## Controversial aspects of the dye-sensitised solar cell

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## Introduction

Several aspects of dye-sensitized nanocrystalline solar cells (DSNC) deserve closer examination. This contribution highlights a number of issues that are currently poorly understood or else the subject of controversy in the literature. Clarification of these issues is important for the existing generation of electrolyte based DSNCs. It also has implications for the development of alternative cells in which the electrolyte is replaced by a solid phase such as a p-type semiconductor or phase such as a redox polymer or a conducting polymer. Due to limitations of space, only one of these issues is considered in any detail in this abstract. It is hoped that related problems such as the nature of electron transport and charge separation will be discussed in the talk and over a few beers.

# The origin of the photovoltage.

There has been controversy in the literature concerning the role of the so-called built-in potential in determining the photovoltage generated by illumination of a DSNC. Schwarzburg and Willig [1] consider that the equilibrium potential difference at the substrate/TiO<sub>2</sub> contact determines the maximum photovoltage. This potential difference, and hence the open circuit voltage under illumination, should depend on the work function of the substrate. This does not appear to be the case experimentally. Cahen et al. [2] as well as Pichot and Gregg [3] contend that the photovoltage arises from the change in chemical potential of electrons in the TiO<sub>2</sub> under illumination. According to these authors, the maximum photovoltage is determined by the difference between the redox energy level and the conduction band energy.

If we consider the equilibrium (dark) situation, the electrochemical potential (partial molar Gibbs energy) of electrons in the three phases (substrate,  $TiO_2$ , electrolyte) must be equal:

$$\mu_{n,TiO2} = \mu_{n,SnO2} = \mu_{n,redox} \tag{1}$$

The electrochemical potential of an electron in a phase  $\alpha$  is defined as

$$\mu_{n,\alpha} = \mu_{n,\alpha} - F \Phi_{\alpha} \tag{2}$$

where  $\Phi_{\alpha}$  is the inner or Galvani potential of the phase. The electrochemical potential of electrons is equivalent to the Fermi energy  $\varepsilon_F$  (strictly at absolute zero). It is important to note that the separation of the free energy into chemical terms and electrical terms is entirely conceptual.

For two phases in contact and in electronic equilibrium it follows that the equilibrium Galvani potential difference is given by

$$\Delta \Phi_{\alpha,\beta} = \frac{1}{F} \left( \mu_{n,\alpha} - \mu_{n,\beta} \right) \tag{3}$$

The equilibrium Galvani potential differences at the three phase contacts in the DSNC must be determined by this relationship. These potential differences are not accessible to measurement.

The work functions of the three phases are given by

$$W_{\alpha} = -\varepsilon_{F,\alpha} + \chi_{dip,\alpha} \tag{4}$$

where  $\chi_{dip}$  is the surface dipole potential. For two phases in contact, the total work done in extracting an electron from phase  $\alpha$ , inserting it into phase  $\beta$  and bringing it across the junction from phase  $\beta$  back to phase  $\alpha$  must be zero

Under illumination at open circuit the system is no longer in electronic equilibrium, so that in principle equilibrium thermodynamics cannot be applied. Nevertheless it is common practice to introduce the concept of the quasi-Fermi level (QFL) to describe the electron occupation probability. It is important to realise that the QFL does not describe the occupation probability of states that are involved in recombination. The occupation of these states is determined instead by the net rates of

electron capture and recombination. In the case of a bulk semiconductor, shallow states can be considered as being in equilibrium with the conduction and valence bands, whereas deeper states involved in recombination are not. The transition between the two types of levels as a function of energy is defined by the demarcation levels for electrons and holes (at the demarcation level the probability of electron or hole release is equal to the probability of recombination). It follows that the careless application of the QFL concept can lead to errors. In the case of the DSNC, we need only consider the electron QFL and the corresponding demarcation level. The occupancy of all electron states under illumination can only be derived using a *kinetic* model. Recombination in the DSNC can be the back reaction of electrons either with the oxidised dye or with  $I_3$ . Under steady state conditions, the total rate of these back reactions equals the rate of electron injection from the photoexcited dye.

Solution of the kinetics of electron generation, trapping, detrapping and recombination leads to the steady state occupation of energy levels. Input functions are the electron capture cross sections for the trapping and recombination processes as well as the density of states function for trapping and recombination centres. The key output information is the steady state density of electrons in the conduction band, since it is these electrons that are involved in the dynamic electron exchange equilibrium at the  $TiO_2$ /substrate interface. The open circuit boundary condition (net current density = zero) implies that electrons in the conduction band can be considered as being in thermal equilibrium with electrons in the substrate, i.e. we recover the QFL approximation, but it applies only to the description of the electron density in the conduction band. It follows therefore that under steady state conditions we can write

$$\mu_{n,TiO2} = \mu_{n,SnO2} \tag{5}$$

where the left hand term represents the electron QFL at the substrate/ $TiO_2$  junction. It is important to realise that a potential difference can only be measured in a single phase. Simple thermodynamic reasoning (thermodynamic equilibrium at all other junctions) then leads to the conclusion that the photovoltage is the difference in outer (or Volta) potentials in the measuring phase (e.g. copper wire), which is given by

$$U_{photo} = \frac{1}{F} \begin{pmatrix} * - & - \\ \mu_{n, T1O2} - \mu_{n, T1O2} \end{pmatrix}$$
(6)

i.e. by the difference between the QFL and the dark (equilibrium) electrochemical potential of electrons in the  $TiO_2$ . The latter is determined by the equilibrium with the redox system. The former depends on the position of the conduction band relative to the redox Fermi level, the density of states function for traps and recombination centres and the kinetics of the back reactions.

The value of the electron QFL in the TiO<sub>2</sub> film can only be obtained by solving the kinetics of generation and recombination (back reaction). This is achieved by solving the continuity equation. As far as  $U_{photo}$  is concerned, it is the value of the QFL *at* x = 0 that matters. In order to simplify the analysis, we have made an a priori assumption that the effects of drift can be neglected. Details of this approach will be given by Alison Walker in another contribution to this workshop.

#### Electron transport

A related controversy concerns the driving force for charge separation under short circuit conditions. Schwarzburg and Willig [1] consider that the built in potential provides the driving force for separation of an electron/ion pair at the junction. In fact the driving force for electron transport in the dark is simply determined by the gradient of electrochemical potential. The situation under illumination can be described adequately using the gradient of the QFL and an appropriate boundary condition for electron extraction at the substrate. This will also be discussed in more detail in our second contribution.

## References

- 1. K. Schwarzburg and F. Willig, Journal of Physical Chemistry B 103:5743 (1999).
- D. Cahen, G. Hodes, M. Gratzel, J. F. Guillemoles, and I. Riess, *Journal of Physical Chemistry* B <u>104</u>:2053 (2000).
- 3. F. Pichot and B. A. Gregg, *Journal of Physical Chemistry* B <u>104</u>:6 (2000).