

Explaining transient behaviour in perovskite solar cells through the interaction between mobile ions and SRH recombination

Daniel Walter, Andreas Fell^{2,3}, The Duong¹, Chog Barugkin¹, Yiliang Wu¹, Nandi Wu¹ and Klaus Weber¹

¹*Centre for Sustainable Energy Systems, Australian National University, ACT 2601, Australia*

²*Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, 79110 Freiburg, Germany*

³*AF Simulations, March, 79232, Germany*

E-mail: daniel.walter@anu.edu.au

Abstract

The origins of slow transient responses of perovskite solar cells (PSCs) – commonly referred to as hysteresis – is a major focus of current research. In this work, we present an overview of our recent insights into PSC hysteresis through a rigorous transient numerical device model based on the Quokka simulation tool. Our approach incorporates mobile ionic charge, which is implemented as effectively a mobile population of ionised dopant impurities. We show how this conceptually simple framework can qualitatively replicate a wide array of hysteresis-related phenomena in PSCs. These range from J-V hysteresis, through to transient responses in current, voltage and luminescence and even long-term (but ultimately reversible) degradation in cell performance. In each case, slow stabilisation, even unusual non-monotonic transients, are shown to simply be varied expressions of the influence of the mobile ionic charge on local rates of recombination through a static population of electronic traps. Although this framework is highly unlikely to fully account for all physical processes relevant to PSC operation, the breadth of agreement with experimental data points toward ion-recombination interactions as fundamental to our understanding of charge transport and hysteresis in perovskite solar cells.

1. Introduction

Perovskite solar cells are a promising evolution in photovoltaic technology. Their most compelling use-case is as a wide band-gap top cell in tandem devices, e.g. on a silicon substrate, for which a current record of 27.3% on a monolithic silicon-perovskite tandem was recently achieved by Oxford PV [1]. However, a great deal of PSC research is based on a broad, and often undirected, investigation of device structures and perovskite mixtures. Yet PSCs still face challenges: (1) how to achieve further efficiency gains, which have ‘stagnated’ (by perovskite standards) at ~22.5% for the last few years [2]; and (2) the challenge of long-term stability, which is still far from resolved, and could prove a major hurdle to commercialisation. A key foundation to addressing these challenges lies in a clearer understanding of loss mechanisms in PSCs, identifying what changes constitute permanent vs reversible degradation, and developing characterisation methods to reveal dominant sources of loss.

So far, fundamental studies in perovskite materials have drawn two major conclusions. The first is that in many ways, perovskites conduct electronic charge in a manner akin to inorganic semiconductors such as GaAs or Si [3], [4]. That is, they are non-excitonic, bivalent conductors of electrons and holes with low effective masses. Secondly, perovskites are also ionic conductors. Ionic conduction is therefore the leading candidate for “abnormal hysteresis”. On the back of this knowledge, we have recently developed a numerical device model of a ‘perovskite’ semiconductor, incorporating multiple mobile ionic charge species, which is highly successful in replicating a range of transient behaviours in PSCs [5]–[8]. This model is built on the widely-used Quokka silicon solar cell simulator, and full details have been published previously [6]. In this contribution, we will present an overview of the key conclusions from our recent investigations into PSC physics based on this model.

2. Results

One manifestation of PSC hysteresis is through slow stabilisation following a change in operating conditions. For example, Figure 1a plots a range of characteristic responses in open-circuit voltage that are measured on PSCs fabricated at ANU. These responses are diverse and in two cases, non-

monotonic in function. In Figure 1b we plot simulated V_{oc} responses, which reveal that each response can be replicated via different configurations of ion concentrations, mobilities and/or the distribution of mid-gap electronic traps. For example, response (3) is characterised by dominant interface recombination, while response (4) is predicted for a device with low levels of bulk and interface recombination. It is notable, therefore, that response (4) was measured on a high-voltage ($V_{oc} > 1.2$ V) PSC with a passivation interlayer at both interfaces, which we suppose to reduce the density of recombination-active defects [9]. It is therefore possible that the characteristic of these responses may point towards the strength and/or location of recombination in the PSC.

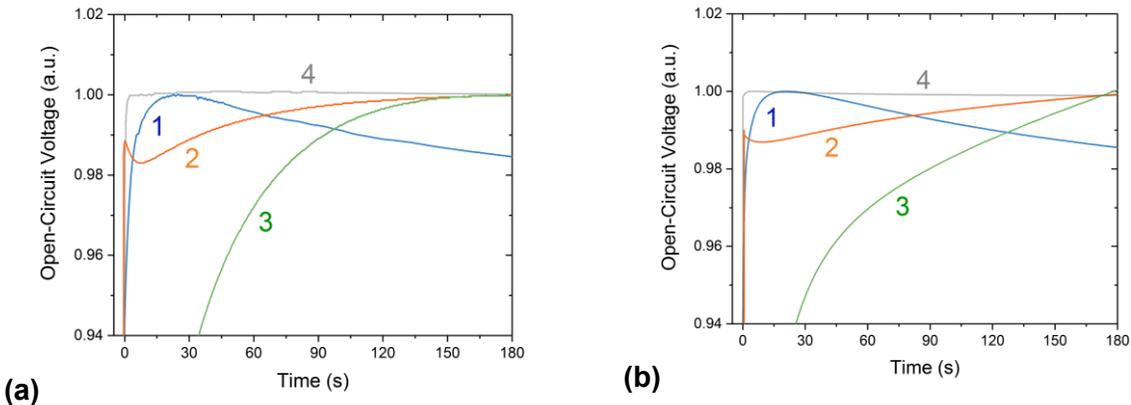


Figure 1: Measured (a), and simulated (b), transients in open-circuit voltage of PSCs following abrupt illumination from dark conditions. Rather than reflecting fundamentally different processes in the devices, our modelling shows that each is a different expression of ion-recombination interaction.

