

# The origin of open circuit voltage of porphyrin-sensitised TiO<sub>2</sub> solar cells

Attila J. Mozer,<sup>\*a</sup> Pawel Wagner,<sup>a</sup> David L. Officer,<sup>a</sup> Gordon G. Wallace,<sup>a</sup> Wayne M. Campbell,<sup>b</sup> Masanori Miyashita,<sup>c</sup> Kenji Sunahara<sup>c</sup> and Shogo Mori<sup>\*\*c</sup>

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Electron lifetime and diffusion coefficient measurements in highly efficient porphyrin-sensitised TiO<sub>2</sub> solar cells showed reduced electron lifetime, and consequently, lower photo-induced electron density under illumination compared to commonly used ruthenium dye (N719)-sensitised solar cells, which is proposed to be the origin of the generally lower open circuit voltage.

Dye-sensitisation by porphyrin dyes – the most common light-harvesting units on the planet – has been extensively researched for several artificial light-harvesting applications including photocatalysis and energy conversion.<sup>1–3</sup> Porphyrin-sensitised TiO<sub>2</sub> solar cells<sup>3</sup> have been highlighted recently due to world-record power conversion efficiencies obtained in both liquid-type cells using I<sup>−</sup>/I<sub>3</sub><sup>−</sup> as a redox couple as well as solid-state devices employing *spiro*-MeOTAD (7.1%<sup>1</sup> and 3.6%, respectively.) The short circuit current ( $J_{sc}$ , mA cm<sup>−2</sup>) of porphyrin-sensitised solar cells is determined by their spectral response and it is fairly well understood and characterised.<sup>1–4</sup> The open circuit voltage ( $V_{oc}$ , mV), on the other hand, is generally 100–200 mV lower than the commonly used ruthenium dye-sensitised analogs, which may be related to either (i) a negative shift of the conduction band potential of the TiO<sub>2</sub> following dye sensitisation; or (ii) a reduced electron density due to reduced electron lifetime.

In this communication, we have determined the electron lifetime and the electron diffusion coefficient in porphyrin-sensitised solar cells using the step-light induced measurements of photocurrent and photovoltage (SLIM-PCV) technique,<sup>5</sup> and compared them to N719-(Bu<sub>4</sub>N)<sub>2</sub>[Ru(dcbpyH)<sub>2</sub>(NCS)<sub>2</sub>] sensitised solar cells fabricated following identical cell fabrication procedures.

The two most efficient porphyrin dyes reported to date, GD1 (cyano-3-(2'-(5',10',15',20'-tetraphenylporphyrinato zinc(II))yl)acrylic acid) and GD2 (2-carboxy-5-(2'-(5',10',15',20'-tetra(3'',5''-dimethylphenyl)porphyrinato zinc(II))yl)-penta-2,4-dienoic acid) were synthesised according to ref. 6. Their chemical structure and the current voltage curves measured for similarly constructed cells under 100 mW cm<sup>−2</sup> AM 1.5 illumination are shown in Fig. 1. The average values and

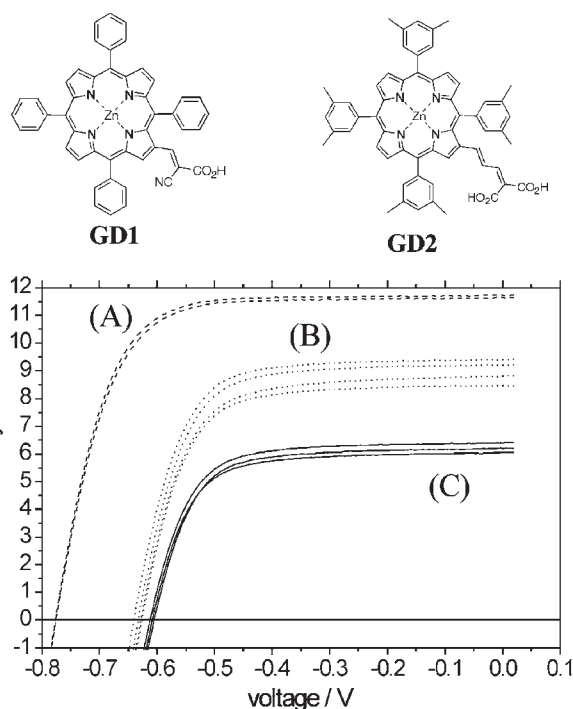


Fig. 1 The chemical structures of GD1 and GD2. Current–voltage curves of (A) N719-, (B) GD2-, (C) GD1-sensitised TiO<sub>2</sub> solar cells.

