REVIEW

Perovskite Solar Cells: The Birth of a New Era in Photovoltaics

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ABSTRACT: One of the most exciting developments in photovoltaics over recent years has been the emergence of organic−inorganic lead halide perovskites as a promising new material for low-cost, high-efficiency photovoltaics. In record time, confirmed laboratory energy conversion efficiencies have increased from a few percent to over 22%. Although there remains uncertainty as to whether materials with the required stability can be found within the associated material system and whether the presence of Pb in highly soluble form will limit commercial application, it is certain that these perovskite cells will remain the focus of concerted research efforts over the coming decade. The early history of the development of this technology leading to the first perovskite cells is documented as are significant recent developments.
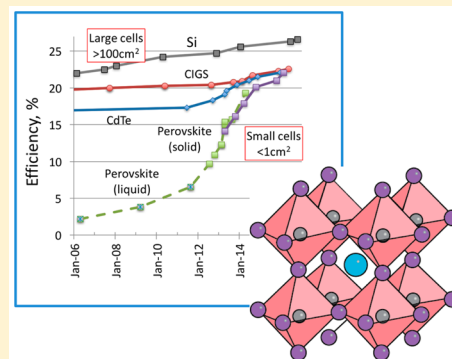
A schematic diagram[1−3] of an organic−inorganic lead halide perovskite solar cell responsible for the high level of recent interest is shown in Figure 1a. A submicrometer thick layer of semiconducting perovskite material is embedded between a low work function electron transport layer (ETL), consisting of a combination of compact and mesoporous titania layers in the case shown (with the latter layer also permeated by the perovskite), and a high work function hole transport layer (HTL). The former is contacted by a transparent conducting oxide (TCO) and the latter by an opaque metal, usually gold (although not an option commercially). When illuminated, electrons are excited from the perovskite valence band to its conduction band leaving vacant hole states in the valence band. The work function difference between the ETL and HTL encourages photogenerated electrons (e−) and holes (h+) to move off in opposite directions as shown, creating a current in any external electrical load connected between these contacts.

The past few years has seen a rapid rise in the efficiency with which sunlight energy can be converted to electrical energy using perovskites. Figure 1b shows this rapid rise for perovskite solar cells compared to progress with the traditional inorganic solar cell semiconductors, silicon, CdTe, and CIGS ($CuIn_{1−x}Ga_xSe$). While confirmed large-area (>100 cm²) silicon cell efficiency now lies at 26.6% for cells fabricated on relatively thick (∼165 μm), self-supporting monocrystalline silicon wafers,[4] small-area (<1 cm²) confirmed efficiencies for the three other materials, all of which are able to be used as micrometer or submicrometer thickness thin films similar to Figure 1a, lie in the 22−23% efficiency range.[5] All previous cells to reach such efficiencies have a simple tetrahedrally

coordinated structure like silicon, with these perovskites the first to differ from this pattern.

Perovskite refers to the distinctive crystal structure shown in Figure 2 adopted by a subset of compounds with the formula ABX_3. A, B, and X are usually elemental atoms, but for the perovskites of present interest, element A can be instead a small organic molecule. Important milestones in the development of perovskites include the material's identification and naming by Rose[6] in 1839; the first report by Wells[7] in 1892 of perovskites where element X was a halide; the discussion of related organic−inorganic halide compounds by Topsöe[8] in 1884; and more recently, the use by Weber[9,10] of methylammonium ($CH_3NH_3^+$) and formamidinium ($CH(NH_2)_2^+$) ions in position A to form Sn and Pb halide perovskites in 1978.

