Enhancement of photocurrent generation and open circuit voltage in dye-sensitized solar cells using Li$^+$ trapping species in the gel electrolyte†

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The influence of the addition of 12-crown-4 ether in a gel polymer electrolyte based to a PEO copolymer and its application in dye sensitized solar cells were investigated. Introduction of these Li$^+$ trapping species brought beneficial contributions to both V_{oc} and J_{sc} values, increasing the device's performance.

Dye-sensitized solar cells (DSSC) have attracted much attention in the last decade since the pioneering work reported by O'Regan and Grätzel,[1] especially in light of their low cost compared to conventional silicon solar cells. DSSC based on TiO$_2$ as the nanostructured electrode are capable of achieving overall conversion efficiencies of 11%.[2] The presence of the liquid electrolyte demands a perfect seal in order to avoid leakage and evaporation of the solvent. However, such perfect sealing is a difficult task and usually the presence of a liquid component makes large scale production difficult. Many efforts have been developed to overcome this drawback, replacing the liquid electrolyte by room temperature ionic liquids,[3,4] organic and inorganic hole transport materials,[5] hybrid electrolytes,[6] polymer and gel-type electrolytes.[7] Polymer electrolytes are usually polyethers, such as PEO and PPO coordinated to a range of inorganic salts, such as LiClO$_4$, LiCF$_3$SO$_3$, LiSCN, NaI, NaSCN, NaClO$_4$ or NaB(C$_6$H$_5$)$_4$.[8] Even for a gel polymer electrolyte where low molar mass, high dielectric constant solvents are introduced to increase the ionic conductivity, the overall conversion efficiency is still low in comparison to devices using a liquid component.[9–11] The major problems result from the low ionic diffusion in a more viscous medium, low penetration of the polymer inside the nanostructured electrode and an increase in the interfacial charge-transfer resistances between the electrodes and electrolyte.[12] To increase the overall conversion efficiency, the conduction properties and also the nature of the polymer systems must be improved/changed. Addition of inorganic nanofillers,[13,14] organic additives,[15,16] ionic liquids,[17–19] oligomers based on ethylene oxide[20,21] and gelators[22,23] have become a common route to elaborate polymer (or gel) electrolytes with improved ionic conductivity. Polymer electrolytes containing crown ethers are usually employed in secondary lithium

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batteries. In general, the addition of crown ethers has been demonstrated to improve the ionic conductivity at low concentrations affecting the rate of the Li electrode reaction[24–26] Shi *et al.* employed an electrolyte containing the ionic liquid 1,2-dimethyl-3-propylimidazolium iodide and 18-crown-6 ether in DSSC. The devices containing crown-ethers exhibited a small enhancement in the short-circuit photocurrent.[27]

In this work we investigated the influence of the addition of 12-crown-4 ether in a gel polymer electrolyte consisting of poly(ethylene oxide–co-2-(2-methoxyethoxy)ethyl glycidyl ether)-P(EO-EM), γ-butyrolactone (GBL), LiI and I$_2$ and its application in dye-sensitized solar cells. The polymer electrolytes were prepared by the dissolution of the copolymer, LiI, I$_2$, the plasticizer GBL (Aldrich) and the 12-crown-4 ether (Aldrich) in acetone. In all cases, the copolymer/plasticizer weight ratio was 0.3 : 0.7. Ionic conductivity measurements, solar cell assembly and device characterization were done according to a well-established procedure developed in our lab and can be found elsewhere.[9,10,28] Solar cells were assembled with 0.25 cm^2 of active area and the *I–V* curves were obtained in the dark and under standard AM 1.5 conditions using a He(Xe) lamp as light source and filters. In addition, a spacer was placed between the two electrodes to avoid short circuit. The apparent diffusion coefficients of I$_3^-$/I$^-$ species in the electrolyte were measured through voltammetry at 10 mV s^{-1} using a Pt disk microelectrode with 30 μm of diameter as working electrode, a Pt foil and a Pt wire as counter and reference electrodes, respectively.

Fig. 1 shows a plot of the ionic conductivity of the gel electrolyte as a function of LiI content. The iodide/iodine ratio was kept 10/1 for all samples. We observe an increase in the ionic conductivity up to 10 wt% of LiI. For a common polymer electrolyte system (polymer and salt), would be expected a decrease in the conductivity after a certain salt concentration due to the formation of ion pairs and crosslinking sites (see
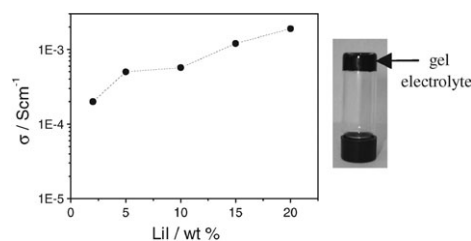

