

Review Article

Charge Transfer in Nanocrystalline Semiconductor Electrodes

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Nanocrystalline electrodes in liquid junction devices possess a number of unique properties arising from their convoluted structure and the dimensions of their building units. The light-induced charge separation and transport in photoelectrochemical systems using nanocrystalline/nanoporous semiconductor electrodes is discussed here in connection with the basic principles of the (Schottky) barrier theory. Recent models for charge transfer kinetics in normal and unipolar (dye-sensitized) cells are reviewed, and novel concepts and materials are considered.

1. Introduction

In electrochemical systems, ionic charge transport in the electrolyte (EL) phase can be coupled to electron transport in the solid electrode via interfacial charge transfer, which may occur in the dark or be stimulated by illumination. Charge transfer characteristics depend mainly on the electrode nature, that is, the particular type and magnitude of conduction in the solid state as determined by bulk and surface properties. Photoelectrochemical cell (PEC) devices use illuminated semiconductor (SC) electrodes for power generation, or electrosynthetic and photocatalytic purposes. The light-induced or light-assisted conversion efficiencies in PECs using compact polycrystalline electrodes are often limited by processes occurring at grain boundaries and are typically inferior to those observed with single crystals, since the individual particles that make up the solid may be small with respect to key properties associated with charge transport (e.g., the minority carrier diffusion length). Fortunately, liquid junctions partly tolerate polycrystallinity, as the active region in which light absorption and separation of photogenerated carriers occurs (i.e., the space charge layer, SCL, with a thickness of the order of *ca.* 100 nm) is located at the SC surface (for typical front-wall illumination); hence, the crystallites need not exceed some tens of nm in size. By contrast, in solid *p/n* junction cells, the crystallites should be of micrometric dimensions since the active region is located

at a depth of 0.1 to 1.0 μm below the illuminated SC surface, and recombination of photocarriers at grain boundaries will considerably decrease the efficacy of the cell. Requirements for crystallinity in the sense relevant to solid state devices may be relaxed in liquid junctions, when the SC particle size or layer thickness is sufficiently small or a porous morphology is present [1, 2].

A mesoporous/nanostructured electrode comprises a porous electrode built up from interconnected particles of crystallite size diameters ranging from 5 to 50 nm. The properties of mesoporous electrodes are unusual compared to the normal polycrystalline ones, mainly as a consequence of the fact that the electrode/electrolyte system consists of two intimately contacted contiguous phases; that is, a solid network interpenetrated with an electrolyte solution all the way to the back contact, creating a large convoluted SC/EL interface. The behavior of this system is largely determined by the (small) structural units and the very large 3D solid/solution interface, that is, the site of interfacial chemistry. It has been firmly established that mesoscopic nanoporous-nanocrystalline thin film electrodes show surprisingly good capability for efficient transport of photogenerated electrons and can thus operate well as components of PEC devices [3]. Studies relevant to this field regard mostly the development of electrochemical dye-sensitized solar cells (DSSC) and photocatalytic systems, both based on the use of nanocrystalline, particulate, aggregated, or

lightly sintered porous coatings or packed pellets of TiO_2 , which comprises the most extensively studied material in this connection [4, 5]. These systems have demonstrated a great potential for applications and are already commercially available.

The mechanism of charge transport in nanostructured electrodes is of prime physical and technical significance and has been examined in several works with varying success in interpretation of experimental results (see, e.g., the seminal review of Lindquist et al. [3], on which a major part of the present brief discussion is based). Simple models regarding uniform, isotropic, nanostructured film electrodes have been presented, and in general the qualitative aspects of charge transfer in nanocrystalline electrodes have been well understood. However, the advancement of theory based on detailed knowledge of their solid state structure and of the transport phenomena in relevant device configurations has been slow due to their complexity and versatile nature. The main arguments and selected attributes of studies in this field are outlined in the following.

