



# Pore-filled electrolyte membranes for facile fabrication of long-term stable dye-sensitized solar cells



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## ARTICLE INFO

### Article history:

Received 6 February 2015

Received in revised form 14 May 2015

Accepted 17 May 2015

Available online 21 May 2015

### Keywords:

pore-filled electrolyte membrane

dye-sensitized solar cells

facile manufacturing process

long-term stability

## ABSTRACT

Pore-filled electrolyte membranes (PFEMs) have been prepared by employing an optimized porous substrate and stable electrolyte composition for a facile manufacturing process of dye-sensitized solar cells (DSSCs). The PFEMs could be easily loaded into a photovoltaic device without adding a traditional electrolyte injection through a hole. In order to meet the requirements of both high energy conversion efficiency and proper long-term stability, three different solvents with high boiling point, *i.e.* valeronitrile, dimethyl sulfoxide, and dimethylacetamide, were appropriately mixed as a volumetric ratio of 7:2:1, respectively. As a result, similar conductivity and viscosity as well as better chemical stability were obtained compared to those of conventional 3-methoxypropionitrile-based electrolyte. In addition, linear relations were observed between the photovoltaic efficiency and porous film properties (*i.e.* porosity and tortuosity). The DSSC employing the PFEM doped with the mixed solvent based electrolyte exhibited the photon-to-current conversion efficiency of 6.30% at one sun condition. Moreover, the long-term stability test fixed at an elevated temperature of 85 °C exhibited outstanding durability of DSSC for 500 h.

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## 1. Introduction

There has been much attention towards dye-sensitized solar cells (DSSCs) in the past decades due to their attractive features such as high energy conversion efficiency of about 12% and low energy production costs [1–5]. A DSSC is typically composed of a photoanode including dye-attached nanocrystalline TiO<sub>2</sub> layer, an electrolyte containing redox shuttles (typically I<sup>-</sup>/I<sub>3</sub><sup>-</sup>), and a counter electrode for the reduction of ions. A large number of studies have been performed over the last two decades to develop efficient photoelectrodes and cathodes for high performance DSSCs [6–8].

Although a respectable photon-to-electricity conversion efficiency has been achieved for a photovoltaic cell employing organic liquid electrolytes, some critical issues, such as the leakage and evaporation of volatile liquid solvents are still considered to be one of the significant factors limiting the long-term stability of the DSSCs. In order to overcome the obstacles, a number of studies have been performed to replace traditional volatile liquid

electrolytes with ionic liquid based gel [9] or polymer gel electrolytes [10–13]. However, for a practical use of highly viscous gel types of electrolytes, their performances such as the ion conductivities and physicochemical properties should be further improved and optimized. Moreover, an effective filling process for highly viscous gel electrolytes has not been successfully established yet even though the electrolyte filling process is of significant importance to commercialize DSSCs [14]. Conventional liquid electrolytes are typically filled into a module by injecting them through holes. However, this traditional method does not seem to be successfully applicable to the injection of highly viscous gel electrolytes. Therefore, the development of a facile and efficient electrolyte filling process should also be achieved especially for manufacturing large-area and flexible DSSC devices employing highly viscous gel electrolytes. Meanwhile, a roll-to-roll continuous process is regarded as one of the most promising manufacturing methods for the mass production of DSSCs and organic photovoltaic cells [15]. The membrane type of quasi-solid-state electrolytes could be well applicable for the cost-effective continuous manufacture of DSSC modules.

Recently, several researchers have reported the development of polymer membrane electrolytes (PMEs) for DSSCs with respectable efficiencies [16–23]. For example, Bella et al. proposed a UV-

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crosslinked type of PME, promising both high efficiency and durability for DSSC applications [16]. In addition, Yang et al. reported ultra-thin PMEs prepared by a phase inversion method using poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as a host polymer [17]. J. Chen et al. also developed PMEs comprised of porous polyethylene membranes and ionic liquid electrolytes, showing the maximum energy conversion efficiency of 2.25% at one sun condition [18]. The results of previous studies demonstrate that the electrolyte membranes, as an alternative to traditional liquid electrolytes, are successfully applicable to DSSC fabrications. However, the PMEs need to be further improved in terms of both the photovoltaic performances and a mechanical stability for easy handling in roll-to-roll processing. In addition, since they were mostly prepared by using volatile solvents such as acetonitrile (ACN), there is a drawback of solvent evaporation during the long-term operation.

In this work, therefore, we have investigated the feasibility of both pore-filled electrolyte membranes (PFEMs) and highly stable electrolyte composition, aiming at a facile manufacturing of efficient and long-term stable DSSCs. The concept of PFEMs employing porous battery separators was originally proposed by Yamaguchi et al. to prepare cost-effective ion-exchange membranes [24]. This type of electrolyte membrane has some advantages, such as low transport resistance, excellent mechanical properties, and easy mass production, etc. A variety of polymeric porous films employed as a separator in secondary batteries can be used for the substrate. The PFEMs could effectively prevent solvent leakage by filling liquid electrolyte inside the pores and also be successfully applied to a cost-effective roll-to-roll manufacturing process. The optimal electrolyte composition for efficient DSSCs was also systematically investigated to obtain a low volatility, high ion conductivity, and good chemical stability by considering solvent properties, such as boiling point, viscosity, and dielectric constant etc. Furthermore, the photovoltaic characteristics of the DSSCs were correlated with the porous properties of the PFEMs, such as porosity and tortuosity for the first time. Finally, the long-term stability of the selected PFEMs was evaluated at 85 °C for 500 h.

