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Synthesis and electrochemical characterization of physically cross-linked gel electrolyte for QSDSSC application

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ABSTRACT

Use of liquid electrolyte in dye sensitized solar cells (DSSC) causes a serious challenge in terms of long-term stability. Quasi-solid-state electrolyte solves this problem to a great extent. In this work a physically cross-linked polyvinyl alcohol (PVA) based quasi-solid-state or gel electrolyte (GE), incorporated with KI/I_2 was synthesized using ethylene carbonate (EC) as plasticizer. Thermal analysis, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) of gel electrolyte were done. Quasi-solid-state dye (N719) sensitized solar cell (QSDSSC) was fabricated with this gel electrolyte and the current-voltage characteristics and electrochemical impedance were tested under irradiance of AM 1.5 (100 mW cm^{-2}). Cell performance was compared with liquid electrolyte based DSSC, where the liquid electrolyte contains KI/I_2 in DMSO/EC mixture without any fillers or additives. Efficiency values of 4.4% and 3.4% were obtained respectively for liquid electrolyte based DSSC and QSDSSC. The effect of plasticizer and the polymeric network gives a comparable performance of QSDSSC. A time-dependent stability of the gel in QSDSSC was studied and the performance was found to be better than that of liquid based DSSC.

1. Introduction

Polymer gel electrolytes are quasi-solid in which liquid electrolyte is trapped within the entangled network of the polymer matrix [1–3]. Gel electrolytes are a very promising substitute for liquid electrolyte in dye sensitized solar cells (DSSC). Its superior properties like non-propensity to leakage, long term stability and its ability to switch between the quasi-solid and viscous state, inspired people around the world to do intense research and development in the field of quasi-solid-state DSSC (QSDSSC) [4,5]. It comprises of a polymer backbone, a plasticizer and a liquid electrolyte. The polymers provide mechanical strength to the electrolyte by increasing the viscosity, whereas, the plasticizers lower the brittleness of the polymer [6,7].

Electrolytes play a key role in converting solar energy into electricity in DSSC. The long-term stability of the device strongly depends on the electrolyte component. The electrolyte usually employed in DSSC contains iodine and its salt that institute a redox shuttle to revive the dye ground state and a suitable solvent which act as the medium for charge transportation between the counter electrode and photoanode [7,8].The highest efficiency reported so far in DSSC with liquid electrolyte is 13% [5]. Liquid electrolytes are widely used for DSSC fabrication because of its ease of preparation, high conductivity, low viscosity, good interfacial wetting between the electrode-electrolyte and resultant high conversion efficiency [7–9]. The practical impediments like, leakage and volatilization of the solvent, corrosion of Pt counter electrode, desorption of attached dye etc. prevent the long term stability of the cell while using liquid electrolyte [2,3,10,11]. To solve this problem, solid-state electrolytes are introduced. The poor mobility of the charge carriers and less interfacial contact between the electrode-electrolyte in solid-state electrolyte due to the lack of solvent deteriorate its application in DSSC [2,7]. Search for a better substitute led to the development and progress of quasi-solid-state electrolyte or gel electrolyte. The first attempt to use gel electrolyte in QSDSSC was done by Cao et al. using a mixture of poly(acrylonitrile), ethylene carbonate, propylene carbonate, acetonitrile and NaI [8]. The performance was poor because of its lower ionic conductivity than that of liquid electrolyte [9]. Many of the problems faced while using liquid electrolyte can be overcome to a great extent by the introduction of gel electrolyte. These gel electrolytes exist in quasi-solid-state at room temperature and as viscous liquid at higher temperature. It has got both the properties of solid and liquid electrolytes like stability, good adhesion and high ionic conductivity [10,12]. This makes the gel electrolyte unique and a better alternative to liquid electrolyte. A recent study by Ramesh et al. reports the use of ionic liquid incorporated rice starch based gel electrolyte in DSSC for a conversion efficiency of 2% [13]. Reports also show the application of gel electrolyte in electrical double layer capacitor [14].

In the current study, polyvinyl alcohol was taken as the gelator for liquid electrolyte. A mixture of solvents like dimethyl sulfoxide (DMSO) and ethylene carbonate (EC) were chosen as the medium for ionic transport which meets almost 80% requirement for a suitable solvent to be used in DSSC [7]. In polymer gel electrolyte, EC has got the

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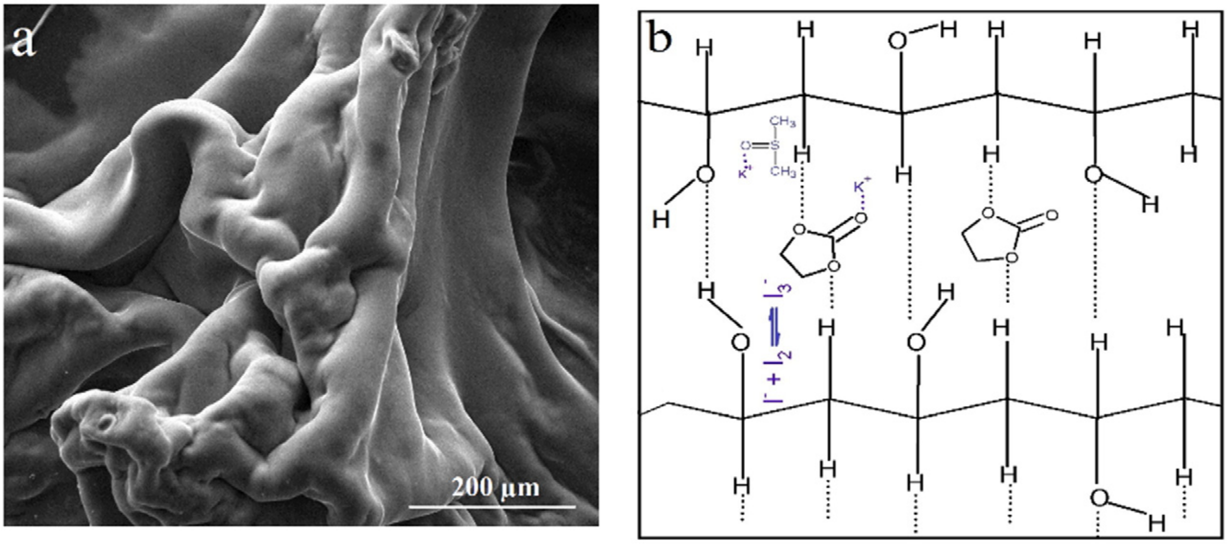

