The influence of the metal cation and the filler on the performance of dye-sensitized solar cells using polymer-gel redox electrolytes

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Abstract

New composite PEO-based polymer-gel electrolytes were developed, using propylene carbonate (PC) plasticizer and iodide/triiodide (I^-/I_3^-) redox couple. The iodide anion was introduced in the form of the corresponding metal salts: CsI, RbI and LiI and the influence of the metal cation was examined. The non-volatile and high polar character of the PC plasticizer results to excellent ionic conductivity values of the electrolyte samples (up to $1.6\,\mathrm{mS\,cm^{-1}}$), as well as remarkable stability over time. Linear sweep voltametry measurements revealed noticeable triiodide diffusion coefficient values (in the order of $2 \times 10^{-6}\,\mathrm{cm\,s^{-1}}$). The thermograms confirm the amorphicity of the electrolytes (crystallinity values below 20%). All the experimental results showed that the introduction of inorganic titania filler (Degussa P25) into the polymer matrix reduces even more the crystallinity of the samples and enhances the mobility of the redox couple. Nanocrystalline photoelectrochemical solar cells were fabricated with the newly developed composite electrolytes and were tested with *I–V* measurements. All cells presented high efficiency values for this type of composite electrolytes, with the best performance attained in the case of the PEO-TiO$_2$-PC(CsI/I$_3^-$) electrolyte, with overall energy conversion efficiency (η) of 2.87% under standard AM1.5 simulated solar irradiation. Our results clearly support the redox couple mobility dependence on the cation nature.
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1. Introduction

Dye-sensitized solar cells (DSSCs) are considered as third generation photovoltaics that combine high-energy conversion efficiency together with low production cost. For these reasons they have attracted great scientific and technological interest as potential alternatives to classical semiconductor-based photovoltaic devices [1]. The active photoelectrode is a nanocrystalline n-type semiconductor, usually TiO$_2$, modified by chemical attachment of a dye monolayer, being usually a ruthenium complex which strongly absorbs light within wide range of the visible spectrum. On the counter electrode, a thin reflecting Pt film is deposited to catalyze the iodide regenera-

tion. The two electrodes are brought in close proximity, while the gap contains a redox electrolyte. The electrolyte assures internal electrical contact between the two electrodes and, mainly, provides the potential barrier necessary for photovoltaic conversion.

Without neglecting the role of the nanostructured film electrode [2] and the photosensitizer [3,4], the composition of a stable and efficient electrolyte remains one of the key parameters limiting the lifetime of dye-sensitized photoelectrochemical solar cells and hindering their industrial production [5]. In fact, liquid electrolytes present serious stability problems under thermal and light stress conditions. These problems are closely related to the solvent leakage and/or evaporation, aggravated by a built-up of pressure inside the cell due to gaseous degradation products of the electrolyte. Besides, perforation of the TiO$_2$ film by the liquid electrolyte results to recapture of photoinjected electrons by the redox couple, thus dark current, the suppression

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of which is enhanced by depositing an additional compact layer between the FTO conductive glass substrate and the TiO_2 nanocrystals [6–9]. In this regard, efforts have been made to replace the liquid electrolyte by a solid thin film conductor, ionic liquids or organic and inorganic hole transport materials [10–12]. Most frequently, with relative success, the liquid electrolyte has been replaced by a solid thin film made by an organic polymer incorporating the redox couple. Among several candidate polymer matrices, the most investigated are PEO, PAN, PVDF, PVDF-HFP and PMMA [13–17]. Unfortunately, although the significantly high efficiencies that have been accomplished, solvent absence in the electrolyte can easily lead to serious problems, such as crystallization of the iodide salt and, consequently, deterioration of the cell. This problem can be overcome by preparation of polymer-gel electrolytes [18–20], which are on the boundary between liquid and solid electrolytes: They are usually obtained by incorporating a plasticizer into a polymer matrix. Thus, a gel is formed between the plasticizer and the polymer host structure, presenting high boiling point and assuring the non-volatile nature of the electrolyte (there is no definite threshold of the lower limit of the boiling point, but 180 °C appears to be reasonable). Owing to their unique hybrid network structure, gels always possess, simultaneously, both the cohesive properties of solids and the diffusive transport properties of liquids. In addition, the plasticizer, usually a low molar mass polyether (e.g. PEG) or a polar organic solvent (e.g. ethylene carbonate or propylene carbonate), is introduced in small fractions into the polymeric matrix in order to enhance the polymer conductivity properties assure the long life of the cell and provide a satisfactory overall conversion efficiency [13].

