

Dye-sensitized solar cells using an aqueous choline chloride-based deep eutectic solvent as an effective electrolyte solution

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Abstract: Dye-sensitized solar cells (DSSCs) using an aqueous (40% w w⁻¹ water content) choline chloride-based deep eutectic solvent as an electrolyte medium have been investigated. The joint combination of the above eutectic mixture and proper hydrophilic sensitizer afforded DSSC with power conversion efficiencies comparable to that using the same electrolyte composition but with conventional, toxic and volatile solvents as media, thereby paving the way to a new generation of eco-friendly, nature-inspired, low-cost solar devices.

Introduction

In the last two decades research focused the attention on third generation photovoltaics (PV), aiming at high-efficiency and low cost cells based on thin film technologies using organic and/or inorganic materials.^[1] Within such 3rd generation PV, dye-sensitized solar cells (DSSCs) hold a great potential for easy-to-fabricate, efficient, and low cost devices.^[2] One of the main issues related to the best performing DSSCs is the use of liquid electrolytes based on hazardous and volatile organic solvents (VOCs), such as acetonitrile. This clearly seriously hampers the widespread use of these devices in our society. In order to overcome these drawbacks, alternative solvents have been proposed as electrolyte media, such as ionic liquids (ILs),^[3] liquid solutions adsorbed in polymeric matrixes,^[2a,4] and solid state cells fully avoiding the use of solvents.^[5] Each of these configurations carries some disadvantages, such as higher costs, limited sustainability, and reduced power conversion efficiencies (PCEs). Therefore, the search for new electrolyte media combining ease of availability, low cost, high sustainability, while maintaining a comparable PCE as that of VOCs is in great demand in order to encourage a wider use of this solar technology.

In the last years, researchers started to investigate DSSCs in water as electrolyte media.^[6] Water fully meets the aforementioned requirements since it is abundant, cheap and non-toxic. However, water is an atypical solvent for DSSCs and

has been carefully avoided for years since it negatively affects the stability of the covalent grafting of the dye-sensitizer to the photoanode semiconductor oxide, typically TiO₂, leading to dye desorption and corresponding shutdown of the device. Furthermore, pure water has a number of additional drawbacks such as shifting of the TiO₂ conduction band (CB) towards the wrong direction, interaction with additives and salts present in the electrolyte solution, and inhibition of interfacial contact between the electrolyte phase and the dye-coated semiconductor surface when common hydrophobic sensitizers are used.^[7] Although very exhaustive works have been recently published using water as the electrolyte solvent,^[6,8] PCEs are low, routinely spanning around values of 1-2%. These reports suggest that, although it successfully addresses some stringent requirements for the industrialization of sustainable and cheap devices, water can hardly be considered as an ideal medium for DSSCs due to the limited compatibility with other components and for the associated limited efficiencies and stabilities.

More recently, after pioneering and systematic work of Abbott and co-workers,^[9] a new generation of unconventional reaction media, namely deep eutectic solvents (DESs), emerged, becoming popular among the scientific community as superior green and bio-renewal media. DESs are fluids generally composed of two or three safe and inexpensive components able to interact each other mainly via hydrogen-bond interactions, thereby forming an eutectic mixture with a melting point lower than either of the individual components. Because of their unusual solvent properties and minimal ecological footprint (high thermal stability, non-flammability and practically no vapour pressure), the ability of DESs to successfully replace conventional VOCs in different fields of modern chemistry has become a topic of growing interest both for academics and industry.^[10] Typical DES components [e.g. glycerol (Gly), urea, natural carboxylic acids, amino acids and carbohydrates, polyalcohols, etc.] come from renewable sources. Thus, their biodegradability and biocompatibility is extraordinarily high, and their toxicity is non-existent or very low. Among all the hydrogen bond donors, choline chloride (ChCl), also known as vitamin B₄, is one of the most widely used ammonium salts. It is a very cheap (ca. 2 € kg⁻¹) and biodegradable material produced on the scale of a million metric tonnes per year (either extracted from biomass or easily synthesized from fossil reserves) as an additive in chicken food for accelerating growth. It is worth noting that although DESs share many physico-chemical properties with traditional ionic liquids (ILs) (e.g. thermal stability, low vapour pressures, refractive index, density, conductivity, surface tension, easy of recycling, etc.) the concept of DESs is quite different from that of ILs.^[11] ILs are indeed composed of weakly coordinated ions with melting points below 100 °C, whereas DESs are not entirely composed of ionic species, and can also be obtained from non-ionic species. Moreover, compared to classic, expensive imidazolium or other organic salts, DESs are very cheap and can be easily prepared by mixing and gently warming the selected

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components without any purification step. In addition, the high toxicity, water stability, and poor biodegradability of ILs still remain a major challenge.^[12] Due to their high viscosity and thus the strong difficulties in homogeneously soaking the ultrathin (few microns) large area PV panels for market needs, ILs are not ideal media for DSSCs as well when up-scaling procedures are to be taken into account. Conversely, the positive impact on the viscosity, density and even conductivity of a DES mixture becomes apparent upon forming ternary mixtures as a result of the addition of a new component, such as water, or an inorganic/organic halide.^[13]

