The balance between efficiency, stability and environmental impacts in perovskite solar cells: a review

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Abstract
Photovoltaic technology is progressing very fast, both in a new installed capacity, now reaching a total of more than 400 GW worldwide, and in big research effort to develop more efficient and sustainable technologies. Organic and hybrid solar cells have been pointed out as technological breakthrough due to their potential for low economical cost and low environmental impact; but despite impressive laboratory progress, the market is still beyond reach for these technologies, especially for perovskite-based technology. In this review, the historical evolution and relationship of efficiency and stability is addressed, including Life Cycle Assessment studies which provide a quantitative evaluation of environmental impacts in several categories, such as human health or freshwater ecotoxicity, with special focus on lead toxicity. The main conclusion is that there is no unsurmountable barrier for the massive deployment of photovoltaic systems with perovskite solar modules, if the stability is extended to lifetimes similar to technologies already in the market. The results of this review provide some recommendations mainly focused on the best options for improved stability (avoiding mainly moisture and oxygen degradation) by using metal oxides, ternary or quaternary cations, or the novel 2D/3D approach, and the encapsulation effort which should also take into account the recyclability of the materials and the low environmental impact processes for up-scaled industrial production. Research guidelines should take into account the end-of-life of the devices and cleaner routes for production avoiding toxic solvents.

1. Introduction

Organic–inorganic perovskite thin films for organic electronic devices were prepared from solution as early as 1998, thus opening a door for a broad range of applications; but stability issues were already raised since the organic salt was not thermally stable and problems due to the stability of the metal valence state were detected [1]. It took more than ten years until Kojima et al [2] developed the first perovskite solar cell with a liquid electrolyte, resembling DSSC solar cells, and delivering a power conversion efficiency (PCE) of 3.8%; all perovskite solar cells (PSC) based on liquid electrolytes showed a large instability, with lifetimes not reported or shorter than a few hours, thus making them useless for power generation. Nevertheless, Park’s group reported in 2011 a stable PSC in electrolyte, with PCE = 6.5% (with a lifetime of 10 min) [3]. A breakthrough was achieved when a long term durable 10.9% perovskite solar cell was reported by Snaith’s group [4]; the new trend was confirmed when an all solid-state perovskite solar cell achieved 9% showing good stability up to 500 h without significant losses [5]; many device architectures are now reaching PCE > 20% since 2015 and 25.2% in 2019 (by KRICT–MIT laboratories, according to NREL efficiency chart). For tandem solar cells where a perovskite cell is grown on top of a silicon cell, efficiencies have boosted up to 23.6% [6] and in 2019 an impressive certified 28.1% (from Oxford PV Ltd); an all-perovskite tandem reached PCE = 19.1% in 2018 [7]. This steady progress is still not enough for successful commercialization of perovskite solar cells, since some challenges remain to be solved:
the main one is to achieve long lifetimes with good stability at module level with $T_{90}$ of a few years of outdoor operation in different environmental conditions; secondly, the toxicity problems must be addressed, especially those arising from the use of lead, and finally, the upscaling of manufacturing towards industrial production must be cost-effective, delivering a levelized cost of electricity (LCOE), which is competitive when compared to other photovoltaic (or any energy) technology. The achievement of a good LCOE will be a consequence of improving the processing routes to address the two main challenges: stability and toxicity.

Improvements of power conversion efficiency have been the main driver for research (and publication rates) so far and the focus on solving the stability problem started later, with first reliable and detailed results about stability published as late as 2013 [8]. Nevertheless, in the past five years, the importance of stability has been emphasized and identified as the main problem to solve for the perovskite solar cells to be able to compete in the market arena [9]. This conviction has led to an increasing number of reports including data about stability and the lifetime of devices, although in very different testing conditions. Recommended standardization about the experimental procedures to carry out stability experiments, initially developed for the study of organic (mainly polymeric) solar cells, has not always been followed by the perovskite community [10]. Therefore, it is still difficult to compare the operational stability of the broad range of alternatives (materials, processes, encapsulation, etc. . . ) and any conclusion about his capability to compete with existing photovoltaic technologies is still preliminary. The concerns about reliability of perovskites for photovoltaic applications can be extended to their use in other devices. Dielectric and ferroic properties of halide perovskites have been recently reported [11, 12]; also, manganese substitution of lead in the CH$_3$NH$_3$PbI$_3$ have generated a great expectation towards the possibility of a light-controlled magnetic recording of information [13].

In this article, a review of the progress of perovskite solar cell technology has been carried out with the focus on the evolution and relationship between power conversion efficiency (PCE) and stability; therefore, data from articles, which at the time were a breakthrough, have also been included to emphasize the evolution trends and this is complemented with parameters from state-of-the-art devices, mostly published in the past two years. More than one hundred different devices, using different materials or architectures, have been considered; all of them have been characterized following standard procedures when electrical parameters are reported, thus making a cross-comparison straightforward. This is not the case when stability is reported, a variety of methods and environmental conditions makes it very difficult for the cross-comparison; the stability data have been organized into two main groups in this review: stability reports for devices which are stored and characterized from time to time, and stability for devices which are characterized under continuous illumination; in both cases data for $T_{90}$ have been considered (sometimes directly reported, in other cases extrapolated from graphs or tables), since this is a recommended parameter to enable fair comparison between devices [14]. As mentioned above, the ‘density’ of information about stability has increased with time; initial reports focused mainly on efficiency and the hysteresis problem; recent reports more often include stability analysis.

Similarly, the environmental impact and economic cost analysis for perovskite solar cells has been carried out recently, mostly in the past four years. Life Cycle Assessment (LCA) is a standardized methodology which provides detailed analysis of the inventory of materials, energy inputs and subprocesses for the whole cycle of fabrication, operational phase (use) and end-of-life of devices. The effort by the scientific community to provide LCA studies for different processing routes of PSCs has increased and some general consensus is arising regarding the main recommendations for a sustainable production of methylammonium based perovskite solar cells or other devices [15–17]; some with more focus on the lead toxicity problems [18, 19]; others focusing on the most recent tandem approaches [20, 21]. Finally, economic cost analysis and first calculations of envisaged levelized cost of electricity for perovskite photovoltaic technology are being published very recently [22].

