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Open-Circuit Photovoltage and Charge Recombination at Semiconductor/Liquid Interfaces

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ABSTRACT

A simple, quantitative relationship between the semiconductor surface recombination velocity (S_r) and the open-circuit photovoltage (V_{oc}) of photoelectrochemical systems was derived and verified experimentally. Experimental results obtained for the n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 junction indicate that V_{oc} is controlled by surface recombination. Quantitative analysis of the results using the derived expression yields values of the barrier height and S_r that compare favorably with published data. Application of the equation to other semiconductor/liquid junction cells suggests that the expression may be important in evaluating and understanding the behavior of a wide range of photoelectrochemical systems.

The open-circuit photovoltage (V_{oc}) of semiconductor/liquid junction solar cells is a critical parameter in determining the energy conversion efficiency. The fundamental process controlling V_{oc} is the recombination of photoexcited electrons and holes.^{1,2} The lower the recombination rate, the larger the V_{oc} . The predominant energy-loss mechanism is determined by competition among the following processes: majority-carrier thermionic emission over the surface barrier,³ majority-carrier charge transfer across the semiconductor/liquid interface,^{3,4} minority-carrier diffusion/recombination in the bulk of the semiconductor,^{5,6} space-charge recombination,⁷ and surface recombination mediated by recombination centers.⁸⁻¹³ The extent to which each of these processes is understood differs considerably. For example, expressions describing the minority-carrier diffusion/recombination in the bulk semiconductor contacting a redox electrolyte is obtained by direct analogy to formulas developed for solid-state p-n junction devices.⁵ When bulk diffusion/recombination is the dominant recombination process, the dependence of V_{oc} on the semiconductor bandgap, doping level, and minority-carrier diffusion length can be expressed in simple analytic forms.⁵ In contrast, surface recombination has generally been treated in a more complex fashion by numerical simulation.⁸⁻¹¹ In cases in which V_{oc} is limited by surface recombination, no simple analytic expression exists for relating V_{oc} and the surface recombination velocity (S_r). Several groups⁸⁻¹¹ have considered theoretically the effect of surface recombination on the performance of photoelectrochemical (PEC) cells. Although each treatment has achieved some success in describing a certain aspect of the effect of surface recombination, these treatments are generally considered qualitative.¹⁴ For the most part, it has been difficult to extract quantitative information on surface recombination from

experimental results because of the number of adjustable (and often arbitrary) parameters involved in numerical analyses. Up to now, only one study¹¹ has dealt directly with the dependence of V_{oc} on the surface recombination current; however, because bias-independent surface recombination currents in arbitrary units were used in the numerical calculation, it is difficult to apply the model of this study for interpreting quantitatively experimental measurements. Other studies⁸⁻¹⁰ have focused mainly on the general shape of the photocurrent-voltage (J - V) curves, without addressing the dependence of V_{oc} on S_r .^b The absence of a theoretical framework relating S_r to V_{oc} impedes the understanding of such processes at the solid/liquid interface.

In this article, we derive a simple quantitative expression, based on semiconductor solid-state theory, that directly relates S_r to V_{oc} . The applicability of the expression to account for the PEC behavior of n-Si/acetone with $\text{FeCp}_2^{+/0}$ (ferrocenium ion/ferrocene) is then investigated. Based on J - V data and the dependence of V_{oc} on both the temperature and the concentration of $\text{FeCp}_2^{+/0}$, we are able to exclude other possible recombination channels and identify surface recombination as the dominant recombination process in determining V_{oc} . The surface recombination velocity deduced from experimental results compares favorably with reported values. The application of the analytic expression to other PEC systems reported in the literature is also discussed.

^b The effect of surface recombination is generally discussed in terms of the photocurrent onset potential. However, unlike the concept of the "open-circuit photovoltage," the "photocurrent onset potential" is an empirical quantity that cannot be precisely defined. The photocurrent onset potential depends on both V_{oc} and the fill factor. The latter two parameters are more definable quantities and are more relevant in calculating the PEC conversion efficiency.

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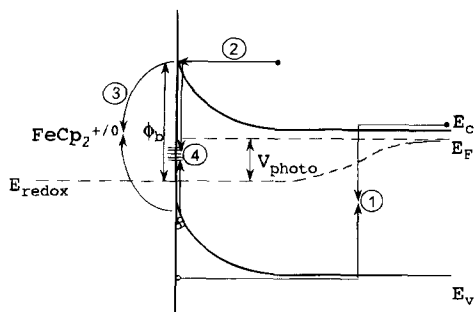


Fig. 1. Major recombination pathways at interfaces between n-type semiconductor and redox electrolyte, under open-circuit condition: 1, recombination in the bulk semiconductor; 2, majority-carrier (electron) transport to the interface; 3, interfacial charge transfer leading to recombination in solution via redox species; and 4, recombination at the interface via surface trapping levels.

