Abstract

In recent years perovskite based solar cells have become a promising photovoltaic technology, most notable for their high power conversion efficiencies and potential for cheap solution-processable module production. This report identifies the ongoing research and development into the behaviour of the perovskite material as a semiconducting active area and the ever improving fabrication of perovskite solar cell devices.

The largest problems and unanswered questions reviewed in this report include the long term stability of perovskite devices, and the challenge associated with up-scaling production of perovskites into high performance large area devices. There is no consensus on whether or not the stability of perovskite photovoltaics will improve enough so that their cost and relative lifetime will be competitive with silicon or cadmium telluride modules. Continued research will determine if the perovskite solar cell will ever become a commercially viable product.

Literature Review

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1 Emergence of the Perovskite Solar Cell

With the race for renewable energy to meet the goals of the climate change act, there has been a surge in large scale photovoltaic (PV) deployment on rooftops and solar farms in the past ten years. Total global PV installed exceeded 100GWp (Giga-watt peak) by the close of 2012[1] and it has been predicted that close to a third of all newly installed electrical generation will be PV by 2030.[2] Government feed-in tariffs across Europe have stimulated growth and investment interest in solar energy, and the ever falling prices of crystalline silicon (c-Si) is bringing c-Si solar energy up to grid cost parity with other energy sources.[3] This drive for solar energy means that there is a future for photovoltaics even alongside the large scale research programs into carbon capture technology and nuclear power.

Thin-film and organic PV active areas are the focal point of a well established scientific community, aiming to provide a semiconducting material to compete with popular solar module materials: c-Si, amorphous silicon (a-Si), cadmium telluride (CdTe) or copper indium gallium selenide (CIGS). Thin film active area materials most commonly have lower efficiencies but rely on using less bulk material and cheaper processing techniques in order to produce a cost competitive device.[4]

A surprise development in this PV community came with the fabrication of the perovskite sensitized solar cell (PSSC). In 2006 a dye sensitized solar cell (DSSC) adapted with perovskite within its nanoporous titanium oxide (titania or TiO2) layer achieved a power conversion efficiency (PCE) of 2.2%.[1,5] This report aims to collate the literature surrounding this development, and every stage of evolution that the PSSC has undergone since. In 2006 the perovskite used was an organometal halide CH3NH3PbBr3, a crystal structure containing methylammonium (CH3NH3), lead (Pb) and bromide (Br). The most prominent perovskite active areas use iodine (I) as the halide. There have been many reiterations and attempts to change the perovskite formula with the goal to improve efficiency, lengthen stability and search for a metal less toxic than Pb, with no carcinogenic manufacturing bi-product.[2,6]

The reason why many articles similar to this literature review are being published, and why the scientific community is so excited by the advent of the PSSC is best explained by observing the rapid increase in reported PCEs. By the end of 2014 a device with an active area made from a formamidinium (FA) and methylammonium (MA) perovskite blend (FAPbI3)0.85(MAPbBr3)0.15 achieved a 20.3% PCE on a reverse bias J-V (current density-voltage) sweep, other devices with the same architecture managed an average of 17.3% steady state PCE.[7]

Perovskites have had the advantage of immediately integrating into the 20 years of engineering already completed on their predecessor DSSC. PSSCs utilize the same architecture as DSSCs and lean on the same chemical and electronic understanding of the supporting electron and hole transport mediums (ETMs & HTMs), the electrode contacts, the transparent conducting oxides (TCOs) and all of the interface physics involved with planar and mesoporous structures between each layer.[2] There are still many problems and unanswered questions surrounding the perovskite, but the scientific community has certainly proved this is an active field that can rise to face these challenges.

1.1 Perovskite Crystal Structure

The perovskite chemical structure is of the form ABX3,[1,2,6,8] consisting of A and B Cations with X Anions forming a crystal structure demonstrated in figure 1. In the organic-inorganic organometal halide hybrid perovskites implemented in typical perovskite solar cells: A is typically the large organic cations MA (CH3NH3) or FA (HC(NH2)2), B has remained as Pb for all high PCE devices but a few research groups are looking at the replacement tin (Sn), and the halides iodine (I), chloride (Cl) and bromide (Br) are all implemented individually or as halide blend perovskites. (APbX4 (A= MA, FA)(X = I, Br, Cl)). Successful perovskite blends include MAPbI3−xClx,[9,10] MAPb(I1−xBrx)3,[11] FAPbI3−xBrx,[12] FAPbI3−xClx,[13] and a recent blend with record breaking PCE, (FAPbI3)0.85(MAPbBr3)0.15.[7]

The perovskite crystal structure is often represented as a cage of organic A cations enclosing a octahedral structure of halide anions X with the metal cation B in the centre. There are several phases of the extended perovskite crystal structure with differing unit cells.
Phase changes are influenced by changes in temperature, pressure and the composition of the perovskite formula. A larger organic A molecule may cause the tilting of the internal octahedra and the shifting of the halide-Pb bond angles. In order for the perovskite cubic crystal structure to form, the relative size of the anions and cations must produce an ideal Goldschmidt tolerance factor ($t$) between $0.8 \rightarrow 1$, lower values of $t$ may cause tetragonal or orthorhombic structures. Ionic radii come with a range of reported values, in the case of MAPbI$_3$, $R_A \sim 1.8$ Å for MA, $R_X \sim 2.22$ Å for iodine and $R_B \sim 1.19$ Å for Pb. MAPbI$_3$ is reported to have $t=0.99$. Other important ionic radii include: FA $\sim 1.9\rightarrow2.2$ Å, Br $\sim 1.96$ Å and Cl $\sim 1.81$ Å. $t$ is calculated using equation 1.

$$t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}}$$

(1)

Figure 2 begins to demonstrate the unit cells of perovskite crystals by showing a typical unit cell for a cubic and pseudocubic phase, it also contains the geometry of the other common tetragonal and orthorhombic phases. In the case of MAPbI$_3$ the perovskite is in a orthorhombic phase (Pbnm) until 162K at which point it becomes tetragonal (I4/mcm). It will remain tetragonal at room temperature and only enters a cubic phase (Pm $\bar{3}$m) state in temperatures above 327K. It is notable that this expected phase state change from tetragonal to cubic occurs within the expected operating temperature of a solar cell (up to $\sim 350$K). The disorientation of the halides is better represented in figure 3. The implementation of different cations or cation blends, and halides or halide blends; leads to different phase structures of perovskite around room temperature. Each phase has different electronic and optical properties, for example, the dielectric constant will change with phase.
Figure 5: From Physical Chemistry,\cite{15} table of band gaps and lattice constants for phases of MAPbX$_3$ (X = I, Br, Cl) calculated from first principle projector augmented-waves with Monte Carlo simulations (Perdew-Burke-Ernzerhof, spin-orbital coupling and hybrid functional method) based on cluster expansion methods (CEM). Also contains some comparable experimental data.