Fig. 1 Variation of the ionic conductivity as a function of LiI for the gel electrolyte P(EO-EM)$_{78:22}$ containing 70 wt% GBL. The inset shows a picture of the inverted electrolyte vessel.
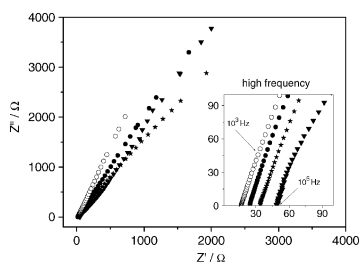
Fig. 2 Nyquist plots from EIE for the electrolyte P(EO-EM) + 20 wt% LiI (2 wt% I_2), 70 wt% GBL with different crown ether contents. (▼) 1 : 1 Li^+/CE (★) 1 : 0.5 (●) 1 : 0.25 and (○) without.

Supplementary Information†). Such effects make the segmental motion of the polymeric chains difficult and, as a consequence, with lower the ionic mobility. However, above 10 wt% of LiI we observe a sharp increase in the ionic conductivity, reaching 1.9 × 10^{-3} S cm^{-1} for the sample with 20 wt% of salt. This value is close to the values observed in a system based on a salt dissolved in an organic solvent. Such high conductivity can be explained by considering the formation of polyiodide species. It is well known that polyiodides can be formed at high concentrations of I_2 in the presence of I^-, improving the conductivity by the introduction of a new electronic conduction pathway.[29–31] We observed the same behavior with other poly(ethylene oxide)-based polymers and its consequence upon the kinetics of the devices will be discussed elsewhere.[32] The inset in Fig. 1 shows a picture of the gel electrolyte containing 20 wt% LiI. As can be seen, almost no fluidity is observed at room temperature even after addition of 70 wt% of GBL. This is an important feature for application as electrolyte in a quasi-solid-state solar cell.

Fig. 2 exhibits the Nyquist plot for the gel polymer electrolyte P(EO-EM) + 20 wt% LiI (2 wt% I_2) and 70 wt% GBL having different 12-crown-4 ether contents. The addition of crown ether with LiI in a 1 : 1 proportion with LiI decreases the conductivity from ∼2.9 to 1.0 mS cm^{-1}. Two factors might be contributing to this result. Morita *et al.*[33] have assigned the decrease in the conductivity because of an increase in the viscosity of the entire polymeric system after a large amount of crown ether addition. However, the trapping of the Li^+ ions by the crown ether can also contribute to this data since Li^+ species are much more mobile than the large polyiodide ions. It is clear that addition of crown ethers compromises the ionic conductivity of the electrolyte, thus a lower device's performance is expected.

Fig. 3 exhibits the *I–V* characteristics of the solar cells assembled with the gel electrolyte at different crown ether contents under AM 1.5 conditions. Detailed electrical parameters at 10 and 100 mW cm^{-2} and ionic conductivity values for the gel electrolyte are summarized in Table 1. The best results were obtained for the device assembled with an electrolyte containing a CE : Li^+ proportion of 1 : 1. At 100 mW cm^{-2}, J_{sc}, V_{oc} and η are 11.39 mA cm^{-2}, 0.78 V and 3.74%, respectively. The low fill factor (0.42) observed in our cells might be a consequence of recombination losses, especially in the dark current due to a high amount of iodine present in the electrolyte.

It is well known that adsorption/intercalation of potential determining cations such as Li^+ into the porous TiO_2 electrode shifts the conduction band edge downwards, lowering the
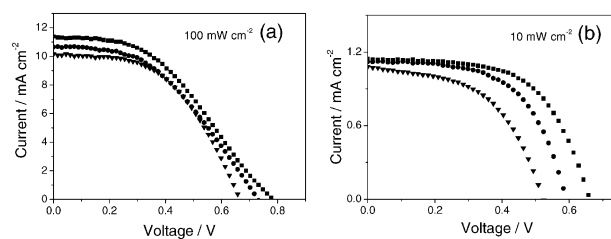

Fig. 3 *I–V* characteristics of DSSC assembled with gel polymer at different 12-crown-4 ether contents (a) 100 and (b) 10 mW cm^{-2}. Active cell area: 0.25 cm^2(■) 1 : 1 Li^+/CE (●) 1 : 0.25 (▼) without.

V_{oc}.[34,35] The 12-crown-4 ether molecules exhibit high size selectivity to Li^+ ions, resulting in a very strong coordinating system, as reported in the literature.[36] As expected, trapping Li^+ ions had a positive effect, increasing V_{oc} from 0.66 to 0.78 V. The low V_{oc} values can be a consequence of the decreased donacity of the system when high amounts of GBL is added. With no GBL, V_{oc} reaches 0.8 V, as observed in our first publication.[10] More remarkable is the increase in the photocurrent values after crown ether addition. As discussed previously, the overall conductivity of the medium decreases after crown-ether addition. So how can we explain this result?