This article is organized as follows: first, the main concern about the toxicity problem of lead, and also other toxic materials used during process is presented and discussed; then a section is devoted to stability and lifetime studies, including the different strategies to overcome the stability problem, followed by a section about how to make processing routes more sustainable and competitive from the environmental and economic point of view. The equilibrium between the challenges: toxicity, stability and economic cost is discussed from a Life Cycle Assessment perspective in the last section. The final section is devoted to summary and conclusions.

2. Lead: the toxicity problem

2.1. Quantification of lead toxicity in perovskite solar cells

Lead toxicity has been pointed out as one of the most challenging barriers towards the commercialization of solar cells, in close competition with stability problems and cost-effective production routes [23]. The dynamics of lead (and tin) intoxication and effects in human health have been thoroughly studied and they pose important

$^{1}$ $T_{90}$ is defined as the time when power conversion efficiency (PCE) drops 20% compared with initial PCE.
risks that must be tackled [19], including possible contamination routes that have been analyzed with special focus in the effect of rain on PSC modules [24]. Toxicity due to lead is also a concern and a possible impediment to large scale deployment of commercial PSCs, which adds to the already existing concern about the disposal of electronic equipment containing lead and other toxic materials [25]. Also possible hazards during the fabrication process for lead contamination by researchers at laboratories, or workers at a future industrial-scale production plant, must be addressed.

One clear way to overcome this problem is to reduce the amount of lead in the halide perovskite, but, how much lead is contained in perovskite solar cells? How does this quantity compare with other lead-containing devices already in the market, such as batteries? We should be able to compare different devices and applications and this cross-comparison is based in a clear definition of the ‘functional unit’ that is chosen for the LCA study. A detailed analysis of the risks that actually suppose the lead content in standard CH$_3$NH$_3$PbI$_3$-based perovskite solar cells is addressed below.

To analyse environmental impacts using Life Cycle Assessment methodology, a ‘functional unit’ has to be clearly defined. The most common one is based on the amount of electricity produced (1 kWh) by the device, with the inconvenience that it is necessary to assume a lifetime for the solar cell in order to perform the calculation. A realistic and cautious assumption is to establish a 1 year lifetime for the solar modules for outdoor operation (compared to commercial technologies, with 25 to 30 years of guaranteed lifetime $T_{90}$, this is a modest assumption). The results for 1 kWh Functional Unit with 1 year lifetime showed that the small amount of toxic lead(II)halide included in the solar cell (0.001% in weight) poses less environmental and health risks than the processing of the methylammonium halide [17]. This result is confirmed by a study on the toxicity impacts of the lead used in the formation of the light absorber layer, that were found to be negligible by Celik et al [26, 27].

Other studies still found emission of lead during production, and emission to water during end-of-life, that are the main contributors to the human toxicity category of impacts, and recommend more research into worker exposure and worker safety measures during processing in a future large scale factory [20]. More recently, a detailed study of lead environmental impacts in electricity production by perovskite solar cell based PV systems throughout its full life cycle found that it can be four times lower and the potential toxic emissions can be 20 times lower than those in representative US electricity mixes, assuming that PV operational lifetimes reach 20 years [28]. A quantification of lead content of perovskite solar modules to supply all of the USA’s demand of electricity per year has been established at 100 tons/year, slightly above the current USA electricity generation mix (in 2011), but well below the emissions from cars or aviation in a year which are one and three orders of magnitude higher, respectively [29].

Despite these variations in lead impact results, the average conclusion of those studies is that the lead based perovskite solar cells do not pose extra concerns which impedes massive fabrication and deployment when compared to other commercial photovoltaic technologies in the cradle-to-gate scenario. Furthermore, there is a strong progress in developing efficient recycling routes for lead used in perovskite solar cells, as explained in the section devoted to recycling issues.

2.2. Lead-free perovskite solar cells

Nevertheless, although these kind of results are promising, a massive deployment of a photovoltaic technology at the GW scale, based on the use of lead, will still pose significant environmental and health risks [30, 31]. Although the concern about lead toxicity of perovskite solar cells tends to be lower than initially expected, it is worth exploring alternatives using lead-free devices [32, 33]. Lead free PSCs reached an efficiency of 6% at a time when lead-based PSCs were at 17%; furthermore, the Sn-based devices show poorer stability than Pb-based devices [34]. The most common approach is substituting lead with tin, but using elements to form halide double perovskites (elpasolites) have also been explored [35]. Interestingly, a lead-free solar cell, based on a CsSnI$_3$ light absorber (as a CH$_3$NH$_3$PbI$_3$ replacement) was also reported, although PCE was very poor and only improved upon the addition of SnF$_2$ to the active layer (best for 20% addition), but on the other hand this showed good stability for more than 250 h, especially those replacing the spiro-OMeTAD by m-MTDATA as HTL [36], while in CH$_3$NH$_3$PbI$_3$ cells, this substitution lead to more than 1000 h stable cells [37]. More recently, the replacement of spiro-OMeTAD by a Zn-derivative porphirin in a lead-free solar cell has led to extended stability up to 60 h for water stability and 100 h for thermal stability, an increment of 75% when compared to control cells [38].

Solar cells with mixed Pb/Sn perovskite have been reported. This is an approach that even if does not eliminate the use of lead, may enable a strong reduction in its use. These devices have shown the best photocurrent at a 50% ratio of mixing (the evolution of band gaps with the addition of Sn does not follow a linear trend and this anomaly emphasizes the effect of Sn addition) [39]. Tin has been included not only in the active layer, SnO has also been used as ETL with good results for PCE (13%) and stability (>700 h storage, no encapsulation) [40, 41]. The environmental impact benefits of lead-free (or lead-reduced) solar cells have been analysed by LCA [15] and in a more detailed comparative analysis of lead versus tin [18]; strikingly, in both cases,
the replacement of lead did not reduce the environmental impacts, since the loss of PCE and stability creates an environmental burden that overcome the advantages of lead-free cells. Those studies are also interesting because they draw attention to other toxicity problems arising from the use of solvents during processing of charge transport layers that were not considered to date and will be analysed in the following section.