A few groups have published work using density function theorem (DFT) which predicts that the band gap of perovskites is relatively insensitive to the size of the organic cation R$_A$. Their results suggest that changing R$_A$ could be a way to tweak perovskite band structure.\cite{8,23} A large amount of effort has been put into the tuning of band gaps, tailoring of absorption ranges, and the optimization of carrier diffusion lengths over many iterations of perovskite. For example, the larger ionic radius of the cation FA $\sim 2$ Å over MA $\sim 1.8$ Å obtains an FAPbI$_3$ tolerance factor of t=1.01,\cite{16} effectively doubles the electron diffusion lengths L$_e$ from $\sim 0.1\mu$m to $\sim 0.18\mu$m, increases the hole diffusion length L$_h$ from $\sim 0.1\mu$m to $\sim 0.81\mu$m\cite{19} and narrows and red-shifts the optical band gap (absorption edge) from 1.52 eV to 1.47 eV.\cite{15,16,19,24} moving the absorption closer to an optimum for the Shockley-Queisser limit ($\sim 1.4$ eV).\cite{24} This is at the expense of a lower absorption coefficient $\alpha$. $\alpha_{MA}$ at 550nm is $\sim 1.5 \times 10^{-4}$ cm$^{-1}$\cite{25} meanwhile it has been found that $\alpha_{FA}$ at 550nm is $\sim 1.3 \times 10^{-4}$ cm$^{-1}$.\cite{24} The X halides are regularly changed and mixed to heavily tune the band gap. Analysis of phase states induced by changing the perovskite formula are often performed as function of mixed halide content x. For example figure 4 covers a study on the previously mentioned MAPb(I$_{1-x}$Br$_x$)$_3$\cite{11} with X-ray diffraction (XRD) to identify the changes in key identifiable peaks and determine the changing lattice parameter. Figure 4 (c) indicates a tetragonal to cubic phase transition for bromide content at x=0.2.\cite{22}

Compendium tables containing the phase symmetry group names, lattice constants, bang gaps (optical and electrical), conduction band minima (CBM) and valence band minima (VBM) for none mixed halide MAPbX$_3$ and FAPbX$_3$ films can be found in figure 5 and 6.\cite{15,19}

Figure 6: From APL Materials,\cite{19} table summarizing perovskites band gaps (eV), structure at room temperature, carrier diffusion lengths and conduction band minima (CBM) and valence band minima (VBM) with energy levels collated from well cited literature. The common chemicals used in the perovskite active layer formulas included are; Iodide (I), Bromide (Br), Chlorid bathe (Cl), with methylammonium (MA, CH$_3$NH$_3$) and formamidinium (FA, HC(NH$_2$)$_2$).

1.2 PSSC Architecture

The success of the perovskite as a semi-conducting active area, capable of achieving high PCE, is due to the remarkable properties of the perovskite. As previously discussed the perovskites large absorption coefficients allow many photons to be collected with the perovskite layer being only a few 100nm thick. A high charge mobility of 8 cm$^2$(Vs)$^{-1}$ for MAPbI$_3$ and 11.6 cm$^2$(Vs)$^{-1}$ for MAPbI$_{3-x}$Cl$_x$ and a low bi-molecular charge recombination encourage a high fill factor (FF).\cite{26} J$_{SC}$ is high as charge generation occurs on the order of picoseconds whilst recombination is on the order of microseconds.\cite{21} A low-non radiative recombination rate means that there is a small difference of $\sim 450$ meV between $V_{OC}$ and $E_g/q$, better than most current PV semiconductors.\cite{21,27}
Figure 7: From Nature, a Dye-Sensitized Solar Cell (DDSC). The well-established DDSC configuration, which was adapted by replacing the dye with halide perovskite to make the first ever perovskite sensitized solar cell (PSSC).

The perovskite was originally implemented in a photovoltaic active area as a hybrid of a standard DSSC in 2006,[5] achieving 2.2% PCE. Figure 7 is the schematic for a typical DSSC. The photoactive dye generates free charges from incoming photons, the electrons transfer into the optically transparent TiO$_2$ mesoporous scaffold and the holes pass through the liquid electrolyte to the electrode and counter electrode respectively. The perovskite directly replaced the dye to produce the first ever PSSC. In 2009 the same group replaced the bromide with iodide in a similar architecture and reached 3.8% PCE,[28] and by 2011 another group had reached 6.2% PCE by sensitizing the TiO$_2$ with perovskite quantum dots (QDs).[25] It was at this time that perovskites were observed to be easily dissolved in the liquid electrolyte, causing damaging losses to the PCE.[8]

In 2012 the move away from PSSCs using the DSSC liquid redox electrolyte occurred with two major pieces of published work, completed by H.Snaith’s and M.Gratzel’s groups. They produced device with PCEs 10.9% and 9.7% respectively.[30,31] The liquid electrolyte was replaced by the HTM spiro-MeOTAD, doped with bis(trifluoromethane) sulfonimide lithium (Li-TFSI) and 4-tert-butylpyridine (TBP). The device structure implemented is similar to schematic (a) in figure 8. These two groups have remained central to the evolution of the perovskite solar cell and are involved in many more of the papers covered in this review.

There has been a lot of attention focused on the use of a scaffold of TiO$_2$ as the ETM. In 2012 a Al$_2$O$_3$ scaffold was implemented to replace TiO$_2$ and it was believed that open circuit voltage (V$_{OC}$) was boosted by this change, producing a 10.9% device.[8,27,30–32] In addition, several articles since have outed TiO$_2$ as having a bad interface with typical perovskite materials.[33,34] A study focusing on the origin of J-V sweep hysteresis (a common problem with perovskite device testing) compared several combinations of perovskite interlayers and came to the conclusion the interface between the scaffold TiO$_2$ and the perovskite could be a significant contributor to hysteresis.[34] Several studies on stability have also led to conclusion that the TiO$_2$/perovskite interface is ultraviolet (UV) unstable as it is a photo-catalyst for oxidizing materials. Iodine may be extracted by the process described in equation 2. The solutions offered by one of these studies recommends the replacement of Al$_2$O$_3$ or the introduction of an antimony sulfide (Sb$_2$S$_3$) interlayer between the perovskite and the TiO$_2$ layer.[21]

$$2I^- \leftrightarrow I_2 + 2e^-$$

$$3CH_3N${}^+ + 3H^+ \leftrightarrow 3CH_3NH_2 + 3H^+$$

$$I^- + I_2 + 3H^+2e^- \leftrightarrow 3HI$$

The next step for perovskite hybrids was the analysis of MAPbI$_{3-x}$Cl$_x$ which was found to have a electron and hole diffusion length L$_{d,e}$ of well over one micron, over 10 times that of MAPbI$_3$ with L$_{d,e}$~100nm. This allows charge to be extracted over thicker perovskite films. In addition experimental evidence revealed the perovskite itself could produce working devices as a thicker perovskite active area, not just as a sensitizing substance[30,31,35] (See Figure 8 (b)).
It was also found that the perovskite later didn’t have to be fully intercalated with an ETM scaffold, in fact, devices could function without an ETM scaffold at all[36] (See Figure 8 (c)). In 2013 a planar compact titania c-TiO$_2$/MAPbI$_{3-x}$Cl$_x$/Spiro-OMeTAD device reached a PCE above 15%. With longer diffusion lengths these perovskite films no longer needed the scaffold to sufficiently extract charges into the HTM.[21] The variation in charge diffusion lengths that occurs with different compositions of perovskite allows flexibility in the device architecture, and opened several avenues of research for the ever growing perovskite community.[27]

Device architectures for perovskites from 2013 onwards typically include the mesoporous structure already shown in figure 8 (b) or the planar structure in figure 8 (c). Devices are not limited to being produced with the HTM above the perovskite (n-i-p devices), and have also been fabricated with alternative HTMs below the perovskite (p-i-n devices).[37] Choices of material for ETMs and HTMs are limited by use of appropriate electron affinity to create an ideal energy landscape for strong charge extraction and also by solvent matching in the fabrication process.[38] Figure 9 shows a device with ETM Phenyl-C61(or C71)-butyric acid methyl ester (PCBM) layer above the perovskite, alongside the energy levels associated with each layer. In this case PCBM could not have been fabricated below the perovskite as the typical solvent used for depositing the perovskite is dimethylformamide (DMF), which also dissolves PCBM. Figure 10 shows the typical energy landscape for the common TiO$_2$/perovskite/spiro-MeOTAD device.

