Modelling Temperature Dependence of Hysteresis in Perovskite Solar Cells

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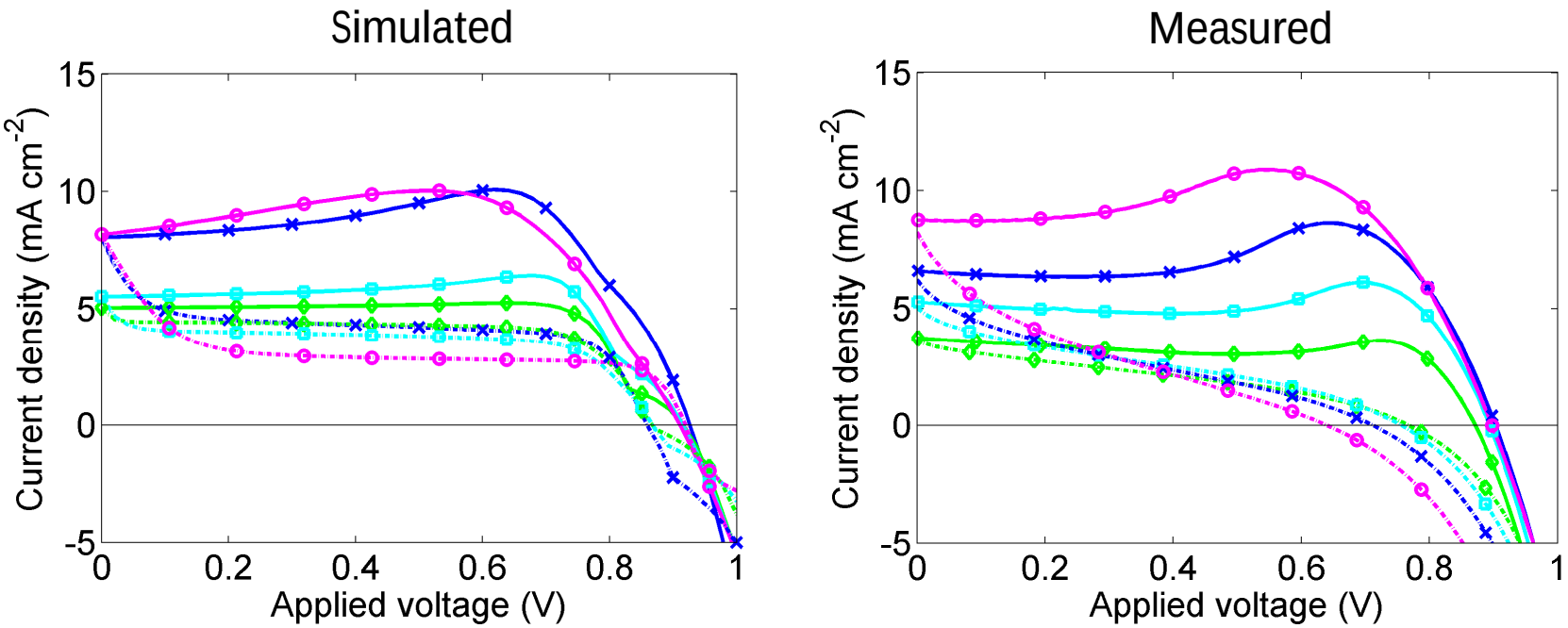
Background

In a paper published in February, we were able to achieve a semi-quantitative fit to measured current-voltage hysteresis loops using a drift-diffusion model that included mobile I^- vacancies and Shockley-Read-Hall recombination.

