

Investigating reverse bias recovery behaviour of perovskite solar cells

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Abstract

Metal halide perovskite semiconductors have been employed in solar cell (Duong et al. 2018; Peng et al. 2021) and light-emitting diode applications (Hassan et al. 2021; Y.-H. Kim et al. 2021). These materials benefit from high mobility (She et al. 2020), easy processing (Hou et al. 2020) and broad absorption spectrum (Ferdowsi et al. 2020). Perovskite solar cell (PSC) research, in particular, has been at the forefront, and power conversion efficiencies (PCEs) of over 30% in tandem structures (S. Kim et al. 2021) and over 25% in single junction (Jeong et al. 2021), have already been achieved. Given the ease of processing and higher PCEs of PSCs, the next target would be the commercialisation of these devices. There are several challenges, however, that need to be overcome to achieve this target.

While most of the recent reports on PSCs have focussed on achieving record PCEs, the reverse bias behaviour has not received much attention and thus, presents itself as one of the major hurdles in the commercialisation of these devices. Achieving reverse bias stability is critical, as a partially shaded solar module causes the shaded cells to be driven into reverse bias by the unshaded cells. To date, there has been very limited investigation into PSC reverse bias behaviour. Bowring *et al.* reported a general mechanism for the breakdown of the devices (Bowring et al. 2018). Tunnelling due to accumulated ion defects was proposed as the cause of cell breakdown, and this hypothesis was supported by drift diffusion simulations. Bertoluzzi *et al.* reported the tunnelling of holes into the perovskite causing oxidation of halides to be one of the contributors responsible for permanent damage of the cells. These halogens then act as recombination zones and are more prone to cause permanent device damage if iodine diffuses out of the absorber (Bertoluzzi et al. 2021). Razera *et al.* provided further insights into factors causing instability under reverse bias. The authors reported formation of shunts in the active area under metal electrodes at high reverse voltages as the most destructive process (Razera et al. 2020). In addition, formation of S-shape in the current-voltage characteristics was also demonstrated due to reversible iodide migration in the organic transport layer. Lastly, phase segregation, caused by irreversible iodide and bromide sub-layer formation, was also shown to occur under heavy reverse biasing. Although, all the above reports provide valuable insights into factors affecting reverse bias degradation of the cells, none of them can demonstrate a comprehensive understanding of the recovery behaviour after removal of reverse bias under different architectures or implement improved device design.

In this work, we present a comprehensive analysis of the device behaviour under reverse bias operation and focus on the factors affecting the recovery of devices after reverse voltage is removed. We focus on studying the electronic behaviour of the perovskite solar cell under reverse bias and consistently show reversible and non-destructive device performance for various choices of perovskite compositions and transport layers. We demonstrate that the transient recovery behaviour of the devices under forward and reverse bias conditions is uniquely different. While under forward bias, suppression of non-radiative recombination can reduce hysteresis; under reverse bias, it is the depletion of carriers in the electron transport layer during reverse bias that limits recovery current flow initially. Previous work has shown that under forward bias, the main impact of ionic movement appears to be to modify the magnitude and location of non-radiative recombination within the perovskite absorber through a modification of electron and hole concentrations (Walter et al. 2018). This change in recombination with ionic movement is then chiefly responsible for the observed hysteresis.

If non-radiative recombination is suppressed through a reduction in the density of defects in the perovskite bulk and at the interfaces, then hysteresis can be reduced even if ionic movement remains unaffected. In contrast, in reverse bias, the depletion of carriers in the electron transport layer create a barrier to current flow. We further exhibit that the cells do eventually recover when the ions move back to their equilibrium position but this process takes several minutes, if not hours, to complete. We show a comprehensive analysis of various perovskite configurations with multiple hole and electron transport layers under reverse bias, and establish that the slow recovery of the PSCs after removal of reverse bias is largely independent of the perovskite composition and choice of hole transport materials and is primarily impacted by the choice of electron transport materials. Some of the key results are highlighted in the next section.

Effect of transport layers and passivation on cell recovery

The nip PSCs were subjected to reverse bias of -3 V and the recovery under maximum power point voltage was recorded.

