Supporting Information

Charge transfer processes at the semiconductor/electrolyte

interface for solar fuels production: insight from impedance

spectroscopy.

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Steady state equations for the direct and indirect charge transfer models

The classical drift diffusion equations that describe the semiconductor systems are the continuity equations for electron and hole conduction currents, the displacement current and Poisson equation, as detailed in ref.¹ In steady state (indicated by the over bar), the displacement current is zero and these equations can be written as a system of 6 first order differential equations that govern the variations of 6 variables: the electron current \bar{j}_n , the hole current \bar{j}_p , the density of electrons \bar{n} and holes \bar{p} , the electrostatic potential ϕ and the electric field \bar{F} :

$$\bar{j}_n = q\bar{n}u_n\bar{F} + qD_n\frac{\partial n}{\partial x} \tag{1}$$

$$\bar{j}_{p} = q\bar{p}u_{p}\bar{F} - qD_{p}\frac{\partial\bar{p}}{\partial x}$$
⁽²⁾

$$\frac{1}{q}\frac{\partial \bar{j}_n}{\partial x} + G - U_r = 0 \tag{3}$$

$$-\frac{1}{q}\frac{\partial \bar{j}_{p}}{\partial x} + G - U_{r} = 0$$
(4)

$$\frac{\partial \overline{F}}{\partial x} = \frac{q}{\varepsilon_0 \varepsilon_r} \left(\overline{p} - \overline{n} + N_D - N_A \right)$$
(5)

$$\overline{F} = -\frac{\partial \overline{\phi}}{\partial x} \tag{6}$$

Where $G = \alpha \phi_0 \exp(-\alpha x)$ is the generation rate, α being the absorption coefficient and ϕ_0 the photon flux. U_r is the band to band recombination rate defined as $U_r = B(\overline{np} - n_0 p_0)$. u_n and u_p are the electron and hole's mobility, respectively, D_n and D_n are the electron and hole's diffusion coefficient, which are linked to the mobility by the Einstein relation: $D_k = u_k k_B T / q \cdot N_D$ and N_A are the total density of ionized donors and acceptors, ε_0 and ε_r are the dielectric permittivity of the vacuum and the relative permittivity of the semiconductor. The total current density is given by $j = j_p + j_n$.

For the system presented in Fig. 1 of the main text, we assume that at the semiconductor/metal interface (x = 0), the majority carrier concentration (electrons) is constant and equal to its equilibrium concentration:

$$\overline{n}(0) = n_0 = N_c \exp(-q\Phi_n / k_B T) \tag{7}$$

Note that in our previous work,² we had neglected the influence of the electric field and the concentration at the contact was directly modulated by the applied voltage as $\overline{n}(0) = n_0 \exp(-qV/k_BT)$, where k_BT is the thermal voltage. We take as the reference for the potentials, the electrostatic potential in x = 0:

$$\phi(0) = 0 \tag{8}$$

We consider the metal to be a perfect electron selective contact (no hole current):

$$\overline{j}_p(0) = 0 \tag{9}$$

At the semiconductor/electrolyte interface, the conduction and valence band edges are pinned and the voltage drop at the Schottky barrier is linked to the electrostatic potential as: $V_{sc} = \overline{\phi}(L) - \overline{\phi}(0) \cdot V_{sc}$ and therefore $\phi(L)$ are directly modulated by the applied voltage as:

$$\overline{\phi}(L) = V_{bi} + V \tag{10}$$

where $V_{bi} = \Phi_n - \Phi_p$ is the built-in potential. Eqn (10) can be also written as:

$$\overline{n}_{L} = \overline{n}(L) = n_{0}e^{-\frac{qV_{sc}}{k_{B}T}} = n_{0}e^{-\frac{q(V_{bi}+V)}{k_{B}T}}$$
(11)

Two boundary conditions on the current must be imposed, depending on the charge transfer model for the semiconductor/electrolyte interface. We give the details of such boundary conditions hereafter.

a) Boundary conditions for the direct charge transfer model.

In the following we model the interface semiconductor/electrolyte as a thin layer of semiconductor of length δL , where all carrier densities are supposed to be uniform.³ For direct charge transfer of holes from the valence band, the hole current flowing through the semiconductor/electrolyte interface (x = L) follows the relation:

$$j_{p}(L) = qk_{vb}\delta L(\overline{p}_{L} - p_{0})$$
⁽¹²⁾

Where $p_0 = N_v \exp(-q\Phi_p / k_B T)$. Finally, the electron current is assumed to be zero at this contact

$$\overline{j}_n(L) = 0 \tag{13}$$

The boundary conditions (7)-(10), (12) and (13) allow obtaining the complete solution to the system of equations (1)-(6).

b) Boundary conditions for the indirect charge transfer model.

