E fficient p-type dye-sensitized solar cells based on disulfide/thiolate electrolytes†

Xiaobao Xu,‡a Bingyan Zhang,‡a Jin Cui,a Dehua Xiong,a Yan Shen,*a Wei Chen,*a Licheng Sun,bc Yibing Chengad and Mingkui Wang*a

Herein, an organic redox couple 1-methyl-1H-tetrazole-5-thiolate (T1/C0) and its disulfide dimer (T2) redox shuttle, as an electrolyte, is introduced in a p-type dye-sensitized solar cell (DSC) on the basis of an organic dye (P1) sensitizer and nanocrystal CuCrO2 electrode. Using this iodide-free transparent redox electrolyte in conjunction with the sensitized heterojunction, we achieve a high open-circuit voltage of over 300 mV. An optimal efficiency of 0.23% is obtained using a CoS counter electrode and an optimized electrolyte composition under AM 1.5 G 100 mW cm−2 light illumination which, to the best of our knowledge, represents the highest efficiency that has so far been reported for p-type DSCs using organic redox couples.

1 Introduction

Recently, dye-sensitized solar cells (DSCs) based on mesoporous semiconductor electrodes have attracted much attention because of their low cost and ease of fabrication. Since the initial report, the power conversion efficiency (PCE) of DSCs has been increased, which is largely due to the systematically study on sensitizers,2,3 electrolytes,4−6 cathodes,7,8 and the device architecture.9,10 Recently, implementation of an active photocathode with a photo-anode has brought about the possibility of fabricating tandem DSC devices.11 Theoretically, the overall PCE of a p–n tandem device can surpass the conventional n-type DSC devices.12 For dye-sensitized photo-cathodes, electron transfer takes place from the valence band of the p-type semiconductor (NiO being the most commonly used to date) to the photoexcited dye.12 Photo-cathodes employing the most efficient sensitizer (P1, see Fig. 1) have been reported in conjunction with a mesoporous NiO nanoparticle film, and an I3−/I− based electrolyte achieved efficiencies of up to 0.15% under simulated sunlight (100 mW cm−2, AM 1.5 G).13 Recently, the photovoltaic performance of p-type DSCs has been largely improved.14−16 Bach et al. have investigated tris(1,2-diaminoethane) cobalt(II)/(III) electrolytes in a p-type DSC device, consisting of mesoporous NiO sensitized with a PMI-6T-TPA sensitizer.16 The system

Fig. 1 The T2/T1 redox couple and its intervention in p-type DSCs. The molecular structure of (a) P1 sensitizer and (b) the T2/T1 redox couple, (c) schematic energy diagram of the p-DSC device components used in this study (D = dye; NHE = normal hydrogen electrode), (d) light-induced electron transfer reactions in p-type DSCs, P1−, the reduced dye; h+ are holes in the valence band of the semiconductor. Electrolyte redox potentials and the valence band edge of CuCrO2 were evaluated according to ref. 4 and 20.

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affords energy conversion efficiencies of 1.3% at 100% sun and open-circuit voltages as high as 709 mV. The photocurrent and photovoltage of the device were found to depend on the steric bulk of the redox species rather than their electrochemical potential. These studies highlighted the possibility of reaching higher voltages when new p-type semiconductor photo-cathodes or new electrolytes were used. The photovoltaic performance of the device is relatively low compared with its counterparts due to number of reasons, mostly as a result of (i) low carrier mobility in the p-type semiconductor; (ii) fast interfacial recombination between the photocathode and redox electrolyte; (iii) narrow photon absorption.

