



New insights in long-term photovoltaic performance characterization of cellulose-based gel electrolytes for stable dye-sensitized solar cells



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ABSTRACT

The gelation of ionic liquid-based solutions with inorganic or organic fillers is one of the strategies commonly adopted in the Dye-Sensitized Solar Cells (DSSCs) field for preparing quasi-solid electrolytes characterized by good photovoltaic performance and long-term stability. In the present paper, the application of a gel electrolyte based on unmodified microcrystalline cellulose and ionic liquids in a DSSC is reported. The gel electrolyte has been characterized evaluating its conductive, thermogravimetric, viscous and crystalline properties, while the photoelectrochemical behavior of the quasi-solid DSSCs has been investigated measuring current-voltage, Electrochemical Impedance Spectroscopy and Linear Sweep Voltammetry curves. The photovoltaic performance of cellulose gel-based DSSCs has been optimized by monitoring some key parameters, such as ionic liquid volume ratios and cellulose content. A maximum photoconversion efficiency of 3.33% has been obtained with the total absence of organic solvents, and a good stability has been demonstrated during more than 8 hours of exposition (replicated over months) to simulated solar light. Moreover, a peculiar and reversible trend in the short-circuit current density and in the overall efficiency of the cell has been observed during prolonged photovoltaic measurements. The present findings suggest the necessity to adopt a new protocol for the measurement of the photovoltaic parameters of quasi-solid DSSCs.

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1. Introduction

Energy is a crucial ingredient of everyday life, its demand is fast raising and the challenge for the next years is to increase the power production from renewable sources using devices fabricated according to the principles of green chemistry [1]. Solar energy has been regarded as a leading actor for the cheap and clean production of power because of its wide availability and inexhaustibility on the human time scale. To this purpose, it is important to improve the photovoltaic performance of solar cells, taking into account their overall environmental impact. In contrast, the commercially available photovoltaic devices are based on inorganic materials that, in the case of silicon, require highly energy consuming preparation methods while, when thin film technology is concerned, are frequently toxic, expensive and have low natural abundance [2].

Organic-based photovoltaics is attracting a lot of attention since it allows the application of a simple fabrication technology with the use of cheap materials and low energy consuming purification processes. Among this class of devices, the most interesting ones are the Dye-Sensitized Solar Cells [3,4]. The working principle of DSSCs is based on the ultrafast electron injection from a photoexcited dye into the conduction band of an oxide semiconductor and on the subsequent hole transportation to the counter electrode by means of an electrolyte [5].

Nowadays, the best photovoltaic performance for DSSCs is around 13% efficiency, obtained using cobalt-based liquid electrolytes [6]. However, some drawbacks exist due to the presence of volatile organic solvents that cause losses in efficiency during stability tests and can solubilize several agents employed to seal the cells.

In order to overcome these issues, several studies about quasi-solid electrolytes (gel-type) have been published [7,8,9], proposing different strategies for preparing gel electrolytes with good photovoltaic performance and guaranteeing long-term stability. Gel electrolytes are usually prepared by mixing ionic liquid-based solutions and inorganic or organic gelators. Ionic liquids have been introduced in DSSCs because of their attractive features such as

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high conductivity, wide electrochemical window, non-volatility, thermal stability and non-flammability [10]. Typical examples of gelators are silica nanoparticles [2,11–13], siloxane [14], sorbitol [15], agarose derivatives [16] and titanium-based materials, such as titanium dioxide (TiO₂) nanotubes [17], titanium carbide [18] and TiO₂ nanoparticles [19]. An interesting class of gelators is represented by natural organic molecules such as cellulose [20,21], which can help to go towards devices with a higher degree of environmental friendliness. Cellulose is the most common natural polymer and it is considered as an almost inexhaustible source of raw material, which can satisfy the increasing demand for environmentally friendly and biocompatible products. Thus, the manufacture of DSSC components with cellulosic materials is starting to be a very stimulating challenge [22,23].

The aim of this work is to prepare a gel electrolyte based on unmodified microcrystalline cellulose (thus avoiding the complex functionalization processes reported in previous papers [20,21]) and ionic liquids, in order to have a more stable and greener DSSC with respect to the standard reference. The novel gel electrolyte we propose was optimized by investigating several key parameters, such as cellulose content and ionic liquid volume ratios, in order to gain the best efficiency, but also material and device stability. Thermal, rheological, spectroscopic and electrical characterizations were exploited to test materials and devices. Materials stability was investigated using gels aged for different times (from freshly prepared to several weeks aged), while device stability was tested by measuring DSSCs for more than one month (every measure lasted more than 8 hours). A new and highly interesting aspect in this work is given by the experimental methodology adopted for the measurement of the photovoltaic parameters: indeed, by means of a long current-voltage test a slow increment of efficiency upon time was observed, mainly due to the enhancement in the photocurrent, with a peculiar reversible behavior. This effect has been attributed to the gradual breaking of the ion-dipole interactions between cellulose OH-groups and ionic liquid iodide ions. Indeed, in systems gelled using a polysaccharide-based material such as cellulose, an activation energy is required to break these chemical bonds and let the ions move towards the semiconductor/dye interface. This phenomenon could be relevant for other gelling agents containing —OH groups and should be taken into account when the best photovoltaic performance of a quasi-solid DSSC is searched and ageing tests are performed.