Additionally, a special concern for toxicity must be raised during experimental work, since hazards in the laboratory arise mainly by the absorption of the toxic lead when manipulated in solution, which is significantly high, especially via the dermal and respiratory routes [42]; some of the lead derivatives used in the laboratory are soluble both in water and fat, posing a high risk [19]. Other routes use dimethylformamide (DMF) and dimethylsulfoxide (DMSO) as solvents, which not only are toxic themselves, but also increase the risk of bio-incorporation since they are miscible with water in all ratios; these solvents have also been considered a major contributor to environmental impact by detailed LCA analysis [17, 43].

3. Stability and lifetime

Any photovoltaic technology, especially for a thin-film solar product to be commercially viable, must pass the IEC 61646 testing standards regarding stability and lifetime [44]. This is an environmental requirement, but it also becomes an economic and marketing requirement since any competing technology (including low-cost inorganic technologies) are already meeting these standards. The organic polymer-based photovoltaic (OPV) research community developed (during a series of conferences) a full set of recommendations in order to perform stability tests for OPVs, which are commonly known as the ISOS protocols [10]. For perovskite solar cells, this is an even stronger requirement, since hysteresis creates an additional uncertainty about how the electrical parameters are measured and also because light induced degradation has been shown to depend on the polarization state of the device and creates metastable modifications of properties of the perovskite film, with a reduction in initial PCE up to ~50% in the first 10 h under short circuit conditions, while in an open circuit, the reduction is 'only' ~20% for the same light irradiance and temperature [45, 46].

Due to the high dispersion of procedures and data that are reported regarding stability of perovskite solar cells it is strongly encouraged that the ISOS protocols be taken into account and used more broadly. This will allow researchers to compare results and to organize inter-laboratory experiments and therefore open a road to a collaborative elaboration of a future standard for perovskite solar cell stability tests [47].

The review presented in this manuscript has selected the articles which reported the most representative device composition and architectures, including those which represented a breakthrough when published for the first time and those with the most recent results for the same structures. The combination of active layers, HTL and ETL layers, substrate and encapsulation alternatives create a challenge when a classification is attempted; on the other hand, a classification based on parameters such as PCE and lifetime (ordered from best to worst), does not provide a clear trend regarding device architectures and selection of materials. The choice of this review has been to classify the articles regarding device structures and performance parameters based on the...
composition of the layers with a focus on toxicity. The criterion for classification is explained below and summarized in Table 1. The results of the classification, including the most relevant electrical and stability parameters, are presented in Table 2.

From the environmental point of view, the rationale behind the classification indicated in Table 1 which led to the order in Table 2 is as follows: first, the principal criterion is active layer composition, with methylammonium lead iodide (MAP) being the main group, followed by derivatives with other halogens or other metals (MAPX, MAXI, respectively). A special category is MASnI lead-free devices, in the previous groups, also Sn, has been used but in combination with lead, so this category emphasizes the approach of completely lead-free devices, since lead is the main toxicity concern in PSC composition. Secondly, the HTL composition divides the main category into subcategories separating it between HTLs containing spiro–OMeTAD from spiro-free HTLs. This choice is due to the important environmental impact of spiro–OMeTAD processing due to the use of toxic solvents; the spiro-free category is separated in subgroups using HTLs composed of carbon derivatives (carbon black, C60, PCBM, carbon nanotubes or graphene), followed by metal oxides, polymers and small molecules. These subcategories have also been used to organize the MAPX, MAXI, MASnI, FA, (MA)PBI and 2D/3D categories. We should emphasize that the 2D/3D category is not (strictly speaking) based on active layer composition, but since this approach is one of the most successful regarding stability and extended lifetimes reaching to more than 10,000 h, a special category has been created for them. The information about different ETLs is included in the tables as a summary, but it is not used to organize or separate subcategories of devices. The final column in Table 1 indicates the number of devices of each group included in Table 2 (a total of 110 devices are included) and the symbol used to identify each category in the graphs of Figures 1 to 3. The colour code also has an orientative meaning; filling colour is red when lead is present and green for lead-free approaches, border colour is red for devices containing spiro–OMeTAD in the HTL and green when it is spiro-free; other combinations are for special categories as indicated above. It is worth mentioning that there is no green/green symbol, i.e. the lead-free active layers all include spiro–OMeTAD in the HTL layer.

From the detailed revision of Table 2 and its graphical representation, some conclusions can be obtained. In all graphs of PCE versus different electrical parameters, a more or less linear trend is followed, more clearly visible in the PCE-I_{sc} dependence with the highest PCEs provided by the FAPI family of devices, also the lead-free devices show a cap in potential I_{sc} which does not evolve beyond PCE > 10%. Since lead has a lower toxicity load than expected, it seems that the effort for lead-free devices is not providing realistic alternatives to lead. On the other hand, spiro-free devices are showing better potential to reduce the environmental impacts. A detailed analysis of the evolution of devices is organized in three subsections: (i) related to structural stability, (ii) replacement of charge transport layers, with special focus on HTLs, (iii) encapsulation approaches.