Fig. 4 shows the steady-state voltammograms obtained using a Pt microdisk electrode for the gel electrolyte at different 12-crown-4 ethers contents. Eqn (1) was used to calculate the apparent diffusion coefficient (D_{app}) of the iodide and triiodide species from the anodic and cathodic steady-state current values:

$$I_{ss} = 4nFD_{app}C \qquad (1)$$

where I_{ss} is the anodic/cathodic steady-state current, n the number of electrons per molecule, F is the Faraday constant, and C is the bulk concentration of electroactive species.[37] The D_{app} values for the iodide and triiodide species are summarized in Table 1.

Increasing the amount of crown ether in the electrolyte, we observe an increase in the steady-state current associated with the diffusion of the iodide/triiodide species. The calculated D_{app} values for the I^- species are about four times higher when compared to the system without crown ether. In a polymer or gel electrolyte system, more than one mobile species is present. Then it is important to know not only the overall conductivity but the proportion of the current which is carried by each species; this proportion is the transport number t for any mobile species n, $t_n = \sigma_n/\sigma_{total}$.[38] In PEO-based electrolytes,
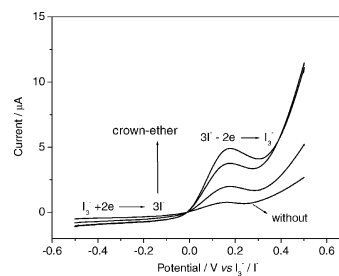

Fig. 4 Steady-state voltammograms for the gel polymer electrolyte at different 12-crown-4 ether contents using a Pt microdisk electrode with 30 μm diameter. Scan rate: 10 mV s^{-1}.

Table 1 Electrical parameters for the devices and for the gel polymer electrolytes containing crown ether

CE : Li$^+$	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)	D_{app}/cm^2 s^{-1} I_3^-/ 10^{-5}	I^-/ 10^{-6}	σ/S cm^{-1} 10^{-3}
100 mW cm^{-2}							
1 : 1	11.4	0.78	0.42	3.7	4.20	6.80	1.0
1 : 0.5	10.7	0.73	0.43	3.4	1.17	5.20	1.3
Without	10.2	0.66	0.50	3.4	0.65	1.59	2.9
10 mW cm^{-2}							
1 : 1	1.14	0.66	0.44	4.5	—	—	—
1 : 0.5	1.12	0.59	0.39	3.4	—	—	—
Without	1.07	0.52	0.47	2.9	—	—	—

the Li$^+$ transport number varies from 0.2 to 0.5 due to the high PEO solvating ability.

Passerini and co-workers[39] observed a similar effect when an ionic liquid is added to PEO for application in lithium ion batteries. Even with a decrease in the ionic conductivity, the introduction of an ionic liquid changed the Li$^+$ cation transport mechanism within the membranes, enabling the batteries to operate at much lower temperature and higher discharge rates. Here the incorporation of 12-crown-4 ether to P(EO-EM) copolymer makes possible the Li$^+$ trapping and contributes to increase the transport number associated to the iodide species, despite a decrease in the overall conductivity of the system. These observations can be supported by an increase in the steady-state current and diffusion coefficients of the iodide species measured by voltammetry. We conclude that it is not the overall ionic conductivity of the electrolyte which is critical, but rather the conductivity of the reactive species, iodide in our case. Another point in favor of the use of crown-ethers is that, with their strong solvating ability, it is possible to dissolve much more salt in the system, precluding formation of ion pairs or triplets. Thus, increasing the amount and the diffusion of such iodide species is of prime importance for a high regeneration rate of the dye cation formed after electron transfer, corroborating with the high values of J_{sc} observed.

Recently, an interesting report by Kang's group[40] demonstrated that for DSSC based on polymer electrolytes the efficiency increases almost linearly with an increase in the log of the ionic conductivity up to 1×10^{-4} S cm^{-1}, above which the efficiency reached a plateau. Their results reveal that ionic conductivity could be a rate-limiting step in determining the photocurrent and efficiency below this threshold. Above it other factors can play an important role in the device's efficiency.

In summary, the incorporation of 12-crown-4 ether in our gel electrolyte was a successful approach to increase the photocurrent generation of the DSSC. Addition of these coordinating molecules also improves the open circuit voltage by inhibiting the Li$^+$ from reaching the TiO$_2$ surface. We conclude that high ionic conductivity of the electrolyte is not the prime demand for polymer-based DSSC, but rather, the "conductivity" of the reactive species. However, other factors, such as recombination and interfacial resistance at the junction of the electrolyte–electrode, are important for improving the overall energy conversion of these devices. Electrochemical investigations are now in progress to determine the transport number of Li$^+$ ions before and after crown ether addition.

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