The Electrochemical Impedance of One-Equivalent Electrode Processes at Dark Semiconductor|Redox Electrodes Involving Charge Transfer through Surface States. 1. Theory

Z. Hens*

Universiteit Gent, Laboratorium voor Fysische Chemie, Krijgslaan 281, B-9000 Gent, Belgium

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Electrode processes at redox electrodes consist of mass transport to and from the electrode|electrolyte interface and of charge transfer across this interface. At n-type semiconductor electrodes, charge transfer may involve either direct exchange of conduction band electrons or direct exchange of valence band holes, accompanied by an electron-hole recombination step, or surface-state mediated transfer of conduction band electrons. In this paper, the electrochemical impedance of the dark n-type semiconductor|redox electrode is derived, taking into account both mass transport and charge transfer through surface states. The impedance expression obtained leads to a novel equivalent circuit. More limited calculations, previously published in the literature, are comprised in the treatment as special cases. Finally, it is shown how the impedance expression obtained may be also used to describe reactions involving direct exchange of majority charge carriers or direct injection of minority charge carriers followed by a recombination step.

1. Introduction

An overall electrochemical process at a redox electrode generally consists of the transport of electroactive species to and from the electrode|electrolyte interface and of the transfer of charge across this interface.[1−3] Usually, charge transfer at the interface means exchange of electrons. When working with a supporting electrolyte, the transport of mass occurs by diffusion.[3,4]

For the exchange of electrons between a semiconductor and an electroactive species in solution, three different reaction paths are possible. First of all, reactions may proceed directly via the conduction band (1) or the valence band (2) of the semiconductor. The first case is described as direct injection or capture of conduction-band electrons, whereas the second one may be considered as direct capture or injection of valence-band holes.[5,6] Next, surface states with energy levels in the band gap of the semiconductor (3) may be involved in charge exchange.[5−7] These surface states, for example, consist of intrinsic levels, defects, or adsorption-type states.[6,7]

Almost 30 years ago, Gomes et al.[8] and Tyagai et al.[9] used the fact that different electron exchange mechanisms may lead to a different response of the electrode to a small-signal sinusoidal perturbation of the applied potential to study electrochemical reaction mechanisms at ZnO, CdS, and CdSe electrodes. Since then, the relation between the nature of the charge transfer and the electrochemical impedance behavior of a semiconductor electrode has been widely studied, both experimentally and theoretically (for a review, see ref 10). Especially the impedance due to a recombination step in the reaction mechanism has received much attention.[11−15] In this way, electrochemical impedance spectroscopy (EIS) has become a powerful tool to determine the charge-transfer mechanism at semiconductor electrodes.

On the other hand, the influence of diffusion on the electrochemical impedance of semiconductor electrodes was discussed only recently.[16,17] The diffusion component of the impedance of the overall electrochemical process was shown to be determined by the charge-transfer mechanism.[16] Hence, both the charge-transfer part and the diffusion part of the electrochemical impedance contain information about the nature of the charge transfer at semiconductor|redox electrolyte systems.

In this paper, we bring both aspects of the overall electrode process together. First, a general expression for the electrochemical impedance of a one-equivalent charge-transfer reaction at a dark n-type semiconductor electrode is derived, taking into account both charge transfer and mass transport. The calculations are based upon treatments presented recently in the literature,[7,16−18] highlighting either the influence of mass transport or of charge transfer on the electrochemical impedance. Next, the general impedance expression obtained is applied to surface-state mediated exchange of conduction-band electrons.[26] This leads to an equivalent circuit for this reaction type, valid if the capacitance of the semiconductor side of the interface is much smaller than the capacitance of the Helmholtz layer.

In the discussion section, it is shown first of all that the expression obtained is a generalization of previously published impedance expressions describing charge transfer through surface states. Moreover, the use of the general impedance formula derived is not limited to surface-state mediated electron transfer. It may be applied directly to direct exchange of majority charge carriers. Under certain conditions, the formalism proposed is even valid for reactions involving injection of minority charge carriers, followed by a recombination step at the semiconductor surface. In this way, the treatment presented here yields a general impedance expression describing one-equivalent charge-transfer reactions at dark semiconductor electrodes, including mass transport.

One-Equivalent Electrode Processes. 1

J. Phys. Chem. B, Vol. 103, No. 1, 1999 **123**
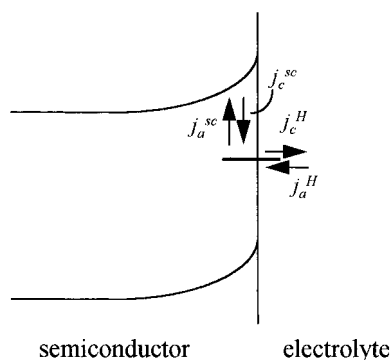
Figure 1. Diagram showing the relevant current densities in the case of surface-state mediated electron transfer.

2. General Electrochemical Impedance of a Dark Semiconductor|Redox Electrode

2.1. Basic Assumptions of the Impedance Calculation. All calculations are performed, considering an n-type semiconductor electrode in contact with supporting electrolyte. Replacing electrons by holes and vica versa, it is possible to describe p-type electrodes using the same formalism.

A potential drop ϕ across the semiconductor/electrolyte interface is assumed to consist of two parts,[27] i.e., a potential drop ϕ_{sc} between the bulk of the semiconductor and the semiconductor surface on the one hand and a potential drop ϕ_H between the semiconductor surface and the bulk electrolyte, i.e. the potential drop across the Helmholtz layer, on the other hand. If a depletion layer exists at the semiconductor side of the interface, the differential capacitance of this part of the interface (C_{sc}) is given, most simply, by the Mott–Schottky relation.[5] To describe the differential capacitance of the Helmholtz layer at the electrolyte side of the interface, no theoretical expression exists. Experimental data indicate that in the case of semiconductors, the value of this capacitance ranges roughly between 4 and 7 μF cm^{-2}.[19-21]

At the semiconductor surface, surface states may mediate charge transfer. We describe these states by their density s (cm^{-2}) and their occupancy θ. Thus, at n-type electrodes, the number of surface states occupied by electrons equals $s\theta$ per cm^2. We consider all surface states to be equal (monoenergetic), their density being constant. Hence, the possibility that the electrode process induces surface states is not taken into account. It is assumed that exchange of electrons may occur between the surface states and both the conduction band of the semiconductor and the electroactive species in solution (cfr. Figure 1). In principle, this implies that the impedance calculated applies neither to reactions involving direct exchange of conduction band electrons nor of valence band holes. In the discussion part, it will be shown how the results may yet be applied to these transfer mechanisms.

