

Dye sensitized solar cell based on poly(vinyl alcohol) doped with ammonium iodide solid polymer electrolyte

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A new polymer electrolyte Polyvinyl alcohol (PVA) doped with ammonium iodide (NH₄I) have been developed, characterized and applied in Dye sensitized solar cell (DSSC). Polymer electrolyte shows enhancement in electrical conductivity by salt doping and then decrease after a certain composition. Infrared spectroscopy (IR) as well as x ray diffraction (XRD) affirmed composite nature of the polymer electrolyte. The polymer morphology has been studied using optical microscopy. Based on maximum conducting sample we have developed a DSSC which shows short circuit current density of 0.46 mA/cm², open circuit voltage of 0.65 volt with overall conversion efficiency of 0.29 % at 1 sun condition.

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1. Introduction

Polymer electrolytes are recently got attention due to their various advantageous properties. They mechanically, behave like solids but internal structure, closely resembles liquid state [1,2]. It is well known that the most of solid state devices need materials with high electrical conductivity (in the range of 10⁻³ to 10⁻² S/cm) which is easily obtainable in polymer electrolyte. Additionally the advantage properties, such as the ability to form thin films, flexibility, light weight, elasticity make them suitable candidate for many electrochemical devices like solid state batteries, supercapacitors, fuel cell, electro chromic display devices, dye sensitized solar cell etc. [3-6].

Polyvinyl alcohol (PVA) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide. Polyvinyl alcohol is produced commercially from polyvinyl acetate, usually by a continuous process. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. The physical characteristics and its specific functional uses depend on the degree of polymerization and the degree of hydrolysis. Polyvinyl alcohol is classified into two classes namely: partially hydrolyzed and fully hydrolyzed. Partially hydrolyzed PVA is used in the foods. Polyvinyl alcohol is an odorless and tasteless, translucent, white or cream colored granular powder [7,8]. PVA's flash point is 79 °C, while its melting point is ≤ 200 °C. Its density ranges from 1.19 to 1.31 g/cm³. It can also release toxic fumes when burned, and reacts with strong acids and oxidants. In large amounts, it

can be hazardous to the environment, especially if it's mixed with water and comes in contact with fish. It is essentially nontoxic for human beings as long as it is not burned or melted with fire. There is also no proof that PVA posts any inhalation risk and physical dangers to humans. PVA complex with many salts forming composite with successive conductivity and applied in many applications [9,10].

Ammonium iodide (NH₄I) used in present study is light sensitive, becomes yellow or brown on exposure to air and light because of liberation of Iodine. It is known that the addition of natural salts to poly(vinyl alcohol) (PVA) modifies its properties. This is of particular interest to science and technology and a range of materials could be developed for electrochemical devices. For device application the prime criteria for a polymer salt complex is to achieve high ionic conductivity which is easily obtained by doping suitable salt in polymer electrolyte matrix.

In present paper we are doping a salt (ammonium iodide) in PVA matrix and try to develop a new PVA:NH₄I polymer electrolyte. The characterizations as well as application of this polymer electrolyte in dye sensitized solar cell are also presented in details. In our knowledge we could not find any literature based on PVA:NH₄I and its application in DSSC area.

2. Experimental

PVA, ammonium iodide (NH₄I) and iodine (I₂) were the starting materials purchased from (Aldrich, USA) and used in the present study. Polymer electrolyte membranes complex with NH₄I (PVA: x wt% NH₄I with x =10 to 90)

were prepared by the solution cast method. First of all PVA was dissolved in deionized water to which NH_4I were added in different stoichiometric ratio along with continuous stirring (~4 hours) to obtain a homogeneous viscous solution. The viscous polymer-salt solutions were then poured and casted in polypropylene petridishes. The solvent was allowed to evaporate slowly resulting in the formation of free standing solid polymer electrolyte films which were finally dried under a vacuum chamber for complete evaporation of water traces. These free standing solid polymer electrolyte were characterized using various techniques.

The maximum conducting polymer electrolyte has been chosen for dye sensitized solar cell application (DSSC). To prepare a laboratory scale DSSC we have prepared a dye soaked mesoporous TiO_2 working electrode (WE) and platinized counter electrode (CE) which details are given elsewhere [6]. Finally, viscous polymer electrolyte solution having maximum conductivity and iodine (I_2 , 10 wt% with respect to NH_4I) were sandwiched between the WE and CE following two step casting process.

