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# Highly efficient gel-state dye-sensitized solar cells prepared using propionitrile and poly(vinylidene fluoride-co-hexafluoropropylene)

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## HIGHLIGHTS

- PVdF-HFP PGE is prepared using PPN solvent.
- $T_p$  value of 60 °C achieved for 18 wt% PVdF-HFP PGE.
- $R_{pt}$  values are lower for the gel-state cells using TiO<sub>2</sub> NFs than TiC NFs.
- Efficiency of 8.38% is obtained for the gel-state cell using 5 wt% TiO<sub>2</sub> NFs.
- The cell with 18 wt% PVdF-HFP and 5 wt% TiO<sub>2</sub> NFs exhibit high stability.

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## ABSTRACT

Propionitrile (PPN) solvent based iodide/triiodide liquid-electrolyte is utilized to prepare highly efficient poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) polymer gel electrolytes (PGEs) of dye-sensitized solar cells, aiming at improving the energy conversion efficiency as well as the stability of gel-state DSSCs. The concentrations effect of the PVdF-HFP on the properties of PGEs and the performance of the corresponding cells are studied. The results show that the in-situ gelation is performed for the PVdF-HFP concentration range of 8–18% at room temperature. However, increasing the concentration of polymer in the PGEs triggers a decrease in the diffusivity and conductivity of the PGEs, but an increase in the phase transition temperature of the PGEs. A high phase transition temperature is obtained for the PGEs with 18 wt% PVdF-HFP, which increase the long-term stability of the gel-state DSSC. By using the 18 wt% PVdF-HFP in the presence of 5 wt% TiO<sub>2</sub> nanofillers (NFs), gel-state cells with an efficiency of 8.38% can be obtained, which is higher than that achieved by liquid-state cells (7.55%). After 1000 h test at room temperature (RT) and 50 °C, the cell can retain 96% and 82%, respectively, of its initial efficiency.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) are attractive to both academics and industry because they are a promising alternative to the classic silicon solar cells in terms of lower cost, simple fabrication processes and high energy conversion efficiencies [1–4]. The DSSCs based on the ruthenium complex and zinc porphyrin dyes have shown energy conversion efficiencies high above 11% and 13%, respectively [5–8]. These high efficiencies were obtained using liquid electrolytes prepared by acetonitrile (ACN). The use of liquid

electrolytes affects the long-term stability of the DSSCs due to evaporation and leakage of the ACN [9,10]. To solve these problems, liquid electrolytes have been replaced by ionic liquids, p-type semiconductors, organic hole transport materials and gelled liquid electrolytes [11–15]. Although cells prepared by these materials have higher stability, their energy conversion efficiencies are much lower than those of the corresponding liquid-state cells. This result is ascribed to the lower conductivity and/or to the poor interfacial contact between the solid materials and nano-structured TiO<sub>2</sub> electrodes [11–15].

Polymer gel electrolytes (PGEs) have received much attention due to their high conductivity and thermal stability and, therefore, are considered a potential alternative for liquid electrolytes [16–26]. However, the measured efficiencies of such gel-state cells have been lower than those of the liquid versions because of the

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poor penetration of the viscous PGEs in the mesoporous matrix of the photoelectrodes. In response, gel-electrolyte with an in-situ gelation property was proposed to improve the filling ability of PGEs in the TiO<sub>2</sub> film. For the in-situ gelation system, the gelation process performs slowly at the room temperature and, therefore, the electrolyte can be injected into the cell at the liquid state and then, performs gelation inside the cell. The in-situ gelation was performed by using poly(acrylonitrile-co-vinyl acetate) PAN-VA as the gelator of an ACN-based liquid electrolyte, the obtained energy conversion efficiency was 9.46% for a gel-state DSSC [27]. This efficiency is even higher than that of its liquid-counterpart. However, this high efficiency was obtained only for the iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple in the ACN system. It was also reported that an in-situ electrolyte gelation comprising poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and Co<sup>2+</sup>/Co<sup>3+</sup> redox couple in an ACN system resulted in a gel-state cell efficiency of 8.7% [28]. This efficiency, however, is 3% lower than that of its corresponding liquid-state cell. Nevertheless, the low boiling point (BP) and high volatility of ACN triggers evaporation of the solvent, decreasing the long term stability of the gel-state cells. To solve this problem, solvents with a high BP should be adopted, and the most common one used for DSSCs is 3-methoxy propionitrile (MPN) [29–36]. Although MPN improves the stability of DSSCs, performing the in-situ gelation using MPN liquid electrolytes is challenging. Therefore, the energy conversion efficiencies of the gel-state cells prepared using MPN solvent are much lower than those of their liquid versions [29–36].

To solve the problems encountered by the ACN and MPN solvents, a new solvent, propionitrile (PPN), is proposed in this work. PPN has a BP (98 °C) higher than that of ACN (82 °C). The higher BP is expected to increase phase transition temperature (T<sub>p</sub>) of the PGEs, thereby improving the long-term stability of the gel-state cells at elevated temperatures. Furthermore, PPN has a lower viscosity than MPN; accordingly, it is able to undergo in-situ gelation for the fabrication of gel-state DSSCs. In other words, the electrolyte-filling difficulty encountered by the MPN gel-electrolyte can be solved and, therefore, the conversion efficiency of the cells can be improved. In this manuscript, PVdF-HFP was utilized as the gelator of the (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple in the PPN system. Various compositions of PVdF-HFP were used to prepare the PGEs, of which the composition effects on the properties of the PGEs are studied. Furthermore, TiC and TiO<sub>2</sub> nanofillers (NFs) were added to improve the performance of the gel-state cells.

