



Polymer electrolyte integrated dye sensitized solar cells endow enhanced stability: Photoanode thickness and light intensity on cell performance[☆]



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ABSTRACT

The study investigates the feasibility of integrating a quasi-solid polymer electrolyte with photoanodes made of titania nanocuboids and enhance the stability of dye-sensitized solar cells. Anatase titania nanocuboids are synthesized employing ammonium fluoride as structure directing agent by hydrothermal route, characterized, made into a homogeneous paste and utilized for fabricating photoanodes of various thicknesses. N719 sensitizer adsorbed on these photoanodes are paired with a new class of polyurethane based semi-IPN electrolyte system supporting I^-/I_3^- redox couple and sandwiched on top with a sputter coated platinum counter electrode. Integrated test cells are evaluated initially for the thickness dependent efficiency of the photoanodes to assess pore-filling ability of the macromolecular electrolyte used and limitations of fabrications. Optimization studies indicated 4 μm thick photoanodes to be ideal for obtaining the most favorable wetting characteristics and appropriate solid-electrolyte interface. The cells made with anatase nanocuboids shows an impressive 2.2% efficiency with a short circuit current density of 4.3 mA and an open circuit voltage of 0.76 V under AM 1.5 and simulated one Sun conditions. It is understood that due to reduced dye loading capacities of these thinner photoanodes, the photoconversion efficiencies and the overall cell efficiency apparently seems to be low, ca. 2–3%, alternate dye molecules with high molar extinction coefficients can effectively offset this loss. The efficiency is certainly seen to improve under 0.25 Sun owing to lower recombination possibilities. Most importantly, the stability tests carried out on these cells stored under ambient conditions demonstrate that these solid-state devices can retain ~ 80% of their initial efficiency for at least 2600 h under the experimental conditions, which is devoid of hermetic sealing.

1. Introduction

Efficient photovoltaic conversion of sunlight into electricity to provide clean energy has remained a subject of intense investigation (Armaroli and Balzani, 2007; Kamat, 2007). Since O'Regan and Gratzel demonstrated the first dye sensitized solar cell (DSSC) with 7% photoconversion efficiency (PCE) using mesoporous titania sensitized by a ruthenium complex in 1991, the possibility of designing cost effective cells for deployment as building integrated photovoltaics (BIPV) has generated tremendous excitement (O'Regan and Gratzel, 1991). The cell components of a DSSC are relatively cheaper and involve comparatively nontoxic processing steps to that of conventional silicon photovoltaics and thin film solar cells materials (CdTe, CIGS) (Greijer et al., 2001). Simply put, DSSC comprises of a photoanode composed of mesoporous nanocrystalline semiconductor layer covered with a

sensitizer paired with a platinum counter electrode and a redox electrolyte filled in between (O'Regan and Gratzel, 1991). To date, highest certified DSSC efficiency over 11% is reported with iodide/triiodide (I_3^-/I^-) electrolyte and a ruthenium sensitizer while ca. 13% is achieved with Co(II/III) based redox electrolyte in combination with a Zn porphyrin dye on titania photoelectrodes (Gao et al., 2008; Yella et al., 2011).

The working mechanism of a DSSC resembles that of natural photosynthesis, and the concept is now very well established (Bisquert et al., 2004). Dye absorbs the light to excite 'n' of its electron from HOMO to LUMO level which is subsequently injected to the conduction band of the semiconductor (TiO_2) and extracted into external circuit. The charged dye molecule is quickly regenerated either by a redox couple or a hole transport material to allow the process to continue uninterrupted (Robertson, 2006). Conventionally used electrolytes are