Net transfer of charge across the interface means current flow. Anodic and cathodic electrical current densities related to charge transfer will be denoted as j_a^{sc} and j_c^{sc}, respectively, at the semiconductor side and j_a^H and j_c^H, respectively, at the electrolyte side of the interface.[28] This distinction is important since only if majority charge carriers are exchanged directly the current densities at both sides of the interface are equal under both dc and ac conditions.[7] We assume that these four different current densities may be a function of the potential drop across the semiconductor, of that across the Helmholtz layer, of the concentration of reducing or oxidizing agent at the interface,

and of the occupancy of the surface states at the semiconductor surface.

The concentrations of oxidizing and reducing agent at the semiconductor/electrolyte interface will be denoted by c_{ox} and c_{red}, respectively.

2.2. Calculation of the Electrochemical Impedance. *2.2.1. Starting Equations of the Calculation.* The calculation of the electrochemical impedance follows the lines of several theoretical treatments presented recently in the literature.[7,16-18] In refs 7 and 18, the total, time dependent current density through the electrochemical cell is written in two ways. At the semiconductor side of the interface, this current density equals the sum of a faradaic component and a part caused by the charging/discharging of the semiconductor side of the interface. Analogously, the current density at the electrolyte side of the interface consists of a faradaic component and a part caused by the charging/discharging of the Helmholtz layer:[29]

$$j = j_a^{sc} + j_c^{sc} + C_{sc}\frac{d\phi_{sc}}{dt} = j_a^H + j_c^H + C_H\frac{d\phi_H}{dt} \quad (1)$$

In this paper, the current densities at the electrolyte side of the interface will be used to calculate the impedance. This simplifies the incorporation of mass transport in the formalism considerably.

If, in addition to a dc potential, a small-signal sinusoidally varying potential perturbation with frequency $\omega/2\pi$ is applied across the interface, the amplitude of the resulting variation of the current density may be written as the complex quantity[30] ($i = \sqrt{-1}$):

$$\tilde{j} = \tilde{j}_a^H + \tilde{j}_c^H + i\omega C_H\tilde{\phi}_H \quad (2)$$

To keep the forthcoming formulas more transparent, the sums $j_a^H + j_c^H$ and $j_a^{sc} + j_c^{sc}$ will be written as j^H and j^{sc} respectively.

The electrochemical impedance is the inverse of the electrochemical admittance. The admittance $Y(\omega)$ itself is defined as the ratio:

$$Y(\omega) = \frac{\tilde{j}}{\tilde{\phi}} = \frac{\tilde{j}^H}{\tilde{\phi}} + i\omega C_H\frac{\tilde{\phi}_H}{\tilde{\phi}} \quad (3)$$

By assumption, the current densities may depend on the potential drop across the semiconductor and the electrolyte side of the interface, the concentration of oxidizing, and reducing agent at the interface and the occupancy of the surface states at the electrode surface. This makes it possible to write the admittance as[31]

$$Y(\omega) = i\omega C_H\frac{\tilde{\phi}_H}{\tilde{\phi}} + \frac{\partial j^H}{\partial \phi_H}\frac{\tilde{\phi}_H}{\tilde{\phi}} + \frac{\partial j^H}{\partial \phi_{sc}}\frac{\tilde{\phi}_{sc}}{\tilde{\phi}} + \frac{\partial j^H}{\partial c_{red}}\frac{\tilde{c}_{red}}{\tilde{\phi}} + \frac{\partial j^H}{\partial c_{ox}}\frac{\tilde{c}_{ox}}{\tilde{\phi}} + \frac{\partial j^H}{\partial \theta}\frac{\tilde{\theta}}{\tilde{\phi}} \quad (4)$$

This formula indicates that the five transfer functions $\tilde{\phi}_H/\tilde{\phi}$, $\tilde{\phi}_{sc}/\tilde{\phi}$, $\tilde{c}_{red}/\tilde{\phi}$, $\tilde{c}_{ox}/\tilde{\phi}$, and $\tilde{\theta}/\tilde{\phi}$ must be known to calculate the admittance $Y(\omega)$. Hence, five independent equations are needed to obtain an expression for the electrochemical impedance.

A first relation originates from the fact that, by assumption, an applied potential perturbation across the interface results in

a variation of the potential drop across both the semiconductor and the Helmholtz layer. This means

$$\tilde{\phi} = \tilde{\phi}_{sc} + \tilde{\phi}_H \tag{5}$$

Next, it is shown in ref 7 that the potential variation across the Helmholtz layer may be written as

$$\tilde{\phi}_H = (1 - \gamma)\tilde{\phi} - \gamma_s \frac{k_B T}{e} \tilde{\theta} \tag{6}$$

In this equation, γ stands for the ratio $C_H/(C_{sc} + C_H)$; γ_s equals $(e^2/k_B T)s/(C_{sc} + C_H)$ whereas k_B represents the Boltzmann constant, T the temperature, and e the elementary electrical charge. The equation indicates that the variation of the potential drop across the Helmholtz layer is the sum of two parts. The first component is simply due to the Helmholtz layer taking part in the capacitance of the interface. The second component describes the influence of a changing occupancy of the surface states on the potential drop across the Helmholtz layer.

To calculate all five transfer functions mentioned, these two equations found in the literature must be completed by three others.