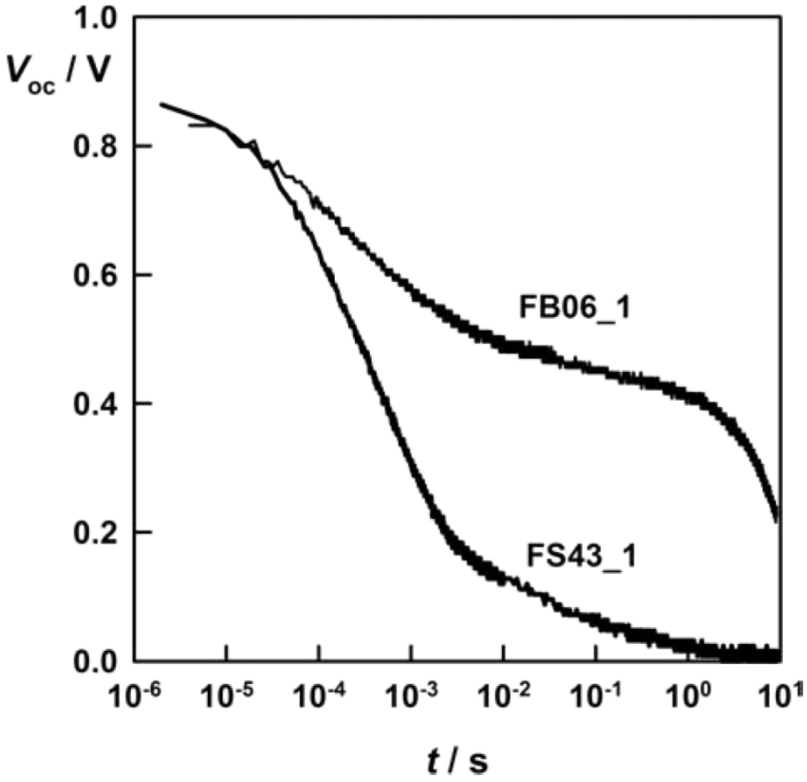


Giles Richardson *et al.*, *Energy Environ. Sci.*, vol. 9, pp. 1476-1485, February 2016

Background

Unusual features in impedance spectroscopy and intensity-modulated photocurrent spectroscopy (IMPS) measurements have been observed at similar timescales to the current-voltage hysteresis, in addition to multiple open circuit voltage decay lifetimes (right). It is likely that these features are also caused by mobile vacancies.

Current decay transients measured at constant voltage are much easier to simulate that any of the above, yet none had been reported in the literature until very recently.



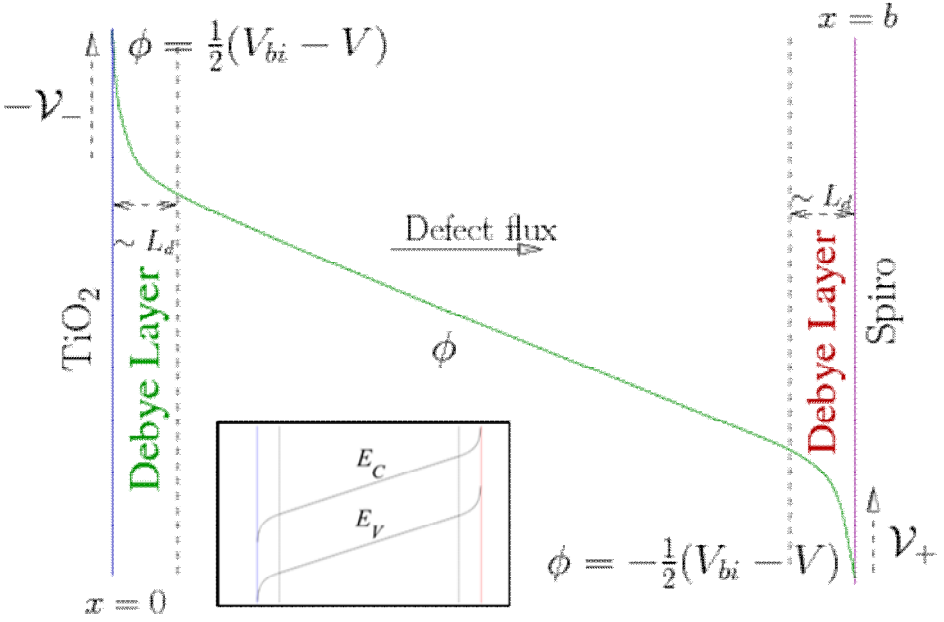
Adam Pockett *et al.*, *J. Phys. Chem. C*, vol. 199, pp. 3456-3465, January 2015

