

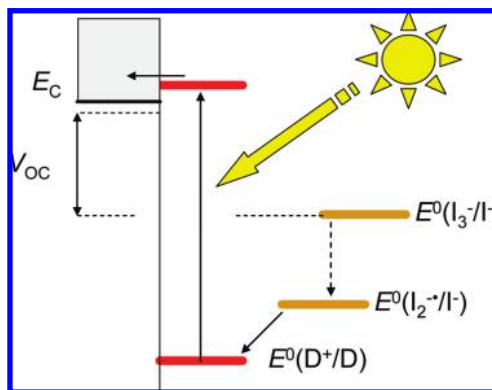
## Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells

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### CON SPECTUS



**D**ye-sensitized solar cells (DSCs) have gained widespread interest because of their potential for low-cost solar energy conversion. Currently, the certified record efficiency of these solar cells is 11.1%, and measurements of their durability and stability suggest lifetimes exceeding 10 years under operational conditions. The DSC is a photoelectrochemical system: a monolayer of sensitizing dye is adsorbed onto a mesoporous  $\text{TiO}_2$  electrode, and the electrode is sandwiched together with a counter electrode. An electrolyte containing a redox couple fills the gap between the electrodes.

The redox couple is a key component of the DSC. The reduced part of the couple regenerates the photo-oxidized dye. The formed oxidized species diffuses to the counter electrode, where it is reduced. The photovoltage of the device depends on the redox couple because it sets the electrochemical potential at the counter electrode. The redox couple also affects the electrochemical potential of the  $\text{TiO}_2$  electrode through the recombination kinetics between electrons in  $\text{TiO}_2$  and oxidized redox species.

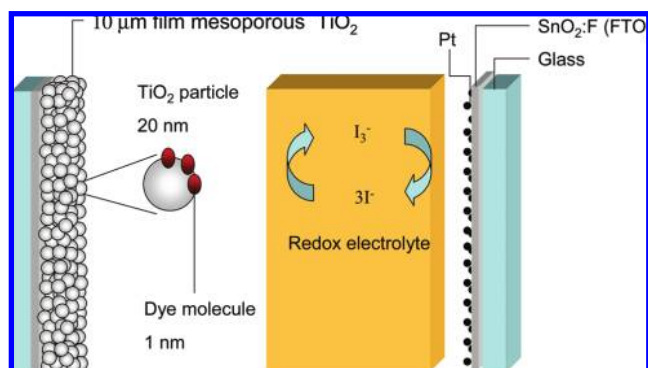
This Account focuses on the special properties of the iodide/triiodide ( $\text{I}^-/\text{I}_3^-$ ) redox couple in dye-sensitized solar cells. It has been the preferred redox couple since the beginning of DSC development and still yields the most stable and efficient DSCs. Overall, the iodide/triiodide couple has good solubility, does not absorb too much light, has a suitable redox potential, and provides rapid dye regeneration. But what distinguishes  $\text{I}^-/\text{I}_3^-$  from most redox mediators is the very slow recombination kinetics between electrons in  $\text{TiO}_2$  and the oxidized part of the redox couple, triiodide. Certain dyes adsorbed at  $\text{TiO}_2$  catalyze this recombination reaction, presumably by binding iodine or triiodide.

The standard potential of the iodide/triiodide redox couple is 0.35 V (versus the normal hydrogen electrode, NHE), and the oxidation potential of the standard DSC-sensitizer ( $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ ) is 1.1 V. The driving force for reduction of oxidized dye is therefore as large as 0.75 V. This process leads to the largest internal potential loss in DSC devices. We expect that overall efficiencies above 15% might be achieved if half of this internal potential loss could be gained.

The regeneration of oxidized dye with iodide leads to the formation of the diiodide radical ( $\text{I}_2^{\cdot-}$ ). The redox potential of the  $\text{I}_2^{\cdot-}/\text{I}^-$  couple must therefore be considered when determining the actual driving force for dye regeneration. The formed  $\text{I}_2^{\cdot-}$  disproportionates to  $\text{I}_3^-$  and  $\text{I}^-$ , which leads to a large loss in potential energy.

