

Theoretical Models for the Action Spectrum and the Current-Voltage Characteristics of Microporous Semiconductor Films in Photoelectrochemical Cells

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Theoretical models for the action spectrum and the current-voltage characteristics of microporous (colloidal) semiconductor films in photoelectrochemical cells have been derived. The derivation is based on the assumptions that the charge carrier transport in the semiconductor occurs via diffusion, and that the diffusion length is constant. Theoretically fitted action spectra and I-V characteristics agree well with experimental results.

Introduction

Recent investigations of microporous semiconductor films forming the working electrode in photoelectrochemical cells have shown¹⁻³ that these films are strikingly different compared to macroscopic polycrystalline or single-crystal semiconductors. Using the observations concerning the microporous colloidal films, we will in this paper present models to describe the photoresponse spectrum and the current-voltage characteristics in microporous semiconductor films.

To facilitate a comparison between the new model for microporous electrodes and conventional semiconductor electrodes, we will briefly mention the model and terminology for macroscopic single-crystal or polycrystalline semiconductors in contact with an electrolyte. We will also take advantage of the recent results obtained for the microporous semiconductor films, which are used to form the model.

For liquid-junction solar cells, often referred to as photoelectrochemical cells, the charge separation process in the semiconductor and the charge transfer at the semiconductor/electrolyte interface (SEI) are fundamental for the operation of the cells. Most experiments in this field are interpreted within the context of a model developed in the 1960's by Gerischer.⁴⁻⁶ An important point in this context is that photogenerated electron-hole pairs in the semiconductor are separated by an electric field, i.e. a depletion layer, often referred to as band bending. By calculating the minority charge carrier concentration in the bulk semiconductor from the diffusion equation and neglecting recombination within the depletion layer, Gärtner⁷ derived an expression for the photocurrent density J .

$$J = q\Phi \left(1 - \frac{e^{-\alpha w}}{1 + \alpha L} \right) \quad (1)$$

Φ is the incident light intensity, α is the reciprocal absorption length, w is the width of the depletion layer, and L is the minority carrier diffusion length. The latter is equal to the square root of the product of the diffusion coefficient and the mean charge carrier lifetime, $L = \sqrt{D\tau}$. Gärtner's equation (eq 1) was derived for a semiconductor-metal Schottky barrier.⁷ The equation was later applied by Butler⁸ to liquid junctions.

Lindquist et al.⁹ measured the action spectra for thin polycrystalline TiO₂ electrodes on quartz substrate, on illumination both through the substrate, denoted SE (substrate/electrode) illumination, and through the electrolyte, denoted EE (electrolyte/electrode) illumination. The terms back-side and front-side illumination were also used, referring to SE and EE illumination,

respectively. They derived a Gärtner-Butler expression for SE illumination. The Gärtner-Butler expressions,^{7,8} both for EE and SE illumination, described the action spectra well.

Taking advantage of the expressions for quantum efficiencies, ϕ , for both EE and SE illumination, Lindquist et al. also derived an equation for the width of the depletion layer (w) divided by the film thickness (d). The equation could be written

$$\phi_{EE} = \frac{w}{d} (\phi_{SE,max}) \quad (2)$$

using the value of the quantum efficiency for EE illumination, ϕ_{EE} , where ϕ_{SE} has a maximum in the action spectra.

The efficient photoelectrochemical solar cell based on a dye-sensitized sintered colloidal TiO₂ film prepared by Grätzel and co-workers¹⁰ directed our interest toward TiO₂ colloidal film electrodes. The size of the colloidal TiO₂ particles is typically about 15-20 nm. The charge separation in colloidal TiO₂ films in the UV region was investigated in ref 2, i.e. without the dye, by measuring the action spectra for SE and EE illumination.

For the colloidal films efficient charge separation was obtained in the UV region,² and it was observed that the shape of the action spectra for SE and EE illumination was just the opposite of that of the spectra for thin polycrystalline TiO₂ films.⁹ This indicates that the most efficient charge separation takes place close to the back contact and that the electron-hole pair separation can be viewed as occurring within the individual colloidal particles, which is reasonable since the electrolyte penetrates the whole colloidal film up to the back contact.