Recently, several p-type semiconductor nanocrystallines have been investigated, including CuO,

CuSCN, CuGaO,

CuCrO,

CuCrO,

and K-doped ZnO, which have shown augmented photovoltaic performances compared to that of the NiO based p-DSC. For example, CuCrO shows promising properties, such as a high flat band potential (~0.6 V vs. SCE) and high hole mobility (about 10–10 to 10 cm s–1). These two advantages are crucial for further improving the performance of p-type DSCs. The organic electrolyte of 1-methyl-1H-tetrazole-5-thiolate (T–) and its disulfide dimer (T2) redox shuttle (see Fig. 1) is a promising redox couple which has the potential to replace triiodide/iodide electrolyte. Herein we report the first application of the T2/T– electrolyte in p-type DSCs, in combination with the P1 sensitizer and CuCrO nanocrystals, achieving an open circuit voltage (Voc) of over 300 mV. To the best of our knowledge, this is the first time that such a high photovoltage has been obtained for p-type DSCs with an organic redox shuttle. The dye regeneration process and the influence of various counter electrodes [Pt, PEDOT (poly(3,4-ethylenedioxythiophene), and CoS] on the photovoltaic performance of p-type DSCs employing this promising organic redox electrolyte have been systematically studied as well.

2 Experimental

In the present work, a high-molar-extinction-coefficient organic dye (coded as P1), was used as a p-type sensitizer (see Fig. 1b), with the triphenylamine moiety as the electron donor and the diethylenetriamine moiety as the electron acceptor. The synthetic protocol of this compound is described in our previous paper. The thiolate redox molecules were synthesized, including the above mentioned 1-methyl-1H-tetrazole-5-thiolate (T–) and its dimer (T2) redox shuttle, through neutralization of the corresponding thiolate in methanol with tetrabutylammonium hydroxide.

The details for the preparation of the CuCrO2 films have been described elsewhere. The CuCrO2 film was sintered at 420 °C for 40 min in air and 550 °C for 40 min in Ar. After cooling to ~80 °C, the film electrodes were dipped into a 300 μM P1 solution in acetonitrile at room temperature for 16 h. After washing with acetonitrile and drying by air flow, the sensitized CuCrO2 electrodes were assembled with the counter electrodes. The working electrodes and counter electrodes were separated by a 45 μm thick hot melt ring (Surlyn, Dupont) and sealed by heating. The internal space was filled with liquid electrolyte using a vacuum back-filling system. The electrolyte for devices A–C and E–F was 0.3 M T2 and 0.9 M T+ with the tetramethylammonium cation in the mixture of acetonitrile and propylene carbonate (volume ratio, 7 : 3) with 0.1 M LiTFSI. Device D being 0.3 M I2 and 1.2 M LiI in a mixture of acetonitrile and propylene carbonate (volume ratio, 7 : 3) with 0.1 M LiTFSI.

A 450 W xenon light source solar simulator (Oriel, model 9119) with AM 1.5 G filter (Oriel, model 91192) was used to give an irradiance of 100 mW cm–2 at the surface of the solar cell. The current–voltage characteristics of the cell under these conditions were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). A similar data acquisition system was used to control the IPCE measurement. A white light bias (1% sunlight intensity) was applied onto the sample during the IPCE measurements with an ac model (10 Hz).

EIS measurements of the p-type DSCs were carried out with an Autolab Frequency Analyzer set-up, which consists of an Autolab PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) producing a small-amplitude harmonic voltage, and a frequency response analyzer module. The recombination rate constant was determined by transient photovoltage decay measurements and charge extraction experiments.