The dye-sensitized solar cell (DSC) provides a molecular approach to photovoltaic solar energy conversion.<sup>2,3</sup> Because of their potential for low-cost solar

energy conversion, research in this field has been rapidly expanding in the last 20 years. The certified efficiency of DSC lies currently at 11.1%.<sup>1</sup>



**FIGURE 1.** Schematic structure of the dye-sensitized solar cell.

The configuration and working mechanism of DSC is very different from those of conventional semiconductor solar cells.<sup>2–4</sup> The DSC is a photoelectrochemical system with an electrolyte containing a redox mediator. It usually has a sandwich configuration, see Figure 1. The working electrode is typically a mesoporous TiO<sub>2</sub> film deposited on a conducting glass substrate (usually glass coated with a thin layer of fluorine-doped tin oxide, FTO). A monolayer of dye (the sensitizer) is adsorbed on the TiO<sub>2</sub> surface. The electrolyte typically consists of the triiodide/iodide redox couple dissolved in an organic solvent. The counter electrode is a conducting glass activated with a platinum catalyst.

Although several alternatives to the I<sup>−</sup>/I<sub>3</sub><sup>−</sup> mediator have been developed for DSCs (e.g., see ref 4 and references therein), the performance of the iodide/triiodide couple remains unmatched. This Account focuses on the special properties of the iodide/triiodide redox couple in dye-sensitized solar cells.

## Energetics of the I<sup>−</sup>/I<sub>3</sub><sup>−</sup> Redox Mediator in the DSC

In solution, iodine will bind with iodide to form triiodide in an equilibrium reaction with an equilibrium constant for formation,  $K_1$ :



If the iodine concentration is high, polyiodide species like I<sub>5</sub><sup>−</sup>, I<sub>7</sub><sup>−</sup>, and I<sub>9</sub><sup>−</sup> may also be formed, but in practice, only triiodide seems to be of importance in DSC electrolytes. Because  $K_1$  is high in the organic solvents typically used for electrolytes in DSCs and the iodide concentration is high, the concentration of free iodine will be very low. For example, in a redox electrolyte prepared from 0.5 M LiI and 0.05 M I<sub>2</sub> in acetonitrile ( $\log(K_1/\text{M}^{-1}) = 6.76$ <sup>5</sup>), a free iodine concentration of  $2 \times 10^{-8}$  M is calculated.

The redox potential of the electrolyte ( $E_{\text{redox}}$ ) is given by the Nernst equation (eq 3), which reads for the triiodide–iodide couple:



$$E_{\text{redox}} = E^{0'} + \frac{RT}{2F} \ln \frac{[\text{I}_3^-]}{[\text{I}^-]^3} \quad (3)$$

where  $E^{0'}$  is the formal potential,  $R$  the gas constant,  $T$  the absolute temperature, and  $F$  the Faraday constant. The validity of eq 3 on a platinum electrode in actual redox electrolytes is demonstrated in Figure 5a.

A number of one-electron redox reactions can occur in the iodide–iodine system. These reactions involve the unstable radicals atomic iodine (I<sup>•</sup>) and diiodide (I<sub>2</sub><sup>•−</sup>). Their redox potentials are related through a series of equilibria and equilibrium constants:

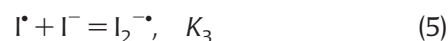
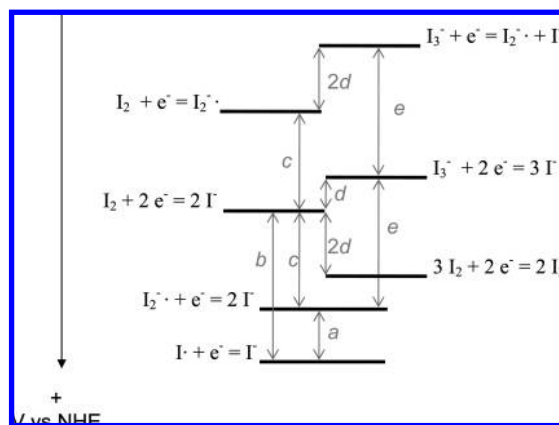


Figure 2 provides an overview of seven redox reactions in the iodide–iodine system and their relative electrochemical potentials. Some of these reactions are important for the DSC. The redox potential of iodine radicals in aqueous solutions has been determined in a number of studies, summarized by Stanbury.<sup>6</sup> Little data is available on the redox potentials of iodine radicals in organic solvents.<sup>7</sup> Redox potentials of the iodide/triiodide system are summarized in Table 1.

In the dye-sensitized solar cell, the two-electron reaction 2 sets the counter electrode at the redox potential of the electrolyte. Reaction 2 is, however, not directly responsible for the regeneration of the oxidized dye, as will be discussed in the section on dye regeneration below. Instead, the one-electron reaction,  $2\text{I}^- \rightarrow \text{I}_2^{\bullet-} + \text{e}^-$ , seems to be responsible for reduction of the oxidized dye.