## 2. Experimental

### 2.1. Materials

Methoxypropionitrile (MPN, 99%), propionitrile (PPN, 99%) and TiC nanopowder (30–50 nm particle size, 99%) were obtained from Alfa Aesar. Anhydrous lithium iodide (LiI, 99%), 4-tert butylpyridine, (tBP, 99%), iodine (I, 99%), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-12% HFP) and TiO<sub>2</sub> nanopowder (<25 nm particle size, anatase, 99.7%) were purchased from Sigma Aldrich. Titanium oxide slurry (80% anatase (d = 21), 20% rutile (d = 50)) was provided by JGC (Catalysts and Chemicals Ltd, Japan). Ruthenizer 535-bis TBA (N719, 99.5%) and 1-propyl-2,2-dimethyl-imidazolium iodide (DMPII, 99%) were procured from Sigma Aldrich. And, ethanol, (99.5%) was obtained from J.T. Baker.

### 2.2. Preparation of the TiO<sub>2</sub> electrode

FTO glass slides were cleaned and dried to prepare the TiO<sub>2</sub> photo electrodes. Two TiO<sub>2</sub> paste layers (18 nm and 400 nm) were coated onto the FTO glass using a screen printing method and then

sintered at 450 °C for 30 min. The total thickness of the TiO<sub>2</sub> film was ~14–15 μm as measured from the cross-sectional image obtained via scanning electron microscopy (SEM). After heat treatment, the TiO<sub>2</sub> coated FTO glass substrates were immersed in an ethanol solution containing N719 for 20–30 h at room temperature (RT). Finally, the dye-sensitized photo electrode was washed with methanol and dried.

### 2.3. Preparation of liquid electrolyte and PGEs

The liquid electrolyte was prepared by dissolving 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.5 M 4-tert-butylpyridine (TBP) and 0.5 M 1-propyl-2, 3-dimethylimidazolium iodide (DMPII) into PPN or MPN solvent. The pristine PGE was prepared by first immersing small pieces of PVdF-HFP in the liquid electrolyte for 1 h at 60 °C in an air-oven to allow swelling of the polymer and then the mixture was kept at 80 °C under stirring for ~1 h to get the homogenous solution. The solution is then allowed to cool at RT to get the PVdF-HFP PGE. As for the TiO<sub>2</sub> and TiC NFs -loaded PGEs, the procedures were the same except that a desired concentrations of NFs were added together with the 18 wt% PVdF-HFP.

### 2.4. Cell assembly

The counter electrode was prepared by sputtering a layer of platinum on the FTO glass. The dye-sensitized photoanode and Pt counter electrode were sandwiched using a 60 μm thick spacer. The active area of the cell was 0.16 cm. Hot PGE was injected into the cell through the holes using a vacuum pump. After the cell was filled with PGE, the holes were sealed with epoxy resin. The cell performance was measured after cooling the cell to RT.

### 2.5. Characterizations

For the measurements of ion-diffusivity and conductivity of the electrolytes (liquid electrolytes, PGEs with and without NFs), we fabricated the dummy electrochemical cells with two Pt-coated FTO electrodes with the electrolytes samples sandwiched between the two electrodes [27,29]. The ion-diffusivity of the electrolytes was evaluated using cyclic voltammetry (CV). The CV was recorded at a scan rate of 20 mV/s. The ion-diffusivity in the electrolytes was evaluated from the saturated current conditions in cyclic voltammograms, where the ion diffusion in the electrolyte is limiting. The I<sub>3</sub><sup>-</sup> ions diffusivity in the electrolytes is proportional to the saturated current density (J) according to Fick's first law:  $J = 2nFCD/l$ , where n is the number of electrons transferred during the reduction of I<sub>3</sub><sup>-</sup> ion (ie. n = 2), F is the Faraday's constant, C is the bulk concentrations of the I<sub>3</sub><sup>-</sup> ions, D = diffusion coefficient of the I<sub>3</sub><sup>-</sup> ions and l is the thickness of the electrolyte layer. The conductivity of the electrolytes and charge transfer resistances at the electrolyte/counter electrode interface (R<sub>pt</sub>) were estimated by electrochemical impedance spectroscopy (EIS). The EIS measurements of the dummy cells with electrolyte samples were carried out using Autolab ECO Chemie PGSTAT 30 in the frequency range from 10<sup>5</sup> Hz to 10<sup>-2</sup> kHz at a potential modulation of 10 mV. The obtained impedance spectra were fitted with the Z-view software (Z view 3.2 b, Scribner Associates, Inc) using appropriate equivalent circuit model. The R<sub>pt</sub> and bulk resistance (R<sub>b</sub>) were extracted from the fitting data. The conductivities of the electrolyte were calculated using the equation  $\sigma = L/R_b A$ , where  $\sigma$  is the conductivity; L and A are the film thickness (60 μm) and area (1.0 cm<sup>2</sup>), respectively. The DSC curves for the 18 wt% PVdF-HFP PGEs with 5 wt% TiO<sub>2</sub> and TiC NFs were obtained on a differential scanning calorimeter (model DSC-7, Perking Elmer). The photovoltaic characteristics of the DSSCs were measured using a solar simulator (New port, oriel class

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