Appendix of PECHouse2 final report - Drift-diffusion model with surface states†

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DOI: 10.1039/b000000x In this file, we present drift-diffusion model with surface state charge transfer along with hematite material

parameters that we used for simulations.

1 Theory

The drift-diffusion model of charge transport from was used for bulk charge transport and recombination

$$\frac{d^2\phi}{dx^2} = -\frac{q(N_D - n(x) + p(x))}{\varepsilon_0\varepsilon_r}, \tag{1}$$

$$\frac{\partial n}{\partial t} = +\frac{1}{q}\frac{\partial j_e}{\partial x} + G_e(x) - R_e(x), \tag{2}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q}\frac{\partial j_h}{\partial x} + G_h(x) - R_h(x). \tag{3}$$

The electron and hole flux consists of two terms (diffusion and drift)

$$j_e = +eD_e\frac{\partial n}{\partial x} - e\mu_e n\frac{\partial \phi}{\partial x}, \tag{4}$$

$$j_h = -eD_h\frac{\partial p}{\partial x} - e\mu_h p\frac{\partial \phi}{\partial x}, \tag{5}$$

where the electrostatic potential is ϕ, electron mobility is μ_e, hole mobility μ_h.

A direct band-to-band nonlinear recombination is assumed

$$R_e = R_h = \frac{1}{N_D\tau_h}(np - n_i^2). \tag{6}$$

We extended the drift-diffusion equations to include effects of electron and hole trapping/detrapping and charge transfer from the surface states. Kinetic model which with corresponding rate constants [2] was extended to 1D model. Trapping/Detrapping rates of electrons β_n, ε_n and holes β_p, ε_p. For the balance on the surface ($x = 0$) the master equation describes evolution of probability f that an electron occupies a surface trap in the semiconductor at level E_t with density N_{ss}

$$\frac{\partial f}{\partial t} = \beta_n(1-f)n(0) - \varepsilon_n f - \beta_p f\, p(0) + \varepsilon_p(1-f) - k_s(f - f_0),$$

where rate of charge transfer from surface traps to electrolyte k_s.

We estimate order of magnitude for $N_{ss} \approx 6\cdot 10^{13}$ cm^{-2} by referring to the number of surface trapped holes as reported by [1]

Electron and hole currents through the SEI

$$j_e(0) = -q(\beta_n(1-f)n(0)N_{ss} + q\varepsilon_n f\, N_{ss}),$$
$$j_h(0) = -q(\beta_p f\, p(0)N_{ss} + q\varepsilon_p(1-f)N_{ss}),$$

Detailed balance at equilibrium (index 0) gives

$$\frac{\varepsilon_n}{\beta_n n_0} = \frac{\beta_p p_0}{\varepsilon_p} = \frac{1-f_0}{f_0} = e^{\frac{E_t - E_{F0}}{k_B T}}$$

The trapping rate is calculated from electron capture cross-section γ_n and thermal velocity of carriers v_{th}

$$\beta_n = \beta_p = \gamma_n v_{th} \tag{7}$$

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Symbol	Fe_2O_3 [2]	Description
N_D [cm^{-3}]	$4.8 \cdot 10^{18}$	Donor concentration
N_A [cm^{-3}]	0	Acceptor concentration
$V_{fb,RHE}$ [V]	+0.5	Flatband potential
χ [eV]	+4.78 [3,4]	Electron affinity
N_C [cm^{-3}	$4 \cdot 10^{22}$ [5,6]	Density of states of CB
N_V [cm^{-3}]	$1 \cdot 10^{22}$	Density of states of VB
ε_r	32	Relative permitivity
E_g [eV]	2.1	Bandgap energy
d [nm]	60	Thickness of semiconductor
τ_e [ms]	0.22	Electron lifetime
τ_h [ns]	0.048 [7]	Hole lifetime
L_e [nm]	50	Electron diffusion length
L_h [nm]	2 [8]	Hole diffusion length
α [cm^{-1}]	$1.18 \cdot 10^5$	Absorption coefficient
pH	6.9	pH value of the electrolyte
E_t [eV]	$E_{c,0i} - \frac{E_g}{2}$	Trap level
γ [m^2]	10^{-25}	Electron capture cross-section

Table 1 Material parameters of hematite used in the simulations.