

New insights into dye-sensitized solar cells with polymer electrolytes†

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Polymer electrolytes or gel polymer electrolytes are interesting alternatives to substitute liquid electrolytes in dye-sensitized solar cells (DSSC). The interest in this research field is growing continuously, reflected in the increase in the number of papers published each year concerning these materials. This feature article presents a brief review of the history and development of polymer electrolytes aiming at applications in DSSC. Recent improvements achieved by modifications of the composition and by introduction of additives such as inorganic nanofillers, organic molecules and ionic liquids are described. The stabilities of DSSC assembled with these materials are also discussed and further improvements that can be introduced to maximize performance of the solar cell, such as photoelectrode modification, will also be presented.

1. Introduction

Dye-sensitized solar cells (DSSC) have been under intensive investigation as a low cost alternative to exploit solar energy since the report by Grätzel and O'Regan¹ in 1991. Usually these cells consist of a transparent electrode coated with a dye-sensitized mesoporous film of nanocrystalline particles of TiO₂, an electrolyte containing a suitable redox couple and a Pt-coated counter-electrode. Since the nanocrystalline DSSC consist of combinations of several materials, the properties of each component directly influence the kinetics and reactions, and consequently the performance of the solar cell. Thus, device

performance depends on the structure, morphology, optical and electrical properties of the porous semiconductor film; the chemical, electrochemical, photophysical and photochemical properties of the dye; the electrochemical and optical properties of the redox couple and solvent in the electrolyte; and the electrochemical properties of the counter-electrode.² DSSC based on Ru bipyridyl complexes and liquid electrolytes can have efficiencies as high as 11%.^{2,3} Nevertheless, there are still some questions about the presence of the liquid component, which requires perfect sealing in order to prevent leakage, and also limits the shape and stability of the cells. Many groups have focused on the substitution of the liquid electrolyte by solid or gel electrolytes, which could aid in reducing costs and make assembly of dye-sensitized solar cells easier. The main alternatives are inorganic or organic hole conductors, gel electrolytes prepared with ionic liquids or by the solidification of liquids, and polymer electrolytes. In this feature article, we present an overview of some recent developments in dye-sensitized solar cells assembled with polymer and gel electrolytes, especially

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Ana Flávia Nogueira

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concerning the modifications introduced to improve the ionic conductivity and mechanical stability of such materials, and how such modifications affect the performance of polymer-based DSSC.

2. Polymer electrolytes

Polymer electrolytes are solid ionic conductors prepared by the dissolution of salts in a suitable high molar mass polymer containing polyether units. It is important to distinguish these materials from polyelectrolytes and gel electrolytes. In polyelectrolytes, charged cationic or anionic groups are chemically bonded to a polymer chain, while their counterions are solvated by a high dielectric constant solvent and are free to move. In a classical gel electrolyte, polymer and salts are mixed with a solvent, usually having a concentration above 50 wt%, and the role of the polymer is to act as a stiffener for the solvent, creating a three-dimensional network, where cations and anions move freely in the liquid phase.⁴

The investigation of polymer electrolytes began in the 1970s, after the pioneering measurements of ionic conductivity in polymer–salt mixtures done by Wright and coworkers⁵ and the proposal of Armand and coworkers⁶ that these systems could be used in secondary batteries. After Wright's work,⁵ the polyethers, such as poly(ethylene oxide) (PEO), coordinated with a range of inorganic salts, such as LiI, NaI, LiClO₄, LiCF₃SO₃, LiSCN, NaSCN, NaClO₄ or LiPF₆, became the classical systems.⁴ In PEO, the repeating unit (–CH₂–CH₂–O–) presents a favorable arrangement for effective interaction of the free electron pair on the oxygen with the alkali metal cations. This occurs because the PEO chains are arranged in a helical conformation with a cavity that presents ideal distances for oxygen–cation interactions. PEO presents a low glass transition temperature ($T_g = -50\text{ }^\circ\text{C}$), but the regular structure favors a high degree of crystallinity (80%), with a melting point $T_m \sim 65\text{ }^\circ\text{C}$. For polymer electrolytes, ionic mobility is closely associated with local structural relaxations which occur in the amorphous phase. Thus solvent-free PEO–

salt complexes usually exhibit conductivity in the range from 10^{-8} to 10^{-4} S cm^{-1} at temperatures between 40 and $100\text{ }^\circ\text{C}$, limiting practical applications at room temperature. The solid-state nature of polymer electrolytes is an advantage; however, the ionic conductivity which occurs in the amorphous phase for the majority of polymer electrolytes is too low for application in photoelectrochemical cells or batteries.

To decrease the degree of crystallinity of the polymer at ambient temperature, and thus increase the ionic mobility, it is necessary to introduce a certain degree of disorder in the structure. This can be achieved by using blends of different polymers, copolymers or cross-linked networks, which can either reduce the crystallinity of the polymer or lower the glass transition temperature. Also, it is possible to introduce a third component in the system, which can act as a plasticizer, increasing the ionic conductivity, as will be discussed in the next sections.

2.1. Copolymers of PEO

The use of copolymers of PEO in electrolytes for solar cells began in 1999. Although PEO polymer electrolytes and their derivatives had been used before in combination with conducting polymers for the assembly of photoelectrochemical cells,^{7,8} the first DSSC assembled with a polymer electrolyte was reported by De Paoli and coworkers.⁹ The device was assembled using poly(*o*-methoxyaniline) as sensitizer and a copolymer of poly(epichlorohydrin-co-ethylene oxide) containing NaI/I₂ as electrolyte. The monochromatic photon-to-current conversion efficiency was 1.3% with 410 nm and 0.1% with 600 nm irradiation.⁹ One year later, the same electrolyte was applied in a device using a ruthenium complex as sensitizer, leading to an open circuit voltage (V_{oc}) of 0.71 V, a short-circuit current (J_{sc}) of 0.46 mA cm^{-2} and overall conversion efficiency (η) of 0.22% under 120 mW cm^{-2} of white-light illumination.¹⁰ But it was only in 2001, 10 years after Grätzel's first announcement of an efficient liquid-electrolyte based DSSC, that devices assembled with polymer electrolytes with efficiencies superior to 1% were reported.^{11,12} Since then, many efforts have concentrated on the search for new polymer electrolytes that could increase the efficiency of the device.

The use of PEO copolymers was initiated with the work of De Paoli and coworkers,¹³ which showed a systematic investigation of the ionic conductivity and thermal properties of three copolymers of ethylene oxide (EO) and epichlorohydrin (EPI) with different monomer ratios. The ethylene oxide/epichlorohydrin ratios in the copolymers were 84/16, 60/40 and 50/50, and they were designated as P(EO–EPI)84–16, P(EO–EPI)60–40 and P(EO–EPI)50–50, respectively. Measurements of the ionic conductivity of copolymers containing LiClO₄ showed that this parameter was dependent both on the concentration of salt and on the molar ratio between the comonomers. For example, the higher the content of ethylene oxide units in the copolymer, the higher was the ionic conductivity of the electrolyte, for the same salt concentration. The best ionic conductivity was obtained for P(EO–EPI)84–16 copolymer mixed with $\sim 5.5\text{ wt}\%$ of LiClO₄ ($4.1 \times 10^{-5}\text{ S cm}^{-1}$ at $30\text{ }^\circ\text{C}$). Cyclic voltammetry studies showed an electrochemical stability window in the range of 4.0 V. The temperature dependence of the ionic conductivity for all copolymer/salt complexes was studied by the empirical



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Marco-Aurelio De Paoli completed his PhD at Universidade de São Paulo in 1974 and became full Professor at UNICAMP in 1990. He worked as a researcher/visiting professor at Max-Planck Institut für Strahlenchemie, IBM Research Laboratory, Università di Roma La Sapienza and Università di Bologna. He is a member of the Brazilian Academy of Sciences and has received several international and national awards. He began his research on polymers at UNICAMP in 1978 and

in the 1990s was a pioneer in the field of polymer electrolytes for electrochemical devices, including DSSCs. He has published 240 scientific papers, two books, several book chapters and patents.

Vogel–Tamman–Fulcher relationship and it was found that the ionic conductivity in these complexes was strongly coupled to the flow behavior of the matrix, as also observed by other groups.¹⁴ The strong decrease of crystallinity observed for the copolymer P(EO–EPI)84–16 after addition of a small amount of salt, together with the conductivity data, indicated that Li⁺ cations interact more strongly with the oxygen atoms from the ethylene oxide units than those from the epichlorohydrin units. The ionic conductivity attained in this work was considered sufficient to motivate the use of the P(EO–EPI)84–16 complexes as polymer electrolytes.¹³

Aiming at applications in solar cells, the thermal and ionic conductivity properties of the elastomer P(EO–EPI)84–16 filled with NaI or LiI and I₂ were explored.^{10,15} Fig. 1 shows plots of the ionic conductivity of the polymer electrolyte as a function of salt concentration, at 26 °C. The ionic conductivity initially increases with the increase in salt concentration, due to the increasing number of charge carriers. However, after reaching a maximum value, the conductivity decreases because larger amounts of salt lead to the formation of ion pairing and cross-linking sites that hinder the segmental motion of the polymer chains and, as a consequence, decrease ionic mobility.¹⁶ For this system, the highest conductivity was $1.5 \times 10^{-5} \text{ S cm}^{-1}$, for the sample containing 9 wt% of NaI.¹⁵ The Na⁺ ions interact with the ethylene oxide repeating units of the polymer chains by means of Lewis type acid–base interactions. The empirical Vogel–Tamman–Fulcher equation was used to model the conductivity and temperature relationships, indicating that conduction occurs in the amorphous phase of the copolymer.¹⁵ Surprisingly, the ionic conductivity was higher for the electrolyte prepared with NaI, when compared to the electrolytes prepared with LiI. At first, it was expected that Li⁺ cations would lead to a better conductivity, since they are smaller than Na⁺ cations. This behavior was attributed to the high energy that is necessary to dissolve LiI in the polymer matrix, in comparison to the energy necessary to dissolve NaI.¹⁷