Theoretical Considerations

Although the expressions that we derive apply to n-type semiconductor/liquid junctions, similar equations can easily be written for p-type semiconductor/liquid contacts. A PEC cell under bandgap illumination behaves similarly to a diode at forward applied bias. The recombination current at an illuminated semiconductor/liquid junction is made up of four major components (Fig. 1): 1, recombination in the bulk semiconductor; 2, majority-carrier transport to the interface; 3, recombination in solution via redox species; and 4, recombination at the interface via surface trapping levels. Under open circuit, the photogenerated current (J_{ph}) is balanced by the recombination current. The open-circuit photovoltage (V_{oc}) is obtained from the relation^{1,5}

$$V_{oc} = n \frac{kT}{q} \ln \frac{J_{ph}}{J_0} \quad [1]$$

where n is the diode quality factor, and J_0 is the saturation current density, which is controlled by the largest among processes 1, 3, and 4. (Process 2, which is in series with interfacial recombination 3 and 4, is important only when its rate is smaller than those of the latter two processes.) In the following, we examine each of these processes.

1. Charge recombination in the bulk semiconductor. This process involves the minority-carrier diffusion and recom-

$$J_{sr} = \frac{q v_{th} \sigma_n \sigma_p N_{st} (p_s n_s - n_i^2)}{\sigma_p [p_s + n_i \exp((E_i - E_t)/kT)] + \sigma_n [n_s + n_i \exp((E_t - E_i)/kT)]} \quad [4]$$

bination in the neutral region of the semiconductor. The bulk-recombination current depends on the characteristics of the bulk semiconductor material and is not affected by the interfacial or redox electrolyte properties. Detailed analysis of this process is given elsewhere.⁵ To date, only the n-Si/methanol junction has been verified to exhibit a bulk-recombination-limited V_{oc} .^{6,15}

2. Majority-carrier transport to the interface. This process is commonly treated as thermionic emission. The thermionic emission current (J_{th}) is given by¹⁶

$$J_{th} = A^* T^2 e^{-q\phi_b/kT} e^{qV/nkT} = J_{th0} e^{qV/nkT} \quad [2]$$

where ϕ_b is the barrier height at the interface, A^* is the effective Richardson constant, V is the applied bias, and J_{th0} is the saturation current for thermionic emission. The thermionic emission treatment provides the proper description of metal/semiconductor contacts, in part, because the recombination rate at semiconductor/metal interfaces is very high ($>10^7$ cm/s). The majority-carrier current is limited by the supply of majority carriers surmounting the surface barrier. At semiconductor/liquid junctions, this process is generally not rate limiting. Studies^{3,4} have shown that charge recombination is the rate-limiting process at semiconductor/liquid junctions.

3. Interfacial charge transfer leading to recombination via redox species in solution. This process entails electron

transfer to oxidized species and hole transfer to reduced species. Because the concentration of reduced species is much higher than that of oxidized species in practical PEC cells, the majority-carrier transfer from the n-type semiconductor conduction band to oxidized species is generally rate limiting for this recombination process. The corresponding recombination current (J_{et}) is described by the equation^{3,4,17}

$$J_{et} = q k_c c_{ox} n_s = q k_c c_{ox} N_c e^{-(q\phi_b/kT)} e^{(qV_s/kT)} = J_{et0} e^{(qV/nkT)} \quad [3]$$

where c_{ox} is the concentration of oxidized species, k_c is the rate constant, n_s is the electron concentration at the interface, N_c is the effective density of states of the semiconductor conduction band, V_s is the change in semiconductor band bending because of applied bias V , and J_{et0} is the saturation current for this process. In order to account for the possible potential drop across the Helmholtz layer and the contribution from space-charge recombination, a diode quality factor n is introduced in Eq. 3.

4. Surface recombination via trapping centers. The existence of surface energy levels that lie within the bandgap allow surface recombination to occur. These trapping states or recombination centers are associated with surface and interfacial states, arising from defect sites and semiconductor-redox electrolyte interactions.^{18,19} Up to now, there has been no suitable theoretical treatment dealing with the quantitative relationship between S_r and V_{oc} . The absence of a suitable model seriously limits our ability to scrutinize and understand charge recombination and interfacial charge-transfer phenomena in PEC systems. As shown in Fig. 1, processes 3 and 4 represent two parallel recombination pathways. Because a low concentration of oxidized species is commonly used in n-type semiconductor PEC cells, the rate of recombination via redox species in solution can be much smaller than that from surface recombination. In such a case, process 4 becomes the controlling factor in determining V_{oc} . In fact, studies of n-GaAs/liquid junction cells indicate that V_{oc} is dominated by surface recombination.^{12,13,20-22} To understand this phenomenon in more detail, we have developed a simple, quantitative relation between V_{oc} and S_r .

