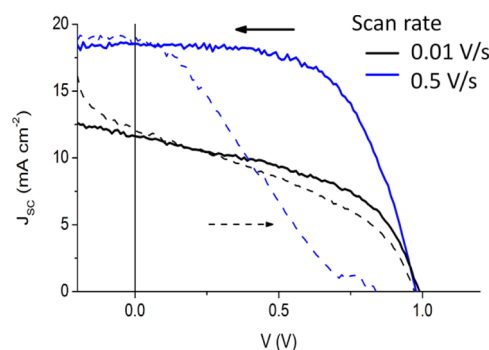


## Perovskite Solar Cells: Do We Know What We Do Not Know?

December 1–4, 2014 saw one of the largest gatherings of scientists and engineers on the topic of hybrid organic–inorganic perovskite solar cells, which dominated symposium W of the fall meeting of the Materials Research Society (MRS) in Boston on *Perovskite-Based and Related Novel Material Solar Cells*.<sup>1</sup> The symposium included many contributions as well as invited talks, open discussion sessions (to highlight major themes and stimulate discussion of unpublished data), and a “rump session”.<sup>2</sup> The latter was intended (and indeed mostly used) for last minute news in the field.<sup>3</sup> Over the 4 days, well over 120 papers were presented, including some 50 posters, 3 of which were awarded the symposium’s poster prizes.<sup>4</sup> Furthermore, on the first day of the symposium, Henry Snaith (University of Oxford) received the 2014 Outstanding Young Investigator award of the MRS and gave a meeting-wide lecture at Symposium X.<sup>5</sup> In this Guest Commentary, we summarize the topics that, in our opinion, were the more salient ones of symposium W, with a focus on recent progress and future challenges in understanding the unique properties of hybrid perovskite solar cells.

The salient issues that were discussed included *hysteresis*, which appears to be, at least in part, an interfacial phenomenon, primarily relevant for interfaces with oxides; *ion migration*, which remains a hypothesis because although it is supported by a variety of experimental results, it still lacks fully conclusive experimental evidence; *materials preparation*, where solvent annealing of the product of a 2-step process seems to be beneficial for cell efficiency, as is the presence of water; and *electronic traps*, where evidence for the presence of traps just below mid gap was presented, which is somewhat inconsistent with the high  $V_{oc}$  of cells and may present a case of photo-induced effects. Furthermore, a variety of *stability* tests give promising short-term results, but the reported very low formation energy of hybrid perovskite materials (from the “binaries”) could be detrimental for long-term stability. For *mixed I–Br perovskites* that are relevant as “ideal bandgap” materials for spectral splitting and tandem cells, phase separation was reported, which, at least for the moment, cannot be explained well by thermodynamics or kinetics. An overall impression is that likely not everyone is, as yet, working with the same material as some effects of *exposure to ambient* could be explained by doping of the perovskite or hole-conducting material. Other results remain puzzling, as even  $N_2$  was seen to change the material’s properties. Finally, not all *efficiency measurements* (and their results) appear to be comparable with each other.

Subsequent to the first public report of *hysteresis* in the current–voltage curves of hybrid-perovskite-based solar cells by Hoke et al. at the MRS 2013 Fall meeting and its discussion in the 2013 “rump session” (see Figure 1),<sup>6</sup> the phenomenon was reported in the literature<sup>7,8</sup> and was the focus of a number of talks at this year’s symposium. Ideas that were brought up to explain it were analyzed in more detail in the discussion sessions of the symposium. Part of the interest stems from the need to arrive at a well-documented, easily reproducible



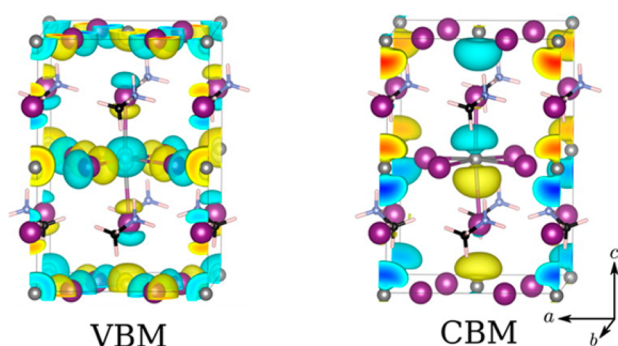
**Figure 1.** Current–voltage measurements of a perovskite-based thin-film device, showing the effects of different scan directions (dashed lines signify 0 V to forward bias, and solid lines signify forward bias to 0 V) and scan rates (from the Fall 2013 MRS Symposium Y talk [ref 6]; we thank E. Hoke for the original figure from his talk).