DSSC were assembled using the polymer electrolyte consisting of P(EO–EPI)84–16, 9 wt% NaI and 0.9 wt% I₂. The film of the polymer electrolyte was deposited onto the sensitized TiO₂

electrodes by casting, using a solution of P(EO–EPI)84–16 with NaI and I₂ in acetone. The assembly of the cells was completed by pressing the Pt counter-electrode against the sensitized electrode coated with the polymer electrolyte. The electrolyte was also used as a kind of adhesive between the working and counter-electrodes, and no sealing step was necessary. The active area of the cells was typically 1 cm². Unsealed devices employing this polymer electrolyte achieved solar to electrical energy conversion efficiencies of 1.6% under 100 mW cm⁻², and 2.6% under 10 mW cm⁻².¹¹ This was the first report of a dye-sensitized solar cell assembled with a pure polymer electrolyte with efficiency superior to 1%. Nevertheless, the efficiency of such “solid” solar cells was much lower than the ~10% obtained for solar cells prepared with liquid electrolytes. The main drawback was attributed to the ionic conductivity of the polymer electrolyte, which was found to be about 2 orders of magnitude lower than the conductivity usually observed with liquid electrolytes. The open circuit voltage of these cells was surprisingly high (0.82 V). Analyses of liquid electrolyte cells have indicated that this voltage is primarily limited by recombination losses from injected electrons interacting with oxidized redox carriers in solution. These recombination losses accelerate as a function of cell voltage due to an increase in the electron density in the titania film. The high Voc value was assigned to the basic character of the polymer in the electrolyte.¹⁸ Protons have been shown to increase the density of electrons in titania films at a fixed applied potential,^{19,20} most probably associated with the ability of these ions to intercalate into titania. The basic nature of the polymer used in the electrolyte is likely to shift the voltage dependence of the electron density in titania to more negative voltages, and therefore minimize the voltage dependence of the recombination losses within the cell. Comparable shifts in the voltage dependence of the recombination dynamics of dye-sensitized TiO₂ films have been observed following the addition of a base to a liquid electrolyte.²¹

Pure PEO has also been used in an electrolyte for DSSC, by combining this polymer with different amounts of KI and I₂.²² Using Raman spectroscopy the authors showed the formation of polyiodide species in the electrolyte upon addition of different salt and iodine concentrations. The highest ionic conductivity achieved at room temperature was $8.4 \times 10^{-5} \text{ S cm}^{-1}$ for the electrolyte composition PEO:KI:I₂ 12:1:0.1. Fourier transform infrared spectroscopy was carried out to show that the K⁺ ions can coordinate to the ether oxygens in PEO chains and a linear Arrhenius type behavior was observed. DSSC assembled with this electrolyte presented J_{sc} = 6.1 mA cm⁻², Voc = 0.59 V, fill factor, FF = 0.56 and $\eta = 2.0\%$ under irradiation of 100 mW cm⁻².

The major problems associated with the use of polymer electrolytes in DSSC arise from the low ionic diffusion in a more viscous medium, low penetration of the polymer inside the nanostructured TiO₂ electrode, and an increase in the interfacial charge-transfer resistance between the electrodes and the electrolyte.²³ In order to enhance the overall conversion efficiency and the transport properties, the nature/composition of the polymer systems must be improved. Further improvements in device performance are readily achievable through optimization of the ionic conductivity. In this context, the addition of inorganic nanofillers, ionic liquids, oligomers based on ethylene oxide, plasticizers and other additives has become a common

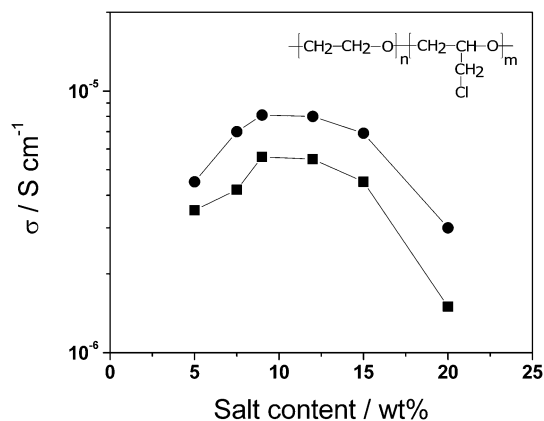


Fig. 1 Effect of salt concentration on conductivity for polymer electrolytes based on P(EO–EPI), I₂ and: (–■–) LiI and (–●–) NaI. The structure of the P(EO–EPI) copolymer is also shown, where n and m are equal to 84 and 16, respectively.

route to elaborate polymer (or gel) electrolytes with improved ionic conductivity properties.

3. Plasticized and gel polymer electrolytes

Adding small molecules or oligomers with coordinating/solvating ability to the polymer is an interesting alternative to overcome the limitations inherent in a mixture of only polymer and salt. Such compounds are known as plasticizers, they possess low molar mass, high boiling points and are routinely added to highly crystalline polymer matrixes to increase the flexibility of the polymer chains. For polymer electrolytes, this additive contributes to increasing the ionic conductivity by several orders of magnitude.²⁴ In fact, DSSC assembled with polymer electrolytes containing plasticizers exhibit much higher efficiencies. However, an increase in the plasticizer content can also be followed by a loss in mechanical properties. One should note that the term “plasticizer” is routinely used for several additives, although it is not necessarily true that these additives will act as a real plasticizer, *i.e.*, by definition, a plasticizer must change the glass transition temperature and reduce the crystallinity degree of the polymer.

It is also important to note that there is a tenuous line between plasticized polymer electrolytes and gel electrolytes. Actually there is not a clear definition or classification system, and misunderstandings in this field are quite common. Classical plasticized polymers are routinely used in industry, when the plasticizers are added (in amounts up to 40 wt%) to a polymer, usually aiming at changing the mechanical properties, but always maintaining the solid-state characteristics (phthalic acid esters added to PVC, for example). In a classical gel electrolyte, a three-dimensional polymer network (not necessarily a coordinating polymer, in fact most gel electrolytes are made of “inert” matrixes) holds an organic solution of a salt. For an “inert” gel electrolyte (polyacrylonitrile, poly(methyl methacrylate) or poly(vinylidene fluoride) derivatives), the ionic transport occurs in the solution phase. However, if the polymer employed possesses the ability to strongly solvate the cation, then both phases can be responsible for ionic transport. As gel electrolytes usually contain a high fraction of liquid components, their mechanical properties are poorer than those observed for pure polymer electrolyte systems, or plasticized polymer electrolytes. The following section contains a brief review about significant improvements made in DSSC assembled with both plasticized and gel electrolytes, without distinguishing between them.

In 2001, a dye-sensitized solar cell assembled with a gel network polymer electrolyte based on polysiloxane and PEO, containing 20 wt% of LiI, 5 wt% of I₂ and 150 wt% of the mixture ethylene carbonate (EC)/propylene carbonate (PC) (3:1 v/v) was reported.¹² EC is a high viscosity solvent with a high dielectric constant, which is favorable for salt dissociation. However, this material has a tendency to crystallize at low temperature, causing phase separation between the plasticizer and the polymer matrix. Thus, organic solvents such as PC are used to form binary organic solvents with EC and homogeneous gel polymer electrolytes can be obtained. The fully crosslinked electrolyte presented ambient conductivity of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ and the solar cells showed an open circuit voltage of 0.69 V and a short-circuit

current density of 1.7 mA cm^{-2} under white light irradiation (28 mW cm^{-2}), yielding an efficiency of 2.9%.¹²

The addition of 50 wt% of the plasticizer poly(ethylene glycol)methyl ether, P(EGME), with molar mass of $\sim 350 \text{ g mol}^{-1}$ to the polymer electrolyte based on P(EO–EPI)84–16, NaI and I₂ increased the ionic conductivity without compromising the electrochemical, thermal and dimensional stabilities. This material was chosen as plasticizer for P(EO–EPI) due to the similarity of its chemical structure with the copolymer matrix. In the P(EPI–EO)/NaI/I₂ system the ionic conductivity of the sample containing 11 wt% of NaI reached a maximum value of $1.9 \times 10^{-5} \text{ S cm}^{-1}$. After addition of P(EGME), an overall increase in the ionic conductivity was observed for the system at all salt concentrations, reaching a maximum value of $1.7 \times 10^{-4} \text{ S cm}^{-1}$ at 13 wt% of NaI. The addition of the plasticizer to the polymer electrolyte even allowed the dissolution of larger amounts of salt without significantly changing the conductivity of the system, which remained on the plateau of $10^{-4} \text{ S cm}^{-1}$.²⁵

Interesting results have also been obtained using γ -butyrolactone (GBL) as plasticizer for P(EO–EPI) copolymer. For the electrolyte prepared with GBL, P(EO–EPI)87–13, 15 wt% of NaI and I₂ for example, the maximum ionic conductivity changed from $3 \times 10^{-5} \text{ S cm}^{-1}$ to $1 \times 10^{-4} \text{ S cm}^{-1}$ after addition of 50 wt% of GBL.²⁶ The apparent diffusion coefficient of ionic species in the electrolyte with and without plasticizer was estimated using complex impedance spectroscopy and the equivalent circuit $R_s[Q_1(R_1O)]$ (Fig. 2) was used to fit the data according to the method proposed by De Paoli and coworkers.²⁷ The Nyquist diagrams are shown in Fig. 2. The response at high frequencies can be attributed to the counter-electrode/electrolyte interface, while the response at low frequencies can be associated with the diffusion processes in the electrolyte.²⁷ From the parameters obtained by fitting the experimental data, the apparent diffusion coefficient can be estimated using Eq. 1,²⁸ where l_e is the thickness of the electrolyte film and B is a parameter related to the element O in the equivalent circuit proposed, which accounts for a finite-length Warburg diffusion (Z_D).

$$D = l_e^2/B^2 \quad (1)$$

Fig. 2 shows that the overall impedance of the system decreases after addition of plasticizer. These data are in