2.2.2. Transfer Functions $\tilde{c}_{red}/\tilde{\phi}$ and $\tilde{c}_{ox}/\tilde{\phi}$. These transfer functions may be calculated along the lines presented in a previous paper.[17] At the interface, a balance exists for every dissolved species S between the reaction rate R^S, the local production rate G^S, and the supply or removal of the species by diffusion J^S. Locating the interface at $x = 0$ this balance becomes, in terms of the small-signal variations of these quantities:[16]

$$\tilde{G}^S|_{x=0} = \tilde{R}^S|_{x=0} + \tilde{J}^S|_{x=0} \tag{7}$$

The relation between the small-signal variation of the diffusion flux of species S and its concentration at the interface equals[16]
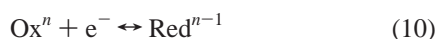
$$\tilde{J}^S|_{x=0} = d(\omega)\tilde{c}^S \tag{8}$$

For diffusion over a finite diffusion length δ with constant bulk concentration, e.g., imposed by rotating a disk electrode, the transfer function $d(\omega)$ was shown to be[16]

$$d(\omega) = \sqrt{i\omega D}\coth\left(\delta\sqrt{\frac{i\omega}{D}}\right) \tag{9}$$

In this equation, D stands for the diffusion coefficient of the electroactive species considered.

Consider now a one-equivalent charge-transfer reaction.

$$Ox^n + e^- \leftrightarrow Red^{n-1} \tag{10}$$

For both the oxidizing and the reducing agent a balance exists at the interface, expressed by eq 7. Furthermore, the reaction rate of the oxidizing agent equals the production rate of the reducing agent and vica versa. Assuming the diffusion coefficient of both species to be equal, this yields[17]

$$\frac{1}{e}\tilde{j}_a^H = -\frac{1}{e}\tilde{j}_c^H + d(\omega)\tilde{c}_{ox}$$

$$-\frac{1}{e}\tilde{j}_c^H = \frac{1}{e}\tilde{j}_a^H + d(\omega)\tilde{c}_{red} \tag{11}$$

Dividing both equations by $\tilde{\phi}$ and using eq 3 and 4, the transfer functions $\tilde{c}_{red}/\tilde{\phi}$ and $\tilde{c}_{ox}/\tilde{\phi}$ become[32]

$$\frac{\tilde{c}_{ox}}{\tilde{\phi}} = -\frac{\tilde{c}_{red}}{\tilde{\phi}} = \frac{\dfrac{1}{e}\dfrac{\partial j^H}{\partial \phi_{sc}}\dfrac{\tilde{\phi}_{sc}}{\tilde{\phi}} + \dfrac{1}{e}\dfrac{\partial j^H}{\partial \phi_H}\dfrac{\tilde{\phi}_H}{\tilde{\phi}} + \dfrac{1}{e}\dfrac{\partial j^H}{\partial \theta}\dfrac{\tilde{\theta}}{\tilde{\phi}}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}} \tag{12}$$

Inserting eq 12 into the admittance expression 4 yields

$$Y(\omega) = i\omega C_H \frac{\tilde{\phi}_H}{\tilde{\phi}} + A(\omega)\left(\frac{\partial j^H}{\partial \phi_H}\frac{\tilde{\phi}_H}{\tilde{\phi}} + \frac{\partial j^H}{\partial \phi_{sc}}\frac{\tilde{\phi}_{sc}}{\tilde{\phi}} + \frac{\partial j^H}{\partial \theta}\frac{\tilde{\theta}}{\tilde{\phi}}\right) \tag{13}$$

In this equation, $A(\omega)$ is defined as

$$A(\omega) = \frac{d(\omega)}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}} \tag{14}$$

2.2.3. Transfer Function $\tilde{\theta}/\tilde{\phi}$. Referring to Figure 1, the time-dependence of the surface-state occupancy θ may be written as[7]

$$\frac{d\theta}{dt} = \Theta(\theta,\phi_{sc},\phi_H,c_{ox},c_{red}) = \frac{1}{es}[(-j_c^{sc}) - j_a^{sc} + j_a^H - (-j_c^H)] \tag{15}$$

If a sinusoidal potential perturbation is applied, the small-signal variation of the occupancy thus becomes:

$$i\omega\tilde{\theta} = \frac{\partial\Theta}{\partial\theta}\tilde{\theta} + \frac{\partial\Theta}{\partial\phi_H}\tilde{\phi}_H + \frac{\partial\Theta}{\partial\phi_{sc}}\tilde{\phi}_{sc} + \frac{\partial\Theta}{\partial c_{ox}}\tilde{c}_{ox} + \frac{\partial\Theta}{\partial c_{red}}\tilde{c}_{red} \tag{16}$$

Using eqs 5 and 12, this equation yields

$$\left(i\omega - \frac{\partial\Theta}{\partial\theta}\right)\tilde{\theta} = \frac{\partial\Theta}{\partial\phi_H}\tilde{\phi}_H + \frac{\partial\Theta}{\partial\phi_{sc}}(\tilde{\phi} - \tilde{\phi}_H) + \left(\frac{\partial\Theta}{\partial c_{ox}} - \frac{\partial\Theta}{\partial c_{red}}\right) \times$$
$$\frac{\dfrac{1}{e}\dfrac{\partial j^H}{\partial\phi_{sc}}(\tilde{\phi} - \tilde{\phi}_H) + \dfrac{1}{e}\dfrac{\partial j^H}{\partial\phi_H}\tilde{\phi}_H + \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}\tilde{\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}} \tag{17}$$

Equation 6 makes it possible to eliminate the potential drop $\tilde{\phi}_H$. This results as

$$\left(i\omega - \frac{\partial\Theta}{\partial\theta}\right)\tilde{\theta} = \left((1-\gamma)\frac{\partial\Theta}{\partial\phi_H} + \gamma\frac{\partial\Theta}{\partial\phi_{sc}}\right)\tilde{\phi} -$$
$$\gamma_s\frac{k_B T}{e}\left(\frac{\partial\Theta}{\partial\phi_H} - \frac{\partial\Theta}{\partial\phi_{sc}}\right)\tilde{\theta} + \left(\frac{\partial\Theta}{\partial c_{ox}} - \frac{\partial\Theta}{\partial c_{red}}\right) \times$$
$$\frac{\left(\dfrac{1-\gamma}{e}\dfrac{\partial j^H}{\partial\phi_H} + \dfrac{\gamma}{e}\dfrac{\partial j^H}{\partial\phi_{sc}}\right)\tilde{\phi} - \left(\gamma_s\dfrac{k_B T}{e^2}\dfrac{\partial j^H}{\partial\phi_H} - \gamma_s\dfrac{k_B T}{e^2}\dfrac{\partial j^H}{\partial\phi_{sc}} - \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}\right)\tilde{\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}$$