2. The Schottky Diode Reconsidered

When a single-crystal or polycrystalline SC (with crystallite size at least some hundreds of nanometers) is brought into contact with a redox electrolyte, adjustment of the electrochemical potentials (Fermi levels) of the two phases leads to creation of a space charge layer at the SC side. In an electrochemical cell with the SC electrode under reverse bias, a depletion SCL for majority carriers is formed. Upon illumination of the SC electrode, the photoexcited electron-hole pairs tend to separate under the influence of the electrostatic field in the SCL region. In an operating PEC comprising, for example, an n -type SC electrode, the electrons in the conduction band of the SC diffuse away from the SCL and through the electrode to the back contact, while the electron holes in the valence band diffuse to the solution interface, where (ideally) they oxidize the reductant component of the electrolyte (Figure 1); the charge transfer and redox chemistry at the counter electrode of the cell complete the process [6].

Analytical descriptions and models involving expressions for the current-voltage characteristics of SC/EL junctions within the theory of SCL formation (Schottky diode), which appeal to the drift and concentration gradients that drive the free carriers through the device by taking into account bulk and surface recombination of carriers and reaction kinetics at the interface, have been worked out widely (e.g., [7, 8]). As a limiting case at high charge transfer rates, most of these models reduce to the Gärtner-Butler formalism, which in its simple form neglects (i) the opposing dark current in the diode, (ii) the space-charge recombination, (iii) the surface state recombination, and (iv) the charge transfer kinetics at the interface. In that case, in an illuminated cell under reverse bias condition, the net photocurrent density J_{ph} is given by (1) as a function of the photon flux Φ_0 incident on the absorber SC electrode, the light absorption coefficient α of the SC material, the diffusion length L of minority carriers in the SC (holes for n -type material), and the depletion layer width w

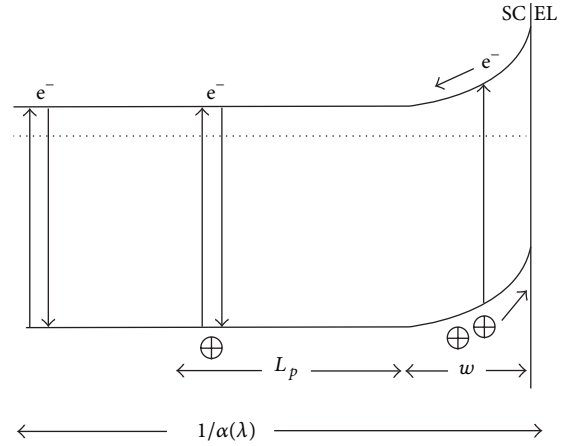


FIGURE 1: The rectifying action of the depletion layer in an n -type SC. L_p is the hole diffusion length in the material, and $1/\alpha(\lambda)$ the penetration depth of light of wavelength λ . If the SCL has a width w , the retrieval length of minority carriers (holes) collected at the electrolyte interface is $(L_p + w)$.

in the SC (q is the absolute charge)

$$J_{\text{ph}} = q\Phi_0 \left[1 - \frac{\exp(-\alpha w)}{1 + \alpha L} \right]. \quad (1)$$

The voltage dependence of J_{ph} is obtained through the variation of the SCL width, w , which is a function of the electrode potential U referred to the flat band potential U_{FB} of the SC, as in equation (2), relevant to n -type electrode material with a donor concentration N_D and relative permittivity ϵ

$$w = \left(\frac{2\epsilon\epsilon_0}{qN_D} \right)^{1/2} (U - U_{\text{FB}})^{1/2}. \quad (2)$$

Equation (1) can be rearranged to give the incident photon-to-current efficiency (IPCE) of the PEC; specifically, at some wavelength λ where the absorption coefficient is $\alpha(\lambda)$, the monochromatic ICPE is given by (3)

$$\text{IPCE} = \frac{J_{\text{ph}}}{q\Phi_0} = 1 - \frac{\exp(-\alpha(\lambda) \cdot w)}{1 + \alpha(\lambda) \cdot L}. \quad (3)$$