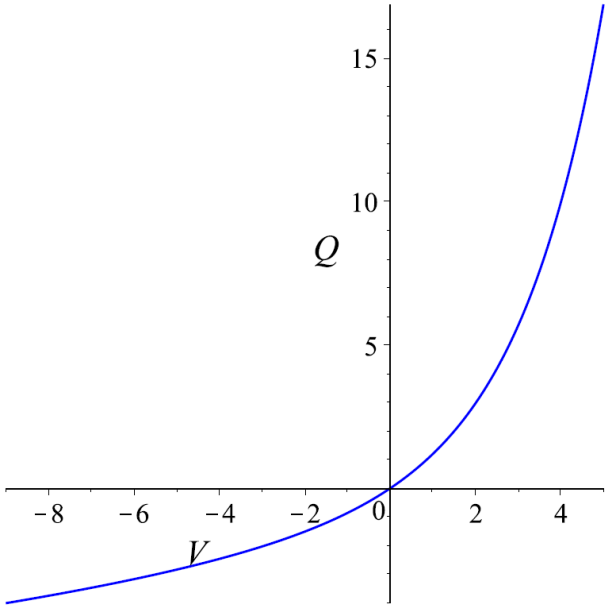
Asymptotic approximation

If the concentration of ions is large enough ($N_0 \sim 10^{24}$ m^{-3}), virtually all of the charge accumulates in small Debye layers causing significant potential jumps $V_{\pm}$.

Assuming only positive charges (I^- vacancies) can move and negative charges are fixed, the Debye charge is given by the equation