As for DES applications, the major research effort to date has been mainly focused on metal finishing applications,^[10e] biomass valorization,^[10n] extraction and separation processes,^[10j, 10k] polymerization and material sciences^[10l, 10m] and various organic transformations.^[10a–10f, 10i, 10o] Emerging applications are in the fields of biotransformations,^[14] organocatalysis,^[15] organometallic chemistry^[16] and metal-catalysed reactions.^[17] To the best of our knowledge, however, applications of DESs in electrochemistry and energy conversion are still in their infancy.^[18] The only example in the literature of exploitation of a DES [namely choline iodide–glycerol (1:3, mol mol⁻¹)] in DSSCs has recently been reported by Wong and co-workers.^[19] In combination with an organic sensitizer, these authors have achieved a PCE of 3.9% vs a value of 4.9% of a control experiment in CH₃CN as the electrolyte solvent. However, in this case, the whole electrolyte solvent was constituted by a mixture of 1-propyl-3-methylimidazolium iodide (PMII) and the aforementioned DES (13:7, v v⁻¹), which resembles more to an adapted IL rather than a "pure" DES medium. Indeed, the same authors classify their work amongst IL-based DSSCs, and the reported efficiency is to be referred to IL-based devices where PCEs higher than in water are routinely achieved.

We herein systematically investigated for the first time the use of a ChCl-based DES as the electrolyte medium in DSSCs in combination with an optimal fraction of water (water-based DES), thereby combining the eco-friendly aspects of both water and DESs into a new healthy, safe, and exceptionally cheap electrolyte solvent. In order to better exploit the interfacial interaction with the water-based medium, we employed an hydrophilic organic sensitizer developed in our group that we have recently employed for the efficient photocatalytic production of hydrogen from water and sunlight.^[20] By carefully adjusting the optimal conditions for electrolyte iodine-based composition, semiconductor layers, electrode materials and device fabrication conditions, we were able to reach a final PCE which is similar to the routine values reported in the literature for water-DSSC and comparable to that using the same electrolyte components in CH₃CN.

Results and Discussion

Since the aim of the present work was to prepare a DSSC working with a water-based electrolyte solvent, the dye acting as a sensitizer has been carefully selected to offer good performance and good compatibility with an aqueous environment and with ultrathin (less than 5 nm) semiconductor layers. Taking into account these requirements, organic dyes are preferred since they exhibit higher molar extinction coefficient than conventional Ru(II) dyes such as N719.^[21] In order to improve the hydrophilic nature of the dye, glycolic chains can be successfully used.^[22] We have met these requirements while designing and investigating organic dyes for photocatalytic hydrogen production in water.^[23] In particular, the selected sensitizer is a donor–acceptor phenothiazine (PTZ) molecule containing thiophene-based spacers and characterized by the presence of a terminal tris(ethylene glycol) monomethyl ether (TEG) substituent (PTZ-TEG, Figure 1).

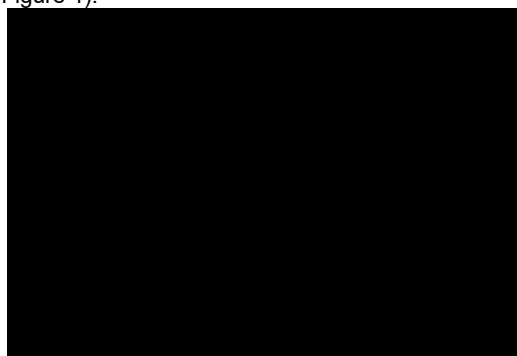


Figure 1. Structure of the hydrophilic PTZ-TEG dye used as a DSSC sensitizer in this work.

A careful evaluation was also dedicated to the choice of the proper co-adsorbent. The commonly used co-adsorbent in DSSC is chenodeoxycholic acid (CDCA) which, upon co-grafting with the dye onto the semiconductor surface, limits the formation of dye aggregates and reduces detrimental charge recombination, thus improving the final cell performance.^[24] We have turned our attention to alternative co-adsorbents able to better interact with hydrophilic media and components and possibly participate to the hydrogen bind interaction operating in the DES medium. For this purpose, we have selected glucuronic acid (GA) which, as far as we are aware, has never been employed as a co-adsorbent in DSSCs. The choice for GA is justified by the simplicity of the structure and the polar nature able to favourably interact with polar molecules. Furthermore, GA is widely available from natural sources (e.g. gum arabic) and is very cheap. The comparative CDCA vs GA study is summarized in Table 1, where the relevant PV characteristics and dye loadings have been included. The replacement of CDCA with GA did not negatively affect the device performance.