### 3.1. Structural stability

The structure and phase transitions of the CH_{3}NH_{3}PbI_{3} (MAP) perovskites have been intensely studied and completely solved for temperatures between 10 K and 350 K in the past few years [115, 116], including the variations of the hybrid perovskites CH_{3}NH_{3}PbX_{3} (X = I, Br and Cl) [117]. An intrinsic problem exists for the MAP perovskite: the existence of a phase transition from tetragonal I4/mcm to cubic Pm-3m when the increasing temperature reaches T = 330 K; this transition temperature is in the range of temperatures that a solar cell may reach when it is operating in ambient conditions. Defects in the structure such as dislocations or crystalline grain boundaries affect the stability of the structure at all temperatures. The phase change of the perovskite active layer, both for lead and for lead-free perovskites, provide structural changes that may be capable of tailoring the relative energy level alignment of defects (e.g. tin vacancies) and therefore reduce the background dopant density and improve charge extraction [118]. An important aspect that has not deserved much attention so far is the residual stress in the structure that may lead to structural instabilities, the residual stresses (tensile) in perovskite films can exceed 50 MPa in magnitude, and simple recommendations such as a bath conversion method to form the perovskite film at room temperature leads to low stress values that are unaffected by further annealing[119]. Therefore, the transition at 330 K and the reduction of stress can be seen as an opportunity for self-healing of the structures.

A good practical test of stability of the molecular and crystalline structure is the amount of hysteresis present during the I–V characterization (forward or reverse, from short circuit to open circuit and vice versa). It is now accepted that the presence of hysteresis is an indication of the lower quality of the device, leading to stability problems. Many devices are now being reported which are completely (or almost) hysteresis-free. Many groups have already achieved this goal: hysteresis-free perovskite solar cells were grown by solution-based, hot-casting techniques to grow continuous, thin films of organometallic perovskites with millimeter-scale crystalline grains, which delivered PCE of 18% with low variability [120]. Other methods, based in sublimation of molecular precursors in high vacuum chambers achieved large crystalline grains and high efficiencies with no hysteresis in the I–V characteristics [64], vapour-deposited perovskites with simplified architectures have delivered...
Table 2. Summary of electrical and stability parameters for 108 devices with different combination of materials and architectures grouped as indicated in Table 1. Lifetimes have been adapted to T80 values (storage with intermittent characterization, or under constant illumination), electrical parameters are included in the table as reported in the references; Voc values marked with asterisk are for tandem or module devices.