The band gap, energy landscape and morphology of every layer involved varies between different choices of: device architectures, perovskite formulas, transport layers and interlayers. Optimization by fabrication or computational models help refine ideal formulas, such as the optimum thickness’s of each layer for charge generation and extraction. Every interface within the perovskite is important, charge extraction processes and degradation effects are often found to depend heavily on the perovskite/transport layer interfaces. Each material and fabrication technique used for a layer will effect the electronic structure and morphology of that layer, which in turn also effects the structure and morphology of the layer deposited above it.[3,14,39,40]

2 The Potential of Perovskite Solar Cells

In 2013 it was predicted that a stabilized perovskite solar cell could potentially cost ∼ 0.30 $ per W$_p$ (Watt peak), lower than the price of c-Si (1 $/W_p$), CIGS (0.55 $/W_p$) and CdTe (0.67 $/W_p$) at the time.[3,41] However the price of silicon has consistently dropped in recent years, by 2015 some prices for c-Si solar cells were estimated at 0.36 $/W_p$.[3]

The cost gap is closing between the thin film technologies and c-Si, but the potential advantages of the perovskite solar cells over conventional c-Si are still enough to encourage progress. As well as all the remarkable electronic and optical properties of the halide perovskites, they also offer the best of both worlds between being a self-assembling solution processable layer and having remarkable crystalline structures.[30,42,43]

2.1 Up-scaling

The dream for the perovskite solar cell is a high efficiency, stable, large area, flexible, transparent device capable of being deposited by reproducible and scalable processes such as: spray coating, slot-dye coating, gravure coating, doctor blade coating or inkjet printing. These up-scaling processes come with many challenges.[44–47] It is commonly observed that large scale print and spray techniques produce films with less surface coverage. This is compounded with the fact that these techniques are often performed in atmospheric conditions where perovskite formulas have been known to produce devices with lower efficiencies and shorter lifetimes than those made in a nitrogen atmosphere or under vacuum.[45] Degradation processes linked with moisture during fabrication have been identified,[48,49] and the commonly used PCBM/electrode interface has been known to cause device failure when deposited in the presence of moisture.[49] Conversely there is also evidence to suggest that slight humidity or oxygen during fabrication can improve perovskite morphology and reduce trapped states in transport layers respectively.[33,50]
The use of alternative material or deposition techniques for the compact TiO$_2$ layer was investigated as this layer often requires annealing temperatures of 450°C for over an hour. The alternatives include: switching the device architecture to that indicated in figure 9 (for which PCBM and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) only require a short anneal at temperatures ~ 100°C or no anneal at all), implementation of graphene into the TiO$_2$, or the use of solution processable TiO$_2$ nanoparticles.\cite{49,51,53–55}

Few high efficiency large area devices (bigger than the typical ~ 0.1 cm$^2$) have been reported, due to the lower surface coverage and the increasing number of shunt inducing pin holes that appear as the device size is scaled up.

Some groups maintain that larger scale spray or slot dye techniques could still be cost effective within vacuum evaporation or in a filtered nitrogen glove box.\cite{40}

### 2.2 Tandem Device

Henry Snaith suggested a major advantage that perovskites might be able to utilize is their absorption band, which efficiently collects wavelengths of light which the major commercial solar cells such as c-Si and CIGS do not.\cite{27} A tandem solar cell was proposed, where a layer of perovskite film could theoretically be deposited on top of one the standard bulk solar cells. Such a tandem cell would require significant optimization on its architecture in order to achieve good lattice matching and charge transfer between any interlayers and ETMs/HTMs used. For feasible up-scaling a device with fewer layers would be preferable as it should incur fewer parasitic losses, however this would increase the likelihood of bad interfaces within the device.\cite{56}

It is estimated that such a tandem cell should reach 1.3 times the maximum amount of photons absorbed than that set for a single junction by the Shockley-Queisser limit. A tandem perovskite/c-Si cell that can limit its parasitic losses and achieve good charge transfer could reach 29.6% PCE.\cite{27} Further studies using an oscillator model on optical n-k data predicted a similar 29% PCE for a perovskite/-CIGS tandem cell.\cite{57,58}

### 3 Research Developments & Unanswered Questions

Despite the progress made on perovskites solar cells so far, our understanding of perovskites is still in its infancy, many groups still have conflicting opinions on properties such as the exact excitonic functionality of perovskites or the origin of hysteresis for J-V sweeps at different speeds. In general the quality of fabrication techniques and optimization of films should continue to reduce imperfections in perovskite devices, this trend will reduce series and shunt resistances, increase maximum power points ($V_{mpp}$) and therefore increase device PCEs.\cite{27} The ever evolving perovskite device architecture may also provide answers to some of the currently unsolved problems that are present in the perovskite community. It is not encouraging that the majority of published research comes with a range of quoted values for many important properties, something as fundamental as the bandgap commonly varies by 20% from group to group. This is one of the many indications that the repeatability of producing perovskite devices between laboratories is still limited. Many groups are careful to only postulate their solutions instead of providing certifying evidence.
3.1 Excitonic or Non-Excitonic Behaviour

After a photon has caused the excitation of a electron within a semi-conductor, the electron and hole generated are generally understood to be extracted in one of two ways. The electron and hole pair are referred to as a quasi-particle known as an exciton and depending on the semi-conductor material this exciton can either be a large weakly bound Wannier-Mott exciton with a binding energy on the order of ~10meV or a small tightly bound Frenkel exciton with a binding energy typically between 0.1 and 1 eV. c-Si active areas generate Wannier-Mott like excitons, where the electron and hole have diffusion lengths large enough to cover the depth of active area and are extracted to the electrodes as free chargers. Typical organic cells have more tightly bound Frenkel excitons, this limits organic cells quantum efficiency as charge can only be extracted if the exciton randomly diffuses to an hole or electron transport interface. Many organic active areas are intercalated with PCBM so that the excitons have to diffuse less distance before reaching an interface.[2,30,31,35]

The consensus is that most MA or FA perovskites with any halide or a mix of halides generate weakly bound Wannier-Mott excitons, resulting in free charge separation. However the experimentally and computational obtained binding energies that form this consensus vary in value between $E_B \sim (1 \rightarrow 50)\, \text{meV}$.[18,26,39,43,57,59–65] If the excitons did indeed have one of the higher quoted values of binding energy, like those approaching 50meV, then there is some contention that the excitons may exhibit tightly bound effects, and reduce the quantum efficiency of a perovskite device.

The impressive PCEs of perovskites devices fundamentally suggest that their generated excitons are unlikely to be tightly bound. After the realization that perovskites did not need a mesoporous scaffold it became apparent that the charge extraction properties of the perovskite were remarkable. This encouraged the investigation of hole and electron diffusion lengths through several time-resolved photoluminescence (PL) studies.[24,26,62,66,67] MAPbI$_3$ has $L_e \sim 0.1\, \mu\text{m}$ with a slightly larger $L_h$, MAPbI$_3$ has $L_e \sim 0.18\, \mu\text{m}$ and $L_h \sim 0.81\, \mu\text{m}$.[7] MAPbI$_{3-x}$Cl$_x$ has $L_e \sim 1\, \mu\text{m}$ and $L_h \sim 1.2\, \mu\text{m}$.[10,26,59] For all of these perovskite formulae the diffusion length is of the order of the typical width of a thin film active area $\sim 0.5\, \mu\text{m}$, but the mixed halide and FA perovskites have the advantage of their diffusion lengths greatly exceeding film thickness.[2,30,31,35]

The calculation to obtain exciton binding energy values usually involves considering the dielectric constant of the perovskite. There is currently a conflict in how to interpret the value of the dielectric constant through the use of n-k data and the Kramers-Kronig relations.[68]