Table 1. Photovoltaic characteristics of DES-based DSSC and dye loadings upon variation of co-adsorbent.^[a]

Co-adsorbent	Dye/co-adsorbent ratio	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]	Dye loading [10 ⁻⁷ mol cm ⁻²]
nothing	-	3.0	0.373	0.57	0.6	2.54
CDCA	1:50	2.5	0.384	0.62	0.6	2.64

GA	1:50	2.6	0.344	$\frac{0.6}{2}$	0.5	0.46
GA	1:10	2.5	0.355	$\frac{0.6}{0}$	0.5	1.37
GA	1:1	2.5	0.349	$\frac{0.6}{0}$	0.5	2.01

[a] Electrolyte composition: 4 M KI, 20 mM I₂.

Indeed, when using GA as a co-adsorbent, a comparable device efficiency in terms of photocurrent J_{sc} , photovoltage V_{oc} , fill factor ff , and PCE have been obtained but with a lower amount of adsorbed dye, which is important for minimization of intermolecular self-quenching and lower manufacturing costs. The presence of GA did not improve the overall PCE compared to the device with no co-adsorbent. However, at variance with CDCA, the cells containing large amounts of GA (dye:GA 1:10 and 1:50) afforded the same efficiency in the presence of much lower amounts of adsorbed dye (up to 5 times lower). It is therefore apparent that the presence of a larger amount of co-adsorbent promotes a more efficient dye organization on the semiconductor surface, minimizing dye excited state self-quenching and improving the photocurrent-dye loading ratio. For the aforementioned considerations, the presence of the co-adsorbent is therefore beneficial and was maintained in the subsequent investigation. The presence of GA as a co-adsorbent is helpful also when comparing with CDCA. In particular, the cell prepared with a ratio of dye:GA of 1:50 afforded the same PV efficiency as with dye:CDCA 1:50, but with an amount of dye adsorbed on the TiO₂ surface of one order of magnitude smaller. Different ratios of dye:GA have been tested, from 1:1 to 1:50. The 1:10 ratio appeared as the best balance between amount of dye and device efficiencies, and was selected for the next steps of the investigation.

The DES-based electrolyte medium was selected according to the following main requisites: abundance and wide availability of starting materials, low cost industrial synthesis, lower viscosity compared to ILs, high sustainability, complete absence of toxic and hazardous materials and synthetic procedures, including chemical precursors. These requirements were established keeping in mind a fast, cheap, and ready industrialization of the corresponding solar devices.

For a proper comparison of our investigation on solar devices with other current application in chemistry and material sciences,^{[10], [10m]} we selected a type III DES based on ChCl:Gly (1:2, mol mol⁻¹)^[9c] (Figure 2) since it is constituted by cheap and widely used materials. In order to further extend the eco-friendly nature of such eutectic mixture and, more importantly, to further decrease the viscosity compared to ILs for an easier application in large area panels, this DES was diluted with water to a final 40% w w⁻¹ composition. To the best of our knowledge, this is the first time that a water-based DES has ever been investigated and/or applied to a technological field. The selection of a hydrophilic organic sensitizer assured the best affinity and interfacial interaction with the water-based DES electrolyte, thus efficiently promoting dye regeneration (electron donation from the reduced form of the redox couple to the oxidized dye following photon absorption of the dye and electron injection to the CB of TiO₂).

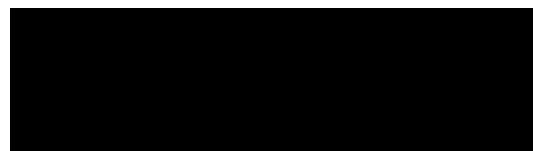


Figure 2. Structures of choline chloride (ChCl) and glycerol.

As far as electrolyte components are concerned, we preferred to limit our investigation to simple and widely available iodine-based chemical species since our main scope was to comparatively test the aqueous DES solvent and CH₃CN rather than achieving high PCEs in absolute terms. We have thus excluded in this work the use of complex mixtures of electrolyte components as well as iodine-free redox species such as cobalt complexes.^[25] In particular, our typical electrolyte used the redox couple I⁻/I₃⁻. KI was chosen as a simple and widely available iodide source. For a more extended comparison, we have also tested organic salts as iodide source [PMII, 1-butyl-3-methylimidazolium iodide (BMII), and 1,3-dimethylimidazolium iodide (DMII)]. It should be noted that in our case the imidazolium iodides have been used as solute species in an aqueous DES and not as solvent-free pure chemical species referred to as ILs. Finally, we have also explored the effect of additives as those routinely found in common liquid DSSC electrolytes, namely *t*-butylpyridine (TBP) and other pyridine-derivatives, and guanidinium thiocyanate (GuSCN).

