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An optimized poly(vinylidene fluoride-hexafluoropropylene)–NaI gel polymer electrolyte and its application in natural dye sensitized solar cells

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ABSTRACT

Gel type polymer electrolytes with PVDF-HFP as polymer host, NaI salt and EC/PC as plasticizers have been prepared and optimized for use in a dye sensitized solar cell (DSSC). The polymer electrolyte containing 48 wt. % (PVDF-HFP)–32 wt. % NaI–20 wt. % (EC/PC) exhibits the highest room temperature conductivity of 1.53×10^{-4} S cm^{-1}. This electrolyte has been used in the fabrication of a DSSC with the configuration FTO/TiO_2/natural dye/electrolyte/Pt/FTO. The natural dyes used anthocyanin and chlorophyll were solvent extracted from black-rice and *pandanus amaryllifolius* leaves respectively. UV-vis absorption spectra of anthocyanin, chlorophyll and the mixture of anthocyanin and chlorophyll in the volume ratio 1:1 were recorded. The anthocyanin shows an absorption peak at 532 nm. In the same region chlorophyll absorption shows a peak at 536 nm and also has a prominant peak at 665 nm. On mixing anthocyanin and chlorophyll two prominant peaks are observed at 536 and 665 nm. The DSSC containing the dye mixture exhibits the best performance with a short-circuit current density of 2.63 mA cm^{-2}, open-circuit voltage of 0.47 V, fill factor of 0.58 and the highest photo-conversion efficiency of 0.72% under the illumination of 100 mW cm^{-2} white light. Under illumination of lower light intensity of 60 mW cm^{-2} and 30 mW cm^{-2}, the fill factor enhanced from 0.58 to 0.59 and 0.60 and the photo-conversion efficiency increased from 0.72% to 1.11% and 1.85% respectively.

1. Introduction

There is considerable interest shown by the research community on polymer electrolytes and their applications in the fabrication of dye sensitized solar cells (DSSCs) that have appealing attributes such as low-cost, easy fabrication and low impact on the environment [1–4]. At present, DSSCs utilizing liquid electrolytes with a iodide/triiodide (I^-/I_3^-) redox couple and ruthenium dyes attract more attention and such DSSCs have reached high overall efficiency of about 11% [5]. Recently, a DSSC with a porphyrin based dye and a liquid electrolyte with a cobalt-based redox couple has produced a record photo-conversion efficiency of 12.3% [6]. Liquid electrolytes however, have life time limitations due to problems such as evaporation and solvent leakage. To overcome these problems, many research groups have been concentrating on alternative electrolytes in the form of solid or gel type polymer electrolytes [7]. Various polymer hosts such as polyacrylonitrile (PAN), poly(vinyl chloride) (PVC), polymethylmethacrylate (PMMA) and Polyvinylidene fluoride (PVDF) have been used to prepare such polymer electrolytes [8]. Recently, Poly(vinylidene fluoride-co-hexafluoropropylene) or PVDF-HFP, has received great attention as one of the promising host polymers for polymer electrolytes because of its excellent mechanical strength and electrochemical stability [9]. The degree of crystallinity of the highly crystalline PVDF is greatly reduced when copolymerised with HFP. The remaining crystallinity in the PVDF-HFP retains sufficient mechanical stability of the system.

Beside electrolytes, dye is another key component in a DSSC. The dye plays the key role in harvesting sunlight and converting solar energy into electric energy. Ruthenium complexes are effective sensitizers that exhibit high energy conversion efficiencies in DSSCs [10]. However, these dyes contain Ru metal compound complexes, which are expensive and produce environmental pollution [11]. Another approach is to use natural dyes extracted from fruits, flowers and plant leaves which are easily obtainable, cheap and simple in their preparation and environment friendly; but suitable natural dyes that can give good efficiencies are yet to be found. Most of the work reported in the literature on natural dye based DSSCs have utilized anthocyanin obtained from different natural sources as the natural dye sensitizer as it is expected to have good

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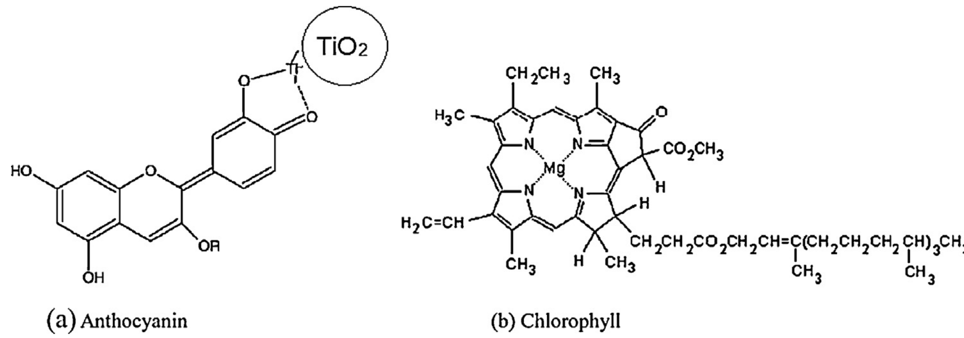

Fig. 1. Basic molecular structures of (a) anthocyanin, and (b) chlorophyll dyes.

binding with TiO_2 surface [12–14]. Chlorophyll is the other popular dye used. Good reviews on various natural dyes used for DSSCs are given in references 15 and 16.

