolita (PVP: $\text{NH}_4\text{I}$ ), izmerjeno pri sobni temperaturi

The ionic conductivity ( $\sigma$ ) in the case of an electrolyte system is given as:

$$\sigma = n q \mu \quad (2)$$

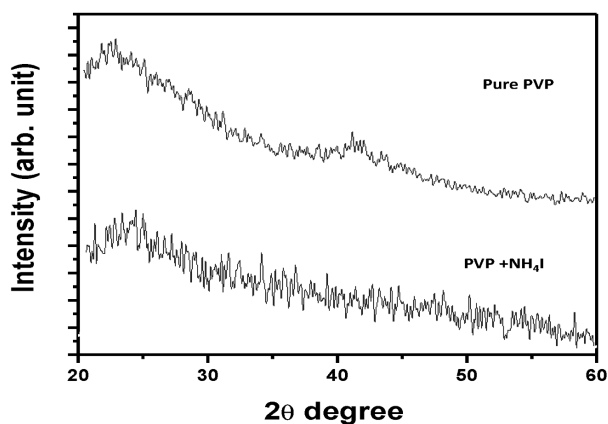
where  $n$  is the charge carrier density,  $q$  is the charge of the carrier and  $\mu$  is the mobility of the carriers. Therefore, any increase in either  $n$  or  $q$  will certainly affect the value of ionic conductivity.

### 3.2 X-ray diffraction

The crystallinity of the polymer electrolyte was further affirmed by X-ray diffraction patterns (XRD) using a Rigaku D/max-2500 XRD diffractometer at a scan rate of  $5^\circ$  min. The recorded X-ray diffraction patterns of pure PVP and  $\text{NH}_4\text{I}$  doped PVP polymer electrolytes are shown in **Figure 3**. It is clear that pure PVP shows well-known amorphous peaks around  $2\theta$  values of  $23^\circ$ . The incorporation of  $\text{NH}_4\text{I}$  into the PVP matrix decreases the intensity of the peaks (the suppression in crystallinity). It also appears that the XRD data relating to the  $\text{NH}_4\text{I}$  doped PVP polymer electrolyte shows only the peaks related to either PVP or  $\text{NH}_4\text{I}$ , which clearly affirms the composite nature of the polymer-electrolyte system. Additionally, the PVP- $\text{NH}_4\text{I}$  data does not contain any other peaks related to the  $\text{NH}_4\text{I}$  sample, affirming a complete dissolution of  $\text{NH}_4\text{I}$  in the Sago Palm matrix.

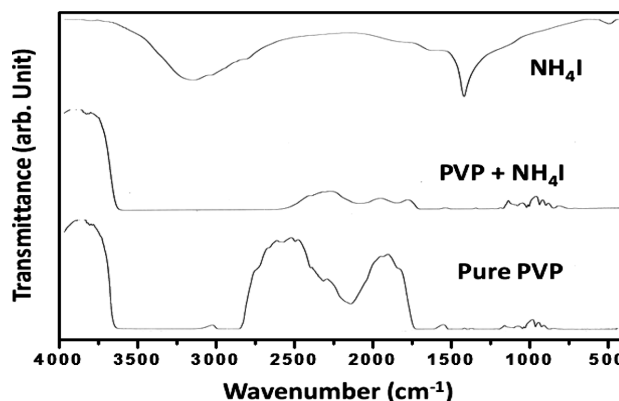
### 3.3 FTIR spectroscopy

The FTIR spectra of pristine PVP,  $\text{NH}_4\text{I}$  and the PVP doped with  $\text{NH}_4\text{I}$  were recorded between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  on a PerkinElmer Spectrophotometer 883 as shown in **Figure 4**. Pure  $\text{NH}_4\text{I}$  shows well defined peaks at  $(3131, 1622$  and  $1398)\text{ cm}^{-1}$ , where the first peak corresponds to the N-H stretch, while the other two correspond to the N-H bending. In the spectrum of pure PVP, the peaks at  $(847, 895$  and  $934)\text{ cm}^{-1}$  correspond to para-, di-substituted and mono-substituted C-H bend-