measurement of cell efficiencies, part from the hope that revealing the origin of such “hysteretic behavior” may help to understand the mechanism behind the photovoltaic properties of hybrid perovskites. Furthermore, the hysteresis might be connected to the long-term stability of the devices. In several talks, layers of organic molecules (discussed in talk W4.06) and device geometry (see, e.g., talk W2.05) were reported to play an important, if not essential, role in the magnitude of the hysteresis effects. These findings suggest that the hysteresis is at least partly an interface phenomenon and highlight the importance of (inter-) surface passivation. On the other hand, several talks throughout the symposium discussed the complementary possibility that reorientation of the polar organic molecules, contained inside the inorganic cage, due to an external electric field could occur. One hypothesis is that such concerted dipole alignment results in ferroelectric domains, which could then be responsible for the observed hysteresis in the current–voltage curves (see talk W1.01). Hysteresis was shown to be independent of light intensity, implying that it is not arising entirely from stored charges—one of the other possible explanations (talk W1.06). While not stated explicitly, we got the impression that without  $TiO_2$  or other electron-conducting hole-blocking oxide layers, there is no or very little hysteresis, suggesting that interface phenomena play a dominant role.

Although there is as of now no fully comprehensive explanation for the hysteretic behavior of hybrid perovskites, it was generally agreed in a number of discussion sessions that at the moment, for generating reliable physical insight in terms of  $I$ – $V$  curves and solar cell efficiencies, it is highly important to report a number of other experimental parameters. These include a steady-state maximum power point, the scan rate, the scan direction, and the preconditioning of the device prior to measuring (e.g., was it electrically biased, illuminated, or measured immediately upon completion of cell fabrication).

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*Ion migration* in hybrid perovskites, in particular, the movement of iodides and/or protons, was suggested as another possible atomistic cause for the hysteresis (see talks W9.05 and W6.03). Experimental work concerning possible iodide migration was reported, but unequivocal evidence for such migration has not yet been presented. Clearly, if such migration occurs, it can affect the operational stability of cells. Furthermore, a descriptive model partly explaining the hysteresis behavior was suggested<sup>10</sup> on the basis of the possible effects that ion migration can have on local doping, especially near the selective contacts, which is important considering the low intrinsic doping of perovskites. It appears to us that this model, which also was put forward by others (see talk W4.06),<sup>11</sup> is rather reminiscent of the so-called light-emitting electrochemical cell, LEC. We note that because the valence band is formed largely from I 5p orbitals (see Figure 2), it is



**Figure 2.** Wave functions of the valence band maximum (VBM) and conduction band minimum (CBM) of methylammonium lead iodide, calculated with density functional theory at the  $\Gamma$  point. Thin lines indicate the unit cell with iodine (violet), lead (gray), carbon (black), nitrogen (blue), and hydrogen (white) atoms. Adapted with permission from ref 9. Copyright 2014, American Chemical Society.

possible that iodine atoms formed by oxidation of the much larger iodide by holes are the migrating species. Clarifying and quantifying the impact of each of the mentioned effects in the current–voltage hysteresis of hybrid perovskites stands out as one of the challenges that lie ahead for future examinations.<sup>12</sup>

In the context of the *preparation* of hybrid perovskites, a number of talks noted improved crystallinity of perovskite films when prepared and also annealed in ambient (generally, ~30% humidity seems to be optimal). Regarding the film preparation step, it was concluded that moisture affects film nucleation. One explanation given for the effect of water is grain boundary movement and possibly also increased ionic diffusion lengths in water that is adsorbed at the grain boundaries.<sup>13</sup> Because water is a solvent for the perovskites, we suggest that it may be another example of the solvent annealing process (W 4.06).<sup>14</sup> It is known that the Pb salt used to prepare the perovskite does not need to be a halide. This notion was taken further, and it was shown that  $\text{Pb}(\text{Ac})_2$  gave more uniform perovskite films (both in thickness and coverage) than other Pb salts.<sup>3</sup> Unlike other methylammonium (MeA) salts, sublimation of MeAAc and decomposition of the  $\text{MeAPbI}_3$  perovskite are well separated in time, which is due to the high vapor pressure of MeAAc. Therefore, no decomposition of the perovskite occurred during the film annealing. To sum up, it appears as if the initial nucleation process and the final evaporation/crystallization stage are of special importance, and when these processes are well controlled and decoupled from decom-

position, more reproducible and higher-efficiency results can be obtained.