standard deviation of the photovoltaic parameters are summarised in Table 1. A rather thin (4.5 μm, Solaronix Nanoxide-T) transparent TiO<sub>2</sub> layer was deposited on FTO glass (Nippon sheet glass, 10 Ω □<sup>−1</sup>) for these studies ensuring that the TiO<sub>2</sub> film thickness was smaller than the diffusion length of the photogenerated electrons. The TiO<sub>2</sub> films were sintered at 550 °C for 30 min and immersed into 2 × 10<sup>−4</sup> M porphyrin in ethanol for 2 hours, or 3 × 10<sup>−4</sup> M N719 in acetonitrile (AN)–*tert*-butanol 1 : 1 mixture for 18 hours. The electrolyte composition for the N719, GD1 and GD2 solar cells was 0.1 M LiI, 0.6 M DMPII (1-propyl-2,3-dimethylimidazolium iodide), 0.05 M I<sub>2</sub> and 0.5 M 4-*tert*-butylpyridine (*t*BP) in AN (electrolyte I). The  $J_{sc}$  of the GD1 and GD2-sensitised cells is approx. 50% and 25% lower than that of the N719, respectively, which is due to the combined effect of the thin TiO<sub>2</sub> film used and the smaller absorption coefficient of the porphyrin dyes in the 500–700 nm region.<sup>6</sup> The  $V_{oc}$ , on the other hand, is on average 166 mV (GD1) and 143 mV (GD2) lower than that for the N719 cell.

Since the change of the redox potential of I<sup>−</sup>/I<sub>3</sub><sup>−</sup> under illumination and in the dark is less than −1 mV, the  $V_{oc}$  of a

<sup>a</sup> ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia. E-mail: attila@uow.edu.au; Fax: +61 42213114

<sup>b</sup> IFS-Chemistry, Massey University, New Zealand. Fax: +64 63505612

<sup>c</sup> Department of Fine Materials Engineering, Shinshu University, Nagano, 386-8567, Japan. E-mail: shogmori@shinshu-u.ac.jp; Fax: +81 268-21-5496; Tel: +81 268-21-5818

**Table 1** Photovoltaic parameters, electron lifetime and electron diffusion coefficient for N719-, GD1- and GD2-sensitised solar cells

Sample (electrolyte)	Thickness/ $\mu\text{m}$	$V_{\text{oc}}$ /mV	$J_{\text{sc}}$ /mA cm $^{-2}$	FF	$\eta$ (%)	$\tau$ /s <sup>a</sup>	$D$ /cm $^2$ s $^{-1}$ <sup>b</sup>
N719 (I)	4.54 $\pm$ 0.06	775 $\pm$ 0	11.68 $\pm$ 0.06	0.72 $\pm$ 0	6.5 $\pm$ 0.08	(5.7 $\pm$ 0.4) $\times 10^{-1}$	(1.0 $\pm$ 0.1) $\times 10^{-5}$
GD1 (I)	4.54 $\pm$ 0.03	609 $\pm$ 3	6.22 $\pm$ 0.16	0.70 $\pm$ 0	2.65 $\pm$ 0.08	(2.6 $\pm$ 0.1) $\times 10^{-3}$	(1.7 $\pm$ 0.1) $\times 10^{-5}$
GD2 (I)	4.57 $\pm$ 0.04	632 $\pm$ 5	8.97 $\pm$ 0.42	0.69 $\pm$ 0.01	3.93 $\pm$ 0.24	(2.9 $\pm$ 0.3) $\times 10^{-3}$	(2.2 $\pm$ 0.1) $\times 10^{-5}$
GD2 (II)	4.52 $\pm$ 0.09	626 $\pm$ 1	9.09 $\pm$ 0.33	0.69 $\pm$ 0.01	3.93 $\pm$ 0.21	(5.1 $\pm$ 1.1) $\times 10^{-3}$	(1.7 $\pm$ 0.5) $\times 10^{-5}$
GD2 (III)	4.45 $\pm$ 0.05	349 $\pm$ 10	10.83 $\pm$ 0.52	0.57 $\pm$ 0.01	2.14 $\pm$ 0.08	(2.4 $\pm$ 1.2) $\times 10^{-4}$	(2.8 $\pm$ 0.1) $\times 10^{-5}$