DSSCs using water-based DESs as electrolyte solvents (DES-DSSCs), in combination with PTZ-TEG as an organic sensitizer, have been prepared and investigated. In order to enhance semiconductor pore diffusion, the preferred TiO₂ architecture consisted in thinner transparent monolayers. Two different transparent TiO₂ thicknesses, 2.5 and 5 μm, have been tested. To further extend the scope of our work for a fruitful comparison with conventional double-layer and solid-state DSSCs, the addition of a second scattering layer, to afford a double transparent+scattering layer, or of a blocking compact layer (BL) of TiO₂, respectively, was also considered. Finally, we have used two types of counter-electrodes, one based on conventional Pt film and one on a poly-ethylenedioxythiophene (PEDOT) layer, since PEDOT-based devices have been reported to better perform in aqueous DSSCs.^[22]

The results pertaining to the first set of experiments are summarized in Table 2. The corresponding J/V curves are illustrated in Figure 3. Inorganic iodide concentrations ranged from 1 to 4 M. Iodine concentration was kept equal to 0.02 M in agreement with the most common values used in conventional liquid DSSCs. The cells filled with an electrolyte based on 1 M and 2 M KI solutions afforded similar results, with the 2 M cells giving a somewhat little higher current. 4 M KI solutions have been tested as well, without any improvement in terms of PV performances but generating a more viscous solution. For this reason, concentration of KI higher than 2 M were avoided in the subsequent investigation.

A significant improvement was recorded when using an organic salt as iodide source. As for KI, three concentrations of PMII, 1 M, 2 M, and 4 M were investigated. 4 M cells showed the best performance, reaching a PCE of 1.7%, almost four times larger than that with KI. However, it should be noted that the high concentration of the imidazolium salt, in this case, approaches that of the pure salt (ca. 6 M), resembling more a IL rather than a solute specie in a DES medium. This value has been thus discarded and not included in the Table. Similarly to KI, the best result for the lower concentrations was obtained when using a 2 M PMII solution, with PCE reaching a 1% efficiency, to be compared to the value of 0.5% obtained with 2 M KI. The better efficiency was mostly due to the enhancement of the photocurrent. Cells containing 2 M BMII and 2 M DMII in aqueous DES afforded analogous performances (see Supporting Information, Table S1). In the subsequent investigation, only PMII was used as imidazolium iodide.

In order to increase the cell photovoltage, TBP and other pyridine derivatives (4-picoline and pyridine) were added to either 2 M KI or 2 M PMII solution.^[26] The solubility of TBP in 2 M KI DES solutions was too poor to give significant results, and this TBP concentration with the KI electrolyte was not investigated. The action of the pyridine derivative is to coordinate to the titania surface through their ring nitrogen lone pair, up-shifting the energy of the CB and Fermi level of the semiconductor. This should result in an increase of the photovoltage, which is proportional to the difference between the CB of the n-type semiconductor and the Nernst level of the redox couple.^[2a] Indeed, the device containing the azine derivative showed a significant increase of V_{oc} , with values going from less than 0.5 to almost 0.7 V, but simultaneously a solid decrease of the current was observed (see Supporting Information, Table S2). We argue that this is likely due to dye desorption from the titania surface (i.e., decrease of active dye concentration) following the hydrolysis in basic aqueous media of the ester bonding between the dye and TiO_2 .^[27]

Table 2. Photovoltaic characteristics of DES-DSSC upon variation of electrolyte composition.^[a]

Cell	Electrolyte	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]
1	PMII 2 M in CH ₃ CN	7.3	0.483	0.70	2.5
2	KI 1 M	1.4	0.452	0.63	0.4
3	KI 2 M	1.9	0.429	0.64	0.5
4	PMII 1 M	1.1	0.467	0.70	0.4
5	PMII 2 M	3.3	0.478	0.67	1.0
6	PMII 2 M + GuSCN	4.1	0.495	0.65	1.3

[a] I_2 concentration = 0.02 M.

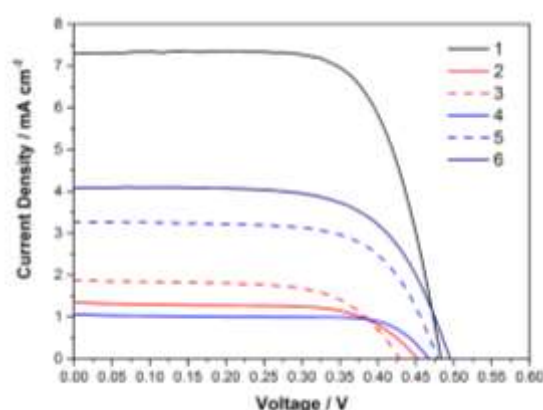


Figure 3. J/V characteristics of DES-DSSCs illustrated in Table 2.

