



Highly stable dye-sensitized solar cells with quasi-solid-state electrolyte based on Flemion

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Abstract

A polymer gel electrolyte containing Flemion[®] (a perfluorocarboxylated polymer) as polymer matrix, lithium iodide, iodine, 1,2-dimethyl-3-propylimidazolium iodide (DMPII) and 4-tert-butylpyridine (TBP) was developed for quasi-solid-state dye-sensitized solar cells (DSSCs). The Flemion-based electrolyte was gelled by heating the Flemion solution to evaporate the ethanol solvent. Scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy suggested three regions in the Flemion-based gel electrolyte: the fluorocarbon polymer frame, the ion cluster, and their interface. The open-circuit voltage, the short-circuit current density, and the fill factor were markedly enhanced by adding TBP and DMPII, respectively, to the Flemion-based gel electrolyte. When irradiated with light at 100 mW cm^{-2} , the DSSC containing the Flemion-based gel electrolyte with 0.6 M DMPII and 0.5 M TBP exhibited an energy conversion efficiency (η) of 4.1%, while η of the acetonitrile-based DSSC was 5.1%. According to electrochemical impedance spectra, gelation greatly increased the charge transfer resistance at the TiO_2 /electrolyte interface in DSSCs containing the Flemion-based electrolyte without DMPII. However, this effect was negated by adding 0.6 M DMPII to the electrolyte. The η of Flemion-gel-based DSSCs stored for up to 4392 h decreased by less than 10%. In contrast, the η of Flemion-liquid-based and acetonitrile-based DSSCs decreased by 95% during 480 h storage, and by 93% during 115 h storage, respectively. This result demonstrates that Flemion-based gel electrolytes solve the leakage problem that degrades the performance of DSSCs.

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1. Introduction

Since their development in 1991 by O'Regan and Grätzel (1991), dye-sensitized solar cells (DSSCs) have been extensively researched because of their simple fabrication process,

potential for low-cost production, mild impact on the environment, and high energy conversion efficiency. A typical DSSC is constructed from transparent conductive substrates, a photoelectrode composed of TiO_2 nanoparticles, dyes, a liquid electrolyte, and a counter electrode (Hagfeldt and Grätzel, 2000; Grätzel, 2001). However, leakage and volatilization of the liquid electrolyte have seriously limited the practical applicability of DSSCs (Wang et al., 2003). To overcome these problems, many researchers have proposed replacing the liquid electrolytes with solid or quasi-solid-state

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electrolytes such as p-type semiconductors (Tennakone et al., 1995), hole-conducting organic or inorganic materials (Kumara et al., 2002; O'Regan et al., 2002), solid ion conductors (Wang et al., 2004; Byrne et al., 2013), solid solvent-free polymers (Han et al., 2005; Nogueira et al., 2001; Stergiopoulos et al., 2002), and polymer gel electrolytes (Kubo et al., 2001). The most promising of these candidate replacement materials are polymer gel electrolytes, owing to their high ionic conductivity, good interfacial filling properties, and relatively excellent long-term stability. In these electrolytes, ionic conductivity is maintained and cell leakage is suppressed because the redox solution is trapped within a polymer matrix. They also provide good contact and filling between the nanoporous TiO₂ electrode and the counter electrode. Among the many polymer gel systems investigated to date are poly(ethylene oxide) (Kim et al., 2004), poly(acrylonitrile) (Cao et al., 1995), poly(methyl methacrylate) (Yang et al., 2008), poly(acrylonitrile-co-styrene) (Wu et al., 2006) and poly(vinylidene fluoride-co-hexafluoropropylene) (Wang et al., 2002).

