Dye-sensitized Solar Cells with an Extremely Thin Liquid Film as the Redox Electron Mediator

G. R. Asoka Kumara,* Shoji Kaneko, Akinori Konno, Masayuki Okuya, and Kirthi Tennakone†
Department of Material Science and Technology, Shizuoka University,
3-5-1, Johoku, Hamamatsu-shi 432-8561
†*Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*

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Dye-sensitized photoelectrochemical and solid-state solar cells are well known. A possible third alternative is a hybrid of both types where an extremely thin film of liquid is interposed between the dye-coated nanocrystalline semiconductor surface and a solid hole collector. To illustrate the principle a model system is constructed with graphite as the hole collector.

Dye-sensitized (DS) solar cells are extensively studied as promising systems for conversion of solar energy. Low cost and environmentally benign technologies of fabrication seem to be the advantageous features of DS solar cells. A nanocrystalline film of wide band gap n-type oxide semiconductor coated with a dye constitutes the light-harvesting component of these devices. DS solar cells considered at present falls into two main categories, DS phtoelectrochemical cells[1–7] (DS PECs) and DS solid-state solar cells (DS SSCs).[8–13] In the former, an electron donor in the electrolyte accepts the positive charge on the dye cations resulting from electron injection by photoexcited dye molecules to the conduction band of the semiconductor. The resulting ionic species then diffusively move up to the electrocatalytically active counterelectrode. In the cells of the latter type, a solid hole collector (e.g., a p-type semiconductor) is deposited as an over layer on the dye-coated nanocrystalline surface. Here, the excited dye molecules inject electrons and holes to the n- and p-type regions respectively. Both types of cells have merits as well as demerits.

The intimate electrolyte–solid surface contact in DS PECs ensures efficient charge separation competing with the back reaction (i.e., the recombination of the dye cation and the injected electron). Thus DS PECs have high energy conversion and quantum efficiencies. The main drawbacks of DS PECs are technical difficulty of leak-proof confinement of a liquid and problems of degradation of the electrolyte and/or the dye. Although DS SSCs in principle are free of the drawbacks of DS PECs, the difficulty of securing a permanent solid-to-solid contact over a surface of high roughness factor makes these devices less efficient and less stable. In this letter we show that a third category DS solar cells, a hybrid of both photoelectrochemical and solid-state versions is feasible, where the dye-coated n-type semiconductor surface and an optically transparent solid conductor (SC) interposes an extremely thin liquid film incorporating a redox ionic species (Figure 1).

A cell of the above configuration (Figure 1) have the following advantages. The liquid film effectively touches solid surfaces on either side and the redox couple (say X^-/X) relays charge between the two surfaces. The mechanism of operation of the cell can be summarized as follows:

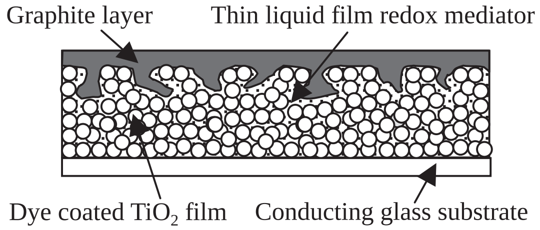

Figure 1. Schematic diagram showing the construction of a dye-sensitized solar cell with an extremely thin redox electrolytic film.

$$h\nu + D \rightarrow D^* \quad (1)$$

$$D^* \rightarrow D^+ + e^- \text{ (CB n-type semiconductor)} \quad (2)$$

$$D^+ + X^- \rightarrow D + X \quad (3)$$

$$X + e^- \rightarrow X^- \text{ (at SC surface)} \quad (4)$$

The excited dye molecule D^* injects an electron to the conduction band of the n-type semiconductor and the species X^- in the liquid film scavenges the positive charge on the dye cation D^+. The solid substrate SC on the other side transfers an electron to X regenerating X^- or equivalently X injects a hole to SC. Most redox couples do not operate via simple kinetics as in (3) and (4) but involve intermediate steps. In the Grätzel type DS PEC, the species that scavenges the positive charge on the dye cation is $X^- = I^-$ and the intermediate state $X = I^\bullet$, resulting from the reaction step $D^+ + I^- \rightarrow D + I^\bullet$, combines with I^- to form the more stable triiodide ion (I_3^-) which moves up to the counterelectrode to accept an electron. If the lifetime of X against a reaction with another species in the electrolyte is τ and D is its diffusion coefficient, X can reach SC and participate in the reaction (4), provided the thickness T of the liquid film satisfies the condition

$$T \leq (D\tau)^{1/2} \quad (5)$$

Thus if the film thickness is made sufficiently thin, even transient redox states leading to first-order kinetics can be utilized. First-order kinetics have many advantages. When the intermediate X (formed by hole scavenging) undergoes stabilization by combination with other species, an energy loss is accompanied (which is ultimately reflected as a loss in efficiency). Again the intermediate states being less massive, these molecules diffuse faster in the electrolytic medium. The other advantage of a cell with an extremely thin film of electrolyte is the following. In a Grätzel type DS PEC, the counter electrode (the platinized conducting tin oxide glass plate) is placed in immediate contact

