

**Digital Simulations in Photoelectrochemistry:
Simulations of the Steady-State, Transient,
and Cyclic Voltammetric Behavior of
Semiconducting Photoelectrodes**

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A series of digital simulations has been performed to obtain insight into the steady-state current density vs potential behavior of semiconductor/liquid interfaces. The TeSCA program, incorporating all of the key kinetic parameters involved with the generation, transport, and recombination of charge carriers both in the semiconductor and across the semiconductor/liquid interface, has been used for this purpose. The simulations confirmed conclusions obtained previously from a simplified analytical model, which state that for "ideal" behavior of a non-degenerately doped semiconducting electrode the photovoltage of an n-type semiconductor/liquid interface should not change if the concentration of the reduced form of the redox species, A⁻, is held constant but the concentration of the oxidized form of the redox species, A, is varied. The simplified analytical model also predicts that the photovoltage will be independent of variation in [A⁻] if [A] is held constant. In contrast, recent work has asserted that "ideal" junction behavior implies that the photocurrent should exhibit shifts in potential that are linearly dependent on the concentration of the minority carrier acceptor species in the solution, with a magnitude of 59 mV per decade change in the acceptor concentration at 300 K. In accord with the predictions of the simplified analytical model, such shifts are not apparent in the simulations presented in this work. Finally, TeSCA simulations have been applied to analyze literature data on the steady-state current density vs potential behavior of p-InP/Fe(CN)₆^{3-/4-}(aq) contacts. Such simulations have established an upper bound for the interfacial charge-transfer rate constant of $10\text{--}20\text{ cm}^2\text{ s}^{-1}$ in this system.

An extensive series of digital simulations of the decay dynamics of photoexcited charge carriers at a semiconductor/liquid interface has been performed using the twodimensional simulation code TeSCA. TeSCA treats majority and minority carrier capture processes separately and incorporates fielddependent carrier mobility terms. These features produce dramatic differences in the output parameters obtained when fitting experimental data with TeSCA relative to those obtained by fitting such data with prior, less complete, simulations.

The simulations revealed that for a typical (n-type in our example) InP electrode in contact with outer-sphere redox reagents dissolved in the contacting liquid phase, the photoluminescence decays were generally insensitive to the value of the minority carrier charge-transfer rate constant, k_{ht} . Instead, diffusion and drift-induced separation of photogenerated carriers in the spacecharge layer of the semiconductor dominated the time decay of the observed luminescence signal under most experimentally accessible conditions. Values of k_{ht} and of the minority carrier lowlevel surface re-

combination velocity, S_p , could be obtained from an analysis of the photoluminescence decays only when the following restricted sets of conditions were satisfied simultaneously: $101\text{ cm}^2\text{ s}^{-1} \leq S_p \leq 105\text{ cm}^2\text{ s}^{-1}$, $10\text{--}18\text{ cm}^2\text{ s}^{-1} \leq k_{ht} \leq 10\text{--}15\text{ cm}^2\text{ s}^{-1}$, and the electrode potential, E , was in the region $0 \leq E \leq +0.15\text{ V}$ relative to the flatband potential of the n-type semiconductor/liquid interface. The simulations demonstrated that it was not possible to extract a "field-dependence" of the charge-transfer rate constant when the semiconductor/liquid contact was maintained in reverse bias ($E \leq +0.15\text{ V}$ vs the flatband potential) and was subjected to light pulses that produced low or moderate carrier injection levels. Under such conditions, the photoluminescence decay dynamics were dominated by drift-induced charge separation in the spacecharge layer of the semiconductor. Under high-level injection conditions, no "field-dependence" could be observed because the majority of the photoluminescence decay dynamics occurred near the flatband condition, so the value of the band bending in the semiconductor under dark, equilibrium conditions had negligible influence on the luminescence transients produced by a high-intensity laser pulse. Additionally, comparison between onedimensional and twodimensional simulations showed that use of onedimensional simulation routines to extract S_p and k_{ht} values from experimental data obtained using focused laser beam excitation can lead to severe overestimates of interfacial charge-transfer rates.

In addition, cyclic voltammograms have been obtained under a variety of conditions using a semiconducting photoelectrode or using a circuit containing a diode in series with a metallic electrode. Simulations of the voltammetry of both types of systems were performed using a model circuit in which electrode non-ideality, double layer capacitance, and parallel resistance effects were accounted for quantitatively. The simulated voltammograms were in excellent agreement with the experimental data for a diode/electrode circuit, yielding a reliable description of the shapes of the voltammograms as well as of the voltage dropped across the diode element as a function of the total potential dropped across the circuit. The digital simulations were in good agreement with the voltammetry of p-Si/CH₃OH-CoCp₂^{+/0} contacts at high light intensities, but could not quantitatively describe the shapes of the voltammograms at low light intensities.