New polymer electrolyte for electrochemical application

Manjeet Singh a,b, Vivek K. Singh a, Karan Surana a, B. Bhattacharya a, Pramod K. Singh a,c,* Hee-Woo Rhee c,*

a Materials Research Laboratory, School of Engineering and Technology, Sharda University, Greater Noida 201 310, India
b Greater Noida Institute of Technology, Greater Noida 201 306, India
c Department of Chemical and Biomolecular Engineering, Soyang University, Seoul, South Korea

A R T I C L E   I N F O

Article history:
Received 18 August 2012
Accepted 22 October 2012
Available online 29 October 2012

Keywords:
Poly vinylpyrrolidone
IR
Conductivity
Dye sensitized solar cell

A B S T R A C T

A solid polymer electrolyte consisting of poly vinylpyrrolidone (PVP) and potassium iodide (KI) were developed, characterized for possible application in dye sensitized solar cell (DSSC) as an electrolyte. Complex impedance spectroscopy revealed the enhancement in electrical conductivity (σ) by salt doping and a conductivity maximum was obtained at 30 wt% KI concentration. Dielectric phenomena also support the σ data. Fourier transform infrared spectroscopy (FTIR) confirmed the composite nature of polymer electrolyte film. Using maximum electrical conductivity film we have fabricated a DSSC which shows 0.14% efficiency at 1 sun condition.

© 2012 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolytes are recently got attention due to their various advantageous properties. They mechanically, behave like solids but internal structure, and consequently the conductivity behavior 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, and high energy density make them suitable candidate for many electrochemical devices including solid state batteries, supercapacitors, dye sensitized solar cell etc. [3–11]. Poly vinylpyrrolidone (PVP), also commonly called polyvidone or povidone, is a polymer made from the monomer N-vinylpyrrolidone. PVP was first synthesized by Prof. Walter Reppe and a patent was filed in 1939 for one of the most interesting derivatives of acetylene chemistry. 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. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. PVP is used in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production. It is used as a binder in many pharmaceutical tablets. PVP added to iodine forms a complex called povidone–iodine that possesses disinfectant properties and it is beneficial for dye-sensitized solar cells (DSSCs) application where iodide/polyiodide redox couple is frequently added in electrolyte. Dye-sensitized solar cells (DSSCs) were first reported by O'Regan and Grätzel in 1991 [12]. Over the past decade, DSSCs have been intensively investigated as potential alternatives to the conventional inorganic photovoltaic devices due to their low production cost and fair efficiency for conversion of solar energy into electricity. The typical cell consists of a nanocrystalline mesoporous titanium dioxide film sensitized by a monolayer dye, electrolyte containing iodide/triiodide as a redox couple and a platinum counter electrode. The electrolyte usually used in these cells is liquid electrolyte and the record energy conversion efficiency over 11% has been reported using volatile liquid electrolyte under irradiation of AM 1.5 [13,14]. However, the usage of liquid electrolyte brings difficulties in the practical application of DSSCs because of its corrosion, evaporation and leakage. In this regards, liquid electrolytes were replaced by solid polymer electrolytes to improve the long term stability of DSSCs [15–20]. In the present paper, we have reported new solid polymer electrolyte films of poly vinylpyrrolidone (PVP) complexed with potassium iodide (KI) and a DSSC has been fabricated using maximum electrical conductivity film.

2. Experimental

Poly vinylpyrrolidone (PVP, $M_w = 130,000$), potassium iodide (KI) and iodine ($I_2$) were purchased from Sigma–Aldrich, USA while
the common solvents were purchased from Qualikems Fine Chem Pvt. Ltd., Vadodara, India.

The electrolytes were prepared according to the following approach. The weighted amount of PVP (500 mg) was dissolved in 4 ml of methanol under continuous magnetic stirring (~30 min) for complete dissolution. The appropriate quantity of KI salts were then added in PVP methanolic solution and stirred continuously. After solvent evaporation the polymer salt complex was poured in polypropylene petridishes. Free standing films of different compositions of PVP:x wt% KI (where x = 20, 25, 30, 35, 40) were obtained and further characterized using various characterization tools. Complex impedance spectroscopy measurements were used to determine the ionic conductivity and dielectric constant of polymer electrolyte. The composite nature and bonding information were affirmed using Perkin Elmer 883 IR spectrophotometer recorded between 4000 and 400 cm⁻¹.

