Solid-state dye-sensitized solar cells: electronic characterization of nano-scale interpenetrating p-n heterojunctions

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This paper describes the transport and recombination characteristics of nanoporous, dye-sensitized TiO_2 films where the pores are filled with the wide-band-gap, p-type conductor CuSCN. These cells will be referred to as Dye Sensitized Heterojunctions (DSHs). Figure 1 shows a typical IV for a DSH. It is obvious that the efficiency is strongly decreased by the low fill factor (~45%). This can be compared to dye-sensitized cells based on similar TiO_2 films filled with liquid electrolytes, which routinely have fill factors of 70%. A low fill factor can be due to series resistance, slow carrier transport in the interpenetrating p-n junction, and/or a high recombination rate. Figure 2a shows a current transient for a DSH under short circuit conditions with 1 sun and 0.1% sun background illumination. The pulse excitation was a 0.1ms white light flash. Figure 2b shows the comparison between the current transients for a DSH and a typical TiO_2/dye/electrolyte cell, both with 1 sun background illumination. It is apparent that the current transients are quite similar, with the exception of a longer tail on the transient for the electrolyte cell.

Figure 3a shows voltage transients for a DSH, at V_{OC}, under the same background illumination and pulse conditions. Figure 3b shows the comparison between the voltage transients for the DSH and the electrolyte cell, at 1 sun, Voc. It is clear that the voltage decay of the DSH is much faster than that of the electrolyte cell. In fact the voltage decay at Voc for this DSH, ($T_{1/2}$ 0.15ms) is essentially the same as the current decay at short circuit ($T_{1/2}$ 0.14ms). This similarity of rates can be taken as evidence that the low fill factor in the DSHs is caused principally by increased recombination, relative to the electrolyte cell. One caveat is that recombination will slower at short circuit than at Voc. A value related to the recombination rate under short circuit conditions can be measured by placing the cell at a constant current (= to Jsc), under 1 sun illumination, and measuring the voltage transient that results from a short light pulse. Figure 4a shows such voltage transients for a DSH and an electrolyte cell. The voltage transient for the DSH cell ($T_{1/2}$ 0.45ms) is only about 3x slower than the current transient, whereas for the electrolyte cell the voltage transient ($T_{1/2}$ 40ms) is more than two orders slower.

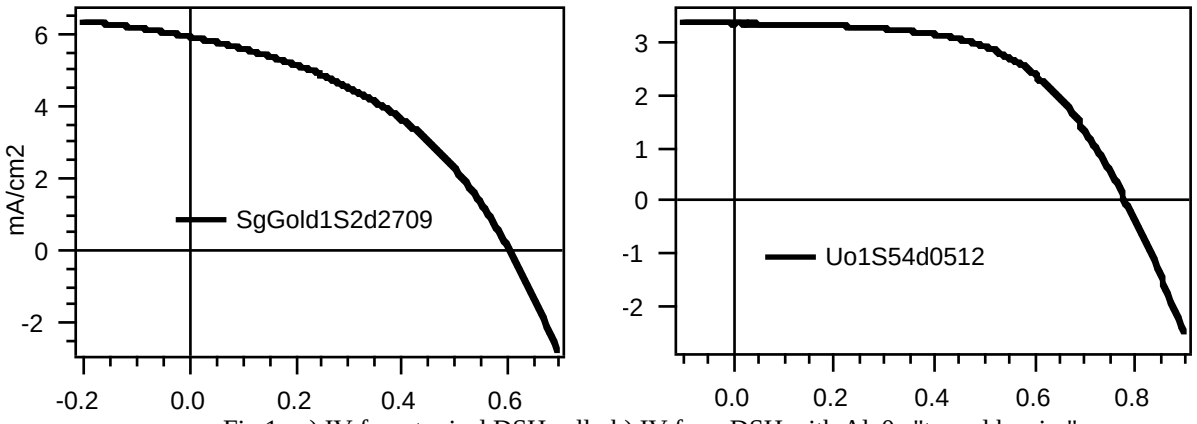

Fig 1. a) IV for a typical DSH cell; b) IV for a DSH with Al_20_3 "tunnel barrier"