$$\tag{18}$$

Rearranging the different terms finally yields the transfer

One-Equivalent Electrode Processes. 1

J. Phys. Chem. B, Vol. 103, No. 1, 1999 **125**

function $\tilde{\theta}/\tilde{\phi}$ as the quotient

$$
\frac{\tilde{\theta}}{\tilde{\phi}} = \left[(1 - \gamma)\frac{\partial\Theta}{\partial\phi_H} + \gamma\frac{\partial\Theta}{\partial\phi_{sc}} + \left(\frac{\partial\Theta}{\partial c_{ox}} - \frac{\partial\Theta}{\partial c_{red}}\right) \times \right.
$$

$$
\left(\frac{\dfrac{1-\gamma}{e}\dfrac{\partial j^H}{\partial\phi_H} + \dfrac{\gamma}{e}\dfrac{\partial j^H}{\partial\phi_{sc}}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}} \right) \right] \Bigg/ \left[i\omega - \frac{\partial\Theta}{\partial\theta} + \gamma_s\frac{k_BT}{e}\left(\frac{\partial\Theta}{\partial\phi_H} - \right.\right.
$$

$$
\frac{\partial\Theta}{\partial\phi_{sc}} \right) + \left(\frac{\partial\Theta}{\partial c_{ox}} - \frac{\partial\Theta}{\partial c_{red}}\right)\left(\frac{\gamma_s\dfrac{k_BT}{e^2}\dfrac{\partial j^H}{\partial\phi_H} - \gamma_s\dfrac{k_BT}{e^2}\dfrac{\partial j^H}{\partial\phi_{sc}} - \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}} \right) \right]
$$

$$(19)$$

2.2.4. General Admittance Expression. If diffusion is important, the admittance of the electrode|electrolyte interface is given in general terms by eq 13. Combining this expression with eqs 5 and 6 enables us to eliminate all unknown transfer functions except $\tilde{\theta}/\tilde{\phi}$. Doing this, the admittance becomes

$$
Y(\omega) = i\omega(1 - \gamma)C_H + A(\omega)\left(\gamma\frac{\partial j^H}{\partial\phi_{sc}} + (1 - \gamma)\frac{\partial j^H}{\partial\phi_H}\right) -
$$
$$
\left[i\omega\gamma_s\frac{k_BT}{e}C_H + A(\omega)\left(\gamma_s\frac{k_BT}{e}\frac{\partial j^H}{\partial\phi_H} - \gamma_s\frac{k_BT}{e}\frac{\partial j^H}{\partial\phi_{sc}} - \frac{\partial j^H}{\partial\theta}\right) \right]\frac{\tilde{\theta}}{\tilde{\phi}} \quad (20)
$$

Inserting eq 19 will finally result in a closed expression for the interfacial admittance $Y(\omega)$. Since no specific conditions for the current densities were assumed (except from their possibilty to depend on either of the 5 variables ϕ_H, ϕ_{sc}, θ, c_{ox}, and c_{red}), eq 20 has a general nature (within the limits of the model). Furthermore, it will be shown in the discussion section how this expression may be used to describe reactions involving direct exchange of majority charge carriers and injection of minority charge carriers. The admittance expression which applies to surface-state mediated charge transfer is obtained by inserting appropriate expressions for the four current densities involved. This is done in the next section.

3. Electrochemical Impedance for Charge Transfer through Surface States

If surface states mediate electron transfer, the charge-transfer reaction is a two-step process. At the semiconductor side of the interface, the cathodic and anodic current densities originate from the capture of a conduction band electron by an empty surface state and the excitation of an electron from an occupied surface state to the conduction band, respectively. Transfer of an electron from a surface state to an empty electronic level of the redox system in solution and vica versa corresponds to cathodic and anodic current flow through the Helmholtz layer. These four current densities may be written as

$$
j_c^{sc} = -e\beta_n n_s s(1 - \theta) \quad (21a)
$$

$$
j_c^H = -el_c s\theta c_{ox} \quad (21c)
$$

$$
j_a^{sc} = e\epsilon_n s\theta \quad (21b)
$$

$$
j_a^H = el_a s(1 - \theta)c_{red} \quad (21d)
$$

In these equations, n_s is equal to the density of conduction band electrons at the semiconductor surface whereas β_n ([cm^3 s^{-1}]) stands for the rate constant of the electron capture process. According to the notation adapted in ref 7, ϵ_n ([s^{-1}]) equals the rate constant of the electron excitation process and l_c ([cm^3 s^{-1}]) and l_a ([cm^3 s^{-1}]) denote the rate constants for cathodic and anodic charge transfer between the surface states and the energy levels in solution, respectively. Under dc conditions, the sum of the faradaic current densities at the semiconductor side of the interface is equal to that at the electrolyte side of the interface; under ac conditions, it is not.

Since the surface states act as intermediates between both sides of the interface, we assume that the current density at the semiconductor side does not depend explicitly on the potential drop across the electrolyte side of the interface and vice versa. This means that in our model, the rate constants β_n and ϵ_n are potential independent whereas the rate constants l_c and l_a only depend on the potential drop across the Helmholtz layer.[33] Consequently, the following four partial derivatives are identically equal to zero:

$$
\frac{\partial j_c^{sc}}{\partial\phi_H} \equiv \frac{\partial j_a^{sc}}{\partial\phi_H} \equiv \frac{\partial j_c^H}{\partial\phi_{sc}} \equiv \frac{\partial j_a^H}{\partial\phi_{sc}} \equiv 0 \quad (22)
$$

These identities simplify the admittance expression for surface-state mediated electron-transfer somewhat, yielding

$$
Y(\omega) = i\omega(1 - \gamma)C_H + A(\omega)(1 - \gamma)\frac{\partial j^H}{\partial\phi_H} - \left[i\omega\gamma_s\frac{k_BT}{e}C_H + \right.
$$
$$
A(\omega)\left(\gamma_s\frac{k_BT}{e}\frac{\partial j^H}{\partial\phi_H} - \frac{\partial j^H}{\partial\theta}\right) \right]\frac{\tilde{\theta}}{\tilde{\phi}} \quad (23)
$$

Nevertheless, this admittance expression remains hard to interpret. The reason for this is clearly the diffusion-related element $A(\omega)$ which is present twice. The factor $A(\omega)$ in the second term on the right hand side of eq 23 is caused by the part the Helmholtz layer takes in the capacitance of the interface. On the other hand, the diffusion element in the fourth term of the admittance expression is caused by the changing occupancy of the surface states. These two components reflect both elements constituting the variation of the potential drop across the Helmholtz layer (eq 6).