| Group            | Active layer | HTL                  | ETL                  | PCE (%) | Jsc (mA/cm²) | Voc (V) | FF | T80 (h) store | T80 (h) Illum. | References |
|------------------|--------------|----------------------|----------------------|---------|--------------|---------|----|---------------|---------------|------------|
| MAPI/ electrolyte| CH₃NH₃PbI₃   | Pt                   | TiO₂, electrolyte: LiI/Li₂ | 3.81    | 11           | 0.61    | 0.57 |               |               | [2]        |
|                  | CH₃NH₃PbI₃   | Pt                   | TiO₂, electrolyte: LiI/Li₂ | 3.13    | 5.57         | 0.96    | 0.59 |               |               | [2]        |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂                 | 9.7     | 17.6         | 0.888   | 0.62 | 500           |               | [48]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | cTiO₂, nanorod        | 9.4     | 15.6         | 0.955   | 0.63 |               |               | [48]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂                 | 15      | 20           | 0.933   | 0.73 | 500           |               | [8]        |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂                 | 17.01   | 21.64        | 1.056   | 0.741|               |               | [49]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂/Au              | 8.2     | 13.4         | 3.36    | 0.778|               |               | [50]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂                 | 15.34   | 20.93        | 1.03    | 0.71 | 400           |               | [51]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | mTiO₂/G               | 16.3    | 22.95        | 1.03    | 0.69 | 400           |               | [51]       |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD         | TiO₂                  | 4.08    | 12.67        | 0.761   | 0.401| 172           |               | 96         |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD/Li-TFSI | TiO₂                  | 12.66   | 19.7         | 0.974   | 0.648| 48            |               | 12         |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD/F4-TCNQ doped | TiO₂                  | 10.59   | 18.72        | 0.946   | 0.568| 172           |               | 50         |
|                  | CH₃NH₃PbI₃   | spiro-OMeTAD/Li-TFSI + FK209 + TBP | TiO₂                  | 12.01   | 20.19        | 1.002   | 0.593| 48            |               | 12         |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | TiO₂                  | 12.3    | 19.55        | 0.91    | 0.69 |               |               | [53]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | cTiO₂/mTiO₂           | 13.24   | 17.4         | 1.021   | 0.745| 800           |               | [54]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Li-TFSI | mTiO₂                 | 8.31    | 14.16        | 0.863   | 0.68 |               |               | [39]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | ZnO NP/PCBM           | 6.4     | 16           | 0.88    | 0.46 |               |               | [55]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | ZnO NP/PEI            | 10.2    | 16.8         | 0.88    | 0.69 |               |               | [55]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO/Ag                | 14.4    | 20.05        | 1.01    | 0.696|               |               | [56]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | ZnO nanorod/NRA       | 5.65    | 12.2         | 0.788   | 0.51 | 500           |               | [57]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO nanorod           | 8.9     | 16.98        | 1.02    | 0.51 |               |               | [58]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO                   | 13.7    | 19.5         | 1.01    | 0.7   | 8             |               | [56]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO nanorod           | 11.13   | 20.08        | 0.991   | 0.56 | 500           |               | [59]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO                   | 15.7    | 20.4         | 1.03    | 0.749|               |               | [60]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO                   | 11.6    | 19           | 0.98    | 0.61 | 14            |               | 14         |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au      | ZnO/MgO/EA+/TiO₂      | 20.05   | 23.08        | 1.12    | 0.775| 30            |               | [61]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Au/graphene | ZnO/MgO/EA+/TiO₂      | 19.82   | 22.92        | 1.12    | 0.772| 500           |               | [61]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD/Li-TFSI/Ag | SnO₂                  | 13      | 19.5         | 1.08    | 0.616| 700           |               | [40]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | ZnO                   | 13.2    | 18.2         | 1.049   | 0.69 | 580           |               | [62]       |
|                  | CH₃NH₃PbI₃   | spiro-MeOTAD         | mZrO₂                 | 10.8    | 17.3         | 1.07    | 0.59 |               |               | [57]       |
|                  | CH₃NH₃PbI₃   | GO/spiro-OMeTAD      | mTiO₂/G               | 18.19   | 22.48        | 1.08    | 0.75 | 400           |               | 4           |
| Group          | Active layer                          | HTL               | ETL               | PCE (%) | Jsc (mA/cm²) | Voc (V) | FF | T80 (h) store | T80 (h) Illum. | References |
|----------------|---------------------------------------|-------------------|-------------------|---------|--------------|---------|-----|---------------|---------------|------------|
| CH₃NH₃PbI₃    | GO/spiro-OMeTAD                        | mTiO₂             |                   | 14.11   | 20.92        | 1.05    | 0.64| 300           | 4             | [51]       |
| CH₃NH₃PbI₃    | carbon                                | cTiO₂/mTiO₂       |                   | 13.26   | 17.59        | 1.016   | 0.575| 800           |               | [54]       |
| CH₃NH₃PbI₃    | NiO:carbon (1:20)                     | cTiO₂/mTiO₂       |                   | 13.26   | 20.93        | 1.035   | 0.612| 800           |               | [54]       |
| CH₃NH₃PbI₃    | PCBM                                  | NMAPIX            |                   | 9.51    | 13.24        | 1.04    | 0.69 |               |               | [63]       |
| CH₃NH₃PbI₃    | PCBM                                  | mPMAPIX           |                   | 12.04   | 16.12        | 1.05    | 0.67 |               |               | [64]       |
| CH₃NH₃PbI₃    | PCBM                                  | C60               |                   | 3.9     | 10.32        | 0.6    | 0.63 |               |               | [65]       |
| CH₃NH₃PbI₃    | PCBM                                  | N45               |                   | 9.11    | 16.27        | 0.882   | 0.635|               |               | [66]       |
| CH₃NH₃PbI₃    | CNT                                   | TiO₂              |                   | 11.6    | 23.9         | 0.9    | 0.54 | 2200          | 650           | [67]       |
| CH₃NH₃PbI₃    | CNT                                   | C60               |                   | 13.2    | 21.8         | 0.94    | 0.62 | 8             |               | [56]       |
| CH₃NH₃PbI₃    | P3HT/SPNHT                            | mTiO₂             |                   | 6.45    | 14.8         | 0.76    | 0.57 |               |               | [68]       |
| CH₃NH₃PbI₃    | P3HT                                  | ZnO               |                   | 10      | 17           | 0.94    | 0.62 | 8             |               | [56]       |
| CH₃NH₃PbI₃    | NiOx                                  | ZnO               |                   | 9.6     | 16.7         | 1.01    | 0.59 | 14            |               | [56]       |
| CH₃NH₃PbI₃    | PEDOT:PSS                             | mTiO₂             |                   | 16.46   | 19.58        | 1.105   | 0.76 |               |               | [69]       |
| CH₃NH₃PbI₃    | PEDOT:PSS                             | mTiO₂             |                   | 12      | 16.5         | 0.997   | 0.727|               |               | [70]       |
| CH₃NH₃PbI₃    | PEDOT:PSS                             | PCBM/Al           |                   | 15.19   | 21.47        | 0.95    | 0.745| 72            |               | [71]       |
| CH₃NH₃PbI₃    | PEDOT:PSS                             | PC₆/BH/Al         |                   | 16.26   | 22.05        | 0.95    | 0.776| 150           |               | [71]       |
| CH₃NH₃PbI₃    | PANI/Al                                | TiO₂/Graphene     |                   | 1       | 2.6          | 0.8     | 0.34 | 96            |               | [72]       |
| CH₃NH₃PbI₃    | TiO₂                                  | P3HT/MoO₃/Ag      |                   | 6.9     | 20           | 0.9     | 0.37 |               |               | [73]       |