By simply replacing ϕ_{EE} with ϕ_{SE} and $\phi_{SE,max}$ with $\phi_{EE,max}$ in eq 2, we estimated the effective zone for charge separation of the colloidal film electrodes to be about 0.5 μm .² Interestingly, this value corresponded with the observation that there was no significant difference between the action spectra for EE and SE illumination of a 0.5 μm thick electrode. The results are intriguing since there is, so far, no physical explanation why it should be possible to switch the ϕ_{EE} and the ϕ_{SE} parameters in eq 2. Furthermore, taking into account transmission of the light through the film, we measured a theoretical quantum efficiency close to 100% for this electrode. Moreover, eq 2 is derived from the Gärtner-Butler expression, which in turn is based on the existence of a depletion layer in the semiconductor.

In the case of colloidal semiconductor particles, the band bending is small and charge separation occurs via diffusion.¹¹ As pointed out by Curran and Lamouche,¹² the potential difference between the particle surface and interior must be at least 50 mV in order for migration to dominate over diffusion. O'Regan et al.¹ calculated the maximum voltage difference between the center and the surface of the colloidal TiO₂ particles constituting the dye-sensitized colloidal film electrodes to be 0.3 mV. This calculation was based on the observation that the colloidal TiO₂

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film had a low doping density, N_D being 10^{17} cm^{-3} . The transport of electrons through the interconnected TiO_2 particles was proposed to occur via diffusion rather than migration. The results in ref 2 support this argument.

Gary Hodes³ measured the photoresponse spectra for microporous CdS and CdSe electrodes consisting of very small particles. The same shape of the action spectra for SE and EE illumination as presented for the colloidal TiO_2 film electrodes² was reported. Hodes also observed that, dependent on particle size and the electrolyte (using efficient electron or hole acceptors), the photocurrent at the same electrode could switch polarities, behaving as p-type or n-type doped semiconductors. Since nothing was done to change the doping of the semiconductor materials, the interpretation was that it is the kinetics of the charge transfer at the SEI of the particles constituting the film which essentially determine the direction and magnitude of the photocurrent. It is obvious that the interpretation of the microporous semiconductor films in photoelectrochemical cells must be made from another point of view compared to the model for macroelectrodes.

Theory

With the above mentioned observations for colloidal semiconductor films we will now derive expressions for the action spectra and the current-voltage behavior for EE and SE illumination. We consider a 3-dimensional isotropic microporous network consisting of nano-sized low-doped semiconducting colloids. The electrolyte is able to penetrate the film all the way to the back contact, and every colloid will be in contact with the electrolyte. This will totally deplete all charge carriers, and there will be no band bending.¹³ The charge concentration in the valence and the conduction bands in the dark is then totally determined by the choice of the redox couple. Let the concentration of the redox couple be sufficiently high that it is unaffected during illumination.

The derivation will be made for electrons as charge carriers in the film, but the electron current will be taken as positive. The following assumptions are made:

(i) The electron transport in the semiconductor occurs via diffusion.

(ii) The diffusion length of the electrons in the semiconductor is constant through the microporous film; i.e. recombination processes are assumed to be of first order.

As an example of a microporous semiconductor electrode, let us consider the colloidal TiO_2 film electrodes investigated in ref 2. A photoexcited hole is taken up by a hole acceptor in the electrolyte, and in order to produce a photocurrent, the electrons have to diffuse to the back contact. At the back contact the electrons are collected and a current is obtained. Since the colloids in the microporous film are surrounded by electrolyte, the electrons may recombine with, e.g., an electron acceptor in the electrolyte all the way to the back contact.

Thus, a constant diffusion length is the case when holes are removed with unit efficiency and the redox couple is homogeneously distributed in the electrolyte.

From the assumptions above it follows that the derivations of the action spectra and the current-voltage characteristics should start with the diffusion equation for the electrons in the microporous semiconductor film

$$Dn''(x) - (n(x) - n_0)/\tau + \Phi\alpha e^{-\alpha x} = 0 \quad (3)$$

where D is the diffusion constant of the electrons in the film, $n(x)$ the excess electron density, n_0 the electron density in the dark, and τ , Φ , and α have the same meaning as in eq 1. The derivation would be equivalent for holes as charge carriers in the porous film.

