

Novel Materials for Photovoltaic Solar Energy Materials

Henry J. Snaith*

**Clarendon Laboratory, Parks Road, Oxford, OX13PU, UK*

My view of the present state of technology and research on renewable energy

The continued development of renewable energy is clearly critical for eliminating the use of fossil fuels. There is no possibility of a sustainable, stable future for humanity or the broader environment and ecosystem on earth, without making this transition to renewables over the next few decades. The renewable power generation technologies are numerous, and many will play a role in our future power generation network, but there exist some clear front runners. Hydroelectric power (HEP) is well established, but the capacity is geographically dependent and the large dams required for HEP can have severe consequences to the local environment. Wind power is widespread and will continue to expand and generate a significant fraction of our future power demands, although the predominant requirement to create off-shore wind farms, rather than on-shore, has and will continue to slow down the price reduction. At some point however, the potential for larger and larger off-shore wind turbines, enabled by advanced composites and optimized designs, will lead to offshore wind being more economic in the future. Solar power is the most abundant power source and even though the levels of irradiance vary, it is ubiquitous across the globe. The primary industrial method for harnessing solar energy is via photovoltaic solar cells, which convert sun light directly into electricity. Here, silicon dominates, and advances in silicon technology have been made by moving from doped positive(p)-negative(n) junctions, to well passivated heterojunctions, with record cell efficiencies having reached between 25 to 27%, and commercial modules at around the 21 to 22% level. The continued scaling of manufacturing and deployment has also lead to continuous price drops in deployed PV, with the lowest cost solar farms having price purchase agreements at around 1\$/kWh (10\$/MWhr). With solar PV, the key driver to cost reduction is now increased efficiency, rather than reduced manufacturing costs. The latter has already been successfully achieved by the existing PV industry. Here, a general approach to deliver higher efficiency than Si is to move towards more advanced concepts. These include more exotic concepts such as hot-carrier collection and photon-multiplication or up-conversion and also more near-term practically realizable concepts such as concentrator PV and multi-junction PV.¹ Concerning the latter, metal-halide perovskites have proven to be

extremely effective and record efficiency perovskite-on-silicon tandem cells have now surpassed 31%.²⁻⁴ Power generation is one piece of the puzzle, and the combination of wind and solar works well in most locations in the world to create a relatively balanced power generation profile. Yet the power generation profile is variable day and night and seasonal depending upon geographic location. There is therefore a major requirement to bring online large-scale power storage to go hand-in-hand with the ramping up of the renewable power generation capacity. The advancements in li-ion battery storage for electric vehicles (EV) is making battery storage affordable for domestic use. However, is it questionable whether the technology developed for EVs will be ideal for grid storage. It is likely that certain elements, such as Co, will need to be replaced. Furthermore, batteries have been optimized for lightweight high-power density. For grid storage weight and arguably round-cycle efficiency are less critical, which may open more diverse possibilities for developing new battery technologies. Hydrogen generation using electroliers is likely to become a major contributor to grid-storage capacity, where the hydrogen can then be stored and used to regenerate electricity in a converted gas-fired power station or through a fuel cell. Although the round cycle efficiency of electrolysis and subsequent combustion of the hydrogen is low, the continued drop in the price of electricity generation form solar and wind make the absolute efficiency of this process less critical, as opposed to the practicality and cost of electrolysis and storage. Beyond hydrogen, a range of other synthetic fuels including ammonia, are likely to also play an increasingly important role.

My recent research contributions to field of photovoltaic solar energy conversion

My research has focuses upon PV technology, specifically investigating and advancing novel materials and device concepts. Over the last decade we have been central pioneers in the development of metal halide perovskite PV, having made some of the key early discoveries of the outstanding optoelectronic properties of lead-halide perovskites, and demonstrating that these materials can be integrated into a simple thin-film device structure which delivers extremely high efficiency.⁴⁻⁷ Metal halide perovskites have an ABX_3 stoichiometry, where A is an organic or alkali metal cation, B is a divalent metal cation (Pb, Sn or Ge) and X is a halide anion. Motivated by the requirement to deliver higher efficiency PV technology to make a positive impact upon the industrialized solar energy generation, we have focused our efforts to enabling and delivering multi-junction perovskite PV cells, both as stand-alone thin-film technologies and in combination with Silicon.⁸⁻¹¹ In **Fig. 1**, we show a cross sectional electron microscope image of an “all-perovskite” triple junction.¹²

