Approaching truly sustainable solar cells by the use of water and cellulose derivatives

(Article begins on next page)

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16

17   **Abstract**: Aqueous dye-sensitized solar cells (DSSCs) are emerging as the first truly safe, cheap
18   and eco-friendly photovoltaic technology, at the same time overcoming the well-known
19   instability upon moisture/water contamination typical of many solar cells. While many
20   aqueous DSSCs recently proposed still contain little amounts of organic solvents or oil-derived
21   polymeric matrices, here we propose the first 100% hydrogel electrolyte, consisting of
22   carboxymethylcellulose as green jellifying agent, water and iodide/triiodide redox mediator.
23   Electrochemical and photoelectrochemical properties of the resulting electrolytes and solar
24   cells are thoroughly investigated, with a special focus on the long-term stability of the aqueous
25   devices under different operating and aging conditions. The obtained promising efficiencies
26   and stabilities, combined with a metal-free sensitizer, lead here to sustainable, stable,
27   transparent and building-integrable solar cells, without suffering any safety and/or toxicity
28   issues.

29

30   **Keywords**: Dye-sensitized solar cells; Aqueous electrolyte; Gel electrolyte; Cellulose;
31   Sustainability.

32

33   **Introduction**

34   About 25 years ago O'Regan and Grätzel developed the dye-sensitized solar cell (DSSC), which
35   was the first photovoltaic device based on (photo)electrochemical reactions. DSSC represented
36   a sparkling revolution for the photovoltaic scientific community in terms of novel approaches
37   for solar energy conversion [1,2]. An enormous research and development work has been
38   carried out in the last decades [3,4], and DSSCs are now the best choice for high efficiency solar

39 cells at low cost, having aesthetic features suitable for architectural integration, and providing
40 full performance even under low irradiance conditions and/or indoor environments [5,6].

41 However, two main aspects have been not yet properly addressed so far, which is indeed
42 rather surprising if one considers that the DSSC was originally conceived to be an eco-friendly
43 bioinspired technology mimicking artificial photosynthesis [7,8,9]. First, the standard electrolyte
44 system is based on volatile organic solvents, such as acetonitrile, methoxypropionitrile, being
45 also flammable and toxic, which certainly affects safety requirements upon module/panel
46 installation in real operating environment [10]. Secondly, either solid or quasi-solid polymer
47 electrolytes introduced so far for targeted stability enhancements are typically oil-derived
48 [11,12,13,14], which in fact definitely clashes the original green and sustainable address for the
49 DSSC technology.

50 Recently green chemistry has contributed significantly to the step forwards of DSSC systems
51 into sustainability by developing devices operating in truly aqueous electrolyte environment
52 [10,15]. The use of water as the only solvent for the redox mediator would assure the
53 realization of safe, cheap and eco-friendly solar cells [16,17], at the same time overcoming the
54 well-known instability of DSSC upon moisture/water contamination [18,19]. Aqueous DSSCs
55 have recently scored an interesting 5.97% efficiency [20]. Presently, research efforts are
56 focused on developing new water-soluble redox mediators [21,22], improving the photoanode
57 wettability [23], and synthesizing water-resistant organic sensitizers [24,25]. Another
58 fundamental step towards stability enhancement is represented by the replacement of the
59 common liquid electrolytes by quasi-solid systems. To this purpose, different polymeric
60 matrices (pure gelatin [26], acrylic acid/gelatin [27] and xanthan gum [28]) are now investigated
61 by several research groups to jellify the aqueous redox mediator. Unfortunately, the acrylic
62 acid/gelatin-based electrolyte demonstrated rather limited stability of the initial power
63 conversion efficiency (PCE) (20% loss in the first 2 h of cell operation) [27], while the xanthan
64 gum-solidified solution cannot be classified as truly aqueous system as it contained 50% of
65 methoxypropionitrile [28]. To our knowledge, Spiccia's group proposed the best jellified
66 system so far, where gelatin (with a 1 wt% addition of PEG-300) was used to prepare a quasi-
67 solid electrolyte providing 4.1% PCE, stable (80%) after 35 days under dark at room
68 temperature [26]. However, even if gelatin represents a suitable and sustainable matrix for
69 aqueous DSSCs, being a polypeptide made by hydrolytic degradation of collagen, this
70 electrolyte also contained polyethylene glycol (oil-derived), 1-methylimidazole (oil-derived,
71 harmful and corrosive) and a heavy metal (cobalt) based redox couple.

72 Considering such a scenario, here we present the first example of truly oil-derived, toxic,
73 corrosive and/or heavy metal-based components free biopolymer electrolyte for aqueous
74 DSSCs. In particular, we make use of the sodium salt of carboxymethylcellulose (CMC) as a
75 green jellifying agent for a 100% aqueous electrolyte based on the iodide/triiodide redox
76 mediator. The effect of the CMC-based gel composition on the electrochemical and
77 photoelectrochemical properties of the resulting electrolytes and solar cells is thoroughly
78 investigated, as well as the long-term stability of the aqueous devices under different
79 operating and aging conditions. We demonstrate how this newly proposed electrolyte system,
80 in conjunction with a metal-free sensitizer, easily leads to sustainable, stable, transparent and
81 building-integrable solar cells, without suffering any safety and/or toxicity issues.

82

83 **Materials and Methods**

84 *Materials*

85 Sodium iodide (NaI), potassium iodide (KI), iodine (I$_2$), sodium carboxymethyl cellulose (CMC,
86 M_w = 250000 g mol^{-1}), chenodeoxycholic acid (CDCA), ethanol, acetone, *t*-butanol (*t*-BuOH)
87 and acetonitrile (ACN) were purchased from Sigma-Aldrich. Deionized water (DI-H$_2$O, 18 MΩ
88 cm at 25 °C) was obtained with a Direct-Q 3 UV Water Purification System (Millipore).

89 Sensitizing dye 2-[{4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-
90 hexahydrocyclopento[b]indole-7-yl}methylidene]-cyanoacetic acid (D131) was purchased from
91 Inabata Europe S.A.