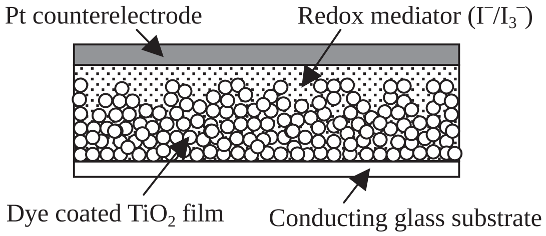

Figure 2. The Counterelectrode/dyed TiO_2 film contact of a Grätzel type DS PEC showing the effect of the unevenness of the film.

with the outer surface of the nanocrystalline dyed TiO_2 film. This is essential to minimize the resistance of the electrolyte. However, because of the unavoidable unevenness of the surface of the TiO_2 film and warping of counter-electrode plates a space is always left between the TiO_2 surface and the counter-electrode surfaces (Figure 2). This is more crucial for large cells. Furthermore, as the amount of liquid electrolyte present is minuscule compared to conventional DS PEC, the sealing problems are less critical.

The challenging problem involved in making cells of this type is finding a suitable SC material, amenable to deposition procedure (i.e., compatible with the dye and the thin film of the electrolyte). Again the ideal SC material should be optically transparent to avoid the blocking of incident light when it interpenetrates to the nanocrystalline TiO_2 matrix. Although not a transparent material, to test our hypothesis, we used graphite as the SC substrate and constructed a cell as follows. A nanocryatalline TiO_2 film ($\approx 10\,\mu m$) was deposited on conducting tin oxide glass plate (resistance 8 ohm/sq, $1 \times 1\,cm^2$) by the method described below. Titanium isopropoxide (5 mL) was mixed with propan-2-ol (15 mL) and acetic acid (5.5 mL) and water (3 mL) is added drop by drop keeping the solution vigorously stirred. Hydrolyzed titanium isopropoxide was mixed with 0.65 g of P-25 TiO_2 powder and the suspension is ultrasonically agitated. Conducting glass substrates were cleaned by 1-h immersion in a solution of KOH in ethanol, rinsed with deionized water, and dried in an air stream. A cleaned CTO glass plate is placed on the surface of a hot plate ($\approx 150\,°C$) and the viscous TiO_2 suspension is spread on the conducting surface by a dropper, allowed to dry and sintered in air at 450 °C for 10 min. Once the plate is cooled, the crust of TiO_2 is wiped with cotton wool to remove loose particles and the coating process and sintering are repeated 5–6 times until a film thickness of $10\,\mu m$ is formed. A nanocrystalline TiO_2 film is coated with the Ru N3 dye following the standard procedure.[6] The film was smeared with the electrolyte (0.1 M LiI, 0.05 M I_2, 0.5 M *tert*-butylpyridine, and 0.6 M dimethylpropylimidazolium iodide in methoxyacetonitrile) and the surface is rubbed with a piece of graphite (over 90% pure natural amorphous graphite) to cover the surface of TiO_2 film and form a level surface. It is unlikely that the micropores in the film get filled with graphite. We believe that the valleys in the gross surface are embeded with graphite (Figure 2). During this processes any excess electrolyte that comes out is wiped off with cotton wool. Resulting graphite film remains firm and the embedded liquid film does not ooze out easily. The platinum sputtered conducting tin oxide glass plate was pressed on the graphite surface and sealed with silicone gum. The *I–V* characteristic ($1000\,Wm^{-2}$, AM 1.5 illumination) and the photocurrent action spectrum of the cell is shown in Figure 3. The observed energy conversion efficiency 3.7% and the photon to photocurrent conversion efficiency (IPCE) 64% are lower than those of a conventional DS PEC. Highly porous and rough TiO_2 nanocrystalline films prepared by standard screen printing technique could not be used for construction of this cell because of abrasion of such films during graphite coating. The roughness factor of TiO_2 films we have made for construction of the present cell is ≈ 400 (i.e., less than half the roughness factor of screen printed films). The above seems to be the main reason for the low current density and, therefore, the low efficiency of the cell. Again some light is cut off by occlusion of graphite lowering the efficiency. Experiments are underway to find optically transparent conducting materials that could replace graphite and also new redox couples. We have not succeeded in elucidating redox species participating in the present cell (i.e., whether I^-/I_3^- or an intermediate species). An advantage of the cells of this type is the extreme ease of sealing and its stability. The present cell, with graphite as SC material could find applications as power source for electrical devices.

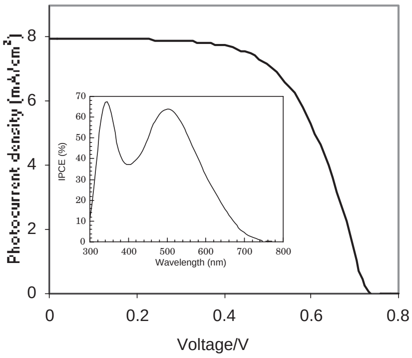

Figure 3. I–V characteristics of the cell with graphite as the SC material. Inset is a photocurrent action spectrum of the cell.

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