

New Biodegradable Polymer Electrolyte for Dye Sensitized Solar Cell

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New biopolymer electrolyte for solar cell has been developed and characterized. Potassium iodide has been added in biopolymer matrix to develop solid electrolyte. Impedance spectroscopy reveals enhancement in ionic conductivity by salt doping and conductivity maxima was obtained at 60 wt% KI concentration. Infrared spectroscopy confirms the formation of composite nature while X-ray Diffraction and Optical microscopy affirms the reduction of crystallinity of biopolymer electrolyte by salt doping. A dye sensitized solar cell has been fabricated using maximum ionic conductivity electrolyte which shows J_{sc} of 5.68×10^{-4} mA/cm², V_{oc} of 0.56 volt and efficiency of 0.63% at 1 sun condition.

Keywords: Biopolymer, IR, XRD, Conductivity, Dye sensitized solar cell.

1. INTRODUCTION

The sources of energy which are either unlimited or can be quickly replaced and regenerated are termed as Renewable energy sources. Though the sources are known since long, may be even before the start of civilization, but their use as per requirement is still a big challenge. These sources are still at the developing stage, a few at the level of commercialization but still needs more research and development to produce and supply 20% electricity by 2020 [1-2]. In most of countries the major emphasis from the government has been focused around development for renewable sources of energy, the awareness and interest towards the use of the renewable sources need to be further enhanced.

Out of all popular renewable energy sources the Solar Energy is probably the most studied and known source of energy which is globally utilized. Sun is known as the source of energy even before the dawn of civilization [3, 4].

There are huge number of reviews, books and papers on the solar cells with different types of materials, different varieties of junctions and their combinations. In short, the first generations of solar cells were based on crystalline silicon. As the next generation, thin film solar cells were developed. The third generation solar cell came after the development of their previous counter parts. These cells evolved with the development of new and advanced technologies. The cells are generally based on nanoparticles and polymers. The two main members of this group are dye sensitized solar cells (DSSC) and organic photovoltaic cells (OPV). This paper is particularly concentrate on development of DSSC using solid polymer electrolyte.

A Dye sensitized solar cell (DSSC) is composed of two electrodes, the anode and the cathode. These electrodes are made from a specific glass that has a Transparent Conductive Oxide (TCO) coating on one side. The space left between the two electrodes is filled with an electrolyte that ensures charge transportation through a redox couple. Till date the DSSC with maximum efficiency reported by Prof. Gratzel group [5-7].

In dye sensitized solar cell (DSSC) polymer electrolyte are proven himself as a novel alternative of liquid electrolyte [8-15]. Till to date the maximum efficient DSSC reported so far was comprises with liquid electrolyte with various other additive [5-7]. Liquid electrolyte has high ionic conductivity albeit other disadvantage like corrosion, solvent evaporation, leakage etc always creates a barrier in developing good efficient DSSC. In solid electrolyte most popular electrolyte are either gel or polymer electrolyte. Gel electrolyte (quasi state solid) shows efficient conductivity albeit liquid entrapped in pores are creates problem when DSSC operates at hot atmosphere and hence long term stability [16-18]. Polymer electrolyte has overcome with these problems stated above.

In this paper we have develop a new polymer electrolyte system containing Arrowroot biopolymer doped with potassium iodide. Arrowroot (*Maranta arundinacea*) is a biopolymer contain about 23% starch (20 to 25% amylose and 75 to 80% amylopectin), starch is basically carbohydrate consisting of a large number glycoside bonded glucose structure obtained from the rhizome's (rootstock) Fig. 1. It is low-cost materials and does not require elaborate apparatus to manufacture.

2. EXPERIMENTAL DETAILS

2.1 Preparation of bio-polymer electrolyte

Most of the chemicals used in present study were purified prior to use in laboratory. Arrowroot starch with average molecular weight ($M_w = 5000$ g/mol) was purchased from HI-MEDIA, Fisher scientific, Mumbai, India) while other chemicals like potassium iodide (KI), iodine (I_2) were obtained from Aldrich, USA. Double distilled water (D2) was used as solvent. All chemicals were stored in desiccators before use.