$$Q_{\pm}(V_{\pm}) = \pm\sqrt{2\left[\exp(V_{\pm}) - 1 - V_{\pm}\right]}$$





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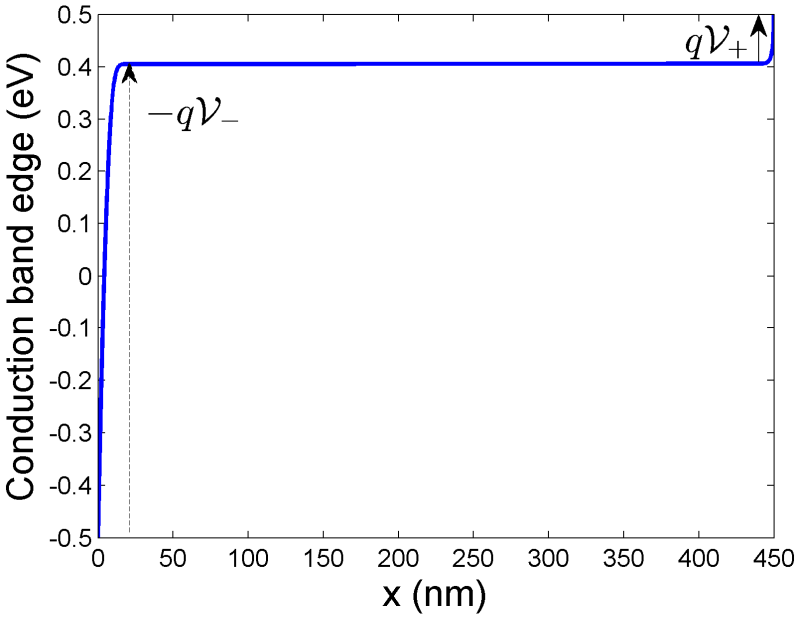
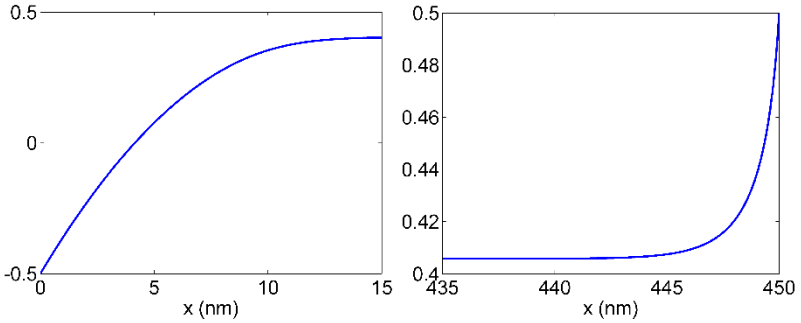
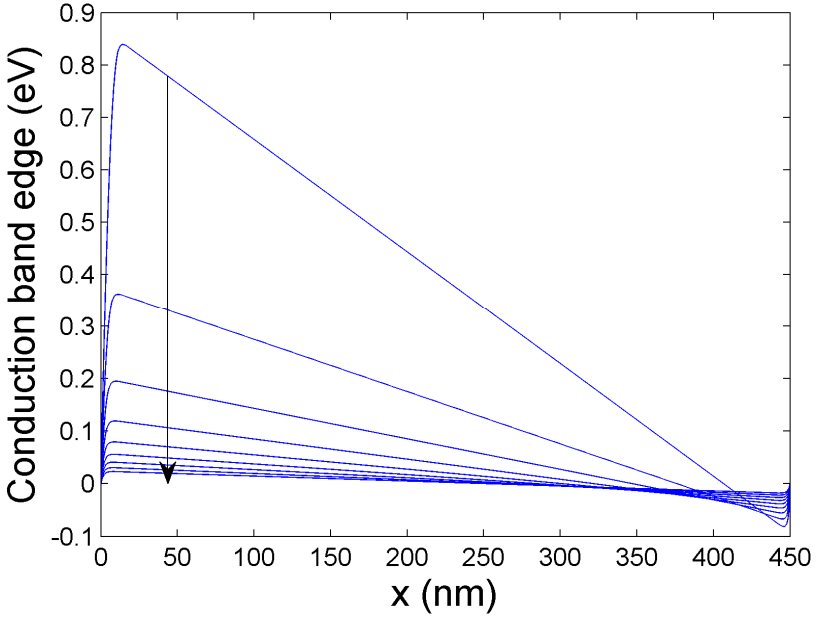
The voltage jump experiment