The study included the effect of the common electrolyte additive GuSCN. As a matter of fact, GuSCN has also been reported to act as a surfactant in aqueous cells.^[28] For this reason, the addition of GuSCN was studied in 2 M PMII DES solution, affording a further improvement of the photocurrent and overall PCE (more than twice higher than with KI), with a value of 1.3%. It should be noted that using the same solute species in CH₃CN as the solvent (cell 1 in Table 2) a PCE of 2.5% was obtained, that is comparable to that using aqueous DES as a solvent. The subsequent investigation was thus focused to further improve PV parameters in order to better compare with the efficiency in CH₃CN. Table 3 collects the study aimed at evaluating the effect of using different photoanodes (in terms of TiO₂ mono-(transparent) or double-layers (transparent+scattering), layer thickness and presence of a compact hole BL. The photoanode investigation was carried out in 2 M PMII solutions, which gave the best performances in the first stage of the study. Figure 4 shows the corresponding current/voltage plots.

The presence of a double transparent+scattering layer, which has often been reported to afford higher photocurrents,^[29] did not lead to any improvement in our case (cell 2 of Table 3). In order to exclude charge recombination phenomena, a ultrathin compact BL of TiO₂ was also deposited via spray-pyrolysis on FTO glass according to a standard procedure. This layer preceded the screen-printing deposition of the mesoporous paste of TiO₂. No improvement was observed in both cases. The BL+monolayer architecture afforded a very poor PCE of 0.2% efficiency (see Supporting Information, Table S3). The BL+double-layer configuration performed better (PCE = 0.9%, cell 3 of Table 3), but still lower than in the absence of the BL. This negative result could be due to reduced charge transport induced by the presence of the compact layer. In contrast, a net improvement was recorded by decreasing the semiconductor mesoporous transparent layer from 5 to 2.5 μ m. The use of thinner films decreases the available surface for dye grafting but improves pore filling and charge transport to the electrode before recombination takes place. In this way, the cell photocurrent (cell 4 of Table 3) increases, with PCE reaching almost 1.5%.

Lastly, PEDOT counter-electrodes were considered in place of Pt, according to literature suggestions.^[22] PEDOT has been polymerised directly on pre-drilled FTO glass according to a modified standard procedure.^[30] The PEDOT counter-electrodes were tested with both 5 and 2.5 μ m TiO₂ photoanodes (Table 3). PEDOT counter electrodes performed actually better in the case of the thicker configuration, but overall PCE for the 2.5 μ m cells was lower than using Pt. It is then apparent that in DES-DSSCs

the use of PEDOT is not beneficial. A conventional Pt counter-electrode thus appears as the best choice.

Table 3. Photovoltaic characteristics of DES-based DSSC upon variation of working and counter electrode.^[a]

Cel	TiO ₂ layer 1	TiO ₂ layer 2	TiO ₂ thickness [μm]	counter-electrode	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
1	Transparent	/	5	Pt	3.3	0.478	0.67	1.0
2	Transparent	Scattering	5 + 5	Pt	2.9	0.471	0.63	0.9
3	Transparent + BL ^[b]	Scattering	5 + 5	Pt	2.9	0.498	0.62	0.9
4	Transparent	/	2.5	Pt	4.6	0.469	0.65	1.4
5	Transparent	/	5	PEDOT	4.2	0.427	0.59	1.1
6	Transparent	/	2.5	PEDOT	4.1	0.421	0.59	1.0

[a] Electrolyte composition: 2 M PMII, 20 mM I₂. [b] Presence of a compact hole blocking layer.

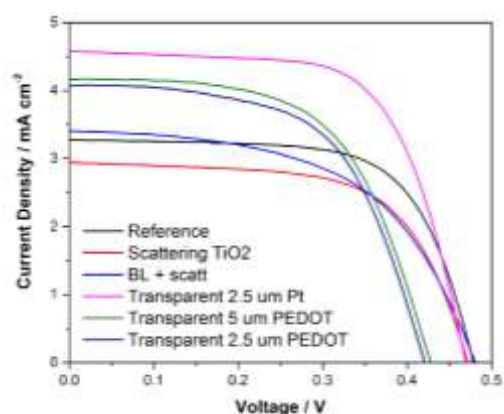


Figure 4. J/V characteristics for DES-DSSC described in Table 3.

By combining all of the above experiments and results we have finally designed the optimal configuration for our prototype DES-DSSC. The best performance was obtained using a 2 M PMII + 0.1 M GuSCN aqueous DES solution in combination with a 2.5 μm transparent TiO₂ layer (Table 4). The J/V curves as well as the incident monochromatic photon-to-electric current conversion efficiency (IPCE) as a function of wavelength (or external quantum efficiency) are presented in Fig. 5. The best cell gave a photocurrent higher than 5 mA cm^{-2} and an overall PCE of 1.7%. This result was further improved at reduced irradiation (0.5 Sun), as those typically found under diffuse light conditions, reaching a conversion efficiency of almost 2%. The DES-DSSC shows IPCE values > 0 over the whole visible wavelength range, exceeding 40% from ca. 480 to 550 nm. This IPCE characteristics

compare well with best performances of water-based DSSC.^[6, 8, 22] In order to check the effect of the co-adsorbent, a similar device prepared under the same conditions of the champion cell but without co-adsorbent GA has been tested (Figure 5). In this case, the IPCE values were smaller (< 30%) although the shape is similar to that with co-adsorbent. It is therefore confirmed the aforementioned beneficial effects of the co-adsorbent on device performances (Table 1).