However, an important issue in the preparation of electrolytes suitable for DSSC applications is the enhancement of the anion mobility. Accomplishment of this task is reported via the immobilization of the cations [21]. At polymer-gel electrolytes the situation is different from that of a liquid one, where, owing to solvation, the smallest ion is the less mobile. It is worth-mentioning that in composite systems, like polymer-gel electrolytes, the larger cations of similar electronic configuration interact more strongly with the polymer due to viscous forces, thus enhancing anionic diffusion [22]. In order to improve the performance of this type of materials, in this work, we developed new polymer-gel electrolytes by adding a liquid plasticizer (propylene carbonate) to polymer electrolytes of the type PEO-XI-I_2, where X = Cs, Rb, Li. We have investigated the influence of the metal cation, X, of the iodide salt on the performance of quasi solid-state DSSCs. In parallel, the influence of the titania filler (Degussa P25), after introduction in the polymer matrix, was also investigated.

2. Experimental

2.1. Preparation of the sensitized nanocrystalline TiO_2 films

Opaque, thin, nanostructured TiO_2 (Degussa P25) films were prepared using the doctor-blade technique on TEC8 transparent conductive glass substrates (Hartford Glass CO, Inc. USA)

according to literature [3]. Surface derivatization of the titanium oxide was achieved by immersing the thin film electrodes overnight, in the dark, in a 3×10^{-4} M ethanolic solution of the dye $[Ru(dcbpbH_2)_2(NCS)_2]$ (Ru535 or N3, Solaronix SA).

2.2. Preparation of the composite polymer-gel electrolytes

For the composite polymer-gel electrolyte preparation, 0.2640 g of poly(ethylene oxide) (PEO, MW = 2×10^6) were added in a mixture of acetonitrile/propylene carbonate (Acros Organics, analytical grade) (25:1, v/v) under continuous stirring, until the resultant mixture become transparently gelatinous. The selection of the propylene carbonate–acetonitrile mixture is due to the fact that PC can dissolve both an alkaline iodide salt and iodine but acetonitrile contains a more polar functional chemical group and thus the resultant solvent mixture simultaneously dissolves the polymer as well. Afterwards, the I^-/I_3^- redox couple was incorporated by dissolution of 0.019 g of iodine (I_2) and each one of the iodide salts: CsI, RbI and LiI, respectively. For all electrolytes the concentration ratio of the iodine and the iodide salt, $[I_2]/[XI]$, was controlled as 0.1 [11]. Moreover, the molar concentration ratio of oxygen in the ethylene oxide repeating units and the cation of the salt, $\eta_{EO} = [O]_{EO}/[cation]$, was equal to 8 [13]. In the case of the filled electrolytes 0.0383 g of TiO_2 (Degussa P25) were incorporated into the polymer matrix, resulting to a mass fraction (filler to polymer percentage ratio) of 14.5 wt.% [23]. In all cases (electrolytes with and without filler) the obtained mixture was magnetically stirred under heating at 80 °C which is below the melting point of PC [24], in order to evaporate acetonitrile. The resulting electrolytes were kept in a desiccator.

2.3. Cell assembly

Quasi-solid-state solar cells were fabricated by sandwiching the composite polymer-gel electrolytes between the derivatized nanocrystalline titania photoelectrode (TEC8/TiO_2/N3) and a TEC8 platinized counter electrode. The two electrodes are brought in close proximity with the help of an adhesive tape mask, in order to avoid short-circuiting between the two conductive glass surfaces.

2.4. Measurements

I–V measurements were performed by illuminating the cell through the active photoelectrode, under solar simulator from a 300 W-Xe light source in combination with standard AM1.5 ($P = 1000$ W m^{-2}) optical filters (Oriel). A cut-off filter was used to exclude wavelengths <400 nm preventing the generation of electron–hole pairs through direct TiO_2 band gap excitation. The active area of the photoelectrode was 0.20 cm^2.