3 Results and discussion

The structure of the P1 dye and T2/T– redox shuttle used in this study is shown in Fig. 1. Compared to the conventional iodide-based electrolyte, the thiolate-based electrolyte shows much lower light absorption in the visible range. The optimized electrolyte composition consists of 0.3 M T2, 0.9 M T+, and 0.1 M LiTFSI (lithium bis(trifluoromethane-sulfonf)amide) in a mixture of acetonitrile and propylene carbonate (volume ratio 7 : 3). Details on the optimization of the concentration for the electrolyte components are presented in Fig. S1 and Table S1. For comparison purposes, an I3–/I– based electrolyte was used in this experiment, containing 1.2 M 1,3-dimethylimidazolium iodide (DMII) and 0.3 M I2 and 0.1 M LiTFSI in a mixture of acetonitrile and propylene carbonate (volume ratio 7 : 3). The photocurrent–voltage curves of the T2/T– based p-type DSCs were measured under simulated AM 1.5 full sunlight and are shown in Fig. 2a. The detailed photovoltaic parameters, the open-circle voltage (Voc), fill factor (FF), short-circuit current density (Jsc), and photovoltaic conversion efficiency (η) are tabulated in Table 1. In the first set of experiments, transparent CuCrO2 films with different thicknesses (from 1 to 3 μm) were loaded with a monolayer of P1, and employed in order to accurately measure the spectral response and internal quantum efficiency of the device. Ultrasmall delafossite CuCrO2 nanocrystals, with a typical size of 15 × 5 nm2 and a high surface area of 87.86 m2 g–1, were fabricated by a hydrothermal method. In this case, a conventional thermally platinized conducting glass was used as the counter electrode. The Jsc, Voc and FF values of device B, with a film thickness of 1.8 μm, are 1.43 mA cm–2, 0.309 V, and 0.38, respectively, which yield an overall PCE of 0.17%, which is much higher than that of 0.019% reported previously.
for the corresponding device using a C343 sensitized CuCrO2 nanocrystal film with an iodide-based volatile electrolyte.20 Under the same conditions, changing the redox couple from T2/T1 to I3−/I− (with the same oxidized species concentration) in device D resulted in a 0.05% overall PCE, attributed principally to the lower photocurrent and photovoltage. This result indicates the promising potential for this organic redox couple in p-DSC devices. Even the thinnest films (about 1 μm) gave an impressive PCE at 0.14%, with a V_{oc} of 0.325 V for device A. The PCE was 0.17% at 3 μm, mainly because of the increase in J_{sc} from 1.14 (device A) to 1.89 mA cm\(^{-2}\) (device C), which is accompanied by a large 75 mV drop in the V_{oc} value.

The left ordinate scale of Fig. 2b refers to the incident photon to current conversion efficiency (IPCE) as a function of the light excitation wavelength. The IPCEs under 390 nm excitation are accompanied by a large 75 mV drop in the voltage curves of the various p-type DSC devices.

Table 1 Photovoltaic parameters of the p-type DSCs based on P1 dye with different electrolytes. Each result was obtained from three DSCs.

<table>
<thead>
<tr>
<th>Thickness [μm]</th>
<th>Counter electrode</th>
<th>V_{oc} [V]</th>
<th>J_{sc} [mA cm(^{-2})]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device A(^a)</td>
<td>1.0 μm</td>
<td>Pt</td>
<td>0.325</td>
<td>1.19</td>
<td>36</td>
</tr>
<tr>
<td>Device B(^a)</td>
<td>1.8 μm</td>
<td>Pt</td>
<td>0.309</td>
<td>1.43</td>
<td>38</td>
</tr>
<tr>
<td>Device C(^b)</td>
<td>3.0 μm</td>
<td>Pt</td>
<td>0.240</td>
<td>1.89</td>
<td>36</td>
</tr>
<tr>
<td>Device D(^b)</td>
<td>1.8 μm</td>
<td>Pt</td>
<td>0.141</td>
<td>0.80</td>
<td>43</td>
</tr>
<tr>
<td>Device E(^b)</td>
<td>1.8 μm</td>
<td>PEDOT</td>
<td>0.293</td>
<td>1.71</td>
<td>43</td>
</tr>
<tr>
<td>Device F(^b)</td>
<td>1.8 μm</td>
<td>CoS</td>
<td>0.304</td>
<td>1.73</td>
<td>44</td>
</tr>
</tbody>
</table>

\(^a\) A sheet UV cut-off film was attached to each DSC surface. \(^b\) 0.3 M T2, 0.9 M T1, and 0.1 M LiTFSI (lithium bis(trifluoromethanesulfonyl)amide) in the mixture of acetonitrile and propylene carbonate (volume ratio 7 : 3).

