

Effect of Different Green Cellulosic Matrices on the Performance of Polymeric Dye-Sensitized Solar Cells

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Carboxymethyl cellulose (CMC) and microfibrillated cellulose (MFC) are here employed as bio-sourced fillers in quasi-solid electrolytes for polymeric dye-sensitized solar cells (DSSCs). High and durable photovoltaic performances are obtained, due the influence of the different cellulosic fillers on the cell parameters which are here compared and discussed. The present findings open up new intriguing prospects in the design of efficient energy conversion devices with eco-friendly/natural additives.

1. Introduction

Solar energy is a resource of primary importance, and the development of technologies for its conversion is the core topic of third millennium scientific research (Ampelli et al., 2013; Ravaghi-Ardebili et al., 2013). Being an efficient alternative to the conventional silicon based solar cells, dye-sensitized solar cells (DSSCs) have been widely considered as a promising practical candidate (Grätzel et al., 2003). One of the main targets for this technology to intrude into the large-scale global market is to improve its long-term stability (Lee et al., 2014), which is at present unsatisfactory due to the evaporation of solvents, poor hermetic sealing and gas permeability (Odobel et al., 2012). In this regard, the replacement of the commonly used liquid electrolyte, prone to leakage and evaporation in real applications, with a solid/quasi-solid one, that can ensure high performance and prolonged durability, is a viable option and a stimulating challenge. In this respect, gels (Bella et al., 2013a), polymer membranes (Bella et al., 2013b), salt-doped solid polymers (Su'ait et al., 2014), p-type direct band-gap semiconductors (Li et al., 2012) and polymeric hole conductors (Baillie et al., 2014) have been widely investigated as valid alternatives.

By trapping a suitable liquid electrolyte in the soft cages of a host polymer matrix, gels and polymer electrolyte membranes can ensure high ionic conductivity and long-term stability. Nevertheless, besides obtaining high-level long term performance, it is also necessary to design products, processes and production systems that can be easily scaled-up, which comply with the main canons of green-chemistry for a sustainable development (Kim et al., 2013). In particular, when considering the components to be used in energy conversion and storage devices electrolytes, bio-based materials deserve to be primarily considered as they are readily available, easy to be functionalized and biodegradable (Gao et al., 2014). Among them, natural cellulose and its derivatives stand out, and their application in flexible Li-ion batteries (Chiappone et al., 2013), supercapacitors (Wang et al., 2012) and hydrogen production (Ruppert et al., 2014) is currently under thorough investigation by the scientific community.

In this work, we compare the characteristics of two different cellulosic materials as fillers in quasi-solid electrolytes for DSSC: carboxymethyl cellulose (CMC) and microfibrillated cellulose (MFC). CMC is an anionic polysaccharide obtained by the modification of cellulose with sodium hydroxide and monochloroacetic acid. It is a low cost, biocompatible and edible product, which has been recently introduced in the field of energy storage and conversion as biopolymer electrolyte for rechargeable proton

battery (Samsudin et al., 2014), substrate for thermal-energy storage (Jayaprakash et al., 2011) and binder for Li-ion batteries graphite anodes (Lee et al., 2005). MFC is obtained by a hydrolysis-free homogenization process; it may be envisaged as a material composed of cellulose greatly expanded in surface area and consisting of aggregates of natural cellulose microfibrils (diameter \approx 20-60 nm, length from 1 to several micrometres) presenting a web-like structure (Siró et al., 2010). Due to this unique feature, MFC exhibits both the crystalline and the amorphous domains of cellulose, with a percentage of crystallinity that ranges between 50 and 70%. In the field of energy technologies, MFC has been proposed as separator (Xu et al., 2014) and reinforcing agent (Chiappone et al., 2011) for Li-ion battery polymer electrolytes. In this paper, CMC- and MFC-based polymeric DSSCs were fabricated and characterized, and outstanding photovoltaic performance and noticeable long-term stability were obtained.

