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Dilemmas of Dye-Sensitized Solar Cells

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Boosted by the urgent need of renewable energies, developments in photovoltaics are turning relatively fast. Just a few years back inorganic thin-film solar cells were a curiosity in a market dominated by crystalline silicon, that now holds about 80% share mainly due to strong progress of CdTe technology that has grown from 2% in 2005 to 13% in 2010. Dye-sensitized solar cells (DSCs) are based on a molecular absorber that emits photogenerated electrons from an excited state to nanostructured TiO₂ and receives ground-state electrons from a liquid redox carrier.^[1,2] Since the seminal paper in 1991,^[3] a series of efficiency increases were reported, but for many years now, the power conversion efficiency has remained about 11% in small-area cells. The DSC holds the prospect for a cost-effective photovoltaic technology due to low cost of the raw constituents and easy processability by automated manufacturing,^[4] and industrialization activities are showing increasing vigor. However, considering the unavoidable losses in scaling up to module size, higher efficiencies are still required, in robust configurations that ensure a long service life. Rather than conforming to a plateau of frustration, an active and growing research community on DSCs is looking for ways out of it, and there is great expectations to see who will shoot the magic bullet.

Herein we discuss the recent development of efficient DSCs based on a new organic dye and ferrocene redox carrier,^[5] and to put this new breakthrough into perspective, we first address which are the general weaknesses of DSC that prevent progress. Take the crystalline silicon solar cell as a reference case. The bandgap of silicon is $E_g = 1.12$ eV, and the optical absorption edge is relatively sharp. Integration of the number of photons above this value with the reference AM1.5G solar spectrum (with total power 100 mW cm^{-2} , usually termed 1 sun) provides a theoretical current of 43.8 mA cm^{-2} (see Figure 1). Short-circuit current as high as 42.7 mA cm^{-2} has been obtained in record cells, which is very close to the theoretical limit.^[6,7] The other crucial element determining power conversion efficiency PCE is the open-circuit voltage V_{oc} . This is given by the separation of electron and hole Fermi levels (E_{Fn} and E_{Fp}) under photoinduced carrier generation at one sun, and amounts to 0.70 V. The PCE obtained in the record cells is 25%, that reduces to 19% in the best commercial modules.

In comparison, we look at the key piece of the DSC, the molecular absorbers. Organic absorbers do not absorb equally at

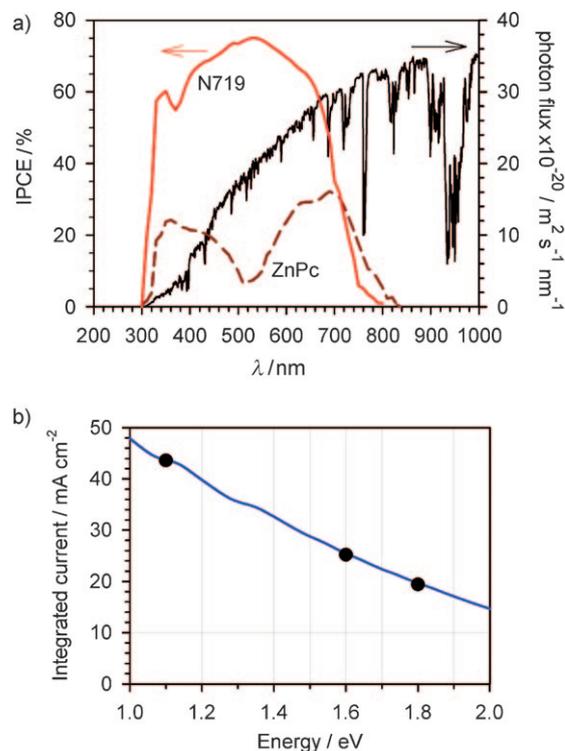


Figure 1. a) Air Mass 1.5 Global (AM1.5G) solar spectrum (photon flux as a function of wavelength) and the measured IPCE of a DSC with N719 dye (PCE 10%) and a zinc phthalocyanine dye (PCE 1%).^[15] b) Integrated current density as a function of the bandgap energy of the absorber, for AM1.5G solar irradiance. Reference points are shown at 1.10, 1.60 and 1.80 eV.