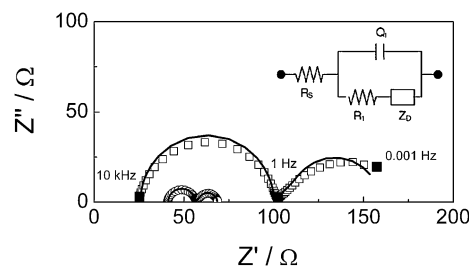


Fig. 2 Nyquist diagrams of the impedance spectra obtained for polymer electrolyte films sandwiched between planar Pt electrodes. Experimental data are represented by symbols and solid lines correspond to the fitting using the equivalent circuit shown in the inset. The polymer electrolytes are based on P(EO–EPI), NaI/I₂ (○) with plasticizer (50 wt% GBL) and (□) without plasticizer.

agreement with the increase observed in ionic conductivity.²⁶ The apparent diffusion coefficient of ionic species in the electrolyte containing GBL was estimated to be $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, one order of magnitude higher than the diffusion coefficient estimated for the polymer electrolyte without plasticizer ($4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). This value is very close to the diffusion coefficient for I_3^- species in highly viscous solvents, such as *N*-methyl oxazolidinone ($2.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$),²⁹ in gels ($3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$),³⁰ gellified ionic liquids ($1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)³¹ and in a TiO_2 membrane soaked in acetonitrile ($3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$),³² but is still one order of magnitude lower than the diffusion in acetonitrile ($\sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).³³

GBL has been used as plasticizer for electrolytes for application in batteries, and it is well known to be able to coordinate Li^+ ions, contributing to the dissolution of lithium salts in polymer systems.^{34,35} Therefore, GBL also made possible the substitution of NaI for LiI in the polymer electrolyte, as shown in the plots of ionic conductivity in Fig. 3. As opposed to what was observed for the non-plasticized polymer electrolyte (Fig. 1), in the presence of GBL, electrolytes prepared with LiI present higher conductivities in comparison to the ones prepared with NaI. The addition of GBL leads to an increase in conductivity of two orders of magnitude, when compared to the non-plasticized polymer electrolyte. Also, the ionic conductivity dependence on salt concentration changes remarkably when 50 wt% of GBL is incorporated in the polymer electrolyte. As discussed before, GBL has an ion solvating ability, which allows the dissolution of larger amounts of salt. Thus, increasing the salt concentration leads to a further increase in the conductivity, reaching $5 \times 10^{-4} \text{ S cm}^{-1}$ for the sample prepared with 20 wt% of LiI. Such behavior is the opposite of that usually observed for polymer electrolytes at high salt concentration.^{13,15} This conductivity value approaches the value for a liquid electrolyte based on organic solvents. The conductivity for the sample containing 30 wt% of LiI was estimated as $6 \times 10^{-4} \text{ S cm}^{-1}$, which is very close to that exhibited by the sample containing 20 wt%, indicating saturation in salt dissolution. Solar cells assembled with P(EO-EPI)87-13 containing 50 wt% of GBL, 20 wt% of LiI and I_2 presented efficiencies of 3.3 and 3.5% at 100 and 10 mW cm^{-2} of

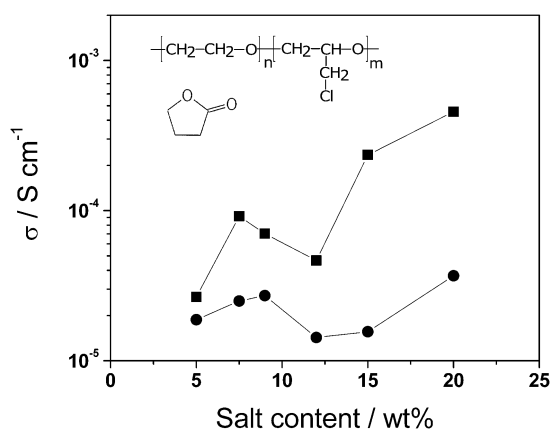


Fig. 3 Effect of salt concentration on conductivity for plasticized polymer electrolytes based on P(EO-EPI), 50% of GBL, I_2 and: (-■-) LiI and (-●-) NaI. The structures of the P(EO-EPI) copolymer ($n = 87$ and $m = 13$) and GBL plasticizer are shown in the inset.

irradiation, respectively.³⁶ Other authors also reported recently that the conductivities and diffusion coefficients of ionic species in gel electrolytes can be changed and improved by varying the composition of the salt, *i.e.*, using different cations.^{37,38}

Other changes can be introduced to further increase the ionic conductivity of such electrolytes. For example, the GBL concentration in relation to the polymer matrix can be increased up to 70% without losses in the mechanical properties, reaching a conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$ (20 wt% LiI).³⁹ In this case, the system presents the conductivity characteristics of a liquid while keeping the mechanical properties of a solid. The high values of ionic conductivity measured were rationalized to originate from a contribution of both ionic transport and a Grothuss-type mechanism introduced by the formation of polyiodides in the electrolytes with high salt concentration. The conversion of iodine to polyiodide species when the LiI salt concentration in the electrolyte exceeds 7.5 wt% was confirmed by Raman spectroscopy measurements,³⁶ and a similar effect was also reported by Yanagida and coworkers⁴⁰ for gel electrolytes.

Recently Nogueira and coworkers³⁹ obtained a very interesting result using the copolymer poly(ethylene oxide)/2-(2-methoxyethoxy)ethyl glycidyl ether containing 78% of EO units P(EO-EM). This material was mixed with LiI, I_2 and the plasticizer GBL. The amount of GBL incorporated into the electrolyte was changed from 30 to 90% and solar cells were assembled with this kind of electrolyte, containing different plasticizer/polymer ratios. The J_{sc} increases when the amount of GBL is increased from 30 to 70%, and this effect was related to the increase of ionic conductivity of the electrolyte. On the other hand, V_{oc} increases in the opposite direction, *i.e.*, with the increase in polymer content. The loss in V_{oc} values observed for PEO-based copolymers as the amount of GBL is increased is shown in Fig. 4. This effect can be attributed to the loss in the basic character of the electrolyte as more GBL is added. It is believed that the polyether units have more donor capability and thus interact more effectively with the Ti(IV) acid sites, inhibiting charge recombination. The electron lifetime in DSSC assembled with electrolytes containing different amounts of GBL was estimated from the voltage decay transients of the solar cells. A decrease in electron lifetime from the electrolyte containing 30%

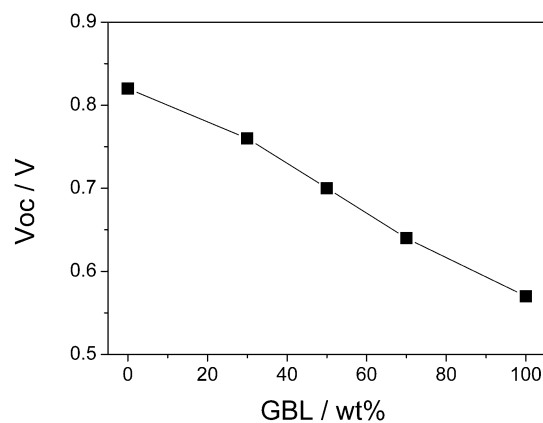
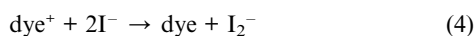
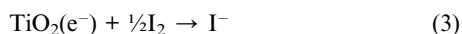
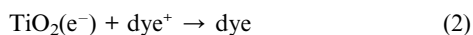


Fig. 4 Effect of GBL concentration on the open circuit voltage of DSSC assembled with polymer electrolyte containing poly(ethylene oxide) copolymers and MI/I_2 ($M = \text{Li}$ or Na).

of GBL to the electrolyte containing 70 wt% of GBL was observed, in agreement with the trend observed in Voc values. These results support the role of the polymer passivating layer in minimizing the charge recombination at the TiO₂/electrolyte interface. It seems that the recombination losses (photoinjected electrons return to the dye cation and/or electrolyte) are accelerated when replacing a very basic polymer by the addition of such additives with lower basicity.

Another important feature of the system poly(ethylene oxide) copolymer/GBL is that the ionic conductivity of the electrolyte is still significantly dependent on the composition of the copolymer.²⁶ It was known from previous works that, for pure polymer electrolytes (without plasticizer), although the crystallinity degree increased with the increase in EO unit content in the copolymer P(EO–EPI), the conductivity also increased due to having more sites available for cation coordination, once the EPI units do not contribute to ionic transport.¹³ The same trend was observed for electrolytes prepared with NaI and P(EO–EPI) even after addition of 50 wt% of GBL to the electrolyte, indicating that the oxygen atoms from the polymer chains are probably still contributing to ionic transport, even in the presence of plasticizer.²⁶

Transient absorption spectroscopy was employed to study electron-transfer dynamics in solar cells incorporating the polymer electrolyte based on ethylene oxide copolymers with and without plasticizer. Electron-transfer kinetics were collected as a function of electrolyte composition, white light illumination, and device voltage. The results were further correlated with the current/voltage characteristics of the solar cells. There are two main recombination pathways which can cause loss in DSSC efficiency: electrons injected into the TiO₂ conduction band can recombine with either dye cations or with the redox electrolyte (Eqs. 2 and 3, respectively).



In a liquid electrolyte DSSC, rapid re-reduction of dye cations by the redox electrolyte (Eq. 4) competes effectively with Eq. 2, and therefore charge recombination to the redox electrolyte, Eq. 3, is the primary recombination loss pathway limiting device efficiency.^{21,41} In polymer electrolyte-based DSSC, however, the low ionic conductivity of the polymer electrolyte introduces the possibility that dye cation re-reduction by the electrolyte may no longer compete effectively with the recombination pathway described in Eq. 2. As a consequence, charge recombination with dye cations may become critical in limiting device efficiency.