■ FIRST PEROVSKITE SOLAR CELLS

Weber's reports stimulated subsequent work exploring material properties,[11−14] with applications such as light emitting diodes (LEDs)[15] starting to become of interest by the early 1990s. In a series of high-profile papers,[16−18] Mitzi also highlighted the use of these and closely related layered organic−inorganic perovskites for applications closely related to photovoltaics, specifically in transistors and LEDs. In an assessment that will perhaps be proven perceptive, Mitzi (private communication) largely discounted their use in photovoltaics because of both the toxicity of Pb and material instability, specifically if Sn was used to replace Pb to address the toxicity issue. According to Ito,[19] the work of Mitzi's IBM team on nonphotovoltaic
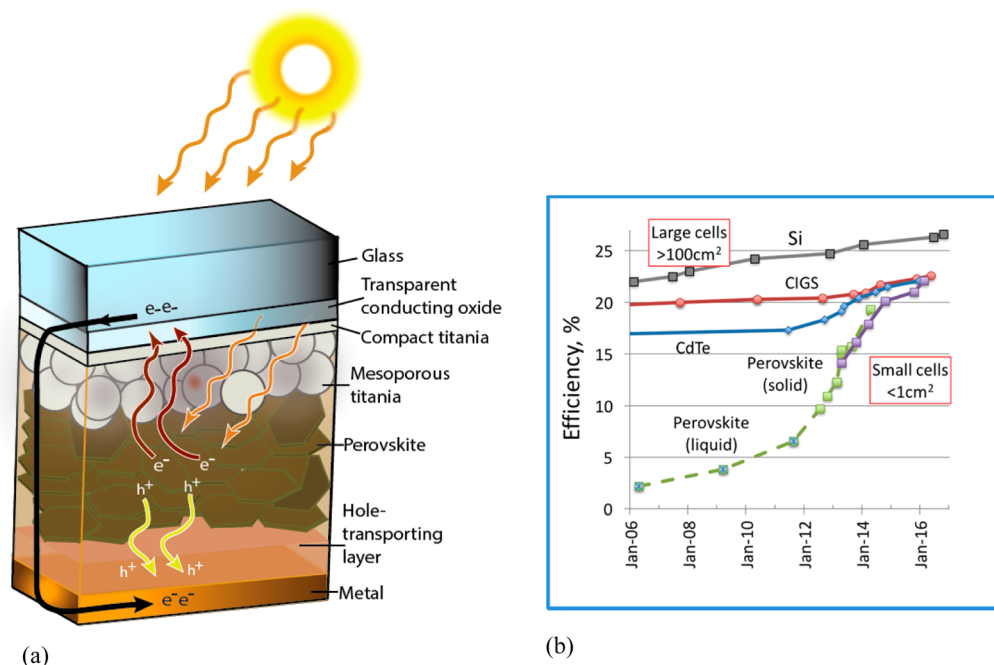
Figure 1. (a) Schematic diagram of a typical perovskite solar cell with the perovskite layer embedded between low and high workfunction layers. (Adapted by permission from ref 3. Copyright 2016 Macmillan Publishers Ltd.) (b) Evolution of laboratory perovskite cell efficiency compared to confirmed results for laboratory cells fabricated from solar cell materials used commercially (Si, CdTe, and CIGS). Note that the silicon cells are 100−2000 times larger than the other cells shown. The dashed green line first links unconfirmed results for perovskite cells with liquid contacts and then continues to link those (green squares) for all solid-state perovskite cells. The purple solid line links confirmed results (purple squares) for all solid-state perovskite cells.
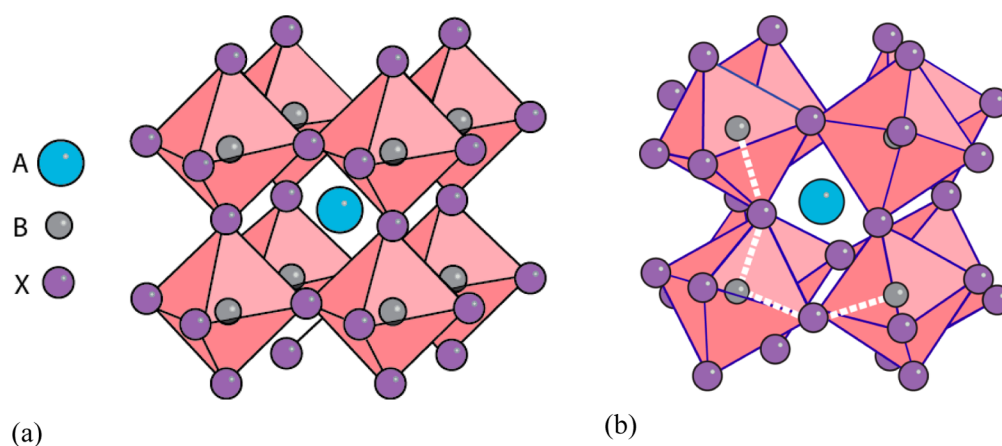

Figure 2. Perovskite crystal structures: (a) cubic phase and (b) less symmetrical orthorhombic phase. For the perovskites of photovoltaic interest, the large cation A has been generally either a methylammonium (MA), formamidinium (FA), Cs, or Rb cation; cation B has been Pb or Sn; anion X has been a halogen (predominantly I, with Br and Cl also of interest). The white dashed lines in panel b define two B−X−B bond angles in the near-vertical (azimuthal) and near-horizontal (equatorial) planes that can be used to characterize deviations from the more symmetrical cubic geometry. (Reprinted from ref 76. Copyright 2015 American Chemical Society.)

applications aroused interest in Japan, where the Japan Science and Technology Corporation (JST) funded a project exploring similar applications under the CREST (Core Research for Evolutionary Science and Technology) program from April 1997 until March 2003.

