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Characterization of poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) nanofiber membrane based quasi solid electrolytes and their application in a dye sensitized solar cell

T.M.W.J. Bandara [a, b, c, d, *], A.M.J.S. Weerasinghe [c, e], M.A.K.L. Dissanayake [c, e], G.K.R. Senadeera [e, f], M. Furlani [b, d], I. Albinsson [d], B.-E. Mellander [b]

[a] *Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka*
[b] *Department of Physics, Chalmers University of Technology, Gothenburg, Sweden*
[c] *Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka*
[d] *Department of Physics, University of Gothenburg, Gothenburg, Sweden*
[e] *National Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*
[f] *The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka*

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ABSTRACT

The electrolyte plays a major role in dye sensitized solar cells (DSSCs). In this work a quasi-solid state (gel) electrolyte has been formed by incorporating a liquid electrolyte made with KI dissolved in ethylene carbonate (EC) and propylene carbonate (PC) co-solvent in poly (vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) co-polymer nanofiber membrane prepared by electrospinning. SEM images of the electrolyte membrane showed the formation of a three-dimensional network of polymer nanofibers with diameters between 100 and 300 nm and an average membrane thickness of 14 μm. The electrolyte was characterized by FTIR and differential scanning calorimetry (DSC) measurements. The DSSCs fabricated with this electrolyte were characterized by current-voltage and Electrochemical Impedance Spectroscopy (EIS) measurements. DSC thermograms revealed that the crystallinity of the PVdF-HFP nanofiber is 14% lower than that of the pure PVdF-HFP polymer while the FTIR spectra showed a reduced polymer-polymer interaction in the nano fiber based gel electrolyte. The DSSCs fabricated with nanofiber based gel electrolyte showed an energy conversion efficiency of 5.36% under 1.5 a.m. solar irradiation, whereas the efficiency of the DSSC made with the liquid electrolyte based cell was 6.01%. This shows the possibility of replacing the liquid electrolyte in DSSCs by electro-spun polymer nanofiber based gel electrolyte and thereby minimizing some major drawbacks associated with liquid electrolyte based solar cells while maintaining a reasonably high efficiency.

1. Introduction

Today, energy has become a key driving force of day-to-day lives of people and economic growth of a country [1]. Solar energy has the potential to meet a substantial part of our future energy demand [2]. A majority of the commercial photovoltaic devices that are available today are based on silicon. However, in recent time dye sensitized solar cells (DSSCs) have gained much attention due to the simple and low cost cell fabrication process compared to conventional silicon solar cells. Most of the DSSCs are primarily composed of a nano-crystalline titanium dioxide (TiO_2) photoanode sensitized by a dye which acts as the photosensitizer, a counter electrode and an electrolyte separating the two electrodes. In a DSSC photo-excitation occurs at the dye adsorbed on to TiO_2 and photo-generated electrons are injected into the conduction band of the semiconducting TiO_2 layer. The oxidized photosensitizing dye is regenerated by redox reactions taking place at the interfaces facilitated by the electrons transferred by the external circuit to the counter electrode [3].

Many studies have been conducted to replace the liquid

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* Corresponding author. Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka.
E-mail addresses: awijendr@yahoo.com, bandara@chalmers.se (T.M.W.J. Bandara).

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electrolyte used in DSSCs by a quasi-solid state (gel) electrolyte in order to overcome durability and stability issues caused by liquid volatility, leakage and dye desorption [4–6]. Gel electrolytes reduce the risk for internal shortening and leakage issues and are more suitable for commercial production [7,8]. Another recent development for DSSC electrolytes is to use quasi solid (gel) electrolytes made by soaking a polymer nano fiber membrane in a solution electrolyte [9]. These gel electrolytes with a structured network of polymer nanofibers exhibit ionic conductivity values close to those of a liquid electrolyte but maintain a quasi-solid structure thereby reducing solvent evaporation and leakage and providing mechanical stability. In addition, since the nano-fiber membrane acts as a separator the fabrication of this kind of cells is relatively easy [10].

There are several methods to produce polymer nano-fibers such as electrospinning, template methods, vapor growth, and phase separation [11–13]. Out of these, the electrospinning method which has been known for more than a century, has become popular for the production of polymer nanofibers for various applications [14–16].

In this study we have used the co-polymer poly-(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP), because when it is in the gel state it shows a low glass transition temperature, high solubility for organic solvents and low crystallinity [17,18]. Accordingly, there are more amorphous domains in PVDF–HFP which could absorb large amounts of liquid electrolytes and gain sufficient mechanical integrity to produce a free-standing electrolyte membrane. PVdF-HFP polymer nanofiber membranes with different thicknesses were produced by electrospinning and used to prepare nanofiber gel electrolytes. Ion/polymer/solvent interactions of the polymer nanofiber gel electrolytes were investigated using Fourier Transform Infrared spectroscopy (FTIR) while thermal transitions were studied using Differential Scanning Calorimetry (DSC). DSSCs were fabricated under identical conditions with (a) a liquid electrolyte, (b) a polymer nanofiber gel electrolyte, and (c) a conventional gel electrolyte and their performances were compared. The interfacial charge transfer resistances of the three different types of DSSCs were investigated by electrochemical impedance spectroscopy measurements (EIS).