all wavelengths. For example Chlorophyll *a*, the absorber that nourishes most of the biosphere, has very strong light absorption around 430 and 660 nm but relatively weak absorption bands in the visible region between these wavelengths. It is therefore useful to assess DSC absorbers by the incident-photon-to-current-conversion efficiency (IPCE), or equivalently, the external-quantum efficiency (EQE). This is the short-circuit current produced by a given dye in an actual DSC device under monochromatic light as a function of wavelength, divided by the theoretical current associated with the incident photon flux. The paradigmatic, ruthenium-based dye $\text{Ru}(\text{Bu}_4\text{NHdcbpy})_2(\text{NCS})_2$ known as N719 starts injection at $\approx 775 \text{ nm}$,^[1] see one example in Figure 1a. N719 can thus be associated with an effective bandgap of 1.60 eV as noted in Figure 2, which provides for a maximum theoretical photocurrent of 25 mA cm^{-2} (see Figure 1b). In practice the photocurrent value must be reduced by about 15% by the optical transparency of the conducting glass that supports the TiO₂ nanoparticle framework and reflection losses. In addition, it is

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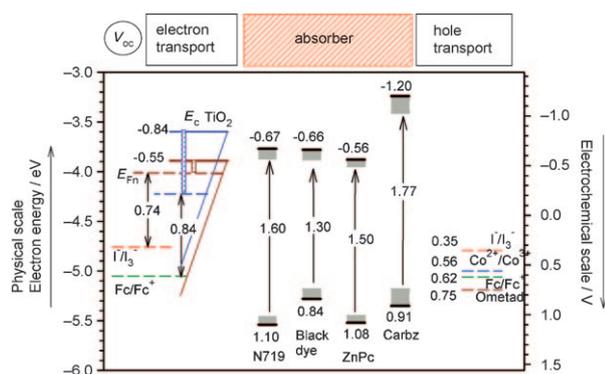


Figure 2. Energy diagram of the materials components of dye-sensitized solar cells. Standard energy levels are given on the electrochemical scale (NHE) where the origin is taken at -4.44 eV (IUPAC value) in the solid-state one-electron energy scale. The arrows indicate excitation energies [eV] derived from IPCE for N719,^[35] black dye,^[11] zinc phthalocyanine (ZnPc),^[15] and Carbz-PAHTDIT.^[5] The grey boxes indicate the broadening of the ground and excited states by interaction of the dye with TiO_2 and electrolyte, allowing a narrower effective bandgap. In general, TiO_2 and dye energy levels are not absolute values as they depend on the solution components.^[36] The conduction band edge E_c of TiO_2 and exponential density of states (DOS) in the bandgap is indicated in two situations, for I^-/I_3^- and ferrocene redox couples in DSC with Carbz dye from ref. [5]. E_{Fn} is the Fermi level of electrons in TiO_2 , the difference to the redox level gives the open-circuit voltage V_{oc} that corresponds to the values obtained. E_c and DOS values are not quantitative (chemical capacitance was not reported in ref. [5]). The shaded squares give an estimation of the distance between the Fermi level and the edge of the conduction band.

observed in Figure 1a that the IPCE takes a high value of 60% only at 670 nm. This corresponds to a great loss in the photon-abundant spectral region 700–800 nm, and in total a current of 19 mA cm^{-2} can be obtained from N719. Therefore, we start with a 50% handicap with respect to the silicon solar cell—we have much less current.

