Kinetic competition in flexible dye sensitised solar cells employing a series of polymer electrolytes

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Received (in Cambridge, UK) 27th October 2005, Accepted 16th December 2005
First published as an Advance Article on the web 18th January 2006
DOI: 10.1039/b515240b

Transient absorption spectroscopy is employed to study electron transfer dynamics in dye sensitised solar cells employing a series of polymer electrolytes, and correlated with device current–voltage characteristics.

Environmental concerns over fossil fuels are motivating the search for low cost photovoltaic devices compatible with reel to reel device fabrication on flexible substrates. Over the last decade dye sensitised solar cells (DSSCs) based upon nanocrystalline TiO_2 films have attracted extensive interest as low cost photovoltaic devices.[1,2] These devices are based upon the use of molecular dyes to sensitise mesoporous, nanocrystalline metal oxide films to solar irradiation. Initial studies of such devices employed liquid electrolytes interpenetrated into the mesoporous film to achieve electrical contact to the device counter electrode. More recently, many studies have focused on solid state or 'quasi-solid state' alternatives to this liquid electrolyte more compatible with low temperature encapsulation on flexible (*e.g.* plastic) substrates, including molecular hole transporters,[3–6] polymer electrolytes[7–9] and polymer gel electrolytes.[10–15]

In this communication we address recombination losses in DSSCs employing a series of polymer electrolytes. In principle there are two recombination pathways of importance in DSSCs, electrons photoinjected into the TiO_2 electrode can recombine with either dye cations or the redox electrolyte (**CR1** and **CR2** in eqn (1) and (2) below).

$$\textbf{CR1}: \mathrm{TiO_2(e^-) + Dye^+ \rightarrow Dye} \quad (1)$$

$$\textbf{CR2}: \mathrm{2\ TiO_2(e^-) + I_2 \rightarrow 2\ I^-} \quad (2)$$

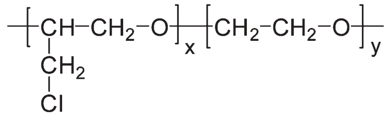
$$\textbf{RR}: \mathrm{Dye^+ + 2\ I^- \rightarrow Dye + I_2^-} \quad (3)$$

In liquid electrolyte devices, rapid re-reduction of dye cations by the redox electrolyte (**RR**, eqn (3)) competes effectively with **CR1**, and therefore charge recombination to the redox electrolyte, **CR2**, is the primary recombination loss pathway limiting device efficiency.[16] However the increasing shift towards more solid state, and therefore typically more viscous, redox electrolytes raises the possibility that dye cation re-reduction by the redox electrolyte may no longer compete effectively with recombination pathway **CR1**. As a consequence, charge recombination to dye cations may become critical in limiting device efficiency. In this communication, we demonstrate that this can indeed be the case with DSSCs employing polymer electrolytes, and furthermore demonstrate that the extent of recombination losses due to **CR1** depends upon the chemical composition of the polymer employed.

DSSCs (1 cm^2) were fabricated as previously[7,17] employing a low temperature compression route[18] to deposit P25 (Degussa Ltd.) TiO_2 nanoparticles as 8 μm thick mesoporous film on ITO–PET sheets. Our studies employed the sensitiser dye $RuL_2(NCS)_2$ (*cis*-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)). The polymer electrolyte was solution cast onto the sensitised film, followed by addition of a platinum coated ITO–PET film in the standard unsealed 'sandwich' configuration. The solution employed for polymer electrolyte deposition comprised 0.3 g of polymer dissolved in 25 ml of acetone, with the addition of 0.03 g of NaI and 0.003 g iodine as redox couple and 0.15 g ethylene carbonate and 0.15 g propylene carbonate as plasticisers. Following polymer electrolyte casting, the film was allowed to dry in air to allow solvent evaporation. As discussed previously, the plasticisers were added to improve the ionic mobility of the polymer electrolyte. Two different poly(epichlorohydrin-*co*-ethylene oxide) co-polymers were used for the polymer electrolyte, EP-16 (Daiso Co., Ltd., Osaka, Japan) and EP-50 (Aldrich, USA) (see Fig. 1), in addition to a control polymer poly(ethylene oxide) (PEO, Mw 100 000).

