



# Functional transparent quasi-solid state dye-sensitized solar cells made with different oligomer organic/inorganic hybrid electrolytes

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## ARTICLE INFO

### Article history:

Received 7 July 2015

Received in revised form

4 January 2016

Accepted 17 January 2016

Available online 2 February 2016

### Keywords:

Hybrid organic–inorganic material

Quasi-solid state electrolytes

Transparent TiO<sub>2</sub> photoanodes

Dye-sensitized solar cells

## ABSTRACT

Five different hybrid organic–inorganic materials were synthesized using either O,O'-Bis(2-aminopropyl) polypropylene glycol of various molecular weights (230, 400, and 2000), O,O'-Bis(2-aminopropyl) polyethylene glycol (900) or O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (600) and 3-isocyanatopropyltriethoxysilane to employ them as gelato agents and ionic conductors for quasi-solid state electrolytes in dye-sensitized solar cells (DSSCs). Initially the electrolytes were liquid enabling the electrolyte molecules to penetrate the semiconductor's nanoparticles and as the acetic acid solvolysis evolved, they jellified, bonding the two electrodes together. The different electrolytes were thermally characterized for their stability while their electrical conductivity was also measured. Functional quasi-solid state DSSCs were accomplished with transparent TiO<sub>2</sub> films which were deposited on conductive glasses using a spin coating method. The structural properties of the photoanodes were investigated with scanning electron microscopy and porosimetry analysis. The experimental results indicated that the thickness of the fabricated transparent films was between 3.5 and 4.2 μm. The dye-sensitized solar cells (DSSCs) made with transparent TiO<sub>2</sub> films were electrically studied to determine if there are any variations to their performance employing the different quasi-solid state electrolytes. The results indicated comparable results for all the cells and an overall performance of 3.3–3.9% to the conversion of the solar light to electrical energy depending on the hybrid material in the quasi-solid electrolyte.

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## 1. Introduction

Electrolyte is one of the main components of dye-sensitized solar cells (DSSCs) having an essential role for the operation of the cell. The presence of a redox couple in the electrolyte, usually I<sup>-</sup>/I<sub>3</sub><sup>-</sup>, is mandatory for restoring the oxidized dye molecules to their ground state. The I<sub>3</sub><sup>-</sup> ions that are formed after the dye regeneration are reduced at the counter electrode to I<sup>-</sup>. Beside the redox couple, other redox mediators have also been studied, such as Cu(I)/Cu(II), Fe(II)/Fe(III), Ni(III)/Ni(IV), V(IV)/V(V) and Co(II)/Co(III) [1–7].

The electrolytes can be divided into three categories mainly based on their physical state, liquid, quasi-solid (gel) or solid [8,9]. While cells employing a liquid electrolyte can exhibit high efficiencies due to the low viscosity of the electrolyte, which allows a good pore filling, the liquid phase has certain drawbacks [10]. The

solvents used in the electrolyte solution can be volatile, may not work well with the sealing materials causing leaking problems leading to poor long-term stability. Respectively, solid state “electrolytes” or more accurately defined, solid state hole conductors, have also significant disadvantages, such as improper pore filling and handling difficulties including their application, which may sometimes result in wasting more than the needed amount of expensive materials [11].

On the other hand, quasi-solid state electrolytes provide a solution to the problems apparent at the use of either liquid or solid electrolytes. Quasi-solid state electrolytes combine the advantages of high ionic conductivity, thermal stability and non-volatility. The fact that the quasi-solid state electrolytes jellify gradually allows them to penetrate into the mesoporous films of nanostructured semiconductor on negative photoelectrode. Many research groups have used several materials to attain the gelation of the electrolyte with satisfactory results [12–18]. Quasi-solid state electrolytes are roughly distinguished into three categories: (a) gel electrolyte could be formed by adding organic or inorganic

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(or both) thickeners [19]. Such materials may be long-chain polymers like poly(ethylene oxide) or inorganic nanoparticles like  $\text{TiO}_2$  or  $\text{SiO}_2$ ; poly(ethylene oxide)-free polymers have also been utilized. The typical polymers used are poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), poly(acrylonitrile) (PAN), poly(styrene) (PS) and poly(methylmethacrylate) (PMMA) derivatives [20–22]. (b) A second route forming quasi-solid state electrolytes is to introduce a polymerizable precursor into the electrolyte solution and in situ polymerization of the mixture [23]; (c) finally, a third route is to produce a gel incorporating the redox couple through the sol-gel process by using a metal alkoxide precursor, like a titanium or silicon alkoxide in combination to an organic conductor [24].

In this work, we studied five different hybrid organic–inorganic materials bearing silicon alkoxide moieties. In particular, the organic sub-phase of the hybrid materials was polypropylene or polyethylene of different oligomer chain length, while the inorganic sub-phase consisted of silica, synthesized by the sol-gel method. We have chosen oligomers with relatively short chain length avoiding any poor penetration within  $\text{TiO}_2$  electrode's pore structure. The hybrid organic–inorganic materials are formed through an acylation reaction through which urea bonds are formed between amino groups ( $\text{NH}_2$ ) and  $\text{N}=\text{C}=\text{O}$ . These hybrid organic–inorganic materials were used to prepare five quasi-solid state electrolytes, which were afterwards used to fabricate transparent dye sensitized solar cells. The gelation of the electrolyte is based on organic acid solvolysis reactions carried out in two steps with an intermediate step where ester is formed [25,26]. The electrolytes were characterized through thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to evaluate their thermal stability while their electrical conductivity was also measured. Finally, all the fabricated quasi-solid state dye sensitized solar cells (QSS-DSSCs) with different organic/inorganic electrolytes were electrically examined under AM 1.5,  $1000 \text{ W m}^{-2}$  artificial solar irradiance to evaluate their performance while all the internal resistances of the cells were also calculated by electrochemical measurements.