One recent study highlights the current discrepancy in the Wannier-Mott model and poses an argument on how the typical use of the optical frequency dielectric constant $\epsilon'$ may be inappropriate as the difference between the static $\epsilon_{SI}$ and high-frequency $\epsilon''$ values is typically very large.[39]

Another common method of determining $E_B$ is by observing the separation of Landau levels using magnetooabsorption measurements, calculated using equation 3 where $N$ is the Landau quantum number, $w_c = eB/m^*$, $B$ is the magnetic field, $m^*$ is the exciton effective mass, $g_{eff}$ is the effective Zeeman splitting and $\mu_B$ is the Bohr magnetron.[60]

$$E(B) = E_g + (N + 1/2)\hbar w_c \pm 1/2 g_{eff} \mu_B B$$

Studies using an $\epsilon'$ for determining $E_B$ typically find a $\epsilon' \sim 6.5$ and hence a higher $E_B \sim 50\, \text{meV}$.[61,65] Alternatively studies using $\epsilon_{SI} \sim 70$ obtain a lower $E_B \sim 2\, \text{meV}$.[39,69] Another paper proposes that this choice of dielectric causes the magnetooabsorption measurements using equation 3 to obtain questionable overestimates of $E_B \sim (37 \rightarrow 50)\, \text{meV}$.[59].

The most recent unpublished (as of 06/2015) attempt to clarify the binding energy of perovskites uses the latest fabrication techniques of quality films and very large fast pulsing magnetic fields up to 150T.[60] This study finds a general $E_B = (16\pm 2)\, \text{meV}$ and $m^* \sim 0.1m$, for the low temperature MAPbI$_3$ orthorhombic phase, which collapses to lower $E_B$ for higher temperatures due to dielectric constant being frequency dependent. This study attributes the cause of previously inaccurate $E_B$ to: the limited range of 1s low magnetic field transitions, the approximation of dielectric constants and the assumption of $E_B$ being a constant function of magnetic field or temperature. Two reports reach a consensus that a MAPbI$_3$ film at room temperature, in the tetragonal phase, has a binding energy which recedes to ~ 5 meV under the influence of dielectric screening from rotating MA cations. Mixed halide films were also found to have reduced excitonic screening due to collective reorientations of the MA cations.[59,60]

3.2 Hysteresis

A common method of determining the PCE is by taking J-V curves under solar illumination Air Mass 1.5 (AM 1.5, 100mWcm$^{-2}$) and obtaining the $V_{OC}$, FF and current density short-circuit voltage $J_{SC}$. Typically the solar cell is held under forward bias (FB), then the voltage is reduced down to short circuit voltage (SC) at a sweep speed $v_s$, to obtain a FB-SC sweep. The opposite can be done to produce a SC-FB sweep. Perovskites have been found to exhibit a significant difference in their J-V curves depending on the direction and speed of the sweep, an anomaly called hysteresis. This process has been previously identified in other DSSC or organic devices, and can be linked to light soaking leading to doping and band bending and/or the effective capacitance of slowly responding devices.
which is observed as a reduced photogenerated charge. Another effect can occur with fast SC-FB scans partially charging the cell generated charge on the backward sweep. Another effect a cell is under FB, which is observed as additional photogenerated charge when forward bias.

During high speed scans a build of charge may occur when a cell is under FB, which is observed as additional photogenerated charge on the backward sweep. Another effect can occur with fast SC-FB scans partially charging the cell which is observed as a reduced photogenerated charge.

A study on hysteresis published in 2014 took particular care to wait for several minutes to achieve steady state scans, and found that hysteresis in perovskites gets more extreme with slower scan rates. This is the opposite of what has been observed in many other photovoltaics, including hysteresis observed in a PSSCs architecture revealed with J-V scans and impedance spectroscopy earlier that year. Figure 11 demonstrates a typical J-V curve and shows the increasing hysteresis with scan speed observed in a planar MAPbI$_3$-xCl$_x$/spiro-OMeTAD perovskite device. J-V curves of other devices containing mesoporous TiO$_2$ yielded the same scan speed trend and demonstrated that the magnitude of hysteresis is highly dependent on device architecture, including: material choices, deposition techniques and layer thicknesses.

Another group used capacitance - voltage (C-V) and capacitance - frequency (C-F) scans of perovskite films to identify the potential changes occurring in perovskite films during light soaking. The accumulation of charge at electrode surfaces was found to neutralise interfacial defects and increases $V_{OC}$, meanwhile PL suggested that photo-generated electrons were more likely to reduce the density of bulk defects, therefore reducing one of the inhibitors of effective charge transport and increasing FF. It was also found the light soaking reduces the bulk polarization of the perovskite film, increasing recombination rates inside the film and decreasing $J_{SC}$. The hysteresis in perovskites is speculated to be caused by any combination of three processes. The first potential cause of hysteresis is that there may be a large number of surface trapped states in the perovskite layer. These states would be filled under FB and create good perovskite interfaces with the ETM/HTMs. These states would then empty fast into the contacts under SC, whereby the performance of device would be reduced until the trapped states were once again filled. This effect would be exaggerated in the architectures with no transport layers. Secondly, hysteresis may be caused by the ferroelectric polarization of the perovskite crystal structure. It has been observed that the organic cations may slowly polarize across the film depending on voltage bias, which could potentially increase charge separation and theoretically allow a $V_{OC}$ higher than the band gap. The final suspect for hysteresis is ion interstitial migration, whereby excess ions may be free to move within the film, screen extra space charge and generate increased charge collection.

By comparing multiple architectures the TiO$_2$ layer has been ruled out as the sole source of hysteresis, however it considered likely that it is the interfaces between the perovskite and ETM/HTMs like TiO$_2$ that are causing hysteresis. It has been shown that hysteresis can be reduced by only using a thicker TiO$_2$ scaffold, due to the increase in surface area allowing a better p-type contact with the perovskite. Hysteresis free films have been reported, with the lack of the hysteresis anomaly attributed to: the high quality morphology of the films, a lower number of trapped states and an increase in crystal grain size. Recently it has been reported that high quality n-i-p structured devices demonstrate negligible hysteresis but it is difficult to significantly reduce hysteresis in p-i-n structured devices.

Groups working on understanding hysteresis have also come to realise that in in order to properly analyse perovskite devices, a consistent method avoiding light soaking and hysteresis must be followed. It is suggested that the steady state J-V curves are recorded at several scan speeds and that the stabilised maximum power point is followed for several minutes. This is important as fast scan speeds can mask hysteresis and trapped states by scanning faster than the emptying of traps. It is also important because the stabilised maximum power point often yields PCEs significantly lower than fast J-V scans. This effect is most prominent in FB-SC scans of planar devices and has been used to question the validity of many reported PCEs.
3.3 Humidity

It has been demonstrated that MAPbI$_{3-x}$Cl$_x$ films deposited from a solution with 3:1 molar ratio of PbCl$_2$:MAI in DMF show significant improvement in morphology for those annealed in ambient air with humidity (35±5)% over those annealed in nitrogen. It is assumed that grain boundary creep caused by moisture between crystal grains encourages grain growth, however films annealed in over 80% humidity showed rapid decay into PbI$_2$. Devices fabricated in this study achieved an increase in PCE from 12% for those annealed in the glove box to 15.4% for those annealed in air, this is attributed to a decrease in non-radiative decay demonstrated by the increase of PL lifetime from 33ns to 99ns. This moisture induced device improvement is expected to occur up to 60% humidity at which point FF begins to fall as more PbI$_2$ is found present in the film.\[50\]

Humidity has been identified as an important factor during device fabrication, but little has been done to isolate the effect of humidity at each point of fabrication. Humidity could potentially change the crystal growth and morphology of the perovskite film as it is spun or spray coated, as it is drying or as it is being annealed. Humidity may alter any interface reaction with the transport layers, or even the deposition and interface reactions of the transport layers with the contacts.\[50\]