| CH₃NH₃PbI₃    | TiO₂                                  | P3HT/MoO₃/Ag      |                   | 12.78   | 26.86        | 0.9     | 0.529|               |               | [73]       |
| CH₃NH₃PbI₃    | TiO₂                                  | P3HT/MoO₃/Ag      |                   | 14.95   | 27.6         | 0.95    | 0.57 |               |               | [73]       |
| CH₃NH₃PbI₃    | ZnO                                   | P3HT/Ag           |                   | 11.94   | 19.8         | 1       | 0.626|               |               | [74]       |
| CH₃NH₃PbI₃    | NiOx                                  | PCBM/C60/Zr/Ag    |                   | 20.13   | 23.47        | 1.08    | 0.794| 500           |               | [75]       |
| CH₃NH₃PbI₃    | NiO                                   | PCBM/ZnO/Al       |                   | 17.3    | 20.8         | 1.001   | 0.84 | 1050          |               | [76]       |
| CH₃NH₃PbI₃    | NiO                                   | P(N(VI)2D-TTCN)   |                   | 17      | 22           | 1       | 0.772| 100           |               | [77]       |
| CH₃NH₃PbI₃    | m-MTDATA                              | C60/BCP/Cu        |                   | 17.76   | 22.55        | 1.018   | 0.77 | 1000          |               | [57]       |
| CH₃NH₃PbI₃    | ZnPpy                                 | cTiO₂/mTiO₂       |                   | 17.82   | 22.29        | 1.09    | 0.731| 100           |               | [58]       |
| CH₃NH₃PbI₃    | CuSCN                                 | mTiO₂             |                   | 12.4    | 19.7         | 1.016   | 0.62 |               |               | [78]       |
| CH₃NH₃PbI₃    | Cu                                    | mTiO₂             |                   | 6       | 17.8         | 0.55    | 0.62 | 1200          | 2             | [79]       |
| CH₃NH₃PbI₃    | NiOx                                  | ZnO or PCBM/Al    |                   | 16.1    | 21           | 1.01    | 0.76 | 1440          |               | [80]       |
| CH₃NH₃PbI₃    | CrO                                   | TiO₂ free cells   |                   | 12.5    | 17.5         | 0.93    | 0.8  |               |               | [81]       |
| CH₃NH₃PbI₃    | TiO₂                                  | NiMgLiO           |                   | 5       | 10           | 0.7     | 0.5  | 1000          |               | [82]       |
| CH₃NH₃PbI₃    | NiOx                                  | PCBM/TiNbO₃/Ag    |                   | 16.2    | 21           | 1.083   | 0.827| 1000          | 1000          | [83]       |
| MAPbI₃−ₓClₓ  | CH₃NH₃PbI₃−ₓClₓ                       | spiro-OMeTAD      |                   | 10.9    | 17.8         | 0.98    | 0.63 |               |               | [4]         |
| CH₃NH₃PbI₃−ₓClₓ | spiro-OMeTAD                          | mAlO₂             |                   | 7.16    | 12.78        | 0.925   | 0.61 |               |               | [84]       |
| CH₃NH₃PbI₃−ₓClₓ | spiro-OMeOTAD                         | mAlO₂             |                   | 15.4    | 21.5         | 1.07    | 0.67 |               |               | [85]       |
| Group | Active layer | HTL | ETL | PCE (%) | Jsc (mA/cm²) | Voc (V) | FF | T80 (h) | T80 (h) | Illum. | References |
|-------|-------------|-----|-----|---------|--------------|--------|-----|---------|---------|--------|-------------|
| CH₃NH₃PbI₃-Cl | spiro-OMeTAD | bY:TiO₂ | 19.3 | 22.75 | 1.13 | 0.75 | 24 | [86] |
| CH₃NH₃PbI₃-Cl | P3HT | TiO₂ | 10.4 | 20.8 | 0.921 | 0.542 | [67] |
| CH₃NH₃PbI₃Cl | PCBDTADD | TiO₂/Al₂O₃ | 10.9 | 17.8 | 0.98 | 0.63 | 1000 | [4] |
| CH₃NH₃PbBr₃ | PDI | mAl₂O₃ | 3.04 | 4.47 | 1.16 | 0.59 | 900 | [88] |
| CH₃NH₃PbBr₃ | PIF8-TAA | mAl₂O₃ | 6.7 | 6.1 | 1.4 | 0.79 | [90] |
| CH₃NH₃PbBr₃ | CBP | mAl₂O₃ | 2.7 | 4 | 1.5 | 0.46 | [91] |
| CH₃NH₃PbI₃(1-x)Brₓ | PTAA | mTiO₂ | 12.3 | 19.3 | 0.91 | 0.702 | 480 | [92] |
| CH₃NH₃PbI₃(1-x)Brₓ | | | 15.4 | 21.5 | 1.07 | 0.67 | [85] |
| CH₃NH₃Sn₇/₉Pb₂/₉Br₁/₉ | spiro-OMeTAD/Li-TFSI | mTiO₂ | 3.74 | 17.55 | 0.376 | 0.5664 | [39] |
| CH₃NH₃Sn₇/₉Pb₂/₉Br₁/₉ | spiro-OMeTAD/Li-TFSI | mTiO₂ | 7.27 | 20.64 | 0.584 | 0.6032 | [39] |
| CH₃NH₃Sn₇/₉Pb₂/₉Br₁/₉ | spiro-OMeTAD/Li-TFSI | mTiO₂ | 7.37 | 15.82 | 0.728 | 0.6401 | [39] |
| CH₃NH₃SnI₃ | P3HT | mTiO₂ | 4.18 | 20.04 | 0.42 | 0.5 | [93] |
| CH₃NH₃SnI₃ | NiO | PCBM/TiO₂ | 14 | 19.57 | 1.02 | 0.702 | 90 | [94] |
| CH₃NH₃SnI₃ | NiO | PCBM/Al-ZnO | 16.79 | 20.71 | 1.025 | 0.792 | 500 | [94] |
| CH₃NH₃SnI₃ | spiro-OMeTAD | mTiO₂ | 6.4 | 16.8 | 0.88 | 0.42 | [34] |
| CH₃NH₃SnI₃ | spiro-OMeTAD | mTiO₂ | 5.23 | 16.3 | 0.68 | 0.48 | 12 | [95] |
| CH₃NH₃SnI₃ | spiro-OMeTAD | mTiO₂ | 5.73 | 12.3 | 0.82 | 0.57 | 12 | [95] |
| CH₃NH₃SnI₃ | spiro-OMeTAD/Li-TFSI | mTiO₂ | 5.44 | 15.18 | 0.716 | 0.5 | [39] |
| FAPbI₃ | FAPbI₃ | mTiO₂ | 4.3 | 6.45 | 0.97 | 0.687 | [96] |
| FAPbI₃ | spiro-OMeTAD | mTiO₂ | 16.01 | 20.97 | 1.032 | 0.74 | 192 | [98] |
| (MAₓFAPbBrₓ)(PbIₓ) | spiro-OMeTAD | mTiO₂ | 14.9 | 21.2 | 1.003 | 0.7 | [99] |
| (MAₓFAPbBrₓ)(PbIₓ) | spiro-OMeTAD/Au | cTiO₂/mTiO₂ | 21.3 | 24.8 | 1.07 | 0.805 | 30 | [100] |
| (MAₓFAPbBrₓ)(PbIₓ) | spiro-OMeTAD/Au | cTiO₂/mTiO₂ | 21.7 | 24.1 | 1.13 | 0.81 | 250 | 250 | [101] |
| (MAₓFAPbBrₓ)(PbIₓ) | spiro-OMeTAD/Au | cTiO₂/mTiO₂ | 18.65 | 21.81 | 1.098 | 0.779 | 150 | [102] |
| (MAₓFAPbBrₓ)(PbIₓ) | spiro-OMeTAD/Au | SnO₂(NP) | 20.27 | 24.87 | 1.09 | 0.747 | 3 | [41] |
| CsFAPbBr₃ | spiro-OMeTAD/Au | ZnO/MgO/EA⁺/TiO₂ | 21.08 | 23.86 | 1.12 | 0.789 | 40 | [61] |
| CsFAPbBr₃ | spiro-OMeTAD/Au/graphene | ZnO/MgO/EA⁺/TiO₂ | 20.91 | 23.71 | 1.12 | 0.787 | 500 | [61] |
| FAPbBr₃ | PEDOT:PSS | ZnO/Ag | 6 | 9.5 | 1.19 | 0.53 | 2 | [103] |
| CsₓFAPbBr₃ | NiO | PCBM/ZnO/Al | 18.6 | 22.2 | 1.023 | 0.82 | 1000 | 60 | [76] |
| CsₓFAPbBr₃ | NiO | PCBM/ZnO/Al | 18.24 | 22.48 | 0.98 | 0.82 | 800 | [104] |
| FAPbBr₃ | Cs₀.7FAPbBr₃ | P3HT | 19.1 | 14.8 | 2.9³ | 0.66 | 340 | [7] |
| FAPbBr₃ | Cs₀.7FAPbBr₃ | DM/Au | 22.3 | 24.8 | 1.11 | 0.81 | 320 | [100] |
| FAPbBr₃ | Cs₀.7FAPbBr₃ | Cs₀.7FAPbBr₃ | 18.5 | 21.71 | 4.36² | 0.779 | 1500 | 1000 | [105] |
| Group | Active layer | HTL | ETL | PCE (%) | Jsc (mA/cm²) | Voc (V) | FF | T80(h) store | T80(h) Illum. | References |
|-------|--------------|-----|-----|---------|--------------|--------|-----|--------------|--------------|------------|
| (FA0.70MA0.16Cs0.03Br0.97Pb(I0.84Br0.16)2.27 | | EH44 | MoOx/Al | 14.9 | 5.75 | 1.047 | 0.62 | 400 | | [106] |
| (CsMAFA)Pb(I0.85Br0.15)3 | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 17.3 | 22.6 | 1.05 | 0.73 | 350 | | [107] |
| (CsMAFA)Pb(I0.85Br0.15)3 (K) | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 21.5 | 23.2 | 1.17 | 0.79 | 350 | | [107] |
| (CsMAFA)Pb(I0.85Br0.15)3 | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 12.3 | 15.3 | 1.12 | 0.72 | 350 | | [107] |
| (FA0.83MA0.17Cs0.05PbI2.55Br0.45 | | NiO | PCBM/BCP/Cr/Cr2O3/Au | 19.8 | 23.8 | 1.08 | 0.81 | 1800 | | [108] |
| Cs0.05FA0.81MA0.14PbI2.55Br0.45 | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 18 | 22.3 | 1.06 | 0.76 | 720 | | [110] |
| (5-AVA)1-x(MA)xPbI3 | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 20.08 | 22.73 | 1.14 | 0.763 | 800 | | [102] |
| (5-AVA)1-x(MA)xPbI3 | | carbon/TiO2/ZrO2 | 12.84 | 22.8 | 0.858 | 0.66 | 1000 | | [111] |
| (5-AVA)1-x(MA)xPbI3 | | mZrO2/carbon | cTiO2/mTiO2 | 14.02 | 23.02 | 0.913 | 0.67 | 8760 | 1000 | [112] |
| (HOOC(CH2)2NH3)2PbI4/CH3NH3PbI3 | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 18 | 22.3 | 1.06 | 0.76 | 720 | | [110] |
| PEA3PbI4/CFMP1B | | spiro-OMeTAD/Au | cTiO2/mTiO2 | 20.08 | 22.73 | 1.14 | 0.763 | 800 | | [102] |
| (5-AVA)1-x(MA)xPbI3 | | carbon | cTiO2/mTiO2 | 14.6 | 18.84 | 1.025 | 0.755 | 12000 | 300 | [113] |
| Others | | m-MTDATA/Au | cTiO2/mTiO2 | 0.003 | 0.19 | 0.01 | 0.21 | 250 | | [56] |
| CsSnI3 | | m-MTDATA/Au | cTiO2/mTiO2 | 0.003 | 0.19 | 0.01 | 0.21 | 250 | | [56] |
| SnF2(20%)/CsSnI3 | | m-MTDATA/Au | cTiO2/mTiO2 | 2.02 | 22.7 | 0.24 | 0.37 | 250 | | [56] |
| CsPb0.995Mn0.005I1.01Br1.99 | | carbon | cTiO2/mTiO2 | 6.14 | 12.15 | 0.96 | 0.53 | 144 | | [114] |
| CsPb0.995Mn0.005I1.01Br1.99 | | carbon | cTiO2/mTiO2 | 7.36 | 13.15 | 0.99 | 0.57 | 300 | | [114] |
PCE = 15% [85]. These processing routes have demonstrated that hysteresis is not an intrinsic characteristic of perovskite-based photocurrent generation, on the contrary, it is an indication of structural defects and chemical or mechanical instability of the perovskite solar cell that should be avoided. It should be emphasized that the presence of hysteresis is an indicator of ion migration, but that ion migration may occur in perovskite solar cells with minimal hysteresis; it has been both experimentally demonstrated and theoretically calculated that electric-field screening, consistent with ion migration, is similar in both high and low hysteresis CH3NH3PbI3 solar cells and that hysteresis requires the combination of both mobile ionic charge and recombination near the perovskite-contact interfaces [121]. Passivation of contacts may lead to reduced hysteresis, while keeping ion mobility high. The ion mobility has effectively been reduced by other strategies (such as including extra cations in the active layer that will be discussed later).