The Quantum Efficiency for Substrate/Electrode (SE) Illumination. The boundary conditions for SE illumination are

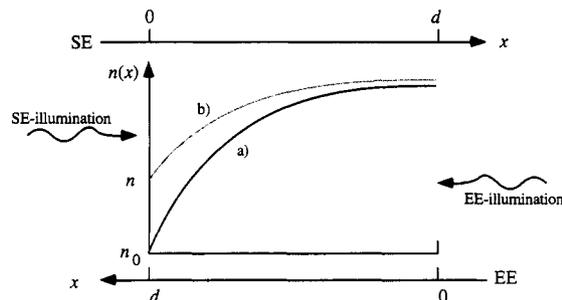


Figure 1. Electron concentration profile in a microporous semiconductor material during illumination. To obtain the boundary conditions for SE and EE illumination the x -axis is in direction of incident light in the respective cases. Curve a) displays the electron concentration when the cell is unloaded (short circuit condition), whereas in curve b) the cell is loaded. The semiconductor/back contact interface is placed at the position of the y -axis, for both SE and EE illumination.

seen in Figure 1, which displays the photogenerated electron concentration profile in the microporous film. At the back contact the electrons are efficiently drawn off as a photocurrent, yielding

$$n(0) = n_0 \quad (4)$$

Electrons reaching the outermost part of the microporous film, $x = d$, will be reflected and will diffuse back into the inner layers of the film (i.e. negligible current flow at $x = d$), and we obtain the second boundary condition for SE illumination as

$$\left. \frac{dn(x)}{dx} \right|_{x=d} = 0 \quad (5)$$

The solution to eq 3 gives the electron concentration in the microporous film. The measured current density, J_{SE}^0 , is proportional to the derivative of $n(x)$ at the back contact $x = 0$. The quantum efficiency is then expressed by

$$\phi_{SE} = \frac{J_{SE}^0}{q\Phi} = \frac{[-L\alpha \cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) + L\alpha e^{-d\alpha}] L\alpha}{[1 - L^2\alpha^2] \cosh\left[\frac{d}{L}\right]} \quad (6)$$

With the assumption that the diffusion length is shorter than the film thickness, i.e. $L < d$, the following equation for ϕ_{SE} is derived

$$\phi_{SE} = \frac{L\alpha}{1 + L\alpha} \quad (7)$$

Dividing the photocurrent in eq 1 with $q\Phi$ to obtain the quantum efficiency and setting $w = 0$, we note that eq 7 is in correspondence with the Gärtner equation (eq 1).

The Quantum Efficiency for Electrolyte/Electrode (EE) Illumination. To obtain the boundary conditions, we place the x -axis in the direction of light; i.e. we place $x = 0$ at the outermost layer of the colloidal film and $x = d$ at the back contact (see Figure 1). The boundary conditions are thus

$$\left. \frac{dn(x)}{dx} \right|_{x=0} = 0 \quad (8)$$

$$n(d) = n_0 \quad (9)$$

The quantum efficiency can then be written as

$$\Phi_{EE} = \frac{J_{EE}^0}{q\Phi} = \frac{[L\alpha \cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) - L\alpha e^{d\alpha}] L\alpha e^{-d\alpha}}{[1 - L^2\alpha^2] \cosh\left[\frac{d}{L}\right]} \quad (10)$$

With the assumption that $d/L > 1$ and $\alpha d \gg 1$, the short-

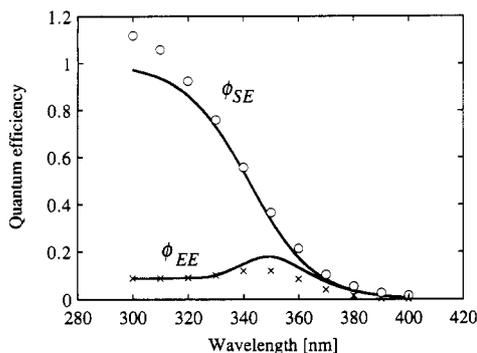


Figure 2. Experimental data for the action spectra of EE (ϕ_{EE}) and SE (ϕ_{SE}) illumination of a 2.5 μm thick colloidal TiO_2 film electrode in 0.1 M KSCN in ethanol with $L = 0.8 \mu\text{m}$. The data have been calculated (solid line) by eqs 6 and 10. The absorption coefficient as a function of wavelength was approximated by $\ln \alpha \text{ (}\mu\text{m}^{-1}\text{)} = 29 - 85\lambda \text{ (}\mu\text{m)}$.