For the electrolyte containing P(EO–EPI)84–16, NaI and I₂, without plasticizer, regeneration of the dye ground state by electron transfer from I[−] ions (Eq. 4) exhibited half times (τ_{1/2}) of 4–200 μs, depending upon the concentration of NaI in the polymer electrolyte.¹⁸ At low NaI concentrations, kinetic competition was observed between Eq. 4 and Eq. 2. The decay kinetics of the dye cation, and the yield of I₂[−], were found to be unchanged by illumination of the cell. From these observations, it was concluded that the charge recombination dynamics in this

cell are not strongly dependent upon the TiO₂ Fermi level over the investigated voltage range and this observation is probably related to the Lewis base nature of the polymer employed, as discussed previously.¹⁸

Plasticized polymer electrolytes of P(EO–EPI)87–13 with 50 wt% of GBL and different amounts of LiI/I₂ were also investigated using this technique.³⁶ For a sample with a moderate concentration of iodide (7.5 wt% LiI), the dye cation signal exhibited a decay with τ_{1/2} = 20 μs, which was only marginally faster than charge recombination of the oxidized dye with electrons injected into the semiconductor, suggesting that kinetic competition between Eq. 2 and Eq. 4 might also be significant for this electrolyte composition. Increasing the amount of LiI to 20 and 30 wt%, regeneration (Eq. 4) became clearly predominant with τ_{1/2} ~ 1 μs in both cases,³⁶ similar to the value reported for acetonitrile based electrolytes.⁴² For 20 and 30 wt% LiI plasticized polymer electrolytes, the transients were less dependent upon white light illumination. The transient data for the plasticized electrolyte containing 7.5 and 20 wt% of LiI are shown in Fig. 5. The data obtained for a non-plasticized polymer electrolyte are also shown for comparison. The results obtained indicate that for polymer electrolytes with high iodide concentration and high ionic conductivity, Eq. 4 competes more effectively with Eq. 2, indicating a more efficient regeneration. Although the high concentration of iodide/iodine in the electrolyte contributed to accelerate dye cation regeneration, it also increased the dark current of the cell by one order of magnitude. In these cells, different from what was observed previously for a DSSC assembled with a polymer electrolyte (polymer and salt only), it is not the competition between Eq. 2 and Eq. 4 that limits the efficiency; instead, Eq. 3 or dark current, together with the low Voc caused by the excess Li⁺ cations on the TiO₂ surface, seems to play the main role in determination of efficiency.³⁶

Further support for the kinetic competition between Eq. 2 and Eq. 4, and Eq. 3 contribution can be obtained by fitting the J–V curves using a two-diode model (Eq. 5),^{18,43} where I_L is the light intensity dependent short-circuit current, k_B is the Boltzmann's constant, T is the temperature and I₀, k, m₁ and m₂ are fitting constants related to the dark current and the ideality factor.

$$I = I_L - I_0[\exp(qV_j/m_1k_B T) - 1] - kI_L[\exp(qV_j/m_2k_B T) - 1] \quad (5)$$

The bias drop across the internal junction, V_j can be related to the externally applied bias, V, through Eq. 6, where R_s is the series resistance of the system. I₀, m and R_s are assumed to be light intensity independent.

$$V_j = V + IR_s \quad (6)$$

Deviations from this model can be interpreted in terms of a voltage dependent loss of charge separation yield due to either lower electron injection yields or kinetic competition between charge recombination (Eqs. 2, 3) and Eq. 4.^{18,42} The first two terms on the right of Eq. 5 compose the usual non-ideal one diode current–voltage characteristic of a solar cell. The final term in Eq. 5 is a light dependent recombination current, and is required to describe adequately the observed behavior for the cells assembled with the polymer electrolyte with and without plasticizer.^{11,18}

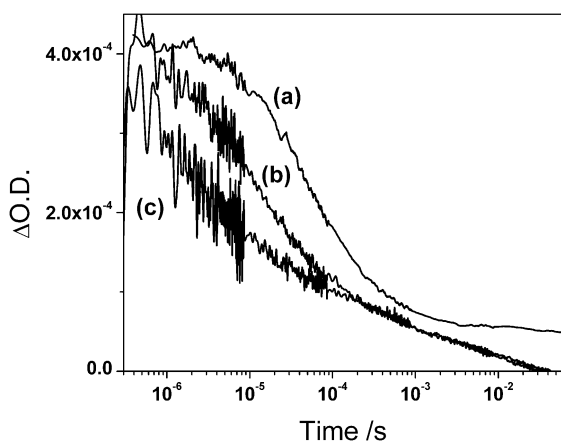


Fig. 5 Transient absorption spectra for dye-sensitized TiO₂ films covered with polymer electrolytes based on P(EO–EPI), MI/I₂ (M = Li or Na): (a) without plasticizer, (b) with GBL and 7.5 wt% of LiI and (c) with GBL and 20 wt% of LiI (O.D. = optical density).

For the non-plasticized polymer electrolyte, the light dependent recombination term was introduced because of the high rate observed for Eq. 2, due to the low ionic conductivity of the electrolyte.¹⁸ For the electrolytes plasticized with GBL, however, it would be expected that the J–V curves could be fitted using the simple one diode model, at least for samples containing larger amounts of salt, due to the high ionic conductivity of these electrolytes, and the data from transient absorption spectroscopy presented earlier.

In Fig. 6 typical J–V curves for DSSC containing polymer electrolytes with and without plasticizer are presented. Fits using the two-diode model are also shown. For the plasticized electrolyte, the need for the second term could be a consequence of the increase in dark current values, due to higher concentrations of iodine/iodide employed, different from the previous case, for the system based on the polymer electrolyte without plasticizer. In other words, the performance at high concentrations of iodide/iodine is no longer expected to be dominated by the conductivity of the medium or by the low rate of dye cation regeneration. These results are in agreement with a report by Kang and coworkers,⁴⁴ which shows that, up to a certain limit,

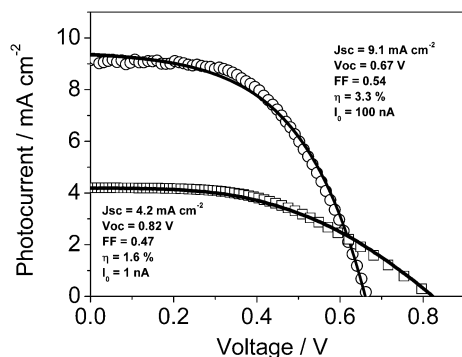


Fig. 6 J–V characteristics (symbols) for the DSSC assembled with the polymer electrolyte containing P(EO–EPI), MI/I₂ (M = Li or Na), (○) with and (□) without GBL as plasticizer, under 100 mW cm⁻². The fits using the two-diode model are also shown as solid lines.

further improvements in the ionic conductivity of the electrolyte do not guarantee any improvements in DSSC performance. Here, the efficiency of this polymer electrolyte DSSC might be dominated by the recombination reactions at the interfaces (mainly Eq. 3 or dark current). Thus, it is expected that the efficiency of these devices can be enhanced even more by improving Voc of the cells containing large amounts of plasticizer and salt. This can be achieved by the incorporation of different additives in the electrolyte, as will be discussed in the following section.

4. Additives in the polymer electrolytes

Besides the plasticizers, other additives can be explored to improve the characteristics of polymer or gel electrolytes. These materials can be incorporated for different purposes, such as the improvement of mechanical and thermal stability, enhancement of the charge transport, open circuit voltage, *etc.*

4.1. Inorganic nanofillers

An interesting approach consists of the addition of nanoscale inorganic fillers, to improve the mechanical, interfacial, and conductivity properties of the (gel) polymer electrolytes.

Since the pioneering work by Scrosati and coworkers,⁴⁵ addition of TiO₂ and other nanoparticles has been extensively employed to improve the ionic conductivity of polymer electrolytes. It is well known that the presence of such nanoparticles changes the conduction mechanisms assigned to the ions introduced in the polymer, however, how these nanoparticles actually act is still unknown. These materials can also improve the mechanical properties of gel electrolytes and ionic liquid-based electrolytes. However, their effect on the mechanical stability can result in a loss in electrolyte penetration.

The most used approach is the addition of TiO₂ nanoparticles to the polymer matrix.^{46–51} Falaras and coworkers^{46,47} investigated the addition of commercially available TiO₂ nanoparticles (P25, Degussa) to the polymer electrolytes of PEO, LiI and I₂. The filler particles, because of their large surface area, prevented recrystallization, decreasing the crystallinity degree of PEO. The increase in the glass transition temperature of the polymer indicated that the polymer electrolyte incorporated a significant quantity of the available inorganic oxide filler. Besides, the large quantity of the filler increased the dissolution of the LiI salt and the system remained mainly amorphous, as confirmed by AFM measurements. The polymer sub-units are held together in a parallel orientation, forming long straight chains of about 500 nm in width, along with TiO₂ spherical particles of about 20–25 nm in diameter. The polymer chains separated by the titania particles are arranged in a three-dimensional, mechanically stable network that creates free space and voids into which the iodide/triiodide anions can easily migrate.⁴⁶ Dye-sensitized solar cells prepared with this nanocomposite polymer electrolyte exhibited Jsc = 7.2 mA cm⁻², Voc = 0.664 V, FF = 0.58 and η = 4.2% (65.6 mW cm⁻²).⁴⁷ Other reports also describe the effects of TiO₂ nanoparticles on gel polymer electrolytes.⁵¹ Kang and coworkers⁵¹ showed that these nanoparticles additionally lead to a light-scattering effect. The DSSC with the ternary component

polymer-gel electrolyte exhibited an energy conversion efficiency of 7.2% (100 mW cm^{-2}).