Improved crystallinity has also been achieved by using 1,8-diiodooctane (DIO) as an additive in the solution process, thus achieving a smoother perovskite morphology with improved coverage area and crystal uniformity, which was achieved with low temperature processing (<150 °C) and delivering good PCE = 12% [122], or in trihalide perovskites reaching PCE = 13.1% with low temperature process [55]. Delivering pure iodine improved structural stability, pushing efficiencies up to 15.58% [123]. Similarly, introducing small amounts of N-cyclohexyl-2-pyridilidone (CHP) as a morphology controller into N,N-dimethylformamide (DMF) has led to superior reproducibility of highly homogeneous film morphology of perovskite solar cells with PCE = 10% [124]. Similar results of better crystallinity were also achieved for bromide-based perovskite solar cells with improved absorption properties and provided a tunable absorption edge depending on the Br content [125].

Structural ionic defects at the surfaces and grain boundaries of organic–inorganic halide perovskite films are detrimental to both the efficiency and stability of perovskite solar cells; the defects can be passivated by using quaternary ammonium halides, the defect healing has proved to be good for boosting efficiency up to more than 20% and at the same time incrementing stability [126], the large variety of possible compositions which combine CH3NH3PbX3 (X = I, Br and Cl) perovskites with the relatively unstable formamidinium lead iodide (FAPbI3, or simply FAPI) have been explored intensively [127]. The poor stability of FAPI devices has been corrected.