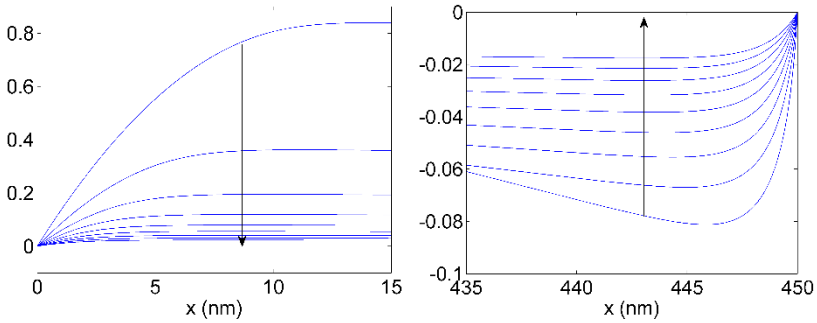
Equilibrium condition (0 V in the dark)





Abrupt jump from equilibrium to 1 V

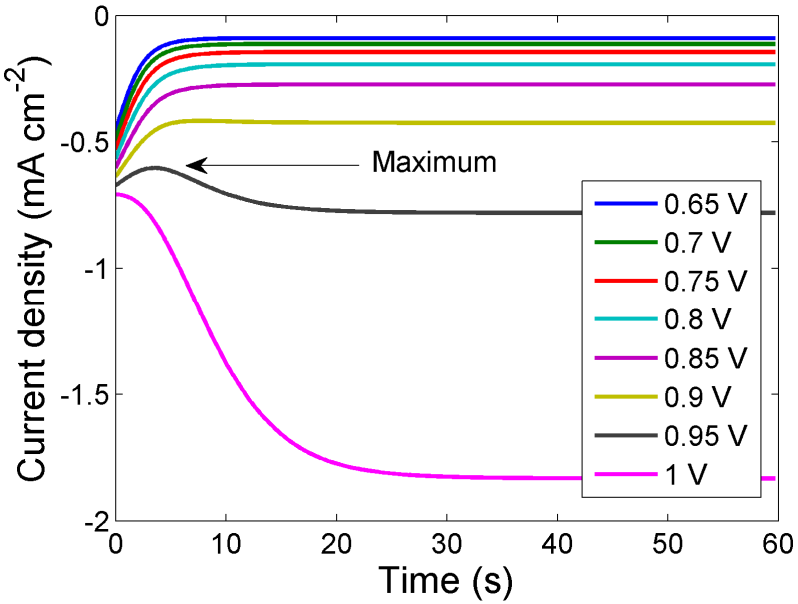




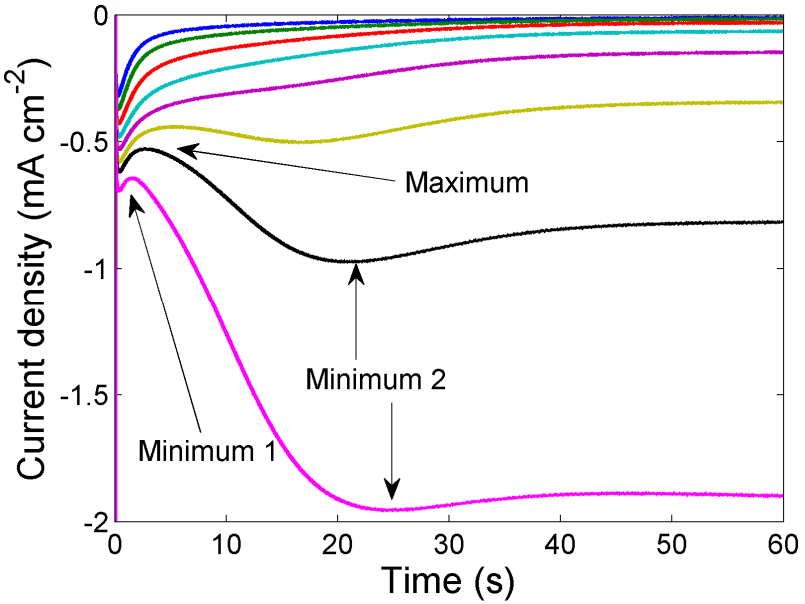
Results: varying jump voltage

For the first experiment, the voltage was jumped from 0 V to one of eight voltages, with temperature fixed at 298 K and no illumination. There is strong agreement between simulation and measurement, except two minima that are absent in the simulation results. Monomolecular hole-dependent recombination was assumed.

Simulated



Measured



Temperature dependence

Temperature affects many aspects of the cell's operation. The vacancy diffusion coefficient D_+ varies as

$$D_+ = D_\infty \exp\left(\frac{-E_A}{k_B T}\right)$$

According to Eames *et al.* (2015), E_A = 0.58 eV and D_+ = 10^{-12} cm^2/s at 320 K, so D_∞ = 3.15 x 10^{-3} cm^2/s. Assuming D_∞ is unchanged, setting D_+ = 7.5x10^{-13} cm^2/s at 298 K requires E_A = 0.55 eV for this cell, so use this to get T dependence of D_+.

The concentration of electrons at the TiO_2 interface and of holes at the spiro interface is temperature dependent:

$$n\big|_{x=0} = N_C \exp\left(\frac{E_{Ft} - E_C}{k_B T}\right)$$

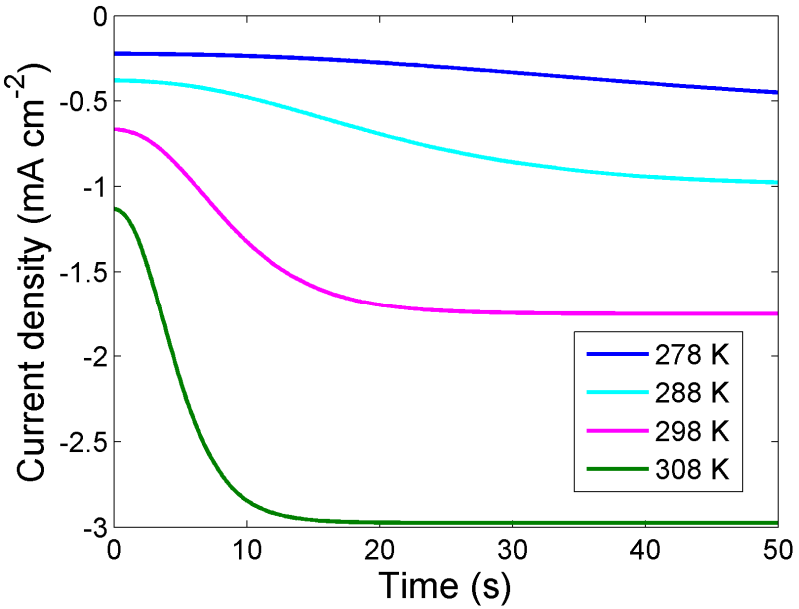
$$p\big|_{x=b} = N_V \exp\left(\frac{E_V - E_{Fs}}{k_B T}\right)$$

where E_{ft} and E_{fs} are the Fermi levels of the TiO_2 and spiro respectively.

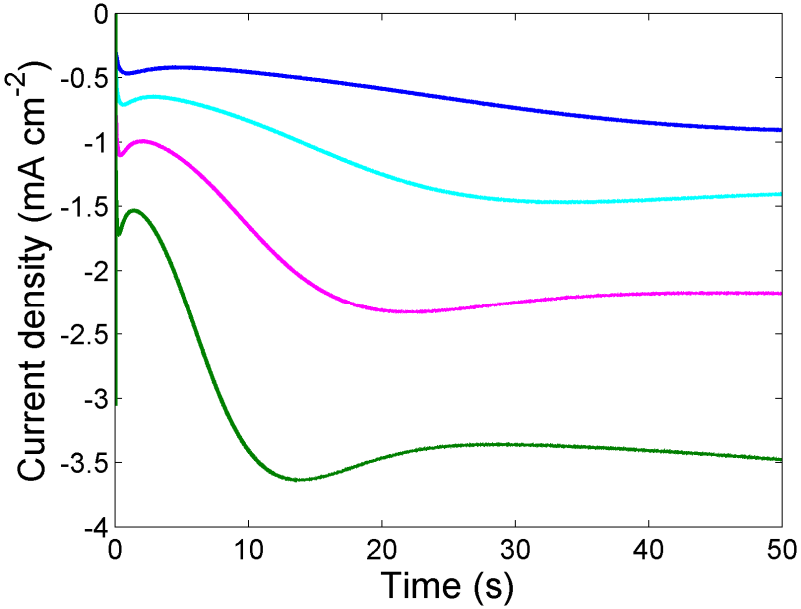
Results: varying temperature

For the second experiment, the jump voltage was fixed at 1 V and the temperature was varied, with no illumination. The agreement is weaker than for the varying jump voltage experiment but the timescale of the decay is similar in both, suggesting the thermally activated behaviour of the vacancy motion is correct.

Simulated



Measured



Summary

- First transient dark current decay measurements on perovskite solar cells
- Simulations show strong agreement with measurement, except for two minima
- Minimum 1 occurs on short timescales & probably due to competing recombination mechanisms
- Minimum 2 occurs when the I^- vacancies have finished moving, suggesting a different process
- Temperature-dependent results imply that vacancy motion is indeed thermally activated

Acknowledgments

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- Philip Schulz
- nanoGE and University of Swansea for organizing

Recombination mechanisms

In our previous work, we assumed Shockley-Read-Hall recombination in the bulk, assuming $\tau_n >> \tau_p$.

$$R = \frac{np - n_{eq} p_{eq}}{\tau_n (n + n_{eq}) + \tau_p (p + p_{eq})} \quad (1)$$

