carboxylate provides only a small direct catalytic advantage, while the latter reveal an essential, and predicted,[5a] role of Asp-102, providing the correct tautomeric form of His-57.

**Acknowledgment**. Funding from the National Institutes of Health (GM39782) and the National Science Foundation (CHE 58202) is gratefully acknowledged. S.C.Z. acknowledges a Dreyfus Teacher-Scholar Award, an Eli Lilly Granteeship, and an NSF Presidential Young Investigator Award.

## Real-Time Measurements of Interfacial Charge Transfer Rates at Silicon/Liquid Junctions

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*Received January 8, 1990*

The rates of interfacial charge transfer from photogenerated carriers in semiconductor electrodes to solution donors and acceptors are fundamentally important in the area of semiconductor electrochemistry.[1-3] However, to date there have been no real-time measurements of the charge-transfer rates between semiconductors and outer sphere redox couples. Previous steady-state current-voltage experiments have led to the suggestion that such rates might be extremely fast ($>10^{11}$ s$^{-1}$), because evidence has been obtained for interfacial charge transfer events competing with thermalization of the photoexcited carriers (i.e. "hot carrier injection processes").[4] Additionally, luminescence decay measurements on CdS surfaces in contact with strongly adsorbing, inner sphere redox reagents such as 1.0 M KOH/1.0 M $S^{2-}$ have indicated high surface recombination velocities ($>10^5$ cm/s) and have yielded photoexcited carrier lifetimes of less than 100 ps.[5] In contrast, simple theoretical estimates of the interfacial charge transfer rate constants for outer sphere redox systems[1,2] can be used to predict carrier lifetimes between $10^{-6}$ and $10^{-3}$ s under common experimental conditions. To address these issues, we report herein the first real-time kinetic rate measurements from carriers in a semiconductor to outer sphere redox donors and acceptors in the liquid phase.

The carrier lifetime measurements in this work were obtained by microwave and radio-frequency (rf) conductivity techniques.[6,7] Previous studies on semiconductors (either in contact with air or with aqueous acids) have shown that, in proper experimental geometries, the intensity of the reflected microwave[6] (38.3-GHz, 180-mW source in our work) or rf[7] power (450 MHz, 1 W), $P_{\text{dark}}$, is proportional to the conductivity ($\sigma$) of the sample. Accordingly, upon creation of a nonequilibrium excess carrier concentration with a light pulse,

$$\Delta P/P_{\text{dark}} \propto \Delta\sigma = (\mu_n\Delta n + \mu_p\Delta p)q \qquad (1)$$

where $\mu_n$ and $\mu_p$ are the electron and hole mobilities, respectively, $\Delta n$ and $\Delta p$ are the excess electron and hole concentrations, $q$ is the electronic charge, and $\Delta P$ is $P_{\text{light}} - P_{\text{dark}}$. Thus, if the mobilities are known, the time dependence of $\Delta P/P_{\text{dark}}$ allows measurement of the time dependence of the photoexcited carrier concentration in the semiconductor.[6,7] The advantages of this method are that it is contactless, has fast time resolution, allows collection of data from a single excitation pulse, and is feasible in a variety of electrolytes. High-injection conditions have been utilized in our work in order to minimize effects of the electric field in the semiconductor;[7-9] thus, only carrier diffusion to the surface of the sample must be considered as an alternative rate-limiting step.

