Solar Energy 160 (2018) 225–250

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Low-cost synthesized organic compounds in solvent free quasi-solid state polyethyleneimine, polyethylene glycol based polymer electrolyte for dye-sensitized solar cells with high photovoltaic conversion efficiencies

P. Karthika[a], S. Ganesan[a,*], M. Arthanareeswari[a]

[a] Department of Chemistry, Faculty of Science and Humanities, SRM University, Kattankulathur 603 203, Kancheepuram District, Tamil Nadu, India

ARTICLE INFO

Keywords:
Quasi solid state polymer blended electrolyte
Polyethyleneimine
Polyethylene glycol
Organic dopants
Dye-sensitized solar cells

ABSTRACT

The present work reports on solvent free quasi-solid state polymer electrolyte comprising of polyethyleneimine, polyethylene glycol, KI, I_2 with newly synthesized N,O,S based organic compounds and application for nano-crystalline dye-sensitized solar cell (DSSC). The synthesized compounds was confirmed by NMR and mass spectra the conductivity and the surface study were analysed by FTIR spectra, impedance spectra, CV, microscope image, UV and XRD. The performance of the fabricated solar cell and conductivity of polymer electrolyte was enhanced by the electron donicity of hetero atom in the synthesized organic compound such as tetraethylene glycol and −O−C−C−O− units. Among all synthesized organic compound, the (4,4′-((((oxybis(ethane-2,1-diyl)) bis(oxy))bis(ethane-2,1diyl))bis(sulfanediyl))dipyridine) dopant (I) showed a strong interaction with nano TiO_2 electrode, redox couple and the electrolyte resulted with short circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (ff) and energy conversion (ŋ) values of about 12.9, 890, 0.56 and 9.2% under the sunlight irradiation of 70 mW/cm^2.

1. Introduction

For several decades, human race faces an enormous level of energy crisis by the depletion of hydrocarbons and other non renewable resources (Su'ait et al., 2015; Ahuja and Tatsutani, 2009; Twidell and Weir, 2012). Thereby usage of renewable energy resources remarkably plays a vital role in eradicating the consumption of the existing exhaustible resources. Recently researchers are concentrating more on exploiting the humongous solar energy for harnessing the electrical energy (Chaurasia and Lin, 2016) with the help of dye sensitized solar cell (DSSC). Henceforth, Dye-sensitized solar cell (DSSC) has gained considerable attention for its high energy conversion, cost-effective, handling and requirement of non-hazardous material. Brian O'Regan and Michael Gratzel primely achieved the dye sensitized solar cell with electric energy efficiency of about 11% (Regan and Gratzel, 1991). The DSSC set up has stellar parts include TiO_2 coated with Ru based N719 dye (di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II))dye Gratzel, 2003; Nazeeruddin et al., 1993; Hirata et al., 2006; Meng et al., 2003 as the working electrode, electrolyte with iodide/iodine as redox couple and platinum as counter electrode. Customarily, the electrolyte takes the vital role in enhancing energy conversion efficiency (Su'ait et al., 2015; Yang et al., 2009). Various types of electrolytes such as liquid (Yu et al., 2011), quasi-solid state (Tao et al., 2014), gel polymer (Shen et al., 2014a, 2014b; Liu et al., 2017), solid state (Ganesan et al., 2011), ionic liquid electrolyte (Song and P., 2015; Wang et al., 2002) and dendrimers (Raja et al., 2011) are being implemented to likely favour the pleasant charge transfer medium due to their legitimate ionic conductivity and enhance electrical, thermal durability in DSSC (Apostolopoulou et al., 2015; Pashaei et al., 2016; Zulkifili et al., 2015).

Generally, the polymer blending technique is chiefly implemented to develop new polymer electrolytes by incorporating two or more polymers by their alluring properties. Formerly, such solid or liquid polymers are blended by heating with protic solvents, casted over petridish and dried at vacuum for several hours to eradicate the solvents (Ganesan et al., 2011; Muthuraaman et al., 2011). This time

* Corresponding author.
E-mail address: ganesan.sh@ktr.srmuniv.ac.in (S. Ganesan).

https://doi.org/10.1016/j.solener.2017.11.076
Received 30 September 2017; Received in revised form 11 November 2017; Accepted 27 November 2017

barrier could lead to sublimation of iodine, which is a major factor in decreasing the energy efficiency. Furthermore, implementing polymer based liquid or solid electrolytes reflects issues like solvent leakage, dye degradation, instability, cathode corrosion, contact problem at the electrodes and efficiency (Gong et al., 2012). Employing quasi solid state electrolyte paved a way to overcome the limitations resulting in better reduction of the recombination life time between electrode and electrolyte, charge transport time, electron diffusion coefficient, stability (Mohamad, 2016; Xia et al., 2015; Aram et al., 2015; Suzuka et al., 2016; Khannam and Dolui, 2017). The recent report based on quasi-solid state electrolyte shows good efficiency (Hwang et al., 2017). Since we started our initial studies with the viscous polymers, such as polyethyleneimine, branched [PEI] and polyethyleneglycol [PEG]. The highly branched PEI with nitrogen as major electronegative group combined of primary, secondary, tertiary amine groups with its high charge density, high poly dispersity and further the presence of nitrogen atoms can in turn enhance the interaction with alkali metal ion. Due to the high viscous nature of PEI and PEG was blended for improving consistency and electrical conductivity. The presence of −O−C−C−O− group in PEG enhances the segmental motion and intensifies the reduction in the recombination of the electrode and reduces the back electron transfer and successively enhances the open-circuit voltage (Voc) Anantharaj et al., 2015; Ganesan et al., 2016, thus making the PEI/PEG polymer combination effectual for increasing the performance in DSSC. In order to obtain rigid setup and to enhance the contact between the dye coated TiO_2 and the Pt electrode, an additional support for the electrolytes such as propylene carbonate is being utilized decisively to refine the efficiency by improvising the ionic conductivity (Aziz et al., 2014; Tarannum and Varishetty, 2017; Ileperuma, 2013). Its paramount role is to cease the chain interaction between the polymers and to expose a wealthy way for the dissociation of the salt.