3.4 Stability

Perovskite devices are as well known for their instability as they for their dramatic rise in efficiency. A typical photovoltaic with encapsulation should aim to retain 80% of its initial PCE after 25 years by being resistant to: continued AM 1.5 illumination (including the UV part of the spectrum), maximum summer operating temperatures (up to ~350K), precipitation and water vapour (up to ~80% relative humidity). Each of these factors may effect the stoichiometry of any of the layers and interfaces in a solar cell and cause degradation to the morphology or crystallinity of the active layer. In perovskites it is commonly observed that the perovskite will degrade into hydrates or its original constituents PbX$_2$ and MAX/FAX (X = I, Cl, Br) under stress testing.\[21,27,76,77\]

Analysis of film constituents before and after stress testing devices are typically done using XRD, X-ray fluorescence (XRF), X-ray photon spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR). Many of these techniques only probe the surface of the perovskite, however some conclusions can be drawn by comparing the spectral data from these techniques to the data obtained by techniques than can probe the bulk of the perovskite, for example XRF. XRF detects more Cl in MAPbI$_{3-x}$Cl$_x$ films than that spotted with surface probing techniques, suggesting that the majority of Cl is in the bulk of the perovskite film, at the opposite interface, or within crystal grain boundaries. Unfortunately it is difficult to probe small volumes with XRF as the spot size must be large. Despite the limitations of these probing techniques much as been learnt about the stability of perovskite devices.\[21,70,78,79\]

The effects of liquid water on unencapsulated perovskite films are expected to follow the degradation described in equation 4.\[21,70\], this has been shown to be a irreversible process. The liquid water travels through the film along grain boundaries and quickly decomposes the crystal structure, visibly changing the perovskite from brown to a yellow-transparent film.\[77\]

\[
\begin{align*}
CH_3NH_3PbI_3 & \leftrightarrow PbI_2 + CH_3NH_3I \\
CH_3NH_3I & \leftrightarrow CH_3NH_2 + HI \\
4HI + O_2 & \leftrightarrow 2I_2 + 2H_2O \\
2HI & \leftrightarrow H_2 + I_2
\end{align*}
\]

(4)

It has been suggested that tetramethylammonium might be a highly moisture resistant substitute for the organic cation, as it offers no protons to initiate the water degradation described in equation 4.\[21\] Another study found that MABr$_3$ or hybrid MAPb(I$_{1-x}$Br$_x$)$_3$ films are significantly less sensitive to moisture with increasing bromide content, but also are bad absorbers due to Br’s larger band gap. MAPb(I$_{1-x}$Br$_x$)$_3$ devices were found to maintain their PCE after 20 days in 55% humidity.\[22\]

It has also been observed that water vapour incident on perovskite films disperses along grain boundaries and forms hydrated crystals CH$_3$NH$_3$PbI$_2$H$_2$O followed by (CH$_3$NH$_3$)$_4$ PbI$_2$2H$_2$O. When saturated with water vapour these hydrates reduce device PCE by an order of magnitude, but after devices are dried in nitrogen for 6 hours PCEs return to their original value, however: a greater level of hysteresis is observed. With insufficient encapsulation for humid environments, the perovskite could fluctuate between an efficient and inefficient state following this reversible hydration (with an ever increasing number of defects). Devices with larger grains could reduce the penetration of water vapour and decrease the number of trapped stated caused by high levels of humidity.\[77\] This could be linked to reports of devices with large grain sizes and high quality morphologies showing negligible amounts of hysteresis.\[39,74\]

As previously stated, the maximum operating temperature a perovskite solar cell should have to endure is ~350K, this is good because the chemical degradation of the perovskites crystal structure starts occurring above ~380K.\[21\] Beyond this temperature many more halide deficiencies are observed, which is the reason why perovskite annealing often does not exceed this temperature.\[52\]
However it has also been identified that there is a phase state change between 327K and 330K from tetragonal to cubic, causing a small decrease in band gap and a switch to an acentric structure exhibiting ferroelectric effects.\textsuperscript{[18–21,80]} FA perovskites have been shown to be more thermally stable showing no degradation or discolouration when exposed up to $\sim 400$K, whilst MA based perovskites fully decompose after $\sim 30$ minutes at such high temperatures. It is unfortunate that FA seems to offer no observable advantages in resistivity to degradation caused by moisture.\textsuperscript{[12]}

FA has often been refereed to as a good potential substitute for MA in perovskite solar cells, this may be best demonstrated by figure 13 showing its smaller band gap and good energy landscape alignment with common transport layers. There is some disagreement in the FAPbI$_3$ crystal phase structure as it has been previously identified as Tetragonal\textsuperscript{[19]} and also as trigonal (P3m1, $\alpha$) at room temperature.\textsuperscript{[7,80]} It is agreed that for MAPbI$_3$:FAPbI$_3$ mixed films the phase state is tetragonal when the MA content makes up $>20\%$ of the total organic anions. It also seems well established that despite the stability of the black $\alpha$ phase in high temperatures up to $\sim 430$K, $\alpha$ is susceptible to ambient humid environments. In a humid environment the $\alpha$ phase is no longer stable and at lower temperatures it slowly converts to a yellow hexagonal $\delta$ phase (P6$_3$mc). The phase change to $\delta$ from $\alpha$ appears to be reversible, the $\alpha$ phase can be re-established by annealing again. The $\delta$ phase contains linear chains of PbI$_6$, has a larger optical band gap and exhibits poor charge separation and transfer properties.\textsuperscript{[7,80]} Figure 14 demonstrates the crystal structure of both the $\alpha$ (a) and $\delta$ (b) reported phases.

The phase instability of perovskites has been combated by the incredibly successfully implementation of (FAPbI$_3$)$_{0.85}$ (MAPbBr$_3$)$_{0.15}$ which maintains the optimum absorption range of FAPbI$_3$ over MAPbI$_3$.

![Figure 12](image12.png)  \(\text{Figure 12: From Physical Chemistry,}\textsuperscript{[80]}\) wide angle XRD analysis of FAPbI$_3$ stabilised with MAI. (a) yellow trigonal $\delta$-phase and (b) stabilised black $\alpha$-phase with 15\% MAI.

![Figure 13](image13.png)  \(\text{Figure 13: From Physical Chemistry C,}\textsuperscript{[24]}\) energy level diagram of mesoporous scaffold TiO$_2$/FAPbI$_3$/spiro-OMeTAD perovskite device.

![Figure 14](image14.png)  \(\text{Figure 14: From Physical Chemistry C,}\textsuperscript{[24]}\) diagrams of the black $\alpha$ (a) and the yellow $\delta$ (b) phases of FAPbI$_3$. The blue polyhedral are the PbI$_6$ octahedral, the Pb and I atoms are the yellow and orange circles respectively. In the $\delta$ phase the larger structure consists of linear chains of face sharing octahedral.
This blend is observed to have no hexagonal δ yellow phase present during or after lifetime testing in an ambient humid atmosphere. Following this development a separate publication has argued that the implementation of bromide content, which increases the band gap of the device, could be a significant limiting factor for its PCE. They suggest that mixing MAPbI$_3$ and FAPbI$_3$ stabilises the trigonal α black phase effectively and does not limit PCE through the presence of bromide. The stability of FAPbI$_3$ with 15% MAI is demonstrated in figure 12 (b) where no phase state change is observed in the crystal XRD spectra after annealing and then re-cooling the samples. Figure 12 (a) shows the un-stabilised perovskite is in a δ phase for temperatures below 400K. Conversely, the original study clearly states that mixing MAPbI$_3$ and FAPbI$_3$ would require too much MA content to phase stabilise FA based devices and hence the performance would be dominated by MAPbI$_3$, which would be counter-productive.