## 2. Experimental details

### 2.1. Materials

Commercially available O,O'-Bis(2-aminopropyl) polypropylene glycol of various molecular weights ( $M_r \sim 230, 400, \text{ and } 2000$ ), O,O'-Bis(2-aminopropyl) polyethylene glycol ( $M_r \sim 900$ ), O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine<sup>®</sup> ED-600,  $M_r \sim 600$ ), 3-isocyanatopropyltriethoxysilane, lithium iodide, iodine, 1-methyl-3-propylimidazolium iodide, *tert*-butyl pyridine, guanidine thiocyanate, chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6$ ), and all solvents were purchased from Sigma-Aldrich and used as received. 3-*Cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium), N719 was purchased from Solaronix S.A., Switzerland.  $\text{SnO}_2:\text{F}$  transparent conductive electrodes (FTO, TEC8)  $8 \Omega/\text{square}$  were purchased from Pilkington NSG Group. For transparent  $\text{TiO}_2$  films, titanium(IV) butoxide (Sigma-Aldrich, 97%), Pluronic<sup>®</sup> P-123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)), glacial acetic acid (AcOH, Aldrich) and *n*-propanol were used to make the  $\text{TiO}_2$  solution.

### 2.2. Preparation of $\text{TiO}_2$ photoanodes

The photoanodes were fabricated via the sol-gel method. In particular, 0.498 g of Pluronic P-123 was mixed with 4 ml of *n*-propanol, followed by addition of 0.4 mL of glacial acetic acid

and 0.37 mL of titanium(IV) butoxide under vigorous stirring [27]. The solution was kept in a well closed vessel when it was not used to slow down alkoxide's hydrolysis due to ambient moisture. After a few minutes stirring, the solution was deposited on the FTO glasses with a spin coating device (Spin150, APT Automation) at 1200 rpm for 10 s. The procedure was repeated several times until an optimum film thickness was obtained for maximum electrical performance at the solar cells. After each film deposition layer, the glasses were heated to  $500 \text{ }^\circ\text{C}$  for 3 min using  $20 \text{ }^\circ\text{C}/\text{min}$  heating ramp rate. When the last film was deposited, the transparent glasses were heated one last time to  $500 \text{ }^\circ\text{C}$  for 30 min.

The  $\text{TiO}_2$  films prepared by the previously described procedure on FTO glass substrates were immersed into a 0.5 mM (ethanol/ acetonitrile 50:50 v/v) solution of N719 dye and were left there overnight to complete the photoanode sensitization. The glasses were removed from the dye solution and were rinsed with acetonitrile to remove the excessive amount of dye and dried in order to remove any acetonitrile or humidity that could be present in the pores of the films.

### 2.3. Preparation of hybrid-organic inorganic materials and quasi-solid state electrolytes

We prepared five different hybrid organic–inorganic materials to be used in five different electrolytes to contribute to their jellification process. The quasi-solid state electrolytes were chosen because they combine the high ionic conductivity of liquids, while they reduce the risk of leaks and minimize sealing problems during the cells' fabrication. The hybrid organic–inorganic materials were prepared according to the following procedure. Either O,O'-Bis(2-aminopropyl) polypropylene glycol of various molecular weights ( $M_r \sim 230, 400, \text{ and } 2000$ ), or O,O'-Bis(2-aminopropyl) polyethylene glycol ( $M_r \sim 900$ ) or O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine<sup>®</sup> ED-600,  $M_r \sim 600$ ) and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine=2) were put to react in a vessel (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part (Scheme 1). The hybrid organic–inorganic materials are abbreviated according to the precursor materials that were used to fabricate them and their molecular weight (PPG230-ICS, PPG400-ICS, PPG2000-ICS, PEG900-ICS and ED600-ICS).

For each quasi-solid state electrolyte prepared, various amounts of the corresponding hybrid organic–inorganic material were tested in order to conclude to the amount that would lead to the optimum solar cell performance. Each quasi-solid state electrolyte was synthesized by the following procedure: a certain amount of the functionalized alkoxide precursor was dissolved in a mixture of 1.6 g of sulfolane and 0.8 g of 3-methoxypropionitrile under vigorous stirring. Then, 0.368 g AcOH were added followed by 0.12 g LiI (0.27 M), 0.12 g 1-methyl-3-propylimidazolium iodide (0.14 M) and 0.06 g  $\text{I}_2$  (0.071 M). To complete the electrolyte solution, 0.204 g of *tert*-butyl pyridine (0.5 M) and 0.036 g of guanidine thiocyanate (0.1 M) were added to the above mixture. The jellified electrolyte solutions are presented in a photo in Scheme 2. The electrolyte that contained the hybrid organic–inorganic material PPG2000-ICS jellified faster than the others, probably because of the higher molecular weight of its precursor material used.

### 2.4. Fabrication of quasi-solid state dye-sensitized solar cells

For the fabrication of the quasi-solid state cells, one drop of the electrolytes was placed on the top of a dye-covered  $\text{TiO}_2$  photoanode, after a few minutes of stirring and a slightly platinized FTO counter electrode was pushed by hand on the top. The platinized FTO glass was made by casting a few drops of  $\text{H}_2\text{PtCl}_6$  solution

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