Yang and coworkers⁵² investigated the use of TiO_2 nanotubes as nanofillers. Electrolytes containing polyethylene glycol and 10% of nanotubes showed high penetration and complete filling of the pores of the TiO_2 film. Using the XPS technique the authors showed that there is an interaction between the titanium atoms of the nanotubes and the polymer network. The ionic conductivity was found to be $2.4 \times 10^{-3} \text{ S cm}^{-1}$, which was achieved due to the decrease in the crystallinity degree of the polymer after introduction of the nanotubes. DSSC fabricated with this composite electrolyte showed the maximum overall conversion efficiency of 4.4%, $J_{sc} = 9.4 \text{ mA cm}^{-2}$, $V_{oc} = 0.73 \text{ V}$ and $FF = 0.65$ under 100 mW cm^{-2} of irradiation.⁵²

Nanoparticles with different compositions, such as ZnO , SiO_2 and Al_2O_3 , have also been used as nanofillers in polymer electrolytes.^{53–56} Caruso and coworkers⁵³ investigated solar cells assembled with a composite polymer electrolyte based on PEO, poly(vinylidene fluoride) (PVDF) and SiO_2 nanoparticles. To fabricate the solid-state DSSC, the composite polymer electrolyte solution was injected into the dye-sensitized TiO_2 electrode using a vacuum technique. For a given TiO_2 film thickness, devices prepared employing the vacuum method exhibited a better performance than those prepared *via* the conventional drop-casting method. Besides, the differences became more pronounced with increasing TiO_2 film thickness. These results are remarkable since they show that not only is the optimization of the composition of the electrolyte an important issue, but it is also important to guarantee the full filling of the photoelectrode with the solid-state or gel electrolyte.

Zhao and coworkers⁵⁴ prepared an electrolyte based on PEO, poly(vinylidene fluoride-co-hexafluoropropylene), SiO_2 and conductive carbon nanoparticles. The conductivity mechanism was analyzed by AC impedance and DC voltage-current measurements. A change in the conduction mechanism was obtained by adding different amounts of carbon nanoparticles. Small amounts of carbon nanoparticles improved the ionic conductivity and a DSSC with 5 wt% of carbon nanoparticles in the electrolyte presented $\eta = 4.3\%$ compared with the original DSSC performance of 3.9%. When the content of nanoparticles was increased to 15 wt%, the efficiency decreased to 3.6%, as a consequence of a decrease in the ionic conductivity and an increase in interface recombination with the electrolyte, because of the electronic conductive path formed by the aggregated carbon nanoparticles.

Xia and coworkers⁵⁵ used an interesting approach to make a composite polymeric electrolyte. First, poly(ethylene glycol methyl ether) with a molar mass of 350 g mol^{-1} was grafted onto the surface of ZnO nanoparticles through covalent bond formation. The electrolyte was composed of KI and I_2 dissolved in a low molar mass poly(ethylene glycol methyl ether), and 24 wt% of the polymer-grafted ZnO nanoparticles were used to solidify the electrolyte. For this system, the ionic conductivity increased as the salt concentration increased, reaching a maximum value of $3.3 \times 10^{-4} \text{ S cm}^{-1}$, and then decreased, behaving like a classical polymer electrolyte system. The authors showed that the V_{oc} increased by 0.13 V after the polymer-grafted nanoparticles were added to the electrolyte, but the J_{sc} decreased, probably due to the high viscosity of the gel formed.

As a result, the efficiency of the solar cell decreased to 3.1% after addition of the polymer-grafted nanoparticles, when compared with the efficiency of 4.0% observed for the device with a liquid electrolyte.

Al_2O_3 particles with different sizes were incorporated into electrolytes based on mixtures of ionic liquids, a PVDF derivative and polyacrylonitrile.⁵⁶ It was observed that the added nanoparticles influenced the diffusion coefficient of I_3^- ions and also the charge transfer rate, and this effect depended on the Al_2O_3 particle size. The authors suggested that the imidazolium cations might adsorb on the nanoparticle surface, and then the counter-anions I^-/I_3^- gather around them.

A few papers have recently reported the addition of clay-like nanoparticles in polymer electrolytes.^{57,58} Nogueira and coworkers⁵⁷ investigated the incorporation of a montmorillonite (MMT) derivative into a polymer electrolyte based on a poly(ethylene oxide) copolymer, the plasticizer GBL and LiI/I_2 . The initial increase of ionic conductivity after addition of MMT was attributed to the large number of charge carriers introduced into the complex as the clay concentration increased (see inset in Fig. 7). The XRD data suggested that the clay was not exfoliated in the nanocomposite electrolyte, but rather kept its lamellar structure. Fig. 7 presents the thermomechanical characterization of the polymer electrolytes prepared with and without the

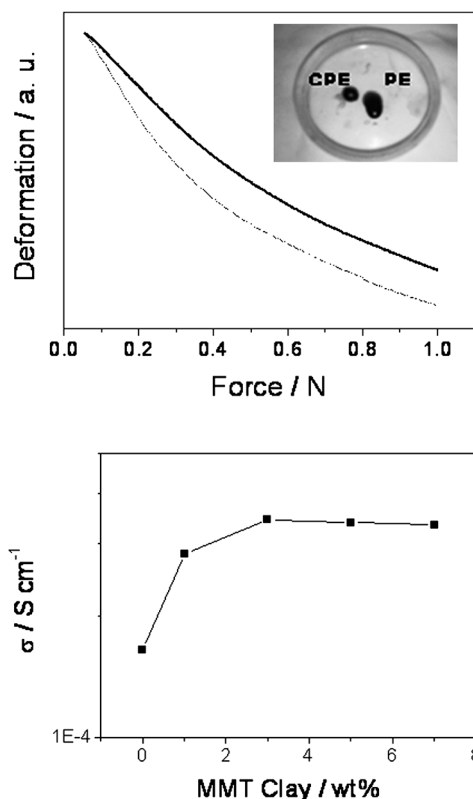


Fig. 7 Thermomechanical analysis (compression mode) for electrolytes based on P(EO–EPI), GBL and LiI/I_2 : (dashed line) without clay and (solid line) with 5 wt % of MMT clay. The inset shows a photograph of spherically shaped samples of the polymer electrolyte prepared with (CPE) and without the clay (PE), after some period of time at ambient conditions. The plot of ionic conductivity as a function of clay content is also shown.

addition of 5 wt% of clay. According to these data, the presence of the MMT promotes an increase in the mechanical stability of the entire system. This can be viewed considering the force applied to the nanocomposite polymer electrolyte film, which promotes a lower deformation comparing to the film without any clay. The difference in the mechanical properties is also illustrated as an inset in Fig. 7, where a picture of spherical shaped samples of both the composite and the plasticized polymer electrolyte prepared without clay is shown. In the case of the system without clay, there is a flow with time due to the action of gravity, leading to the disruption of the spherical shape. For the electrolyte with clay, the spherical shape remains unchanged. These results showed that the addition of MMT clay to the plasticized polymer electrolyte led not only to an increase in the ionic conductivity, but also to the solidification of the electrolyte, reflected as an improvement in the mechanical stability of the films. The solar cell devices containing the nanocomposite polymer electrolyte presented efficiencies of 1.6% and 3.2% at 100 mW cm⁻² and 10 mW cm⁻², respectively. The FF values were very poor, only 40% under 100 mW cm⁻², which was attributed to the low penetration of the composite electrolyte inside the pores of the TiO₂ film.⁵⁷

Lin and coworkers⁵⁸ prepared a nanocomposite of poly(*n*-isopropylacrylamide) with MMT clay and applied it to a liquid electrolyte system as gelator. The DSSC assembled with the polymer nanocomposite electrolyte presented Jsc = 12.6 mA cm⁻², Voc = 0.73 V, FF = 0.59 and η = 5.4% while the DSSC prepared with the electrolyte gelled with the pure polymer presented Jsc = 7.28 mA cm⁻², Voc = 0.72 V, FF = 0.60, and η = 3.2% (100 mW cm⁻²). Electrochemical impedance spectroscopy of the DSSC revealed that the nanocomposite-gelled electrolyte presented a significant decrease in impedance values. The resistance due to the electrolyte and electric contacts, the impedance across the electrolyte/dye-coated TiO₂ interface, and the Nernstian diffusion within the electrolytes were reduced. An increase in the molar conductivity of the nanocomposite-gelled electrolytes was also reported.⁵⁸

4.2. Organic molecules

Pyridine derivatives, such as 4-*tert*-butylpyridine (TBP), are frequently added to the electrolytes as additives to enhance the open-circuit photovoltage, and thus the efficiency of DSSC. The open-circuit voltage and FF of the DSSC are affected by TBP due to the suppression of dark current at the semiconductor/electrolyte junction, since TBP blocks the surface states that are active in the charge transfer.⁵⁹ Wu and coworkers⁶⁰ investigated DSSC with a polymer electrolyte based on a blend of poly(acrylamide) and poly(ethylene glycol). Using poly(ethylene glycol) as both reactant and plasticizer, TBP as additive and the mixture EC/PC or GBL as solvent, a gel polymer electrolyte with quasi-solid state was prepared. The ionic conductivity of the electrolyte was enhanced because of the complexation of the carbonyl, amine and hydroxyl groups on poly(acrylamide) and poly(ethylene glycol) chains to the K⁺ ions present in the electrolyte. The maximum ionic conductivity (at 30 °C) was ~2.0 mS cm⁻¹. DSSC were fabricated using the gel polymer electrolyte with different amounts of TBP. On the other hand, Jsc decreased with the increase in the TBP concentration. Considering the

influence of the amount of TBP on both Jsc and Voc, the optimized quantity of TBP was determined to be ~2 wt%. Under irradiation of 60 mWcm⁻², the optimized DSSC presented Voc = 0.69 V and Jsc = 4.6 mA cm⁻² while the overall energy conversion efficiency was ~3%.

Xia and coworkers⁵⁵ added TBP to the electrolyte composed of poly(ethylene glycol methyl ether), KI, I₂ and 24 wt% of polymer-grafted ZnO nanoparticles. The addition of TBP into the electrolyte resulted in a dramatic improvement in Jsc and overall efficiency, from 3.1% to 5.0%. However, the open circuit voltage and fill factor remained insensitive to the presence of this additive. The same phenomenon was also observed in a solar cell based on a room temperature molten salt reported by Kloo and coworkers.⁶¹ Although the detailed mechanism was not given, the improvement was attributed to a lower viscosity and better interfacial contact of the electrolyte after addition of TBP. The authors suggested that the effect of TBP on the electrode surface is less significant than the effect on the viscosity, for solar cells that utilize highly viscous electrolytes.⁵⁵ These reports suggest that the TBP effect on DSSC with polymer electrolytes is still under debate and that the results depend strongly on the type and composition of the electrolyte.

