



# Use of fumed silica nanoparticles to attain polymer free novel quasi-solid state electrolyte for high-efficiency dye-sensitized solar cells



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## ABSTRACT

Novel gel electrolyte is prepared by replacing conventional polymers solely by fumed silica nanoparticles. In the gel composition, ethylene carbonate and propylene carbonate are used as solvents with the tetrapropylammonium iodide/iodine redox couple. The molar ratio of total oxygen moles of ethylene carbonate and propylene carbonate to iodide moles of tetrapropylammonium iodide ( $O:I^-$ ) is varied from 80:1 to 40:1 and the best room temperature ionic conductivity of  $6.90 \times 10^{-3} \text{ S cm}^{-1}$  is achieved for the system with the molar ratio at 50:1. The dye-sensitized solar cell (DSC) employing this gel electrolyte gives a light-to-electricity conversion efficiency of 7.46% under irradiation of  $100 \text{ mW cm}^{-2}$ . The electrolyte and the fabricated DSCs are characterized using linear sweep voltammetry, FT-IR spectroscopy, current-voltage characteristics and photocurrent action spectra.

## 1. Introduction

Dye-sensitized solar cells (DSCs) have emerged as promising candidates in photovoltaic devices, because of their easy fabrication, low production cost and environmental friendliness when compared to conventional single crystal silicon-based solar cells (O'Regan and Grätzel, 1991; Kalyanasundaram and Grätzel, 1997). The Grätzel cell consists of an interconnected nanoporous  $\text{TiO}_2$  working electrode sensitized with a ruthenium bipyridine dye (Nazeeruddin et al., 1993), liquid electrolyte containing  $I^-/I_3^-$  redox couple dissolved in acetonitrile and a Pt counter electrode. However, these solar cells deteriorate with time due to solvent evaporation, sealing imperfections, dye degradation and also due to corrosion of the Pt counter electrode. These are the major problems in commercializing the device with a liquid electrolyte to produce robust large-area solar panels. Some of the efforts to solve the above problems include the use of p-type semiconductors (Tennakone et al., 1995), organic hole conductors (Bach et al., 1998), polymer electrolytes or gel electrolytes (Ileperuma et al., 2002; Dissanayake et al., 2002; Yuan et al., 2014a, 2014b, 2014c; Li et al., 2014, 2013a, 2013b). Replacement of the liquid electrolyte with a quasi-solid-state electrolyte is an attractive strategy to improve the long-term stability of the cells with comparable efficiencies due to the

cohesive nature of the solids and the diffusive nature of liquids trapped in the solid matrix which results in relatively high ionic conductivities.

The gelation of the liquid electrolyte is achieved chemically or physically upon addition of polymers (Wang et al., 2004), low molecular weight gelators (Kubo et al., 2001) and by incorporating inorganic nanoparticles (Wang et al., 2003). The addition of inorganic nanoparticles, such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$  in gel electrolytes enhances the overall cell performance by increasing the amorphousness of the polymer matrix and thereby forming transport channels (Kang et al., 2008) and reducing charge recombination (Huo et al., 2007). In addition, they possess excellent thermal stability making them suitable for practical applications.

This study focuses on using fumed silica nanoparticles to form the gel matrix without the support of a polymer. When use of fumed silica nanoparticles, these particles possess the ability to make thixotropic like gels by forming network structures in liquids via hydrogen bonds with their surface silanol groups (Cab-O-Sil Properties and Functions, 1987; Technical Bulletin Pigments No. 23, 1989). Fumed silica is an amorphous, nonporous and electrochemically inert material. These nanoparticles are synthesized by the flame hydrolysis of  $\text{SiCl}_4$  in  $\text{H}_2$  and  $\text{O}_2$  and the particle sizes are in the range of 7–40 nm with high surface area ( $50\text{--}400 \text{ m}^2 \text{ g}^{-1}$ ) Khan et al., 1994. Pristine fumed silica inhibits a