In a common preparation method of polymer electrolyte, a fixed amount of Arrowroot powder (0.172 g) was dissolved in D2 water (20 ml) in a beaker with continuous stirring at constant heating of 70 °C for 30min . This ratio was used as stock solution for overall experiment (written here as B1). Stoichiometric ratio's of potassium iodide (KI) was then dissolve in D2 water (~ 5ml.) in another beaker (written here as B2). Adding B2 (drop by drop) in B1 formed clear transparent biopolymer electrolyte solution. During this process the biopolymer-salt solution was continuously stirred. Finally this clear solution of the mixture was poured in polypropylene petridish. After water evaporation we get free standing biopolymer electrolyte film

2.2 Device Fabrication

Cut FTO glass plate and cleaned it in ultrasonic bath with ethanol, methanol and distilled water then a blocking layer is coated on electrode on FTO electrode with the help of spin coater and then calcinated it at 450°C for 30 min in programmable muffle furnace. Also counter electrode is prepared by coating chloroplatinic acid on spin coater and calcinated for 400°C for 30 min in muffle furnace then after that fabricate the TiO₂ electrode with doctor blade method, then calcinated in muffle furnace for 30 min at 500°C after that put that working electrode into N3 dye solution for overnight. Now biopolymer electrolyte is sandwiched between the working and counter electrode [17].

3. RESULTS AND DISCUSSION

3.1 Electrical measurement

The ionic conductivity measurement of the Arrowroot-KI based biopolymer electrolyte films were carried out using CH instrument workstation (model 604D, USA) over frequency range 100 Hz to 1 MHz.

Table 1. The room temperature electrical conductivity data of Arrowroot-KI composite electrolyte system.

Composition (wt.% of KI)	σ (S/cm)
10	1.03×10^{-7}
20	1.67×10^{-7}
30	7.70×10^{-7}
40	9.92×10^{-6}
50	2.08×10^{-5}
60	1.04×10^{-4}
70	5.63×10^{-5}
80	3.62×10^{-5}

To measure ionic conductivity we have sandwiched free standing biopolymer electrolyte films between steel electrodes and the electrical conductivity was evaluated using formula

$$\sigma = R_b (l/A)$$

where, σ is ionic conductivity, R_b is the bulk resistance where the Nyquist plot intercepts with the real axis, l is thickness of sample, A is the area of given sample.

The calculated values of ionic conductivity are listed in Table 1 and plotted in Fig.3(a). It is clear that adding KI in Arrowroot matrix enhances the ionic conductivity and conductivity maxima were obtained at 60 wt% KI concentration where conductivity value approaches at 1.04×10^{-4} S/cm and then decreases.

The increase in the ionic conductivity with increasing KI concentration can be further affirmed related to the increase in the number of mobile charge carriers while the possible decrease in the ionic conductivity at a KI concentration greater than 60 wt% can be attributed to the formation of ion multiples.

The ionic conductivity (σ) in case of electrolyte system is given as

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

where n is charge carrier density, q is the charge of the carrier, μ is mobility of the carriers. Therefore any increase in either of the parameters n or q will certainly affected the value of ionic conductivity. Adding KI in Arrowroot matrix provides additional mobile charge species i.e. in present case K^+ cation and I^- anion and hence ionic conductivity enhances while decrease in ionic conductivity could be explained on the basis of charge pair model [19, 20]. Moreover, the ionic hopping mechanism (K^+ and I^-) is responsible for ion conduction in Arrowroot polymer electrolyte [22].

