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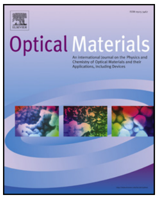

Effect of lithium iodide on the performance of dye sensitized solar cells (DSSC) using poly(ethylene oxide) (PEO)/poly(vinyl alcohol) (PVA) based gel polymer electrolytes

L.P. Teo, T.S. Tiong, M.H. Buraidah, A.K. Arof*

Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia

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ABSTRACT

In this work, different concentrations of lithium iodide (LiI) have been added to the gel polymer electrolyte (GPE) containing PEO and PVA in equal ratio, tetrabutylammonium iodide (TBAI), ethylene carbonate (EC), dimethyl sulfoxide (DMSO) and iodine crystals (I_2). The effect of introducing lithium iodide (LiI) into PEO-PVA blended GPE system having TBAI has been investigated in terms of optical, electrical, thermal and electrochemical characteristics. Fourier transform infrared (FTIR) spectroscopy has been carried out to study the interaction of LiI with the GPEs. The GPE without LiI showed the highest conductivity of 5.50 mS cm^{-1} at room temperature. With the incorporation of LiI, decrement in conductivity was observed. Dye-sensitized solar cells (DSSCs) with configuration FTO/TiO_2/N3-dye/GPE/Pt/FTO have been fabricated and tested under white light of intensity 100 mW cm^{-2}. The DSSC made of GPE with 1.34 wt% LiI exhibited highest efficiency, η of 6.26%.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been chosen as potential candidate for the next generation solar cells, owing to their appealing features such as low cost, easy fabrication method, flexibility, color availability and potential for indoor application [1]. To date, the highest photo conversion efficiency of DSSCs has been recorded at 14.3% using co-sensitization of silyl- and carboxy-anchored dyes with liquid electrolyte [2]. Although its efficiency is lower than the recently emerging perovskite solar cells, the DSSCs are eco-friendly and more stable [3]. A DSSC comprises three main constituents i.e. dye-adsorbed photoanode, electrolyte and counter electrode, in which the electrolyte plays an important task as charge transport medium. Liquid electrolytes usually offer high efficiency since they can give good ionic conductivity and make good contact with the porous surface of the photoanode. However, they are likely to leak, evaporate, and corrode which makes them unstable for long run. With comparable conductivity and good interfacial filing properties, gel polymer electrolytes (GPEs) are good substitute to liquid electrolytes without compromising the flexibility. Moreover, the leakage problem can be minimized in GPEs since the salt that has been dissolved in solvent is confined inside the polymer network.

GPEs for DSSCs must also contain redox mediator in order to regenerate the oxidized dye after electron injection process. The iodide/triiodide (I^-/I_3^-) redox couple is a good choice due to its excellent solubility, appropriate redox potential, fast dye rejuvenation and unfavorable electron recombination [4]. Other common ingredients that can be added into GPEs include secondary polymer matrix, secondary/ternary salt, plasticizers, additives and fillers. Blending of two or more polymers allows better properties in terms of ionic conductivity, flexibility, thermal stability, mechanical strength and electrochemical process as compared to the electrolytes having one polymer matrix. The rationale behind incorporation of double salts in electrolytes lies in the fact that both anions and cations play significant role in influencing the performance of DSSCs. It is clear that the anions are very important not only in ensuring good iodide anionic conductivity and thus number of iodide ions but also in determining the short-circuit current density (J_{sc}) and thereby the efficiency (η) of DSSCs. Salts in electrolytes having cations of large size such as tetraethylammonium (TEA^+ or Et_4N^+), tetrapropylammonium (TPA^+ or Pr_4N^+) and tetrabutylammonium (TBA^+ or Bu_4N^+) to name a few can be easily dissociated from the iodide anions due to low lattice energy. Since they are bulkier and less mobile than the iodide ions, it is expected that the cationic conductivity will be reduced while increasing the anionic conductivity. This will lead to improvement in J_{sc} and efficiency.

On the other hand, if small-sized cations such as lithium (Li^+), potassium (K^+) and sodium (Na^+) are used, they are able to be adsorbed onto the TiO_2 photoanode surface or intercalate into TiO_2

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* Corresponding author.
E-mail address: akarof@um.edu.my (A.K. Arof).

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nanoparticles thereby affecting the interfacial process at the TiO_2/dye/electrolyte. With the cation adsorbed on the TiO_2 surface, the TiO_2 Fermi and conduction band edge levels will be shifted positively and strengthen the electronic coupling between dye and TiO_2 thereby enhancing the electron injection rate and improve J_{sc} and at the same time lowering the open-circuit voltage (V_{oc}) [5]. Unlike small cations, the large cations might not attach on TiO_2 surface or intercalate into TiO_2 and thus the V_{oc} will be higher [6,7]. Therefore, many researchers have attempted to use two salts with large and small cations with the aim to have synergistic influence or better known as mixed cation effect towards contributing to good performance of DSSCs [8–13]. Bandara et al. [10] have fabricated DSSCs with GPEs containing polyacrylonitrile (PAN) as polymer host and binary salts of tetrahexylammonium iodide (THAI) and magnesium iodide (MgI). Highest efficiency of 3.50% was achieved for DSSC using two salts as compared to the cells having single salt of MgI (η = 2.00%) and THAI (η = 3.10%). In the work of Wanninayake et al. [13], an efficiency of 6.40% was obtained for DSSC employing PAN-based GPE with tetrapropylammonium iodide (TPAI) and lithium iodide (LiI) salts. With electrolyte containing single salt only, the efficiencies were 5.36% and 6.10% for TPAI and LiI, respectively.

