Semiconductor Electrodes

IX. Digital Simulation of the Relaxation of Photogenerated Free Carriers and Photocurrents

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ABSTRACT

A digital simulation of the photoprocess at a semiconductor electrode is described. The simulation model accounts for photogeneration, recombination, and transport of excess free carriers within the semiconductor phase. The origin of the photopotential in the absence of faradaic current is elucidated. Quantitative current efficiency-potential curves for the photocurrents under a variety of conditions are calculated for n-type TiO₂ and these are compared to experimental results.

In previous papers in this series we have introduced the use of digital simulation methods for the treatment of semiconductor electrodes. In Ref. (1) the relaxation of free carriers following charge injection, with and without surface states, was described. In Ref. (2) a method of deriving the semiconductor electrode characteristics, equilibrium or steady state, at open circuit in the dark or under constant illumination, was presented. When a semiconductor electrode is at equilibrium and in contact with solution, a certain time elapses before the photoeffects are observed. During this time a redistribution of free carriers and charges in the electric field in the space charge region occurs. [When the semiconductor electrode/solution interface is blocked to charge transfer, the new distribution of free carriers in the space charge region under illumination will cause a change in the potential of the electrode (the photopotential effect).] Frequently, illumination of the electrode is accompanied by charge transfer to solution species and this gives rise to a photocurrent. For example, irradiation of n-type TiO₂ with light of energy larger than the bandgap energy will result in the oxidation of water (3, 4), while

Fig. 7. The dependence of the photopotential for n-type Ge (sample as in Fig. 3) on dark surface potential $V_s$; $I_0 = 10^{16}$ photons/cm²·sec. Dashed line, calculated according to Johnson's method (4) assuming $n_I = 1.3 \times 10^{13}$ cm⁻² (see text).

Fig. 8. Dependence of photopotential for n-type Ge (sample as in Fig. 2) on illumination intensity, $I_0$ (dark) = 250 mV. Points are simulations and the dashed line was calculated by Johnson's method (4) assuming that the injection level was proportional to the light intensity and was $1.3 \times 10^{13}$ cm⁻² at an illumination intensity of $10^{16}$ photons/cm²·sec.

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10. Ibid., p. 53.

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cathodic photocurrents arise at p-type semiconductor electrodes (5, 6). Numerous examples of photogalvanic effects and analytical treatments of these have been given (7, 8).

In this paper we treat the transient behavior of a semiconductor electrode following the onset of illumination and the photocurrents which are produced. The semiconductor electrode characteristics which affect the magnitude of the photocurrent are discussed and a comparison of the simulated light intensity-current and current-potential behavior with some experimental results given.

**Relaxation of Photogenerated Carriers in the Absence of Faradaic Current: Physical Model**

The rate of change of the concentration of excess free carriers (e.g., holes, the minority carriers in an n-type semiconductor) during illumination is governed by their rate of generation by the adsorbed light, their recombination, and their transport

\[
\frac{\Delta p}{\Delta t} = g(x) - \left(1/\tau_p\right) (n(x)/n_0) \Delta p + D_p \frac{\partial^2 \Delta p}{\partial x^2} + U_p \frac{\Delta E(x)}{\Delta x}[1]
\]

where \(\Delta p = p(x) - p(x)_{eq}\), \(\Delta E = E(x) - E(x)_{eq}\). A similar expression can be written for excess electrons, \(\Delta n\). The electrical field vector in the x direction is governed by Gauss' law

\[
\frac{dE(x)}{dx} = e \frac{\Delta p}{\varepsilon_0 \varepsilon_r} \Delta n\frac{\partial}{\partial x} \left[ \frac{d}{dt} (p - n) \right] \Delta x[2]
\]