**Figure 3:** XRD pattern of pure PVP and PVP +  $\text{NH}_4\text{I}$  polymer electrolyte

**Slika 3:** XRD-posnetek čistega PVP in PVP +  $\text{NH}_4\text{I}$  polimernega elektrolita



**Figure 4:** FTIR spectra of pure PVP,  $\text{NH}_4\text{I}$  and PVP +  $\text{NH}_4\text{I}$  polymer electrolyte

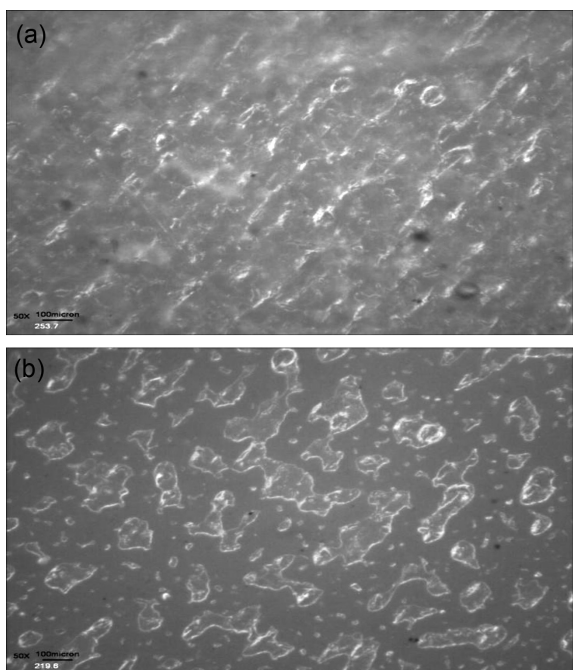
**Slika 4:** FTIR-spektri čistega PVP,  $\text{NH}_4\text{I}$  in PVP +  $\text{NH}_4\text{I}$  polimernega elektrolita

ings. The bands between  $1450\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  correspond to the C=C stretching. The peaks at  $1075\text{ cm}^{-1}$  and  $2135\text{ cm}^{-1}$  correspond to the C-N stretching, while the ones at  $1018\text{ cm}^{-1}$  and  $1172\text{ cm}^{-1}$  correspond to the C-C stretching. The  $\text{CH}_3$  bending is shown at  $1375\text{ cm}^{-1}$ . The peak at  $1835\text{ cm}^{-1}$  corresponds to the presence of C=O bonds. In the spectrum of PVP +  $\text{NH}_4\text{I}$  the peaks at  $843\text{ cm}^{-1}$  and  $934\text{ cm}^{-1}$  correspond to the C-H bending. The peaks at  $1100\text{--}1300\text{ cm}^{-1}$  correspond to the C-C stretching. The C-N stretching is shown at  $1074\text{ cm}^{-1}$ . The  $\text{CH}_2$  bending is given by the peak at  $1439\text{ cm}^{-1}$ . The bands between  $1550\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  correspond to the N-H bending. The peak at  $1848\text{ cm}^{-1}$  corresponds to the C=O stretching, while the C=C peaks are indicated by the peaks between  $1450\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ .

It is also clear from the figure that almost all the peaks related to the host materials (PVP and  $\text{NH}_4\text{I}$ ) are present in the  $\text{NH}_4\text{I}$  doped PVP polymer-electrolyte sample. The disappearance of any new peaks other than those of the host materials clearly affirms the composite nature of the samples, also supported by our XRD data.

### 3.4 Light microscopy

Light microscopy (LM) of a polymer-electrolyte sample with the dimensions of  $1\text{ cm} \times 1\text{ cm}$  was carried out using a Leica Leitz DMRX light microscope. The obtained photographs are shown in **Figure 5**. It is noted that the pure PVP film (**Figure 5a**) shows well-ordered patches, confirming its semicrystalline nature. This pattern is a bit different from the micrographs of the PEO matrix. Due to an addition of  $\text{NH}_4\text{I}$  to the PVP matrix (**Figure 5b**) the patch size becomes random and the crystallinity seems to be disturbed. The decrease in the crystallinity (an ordered pattern) showed a further increase in the amorphicity (a non-ordered pattern) where different sizes of rough patches are distributed randomly within the polymer matrix. It is believed that the amorphous regions (the non-ordered pattern) are conductivity-rich regions and, hence, our light micro-