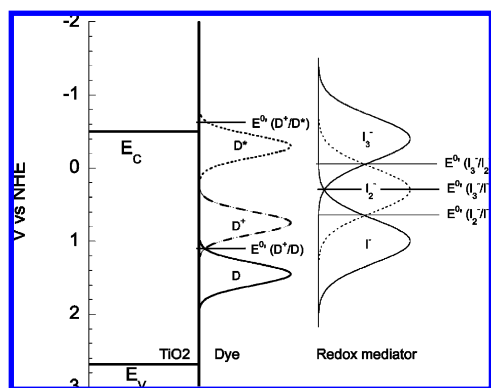


**FIGURE 2.** Redox reactions of the iodine–iodide system and their relative electrochemical potentials. The indicated differences in formal potentials are  $a = (RT/F)\ln(K_3)$ ;  $b = (RT/(2F))\ln(K_2)$ ;  $c = b - a$ ;  $d = (RT/(2F))\ln(K_1)$ ;  $e = c + d$ .

**TABLE 1.** Redox Potentials (V vs NHE) of the Iodide–Triiodide System

solvent	$E^0(I_3^-/I^-)$	$E^0(I^{\bullet}/I^-)$	$E^0(I_2^{\bullet-}/I^-)$	$E^0(I_3^-/I_2^{\bullet-})$
water	+0.536	+1.33 <sup>6</sup>	+1.03 <sup>6</sup>	+0.04 <sup>b</sup>
acetonitrile <sup>a</sup>	+0.29 <sup>c</sup> +0.354 <sup>5</sup>	+1.23 <sup>7</sup>	<+0.93 <sup>7</sup>	>-0.35

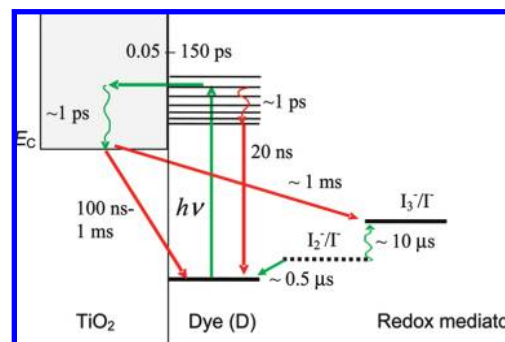
<sup>a</sup> Values reported vs  $Fc^+/Fc$  are converted to NHE by addition of 0.63 V. <sup>b</sup> A value of +0.21 V for  $E^0(I_2^{\bullet-}/I_2^-)$  is reported by Stanbury.<sup>6</sup> <sup>c</sup> Average value from studies summarized in ref 7.

**FIGURE 3.** Energy scheme of the *cis*-Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>-sensitized TiO<sub>2</sub> solar cell with I<sup>−</sup>/I<sub>3</sub><sup>−</sup> redox mediator. Reorganization energies were assumed to be 0.35 eV for the dye and 0.7 eV for the redox species. The energy distribution for D<sup>•+</sup> is obtained by addition of E<sub>0-0</sub> of 1.75 eV<sup>8</sup> to the ground-state level of D.

An energy scheme of the DSC is shown in Figure 3. For the standard sensitizer *cis*-Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>, also known as N3 (in its fully protonated form) or N719 (as the double tetra-butyl-ammonium salt),  $E^0(D^+/D)$  is 1.10 V vs NHE if the dye is fully protonated.<sup>8</sup> Electrochemistry of Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> adsorbed onto a conducting tin oxide glass gave the same value, for both N3 and N719 (unpublished results). The potential difference between  $E^0(D^+/D)$  and  $E^0(I_3^-/I^-)$  amounts to 0.75 V. This potential is used to drive the forward reactions in the DSC. Based on the reaction scheme for dye regeneration, which will be discussed below, the driving force for dye regeneration reaction is given by the difference between  $E^0(I_2^{\bullet-}/I^-)$  and  $E^0(D^+/D)$ . The unstable I<sub>2</sub><sup>•−</sup> radical, which is formed during dye regeneration, is converted into I<sub>3</sub><sup>−</sup>. This corresponds to a potential loss of several hundred millivolts [ $E^0(I_2^{\bullet-}/I^-) - E^0(I_3^-/I^-)$ ] in the DSC.