Habitually organic molecules create an eloquent presence in photovoltaic and light harvesting systems. Nowadays, doping of hetero organic molecules comprising of N, O, S atoms into the polymer matrix has been extensively practiced to enrich conductivity in DSSC (Ganesan et al., 2016, 2008). Due to the existence of lone pair of electrons in such organic molecules, sublimation of iodine can be gradually decreased by the formation of charge transfer complexes with iodine in the redox couple, apparently improving the conducting and photo voltaic behaviour of polymer (Ganesan et al., 2013). Cumulatively, pair of electrons in the polymer and the hetero dopants establishes an effective interaction with alkali ion owing to the redox couple's mobility (Muthuraaman et al., 2011). Hence it enforces us to synthesize such new electron donating conjugated compounds via rapid synthetic route, simple work up, good yields and blending with the conducting polymer to examine the energy conversion efficiency (ŋ) in dye sensitized solar cell. In our present study, commendable combination of liquid/viscous liquid polymer and subsequent doping of synthesized organic compounds is quite challenging in our criteria. Predominantly this polymer blend reveals us the amorphous nature due to their high miscibility with organic dopants and redox couple, resulting in better ionic conductivity due to the ionic mobility. In our present study, we have comparatively investigated the effect of doping of congenitally synthesized compounds and the conductivity of electrolytes to explore its photovoltaic properties of DSSC. The quasi solid state polymer electrolyte with the organic dopants and redox couple are subjected to XRD, FTIR, UV–Vis, Cyclic voltammetry, Electrochemical impedance spectroscopy (EIS) studies. The results demonstrated the impact of the organic dopants in the conductivity and performance of the fabricated DSSCs.

2. Experimental methods

2.1. Chemicals and reagents

The polymers polyethylenimine, branched (M_w ~ 25,000) and poly (ethylene glycol) (M_w ~ 400) and the organic compounds 2,6-dibromo pyridine, 2-mercapto benzimidazole, 2-mercaptopyridine-3-carboxylic acid, 3-hydroxy-2-methylpyridine, 3-hydroxy acetophenone were purchased from sigma aldrich. Fluorine doped Tin oxide coated glass slide L × W × D 100 mm × 100 mm × 2.3 mm surface resistivity ~ 7 Ω/sq were purchased from sigma aldrich. Tetraethylene glycol, phosphorous tribromide, 4-mercapto pyridine was purchased from TCI. DMSO, acetone, ethanol, KOH, Na_2CO_3 were procured from avra synthesis Pvt. Ltd.

2.2. Synthesis of organic dopants

2.2.1. Synthesis of 4,4′-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1diyl))bis(sulfanediyl))dipyridine (dopant I)

2.2.1.1. Step 1: synthesis of (1-bromo-2-(2-(2-(2-romoethoxy)ethoxy) ethoxy)ethane). Initially tetraethylene glycol 33.56 g (0.1727 mol) was cooled to 0 °C, and then PBr_3 34.61 g (0.1278 mol) was added dropwise to the cooled tetraethylene glycol over a period of 1 h. Then the

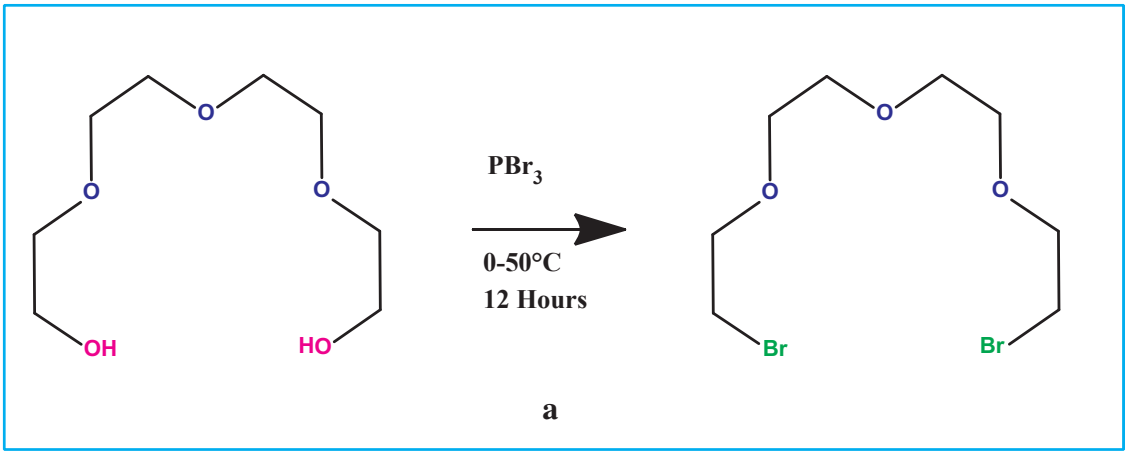

Fig. 1. (a) Schematic representation of 1-bromo-2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethane (1), (b) ^{1}H NMR of 1, (c) ^{13}C NMR of 1 and (d) Mass Spectrum of 1.