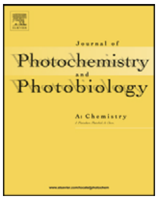
Journal of Photochemistry and Photobiology A: Chemistry 207 (2009) 224–230

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



High efficiency quasi-solid-state dye-sensitized solar cell based on polyvinyidene fluoride-*co*-hexafluoro propylene containing propylene carbonate and acetonitrile as plasticizers

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ARTICLE INFO

Article history:
Received 14 January 2009
Received in revised form 15 May 2009
Accepted 16 July 2009
Available online 24 July 2009

Keywords:
Dye-sensitized solar cell
Gel polymer electrolyte
TiO_2 morphology
Organic iodide
Electrochemical impedance spectroscopic

ABSTRACT

Quasi-solid-state dye-sensitized solar cells (DSSCs) with different weight ratios of polyvinyidene fluoride-*co*-hexafluoro propylene (PVDF-HFP) containing two different plasticizers such as propylene carbonate (PC) and acetonitrile (AN) were fabricated and the effects of TiO_2 morphology, light intensities as well as different organic iodides on the solar cell performance were studied. Two TiO_2 photoelectrodes were designed by the coating of low (P1) and high molecular weight poly(ethylene glycol) (P2) incorporated into the TiO_2 suspension. The DSSCs fabricated with the P2 TiO_2 electrode show better performance in terms of short-circuit current densities (J_{SC}) and conversion efficiencies than the P1 for all the weight percentages of PVDF-HFP containing both plasticizers. Further, the maximum current density (J_{SC}) and conversion efficiency of PVDF-HFP containing different organic iodides follow the order: TBAI > TPAI > NH_4I irrespective of the solvents and light intensity. A good conversion efficiency of 6.74% with J_{SC} of 16.04 mA/cm^2, an open-circuit voltage (V_{OC}) of 0.657 V and a fill factor of 0.64 under illumination of 100 mW/cm^2 was obtained for the DSSC with 10% of PVDF-HFP containing 0.4 M of TBAI and 0.04 M of I_2 in PVDF-HFP/AN system.

1. Introduction

Photoelectrochemical solar cells based on nanostructured dye-sensitized titanium dioxide have attracted great interest in the scientific community as a low cost alternative to the convention silicon solar cells [1,2]. A recent review work presenting an extensive listing of the highest independently confirmed efficiencies for solar cells and modules quotes that an impressive solar to electrical energy conversion efficiency of 11% can be achieved by using these types of solar cells [3]. The electrolyte used in the cell is composed of I^-/I_3^- redox couple dissolved in organic solvents [4]. However, liquid electrolytes can lead to major technological problems associated with performance limitation in long-term operation due to sealing difficulties. Hence, in order to improve the long-term stability, several kinds of strategies have been attempted to replace the liquid electrolytes by solid-state conductors such as p-type inorganic semiconductors [5] or with solid-state hole conductors [6,7]. However, the imperfect contact between the dye anchored electrode and the hole conductor in the above systems leads to inefficient hole transport resulting in the low efficiency.

In order to overcome the above problem, few alternative research works have been explored recently employing solid polymer electrolytes (SPEs). These SPEs have emerged as an exciting class of novel polymer materials with potential applications in electrochromic windows, rechargeable batteries and other devices [8]. They offer many advantages such as fast ion transport, plasticity, electrochemical stability and the ease of fabricating thin films. In one such class of polymer electrolytes, widely known as “gel polymer electrolytes”, high conductivities are obtained by trapping a liquid electrolyte solution in polymer cages formed by the host matrix. Owing to their unique hybrid network structure, gels have both the cohesive properties of solids and diffusive transport of liquids and they have been characterized by high ambient ionic conductivity and long-term durability on the devices.

It is well-known that the ionic conductivity of polymer electrolytes can be enhanced using plasticizers. A plasticizer can be defined as a chemical which reduces the stiffness of an amorphous polymer. It can interact with the polymer chains on the molecular level so as to speed up the viscoelastic response of the polymer and increase the ionic mobility in the electrolyte significantly.

The first attempt to use gel electrolytes in quasi-solid-state dye-sensitized solar cells (DSSCs) was done by Cao et

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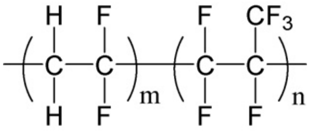
doi:10.1016/j.jphotochem.2009.07.014



Scheme 1. The chemical structure of PVDF-HFP.

al. using poly(acrylonitrile) dissolved in ethylene carbonate/ propylene carbonate/acetonitrile with specific concentration of NaI [9]. After this, there are lot of reports in the literature on the quasi-solid-state photoelectrochemical solar cells constructed with various gel electrolytes such as poly(acrylonitrile) [10–14], poly(ethyleneoxide) [15–17], poly(oligoethyleneglycol methacrylate) [18], poly(siloxane-*co*-ethylene oxide) [19], poly(butylacrylate) [20] and polyvinyidene fluoride-*co*-hexafluoro propylene (PVDF-HFP) [21–25] with different plasticizers. Among the various gel electrolytes mentioned above, PVDF-HFP (Scheme 1), shows relatively high ionic conductivities at ambient temperatures and it has been successfully used as the quasi-solid-state materials in combination with room temperature ionic liquids [23–25] showing good conversion efficiencies. Further, fluorinated polymers are potentially stable even in the presence of TiO_2 and Pt nanoparticles, which underline their suitability as a quasi-solid electrolyte in terms of long-term stability of the DSSCs [26–27]. Hence, at first, performances of the DSSC fabricated with PVDF-HFP containing PC and AN as the plasticizers having TiO_2 photoelectrodes prepared under two different conditions were investigated in this work. Further, the influence of different light intensities at different weight percentages of PVDF-HFP on the photovoltaic behavior was characterized. Finally, the effect of different cations on the redox behavior of $I^-/I_3{}^-$ was also studied.