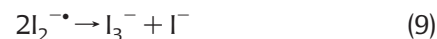
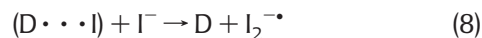
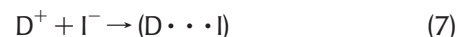
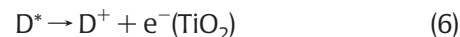
## DSC Working Mechanism and Kinetics

**Electron Injection and Regeneration of the Oxidized Dye.** The working mechanism of the dye-sensitized solar cell is summarized in Figure 4. Sunlight is absorbed by the dye, and the excited dye can inject an electron into the conduction band of TiO<sub>2</sub>. The time scale of this process is tens of femtoseconds to hundreds of picoseconds and depends on the electronic coupling and energetic overlap between donor and

**FIGURE 4.** Kinetics of the *cis*-Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>-sensitized TiO<sub>2</sub> solar cell with I<sup>−</sup>/I<sub>3</sub><sup>−</sup> redox mediator. Typical time constants of the forward reactions (green) and recombination reactions (red) are indicated.

acceptor states.<sup>9</sup> The remaining oxidized dye is reduced by the iodide in the electrolyte. The half-time for regeneration of the most common sensitizer, *cis*-Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>, in the presence of about 0.5 M iodide is in the range of 100 ns to 10 μs, depending on the precise composition of the electrolyte.<sup>10–15</sup> (Note that values as small as 10 ns have been reported,<sup>3,16</sup> but these appear to be in error.) The nature of the cation in the electrolyte plays a significant role. Pelet et al. observed faster dye regeneration when using electrolytes containing cations that adsorb at the TiO<sub>2</sub> surface.<sup>11</sup> This was attributed to a higher local concentration of the iodide anion near the TiO<sub>2</sub>/electrolyte interface. Several studies report on the regeneration by iodide of other sensitizers, such as Ru- and Os-based complexes,<sup>13,17,18</sup> metal–organic compounds such as phthalocyanines and porphyrins,<sup>14,19</sup> and fully organic dyes.<sup>20</sup> Notably, Os(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>, having an oxidation potential 0.23 V more negative than that of Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>, is not efficiently reduced by iodide after electron injection.<sup>13</sup>

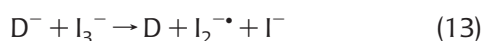
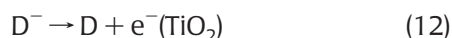
The reaction between oxidized dye and iodide leads to the formation of diiodide radicals (I<sub>2</sub><sup>•−</sup>).<sup>14,18,21–23</sup> This radical was observed in dye-sensitized solar cells using nanosecond-laser spectroscopy<sup>14,18,23</sup> and pseudo-steady-state photoinduced absorption spectroscopy.<sup>24</sup> The pathway for the reduction of the oxidized dye (D<sup>•+</sup>) by iodide is given by reactions 6–9.<sup>11,12,17</sup>



After electron injection from the excited dye (D<sup>•+</sup>), the oxidized dye D<sup>•+</sup> is reduced by iodide, under the formation of a complex (D<sup>•+</sup>⋯I). The formation of such a complex was

recently demonstrated by Clifford et al. for the sensitizer *cis*-Ru(dcbpy)<sub>2</sub>(CN)<sub>2</sub>.<sup>12</sup> Fitzmaurice et al. proposed earlier the formation of a (D<sup>••</sup>·I<sub>2</sub><sup>−</sup>) complex in the case of a Ru(dcbpy)<sub>3</sub><sup>2+</sup> sensitizer.<sup>25</sup> Quantum chemical calculations confirm that formation of such complexes is energetically favorable.<sup>26</sup> The complex dissociates when a second iodide ion comes in and dye in the ground state D and I<sub>2</sub><sup>−•</sup> are formed, reaction 8. Two diiodide radicals react to form triiodide and iodide (disproportionation, reaction 9). The concentration of I<sub>2</sub><sup>−•</sup> in a DSC under operation can be estimated as follows: If we assume that the solar cell generates a photocurrent of 10 mA cm<sup>−2</sup>, the formation rate of I<sub>2</sub><sup>−•</sup> is 10 × 10<sup>−3</sup>/F = 1.0 × 10<sup>−7</sup> mol cm<sup>−2</sup> s<sup>−1</sup>. The generation is confined to the pores in the TiO<sub>2</sub> film. Assuming a 10 μm film with 50% porosity, the pore volume is 5 × 10<sup>−4</sup> cm<sup>3</sup>, and the I<sub>2</sub><sup>−•</sup> generation rate per volume is 0.2 mol L<sup>−1</sup> s<sup>−1</sup>. With the second-order rate constant for reaction 9 in acetonitrile of 2.3 × 10<sup>10</sup> M<sup>−1</sup> s<sup>−1</sup>,<sup>27</sup> the steady state concentration of I<sub>2</sub><sup>−•</sup> is calculated to be 3 μM. This is 2 orders of magnitude higher than the concentration of free I<sub>2</sub> in a typical acetonitrile-based redox electrolyte.