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hydrophilic nature because of its surface silanol groups. However, depending on the applications, these hydrophilic silanols may be replaced by hydrophobic ligands. Even so, the suspending medium, the amount of fumed silica added and its' hydrophilic or hydrophobic nature directly influence the amount of network formed in a liquid by fumed silica nanoparticles. Khan et al. (Khan et al. (1994)) have studied the rheology and the ionic conductivity of composite polymer electrolytes using fumed silica. Raghavan et al. (Raghavan et al. (2000)) have also studied the fumed silica dispersions in organic liquids and they showed that their solvation forces are composed of hydrogen bonds. When suspending medium of the electrolyte contains cyclic carbonates, end-capped oligoethers or higher *n*-alkanols, they tend to form weak hydrogen bonds with the surface silanol groups of the fumed silica nanoparticles. This allows silica particles to directly interact with each other through hydrogen bonding via the surface silanol groups and ultimately this kind of bonds throughout the matrix tend to convert the liquid electrolyte to a gel.

In gel polymer electrolytes, polymer could gelate the liquid electrolyte effectively by trapping the liquid electrolyte in the polymer matrix. However, the gel network formed hinders the charge transport ability of the electrolyte thus reducing the overall cell performance. Therefore, lots of studies have been carried out by introducing SiO<sub>2</sub>, TiO<sub>2</sub> nanoparticles to the polymer matrix to increase the amorphousness of the gel polymer (Huo et al., 2007; Lee et al., 2012; Benkstein et al., 2003; Yanagida, 2006; Yang et al., 2006). When ionic liquids are used, the latter can be converted to a gel electrolyte simply by adding nanoparticles to solidify the viscous liquid.

Consequently, these observations have triggered us to explore the behaviour of fumed silica nanoparticles with organic solvent to form a fully amorphous gel electrolyte to be used in DSCs. For the first time, we were able to gelate polymer and ionic liquids free, organic solvent based liquid electrolytes using fumed silica nanoparticles. The electrolyte comprises of plasticizers ethylene carbonate (EC) and propylene carbonate (PC), tetrapropylammonium iodide (Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>), and iodine to generate the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple. In this system, EC and PC were used as cyclic carbonates and this solvent mixture forms weak hydrogen bonds with the surface silanol groups of fumed silica nanoparticles. Then, these silica particles directly interact with each other via hydrogen bonds resulting a gel throughout the liquid.

The novelty of this work is that we solely used the gelation property which is shown by fumed silica nanoparticles when they are in a solvent composed of cyclic carbonates. However, if fumed silica nanoparticles are replaced by silica nanoparticles, it will result a paste instead of a gel electrolyte. On the other hand, EC and PC are much less expensive and less viscous compared to ionic liquids. The other added advantage of fumed silica based electrolytes is their fully amorphous nature which cannot be achieved in composite polymer electrolytes.

In this study, we assembled DSCs with the above gel electrolyte according to the configuration of glass/FTO/TiO<sub>2</sub>/N719 dye/gel electrolyte/Pt/FTO/glass and their photoelectrochemical properties were investigated.

## 2. Experimental

EC, PC, Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>, fumed silica (powder, 7 nm), iodine, acetic acid, ethanol, triton X-100 and titanium tetraisopropoxide with purity > 99% were purchased from Sigma-Aldrich. N719 dye was purchased from Solaronix and all the chemicals were used as received.

### 2.1. Preparation of the quasi-solid-state electrolyte

First, EC and PC were mixed in a 1:1 mass ratio, and Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> was added varying the molar ratio of the total moles of oxygen in EC and PC to moles of iodide from 80:1 to 40:1. After dissolving the Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> salt, iodine was added to the mixture keeping the I<sup>-</sup>:I<sub>2</sub> molar ratio at 10:1. Then, fumed silica was added to the mixture at 10% of the total mass of

EC, PC and the iodide salt. This mixture was stirred for 24 h and, subsequently, allowed to form a gel, at room temperature.