This CREST "Self-Organized Quantum Confinement Structures" program involved researchers from a number of Japanese universities, producing 59 English journal publications and 65 international conference presentations (the final project review[20] noted more of both would have been better!). One university involved was Tokyo Polytechnic where Dr. Kenjiro Teshima was leader of the Basic Material Design group within

the project.[21] After completion of the CREST project, he continued perovskite research with a graduate student, Akihiro Kojima, presenting results on lead bromide-based organic−inorganic layered perovskite compounds[22] at the Fall Meeting of the Society of Photographic Science and Technology of Japan (SPSTJ) in December 2005. At the next meeting of this society, the Annual Meeting in Chiba in June 2006, a notable development was presentation of a paper with extended authorship reporting a lead bromide organic−inorganic perovskite sensitized solar cell.[23]

Professor Tsutomu Miyasaka, on joining Toin University of Yokohama in 2001, had established a group working on

traditional dye-sensitized solar cells. In March 2004, he was encouraged by the local government to start a company, Peccell Technologies, to investigate commercial prospects and to market associated measurement equipment, recruiting Teshima from Tokyo Polytechnic.[24] This provided the first direct link between perovskites and dye-sensitized solar cells. It also provided the link to Kojima who became one of Miyasaka's students, transferring to the University of Tokyo where the latter had a visiting appointment. The first presentation[25] on the use of perovskites in dye-sensitized cells was at the 73rd Congress of the Electrochemical Society of Japan at Tokyo Metropolitan University on April 1, 2006, followed by the presentation in Chiba in June mentioned above.[20] The latter documents a dye-sensitized cell using MAPbBr$_3$ as the sensitizer with 2.2% efficiency. The first report outside Japan appears to be at the 210th meeting of the Electrochemical Society in Cancun later that year, where similar results were reported.[26]

> The first presentation on the use of perovskites in dye-sensitized cells was at the 73rd Congress of the Electrochemical Society of Japan at Tokyo Metropolitan University on April 1, 2006.

International conference presentations in 2007 included those the 212th Meeting of the above society in October, where operational dye-sensitized cells using MAPbI$_3$ sensitization were additionally reported,[27] and also at the 17th International PV Science and Engineering Conference (PVSEC-17) in Fukuoka in December, where efficiency increases to 2.6% and 1.2% were reported[28] for the bromide and iodide perovskites, respectively. Additionally, an oral presentation was made at the second International Conference on Industrialization of Dye Sensitized Solar Cells in Switzerland in September 2007 by Miyasaka.[29]

Also presenting on dye-sensitized solar cells at this latter conference was Professor Nam-Gyu Park, now at Korea's Sungkyunkwan University (SKKU), who attended Miyasaka's talk. Both Park and Miyasaka agree that Park was one of the few showing interest in Miyasaka's presentation, because it resonated strongly with Park's previous work on more traditional perovskites that had formed part of both his Masters and Ph.D. research.[30,31] One of Park's postdoctoral students, Song Rim Jang, attempted to duplicate the work, but ran into difficulties that she documented in a mid-2008 internal report.[32] The first journal publication[33] of the Miyasaka group's work appeared in 2009, with this stimulating Park's group into additional efforts to repeat and extend this work with improved efficiency of 6.5% reported[34] in mid-2011, still using liquid contact giving rise to the same poor stability earlier noted (10 min durability mentioned).

■ PUSH TO SOLID-STATE DEVICES

The poor stability noted above was due to the perovskite being attacked by the polar iodine solutions traditionally used for hole transport in dye-sensitized cells. Attempts to replace these solutions by conductive carbon and polymers to prevent this attack were reported by the Miyasaka group in 2008, but results were not very encouraging.[35]

A link to the successful solution to this problem was provided by an academic, Takurou Murakami, who had joined a different department of Toin University (private communication). A Toin University graduate cosupervised by Miyasaka, Murakami had completed postdoctoral research in Grätzel's group at École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, overlapping with a similar postdoctoral period there spent by Henry Snaith. Snaith subsequently established the well-known solar group at Oxford and a company (Oxford PV) in 2010, originally targeting the nontrivial task of commercializing dye-sensitized cells.