The room temperature ionic conductivity of the polymer electrolyte films were carried out using complex impedance spectroscopy. To evaluate electrical conductivity (σ), we have used LCR source measure unit (CHI, USA) operated with frequency range between 100 Hz to 1 MHz. The infrared spectra (IR) of PVA: NH_4I films were recorded using Thermo Electron Corp./ Nicolet 380 FTIR spectrophotometer in the range of 4000 - 500 cm^{-1} while X-ray diffraction (XRD) spectra of these films were carried out using X-ray diffractometer (Rigaku D/max-2500) in the range of $2\theta = 20^\circ$ to 65° with scan rate of $5^\circ/\text{min}$. The optical micrographs were taken using Leica-Leitz DMRX optical microscope. Photocurrent and voltage of DSSC were measured with Keithley 2400 source meter operated at one sun condition ($100 \text{ mW}/\text{cm}^2$).

3. Results and discussions

3.1 Ionic conductivity

The ionic conductivity (σ) can be evaluated using formula

$$\sigma = G.l/A$$

where G is the conductance ($1/R_b$, R_b is bulk resistance) which is evaluated using intercept on Nyquist plot in real axis, l is thickness of sample and A is the area of given sample. The calculated values of ionic conductivity are listed in Table 1 and plotted in Fig. 1. From this table and figure, it was clear that addition of NH_4I in PVA matrix enhances the ionic conductivity at 60 wt% NH_4I concentration and then decreases. The conductivity maxima was observed at 40:60 compositions with conductivity value $5.80 \times 10^{-5} \text{ S.cm}^{-1}$. It is well known that the values of conductivity are depends on the number of charge carriers (n) and the mobility (μ) since

$$\sigma = n.q.\mu$$

Therefore, a change in the conductivity implies either a change in n or μ or both. In present system it has been found that conductivity increased with increasing salt concentration due to enhanced concentration of free ions from salt [11-13]. The conductivity enhancement by salt doping can be understood by the fact that the salt contains cations as well as anions. The addition of salt provides additional charge carriers which enhances ionic conductivity while decrease in conductivity after 60 wt% salt concentration was due to formation of charge pair model [13].

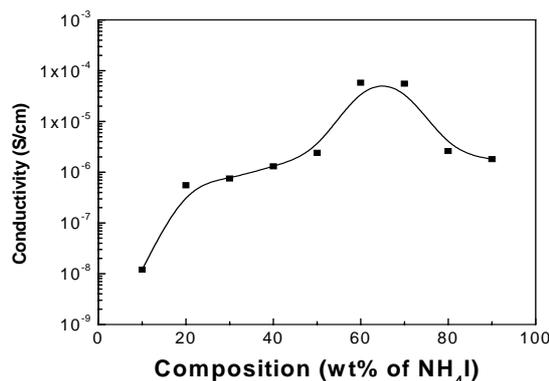


Fig. 1. The conductivity vs composition of NH_4I wt% plot in PVA: NH_4I polymer electrolyte system.

Table 1. Room temperature ionic conductivity in PVA: NH_4I polymer electrolyte system.

Composition (PVA : NH_4I in wt%)	Conductivity (S.cm^{-1})
90:10	1.20×10^{-8}
80:20	5.53×10^{-7}
70:30	7.51×10^{-7}
60:40	1.30×10^{-6}
50:50	2.40×10^{-6}
40:60	5.80×10^{-5}
30:70	5.53×10^{-5}
20:80	2.60×10^{-6}
10:90	1.80×10^{-6}

3.2 Infrared spectroscopy

Infrared spectroscopy (IR) of PVA doped NH_4I films along with pristine PVA and NH_4I were recorded using Perkin Elmer 883 IR spectrophotometer. Fig. 2 shows the recorded IR patterns and corresponding peak position are listed in Table 2. Pure PVA shows a strong peak at 3442 cm^{-1} which is due to the intermolecular hydrogen-bonded O-H stretching frequency of PVA while peaks appears at 2925 and 2854 cm^{-1} is due to C-H stretching in PVA matrix. The other peaks appear at 1737, 1639, 1459, 1383, 1096 cm^{-1} are due to C=O stretch, C-C stretch, C-H bend, C-H wagging, C-N stretch respectively. Ammonium iodide (NH_4I) shows well defined peaks at 3128, 2787, 1629, 1397 cm^{-1} which corresponds to N-H stretch,