In polycrystalline semiconductors, the grain boundaries influence the diode characteristics and may even control the electrical transport properties. The major mechanisms for this effect include impedance to the flow of majority carriers, recombination sites for minority carriers by enhanced attractive fields due to boundary depletion regions, and possible electrical shunts that can limit the reverse saturation currents in the diode structures. In any case, the photoelectrochemical behavior of nonporous, polycrystalline thin films has been illustrated satisfactorily using standard models based on compact materials. For instance, polycrystalline TiO_2 photoelectrodes could be described by the simple theory, both in the case of illumination through the electrolyte and through the backside contact, on the basis of photocurrent action spectra [9].

On the other hand, the way that porosity-nanocrystallinity affects the properties of (photo) electrodes prompts to reconsider the basic attributes of the diode model. To be sure, the net flux of charge through a nanocrystalline-nanoporous electrode is a function of parameters such as particle and pore size, as well as the redox and other properties of the electrolyte solution. Some novel features, though, emerge. When the dimensions of the porous structure are comparable to the illumination wavelength, the absorption of incident light is much more effective than in a nonporous medium, due to scattering and internal reflection. In addition, quantum size effects may emerge when the particle dimensions reach the point where “molecular” properties are manifested. But, what interests us here is that, because of the low structural dimensions, the absorbed light generates minority carriers close to the solid/solution interface so that if the kinetics of their transfer to solution are fast, a high quantum yield can be obtained, insofar as minority carriers are concerned [10]. The size D of the individual subunits or particles that make up the nanocrystalline solid becomes then a key parameter rather than the bulk material properties, and the criterion for capture of minority carriers by the electrolyte is no longer $1/\alpha(\lambda) \leq L_p + w$ as in Figure 1, but $D/2 \leq L_p + w$. However, photophysical calculations predict little or no band bending at the surface of colloidal SC materials having diameters smaller than the thickness of the SCL. Thus, at a certain point of a solid crystal partition, that is, when the crystal particle is so small that it can no longer support an effective depletion layer, the Gärtner-Butler formalism breaks down. It means that with particles smaller than, say, 20 nm, both drift and concentration gradients are essentially absent, and consequently one would expect minimal charge carrier separation [1, 2]. Still, for generating a photocurrent from a nanocrystalline electrode, it is essential that the photogenerated carriers will be spatially separated in order to avoid recombination, while, in addition, majority carriers should “survive” a long journey through numerous crystallites to reach the back contact of the electrode.

Hodes et al. [11] undertook this problem by analyzing action spectra of nanocrystalline porous CdS and CdSe thin films (n -type) in liquid junctions and were led to conclude that charge separation occurs at the SC/EL interface throughout the porous film rather than in a built-in space charge field. On the one hand, rapid removal of photogenerated holes to the electrolyte diminished the extent of bulk recombination with electrons (although holes were still susceptible to surface recombination); on the other hand, most free electrons were able to reach the back contact without recombining with holes or annihilated by reductive back reactions with electrolyte species (Figure 2).

The conclusion, corroborated by later analyses, was that minority carriers in nanocrystalline SC electrodes could escape “bulk” recombination by virtue of *interfacial kinetics*, as a result of chemical rather than electric potential gradients, while the majority carriers could effectively pass a number of grain boundaries and give high collection efficiency at the back contact. The actuality of electron conduction through numerous crystallites has been proved, for instance, by