Murakami and Snaith were successful in a grant application for dye-sensitized cell research under the Japan Science and Technology Agency (JST) − U.K. Engineering and Physical Sciences Research Council (EPSRC) Strategic International Cooperative Program ("Enhanced Solar Light Harvesting and Charge Transport in Dye-Sensitized Solar Cells": FY2009−2011). In a project meeting at Toin University in October 2009, not long after the journal publication of Miyasaka group's work on the liquid contacted perovskite devices, Snaith outlined plans for fabricating a solid-state version of the device. Murakami (private communication) reports that a student (Michael Lee) from the Snaith team spent 6 weeks in Murakami's group at Toin University in late-2010 with a view to fabricating such devices, with this successfully completed on his return to Oxford using spiro-MeOTAD (2,2′, 7,7′-tetrakis (N,N-di-p-methoxyphenamine)-9,9′-spirobiflourene) to replace the liquid. This resulted in the submission of a joint Oxford/Toin University paper[36] to Science in May 2012 (published online in October), the first describing solid-state results using perovskites for light absorption by submission date (Figure 3), with the paper noting that the "University of Oxford has filed three patents related to this work".
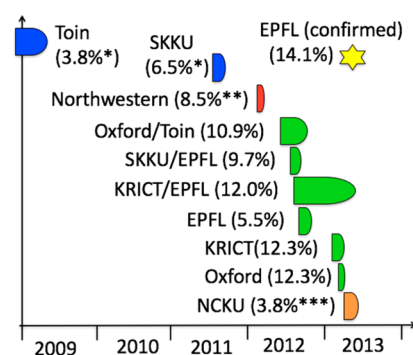

Figure 3. Timing and reported efficiencies (in brackets) of early perovskite solar cell papers. The left side of the bullet-shaped symbols represents paper submission date, while the right extremity represents publication date (* liquid contacting; ** perovskite as hole contact; *** inverted cell).

Predating this paper by several months was work investigating perovskites for photovoltaics from a slightly different perspective. The Kanatzidis group at Northwestern University, Illinois, had become interested in the use of the inorganic perovskite CsSnI$_3$ as a p-type solid-state conductor for use in dye-sensitized cells that remained sensitized by the traditional N719 dye. Masked cell efficiency up to 8.5% was reported,[37] although it was dependent on synergistic effects between the N719 dye and the CsSnI$_3$, with devices with the dye excluded giving efficiencies of only 0.2%. Important direct consequences of this work were detailed studies of the

temperature-dependent $CsSnI_3$ phases,[38] as well as very timely studies of $MASnI_3$, $FASnI_3$, $MAPbI_3$, $FAPbI_3$, and their phases, as well as of some solid solutions of these.[39]

However, the perovskite paper of the Oxford/Toin University team[36] not only removed the need for a dye but, in addition to the successful use of spiro-MeOTAD, also reported four other developments that were to have significant further implications. One was the use of a solid solution of $MAPbI_3$ and $MAPbCl_3$ that gave improved properties (although the miscibility of these compounds may have been overestimated). A second was to go beyond earlier quantum dot structures by coating the nanoporous TiO_2 with a thin but continuous layer of the perovskite. A third and perhaps the most significant development was replacing the nanoporous TiO_2 layer by nonconducting Al_2O_3, with an efficiency of 10.9% reported with this structure. This demonstrated that these perovskites could transport both electrons and holes between cell terminals, showing that they had the potential to do more than merely replace dye sensitizers. Finally, this ambipolar transporting property was exploited by demonstrating simple planar cells with the mesoporous layer completely eliminated.

> Perhaps the most significant development was replacing the nanoporous TiO_2 layer by nonconducting Al_2O_3.

Independent work almost simultaneously led Park's group to the successful replacement of the problematic liquid contacts. After achieving the results with liquid contacted devices reported in their 2011 paper,[34] Park's group (private communication) found that replacing the iodine solution by P3HT gave efficiencies of only 4%, while spiro-MeOTAD increased efficiency to 6% for devices with 2 μm thick mesoporous layers, as is standard for dye-sensitized cells. Hui-Seon Kim, the researcher involved in this work, decided to decrease the TiO_2 film thickness because she knew that the absorption coefficient of the perovskite was more than 10 times higher than that of ruthenium dye from the group's earlier work.[34] Decreasing thickness to 0.6 μm boosted efficiency to 9.7%.

Targeting a high impact publication, Park (private communication) arranged for Kim to visit Grätzel's group at EPFL taking with her approximately 100 cells for more detailed device and material characterization. This resulted in a joint publication originally submitted to *Nature Communications*, with a request for urgent publication. *Nature Communications* suggested transfer to *Scientific Reports* for the most rapid response. This seems to have been good advice, with the article being published online in August 2012, less than 7 weeks after submission, ahead of the earlier submitted *Science* paper, becoming the first published report of good performance from an all solid-state, perovskite-sensitized device.[40] Those two papers had enormous impact in alerting the research community to the enormous potential of perovskites in photovoltaics.