For indirect hole transfer from surface states the recombination current at the interface semiconductor/electrolyte must be calculated. One procedure to obtain such current consists in solving the continuity equations coupled to the master equation for the occupation probability, \bar{f} , of the surface states. We neglect direct charge transfer of electrons and holes at the interface, so that: $\bar{j}_n(L + \delta L) = \bar{j}_p(L + \delta L) = 0$. The recombination current can be calculated by solving the following continuity equations:

$$\frac{1}{q}\frac{\partial j_n}{\partial x} - \beta_n \overline{n}_L (1 - \overline{f})N_{ss} + \varepsilon_n \overline{f}N_{ss} = 0$$
(14)

$$-\frac{1}{q}\frac{\partial \bar{j}_{p}}{\partial x} - \beta_{p}\bar{p}_{L}\bar{f}N_{ss} + \varepsilon_{p}(1-\bar{f})N_{ss} = 0$$
(15)

where \bar{f} is determined by the master equation:

$$\beta_n \bar{n}_L (1 - \bar{f}) - \varepsilon_n \bar{f} - \beta_p \bar{p}_L \bar{f} + \varepsilon_p (1 - \bar{f}) - k_s (\bar{f} - f_0) = 0$$
(16)

In addition, by using the relation imposed by the detailed balance $(\varepsilon_n \varepsilon_p = \beta_n n_0 \beta_p p_0)$,

and integrating eqn (14) and (15), we obtain:

$$\bar{j}_{n}(L) = -q \,\delta L N_{ss} \left[\frac{\beta_{n} \beta_{p} \left(\bar{n}_{L} \bar{p}_{L} - n_{0} p_{0} \right)}{\beta_{n} \bar{n}_{L} + \varepsilon_{n} + \beta_{p} \bar{p}_{L} + \varepsilon_{p} + k_{s}} + \frac{k_{s} \left(1 - f_{0} \right) \beta_{n} \left(\bar{n}_{L} - n_{0} \right)}{\beta_{n} \bar{n}_{L} + \varepsilon_{n} + \beta_{p} \bar{p}_{L} + \varepsilon_{p} + k_{s}} \right] (17)$$

$$\bar{j}_{p}(L) = q \,\delta L N_{ss} \left[\frac{\beta_{n} \beta_{p} \left(\bar{n}_{L} \bar{p}_{L} - n_{0} p_{0} \right)}{\beta_{n} \bar{n}_{L} + \varepsilon_{n} + \beta_{p} \bar{p}_{L} + \varepsilon_{p} + k_{s}} + \frac{k_{s} f_{0} \beta_{p} \left(\bar{p}_{L} - p_{0} \right)}{\beta_{n} \bar{n}_{L} + \varepsilon_{n} + \beta_{p} \bar{p}_{L} + \varepsilon_{p} + k_{s}} \right] (18)$$

Equations (17) and (18) are the two last boundary conditions that are needed to obtain the complete solution to the set of differential equations (1)-(6) for indirect hole transfer from the surface states. In the case that both the indirect charge transfer model and direct transfer model are considered, the hole current density charge at the semiconductor/electrolyte interface is given by the sum of (12) and (18) and the electron current density is given by (17). Several points should be remarked about eqn (17) and (18). First, in the expression of the recombination currents the first right hand side term correspond to a generalized Shockley Read Hall recombination including charge transfer kinetics, while the second term corresponds to charge transfer from these surface states. Second, it should be remarked that the total photo-anodic current is given by:

$$\bar{j}(L) = \bar{j}_n(L) + \bar{j}_p(L) = -q \,\delta L k_s N_{ss} \left(\bar{f} - f_0 \right)$$
⁽¹⁹⁾

Consequently, at high applied anodic potential, the surface states are filled with holes and $\bar{f} \rightarrow 0$. Therefore, the maximum theoretical anodic current is $q \delta Lk_s N_{ss} f_0$.



Influence of the trap assisted recombination on the anodic current.