<sup>a</sup> Calculated at  $10^{18}$  and  $10^{17}$  electron density, respectively. Electrolyte I: 0.1 M LiI, 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.5 M (rBP) in AN, Electrolyte II: 0.1 M LiI, 0.9 M DMPII, 0.05 M I<sub>2</sub>, 0.5 M (rBP) in AN; Electrolyte III: 0.7 M LiI and 0.05 M I<sub>2</sub> in AN. <sup>b</sup> Calculated at  $10^{18}$  and  $10^{17}$  electron density, respectively. Electrolyte I: 0.1 M LiI, 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.5 M (rBP) in AN, Electrolyte II: 0.1 M LiI, 0.9 M DMPII, 0.05 M I<sub>2</sub>, 0.5 M (rBP) in AN; Electrolyte III: 0.7 M LiI and 0.05 M I<sub>2</sub> in AN.

dye-sensitised solar cell is proportional to the electron density in the TiO<sub>2</sub> under illumination and in the dark.<sup>7</sup> The decay of the  $V_{\text{oc}}$  caused by a small perturbation in electron density can be approximated to a single exponential decay, where the exponent equals the electron lifetime ( $\tau$ ). The short circuit current decay, on the other hand, is determined by the electron diffusion coefficient if the diffusion length is larger than the TiO<sub>2</sub> film thickness ( $l$ ). The electron diffusion coefficient  $D$  (cm $^2$  s $^{-1}$ ) can be calculated as  $D = l^2/(\tau_c \times 2.77)$ , where  $\tau_c$  is the short circuit current decay constant.<sup>5</sup>

We have recorded short circuit current and  $V_{\text{oc}}$  decays in N719-, GD1- and GD2-sensitised solar cells by illuminating them with a 635 nm diode laser. Less than 10% of the light intensity was turned down and the voltage or current response was measured using a fast multimeter. Electron densities (ED, cm $^{-3}$ ) at the same illumination intensities were determined by a charge extraction method, in which the light intensity was

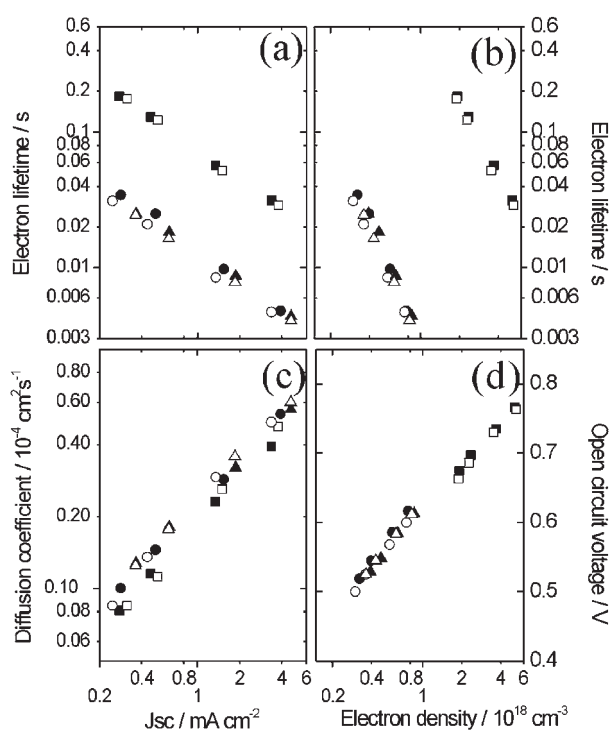
switched off completely, and simultaneously the solar cell was switched from open circuit to short circuit. The resulting current was integrated and from the amount of extracted charge, the electron density was calculated.<sup>8</sup>

