photonics

Insights of Hysteresis Behaviors in Perovskite Solar Cells from a Mixed Drift-Diffusion Model Coupled with Recombination

Chongqiu Yang, Xiaobiao Shan and Tao Xie *

Harbin Institute of Technology, School of Mechatronics Engineering, Harbin 150001, China; 14B908006@hit.edu.cn (C.Y.); shanxiaobiao@hit.edu.cn (X.S.)
* Correspondence: xietao@hit.edu.cn

Mathematical equations

Drift-diffusion equations and Poisson's equation of charge carriers and ions are present as follow

(1) Perovskite layer

Drift-diffusion equations

$$J_n = q\mu_n nE + qD_n \frac{\partial n}{\partial x} \tag{1}$$

$$J_p = q\mu_p pE - qD_p \frac{\partial p}{\partial x} \tag{2}$$

$$J_N = q\mu_N NE + qD_N \frac{\partial N}{\partial x} \tag{3}$$

$$J_P = q\mu_P PE - qD_P \frac{\partial P}{\partial x} \tag{4}$$

Where n, p, N, P are electron, hole, anion and cation density, $\mu_{n,p,N,P}$ and $D_{n,p,N,P}$ are there drift mobility and diffusion coefficient, respectively, defined as follow

$$D_{n,p,N,P} = \frac{k_B T}{q} \mu_{n,p,N,P} \tag{5}$$

$\varepsilon_0, \varepsilon_r, q, k_B, T$ are vacuum permittivity, relative permittivity, elementary charge, Boltzmann constant and absolute temperature.

The conservation of charge carriers and ions are defined using the semiconductor transport equations

$$\frac{\partial n}{\partial t} = \frac{1}{q}\frac{\partial J_n}{\partial x} - R + G \tag{6}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q}\frac{\partial J_p}{\partial x} - R + G \tag{7}$$

$$\frac{\partial N}{\partial t} = \frac{1}{q}\frac{\partial J_N}{\partial x} \tag{8}$$

$$\frac{\partial P}{\partial t} = -\frac{1}{q}\frac{\partial J_P}{\partial x} \tag{9}$$

$R = R_{rad} + R_{SRH}$ is the recombination rate for electrons and holes. The radiative recombination rate is

$$R_{rad} = B_{rad}(np - n_i p_i) \tag{10}$$

Where B_{rad} is radiative recombination coefficient, n_i and p_i are intrinsic carrier density. The SRH recombination rate is

$$R_{SRH} = \frac{np - n_i p_i}{\tau_n p + \tau_p n} \tag{11}$$

Where $\tau_{n,p}$ are electron and hole pseudo-lifetime, respectively. For all cases, we assume that $\tau_n = \tau_p$. G is a uniform electron/hole generation rate applied to the perovskite layer. And in the status of thermal balance, we have

$$n_i p_i = N_C N_V e^{-E_g/k_B T} \tag{12}$$

where N_C is the effective conduction band density of states (DoS), N_V is the effective valence band DoS. In this work, the values of N_C and N_V are defined to be 5×10^{24} m^{-3} in perovskite layer.

Poisson's equation about the electric potential

$$\frac{\partial^2 \varphi}{dx^2} = \frac{q(n + N - p - P)}{\varepsilon_0 \varepsilon_P} \tag{13}$$

ϕ and $E = -\frac{d\phi}{dx}$ are electric potential and electric field.

(2) Electron transport layer (ETL)

$$J_n = q\mu_n nE + qD_n \frac{\partial n}{\partial x} \tag{14}$$

$$\frac{\partial n}{\partial t} - \frac{1}{q}\frac{\partial J_n}{\partial x} = 0 \tag{15}$$

$$\frac{\partial^2 \varphi}{dx^2} = \frac{q(n - D_E)}{\varepsilon_0 \varepsilon_E} \tag{16}$$

D_E is the n-type doping concentration, ε_E is the relative permittivity of ETL.

(3) Hole transport layer (HTL)

$$J_p = q\mu_p pE - qD_p \frac{\partial p}{\partial x} \tag{17}$$

$$\frac{\partial p}{\partial t} + \frac{1}{q}\frac{\partial J_p}{\partial x} = 0 \tag{18}$$

$$\frac{\partial^2 \varphi}{dx^2} = \frac{q(D_H - p)}{\varepsilon_0 \varepsilon_H} \tag{19}$$

D_H is the n-type doping concentration, ε_H is the relative permittivity of ETL.

Calculation method

The J-V hysteresis phenomenon was calculated used COMSOL Multiphysics 5.4 software. The radiative recombination $B_{rad} = 2\times10^{-11} cm^3 s^{-1}$ was always enabled in the perovskite layer to yield an open-circuit voltage of about 1.3V. For the bulk recombination, $\tau_n = \tau_p = 10ns$, and for the interfacial recombination, $\tau_n = \tau_p = 0.2ns$. The ionic movement and redistribution were only constrained inside the perovskite layer. For the initial conditions and measurement protocol, the device was generally pre-biased with a positive voltage 1.2 V to reach an equilibrium condition. Then the external applied voltage swept from 1.2 V to −0.2 V (Reverse, R), and turn back to 1.2 V (Forward, F) immediately to fulfill a complete J-V loop. While in case of F-R measurement protocol, the voltage swept from −0.2 V to 1.2 V, and back to −0.2 V. The voltage varied with a step of 20 mV, and the scan rate could be varied among 2.4 V/s, 240 mV/s, 24 mV/s and 4 mV/s, as seen in Figure. S1.

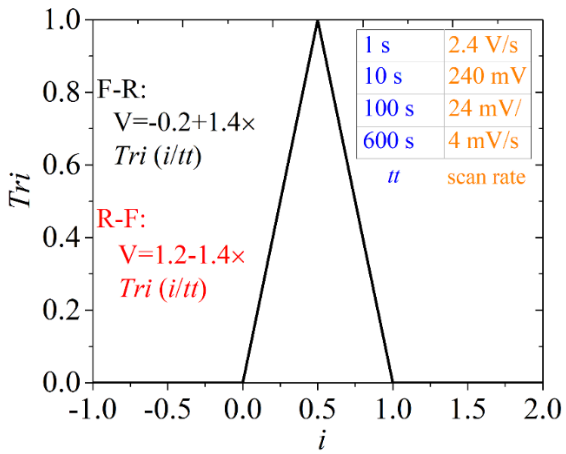

Figure S1. Scan rate determined by a triangle function.