wavelength side of the action spectrum, eq 10, is simplified to

$$-\ln \phi_{EE} = \frac{L}{d} \quad (11)$$

Equation 11 predicts that the quantum efficiency will be constant at the short-wavelength side of the photoresponse spectrum. This is due to the fact that short-wavelength light with a high absorption coefficient will be absorbed, in an interval shorter than the diffusion length, at the outermost layers in the microporous film. This is actually observed for EE illumination of a 2.5 μm thick colloidal TiO_2 film electrode (cf Figure 2). As can be seen in the same figure, a maximum in ϕ_{EE} is also observed. To search for $\phi_{EE,\text{max}}$, we have to take the derivative of ϕ_{EE} with respect to α , but first we have to realize that the condition $(L\alpha)^2 \ll 1$ must be fulfilled. Otherwise the electron-hole pair would just be created within a distance ranging from a layer in the microporous film to the back contact shorter than L , and no maximum in ϕ_{EE} would appear. Using this condition together with $d/L > 1$, it is seen that ϕ_{EE} has a maximum when

$$\alpha = \frac{1}{d} \quad (12)$$

Since, for the solid state, α is a decreasing function of λ , eq 12 predicts that $\phi_{EE,\text{max}}$ will occur at lower absorption coefficients, i.e. $\phi_{EE,\text{max}}$ is red-shifted, when d increases. This has been observed experimentally.² We note that eq 12 is in correspondence with the expression for the maximum in ϕ_{SE} for a macroscopic semiconductor electrode derived by Lindquist et al.⁹

Finally, we can now derive an expression for ϕ_{SE} where ϕ_{EE} has a maximum by inserting eq 12 into eq 7,

$$\phi_{SE} = \frac{L}{d} \quad (\phi_{EE,\text{max}}) \quad (13)$$

If we replace ϕ_{SE} with ϕ_{EE} and $\phi_{EE,\text{max}}$ with $\phi_{SE,\text{max}}$, we obtain eq 2, which was derived for a macroscopic semiconductor electrode⁹ with the Gärtner–Butler equations. Equation 13 explains why it was possible to switch the ϕ_{SE} and ϕ_{EE} parameters in eq 2 for a colloidal film electrode,² as described in the Introduction. The zone (defined in ref 2) ranging from the back contact to the layer in the colloidal film, where the electron transport is not affected by recombination losses, is readily interpreted by eq 13 as the electron diffusion length.

The Current–Voltage Characteristics. The I–V characteristic is recorded by varying external voltage opposite the photovoltage and at the same time measuring the current. When no external potential is applied, the short-circuit current is measured. The I–V characteristics can also be measured by varying an external resistance.

If we forward-bias the microporous semiconductor film in order to record the I–V characteristics, the Fermi-level at the back contact/semiconductor interface is assumed to increase compared to dark¹⁴ and consequently the electron concentration will also increase, from n_0 to n (see Figure 1). The change in potential at the back contact/semiconductor interface can then be written as

$$V_{sc} = \frac{kT}{q} \ln \frac{n}{n_0} \quad (14)$$

where T is the absolute temperature and k is Boltzmann's constant.

The measured photopotential, V , must also include potential drops at the semiconductor–electrolyte interface and in the electrolyte. The most significant contributions will come from (i) the double layer at the semiconductor electrode interface, as well as from the counter electrode/electrolyte interface, (ii) the light-induced Nernstian shift caused by electrochemical reaction in the electrolyte changing the relative amount of redox couples, and (iii) at high current densities (high light intensities), the Nernstian shift (along the axis of the charge flow in the electrolyte), caused by the diffusion limitation of the redox couples. These potential drops will all cause a deviation in V , which in a similar way as in semiconductor physics¹⁵ may be corrected for by the introduction of an ideality factor, m ,

$$V_{sc} = V/m \quad (15)$$

By solving the diffusion equation for the electrons in the semiconductor with appropriate boundary conditions, we will now derive expressions for the photocurrent as a function of the voltage, i.e. the I–V characteristics.