Speed of the reviewing and publication process had even more impact upon a third paper[41] submitted to *Nature Photonics* less than 2 weeks after the previous but not published until well into 2013. Another Korean group, Seok's at KRICT (Korea Research Institute of Chemical Technology), also reported all solid-state devices jointly with EPFL who were cooperating with Seok within the framework of the Korean

Global Research Laboratory (GRL) program, funded over 10 years to develop solid-state quantum dot-based mesoscopic solar cells. Seok's past work had focused more on these quantum dot cells, with good results reported on Sb_2S_3 solar cells[42] in 2010. Little progress had since been made, encouraging Seok to begin investigating perovskite cells in early 2012, coming from a different direction from most of the other researchers involved at this stage. He was interested in a range of organic hole contact layers to the perovskites. PTAA (poly triarylamine) gave the best results, with efficiency up to 12% reported in the final paper,[41] although results may have evolved somewhat during the prolonged review process.

The long publication delay meant that a second paper from the KRICT group,[43] submitted in early 2013, was published before the first. This second paper reported improved efficiency to 12.3% by using the mixed halide solid solution $MAPbI_{3-x}Br_x$. Low Br content (<10%) gave the best initial efficiency, but higher Br content (>20%) gave the best stability, with the moisture sensitivity of these cells starting to be more widely recognized as a serious problem by this stage. Published 1 week after KRICTs 12.3% cell was reported, Snaith's group also reported a 12.3% cell with a device architecture comprising a thin mesoporous Al_2O_3 scaffold, infiltrated and capped with a solid perovskite absorber layer.[44] This latter publication provided additional clear evidence that a solid perovskite thin film could operate very efficiently as both the absorber and charge transport layer within a photovoltaic device.

Another significant development that built on the realization of these charge-transporting capabilities and the consequent feasibility of planar devices was the application of architectures developed for organic photovoltaics (OPV) to perovskites, initially by a team at the National Cheng Kung University (NCKU), Taiwan.[45,46] One difference is that the HTL, usually PEDOT:PSS, lies closest to the glass with the ETL, frequently $PC_{61}BM$, furthest from the glass, giving the cell an "inverted" polarity.[46] Although often referred to as the "inverted" structure, it might be better referred to as a p-i-n structure, as opposed to the normal n-i-p, if n and p are taken to refer to the regions that become negative or positive, respectively, on illumination as originally intended and i is taken to mean "not intentionally doped".

The pace of development then escalated. Many researchers previously working on dye-sensitized cells or organic photo-

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voltaics, where progress had largely stagnated, converted to this new field. At the European Materials Research Symposium in May 2013, two groups reported efficiency above 15%. Grätzel and co-workers reported a 2-step iodide deposition process that improved morphology and efficiency.[47,48] Importantly, this group reported the first independently confirmed efficiency for a perovskite cell of 14.1%, giving credibility to the efficiency levels being claimed. Snaith and co-workers[49] also reported efficiency above 15% using cells with a completely different planar cell structure formed by vacuum evaporation of

$MAPbI_{3-x}Cl_x$ rather than the wet chemical processes previously used, although these results were not independently confirmed.

RAPID EFFICIENCY IMPROVEMENT

The initial developmental period documented in Figure 3 was followed by a period of very rapid progress in efficiency dominated by Seok and colleagues at KRICT. At the end of 2013, 16.2% efficiency was independently confirmed[50] for a cell including all layers of Figure 1a using $MAPb(I_{1-x}Br_x)_3$ (with 10−15% Br) followed by a 17.9% confirmed result[51] in early 2014. This was followed by a 19.7% result[52] and a landmark value of 20.1% confirmed in November 2014. This cell again used all the layers of Figure 1a but with $MAPbI_3$ replaced[53] by lower band gap $FAPbI_3$.

Although cells based on both $FAPbI_3$ and $FAPbBr_3$ had been earlier reported, one problem with the iodide is the existence of an isomorphous room-temperature hexagonal phase with much poorer photovoltaic properties. Techniques for stabilizing the desired perovskite phase include high-temperature annealing postdeposition; sequential deposition of PbI_2 followed by FAI reducing the required annealing temperature; intramolecular exchange during sequential deposition; or forming solid solutions $FA_{1-x}MA_xPb(I_{1-y}Br_y)_3$ with both mixed cations and anions,[54] where x is typically 10% and y ranges from 0 to 20%.