The surface recombination current (J_{sr}) for process 4 under steady-state conditions is given by the Shockley-Read-Hall formula^{16,19}

where

$$n_s = N_c \exp(-q(\phi_b - V_s)/kT) \quad [5]$$

and

$$p_s = N_v \exp(-(E_G - q\phi_b)/kT)$$

are the respective densities of electrons and holes at the interface. n_i is the intrinsic carrier concentration of the semiconductor, N_{st} is the recombination center density per unit area in the surface region, N_v is the effective density of states of the semiconductor valence band, v_{th} is the thermal velocity of the carriers, σ_n and σ_p are the respective capture cross sections for electrons and holes, E_i is the intrinsic Fermi level, and E_t is the energy level of the recombination centers. Assuming $\sigma_n = \sigma_p = \sigma_s$ and $n_s p_s \gg n_i^2$, Eq. 4 simplifies to

$$J_{sr} = q S_r \frac{n_s p_s}{n_s + p_s} \quad [6]$$

where

$$S_r = \frac{v_{th} \sigma_s N_{st}}{1 + \frac{2n_i}{n_s + p_s} \cosh((E_t - E_i)/kT)} \quad [7]$$

is the experimentally measurable surface recombination velocity.^{18,19,c} Depending on the quality of the semiconductor surface and interactions of interfacial electronic states, S_r typically varies from 10^2 to 10^6 cm/s for Si-based junctions.

In previous studies,^{9,15} further simplification of Eq. 6 was typically made by assuming the inequality $p_s \ll n_s$ for n-type semiconductors. Under this condition, a low-barrier height is implied, and surface recombination centers are always occupied by electrons as a result of their high surface concentration. The surface recombination current is thus limited by hole capture, and Eq. 6 simplifies to the familiar expression: $J_{sr} = qS_r p_s$. Because p_s is determined by Eq. 5, which is independent of applied bias, the resultant J_{sr} is also independent of applied bias. Consequently, V_{oc} cannot be related to S_r under the usual assumption of $p_s \ll n_s$. In this case, V_{oc} is controlled by other recombination processes (e.g., space-charge recombination). For situations in which p_s is comparable to, or is much greater than n_s , however, the surface recombination current can be very large and dominate recombination processes. This condition applies to many semiconductor/liquid junction solar cells in which high surface barriers are employed to achieve high photoconversion efficiencies. For PEC cells with high-barrier heights, the assumption $p_s \ll n_s$ becomes invalid. Because the expression for S_r corresponding to the condition $p_s \sim n_s$ is qualitatively similar to that of $p_s \gg n_s$,^d we will focus on the latter inequality to demonstrate the concept and to gain insight into the charge-recombination phenomena. Under the condition $p_s \gg n_s$, the surface recombination current (J_{sr}) is limited by electron capture, and Eq. 6 simplifies to

$$J_{sr} = qS_r n_s = qS_r N_c e^{-(q\phi_b/kT)} e^{(qV_s/kT)} = J_{sr0} e^{(qV_s/kT)} \quad [8]$$

where J_{sr0} is the saturation current for surface recombination. As in the case of Eq. 2 and 3, a diode quality factor n is introduced in Eq. 8. When the dominant charge transport/recombination mechanism is surface recombination, J_{sr0} can be substituted for J_0 in Eq. 1 to yield the surface-recombination-limited open-circuit photovoltage

$$V_{oc} = n \left(\phi_b - \frac{kT}{q} \ln \frac{qS_r N_c}{J_{ph}} \right) \quad [9]$$

An analogous expression to Eq. 9 can be written for p-type semiconductor/liquid junctions by substituting N_v for N_c . Equation 9 relates the open-circuit photovoltage, the interfacial barrier height, and the surface recombination velocity. Moreover, all of the parameters in Eq. 9 are independently measurable quantities. More complex treatments of surface recombination⁸⁻¹¹ involve several adjustable parameters, making it difficult to compare directly the simulated and experimental results and to extract useful information from experimental observables.

Equation 9 can be used to estimate S_r under steady-state conditions. If it can be established that the open-circuit photovoltage is controlled by surface recombination, S_r can be deduced from measurements of V_{oc} at room temperature and ϕ_b . The surface-barrier height can be determined from capacitance-voltage measurements (Mott-Schottky plot) or from the temperature dependence of V_{oc} . This method of

^c To be precise, an integration of contributions from all energy levels within the semiconductor bandgap should be used in Eq. 4 and 7. For clarity reasons, we did not use the integration notation. The readers can verify that incorporation of the integration would not affect the result. Most information on trap locations and their capture cross sections is lost when a single S_r value is used in the place of the more complete set of parameters (E_t , σ , N_t). However, the knowledge of S_r , which by itself is an experimentally measurable quantity, is often sufficient to provide a quantitative description for most device applications.

