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

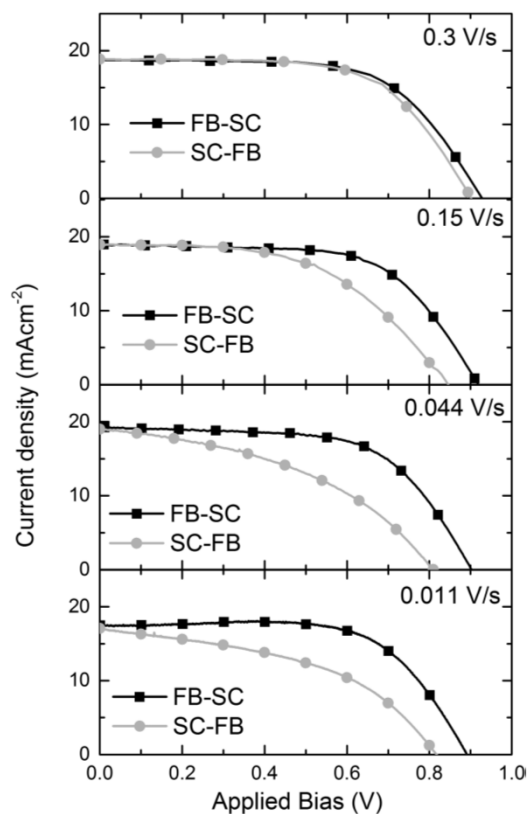
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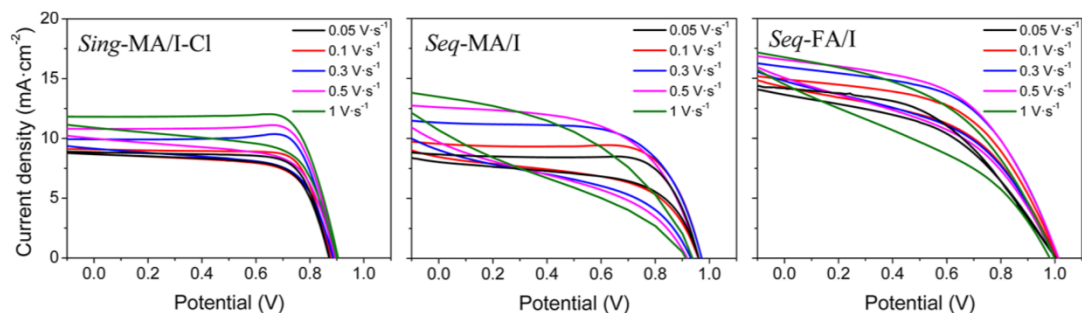


Motivation



Henry Snaith *et al.*, *J. Phys. Chem. Lett.*, vol. 5, no. 9, pp. 1511-1515, March 2014

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'.