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Fig. 2 (a) Photocurrent density–voltage curves of the various p-type DSC devices sensitized with P1 dye under full sunlight (100 mW cm\(^{-2}\)). (b) Left ordinate: incident photon-to-current conversion efficiency as a function of wavelength for the p-type DSC devices; right ordinate: the transmission spectra of the two different electrolytes (red, T2/T1: blue, I3−/I−) at a concentration of 10 mM in a mixture of acetonitrile and propylene carbonate. Devices A–C and devices E–F have the same electrolyte containing 0.3 M T2, 0.9 M T1, and 0.1 M LiTFSI, and device D has an electrolyte of 0.3 M I3−, 1.2 DMMI and 0.1 M LiTFSI. The counter electrode of devices A–D is Pt, device E PEDOT and device F CoS.

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Fig. 3 Normalized SECM feedback approach curves for the approach of a Pt disk electrode towards a CuCrO2/P1 film under illumination of a blue LED with (a) [I−] and (b) [T−] in mM: 0.03, 0.10, 0.30, 0.60, 0.80 and 1.0 in acetonitrile, respectively. Scan rate = 1 μm s\(^{-1}\), E_f = −0.7 V, t_f = 12.5 μm. Solid lines are calculated curves for an approach of an UME with RG = 10 towards an inert insulating surface. (c) Plot of experimental values of x_{Dir} vs. the concentration of the reduced species of redox shuttle.

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CrCuO₂ film for T⁻ and I⁻ with various concentrations under illumination of the film with blue LED (470 nm, incident photon flux: 1.35 × 10¹⁶ cm⁻² s⁻¹). In each figure, the effect of the concentration of the reduced state of the redox couples on the approach curves was investigated. The ultra-microelectrode (UME) current curves under illumination are typical for SECM feedback experiments with finite electron transfer at the sample. Under these particular experimental conditions, it is reasonable to assume that the UME current response in this region is governed by a photo-induced charge transfer reaction at the illuminated film/electrolyte interface. Experimental approach curves iᵣ(z) were normalized to iᵣ(L) and the normalized heterogeneous rate constants kᵣₑ were extracted by fitting them to an analytical approximation suggested by Cornut and Lefrou for a first-order reaction at the sample and an infinitely fast reaction at the UME.

\[ I^\text{cond}(L, \kappa, \text{RG}) = \frac{i^\text{ins}(L, \text{RG}) - 1}{(1 + 2.47 \text{RG}^{0.31} L)^{(1 + \kappa 0.006 \text{RG} + 0.113 \kappa - 0.023 \text{RG} + 0.91)}} \]

where \( I^\text{ins}, I^\text{cond} \), and the normalized UME current, when the reaction at the sample is diffusion controlled, and are calculated according to the following equations, respectively.

\[ I^\text{ins}(L, \text{RG}) = \frac{(2.08/\text{RG}^{0.35})(L - (0.145/\text{RG}) + 1.585}{(2.08/\text{RG}^{0.35})(L + 0.00238 \text{RG}) + 1.57 + (\ln \text{RG}/L) + (2/\pi \text{RG}) \ln(1 + (\pi \text{RG}/2L))} \]  

(1a)

\[ I^\text{cond}(L + \kappa^{-1}, \text{RG}) = \alpha(\text{RG}) + \frac{\pi}{4 \beta(\text{RG}) \arctan(L + \kappa^{-1})} \]

\[ + \left(1 - \alpha(\text{RG}) - \frac{1}{2 \beta(\text{RG})}\right) \frac{2}{\pi} \arctan(L + \kappa^{-1}) \]

(1b)

\[ \alpha(\text{RG}) = \ln 2 + \ln 2 \left(1 - \frac{2}{\pi} \arccos \left(\frac{1}{\text{RG}}\right)\right) \]

\[ - \ln 2 \left(1 - \frac{2}{\pi} \arccos \left(\frac{1}{\text{RG}}\right)^2\right) \]