^d For the intermediate situations $p_s \sim n_s$, Eq. 6 must be used without further simplifications. Under open-circuit conditions ($V = V_{oc}$), the photogenerated current J_{ph} equals the recombination current J_{sr} (Eq. 5 and 6). V_{oc} is then given by an equation similar to Eq. 9: $V_{oc} = \phi_b - (kT/q) \ln (qS_r N_c / J_{ph})$, where $S_r = S_r - (J_{ph}/qN_v) \exp[(E_G - q\phi_b)/kT]$.

estimating S_r circumvents certain ambiguities inherent in other techniques in which the theoretical conditions are not always experimentally verifiable. For example, measurements of S_r by transient photoconductivity or photoluminescence require a flatband condition in which band bending is supposedly eliminated by illuminating the semiconductor with intense light. Unfortunately, high-intensity illumination can often promote surface decomposition. If some band bending is still present, then only an effective surface recombination velocity is obtained. For instance, 60 mV of residual band bending will lead to one order of magnitude uncertainty in S_r .²⁴ Provided the barrier height is sufficiently high to satisfy the condition that $p_s \gg n_s$, the S_r value determined from Eq. 9 corresponds to the intrinsic surface recombination velocity.

Experimental

n-Type [100] oriented Si wafers (resistivity 2 to 4 $\Omega \cdot \text{cm}$) were cut into 5 to 6 mm square plates. Electrical contacts were made on the back surface with an indium-gallium eutectic. The back contact and edges of the crystal were sealed with Torr-Seal[®] epoxy. Prior to immersion into the electrolyte, the electrodes were subject to two 30 s etches in HF solution (49% by weight), rinsed with distilled water, and then dried under an N_2 stream. The redox electrolyte was prepared with reagent-grade chemicals. The supporting electrolyte, LiClO_4 , was dried by heating under vacuum at 170° for 4 h prior to use. Acetone was dried over an activated molecular sieve. FeCp_2 was used as received. The oxidized species (FeCp_2^+) was generated by electrolysis in a two-compartment cell consisting of a reticulated vitreous carbon electrode (40 pores/cm; Electrosynthesis Co.), a Pt mesh counterelectrode, and an Ag wire quasi-reference electrode. Photoelectrochemical measurements were performed with a two-electrode one-compartment cell containing a Pt foil counterelectrode (10 cm^2). Typically, solutions used in this study consisted of FeCp_2 (75 mM) and LiClO_4 (1.0M) in acetone. Except for the study of the dependence of V_{oc} on the concentration of FeCp_2^+ , no intentional FeCp_2^+ was added to the solution; FeCp_2^+ generated *in situ* at the n-Si electrode during the initial stage of the experiment was found to be sufficient to maintain the stable performance of the PEC cell. The solutions were rigorously stirred in all experiments. The cell temperature was controlled by a circulating bath using methanol as the working medium and was measured with an Si diode sensor connected to a Scientific Instrument (Model 9620) temperature controller. An Oriel 250 W tungsten-halogen lamp fitted with a water jacket was used as the light source. The stability of the photocurrent and photovoltage over the period of measurement indicates the absence of significant photodegradation of the Si electrodes.

Results and Discussion

The diode quality factor n was obtained from a plot of V_{oc} vs. $\log(J_{sc})$ (Fig. 2), which was linear over the voltage range

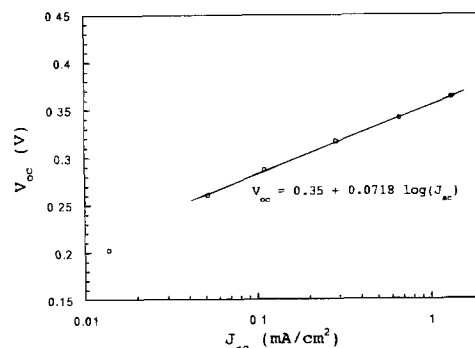


Fig. 2. Open-circuit photovoltage V_{oc} at room temperature as a function of short-circuit photocurrent density J_{sc} for n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 system.