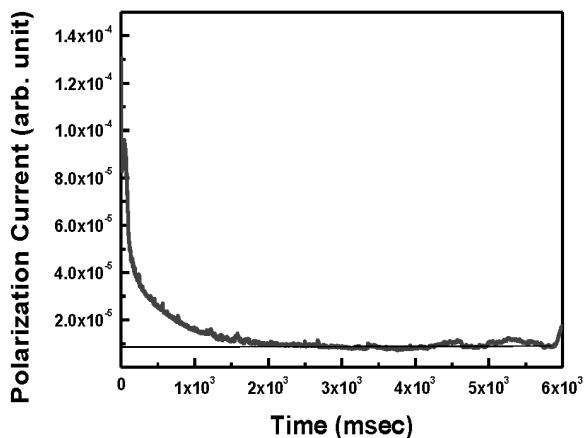
**Figure 5:** Light microscope photographs of: a) pure PVP, b) PVP + 40 % NH<sub>4</sub>I polymer-electrolyte matrix

**Slika 5:** Posnetka s svetlobnim mikroskopom: a) čisti PVP, b) PVP + 40 % NH<sub>4</sub>I osnova polimernega elektrolita

graphs showed good agreement with the ionic-conductivity data.

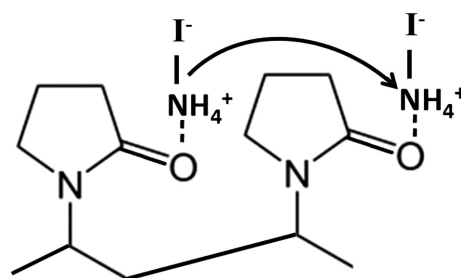
To further specify the nature of the charge carriers (ionic or electronic) we carried out the ionic-transference-number measurement. **Figure 6** shows the current-versus-time measurement for a typical sample of the arrowroot-60 % NH<sub>4</sub>I polymer-electrolyte matrix. In this study we applied a fixed DC voltage and the current was recorded with respect to time following a well-established formula:

$$t_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}} \quad (3)$$



**Figure 6:** Current-versus-time plot ( $t_{ion}$  measurement) of a typical PVP:NH<sub>4</sub>I polymer-electrolyte matrix measured at room temperature

**Slika 6:** Odvisnost toka od časa ( $t_{ion}$  meritev) značilne PVP:NH<sub>4</sub>I osnove polimernega elektrolita, izmerjena pri sobni temperaturi



**Figure 7:** Mechanism of ion transport in the PVP:NH<sub>4</sub>I polymer-electrolyte matrix

**Slika 7:** Mehanizem potovanja ionov v osnovi polimernega elektrolita PVP:NH<sub>4</sub>I

where  $I_{initial}$  is the initial current and  $I_{final}$  is the final residual current.

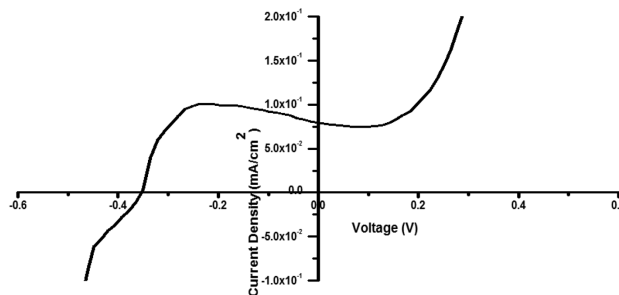
The observed ionic-transference number is 0.93 showing that our biopolymer electrolyte is essentially an ion-conducting system.<sup>10</sup>

### 3.5 Ion-transport mechanism

The ion-transport mechanism in the PVP polymer-electrolyte matrix can be easily understood using **Figure 7**. According to the literature, in most of the polyethers incorporated with alkali halides the anion contribution is more dominant.<sup>14</sup> However, in the case of the polyethers doped with the other salts like NH<sub>4</sub>ClO<sub>4</sub> the cationic part is more dominating<sup>15,16</sup>. The NH<sub>4</sub><sup>+</sup> ions of NH<sub>4</sub>I are coordinated with the ether oxygen of PVP and I<sup>-</sup> anions hang outside. The weakly bonded H in NH<sub>4</sub><sup>+</sup> can be easily dissociated under the influence of a DC electric field forming H<sup>+</sup> ions. These H<sup>+</sup> or NH<sub>4</sub><sup>+</sup> ions can jump via each coordinating site as shown in **Figure 7**.