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mostly liquids which impose design limitations. Whether the liquid electrolytes used are volatile (acetonitrile, valerionitrile, etc.)/non-volatile (ionic liquids), they invariably present a problem with sealing of the device. While leak-proof sealing remains a major bottleneck for large scale module fabrications, inability to achieve roll-to-roll processing make them commercially unattractive (Wang et al., 2004, 2003; Yu et al., 2012, 2011; Papageorgiou et al., 1996; Matsumoto et al., 2001). Researchers have long been looking forward to achieve all solid-state devices employing *p*-type inorganic semiconductors (Kumara et al., 2002; O'Regan et al., 2002), polymer electrolytes (Freitas et al., 2009) and organic/polymer hole transport materials (Bach et al., 1998; Kruger et al., 2002), to substitute liquid electrolytes. However, these materials pose unusual challenges owing to their limited pore filling ability, light absorptive nature and high degree of crystallinity apart from the complicated synthetic routes involved to achieve high purity requirements for device applications (Wu et al., 2015).

During the last two decades a remarkable international research effort has been dedicated to the development of solvent-free solid polymer electrolytes (Yum et al., 2008; Li et al., 2009; Suait et al., 2015). The conceptualization of polymeric electrolytes (Li^+ -ion polymer complexes) in early seventies though promised to deliver thinner better electrochemical devices, such as, Li-ion batteries, ECDs, DSSCs, etc., practical devices are yet far from achieving commercial realization (Lewis, 2007; Gratzel, 2001; Alamgir et al., 1991, 1994; Freitas et al., 2009; Gray, 1997). De Paoli and co-workers first demonstrated the possibility of replacing the liquid electrolyte incorporating polymer-salt complexes with NaI/I_2 as a redox system (Freitas et al., 2009). Successive reports, however, highlighted the constraints imposed by the sluggish ion-transport in macromolecular matrices that restricted fast regeneration of the dye. Use of ionic liquids and polymeric gels with high liquid entrapment could only partially address certain issues (Gao et al., 2010; Upadhyaya et al., 2006; Wu et al., 2007). Nevertheless, in recent years; several successful attempts by notable groups have revived the hope to achieve functional devices (Wu et al., 2015).

The present investigation showcases the ease and feasibility of integrating a semi-IPN electrolyte with nanostructured titania photoanodes that imparts appreciable stability for the DSSC devices. In persistent efforts from our group towards achieving the elusive polymer electrolytes with requisite ionic conductivity, a significant milestone was reached in the last couple of years (Bar et al., 2014; Bar and Basak, 2014). Ionic conductivity, $\sigma_{\text{Li}^+} \sim 10^{-4} \text{ S cm}^{-1}$ at ambient temperatures was achieved for a new class of quasi-solid random semi-IPN systems notably without any external plasticization (Bar et al., 2014; Bar and Basak, 2014). Efficiency of a DSSC largely depends upon the *physico-chemical* properties of titania including the surface area-to-volume ratio, particle size, phase, morphology, crystallinity and dye absorption capability. Over the years, various nanostructured titania with different particle sizes, morphologies, and crystalline phases have been evaluated as photoanodes in attempts to enhance the overall cell efficiency (Yu et al., 2011, 2013; Shiu et al., 2012; Cheng et al., 2013; Tetreault and Gratzel, 2012). In recent efforts, anatase nanocuboids with exposed high energy (001) facets and high surface area is demonstrated to yield photoanodes with improved efficiencies owing to better electron transport, improved dye adsorption and better scattering ability (Illa et al., 2016; Peng et al., 2016). This study combines the advantage offered by such photoanodes fabricated from anatase nanocuboids (Illa et al., 2016) and paired with a quasi-solid polymeric electrolyte (Bar et al., 2014) to successfully achieve enhanced efficiencies along with prolonged stability. A comprehensive performance evaluation of the test cells as a function of photoanode and light intensity reaffirms the distinct possibility of achieving stable DSSCs with prolonged lifetime.