Equations [1] and [2] were written in finite difference form using the same space division and representation of fluxes given in Table I of Ref. (2); the actual expressions are given in the Appendix. The general notation and the terms in Eq. [1] and [2] are the same as those used in Refs. (1) and (2) and are discussed only briefly here. The generation function for free carriers by light, \(g(x)\), can be written as

\[
g(x) = I_0 n_0 \exp(-a x) \quad [cm^{-3}\cdot sec^{-1}][3]
\]

\(I_0\) is the incident light flux at the electrode surface \((cm^{-2}\cdot sec^{-1})\) and \(a\) is the absorptivity of the light \((cm^{-1})\). We assume here that all of the light absorbed leads to free carrier formation. The treatment is easily modified for cases in which the generation by the introduction of a quantum efficiency factor. The term \((1/\tau_p)\Delta p\) is the usual expression (9) for the recombination rate of excess minority free carriers in the semiconductor bulk, where the process is assumed to be pseudo-first order with respect to the excess minority carriers \((i.e., 1/\tau_p = k_p n_0\), where \(n_0\) is the bulk concentration of electrons and \(k_p\) is the rate constant). The term \((n(x)/n_0)\Delta p\) is introduced to account for this effect inside the space charge region, where the concentration of electrons is not equal to the bulk value. The last two terms on the right-hand side of Eq. [1] are the divergence of the flux of excess free carriers by diffusion and migration. For a numerical calculation of the migration term, the properties of the semiconductors at equilibrium \((p(x)_{eq}\) and \(E(x)_{eq}\)) have to be known. Similarly, calculation of the recombination term requires knowledge of \(n(x)_{eq}\). Thus, a simulation of the semiconductor electrode free carrier and electric field distribution in the dark at a given potential \(V_n\) as given in Ref. (2), provides the initial conditions which precede simulation of the photoeffects. The usual simulation techniques were employed [see the Appendix and Ref. (10) and (11)]. Changes in \(\Delta p\) and \(\Delta n\) which occur during a short time interval, \(\Delta t\), based on the carrier concentrations and fields from the previous time interval, were calculated. These changes are used to calculate new values of \(p(x)\) and \(n(x)\), as well as a new field distribution \(E(x)\), by Eq. [2]. These new values are then used for calculation of the values of \(\Delta p\) and \(\Delta n\) in the next time interval, etc. The distribution of excess free carriers and electric field are mutually dependent, since \(E(x)\) depends upon the charge and the migration of the free carriers depends upon the field.

**Results**

The distributions of excess carriers for an n-type TiO2 electrode at two different times after the onset of illumination are shown in Fig. 1. In this example, the n-TiO2 electrode at equilibrium in the dark was assumed to be initially biased positively \((V_n = 0.8V)\) to form a depletion layer. In the time interval considered, only very slight changes in electric field are observed. The changes in the charge density distribution, although noticeable, are still very small compared to the charge density at equilibrium or to the changes in charge density which exist at the steady state. Consider some aspects of the relaxation process which can be observed from the transient behavior. The generation function is an exponential one with respect to distance, the steep concentration and field profiles which exist inside the space charge region/bulk boundary. At this stage, some of the holes which are produced outside the space charge region and which escape recombination enter the space charge region by diffusion. Only at a later time, when the surface concentration of holes increases further, are they reflected back from the surface by diffusion, so that at the steady state \((as in Ref. (2))\) a flux of holes leaves the space charge region toward the bulk. At this time the concentration excess of holes outside the space charge region is about equal to the concentration excess of electrons \((\Delta n = \Delta p)\). This steady-state situation could not be achieved within the time domain of the transient simulation (assuming no outlet to solution), while the electrons accumulate near the space charge region/bulk boundary.