## 2. Experimental

### 2.1. Preparation and characterizations of electrolytes and porous substrate

Liquid electrolytes were prepared by dissolving 1-butyl-3-methylimidazolium iodide (BMImI, 0.62 M), I<sub>2</sub> (0.05 M), LiI (0.1 M)

and *t*-butylpyridine (TBP, 0.5 M) in mixed organic solvent with a high boiling point (> 150 °C). Details of the preparation for the Mixed solvent based electrolytes are described in the results and discussion section. Commercial porous battery separator films were employed as the substrate for preparing pore-filled film electrolytes and the properties of the porous substrates are shown in Table S1 (in the supplementary materials). The initial character in the code name stands for the corresponding manufacturer (i.e. S of SK Chemicals (Korea), A of Asahi Kasei E-materials Corp. (Japan), and G of W. L. Gore & Associates, Inc. (USA)) and the following number is the thickness of the substrate film. The porosity ( $\epsilon$ ) and the tortuosity ( $\tau$ ) of the porous substrates were determined by the Smolder-Franken equation and the correlation suggested by Macki-Meares, respectively [25,26]. We have also prepared porous substrates using PVdF-HFP (avg. Mw = 400,000, Aldrich) via conventional phase inversion method. A casting solution was prepared by dissolving PVdF-HFP in *N*-methyl-2-pyrrolidone (NMP) as a 10 wt% and then cast onto a glass plate using a Meyer bar coater (KP-3000 V, KIPAE E&T Co., Korea). The polymer solution coated plate was then immersed in non-solvent (i.e. distilled water, D.W.) for 20 min to induce a phase inversion. After a series of washing with D.W., the prepared porous membranes were dried in a convention oven at 80 °C for 24 h. After cleaning the porous substrates with 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution and acetone, the PFEMs were prepared by dipping them into liquid electrolyte solution for a specific time. The porous substrates were also filled with quaternized polymer electrolytes. Poly(ethylene glycol) diacrylate (PEGDA) and vinylbenzyl chloride (VBC) were chosen as the base monomers and benzoyl peroxide (BPO) was utilized for the initiation of radical polymerization. The mole ratio of PEGDA and VBC was fixed as 7:3 and BPO was added into the monomer mixture as the content of 2 wt%. The porous substrates were immersed in the monomer mixture for one hour, followed by a radical polymerization process conducted in an oven at 80 °C for 3 h. An amination process was conducted by soaking the polymerized film in a 0.5 M trimethylamine (TMA) aqueous solution for 3 h. Finally, the prepared pore-filled membranes were washed with deionized water and then dried in a vacuum oven for more than 24 h before the electrolyte doping. All chemicals were purchased from Aldrich and used without further purification.

### 2.2. DSSC fabrication

Transparent glass coated with conductive SnO<sub>2</sub>:F (FTO, 8 Ω/sq., purchased from Pilkington Co. Ltd.) was utilized as a substrate to prepare both the photoanode and counter electrodes. For the preparation of photoanode, commercial TiO<sub>2</sub> paste (18NR-T, Dyesol Ltd.) was cast onto a TCO substrate via a doctor-blade technique and successively sintered at 500 °C for 30 min (*nc*-TiO<sub>2</sub> layer thickness = ca. 9 μm). The photoelectrodes were sensitized with Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> dye (here, dcbpy = 2,2'-bipyridyl-4,4'-dicarboxylato) solution (N719, Solaronix, 40 mM, dissolved in ethanol) overnight. A platinum layered counter electrode was prepared by spin-coating H<sub>2</sub>PtCl<sub>6</sub> solution (0.05 M in isopropanol) onto a TCO substrate and successive sintering at 400 °C for 30 min. Hot-melt film (Bynel<sup>®</sup>, DuPont) with a thickness of about 60 μm was employed as a sealant. It was inserted between the photoanode and counter electrode together with prepared PFEM and then hot-pressed for the fabrication of the cells (at 130 °C for 15 sec).

### 2.3. Characterizations

The ion conductivity of the electrolytes was measured using a lab-made four-point probe conductivity cell connected to impedance analyzer (1260A, Solartron). The photovoltaic characteristics of the prepared DSSCs (i.e. short-circuit current ( $J_{sc}$ ), open-circuit

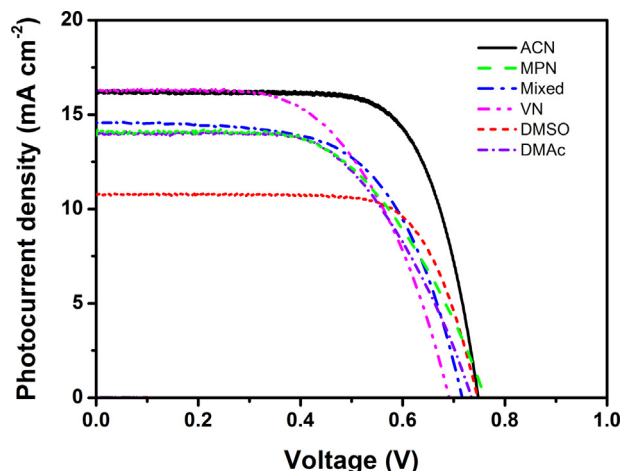


Fig. 1. J-V curves of DSSCs employing liquid electrolytes with different solvents (measured at one sun illumination).

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