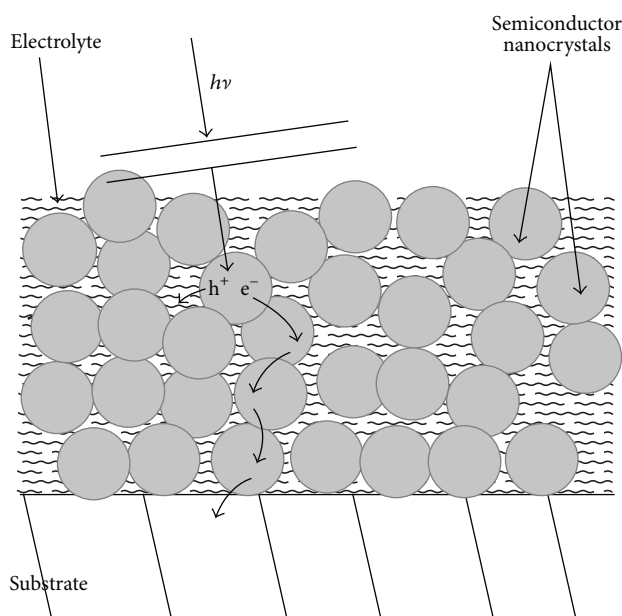


FIGURE 2: Model of porous-nanocrystalline film showing electrolyte contact with individual crystallites. Illumination produces an electron/hole pair in one crystallite. The hole transfers to the electrolyte and the electron transverses several crystallites before reaching the substrate (adapted from [11]).

experiments with nanostructured TiO_2 showing that the very low dark conductivity of this wide gap semiconductor ($\approx 10^{-9} \Omega^{-1} \text{cm}^{-1}$ at room temperature in vacuum) is solely due to a low electron concentration in the conduction band rather than to poor electrical contact between the particles, since it is strongly increased under UV light illumination [12]. Thus, the absence of continuous crystal regions is not decisive for hindering conduction in nanostructured electrodes. It is found, though, that the transport of majority carriers in such electrodes is relatively slow and their lifetime surprisingly long; in fact, n -type porous electrodes have exhibited transit times for electrons about nine orders of magnitude longer than through the depletion layer of a conventional (non-porous) electrode [2]. It appears that an effective shielding of photoinjected electrons by a high ionic strength electrolyte permeating the porous SC network, resulting in the absence of an electrical field component normal to the substrate [3], is essential to prevent back reactions and increase the electron life time, while the slow advancement of these carriers within the electrode material can be attributed to *electron trapping-detrapping* events in intrinsic states and/or surface states at the nanocrystalline electrode. Remarkably, such features have been found to be common to nanostructured electrodes, independent on morphology.

Many works published within the previous fifteen year have revealed quite interesting aspects of the problem in hand. We only refer to Södergren et al. [13] who proposed a first model for the charge separation and transport in nanostructured TiO_2 electrodes and the work of Bisquert et al. [14] in modeling the electric potential distribution in nanocrystalline porous SC electrodes.

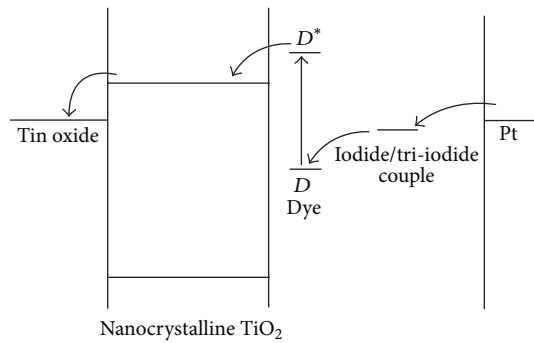


FIGURE 3: Energy scheme for the typical regenerative dye-sensitized TiO_2 cell. Electrons collected at the tin oxide substrate pass via the external circuit to the counter electrode where they reduce I_3^- back to I^- . Normally, illumination is incident from the substrate side.