Dye-sensitized solar cell with an active area of 0.25 cm² was fabricated as procedure reported elsewhere [17]. In a common procedure the TiO₂ paste was coated on fluorine-doped SnO₂ substrate (FTO) using doctor blade method. The thickness of an as-coated TiO₂ film was controlled by adhesive Scotch tape with thickness around 50 μm and followed by heat treatment at 500°C for 30 min. The porous TiO₂ films formed on the FTO substrate were 10 μm thick and pore with diameter 10–15 nm in size [15–20]. The TiO₂ porous film on FTO substrate was then immersed in ruthenium sensitizer dye solution (0.5 mmol N-719, Solaronix, in ethanol) for whole night for sufficient dye adsorption. This TiO₂ working electrode with dye was then rinsed off with deionized water and ethanol solution. A Pt thin film coated counter electrode was prepared separately by spin-coating H₂PtCl₆ solution on to FTO substrate. The viscous polymer electrolyte solution (~400 μL) containing PVP:KI (maximum α) were finally casted on working electrode (two step casting) and sandwiched between platinized counter electrode and TiO₂ working electrode. Prior to photovoltaic measurement the DSSC assembly was dried under vacuum for ~2 h.

3. Results and discussion

The ionic conductivity of the poly vinylpyrrolidone based polymer electrolyte film was carried out using CH instrument workstation (model 604D, USA) over frequency range 10²–10⁵ Hz. To measure ionic conductivity (σ) we have used steel electrodes and calculated ionic conductivity values using formula

\[ \sigma = \frac{G \lambda}{A} \]

where σ is ionic conductivity, G is conductance (1/R₀), R₀ is bulk resistance where the Nyquist plot intersects with the real axis, λ is thickness of sample and A is the area of given sample. The room temperature ionic conductivity of polymer electrolytes as a function of KI concentration is shown in Fig. 1 and values are listed in Table 1. As observed in Fig. 1, the ionic conductivity (σ) increases with the increase in KI concentration and reaches maxima at 30 wt% KI (σ = 4.69 × 10⁻⁵ S/cm) concentration and then decreases. The increase in the ionic conductivity with increasing KI concentration can be 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 30 wt% can be attributed to the formation of ion multiples. The ionic conductivity (σ) is defined by

\[ \sigma = nq\mu \]

where n the is charge carrier density, q is the charge of the carrier, \( \mu \) is mobility of the carriers. Therefore any increase in either of the parameters n or \( \mu \) will led to the increase in the conductivity σ. According to electrolyte dissociation theory of Barker [21]

\[ n = n_0 \exp \left\{ -\frac{U}{2kT} \right\} \]

where U is dissociation energy of the salt, k is Boltzmann constant, \( \varepsilon \) is dielectric constant of the system, and T is temperature of the sample.

<table>
<thead>
<tr>
<th>Composition (wt % of KI)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.29 × 10⁻⁵</td>
</tr>
<tr>
<td>15</td>
<td>9.76 × 10⁻⁵</td>
</tr>
<tr>
<td>20</td>
<td>4.69 × 10⁻⁵</td>
</tr>
<tr>
<td>25</td>
<td>1.44 × 10⁻⁵</td>
</tr>
<tr>
<td>30</td>
<td>1.37 × 10⁻⁵</td>
</tr>
<tr>
<td>35</td>
<td>1.30 × 10⁻⁵</td>
</tr>
<tr>
<td>40</td>
<td>1.26 × 10⁻⁵</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of KI content on the conductivity of the polymer electrolyte (PVP:KI) measured at room temperature.

Fig. 2. Change in relative number of charge carriers with increasing amount of KI in PVP:KI polymer electrolyte matrix.
To check the role of charge carriers in polymer electrolyte matrix we have calculated the room temperature relative number of charge carriers ($n/n_0$) for our samples. Change in the relative number of charge carriers ($n/n_0$) with increasing amount of KI is shown in Fig. 2. At the doping limit (~30 wt%), the $n/n_0$ is maximum and then shows a decreasing trend, which explains the variation in the conductivity in terms of the relative number of charge carriers ($n/n_0$). The conductivity, therefore, in this PVP:KI system is predominantly governed by the number of charge carriers. 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.