(Fig. 2a). The spectrum of PVA:NH₄I polymer electrolyte show well define broad peak at 3460 and 3254 cm⁻¹ which are correlated with water related peak. The peak at 2938 cm⁻¹ is attributed to the characteristic stretching vibrations of C-H while at 1737, 1440 cm⁻¹ are corresponds to C=O stretch, C-C stretch (in ring), C-H bending respectively. Peaks at 1136, 1028 cm⁻¹, suggesting the existence of some C-N stretching peaks in polymer electrolyte. If the NH₄⁺ ions of NH₄I were coordinated with hydroxyl group, we would expect some prominent changes in vibrational or deformation modes. In PVA: NH₄I complex system (Table 2) we have observed a significant change in peak position (1639 cm⁻¹ to 1630 cm⁻¹, 1459 cm⁻¹ to 1440 cm⁻¹) which is clearly assist our observation stated above.

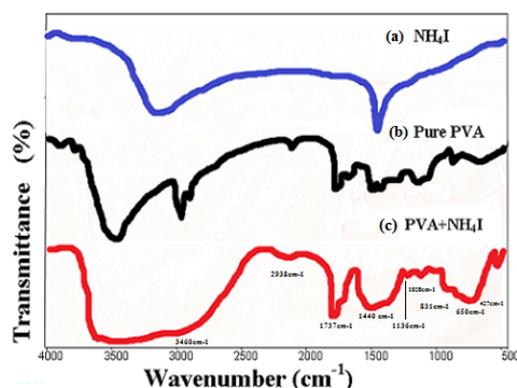


Fig. 2. IR spectra of pure NH₄I (a) PVP:NH₄I (b) and pure PVA (c).

Table 2. Infrared bands of PVA and PVA:NH₄I polymer electrolyte system.

S No.	PVA (cm ⁻¹)	NH ₄ I (cm ⁻¹)	PVA+NH ₄ I (cm ⁻¹)	ASSIGNMENT
1			3460	O-H stretch, H bond, alcohol, phenols
2	3442			O-H stretch, H bond, alcohol, phenols
3			3254	O-H stretch, H bond, alcohol, phenols
4		3128		N-H stretch, alkynes
5			2938	C-H stretch, alkanes
6	2925			C-H stretch, alkanes
7	2854			C-H stretch, alkanes
8		2787		H-C=O : C-H stretch, aldehydes
9	2081			
10			1737	C=O stretch, aldehydes
11	1737			C=O stretch
12	1639			C-C stretch
13			1630	C-C stretch(in ring), aromatic
14		1629		C-C stretch(in ring), aromatic
15	1459			C-H bend, alkanes
16			1440	C-H bend, alkanes
17		1397		NH ₄ asymmetric H-N-H deformation
18	1383			C-H wagging
19			1136	C-N stretch, aliphatic amines
20	1096			C-N stretch, aliphatic amines
21			1028	C-N stretch, aliphatic amines

Some additional new bands appear at 3254, 1737, 1440 and 1136 cm⁻¹ which is due to complexation. It is also clear from the figure and table that almost all the peaks related to host materials (PVA and NH₄I) are present in PVA doped NH₄I sample (Fig. 2b). Disappearance of any new peaks other than host materials clearly affirms the composite nature of the samples.

3.3 X-ray diffraction

To further affirm the composite nature, we have recorded the X-ray diffraction pattern (Rigaku D/max-2500) in the range of 2θ = 20–65°. The recorded X-ray diffraction patterns of host materials PVA (blue color), NH₄I (red color) as well as polymer electrolyte doped with NH₄I salt (black color) are shown in Fig. 3.