Table 4. Photovoltaic characteristics of best-performing DES-based DSSC.^[a]

Light power [Sun]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
1	5.1	0.504	0.66	1.7
0.5	3.0	0.478	0.66	1.9

[a] Electrolyte composition: 2 M PMII + 0.1 M GuSCN; transparent TiO₂ thickness: 2.5 μm ; counter-electrode: Pt.

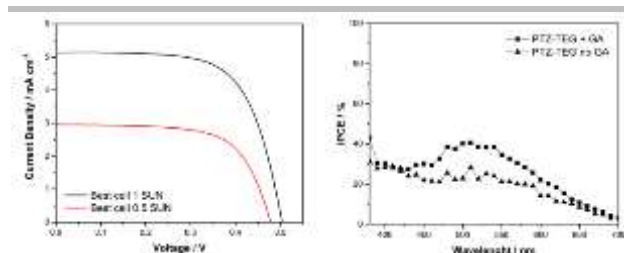


Figure 5. Left) J/V characteristics of the best performing cell (Table 4) at 1 and 0.5 Sun. Right) Corresponding IPCE plot (1 Sun). For comparison the IPCE plot of the same device without co-adsorbent GA has been added.

Electrochemical impedance spectroscopy (EIS)^[31a, 31b] was used to further investigate the comparative behaviour of the cells of Table 3 as a function of semiconductor layer structure and thickness. Only devices with a Pt counter-electrode (cells 1-4) have been considered since this architecture afforded the most relevant results (Table 4). In a EIS experiment, a small sinusoidal voltage stimulus of a fixed frequency is applied to an electrochemical cell and its current response measured. The ac behaviour of an electrochemical system can be investigated by sweeping the frequency over several orders of magnitude (generally from a few mHz to several MHz). The analysis of the impedance spectra is usually performed in terms of Nyquist plots where the imaginary part of the impedance is plotted as a function of the real part over the range of frequencies. The properties of the TiO₂/dye/electrolyte interface can be derived from the central arc in terms of recombination resistance (R_{rec}) and chemical capacitance for charge accumulation (C_{μ}). Both parameters are associated to charge transfer (recombination) phenomena representing detrimental back-processes between the injected electrons in the oxide and the oxidized form of the electrolyte. EIS analysis has been performed in dark condition to deeply investigate the charge-transfer phenomena at the TiO₂/dye/electrolyte interface. Charge recombination resistance (R_{rec}) and chemical capacitance for charge accumulation (C_{μ}) have been determined as a function of the bias potential (V_b) by fitting the experimental data with an equivalent electrical model.^[32] The apparent electron lifetime in the oxide τ_n can be calculated from $\tau_n = R_{\text{rec}} \times C_{\mu}$. The data are illustrated in Figure 6. The EIS study clearly demonstrates the superior performance of the TiO₂ transparent monolayer (cells 1 and 4) compared to the double-layer geometry (cell 2 and 3). The higher electron lifetime of the former cells mostly derives from the higher recombination resistance, whereas differences in the chemical capacitance are not significant. The lower back-electron transfer, as a consequence of the higher resistance, results in higher photocurrents and, eventually, higher PCE. These data therefore suggest that the best semiconductor layer architecture, in combination with the DES-based electrolyte, is the monolayer and not the double layer geometry, the latter being typically used in combination with conventional liquid electrolytes in organic solvents. No significant differences in terms of electron lifetime and recombination resistance have been found by comparing the two monolayer cell with different thickness (cells 1 and 4).

