



Poly(ethylene oxide) polymer matrix coupled with urea as gel electrolyte for dye sensitized solar cell applications



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ABSTRACT

In this paper, a new series of gel polymer electrolytes modified with various weight percent of urea in Poly(ethylene oxide) polymer matrix and iodine-iodide based redox couple were reported for the application of dye-sensitized solar cell. The effect of urea on both molecular mobility and final morphology of GPE are characterized by Fourier Transform Infrared spectroscopy and Scanning Electron Microscopy. Electrochemical Impedance Spectroscopy and Linear Sweep Voltammetry show that the addition of urea gives a general increment in both ionic conductivity (σ) and tri-iodide diffusion coefficient. In particular, GPE containing 4 wt% of urea has an ionic conductivity, $\sigma = 4.28 \times 10^{-4} \text{ S cm}^{-1}$ and tri-iodide diffusion coefficient, $D_{I_3} = 2.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. A maximum power conversion efficiency of 6.82% in the photovoltaic performance is achieved. Further, a variation of charge transfer resistance and chemical capacitance at the $\text{TiO}_2/\text{dye}/\text{interfaces}$ as a function of bias voltage is observed. It suggests an upward shift in the conduction band of TiO_2 in the case of gel electrolytes.

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1. Introduction

Researchers are focusing on finding new renewable green energy sources to meet the increased energy requirements towards increasing population and developing technology. Dye-sensitized solar cell (DSSC), introduced by Gratzel [1], is one among the various types of solar cells and has attracted attention due to its comparatively low cost and simple fabrication method [2]. In addition, efficiencies up to 13% were achieved for conventional liquid electrolytes based DSSCs [3]. However, the actual devices still have serious drawbacks such as volatile and flammable nature of organic solvents used, stability issues due to the degradation of dyes in the photoanode, corrosion of counter electrode and severe leakage and sealing issues in practical applications [4]. Up to now, numerous attempts have been made to replace liquid electrolyte with polymer electrolytes [5–7], solid state hole transport materials (SSHTMs) [8,9] and room temperature ionic liquids (RTILs) [10,11]. RTILs has shown efficiencies 7–10% [12–15] but has the drawback of low ionic mobility due to high viscosity and poor stability [16]. SSHTMs have good long-term stability, but their efficiencies were lower than analogous liquid electrolyte based

DSSCs due to the poor interfacial contact. Efficiencies up to 7% were reached by various methods such as surface modifications, doping, etc [17].

Among the various types of electrolytes, polymer electrolytes have shown wide potential applications in solid state electrochromic devices [18], super capacitors [19], fuel cells [20], rechargeable batteries [21] and dye-sensitized solar cells due to its flexibility, easy availability and non-toxic nature. But unfortunately, DSSCs made with solid polymer electrolytes (SPEs) shows very low efficiency (4%) [22] due to their low ionic conductivity [23,24]. To overcome this problem, gel polymer electrolytes (GPEs) were recently introduced. Despite, the higher efficiency of GPEs and a considerable stability, their efficiency values are still lower than that of liquid electrolytes. Hence, numerous attempts were made to increase the cell performance of DSSCs containing GPE by using various synthetic polymers, bio-polymers and additives such as nanofillers and plasticizers [25,26]. In particular, the addition of plasticizer has proven to reduce final crystallinity and provides free space for ionic mobility. Some commonly encountered plasticizers are nitrogen or oxygen containing heterocyclic compounds like ethylene carbonate, propylene carbonate [27], *tert*-butyl pyridine [28,2] and γ -butyrolactone [29]. Urea is practically non-toxic and it has two $-\text{NH}_2$ groups which can interact with polymer matrices like (poly(ethylene oxide) and poly(vinyl chloride)) to form

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polymer-urea complexes with interesting electrochemical properties [30,31]. According to our best knowledge, up to now, there were no reports available on the use of urea as a plasticizer in DSSC.

In this paper, a series of GPEs utilizing various Wt% of urea as a plasticizer in PEO polymer matrix and LiI/I_2 redox couple in propylene carbonate are prepared. PEO is taken as polymer matrix because of its higher miscibility with inorganic salts in the redox electrolyte due to the presence of ether oxygen group. Urea is shown as plasticizer, because it a simple molecule with one carbonyl and two $-\text{NH}_2$ groups. The conformational changes in urea modified gel polymer electrolyte are studied using FT-IR and SEM. Electrochemical characteristics like ionic conductivity and tri-iodide diffusion coefficient were determined. Finally, DSSCs are assembled using the urea modified GPEs and characterized by linear sweep voltammetry and electrochemical impedance spectroscopy. Further, variation of charge transfer resistance and chemical capacitance at the working electrode/electrolyte interface with respect to applied voltage are also studied.

2. Experimental section

2.1. Materials

Poly(ethylene oxide), Titanium(IV) chloride, Acetyl acetone (99%), Triton-X (95%), Poly(ethylene glycol) (PEG, MW = 10,000), N719 dye, Lithium Iodide (99.9%), Iodine (99.8%) and urea were purchased from Sigma-Aldrich, India. TiO_2 (P25) (Degussa), Nitric acid (Merck) and Propylene Carbonate (Alfa-Aesar) were also used. All purchased chemicals and reagents were of analytical grade and used as received without any further purification.