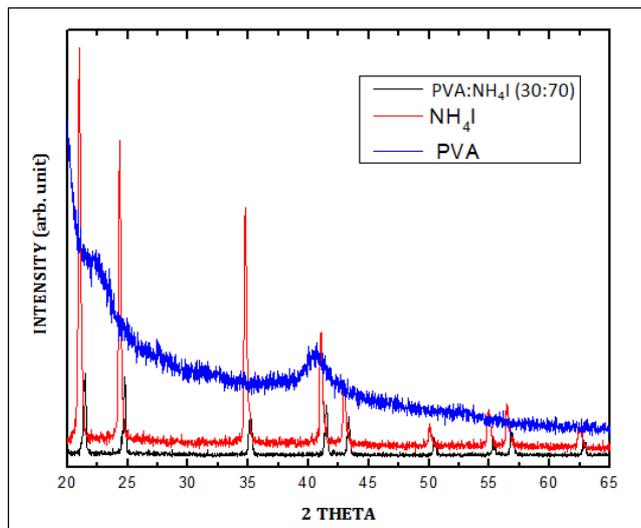


Fig. 3: X-ray diffraction pattern of PVA:NH₄I composite polymer electrolyte along with pure PVA and NH₄I.

Pure PVA shows well defined peaks around $2\theta = 21^\circ$, 41° while NH₄I shows peaks around $2\theta = 21^\circ$, 41° . It is clear that XRD pattern of NH₄I doped polymer electrolyte sample do not contain any additional peaks other than PVA and NH₄I which clearly affirm the “composite nature” of polymer electrolyte system which we have already observed in IR results stated earlier.

3.4 Optical Microscopy

The optical micrographs of PVA:NH₄I polymer electrolyte along with pure PVA are shown in Fig. 4. It is clear that pure PVA shows rough patches like structure (Fig. 4a) which is much different than PEO polymer matrix which we have studied earlier in detail [14-16]. Doping of salt (NH₄I) produces a matrix where the matrix shows a rough distribution of small size spherulites (Fig. 4b). Further addition of salt diminished the spherulitic structures and observed micrographs shows more amorphous nature (Fig. 4c).

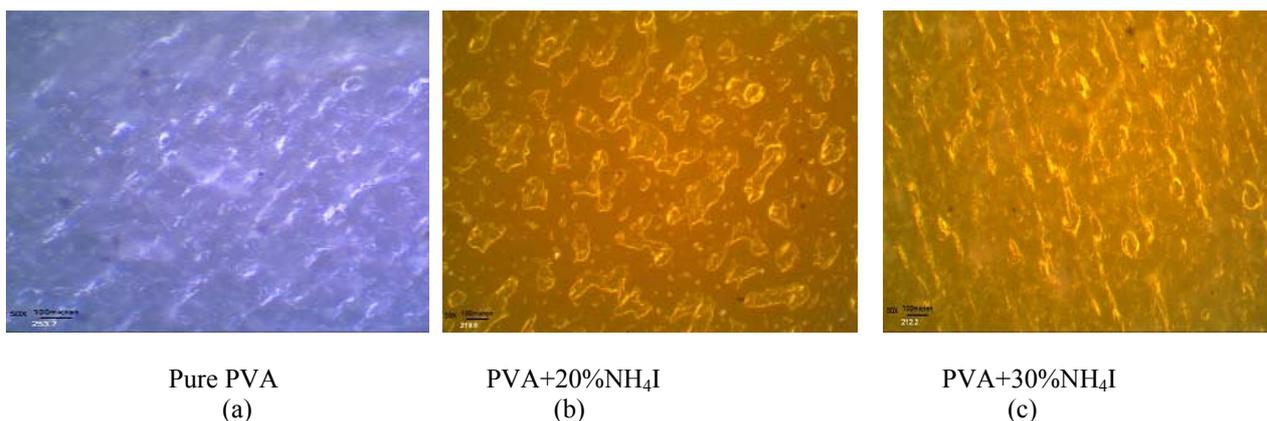


Fig. 4. Optical micrograph of (a) pure PVA (b) PVA:20 wt% NH₄I and (c) PVA:30 wt% NH₄I polymer electrolyte samples.

3.5 Dye sensitized solar cell performance

The DSSC performance with PVA:NH₄I/I₂ polymer electrolyte film with the highest ionic conductivity (60 wt% of NH₄I) and is shown in Fig. 5. For developing redox couple to use in present DSSC iodine has been added (10 wt% with respect to iodide salt) in PVP:NH₄I matrix. The DSSC shows overall efficiency of 0.29 with short circuit current density (J_{sc}) of 0.46 mA/cm^2 , open circuit voltage (V_{oc}) of 0.65 V and fill factor (FF) of 0.29 at 100 mW/cm^2 . The observed efficiency was quite low in comparison of liquid electrolyte since observed conductivity was much low (10^{-5} S/cm) as compared to liquid electrolyte where conductivity values lies between 10^{-1} to 10^{-2} S/cm .

