

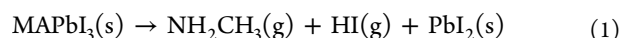
The Causes of Degradation of Perovskite Solar Cells

Last year, two important milestones were reached in the field of perovskite solar cells that would bring us closer to imminent commercial use of this light-harvester material. One was the first perovskite-based building integrated photovoltaic (BIPV) product demonstration by Saule Technologies.¹ Another significant landmark was a new certified world record for a 1 cm² perovskite–silicon tandem solar cell achieving 28% conversion efficiency achieved by Oxford PV,² which surpassed their previous certified record of 27.3% efficiency announced earlier during 2018. The first achievement outlined above is a technological and symbolic tied match with the emergent antonoma dye-sensitized solar cell technology that also became integrated in buildings for demonstration purposes.³ The next achievement is more relevant due to the excellent integration demonstrated with mature Si-based solar cell devices, even rather than the terrific efficiency record achieved by the tandem device. With these two encouraging checkpoints in mind, we start 2019 optimistic of the two harshest criticisms for hybrid perovskite coming, in principle, from two different fronts. First, what will be the expected stability of the devices, and second, but no less important, how will the environmental problem of the lead content be addressed. Would it not be great if these two problems were solved using the same countermeasure? Is encapsulation such a solution?

In principle, the failure of a perovskite solar cell to release maximum efficiency over a prolonged time interval may be due to degradation of the light-harvester material and/or necessary components for proper operation of the device, such as selective contacts. Much of the work done until now focused on the understanding of the mechanism of degradation of the perovskite material, which noted that the main underlining process occurring is an evaporation-like process of the organic part of the hybrid perovskite. The process results in a mostly intact inorganic framework solid residue that is no longer useful for light harvesting, but gracefully, the perovskite phase could be recovered by reincorporating the organic cation. Therefore, why then do encapsulated devices so often slowly lose their efficiency in the long term until total exhaustion? In this collection of perspectives on the topic of “The Causes of Degradation of Perovskite Solar Cells”, different approaches are reviewed to unravel the fade away of the hybrid perovskite material acting as an active material in solar cells.

The first perspective article, entitled “Prospects for Mitigating Intrinsic Organic Decomposition in Methylammonium Lead Triiodide Perovskite”⁴ and authored by McLeod and Liu, summarizes insights into the intrinsic stability of methylammonium-based lead iodide perovskite (MAPbI₃). The authors focus on the so-called “intrinsic” decomposition rather than the “extrinsic” decomposition driven by external agents such as moisture and/or oxygen. In fact, inducing thermal decomposition in MAPbI₃ in the absence of these external agents may be the best way to understand its decomposition, as expected to apply for encapsulated perovskite. The most recent pathways for methylammonium-based perovskite decomposition are discussed in this Perspective in

light of the output results from X-ray photoelectron and absorption fine structure spectroscopies (XPS and XAFS) and infrared spectroscopy (FTIR) measurements. A special emphasis is made on the C and N 1s states in XPS and their interpretation becoming experimental evidence that MAPbI₃ may decompose following two different routes



The predominant reaction depends on whether the decomposition occurs under kinetic or thermodynamic control. In other words, it depends on the surrounding temperature. Remarkably, McLeod and Liu elaborate a figure including all different CH₃NH₂/CH₃I molecular ratios vs temperature experimentally reported from several experimental sources. According to the authors, examining the morphology of MAPbI₃ during decomposition is essential, and evidence collected showed that this material may already contain a significant concentration of organic defects even in freshly formed film.

The second Perspective in this collection is entitled “Stability and Degradation in Hybrid Perovskites: Is the Glass Half-Empty or Half-Full?”⁵ This Perspective is also devoted entirely for pristine MAPbI₃ but includes the extrinsic factors’ effects on degradation. Deretzis et al. note a “half-full” glass of remarkable stability for perovskite thin-film samples aged in nitrogen atmosphere for 15 months at room temperature (RT) as well as fast deterioration in 3 days in atmospheric conditions at temperatures above RT (the half-empty glass of stability). This Perspective reviews chemical, structural, and thermodynamic strengths of perovskite under different ambient conditions using X-ray diffraction, SEM, and optical absorption to monitor perovskite integrity. The authors analyze significant insights as the defect generation process is highly localized on surfaces and interfaces; how external pressure can significantly affect the degradation process and demonstration that the degradation of MAPbI₃ is overall a desorption process. After considering all degradation mechanisms observed, the authors wonder if the stabilization of MAPbI₃ is feasible for commercial applications. They argue that proper surface passivation in order to simultaneously hinder molecular desorption and prevent infiltration of external agents within the perovskite bulk would work but remark that such a passivation agent would be a gas-phase component. In fact, the authors envisage the encapsulation of solar cell devices in a pressurized N₂ ambient as a viable preservation method but note that industrial realization of similar systems is still missing.