After a brief hiatus, another burst of activity was reported by Hagfeldt, Grätzel, and colleagues at EPFL. An efficiency of 21.0% was independently confirmed in late 2015 again for a small-area cell that used poly(methyl methacrylate) (PMMA) as a template to control nucleation and crystal growth to prepare perovskite films of high electronic quality[55] in conjunction with $[(FAI)_{0.81}(PbI_2)_{0.85}(MAPbBr_3)_{0.15}]$ precursor solution.

In related work with mixed compounds, using a vacuum-assisted solution-processing method to give good crystal quality, EPFL reported[56] an independently confirmed value of 19.6% for a larger 1 cm^2 device, about 10 times larger than most earlier devices attaining this performance level. Devices of this size give a more realistic comparison with established technologies such as silicon (Figure 1b), because smaller devices artificially avoid resistive and/or shading losses that cannot be bypassed in devices of a practical size.

KRICT together with Ulsan National Institute of Science and Technology (UNIST) more recently surpassed both milestones, with 22.1% efficiency confirmed for a 0.095 cm^2 cell and 19.7% efficiency for a much larger 1 cm^2 device, both in March 2016.

Although the basis of such work has not yet been published, a recent publication[57] with KRICT coauthorship outlines a path to efficiencies above 22%. The role of a mediator "to retard the rapid crystallization between organic cations and PbI_2" is stressed as is the role of manipulating "the chemical composition of the perovskites via solvent engineering and intramolecular exchange process". An interesting comment is that to go beyond 22%, the luminescent properties of the perovskite materials need to be better understood to improve open-circuit voltage (V_{oc}), "because J_{sc} and FF have already attained realistic values".

RECENT PROGRESS

Although the gains in perovskite cell performance documented in Figure 1b have been impressive, some caution is needed. All the perovskite cells shown in this chart are unstable, with likely durability of months at best (some of the cells shown degrade in less than 10 min during the measurement procedure itself). The performance certificate issued for these devices contain the following particularly relevant advice: "The performance parameters reported in this certificate apply only at the time of the test, and do not imply future performance".

Progress over the last year has been more in improving device stability rather than efficiency. Clear guidelines are beginning to emerge about how best to avoid instabilities. These are clearly explained by one prominent researcher[58] reporting improved stability in November, 2016: "Degradation is one of the main concerns here and, I have to say, I was trying to be very cautiously optimistic about a year ago (November 2015). Back then, our cells were only lasting a few minutes. We have improved this by well over four orders of magnitude in the last year. The key is you've got to replace metal electrodes with something like indium−tin oxide because the halogens in the perovskite reacts with most metals; you've got to get the methylammonium out of there; and then you have to package it".

Note that 4 orders of magnitude improvement from a baseline of few minutes amounts to about 500 h or 20 days, suggesting that, notwithstanding the good recent progress, multiple orders of magnitude improvement are still required.