2. Experimental

2.1. Materials

The chemicals for the synthesis of polyurethane based semi-IPN network are castor oil (CO, BSS grade), polyethylene glycol (PEG, $M_n = 4000$, Sigma-Aldrich), polyethylene glycol dimethylether (PEGDME, $M_n = 500$, Sigma-Aldrich), 4,4'-methylene bis(phenyl isocyanate) (MDI, Merck), N,N-dimethylaniline (DMA, Sigma-Aldrich), Lithium iodide (LiI , Sigma-Aldrich), Iodine (I_2 , Sigma-Aldrich) and used as received without further purification. The solvents tetrahydrofuran (THF, Rankem) and acetonitrile (CH_3CN , S.D. Fine-Chem Ltd., India) were dried prior to use. For the synthesis of anatase nanocuboids, chemicals used are ammonium fluoride (NH_4F , Sigma-Aldrich), titanium tetrachloride (TiCl_4 , Merck) along with deionized water (18 M Ω -cm). Chemicals used for fabrication of photoanode paste are ethylcellulose (Sigma-Aldrich), α -terpineol (Sigma-Aldrich) and ethanol (s.d. Fine Chemicals). *Cis-bis(isothiocyanato) - bis (2,2'-bipyridyl-4,4'-dicarboxylato) - ruthenium(II) bis-tetrabutyl ammonium* (N719 dye, Sigma-Aldrich) was used as a dye, acetonitrile (Sigma-Aldrich), valerionitrile (Sigma-Aldrich), *tert*-butanol (> 99.0%, Sigma-Aldrich), 4-*tert*-butylpyridine (Sigma-Aldrich), iodine (Sigma-Aldrich), 1-butyl-3-methyl-imidazolium iodide (BMII, Sigma-Aldrich), guanidinium thiocyanate (GSCN, Sigma-Aldrich) were used to prepare the conventional liquid electrolyte. Commercially available titanium dioxide nanopowder (P25, 21nm, Sigma-Aldrich) is used as reference material and surlyn (25 μm obtained from Dyesol) is used as separator and sealant.

2.2. Synthesis of PEG-PU/PEGDME semi-IPN electrolytes

The semi-IPN electrolytes are synthesized following the previously established protocol (Bar et al., 2014; Bar and Basak, 2014). In a typical synthesis, isocyanate terminated polyurethane is synthesized by reacting castor oil and MDI in THF for one hour in an inert atmosphere. To this pre-polymer, PEG, $M_n = 4000$ is added along with DMA to catalyze the network formation. Concurrently, requisite amount of LiI/I_2 in mole ratio 1:0.1 was dissolved in PEGDME $M_n = 500$ in THF/acetonitrile (1:1 v/v) mixed solvent system and added to the reaction mixture so as to achieve an overall salt concentration of ca. 1 M in the final electrolyte composition. The weight ratio of PEG-PU/PEGDME is (30:70) and a total $-\text{NCO}/-\text{OH}$ ratio = 1.2 is maintained. The reaction is carried out until a viscous homogeneous polymer mix is obtained. The polymer so synthesized is casted in a Teflon mould and cured at room temperature for 24 h followed by further curing at 80 °C for 48 h to ensure the completion of isocyanate reaction. Post curing the films of quasi-solid semi-IPN matrices are characterized to ascertain their *physico-chemical* and electrochemical properties. For test cells fabrication, the electrolyte solutions are directly casted and spin-coated on the dye adsorbed photoanodes followed by the curing steps.

2.3. Synthesis of anatase titania nanocuboids

Following a previously optimized method in our group anatase TiO_2 nanocuboids with exposed high energy (001) facets are achieved via a simple one-step hydrothermal route (Illa et al., 2016). In a typical synthesis, 13.6 mM of TiCl_4 is added to 50 mL of deionized water containing ammonium fluoride (NH_4F , 27 mM). The solution is immediately transferred into a 75 mL Teflon lined autoclave and kept in an oven at 180 °C for 24 h. After completion of reaction, the autoclave is allowed to oven cool prior to recovering the product. Repeated centrifugation and washing cycles of the precipitate carried out with deionized water and finally with ethanol is followed by drying the samples overnight at 60 °C.

DSSC test cell fabrication: Titania paste is made following a previously reported method (Illa et al., 2016). The synthesized anatase nanocuboids are dispersed in ethanol and sonicated for 30 min. To this

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