**Alternative Pathway for Dye-Sensitization: Reductive Quenching of Excited Dye Molecules.** Under certain conditions, an alternative pathway is possible in dye-sensitized solar cells involving the reductive quenching of excited dye molecules by iodide:<sup>28–31</sup>



This pathway can be significant if electron injection for the excited dye into the conduction band of the semiconductor is relatively slow or in the presence of very high concentrations of iodide. The excited dye is reduced by iodide, leading to the formation of the reduced dye D<sup>−</sup> and I<sub>2</sub><sup>−•</sup>. Initially, iodine radicals may be formed (reaction 10).<sup>31</sup> The reduced dye can either inject an electron into the conduction band of TiO<sub>2</sub> (reaction 12)<sup>29</sup> leading to photocurrent or react with triiodide (reaction 13), which is a recombination reaction. In practical dye-sensitized solar cell devices, the reductive quenching pathway may play a role in ionic liquid electrolytes, where iodide concentration can be very high (>5 M). Wang et al. reported that optimum solar cell performance was obtained in a binary ionic liquid electrolyte containing 50% 1-phenyl 3-methyl imidazolium iodide, while higher concentrations led to a decrease in photocurrent, suggesting that reaction 13 is dominant over

reaction 12 after reductive quenching (the Ru complex Z907 was used as a sensitizer).<sup>30</sup>

**Reaction at the Counter Electrode.** At the counter electrode triiodide should be efficiently reduced to iodide (reaction 2). The counter electrode must be catalytically active to ensure rapid reaction and low overpotential. The overpotential  $\eta$  needed to drive the reaction at a certain current density  $J$  gives rise to a charge transfer resistance ( $R_{CT} = \eta/J$ ), which acts as a series resistance in the solar cell. Ideally  $R_{CT}$  should be down to ~1 Ω/cm<sup>2</sup> to avoid significant losses. Counter electrodes prepared from conducting glass onto which thermal Pt clusters are deposited are very suitable.<sup>32</sup> Low Pt loadings (5 μg cm<sup>−2</sup>) are needed so that the electrode remains transparent. Iodine adsorbs dissociatively onto the Pt surface, enabling a rapid one-electron reduction. Alternative materials that were successfully used as counter electrodes in DSCs are carbon<sup>33</sup> and the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT).<sup>34</sup>

## Loss Mechanisms in the DSC

**Recombination Reactions.** A series of recombination reactions compete with the forward reactions in the DSC, see Figure 4. Radiative and nonradiative decay of the excited dye is competing with electron injection. Injection efficiencies approaching 100% are found for sensitizers with favorable energetics and good electronic coupling to TiO<sub>2</sub> conduction band states. After injection, electrons can recombine with oxidized dye molecules. Although this process is slow under low light intensity (when the electron concentration per TiO<sub>2</sub> particle is about one), it has been shown that this recombination accelerates dramatically under conditions of high electron concentration in the TiO<sub>2</sub>, for example, at high light intensities or at the maximum power point, and may compete with dye regeneration.<sup>10</sup>

Photoinjected electrons travel a relatively long path through the mesoporous TiO<sub>2</sub> structure before reaching the conducting substrate. During transport, they are always near the semiconductor/electrolyte interface and may recombine with electron acceptors in the electrolyte. Here, the I<sub>3</sub><sup>−</sup>/I<sup>−</sup> couple distinguishes itself from one-electron couples, such as ferrocenium/ferrocene (Fc<sup>+</sup>/Fc); while nearly all injected electrons are collected in the DSC under short-circuit conditions in case of I<sub>3</sub><sup>−</sup>/I<sup>−</sup>, most electrons recombine in case of Fc<sup>+</sup>/Fc.<sup>35</sup>

The recombination of electrons in mesoporous TiO<sub>2</sub> with acceptors in the electrolyte has been mostly studied using steady-state<sup>36–38</sup> or dynamic<sup>39–43</sup> measurements of the open-circuit potential ( $V_{oc}$ ). This electron transfer can occur both at the interface between the TiO<sub>2</sub> and the electrolyte and