*Electronic charge traps* in the perovskites (the discussions focused primarily on the Pb iodide one, prepared with or without chloride or bromide) were invoked to explain optical (cf. talks W3.04, W4.03; and with respect to room temperature annealing, cf. W6.06) and electrical transport results, with  $\text{TiO}_2$  as the electron-conducting hole-blocking layer, but also for oxide-free systems. The traps were reported to be electron traps (W2.01). Ultraviolet photoelectron spectroscopy (UPS) data showed direct evidence for tail states near the valence band (W4.08, W7.04) that may function as shallow hole traps. The macroscale experimental results were complemented by nanoscale ones (W5.04) and by computational studies on defect chemistry and structural dynamics of the materials (W1.01, W6.03, W6.04, and W8.09). Furthermore, (de)-trapping at grain boundaries was suggested as cause for the *I–V* hysteresis (W4.06). Revealing the origin of illumination-induced structural changes and migration of species is another highly interesting avenue for future research in hybrid perovskite solar cells.

In many cases, the traps were identified as interface ones (cf. W4.11), and *interface treatments* with small molecules (W 4.03 and rump session) or with Pb-dihallide (e.g., W 4.04), or interlayers with fullerenes or C nanotubes were used to minimize the effects ascribed to the traps (as reflected in the optical or electrical transport response of the cell). In illuminated cells that used  $\text{TiO}_2$ , trapped charges were reported to decay in about a minute. In a separate report, the trap states' energy was estimated to be 0.6–0.7 eV above the valence band top (W4.08), a finding that seems to fit measurements of the Pb iodide perovskite's work function in the dark by several groups (cf. W5.01, P5.05). However, due to the relatively small ( $E_G - qV_{oc}$ ) that can be achieved with these cells, this leads to an interesting question, namely, do the traps persist under illumination and if not, what is the mechanism for their disappearance/passivation under illumination?

UPS/XPS measurements have shown the Fermi level to vary between close to the conduction band and slightly below midgap, that is, hitherto, no direct evidence for a Fermi level near the valence band has been presented. Yet, the high  $V_{oc}$  obtained means that the quasi-Fermi level (i.e., under ~AM1.5G insolation) must be near the valence band at the hole conductor. Surface photovoltage (SPV) measurements in various atmospheres,<sup>15</sup> samples of which lack at least one of the interfaces of complete cells, so far do not show a Fermi level near the valence band either. This indicates that the problem is not due to the vacuum (that might, e.g., cause a switch from p-type to n-type due to loss of, e.g., MeAX). During the discussion sessions, ideas such as self-healing/self-annealing were brought up, but at present, no experimental evidence or model has been put forward. Summarizing our impressions and own experience, we note that for a clearer, more detailed understanding, the issue of electronic traps should be separated into interface traps and bulk traps. At the moment, most models and calculations do not include interfaces, while in most measurements, they are ubiquitous.

The issue of *stability* was present, often as the gorilla in the room but at times also explicitly (see talks W6.05, W9.01, W9.02). It is not clear if there is any connection to the current–voltage hysteresis phenomena or the above-mentioned suggested ion mobility. Heating at 85 °C in ambient air,  $\text{O}_2$ , or  $\text{N}_2$  was reported to lead to  $\text{PbI}_2$  formation and ultimately to

Pb(0) particles (W6.05), supposedly not due to exposure to the X-ray or electron beam. The reported N<sub>2</sub> annealing effect is one of morphological changes (including very small PbI<sub>2</sub> grain formation), and reference to work on Cu-phthalocyanine could be relevant in this context.<sup>16</sup> At the same time, there were reports of cells that are stable for many hours at maximum power and for 45 days in a UV-filtered Ar ambient (W1.06). Use of C-nanotube-containing electrodes (especially when functioning as the anode) was shown in multiple studies to improve stability (and decrease hysteresis; see, e.g., W4.06). The reported stabilities are intriguing in view of reports in which very low energies of formation ( $\sim 0.1$  eV) of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite from its CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> precursors were calculated (talk W8.09).