**Fig. 1.** Excess carrier concentrations in n-type TiO2 (dashed line) \(1.44 \times 10^{-11} \ sec\) and (solid line) \(1.16 \times 10^{-9} \ sec\) after turning on illumination \(10^{16} \ photons \ cm^{-2} \ sec^{-1}\). \(V_n = 0.8V\) (in dark); \(n_o = 1 \times 10^{16} \ cm^{-3}\); \(p_o = 0\); \(\tau_p = 10^4 \ esu\); \(U_p = 100\) and \(U_n = 50 \ cm^{-2} \ sec^{-1}\). \(V_n = 5 \times 10^3 \ cm^{-1}\); \(\tau_p = 10^{-4} \ sec\). Vertical dashed line shows space charge region/bulk semiconductor boundary.
fine division of space elements ($\Delta x \approx 20-50\text{Å}$) to represent the quantities there to a sufficient accuracy in the digital simulation. Because of this, combined with the high value of the transport coefficients of the free carriers, a very short time interval must be used as a simulation time step (ca. $10^{-14}\text{ sec}$) and the total simulated time is limited to the nanosecond range even after $10^5$ simulation steps. For reasonable fluxes of light to be calculated (e.g., $10^{16}\text{ photons cm}^{-2}\text{ sec}^{-1}$), the excess of free carriers added to the space charge region within this time interval is far smaller than the amount which will be present there at the steady state to produce the photopotential. An attempt to overcome this problem by using higher light fluxes or slower transport coefficients (which, numerically, have the same effect) results in a distorted picture in which the generation of carriers is very exaggerated with respect to their transport. Thus the transport processes (migration and diffusion) dominate all others. The speed at which these driving forces, especially inside the space charge region, dissipate a large portion of any local perturbation (provided it is not too large) is what underlies the possibility of using the Boltzmann distribution in cases where actual equilibrium does not exist (7, 8). The simulated transient behavior allows us to deduce the sequence of events which leads to the steady state and causes the photopotential effect. This is shown schematically in Fig. 2. The charge density distributions at equilibrium in the dark and under illumination are given in Fig. 2a, b. Figure 2b shows the redistribution of the charge density caused by the changes $\Delta p$ and $\Delta n$ in the surface field, but its distribution shows an accumulation of positive charge at the surface and a loss of positive charge at the space charge region/bulk boundary (where the excess of electrons which accumulate there compensates for the diffuse positive charge of the space charge region). The corresponding electric field distributions are shown in Fig. 2c. The area between the field curves, i.e., the integration of the difference in the electric field with respect to distance from the bulk semiconductor to the surface, is the decrease in surface potential due to illumination, the photopotential

**Photocurrent in the Absence of Kinetic Complications**

If charge transfer across the semiconductor/solution boundary is possible, the situation differs from the open-circuit case described above. Two extreme cases can be considered. If the rate constant for charge transfer is infinitesimal, the open-circuit case, which is characterized by very small faradaic currents and the photopotential effect, is approached. At the other extreme, if the charge transfer to solution is limited only by the combined effect of generation/recombination and transport of carriers within the semiconductor phase, only a small accumulation of excess free carriers occurs leading to a smaller photopotential and larger faradaic currents. Thus, the rate constant for charge transfer to solution will have a key role in determining both the photocurrent and the electrical state of the semiconductor.

We simulate here the fast charge transfer case and calculate the photocurrent which is determined by the processes within the semiconductors phase. We use n-Type TiO$_2$, a stable semiconductor electrode for which the photocurrent has been widely described (5, 4), as a model. The very low concentration of minority carriers (holes) in this sample somewhat simplifies the calculation because no oxidation current (hole injection to solution) exists in the dark.