However, it is possible to obtain an impedance representation in terms of separate circuit elements if one assumes that the semiconductor space-charge capacitance dominates the interfacial capacitance (hence $C_{sc} \ll C_H$). This assumption is generally valid if a depletion layer exists at the semiconductor side of the interface. The inequality $C_{sc} \ll C_H$ means that $\gamma \cong 1$ and that $(1 - \gamma)C_H \cong C_{sc}$. Consequently, the admittance expression 23 now becomes

$$
Y(\omega) = i\omega C_{sc} - \left[i\omega\gamma_s\frac{k_BT}{e}C_H + A(\omega)\left(\gamma_s\frac{k_BT}{e}\frac{\partial j^H}{\partial\phi_H} - \frac{\partial j^H}{\partial\theta}\right) \right]\frac{\tilde{\theta}}{\tilde{\phi}} \quad (24)
$$

Using the same assumption $C_{sc} \ll C_H$, the transfer function $\tilde{\theta}/\tilde{\phi}$

simplifies to

$$\frac{\tilde{\theta}}{\tilde{\phi}} = \frac{\dfrac{\partial\Theta}{\partial\phi_{sc}}}{i\omega - \dfrac{\partial\Theta}{\partial\theta} + \gamma_s\dfrac{k_BT}{e}\left(\dfrac{\partial\Theta}{\partial\phi_H} - \dfrac{\partial\Theta}{\partial\phi_{sc}}\right) + \left(\dfrac{\partial\Theta}{\partial c_{ox}} - \dfrac{\partial\Theta}{\partial c_{red}}\right)\left(\dfrac{\gamma_s\dfrac{k_BT}{e^2}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\right)} \tag{25}$$

Inserting eq 25 into the expression for the interfacial admittance (eq 24) combined with the definition of $A(\omega)$ yields

$$Y(\omega) = i\omega C_{sc} + \left(-\dfrac{\partial\Theta}{\partial\phi_{sc}}\right)\left[i\omega\gamma_s\dfrac{kT}{e}C_H + \dfrac{d(\omega)}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\left(\gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{\partial j^H}{\partial\theta}\right)\right]\Bigg|$$

$$\left[i\omega - \dfrac{\partial\Theta}{\partial\theta} + \gamma_s\dfrac{k_BT}{e}\left(\dfrac{\partial\Theta}{\partial\phi_H} - \dfrac{\partial\Theta}{\partial\phi_{sc}}\right) + \left(\dfrac{\partial\Theta}{\partial c_{ox}} - \dfrac{\partial\Theta}{\partial c_{red}}\right)\left(\dfrac{\gamma_s\dfrac{kT}{e^2}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\right)\right] \tag{26}$$

This admittance consists of two parts. The first part is the capacitance of the semiconductor depletion layer which dominates, by assumption, the interfacial capacitance. The influence of charge transfer and mass transport on the admittance is lumped in the second part of eq 26, which corresponds to the faradaic part of the admittance. Calculating the electrochemical impedance from this admittance expression yields a parallel connection of the capacitance of the semiconductor and the faradaic impedance. Using the definition of γ_s and the inequality $C_{sc} \ll C_H$, the latter is given by

$$Z_F(\omega) = \frac{i\omega - \dfrac{\partial\Theta}{\partial\theta} + \gamma_s\dfrac{k_BT}{e}\left(\dfrac{\partial\Theta}{\partial\phi_H} - \dfrac{\partial\Theta}{\partial\phi_{sc}}\right) + \left(\dfrac{\partial\Theta}{\partial c_{ox}} - \dfrac{\partial\Theta}{\partial c_{red}}\right)\left(\dfrac{\gamma_s\dfrac{k_BT}{e^2}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{1}{e}\dfrac{\partial j^H}{\partial\theta}}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\right)}{\left(-\dfrac{\partial\Theta}{\partial\phi_{sc}}\right)\left[i(es)\omega + \dfrac{d(\omega)}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\left(\gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{\partial j^H}{\partial\theta}\right)\right]} \tag{27}$$

Using expression 15 and the identities 22, this expression may be rewritten and simplified, yielding

$$Z_F(\omega) = \frac{1}{\dfrac{\partial j^{sc}}{\partial\phi_{sc}}}\left[1 + \dfrac{\dfrac{1}{es}\left(\dfrac{\partial j^{sc}}{\partial\theta} + \gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)}{i\omega + \dfrac{1}{es}\dfrac{d(\omega)}{d(\omega) - \dfrac{1}{e}\dfrac{\partial j_c^H}{\partial c_{ox}} + \dfrac{1}{e}\dfrac{\partial j_a^H}{\partial c_{red}}}\left(\gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{\partial j^H}{\partial\theta}\right)}\right] \tag{28}$$

   The impedance of the semiconductor|electrolyte system as a whole is the parallel connection of the impedance $Z_F(\omega)$ and the capacitance of the interface; the corresponding equivalent circuit is shown in Figure 2. The faradaic part $Z_F(\omega)$ consists of the series connection of a resistance (R_1) and an impedance which is in itself the parallel connection of a capacitance (C_2) on the one hand and a resistance (R_2) in series with a diffusion impedance (Δ) on the other hand. Quantitatively, these four circuit elements are given by
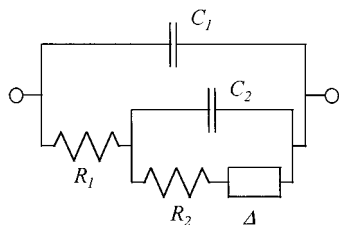
$$R_1 = \left(\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)^{-1} \tag{29}$$