Recently it was shown that the incorporation of the additive 2,6-bis(*N*-pyrazolyl)pyridine to the electrolyte of PEO, KI and I₂ improved both the interfacial contact and the ionic conductivity in DSSC. X-Ray diffraction and impedance spectroscopy results have shown that this additive forms a stable complex with the polymer matrix and decreases the crystallinity of PEO. Due to the coordinating and plasticizing effect of this additive, the ionic conductivity of the polymer electrolyte was enhanced. The DSSC assembled presented Jsc = 21 mA cm⁻², Voc = 0.70 V and η = 8.8% under direct solar irradiation of 80 mW cm⁻².⁶²

A few reports are found describing the use of pyridine polymers. Polyvinylpyridine (PVP) and its derivatives are the only pyridine polymers which have been used so far to treat the dye-sensitized TiO₂ electrode surface.^{63–66} For PVP, a 150 mV enhancement in Voc was observed.⁶³ Lin and coworkers⁶⁶ investigated the addition of poly(vinylpyridine-co-acrylonitrile) to an electrolyte containing EC/PC, KI and I₂. The copolymer was used instead of pure PVP because of the incompatibility of PVP with electrolytes containing alkali iodides. The authors observed that Voc increased by ~100 mV, and the efficiency for the quasi-solid DSSC achieved 6.7%, which is higher than the 6.0% obtained for the initial EC/PC/KI/I₂ liquid electrolyte.

Different additives containing functional end-groups can be used to chemically modify the electrolyte and its interface with the photoelectrode and counter-electrode. Zhao and coworkers⁶⁷ employed a NH₂-terminated functional silane (3-aminopropyltriethoxysilane) to functionalize the electrolyte composed of PEO and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)). The newly formed Si–O–Si network and interactions influenced the ionic conductivity of the modified polymer electrolyte and also enhanced the connection of the polymer electrolyte with the electrodes. The additive deprotonated the TiO₂ photoelectrode surface, causing a change in the Fermi level energy that effectively reduced the interface recombination in the DSSC and improved the open circuit voltage. With a moderate concentration of the additive, they achieved an efficiency of 5.1% compared with 3.7% of the original DSSC. The

end-group-functionalized silicone coupling agent dodecyl-trimethoxysilane was also used to modify the PEO/P(VDF-HFP)/SiO₂ nanocomposite polymer electrolytes. The introduction of optimized contents of this additive improved the ionic conductivity and the connections with the photoanode and counter electrode. Optimal efficiencies of 6.4% and 4.9% under 30 mW cm⁻² and 100 mW cm⁻², respectively, were obtained.⁶⁸

Another possibility to improve DSSC performance is the addition of crown ethers (CE) to the electrolyte. Polymer electrolytes containing crown ethers are usually employed in secondary lithium batteries, but some papers have shown the use of this material in electrolytes for DSSC. For example, Dai and coworkers⁶⁹ added 18-crown-6 ether to an electrolyte containing the ionic liquid 1,2-dimethyl-3-propylimidazolium iodide. The devices containing crown ethers exhibited a small enhancement in the short-circuit current. On the other hand, the addition of crown ethers to polymer electrolytes has been shown to decrease the overall ionic conductivity.⁷⁰ Nogueira and coworkers³⁹ investigated the influence of the addition of 12-crown-4 ether to a polymer electrolyte consisting of P(EO-EM), GBL, LiI and I₂, and its application in dye-sensitized solar cells. The copolymer/plasticizer weight ratio was 3:7. The 12-crown-4 ether molecules exhibit high size selectivity for Li⁺ ions, resulting in a very strongly coordinating system, as reported previously.⁷¹ As expected, trapping Li⁺ ions had a positive effect, increasing Voc. Even more remarkable was the increase in the photocurrent values after crown ether addition, since the overall conductivity of the electrolyte decreased from 3.0 to 1.0 × 10⁻³ S cm⁻¹ after addition of CE. On the other hand, the addition of crown ether to the electrolyte increased the steady-state current associated with the diffusion of the iodide/triiodide species. The steady-state voltammograms for the redox reaction of triiodide/iodide in the polymer electrolyte were obtained using Pt disk microelectrodes, and are depicted representatively in Fig. 8. The apparent diffusion coefficients of the iodide species increased when compared to the system without the crown ether. This suggests that the incorporation of 12-crown-4 ether to P(EOEM) copolymer makes possible Li⁺ trapping and contributes to increasing the transport number associated with the iodide species, despite a decrease in the overall conductivity of the system. DSSC

assembled with the polymer electrolyte containing CE:Li⁺ in the proportion 1:1 presented J_{sc} = 11.4 mA cm⁻², Voc = 0.78 V and η = 3.7% under 100 mW cm⁻². The same devices presented J_{sc} = 10.2, Voc = 0.66 and η = 3.4% when prepared without crown ether.³⁹

Room temperature ionic liquids have also been used as additives for gel or polymer electrolytes. A complete review about the general application of ionic liquids in dye-sensitized solar cells has been published recently by Gorlov and Kloo.⁷² Thus, this important topic will not be further discussed in this feature article.

5. Stability of polymer electrolyte-based DSSC

The stability of DSSC with polymer electrolytes is very important, although few studies involving this issue can be found. One of the motivations for the substitution of the liquid electrolyte is that the use of a solid electrolyte can minimize leakage and solvent evaporation problems and provide long-term stability, thus extending the life of the devices. At the same time, many questions concerning the stability of such organic materials when used in the conditions of device operation have already been raised.

De Paoli and coworkers⁷³ investigated solar cells assembled with the polymer electrolyte of P(EO-EPI)84-16, NaI and I₂, using flexible and rigid glass substrates. These cells were irradiated under a Xe lamp with UV and IR filters for long periods, alternating with dark periods. An initial decay in the performance was observed in the first 15 days, followed by a plateau of stability during at least 30 days. In another study, Nogueira¹⁷ investigated solid-state solar cells assembled with a similar polymer electrolyte, continuously irradiated using the same light source. A similar decay profile was observed in the first 600 h of irradiation, followed by 1080 h of stability. De Paoli and coworkers⁷⁴ also investigated DSSC with a plasticized polymer electrolyte, based on the copolymer P(EO-EPI)87-13, NaI, I₂ and the plasticizer GBL. The devices were irradiated under direct sunlight, and present a similar decay profile during the first 40 days after device assembly, reaching a constant performance after this period. Durrant and coworkers⁷⁵ also investigated the stability of unsealed DSSC containing plasticized polymer electrolytes based on P(EO-EPI), EC/PC NaI and I₂. With continuous illumination for 80 h at 20 mW cm⁻² the devices lost only 15% of the initial performance. All these results suggest that the initial decay in performance followed by a plateau of stability might be an intrinsic property of DSSC assembled with polymer electrolytes and appears to be independent of the cell size, type of substrate employed and exposure time. Fig. 9 presents a typical behavior of the variation of DSSC parameters with time, under direct sunlight exposure. De Paoli and coworkers²⁵ demonstrated that no degradation of the plasticized polymer electrolyte occurs with time or during the operation of the solar cell under ambient conditions. Deposition of the polymer electrolyte under heating leaves almost no residual solvent in the electrolyte. Therefore, the loss of performance observed can not be attributed to residual solvent evaporation.²⁵

Some controversy in the literature concerning the ruthenium dye still persists. The *cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) dye (N3, Solaronix) usually

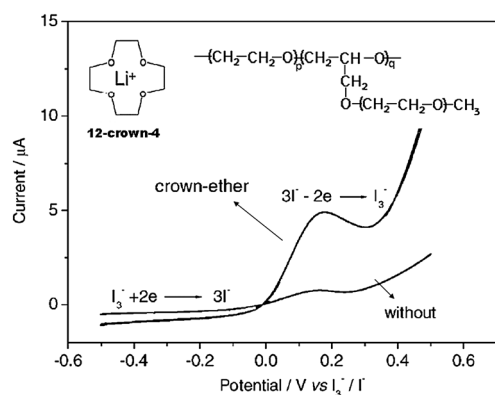


Fig. 8 J–V steady-state voltammograms for a gel polymer electrolyte with and without the addition of 12-crown-4 ether, using a Pt microdisk electrode with 30 µm diameter (scan rate = 10 mV s⁻¹). The structures of the crown ether and the copolymer are shown in the inset.

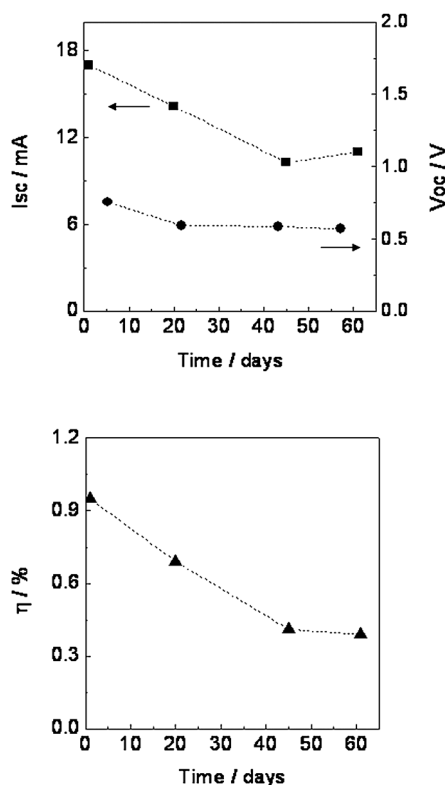


Fig. 9 Variation of I_{sc} , V_{oc} and η as a function of time for a DSSC assembled with a polymer electrolyte, exposed to direct sunlight for 1 h each day (at noon).

employed is believed to be able to sustain 10^8 redox cycles without noticeable loss of performance, corresponding to 20 years of operation under sunlight.² However, when this dye is maintained in the oxidized state for long periods, it degrades through loss of the $-NCS$ ligand. Therefore, regeneration of the dye in the photovoltaic cell should occur rapidly to avoid this unwanted side reaction, as the lack of adequate conditions for regeneration of the dye may lead to dye degradation.⁷⁶ This is especially true for devices comprising polymer electrolytes, due to several factors, such as low ionic mobility that can lead to slow regeneration or the incomplete filling of the TiO_2 sensitized electrode by the electrolyte. Also, upon exposure for prolonged periods of time at higher temperatures, such as 80–85 °C, degradation of performance in DSSC is frequently observed. Considering this, a few years ago Grätzel and coworkers⁷⁷ synthesized a new amphiphilic ruthenium dye (Z-907), which was applied in a DSSC in combination with a heat resistant quasi-solid state electrolyte based on a mixture of imidazolium iodide, methoxypropionitrile and a fluorinated polymer. This device showed stability for 1000 h at 80 °C for the first time.