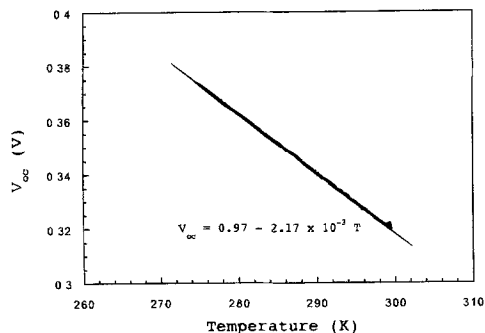


Fig. 3. Open-circuit photovoltage V_{oc} as a function of temperature of n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 system. The experiment was performed at reduced light intensity (0.5 mW/cm^2). The short-circuit photocurrent was 0.2 mA/cm^2 in the temperature range investigated.

of 0.30 to 0.38 V. With the aid of Eq. 1, a diode quality factor of 1.20 was evaluated. Higher n values were obtained at lower light intensities (or lower V_{oc}) because of the increased contribution from space-charge recombination. Measurements were thus confined to the voltage range of 0.30 to 0.38 V, and an n value of 1.20 was used in assessing recombination processes.

Figure 3 displays a plot of V_{oc} vs. temperature at low light intensity (0.5 mW/cm^2). At this illumination level, a V_{oc} of 0.32 V and a J_{sc} of 0.20 mA/cm^2 were obtained at room temperature. As the temperature declined from 300 to 275 K, V_{oc} increased linearly as expected from Eq. 9; J_{sc} , on the other hand, was unchanged¹ (variation less than 2%). Because of the limited solubility of the redox species and the supporting electrolyte, measurements were restricted to this temperature range. To reduce the measurement uncertainty in the narrow temperature range available, we accumulated data with improved statistics. The data shown in Fig. 3 consist of more than 300 points. Each V_{oc} value is an average of 10 measurements and has an uncertainty of less than $\pm 1 \text{ mV}$. The accuracy of the relative temperature measurement is less than $\pm 0.1 \text{ K}$. The cooling rate was typically 0.5 K/min . The reproducibility of the data is reflected by the observation that V_{oc} vs. T plots measured during the cool-down and the warm-up processes were identical. Similar V_{oc} vs. T measurements were made on Au/n-Si Schottky diodes using the same Si wafers over the same temperature range. Using Eq. 1 and the thermionic emission equation (Eq. 2), we obtained an effective Richardson constant of 2.5 for the Schottky diodes, in good agreement with the theoretical value,¹⁶ indicating that the V_{oc} vs. T data provide reliable information.

The V_{oc} vs. T data in Fig. 3 can be fitted with an expression for a straight line: $V_{oc} = 0.97 - 0.00217 T$. The intercept of the plot ($V_{oc}^{\text{intercept}} = 0.97 \text{ V}$) is 0.15 V smaller than E_c/q of silicon (bandgap of Si is 1.12 eV) at room temperature, implying that V_{oc} is not bulk-recombination limited. For comparison, the V_{oc} vs. T plot for n-Si/methanol junction cells yields a $V_{oc}^{\text{intercept}}$ value of 1.17 V.^{6,23} In the case of the Si crystals used in our experiments (resistivity 2 to $4 \Omega \cdot \text{cm}$, minority-carrier diffusion length $> 100 \mu\text{m}$), the room temperature bulk-recombination-limited V_{oc} (V_{oc}^{max})⁵ is calculated to be at least 0.44 V at a photocurrent density level of 0.2 mA/cm^2 . V_{oc}^{max} is much larger than the experimentally observed value of 0.32 V for the Si/acetone junction at room temperature. The discrepancies between the observed values ($V_{oc} = 0.32 \text{ V}$, $V_{oc}^{\text{intercept}} = 0.97$) and those predicted by bulk-recombination-limited V_{oc} ($V_{oc}^{\text{max}} > 0.44 \text{ V}$, $V_{oc}^{\text{intercept}} = E_c/q > 1.12 \text{ V}$) rule out the possibility that bulk diffusion/recombination is rate limiting.

The possibility that thermionic emission is the dominant process in determining V_{oc} can also be excluded. The thermionic emission controlled V_{oc} is given by

$$V_{oc} = n \left(\phi_b - \frac{kT}{q} \ln \frac{A^* T^2}{J_{ph}} \right) \quad [10]$$

Using the effective Richardson constant for n-Si(100), $A^* = 300 \text{ A/cm}^2/\text{K}^2$, $n = 1.20$, and $J_{ph} = 0.2 \text{ mA/cm}^2$ for the temperature range of 275 to 300 K, the expected value of the slope of the V_{oc} vs. T plot, based on Eq. 10, is 2.65 mV/K , which is substantially larger than the experimentally observed slope of $2.17 \pm 0.01 \text{ mV/K}$ (Fig. 3), implying that thermionic emission does not significantly affect V_{oc} .