92 Fluorine-doped tin oxide (FTO) glass plates (sheet resistance 7 Ω sq^{-1}, purchased from
93 Solaronix) were cut into 2 cm × 1.5 cm sheets and used as substrates for the fabrication of
94 photoanodes and counter electrodes.

95

96 *Electrolytes: preparation and characterization*

97 The experimental work related to the proposed aqueous electrolyte can be summarized in
98 three sections.

99 In the first one, gel electrolytes containing aqueous NaI 0.50 M and various weight
100 percentages (3.5 – 5 – 7.5 – 10 – 12.5 – 15 – 20) of CMC were prepared by weighting the
101 polymer in a vial and adding dropwise the proper amount of the iodide stock solution (NaI 0.50
102 M). Gel electrolytes were gently stirred overnight (18 h). In the case of the sample containing
103 20 wt% CMC, the gel was stirred in a warm bath setting the hot plate at 50 °C to get an
104 homogeneous mixture.

105 The resulting gels were tested for their ionic conductivity (σ) in lab-scale cells (ECC-Std, EL-CELL
106 GmbH) by means of electrochemical impedance spectroscopy (EIS), using a potentiostat
107 (PARSTAT 2273, Princeton Applied Research) in the range of frequencies between 10 kHz and 1
108 Hz. Gels were sandwiched between two stainless steel blocking electrodes separated by a 100
109 μm-thick spacer featuring a round shape (14 mm inner diameter). The amplitude of the AC
110 signal was 10 mV. The reference electrode was short-circuited with the counter-electrode in all
111 cases. The ionic conductivity was calculated according to:

112

113 $\sigma = \frac{l}{A \cdot R_b}$ (Eq. 1)

114

115 where l stands for the cell thickness, A is the area of the electrode in contact with the gel
116 electrolyte, and R_b is the bulk-resistance to ion diffusion. R_b was determined directly as the
117 value on the Z_{re} axes at Z_{im} = 0 in the Nyquist plot. For ionic conductivity measurements at
118 different temperatures, ECC-Std cells were placed in a climatic chamber (MK 53, BINDER
119 GmbH). After proper cell equilibration at 70 °C, the temperature was decreased by 10 °C
120 stepwise in the range from 70 to −25 °C. Each measurement was made 1 h and 30 min after

121 the chamber had reached the thermal equilibrium at the set temperature. The ionic
122 conductivity of aqueous NaI 0.50 M was also measured for comparison.

123 In a second phase of the study, and for a more in depth investigation of both the electrolyte
124 and the cathode/electrolyte interfaces, symmetrical (dummy) cells were assembled. Gel
125 electrolytes containing aqueous NaI 0.50 M, I_2 30 mM and CMC 10 wt% (this value was chosen
126 as intermediate value within the investigated experimental domain) were prepared by
127 weighing the polymer in a vial and adding dropwise the proper amount of the aqueous
128 electrolyte solution. The gel electrolyte was gently stirred overnight (18 h) in a warm bath at
129 50 °C. The FTO-coated glass plates used for dummy cell assembly were platinized by a sputter
130 coater (Q180T ES by Quarum Technologies Ltd). A small amount of gel electrolyte was casted
131 onto one platinized electrode using a spatula. The dummy cell was then assembled clamping
132 the two electrodes separated by a spacer (with an internal round area of 0.785 cm^2 and a 70
133 μm thickness).

134 In the final part of the work, the cellulosic matrix was also used to jellify solutions with
135 optimized I^-/I_3^- content for aqueous DSSC application [29]. In detail, both potassium- (KI 5.5 M
136 and I_2 50 mM) and sodium-based (NaI 4.5 M and I_2 50 mM) mixtures were used to prepare gel
137 electrolytes. For DSSCs application, these quasi-solid electrolytes were obtained by weighing
138 the redox mediator aqueous solution in a vial and adding the proper amount of biopolymer
139 under gentle stirring. CMC was added in 3.5, 4.5, 5.5, 6.5 and 7.5 wt% weight percentages.
140 After gelation, samples were left in a bath at 30-40 °C for 20 min to allow a proper
141 homogenization. Besides DSSCs fabrication, a dummy cell assembled as previously described
142 was used to measure the diffusion limited current by steady state cyclic voltammetry. The gel
143 electrolyte tested contained aqueous KI 5.5 M, I_2 50 mM and CMC 6.5 wt%. Its liquid
144 counterpart was tested under the same conditions for comparison. The diffusion coefficient D
145 of triiodide was calculated according to:

146

147 $$D = \frac{1}{2} \frac{d}{nFc_i} J_{\lim} \quad \text{(Eq. 2)}$$

148

149 where d is the distance between the two electrodes, n is the number of electrons involved in
150 the electrode reaction, F is the Faraday constant, c_i is the initial concentration of I_3^- and $J_{\lim}$ is
151 the diffusion-limited current density.

152 All electrolyte samples and cells were freshly prepared before each single testing and each of
153 the experiments was repeated at least three times.

154

155 *DSSC devices: fabrication and characterization*

156 FTO covered glasses were rinsed with acetone and ethanol in an ultrasonic bath for 10 min.
157 Then, all traces of solvents were removed by a compressed air gun. Front electrodes were
158 prepared by depositing a single layer of porous TiO_2 on top of conductive substrates using a
159 screen printer equipped with a 43T mesh frame. After paste (18NR-T, Dyesol) deposition and
160 20 min rest to let the paste relax, the TiO_2 layer was dried at 80 °C for 20 min and sintered

