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Tracking ionic migration in organic-inorganic metal-halide perovskite solar cells using in situ and ex situ transmission electron microscopy

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Organic-inorganic metal-halide perovskite solar cells are a promising low cost technology for photovoltaic applications, with record efficiencies that have increased from 3% in 2009 to >22% in 2016.1,2 Although the absorber and contact materials can be tuned to combine the technology with high-efficiency Si solar cells in tandem devices,3 commercial applications are hindered by stability issues that are still under debate.4 In particular, the migration of ions from the absorber material to the hole and electron selective contacts is thought to result in hysteresis in the current-voltage (*J-V*) characteristics of the cell. However, this behavior has not been visualized experimentally.5,6
Here, *ex situ* and *in situ* electrical biasing in the transmission electron microscope (TEM) were performed to assess the migration of species during the fabrication of a cell and its operation. Thin lamellae were extracted from both as-fabricated and tested single junction and tandem cells using a conventional focused ion beam (FIB) lift-out method. The original materials contained either a methylammonium lead iodide (MAPbI3) or a cesium formamidinium lead halide (CsFAPbI3-xBrx) absorber. *In situ* experiments involved contacting the as-deposited FIB-prepared samples to a microelectromechanical systems (MEMS) chip in an electrical biasing TEM specimen holder6 (Fig. 1a). TEM characterisation of the electrically contacted samples involved using (scanning) TEM (STEM) imaging, selected-area electron diffraction, energy-dispersive X-ray spectroscopy and electron energy-loss spectroscopy at 200 kV.
The manufacturing parameters were found to result in iodide diffusion into the Spiro-OMeTAD hole collector, with the amount of iodide in the contact increasing when the hole transport layer was positively biased in both *ex situ* and *in situ* experiments. Reversing the polarity had the effect of driving some of the iodide back towards the absorber and eventually into the fullerene-based electron contact. The migration of iodide towards the positive contact, which may explain the hysteresis phenomena, was found to be associated with the formation of PbI2 nanoparticles and nanometric voids at the interface between the perovskite and the positively biased contact (Fig. 1b). Hole transport material dopants appeared to segregate at some of the interfaces in the cell, likely affecting carrier transport.
Different mechanisms that can contribute to a change in the optoelectronic properties of the cell, including dopant and ion migration, PbI2 particles and void formation, were identified both *ex situ* and *in situ*. This work highlight the need for detailed analysis of perovskite/hole transport layer interactions during cell operation to improve the stability of such devices.

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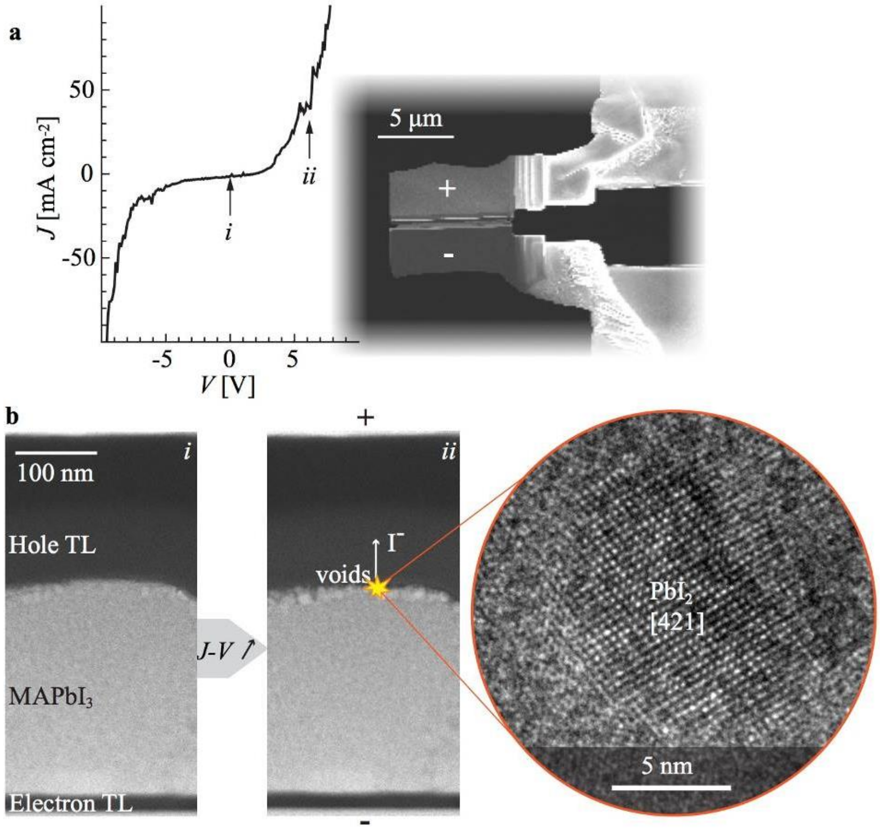

Figure 1. (a) *J-V* curve recorded *in situ* in the TEM alongside the MEMS-contacted TEM lamella. (b) STEM high-angle annular dark-field images recorded (i) before and (ii) after applying a bias of 6 V to the sample, resulting in ~50 mA cm-2 passing through it, the migration of iodide towards the positively biased electrode and the formation of voids and PbI2 at the interface with the hole transport layer (TL).