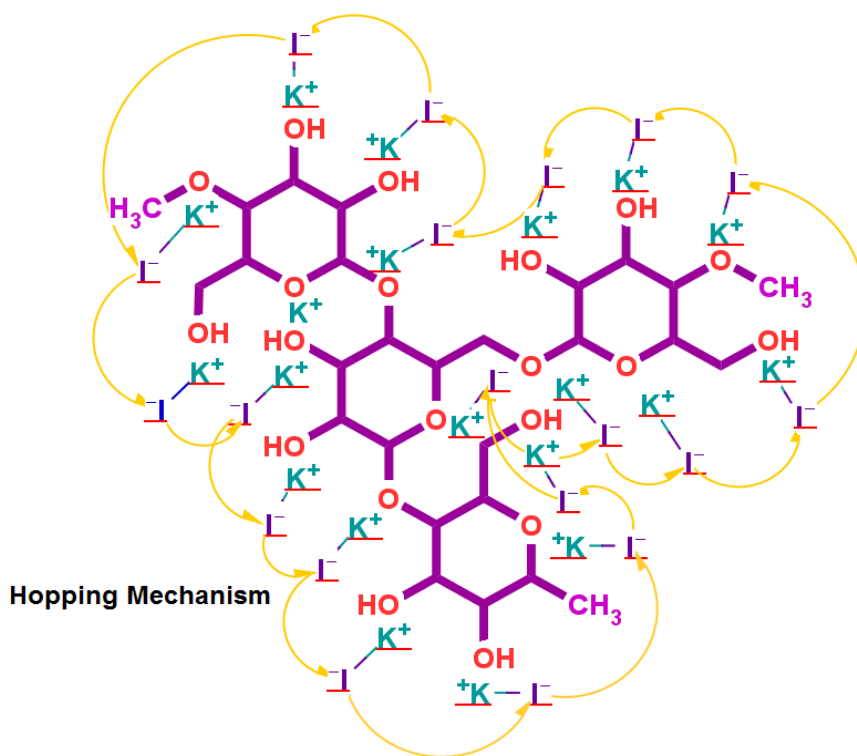


Figure 1. Arrowroot-KI polymer electrolyte matrix showing hopping mechanism.

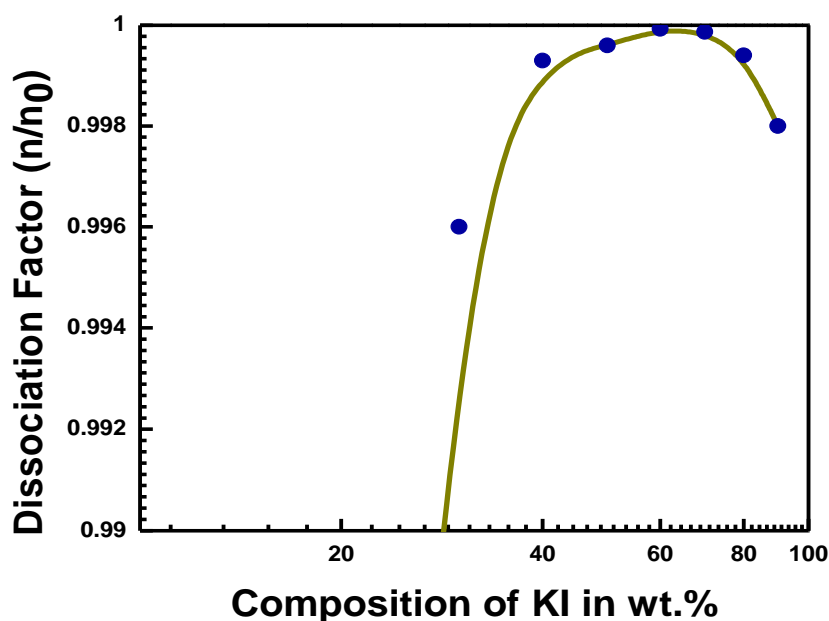


Figure 2. Change in relative number of charge carriers with increasing amount of KI in Arrowroot : KI polymer electrolyte matrix.

To further clarify the role of charge carriers in biopolymer electrolyte matrix we have evaluated the room temperature relative number of charge carriers (n/n_0) for all samples. The change in the relative number of charge carriers (n/n_0) with increasing amount of salt (KI) concentration is shown in the Fig. 2. The dissociation energy of the salt (KI) is 3.33 eV. It is observe that at the maximum doping limit (~ 60 wt % KI) the n/n_0 is maximum and then shows a decreasing trend. It follows the similar trend as we have observed in conductivity measurements. The conductivity, therefore, in biopolymer – KI matrix is predominantly governed by the number of charge carriers.

According to electrolyte dissociation theory of Barker [21].

$$n = n_0 \exp \{-U/2\epsilon kT\}$$

where,

U = Dissociation energy of the salt, k = Boltzmann constant, ϵ = Dielectric constant of the system, T = Temperature of the sample.

To justify the overall contribution of the number of free charge carriers in the total conductivity, the dielectric constant (ϵ) of the film was calculated. Fig. 3 shows the change in dielectric constant, ionic conductivity with increasing amount of KI in the biopolymer electrolyte at three different frequencies 825200 Hz, 82520 Hz and 8301 Hz. It is clear that conductivity data well matches with dielectric data. The addition of KI results in the change in the dielectric constant of the matrix, which results in the change in the number of free charge carriers and thereby the conductivity.