### 2.2. Assembling the quasi-solid-state dye-sensitized solar cell

Titanium tetraisopropoxide (20 cm<sup>3</sup>), acetic acid (2.5 cm<sup>3</sup>), ethanol (25 cm<sup>3</sup>) were mixed and steam was passed to the above mixture until it turned to a light blue colour. Then de-ionized water (50 cm<sup>3</sup>) was added to the above mixture and stirred. Next, this mixture was autoclaved at 150 °C for 3 h to obtain titanium dioxide colloidal solution. After that, prepared titanium dioxide colloidal solution (20 cm<sup>3</sup>), acetic acid (5.5 cm<sup>3</sup>), triton X-100 (5 drops) and ethanol (20 cm<sup>3</sup>) were mixed and this solution was sprayed on to the previously cleaned (with water using a detergent followed by ultrasonic cleaning in a 1:1 v/v mixture of ethanol: acetone) FTO glass substrates (15 Ω cm<sup>-2</sup>) which was heated to 150 °C on a pre-heated hot plate. Next, these cells were sintered at 500 °C for 30 min and allowed to cool to 80 °C. The final film thickness of the TiO<sub>2</sub> film was 10 μm and the nanoparticle size of TiO<sub>2</sub> was 20 nm. These cells were then immersed in a N719 dye solution, for 12 h. Finally, the gel electrolyte prepared was sandwiched between the dyed TiO<sub>2</sub> working electrode and the lightly-platinized counter electrode. Then these cells were used as prepared.

### 2.3. Measurements

Photovoltaic characteristics were measured using a solar simulator (PECCELL PEC-L01) with a source meter (Keithley 2400) at 25 °C. Light intensity of AM 1.5 (100 mW cm<sup>-2</sup>) and active cell area of 0.25 cm<sup>2</sup> were used. Ionic conductivities of the above electrolytes were measured, in the temperature range of 25–60 °C, using a computer-controlled Schlumberger 1260 Impedance Analyzer, in the frequency range of 20 Hz–10 MHz, and an applied voltage of 20 mV using stainless steel electrodes. The electrolyte samples were incorporated into stainless steel electrodes were kept in a Faraday cage while taking measurements and the temperature was measured with a digital thermometer which was attached to the Faraday cage. The electrode area was 0.724 cm<sup>2</sup>. Here, bulk resistance values which were obtained using the impedance plots were used to calculate the ionic conductivities of the electrolyte samples. The scanning electron microscope (SEM) image of the best electrolyte composition was taken using EVO/LS 15 (ZEISS) scanning electron microscope. DC polarization measurements were taken by sandwiching the electrolyte between two stainless steel (SS) blocking electrodes under bias voltage of 1 V at 25 °C. Then current through the cell was measured as a function of time. The device configuration was SS/gel electrolyte/SS. In this study, FTIR measurements were obtained for the gel electrolytes prepared, using a Thermo Nicolet 6700 FTIR spectrometer in the range of 400–4000 cm<sup>-1</sup>. Both attenuated total reflection mode (ATR) and transmission modes were used to obtain the spectra for the gel electrolytes. For transmission mode IR inactive KBr pellets were used. In order to prepare these pellets, a small amount of the sample was mixed well with pre-calcinated KBr in an alumina mortar. Then, using a mould which has a diameter of 1 cm, the mixture was pressed up to a pressure of 5 ton in order to make 2 mm thick pellets. In our study, spectra were recorded for pure salt Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>, EC and PC and gels composed of Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>/EC/PC/fumed silica. These spectra were then compared to the spectrum of gel electrolyte composed of LiI salt instead of Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> salt, in order to verify cation/solvent interactions. This LiI based gel electrolyte was prepared according to the same procedure given in Section 2.1. To investigate the diffusion coefficient of triiodide ions, linear sweep voltammetric measurements were carried out for each gel electrolyte using an Autolab (PGSTAT12) potentiostat. Here, corresponding voltammograms were obtained by sandwiching the corresponding gel electrolyte between stainless steel electrodes in a two electrode configuration. The applied potential was varied from -0.6 V to 1.0 V at a scan rate of 1 mV s<sup>-1</sup> at 25 °C. The electrode area was 0.724 cm<sup>2</sup>. Then photocurrent action spectra were

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