The thermal properties of the composite polymer-gel electrolytes were investigated with modulated differential scanning calorimetry (MDSC), using a TA Instruments 2920 Modulated DSC. The samples (~10 mg) were heated from −50 up to 108 °C with a rate of 5 °C/min under nitrogen atmosphere. The conductivity of the various gel-type electrolytes was determined by elec-

trochemical impedance spectroscopy (EIS). All measurements were conducted with an AUTOLAB12/FRA2 electrochemical analyzer (EcoChemie, The Netherlands). The electrolyte was sandwiched between two platinized conductive glasses. The conductive side in one of these was properly masked with an insulating tape, leaving an opening area of $0.5\,cm \times 0.5\,cm$. All the experiments were carried out at a $30\,kHz$ frequency (the voltage amplitude of the sine waveform was $10\,mV$), in order to drastically suppress the contribution of the capacitance to the overall impedance and to ensure thus that the recorded impedance is largely attributed to the film resistance.

The triiodide apparent diffusion coefficient $D^*_{I_3^-}$ was determined by measuring the triiodide diffusion-limited current in linear sweep voltammetry (LSV) experiments. The electrochemical cell consists of two similar platinized conducting glass electrodes which are held at a distance of $d = 50\,\mu m$ (measured by an optical microscope), whereas the electrolyte was enclosed in between. The system was polarized from -0.75 to $+0.75\,V$ versus Pt at a rate of $10\,mV\,s^{-1}$. Three subsequent scans were recorded and mean values of the limiting current densities were obtained.

3. Results and discussion

The composite electrolytes were thoroughly characterized by examining their thermal, conductivity and diffusion properties. modulated differential scanning calorimetry (MDSC) was used to investigate the thermal properties of polymer-based composites. The temperature that corresponds to the lowest point of the endotherm peak is obtained as the melting temperature of the material, T_m. The melting enthalpy ΔH_m is obtained by integrating the area under the melting transition. This parameter stands for the energy given to the polymer in order to melt the crystals. In Table 1, the T_m values are shown where no spectacular differences are observed for all the electrolytes. The crystallinity values (X_c) of the samples were calculated according to the Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_{m,c} \times f_{PEO}} \tag{1}$$

where ΔH_m is the melting enthalpy of each sample (experimentally measured from the MDSC thermograms represented in Figs. 1 and 2), $\Delta H_{m,c} = 196.4\,J/g$ the melting enthalpy of 100% crystalline PEO and f_{PEO} is the weight fraction of polyethy-

Table 1
Melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity ($X_c\%$) values for the PEO-TiO$_2$-PC(XI/I$_3^-$) and PEO-PC(XI/I$_3^-$) composite polymer electrolytes

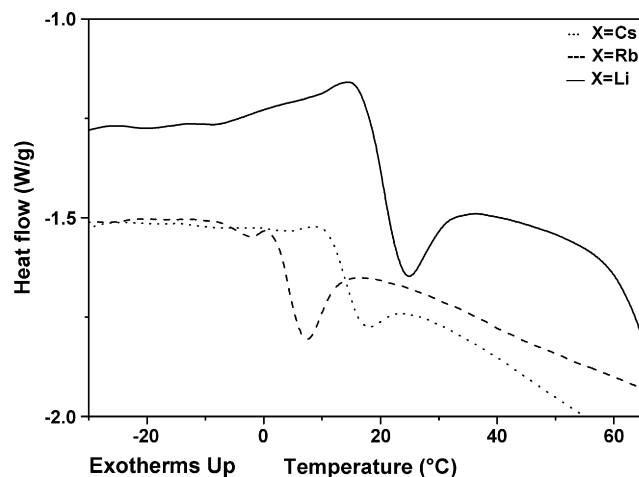| Sample	T_m (°C)	ΔH_m (J/g)	X_c (%)
PEO-TiO$_2$-PC(CsI/I$_3^-$)	18.1	0.42	2.4
PEO-PC(CsI/I$_3^-$)	16.9	0.89	4.9
PEO-TiO$_2$-PC(RbI/I$_3^-$)	19.3	0.62	3.4
PEO-PC(RbI/I$_3^-$)	7.1	1.73	9.5
PEO-TiO$_2$-PC(LiI/I$_3^-$)	19.1	0.77	4.2
PEO-PC(LiI/I$_3^-$)	24.3	3.73	20.0

X = Cs, Rb, Li.

