

## Addressing the stability of lead halide perovskites

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*The rapid rise in efficiencies of lead halide perovskite solar cells has hastened the case for commercialisation, one of the key barriers, however, is stability of devices. Recently, in Joule, Zhou et al. have studied the degradation mechanism of a FA-Cs mixed cation perovskite based solar cells with experimental and modelling techniques to show that phase separation into FA-rich and Cs-rich compositions accounts for the observed degradation.*

### Main Text

We are on the brink of significant climate change and need rapid deployment of renewable energy technologies to mitigate the associated global impacts. Photovoltaic (PV) technologies are a key component of current and future renewable energy; however, the sustainability of available PV technologies needs to be maximised to transition to a sustainable and clean energy future. It is likely that the vital transition to cleaner energy sources will be accelerated with a greater range of technologies available, mass production resulting in reduced costs, and the development of emerging low-cost printable photovoltaics, particularly halide perovskite PV, to complement the market leading Si technologies. This will also act to reduce the risk of widespread deployment of technologies being limited by the availability of critical raw materials. For the dream of a clean renewable energy future to become a reality we need to transition to a circular economy with widespread deployment of sustainable green energy technologies to provide resource security, minimise environmental damage, and reduce primary resource consumption.<sup>1</sup> For halide perovskite photovoltaics this means that stability issues must be addressed to produce devices with improved longevity that are inherently more sustainable, and use of toxic materials in manufacture minimised for large scale commercialisation.

The rise of lead halide perovskite-based solar cells during the last few years, reaching certified power conversion efficiencies (PCEs) over 25% have confirmed perovskite PV as an extremely strong candidate for potential low cost, low embodied energy, performance-competitive solar technology that can potentially be manufactured at scale through printing techniques.<sup>2</sup> Perovskites generally have the chemical formula  $ABX_3$ , where A is a monovalent cation, such as methylammonium ( $MA^+$ ), B is  $Pb^{2+}$  (although alternatives are available none are yet to match the performance of lead) and X is a monovalent halide anion, such as  $I^-$ ,  $Cl^-$ ,  $Br^-$  etc. It is possible to mix/substitute the cations and anions which has resulted in significant amount of research into mixed cation/anion perovskites with the aim of improving stability. The first report of a perovskite solar cell, where a perovskite modified dye-sensitized solar cell achieving a 3.8 % PCE using a liquid electrolyte,<sup>3</sup> represented a particular stability challenge; the liquid electrolyte dissolved the perovskite material limiting the lifetime of the device to just a few seconds. However, the full extent of the stability challenges of perovskites was still not evident and, since then, a great deal of research has been dedicated to understanding the causes and consequences of instability along

with materials and device architectures to improve stability. While significant progress is being made towards improving the stability of lead halide perovskite devices the challenge is not an easy one, with commonly used perovskites such as methylammonium lead triiodide perovskite (MAPI) being sensitive to oxygen, moisture, light, electrical stress, thermal stress and combinations of these.<sup>4,5</sup>

Oxygen can quickly diffuse through the perovskite layer and passivate traps states, leading to the photobrightening often seen in the photoluminescence behavior of perovskite thin films,<sup>6</sup> which in turn leads to the formation of superoxide which can cause degradation.<sup>7</sup> Iodide vacancies occupied by a trapped electron are thought to be the sites for the formation of superoxide and thus the stability towards oxygen is directly correlated to the morphology, crystal size and degree of traps states (vacancies) within the film.<sup>5</sup> This susceptibility to the formation of superoxide means that devices deposited on a mesoporous semiconductor such as titanium dioxide (TiO<sub>2</sub>) are more stable towards oxygen than those deposited on an insulating material (e.g. Al<sub>2</sub>O<sub>3</sub>).<sup>7</sup> This is due to the fact that, in the case of an insulator, excited state electrons are not injected into/extracted-by the scaffold and thus they are more likely to react with molecular oxygen to form superoxide. However, in the case of instability to light as a stressor, TiO<sub>2</sub> presents a possible degradation pathway as UV light can degrade halide perovskites through the photocatalytic effect of the mesoporous TiO<sub>2</sub> layer. Light has also been shown to induce ionic movement which in turn leads to vacancies in the film which can catalyze degradation. Electrical stress has been shown to have a similar effect.<sup>4</sup>

The methyl ammonium cation (MA<sup>+</sup>) is thermally unstable and relatively easily dissolved by moisture, resulting in degradation through the loss of MA, leaving the characteristic yellow colour of a PbI<sub>2</sub> thin film. Thus, to enhance stability many have looked to replace, or reduce the quantity of, the MA cation with combinations of formamidinium (FA), cesium (Cs) and rubidium (Rb) to produce single, double and triple cation perovskites.<sup>8</sup> There is, however, the requirement to ensure the Goldschmidt tolerance factor is kept between 0.8 and 1.0 to produce the required photoactive black phase which limits the materials available, Rb for example is too small to be used as the single cation but can be used in combinations with other cations. Indeed, MA is sometimes used in a fractional amount in order to adjust the tolerance factor as MAPI sits in the middle of the required range with a tolerance factor of ca. 0.9, but with improved stability arising from the use of more thermally stable cations such as FA and Cs.<sup>4</sup> Strategies other than changing the composition of the perovskite, have also showed some success in improving stability. Additives and solvent treatments, particularly of spin-coated perovskite films, can help reduce defects and produce more stable and uniform films. The architecture and contact layers also have a significant effect on the stability of the device. Of particular note are carbon electrode based triple mesoporous solar cells with MAPI perovskite and an aminovaleric acid additive which have demonstrated zero PCE loss over more than 10,000 h under ISOS standard conditions for a 100 cm<sup>2</sup> device.<sup>9</sup> The improved stability of MAPI with this architecture and additive is thought to be due to, at least in part, improved penetration of the perovskite precursor and improved uniformity and morphology of the annealed film resulting in less superoxide formation.<sup>5</sup> However, PCEs of these devices need to be improved upon.

In this recent work by Zhou et. al. they have investigated the performance and stability of the MA-free FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub> perovskite under combinations of different stressors.<sup>10</sup> While the devices show

decent thermal stability, they are still not to the standard of commercial demands. It is demonstrated that light drives phase segregation within the film resulting in Cs rich phases which are photoinactive and act as current blocking sites. It seems, while perovskite devices have a plethora of excellent properties for photovoltaics the mobility of ions within the film is a challenge that needs to be addressed to prevent phase segregation and loss of performance in these materials. Studies such as this by Zhou et. al. increase our knowledge of the causes and consequences of instability to help develop strategies to overcome these issues. Given the vast progress being made to understand and overcome the instability of perovskites, and with companies such as Oxford PV pioneering the technologies, one hopes that perovskites realise their goal of commercialisation in the not too distant future – but there is still much research to be done!

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