The spectroscopic break down of a comparable FAPbI$_{3-x}$Br$_x$ (3−y) device architecture reaching 14.2% PCE is given in figure 16, which identifies the implementation of a high bromide content into FA perovskite causing cubic and tetragonal crystal structures similar to MA only perovskite devices.

In terms of UV stability the potential instability of TiO$_2$ has already been addressed in the first few iterations of perovskite solar cells. Further theoretical work has been done to suggest that exposure to oxygen is needed on the TiO$_2$ surface in order to passivate surface trapped states. This should increase UV stability and reduce hysteresis originating from the bad perovskite/TiO$_2$ interface.

### 3.5 Material Replacements

This report has already covered some iterations of perovskite device architectures used to study the functional properties of perovskite. Many more steps have been taken by research groups to increase stability and efficiencies, some of which are reviewed in the following sections. The experimentally determined energy levels for further alternative device materials are presented in figure 15. This includes the antimony sulfide (Sb2S3) and the photosensitive dye N719. The popular MA replacement FA has already been discussed, however it is worth clarifying that in general FA films need to be slightly thicker (~500nm → ~600nm) than MAI:PhCl$_2$ films (~350nm → ~500nm) or MAI:PI$_2$ (~200nm)[67] due to FA’s weaker absorption.[75]

#### 3.5.1 Perovskite Formula

The band gap of the common perovskite film MAPbI$_3$ has already been established as ~1.52eV. This is reduced by ~50meV and ~150meV by the direct replacement of iodide for bromide and chloride respectively.

The implementation of these halides causes contraction of the octahedra, decreases the unit cell size and causes strain in the crystal lattice that blue shifts the absorption range.[15,19]

The role of phases in mixed halide perovskites has been addressed several times but is still not fully understood. The introduction of bromide into FA is summarised in a spectroscopic breakdown in figure 16. The effect of bromide in MA can be summarised by considering figure 17 where for MAPb(1−x)Br$_x$I$_3$ devices: the absorption shift with additional bromide is shown in (a), the change in optical band gap is fitted in (b) and the efficiency change as a function of x in (c). It is prompted that a Br content of x=0.2 might be a sweet spot, maintaining high PCE but gaining the extended stability previously reported in perovskites containing bromide.[22] It is worth noting that this x=0.2 bromide content is also where the shift from tetragonal to cubic phase in MAPb(1−x)Br$_x$I$_3$ films occurred.

The uniformity of halide distribution in mixed halide perovskite films is still uncertain. An anomalous PL change has been observed in MAPb(1−x)Br$_x$I$_3$ films under light soaking. Figure 18 (a) shows how the expected PL signal from a fully mixed halide phase (x=0.4, PL peak ~1.85 eV) shrinks and is replaced by a PL with peak at 1.68 eV, similar to that observed in MAPbI$_3$ (iodine only) films. This new PL peak returns to its original location and intensity after the film is left in the dark for 5 minutes, as demonstrated in figure 18 (c) for a x=0.6 film. It has been suggested that this effect can be attributed to a change in perovskite film morphology under illumination, whereby the mixed halide film converts into bromide and iodide rich phases. If this is the case, then any value of overall bromide content x would still cause a PL peak at ~1.68 eV under illumination, where the photo-excited bromide rich states are relaxing to iodide rich states before charge extraction or recombination occurs.

![Figure 15: From Materials Today, energy levels for alternative materials of HTM, ETM and Perovskite active layers.](Image)
Figure 16: From Energy & Environmental Science,[12] analysis of the FAPbI$_x$Br$_{3-y}$ perovskite films with varying $y$. (a) Absorbance. (b) Steady-state Photoluminescence (PL). (c) Images of films, $y$ increases from 0 to 1 from left to right. (d) XRD indicating that as $y$ decreases, the (100) cubic peak changes to the (110) tetragonal peak. (e) Variation of band gap as a function of pseudocubic lattice parameter.
Figure 17: From Nano Letters,[22] analysis of MAPb(Br$_x$I$_{1-x}$)$_3$ films and devices. (a) Absorbance of films with varying bromide content $x$, with image of each film. (b) Band gap variation with increasing $x$. (c) PCE of the devices with structure mesoporous TiO$_2$/perovskite/polytriarylamine (PTAA).

Figure 18: From Chemical Science,[81] PL spectra under 457nm at 300K light for MAPb(Br$_x$I$_{1-x}$)$_3$. (a) PL spectra of $x=0.4$ film over 45 seconds in 5 seconds increments showing growth of peak at 1.68ev. (b) Normalised PL spectra after films have been illuminated for 5-10 minutes. (c) PL spectra of $x=0.6$ film before illumination and after illumination for 2 minutes, where films are left in the dark for 5 minutes before the next set of measurements.
The exact composition and halide uniformity in MAPbI$_{3-x}$Cl$_x$ films has been a cause of disagreement since the advent of the first mixed halide devices. Despite the common MAI: PbCl$_2$ 3:1 molar ratio implemented by most research groups, the films appear to only possess a Cl content between 2% and 4% after annealing. One study measured an absolute upper boundary of 300 ppm (parts per million) for Cl in their MAPbI$_{3-x}$Cl$_x$ devices,$^{[10,52]}$

$$\text{PbX}_2 + 3\text{CH}_3\text{NH}_3\text{I} \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3 + 2\text{CH}_3\text{NH}_3\text{X}$$

(\(X = \text{I, Cl, Br}\)) \hspace{1cm} (5)

Consider the perovskite formation equation 5 which demonstrates the generation of the by-product 2CH$_3$NH$_3$X. The energetic requirements of the decomposition of these by-products can be calculated as 226.7°C for MACl and 245°C for MAI, which would suggest that it is unlikely that the majority of Cl could decompose and evaporate off the surface of the film, and so does not explain the apparent lack of Cl commonly measured. The possibility for the majority of Cl to be located in the perovskite/transport layer interfaces or amongst grain boundaries has already been considered, however; it is suggested that a large amount of Cl must still be subliming and out-gassing off of the films given the quantity of Cl unaccounted for.$^{[79]}$ Some publication suggests that the high surface area:volume ratio and efficient heat dissipation through perovskite films allow MACl to sublime at only 100°C instead of 245°C, and suggest that the out-gassing of MA and Hydrochloric Acid (HCl) occurs instead of MACl. This is strongly backed up by in situ evidence of slowly decreasing Cl content during annealing. It is also mentioned that whilst MACl is not the major out-gassing component, it has been measured on petri dishes used to contain old films.$^{[52,78]}$ Other separate studies conclude that no MAI is given off during deposition or annealing, but that HCl can be seen coming off old films heated to 150°C.$^{[70,79]}$ Conversely, there is published evidence that shows only solvent out-gassing can be observed during the annealing process.$^{[78]}$ These disagreements do not help to solve what actually occurs during deposition and annealing to produce the resultant Cl deprived MAPbI$_{3-x}$Cl$_x$ films.

Despite some unanswered questions, the perovskite community’s understanding of decomposition temperatures and energetically favourable reactions has improved and has inspired one of the biggest developments in perovskite formula to date. The by-product produced by using lead acetate (PbAc$_2$) in MAI:PbAc$_2$ perovskite films is MAAc, which decomposes at 97.4°C, making it energetically favourable compared to other potential by-products MACl and MAI. Implementation of lead acetate as a lead source instead of the typical halide lead sources PbX$_2$ is demonstrated in scanning electron microscopy (SEM) images of films in figure 19.