Some authors reported the stability of DSSC assembled with polymer electrolytes with different compositions and related this behavior to the properties of the electrolyte. For example, solar cells were assembled with electrolytes combining the ionic liquid 1-methyl-3-propylimidazolium iodine and PEO, poly(propylene oxide) or the copolymer poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide).⁷⁸ After introducing less than 10 wt% of the polyether into the liquid

electrolyte, the parameters of these quasi-solid state solar cells were still comparable to those of the liquid photochemical cells. It was believed that the polymer can contribute to the maintenance of the efficiency of the solar cells by holding the organic solvent. All devices were sealed with paraffin wax. The cell assembled with liquid electrolyte lost half of the conversion efficiency after five days, while the cells fabricated with the polyether electrolytes had only 10–15% losses of efficiency. AFM images were obtained after one week, showing that for the liquid electrolytes the morphology presented holes, indicating a possible evaporation of the solvent, while the morphology for polymer electrolyte films showed more homogenous surfaces.

Using poly(methyl methacrylate) as polymer host, EC, 1,2-propanediol carbonate and dimethyl carbonate as organic solvents and NaI/I_2 , Wu and coworkers⁷⁹ prepared a gel electrolyte with high conductivity ($6.9 \times 10^{-3} \text{ S cm}^{-1}$). The long-term stability of DSSC with the polymer gel electrolyte was compared to that of a device prepared with liquid electrolyte, where both cells were fabricated using the same methods, employing a cyanoacrylate adhesive and epoxy resin as sealants. After 5 days, the efficiency of the DSSC with the polymer gel electrolyte decreased by 8%, while the DSSC with liquid electrolyte lost 40% of the initial efficiency. After 40 days, the DSSC with the polymer gel electrolyte had maintained 83% of the original energy conversion efficiency, and the DSSC with liquid electrolyte had only 27% of the initial conversion efficiency. Recently, Xia and coworkers⁸⁰ also observed that a polymer gel electrolyte-based DSSC using a PVDF-HFP membrane maintained 77% of its initial efficiency in the same period, indicating that the liquid retaining ability of the porous polymer framework is extremely high.

Addition of TiO_2 nanoparticles can also extend the thermostability of the composite electrolyte in comparison to regular gel electrolyte and liquid electrolyte devices. The results of accelerated aging tests showed that the composite electrolyte-based devices containing PVDF-HFP and TiO_2 could maintain 90% of their initial value after heating at 60 °C for 1000 h.⁸¹ Two different kinds of composite electrolyte, solidified with pure ZnO nanoparticles or with polymer-grafted ZnO nanoparticles, were applied to DSSC. These cells were sealed with thermal plastic tape for long-term testing. The devices were stored at 55 °C and their efficiencies were measured once a week. The solar cell containing the nanocomposite electrolyte with polymer-grafted nanoparticles kept 93% of its initial efficiency value, even under heating at 55 °C for 34 days, while the efficiency of a solar cell solidified with pure ZnO nanoparticles decreased to 60% of its initial value, which was attributed to a phase separation that occurs when the non-modified particles are used.⁵⁵

The stability of DSSC assembled with thermosetting gel electrolytes (TSGE) was also investigated. Wu and coworkers⁸² reported a TSGE based on poly(acrylic acid)-(ethylene glycol). In this copolymer, the liquid electrolyte absorbed is kept in the networks of the copolymer through chemical reactions, minimizing leakage or volatilization over an extended time. The solar cells assembled with this material presented an initial increase of performance during the first 18 days of measurement, which was attributed to a better penetration of the electrolyte into the pores of the TiO_2 photoelectrode. The DSSC did not lose performance significantly for 50 days. Wu and coworkers⁸³ also investigated

a thermoplastic electrolyte prepared by heating a mixture of PEG, PC, KI and I₂. This electrolyte was applied to a DSSC and presented similar stability behavior as that observed for the TSGE electrolyte.

So far, all studies involving the stability of polymer electrolyte-based DSSC show the benefit of the replacement of the liquid component. The positive effect after long-term operation is more evident in the J_{sc} parameter. Besides, the use of the polymer electrolyte allows for easier assembly while different types of materials can be used as sealants.

6. New anode structures

In the previous sections the properties and optimizations of polymer electrolytes were presented. However, optimizing the electrolyte composition is not the only critical issue in the matter of highly efficient solid-state DSSC. Other parameters must be controlled and optimized, in order to allow better usage of a solid electrolyte.

In DSSC, the TiO₂ film deposited on the conductive glass substrate comprises a three-dimensional highly porous network of spherical interconnected nanoparticles. This structure is obtained using viscous colloidal dispersions of the oxide prepared by a combination of sol-gel chemistry under hydrothermal conditions and a suitable deposition technique. However, there are several drawbacks related to this kind of structure, especially considering the use of polymer electrolytes. These materials are usually highly viscous, having difficulty in penetrating the porous titania electrode. This can lead to solar cells with poor fill factors and efficiencies. The nanoporous film electrode must be completely penetrated by the polymer

electrolyte, and deep penetration is not a simple task, being directly related to the polymer molar mass.⁸⁴ New deposition methods, such as the use of vacuum techniques, have been shown to minimize this effect, leading to a better filling of the porous electrode.⁵³ Another elegant alternative is the modification of the porous electrode, so that its porosity can be enhanced, facilitating the penetration of highly viscous polymer electrolytes.

Several reports in the literature concerning the fabrication of ordered titania nanotubes grown by controlled Ti anodic oxidation and their application in solar cells have been published.^{85–88} However, few of them explore the use of these electrodes in combination with solid-state electrolytes.^{89,90} Falaras and coworkers⁸⁹ recently reported the use of a self-organized TiO₂ nanotube layer as photoelectrode in a DSSC using a polymeric electrolyte based on PEO, LiI and I₂ with TiO₂ nanoparticles as nanofillers. The as-grown tubes presented a high aspect ratio, diameter of 80–100 nm and thickness of 20 μm (Fig. 10a). The amount of the dye adsorbed on the surface and inside the pores was estimated by adsorption-desorption measurements. It was found that the amount of adsorbed dye molecules was 8.42×10^{-8} moles or 5.07×10^{15} molecules, very similar to other titania tubes⁹¹ and nanoparticulate TiO₂ films (5.68×10^{-8} moles cm⁻² for a ~14 μm mesoporous film⁹²). Under 100 mW cm⁻², the DSSC using polymer electrolyte presented J_{sc} = 3.34 mA cm⁻², Voc = 0.53V, FF = 0.49 and η = 0.85%. This efficiency was further increased to 1.65% using a commercial liquid electrolyte.⁸⁹ Sung and coworkers⁹⁰ prepared similar titania nanotube substrates. The tubes presented an average length of 3 μm. Under reverse illumination the DSSC presented Voc = 0.64 V, a J_{sc} = 2.38 mA cm⁻², FF = 0.38 and η = 0.58%. The efficiency was further improved by the post-treatment of the

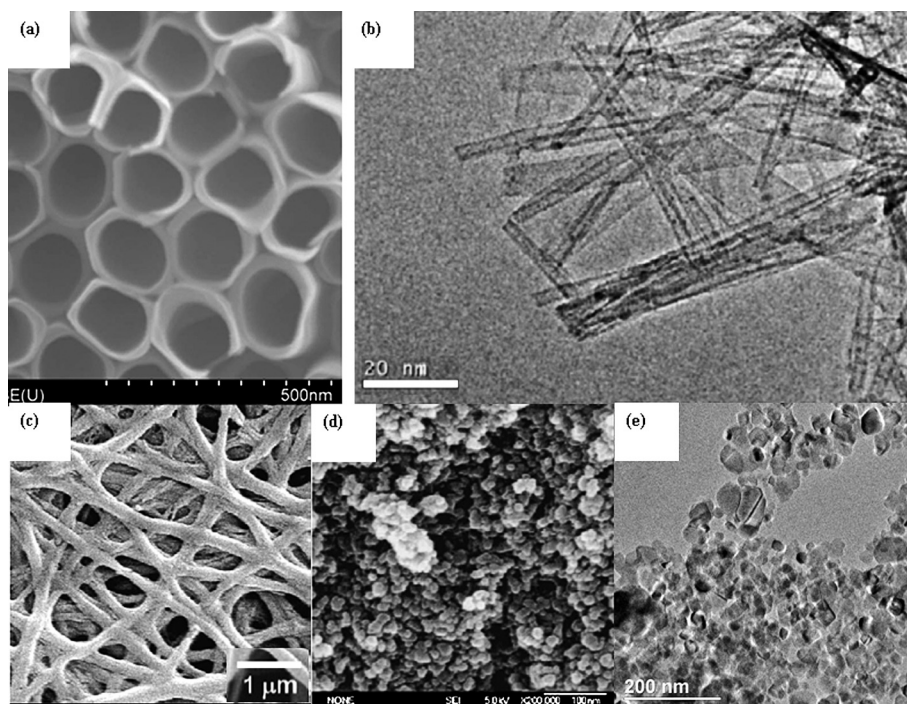


Fig. 10 SEM and TEM images of different anodes structures: (a) aligned TiO₂ nanotube electrode,⁸⁶ (b) TiO₂ nanotubes, (c) electrospun TiO₂ electrode after calcination at 450 °C,⁹⁴ (d) TiO₂ electrode with textural channels⁹⁶ and (e) core-shell SrTiO₃-TiO₂ nanoparticles.