Fig. 2(a) shows the electron lifetime for N719-, GD1- and GD2-sensitised solar cells under various laser light intensities. The  $x$ -axes show  $J_{\text{sc}}$  measured under the same light intensity as used for lifetime measurements. Two set of measurements for each dye are shown, as indicated by the open and full symbols. The electron lifetime in both porphyrin dyes is reduced by approximately a factor of 5 at all illumination intensities, independent of their chemical structure. This difference is even more pronounced when the electron lifetime is compared at the same ED determined by the charge extraction method (Fig. 2(b)).  $\tau$  values at  $10^{18}$  cm $^{-3}$  ED were calculated assuming a linear dependency of  $\log \tau$  versus  $\log$  ED (a functional dependence frequently observed in DSSCs)<sup>5,8</sup> in Fig. 2(b). The calculated values are shown in Table 1, and indicate a factor of 200 shorter  $\tau$  in porphyrin-sensitised solar cells at matching electron densities. This difference is largely due to an approximately 8 times lower ED in porphyrin-sensitised solar cells at short circuit at the same illumination intensity (not shown). The electron diffusion coefficient, on the other hand, appears to be very similar for all dyes measured, as shown in Fig. 2(c). As a result of the shorter electron lifetime (increased recombination), the electron density and therefore the  $V_{\text{oc}}$  is smaller in porphyrin-sensitised solar cells, as shown in Fig. 2(d). The  $V_{\text{oc}}$  logarithmically depends on ED with a slope of around 200 mV for each order of magnitude increase in ED. As clearly seen in Fig. 2(d), neither the slope nor the intercept of  $V_{\text{oc}}$  versus  $\log$  ED on the  $y$ -axis differs between N719-, GD1- and GD2-sensitised solar cells. This shows that the lower  $V_{\text{oc}}$  of porphyrin-sensitised solar cells is not due to a shift of the conduction-band potential following dye uptake. We anticipate that by increasing the electron density by one order of magnitude by eliminating recombination pathways, open circuit voltages similar to N719-sensitised solar cells will be obtained.

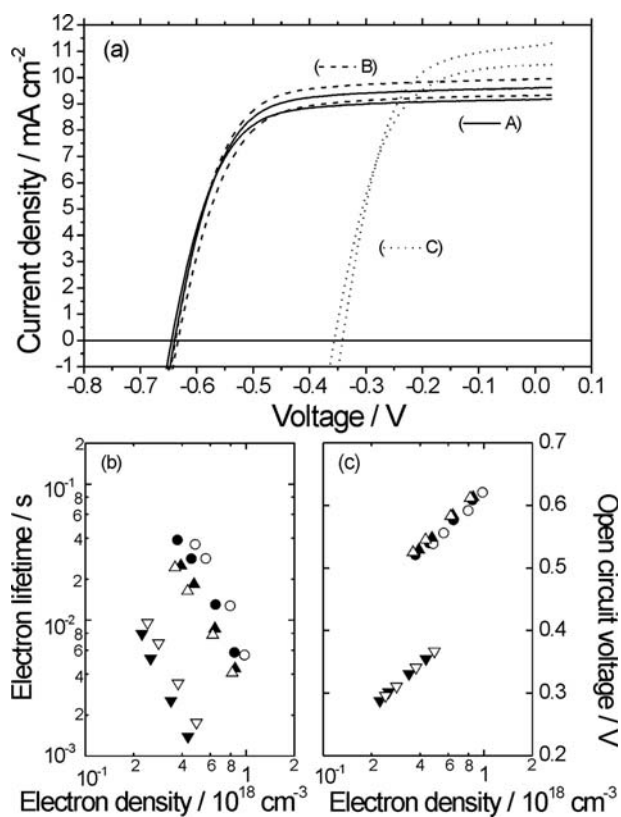
The electron lifetime determined by  $V_{\text{oc}}$  is the product of two recombination reactions occurring simultaneously, as described by eqn (1),<sup>5</sup>

$$\frac{\partial n}{\partial t} = G - \frac{n}{\tau_1} - \frac{n}{\tau_D} \quad (1)$$

where  $\tau_1$  and  $\tau_D$  are the lifetimes determined by the recombination reactions of conduction band electrons with I<sub>3</sub><sup>-</sup> and oxidised dye, respectively. The measured shorter lifetime in



**Fig. 2** (a) Electron lifetime and (c) diffusion coefficient versus short circuit current density. (b) Electron lifetime and (d) open circuit voltage versus electron density for N719- (■, □), GD1- (●, ○) and GD2- (▲, △) sensitised TiO<sub>2</sub> solar cells.