161   increasing the temperature up to 480 °C in 45 min. The fabricated photoanodes (with a
162   thickness of ≈6 µm and a covered area of 0.25 cm^2) were finally activated by heating at 450 °C
163   for 20 min and, after cooling, soaked into a D131 dye solution (0.50 mM in *t*-BuOH:ACN 1:1).
164   CDCA 0.90 mM as coadsorbent in the dye solution was added. Dipping in dye solutions was
165   carried out at 22 °C for 5 h in the dark under shaking in a Buchi Syncore platform equipped
166   with a cooling plate. After dye-loading, the photoanodes were washed in acetone to remove
167   residual dye not specifically adsorbed on the TiO$_2$ layer. As regards the preparation of the
168   counter electrodes, FTO conductive glasses were platinized by spreading a H$_2$PtCl$_6$ solution (5
169   mM in ethanol) on the plate surface and heating. A thermoplastic Surlyn frame (3-4 mm large
170   and with an internal area of 0.8 cm × 0.8 cm) was used as spacer. The amount of gel electrolyte
171   required to fill a cell was determined assembling several trial cells. For each DSSC, a drop of gel
172   electrolyte (5.4-5.6 mg) was casted onto the platinized counter-electrode by a spatula. The
173   complete DSSC was then assembled by hot-pressing at 100 °C for 20 s. All DSSCs assembled in
174   this phase were stored in the dark for six days. After this period, one cell for each electrolyte
175   experimented was stored at 60 °C under dark condition. I-V curves of these cells were
176   periodically recorded right after the extraction from the oven and after 24 h of cooling at RT.
177   The photovoltaic performances were evaluated recording three consecutive I-V curves using a
178   Keithley 2420 Source Measure Unit. Cells were irradiated under simulated sun light at 1 sun
179   (AM 1.5G) after calibration using a silicon diode.

180

181   **Results and Discussion**

182   *Electrochemical characterisation of CMC as jellifier for aqueous electrolytes*

183   Here we attempt to exploit CMC, often cited as "cellulose gum", as a green jellifying agent for
184   aqueous DSSC electrolytes, which assure quasi-solid-like features. In CMC the hydroxyl groups
185   of the glucopyranose monomers of cellulose are bound with carboxymethyl groups; the
186   functional properties of the resulting product depend on the degree of substitution of the
187   initial cellulose structure (0.9 in the present study).

188   As a first experiment when proposing a novel macromolecular matrix for polymer electrolytes,
189   we assessed whether CMC at M_w = 250000 g mol^{-1} could behave as a proper jellifier for
190   aqueous electrolytes. To this purpose, an aqueous solution containing NaI 0.5 M was jellified
191   by CMC in various amounts up to 20 wt% (**Fig. 1A-G**). In this phase, I$_2$ was not yet introduced
192   since our aim was that of investigate the proposed hydrogel step-by-step by adding a
193   component at a time. All samples were clearly homogeneous, and showed enhanced
194   viscoelastic characteristics upon increasing the jellifier content; above 5 wt%, we clearly
195   experienced the proper gelation of the electrolytes that formed a homogeneous sticky gel well
196   consistent and self-standing even when overturning the vessel (**Fig. 1C**). The homogeneity was
197   retained up to 20 wt%; samples at higher CMC content were excluded from our investigation.

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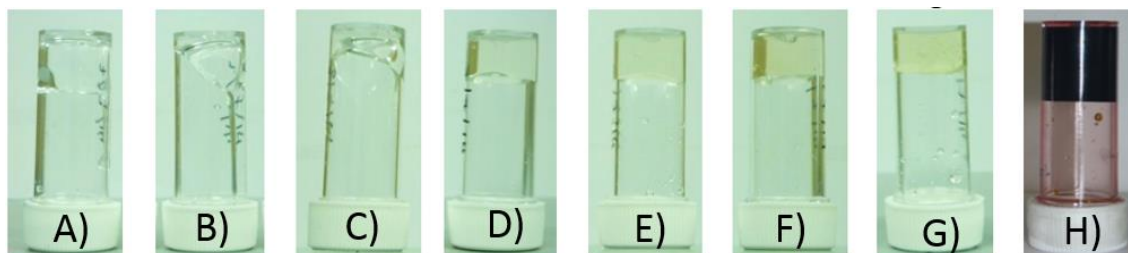
Fig. 1. Gel electrolytes containing aqueous NaI 0.5 M and 3 (A), 5 (B), 7.5 (C), 10 (D), 12.5 (E), 15 (F) and 20 wt% (G) CMC. The image of a gel electrolyte containing aqueous NaI 0.5 M, I_2 30 mM and CMC 10 wt% is also shown (H).

The promising prospects of the obtained materials as electrolytes for DSSCs were determined by ionic conductivity (σ) measurements through EIS analysis. Gels containing CMC in the 2.5-20 wt% range displayed very similar σ values, in the range of 10 mS cm^{-1} at ambient temperature (**Fig. 2A**, **Table S1**). This value is lower with respect to that (48.4 mS cm^{-1}) of the liquid counterpart, which suggests, as expected, a slightly restricted ion mobility in the gel electrolytes. Anyway, it is worth noting that our hydrogel electrolyte shows room temperature σ values one order of magnitude higher than pure ionic liquids, such as 1-hexyl-3-methylimidazolium iodide (HMII), which was successfully proposed in efficient DSSCs [30].

Gels containing 5, 10 and 20 wt% of CMC were further tested for their ionic conductivity between 70 and −25 °C (**Fig. 2B**, **Table S2**), to cover the practical operational conditions of a DSSC. The variation of Logσ as a function of T^{-1} in the range from 70 to −10 °C was barely compatible with the linear correlation predicted by the Arrhenius model. On the other hand, a dramatic decrease of σ was observed below −10 °C, likely ascribable to water solidification. As a result, we can confidently assume that our proposed biosourced aqueous electrolyte can be safely employed in DSSCs operating in places where the temperature frequently drops below zero, without affecting the charge transport properties up to −10 °C.