Figure 19: From Nature Communications,$^{[52]}$ scanning electron microscopy (SEM) images showing the morphology of FTO/TiO$_2$/MAI:PbX with differing lead sources. (a) PbCl$_2$, (c) PbI$_2$ and (e) PbAc$_2$, are top down SEM images of the perovskite films. Also included are cross-sections of full devices using the (b) PbCl$_2$, (d) PbI$_2$ and (f) PbAc$_2$ lead sources.

An example of a smooth and even film obtained from MAI: PbAc$_2$ with a 3:1 molar ratio is shown in figure 19 (c), the quality of the film is described by the group who made it as comparable to a vapour deposited sample. The average PCE of devices using PbAc$_2$, PbI$_2$ and PbCl$_2$ were 14.0%, 9.3% and 12% respectively; demonstrating the improvement from using this alternative lead source.$^{[52]}$

Another notable addition to the perovskite formula is the use of iodopentafluorobenzene (IPFB), this material is deposited before the HTM in n-i-p structured devices and has been shown to passivate trapped states in the perovskite.$^{[82]}$

The idea of producing lead-free non-toxic perovskites solar cells has received a lot of attention in research level and popular science publications. The best potential candidate so far is tin (Sn). To demonstrate the functionality of Sn, one study integrated Sn into a lead halide perovskite hybrid cell with the formula MASn$_{12}$Pb$_2$I$_3$. This hybrid cell was found to have a bang gap tunable between 1.17 → 1.55 eV with the highest device PCE only reaching 3%. With confirmation that Sn could work another group went on to produce the first ever MASnI$_3$ lead free device, and reached a champion PCE of 5%.$^{[8]}$ No doubt research into lead-free perovskites will continue to remain a popular topic, however Henry Snaith’s group maintain that the restrictions within the European Union will not stop perovskites containing lead from reaching a commercial market.
3.5.2 Electron Transport Mediums & Hole Transport Mediums

Despite TiO$_2$ being one of the most common ETMs employed in perovskite n-i-p architectures, common TiO$_2$ layers require a 500°C calcination, and have also been linked to interfacial UV degradation when in contact with perovskite materials. A recent publication has attempted to overcome the first of these problems by developing a solution processable TiO$_2$ layer which could eventually replace the high temperature TiO$_2$ deposition for n-i-p devices that do not need a precisely engineered TiO$_2$ scaffold. In addition, a solution processable TiO$_2$ could be used as an interlayer or transport layer in p-i-n architectures to replace or lie below PCBM. Since TiO$_2$ is often deposited in air this may provide a route to fabricate a p-i-n device architecture that is fully air-processable; using PEDOT:PSS as an HTM and TiO$_2$ as an ETM. Unfortunately the champion devices using this new solution processable TiO$_2$ currently have less that half the champion PCE of those without TiO$_2$ or using standard calcinated TiO$_2$. Another alternative to the traditional TiO$_2$ layer is the implementation of intercalated graphene flakes into the TiO$_2$ layer, which recently have produced devices yielding a maximum PCE of 15.6% with fabrication temperatures not exceeding 150°C.\[7,44,53\]

Spiro-MeOTAD is a common HTM used in n-i-p device architectures which requires doping with li-TSFI in order to increase hole mobility, however it also makes the Spiro-MeOTAD more susceptible to moisture. Another dopant used in Spiro-MeOTAD is TBP which has been shown to react with perovskite and also increase measurable parasitic resistance when used in conjuncture with li-TSFI. This resistance may be caused due to it being energetically favourable for li-TSFI to migrate to the TiO$_2$ surface in the presence of TBP, decreasing V$_{OC}$ and FF.\[70\] It has been suggested that TBP could be replaced with montmorillonite in order to improve the effectiveness of Spiro-MeOTAD without causing these additional resistances and degradation effects.\[70\]

Another low temperature solution processable ETM is zinc oxide (ZnO) which has been demonstrated to work as an interlayer alongside PCBM in a p-i-n architecture producing a device with 16.8% PCE.\[83\]

In a traditional p-i-n architecture PEDOT:PSS should be deposited onto hot ITO held at 120°C in order to create a smooth surface on which to deposit the perovskite.\[84\] An alternative method for perovskite solar cells is to remove the ETM entirely, one group demonstrated a FTO/Mapb$_{3-x}$Cl$_x$/Spiro/Au device that achieved 14.4% PCE.\[85\] ETM free devices may not ever reach higher PCE’s given that hole and electron transport rates should be balanced in order to achieve the maximum theoretical PCE for a particular solar cell.\[7\]

![Figure 20: From Advanced Functional Materials,\[46\] dependence of perovskite morphology on annealing temperature and thickness. (a) SEM of film perovskite MAPb$_{3-x}$Cl$_x$ morphologies. Top row: annealing temperatures 90 170°C with constant film thickness 650 ± 50 nm. Bottom row: film thickness 50-700 nm with constant annealing temperature 95°C. (b) Perovskite film coverage as a function of annealing temperature. (c) Perovskite film coverage as a function of film thickness.](image)

3.6 Deposition Optimization

It is clear that the formation of the perovskite film will depend heavily on the choice of contacts, transport layers and perovskite formula used, for example the inclusion of Cl has shown evidence of increasing the MA out-gassing during annealing.\[10\] There are other additional fabrication techniques that have been reported to improve the formation of perovskite films in order to increase the stability and performance of perovskite devices.

The choice of solvent (or solvents) used to dissolve the perovskite precursor can change the morphology of the film. Common solvents used are DMF, γ-butyrolactone and Dimethyl sulfoxide (DMSO). For the current record efficiency perovskite devices an improvement in film coverage and smoothness has been partially attributed to the use of γ-butyrolactone: DMSO solvent blend (7:3, volume ratio).\[7\]

Two obvious factors affecting the morphology of perovskite devices are the thickness of the layer being deposited and the annealing temperature chosen. Figure 20 give an example of how a Mapb$_{3-x}$Cl$_x$ film is affected by these two properties and demonstrates how detrimental over-annealing can occur at temperatures above 110°C.\[46\] Annealing causes crystallisation only after the excess organic component is crystallisation only after the excess organic component is...
Crystallisation should be driven only by temperatures below 110°C for MA based devices, as it is calculated that a large increase in halide deficiencies occur over 110°C.[52]

The deposition of the perovskite can be completed using co-evaporation to produce a very uniform and smooth film,[84] however most research groups try to avoid this time consuming and expensive technique and use spin coating instead. Spin coating has achieved resounding success when combined with several additional techniques. A toluene wash is commonly deployed in a second spin cycle quickly following the deposition of the perovskite, the toluene washes away excess unreacted organic material and encourages an earlier initiation of the crystallisation process. This is been associated with large crystal grains and a overall smoother, pin-hole free film morphology.[7,51,80] A similar improvement in perovskite devices has been observed by the implementation of vapour or solvent annealing, where the film crystal growth is made slower in the presence of excess solvent, encouraging much larger crystal grain sizes.[83] Hot casting the perovskite precursor at a high temperature (∼70°C) onto a hot substrate (∼180°C) has reported increased grain sizes of up to millimetres in length achieving PCE’s of up to 18%.[74] Various groups use either hot solution or hot substrates at some point in their fabrication routines but there seems to be no universal standard technique to improve device morphology. Several groups have reported that an additional amount (∼ 6% volume) of stabilised HI can be added to the precursor ink to form much smoother films.[12]

Common 2-step fabrication processes include the deposition of the lead source PbX₂ in DMF and organic halide component MAX in IPA one after the other.[84] These are often spin coated sequentially or, in some cases, a 2-step solution dump has been used where a PbI₂ film has been dipped in a bath of MAI in IPA. Devices fabricated using a 2-step-dip process kept 4/5ths of their original PCE after 500 hours of ageing in ambient conditions.[87] MAI has recently proved itself a capable MA replacement again as FAPbI₃ films with over 20% PCE have been made by using intramolecular exchange. These impressive devices utilize the reaction PbI₂-DMSO + FAI ↔ PbI₂-FAI + DMSO, whereby it is energetically favourable for a PbI₂(DMSO) precipitate obtained from PbI₂(DMSO)₂ to replace DMSO with the FAI deposited on top through intermolecular exchange. A similar process worked for producing the formidable FAPbI₃:MAPbBr₃ devices.[75]

Other additional factors that may also improve the device quality include the implementation of a drying step before annealing, or the removal of airflow by the switching off glovebox circulation and/or lamina flow hoods during perovskite and transport layer deposition and annealing. A reduction in airflow could be a contributing factor to the success of scaled solvent annealed perovskite films.[83]

Figure 21: From Nano Letters,[86] schematic of a scaffold mesoporous Al₂O₃/Perovskite with a novel HTM-encapsulate hybrid of P3HT/SWNTs capped with PMMA.