To further specify the nature of charge carriers (ionic or electronic) we have carried out ionic transference number measurement. Fig. 4 shows current vs time measurement of one typical sample

Arrowroot-60 wt% KI polymer electrolyte matrix. In this study we have applied a fixed DC voltage and current is recorded with respect to time following the well establish formula

$$t_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}}$$

Where, $I_{initial}$ = initial current, I_{final} is the final residual current

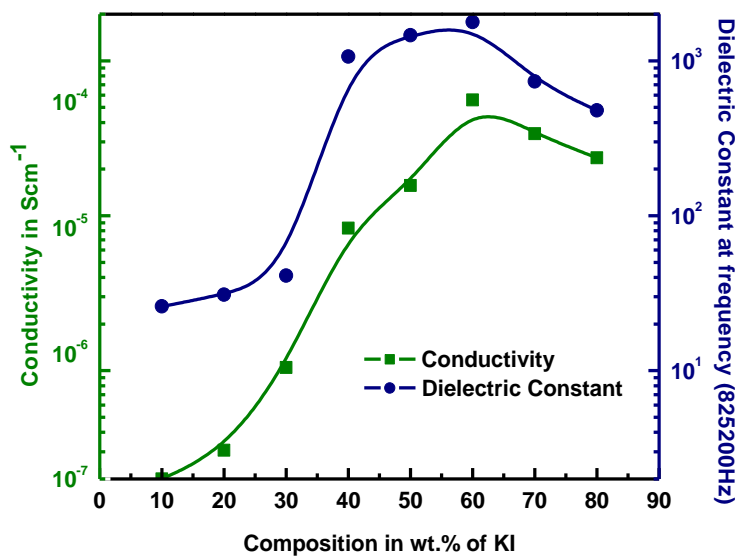


Figure 3. Dielectric constant , ionic conductivity vs composition of KI plot in biopolymer:KI polymer electrolyte system.

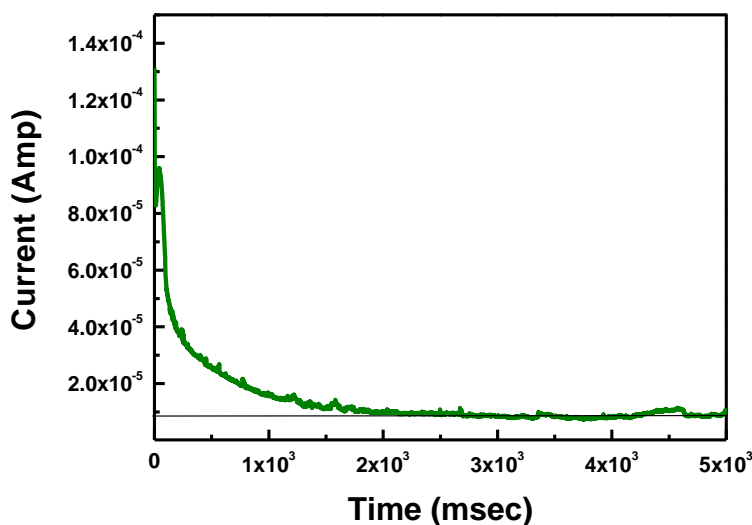


Figure 4. Current vs time measurement of a typical Arrowroot-60 wt.% KI biopolymer electrolyte film.

The observed ionic transference number is 0.93 which show that our bio polymer electrolyte is essentially an ion conducting system.

3.2 Structural measurement

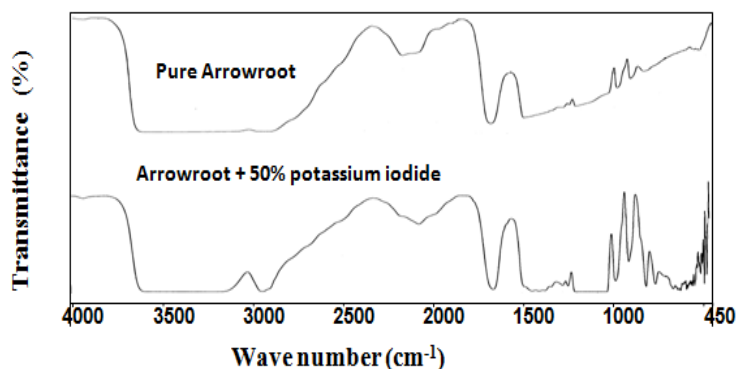


Figure 5. Infrared spectroscopy of pure Arrowroot and Arrowroot-potassium iodide samples.