Overall, the data collected suggest that supply of I$^-$ ions at the photoanode is likely not limited by the slow diffusion through the three-dimensional CMC network in a wide range of temperatures. Indeed, efficient I$^-$ ions supply is a fundamental requirement to ensure fast regeneration, since it is well known that a slow regeneration with respect to the rate of back electron transfer from the semiconductor to the oxidized dye molecules would affect the photovoltaic performance [2,31,32]. Evidences of this phenomenon ascribed to the low ionic conductivity of some classes of polymer electrolytes were reported by Nogueira *et al.* [33], who showed that the ionic conductivity of polymeric systems increased up to ≈10^{-5} S cm^{-1} with increasing [NaI] values [34]. However, one should consider that this value is lower by two orders of magnitude when compared to the one we obtained here with the water-based NaI/CMC gel electrolytes.
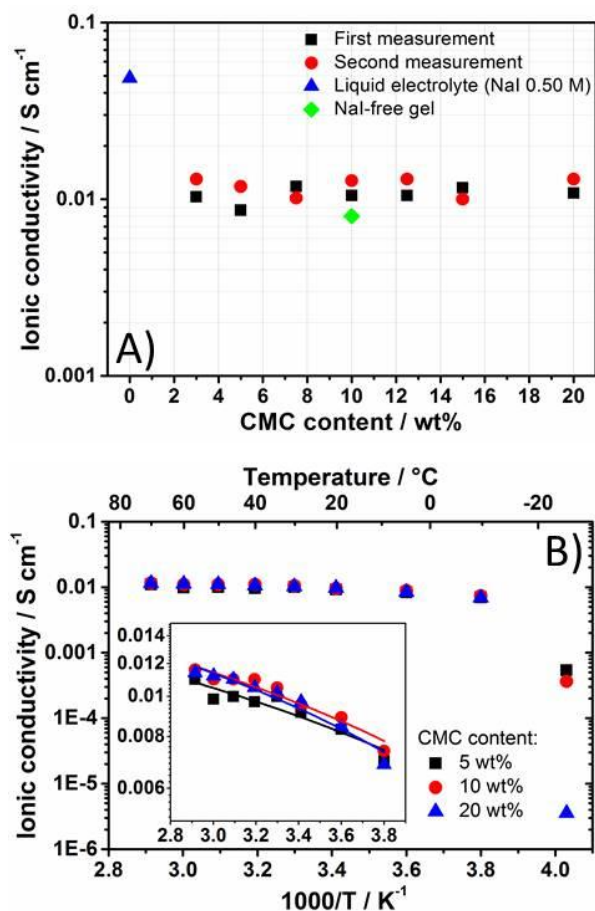
Fig. 2. A) Ionic conductivity at ambient temperature of aqueous NaI 0.50 M gelled with different amounts of CMC. The ionic conductivity of pristine aqueous NaI 0.50 M and of a NaI-free gel containing 10 wt% CMC are also shown for comparison; **B)** Ionic conductivity, in the temperature range of −25/+70 °C, of aqueous NaI 0.50 M gels containing different amounts of CMC. The inset shows data points up −10 °C fitted as lines. The corresponding R^2 values are 0.87 (5 wt%), 0.93 (10 wt%) and 0.95 (20 wt%).

A self-standing gel composed of CMC 10 wt%, aqueous NaI 0.50 M and I_2 30 mM (**Fig. 1H**) was used to fill a dummy cell and investigated in depth by means of EIS analysis. It is worth noting that this gel electrolyte was not fully homogeneous; indeed, small brownish aggregates (also recalled and shown later on in the followings) randomly appeared in the sample likely ascribable to the formation of polymer−I_2 complexes. The formation of polymer−I_2 complexes is common in many cellulose derivatives and other natural and synthetic polymers; indeed, literature studies showed that binding sites were found to be located in the amorphous regions [35]. Anyway, the slight inhomogeneity did not affect at all the electrochemical performance of the sample, which remained constant upon time. The value of R_{Pt} from the impedance measurement was lower than 1 Ω cm^2, similarly to what observed in the case of liquid NaI 1.50 M + I_2 50 mM (**Fig. 3**).

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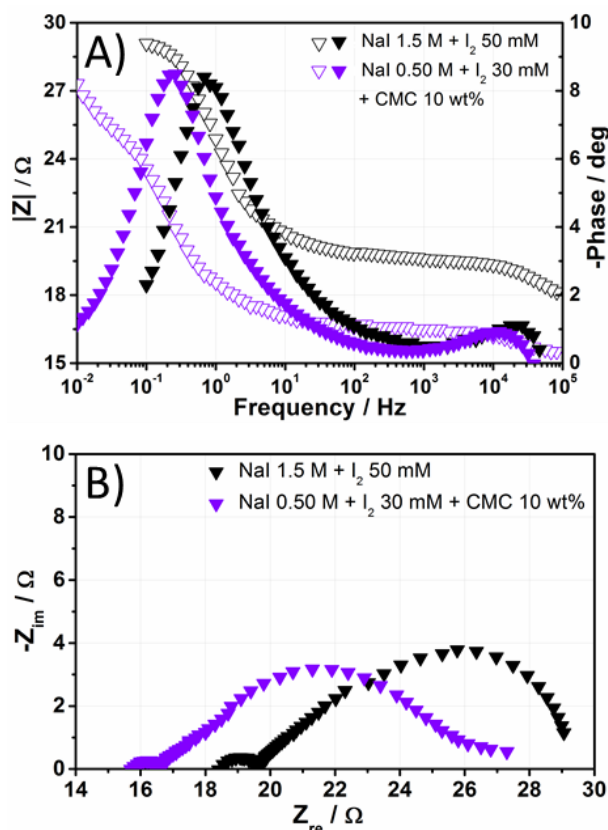
Fig. 3. A) Bode (modulus = open triangles; phase = filled triangles) and **B)** Nyquist plots of a dummy cell filled with aqueous NaI 0.50 M, I_2 30 mM and CMC 10 wt%. The spectra of a dummy cell filled with aqueous NaI 1.5 M + I_2 50 mM are shown for comparison.

Effect of CMC content on the photovoltaic performance of aqueous DSSCs

The data reported in the previous paragraph suggest that CMC-containing electrolytes are likely to be successfully applied in truly aqueous DSSCs, and the faint inhomogeneity (brownish spots) in the gels containing both I_2 and NaI does not affect significantly the electrochemical performance.

The most performing aqueous liquid electrolytes (according to our previous work focused in the unravelling of the I^-/I_3^- chemistry in water [29]) were used to prepare gel electrolytes at various CMC amounts. These starting electrolyte solutions contained I_2 50 mM and NaI 4.5 M or I_2 50 mM and KI 5.5 M. When CMC 10 wt% was introduced in these liquid electrolytes, the gel point was surpassed in both cases. Thus, we added CMC amounts in the range of 3.5 (viscous fluid) to 7.5 wt% (self-standing gel).