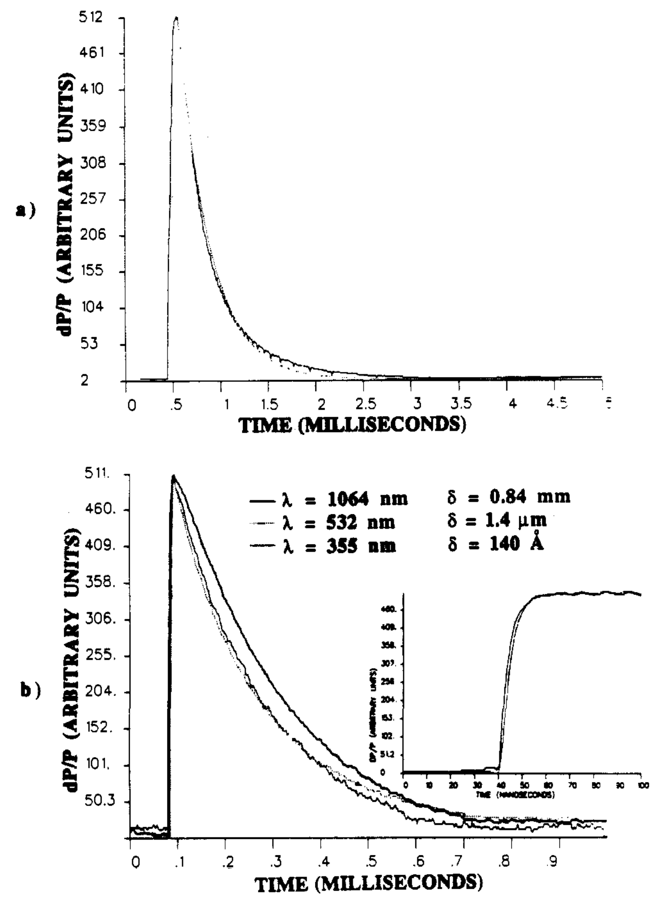

**Figure 1.** (a) Microwave conductivity decay (solid curve) under high injection ($10^{15}$ injected carriers/cm$^2$ in a 190-$\mu$m-thick sample of n-Si) in contact with concentrated sulfuric acid. A simulation with a surface recombination velocity of 25 cm s$^{-1}$ and a bulk lifetime of 2 ms is shown (dashed line) for comparison. Similar decay curves were obtained with a 450-MHz rf conductivity apparatus. (b) Microwave conductivity decays for the same material as in Figure 1a, but in contact with a methanol solution containing 0.34 M $Me_2Fc$, 5 mM $Me_2Fc^+$, and 0.10 M $LiClO_4$. Decays are displayed for three separate excitation wavelengths of penetration depth $\delta$. The ratio of absorbed photons-cm$^{-2}$(Si) to maximum signal intensity is the same for all three curves. Absorbed photons per square centimeter (Si) were $2.2 \times 10^{13}$ photons cm$^{-2}$ at 1064 nm, $9.1 \times 10^{12}$ photons cm$^{-2}$ at 532 nm, and $1.7 \times 10^{13}$ photons cm$^{-2}$ at 355 nm. The light pulses were obtained from a Nd:YAG laser (Spectra-Physics Model DCR-1) with a 9-ns pulse width (fwhm). The inset shows the early time signals for all three wavelengths, and the rise time in these traces is preamplifier response limited.

Figure 1a shows the time dependence of the reflected microwave power for a 130 Ω cm resistivity (donor density = $3.4 \times 10^{13}$ cm$^{-3}$),

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long bulk lifetime (>2 ms),[10] (100) oriented, 190-$\mu$m thick sample of n-Si in contact with concentrated $H_2SO_4$. Both sides of this wafer were optically polished, and both sides were in contact with the solution. In agreement with prior work,[7a] the excess carrier concentration decays with a remarkably long time constant in contact with aqueous acid solutions. Using the known expression that $k_{obsd} = k_{bulk} + k_{surf}$,[9] and the knowledge that $k_{bulk} < 5 \times 10^2$ $s^{-1}$ for these samples,[10] we calculate that the surface recombination velocity is 25 cm/s (from $k_{obsd} \approx 2S/L$ where $L = 190$ $\mu$m and $S$ is the surface recombination velocity in cm/s) under our conditions.

The presence of electron donors or acceptors in the solution should decrease the observed lifetime, especially if electron transfer is occurring on a rapid time scale. Figure 1b displays the reflected power decay curves for this same n-Si sample in contact with 0.34 M dimethylferrocene ($Me_2Fc$), 5 mM $Me_2Fc^+$, and 0.10 M $LiClO_4$ in $CH_3OH$. The excess carriers were remarkably long-lived, with excess carrier lifetimes of 0.24 ms, corresponding to a surface recombination velocity of 40 cm/s for this system. At 0.34 M $Me_2Fc$, this corresponds to an upper limit on the bimolecular hole transfer rate constant of $1.95 \times 10^{-19}$ $cm^4/s$. This result has been obtained with both the microwave and the rf conductivity apparatus, confirming that it is not an artifact of the measurement technique.

The reflected power decay profiles have also been investigated as a function of excitation wavelength (Figure 1b). Even with excitation at 355 nm, where the photoexcited carriers have over 2.3 eV of excess unthermalized energy and are initially confined to the 140-Å penetration depth of the incident light,[11] we observed lifetimes of greater than 0.2 ms for these carriers in the presence of the $Me_2Fc^{+/0}$. These long lifetimes were also obtained with the $Me_2Fc^{+/0}$ system in other solvents, including propylene carbonate and acetonitrile.