$$C_2 = \left(\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)\left(\dfrac{1}{es}\dfrac{\partial j^{sc}}{\partial\theta} + \dfrac{1}{C_H}\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)^{-1} \tag{30}$$
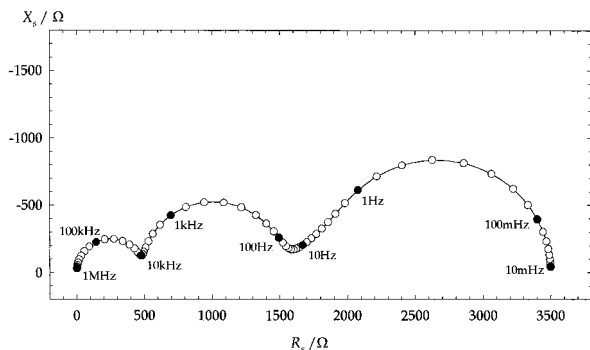
$$R_2 = \left(\dfrac{\partial j^{sc}}{\partial\theta} + \gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)\left(\dfrac{\partial j^{sc}}{\partial\phi_{sc}}\right)^{-1}\left(\gamma_s\dfrac{k_BT}{e}\dfrac{\partial j^H}{\partial\phi_H} - \dfrac{\partial j^H}{\partial\theta}\right)^{-1} \tag{31}$$

$$\Delta = R_2\left(\dfrac{\partial j_a^H}{\partial c_{red}} - \dfrac{\partial j_c^H}{\partial c_{ox}}\right)(ed(\omega))^{-1} \tag{32}$$

Figure 2. Equivalent electrical circuit corresponding to the impedance for electron transfer through surface states under the condition that $C_{sc} \ll C_H$. Detailed expressions for the circuit elements are given in the text (formulas 29−32).

Figure 3. Impedance plot calculated according to the equivalent circuit for surface-state mediated electron transfer. A Warburg impedance is used instead of the more complicated diffusion impedance for finite diffusion length. The values of the respective circuit elements are $C_1 = 5$ nF, $R_1 = 0.5$ kΩ, $C_2 = 300$ nF, $R_2 = 1$ kΩ, $\Delta = 2 \tanh(\sqrt{i\omega})/\sqrt{i\omega}$ kΩ.

The resulting Nyquist plot calculated for typical values of the different circuit elements is shown in Figure 3. Obviously, the shape of this plot may vary depending on the values of the five circuit elements. A detailed discussion of the circuit elements and their relation to the electrode reaction can be found in part 2.[24]

4. Discussion

Up till now, we have made a mathematical calculation of the electrochemical impedance of a one-equivalent electrode process involving diffusion and charge transfer through surface states. In this section, the correspondence between the impedance expression obtained and formulas proposed in the literature will be pointed out. Furthermore, we will show that the calculations performed may be used to describe direct majority charge carrier exchange reactions and, under certain conditions, reactions involving direct injection of minority charge carriers.

4.1. Correspondence to Impedance Expressions Found in the Literature. The electrochemical impedance obtained for surface-state mediated charge transfer corresponds to the equivalent circuit shown in Figure 2. Other impedance expressions and equivalent circuits describing electron transfer through surface states have been published previously.[19,25] It is instructive to compare these results with the impedance obtained here.

More then 25 years ago, Cardon proposed an impedance expression for a semiconductor|electrolyte interface with electron transfer through surface states.[25] He assumed no concentration polarization and neglected the variation of the potential drop across the Helmholtz layer (which amounts to an infinite diffusion coefficient and an infinite Helmholtz-layer capacitance, respectively). According to the author, the resulting impedance
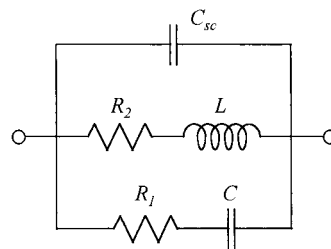
Figure 4. Equivalent electrical circuit corresponding to the impedance for electron transfer through surface states as proposed by Cardon. For the explicit expressions of the different circuit elements, see ref 25.

corresponds to the equivalent circuit shown in Figure 4. At first glance, this circuit has nothing in common with the equivalent circuit obtained by the calculation performed here. Especially the self-inductance appearing in the circuit of Figure 4 seems to lack a counterpart in the equivalent circuit of Figure 2. However, an equivalent circuit is never a unique representation of an impedance expression. Using the notation adopted in the present paper, the impedance obtained by Cardon equals[25,34]

$$Z = \frac{k_B T}{e^2 \beta_n n_s \theta (1-\theta)s} \left[\frac{i\omega\theta + (l_a c_{red} + \beta_n n_s)}{i\omega + (l_a c_{red} + l_c c_{ox})} \right] \quad (33)$$

In Appendix A, it is shown that this impedance may equally well be written as

$$Z = \frac{k_B T}{e^2} \frac{1}{\beta_n n_s s (1-\theta)} + \frac{k_B T}{e^2} \frac{\epsilon_n + \beta_n n_s}{i\omega\beta_n n_s s (1-\theta) + (l_a c_{red} + l_c c_{ox})\beta_n n_s s (1-\theta)} \quad (34)$$

This impedance expression now corresponds directly to the equivalent circuit shown in Figure 2 with the diffusion-related element equal to zero. The three remaining impedance elements are given by

$$R_1 = \frac{k_B T}{e^2 \beta_n n_s (1-\theta)s} = \left(\frac{\partial j^{sc}}{\partial \phi_{sc}} \right)^{-1} \quad (35)$$

$$C_2 = \frac{e^2}{k_B T}(1-\theta)s \frac{\beta_n n_s}{\beta_n n_s + \epsilon_n} = \left(\frac{\partial j^{sc}}{\partial \phi_{sc}} \right)\left(\frac{1}{es} \frac{\partial j^{sc}}{\partial \theta} \right)^{-1} \quad (36)$$

$$R_2 = \frac{k_B T}{e^2 \beta_n n_s (1-\theta)}\left(\frac{\beta_n n_s + \epsilon_n}{l_a s c_{red} + l_c s c_{ox}} \right) = \left(\frac{\partial j^{sc}}{\partial \phi_{sc}} \right)^{-1}\left(\frac{\partial j^{sc}}{\partial \theta} \right)\left(\frac{\partial j^H}{\partial \theta} \right)^{-1} \quad (37)$$

These circuit elements are identical to the elements 29−31, respectively, if C_H and D are set equal to infinity. This agrees with the assumptions made in ref 25 for the impedance calculation (no concentration polarization and no potential variation across the Helmholtz layer).