The photovoltaic parameters referred to the best performances of the solar cells co-sensitized with D131 and CDCA (D131 : CDCA = 1 : 1.8) are shown in **Fig. 4** and **Table S3**. Data were selected among those recorded during the first week of dark storage at ambient temperature (all results are shown in **Tables S4-S13**). The cells filled with the electrolyte containing CMC 6.5 wt% and NaI were excluded because of massive air infiltration during sealing by hot-pressing.

8

273 It was noted that the short circuit photocurrent density (J_{sc}) was the main factor affecting
274 efficiency. With both NaI- and KI-containing electrolytes, the best photovoltaic performances
275 were achieved at CMC 5.5 wt%. The best efficiencies reached by the gels containing KI were
276 similar at different CMC content. This is likely ascribable to the fact that the ionic conductivity
277 of the gels containing iodide and CMC did not change as a function of the cellulose content.
278 When discussing these PCE values, it must also be noticed that no additives were used to
279 selectively improve the photovoltaic parameters; indeed, our purpose is to evaluate the
280 characteristics of a pure aqueous electrolyte upon addition of the natural cellulose-based
281 jellifier. Moreover, almost none of the additives conventionally used in the DSSC field, such as
282 4-*tert*-butylpyridine (TBP) and *N*-methylbenzimidazole (NMBI), are soluble in water. In this
283 regard, it is rather surprising that some research groups recently proposed TBP- and NMBI-
284 based aqueous DSSCs [36,37]; in our laboratories we were not able to solubilize them in water,
285 even in the presence of surfactants.

286 By comparing the photovoltaic parameters of this work with our recent outcomes in the field
287 of aqueous liquid electrolytes [29], it emerges that the efficiency values reached by the cell
288 containing CMC and NaI were about 0.1% lower than those achieved with CMC and KI. We also
289 noticed that the J_{sc} value achieved by the cell containing NaI and CMC 5.5 wt% was higher than
290 its liquid counterpart, thus confirming the excellent transport properties of the quasi-solid
291 electrolyte proposed in this work. In all of the other cases, J_{sc} and open-circuit potential (V_{oc})
292 values were lower in gel electrolytes. In particular, V_{oc} values achieved with CMC and NaI were
293 significantly low. Moreover, such a reduction of V_{oc} values in the gel electrolytes was
294 somewhat unexpected. Actually, CMC hydrogels are supposed to be basic because of the
295 protonation of carboxylic moieties leading to the release of hydroxyl groups. Under this
296 condition, a shift of the flat band potential of the semiconductor towards negative potentials
297 *vs.* SHE is expected, with a consequent increase of V_{oc} values. Anyway, the flat band potential
298 also depends upon the surface dipole moment due to the anchored dye layer, which can be
299 affected by the interactions with the electrolyte. The increase of dark current in the solar cells
300 filled with gel electrolytes would explain the decrease of V_{oc} when compared to the liquid
301 counterparts. Anyway, under this condition, the fill factor (*FF*) should be decreased as well,
302 and this was not found to be the case. Sealing problems may have played a role, as well;
303 however, we may almost completely exclude this hypothesis as the long-term stability of these
304 cells is excellent (see the followings).

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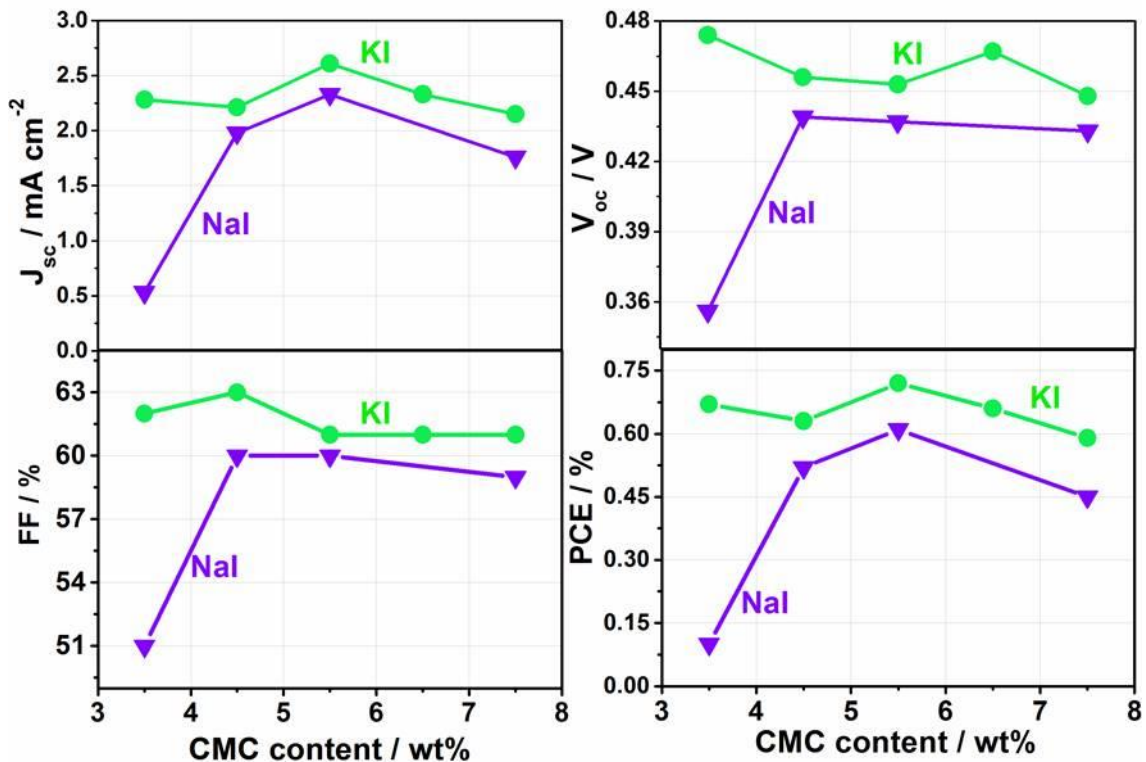
Fig. 4. Photovoltaic parameters referred to the best performance of the DSSCs stored at ambient temperature during the first week after assembly. The solar cells were filled with gel electrolytes containing NaI 4.5 M or KI 5.5 M at various CMC content. I_2 was 50 mM in all cases. All the photoanodes were co-sensitized with D131 and CDCA (D131 : CDCA = 1 : 1.8). Data refer to the third of three consecutive measurements at 1 sun. Lines just connect data points and have no physical meaning.