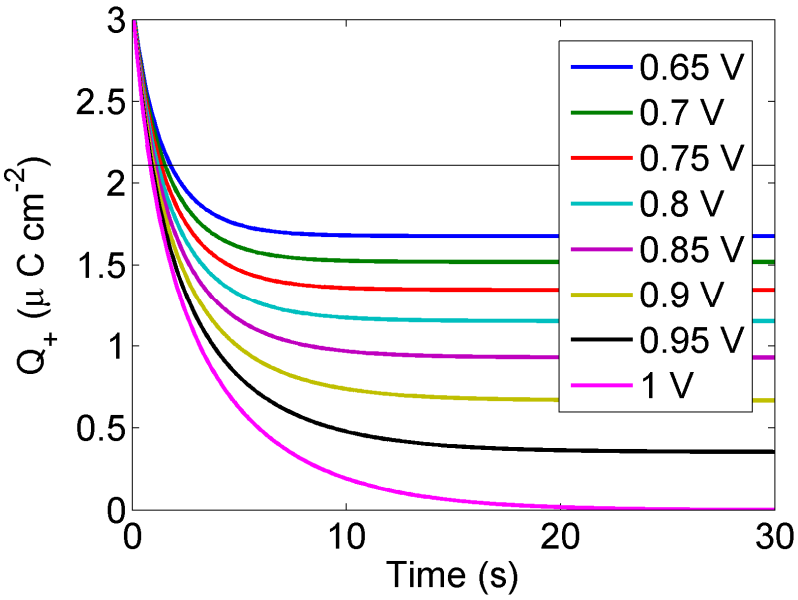
However, due to the large electric field that arises when the voltage is jumped, (1) becomes very difficult to solve computationally. Substitute τ_p = 0 into (1):

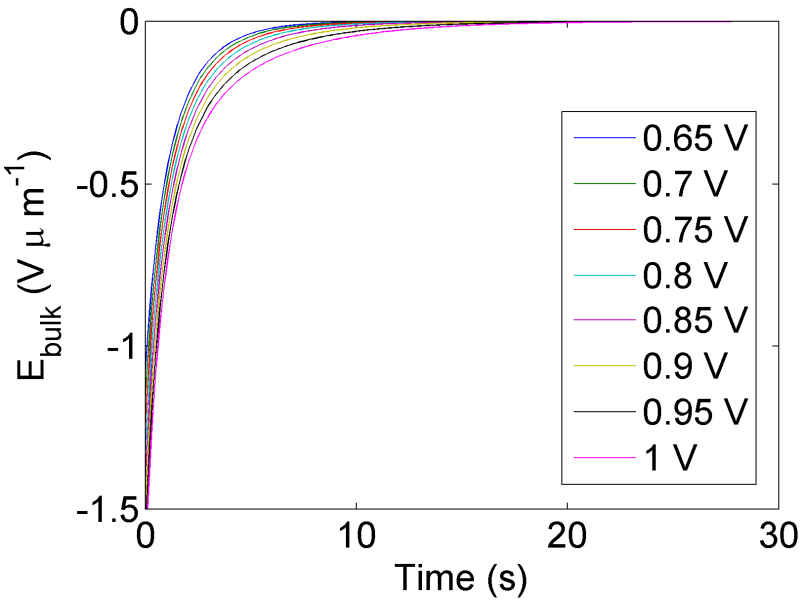
$$R = \frac{np - n_{eq} p_{eq}}{\tau_n (n + n_{eq})} \quad (2)$$