2. Materials and methods

2.1 Materials

Carboxymethyl cellulose sodium salt (CMC, average M_w : 250000), bisphenol A ethoxylate dimethacrylate (BEMA, average M_n = 1700), poly(ethylene glycol) methyl ether methacrylate (PEGMA, average M_n = 475), polyethylene oxide (PEO, average M_w : 400000), acetonitrile (CH_3CN), sodium iodide (NaI), 1-methyl-3-propylimidazolium iodide (MPII), 4-tert-butylpyridine (TBP) and iodine (I_2) were purchased from Sigma-Aldrich. MFC particles were prepared as described elsewhere (Chiappone et al., 2013) from a sulphite bleached spruce pulp (supplied by Domsjo); a MFC aqueous suspension (2 wt%) was used in the present work. 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173, free radical photoinitiator) was obtained from Ciba Specialty Chemicals.

Conducting glass plates (FTO glass, Fluorine doped Tin Oxide over-layer, sheet resistance $7 \Omega \text{ sq}^{-1}$, purchased from Solaronix) were cut into $2 \times 2 \text{ cm}^2$ pieces and used as substrate for both the deposition of a thin porous layer of TiO_2 from a paste (DSL 18NR-AO, Dyesol) and the fabrication of platinized counter-electrodes. Sensitizing dye cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), i.e. N719 - Ruthenizer 535 bis-TBA, was purchased from Solaronix.

2.2 Preparation of the CMC-based gel-polymer electrolyte

A homogeneous liquid electrolyte solution was prepared by thoroughly mixing NaI, I_2 , MPII and TBP in acetonitrile (see Bella et al. 2013a). To produce the gel-polymer electrolyte, the liquid solution was mixed with specific amounts of PEO and CMC. In preliminary experiments, a chemometric design of experiments (DoE) approach was adopted to determine the best gel-polymer electrolyte composition. The formulation used in this work is the following: 55 wt% liquid electrolyte, 45 wt% solid components (9 wt% CMC in PEO). This system was kept under constant stirring for 2 h at $50 \text{ }^\circ\text{C}$, until a homogeneous highly viscous jelly-like mixture was obtained.

2.3 Preparation of the MFC-based polymer electrolyte membrane

Differently from the physical gel-polymer electrolyte preparation, the fabrication of the MFC-based polymer electrolyte membrane was performed through photoinduced polymerization. It is a fast, cost effective, easily up-scalable and environmentally friendly process, that does not involve the use of any solvents and catalysts (Bella et al., 2013c). A BEMA:PEGMA (30:70 weight ratio) reactive mixture was prepared, along with 2 wt% of photoinitiator. A MFC suspension was added to the reactive formulation in order to obtain a composite containing 30 wt% of filler. The liquid mixture was coated on a polypropylene (PP) substrate and left 24 h in an oven at $70 \text{ }^\circ\text{C}$ to assure the water evaporation. Subsequently, it was UV-cured for 3 min under N_2 flux by using a medium vapour pressure Hg lamp (Helios Italquartz), having a irradiation intensity on the surface of 30 mW cm^{-2} . The resulting self-standing films were peeled off from the PP substrate and treated in high vacuum at $80 \text{ }^\circ\text{C}$ overnight, to completely remove traces of moisture and impurities. Polymer membranes having a final thickness of $100 \pm 5 \mu\text{m}$ (measured with a Mitutoyo series 547 thickness gauge equipped with an ABSOLUTE Digimatic Indicator model ID-C112XBS, with a resolution of $\pm 1 \mu\text{m}$ and a max measuring force of 1.5 N) were obtained.

2.4 Fabrication and characterization of quasi-solid DSSCs

As regards the photoanode preparation, FTO covered glasses were rinsed with acetone and ethanol in an ultrasonic bath for 10 min. Then, traces of solvents were removed by flash evaporation at $500 \text{ }^\circ\text{C}$ on a hotplate. A TiO_2 paste layer with a circular shape ($\varnothing = 1 \text{ cm}$) was deposited twice onto FTO by screen printing technique (AT-25PA, Atma Champ Ent. Corp.) and dried at $100 \text{ }^\circ\text{C}$ for 10 min on a hot plate. A sintering process ($525 \text{ }^\circ\text{C}$, 30 min) led to obtain a mesoporous TiO_2 film with an average thickness of 12 μm , measured by profilometry (P.10 KLA-Tencor Profiler). The sensitization of the photoelectrodes was

performed by soaking in a 0.4 mM N719 dye solution in ethanol for 16 h at ambient temperature, followed by washing in ethanol to remove the unadsorbed dye.