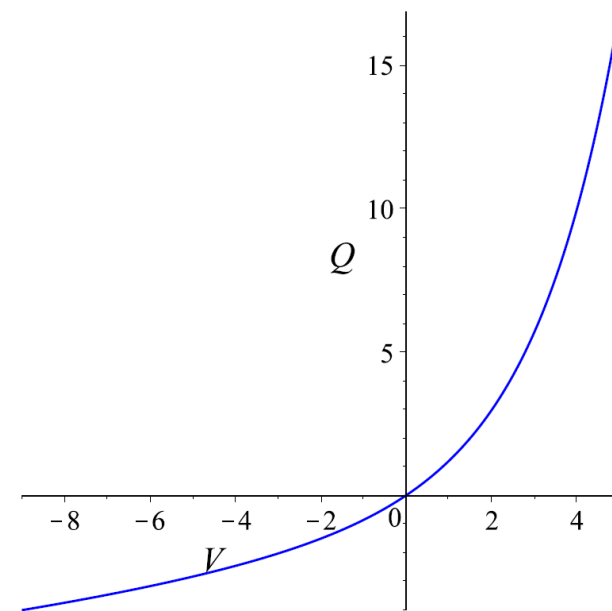
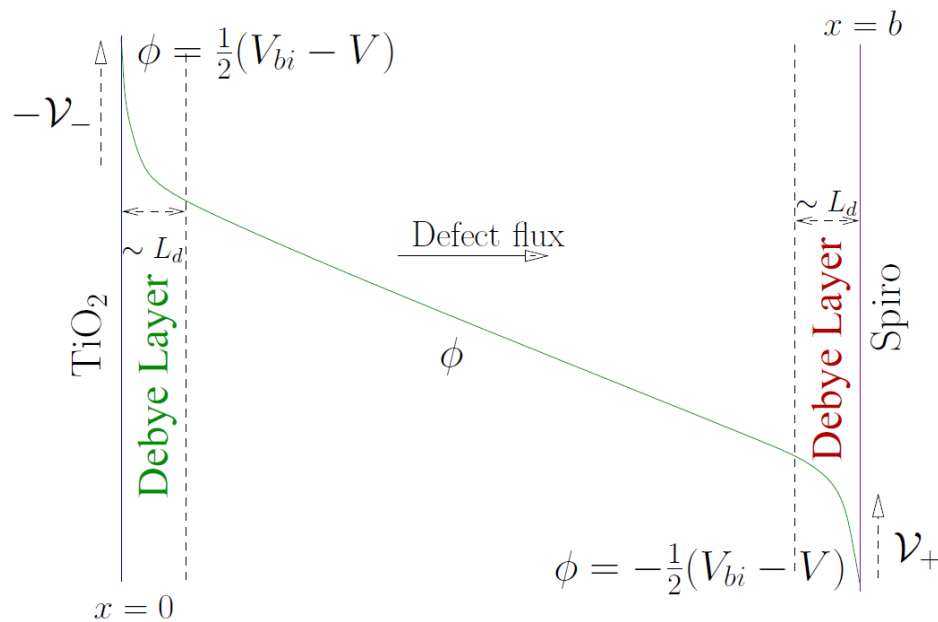
Rafael Sanchez *et al.*, *J. Phys. Chem. Lett.*, vol. 5, no. 13, pp. 2357-2363, June 2014

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} .

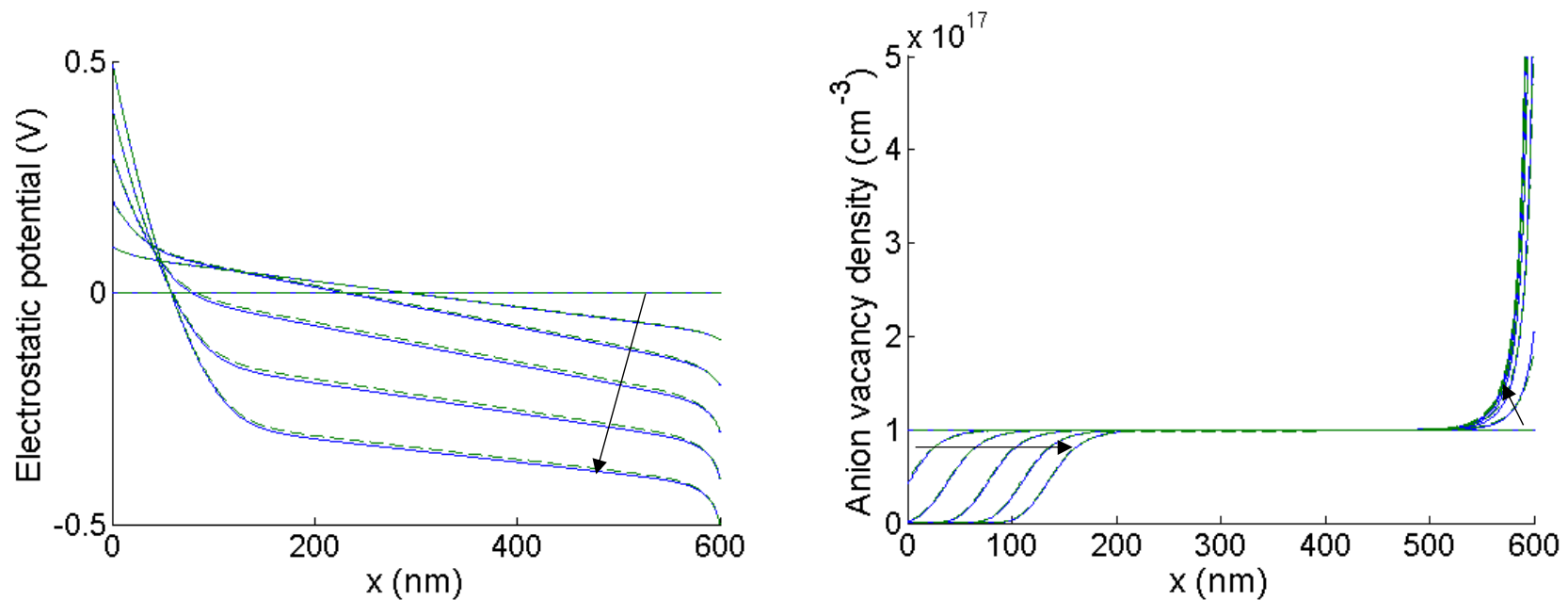
Assuming only positive charges (I⁻ vacancies) can move and negative charges are fixed, the Debye charge is given by the equation