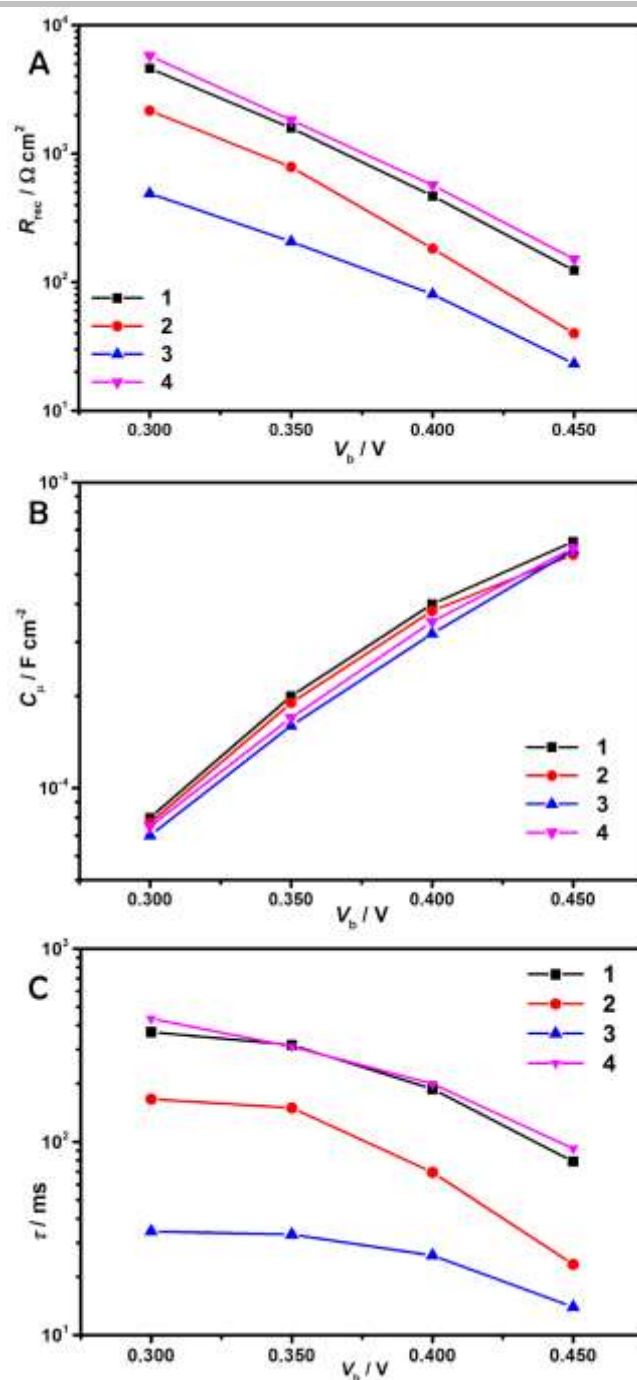


Figure 6. Recombination resistance (A), chemical capacitance (B), and electron lifetime (C) determined as a function of the bias potential of devices 1 - 4 of Table 3.

Conclusions

In conclusion, a new paradigm for the sustainable use of DSSCs for renewable energy storage has clearly emerged, and in this paper we have described the first example of a DSSC using an aqueous ChCl-based DES as an effective electrolyte solvent. Different cell configurations, upon varying electrolyte composition

and concentration, TiO₂ layer architecture, chemical nature of the counter-electrodes, co-adsorbents and electrolyte additives, have been tested in order to optimize at the best the above-described DES-DSSC technology. In this way, we have been able to successfully improve the cell parameters and overall PCE from values close to 0% to a value up to nearly 2%, which is quite comparable in absolute terms to mid-to-high ranked water-based DSSCs. In a world with dwindling petroleum resources, future work should thus mainly focus on further exploring the potential of using DESs as new, "green" media for solar devices in order to entirely replace hazardous and toxic VOCs, which are still massively employed. Indeed, many DES components come from natural sources and do exhibit extremely low toxicity, and high biodegradability and renewability levels. What is remarkable and auspicious for future developments is the high compositional flexibility of DESs with the possibility of fine-tuning their physico-chemical properties^[33] to match the structure and features of dye-sensitizers and of other cell components. Thus, there is plenty of room to develop both fundamental and applied research in this field. We hope that this preliminary work may contribute to popularize even more the use of DESs in energy conversion, thereby boosting the generation of new industrially relevant DES-based families with unforeseen improved efficiency.

Experimental Section

Reagents and materials

All common reagents were obtained from a commercial supplier (Sigma-Aldrich) at the highest purity grade and used without further purification. The photosensitizer 3,3'-[5,5'-[10-[2-(2-methoxyethoxy)ethoxy]ethyl]-10H-phenothiazine-3,7-diyl]bis(thiophene-5,2-diyl)]bis(2-cyanoacrylic acid) (PTZ-TEG) has been prepared according to the literature.^[23] The co-adsorbents chenodeoxycholic acid (CDCA) (Sigma-Aldrich) and glucuronic acid (GA) (Sigma-Aldrich) have been obtained from a commercial supplier and used without further purification. FTO-coated glass plates (2.2 mm thick; sheet resistance ~7 ohm per square; Solaronix), Dyesol 18NR-T TiO₂ blend of active 20 nm anatase particles and Solaronix R/SP TiO₂ blend of > 100 nm anatase scatter particles were purchased from commercial suppliers. UV-O₃ treatment was performed using Novascan PSD Pro Series-Digital UV Ozone System. The thickness of the layers were measured by means of a VEECO Dektak 8 Stylus Profiler.

DES preparation

The eutectic mixtures of choline chloride (Alfa Aesar)-glycerol (Alfa Aesar) (1:2 mol mol⁻¹) was prepared by heating under stirring up to 60 °C for 10 min the corresponding individual components until a clear solution was obtained.