More recently, Vanmaekelbergh published a study on the admittance of surface-state mediated electron transfer at semiconductor/electrolyte junctions.[18] In that work, the variation of the potential drop across the surface states is accounted for, but concentration polarization is, again, neglected. Assuming $C_{sc} \ll C_H$, the faradaic impedance resulting from his study equals[18]

$$Z = \left[-\gamma_s \frac{k_B T}{e} \frac{\partial \Theta}{\partial \phi_{sc}} \Big|_{\phi_H,\theta} \right]^{-1}$$
$$\left[\frac{i\omega - \frac{\partial \theta}{\partial \theta} + \frac{kT}{e}\gamma_s \left(\frac{\partial \Theta}{\partial \phi_H} \Big|_{\phi_{sc},\theta} - \frac{\partial \Theta}{\partial \phi_{sc}} \Big|_{\phi_H,\theta} \right)}{i\omega C_H + \frac{\partial j^H}{\partial \phi_H} \Big|_{\phi_{sc}}} \right] \quad (38)$$

This expression corresponds to eq 28 if it is assumed that the diffusion coefficient is infinite.[35]

4.2. Direct Exchange of Majority Charge Carriers. The general impedance expression (eq 20) applies to direct exchange of majority charge carriers if the term in $\tilde{\theta}/\tilde{\phi}$ is dropped. This procedure is justified since the terms in $\tilde{\theta}/\tilde{\phi}$ or $\tilde{\theta}$ now disappear from eqs 4, 5, 6, and 12. Thus, using eq 20, the admittance for direct majority charge carrier exchange equals

$$Y(\omega) = i\omega(1 - \gamma)C_H + D(\omega)\left(\gamma \frac{\partial j^H}{\partial \phi_{sc}} + (1 - \gamma)\frac{\partial j^H}{\partial \phi_H} \right) \quad (39)$$

This admittance is the sum of the capacitance of the interface and a faradaic element describing charge transfer and diffusion. Therefore, the impedance consists of the parallel connection of the inverse of both terms of eq 39. This corresponds to the well-known Randles equivalent circuit.[1,17]

For direct exchange of majority charge carriers, the expressions for the anodic and cathodic current densities are equal at the semiconductor and the electrolyte side of the interface. According to the Gerischer model, they are expressed by the following equations:[5,23]

$$j_c^H = -ek_c c_{ox} n_s$$
$$j_a^H = ek_a c_{red} \quad (40)$$

Here, k_c and k_a stand for the rate constants of the cathodic and the anodic partial reaction, respectively, whereas n_s equals the concentration of conduction-band electrons at the semiconductor surface. All partial derivatives needed may be calculated using these equations. Those with respect to both concentrations are trivial. Vanmaekelbergh calculated the partial derivatives with respect to ϕ_H and ϕ_{sc}.[7] They are given by

$$\frac{\partial j^H}{\partial \phi_H} = \frac{e}{k_B T}((1 - \alpha)j_a^H + \alpha(-j_c^H))$$

$$\frac{\partial j^H}{\partial \phi_{sc}} = \frac{\partial j_c^H}{\partial \phi_{sc}} = \frac{e}{k_B T}(-j_c^H) \quad (41)$$

In this equation, α and $(1 - \alpha)$ stand for the transfer coefficient of the anodic and cathodic partial reaction, respectively.

Inserting these partial derivatives in eq 39 allows us to calculate the faradaic part of the electrochemical impedance. This yields

$$Z_F(\omega) =$$
$$\frac{k_B T}{e} \frac{1}{\gamma |j_c^H| + (1 - \gamma)[\alpha|j_c^H| + (1 - \alpha)j_a^H]}\left(1 + \frac{k_c n_s + k_a}{d(\omega)} \right) \quad (42)$$

For a detailed discussion of this result, we refer to ref 17.

4.3. Description of Reactions Involving Minority Charge Carriers. Besides direct exchange of majority charge carriers, the proposed formalism may be applied under certain conditions
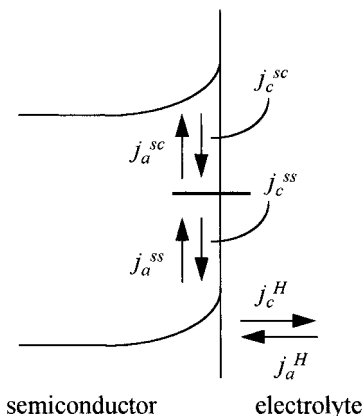
Figure 5. Diagram showing the relevant current densities in the case of direct transfer of minority charge carriers.

to reactions involving direct injection of minority charge carriers as well. The main problem here is that the calculations performed in section 2 and 3 are based on one dynamic equation only, describing the evolution in time of the occupancy of the surface states. In this way, the theory makes it possible to describe reactions involving either two (surface-state mediated transfer) or one (direct exchange) reaction steps. However, if charge transfer at n-type semiconductors involves exchange of valence-band holes, at least three reaction steps occur. Electrons must be transferred between the electroactive species in solution and the valence band, between the valence band and a recombination level and finally between the recombination level and the conduction band[36] (cf. Figure 5). Therefore, the general admittance (eq 20) does not apply to hole exchange at n-type semiconductors in principle.

Thus, two dynamic equations are needed to describe reactions involving transfer of valence band holes, if all holes injected either recombine at the semiconductor surface or are captured by the reducing agent in solution (reverse reaction). The first equation describes the time-dependence of the occupancy of the recombination centers; the second models the time dependence of the total number of holes in the valence band of the semiconductor near the semiconductor surface (P).[37] Referring to Figure 5, these two equations may be written as

$$\frac{d\theta}{dt} = \Theta(\theta,\phi_{sc},P) = \frac{1}{es}[(-j_c^{sc}) - j_a^{sc} + j_a^{ss} - (-j_c^{ss})] \quad (43)$$

$$\frac{dP}{dt} = \Pi(\theta,P,\phi_H,c_{ox},c_{red}) = \frac{1}{e}[(-j_c^{ss}) - j_a^{ss} + j_a^H - (-j_c^H)] \quad (44)$$

As shown in Figure 5, j_c^{ss} and j_a^{ss} denote the current densities associated with the transfer of electrons between the valence band and recombination levels at the semiconductor surface.