Fig. 5 (blue curve) shows the steady state cyclic voltammogram of the gel electrolyte containing CMC 6.5 wt% and KI, as representative sample that also allowed the solar cells to retain most of their efficiency over time, both at ambient temperature and at 60 °C. The diffusion limited current density in the gel electrolyte is nearly halved as compared to that of the liquid electrolyte (red curve). Anyway, its value is much higher ($\approx$ 15 mA cm^{-2}) than the photocurrent generated by the cells. This result suggests that mass transport through the electrolyte is not supposed to limit the photocurrent, unless diffusion is somewhat restricted inside the nanostructured semiconductor layer. The diffusion coefficient of triiodide was calculated assuming $[I_3^-]$ = 50 mM is 5.2×10^{-6} cm^2 s^{-1}. It is comparable with the values reported by Hauch and Georg for liquid nitrile-based electrolytes [38] and, in fact, one order of magnitude higher to those obtained with aqueous gels based on amphiphilic copolymers such as Pluronic F77 and P123 mixed with an aqueous solution of 1-butyl-3-methyl imidazolium iodide (BMII) [37]. Such a high value can be also due to the fact that, at high I$^-$ concentration such as those experimented here, sizeable amounts of polyiodides are supposed to be present in the electrolyte solution. This fact may promote the Grotthuss-type charge transfer mechanism in the gel electrolytes [39].
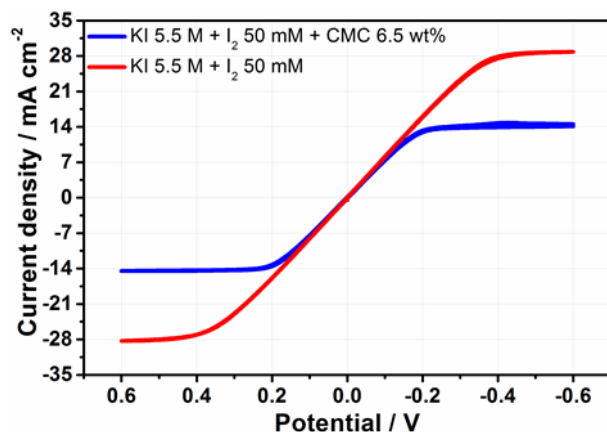
**Fig. 5.** Steady state cyclic voltammograms (scan rate = 10 mV s^{-1}) of dummy cells filled with aqueous liquid and gel electrolytes.