Although each response is characteristically different, our model reveals a common cause: the movement of ionic charge creates a time-varying net doping profile (akin to compensation in silicon). This net ionic-doping profile redistributes electron and hole populations, creating time- and spatially-varying recombination profiles in the perovskite absorber through SRH recombination statistics (Fig. 2).

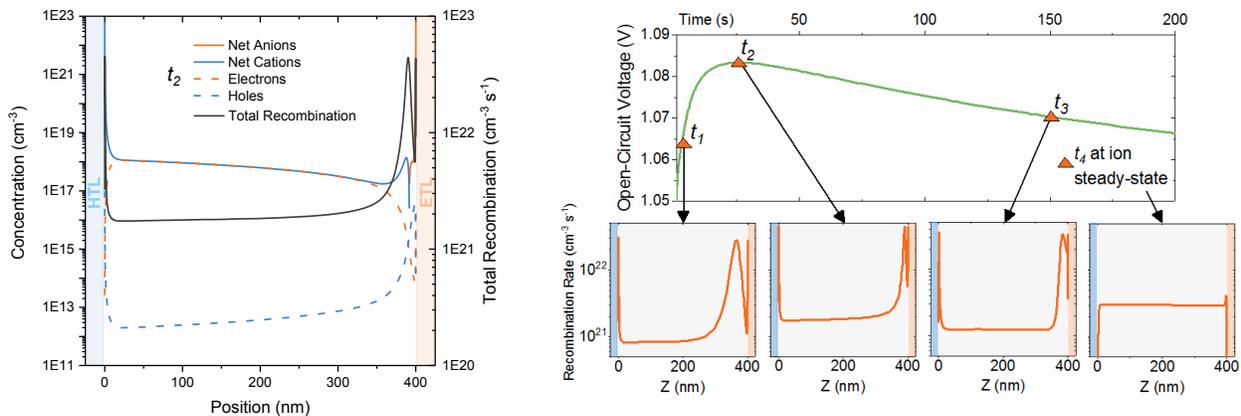


Figure 2: (a) a spatial plot of the distribution of net ionic charge (i.e net ionic doping), electron-hole populations and total recombination at one point in the transient voltage, demonstrating the influence of ion distribution on recombination rates. And (b), the evolution of spatial recombination over time for response (1) of figure 1.

In the final contribution, we will present similar data and simulation for transient responses in photocurrent and luminescence, for which we see similarly qualitative agreement, and which are ultimately dependent on the same ion movement-recombination interaction. Furthermore, we will show that when there is a very slow-moving population of ionic defects (e.g. MA⁺ vacancies), this can result in extremely slow changes in device voltage or current (on the order of hours to days), that nonetheless are reversible and do not represent permanent degradation. Consequently, it is important to account for the possibility of slow-moving ions when assessing degradation.

Bibliography

- [1] “Oxford PV sets world record for perovskite solar cell [Oxford PV.]” [Online]. Available: <https://www.oxfordpv.com/news/oxford-pv-sets-world-record-perovskite-solar-cell>. [Accessed: 16-Jul-2018].
- [2] NREL, *NREL Research Cell Record Efficiency Chart*. .
- [3] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, “Hybrid organic—inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties,” *Nat. Rev. Mater.*, vol. 1, no. 1, p. 15007, Jan. 2016.
- [4] A. M. Soufiani *et al.*, “Impact of microstructure on the electron–hole interaction in lead halide perovskites,” *Energy Environ. Sci.*, vol. 10, no. 6, pp. 1358–1366, 2017.
- [5] A. Fell, D. Walter, and S. Glunz, “A Fast and Easy Perovskite Solar Cell Simulation Tool Featuring Ion Migration,” in *33rd European Photovoltaic Solar Energy Conference and Exhibition*, Amsterdam, Netherlands, 2017.
- [6] D. Walter *et al.*, “Transient Photovoltage in Perovskite Solar Cells: Interaction of Trap-Mediated Recombination and Migration of Multiple Ionic Species,” *J. Phys. Chem. C*, vol. 122, no. 21, pp. 11270–11281, May 2018.
- [7] D. Walter, A. Fell, Y. Wu, T. Duong, and K. Weber, “The Interaction of Ion Migration with Shockley-Read-Hall Recombination in the Bulk of Perovskite Solar Cells Explains Anomalous Voltage and Luminescence Transients,” in *Proceedings of the 7th World Conference on Photovoltaic Energy Conversion*, Waikoloa, Hawaii, 2018.
- [8] De Bastiani, Michele *et al.*, “Ions, charge accumulation, and transient currents: The role of contact passivation in perovskite solar cells,” *Submitted*, 2018.
- [9] J. Peng *et al.*, “Interface passivation using ultrathin polymer–fullerene films for high-efficiency perovskite solar cells with negligible hysteresis,” *Energy Environ. Sci.*, vol. 10, no. 8, pp. 1792–1800, 2017.