Unravelling hysteresis in hybrid perovskite solar cells with transient optelectronic

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Hysteresis in the current voltage characteristics of hybrid perovskite solar cells is commonly observed for many preparations, particularly after aging the devices (figure 1).[1-4] We have found that even devices that have apparently stable current voltage curves at room temperature do show hysteresis when they are cooled to lower temperatures.[5] Ferroelectric effects have been proposed as a possible explanation for the phenomenon[6] however there is now increasing evidence that hysteresis results from the migration of ionic defects within the perovskite layer.[7-10] These mobile ions may form as a consequence of Schottky defect formation with concentrations as high as 0.4 %.[7] These charged defects are proposed to move to compensate the built in or applied electric field in the device (see figure 1). A consequence of this is the creation of space charge regions in the material close to the material interfaces, while the bulk of the material becomes free of electric field at equilibrium.

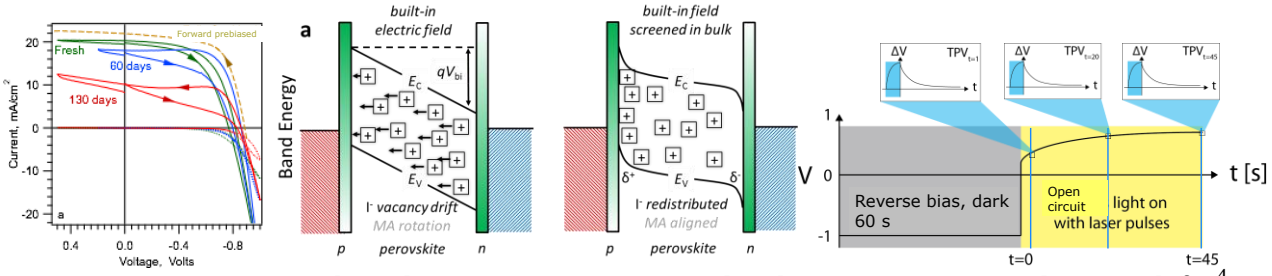

Figure 1. Current-voltage hysteresis in a $CH_3NH_3PbI_3$ device increasing with aging (left).[4] Proposed mechanism for the screening of the built in electric field (middle).[7] Schematic showing the experimental protocol for 'transient of the transient' measurements (right).

The compensation of internal electric fields in this manner was thought to cause hysteresis in the photocurrent-voltage characteristics due to the absence, or reversal of, the internal electric field in the device resulting in reduced charge collection efficiency. However, recently Reenen et al. used simulations to propose that recombination via interfacial traps was necessary, in addition to ionic migration, for hysteresis to be observed.[11]

Here we test the possible mechanisms by which photocurrent and photovoltage is lost in devices exhibiting hysteresis. To achieve this we have performed chronophotovoltametry measurements with a superimposed series of transient photovoltage measurements. The chronophotovoltametry measurements record the slow evolution of the photovoltage (over 10s of seconds) following preconditioning the device at different potentials in the dark. The transient photovoltage measurements allow the kinetics of recombinations (microsecond) to be tracked simultaneously (figure 1).

For devices showing hysteresis, the photovoltage after short circuit (or reverse bias) preconditioning rises steadily towards an equilibrium value (figure 2). The transient photovoltage behaviour shows anmalous behaviour: during the initial phase of the photovoltage evolution, the small perturbation photovoltage transients are negative during the pump pulses, followed by relaxation towards a positive response which then decays to the background level. Later during the background photovoltage rise the transient photovoltage signal is purely positive. Throughout the evolution of the photovoltage towards equilibrium the time constants for the positive component of the transient decays show only a minor change. This suggests that as the photovoltage of the device rises its recombination rate constant does not change significantly.

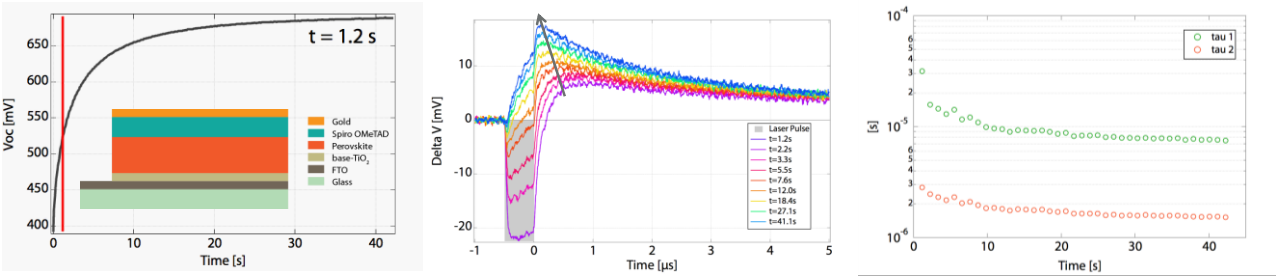

Figure 2. Evolution of the photovoltage of a bottom cathode hybrid $CH_3NH_3PbI_3$ under 1 sun equivalent illumination after preconditioning in the dark at short circuit (left). The midle panel shows the evolution of photovoltage transients recorded during the evolution of the steady state photovoltage shown in the left panel. The region shaded in grey corresponds to the duration of the laser pulse. The right hand panel shows the time constants of a double exponential function fitted to the decay component of the transients in the middle panel.

Using numerical drift-diffusion modelling including mobile ionic defects we show that the negative transients result from the reversal of electric fields in the device immediately following the photovoltage turn on. In addition the simulations revealed that surface recombination is also required to explain the behaviour, for example via trap states (consistent with Reenen et al.[11]) or through pinholes. During the evolution of the photovoltage the mobile defects migrate towards a new equilibrium distribution which reduces the influence of the reversed electric fields until no negative deflection is seen in the transient photovoltage. The chronophotoamperometry also allows us to demonstrate that, for some device architectures, the nature of the dominant recombination mechanism changes as the ionic defect distribution in the device changes.

These observations not only appear to explain the causes of current-voltage hysteresis in hybrid perovskite solar cells, but also suggest likely explanations for observations of other peculiar behaviour observed in these devices such as slowly varying photoluminescent yields.

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