2. Experimental details

2.1. Materials

Anhydrous LiI, I_2, poly(ethylene glycol) (PEG) and 4-tertiary butyl pyridine (TBP), acetonitrile (AN), propylene carbonate (PC) and tertiary butanol were obtained from Merck. Tetrabutylammonium iodide (TBAI, +98%), tetrapropylammonium iodide (TPAI, +98%) and titanium (IV) isopropoxide (+98%) were from Acros and used as such. Ammonium iodide (NH_4I) and PVDF-HFP (molecular weight = 400,000) were obtained from Aldrich. The cis-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium (II) (N3) was obtained from Solaronix, (Aubonne, Switzerland).

2.2. Preparation of the TiO_2 electrode

The TiO_2 electrodes were prepared by sol–gel process in acid medium according to the procedure reported in the literature [4,28]. Titanium (IV) isopropoxide (72 ml, 98%, Acros) was added to 430 ml of 0.1 M nitric acid solution with constant stirring and the colloidal solution was heated to 85 °C simultaneously for 8 h. The mixture was cooled down to room temperature and filtered. Then the filtrate was heated in an autoclave at 240 °C for 12 h in order to allow the TiO_2 particles to grow uniformly. The solution was concentrated to 13 wt% and two types of pastes namely P1 and P2 were prepared by adding 30 wt% (with respect to TiO_2) of PEG with the corresponding molecular weights of 20,000 and 200,000, respectively to the above solution in order to control the pore diameters and to prevent the film from cracking during drying.

These two TiO_2 pastes (P1 and P2) were coated on a fluorine-doped tin oxide (FTO) glass plate using glass rod (the sheet resistivity of FTO is 8 Ω/square). After this, these TiO_2 photoelectrodes were dried in the air at room temperature for 30 min followed by sintering at 500 °C in a hot-oven at a rate of 5 °C/min for another 30 min. An active area of 0.25 cm^2 was selected from sintered electrode and the electrodes were immersed in 3×10^{-4} M solution of N3 dye containing acetonitrile and tertiary butanol (volume ratio of 1:1) for 24 h. Pt (100 nm thick) sputtered on FTO was used as the counter electrode.

2.3. Preparation of PVDF-HFP gel electrolytes and cell assembly

The supporting electrolyte was prepared as follows: the required weight percentage of PVDF-HFP along with I_2 (0.05 M), (0.5 M of XI, where X = $NH_4{}^+$, TBA^+, and TPA^+) were dissolved in either AN or PC and stirred at 70 °C for 6 h. When the electrolyte was cooled down, it became gel and was used as such. For measuring long-term stability, the cell was fabricated by keeping an ionomer resin (thickness of 50 μm, Dupont, USA) between the two electrodes and two holes were made on the resin. The whole set-up was heated at 100 °C on a hot plate till all the resin had been melted and the electrolyte was injected into the space between the electrodes through these two holes. Finally, these two holes were sealed completely by the Torr Seal® cement (Varian, MA, USA). For other measurements, the gel electrolyte was heated at 70 °C and immediately, it was sprayed onto the dyed TiO_2 electrode followed by clipping it with Pt electrode.

2.4. Photovoltaic measurements

The TiO_2 film thickness was measured using a profilometer (Sloan Dektak 3030). The TiO_2 surface area, pore diameter, pore volume, and particle diameter were measured by Brunauer–Emmett–Teller (BET) method, using accelerated surface area and porosimetry (Micrometrics Instruments ASAP 2010). The photoelectrochemical characterizations of the DSSCs were carried out by using an AM 1.5 simulated light radiation. The light source was a 450 W Xe lamp (#6266, Oriel) equipped with a water-based IR filter and AM 1.5G filter (#81075, Oriel).

Conductivity measurement of solution was performed by impedance spectroscopy with two Pt electrodes conductance cell where the area of the each Pt electrode is 1 cm^2 and the distance between the two electrodes is 1 cm. The cell constant is 0.54 as calibrated from the standard aqueous KCl solution. Photoelectrochemical characteristics and the electrochemical impedance spectra measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands) under different light illuminations. The frequency range explored was from 10 mHz to 65 kHz. The applied bias voltage and ac amplitude were set at open-circuit voltage of the DSSCs and 10 mV between the FTO/Pt counter electrode and the FTO/TiO_2/dye working electrode, respectively [29]. The impedance spectra were analyzed by an equivalent circuit model interpreting the characteristics of the DSSCs [25,30]. The structural nature of TiO_2 was investigated using Scanning Electron Microscopy (SEM, Hitachi S-4700).

3. Results and discussions

3.1. Photovoltaic studies of the DSSC

3.1.1. The influence of TiO_2 morphology on DSSC

Micrographs of the TiO_2 electrodes with the corresponding coating material of P1 and P2 obtained from SEM were shown in Fig. 1a and b respectively. Highly porous nanostructure could be observed for both the thin films from the SEM micrographs. However, it is also observed that the TiO_2 electrode coated with P2 shows high porosity and P1 shows denser structure. Further analysis of various parameters such as surface area, pore volume and pore diameter