The third Perspective in this collection, authored by Ciccioli and Latini, is entitled “Thermodynamics and the Intrinsic Stability of Lead Halide Perovskites CH₃NH₃PbX₃”.⁶ The review consists of two parts. The first part is focused on general

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thermodynamic analysis of the hypothetical decomposition of MAPbX_3 to precursors $\text{CH}_3\text{NH}_3\text{X}(\text{s})$ and $\text{PbX}_2(\text{s})$, pointing out the importance of the entropic factor playing a stabilizing role for the perovskite structure. The authors discuss the scarcity of studies available currently to quantify the thermodynamic stability of MAPbX_3 based on this macroscopic approach, sometimes noting uncertainties and inconsistencies even capable of precluding the prediction of the relative stability in the halide series ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).⁷ Nonetheless, this thermodynamic stability determination reviewed by Ciccioli and Latini is essential for the future of perovskites. If the material is found unstable for working temperatures and pressures using this approach, no protection strategy may be used safely for the long-term stability requirement in photovoltaics. The second part of the Perspective is devoted to the specific decomposition processes leading to the release of gaseous products from MAPbI_3 perovskite. As noted by the authors, envisaging all possible degradation pathways for perovskite could be difficult or impossible to guess. However, it is a priori necessary information to predict from the thermodynamics point of view if the system undergoes spontaneously such a type of chemical/physical transformation or remains unmodified. The authors review the two well-established degradation pathways for MAPbI_3 as did McLeod and Liu in the first Perspective of this collection (eqs 1 and 2) but including a third pathway assuming full MAI evaporation for completeness. Ciccioli and Latini explain that there is a kinetic limitation for reaction 2 to proceed because it implies the breaking of a strong C–N bond, and consequently, the nonspontaneous reversal of the neutralization reaction 1 is predominantly observed as the dominant kinetic decomposition pathway at low temperature. Gas-releasing decomposition via reaction 2 is of crucial importance for investigating the stability of MAPbI_3 because pathway reaction 2, in contrast with reaction 1, is not reversible and not selective for MAI back formation.⁸ Indeed, there is a key issue for the stability of MA-based perovskite. Currently, the determination of the temperature threshold favoring degradation reaction 2 instead of the benign evaporation-like process in reaction 1 is a matter of debate. Ciccioli and Latini observed, according to KEMS results, that even at temperature as high as 250 °C reaction 2 could not come out to the extent predicted from equilibrium thermodynamics. However, there were recently two independent determinations of CH_3I release at ~180° and ~60 °C^{10,11} using quadrupole mass spectrometry measurements.


MA-based perovskite light-harvesting materials must afford exceptional stability properties in the long-term if used for photovoltaic applications. Luckily, the decomposition route to $\text{NH}_3(\text{g})$ and $\text{CH}_3\text{X}(\text{g})$ at photovoltaic working temperatures is not the most largely favored route from a kinetic point of view. It is all good news as long as one does take into account that there would still be a small portion of MA degrading irreversibly and Le Chatelier's principle is in compliance. On the other hand, nowadays, there is a strong movement in favor of MA-free but mixed formamidinium with inorganic cations (Cs, Rb) obtaining high performance and stable perovskite solar cells.^{12,13} Indeed, we would be facing a Gordian knot problem. What would be a more economically viable approach to synthesize a high-performance perovskite light harvester material? (1) Use a perovskite formula whose A position is fully based on inexpensive MA (or mixed FA/MA) organic components at the expense of short use or (2) include

expensive and scarce inorganic cations such as Cs or Rb that clearly outperform pure organic A site composition?

One could wonder if a compromised solution would be the conception of a methylamine gas rechargeable solar cell device similar to the N_2 pressurized preservation device proposed by Deretzi et al. in their Perspective. Once encapsulation is accepted as a mandatory design constraint, not only to minimize gas desorption and ambient-driven degradation but to prevent Pb leaks, an encapsulated device would be purged and flushed again to refill with an inexpensive methylamine/HI gas mixture to recover the methylammonium cation lost by route 2. This refilling procedure would have to be carried out at the very first sign of loss of efficiency and/or yellowing observed by the naked eye of the light-harvester material. Of course, all other components in the device should have been chosen to be compliant and robust against the gas-transfer and perovskite regeneration processes, i.e., using carbon electrodes and avoiding delicate organic selective contact layers.

Juan Bisquert, Reference Editor

Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain

Emilio J. Juárez-Perez,* Collection Organizer 

ARAID Foundation, Institute of Nanoscience of Aragon (INA), University of Zaragoza, 50018 Zaragoza, Spain

AUTHOR INFORMATION

Corresponding Author

*E-mail: ejjuarezperez@unizar.es.

ORCID

Emilio J. Juárez-Perez: 0000-0001-6040-1920

Notes

The authors declare no competing financial interest.

The Perspective Collection organized by Juan Bisquert and Emilio J. Juárez-Perez for the *Journal of Physical Chemistry Letters* can be found at <https://pubs.acs.org/page/jpcld/vi/perspective-collections-perovskites>.

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