Fig. S1 Full drift diffusion simulation with two values of the hole trapping kinetic constant (β_p) indicated in the Figure. Higher hole trapping kinetics induce higher electron-hole recombination and therefore a lower anodic current. For this simulation we chose $k_{vb} = 5 \times 10^6 \text{ s}^{-1}$ and the other parameters are the one indicated in Table S1.

Parameters	Values
L	100 (nm)
δL	10 (nm)
k _B T	26 (meV)
$\mu_n = \mu_p$	$10 (cm^2 V^{-1} s^{-1})$
E _r	10
N _D	10^{17} (cm ⁻³)
N _A	0 (cm ⁻³)
N _{ss}	$10^{20} (\text{cm}^{-3})$
$N_c = N_v$	$10^{20} (\text{cm}^{-3})$
E	1.2 (eV)
Φ_n	0.1 (eV)
Φ_n	0.4 (eV)
G ₀	$5 \times 10^{19} \text{ (cm}^{-3}\text{s}^{-1}\text{)}$
α	$10^3 (cm^{-1})$
k _{vb}	10^{6} (s ⁻¹)
k _s	1 (s ⁻¹)
β_n	$10^{-8} (cm^3s^{-1})$
β_n	$10^{-12} (\text{cm}^3\text{s}^{-1})$
<i>E</i> _n	2×10^3 (s ⁻¹)
E _p	$4 \times 10^{-4} (s^{-1})$
f_0	0.99

Table S1.Parameters of the simulations

Note that β_n , β_p , ε_n , ε_p and f_0 must satisfy the detailed balance.² In addition, we have chosen the values of k_s and k_{vb} such that the maximum achievable anodic currents from the surface states and valence band are comparable. According to equations (12) and (19), the ratio between both currents is $k_s f_0 N_t / (k_{vb} \overline{p}_L)$. Therefore, since the maximum value of \overline{p}_L is of the order of 10¹⁵ cm⁻³ (see Figure 2b of the main text), we must have k_s / k_{vb} of the order of 10⁻⁶.

Calculation of the equivalent circuits of Fig. 3 of the main text.

In the following we derive the small perturbation equations that are used to obtain the ECs of Fig. 3 of the main text. We focus on the processes that occur at the interface and neglect all the transport limitations, which would give rise to transmission line behavior. In addition, the geometric capacitance, C_g , associated to the displacement current is usually much smaller than the classical chemical capacitance of free or trapped carriers. This capacitance is therefore observed at much higher frequencies. For this reason, we can decouple the geometric capacitance from the rest of the circuit,¹ represented with the impedance Z_{el} in Fig. S2. In the following we calculate the impedance Z_{el} .



Fig. S2 General simplified EC for both interfacial charge transfer models displayed in Fig. 1b and c of the main text. In this approximation, the geometric capacitance has been decoupled from the electronic transport as in ref.⁴

a) Direct hole transfer model.

For direct hole transfer, the continuity eqn (3) and (4) can be written as:

$$\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial j_n}{\partial x} + G - U_r$$
⁽²⁰⁾

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial j_p}{\partial x} + G - U_r \tag{21}$$

Since we can neglect all transport limitation, all densities are homogeneous and we can integrate eqn (20) and (21) over the whole semiconductor layer. By applying boundary conditions (9), (12) and (13), we obtain the total extracted current:

$$qL\frac{\partial n_L}{\partial t} = -j_n + qL(G - U_r)$$
⁽²²⁾

$$L\frac{\partial p_{L}}{\partial t} = L(G - U_{r}) - k_{vb}\delta L(p_{L} - p_{0})$$
⁽²³⁾

We now use the small perturbation theory, which consists in applying a small perturbation \hat{V} to the steady state voltage \overline{V} . The carrier densities n_L and p_L can then be written as: $n_L = \overline{n}_L + h$ and $p_L = \overline{p}_L + p$. Using eqn (11), we can identify h as:

$$\hat{n} = -\frac{q\hat{V}}{k_B T}\bar{n}_L \tag{24}$$

In addition we have:

$$\hat{U}_r = B(\hat{n}\overline{p}_L + \overline{n}_L p)$$
(25)

After applying the Laplace transform to eqn (22) and (23), we obtain:

$$j_n = -qL(i\omega\hat{n} + B(\hat{n}\overline{p}_L + \overline{n}_L \not p))$$
⁽²⁶⁾

$$\hat{p} = -\frac{B\overline{p}_L}{i\omega + B\overline{n}_L + k_{vb}}\frac{\delta L}{L}\hat{n}$$
(27)