The first boundary condition for SE illumination is analogous to eq 4, but as described above, an applied external voltage will increase the electron concentration (see Figure 1)

$$n(0) = n \quad (16)$$

The second boundary condition is described by eq 5. Solving the diffusion equation with these boundary conditions gives the photocurrent as

$$J_{SE} = J_{SE}^0 - \frac{qDn_0 \sinh\left(\frac{d}{L}\right)}{L \cosh\left[\frac{d}{L}\right]} (e^{qV/kTm} - 1) \quad (17)$$

where J_{SE}^0 is identical to eq 6. Equation 17 can be simplified if the diffusion length is small compared to the film thickness, i.e. $L < d$. The photocurrent is then

$$J_{SE} = J_{SE}^0 - \frac{qDn_0}{L} (e^{qV/kTm} - 1) \quad (18)$$

An optimal solar cell requires that the diffusion length be larger than the film thickness ($L > d$), which gives

$$J_{SE} = J_{SE}^0 - \frac{qDn_0 d}{L^2} (e^{qV/kTm} - 1) \quad (19)$$

We note that $D/L^2 = 1/\tau$, and τ is determined by recombination kinetics at the SEI.

For EE illumination the first boundary condition is

$$n(d) = n \quad (20)$$

and the second condition equals eq 11. The expression for the photocurrent at EE illumination can then be expressed by

$$J_{EE}^0 = J_{EE}^0 - \frac{qDn_0 \sinh\left(\frac{d}{L}\right)}{L \cosh\left[\frac{d}{L}\right]} (e^{qV/kTm} - 1) \quad (21)$$

where J_{EE}^0 is identical to eq 10.

If the area of the device is not considered, the current expression of a microporous photoelectrochemical cell can be generalized to

$$I = I_L - I_S (e^{qV/kTm} - 1) \quad (22)$$

where I_L is the photocurrent due to the incident light and I_S is the saturation current. Thus I_S is constant for a given solar cell, as can be seen from eqs 17 and 21. Equation 22 is similar to the expression for a p-n junction solar cell.¹⁵

A Comparison with Experimental Data

As mentioned above, O'Regan et al. calculated the band bending to be 0.3 mV in a colloidal TiO₂ film. This indicates that assumption (i) in the Theory section should be valid for such films. In Figure 2 we present experimental action spectra for SE and EE illumination of a 2.5 μm thick colloidal TiO₂ film electrode. These curves are fitted to the theoretical expressions of eqs 6 and 10, assuming an electron diffusion length of 0.8 μm (see below). If the experimental errors are considered in the procedure when the photoresponse spectrum was obtained (measuring the light intensity, film thickness, absorption coefficients, etc.), the agreement between the experimental and the theoretical curves is satisfactory.

If a constant value of ϕ_{EE} is observed, the diffusion length of the electron can be calculated by eq 11. In Figure 2 we observe a constant value of $\phi_{EE} = 0.09$ at the short-wavelength side of the action spectrum, which corresponds to an electron diffusion length of 0.8 μm. This can be compared to the value of $L = 0.9$ μm by inserting $\phi_{SE} = 0.12$ where ϕ_{EE} has a maximum in eq 13.

A comparison between experimentally observed current-voltage characteristics for SE illumination and theoretically fitted curves according to eq 22 is seen in Figure 3. A dye-sensitized colloidal TiO₂ solar cell, with a film thickness of about 2 μm, was prepared in a manner similar to that described in ref 10. Different low light intensities were used with a wavelength of 520 nm. Thin film and low light intensity will suppress mass transport limitations. All measurements were made at room temperature (20 °C).

The numerical values of the parameters yielding the best curve fit are given in Table 1. As mentioned above, the saturation current must be constant, and it was found to be 7.5×10^{-5} mA. Deviation from ideality is reflected by the ideality factor, m , which was found to be about 2.1, but it decreases slightly, linearly, with increasing light intensity. The short-circuit current, I_L , is linear with light intensity, indicating negligible mass transport limitations.