Fig. 1. MDSC thermograms for the PEO-PC(XI/I$_3^-$) composite electrolytes. X = Cs, Rb, Li.

lene oxide in the polymer electrolyte [25]. The obtained values of X_c for the composite polymer-gel electrolytes, presented in Table 1, confirm that we deal with almost amorphous materials ($X_c < 20\%$). It is obvious that the electrolytes based on Cs and Rb are much more amorphous than the Li one (especially for Cs, a crystallinity lower than 5% is presented), indicating a clear dependence of the polymer thermal properties on the cation radius. That is, X_c values increase in the following order: Cs < Rb < Li. This suggests a clear interaction of the polymer with the alkali metal cations. Specifically for PEO, the repeating unit (–CH$_2$–CH$_2$–O–) seems to present a favorable arrangement for such effective interactions via the free electron pair on its oxygen atoms. This may occur because the PEO chains are capable of adopting a helical conformation with an oxygen-lined cavity that presents ideal distances for oxygen–cation interactions [13].

It is generally accepted that conductivity is enhanced inside the amorphous parts of a polymer electrolyte [26]. For this reason, it is important to introduce a certain degree of disorder in the polymer host structure, by, for example, the addition of inor-
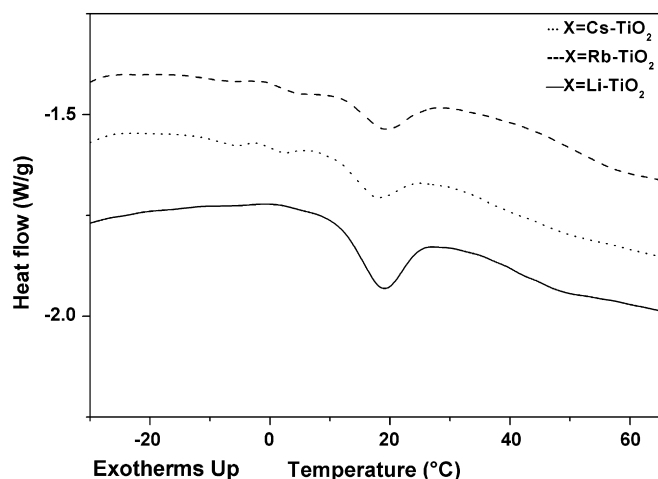

Fig. 2. MDSC thermograms for the PEO-TiO$_2$-PC(XI/I$_3^-$) composite electrolytes. X = Cs, Rb, Li.

ganic fillers in the host polymer [27–29]. Indeed, the strategy of incorporating nanosized oxides into PEO/I_3^-/I^- electrolytes has already successfully been used in order to prepare highly efficient DSSCs [16,17]. As seen in Table 1, the X_c values are further reduced by the addition of titania filler into the electrolytes. It is remarkable that all electrolytes present a crystallinity below 4.2%. Once again the lowest value is obtained in the case of the larger cation, Cs, although we should notice that the most spectacular change in amorphicity comes for the Li-based electrolyte (about 80% relative decrease). The filler particles, because of their large surface area, prevent the recrystallization of the PEO. The same effect was observed also with other inorganic fillers used. Preliminary work with different metal oxides in the form of nanocrystalline fine powder, like SnO_2, MgO and Al_2O_3, has been carried out. The first results (not shown) confirmed a significant dependence of the cell efficiency on the nature of the filler, particle size and BET surface area. Nevertheless, TiO_2 nanoparticles were still those presenting the highest efficiency among all fillers. This effect can be attributed to structure modification of the polymer electrolyte produced by a combination of steric hindrance effects or/and of acid–base interactions between the Lewis acid character filler polar surface groups and the oxygen of the PEO [30].

The MDSC results concerning the amorphicity, have been further supported by conductivity measurements. As can be seen in Table 2, all samples present excellent ionic conductivity values, σ, (ranging from 0.8 to 1.6 mS cm^{-1}) comparable with the ones reported in literature [24]. It is also noteworthy that they exhibit a remarkable stability, as the same values were confirmed again at least 2 days after their preparation. In good agreement with the MDSC results, the addition of the filler further increases the conductivity of all the electrolytes. However, it is noticeable that all composite samples present almost similar σ values despite their different thermal properties. It is evident that the transport properties in the polymer electrolytes depend strongly on the polymer-salt and polymer-plasticizer interactions that play a key role to the conductivity behavior of the electrolyte. Due to the interaction of the free electron pair on the oxygen atom of PEO with the alkali metal cation, the ionic conductivity is associated with the concentration ratio of oxygen in the ethylene oxide repeating units and the cations of the salt [13]. The above arguments are supported by recent ^{7}Li NMR measurements [31] on similar type electrolytes which show severe reduction of the Li diffusion coefficient relative to that determined in the corresponding liquid ones. Moreover, liquid (PC) plasticizers or solid

filler particles, remaining between the adjacent polymer chains, reduce the polymer–polymer chain interaction and increase the free volume of the system, all these resulting in enhanced mobility of the I^-/I_3^- redox couple. Therefore, while, in gels, the cations are strongly immobilized via interactions with the polymer and the filler, the anions remain mobile, at a large extend and are able to diffuse.