2. Experimental

2.1. Materials and chemicals.

Cellulose powder (~20 μm size), 1-methyl-3-propylimidazolium iodide (MPII), 1-ethyl-3-methylimidazolium thiocyanate (EMISCN), iodine (I₂), lithium iodide (LiI) and 4-tert-butylpyridine (TBP) were purchased from Sigma-Aldrich. Ionic liquids and cellulose were dried in vacuum at 100 °C overnight before use.

Conducting glass plates (FTO glass, Fluorine doped Tin Oxide over-layer, sheet resistance 7 Ω/sq, purchased from Solaronix) were cut into 2×2 cm² sheets and used as a substrate for the deposition of TiO₂ porous film from a paste (DSL 18NR-AO, Dyesol) and for the fabrication of platinized counter electrodes. Sensitizing dye cis-diisothiocyanato-bis(2,2'-bipyridil-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719, Ruthenizer 535 bis-TBA) was purchased from Solaronix. All the quasi-solid (gel) electrolytes were composed of different volume percentage ratios of the two ionic liquids (with and without iodide as anion, respectively), 2 wt% of lithium iodide, iodine (10 wt% of the whole iodide weight) and 3 to 6 wt% of cellulose microcrystalline powder. 10 wt% of TBP was also added as an additive to increase the open-circuit voltage (V_{oc}).

2.2. Methods.

2.2.1. Gel electrolytes preparation.

All the reagents listed in Section 2.1 were introduced in a glass recipient, that was subsequently sealed with an aluminum foil, in order to avoid the contact with the ambient moisture. Each sample was stirred and heated at 90 °C for 24 hours.

After 24 hours, the mixture was spontaneously cooled down at room temperature; then, it was poured into a plastic Petri dish filled with several absorbing paper sheets, in order to remove the ionic liquid excess and to let the gelation occur.

After 1 day of this treatment, a gel electrolyte was obtained. The gel was rinsed twice with ethanol and dried in vacuum at 60 °C overnight before use.

A few hours before setting the DSSC up, the gel was mixed with TBP. This addition was performed after gelation, because the temperature used to dissolve cellulose (90 °C) caused a partial evaporation of TBP, thus leading to a decrease of the photovoltaic performance.

2.2.2. Liquid electrolyte preparation.

A liquid electrolyte (0.8 M MPII, 0.9 M EMISCN, 0.03 M LiI, 0.087 M I₂ and 0.015 M TBP in 2 mL acetonitrile) was prepared for comparison with the most efficient gel electrolyte.

2.2.3. DSSCs fabrication protocol.

FTO-covered glasses were rinsed with acetone and ethanol in an ultrasonic bath for 10 min and then thermally treated at 540 °C for 5 min. Afterwards, a titanium dioxide paste was deposited with a circular shape on FTO by doctor-blade technique. The coated films were baked at 100 °C for 10 min and subsequently calcined at 525 °C for 30 min in order to obtain ~8.5 μm-thick TiO₂ layers, as measured by profilometry (P.10 KLA Tencor Profiler). For dye absorption, photoanodes were soaked into a 0.35 mM N719 dye solution in ethanol for 18 hours at room temperature and then rinsed in ethanol to remove the unadsorbed dye.

FTO/glass counter electrodes were cleaned with the same rinsing method described above and a 5 nm Pt thin film was deposited by means of thermal evaporation.

A quasi-solid state DSSC was assembled by smearing the cellulose-based gel polymer electrolyte onto the sensitized photoanode by doctor-blade technique. The two electrodes were clipped together and an inert 50 μm-thick spacer was used to keep them separated. A thermal treatment was carried out before cell characterization in order to increase the gel penetration into the porous photoanode layer. Temperatures rising from 45 up to 75 °C degrees and time intervals from 1 to 3 hours were employed.

It is worth noting that no sealants were required to prevent electrolyte leakages, due to the spontaneous good adhesion of the gel polymer on the platinized counter electrode. On the contrary, the cell prepared with the liquid electrolyte was assembled by drop casting the electrolyte on the photoanode and positioning the counter electrode directly above it, then locking the cell with two binder clips. Also in this case, an inert 50 μm-thick spacer was used to separate the electrodes.

2.3. Characterizations.

2.3.1. Gel electrolytes characterization.

Conductivity measurements were performed by means of a Metrohm EC.AUT.MAC multipotentiostat equipped with a FRA 32 module. Impedance tests were performed at room temperature in a frequency range between 1 and 100 Hz. The resistance of the electrolyte was given by the low frequency intercept determined by analyzing the impedance response using a fitting program provided by Metrohm. The measurements were

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