Discussion of the Model

Since band bending is probably negligible in the porous film, the charge separation must be kinetically determined. The reaction of a photogenerated hole with a hole acceptor is assumed to be fast, whereas the recombination of a photoexcited electron with an electron acceptor is assumed to be slow.

The detailed properties of the porous electrochemical cell are hidden in the diffusion length and the diffusion constant. We have assumed that the recombination of the electrons is of first order; in the real case this can only be true when the electron concentration is low enough to let the photogenerated holes leave with unit efficiency, and when there is no concentration gradient in the electrolyte. Otherwise there would be a gradient of electron acceptors leading to a nonconstant diffusion length with distance from the back contact. However, it is probably always possible to determine an average diffusion length from the model.

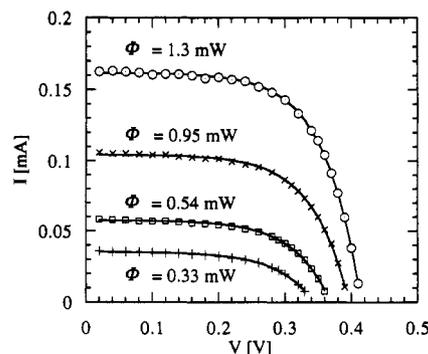


Figure 3. Current-voltage characteristics of a 2-μm dye-sensitized colloidal TiO₂ film at different monochromatic light intensities of 520 nm (FMHW = 10 nm). Dots indicate experimentally measured points, and the solid lines are curves fitted to eq 22. The cell was prepared according to ref 10, with a film thickness of about 2 μm and 0.4 M LiI and 0.1 M I₂ in a propylene/ethylenecarbonate mixture (20/80 by weight) as electrolyte.

TABLE 1: Light Intensities (Φ) and the Corresponding Parameters to Fit Experimentally Measured I-V Characteristics (Figure 3) by Eq 22

| Φ (mW) | I_L (mA) | I_S (mA) | m |
|--------|------------|----------------------|------|
| 0.33 | 0.035 | 7.5×10^{-5} | 2.19 |
| 0.54 | 0.058 | 7.5×10^{-5} | 2.18 |
| 0.95 | 0.104 | 7.5×10^{-5} | 2.15 |
| 1.30 | 0.162 | 7.5×10^{-5} | 2.12 |

Because of grain boundaries and constrictions in the microporous film, the diffusion constant of electrons is not the same as in a single crystal. The constriction occurs because the contact areas between the colloidal particles are limited. (A similar constriction will also be present for the redox couple.¹⁶)

In a dye-sensitized porous film the situation is similar. An electron is injected with unit efficiency to the conduction band, leaving the hole on the surface-adsorbed dye. This means that the model should be valid for this case as well.

Concluding Remarks

Sintered colloidal semiconductor film electrodes, with a microporous morphology, in liquid-junction solar cells, have shown striking different results¹⁻³ from those obtained by single-crystal or polycrystalline electrodes. In this paper we have derived models for the action spectra and the I-V characteristics for SE and EE illumination in microporous semiconductor materials. This has been done by assuming that (i) the electron transport in the microporous semiconductor material to the back contact occurs via diffusion and (ii) the diffusion length of the electrons in the semiconductor is constant.

Theoretical photoresponse spectra for SE and EE illumination of a 2.5 μm thick colloidal TiO₂ film electrode fit well with experimental data. Simple relations to calculate the electron diffusion length have been derived (eqs 11 and 13). Calculations of the electron diffusion length from both eqs 11 and 13 were in good agreement for a colloidal TiO₂ film electrode with a film thickness of 2.5 μm.

The electron diffusion length is dependent on the rate of recombination losses; i.e. a high probability for recombinations will give a short diffusion length. Thus, by estimating the diffusion length, we can get information about recombination processes for microporous semiconductor films.

The derived current-voltage characteristics of microporous photoelectrochemical cells are in correspondence with the expression for a p-n junction solar cell. Theoretically fitted curves agree well with experiments.

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