tubes with H₂O₂ and a ZnO coating on top of the nanotubes. This treatment was found to improve both the fill factor (FF ~ 0.37–0.49) and the conversion efficiency (η ~ 0.70–0.91%).⁹⁰

Nogueira and coworkers⁹³ employed randomly oriented titania nanotube electrodes in combination with a plasticized polymer electrolyte, based on a PEO copolymer and 50 wt% of poly(ethyleneglycol)dibenzoate, NaI and I₂. The TiO₂ nanotubes were prepared by a simple sol–gel route and the resulting suspension was deposited by the doctor blade technique. The nanotubes had diameters of ~3 nm, with transversal and longitudinal lengths of up to ~100 nm and 1 μ m, respectively (Fig. 10b). The performance of this photoelectrode in solar cells was compared to that of electrodes prepared with standard TiO₂ nanoparticles (Degussa P-25). For the same film thickness, the DSSC assembled with the titania nanotubes showed higher efficiency in comparison with the device using nanoparticles. Under irradiation of 100 mW cm⁻², the DSSC assembled with TiO₂ nanotubes had J_{sc} = 9.6 mA cm⁻², Voc = 0.85 V, FF = 0.49 and η = 4.0%, while the solar cell assembled with standard TiO₂ nanoparticles had J_{sc} = 7.7 mA cm⁻², Voc = 0.78 V, FF = 0.47 and η = 2.8%. The increases in the current density and in open circuit voltage observed when using the nanotubes were assigned as a consequence of two effects: the much higher surface area of this material, which allows more sensitizer dye to be chemically anchored in the electrode, improving light harvesting and the better penetration of the plasticized polymer electrolyte through the film, as a consequence of the open structure of the nanotubes.⁹³

A TiO₂ fibre electrode was electrospun directly onto a conducting glass substrate from a mixture of titanium(IV) isopropoxide and poly(vinyl acetate) in DMF.⁹⁴ SEM images of the electrodes showed that the TiO₂ fibres had diameters of 200–600 nm and are composed of one-dimensionally aligned nanofibrils with ~20 nm thickness (Fig. 10c). These electrodes were used in a DSSC with an electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene), 1-hexyl-2,3-dimethylimidazolium iodide and I₂ in a mixture of EC/PC. The porous structure of the electrospun electrode was found to favor an efficient penetration of the viscous polymer gel electrolyte. The performance of the devices was improved after deposition of TiO₂ nanocrystals onto the electrospun electrodes from TiCl₄ treatment, which is known to improve the light scattering properties.⁹⁵ The diameter of the fibres increased after TiCl₄ treatment, but the macroscopic porous morphology was maintained. This increase resulted in an increase in the total volume fraction of TiO₂ and, consequently, in the amount of sensitizer molecules adsorbed in the electrode. The optimized DSSC presented J_{sc} = 10.52 mA cm⁻², Voc = 0.78 V, FF = 0.56 and η = 4.6%.⁹⁴

The design of nanoparticulate TiO₂ films with more suitable meso- and macro-pores is another alternative to improve the interfacial contact and reaction between the dye-sensitized TiO₂ film and the electrolyte. Huang and coworkers⁹⁶ reported a simple approach to prepare TiO₂ electrodes with textural channels, *i.e.* micro-sized cracks on the surface and about 41 nm nanopores in the bulk. This novel material was prepared *via* packaging ZnO nanowires with diameters of 30–50 nm into TiO₂ films and subsequently etching the nanowires with HCl (Fig. 10d). DSSC were assembled using a hybrid polymer electrolyte composed of two types of ionic liquids and a copolymer of

PVDF, PEO and TiO₂ nanofillers. These textural channels in the TiO₂ film enhanced the penetration of the electrolyte and therefore led to an improvement in efficiency of 20–30% compared to that from the non-modified TiO₂ films.

An interesting approach consists of the assembly of flexible, solid-state DSSC. Flexible plastic electrodes like polyethylene terephthalate sheets coated with tin-doped indium oxide (ITO) possess many technological advantages in comparison to F:SnO₂ conductive glass (TCO) usually employed in DSSC, such as low weight, reduced production cost and fewer size and shape limitations. On the other hand, the use of such plastic substrates requires that all processes during the fabrication of the device are performed at temperatures lower than 150 °C. This limits the formation of the TiO₂ nanocrystalline film, since a calcination step with temperatures above 400 °C is necessary for making films with good characteristics. Several different approaches have been proposed to overcome the lack of high temperature annealing of the photoelectrode.^{97–100} However, few reports have concentrated on the combination of such flexible photoelectrodes with solid or quasi-solid electrolytes.

De Paoli and coworkers^{27,73} investigated solar cells assembled with the electrolyte based on P(EO–EPI)84–16, NaI and I₂ using flexible ITO–PET substrates. The efficiency obtained by simply depositing the TiO₂ film from a colloidal commercial suspension (Ti-nanoxide T, Solaronix) by doctor blading and annealing at 130 °C for 4 h was only 0.1%, 10 times lower than the efficiency obtained when using a glass TCO substrate and an annealing temperature of 450 °C.²⁷ In another work, UV radiation was used to remove the organic residues from the TiO₂ film spread onto the flexible substrate.⁷³ This was possible due to the well-known activity of TiO₂ to degrade organic compounds upon UV exposure.¹⁰¹ The best results were obtained for films exposed for 15 min to UV radiation, followed by heating at 140 °C for 2 h in a dry box, leading to DSSC with an efficiency of 0.3%.⁷³ Similar approaches using UV radiation for the low-temperature fabrication of TiO₂ electrodes have been reported by other authors.^{102–104} Recently, Stathatos and coworkers¹⁰⁵ synthesized nanocrystalline TiO₂ films without using any surfactant to prepare films on plastic substrates at low temperature. The films were formed by dip coating and the highest temperature used was 100 °C to remove humidity. The DSSC prepared with a quasi-solid gel electrolyte based on a mixture of a polymer and an ionic liquid presented overall solar to electric energy conversion efficiency of 3.2% (under 100 mW cm⁻²).

Another important feature that can limit the performance in DSSC assembled with polymer electrolytes is the reduced mobility of I₃⁻, which may lead to the build-up of triiodide in the TiO₂ pores relative to the bulk of the electrolyte, increasing the probability of electron recombination (the so-called “dark current”). This reaction drastically affects the Voc values.¹⁰⁶ One possibility, therefore, is the use of an oxide blocking layer in the TiO₂ electrodes (core–shell structures), which can change the Fermi level energy in the photoelectrode, thus reducing the probability of recombination of injected electrons. This approach has been successfully used in DSSC with liquid electrolytes,^{107–110} and is also an elegant way to improve the efficiency of devices using polymer electrolytes.

Durrant and coworkers⁷⁵ showed the application of a shell of Al₂O₃ to the photoelectrode of TiO₂ on ITO–PET flexible

substrates, prepared by a compression route. These electrodes were combined with a plasticized polymer electrolyte of P(EO–EPI), EC/PC and NaI/I₂ to make flexible DSSC with efficiencies higher than 5% (10 mW cm⁻²) and 2.5% (100 mW cm⁻²). The addition of the Al₂O₃ coating was shown to improve all cell parameters, including a ~20% enhancement in the efficiency. Using transient absorption spectroscopy the authors showed that the use of the core–shell structure resulted in a 10-fold retardation in the recombination dynamics of injected electrons with dye cations, in comparison to the uncoated films. Nogueira and coworkers¹¹¹ investigated for the first time a series of different core–shell electrodes based on TiO₂ covered with different oxides and their application in gel-electrolyte based dye-sensitized solar cells. The TiO₂ electrodes were prepared from TiO₂ powder (P25 Degussa) and coated with thin films of Al₂O₃, MgO, Nb₂O₅, or SrTiO₃ prepared by a sol–gel route, giving core–shell type electrodes. The electrolyte was composed of P(EO–EM), 70% of GBL, LiI and I₂. Optimum performances were achieved with solar cells based on TiO₂/MgO core–shell electrodes: J_{sc} = 11 mA cm⁻², V_{oc} = 0.78 V, FF = 0.57 and η = 4.9%. Devices prepared with pure TiO₂ electrodes presented the same photocurrent, but reduced V_{oc} and η values. Fig. 10e presents TEM images obtained for SrTiO₃-coated TiO₂ nanoparticles. Photovoltage decay measurements under open-circuit conditions were carried out to evaluate the influence of the oxide layer on the charge recombination dynamics of the DSSC. The results showed that the core–shell electrodes provide longer electron lifetime values compared to uncoated TiO₂ electrodes, corroborating the minimization in the recombination losses at the nanoparticle surface/electrolyte interface. These results prove the effectiveness of this approach to improve solar cells containing gel or polymer electrolytes.

7. Conclusions and perspectives

The effective application of polymer electrolytes in dye-sensitized solar cells began only 10 years after the first announcement of efficient devices containing liquid electrolytes. Since then, interest in this kind of technology has increased considerably, which is evident through the increasing number of papers published every year describing the assembly of dye-sensitized solar cells with polymer or gel electrolytes. A direct comparison between results reported by different groups, however, is not straightforward, since many parameters other than the electrolyte composition and conductivity can affect device performance, such as the TiO₂ film thickness. Also, as is the case for DSSC with liquid electrolytes, the active area of the device still has a major role in the overall efficiency.

Many techniques have already been used to understand and explain the charge transport mechanisms and reactions occurring inside the solid or gel electrolyte, such as transient absorption spectroscopy, complex electrochemical impedance spectroscopy, microelectrode voltammetry, Raman spectroscopy and NMR, providing powerful tools for the improvement of the so-called “solid-state” DSSC. Efficiencies can be further improved, although, considering the solid-state nature of the materials and the diffusion limited photocurrent, they are unlikely to reach the 11% efficiencies obtained for liquid solar cells. Nevertheless, the 7–8% efficiencies reached so far can be considered very promising

and, along with the stability results, might motivate the research in this field to bring these devices to the market. Efforts should now be directed to up-scaling such devices and also to the assembly of “all-flexible” devices, combining the application of polymer electrolytes with flexible conductive substrates instead of the glass TCO routinely employed.

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