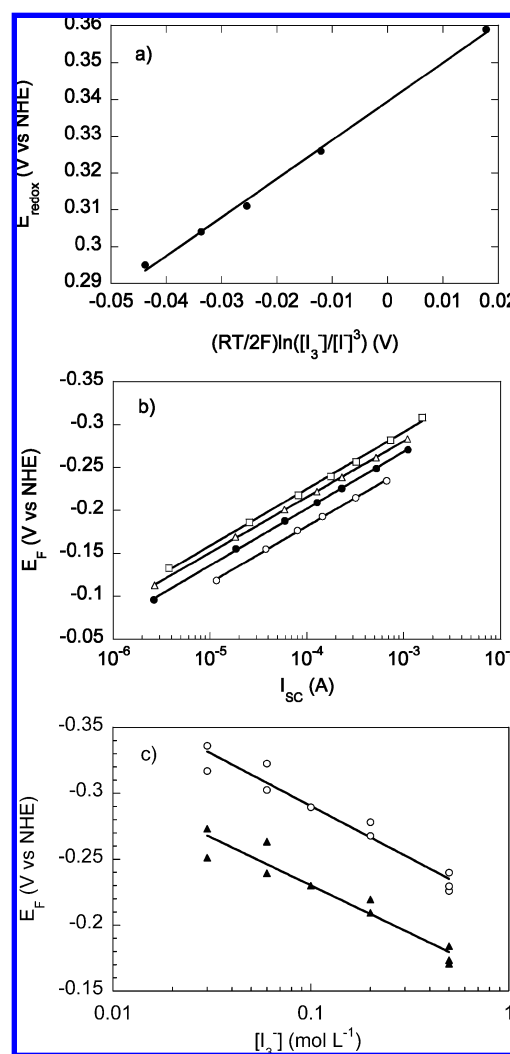
at the part of the conducting substrate that is exposed to the electrolyte. The second route is usually less important in case of  $\text{I}_3^-/\text{I}^-$  and can be suppressed further by using a compact blocking layer of the metal oxide.<sup>38</sup> We will therefore consider only the first route here. When the DSC is illuminated under open circuit conditions, the net rate of electron injection from dyes into the  $\text{TiO}_2$  is balanced by the net rate of electron transfer from the electrode to the electrolyte. Because the  $V_{\text{OC}}$  depends on the electron concentration in the  $\text{TiO}_2$ , changes in  $V_{\text{OC}}$  can be related to the recombination process. The following expression has been derived for the steady-state  $V_{\text{OC}}$  in the DSC:<sup>8,36,44</sup>

$$V_{\text{OC}} = \frac{kT}{e} \ln\left(\frac{J_{\text{inj}}}{k_{\text{rec}} n_{\text{c},0} [\text{I}_3^-]}\right) \quad (14)$$

where  $J_{\text{inj}}$  is the flux of injected electrons,  $k_{\text{rec}}$  is the rate constant for triiodide reduction, and  $n_{\text{c},0}$  the conduction band electron density in the dark. First-order recombination kinetics for both electrons and triiodide are assumed in eq 14. Huang et al. included an additional electron transfer coefficient in their expression,<sup>36</sup> which seems inappropriate because  $\text{TiO}_2$  is a semiconductor. Equation 14 predicts that  $V_{\text{OC}}$  will increase by 59 mV for a 10-fold increase in light intensity, because  $J_{\text{inj}}$  is proportional to light intensity. Values close to 60 mV are indeed frequently found,<sup>36–38</sup> but higher values have also been reported. Figure 5b shows a recent example from our laboratory of the light-intensity dependence of  $V_{\text{OC}}$  in DSCs with varying concentrations of triiodide in the electrolyte. The slopes are  $66 \pm 1$  mV per decade increase in light intensity.

In a number of studies, the effect of the concentration of triiodide on recombination kinetics was investigated.<sup>36,37,39,41</sup> As expected, the recombination rate increases with increasing  $\text{I}_3^-$  concentration. Analysis of  $V_{\text{OC}}$  under steady-state conditions in DSCs with varying triiodide concentration gave values of 1.9<sup>36</sup> and 1<sup>37</sup> for the reaction order of triiodide in the recombination reaction. Changes in the redox potential were, however, unaccounted for in these studies, so the validity of these values is questionable. Figure 5c shows the dependence of the electrochemical potential ( $E_{\text{F}}$ ) of the  $\text{TiO}_2$  electrode in a DSC as a function of triiodide concentration, taken from our recent work. By using  $E_{\text{F}}$  rather than  $V_{\text{OC}}$ , the shifts in redox potential of the electrolyte are taken into account. Using the method outlined by Huang et al.,<sup>36</sup> a reaction order of 1.1 is determined for  $\text{I}_3^-$  in the recombination reaction. Equation 14 appears therefore to be valid.

