Time-Dependent Drift-Diffusion Modelling of Perovskite Solar Cells with Moving Ions

Simon O’Kane¹, Timo Peltola¹, Jamie Foster², Giles Richardson² and Alison Walker¹

¹Department of Physics, University of Bath
²Department of Mathematical Sciences, University of Southampton
Motivation

Slow-moving ions within the perovskite have been proposed as the cause of hysteresis observed in current-voltage measurements. Several authors have suggested iodide vacancies arising from Schottky defects, while foreign ions (H\(^+\), OH\(^-\), Li\(^+\) etc.) have also been suggested. Time-dependent drift-diffusion models provide a way of testing the ‘moving ion hypothesis’.


Asymptotic approximation

If the concentration of ions is large enough \( N_0 \sim 10^{24} \text{ m}^{-3} \), 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

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

To test the asymptotic approximation, a numerical calculation (solid blue lines) was performed for ion concentration $N_0 = 10^{23} \, \text{m}^{-3}$, scanning from $V = V_{bi} = 1 \, \text{Volt}$ to short circuit ($V = 0$). The same calculation was performed with the asymptotic model (dashed green lines) and the two show strong agreement. Assuming an ionic diffusion constant of $10^{-14} \, \text{m}^2 \, \text{s}^{-1}$, the scan rate corresponds to about 0.9 \, \text{V} \, \text{s}^{-1}.$
How does this cause hysteresis?

On the reverse scan, the bulk field drives electrons and holes towards their selective contacts, decreasing recombination hence increasing output current. On the forward scan, residual charge in the Debye layers causes the bulk field to reverse direction, increasing recombination and hence decreasing output current. This analysis assumes there is little/no surface recombination!
J-V curves using asymptotic model

The real ion density $N_0 \sim 10^{25} \text{ m}^{-3}$, which makes the problem too stiff for numerics. The asymptotic approximation was used to find $V_\pm$ and the bulk voltage drop $V_{bulk}$. A numerical model was then used to calculate carrier densities in the bulk region.

Shockley-Read-Hall recombination

Langevin (bimolecular) recombination

Fast scan $\approx 9 \text{ V s}^{-1}$, slow scan $\approx 1.8 \text{ V s}^{-1}$ assuming an ion diffusion coefficient of $10^{-14} \text{ m}^2 \text{ s}^{-1}$
Comparison with measurements

- Intersecting J-V curves not observed in measurements
- Behaviour close to short circuit similar to that observed by Tress et al. (2015)
- Predictions similar to those for measurements for slower scan rates, suggesting the ionic diffusion coefficient is closer to $10^{-15}$ m$^2$ s$^{-1}$

Explaining the unusual behaviour

Note the maxima in $V_{\text{bulk}}$ that arise during the reverse scan.

The black line represents what $V_{\text{bulk}}$ would do if there were no ions.
Future work

The current model assumes ions cannot leave the perovskite. What if this isn’t true?

\[ R_{SRH} = \frac{np - n_{eq}p_{eq}}{\tau_n(n + n_{eq}) + \tau_p(p + p_{eq})} \]

So far been assuming that \( \tau_n = \tau_p \). What if that isn’t true?

Large parameter space to explore!

There have been very few studies of interface energetics in perovskite cells, so try experimenting with these
Summary

• Hypothesis: ionic charge accumulates in narrow Debye layers, leaving the bulk virtually charge-free
• Asymptotics and numerics show strong agreement
• The model predicts hysteresis but the forward and reverse J-V curves intersect; this has never been observed in measurements
• Qualitatively similar behaviour for Langevin and SRH recombination but SRH fill factor more realistic
• Model can be applied to any ion species, not just I⁻
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