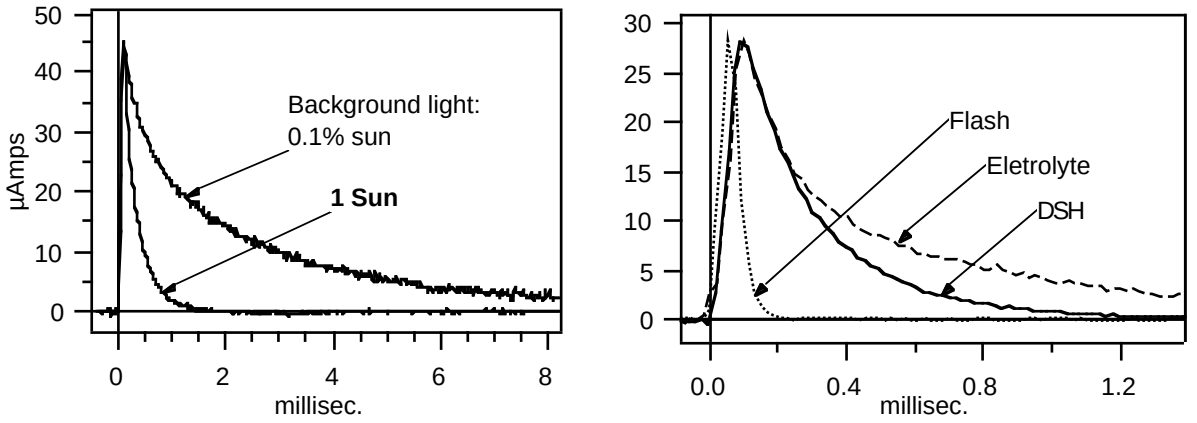

Fig 2. a) Current transients for DSH, low and high background light. b) Current transients, DSH and electrolyte cell.

Comparing Fig 3a and 4a, shows the recombination rate in the DSH at V=0, under 1 sun, is 2 orders of magnitude faster than that at Voc (=330mV) under 0.1sun. We believe that this acceleration is due to the increase in electrons stored in the TiO_2, that occurs even at short circuit conditions. The CuSCN is intentionally doped, and has a dark conductivity several orders of magnitude higher than the TiO_2. Thus the addition of the same number of electrons to TiO_2 as holes to CuSCN, as required by charge balance in this system, will cause a much larger relative increase in the concentration of electrons than of holes. Crudely, the recombination rate at short circuit, under 1 sun, is similar to that at Voc under ~1/10 sun, or about 100mV positive of the 1 sun Voc. Apparently, for the TiO_2 to become sufficiently conductive to carry the 1 sun current, the Fermi level in the TiO_2 must move up to within 100mV of the open circuit position. The work function of CuSCN is ~400 mV larger than that of the I_3/I^- electrolyte. Thus, the dark Fermi level in TiO_2 in the DSH is farther below the conduction band than in the electrolyte cell, and the relative upward movement of the Fermi level is probably larger.

Insulating oxide "tunnel barriers" have been applied to metal oxide films in dye sensitized electrolyte cells to increase the voltage. This technique is also very effective in DSH cells. Figure 1b shows the IV of a DSH with an aluminum oxide tunnel barrier. The typical fill factor increases from 45% to 55-60% with the presence of the tunnel barrier. Figure 4b shows the voltage transient at short circuit ($T_{1/2}$ 8mS) and at 600mV, ($T_{1/2}$ 4mS). At both potentials, the recombination is much slower than in the untreated DSH. This is evidence that in these cells, the "tunnel barrier" does work by reducing the recombination rate constant. If the tunnel barrier only made the surface charge more negative, thus moving the band edge of TiO_2 negative relative to CuSCN, then (to first order) the capacitance at Voc would be the same as without the tunnel barrier, and the recombination rate constant at Voc should be the same as in the untreated cell. If the tunnel barrier works by reducing the rate constant, then the Fermi level at Voc will be closer to the conduction band, the capacitance higher, and the rate constant slower, as observed.