The photocurrent density due to photogenerated holes within the semiconductor biased to positive potentials is expressed as the product of the charge transfer rate constant $k_p$ (cm$^2$ sec$^{-1}$) and the hole concentration at the surface ($x = 0$) (or in the simulation for space element, $K = 1$)

$$i_{p,f} = e k_p p(0)$$  \[4\]

The rate constants were chosen to be sufficiently large that the steady photocurrent calculated in the simulated time domain was independent of the value of $k_p$. The surface concentration of holes was found to be inversely proportional to $k_p$. The effect of the magnitude of $k_p$ is shown in Fig. 3. The electron distribution is also affected by $k_p$, because for every hole which is injected into the solution, an electron is collected by the metallic contact to the semiconductor electrode.
and is delivered to the counterelectrode. Although the effect of $k_p$ is most prominent at the semiconductor surface, it also determines the whole level of excess holes inside the space charge region and hence the flux of holes which will enter this region. Under actual conditions the situation may be far more complex because $k_p$ may depend upon the potential drop in the Helmholtz layer at the semiconductor/solution interface. Assuming $\Delta \phi_H$, e.g., it could be given by $k_p e^{\Delta \phi_H} (\beta a_{\text{ph}})$ and where $k_p$ may have a much smaller value than that used in the simulation. At the instant after illumination only a small photocurrent is expected, resulting in a pronounced accumulation of excess carriers in the space charge region, in a manner similar to that for the open-circuit case. This accumulation causes a photopotential to be built up gradually, which in a potentiostatic experiment will result in a gradual change in $\Delta \phi_H$ and an increase in $k_p$. At the steady state the charge transfer rate will be sufficiently fast to prevent any further accumulation of excess free carriers inside the space charge region. We did not simulate this suggested sequence of events which extends over two completely different time domains. Moreover, $k_p$ could not be made too small because under these conditions, even after a lengthy computation, a steady state was not achieved. Therefore, we can only speculate that as long as migration is the predominant driving force (high fields and band bending) and not so small that a high accumulation of excess carriers is produced inside the space charge region thus changing considerably the fields there, only a minor dependence of photocurrent on $k_p$ is expected. At low band bending, on the other hand (which would usually occur at the foot of the photocurrent-potential wave), diffusion may be the main transport process. The photocurrent will then strongly depend upon the diffusion of the holes inside the space charge region and towards the surface, which in turn will be determined by the concentration profile present and thus on $k_p$.

**Results**

Photocurrent-potential curves assuming rapid charge transfer to solution under several different sets of conditions were simulated (Fig. 4). Curve a represents the steady-state currents for the electrode initially held at the (dark) held at the indicated potential where all of the imposed potential is assumed to drop inside the semiconductor space charge region. No photopotential is observed. The dashed line a shows the calculated curve if electrons are allowed to cross the surface as well, to reduce the species just formed by the hole injection process, or to react with holes at the surface at a rate which is proportional to the absolute concentration of electrons at the surface. Both processes will have the same effect in reducing the net oxidation current. This back-reaction effect could be of importance, since the photosensitized oxidation of the semiconductor electrode frequently produces a species which is thermodynamically reducible at the electrode potential. For any value for the rate constant, $k_{en}$ chosen for this "back-reaction" effect, the observed photocurrent is found to rise very steeply (almost discontinuously) with potential. This steep rise is caused by the fact that the absolute electron concentration at the surface is an exponential function of potential. Such abrupt rises in photocurrent are not observed experimentally. A calculation in which the excess of electrons at the surface, rather than their absolute numbers, determines their contribution to the photocurrent is shown as curve a'. A simple model for surface recombination, similar to that which was presented previously (1) results in the expression

$$i_e = e[k_p \Delta n(o) - k_p \Delta n(o)]$$

For the case under consideration, for holes, $\Delta p \sim p$, while for electrons, $\Delta n = n - n^*$. This effect modifies somewhat the foot of the photocurrent-potential wave.