As for the counter electrodes, 6 nm Pt thin films were deposited by sputtering (Q150T ES, Quorum Technologies Ltd) onto FTO glasses, previously cleaned with the same rinsing method described above.

CMC-based DSSCs were assembled by spreading with a spatula the gel-polymer electrolyte over the sensitized photoanode surface. Then, the two electrodes were clamped together, and kept at a distance of 70 μm by means of a layer of inert tape.

As regards the MFC-based polymer electrolyte membranes, they were activated by rapid soaking into a liquid electrolyte (0.45 M NaI, 0.056 M I_2 , 0.55 M TBP), and then placed between the two electrodes.

A cyanoacrylate based glue was used for the final sealing of both kinds of cells.

The active area of the cells was 0.78 cm^2 and the photovoltaic measurements were performed with a 0.22 cm^2 rigid black mask. I-V electrical characterizations under AM1.5G illumination (100 mW cm^{-2}) were carried out using a class A solar simulator (91195A, Newport) and a Keithley 2440 source measure unit. The photoelectric performances (i.e., fill factor FF and light-to-electricity energy conversion efficiency η) were calculated by the following equations:

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta(\%) = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100 \quad (2)$$

where V_{oc} is the open-circuit potential (V), J_{sc} the short-circuit current density (mA cm^{-2}), P_{in} the incident light power density (mW cm^{-2}), V_{max} (V) and J_{max} (mA cm^{-2}) are the potential and the current density in the J-V curves, respectively, at the point of maximum power output. I-V measurements were also performed at light intensities in the range of 0.4-1 sun, by using neutral density filters.

3. Results and discussion

3.1 Gel-polymer electrolyte and polymer electrolyte membrane

Two different quasi-solid electrolytes are investigated in this work, with a dual aim. First of all, we would like to demonstrate the possibility of using green, cellulose-based resources for the preparation of sustainable photovoltaic devices. The second aim is to present the characteristics of two different electrolyte systems, one in the form of membrane, the other in the form of gel.

The CMC-based gel-polymer electrolyte was dense, translucent, not flowing; it could stay stable for long time even in horizontal line and it did not droop when overturned, as shown in Figure 1(A-B). The polymeric and cellulosic matrices were homogeneously mixed, and no phase separation occurred even after a prolonged storage.

Concerning the MFC-based polymer electrolyte membrane, the photoinduced polymerization process led to a rapid light-driven curing of a macromolecular network which helped in maintaining a homogeneous dispersion of the filler. As can be seen in Figure 1C, the composite membrane appeared highly homogeneous, and the interpenetration between the polymeric matrix and network of fibres was excellent, especially considering that no functionalization of MFC was carried out. After activation in the iodide/triiodide-based liquid electrolyte, the membrane remained free-standing, easy to handle, non-tacky and extremely flexible, as clearly visible in Figure 1D.

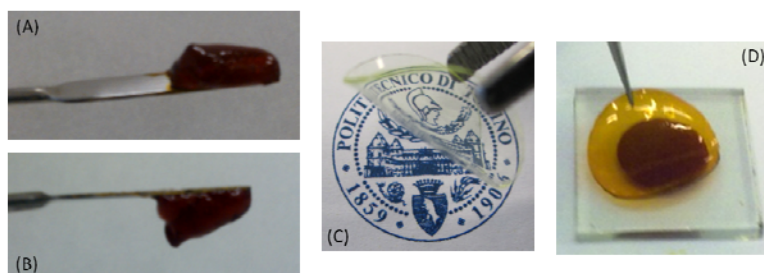


Figure 1: Aspect of the quasi-solid electrolytes under study. A) CMC-based gel-polymer electrolyte on a spatula; B) CMC-based gel-polymer electrolyte being overturned for 10 min; C) MFC-based polymer membrane; D) activated MFC-based polymer electrolyte membrane.