Opportunities to improve the DSC appear from the fact that it is formed by a combination of materials. Internal energetics can be changed by the chemistry of the components and their physical interactions. In general, new degrees of freedom for tailoring materials properties exist, which are inaccessible for single semiconductor solar cells. One central aspect of the electron injection process that launches the photocurrent is the absolute position of dye's excited state S^+/S^* in the energy scale, as plotted in Figure 2. This state must be *higher* than the conduction band of the electron acceptor TiO_2 , otherwise the excited electrons have nowhere to go.^[8,9] Light absorption properties of dyes and injection to titania may change strongly due to the specific components of the liquid electrolyte, aggregation, solvatochromic shift, and so on. The dye's excited state S^+/S^* consists on a complex manifold of vibrationally unrelaxed and relaxed states.^[10,11] The reported bandgap of N719 taken from the excitation transition energy varies between 1.60 and 1.70 eV, whereas the ground state lies at $V_{\text{NHE}} = +1.10$ V (up to +0.91 V) with respect to the reference normal hydrogen electrode (NHE).^[12–14]

One way to heal the photocurrent limitation of DSCs is to extend dye absorption to the red part of the spectrum. Phthalocyanine (Pc) dyes, for example, have a narrower energy gap

than N719, hence the IPCE is broadened as indicated in Figure 1a. We believe that S^+/S^* is lower for Pc than N719 dye, which causes a decrease in the injection that is visible as a strong reduction of IPCE of Pc-based DSCs, as illustrated in Figure 1a.^[15] Other Zn–Pc dyes, such as the popular TT1, can give 70% at the summit of IPCE, at the price of shifting the current onset below 800 nm, thus with a wider excitation gap approaching that of N719.^[16] Overall, Pc dyes provide photocurrents of about 8 mA cm^{-2} .

But we recall that power production in the solar cell has, like the Janus god of mythology, two oppositely looking faces: less current should give scope for more voltage. In the silicon solar cell $E_g - qV_{\text{oc}} = 0.5$ V at 1 sun (q being the elementary charge), then at *similar electron density* one may ask for $V_{\text{oc}} = 1.1$ eV from the N719 dye. Actually this dye gives a photovoltage of 0.8 V, and the reason why this falls short of expectation is well known.^[17] The liquid electrolyte in the DSC forms a perfect large-area electronic junction in the intricate framework of the nanostructured metal oxide. At the same time, the photovoltaic operation of DSCs relies to a large extent on unique properties of the I^-/I_3^- redox couple, the redox hole carrier that ensures excellent kinetically induced rectification of electron transfer both at TiO_2/dye and liquid/counter-electrode contacts.^[3,18] However, the redox energy (corresponding to the Fermi level in solution) of this vital element of the DSC lies high in the energy scale, at $+0.35 V_{\text{NHE}}$ (Figure 2). The distance to the ground state of N719 is huge, hence the strong reduction of photovoltage [which is given by $V_{\text{oc}} = (E_{\text{Fn}} - E_{\text{redox}})/q$] with respect to the bandgap of the molecular absorber.

The way of escape out of the high hole energies is to find another hole carrier with a lower Fermi level that cuts the distance to the dye ground state. Alternative hole conductors that are less aggressive to metal substrates and collector grids also have the great benefit of enabling cheaper device configurations for large-scale production. This idea has in effect been realized, for example with the organic hole conductor Spiro-OMeTAD, which is 400 mV deeper than N719 (Figure 2) and allows for a DSC with $V_{\text{oc}} \approx 1.1$ eV to be realized.^[19] Essential to this development has been the design of new sensitizers with a large extinction coefficient,^[20] including metal-free organic dyes, that allows the reduction of the thickness of the TiO_2 film.^[21] Nonetheless, the thinner film used to avoid the penalty of hole transport in a slower medium such as OMeTAD, or with the new molecular complexes,^[22] imposes a loss in photocurrent, although recently cells of efficiency close to 7% have been realized with cobalt polypyridine redox mediators.^[23,24] It must also be noted that variations in the DSC configuration that look for a particular gain may have adverse effects in other aspects of the device. Recombination, the loss of electrons in the TiO_2 electron conductor to the hole carrier, is one important process that is severely affected by properties of the materials and the surface conditions. It has been observed that some otherwise efficient dyes increase the recombination rate,^[25] and recombination also produces a strong limitation for solid-state OMeTAD cells.^[26]