IR spectra of pure biopolymer (Arrowroot) and Arrowroot doped with KI were recorded using Perkin Elmer 883 IR spectrophotometer between 4000 and 450 cm^{-1} . The different bands assigned with various functional groups are listed in Table 2. It is clear from the figure (Fig. 5) and table (Table 2), that all the peaks related to host materials (Arrowroot and KI) are present in Arrowroot doped KI sample. Pure potassium iodide IR spectra shows well defined peaks at 3435, 1623, 1399, 1123 cm^{-1} [23]. In the spectrum of pure arrowroot (Fig. 5) a sharp and strong peak was observed at 3584 cm^{-1} which is correlated with water related peak and weak peak of c-c stretch also shown at 2149 cm^{-1} and 1462 cm^{-1} .

Table 2. Infrared spectra data of pure Arrowroot and KI doped Arrowroot polymer electrolyte system.

Pure Arrowroot Wavenumber (cm^{-1})	Arrowroot+KI Wavenumber (cm^{-1})	Freq. ranges	Groups (bonds)	Functional groups
3584	3372	3500-3200 (s,b) 3640-3610(s,sh)	O-H stretch, free hydroxyl, H-bonded	alcohols, phenols
	2929	3000-2850 (m)	C-H (stretch)	Alkane
2149		2260-2100 (w)	-CC- stretch	Alkynes
	1626	1680-1640 (m)	-C=C- stretch	Alkenes
1645		1650-1580 (m)	N-H bend	1° amines
1462	1408	1500-1400 (m)	C-C stretch (in-ring)	Aromatics
1169	1234, 1203, 1075	1250-1020 (m)	C-N stretch	Aliphatic amines
936	935	950-910 (m)	O-H bend	Carboxylic acid
863, 787	860, 762, 709	900-675 (s)	C-H "oop"	Aromatics
482	607, 588	690-515 (m)	C-Br stretch	Alkyl halides

m = medium, w = weak, s = strong, n = narrow, b = broad, sh = sharp

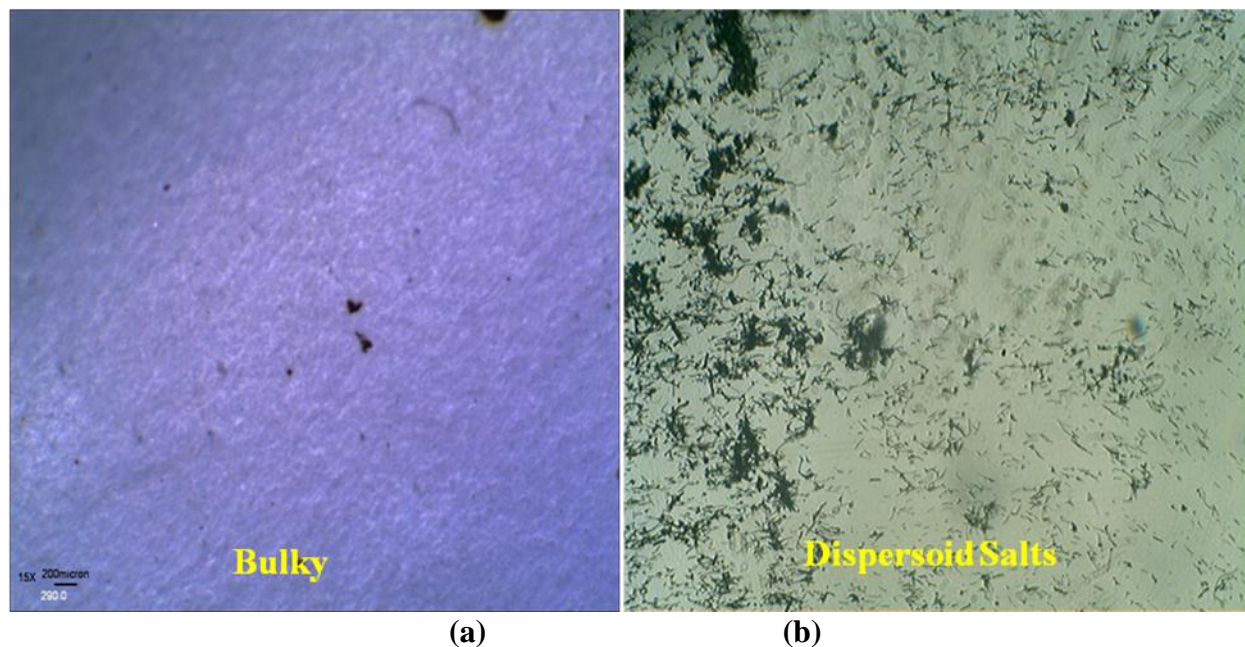


Figure 6. Optical micrographs of (a) Arrowroot (b) KI doped Arrowroot biopolymer electrolyte composite at 15X (200 micron/290).