(1c)

\[ \beta(\text{RG}) = 1 + 0.639 \left(1 - \frac{2}{\pi} \arccos \left(\frac{1}{\text{RG}}\right)\right) \]

\[ - 0.186 \left(1 - \frac{2}{\pi} \arccos \left(\frac{1}{\text{RG}}\right)^2\right) \]

(1d)

In eqn (1), \( \kappa \) is a normalized, dimensionless, first order rate constant which is obtained by fitting the experimental approach curves to the analytical approximations. Thus, the apparent heterogeneous rate constants \( kᵣₑ \) for the regeneration of the reduced dye (after injection the hole into the valence band of semiconductor) by the oxidized state of redox shuttle at incident light of given intensity can be obtained from eqn (2).

\[ kᵣₑ = \frac{2x \cdot D \cdot \phi \cdot j_{\text{in}}}{3d \cdot [S] \cdot \phi \cdot j_{\text{in}} - 6k \cdot D \cdot [\text{re}]/j_{\text{in}}} \]  

(2)

where \( D \) is the diffusion coefficient of the redox shuttle in electrolyte, \( rᵣ \) is the particular UME radius, \( d \) is the film thickness, \([\text{re}]\) is the concentration of the reduced state of redox couple, \([S]\) is the concentration of the oxidized state of redox couple, \( j_{\text{in}} \) is the incident photon flux, \( \phi \) is the excitation cross-section, respectively. Fig. 3c presents the calculated heterogeneous rate constants \( kᵣₑ \) as a function of the concentration of the reduced state of redox couple, showing that the \( kᵣₑ \) values are approximately 1000 fold higher with the thiol-based electrolyte than with the iodide-based electrolyte. Under illumination of the thin film with a blue LED, the rate constants extracted by fitting with a single exponential are \( kᵣₑ = 4.6 \times 10⁻⁴ \) and \( 2.2 \times 10⁻⁵ \) mol⁻¹ cm⁻² s⁻¹ for the regeneration of the P1 dye by T⁻ and T⁺, respectively. Taking into consideration the similar diffusion coefficients (about 3–5 × 10⁻⁵ cm² s⁻¹) of different electrolytes used here, the fast regeneration process observed with the thiol-based electrolyte is particularly noteworthy as this electrolyte is attractive for use in p–n tandem devices due to its transparency. However, the rate constants are relatively lower for the p-type dye regeneration compared with those of the n-type DSCs using these two electrolytes, indicating that an expected large improvement in the p-DSC with a suitable electrolyte would be fulfilled. The lower dye regeneration rates of the p-type dyes compared to that of n-type dyes could be due to the large driving force of the reaction, the diffusion of the redox shuttles, and the molecular structures of the mediators, etc.

The dark current–voltage characteristics of devices B and D are shown in Fig. S2.† The onset of the dark current of device D occurred at a low forward bias, whereas the use of the organic
redox couple suppressed the dark current, shifting its onset by about 120 mV. This result agrees with the difference in the open-circuit voltage. The $V_{oc}$ corresponds to the increase of quasi-Fermi level of the semiconductor ($E_{F,p}$) with respect to the dark value ($E_{F,0}$), which equals the electrolyte redox energy ($E_{redox}$). To understand the difference in photovoltaic performance among the various devices, the interfacial charge recombination kinetics between the holes of the CuCrO$_2$ nanoparticles and the reduced state of the redox shuttles were investigated by photovoltage decay experiments and charge extraction measurements. Fig. 4a presents the injected hole density ($n_i$) as a function of the $V_{oc}$. The linear fitting of the data (in logarithmic scale) gives rise to different slope values, which remains approximately constant (about 0.7 per decade) over the potential range of 0.05 V to 0.1 V for devices B and D, largely changes over 0.1 V and then remains almost constant (about 2.0 per decade) from 0.16 V to 0.31 V for device D. The open-circuit voltage is lower for device B at the low charge density examined (ca. 50 mV difference at a charge density of 1.0 $\times$ 10$^{18}$ cm$^{-2}$). This result could be attributed to the redox potential difference (ca. 50 mV) between the two electrolytes. This argument is further proved in Fig. 4b, showing that device B had a much longer hole lifetime in comparison to device D at an identical charge density. Therefore, the slow recombination process between the injected holes and $T_2$ in device B, as well as the transparency of the electrolyte, could result in the high $V_{oc}$ values recorded. Assuming that there is a similar hole diffusion coefficient in both devices, a longer hole diffusion length ($L_{D, D} = \sqrt{D_{D} \tau}$, where $D_{D}$ being the hole diffusion coefficient, $\tau$ being the charge recombination lifetime) would be expected for device B than that of device D, which may also contribute to the higher IPCE values observed for the former, as presented in Fig. 2.