Fig. 2 shows typical current–voltage data for DSSCs fabricated with the three different polymer electrolytes. It is apparent that these data are strongly dependent upon the polymer composition, with EP-50, comprising the highest epichlorohydrin content, yielding the highest short circuit current and fill factor, but also the highest dark current and lowest open circuit voltage.

The trend in V_{oc} observed for the three polymer electrolytes clearly follows the trend in dark current. This trend most probably originates from the Lewis acid/base properties of the polymer.[8,9] The dark current originates from the recombination pathway **CR2** above. More basic electolytes raise the conduction band energy of the TiO_2 electrode, resulting at a given voltage in a reduced TiO_2 electron density, and therefore from eqn (2) in a lower dark current density. The dark current data shown in Fig. 2 are consistent with



$$\left[\mathrm{CH(CH_2Cl)-CH_2-O}\right]_x\left[\mathrm{CH_2-CH_2-O}\right]_y$$

Fig. 1 Chemical structure of the poly(epichlorohydrin-*co*-ethylene oxide) co-polymers employed in this study: EP-50, $x = y = 50$ and EP-16, $x = 16$, $y = 84$. The control polymer poly(ethylene oxide) corresponds to $x = 0$, $y = 100$.

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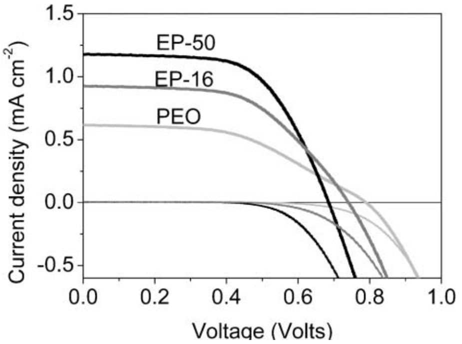

Fig. 2 A comparison of the *J–V* characteristics of typical flexible DSSCs using EP-50, EP-16 and PEO polymer electrolytes in the dark (gray lines) and under 10 mW cm^{-2} AM1.5 simulated irradiation (black lines). The device performance characteristics (J_{sc}, V_{oc}, *ff* and η) are 1.20 mA, 0.70 V, 62% and 5.2% for EP-50; 0.95 mA, 0.76 V, 55% and 3.9% for EP-16; 0.60 mA, 0.82 V, 48% and 2.4% for PEO.

this behaviour, with the most basic polymer (PEO) giving the highest V_{oc}; the inclusion of less basic epichlorohydrin groups into the polymer results in progressively lower V_{oc}'s for EP-16 and EP-50.

Determining the origins of the trends in *ff* and I_{sc} shown in Fig. 2 is less straightforward. Impedance studies determined ionic conductivities of $\sim 2 \times 10^{-4}$ S cm^{-1} for both the EP-16 and EP-50 polymer electrolytes, suggesting that these trends do not result from differences in charge transport in the polymer electrolytes. Alternatively these trends may originate from differences in interfacial electron transfer dynamics. Transient absorption studies were therefore employed to address these interfacial dynamics directly.

Fig. 3 shows transient absorption data for dye sensitised TiO_2 films covered in the EP-16 and EP-50 polymer electrolytes studies, employing pulsed laser excitation at 550 nm, and monitoring the change in optical density of the sample at 800 nm (for experimental details see ref. 8). For ease of data collection, experiments were conducted without the addition of the counter electrode to the film. Following assignments made in our previous studies of analogous films with both liquid and polymer electrolytes,[8] the initial absorption increase is assigned to the absorption of $RuL_2(NCS)_2$ cations generated by photoinduced electron injection into the TiO_2 electrode. The fast (microsecond) decay phase of this transient absorption signal is assigned to loss of dye cation absorption due to re-reduction by the redox electrolyte (**RR**) and/or charge recombination with injected electrons (**CR1**). The residual long lived (millisecond lifetime) is assigned to absorption of I_2^- species generated by the re-reduction reaction **RR**, and the concomitant absorption of long lived electrons. Decay of this long lived signal is assigned to I_2^- dismutation and charge recombination with TiO_2 electrons, **CR2**.