The reaction of electrons in  $\text{TiO}_2$  with triiodide is strongly temperature dependent and is an activation-controlled process.<sup>43</sup> It can be suppressed by additives in the electrolyte,



**FIGURE 5.** (a) Redox potential of the iodide–triiodide electrolyte measured on a platinum electrode as function of  $(RT/2F)\ln([\text{I}_3^-]/[\text{I}^-]^3)$ . The slope is 1.0, showing the validity of eq 3. The electrolyte was composed of 1.0 M 1-propyl 3-methylimidazolium iodide and various amounts of iodine in acetonitrile. (b) Light intensity dependence of the electrochemical potential  $E_{\text{F}}$  in  $\text{TiO}_2$  in a *cis*- $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ -sensitized solar cell.  $E_{\text{F}} = V_{\text{OC}} - E_{\text{redox}}$ , where  $V_{\text{OC}}$  is taken as a negative value. The  $\text{I}_3^-$  concentration was 0.03, 0.1, 0.2, and 0.5 M from top to bottom. (c) Dependence of  $E_{\text{F}}(\text{TiO}_2)$  in the same DSCs on  $\text{I}_3^-$  concentration for two light intensities.

such as 4-*tert*-butylpyridine<sup>8,36,42</sup> and guanidium thiocyanate.<sup>45</sup> Both additives give a decreased recombination rate, as well as a shift of the conduction band edge of  $\text{TiO}_2$ : toward negative potential for 4-*tert*-butylpyridine and toward more positive potential for guanidium thiocyanate. The most probable mechanism is that these additives adsorb at the  $\text{TiO}_2$  surface, blocking active reduction sites or preventing close approach of electron acceptors to the surface. Co-absorbers, added to the dye bath upon dye adsorption, can have a similar effect as the additives in the electrolyte. For example,

$\omega$ -guanidinoalkyl acids gave reduced recombination as well as a  $\text{TiO}_2$  conduction band edge shift toward negative potential.<sup>46</sup>

Green et al.<sup>47</sup> reported that recombination of electrons in bare mesoporous  $\text{TiO}_2$  with  $\text{I}_3^-$  is 2 orders of magnitude slower than with  $\text{I}_2$ . This may imply that  $\text{I}_2$  is the main electron acceptor in the electrolyte in DSCs. Interestingly, the  $\text{I}_2^{\cdot -}$  intermediate was not observed spectroscopically in their experiment. This can be explained by a dissociative reduction process of iodine on the  $\text{TiO}_2$  surface. The kinetics appeared to be first order with respect to the  $\text{I}_2$  concentration.

Dyes adsorbed at the mesoporous  $\text{TiO}_2$  electrode affect the reduction of triiodide. Dyes with additional hydrophobic chains can reduce the rate of recombination by a blocking effect, as was demonstrated for the Z907 dye in comparison with N719.<sup>15</sup> Certain dyes adsorbed on  $\text{TiO}_2$  increase the recombination rate.<sup>48–51</sup> Miyashita et al.<sup>50</sup> proposed that this is due to a locally increased concentration of triiodide near the dye, while O'Regan et al.<sup>51</sup> suggested that this is due to binding of the dye with iodine.

**Diffusion Limitations.** In order to have rapid regeneration of the oxidized dye, iodide should be present in high concentration or diffusion of iodide should be fast. In nonviscous electrolytes such as acetonitrile, an iodide concentration of 0.3 M is sufficient, while in viscous ionic liquids a higher concentration may be necessary.<sup>30</sup>

Transport of triiodide to the counter electrode can be a rate-limiting step in the DSC if the concentration of triiodide is low or if the solvent is viscous.<sup>52</sup> Depletion of triiodide at the counter electrode causes an overpotential, lowering the voltage output of the solar cell. Transport of triiodide is mostly driven by diffusion. When a high concentration of high triiodide is present, a Grotthuss mechanism, illustrated below, may increase the observed diffusion coefficient.<sup>53</sup>