The above noticeable conductivity values for the composite electrolytes are in agreement with the corresponding triiodide effective diffusion coefficient values, calculated from linear sweep voltametry experimental results. During the redox couple regeneration cycle, the ionized dye molecules are reduced by iodide in the electrolyte by the reaction:

$$2D^+ + 3I^- \leftrightarrow 2D + I_3^- \tag{2}$$

At the Pt electrode the reverse reaction takes place:

$$I_3^- + 2e^- \leftrightarrow 3I^- \tag{3}$$

The linear sweep voltametry experiments monitor the above redox reaction of I^-/I_3^- couple at the Pt electrode. Above about ±300 mV versus Pt, the current density saturates for both polarities with similar anodic and cathodic limiting current plateaus which indicate steady-state conditions. For our electrolytes, the excess iodide concentration over triiodide (10:1) ensures that triiodides are the limiting current ions [11]. Therefore, limiting current densities (J_{lim}) can only be used to calculate the triiodide apparent diffusion coefficient $D_{I_3^-}^*$ according to the following relation [11]:

$$J_{lim} = \frac{2nFC_oD_{I_3^-}^*}{d} \tag{4}$$

where $n = 2$ is the electron number required for the reduction of triiodide to iodide, C_o the initial concentration of the triiodide ions, d the thickness of the cell and F is the Faraday constant. Values of $D_{I_3^-}^*$, presented in the following Table 2, routinely increase in the previously presented order concerning the cation radius: Cs > Rb > Li. Furthermore, in agreement with the reported σ values in Table 2, the inclusion of the TiO_2 filler turns out decisive in the increase of $D_{I_3^-}^*$, attaining values of 3.2×10^{-6} cm s^{-1} for the Cs-based electrolyte. Taking into account the gel-like nature of the electrolytes [31], this can be considered as a very high value which is comparable with that obtained with classical liquid electrolytes.

Table 2

Ionic conductivities (σ), triiodide effective diffusion coefficients ($D_{I_3^-}^*$) for the composite electrolytes and performance parameters, under AM1.5, of the TiO_2 (P25 Degussa)/Ru535 dye-sensitized solar cell using the PEO-TiO_2-PC(XI/I_3^-) and PEO-PC(XI/I_3^-) composite polymer electrolytes

Sample	σ (mS cm^{-1})	$D_{I_3^-}^*$ (10^{-6} cm^2 s^{-1})	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
PEO-PC(CsI/I_3^-)	1.1	2.1	5.78	667	0.54	2.08
PEO-TiO_2-PC(CsI/I_3^-)	1.5	3.2	10.10	618	0.46	2.87
PEO-PC(RbI/I_3^-)	0.9	2.1	6.06	685	0.51	2.11
PEO-TiO_2-PC(RbI/I_3^-)	1.6	2.1	6.55	666	0.50	2.18
PEO-PC(LiI/I_3^-)	1.0	0.7	3.60	610	0.50	1.10
PEO-TiO_2-PC(LiI/I_3^-)	0.8	1.1	6.00	534	0.45	1.44

X = Cs, Rb, Li.
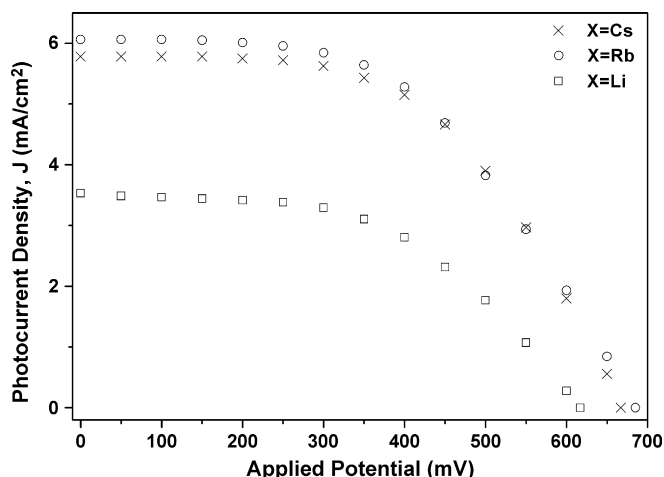
Fig. 3. Photocurrent density–voltage (J–V) curve of the TiO_2 (P25 Degussa)/Ru535 dye-sensitized solar cells using the PEO-PC(XI/I_3^-) composite polymer electrolytes. X = Cs, Rb, Li. Temperature: 25 °C, Area: 0.20 cm^2, solar irradiance: 1000 W m^{-2}.