Long-term stability of lab-scale DSSCs based on aqueous gel electrolyte

Fig. 6 shows the photovoltaic parameters of the solar cells stored at ambient temperature. At low CMC contents of 3.5 and 4.5 wt%, the efficiency values slightly increased over time both in NaI- and KI-based devices. At high CMC contents, the cell performance worsened over time in the case of KI-containing gels. Overall, the most stable cell from the KI pool (CMC 6.5 wt%) retained 85% efficiency after about one month. The conversion efficiency of the cells filled with NaI-based gels at high CMC content fluctuated over time, but the values observed after about one month were similar to those recorded right after cell assembly. The most efficient cell from the NaI pool retained 93% efficiency at the end of the monitoring period. This is a truly impressive result if one considers that other biosourced polymer matrices (e.g., gelatin) reported in the literature showed poor stability, with >20% loss in PCE in about 2 h after cell assembly [27].
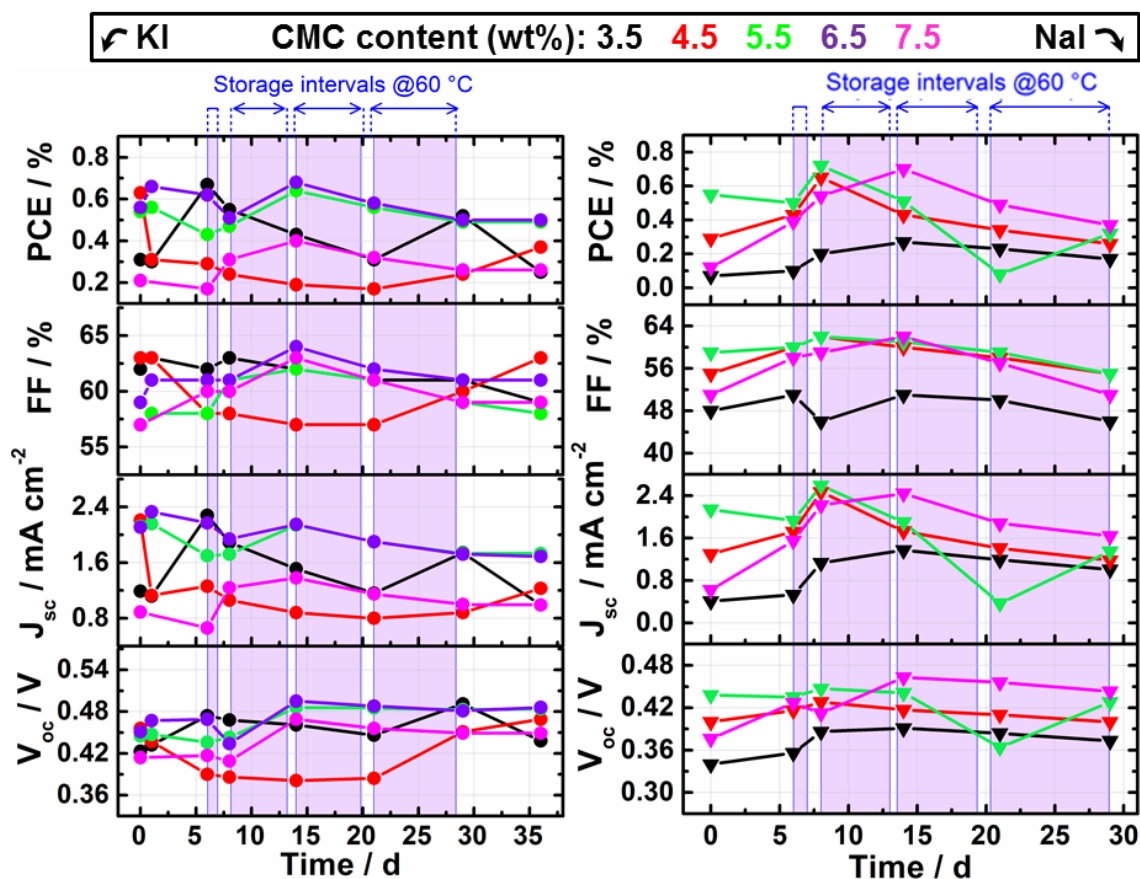
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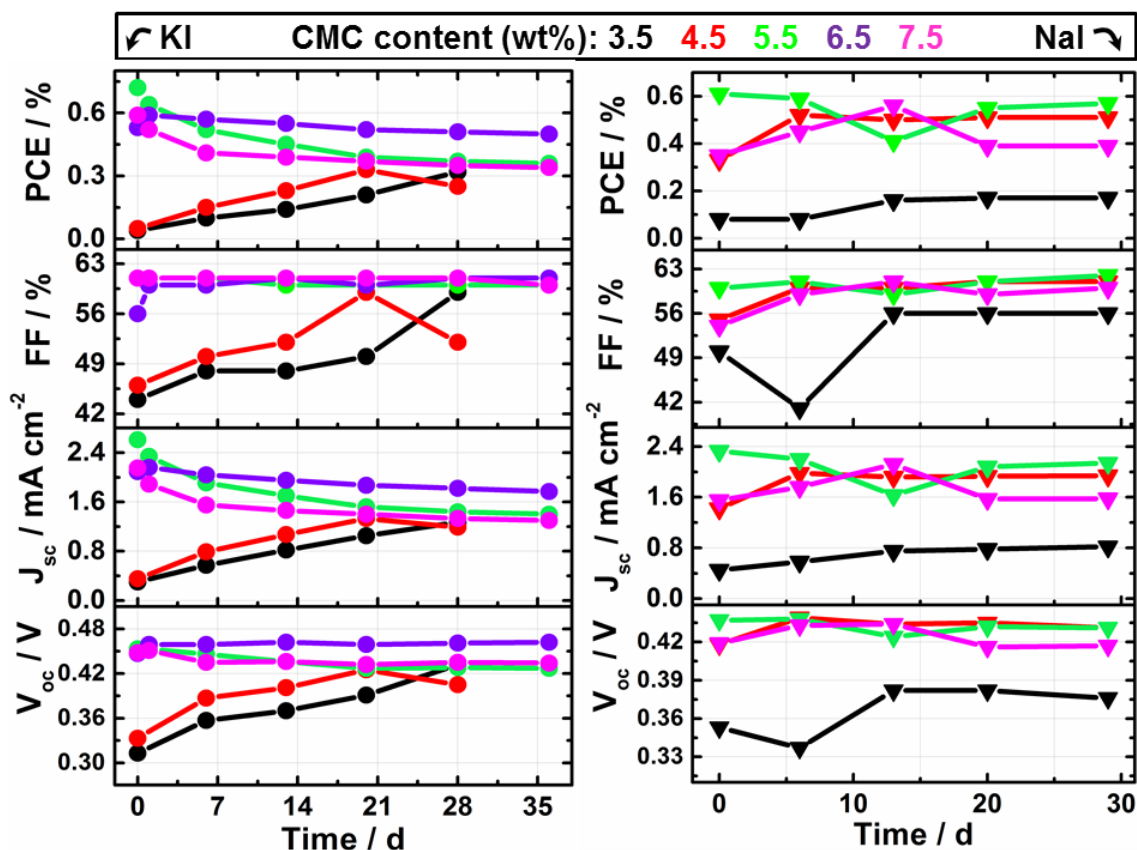
Fig. 6. Photovoltaic parameters versus time of the solar cells co-sensitized with D131 and CDCA
(D131 : CDCA = 1 : 1.8) stored in the dark at ambient temperature. The solar cells contained KI
5.5 M + I_2 50 mM (left panel) or NaI 4.5 M + I_2 50 mM (right panel), jellified with different
amounts of CMC. Data points refer to the third of three consecutive measurements at 1 sun.
Lines just connect data points and have no physical meaning.

The stability of our aqueous solar cells was more deeply investigated by inducing a thermal
stress at 60 °C in a 35 days aging test. The photovoltaic performances of the cells stored at 60
°C fluctuated over time (**Fig. 7**, **Tables S4-S13**). The highest efficiency values after ageing were
recorded at 5.5 and 6.5 wt% CMC with KI-containing electrolytes. In most cases, efficiency
values peaked during the first week of storage at 60 °C. Exceptions are represented by the cells
filled the KI containing electrolytes at 3.5 and 4.5 wt% CMC. This may be due to better pore
filling due to both the rearrangement of the biosourced macromolecules and the lowered
viscosity of the gel promoted by heat. Actually, the slight inhomogeneity of the gels appeared
to be reduced right after cell extraction from the oven. The brownish spots reappeared after
cooling at ambient conditions; anyway, their presence surprisingly did not detrimentally affect
both the performance and the stability of the cells, as for the data plotted in **Fig. 7**.

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Fig. 7. Photovoltaic parameters of the solar cells co-sensitized with D131 and CDCA (D131 :
CDCA = 1 : 1.8) stored in the dark at 60 °C versus storage time. The solar cells contained KI 5.5
M + I_2 50 mM (left panels) or NaI 4.5 M + I_2 50 mM (right panels) jellified with different
amounts of CMC. The time intervals during which the cells have been stored at 60 °C are
represented by filled coloured areas. The cells were cooled at ambient temperature for 24 h
before recording the J-V curves. Data points refer to the third of three consecutive
measurements at 1 sun. Lines just connect data points and have no physical meaning.