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



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 $V = V_{bi} = 1$ 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 V s^{-1} .

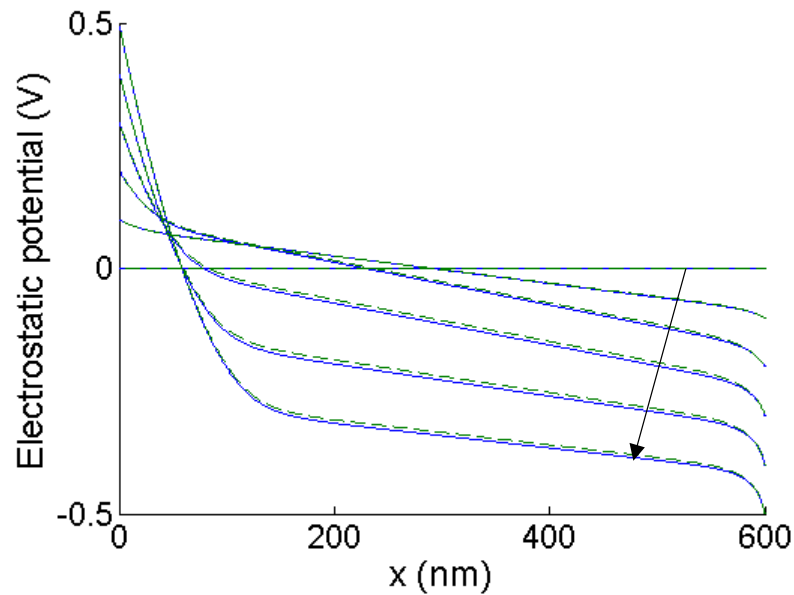


How does this cause hysteresis?

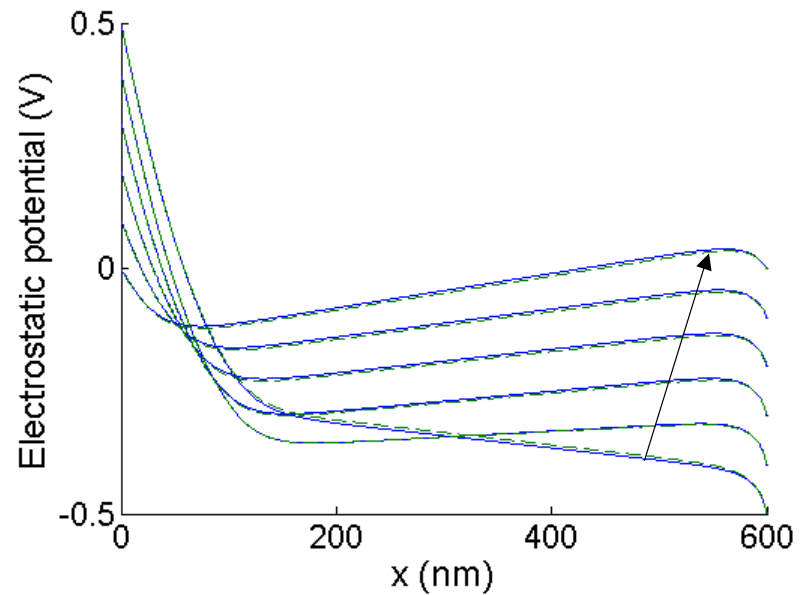
On the reverse scan, the bulk field drives electrons and holes towards their selective contacts, decreasing recombination hence increasing output current.
On the forward scan, residual charge in the Debye layers causes the bulk field to reverse direction, increasing recombination and hence decreasing output current.