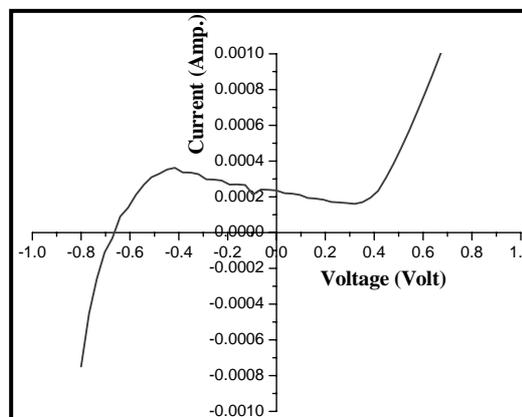


Fig. 5. Current-voltage characteristic of PVA:60 % NH₄I/I₂ polymer electrolyte film at 1 sun condition

4. Conclusions

Polymer electrolyte system consisting PVA and NH₄I was developed for DSSC application. Complex impedance spectrum shows the ionic conductivity enhancement by salt doping and conductivity maxima was obtained at 60 wt% NH₄I concentration with conductivity value of 5.80×10^{-5} S/cm. The conductivity enhancement could be due to the free mobile charge carrier. The composite nature of film was confirmed by IR as well as XRD. A Dye sensitized solar cell (DSSC) has been fabricated using maximum conducting film which shows 0.29 % efficiency at 1 sun condition.

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References

- [1] J. R. MacCallum, C. A. Vincent (Eds.) Polymer Electrolyte Reviews-1, Elsevier, London (1987).
- [2] J. R. MacCallum, C. A. Vincent (Eds.) Polymer Electrolyte Reviews-2, Elsevier, London, (1989).
- [3] R. K. Nagarale, B. Bhattacharya, N. A. Jadhav, P. K. Singh, *Macromolecular Chemistry and Physics*, **212**, 1751 (2011).
- [4] S.A. Mohamad, R. Yahya, Z.A. Ibrahim, A.K. Arof, *Solar Energy Materials and Solar Cells*, **91**, 1194 (2007).
- [5] R. C. Agrawal, G. P. Pandey, *Journal of Physics D: Applied Physics* **41**, 223001 (2008).
- [6] P. K. Singh, R. K. Nagarale, S. P. Pandey, H. W. Rhee, B. Bhattacharya, *Advances in Natural Sciences: Nanoscience and Nanotechnology*, **2**, 023002 (2011).
- [7] K. Leja, G. Lewandowicz, *Polish J. of Environ. Stud.*, **19**, 255 (2010).
- [8] M. Kobayashi, H. S. Hyu, *Materials*, **3**, 2753 (2010).
- [9] R.I. Mohamed, *Journal of Physics and Chemistry of Solids* **61**, 1357 (2000).
- [10] S. Pandey, S. K. Pandey, V. Parashar, G. K. Mehrotra A.C. Pandey, *Journal of Materials Chemistry*, **21**, 17154 (2011).
- [11] M. J.Reddy, P. P.Chu, *Electrochimica Acta*, **47**, 1189 (2002).
- [12] Pramod K. Singh, A. Chandra, *J. Phys.D: Appl. Phys.*, **36**, L93 (2003).
- [13] S. A. Hashmi, A. Kumar, K.K. Maurya, S.Chandra, *Journal of Physics D: Applied Physics*, **23**, 1307 (1990).
- [14] Pramod K Singh, B. Bhattacharya, *Optoelectron. Adv. Mater.-Rapid Comm.*, **7**, 157 (2013).
- [15] R. Singh, N. A. Jadhav, S. Majumder, B. Bhattacharya, Pramod K Singh, *Carbohydrate Polymers*, **9**, 682 (2013).
- [16] M. Singh, V. K. Singh, K. Surana, B. Bhattacharya, Pramod K Singh, *Journal of Industrial and Engineering Chemistry* **19**, 819 (2013).

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