Arrowroot doped with KI system shows two sharp and two broad peaks are present at 3372cm^{-1} and 935 cm^{-1} due to the presence of hydroxyl stretching vibrations and carboxylic group bending vibrations, peak at 2929 cm^{-1} shows due to stretch between C-H bonds, 1626 cm^{-1} and 1408cm^{-1} are peaks due to the stretching vibrations C=C double bond and C-C single bond. The bands at $1250\text{--}1000$ are due to the stretching vibrations of C-N. It can be seen that all the peaks of Pure Arrowroot (Fig. 5) are retained in the spectra of the composite as well. Similarly, it is also obvious that the doped KI-related peaks also manifest themselves in the IR spectra of the composite. In brief, thus, we can state that both the host bio polymeric matrix and the dispersoid KI retain their identity and hence, Arrowroot:KI is essentially a polymeric composite film.

Optical microscopy has been recorded using optical microscope (Leica-Leitz DMRX) to further clarify the role of doping of KI salt in biopolymer matrix. The observed micrographs of pure as well as KI doped biopolymer matrix are shown in Fig. 6. It is clear that pure biopolymer (Arrowroot) shows well commented rough matrix (Fig. 6a). Doping of salt (KI) enhances amorphous matrix where blackish portion increases drastically (Fig. 6b) and appears as opaque. This shows good agreement with our conductivity data. Basically pure biopolymer film has a whitish color where as salt doped film has a brown and yellowish color portions. The surface (Fig. 1b) has a dark yellowish color indicates potassium iodide ions are entered in that portion of starch matrix or it indicates amylopectin portion. But when iodine is added in excess the film color appears bluish and brownish [11]. Arrowroots starch shows coloration effect in presence of iodine and color varies from yellow to brown and then brown to blue depending upon content of starch and/or iodine enter the starch matrix. KI can be easily dissociate in the starch matrix and appears yellowish and brownish color due to low concentration of iodine ion whereas in case of starch + potassium iodide + Iodine system dark blue color is appearing due to its low dissociation constant and acidic nature of KI.

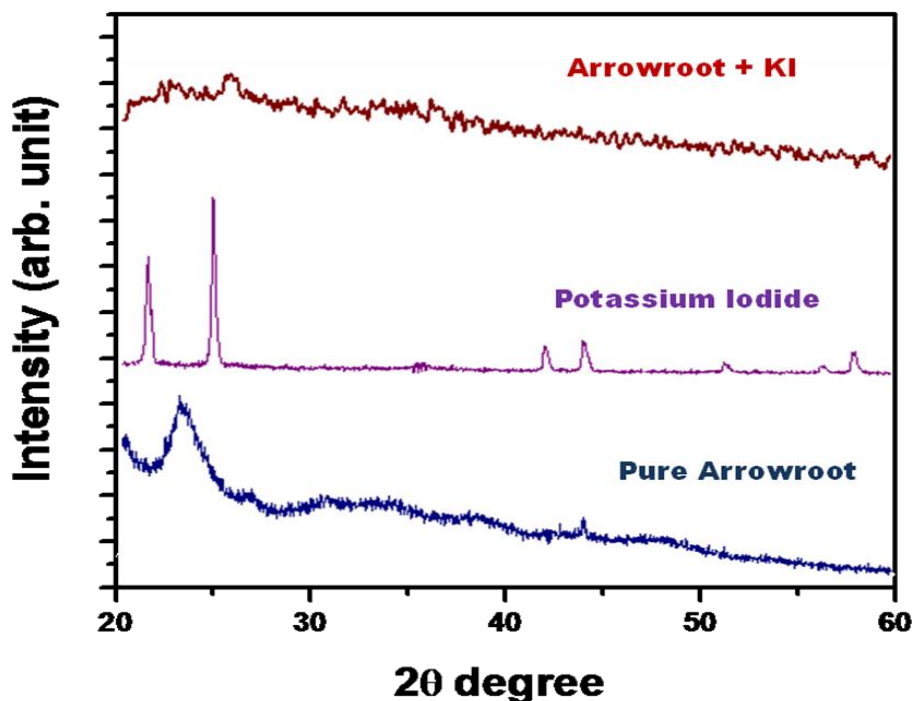


Figure 7. The XRD pattern of pure arrowroot, pure KI and KI doped arrowroot biopolymer.