Figure 4 shows the dependence of V_{oc} on the concentration of FeCp_2^+ . The FeCp_2 concentration was held constant at 75 mM , and the light intensity was adjusted to maintain a constant J_{sc} of 0.3 mA/cm^2 . Over a two-decade concentration range of FeCp_2^+ , from 0.003 to 0.3 mM , V_{oc} varied logarithmically with the concentration of FeCp_2^+ . Significantly, the slope of the plot equaled 34 mV/decade . If recombination in solution were the principal pathway and ϕ_b were independent of the concentration of FeCp_2^+ (i.e., bandedges varied with $[\text{FeCp}_2^+]$; Fermi-level pinning occurred), then Eq. 1 and 3 would predict that V_{oc} should decrease by at least 60 mV for a ten-fold increase in the concentration of FeCp_2^+ . The data of Fig. 4 is inconsistent with this expectation. Also, even if ϕ_b varied with the concentration of FeCp_2^+ (i.e., bandedges were fixed; no Fermi-level pinning occurred), V_{oc} would still remain invariant with increasing concentration of FeCp_2^+ ²⁶ because the increase in FeCp_2^+ concentration is offset by a corresponding decrease in the surface electron concentration (n_s) due to an increased barrier height. The fact that a 34 mV/decade increase in V_{oc} was observed with increasing concentration of FeCp_2^+ clearly indicates that the Fermi level at the semiconductor/liquid interface is not pinned and that recombination via redox species is not the dominant process in controlling V_{oc} .

The explanation most consistent with the data is that surface states control the recombination current. Using $n = 1.20$ and Eq. 9, the data of Fig. 3 yield a surface barrier height of 0.81 V, in close agreement with the observation of others (0.83 V).²⁷ Substituting $\phi_b = 0.81 \text{ eV}$ and $V_{oc} = 0.32 \text{ V}$ (at 299 K) into Eq. 9 yields an S_r of $6 \times 10^4 \text{ cm/s}$, which concurs with values measured for the n-Si/air interface.²³ Although steady-state measurements of S_r at semiconductor/liquid junctions have been scarce, a maximum surface recombination velocity of $5 \times 10^5 \text{ cm/s}$ has been reported for the n-Si/methanol junction.¹⁵

For Eq. 9 to be valid for n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 , it is important to establish that $n_s \ll p_s$. Figure 1 can be used to compare the energy differences between the bandedges and quasi-Fermi levels of electrons and holes. The closer the quasi-Fermi level is to the respective bandedge, the higher the concentration of corresponding charge carriers. For a barrier height of 0.81 eV, the energy difference between the valence-band maximum (VBM) and the hole quasi-Fermi level (E_{Fp}) is ($E_G - q\phi_b = 0.31 \text{ eV}$ (Fig. 1)). For a V_{oc} of less than 0.4 V, the energy difference between the

⁶ The experimental V_{oc} vs. T data set in Fig. 3, which consists of 300 data points, have a correlation coefficient of > 0.999 . The standard error of the slope is calculated to be 0.005 mV/K , corresponding to an uncertainty of $\pm 0.01 \text{ mV/K}$ at a 95% confidence level.

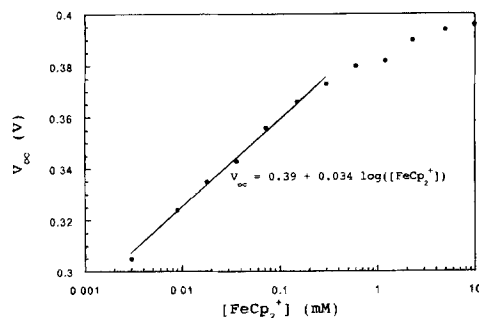


Fig. 4. Open-circuit photovoltage V_{oc} as a function of the FeCp_2^+ concentration of n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 system. The FeCp_2 and LiClO_4 concentrations were kept at 75 mM and 1 M , respectively. The short-circuit photocurrent was maintained at 0.3 mA/cm^2 .

conduction-band minimum and the electron quasi-Fermi level (E_{Fn}) is at least $q\phi_s - V_{oc} = 0.41$ eV, which is larger than the difference between VBM and E_{Fp} . With the assistance of Eq. 5, this implies that the concentration of electrons at the surface is at least one-order of magnitude lower than that of holes. The inequality $n_s \ll p_s$ is thus valid, and the surface recombination current is rate-limited by electron capture.

The possibility that charge recombination via surface states plays a dominant role in other PEC systems^{21,25,28} was also explored. Photoluminescence time-decay measurements²² indicate that chemisorption of Ru ions on the surface of n-GaAs reduces S_r from 5×10^5 to 3.5×10^4 cm/s. This reduction in S_r is accompanied by a 90 mV improvement in V_{oc} .¹² Using the relative change in S_r reported for n-GaAs, Eq. 9 predicts an increase in V_{oc} of 90 mV assuming a diode quality factor of 1.3, which is a typical value for majority-carrier semiconductor/liquid junction devices.²⁹ The quantitative agreement of these results gives credence to the use of Eq. 9 to describe the effect of surface recombination on V_{oc} .