The low FF in devices A–C could be due to the slow catalytic oxidation of the reduced species of the thiolate redox shuttle at the platinum-loaded counter electrode. Thus, two platinum-free counter electrodes were taken for further experiments herein, namely PEDOT and CoS, for thiolate-to-disulfide oxidation in p-type DSCs. As presented in Fig. 2a and Table 1, a high FF of about 0.44 was obtained when using PEDOT or CoS as a counter electrode, leading to an impressive overall power conversion efficiency of 0.22 and 0.23%, respectively. Electrochemical impedance spectroscopy (EIS) was employed to scrutinize the effect of different redox couples on the dark current generated under a forward bias at the nanocrystalline CuCrO$_2$/electrolyte junction through the oxidation of reduced ions of the shuttle by valence band holes. Fig. 5a shows the corresponding EIS spectra of devices B and D at a bias of 0.125 V. The resulting frequency analysis shows two well-separate semicircles in the Nyquist diagram. In the order of increasing frequency these are attributed to the hole recombination at the oxide/electrolyte interface, and the electrochemical reaction at the counter electrode. Clearly, device D, with an iodide-based electrolyte, shows a much smaller impedance compared with that of device B, with a thiolate-based electrolyte. Because the impedance arcs of the photocathode and counter electrode are partially overlapped in the Nyquist plots, information of the transport resistance could not be directly extracted from the data. For this reason the photo-cathode impedance was fitted with a lumped RC-circuit instead of a transmission line model in this paper. The important elements, including the charge transfer resistance of the counter electrode ($R_{ct}$), and the photocathode/electrolyte interfacial charge recombination resistance ($R_{ct}$), were derived by fitting the impedance data. The charge transfer resistance $R_{ct}$ at the counter electrode/electrolyte interface is presented in Fig. 5b. Compared to other devices, device B which uses a thiolate-based electrolyte with Pt as a CE exhibits higher $R_{ct}$ value (about 36 $\Omega$ cm$^2$) than those of devices E and F (about 1.8–8 $\Omega$ cm$^2$) with the PEDOT or CoS counter electrodes at a given dark current (0.8 mA cm$^{-2}$), indicating a higher over-potential in this device under operating conditions. It is interesting to note that both Pt free counter electrodes exhibit good electrochemical activity in the thiolate-based electrolyte, explaining the higher FF obtained in these devices. Early investigation has shown that the high electro-catalytic activity could be attributed to the nanoporous structure and high surface area of those counter electrodes. Even though the $R_{ct}$ was largely reduced by using a PEDOT or CoS counter electrode, their catalytic activity is lower compared with Pt to the iodide-based electrolyte, as presented in Fig. 5b. Under the same conditions, device D using $I_x$ $\equiv$ $I$ electrolyte with a Pt counter electrode shows much lower $R_{ct}$ value (about 1 $\Omega$ cm$^2$). Ruling out the effect from the diffusion process of the redox species on the interfacial charge transfer at the counter electrode (i.e., the
rate of charge transfer is much slower than the diffusive processes in the system), the value of $R_{Ce}$ can be evaluated with following equation:

$$R_{Ce} = \frac{RT}{n^2F^2k_{Ce}(C_{ox})(C_{re})^{-\alpha}}$$  (3)

where $C_{ox}$ and $C_{re}$ are the known concentrations of the redox species, $n$ is the number of electrons transferred, $F$ is Faraday’s constant, $k_{Ce}$ is the rate constant for the electrochemical charge transfer reaction on the counter electrode, $\alpha$ is the electrochemical transfer coefficient, $R$ is the idea gas constant, and $T$ is the absolute temperature, respectively. Thus, by assumption of $\alpha$ being 0.5 for a reusable reaction, the heterogeneous rate constant $k_{Ce}$ values were calculated to be $1.8 \times 10^{-5}$, $6.7 \times 10^{-4}$, $7.9 \times 10^{-5}$ cm s$^{-1}$ for the reduction reaction of T$_2$ on a Pt, PEDOT, and CoS surface, respectively. The rate constant $k$ for the reduction of I$_3^-$ on Pt was about $3.9 \times 10^{-4}$ cm s$^{-1}$. The higher heterogeneous rate constant $k_{Ce}$ values may result in higher $J_{sc}$ and FF values, leading to better photovoltaic performances.

The dark current reaction contributes to the loss of photovoltaic performance in p-type DSCs, which can be investigated with the photocathode/electrolyte interfacial charge transfer resistance ($R_{ct}$). Fig. 5c presents the variation of the $R_{ct}$ resistance with the applied bias. It should be noted that the redox potential level offset (about 50 mV) between these electrolytes has been considered. By increasing the potential, the $R_{ct}$ resistance becomes smaller due to the higher CuCrO$_2$ valence band hole concentration. The $R_{ct}$ for a cell with the $I^-/I^-$ based electrolyte and Pt counter electrode (device D) is ca. 24 times lower than that for the cells with the T$_2$/T$_{-}$ based electrolyte (device B) at a given potential of 0.2 V, which is qualitatively consistent with the lower $V_{oc}$ under 1 sun illumination. According to the Marcus–Greschener model, the $R_{ct}$ can be expressed as follows:

$$R_{ct}(E_p) = R_0 \exp \left( -\frac{E_{F_p} - E_{F,redox}}{k_BT} \right)$$

$$= R_0 \exp \left( -\frac{E_{vb} - E_{F,redox}}{k_BT} \right) \exp \left( -\frac{E_{F_p} - E_v}{k_BT} \right)$$

(4)

where $E_{vb}$ is the value band level of the p-type semiconductor, $E_{F,p}$ is the Fermi level of hole in the p-type semiconductor, $E_{F,redox}$ is the quasi equilibrium potential of the redox shuttle on the counter electrode, $\beta$ is the Tafel parameter. The fitting of $R_{ct}$ shows that the $\beta$ values of device D (with iodide, about 0.9) is much higher than that of the devices with thiol-based electrolyte (about 0.6), indicative of different recombination mechanisms in those devices. The device parameters obtained from the analysis of the EIS signals in the dark match those obtained from photovoltage transient decay measurements under illumination.

**4 Conclusions**

Electrolytes based on T$_2$/T$^{-}$ are optically transparent, making them very suitable for applications in p–n tandem dye-sensitized solar cells. The effects of the dye-regeneration process and electro-catalytic activity of the counter electrodes on solar conversion efficiencies have been explored in detail. The study herein shows that the interfacial charge transfer kinetics is faster in the dye regeneration process for the T$_2$/T$^{-}$ electrolyte compared to that of the conventional iodide electrolyte, which is attractive to p-DSC applications. The transparent T$_2$/T$^{-}$ electrolyte leads to higher levels of light utilization than the conventional iodide electrolyte, and thus has a higher solar conversion efficiency.

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**Notes and references**