Here, we report on a quasi-solid state (polymer gel) Flemion[®] [(CF₂CF₂)_n-CF₂CF-O-(CF₂)_mCOOH]-based electrolyte produced by heating the Flemion solution to evaporate the ethanol solvent. Flemion, a perfluorocarboxylated polymer prepared by copolymerization of tetrafluoroethylene and carboxylated perfluorovinyl ether, was developed in 1975 by the Asahi Glass Co. Ltd. Although Flemion film is a well-known ion-exchange membrane, to our knowledge, it has not been applied in DSSC electrolytes. The resulting polymer gel electrolytes were characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The photovoltaic performance of the Flemion-gel-based DSSCs was compared with those of Flemion-liquid-based DSSCs and acetonitrile liquid-based DSSCs. The photovoltaic performance of electrolytes containing different concentrations of 1,2-dimethyl-3-propylimidazolium iodide (DMPII) was investigated in detail. The electronic and ionic processes in the Flemion-gel-based DSSCs were explored and characterized by electrochemical impedance spectroscopy (EIS). The long-term leakage resistance was evaluated in storage tests of the Flemion-gel-based DSSCs and DSSCs containing liquid electrolytes.

2. Experimental

2.1. Materials

The DSSCs were fabricated from the following materials: Flemion solution (FSS-2, a mixture of fluoropolymer and ethanol, Asahi Glass Co. Ltd), glass substrate with ITO-based transparent conductive oxide (TCO) film with a sheet resistance of approximately 10 Ωsq⁻¹ (No. 0052, Geomatec Co., Ltd.), iodine, 1,2-dimethyl-3-propyl imidazolium iodide (DMPII) and acetonitrile (Tokyo Chemical Industry Co., Ltd., Japan), anhydrous lithium iodide (Wako Pure Chemical Industries, Ltd.), di-tetrabutylam-

monium *cis*-bis (isothiocyanato) bis (2,2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) (N-719), 4-*tert*-butylpyridine (TBP) and chloroplatinic acid hexahydrate (Sigma-Aldrich), and titanium oxide paste with a particle size of approximately 20 nm (PST-18NR, JGC Catalysts and Chemicals Ltd.). The above ITO-based TCO 0052 has heat resistance properties, unlike conventional ITO-based TCO. We confirmed that the transmittance and the sheet resistance of TCO sample No. 0052 were almost same even after sintering at 500 °C for 60 min.

2.2. Preparation of electrolytes

Four kinds of electrolytes, labeled A–D, were prepared by adding iodine, lithium iodide, various concentrations of DMPII and TBP to Flemion solution by this order and stirring sufficiently and mixing under ultrasonic vibration for 30 min. The constituents of the electrolytes are summarized in Table 1. For comparison of the photovoltaic properties, a fifth electrolyte (E) was prepared using acetonitrile as a solvent instead of the Flemion solution. The Flemion-based solution was gelled by heating, first in an oven and then on a hot plate.

2.3. Fabrication of DSSCs

Fig. 1 shows the schematic of the DSSC fabrication process. The TiO₂ paste was deposited on TCO-coated glass by the screen-printing method. The obtained TiO₂ layer was annealed in a furnace at 500 °C in an N₂ atmosphere. The approximate thickness and area of the prepared porous TiO₂ layer were 9.0 μm and 25 mm² (5 mm × 5 mm), respectively. Dye adsorption was carried out by immersing the TiO₂ electrode in a 0.3 mM ethanol solution of N719 at 25 °C for 20 h. The TiO₂ electrode was removed from the N719 solution, washed with ethanol and dried. The electrolyte spacer was an 85-μm-thick polyimide film with adhesives on both surfaces and a 6 mm × 6 mm square hole. This film was then affixed to the TiO₂ electrode. Electrolyte solutions were dripped through the spacer until the electrode just began to swell. Next, the TiO₂ electrode was heated in an oven at 50 °C for 5 min followed by continuous heating on a hot plate at 125 °C for 1 min to evaporate the ethanol and to gel the electrolyte. To prepare the counter electrode, a few drops of 2 mg chloroplatinic acid hexahydrate in 1 ml ethanol solution were placed on the TCO-coated glass plates drilled with a 1 mm diameter hole. The counter electrode was heated at 400 °C for 30 min and then assembled with the TiO₂ electrode, removing any surplus electrolyte overflowing from the hole in the counter electrode. The two electrodes were separated by the spacer. Finally, the hole was sealed with vinyl tape. Four cells per each electrolyte were fabricated, and the performance on the average of four cells was compared.

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