2. Experimental

2.1. Materials

Ethylene carbonate (EC), propylene carbonate (PC), iodine chips (I_2) and KI with purity greater than 98% were purchased from Fluka. PVdF-HFP pellets (Mw ~ 400,000) were purchased from Sigma Aldrich. Ruthenizer 535-bisTBA (N719) sensitizer dye and fluorine doped SnO_2 coated (FTO) glass (sheet resistance 12 Ω/sq) was purchased from Solaronix SA.

2.2. Preparation of the PVdF-HFP nanofiber membranes

PVdF-HFP nano fibers were prepared using a Nabond electrospinning system (NaBond Technologies, Hong Kong). The electrospinning solution was prepared by dissolving PVdF-HFP pellets (1.0 g) in 9.0 ml of DMF (Sigma Aldrich) and stirring overnight to form a transparent homogenous solution. A 10 kV DC voltage was applied between the spinneret and the drum collector and the syringe pump flow rate was adjusted to 1 ml h^{-1}. The electro-spun PVdF-HFP nano fibers were collected onto platinized glass plates attached to the drum collector for about 3 min. For SEM measurements the electro-spun PVdF-HFP nano fibers were collected onto FTO glass plates. The rotational speed of the drum collector during nanofibre deposition was 825 rpm and the distance between the collector and the syringe tip was 6.5 cm.

2.3. Fabrication of the DSSC's

The first colloidal suspension was prepared by grinding together 0.25 g of TiO_2 (Evonic P90 Aeroxide) and 0.1 M HNO_3. A compact layer of TiO_2 of fine particles of size ~14 nm was deposited on precleaned fluorine doped tin oxide (FTO) glass plate (Nippon sheet glass 10–12 Ω/sq) by spin coating the suspension at 3000 rpm, sintering it at 450 °C for 45 min and by slowly cooling it down to ambient temperature. The size of the FTO glass plate was ~1 cm × 0.5 cm and a half of the FTO plate was covered by a peace of scotch tape to prevent coating TiO_2 on the area needed for the electrical contact. Therefore, TiO_2 coated area of the cell was ~0.5 cm × 0.5 cm. Another TiO_2 colloidal suspension was prepared by mixing 0.25 g of TiO_2 (Degussa P-25), 0.1 M nitric acid, 0.02 g triton X-100 and 0.05 g PEG 1000 (Fluka) and the resulting paste was spread over the first TiO_2 compact layer by doctor blade technique to obtain a photoanode with larger particle size (~21 nm) and an active cell area of 0.25 cm^2 was used. The resulting two layer TiO_2 photoanode was finally sintered again at 450 °C and allowed to cool back to room temperature. These electrodes were then immersed in an ethanolic (Di-tetrabutylammonium *cis*-bis(isothiocyanato)bis (2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium (II)) dye solution for 24 h for dye absorption in order to prepare the dye sensitized TiO_2 photo-anode.

The electrolyte solution was prepared by dissolving 0.06 g of KI and 9.2 mg of I_2 in an EC (0.4 g) and PC (0.4 g) mixture. Few drops of the liquid electrolyte were carefully placed on the nanofiber membrane deposited platinum plate and kept for about 1 h for the absorption of the electrolyte solution by the nanofiber matrix to form a quasi-solid-state (or gel) electrolyte. The excess electrolyte was carefully wiped off to make sure that no free electrolyte solution was left on the platinized counter electrode. Dye sensitized solar cells were fabricated in the configuration FTO/TiO_2/electrospun nanofiber membrane gel electrolyte/Pt/FTO with an active cell area of 0.25 cm^2. For comparing the device performance two other types of DSSC's were also fabricated, one with the liquid (solution) electrolyte and the other with a conventional gel electrolyte with PVdF-HFP co-polymer.

The liquid electrolyte was prepared using the same composition given above and the conventional gel polymer electrolyte samples were prepared by using the weights of PVdF-HFP (0.1 g), EC (0.40 g) PC (0.40 g) KI (0.06) and iodine (0.009). The relevant weights of EC, PC, Pr_4NI and KI were mixed in a closed glass bottle by continuous stirring at room temperature for a few hours. Subsequently, PVdF-HFP was added to the above mixture and heated to about 125 °C for a few minutes until a transparent slurry was obtained. After the mixture was cooled down to about 50 °C, I_2 chips were added and the mixture was continuously stirred for about an hour to get the conventional gel polymer electrolyte.

2.4. Measurements

The morphology of the electro-spun polymer nanofiber membranes were observed by Scanning Electron Microscopy (SEM; HITACHI-SU8220). The thicknesses of the membranes were determined from the SEM images of their cross sections. The current density versus cell potential (*J-V)* characteristics of the DSSCs having an active cell area about ~0.25 cm^2 were measured using a computer-controlled Keithley 2000 multimeter with Potentiostat/Galvanostat HA-301 under the illumination of 1000 W m^{-2} using a Xenon 500 lamp with an AM 1.5 filter. Electrochemical Impedance Spectroscopy (EIS) measurements were performed on the DSSCs using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N coupled to a FRA32 M Frequency Response Analyzer (FRA) covering the 2 Hz to 100 kHz frequency range and using an AC voltage signal