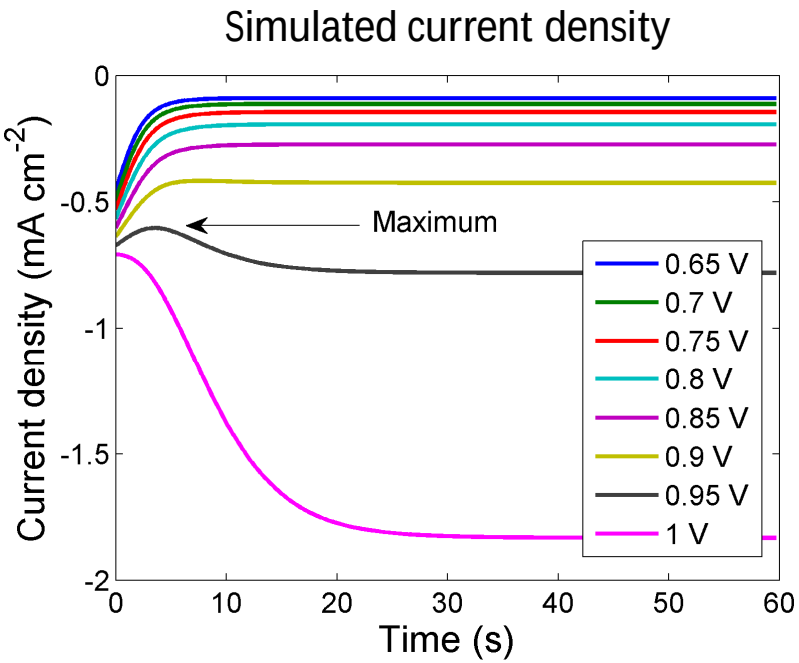
If $n >> n_{eq}$, (2) is approximately monomolecular:

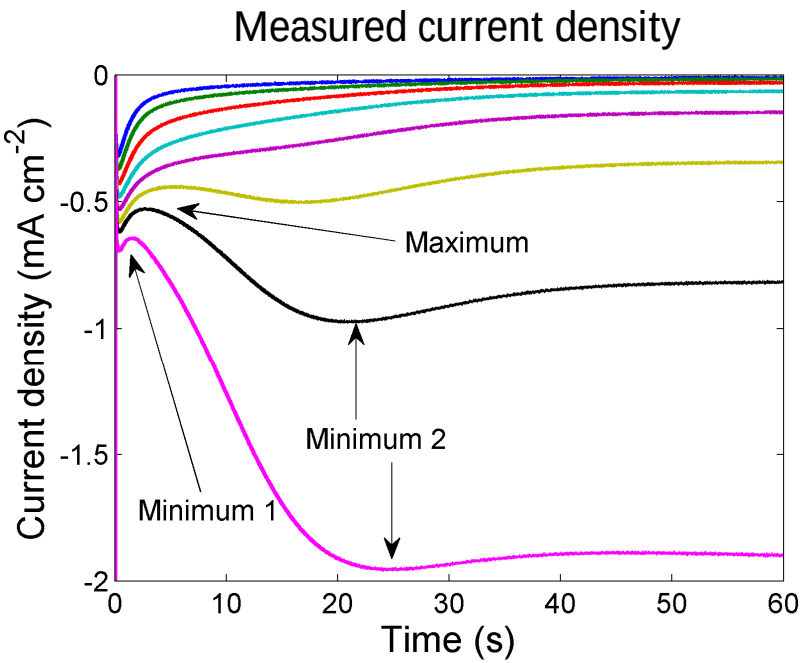
$$R \approx \frac{p}{\tau_n} \quad (3)$$

At 298 K, (3) is a valid approximation when $Q_+ < 2.1$ μC cm^{-2}


3
2.5
2
1.5
1
0.5
0
0
10
20
30
Time (s)
Q_+ (μ C cm^{-2})
0.65 V
0.7 V
0.75 V
0.8 V
0.85 V
0.9 V
0.95 V
1 V


0
-0.5
-1
-1.5
0
10
20
30
Time (s)
E_{bulk} (V μ m^{-1})
0.65 V
0.7 V
0.75 V
0.8 V
0.85 V
0.9 V
0.95 V
1 V


Simulated current density
0
-0.5
-1
-1.5
-2
0
10
20
30
40
50
60
Time (s)
Current density (mA cm^{-2})
Maximum
0.65 V
0.7 V
0.75 V
0.8 V
0.85 V
0.9 V
0.95 V
1 V


Measured current density
0
-0.5
-1
-1.5
-2
0
10
20
30
40
50
60
Time (s)
Current density (mA cm^{-2})
Maximum
Minimum 2
Minimum 1