In this work, a plasticized polymer electrolyte system composed of PVDF-HFP, sodium iodide (NaI) and equal weight of ethylene carbonate (EC) and propylene carbonate (PC) as the binary plasticizer was used to fabricate DSSCs with natural dye sensitizers. To find the best composition of the electrolyte for the DSSC fabrication, different compositions of polymer elecrolytes were prepared and characterized by FTIR, XRD and EIS measurements. The ethylene carbonate (EC) and propylene carbonate (PC) were chosen as plasticizers due to their promising and compatible properties for ionic conduction in polymer electrolytes such as high dielectric constant and low viscosity. EC has a dielectric constant of 89 and viscosity of 1.90 cp while PC has a dielectric constant of 64.4 and viscosity of 2.53 cp at 25 °C [17]. Anthocyanin extracted from black rice and chlorophyll from *pandanus amaryllifolius* leaves were used individualy and as a 1:1 mixutre as natural dye sensitizers. Basic molecular structures of anthocyanin and chlorophyll are shown in Fig. 1. The carbonyl and hydroxyl groups present in anthocyanin molecules help it to bind well to the surface of TiO_2 of the porous film and thereby help the photoelectric conversion in the DSSC [18]. Chlorophyll, a natural photosensitizer for photosynthesis in green plants, is another potential compound as a photosensitizer in the visible region, has already been tested in DSSCs [19].

Earlier work reported in the literature on DSSCs with natural chlorophyll and anthocyanin dyes were fabricated with liquid based iodide electrolytes which are prone to leakage and flammability [20,21]. In this work we have used PVDF-HFP based plasticized plolymer electolytes to overcome the problems faced with liquid electrolytes. To our best knowledge no such work has been reported in the literature.

2. Experimental

2.1. Materials

Poly(vinylidenefluoride-hexafluoropropylene) of MW 400,000, sodium iodide salt and chloroplatinic acid were procured from Sigma-Aldrich. High purity (99%) acetone, ethylene carbonate and propylene carbonate were purchased from Fluka. TiO_2 paste PST-18NR was obtained from JGC Catalyst and Chemicals Ltd. Japan. The TiO_2 compact layer solution, diisopropoxytitanbis(acetylacetonate), purchased from Aldrich was diluted with ethanol to obtain 0.38 M and fluorine-doped tin oxide (FTO) glasses were supplied by Solaronix.

2.2. Preparation of polymer electrolytes

In this work, electrolytes with PVDF-HFP as the polymer host, sodium iodide as the doping salt and a mixture of equal weight (EC/PC) as a binary plasticizer were prepared by solvent casting method. The compositions of unplasticized electrolyte (i) and plasticized electrolyte (ii) are as shown below:

(i) x wt. % (PVDF-HFP)–y wt. % NaI, where x = 100, 90, 80, 70, 60, 50 and y = 0, 10, 20, 30, 40 and 50.
(ii) x wt. % [(PVDF-HFP)/NaI]–y wt. % (EC/PC), where x = 90, 80, 70, 60, 50 and y = 10, 20, 30, 40 and 50; (PVDF-HFP)/NaI fixed at 60/40 wt. ratio.

(PVDF-HFP)-NaI electrolytes were prepared using the following procedure. A fixed amount (1.00 g) of PVDF-HFP was continuously stirred at 60 °C in acetone under reflux for 1 hour to form a homogenous polymer solution and it was allowed to cool down. When the solution reached room temperature, various amounts of NaI salt from 0 to 50 wt.% were added into the polymer solution and stirred vigorously for about 24 hours until the polymer-salt solution becomes homogenous. These polymer-salt solutions were cast onto separate clean glass petri dishes to allow the solvent to evaporate slowly until films are formed. The films were kept in a dessicator for further drying before they were chracterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Electrochemical impedance spectroscopy (EIS). EIS technique was used to determine the conductivity of each composition. The highest conducting (PVDF-HFP)-NaI composition was chosen to make the plasticized polymer electrolytes. A mixture of EC and PC of 1:1 weight ratio was prepared to be used as the binary plasticizer. 10–50 wt. % of the plasticizer mixture were added to the highest conducting polymer-salt composition in order to find the best composition of polymer-salt-plasticizer for the DSSC fabrication. 10 wt. % iodine (of salt content) was added into the best conducting plasticized polymer electrolyte system to have I^-/I_3^- redox couple in the polymer electrolyte.

2.3. Preparation of dye materials

Three types of dye solutions were prepared for this study. (i) anthocyanin dye solution prepared from 100 g black rice immersed in 100 ml ethanol. (ii) chlorophyll dye solution prepared from 50 g fresh leaves of *pandanus amaryllifolius* or locally known as *pandan* leaves. For this, the leaves were cleaned with distilled water, rinsed with ethanol and were cut into small pieces and immersed in 50 ml ethanol. Both anthocyanin and chlorophyll solutions were kept for 24 hours in the dark before filtration to remove residues. (iii) A mixed dye solution was prepared by mixing equal volumes of anthocyanin and chlorophyll solutions. The dye solutions were mixed with tartaric acid and the *pH* was adjusted to 1 since it has been shown in our previous work that at this *pH* the absorbance of the dye is highest compared to those at other *pH* values [22].