3. Dye-Sensitized Solar Cells

The previous discussion is extended here to the dye-sensitized cell proper, due to its leading role in current photoelectrochemistry of nanostructured electrodes. The basic principle of the thin layer DSC is shown in Figure 3. A light-harvesting dye is adsorbed on the surface of a porous nanocrystalline film composed of a wide bandgap metal oxide SC such as TiO_2 , ZnO , or SnO_2 . The porous oxide is spread as a thin film (typically $10\ \mu\text{m}$ thick) on a transparent conducting glass substrate and is contacted by an electrolyte containing a redox system (usually iodide/tri-iodide). Photoexcitation of the dye is followed by rapid electron injection into the conduction band of the oxide. The dye is regenerated rapidly from its oxidized state by iodide ions (I^-). The oxidized form of the redox couple (I_3^-) diffuses to a platinum-coated counter electrode where it is reduced to complete the cycle.

DSC differs from a p/n cell or a conventional PEC in that light absorption occurs in the dye and not in the SC. As a result, only majority carriers are present in the SC and there is no need of a strong depletion layer or other mechanism in the SC to effectively separate carriers. Therefore, despite the enormous surface area of the nanoporous photoactive SC+dye/EL interface, recombination is minimized because of the *unipolar* character of charge transport. Besides this difference, the ideas outlined in the previous section are applicable also to the problem of charge transport in DSC devices.

The carrier generation/collection problem in DSCs is usually formulated using as a starting point the one-dimensional continuity equation (4) with the drift term omitted [15, 16], as

$$\frac{\partial n(x, t)}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} - \frac{n - n_0}{\tau_n} + \eta \alpha(\lambda) \Phi_0 e^{-\alpha(\lambda) \cdot x}. \quad (4)$$

Equation (4) describes the injection, collection, and back reaction of electrons in the DSC in terms of the electron concentration n (n_0 at equilibrium), the net electron injection efficiency η , the electron diffusion coefficient D_n , and its lifetime τ_n in the conduction band. The latter is determined by recombination in the solid or by electron transfer to redox

species in the electrolyte, that is, the back reaction with the oxidant in solution (normally assumed as being of a first order rate constant). Screening effects of ions and dipoles in solution acting on electrons located in the SC particles are important in this connection.

The efficiency of DSC depends on several parameters, which can be concisely taken into account in the overall external quantum efficiency (IPCE) of the photocurrent generation process as given in (5) by the product of the efficiencies for light absorption (η_{abs}) in the electrode, electron injection (η_{inj}) in the SC material, and electron collection (η_{coll}) at the back contact, as follows

$$\text{IPCE} = \eta_{\text{abs}} \times \eta_{\text{inj}} \times \eta_{\text{coll}}. \quad (5)$$

Solutions of the continuity equation using appropriate boundary conditions have been elaborated on the basis of experimental results from various dynamic and time-resolved electrochemical characterization techniques, including photovoltammetry, intensity-modulated photocurrent spectroscopy (IMPS), and intensity-modulated photovoltage spectroscopy (IMVS). The latter have allowed characterization of electron transport and back reactions over five orders of magnitude of light intensity.

A large body of results indicates [17] that the operation of typical DSCs relies on *differential kinetics* effects consisting in a rival between (i) *slow back-transfer* of electrons from the photoelectrode to oxidized ionic species in solution, leaving thus a high concentration of conduction band electrons in the electrode to generate a useful photovoltage; (ii) *relatively fast electron transfer* through the nanocrystalline oxide film to the back contact and the external circuit to reduce the same species at the regenerating electrode. Electron transport in the solid electrode can most well be explained by assuming a *trap-limited diffusion process*, in which the conductive electrons move through the interconnected network of the oxide nanoparticles by a random-walk course involving multiple trapping at states in the bandgap of the SC. The transport process is limited by the surface traps rather than those located in the bulk or at grain boundaries, as suggested by the observed scaling of the electron diffusion coefficient with the internal surface area of the films [18]. On the other hand, the rate of back reactions is controlled by the SC/EL interface properties, so the role of the redox electrolyte phase is very important in this connection. It appears that the I_3^-/I^- couple is unique in providing the kinetic asymmetry that makes functional a typical DSC device. Differential kinetics is more difficult to obtain in the case of *fast* one-electron outer-sphere redox systems; for example, a DSC based on the ferrocene/ferrocenium couple does not generate a photovoltage unless both the exposed conducting glass substrate of the active electrode and the surface of the nanocrystalline TiO_2 are blocked somehow in order to inhibit the back reaction. On the other hand, electrolytes with redox couples based on cobalt complexes provide some degree of kinetic asymmetry, possibly arising from adsorption on the electrode, but these cells only function when a blocking layer of compact TiO_2 on the glass substrate is used to prevent “shunting.” Similar results have been obtained for DSCs based