This analysis assumes there is little/no surface recombination!

Reverse scan ($V_{bi} \rightarrow$ short circuit)

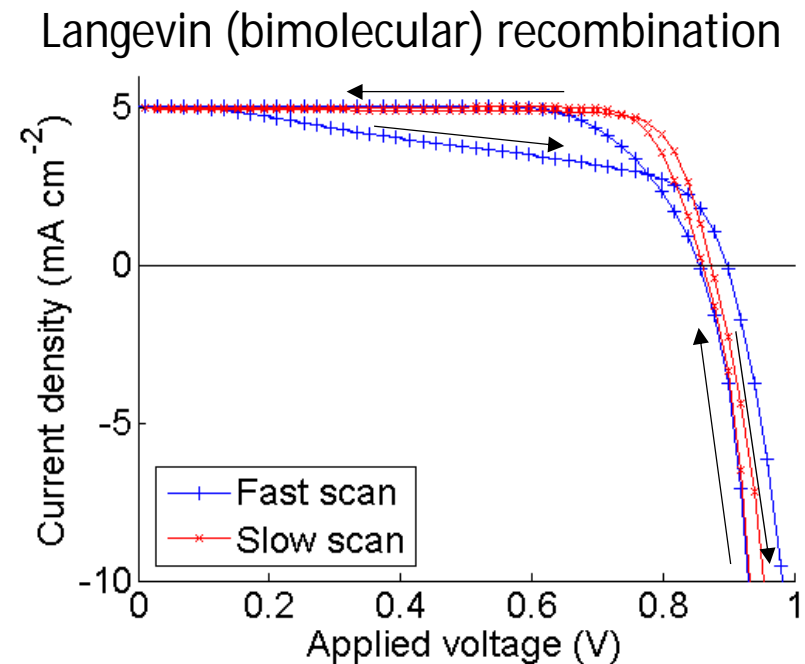
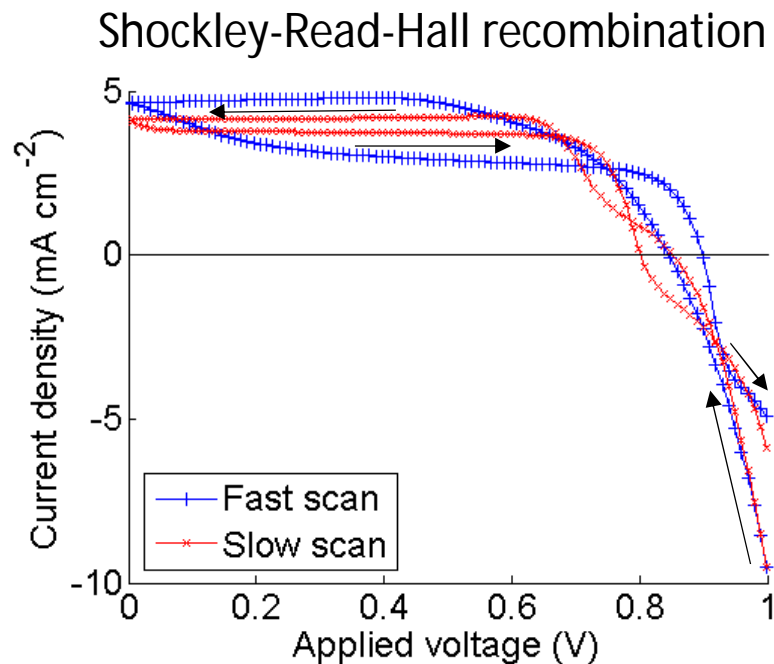


Forward scan (short circuit $\rightarrow V_{bi}$)