Fig. 7 shows the X-ray diffraction patterns of different samples of biopolymer composite electrolyte using Rigaku D/max-2500 with scan rate 2 (deg/min) and X-ray tube target is Cu and applied voltage is 40.0 (kV) and current is 30.0 (mA). The X-ray diffraction patterns of Arrowroot shows well defined amorphous peak around $2\theta = 23^\circ$. The potassium iodide shows well defined crystalline peaks. It is clear that doping KI in arrowroot matrix the amorphous peak display which is clearly indication of enhancement in amorphous nature of film. It is believe that amorphous region has conductivity rich region and hence our XRD data is well supported by conductivity and optical microscopy data explained earlier. Additionally arrowroot-KI XRD data do not contains any other peaks related to KI sample which affirms the complete dissolution of KI in Arrowroot matrix.

3.3 Photovoltaic measurement

The photovoltaic performance (I–V curve) of the DSSC was measured with Keithley 2400 source meter under 1 sun condition. For developing redox couple in Arrowroot-KI matrix we have added iodine (10 wt% with respect to iodide salt) in Arrowroot-KI matrix (with the highest ionic conductivity).

The photoelectrochemical performance of DSSC was calculated by the following equations:

$$FF = V_{max} \cdot J_{max} / V_{oc} \cdot J_{sc}$$

$$\eta = V_{max} \cdot J_{max} / P_{in} \times 100 = V_{oc} \cdot J_{sc} \cdot FF / P_{in} \times 100$$

where FF is fill factor, η is the light-to-electricity conversion efficiency, J_{sc} is the short-circuit current density (mAcm^{-2}), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mAcm^{-2}) and V_{max} (V) are the current and voltage in the J - V curve respectively at the point of maximum power output.

The photocurrent density-voltage curves for the DSSC are shown in Fig. 8 and its various parameters are listed in Table 3. The fabricated DSSC shows overall DSSC efficiency (η) of 0.63 % at 1 sun condition with short circuit current density (J_{sc}) of $5.68 \times 10^{-4} \text{ mA/cm}^2$, open circuit voltage (V_{oc}) of 0.56 V.

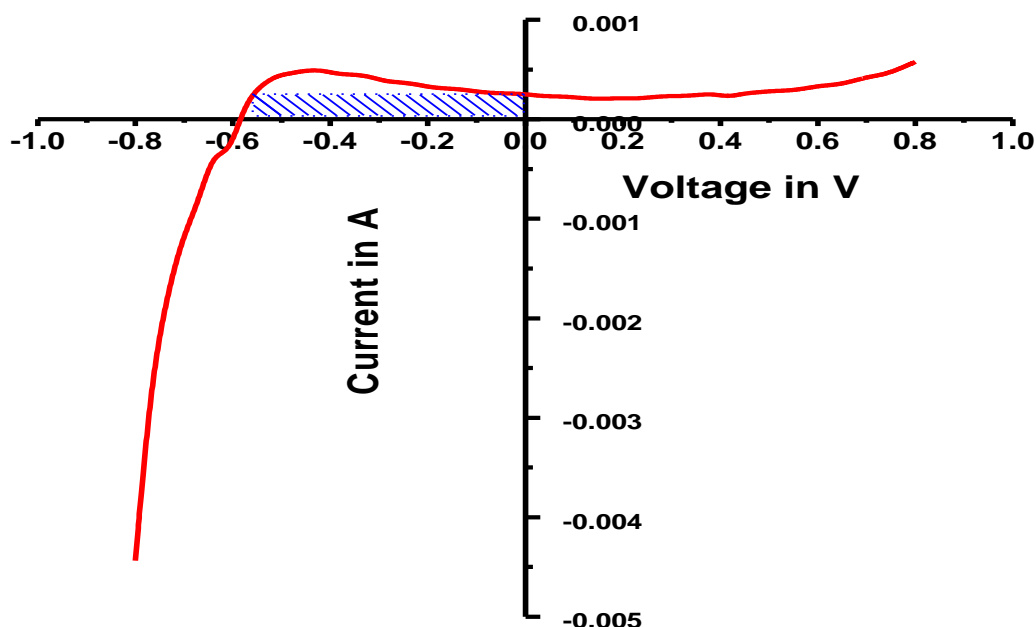


Figure 8. Current-voltage characteristic of Arrowroot:60 wt% KI/I₂ polymer electrolyte film at 1 sun condition.