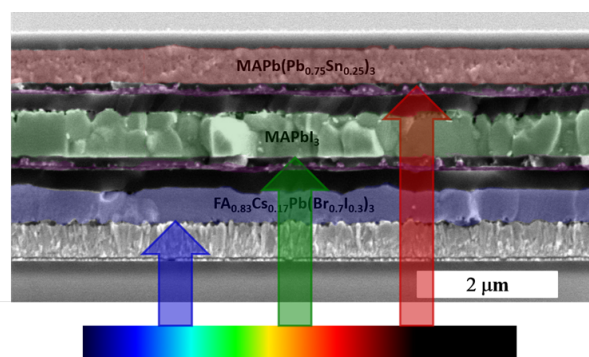


Fig. 1. Cross sectional electron microscope image of an all-perovskite triple junction cell. Reproduced with permission from reference [12]

A key challenge for the multi-junction perovskites has been to enable high open-circuit voltage from the wide gap perovskites and large “deficit” in voltage existed between the band gap energy and the open-circuit voltage. In order to obtain wide band-gaps, we need to form alloys of I/Br at the X-site. Early observations saw that under illumination the halides tended to segregate into at least two different domains. This resulted in the formation of lower band gap I-rich domains within the perovskite and subsequent emission of light through the low band gap domains.¹³ This was thought to be the cause of the voltage issue with wide band gap perovskite cells. We performed a combined optical and thermodynamic simulation to quantify the impact of halide segregation upon open-circuit voltage deficit, and surprisingly we found that the halide segregation alone could only account for a small fraction of the voltage deficit.¹⁴ We thus identified that suppressing trap-assisted charge carrier and recombination at the perovskite absorber/charge extraction layer heterojunction was the area that required most effort to improve. Since then, we have made significant progress on delivering higher voltage wide gap perovskite PV cells by focusing upon both internal and interfacial passivation of the absorber layers.¹⁵

A central challenge for metal-halide perovskites is to enable long term operational stability commensurate with Si PV. Early compositions employed methylammonium as the organic cation, which suffers from poor thermal and chemical stability.¹⁶ Moving towards formamidinium (FA) as the organic cation lead to a substantial enhancement in the thermal stability,¹⁷ [ref GE] and alloying FA with cesium, in addition to I with Br lead to highly stable perovskite thin films with tunable and stable band gaps.¹¹ With these adaptations to the perovskite, the “weakest-link” ceased to be the organic-inorganic nature of the perovskite, and became the photochemical degradation of the metal-halide framework. Here, under the combined stresses of light and temperature, I_2 gas is generated, which is considered to originate from holes being trapped on interstitial iodide.^{18,19} [ref two past papers] We found that crystallizing the perovskite in the presence of quaternary ammonium salts, greatly suppressed this degradation leading to significant enhancements in the long term stability.^{20,21}

Outlook to future developments of research on novel materials for PV

As for perovskites, key challenges remain; i) obtaining very high voltages for the wide gap cells, but the road map to achieve this is very clear, via controlled crystallization and growth to achieve homogeneous alloyed compositions with low defect densities, coupled with bulk and interface passivation. This may include molecular passivation, or the inclusion of lower dimension perovskite phases forming heterojunctions with the bulk 3D ABX_3 perovskite material. ii) The second main challenge is long-term stability. Unlike efficiency, this cannot be quantified unambiguously in a lab, and will require a combination of laboratory-based stress test and real-world outdoor testing. According to our present knowledge, understanding the photochemical degradation process in metal halide perovskites, and how and why certain additives suppress this is central to both delivering a highly stable technology, and having the confidence that it will last for 25 years in the field. In addition to the academic works, there is much industrial activity advancing the perovskite PV technology, which has a central focus upon long-term stability. As scientists we are best placed to stress these materials and devices via diverse methods, so that we can discover and understand instabilities from a fundamental basis.

Beyond lead halide perovskites, there are many possible new materials which may deliver complementary functionality or enhanced properties for a broad range of PV applications. Specifically, the lower band perovskite which is composed of an alloy of Pb and Sn, does not have the same stability as the wider band neat-Pb perovskites. There is therefore an opportunity to discover a new compound which has a much lower band gap, to enable more efficient and stable thin-film multi-junction cells. Here, AgBi compounds (halides and chalcogenides) have attracted recent interest, but nothing has yet become anywhere near as promising as the metal-halide perovskites. A notable importance for new compounds, is to ensure that they are sustainable for TW scale PV production. Unfortunately, both Ag and Bi are materials that the present PV industry is trying to reduce the use of due to their scarcity of supply. Hence, this has to be considered when embarking on a large program to discover new compounds for PV.