on solid organic hole-conductors, which are effectively one-electron redox systems.

One of the most important keys to the commercialization of DSCs is to further improve the rather low energy conversion efficiency attained—an intricate task presenting multiple aspects [19]. In particular, electron transport at the nanocrystalline oxide electrode by trap-limited diffusion does not consent to reaching high device efficiencies as being essentially a slow process amenable to increased recombination events. Significant enhancement could be achieved by using nanocrystalline materials that provide more facile kinetics for charge transfer, enabling at the same time extensive interpenetration of the sensitization dye and the electrolyte with the electrode nanoparticles. Tough candidates in this connection, on account of their unique physical characteristics, are specially engineered microstructures possessing exotic “nanoplant-like” morphologies, as exemplified by zinc oxide (ZnO) coatings, which have been grown by means of a low temperature (<150°C) process on a variety of amorphous, semiconductor, and crystalline substrates [20]—the preparation technique can be used alike to obtain similar morphologies with other metal oxides such as TiO₂ and SnO₂. In contrast to sintered nanoparticle-based DSCs, these novel plant-like nanostructures provide direct electrical pathways between interconnected nanoplants, which allow rapid collection of carriers generated throughout the material, featuring thus improved conduction characteristics for DSC cells.

Regarding the redox electrolyte phase, stability reasons prompt for prospective replacement of the liquid medium by solid charge-transport materials that would possess adequate transparency, scavenging ability, and conduction properties, while preserving the basic mechanism of DSC operation. Organic and inorganic *p*-type semiconductors have been tested in this regard as hole-collectors in DSCs [21]. Among the various investigated systems, great promise is offered by the *p*-type, transparent oxide semiconductors belonging to the copper delafossite series (CuMO₂, M = Al, Ga, In) [22]. In effect, the boron-analogue, CuBO₂, as grown in high quality thin films by pulsed laser deposition, has been found to exhibit excellent light-transmission properties (exceeding 85% for wavelengths above 550 nm) together with high room-temperature conductivity and hole mobility [23] and can be considered as a key step in the technology for hole-collector application in solid-state DSCs towards completely transparent oxide electrolytes.

4. Concluding Remarks

The differential kinetics invoked in DSC cells for the forward and back reactions of majority carriers along with the chemical gradients driving minority carriers to a contact phase seem to have a general significance for photovoltaic devices. A broad spectrum of results regarding photoinduced charge transfer in various types of cells suggests that a rectifying junction is not as essential for photovoltaic conversion as stressed in the past. Even with *p/n* junctions, it has been argued that the contact electric field and concomitant band bending is rather incidental to the cell operation; this

principally relies on the fact that the *n*-type region allows selective contact to the conduction band (excited states), while the *p*-type region allows selective contact to the valence band (ground state). Yet, selectivity of contacts to electrons and holes can be achieved not only via potential barriers at interfaces, but also by details of interfacial charge transfer depending both on kinetic rate constants and on the overlap of the energy levels determining the transfer events [24]. This is exactly the case of “electrochemical,” liquid or solid junction cells using porous/nanocrystalline semiconductor electrodes, where the excited state is selectively contacted by the semiconductor conduction band, and the ground state is selectively contacted by the redox couple in the electrolyte.

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