3.7 Encapsulation

Encapsulation can stop many of the degradation effects which destabilise perovskite solar cells. Typical laboratory UV activated encapsulation is relatively ineffective compared to some novel encapsulates that have been developed specifically to target degradation effects and increase the lifetime of perovskite and organic solar cells.

The nano-phosphor layer europium doped yttrium vanadate (YVO₄:Eu³⁺) has been implemented as an extra encapsulation layer to protect the perovskite device beneath from UV illumination. The YVO₄:Eu³⁺ red shifts UV photons into the absorption region of the perovskite which protects the UV sensitive interfaces in the perovskite whilst simultaneously increasing the PCE of the devices. It is predicted that an extra 8.5% PCE could be achieved from a well engineered down shifting layer. Sample devices implementing YVO₄:Eu³⁺ retained half of their original PCE instead of a third for those without YVO₄:Eu³⁺ after prolonged UV illumination.[21]

A very successful encapsulating layer that has been developed is a HTM P3HT/Single walled nanotube (SWNT) layer.[89] This layer fits into a typical n-i-p perovskite architecture as demonstrated in figure 21. It has remarkable hole extraction properties which allow it to entirely replace the typical doped spiro-OMeTAD layer. P3HT/SWNT capped with Polymethyl methacrylate (PMMA) protects the device from moisture whilst removing the degradation of perovskite associated with li-TSFI and TBP. Figure 23 shows the images taken of perovskite/HTM samples over 98 hours held at 80°C in ambient atmospheric conditions, it is clear that P3HT/SWNT-PMMA layers stabilise the perovskite.[89]
Figure 22: Edited from Nature Communications,[14] density function theorem (DFT) calculations on tuning of A cations steric size influencing the X-B halide-metal bond angle as the octahedral tilt and band gap of the perovskite APbI$_3$ changes. (a) Octahedra $0_1$, $0_2$, $0_3$, $0_4$ of different tilts demonstrating the apical and equatorial bond angle ($\alpha_a$ and $\alpha_e$). (b) Map of the DFT calculated band gaps as a function of $\alpha_a$ and $\alpha_e$. The dashed line shows the crystalline symmetry where $\alpha_a = \alpha_e$. Dark circles are DFT calculated perovskites and white circles are previously synthesised perovskites. The size of circles indicates the Pb-I bond length varying away from the MA-PbI$_3$ (3.18 Å). (c) Assuming $\alpha_a \sim \alpha_e$ this graph shows the correlation between bond angle and the size of the replacement A cation.

Figure 23: From Nano Letters,[88] pictures showing the degradation of MAPbI$_{3-x}$Cl$_x$/HTMs over 98 hours at 80°C in ambient atmospheric conditions. The HTMs used are: Li-spiro-OMeTAD (spiromer-OMeTAD doped with Lithium bis(trifluoromethane sultonyl) imide), P3HT (Poly(3-hexylthiophene-2,5-diyl)), PTAA (Poly(triarylamine)), PMMA (Poly(triarylamine)) and P3HT/PMMA-SWNT (Single-walled carbon nanotubes).

3.8 Modeling the Perovskite

Computational models can sometimes save time in the laboratory by removing the need for rigorous trial and error experimentation to reach a device architecture that works. For example the band gaps, VBM and CBM’s found in figure 6 were determined using computational spin orbital coupling SOC-GW and QSGW quasiparticle self-consistent GW DFT models (Using the GW approximations). Some of the predicted band gaps of MAPbX$_3$ and FAPbX$_3$ (X = I, Br, Cl) are within ~ 0.1 eV of experimental obtained values.[19] We can now be fairly sure that a DFT model can produce an decent estimate of a semiconductor’s band gap. This means the functionality of any new potential iterations of perovskite (with replacement organic cations) can be tested computationally before they are implemented in the laboratory.[52]

An example of a piece of published computational engineering is shown in figure 22, where changes in apical and equatorial (X halide)-(B Metal) bond angle ($\alpha_a$ and $\alpha_e$ shown in (a)) caused by the various steric sizes (95% Density of ionic radii) of possible A cation replacements are mapped against their DFT calculated band gap (shown in (b)).[14]
n-k data of the perovskite and transport layers can be used to model the device as an optical cavity and determine the optimum architecture of a perovskite device. One group used such a model to produce ideal thicknesses for a device with architecture: ITO(850nm)/PEDOT:PSS (15nm)/PCD-TBT(5nm)/perovskite(350nm)/PC60BM/Ag. The device achieved 16.5% PCE with minimal laboratory optimization.[39]

4 A solar cell to compete with silicon?

Ultimately, the perovskite community needs to produce a stress tested perovskite device that emulates enough years of operational life time to be cost competitive with c-Si and CIGS. Oxford-PV and Snaith’s research group believe that this goal is soon to be reached with a first generation of commercial glove-box or vacuum processed devices. These groups have identified that perovskites can pass many of the governmental and European Union restrictions pertaining to lead and have applied for several patents surrounding the perovskite solar cell.

There is still promise for air processed p-i-n devices such as ITO/PEDOT:PSS/Perovskite/PCBM/Ca/Al. Ambient humidity has been proved advantageous for some perovskite formulae, but a new deposition technique or replacement material for PCBM is needed to get ETMs integrated into fully air-processable p-i-n devices.

Device stability and efficiencies have continued to improve alongside a reduction in hysteresis by using new formulae and deposition techniques. Smooth spin cast films of FA/MA perovskite blends have produced supposedly hysteresis free n-i-p devices by implementing either intramolecular exchange or toluene washes.

Publications using the FAI:MAX:PbI2:Px2 blends have so far only used devices architectures that implement the expensive 500°C calcination step for the TiO2 layer. It also appears that the lead acetate source has not been used in combination with any FAI:MAX blend or in any fabrication routine in air. This may be a potential avenue for future research but it is likely that lead acetate perovskite fabrication routines will not work will in air. A new formula that could prove successful is a FAI:MA(Br/Cl):PbAc2 blend in a ITO/PEDOT:PSS/Perovskite/PC70BM/Ca/Al device, using an acetate lead source to obtain short annealing times. An air-processable version may need a solution processable oxide ETM layer instead of PC70BM and an alternative conventional PbX2 halide lead source since PbAc2 may not improve film morphology in air.

A toluene wash to quench excess solvent could be implemented instead of PbAc2 to maintain high quality morphology.

If you extrapolate the amazing steps taken by the perovskite community so far then the future of perovskite solar cells looks promising... and if you are feeling cynical about the devices’ undesirable muddy-brown appearance holding them back, there are even groups working specifically on making them rose tinted.

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Brian O’Regan and Michael Grätzel. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. 1991. DOI: 10.1038/353737a0.

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