The central target for novel materials has to be to deliver higher efficiency than existing technologies, and the multi-junction cells are a means to do this. Since tandems with perovskites have progressed so quickly to becoming industrialized, we may see reinvigorated efforts towards realizing other more exotic higher efficiency concepts being developed in the near future, including the conceptualization and demonstration of yet to be conceived ideas.

Acknowledgments

We have received funding from the engineering and physical sciences research council (EPSRC), UK, the European commission through the FP7, Horizon 200 and Horizon Europe frameworks, the office of naval research (ONR and ONR-G) and the air force

office of scientific research (AFOSR) (USA), the Royal Society Wolfson Fund, Oxford PV, and the Bink's Trust.

References

- 1 Green, M. A. Third generation photovoltaics: solar cells for 2020 and beyond. *Physica E: Low-dimensional Systems and Nanostructures* **14**, 65, doi:[https://doi.org/10.1016/S1386-9477\(02\)00361-2](https://doi.org/10.1016/S1386-9477(02)00361-2) (2002).
- 2 <https://www.nrel.gov/pv/cell-efficiency.html>, (accessed 14th August 2020).
- 3 Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society* **131**, 6050, doi:10.1021/ja809598r (2009).
- 4 Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **338**, 643, doi:10.1126/science.1228604 (2012).
- 5 Liu, M. Z., Johnston, M. B. & Snaith, H. J. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **501**, 395, doi:10.1038/nature12509 (2013).
- 6 Stranks, S. D. *et al.* Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **342**, 341, doi:10.1126/science.1243982 (2013).
- 7 Ball, J. M., Lee, M. M., Hey, A. & Snaith, H. J. Low-temperature processed meso-superstructured to thin-film perovskite solar cells. *Energy & Environmental Science* **6**, 1739, doi:10.1039/c3ee40810h (2013).
- 8 Bush, K. A. *et al.* 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nature Energy* **2**, doi:10.1038/nenergy.2017.9 (2017).
- 9 Eperon, G. E., Horantner, M. T. & Snaith, H. J. Metal halide perovskite tandem and multiple-junction photovoltaics. *Nature Reviews Chemistry* **1**, doi:10.1038/s41570-017-0095 (2017).
- 10 Eperon, G. E. *et al.* Perovskite-perovskite tandem photovoltaics with optimized band gaps. *Science* **354**, 861, doi:10.1126/science.aaf9717 (2016).
- 11 McMeekin, D. P. *et al.* A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* **351**, 151, doi:10.1126/science.aad5845 (2016).
- 12 McMeekin, D. P. *et al.* Solution-Processed All-Perovskite Multi-junction Solar Cells. *Joule* **3**, 387, doi:<https://doi.org/10.1016/j.joule.2019.01.007> (2019).
- 13 Hoke, E. T. *et al.* Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chemical Science* **6**, 613, doi:10.1039/C4SC03141E (2015).
- 14 Mahesh, S. *et al.* Revealing the origin of voltage loss in mixed-halide perovskite solar cells. *Energy & Environmental Science* **13**, 258, doi:10.1039/C9EE02162K (2020).
- 15 Oliver, R. D. J. *et al.* Understanding and suppressing non-radiative losses in methylammonium-free wide-bandgap perovskite solar cells. *Energy & Environmental Science* **15**, 714, doi:10.1039/D1EE02650J (2022).

- 16 Habisreutinger, S. N. *et al.* Carbon Nanotube/Polymer Composites as a Highly Stable Hole Collection Layer in Perovskite Solar Cells. *Nano Letters* **14**, 5561, doi:10.1021/nl501982b (2014).
- 17 Eperon, G. E. *et al.* Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy & Environmental Science* **7**, 982, doi:10.1039/c3ee43822h (2014).
- 18 Motti, S. G. *et al.* Controlling competing photochemical reactions stabilizes perovskite solar cells. *Nature Photonics* **13**, 532, doi:10.1038/s41566-019-0435-1 (2019).
- 19 Kim, G. Y. *et al.* Large tunable photoeffect on ion conduction in halide perovskites and implications for photodecomposition. *Nature Materials* **17**, 445, doi:10.1038/s41563-018-0038-0 (2018).
- 20 Bai, S. *et al.* Planar perovskite solar cells with long-term stability using ionic liquid additives. *Nature* **571**, 245, doi:10.1038/s41586-019-1357-2 (2019).
- 21 Lin, Y.-H. *et al.* A piperidinium salt stabilizes efficient metal-halide perovskite solar cells. *Science* **369**, 96, doi:10.1126/science.aba1628 (2020).