Fig. 1. SEM image (a) and 3-D network structure of polymer gel electrolyte (b).

role of solvent and plasticizer which holds the polymer chain segments together resulting in the formation of a network structure [4,7,10]. The gelation process prevents leakage and volatilization of liquid electrolyte and extends its stability and durability. In this part of study, synthesis and characterization of gel electrolyte is done. The impact of three dimensional network structure and effect of plasticizer on the kinetics of electron transfer at TiO_2-electrolyte interface and Pt-electrolyte interface is also studied. The gel stability study and stability of QSDSSC are also done.

2. Experimental

2.1. Materials

Fluorine doped tin oxide (FTO-7 Ω/cm^2), N719 (Ru(dcbpy)$_2$(NCS)$_2$) − 95%), ethylene carbonate(EC-98%), hexachloroplatinic acid (H_2PtCl_6), potassium iodide (KI) (bio ultra, 99.5%), polyvinyl alcohol (PVA, 99% hydrolyzed) were from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and iodine (I_2) were from MERCK.

2.2. Gel electrolyte synthesis

Liquid electrolyte was prepared by dissolving 0.5 M KI and 0.03 M I_2 in 13 mL of DMSO/EC mixture and stirred until the salt was completely dissolved to obtain a homogenous solution. To this electrolyte 1.25 g of PVA was added and heated at 100 °C and stirred till the polymer was completely dissolved in the organic solvent. This resulted in the formation of a highly viscous solution. The temperature was lowered and stirring continued till the system cooled down to ambient condition. The solution was then kept overnight for complete polymerization to obtain PVA based gel electrolyte.

2.3. DSSC assembly

Transparent conducting oxides are usually taken as substrate material for photoanode and platinum coated FTO as counter electrode in DSSC. TiO_2 paste was made in ethanol with Triton X-100 as a binder material. This TiO_2 paste was spread on the FTO substrate by using a glass rod. The film was then air dried and sintered at 450 °C for 30 min to remove the organic contents present and to get a continuous network of TiO_2 particles. The FTO/TiO_2 electrode was then loaded with the photosensitizer by dipping in a solution of N719 dye overnight. The photoanode was then rinsed with ethanol and dried. Pt deposited FTO was used as the counter electrode [8,15]. Cell assembly was completed

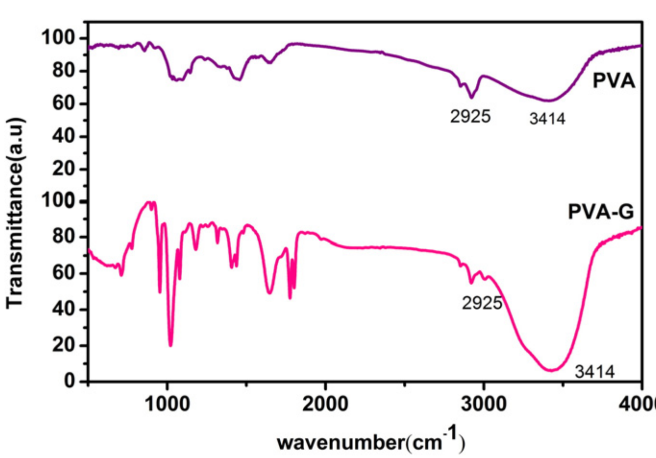

Fig. 2. FT-IR spectra of pure PVA and PVA gel (PVA-G).

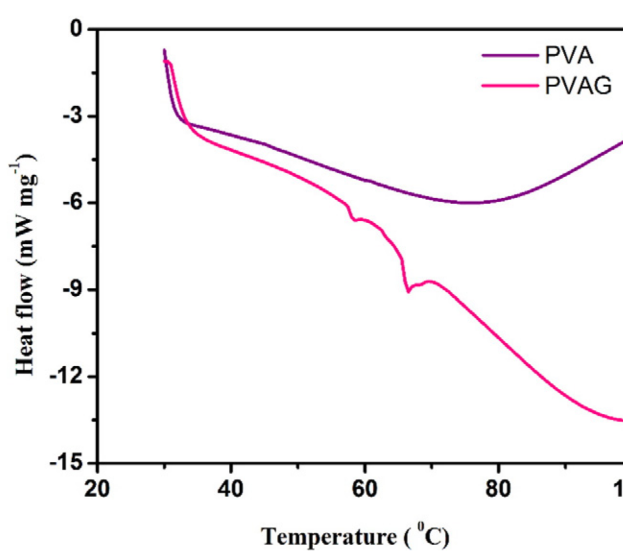

Fig. 3. DSC curves of pure PVA and PVA gel electrolyte.