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![Fig. 4. Simulated photocurrent-potential curves for n-TiO₂ Electrode as in Fig. 1, $n_o = 10^{16}$ photons cm⁻²sec⁻¹, $k_p = 2.78 \times 10^4$ cm²sec⁻¹, except as noted below. Efficiency = $i_{p,f}/i_{p}$ given in holes per second. (a) $\tau_p = 10^{-9}$ sec; (a') as in (a), assuming electrons cross to solution at a rate proportional to their absolute number at the surface, with a rate constant $k_n = 1.39 \times 10^5$ cm⁻²sec⁻¹; (a'') as in (a) assuming electrons cross to solution at a rate proportional to their excess number at the surface, $k_n = 1.39 \times 10^5$ cm⁻²sec⁻¹; (b) as in (a'), $a = 3 \times 10^8$ cm⁻²; (c) as in (b), $\tau_p = 10^{-10}$ sec; (d) $a = 3 \times 10^4$ cm⁻², $\tau_p = 5 \times 10^{-11}$ sec, $n^* = 4 \times 10^{17}$ cm⁻³; (e) experimental efficiency curve for a single crystal TiO₂ for water photo-oxidation (c axis normal to solution) measured at 375 nm; solution pH = 4.0; the potential axis in this case is the electrode potential vs. SCE.](image_url)

![Fig. 5. Effect of bulk recombination rate constant for excess holes on the photocurrent and concentration profiles of excess free carriers. Electrode and illumination as in Fig. 1; $V_o = 0.4V$. (a) $\tau_p = 10^{-9}$ sec, $i_{p,f} = 1.596$ mA; (b) $\tau_p = 10^{-10}$ sec, $i_{p,f} = 0.886$ mA; (c) $\tau_p = 10^{-11}$ sec, $i_{p,f} = 0.718$ mA.](image_url)
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APPENDIX

The calculation cannot be extended in reasonable simulation times to K values that rigorously will satisfy the conditions of Eq. [A-7]. Instead, the following boundary condition was chosen

$$\Delta p_{K=0} = 0, \; \Delta n_{K=0} = 0, \; E_{K=0} = 0$$  [A-7]

The following boundary conditions apply

$$\Delta p_{K=K_{MAX}} = \Delta p_{K_{MAX}-1} \exp\left(-\frac{\Delta x}{(\chi_D)_{1/2}}\right)$$  [A-8]

$$\Delta n_{K=K_{MAX}} = \Delta n_{K_{MAX}} = 0$$

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$$\Delta n_{K=K_{MAX}} = \Delta n_{K_{MAX}} = 0$$

**LIST OF SYMBOLS**

- \(a\) : absorptivity of light
- \(D_p, D_n\) : diffusion coefficients of holes, electrons
- \(E(x)\) : electric field
- \(E(x)_{eq}\) : electric field at equilibrium
- \(\Delta E(x)\) : change in electric field with respect to equilibrium \([E(x) - E(x)_{eq}]\)
- \(g(x)\) : generation function of light
- \(I_f\) : total faradaic current
- \(I_p\) : faradaic current due to holes
- \(\alpha\) : absorption coefficient
- \(\kappa\) : recombination rate constant
- \(K\) : simulation distance index
- \(n(x)\) : electron concentration
- \(n(x)_{eq}\) : electron concentration at equilibrium
- \(n_0\) : electron concentration in bulk semiconductor
- \(\Delta n\) : excess concentration of electrons \([n(x) - n(x)_{eq}]\)
- \(p(x)\) : hole concentration
- \(p(x)_{eq}\) : hole concentration at equilibrium
- \(p_0\) : hole concentration in bulk semiconductor
- \(\Delta p\) : excess concentration of holes \([p(x) - p(x)_{eq}]\)
- \(\Delta t\) : simulation time interval
- \(U_p, U_n\) : mobility of hole, electron
- \(x\) : distance from electrode surface
- \(\Delta x\) : simulation space element thickness
- \(\alpha\) : absorption coefficient
- \(\epsilon_0\) : permittivity of free space (mks)
- \(\epsilon_r\) : dielectric constant
- \(\tau\) : average lifetime of excess minority carrier (hole) in bulk n-type semiconductor

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Analysis of Multiple Reaction Sequences in Flow-Through Porous Electrodes

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ABSTRACT

The role of multiple reactions in flow-through porous electrodes has been investigated theoretically. The reaction sequences studied include simultaneous deposition of several metals, deposition of a metal in the presence of a redox system, and an ECE sequence which is characteristic of many electro-organic synthesis reactions. The model accounts for mass transport, multiple charge transfer reactions, homogeneous chemical reactions, ohmic and geometric parameters. Results are compiled in a series of graphs which elucidate electrode behavior over a wide region of parameter space.