Regardless of whether charge stored in the surface states originates from the valence band or from electroactive species in solution, its effect on the potential drop across the Helmholtz layer is the same. Hence, the role played by eq 43 in the description of the charge-transfer mechanism is analogous to the role eq 15 plays in surface-state mediated electron transfer.

If a small-signal potential perturbation is applied across the interface, eqs 43 and 44 may be written using small-signal quantities. The relation known from the literature between the number of holes in the valence band and the concentration of valence-band holes at the surface of the semiconductor[15] makes it possible to calculate the electrochemical impedance for this particular charge-transfer mechanism, leading to a long and hardly surveyable calculation.

Therefore, let us assume that the dynamics of valence-band holes are sufficiently fast, such that

$$i\omega P = \frac{1}{e}[(-\tilde{j}_c^{ss}) - \tilde{j}_a^{ss} + \tilde{j}_a^H - (-\tilde{j}_c^H)] \cong 0 \qquad (45)$$

for all measuring frequencies of interest. If so, the dynamic eq 45 may be inserted directly into eq 43, yielding

$$i\omega\theta = \frac{1}{e}[(-\tilde{j}_c^{sc}) - \tilde{j}_a^{sc} + \tilde{j}_a^H - (-\tilde{j}_c^H)] \qquad (46)$$

The calculation of the electrochemical impedance is now completely identical to that of the impedance for charge transfer through surface states, except for the explicit expression of the current densities at the electrolyte side of the interface. Therefore eq 20 will yield the impedance if the appropriate current density expressions are used. Furthermore, if the condition $C_{sc} \ll C_H$ is valid, the faradaic impedance is equally given by formula 28. This means that, if condition 45 is fulfilled, charge-transfer involving direct transfer of valence band electrons accompanied by electron−hole recombination cannot be distinguished in general from surface-state mediated electron transfer.[38] Evidently, the question remains whether the assumptions made in eq 45 have any physical meaning. In ref 16, it is argued that this is indeed the case for reactions involving a recombination step at n-GaAs. However, it is evident that this condition should be checked every time the approximation is introduced.

Appendix A

As mentioned in the text, if hole excitation from the valence band to the recombination level is neglected, the impedance calculated by Cardon equals 25:

$$Z = \frac{k_B T}{e^2 \beta_n n_s \theta(1-\theta)s}\left[\frac{i\omega\theta + (l_a c_{red} + \beta_n n_s)}{i\omega + (l_a c_{red} + l_c c_{ox})}\right] \qquad (a1)$$

This expression may be written as

$$Z = \frac{k_B T}{e^2 \beta_n n_s \theta(1-\theta)s}$$
$$\left[\frac{i\omega\theta + \theta(l_a c_{red} + l_c c_{ox}) - \theta(l_a c_{red} + l_c c_{ox}) + (l_a c_{red} + \beta_n n_s)}{i\omega + (l_a c_{red} + l_c c_{ox})}\right]$$
$$\qquad (a2)$$

and hence

$$Z = \frac{k_B T}{e^2 \beta_n n_s(1-\theta)s}\left[1 + \frac{\beta_n n_s + (1-\theta)l_a c_{red} - \theta l_c c_{ox}}{i\omega\theta + (l_a c_{red} + l_c c_{ox})\theta}\right] \qquad (a3)$$

This expression may be simplified using the equality between the net dc current densities at both sides of the interface:

$$-e\beta_n n_s s(1-\theta) + e\epsilon_n s\theta = -el_c s\theta c_{ox} + el_a s(1-\theta)c_{red} \qquad (a4)$$

Inserting this equality into (eq a3) yields finally the impedance calculated by Cardon in the form corresponding to the equivalent circuit proposed in the present paper:

$$Z = \frac{k_B T}{e^2}\frac{1}{\beta_n n_s(1-\theta)s} +$$
$$\frac{k_B T}{e^2}\frac{\beta_n n_s + \epsilon_n}{i\omega\beta_n n_s(1-\theta)s + (l_a c_{red} + l_c c_{ox})\beta_n n_s(1-\theta)s} \qquad (a5)$$

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(26) It is assumed that the surface states mediating the charge transfer are not induced by the electrode process itself.

(27) This means that the semiconductor surface is a surface of equal potential.

(28) According to the electrochemical sign convention, cathodic currents are taken as negative, anodic currents as positive.

(29) Assuming the non-faradaic current to be purely capacitive limits somewhat the generality of the proposed model. For example, reactions in nonsupported electrolyte[22] or reactions involving changes of the structure of the Helmholtz-layer apart from the filling or unfilling of surface states are excluded.

(30) Sinusoidally varying quantities derived from a given quantity a are written as $\tilde{a}\exp(i\omega t)$.

(31) In what follows, neither the dependence of the small signal variables on the pulsation ω nor the fact that, when taking a partial derivative, all other independent variables remain constant is indicated explicitly.

(32) It is assumed that the cathodic and anodic current density depend only on the concentration of oxidizing and reducing agent at the interface, respectively.

(33) The magnitude of the electric field at the interface might influence these rate constants causing a dependence of the current densities at the semiconductor side on the potential drop across the Helmholtz layer and vice versa. The assumption made considers this to be a minor effect only.

(34) Hole excitation from the valence band to the surface state is not accounted for in this expression.

(35) A difference remains between the formulas 31 and 38. In formula 38, only the potential drop across the semiconductor is kept constant in the partial derivative $\partial j^H / \partial \phi_H$. In formula 31, both the potential drop ϕ_{sc} and the occupancy of the surface states θ are kept constant in this partial derivative. The final result, obtained by calculating the partial derivatives explicitly, is nevertheless the same for both.

(36) It is assumed that all injected holes either recombine at the semiconductor surface or are captured by the reaction product (reverse reaction). This is justified if parallel recombination mechanisms (band to band recombination, recombination in the space-charge layer, ...) and other hole consuming reactions (anodic dissolution) are negligible as compared to these two processes.

(37) This quantity should not be confused with the surface concentration of valence-band holes, see ref 15.

(38) In the case of hole injection without reverse reaction, distinction is still possible if the energy levels of the oxidizing agent overlap completely with the valence band. Then the partial derivative $\partial j^H / \partial \phi_H$ is equal to zero such that no diffusion impedance appears in the electrochemical impedance, cfr. ref 16.