J-V curves using asymptotic model

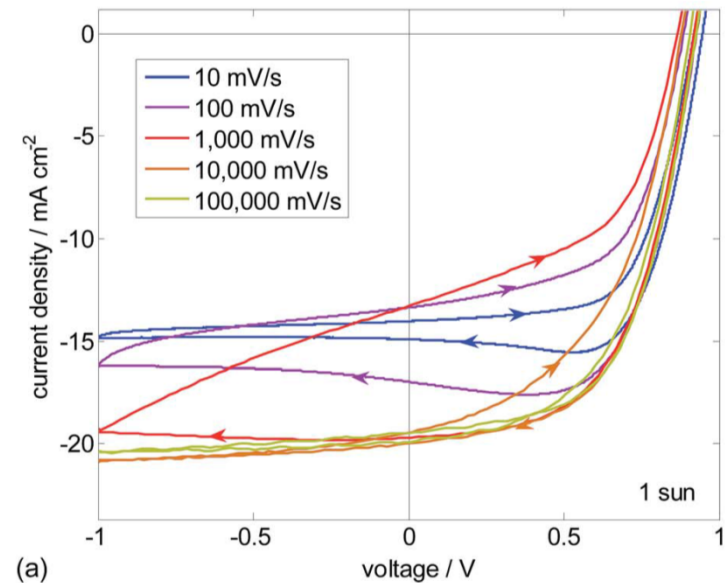
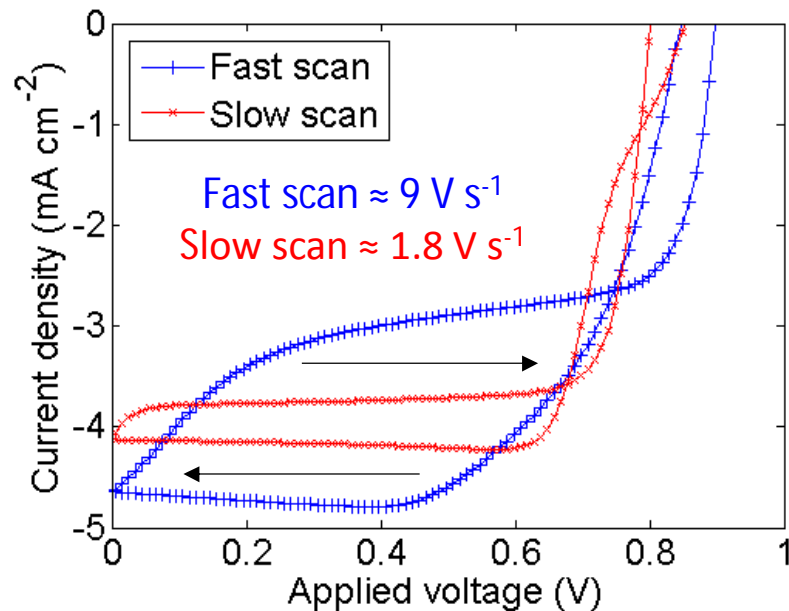
The real ion density $N_0 \sim 10^{25} \text{ m}^{-3}$, which makes the problem too stiff for numerics. The asymptotic approximation was used to find V_{\pm} and the bulk voltage drop V_{bulk} . A numerical model was then used to calculate carrier densities in the bulk region.