After the electrochemical characterization, the developed polymer redox electrolytes were incorporated in dye-sensitized solar cells. The current density–voltage (J–V) curves, obtained under simulated solar illumination of 1000 W cm^{-2} for the [TEC8/TiO$_2$-Ru535//Electrolyte//Pt/TEC8] DSSCs employing the different unfilled and filled electrolytes, are exhibited in Figs. 3 and 4, respectively, and Table 2 summarizes the photovoltaic characteristics obtained from the J–V curves analysis. The results strongly verify the dependence of the cells performance from the I$^-$/I$_3^-$ redox couple mobility and the nature of the metal cation of the iodide salt. It is evident that cells with the unfilled Li-based electrolyte present again the lowest efficiency compared with the other two electrolytes. On the other hand, the use of electrolytes with Cs and Rb cations leads to almost the same efficiencies. This behavior reflects the similar values of σ and $D^*_{I_3^-}$ for the above electrolytes.
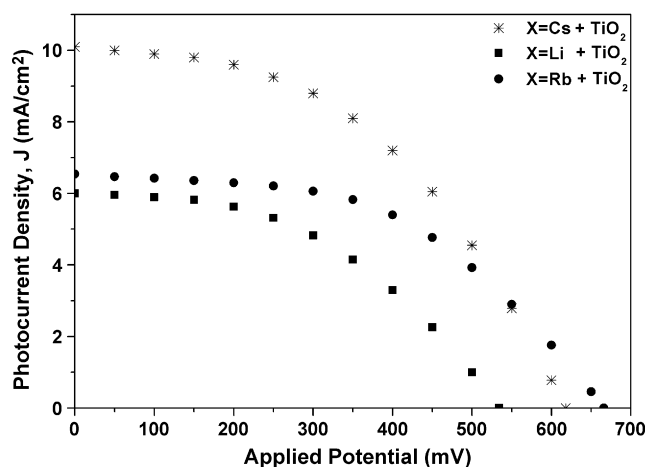

Fig. 4. Photocurrent density–voltage (J–V) curve of the TiO_2 (P25 Degussa)/Ru535 dye-sensitized solar cells using the PEO-TiO$_2$-PC(XI/I_3^-) composite polymer electrolytes. X = Cs, Rb, Li. Temperature: 25 °C, area: 0.20 cm^2, solar irradiance: 1000 W m^{-2}.

In the case of the TiO_2-filled composite electrolytes, enhanced photovoltaic performance accompanied by remarkable stability for several weeks is exhibited for all the samples. The efficiency increases again according to the cation size, in agreement with literature [18]. In fact, the larger the cation, the smaller its solvation layer is. This results to a more intensive interaction of the cation with the polymer chains and subsequently to an increase of the I$^-$/I$_3^-$ redox couple mobility and thus the photocurrent. The optimum performance was obtained in the case of the DSSC containing the PEO-TiO$_2$-PC-(CsI/I$_3^-$) electrolyte, yielding fill factor (FF) of 0.46, short-circuit current density (J_{sc}) of 10.10 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.618 V and overall energy conversion efficiency (η) of 2.87%.

As shown in Table 2, the addition of the filler improves significantly the efficiency of the corresponding solar cell devices by an overall 30–70%. This is attributed to the morphological changes of the polymer structure in an extended network which permits the ionic movement monitored by the enhancement of the apparent diffusion coefficient and the ionic conductivity. In this way, the use of the gels with the inclusion of the filler, combines a decisive enhancement in the short circuit photocurrent J_{sc} which approaches that of the liquid electrolytes while maintaining a high V_{oc} characterizing the quasi-solid electrolytes. However, a close inspection of the data in Table 2, shows a slight decrease of FF and a wider variation to the V_{oc}, as a cost for the improvement of the ionic motion. In fact, variations of V_{oc} values are also observed regarding the different cations of the electrolyte. This is easily explained if anyone takes into account that wetting of the semiconductor by the electrolyte results in the presence of iodides inside the porous network. To assure charge neutrality, the corresponding cationic species are also incorporated. Well-known intercalation effects in nanostructured titania [32] support the above statement. Under these conditions, the semiconductor/electrolyte interface is modified by the specific adsorption of cations [33]. As these positive charges are adsorbed on the semiconductor, the Fermi level position is lowered and consequently, the obtained photopotential decreases.