One advantage of electrochemical processes is that a high level of selectivity for a desired reaction product can often be achieved through careful control of the potential under which reaction proceeds. On the other hand, the attainment of economically high volumetric reaction rates often requires optimizing around competing needs for large surface area, adequate mass transfer, and low ohmic resistance. Although flow-through porous electrodes are advantageous for achieving high reaction rates per unit volume, these devices often exhibit substantial potential variations over their interior surface so that the original electrochemical advantage of selectivity may thereby be lost. The purpose of this investigation is to develop theoretical methods for predicting the selectivity of flow-through porous electrodes in systems where multiple reactions occur, and to illustrate how such predictions can be compiled for use in engineering design.

Literature Review

The use of fixed bed porous electrodes with a single electrode reaction has been recently reported for stripping copper (1), depositing antimony (2) and copper (3-5), carrying out redox reactions with iron (6) and ferricyanide couples (5, 7, 8), detecting dissolved gases (9-11), and for precipitating anionic species (12). Earlier work has been reviewed with emphasis on battery applications (13) for which a single electrode reaction is the preferred mode of operation. The extensive publications of Sioda, reviewed in Ref. (13), are especially noteworthy since they established many experimental procedures and theoretical methods of analysis. Many additional porous electrode studies are known which involve multiple electrochemical reactions in order to accomplish simultaneous removal of several metal ions from mixed solutions (14-21); separation of quinones (22), radioactive nuclides (23), and halide ions (24); and reduction of metal ions in the presence of competing reactions (25). Reaction schemes involving coupled electrochemical and homogeneous chemical steps have also been used in porous electrode cells for coulometric and preparative applications (12, 26-29), and for electro-organic synthesis applications (30-36). It is abundantly clear that multiple reaction sequences are commonly encountered in many fixed bed porous electrode applications.

Theoretical considerations of multiple reaction effects in porous electrodes have led to the development of simple criteria for choosing the flow velocity and applied current such that (i) the potential distribution is sufficiently uniform that side reactions are avoided (8, 13, 37), or (ii) the residence time is convenient for maximizing the production of an intermediate species in a sequential reaction (27). In both cases, the approximate procedures are based on the need to attain a high degree of selectivity in the presence of multiple reactions. Therefore it seems appropriate to develop a more extensive theoretical basis for predicting the current and potential distribution behavior of porous electrodes in the presence of multiple homogeneous and heterogeneous reactions.

Theoretical Formulation

The geometry of the porous electrode system under study is indicated in Fig. la. Electrolyte flows in the direction of the y coordinate; the electrode is of thickness l. The counterelectrode may be located either upstream or downstream from the porous electrode; in Fig. 1a, a downstream location is shown. Other details of cell construction are not shown since they are not included in the model equations. Electrolyte flows through the porous electrode, supplying reactants to the interior surface where electrochemical reaction occurs. The local reaction rate is a function of position since the potential and species concentrations vary along the reactor length owing to ohmic and transport limitations.

Figure 1b illustrates how the processes in the interior region of the porous electrode are envisioned by the model. The solid surface of the interior region, upon which electrochemical charge transfer occurs, is of arbitrary shape and is accounted for in the model only by a specific area term. The species concentration distributions at the solid surface, c* (y), are different from the species concentration distributions in the well-mixed core, c(y), owing to the presence of a mass transfer diffusion layer between core and surface. The diffusion layer is assumed to occupy only a small fraction of the electrolyte volume so that (i) if homo-