Although solid solutions of FA and MA lead-halide perovskites have been important in contributing to efficiency increase, noted earlier, these have also been assessed as too unstable for practical application.[58,59] Encouraging stability results, however, have recently been reported for solid solutions of Cs and FA lead-halide perovskites.[58] Modules involving small area cells encapsulated between two glass sheets bonded together with industry standard ethylene vinyl acetate (EVA) or Surlyn thermoplastic resin and using standard butyl rubber edge sealants (Figure 4) have passed both the new industry standard IEC61215:2016 damp-heat module qualification test (MQT13: 1000 h exposure to 85% relative humidity at 85 °C) and thermal cycling test (MQT11: 200 cycles from −40 to 85
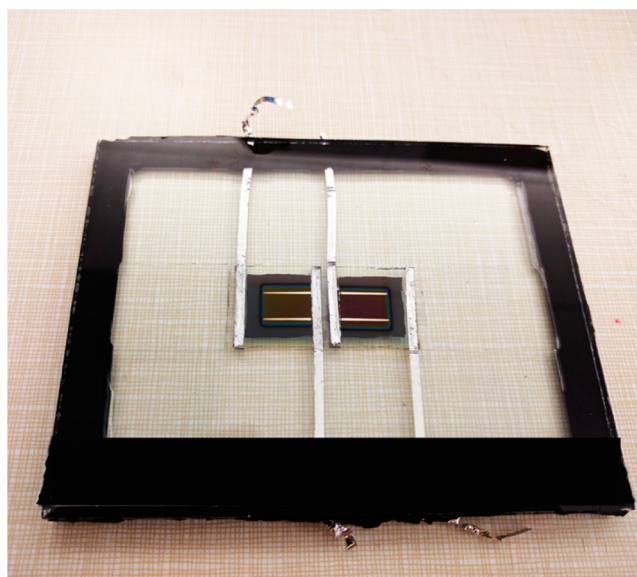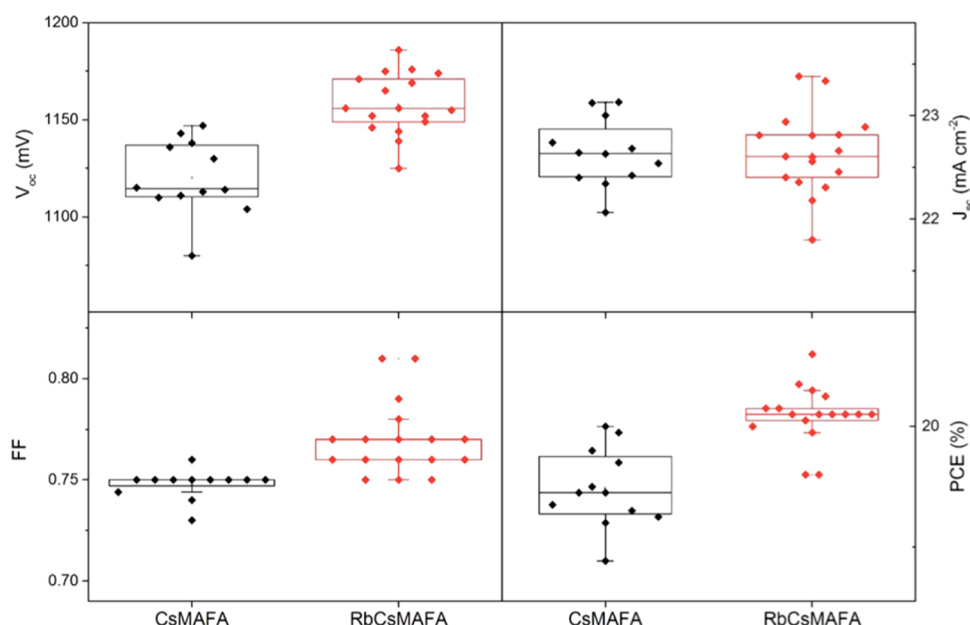

Figure 4. Small perovskite cell module using commercial module materials that has passed IEC 61215 module damp heat and thermal cycling qualification tests. (Reproduced with permission from ref 58.)

Figure 5. Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) statistics of 12 $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ (CsMAFA) and 17 $Rb_{0.05}[Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}]_{0.95}Pb(I_{0.83}Br_{0.17})_3$ (RbCsMAFA) devices measured with a scan rate of 10 mV s^{-1} without preconditioning, such as light soaking or long-term forward voltage biasing. Note that the V_{oc} improved from 1120 to 1158 mV, the FF from 0.75 to 0.77, and the PCE from 18.9 to 20.2% for devices including both Cs and Rb cations. (Reprinted with permission from ref 65. Copyright 2016 AAAS.)

°C) with less than 10% degradation (the new standards combine earlier separate standards for silicon and thin-film modules[60]). The sputtered ITO electrodes used in these cells were found to contribute significantly to this improved stability. More challenging was a 1000 h test under illumination, although results were reported to be encouraging.[58]

The company Oxford PV is reporting the ability to pass all three tests when the perovskite cells are deposited onto a silicon cell in a tandem cell configuration, although few relevant details are publicly available.[59,61,62] This is just the first step toward meeting commercial requirements.[61] Standard silicon modules, for example, will generally pass a damp heat test three times longer than the standard test, but this is not necessarily sufficient to ensure a 25 year life in some climates.[63] Commercial CdTe modules are reported by one manufacturer to pass 6000 h under the damp heat test and 1000 thermal cycles,[64] 5−6 times more severe than required for module qualification testing.

As discussed above, the choice of cation A can have a large effect upon both stability and performance, with a solid solution with $Cs_{0.17}FA_{0.83}$ giving good efficiency and stability. Tuning the anion choice can also enhance stability with solutions with Br and I anions in the same ratio ($Br_{0.17}I_{0.83}$) also performing well. More recently, Rb has been added to the cation mix,[65−67] with synergistic effects between Rb and Cs additions noted.[65] Solid solutions with the formula $Rb_{0.05}[Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}]_{0.95}Pb(I_{0.83}Br_{0.17})_3$ (RbCsMAFA) have given tightly distributed cell performance (Figure 5), superior to that of Rb-free devices, as well as better stability. It remains to be seen whether removing MA from the devices reported in Figure 5 further improves stability.