In our previous work [14], GPEs containing poly(vinyl alcohol) (PVA) blended with poly(ethylene oxide) (PEO) at equal weight ratio of 1:1 and tetrabutylammonium iodide (TBAI) salt with ethylene carbonate (EC) and dimethyl sulfoxide (DMSO) as solvent and plasticizer have been prepared and tested in DSSCs. The ionic transport characteristics of PVA-PEO-TBAI GPEs concerning ionic mobility, number density of mobile ions and diffusion coefficient with their performance in DSSCs have been discussed in that work [14]. Systematic research effort has prompted us to incorporate 1-butyl-3-methylimidazolium iodide which is larger than TBAI into the PVA-PEO-TBAI GPEs [15]. As anticipated, the J_{sc} and efficiency have been enhanced. As a continuation of the work, we have employed instead a smaller cation salt than TBAI, *viz.* LiI and tried to investigate its influence in PVA-PEO blended GPEs on the DSSCs performance in this study. Also, this manuscript will shed some light on the effect of LiI addition on conductivity and reveal the interactions that occur between LiI, TBAI, PVA, PEO, EC and DMSO in the GPEs system. To the best of our knowledge, there is no report on the utilization of TBAI and LiI binary salts in PVA-PEO blended GPEs for DSSCs.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), ethylene carbonate (EC), tetrabutylammonium iodide (TBAI), lithium iodide (LiI), carbowax and triton X-100 surfactant were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and nitric acid were procured from Friedemann Schmidt Chemical whereas iodine (I_2) crystals were acquired from Amcochemie-Humburg. Titanium dioxide (TiO_2) with ~21 nm (P25) and ~15 nm (P90) particles size were obtained from Evonik Industries. Cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) dye (N3), platinum (Pt) solution and fluorine doped tin-oxide (FTO) glass substrates were purchased from Solaronix.

2.2. Preparation of gel polymer electrolytes (GPEs)

The GPEs preparation is similar to our previous work [14]. From the highest conducting electrolyte composition (7.02 wt% PEO - 7.02 wt% PVA - 30.11 wt% EC - 30.11 wt% DMSO - 24.08 wt% TBAI - 1.66 wt% I_2) [14], lithium iodide has been added. Some portions of TBAI have been substituted with LiI so that the total weight composition remained the same. Other materials have been fixed (0.21 g PVA, 0.21 g PEO, 0.9 g EC, 0.9 g DMSO and 0.0496 g I_2). A total of six samples of GPEs having different ratios of TBAI and LiI have been prepared and listed in Table 1.

Table 1
The salt composition of PVA-PEO blended GPEs with their designation.

GPE	LiI (wt.%)	TBAI (wt.%)
A	0.00	24.08
B	0.33	23.75
C	1.34	22.74
D	2.68	21.40
E	4.01	20.07
F	5.35	18.73

2.3. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

Thermoscientific Nicolet iS10 FTIR Spectrometer (from USA) was used to perform ATR-FTIR study on the GPEs. This spectrometer is equipped with an ATR internal reflection system. The FTIR spectra were recorded with a resolution of 4 cm^{-1} in transmittance mode over the wavenumber range from 4000 to 650 cm^{-1}. The FTIR spectra were analyzed by OMNIC 8 software which is provided by Thermo Fischer Scientific Inc.

2.4. Electrochemical impedance spectroscopy (EIS)

The bulk resistance (R_b) of GPEs was obtained from EIS measurements. The measurements were performed using the Hioki 3531 Z Hi Tester in the frequency range from 50 Hz to 5 MHz at temperatures between 303 K and 363 K. From the bulk resistance, the ionic conductivity (σ) of each GPE can be calculated from equation below:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where A and t are the area and thickness of the GPEs, respectively.

2.5. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA)

Thermal analysis of the GPEs was conducted using a simultaneous TGA-DTGA apparatus TGA Q500 (TA instruments) which is connected to a computer with software version TA Universal Analysis. The measurements were carried out from 24 to 600 °C at a heating rate of 50 °C min^{-1} under nitrogen flow of at 40 mL min^{-1}.

2.6. Fabrication and characterization of dye sensitized solar cells (DSSCs)

Two layers of TiO_2 were deposited on the clean conducting side of FTO glass. The first TiO_2 layer was prepared by grinding 0.5 g of TiO_2—P90 powder in 2 mL dilute nitric acid before being spin-coated on FTO glass. The spin-coated FTO glass was then sintered at 723 K for 30 min. For the second layer, 0.5 g of TiO_2—P25 powder and 0.1 g carbowax were added into 2 mL nitric acid and ground for about 60 min. Few drops of surfactant (triton-X) were added to the TiO_2 paste and mixed properly. The TiO_2 paste was then coated on the blocking compact layer (sintered TiO_2—P90 layer) using the doctor blade method and sintered at 723 K for 30 min. The thickness of the TiO_2 layer was around 50 μm. The double layered TiO_2 electrodes were then soaked in 0.3 mM photosensitive dye (N3) for 24 h for dye adsorption. Meanwhile, Pt counter electrode of DSSC was prepared by spreading a platinum solution on top of the conducting side of FTO glass and sintered at 723 K for 30 min.

The DSSCs were fabricated by sandwiching the GPEs between the dye-adsorbed TiO_2 photoanode and Pt counter electrode to have the configuration FTO/TiO_2/N3 dye/GPE/Pt/FTO. The active area of the