Annealing in a (partial) O<sub>2</sub> atmosphere was reported to improve cells, but we note that such annealing is known to improve the conductance of the hole conductor that was used (spiro-OMeTAD) by doping it. Thus, we can surmise that much of the reported annealing effects (cf. W2.03) are not necessarily due to doping of the perovskite material.

Other environmental effects on hybrid-perovskite-based cell performance that were presented are the preparation in Pb-rich or -poor conditions (see talk W8.09), which led to lower and higher ionization potentials (W4.08), respectively. We note that oxidizing agents might affect the polarity of the device (n-type versus p-type), but at present, systematic work is lacking to separate effects originating from the hybrid perovskite from those of other cell components or interfaces.

Mixed iodide–bromide perovskites have been studied mainly to tailor the band gap and, by so doing, to obtain an intermediate band gap semiconductor suitable for a high-band-gap tandem/spectrally split cells (see talks W1.04, W5.06, and W2.04). In the reported cases, the general conclusion was that for MeAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, when  $x$  increased above  $\sim 0.2$ , phase segregation occurred to some extent. This resulted in a phase with a photoluminescence (PL) peak at  $\sim 1.7$  eV that was independent of the composition (for  $0.2 < x < 1$ ) and dominated the PL. It was suggested (W2.04) that photo-excitation may induce or enhance halide migration. We note that this migration can result in iodide-rich domains or in traps that pin the open-circuit voltage. Both could explain the lower  $V_{oc}$  in the mixed phase. The apparent pinning occurs well below what is aimed for in the use of such materials in spectral splitting cells. This might explain the use of Br-free I perovskite in such systems as a type of “next best choice” (cf. W8.01). Furthermore, domains with different compositions of  $1\text{--}2\ \mu\text{m}$  in size were measured (see talk W1.04). It was also shown that aging the mixed perovskite films (in inert environment, in the dark) changed both their absorption and PL spectra, greatly reducing the amount of the 1.7 eV phase. Other results on mixed perovskites (see talk W2.04) showed that segregation was induced/accelerated by illumination (by any light that was absorbed by the perovskite).

These studies highlight the importance of studying the phase diagram of these materials as an important step on the route for (stable) intermediate-band-gap perovskite solar cells (and other devices). Furthermore, the findings presented on this segregated “1.7 eV phase” suggest that, in order to have a chance of increasing  $V_{oc}$  by increasing  $E_g$  in these mixed perovskites, the composition will need to be confined to  $x \leq 0.2$  to prevent such segregation and loss. This is because of the *presumed* energy and/or charge transfer from the excited state of a higher  $E_g$  material to the 1.7 eV domains. We note that

such a conclusion may also be derived from a consideration of the optical absorption spectra of ref 17, where sub- $E_g$  tailing increased substantially for  $x > \sim 0.2$ . It must be noted that this tail was not seen in the spectra of ref 18, except for one composition of  $x = 0.5$ . This is an important difference, which exemplifies one of the main problems that perovskites face at this stage, namely, that one person’s hybrid perovskite is often not the same as that of his/her neighbor’s (or even that of the same person a day later).

In summary, symposium W at this year’s fall meeting of the Materials Research Society in Boston showed that the field of hybrid perovskite solar cells is progressing fast, and interest of the scientific community is growing strongly.

Some major conclusions that can be drawn are that

- likely not everyone is, as yet, working with the same material, even if the procedure that is followed seems to be the same;
- there still is a problem that not all efficiency measurements (and their results) are comparable;
- the device areas of nearly all reported devices remain small.

At the same time, it is more and more realized that these materials are special in the sense that many different microscopic phenomena could, in principle, contribute to their remarkable macroscopic properties and the performance of the solar cells that employ them.

We strongly emphasize that it will be crucial to provide insight into the “inner workings” of the hybrid perovskite materials, especially in terms of what happens under supra-band-gap illumination, and reveal how these are related to the intriguing electrical features of the highly efficient devices that use them. Together with an understanding of effects that are more related to the long-term properties and stability of the devices, such fundamental understanding will be imperative, not only for helping hybrid perovskite solar cells along but, and maybe more important for the Materials Research community, as a window on what may be a new class of materials, in terms of the combination of properties that it can have.

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