### 3.6 DSSC performance

A dye-sensitized solar cell (DSSC) was prepared with the PVP:NH<sub>4</sub>I/I<sub>2</sub> polymer electrolyte with the maximum ionic conductivity ( $w(\text{NH}_4\text{I}) = 50\%$ ). Iodine was also added to prepare the redox couple (10 % with respect to the iodide salt). The recorded J-V characteristic is shown in **Figure 8**. The fabricated DSSC shows



**Figure 8:** Current density versus voltage characteristic of the PVP:50 % NH<sub>4</sub>I/I<sub>2</sub> polymer-electrolyte film at the 1 sun condition

**Slika 8:** Gostota toka v odvisnosti od značilnosti napetosti v plasti polimernega elektrolita PVP:50 % NH<sub>4</sub>I/I<sub>2</sub> v razmerah 1 sun

an open-circuit voltage ( $V_{oc}$ ) of 0.35 V and a short-circuit-current density ( $J_{sc}$ ) of 0.1 mA/cm<sup>2</sup> with the overall efficiency of 0.025 %.

The observed efficiency was much lower when compared to the other polymeric systems reported in<sup>11–13</sup>. This was expected since the observed conductivity in the present case was much lower (by  $\approx$  1–2 order of magnitude).

#### 4 CONCLUSION

A solid polymer-electrolyte film consisting of PVP doped with the NH<sub>4</sub>I salt was successfully prepared and characterized. It was observed that NH<sub>4</sub>I doping enhances the ionic conductivity and the conductivity maximum was obtained at the 50 % NH<sub>4</sub>I salt mass concentration with the conductivity value of  $7.55 \times 10^{-4}$  S/cm. XRD and IR affirmed the composite nature of the polymer electrolyte, while optical micrograph and XRD affirmed the reduction in the crystallinity due to the NH<sub>4</sub>I doping. Using a solid polymer electrolyte with the maximum ionic conductivity, we fabricated a DSSC that shows a reasonable photo response at the 1 sun condition.

#### Acknowledgments

This work was supported by a DST project (DST/TSG/PT/2012/51) of the Government of India.

#### 5 REFERENCES

- <sup>1</sup> D. E. Fenton, J. M. Parker, P. V. Wright, *Polymer*, 14 (1973), 589
- <sup>2</sup> K. N. Kumar, T. Sreekanth, M. J. Reddy, U. V. S. Rao, *J. Power Sources*, 101 (2001), 130–133
- <sup>3</sup> T. M. W. J. Winjendra, P. Ekanayake, M. A. K. L. Dissanayake, I. Albinsson, B. E. Mellander, *J. Solid State Electrochem.*, 14 (2010), 1221–1226
- <sup>4</sup> R. Chandrasekaran, S. Selladurai, *J. Solid State Electrochem.*, 5 (2001), 355–361
- <sup>5</sup> X. Li, D. Zhang, X. J. Yin, S. Chen, J. Shi, Z. Sun, S. Huang, *J. Solid State, Electrochem.*, 15 (2011), 1271–1277
- <sup>6</sup> B. O'Regan, M. Grätzel, *Nature*, 353 (1991), 737–740
- <sup>7</sup> M. Singh, V. K. Singh, K. Surana, N. A. Jadhav, P. K. Singh, B. Bhattacharya, H. W. Rhee, *J. Ind. Eng. Chem.*, 19 (2013), 819–822
- <sup>8</sup> A. F. Nogueira, J. R. Durrant, M. A. De Paoli, *Advanced Materials*, 13 (2001), 826–830
- <sup>9</sup> M. Saito, S. Fujihara, *Energy & Environmental Science*, 1 (2008), 280–283
- <sup>10</sup> A. Saxena, P. K. Singh, B. Bhattacharya, *Mater. Tehnol.*, 47 (2013) 6, 799–802
- <sup>11</sup> P. Kumar, P. K. Singh, B. Bhattacharya, *Ionics*, 17 (2011), 721–725
- <sup>12</sup> P. K. Singh, B. Bhattacharya, R. K. Nagarale, *J. Appl. Polym. Sci.*, 118 (2010), 2976–2980
- <sup>13</sup> P. K. Singh, B. Bhattacharya, R. M. Mehra, H. W. Rhee, *Current Applied Physics*, 11 (2011), 616–619
- <sup>14</sup> B. Bhattacharya, R. K. Nagarale, P. K. Singh, *High Performance Polymers*, 22 (2010), 498–512
- <sup>15</sup> S. A. Hashmi, A. Kumar, K. K. Maurya, S. Chandra, *J. Phys. D: Appl. Phys.*, 23 (1990), 1307–1314
- <sup>16</sup> A. Sachdeva, R. Singh, P. K. Singh, B. Bhattacharya, *Mater. Tehnol.*, 47 (2013) 4, 467–471