DES-DSSC preparation

DSSCs have been prepared adapting a procedure reported in the literature.^[34] In order to exclude metal contamination, all of the containers were in glass or Teflon and were treated with EtOH and 10% HCl prior to use. Plastic spatulas and tweezers have been used throughout the procedure. FTO glass plates were cleaned in a detergent solution for 15 min using an ultrasonic bath, rinsed with pure water and EtOH. After treatment in a UV-O₃ system for 18 min, the FTO plates were treated with a freshly prepared 40 mM aqueous solution of TiCl₄ for 30 min at 70 °C and then rinsed with water and EtOH.

In the case of the cells with blocking layer, the treatment with TiCl₄ is replaced by a spray pyrolysis deposition of a solution of 20 mM titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich) in anhydrous isopropanol at 450 °C for 30 min and then allowed to cool down to room temperature.

A transparent layer of 0.20 cm² was screen-printed using a 20-nm transparent TiO₂ paste (Dyesol 18NR-T). The coated transparent film was dried at 125 °C for 5 min and when needed another layer was screen-printed by using a light scattering TiO₂ paste with particles >100 nm (Solaronix R/SP). The coated films were thermally treated at 125 °C for 5 min, 325 °C for 10 min, 450 °C for 15 min, and 500 °C for 15 min. The

heating ramp rate was 5-10 °C/min. The sintered layer was treated again with 40 mM aqueous TiCl₄ (70 °C for 30 min), rinsed with EtOH and heated at 500 °C for 30 min. After cooling down to 80 °C, the TiO₂ coated plate was immersed into a 0.2 mM solution of the dye in the presence of the co-adsorbent (typically 1:10 glucuronic acid) for 20 h at room temperature in the dark.

Platinum-based counter electrodes were prepared according to the following procedure: a 1-mm hole was made in a FTO plate, using diamond drill bits. The electrodes were then cleaned with a detergent solution for 15 min using an ultrasonic bath, 10% HCl, and finally acetone for 15 min using an ultrasonic bath. Then, a 10 mL of a 5 × 10⁻³ M solution of H₂PtCl₆ in EtOH was added and the electrodes were thermally treated at 500 °C for 30 min.

PEDOT-based counter electrodes were prepared adapting a literature procedure.^[30] Electropolymerization of EDOT (Sigma-Aldrich) was performed with an Autolab Potentiostat/galvanostat PGStat302N in the galvanostatic mode. A two-electrode cell with a 2 cm × 3.75 cm FTO glass as counter electrode and a predrilled washed 2 cm × 3.75 cm FTO glass as working electrode was used and a constant current of 0.602 A was applied for 400 s (film thickness about 560 nm, measured by profilometry).

The dye adsorbed TiO₂ electrode and the counter electrode were assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer-class resin (Surlyn 30- μ m thickness) as a spacer between the electrodes.

The electrolyte solution was prepared by mixing at room temperature iodine, KI or PMII, and additives (*i.e.* GuSCN, 4-picoline, or pyridine) in a 40% aqueous solution of DES and kept in the dark under air. The electrolyte solution is used within one week from preparation. A drop of the electrolyte solution was added to the hole and introduced inside the cell by vacuum backfilling. Finally, the hole was sealed with a sheet of Surlyn and a cover glass. A reflective foil at the back side of the counter electrode was taped to reflect unabsorbed light back to the photoanode.

DES-DSSC measurements

Photovoltaic measurements of DSSCs were carried out using a 500 W xenon light source (ABET Technologies Sun 2000 Solar Simulator). The power of the simulated light was calibrated to AM 1.5 (100 mW cm⁻²) using a reference Si photodiode. Values were recorded immediately after cells assembling. I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. Incident photon-to-current conversion efficiencies (IPCEs) were recorded as a function of excitation wavelength (between 300–800 nm), using a monochromator (HORIBA Jobin Yvon) and a 400 W xenon lamp as incident light, in AC mode. The monochromatic light was mechanically chopped (chopping frequency of 1 Hz) and the AC-photocurrent response was measured using a lock-in-amplifier. A white light bias (0.3 sun) was applied to the sample during IPCE measurements.

Dye loading

The amount of adsorbed dye has been measured for each sample by desorbing the dye, after the photovoltaic investigation on the dye-coated films, using a 0.1 M solution of NaOH in EtOH-H₂O (1:1) and by measuring its UV-Vis spectrum in a known volume of the solution. Comparison with the spectra of freshly prepared solutions of the dye in the same solvent, at known concentrations, are used to determine the amounts of desorbed dye.

Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) spectra were obtained using an Eg&G PARSTAT 2263 galvanostat-potentiostat. Measurements were performed in the 100 kHz - 0.1 Hz frequency range under dark conditions and with different applied voltages including open circuit conditions. The resulting impedance spectra were fitted with the ZView software (Scribner Associates).

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Solar cells**FULL PAPER**

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Chiara Liliana Boldrini, Norberto Manfredi, Filippo Maria Perna, Vito Capriati, and Alessandro Abboto**

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Dye-sensitized solar cells using an aqueous choline chloride-based deep eutectic solvent as an effective electrolyte solution