Although it has been established that recombination in the bulk semiconductor is the dominant process at room temperature for the n-Si/methanol- $\text{Me}_2\text{Fc}^{+/0}$ - LiClO_4 junction,⁶ the recombination mechanism at low temperature is still controversial.^{25,28} It has been reported²⁸ that the V_{oc} vs. T plot for n-Si/methanol- $\text{Me}_2\text{Fc}^{+/0}$ - LiClO_4 indicates a temperature-dependent charge-transport mechanism. In the temperature range of -20 to 20°C , the plot yielded a $V_{oc}^{\text{intercept}}$ that was close to the bandgap of Si, implying that bulk recombination is the dominant recombination process. At temperatures below -20°C , however, the V_{oc} vs. T data yielded a $V_{oc}^{\text{intercept}}$ of 1.0 eV, suggesting that majority-carrier transport is important.²⁸ The low-temperature result was interpreted using a modified thermionic emission theory in which a very small electron-transfer probability ($P = 0.01$) was assumed to account for the shallow slope of the V_{oc} vs. T curve. A surface-recombination-limited V_{oc} offers an alternative explanation to this result, without the necessity of invoking an extremely small electron-transfer probability. When Eq. 9 is applied to the low-temperature result, an S_r of 10^5 cm/s is obtained, which is consistent with experimental measurements of others.¹⁵

Charge recombination by means of consecutive oxidation and reduction of solution species (process 3 in Fig. 1) provides a parallel path to surface recombination (process 4 in Fig. 1). Taking into consideration that the rate of surface recombination exceeds the rate of recombination in solution ($qk_c c_{ox} n_s < qS_r n_s$) up to a FeCp_2^+ concentration of at least 0.5 mM, we can estimate the upper limit of the electron-transfer rate from the Si conduction band to FeCp_2^+ solution. Substituting $c_{ox} = 0.5$ mM and $S_r = 6 \times 10^4$ cm/s into the inequality $qk_c c_{ox} n_s < qS_r n_s$, we obtain $k_c < 2 \times 10^{-13}$ cm⁴/s. This estimation is close to the rate constant reported for the GaAs/liquid junction cell ($k_c = 2.3 \times 10^{-12}$ cm⁴/s),³⁴ considering the wide scattering of k_c values (over seven orders of magnitude) reported in the literature.^{30,31}

It has been suggested that competition between hole transfer to reduced species in solution and hole trapping by surface states is important for determining the efficiency of PEC cells.^{32,33} Although such competition is crucial when the system is operated away from open circuit, thereby affecting the shape of the J - V curve and the fill factor, it is not important under open-circuit conditions for the systems (narrow bandgap semiconductors with a high interface barrier) that are discussed in this paper. Because the concentration of holes at the semiconductor surface is much greater than the concentration of electrons, recombination via surface states is limited by the rate of electron capture. Since surface recombination centers are always occupied by holes at open circuit under steady state, the rate of hole capture is not rate limiting in the surface recombination process and does not affect V_{oc} . Furthermore, increased rates of hole transfer to reduced species in solution must be accompanied by increased rates of electron transfer to oxi-

dized species to maintain open-circuit conditions, and cannot therefore explain the improved V_{oc} observed at the Ru-treated n-GaAs/liquid junction.

An exact determination of the surface recombination current is complicated. The energy distribution of recombination centers within the bandgap and their capture cross sections for electrons and holes must be known for each individual interface system. Much work has been carried out to obtain this information for the SiO_2/Si interface, which is of technological importance. In contrast, this type of information is nonexistent for Si/liquid interfaces. Furthermore, even for SiO_2/Si , simplifications of the original Shockley-Read-Hall formula (Eq. 4) were often made by neglecting the energy distribution of recombination centers and differences in capture cross sections, without sacrificing the usefulness of the formula in evaluating surface recombination processes in practical semiconductor devices.³⁴ The success of Eq. 9 in explaining the data for the n-Si/acetone and n-GaAs/liquid junction cells indicates that the simplifications that were made in deriving Eq. 9 do not significantly affect the final results.

In summary, we have derived a simple, quantitative relationship between the surface recombination velocity and the open-circuit photovoltage of semiconductor/liquid junction solar cells. Experimental studies of the n-Si/acetone- $\text{FeCp}_2^{+/0}$ - LiClO_4 junction indicate that surface recombination mediated by surface states is the dominant process that determines V_{oc} . The V_{oc} - S_r expression yields values of the barrier height and the surface recombination velocity that are in good agreement with published data. The application of the surface-recombination-limited V_{oc} analysis to other semiconductor/liquid junction cells suggests that Eq. 9 may be useful in evaluating the charge-transport/recombination mechanisms of other PEC systems.