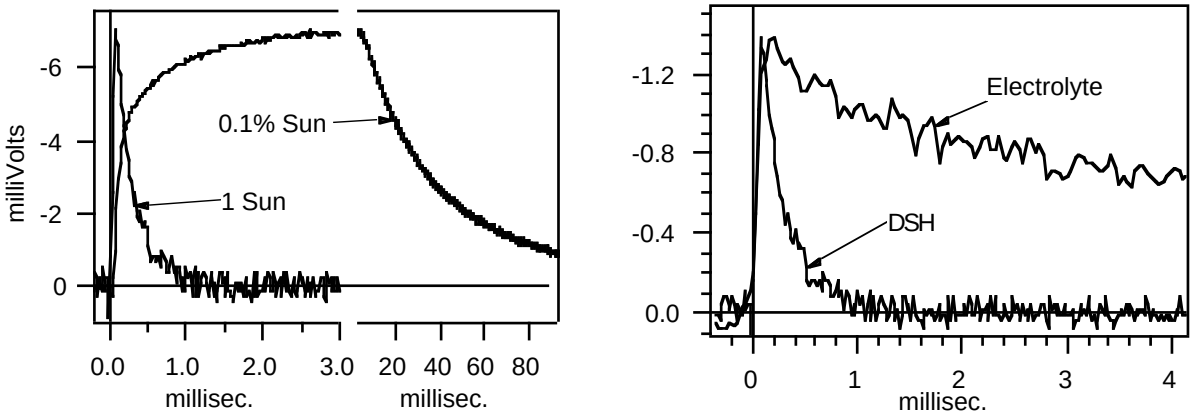

Fig 3. a) Voltage transients at Voc, 1 Sun, for DSH. b) Comparison of voltage transients for DSH and electrolyte cell,

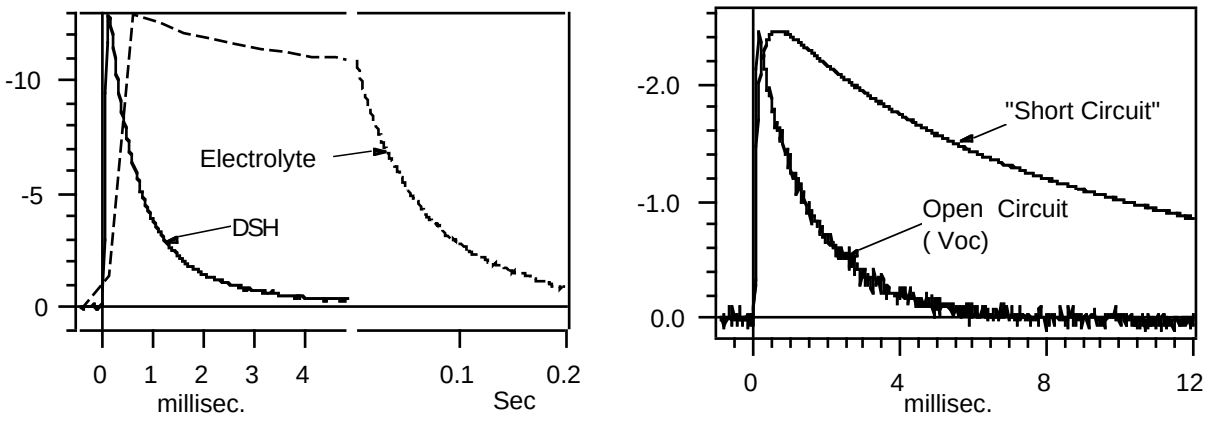

Fig 4. a) Voltage transients, at 0V bias, DSH and electrolyte cells. b) Voltage transients 0V and Voc for DSH with an Al_20_3 tunnel barrier