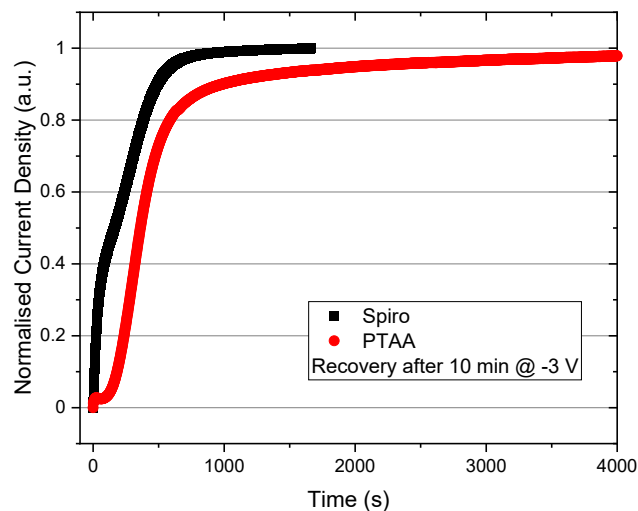


Fig. 1 Comparison of recovery times of Spiro-OMeTAD and PTAA transport layers. The recovery times of the two transport layers are over 1000 s after being subjected to -3 V for 10 min.

It can be seen from Fig. 1 that the recovery of Spiro and PTAA-based n-i-p devices show a slow recovery after being subjected to reverse bias. Both types of cells take more than 1000 s to recover fully. Choice of electron transport layers were also varied to demonstrate their impact on the recovery. Fig. 2 shows that the recovery of SnO₂ was slow (>5000 s) as compared to TiO₂ recovery, with rest of the n-i-p device structure being the same. The slow response of the tin oxide devices can be attributed to lower charge carrier concentration ($\sim 10^{-13} \text{ cm}^{-3}$) as compared to TiO₂ (10^{-16} cm^{-3}). Further study was performed on evaluating the effect of PMMA:PCBM passivation on mesoporous titania. It can be seen in Fig. 3 that the lack of PMMA:PCBM passivation results in a very slow recovery (>4000 s) after reverse stress as compared to the device with the passivation. This behaviour of the non-passivated devices can be assigned to the non-uniform on the mesoporous surface resulting in the presence of traps, slowing recovery of ions.

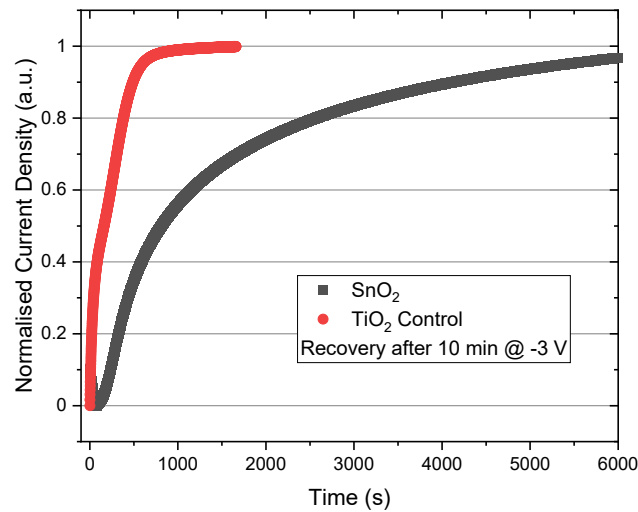


Fig. 2 Comparison of recovery times of TiO₂ and SnO₂ transport layers. Slower recovery of SnO₂ is a result of lower carrier concentration as compared to TiO₂ after being subjected to -3 V for 10 min.

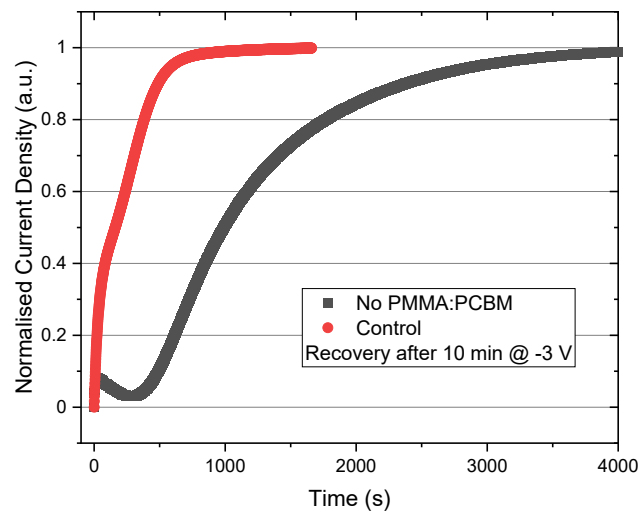


Fig. 3 Comparison of recovery times of devices without PMMA:PCBM passivation and control titania transport layers. The insulating nature of PMMA:PCBM potentially prevents ions from entering electron transport layer, resulting in faster recovery after being subjected to -3 V for 10 min.

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