Another significant recent development has been progress with tandem perovskite solar cells with an unconfirmed efficiency of 17% reported for the monolithic 2-terminal tandem stack of Figure 6, consisting of 1.8 and 1.2 eV cells of
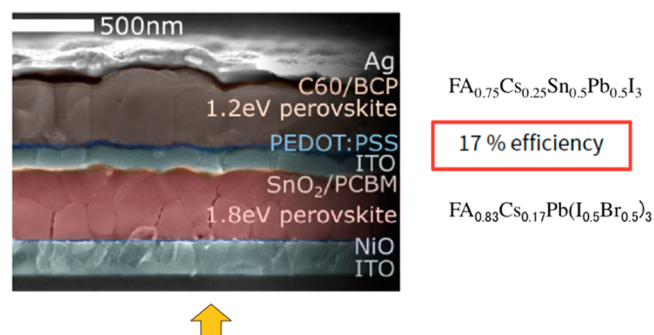
Figure 6. Monolithic 2-terminal all perovskite tandem cell structure demonstrating a reported value of 17% energy conversion efficiency. Illumination is from the direction indicated by the arrow. (Reprinted with permission from ref 68. Copyright 2016 AAAS.)

the composition shown.[68] Replacing the 1.8 eV cell by a better-performing 1.6 eV cell with the formula $FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})_3$ and using a 4-terminal configuration increases efficiency to 20%. Improvements to the 1.8 eV cell should reduce these differences in the future (experimental V_{oc} for the 1.8, 1.6, and 1.2 eV band gap cells were reported as 1.12, 0.97, and 0.74 V, respectively[68]). Note the "inverted" p-i-n structure used for these cells.

Following on from this work, Stanford and Arizona State Universities have combined to produce a 1 cm^2 monolithic 2-terminal perovskite on silicon tandem cell[69] with a confirmed efficiency of 23.6%. This is the highest confirmed efficiency for any perovskite cell, being comfortably above the 19.7% record for a stand-alone perovskite cell of this size but still below the recent 26.6% record result for a silicon cell (Figure 1b). This gap is expected to be breached over the next year or two.

■ SUMMARY AND FUTURE OUTLOOK

There have been massive improvements in both efficiency and stability of perovskite solar cells since the first reports of 2.2% efficient, highly unstable devices a little over a decade ago, as outlined above.

As shown, a strong contributor to this rapid progress has been the research networks developed for dye-sensitized solar cell research and, to a significant but lesser extent, for OPV research. Efficiency over 22% was confirmed in early 2016, although it should not be forgotten that some of these record devices will maintain their record-breaking performance for periods that may be as short as 10 min. Good progress on the efficiency front since then has been made with both all-perovskite and perovskite/silicon tandem cells, with confirmed efficiencies of 23.6% demonstrated for the latter.

Over the last year, the other area where good progress has been made is stability. One contributor to this has been the development of more robust perovskite solid solutions involving up to four different "A" position cations and two different "X" position anions. With appropriate encapsulation, small-area perovskite cells have passed the standard module qualification damp heat and thermal cycling tests. Although a big step forward, this does not by itself ensure the ruggedness to meet industry standard 25 year warranties, with commercial modules able to pass tests several times more extreme. Light exposure tests, where good performance would seem fundamental for a material to be used as a solar cell, presently seem the most challenging.

Some ground rules are emerging that preclude the very device structures responsible for the present interest in these perovskites. Specifically, these are to avoid the methylammonium cation and metals in the device layers, with the latter likely to be attacked by iodine decomposition byproducts. Avoidance of TiO_2 seems to be another feature of the modules demonstrating good performance.

Apart from lack of stability, the high Pb content of all high-efficiency perovskite cells to date may provide another barrier to commercialization.[70] Although the amount of Pb in a perovskite module is small, about the same total content as in a 1 cm thick layer of natural soil that might underlie it,[2] the present perovskites can easily degrade into very soluble toxic byproducts, significantly increasing their bioavailability and hazard for human and other lifeforms.[70] One recent study suggests that 100% reliable containment of degradation products from perovskite modules may be required.[70] This may be an almost impossible result to achieve in practice with field data showing that glass breakage is the most common thin-film solar module failure mode.[71]

It is becoming clear that available options within the generic perovskite material system may be more restrictive than originally imagined because of the challenge of producing material with band gap in the required range. For example, 2-D geometries for these perovskites have been found to improve stability but increase the band gap, reducing efficiency.[72] Similarly, Pb-free compounds such as MA_2AgBiI_6, with a double-perovskite unit cell, also have excessively high band gap.[73−75] Only Sn- or Pb-based perovskites have produced efficient cells with band gaps in the required range, although this range may be extended for the uppermost cells in tandem stacks. Notwithstanding these challenges, the rapid pace of progress and the huge number of researchers contributing to this field suggest that solutions to these challenges, if available, will be found.

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