**Fig. 3** (a) Current density–voltage curves of GD2-sensitised solar cells using electrolyte I (A), electrolyte II (B), and electrolyte III (C); Electron lifetime (b) and open circuit voltage (c) versus electron density using electrolyte I (●, ○), electrolyte II (▲, △) and electrolyte III (▼, ▽).

porphyrin-sensitised solar cells is thus related to either a faster recombination with dye cations or  $I_3^-$  ions.

Using nanosecond transient absorption spectroscopy we have shown that the reaction of conduction band electrons with oxidised dye happens comparatively slowly, as in N719-sensitised films when only an inert solvent is used. Alternatively, a shorter  $\tau_D$  may be attributed to the slow re-reduction of the dye cations by  $I^-$ . The reaction rate of dye cations with  $I^-$  ions should depend on the  $I^-$  concentration.<sup>9</sup>

In the following, we have determined  $\tau$  and  $D$  in GD2-based solar cells using an electrolyte containing (i) increased concentration of  $I^-$  (0.1 M LiI, 0.9 M DMPII, 0.05 M  $I_2$  and 0.5 M *t*BP in AN, electrolyte II) or (ii) using a simple electrolyte containing only LiI as  $I^-$  source (0.7 M LiI and 0.05 M  $I_2$  in AN, electrolyte III). The current density–voltage curves recorded under 100 mW cm<sup>-2</sup> AM 1.5 illumination are shown in Fig. 3(a) using electrolyte I (A), electrolyte II (B) and electrolyte III (C), respectively. We observed no significant change in the performance of the GD2-sensitised solar cells by increasing the total  $I^-$  concentration from 0.7 M to 1.0 M. In addition, neither the electron lifetime (Fig. 3(b)) nor the  $V_{oc}$  (Fig. 3(c)) of these cells was affected by the increase in  $I^-$  concentration, which suggests that slow re-reduction of the dye cation by  $I^-$  is not the major reason for the shorter electron lifetime.

Using electrolyte III has a dramatic effect on the solar cell performance. The  $V_{oc}$  dropped by almost 50%, and the  $J_{sc}$

increased (Table 1). Moreover, the  $V_{oc}$  versus ED plot (Fig. 3(c)) shows a shift of nearly  $-200$  mV along the  $V_{oc}(x)$  axis. We attribute this change primarily to the absence of *t*BP and the increase of  $Li^+$  concentration in electrolyte III. It has been shown that the conduction band potential of  $TiO_2$  is shifted negatively by the addition of *t*BP, resulting in higher  $V_{oc}$  but slower charge injection from the photo-excited state of the sensitizer into the conduction band of  $TiO_2$ .<sup>10</sup> The difference in  $D$  shown in Table 1 for various electrolytes was too small to explain the large difference in electron lifetime, therefore we also conclude that the smaller electron lifetime in porphyrin-sensitised solar cells is not due to faster electron transport in these films.

The shorter electron lifetime may originate from the different shape and symmetry of the Zn-porphyrins compared to N719. The former has a planar structure<sup>11</sup> and is likely to bind close to orthogonal to the  $TiO_2$  surface. Thus,  $I_3^-$  can be attracted to the positively charged Zn atom at the center, enhancing recombination through the proximity of  $I_3^-$  to the  $TiO_2$  surface. In contrast, the spherical N719 dye<sup>12</sup> binds to the surface such that the approach of  $I_3^-$  to the  $TiO_2$  surface is shielded by the negatively charged NCS ligands. Voltage decay measurements performed in the dark revealed similarly short lifetimes, which suggest similar proximity of  $I_3^-$  ions to the  $TiO_2$  interface in both the dark and under illumination.

In summary, we have observed a significantly reduced electron lifetime in porphyrin-sensitised solar cells, which is the main reason for their generally lower open circuit voltage. We proposed that the short electron lifetime is intrinsic to the symmetric nature of the Zn-porphyrin dyes studied.

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