

Compact TiO<sub>2</sub> Blocking Layers in Dye Sensitized  
Nanocrystalline Solar Cells  
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The aim of this work was to investigate blocking underlayers in dye-sensitized nanocrystalline (DSNC) solar cells. Compact TiO<sub>2</sub> underlayers are widely used, but remarkably little is known about their properties. Interesting information has been obtained about the effects of blocking layers on the kinetics of back reaction in DSNC cells.

The working electrode of a DSNC solar cell consists of a sensitizing dye adsorbed onto a mesoporous nanocrystalline oxide film. Upon illumination the excited sensitizer injects an electron into the conduction band of the oxide. The electrons diffuse through the oxide and are collected at a fluorine doped tin oxide [SnO<sub>2</sub>(F)] substrate. The ground state of the sensitizer is regenerated by electron donation from a redox mediator that is in intimate contact with the nanocrystalline film. A platinum coated counter electrode completes the cell and catalyses the reduction of the mediator.

There are several recombination processes that compete with desired pathways to reduce cell efficiency. An injected electron can back react via three mechanisms [figure 1]. It can undergo recombination with the oxidised sensitizer. Alternately it can back react with the redox mediator, either at the TiO<sub>2</sub>/electrolyte interface or at the SnO<sub>2</sub>/electrolyte interface. In the presence of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple the kinetics of interfacial recombination is slow enough to allow reasonable cell efficiencies. In contrast, cells that use other hole transport media exhibit more rapid back reaction (particularly at the substrate), so that passivation strategies are required [1].

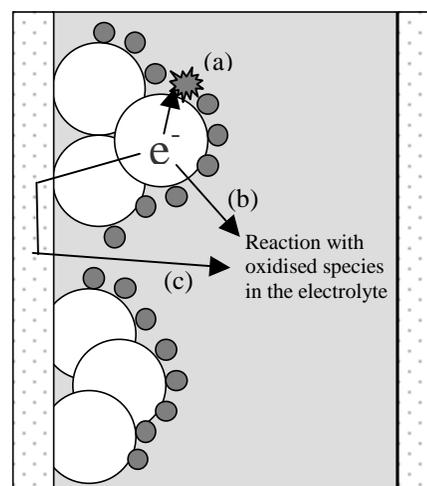
To prevent recombination of electrons in the SnO<sub>2</sub>(F) with the oxidized species in the electrolyte a thin insulating layer (called a blocking layer or more specifically a blocking underlayer) can be placed between the mesoporous oxide and the SnO<sub>2</sub>(F) glass. Recently such a blocking layer was used in a 5.2% efficient cell containing the novel one electron redox mediator Co(II)(dbbip)<sub>2</sub><sup>2+</sup>[2]. Blocking layers are also widely used in polymer-based solid-state cells to prevent the hole conductor permeating through pores in the oxide to form an ohmic contact with the SnO<sub>2</sub>(F) substrate, short-circuiting the cell.

Insulating TiO<sub>2</sub> layers of various thickness were deposited onto SnO<sub>2</sub>(F) glass substrates and a variety of techniques were used to investigate their properties. A three-pronged attack was attempted. Firstly the fundamental characteristics of the films were investigated using electrochemistry and impedance spectroscopy. This gave useful information about the apparent unidirectional electron transfer through the blocking underlayer [figure 2].

Secondly DSNC cells were fabricated incorporating blocking layers and the kinetics of the back reaction was probed using the charge extraction technique [3]. In this experiment the cell is illuminated at open circuit and the subsequent decay of the open circuit photovoltage (U<sub>photo</sub>) in the dark is monitored. It has been shown that the open

circuit photovoltage decays much more rapidly in cells without blocking layers when compared to cells with blocking layers.

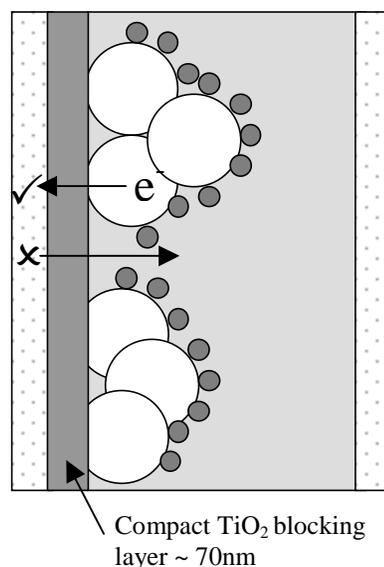
Finally a model was constructed to calculate the fraction of electrons back-reacting via the TiO<sub>2</sub> and the SnO<sub>2</sub>(F) glass at open circuit as a function of U<sub>photo</sub>. Interesting results have been obtained that throw new light on the observed results from the charge extraction experiments.



**Figure 1**

The three pathways for back reaction of electrons in a DSNC cell:

- (a) with the oxidised dye
- (b) with the electrolyte via the TiO<sub>2</sub>
- (c) with the electrolyte via the SnO<sub>2</sub>(F) substrate



**Figure 2**

Unidirectional electron transfer through the blocking layer

[1] B.A.Gregg, F.Pichot, S.Ferrere, C.L.Fields. *J.Phys.Chem. B.* **2000** 104, 949-958

[2] H. Nusbaumer, J.E.Moser, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel. *J.Phys.Chem. B.* **2001** 105, 10461-10464

[3] N.W. Duffy, L.M. Peter, R.M.G. Rajapakse, K.G.U. Wijayantha, *J.Phys.Chem. B.* **2000** 104, 8916-8919