Combining eqn (24), (26) and (27), we obtain:

$$Z_{el}^{-1} = \left(i\omega C_{\mu}^{(cb)} + \frac{1}{R_{rec} + \frac{1}{i\omega C_{\mu}^{(vb)} + \left(R_{ct}^{(vb)}\right)^{1}}} \right)$$
(28)

where:

$$C_{\mu}^{(cb)} = \frac{q^2 L}{k_B T} \overline{n}_L \tag{29}$$

$$C^{(\nu b)}_{\mu} = \frac{q^2 L}{k_B T} \overline{p}_L \tag{30}$$

$$R_{rec} = \left(\frac{q^2 L}{k_B T} B \overline{n}_L \overline{p}_L\right)^{-1}$$
(31)

$$R_{ct}^{(vb)} = \left(k_{vb}\frac{\partial L}{L}C_{\mu}^{(vb)}\right)^{-1}$$
(32)

Note that charge transfer from the valence band is optimum for nanostructured semiconductors since in this case charge transfer occurs at all points and $\delta L/L \rightarrow 1$.

From eqn (28) we obtain Z_{el} and consequently, from Fig. S2, we deduce the EC of Fig. 3a of the main text where the external capacitance, $C_{out}^{(cb)}$, is the parallel combination of $C_{\mu}^{(cb)}$ and C_g :

$$C_{out}^{(cb)} = \frac{C_{\mu}^{(cb)} C_g}{C_{\mu}^{(cb)} + C_g}$$
(33)

b) Indirect hole transfer model.

We apply the same procedure as the one used for the direct hole transfer model. However in this case we neglect the valence band capacitance (i.e $\partial p / \partial t \approx 0$) as well as the bulk recombination U_r . In this case, after integrating eqn (3) and (4) over the semiconductor layer and applying eqn (9), (14) and (15) and considering the time dependent master eqn, we get:

$$qL\frac{\partial n_L}{\partial t} = -j_n + qLG + q\left(-\beta_n n_L(1-f)N_{ss} + \varepsilon_n fN_{ss}\right)\delta L$$
(34)

$$0 = GL + \left(-\beta_p p_L f N_{ss} + \varepsilon_p (1 - f) N_{ss}\right) \mathcal{D}L$$
(35)

$$\frac{\partial f}{\partial t} = \beta_n n_L (1 - f) - \varepsilon_n f - \beta_p p_L f + \varepsilon_p (1 - f) - k_s (f - f_0)$$
(36)

From eqn (35) and (36), we deduce:

$$\bar{f} = \frac{\beta_n \bar{n}_L + k_s f_0 - GL/(N_{ss} \delta L)}{\beta_n \bar{n}_L + \varepsilon_n + k_s}$$
(37)

$$\frac{\partial f}{\partial t} = \beta_n n_L (1 - f) - \varepsilon_n f - k_s (f - f_0) - GL/(N_{ss} \delta L)$$
(38)

Applying the small perturbation method and the Laplace transform to eqn (34) and (38), we obtain:

$$)_{j_n} = -qL \left(i\omega \hat{n} + \left(\beta_n \hat{n} (1 - \bar{f}) - \left(\beta_n \bar{n}_L + \varepsilon_n \right) \hat{f} \right) V_{ss} \frac{\delta L}{L} \right)$$
(39)

$$\hat{f} = \frac{\beta_n \hat{n}(1 - \bar{f})}{i\omega + \beta_n \bar{n}_L + \varepsilon_n + k_s}$$
(40)

We deduce the total impedance Z_{el} for indirect charge transfer:

$$Z_{el} = \left(i\omega C_{\mu}^{(cb)} + \frac{1}{R_{tdn}^{(ss)} + \frac{1}{i\omega C_{\mu p}^{(ss)} + (R_{p}^{(ss)})^{-1}}} \right)$$
(41)

with:

$$C_{\mu p}^{(ss)} = \frac{\delta L}{L} \frac{\beta_n N_{ss} (1 - \bar{f})}{\beta_n \bar{n}_L + \varepsilon_n} C_{\mu}^{(cb)}$$
(42)

$$R_{tdn}^{(ss)} = \left(\left(\beta_n \overline{n}_L + \varepsilon_n \right) C_{\mu p}^{(ss)} \right)^1$$
(43)

$$R_p^{(ss)} = \left(k_s C_{\mu p}^{(ss)} \right)^{-1} \tag{44}$$

From eqn (41) we deduce the EC of Fig. 3b.

References.

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