However, the observed differences regarding the efficiency values of the DSSCs are mainly due to the short-circuit photocurrent differences, which can in turn be assigned to triiodide diffusion coefficient and/or conductivity differences (Table 2). Firstly, in order to give insight into the crucial role of the above parameters on the performance of the cells, the current densities tabulated in Table 2 for the various cells have been plotted versus $D^*_{I_3^-}$ of the corresponding gel electrolytes used (Fig. 5). A linear increase of J_{sc} versus $D^*_{I_3^-}$ is observed, which verifies the importance of optimizing $D^*_{I_3^-}$ in our cells. The $D^*_{I_3^-}$ enhancement was identified as the most significant reason for the short circuit photocurrent increase in [34], too, where, however, J_{sc} tends to level off for very high $D^*_{I_3^-}$ values (above 5×10^6 cm^2 s^{-1}), limited by recombination effects of the injected electrons at the photoelectrode. Moreover, it should be noticed here that, while analyzing the gel-electrolyte properties, the $D^*_{I_3^-}$ and σ parameters were determined in Pt sandwiched electrodes thus, they
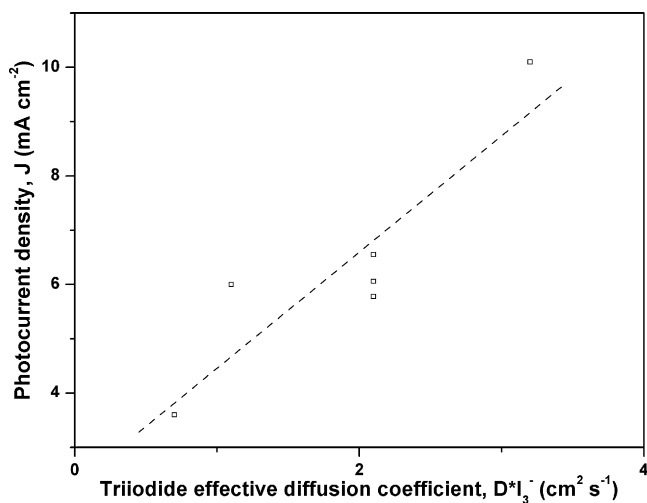
Fig. 5. Dependence of the photocurrent density, J, of DSSCs containing various polymer-gel electrolytes on their triiodide effective diffusion coefficient.

are expected to be significantly altered inside the DSSC, as they are affected by the photoelectrode porous network which is not accessed in the conductivity and electrochemical experiments. In fact, the TiO_2 photoelectrode has a mesoporous structure [35,36] and it is anticipated to restrict seriously the ionic motion through gellation and restricted percolation of the electrolyte through its pores. Consequently, the photoelectrode severely restrains the ionic motion in the corresponding solar cells [37].

4. Conclusions

In summary, new, almost amorphous, highly conductive polymer-gel electrolytes were developed. We have successfully fabricated dye-sensitized nanoporous TiO_2 photoelectrochemical cells using these electrolytes and the influence of the metal cation of the iodide salt and the introduction of TiO_2 filler on the performance of the cells was investigated. The PEO-TiO_2-PC(CsI/I_3^-) composite polymer electrolyte presents the optimum redox couple diffusion characteristics and the highest degree of amorphicity. Under standard AM1.5 solar irradiation, the DSSC incorporating the above electrolyte gives maximum overall energy conversion efficiency of 2.87%. The quasi-solid-state DSSCs filled with titania nanoparticles into the polymeric electrolyte clearly exhibit a considerable enhancement in their photovoltaic performance. Thanks to these electrolytes, we have avoided the problems caused from the use of both liquid and solid electrolytes as well as the necessity of the blocking layer deposition on the working electrode, demonstrating that a polymer-gel electrolyte helps to improve long-term stability and solar energy conversion efficiency to a remarkable extent. Optimization of the electrolyte parameters and of the cell assembly should help to further improve the photovoltaic performance.

Acknowledgements

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