3.2 Photovoltaic characterization of quasi-solid DSSCs

The two cellulose-based quasi-solid electrolytes were sandwiched between cell electrodes and their I-V characteristics were measured under 1 sun irradiation. The photovoltaic parameters are listed in Table 1; the values of the corresponding liquid cell (i.e., a DSSC assembled with the same standard electrodes and filled with the same liquid electrolyte used for the activation of the quasi-solid electrolytes) are also reported for comparison purposes. Furthermore, gels and membranes were also prepared in the absence of the cellulosic matrix, in order to unravel its effective role.

As regards CMC-based gel-polymer electrolyte, a light-to-electricity conversion efficiency of 5.18 % ($J_{sc} = 10.03 \text{ mA cm}^{-2}$, $V_{oc} = 0.75 \text{ V}$, $FF = 0.69$) was measured. The performance of this bio-based cell is much better than those reported in the literature for other types of biopolymers, such as agarose (Singh et al., 2013) and κ -carrageenan (Mobarak et al., 2012).

Concerning the MFC-based polymer electrolyte membrane, a remarkable efficiency of 7.03 % ($J_{sc} = 15.20 \text{ mA cm}^{-2}$, $V_{oc} = 0.76 \text{ V}$, $FF = 0.61$) was obtained. To the best of our knowledge, this is the best performance ever measured for a green polymer electrolyte-based DSSC under 1 sun irradiation. Furthermore, the efficiency values is even higher than that of the standard liquid cell ($\eta = 6.92 \%$).

Table 1: Photovoltaic parameters of DSSCs assembled with CMC-based or CMC-free gel-polymer electrolytes and MFC-based or MFC-free polymer electrolyte membranes. Values for the corresponding liquid cell used as reference are also reported.

Electrolyte	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
CMC-based gel	10.03	0.75	0.69	5.18
CMC-free gel	10.32	0.70	0.71	4.39
MFC-based membrane	15.20	0.76	0.61	7.03
MFC-free membrane	11.70	0.65	0.59	4.42
Liquid	16.30	0.69	0.60	6.92

A detailed analysis of the photovoltaic parameters listed in Table 1 allows a comparison between the different electrolytes presented in this work.

As regards J_{sc} , the introduction of CMC did not cause any relevant variation in the photocurrent density values. On the contrary, J_{sc} noticeably increased from 11.7 to 15.2 mA cm⁻² when MFC was introduced in the polymer electrolyte membrane. This was ascribed to the partial crystalline structure of the MFC network of fibers, thus resulting in a multiplanar light scattering grating. As a consequence, photons which passed unharmed through the photoanode were recovered and reflected back to the N719 dye molecules, thus increasing the sensitizer excitation and, as a consequence, the charge photo-injection. By means of diffused reflectance measurements, we found that the MFC-based polymer electrolyte had a scattering value equal to 76%, at the wavelength of 530 nm (absorption peak of the N719 dye). The corresponding value for the MFC-free sample was ~ 10%. Regardless of the type of quasi-solid electrolyte, Table 1 shows that the highest J_{sc} was measured for the liquid cell: this is a consequence of the fact that the polymer matrix partially inhibits the ionic diffusion between the two electrodes.

As regards V_{oc} values, it was observed that both CMC and MFC markedly improved the cell photovoltage, which is given by the difference between the Fermi level of TiO₂ and the redox potential of the electrolyte. Cellulosic materials can establish hydrogen bonds with the TiO₂ active material particles in the photoelectrode, thus hindering the charge recombination between I₃⁻ ions and electrons in the conduction band of the semiconductor. The reduced recombination phenomena increases the recombination resistance at the TiO₂/electrolyte interface, thus resulting in improved V_{oc} values.

The ameliorated recombination resistance at the TiO₂/electrolyte interface in the presence of cellulosic matrices also enhanced FF values. It was also observed that FF values of gel-polymer electrolytes-based DSSCs were higher than the polymer electrolyte membrane-based ones. This is due to the fact that gels, being spreadable and deformable under pressure, can more deeply penetrate the TiO₂ mesoporous structure, thus contacting a higher portion of dye molecules to be regenerated. On the contrary, membranes are self-standing and their penetration into the electrode structure is less effective.