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

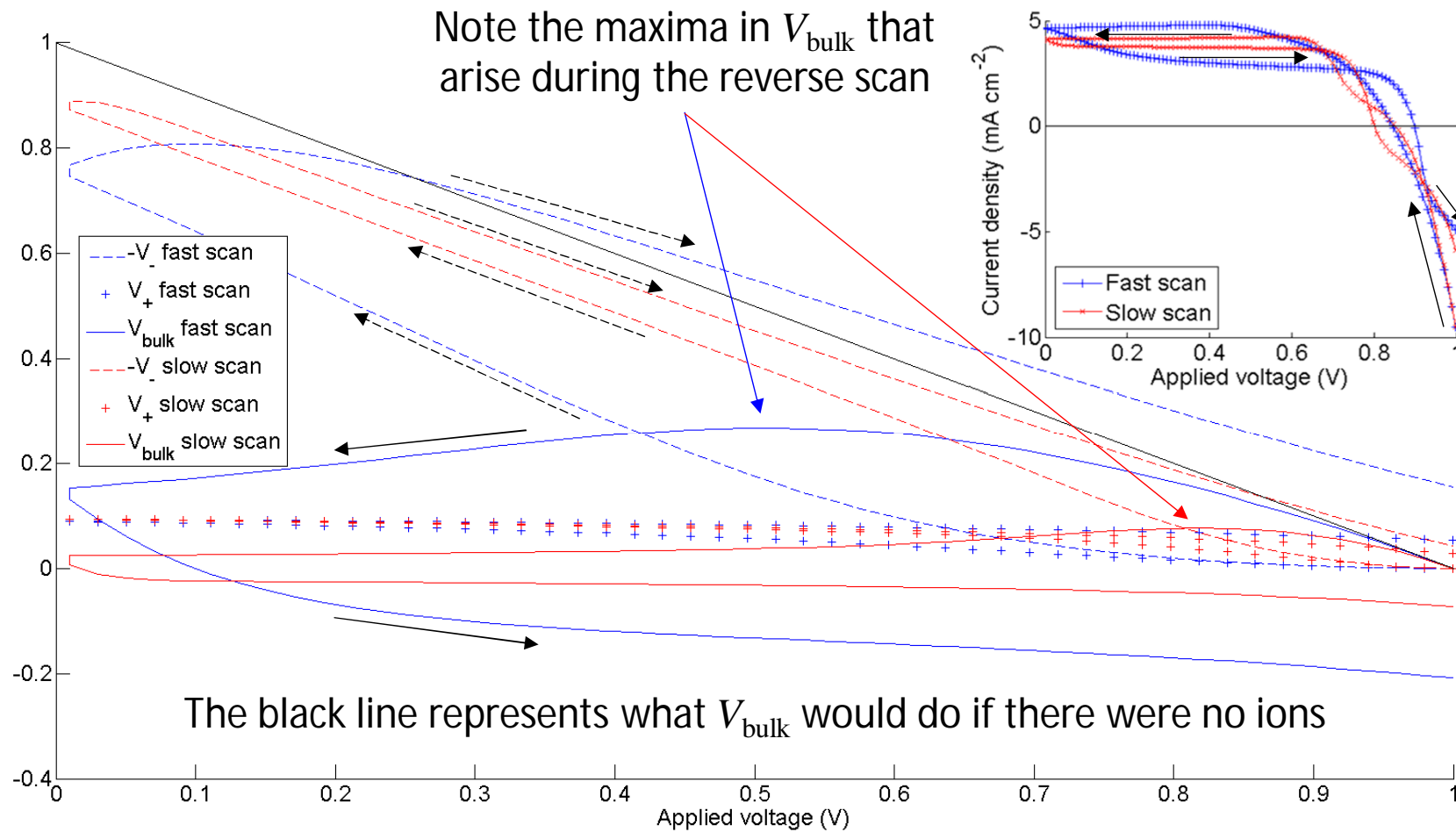
Comparison with measurements

- 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 $10^{-15} \text{ m}^2 \text{ s}^{-1}$

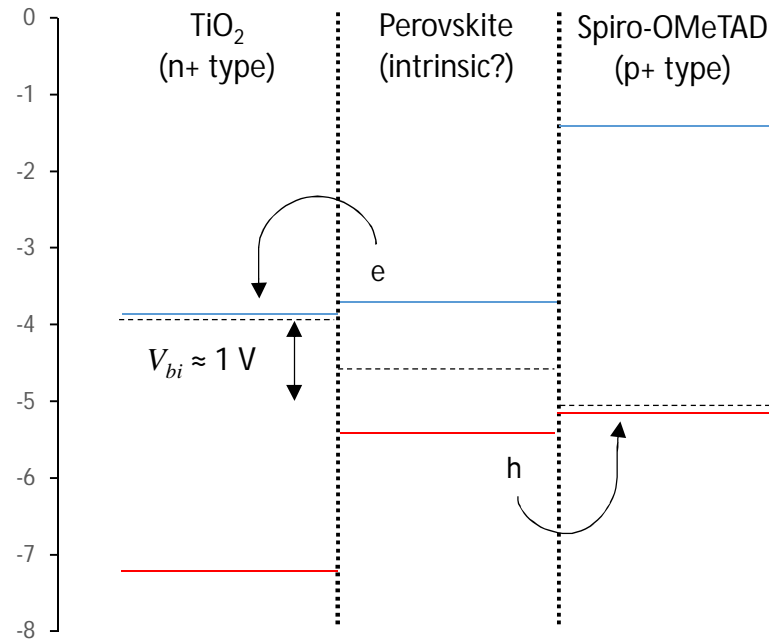


Tress *et al.* *Energy Environ. Sci.* vol. 8 pp. 995, January 2015

Explaining the unusual behaviour



Future work



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

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!

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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