In order to estimate the contribution of the number of free charge carriers in the total conductivity, the dielectric constant of the film was calculated. Change in dielectric constant with increasing amount of KI in the polymer electrolyte at frequencies 82,520 Hz and 8301 Hz are shown in Fig. 3. For comparative study, the variation in dielectric constant (at 82,520 Hz frequency) and ionic conductivity data at different KI concentrations in PVP:KI system was shown in Fig. 4. It was clear from the figure (Fig. 4) that dielectric data well matches with ionic conductivity, $n/n_0$ data's.

FTIR spectra of pristine PVP, KI and PVP doped with KI were recorded between 4000 and 400 cm$^{-1}$, using Perkin Elmer 883 IR spectrophotometer. Fig. 5 shows the recorded FTIR spectra of pristine PVP, KI as well as PVP:KI polymer electrolyte films. Pure potassium iodide IR spectra (Fig. 5a) shows well defined peaks at 3435, 1623, 1399, 1123 cm$^{-1}$. In the spectrum of pure PVP (Fig. 5c) a broad peak was observed at 3391 cm$^{-1}$ which is correlated with water related peak. A vibrational band of C=O group was observed at 1682 cm$^{-1}$, suggesting the existence of some H-bonding carbonyl groups in PVP. Bands at 2954 cm$^{-1}$ and 2893 cm$^{-1}$ are attributed to the characteristic stretching vibrations of C–H respectively. Broad bands at 1500–1400 cm$^{-1}$ are noted due to the stretching vibrations of C–C. The bands at 1300–1150 are due to the stretching vibrations of C–H (wag). The bands at 1250–1000 are due to the stretching vibrations of C–N. A broad peak at 918 cm$^{-1}$ is due to the outer face vibration oscillation of the hydroxyl group, and strong peaks at 1464 cm$^{-1}$ and 1423 cm$^{-1}$ are assigned to the inner face of the bending vibrations of the hydroxyl group.
A close look and comparison of the IR spectra of pure KI, pure PVP and PVP doped with KI leads to the conclusion that PVP:KI polymer electrolyte system shows “composite” nature. It can be seen that all the peaks of PVP (Fig. 5c) are retained in the spectra of the composite (Fig. 5b) as well. Similarly, it is also obvious that the doped KI-related peaks (Fig. 5a) also manifest themselves in the IR spectra of the composite (Fig. 5b). In brief, thus, we can state that both the host polymeric matrix and the dispersoid KI retain their identity. Hence, PVP:KI is essentially a polymeric composite film.

The DSSC performance with PVP:KI/I$_2$ polymer electrolyte film with the highest ionic conductivity (30 wt% of KI) is shown in Fig. 6. For developing redox couple to use in present DSSC iodine has been added (10 wt% with respect to iodide salt) in PVP:KI matrix. The DSSC shows overall efficiency of 0.14 with short circuit current density ($J_{sc}$) of 0.97 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.48 V and fill factor (FF) of 0.29 at 100 mW/cm$^2$.

4. Conclusions

A new polymer electrolyte system consisting poly vinylpyrrolidone (PVP) and KI was developed for DSSC application. A complex impedance spectrum shows the ionic conductivity enhancement by KI doping and highest ionic conductivity was obtained at 30 wt% KI concentration with conductivity value of 4.69 × 10$^{-4}$ S/cm. The conductivity enhancement could be due to the free mobile charge carrier which is supported by our dielectric and $n/n_0$ evaluated by $n/n_0$ measurements. The composite nature of film was confirmed by FTIR data. A dye sensitized solar cell (DSSC) has been fabricated using maximum conducting film which shows 0.14% efficiency at 1 sun condition.

Acknowledgements

This work was supported by DST project (SR/S2/CMP-0065/2010) Government of India and Global Frontier R &D Program on Center for Multiscale Energy System funded by the National Research Foundation under the Ministry of Education, Science and Technology, Korea.

References