2.2. Preparation of bare and urea-modified gel polymer electrolytes

The bare and urea-modified Gel Polymer Electrolytes were prepared as follows: about 0.264 g of PEO is added to propylene carbonate and acetonitrile in v/v ratio of 1:20 and then stirring at 80°C for 2 h; the LiI/I_2 redox couple in the concentration ratio of 10:1 and various wt% of urea (0, 2, 4, 6 and 8% with respect to the weight of PEO) were then added and the stirring process is continued for another 2 h at refluxing condition. This mixture was stirred overnight at room temperature. After that, temperature was raised at 80°C in order to allow acetonitrile evaporation. GPEs containing 0%, 2%, 4%, 6% and 8% of urea were named as A, B, C, D and E respectively. A liquid electrolyte with the same molar concentration of redox couple was also prepared for comparison.

2.3. Dye sensitized solar cell fabrication

The photoanodes were fabricated according to the procedure reported elsewhere [32]. In particular, TiO_2 paste was prepared by sonicating and stirring the mixture of 0.5 g of TiO_2 (P25) nanoparticles in 1 M HNO_3 with 1.6 mg of PEG, 0.21 mL of acetyl acetone and 0.04 mL of Triton-X for 1 h and 24 h respectively. The as prepared paste was then coated by doctor blade technique on the pre-cleaned and TiCl_4 treated FTO plates. TiCl_4 treatment was performed using a 40 mM solution of TiCl_4 at 70°C for 30 min. In order to provide cross linking and additives removal, TiO_2 coated plates were sintered at 450°C for 30 min in a tubular furnace. Finally, the photoanode was obtained by sensitizing the TiO_2 films using a 3×10^{-4} M solution of N719 dye in acetonitrile and *tert*-butanol at volume ratio of 1:1 for 24 h. The active area of the photoanodes was 0.25 cm^2 . To enhance the contact between TiO_2 and electrolytes all the prepared photoanodes were treated with a dilute solution of LiI in acetonitrile [33]. Platinum counter electrodes were prepared by drop casting 5×10^{-4} M solution of $\text{H}_2[\text{Pt}(\text{Cl})_6]$ on cleaned FTO plates and sintering them at 450°C for

30 min. Finally, to obtain the DSSCs the electrolyte layer (either liquid electrolyte or gel polymer electrolyte) with a thickness of about $50\ \mu\text{m}$ was sandwiched in between the two electrodes.

2.4. Characterization techniques

Fourier transform infrared spectra were obtained using a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Morphological study was performed by using FEI, model quanta 200 3D, SEM instrument.

The ionic conductivity of the electrolytes was determined using bulk resistance from electrochemical impedance spectroscopy (EIS) whereas the tri-iodide apparent diffusion coefficient $D_{\text{I}_3^-}$ was determined by using the tri-iodide diffusion-limiting current from linear sweep voltammetry (LSV). In that case, experiments was performed in a symmetrical cell obtained by sandwiching the electrolytes in between two Pt coated FTO electrodes one of which is masked properly leaving an open area of 0.25 cm^2 for measuring conductivity and 1 cm^2 for diffusion, respectively.

The photovoltaic properties of the fabricated DSSCs were characterized under illumination from a solar simulator of 150 W Xe light source in combination with standard AM1.5 (85 mW cm^{-2}). Electrochemical impedance spectra (EIS) of the cells were obtained under forward bias at open circuit voltage in dark conditions from 1 Hz to 10^6 MHz with a perturbation voltage of 10 mV. Further, EIS analysis by varying bias voltage is also performed. All the above electrochemical and photo-electrochemical measurements were conducted by using an AUTOLAB12/FRA2 electrochemical analyzer.

3. Results and discussion

A schematic representation of the resonance mode of urea molecules is shown in Fig. 1a. As shown in Fig. 1b, possible interactions of urea with the GPE molecules is through both H-bonding of amino protons with ether oxygen of PEO and polar interactions of carbonyl group with Li^+ ions in the redox couple, forming a six membered complex.

3.1. Fourier transform infrared spectrum

To identify the ionic interactions in polymeric electrolytes FT-IR analysis was performed. Fig. 2 shows the FT-IR spectra of pristine urea, bare GPE and urea modified GPEs. The adsorption bands centred around 945 and 956 cm^{-1} are assigned to the symmetric and asymmetric rocking modes of $-\text{CH}_2$ groups of PEO, respectively. As previously reported, these bands are sensitive to the changes of macromolecular conformations [34]. With the addition of urea to the electrolytes, the relative intensity of the band at 956 cm^{-1} increase with respect to the 945 cm^{-1} band. A triplet band observed at 1100 cm^{-1} is due to $\text{C}-\text{O}-\text{C}$ stretching mode of crystalline PEO. A doublet peak around 1352 and 1387 cm^{-1} is due to the wagging modes of $-\text{CH}_2$ group, whereas the stretching vibrations of $-\text{CH}_2$ group is observed around 2900 cm^{-1} . The $\text{C}=\text{O}$ stretching vibrations of urea is observed at 1602 cm^{-1} whereas the deformation modes [35] are observed at 1625 cm^{-1} and 1683 cm^{-1} . The bands in the region $3300-3500\text{ cm}^{-1}$ are due to symmetric and asymmetric stretching vibrations of two urea $-\text{NH}_2$ groups. For urea modified GPEs, urea bands were observed with significant changes: the 1602 cm^{-1} shifts to higher wave number and superimposed to the band at 1625 cm^{-1} . Stretching vibrations of urea $-\text{NH}_2$ groups gets broadened: this may be due to the formation of hydrogen bonds between ether oxygen of PEO [30,36]. From the above observations, it is deduced that urea interacts with the ether oxygen in PEO

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