The efficiency values recorded about one month after cell assembly and ageing at 60 °C were
similar to those recorded during the first week in the case of the less performing cells. As
regards the photovoltaic performance of the cells that displayed efficiency values ≥0.5%,
some of them were found to slightly decrease during the same period. Anyway, devices
demonstrated proper operation during the whole test, thus accounting for the stable
performance of the proposed electrolyte.

Upon observation of the devices subjected to the aging test, dye desorption is likely one of the
causes of the slight J_{sc} decrease observed for some of the cells. Indeed, the discoloration of the
active area was clearly observed in the cell filled with the electrolyte containing CMC 4.5 wt%
and KI (**Fig. 8**, top). In some other cases, the electrolyte partially depleted over time near the
active area (**Fig. 8**, bottom). This typically arises from an unsuitable sealing, which may result in
gel deswelling (leading to the leakage of the liquid phase). In the present work, we rarely
experienced electrolyte traces out of the active area; therefore, we hypothesised that the
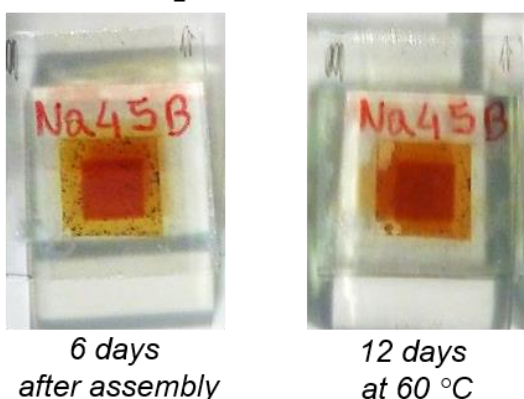
13

389 CMC-based gel penetrated the semiconductor pores left unfilled after cell sealing. Indeed, it is
390 well known in the literature that DSSC filling with a gel electrolyte is rather tricky, especially
391 when the gel consistence renders it impossible to introduce it by vacuum-filling. Therefore,
392 electrolyte deposition must be performed manually or by screen-printing, and the proper
393 dosage of gel amount in the first case (like in our study) is difficult to be pursued.

394

KI 5.5 M + I$_2$ 50 mM + CMC 4.5 wt%

Just assembled | 12 days at 60 °C

NaI 4.5 M + I$_2$ 50 mM + CMC 4.5 wt%
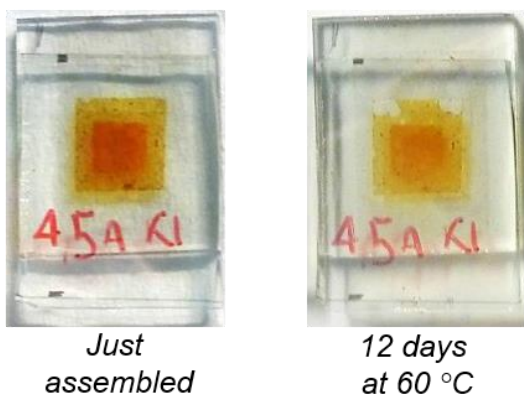
6 days after assembly | 12 days at 60 °C

395

396 **Fig. 8. Top**: cell K45A filled with aqueous KI 5.5 M + I$_2$ 50 mM + CMC 4.5 wt% after cell
397 assembly and after 12 days of storage at 60 °C. **Bottom**: cell Na45B filled with aqueous NaI 4.5
398 M + I$_2$ 50 mM + CMC 4.5 wt% 6 days after cell assembly and after 12 days of storage at 60 °C.
399 Both the cells were cosensitized with D131 and CDCA (D131: CDCA = 1 : 1.8).

400

401 Overall, the most important outcome of this experiment is the truly impressive stability of the
402 CMC-based aqueous electrolytes upon thermal aging. To the best of our knowledge, this is the
403 first report showing the long-term (≈800-875 h) stability of an aqueous DSSC upon thermal
404 aging at 60 °C; the only study on 100% aqueous DSSCs stressed under heat shows an aging test
405 limited at 200 h [40]. Thus, we here demonstrate that CMC can successfully jellify the aqueous
406 solution of the redox mediator, at the same time ensuring its effective trapping within the
407 macromolecular matrix without affecting the diffusion of the shuttle ions between the
408 electrodes in the cell.

409

Conclusions

411 CMC hydrogels have demonstrated suitable characteristics as electrolytes in 100% aqueous
412 DSSCs. Hydrogels containing both NaI and I_2 allowed for efficient charge transfer at the
413 Pt/electrolyte interface. The ionic conductivity of NaI-containing hydrogels and the diffusion
414 coefficient of I_3^- ions were slightly lower than in the liquid counterpart, anyway they were
415 comparable and/or higher than the recent literature reports on ionic liquids and water-based
416 gel electrolytes. The truly promising electrochemical characteristics suggested that the
417 photocurrent generation should not be limited by slow diffusion of I^- or I_3^- ions, as for an ionic
418 mobility kept constant even down to −10 °C.

419 The newly developed biosourced aqueous gel electrolytes were tested in lab-scale solar cells
420 and the best photovoltaic performances (0.72%) were achieved in the presence of CMC 5.5
421 wt%. In this work, no additives were added to the electrolyte and no surface treatment of the
422 photoanodes was performed, in order to keep the whole system as simple, sustainable and
423 cheap as possible; this also means that there is much room for improving PCE values. The most
424 stable cell demonstrated a remarkable 93% efficiency retention after 29 days of dark storage;
425 the CMC-based devices also showed a robust stability when subjected to a further month of
426 thermal aging at 60 °C in oven. We found a few difficulties when manually dosing the exact
427 amount of quasi-solid electrolyte in the cell, therefore we think that future works should be
428 addressed towards in situ gelation of cellulose derivatives, that surely would allow reducing
429 the impact of sealing and ensuring an in depth pore filling.

430 Overall, we here demonstrated that photovoltaic cells can be fabricated with (heavy) metal-
431 free redox shuttles and dye sensitizers, organic solvent-free electrolytes, bioderived cellulosic
432 gellifiers by simple and cost-effective preparation procedures, thus opening the way to the
433 next-generation of green solar energy conversion.

434

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