The large concentration of $Me_2Fc$ donors might be expected to act as effective hole traps, and this should reduce the measured signal by 25% even if all of the electrons remained in the solid (from eq 1 and the fact that $\mu_n/\mu_p \approx 3$ for Si). However, no fast component of the concentration decay was observed even on the nanosecond time scale (Figure 1b inset). We note that, for excitation at 1064 nm, the photon penetration depth in Si is 0.84 mm.[11b] When excess carriers are created uniformly throughout the 190 $\mu$m thick Si sample, the half-life for carriers to be captured at a diffusion-limited rate to the surface (with the ambipolar $D$ = 10 $cm^2/s$)[3] is 7 $\mu$s;[9] thus, the time response of the experimental system is more than adequate to observe any fast-decay components associated with the postulated trapping processes. We have also examined the Si surface after a laser flash to see whether an insulating layer was formed that could impede electron transfer, but after exposure to three light pulses ($3 \times 10^{13}$ photons/$cm^2$ per pulse) in $CH_3OH/Me_2Fc^{+/0}$ at 1064 nm, we observed only Si, adventitious C, and less than 0.25 monolayers of silicon oxide by high-resolution X-ray photoelectron spectroscopy.[12] We therefore conclude that the carrier lifetimes are very long in these Si samples and that no light-induced insulating layer is leading to spuriously low rate constants in these experiments. Our analysis places an upper limit to the interfacial charge transfer rate constant of 40 cm/s, as compared to charge transfer rate constants of $10^7$ cm/s observed for semiconductor/metal interfaces.[9]

Taken at face value, these results seem to contradict the impressive current–voltage properties and high energy conversion efficiencies displayed by the n-Si/$CH_3OH$ interface in contact with the $Me_2Fc^{+/0}$ redox system.[13] However, the ratio of the minority carrier injection rate into the electrolyte relative to the minority carrier recombination rate will determine the net photocurrent quantum yield;[1,2,14] therefore, if the surface nonradiative recombination rates are sufficiently small, a slow interfacial charge transfer rate still can produce high net quantum yields in steady-state experiments. Current continuity arguments can be used to place a lower limit on the hole capture velocity of 1 cm/s and an upper limit on the electron capture velocity of $10^4$ cm/s in the n-Si/$Me_2Fc^{+/0}$ cell;[13-16] thus, there is no actual contradiction between the real-time data and the steady-state photoelectrochemical efficiency measurements. However, the unexpectedly slow injection rates do underscore the usefulness of real-time techniques in elucidating the magnitude of the charge-transfer kinetics.

These results, in conjunction with those obtained for CdS,[5] imply that a wide range of electron-transfer rate constants may be found at semiconductor/liquid interfaces. They also demonstrate that these rate constants may be over 6 orders of magnitude slower than previously postulated for semiconductors and still be consistent with established steady-state voltammetric experiments. The real-time methods described above can be used to obtain rate constant information in aqueous media and for a variety of other redox systems, and such work is in progress at present.

**Acknowledgment**. We thank B. J. Tufts for running the XPS experiments, P. G. Santangelo and A. Kumar for experimental assistance, and E. Yablonovitch, T. Gmitter, M. Kunst, J. Warman, and H. Tributsch for helpful discussions regarding the experimental setup. We are also grateful to R. Swanson and R. Sinton of Stanford University for providing the Si samples. M.D.E.F. is grateful for financial support from the National Science Foundation through its Postdoctoral Fellowship Program in Chemistry. This work was supported by Grant No. CHE-8814263 from the National Science Foundation.

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## Palladium-Catalyzed Stereocontrolled Intramolecular 1,4-Additions to Cyclic 1,3-Dienes Involving Amides as Nucleophiles

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Regioselective metal-mediated additions to conjugated dienes have attracted considerable interest recently.[1] In the palladium-catalyzed oxidation of conjugated dienes, two nucleophiles are added in a regio- and stereospecific manner across the diene (Scheme I).[1-3] The latter type of reaction occurs in the presence of an acid with benzoquinone being used as electron-transfer catalyst or oxidant. Nucleophiles that can be used include carboxylates, alcohols, and halides. It would be of great synthetic interest to extend these selective 1,4-oxidations to other nucleophiles, such as carbon and nitrogen nucleophiles. In this communication, we report for the first time the use of nitrogen nucleophiles in the palladium-catalyzed 1,4-oxidation of 1,3-dienes.

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