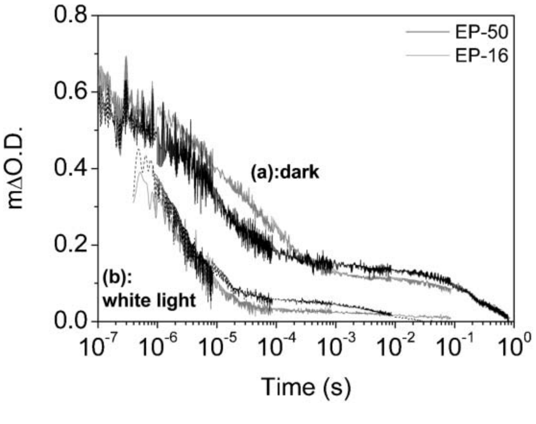

Fig. 3 Transient absorption for $RuL_2(NCS)_2$ sensitised TiO_2 films covered in polymer electrolytes with EP-50 (black) and EP-16 (grey). Data collected at a probe wavelength of 800 nm, in the absence (a) or presence (b) of $\sim$25 mW cm^{-2} of continuous white light irradiance.

The data shown in Fig. 3 provide clear evidence that kinetic competition between charge recombination to dye cations (**CR1**) and dye cation re-reduction by the polymer electrolyte (**RR**) limits the performance of DSSCs employing these polymer electrolytes. We will consider first the data collected in the absence of white light illumination (a). Under such 'dark' conditions, charge recombination to the $RuL_2(NCS)_2$ cation (**CR1**) is dispersive and exhibits a half time of $\sim$1 ms.[8] In liquid electrolytes, $RuL_2(NCS)_2$ cation re-reduction by iodide ions (**RR**) exhibits a half time of $\sim$1 µs, and therefore competes efficiently with charge recombination to the redox electrolyte.[16,17] The decay dynamics of dye cation absorption in Fig. 3 (half times, $t_{50\%}$, of 20 and 6 µs for EP-16 and EP-50 respectively) are clearly indicative of slower re-reduction dynamics. For the EP-16 electrolyte, the yield of I_2^- product states of the re-reduction reaction is also reduced (apparent as the lower amplitude slow decay phase), indicating that for this polymer electrolyte, dye cation re-reduction is so slow that it no longer competes effectively with charge recombination **CR1**. The 20% lower yield of dye regeneration (**RR**) observed from these transient studies is in good quantitative agreement with the lower I_{sc} obtained for this polymer electrolyte.[19]

The presence of continuous illumination raises the TiO_2 Fermi level (corresponding to open circuit conditions), resulting in an acceleration of both charge recombination pathways. As shown in Fig. 3, this illumination results both in an acceleration in dye cation decay dynamics ($t_{50\%}$ of 1 and 2 µs for EP-16 and EP-50 respectively) and a reduction in I_2^- yield, indicating increased charge recombination losses due to the acceleration of **CR1**. These observations contrast with our studies of MeCN based electrolytes where the faster re-reduction dynamics compete effectively with **CR1** even under white light bias, resulting in the dye cation decay dynamics and I_2^- yields being independent of bias light.[16] The recombination losses are most significant for EP-16, consistent with the slower dye re-reduction dynamics observed for this electrolyte and resulting in the observed lower fill factor observed in the device *J–V* data.