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Theory of Thermocells

Transported Entropies, and Heat of Transfer in Sulfate Mixtures

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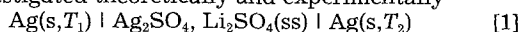
ABSTRACT

The transported entropy of silver ion, $S_{Ag^+}^*$, and the heat of transfer, q_2^* for Ag_2SO_4 , have been calculated from electromotive force (EMF) measurements in the cell $Ag(T_1) | Ag_2SO_4-Li_2SO_4 | Ag(T_2)$. Results give $S_{Ag^+}^* = 102 \pm 6 \text{ JK}^{-1} \text{ mol}^{-1}$ when $0.1 < x_{Ag_2SO_4}$. From this we derive $S_4^{2-} = 220 \text{ JK}^{-1} \text{ mol}^{-1}$ in pure silver sulfate and $S_{Li^+} = 54 \text{ JK}^{-1} \text{ mol}^{-1}$ in lithium-silver sulfate mixtures. For smaller mole fractions of Ag_2SO_4 , $S_{Ag^+}^*$ increases. The heat of transfer, q_2^* , is negative and varies with composition. The sign indicates that Ag_2SO_4 is enriched on the hot side. The Thomson coefficient for molten pure $AgSO_4$ is $\tau_{Ag^+} = 30 \text{ JK}^{-1} \text{ mol}^{-1}$. From this we derive $\tau_{SO_4^{2-}} = 140 \text{ JK}^{-1} \text{ mol}^{-1}$. Kinetic and thermodynamic models for the transported entropy and heat of transfer are discussed. Some models can be rejected.

Knowledge about transported entropies,^a S^* , and heats of transfer, q^* , is important for calculation of local heat effects in electrolysis cells,^{1,2} fuel cells,^{3,4} and thermoelectric generators. These parameters can be obtained from measurements of EMFs of thermocells; thermoelectric powers.¹ Data of S^* and q^* are scarce in the literature. Transported entropies are reported, but mainly for single salts.⁵⁻¹⁰ Some transported entropies on mixtures have been reported by Richter and coworkers^{11,12} and by Grimstvedt.¹³

Kinetic as well as thermodynamic interpretations of S^* and q^* exist. For a pure salt, Pitzer¹⁴ related the transported entropy of an ion to its thermodynamic entropy. Rice and Roth¹⁵ related the thermoelectric power (*i.e.*, S^*) to the activation energy of electric conductivity of the solid-state conductor. Payton and Fuller¹⁶ did the same with q^* for aqueous solutions. Haase¹⁷ and Kempers¹⁸ related the heat of transfer to the partial molar enthalpies in a liquid mixture. Howard and Lidiard¹⁹ and later Agar²⁰ related thermoelectric power to heats of transfer of vacancies and interstitial ions in a solid.

The main purpose of this work is to contribute to the understanding of transported entropies and the heat of transfer in electrochemical systems. The following cell has been investigated theoretically and experimentally



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^a The name "transported entropy" is commonly used in the literature. It relates to heat production or consumption in various parts of a system, and a more appropriate name on a phenomenological basis is therefore "entropy of transfer."

The solid solution (ss) was chosen because thermodynamic entropies, transference numbers, and specific conductivity of the system are known.²¹⁻²³ This allows for a discussion of the mechanism of heat transport. We shall see that neither of the existing models proves satisfactory for our system. New experiments are therefore suggested to reveal further the properties of S^* and q^* .

Another advantage of the chosen system is that interdiffusion is rapid. Thus one can easily prepare a homogeneous solid solution by annealing the mixture. Mixtures of Ag_2SO_4 and $Li_2SO_4(ss)$ have different high-temperature solid phases.^{21,24} We consider here the Li-rich phase in the solid state and molten and solid Ag_2SO_4 .

The transported entropy has been reported for pure molten and solid Ag_2SO_4 .⁹ Transported entropy of silver and heats of transfer for the mixture are not known from thermoelectric power studies, but thermal diffusion studies have been performed by Lunden and Olsson.²⁵ Consistency checks on our experimental results are thus possible.

Principles

Flux equations.—Our theoretical derivations follow from Førland *et al.*¹ We denote Li_2SO_4 as component 1 and Ag_2SO_4 as component 2. The symbol x_i is used for mole fraction, and S_i for partial molar entropy.

In cell 1 there are five forces; $-\nabla \ln T$, $-\nabla \mu_{1,T}$, $-\nabla \mu_{2,T}$, $-\nabla \mu_{Ag,T}$ and $-\nabla \phi$. Here T is the absolute temperature, $\mu_{i,T}$ is the chemical potential at constant T , and $\Delta \phi$ is the electric potential measured with $Ag | Ag^+$ electrodes. The fluxes are J_q (heat flux), J_1 , J_2 , J_{Ag} (mass fluxes), and j (electric current