A decade ago the photovoltaic mechanisms of DSC were still under intense discussion, and the physical basis for $V_{\text{oc}} =$

$(E_{\text{Fn}} - E_{\text{redox}})/q$ was questioned. In this context Brian Gregg presented the results of DSC using different redox couples, to show that V_{oc} is not influenced by the material of the collecting substrate.^[27] Although he succeeded in making the main point, the V_{oc} of the ferrocene sample was considerable less than that of I^-/I_3^- , despite the ferrocene being 270 mV deeper (Figure 2). It was recognized that ferrocene shows an enormous charge transfer rate (recombination) and this popular redox couple (largely available, and with simpler charge transfer properties than those of iodide complexes), was largely discredited for DSC applications until recently Brian O'Regan spoke at conferences about aqueous DSCs using this redox carrier. The results reported now by Bach, Spiccia and coworkers, constitute an important achievement.^[5] They combine a new metal-free Carbz-PAHDTT dye with the ferrocene mediator and reach a PCE of 7.5% with $V_{\text{oc}} = 0.84$ V. To obtain this result the authors wisely combine a battery of tools concerning, for example, the blocking of substrates to avoid recombination and the control of electrolyte additives as *tert*-butyl pyridine (TBP) and chenodeoxycholic acid (cheno). This illustrates the progress in controlling the factors determining DSC properties resulting from extensive investigation in recent years. TBP (and avoiding using lithium ions, which produce the opposite effect^[28]) is applied to shift up the conduction band of TiO_2 , which increases the photovoltage.^[29] Additives, in combination with tailored dye properties, also protect electrons in titania from being charge-transferred to solution.^[30,31] These properties of the DSC are now well-understood and routinely checked by measuring the chemical capacitance and recombination resistance with impedance spectroscopy.^[15,32,33]

Still, the main question concerning the results of Daeneke et al.^[5] is how the large V_{oc} is explained in a redox medium that produces large recombination. A salient aspect of their report is the high position of S^+/S^* of the new dye, just opposite to the tendency of phtalocyanine dyes mentioned above. Figure 2 shows that S^+/S^* stands higher than most common dyes. Shifting up the dye levels, to reduce the regeneration gap, has been a relatively little explored avenue, producing no improvement in some cases.^[34] Following the nomenclature of the titania density of states (DOS)^[32] we have plotted in Figure 2 (left) an estimation of energy levels. The DOS is inferred from charge extraction measurements in ref. [5], which suggest a low charge density in the ferrocene DSC, as expected, and also an enormous upward shift of the TiO_2 conduction band of about 190 mV for the ferrocene cell with respect to the control I^-/I_3^- cell. This high position of the band of the electron carrier allows one to take full advantage of the high dye levels to obtain the remarkable $V_{\text{oc}} = 0.84$ V in a situation of strong recombination.

As mentioned before, the DSC has several internal degrees of freedom in the energy space. For some years the tendency has been to go down with the redox carrier to improve the V_{oc} and now we see that an interesting route is to go up with the dye's excited state, with the concomitant achievement of a high position of the TiO_2 conduction band. It will be useful to further determine if such a high position is induced by the ferrocene mediator (in which the electron acceptor has a +

charge in contrast to I_3^-) in combination with other additives. It also appears important to assess the stability of ferrocene-based DSCs, as this is one of the main requirements for fabrication. Overall the work of Daeneke et al. explores an interesting dimension of DSC, which is to shift up the dye excited state to improve photovoltage while maintaining a reasonable photocurrent, and demonstrates that playing with the energetics inside the DSC gives still room for plenty of improvements.

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