The effect of different light intensities on the photovoltaic performance of the different quasi-solid systems under study was then investigated. As shown in Figure 2, J_{sc} values of both cells increased with an increased irradiation intensity, while V_{oc} remained almost constant. The CMC-based gel DSSC demonstrated a 6.98 % light-to-electricity conversion efficiency under the illumination of 40 mW cm⁻² (Figure 2A), thus showing excellent performances even under conditions of not optimal lighting (which usually occur in real outdoor applications). Under the same irradiation, the MFC-based DSSC showed a 8.25 % efficiency (Figure 2B), which is an outstanding value for a quasi-solid device. The inset graphs of

Figure 2 also show the linear dependence of J_{sc} on the light intensity from 0.4 to 1 sun, indicating that neither the I^-/I_3^- transportation nor electron transfer at the Pt/electrolyte interface represent the rate-determining step.

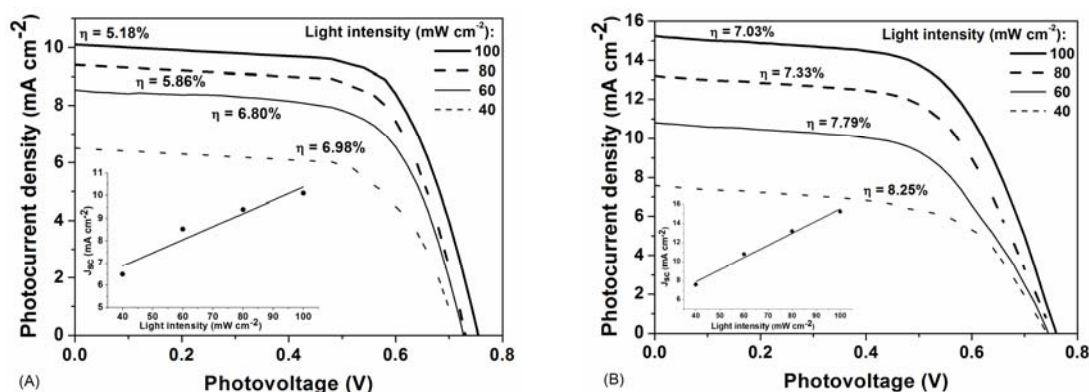


Figure 2: J-V curves of DSSCs assembled with CMC-based gel-polymer electrolyte (A) and MFC-based polymer electrolyte membrane (B), measured under different light intensities. Inset graphs: J_{sc} values plotted as a function of the different light intensity.

3.3 Aging test of quasi-solid DSSCs

In order to assess the long-term stability of the fabricated DSSCs, a 250 h aging tests was carried out at the temperature of 60 °C under dark. As shown in Figure 3, both the quasi-solid cells showed an improved efficiency in the initial 100 h of ageing, due to the achievement of the optimum filling of the electrolytes into the mesoporous photoanode. After 250 h, the CMC-based cell showed an efficiency equal to the 98% of the initial value, while the MFC-based device performance was even higher than the initial value. Such excellent results, especially if compared with the 24 % efficiency decrease of the standard liquid cell, are definitely impressive in view of the real-world application of bio-based polymeric DSSCs.

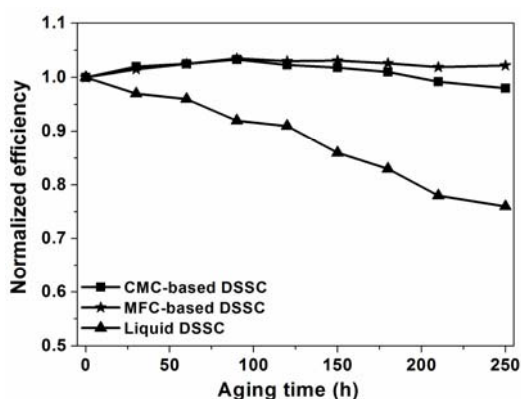


Figure 3: Normalized light-to-electricity conversion efficiencies versus conservation time at 60 °C of DSSCs assembled with the CMC-based gel-polymer electrolyte and the MFC-based polymer electrolyte membrane. Curve for the corresponding liquid cell is also reported.

4. Conclusions

We herewith presented the smart efficacy of cellulosic matrices in cumulatively increasing the photocurrent, photovoltage and long-term stability of polymeric DSSC devices. This is even more relevant considering that cellulose derivatives are green bio-sourced materials which can be easily incorporated in various polymeric systems obtained via different polymerization processes as demonstrated in this work.

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