Further support for kinetic competition between **CR1** and **RR** limiting device performance can be obtained from simulating the device current–voltage data in terms of the non-ideal diode equation:[8]

$$I = I_L - I_0\left(e^{qV_j/mk_BT} - 1\right) \qquad (4)$$

where I_L is the light intensity dependent short circuit current, k_B is Boltzmann's constant, T is temperature and I_0, m are fitting constants. The bias dropped across the internal junction, V_j, can be related to the externally applied bias, V, through:

$$V_j = V + IR_s \qquad (5)$$

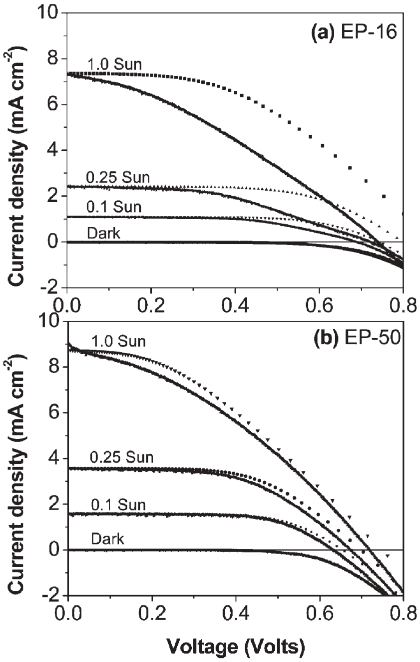

Fig. 4 *J–V* characteristics (solid lines) of the flexible DSSCs using polymer redox electrolytes with (a) EP-16 and (b) EP-50 as a function of irradiation intensity. Also shown (dotted lines) are fits to the single diode model, eqn (4), with all parameters except I_L being assumed to be independent of light intensity.

where R_S is the series resistance of the system. I_0, m and R_s are assumed to be light intensity independent. As we have discussed previously,[8,17] deviations from this model can be most easily interpreted in terms of a voltage dependent loss of charge separation yield due to either lower electron injection yields or kinetic competition between **CR1** and **RR**. For MeCN based electrolytes, experimental data show an excellent fit to this model, indicating that recombination losses are limited only to recombination the redox electrolyte **CR2**. For the EP-50 polymer electrolytes, the experimental data only deviate marginally from this model (Fig. 4(a)), indicating minor recombination losses from **CR1**, whilst for the EP-16 polymer electrolyte, the experimental data show significantly lower fill factors than those predicted by the model calculations, consistent with significant efficiency losses due to charge recombination to dye cations (**CR1**).[20]

We conclude that the improved I_{sc} and *ff* observed for EP-50 polymer electrolyte originate from faster dye cation re-reduction by iodide ions, eqn (3) above. These faster dynamics may result from the less basic nature of EP-50 compared to EP-16 and PEO, as discussed above. Pelet *et al.* have previously reported faster re-reduction dynamics for less aprotic electrolytes, assigned to a more positive TiO_2 surface charge.[21] Alternatively the faster dynamics may result from a higher iodide mobility in this polymer electrolyte due to the epichlorohydrin component resulting in an amorphous structure.

We note that our observation of kinetic competition between **CR1** and **RR** contrasts with the conclusion of our previous study of DSSCs employing a polymer electrolyte without added plasticisers. In our previous study,[8] the absence of plasticisers resulted in a lower ionic conductivity, resulting in accumulation of I_2^- and I_3^- species in the film pores under illumination, and therefore causing recombination losses to the redox electrolyte **CR2** to limit device performance.

We have previously demonstrated that careful consideration of the correlations between charge separation and recombination are critical to optimisation of the efficiency of dye sensitised solar cells, with optimisation requiring the minimisation of 'kinetic redundancy' within the device.[22] Our previous study has focused on the correlation between electron injection into metal oxide and charge recombination to the redox electrolyte in liquid electrolyte devices. The study we report here emphasises that the use of higher viscosity, more solid state electrolytes may result in the secondary charge step, electron transfer from the electrolyte to the dye cation, also playing a key role in determining device efficiency.

We acknowledge the EPSRC Supergen Programme and Commission of the European Community (Project Molycell, Contract No. 502783) for financial assistance. We also thank Daiso Co., Ltd., Osaka, for EP-16 supply, Degussa Ltd. for supply of P25, and Johnson Matthey Ltd. for supply of $RuL_2(NCS)_2$ sensitiser dye.

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