**Light Absorption by Triiodide and Photochemical Reactions.** The  $\text{I}_3^-/\text{I}^-$  redox electrolyte possesses a yellow to brown color and will thus absorb some sunlight. It has been calculated that a very high concentration of 1 M triiodide in an ionic liquid electrolyte gives a 13% reduction in photocurrent as a result of light absorption for a solar cell with the standard N719 dye.<sup>54</sup> Excitation of triiodide leads to the following photochemical reactions in the electrolyte:<sup>55</sup>



In the presence of iodide, the iodine radical formed in reaction 16 is rapidly converted to  $\text{I}_2^{\cdot -}$ , which is more stable. Diiodide radicals will decay by disproportionation reaction 9. The reactive iodine radical could give unwanted side reactions, but we did not find evidence for this in the literature. Photogenerated  $\text{I}_2^{\cdot -}$  gives rise to a cathodic photocurrent in mesoporous  $\text{NiO}$  solar cells.<sup>56</sup> The system acts as photogalvanic solar cell: photogenerated  $\text{I}_2^{\cdot -}$  in the electrolyte injects holes into the valence band of the wide bandgap p-type semiconductor  $\text{NiO}$ . In  $\text{TiO}_2$ -based DSCs,  $\text{I}_2^{\cdot -}$  is expected to accept electrons from the  $\text{TiO}_2$  conduction band or the conducting substrate, giving additional recombination.

Long-term exposure of a DSC to sunlight can lead to loss of triiodide in the cell. Absorption of UV light by  $\text{TiO}_2$  leads to formation of an electron–hole pair. If the hole reacts with iodide, no harm is done, and the DSC will function as usual. If the hole reacts with an organic molecule, for instance, a solvent molecule, no triiodide is formed. The electron still reduces  $\text{I}_3^-$  at the counter electrode. Eventually, this will lead to depletion of  $\text{I}_3^-$  in the DSC. It is therefore essential to prevent direct excitation of  $\text{TiO}_2$  in DSCs by a UV-filter.

**Corrosion.** The iodide/triiodide redox electrolyte is highly corrosive and attacks most metals. Even vapor-deposited platinum, frequently used as a catalyst on the counter electrode, is reported to dissolve in this electrolyte.<sup>57</sup> Thermally platinized conducting glass, on the other hand, appears to be stable in long-term solar cell tests. DSC modules generally use metal current collectors (usually silver) on the FTO substrates to reduce series resistance losses. An imperfect DSC sealing can result in electrolyte leakage and degradation of the current collectors. The use of a gelled electrolyte can prevent leakage.

## Alternative Redox Mediators

Bromide and pseudohalides have a similar chemistry as iodide, behave similarly in DSCs, and have therefore also similar drawbacks. The  $\text{Br}^-/\text{Br}_3^-$ ,<sup>58</sup>  $\text{SCN}^-/(\text{SCN})_3^-$ ,<sup>59</sup> and  $\text{SeCN}^-/(\text{SeCN})_3^-$ <sup>59,60</sup> redox couples have been tested with some success. Selenocyanate-based ionic liquid electrolytes gave very encouraging performance.<sup>60</sup>

Some success was also obtained with one-electron redox systems, such as cobalt(II/III)<sup>61</sup> and copper(I/II)<sup>62</sup> coordination complexes, and organic mediators, such as TEMPO.<sup>63</sup> Rapid electron recombination was found in case of the  $\text{Fc}^+/\text{Fc}$ , but this couple could be made to function by passivating the  $\text{TiO}_2$  surface using polysiloxane.<sup>35</sup> The redox electrolyte in the DSC

may also be replaced by a solid-state organic hole conductor, such as 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-MeOTAD).<sup>64</sup>

## Outlook

The iodide/triiodide couple will probably be unsurpassed as a redox mediator for dye-sensitized solar cells for some time to come. The kinetics of recombination between electrons in the TiO<sub>2</sub> and triiodide in the electrolyte are extremely slow and favorable compared with most alternatives investigated to date. The regeneration of the oxidized dye is rapid, but this comes at the high cost of a potential loss of about 0.75 V. There is still limited room for improvement for DSCs with I<sup>−</sup>/I<sub>3</sub><sup>−</sup> as the redox mediator: dyes with improved light absorption and less potential loss during the regeneration process compared with Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> may be developed.

With the growing ability to master the semiconductor/dye/electrolyte interface and control recombination reactions, we will be able to use alternative redox mediators or hole conductors that have redox potentials up to 0.5 V more positive than that of iodide/triiodide. Eventually, DSCs based on these mediators may match or overtake I<sup>−</sup>/I<sub>3</sub><sup>−</sup>-based DSCs in terms of solar cell efficiency.

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