Table 3. The recorded photovoltaic parameters of developed dye sensitized solar cell.

Composition (60:40)	J_{sc} (mAcm^{-2})	V_{oc} (V)	Area (cm^2)	η (%)
Arrowroot + KI	5.68×10^{-4}	0.56	0.45	0.63

4. CONCLUSIONS

We have successfully prepared dye sensitized solar cell based on carbohydrate (biodegradable) polymer electrolyte (Arrowroot starch and KI). The conductivity measurement shows that conductivity enhances with doping KI in biopolymer (carbohydrate based matrix) and maximum conductivity approaches near 10^{-4} S/cm which may be desirable for electrochemical devices. IR confirms the

composite nature while XRD and OM affirms the suppression in crystallinity (increase in amorphous matrix) of the biopolymer matrix. Applying maximum conductivity Arrowroot-KI/I₂ solid biopolymer electrolyte, we have developed an all-solid-state DSCC with total photoelectric conversion efficiency of 0.63% at one sun condition.

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References

1. M. A. Green, PV modules: operating principles, technology and system applications, Sydney: UNSW, (1992).
2. E. Radziemska, E. Klugmann, *Energ Convers Manage*, 43 (2002) 1889–900.
3. W. Zhou, H. Yang, Z. Fang., *Appl. Energy*, 84 (2007)1187-1198.
4. R. W. Lenz., *Advances in Poly. Sci.*, 107(1993)1–40.
5. A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo, H. Pettersson., *Chem. Rev.*, 110 (2010) 6595–6663.
6. M. Gratzel., *Acc. Chem. Res.*, 42(2009)1788–1798.
7. M. Gratzel., *Nature.*, 414(2001)338–344.
8. M. Kaneko, T. Hoshi, Y. Kaburagi, H. Ueno., *J Electroanal Chem.*,572 (2004)21–27.
9. J. C. H. Koh, Z. A. Ahmad, A. A. Azmin., *Ionics.*, 18(2012)359–364.
10. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada, S. Yanagida., *Chem. Comm.*, (2002)374–375.
11. M. Kumar, T. Tiwari, N. Srivastava., *Carbo. Poly.*, 88(2012)54–60.
12. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska., *J A. Chem Soc.*, 115(1993)6382–6390.
13. J. Nemoto, M. Sakata, T. Hoshi, H. Ueno, M. Kaneko., *Journal J Electroanal Chem.*, 99(2007)23–30.
14. W. Ning, Z. Xingxiang, L. Haihui, W. Jianping., *Carbo Poly.*, 77(2009)607–611.
15. C. Rochas, M. Lahaye., *Carbo. Poly.*, 10(1989)289–298.
16. I. Chung, B. Lee, J. He, R. P. H. Chang, M. G. Kanatzidis., *Nature*, 485(2012)486-490.
17. P. K. Singh, R. K. Nagarale, S. P. Pandey, H. W. Rhee, B. Bhattacharya., *Adv Nat Sci.: Nanosci Nanotechnol.*, 2 (2011) 023002–0203015.
18. S. Yanagida, Y. H. Yu, K. Manseki., *Acc. Chem. Res.*, 42(2009)1827–1838.
19. P. K. Singh, K. W. Kim, K. I. Kim, N. G. Park, H. W. Rhee., *J. Nanosci. Nanotechnol.*, 8 (2008)5271–5274.
20. K. Suzuki, M. Yamaguchi, M. Kumagai, N. Tanabe, S. Yanagida., *Comptes Rendus Chimie.* 9(2006)611–616.
21. R. E. Barker, C. R. Thomas., *J. Appl. Phys.*, 35(1964)3203-3216.
22. K.K. Maurya, N. Srivastava, S.A. Hashmi, & S. Chandra, *J. Mat. Sci.*, 27 (1992) 6357-6364.
23. Manjeet Singh, Vivek K. Singh, Karan Surana, B. Bhattacharya, Pramod K. Singh, Hee-Woo Rhee, *J. Ind. Eng. Chem.* 19 (2012)819–822.