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upon the addition of Cs cations, with the objective of reducing ion migration, but Cs inclusion in the perovskite structure has been elusive so far, due to the difficulties of two step processing to deliver good perovskite structures with the efficient incorporation of Cs; a new growth technique based on seeding the nanocrystals has been recently proposed and led to better PCE and stabilities [101]. It is worth mentioning that the stability experiment by Zhao and co-workers emulated real operating conditions by cycling intervals of 10 h under 1 Sun illumination followed by 10 h in dark and formamidinium (FA) and guanidinium (FA) and I and Br, indicated the higher impacts of using FA and the recommendation to avoid chlorobencene as solvent. In the end, multiple cations will need longer lifetimes to compete with the standard MA approach [129, 130].

Structural stability is not a problem for future extensions of lifetime with reduced environmental impact in the processing route. Oxygen and moisture chemical degradation remains a more challenging issue, and strategies to keep devices dry and oxygen free (encapsulation or layered structures) are being developed. A first indirect approach is the exploration of different charge transport layers, which have been intensely researched [132]. Also organic carbon-based layers have been considered, such as carbon black, C60, PCBM, carbon nanotubes, graphene or polymers and small molecules. The other, more recent approach, is the stabilization of the structure of the perovskite layers upon controlling interfaces (the 2D/3D approach, but also intrinsic stabilization of the 3D ‘bulk’ perovskite). In both cases, the interfacial control led to i) improved charge transport at interfaces between perovskite and charge (electron- and hole-)selective contacts, since they control the charge extraction, accumulation, and recombination processes, and ii) passivation of bulk and interface defects of the perovskite layer. From the environmental impact analysis, neither of the two approaches will pose an additional toxicity concern, and therefore the reduction of impacts will come from optimization of processing, specially the use of green-solvents or low temperature processing.

3.2. Interlayers with focus on stability

Interfacial engineering has been the best drivers for perovskite solar cell evolution combining simultaneous improvements in efficiency and stability [131]. Two main approaches have been used when considering interlayers to boost both PCE and stability, the first and more extensively explored one is the use of transition metal oxides, thus including inorganic structures in the device; this approach was successfully used in organic polymeric solar cells and can be extended to hybrid perovskites [132]. Also organic carbon-based layers have been considered, such as carbon black, C60, PCBM, carbon nanotubes, graphene or polymers and small molecules. The other, more recent approach, is the stabilization of the structure of the perovskite layers upon controlling interfaces (the 2D/3D approach, but also intrinsic stabilization of the 3D ‘bulk’ perovskite). In both cases, the interfacial control led to i) improved charge transport at interfaces between perovskite and charge (electron- and hole-)selective contacts, since they control the charge extraction, accumulation, and recombination processes, and ii) passivation of bulk and interface defects of the perovskite layer. From the environmental impact analysis, neither of the two approaches will pose an additional toxicity concern, and therefore the reduction of impacts will come from optimization of processing, specially the use of green-solvents or low temperature processing.

3.2.1. Solution processed metal oxide interlayers

The main approach to interlayers is provided by the use of transition metal oxides. Inorganic metal oxide interlayers provide good processability that can be enabled by progress in research on low temperature solution-processable metal oxides and their functionality may be enhanced using a tuning of work function via doping or multication oxide systems.

Using nanocrystalline NiO as a p-type electrode material lead to a significant improvement in stability of a NiO/perovskite/PCBM cell [63], this is due to the more robust architecture of the cell, opening the door to stable tandem devices. A solvent–processed NiO nanocrystal (NC) layer has been used as the hole-transporter [66]; also a p–i–n structure (glass/indium tin oxide/NiOx/perovskite/ZnO/Al), in which the ZnO layer isolates the perovskite and Al layers, thus preventing degradation [80]; and a similar approach using chromium oxide on flexible substrates [81]. More recently p-type NiO nanoparticles embedded in a carbon matrix delivered $PCE = 13.26\%$ and long term stability of 800 h in storage [54]. The use of ZnO enables low-cost processing routes as has already been demonstrated for polymeric solar cells with inverted architecture [133]. Heavily
p-doped (p⁺) NiₓMg₁₋ₓO and n-doped (n⁺) TiO₂ contacts to extract selectively photogenerated charge carriers from an inverted planar MAPbI₃-PCBM film architecture delivered PCE efficiencies up to 16% (hysteresis-free) and stability up to 1000 h under 1 Sun illumination [83]. More recently NiOₓ used as an inorganic HTM layer in inverted PSCs led to PCE > 16% with 90% stable performance for over 60 days of storage in air [80]. ZnO nanorods achieved long term stability, although PCE is lower due to more recombination losses [57]. The thin film of ZnO nanoparticles used as an electron-transport layer achieved PCE = 15.7% [60]. Sb₂S₃ layers were inserted between the TiO₂ and CH₃NH₃PbI₃ were used to protect the perovskite against light induced degradation [134]. CuI has been used as a cost-effective competitor to spiro-OMeTAD in perovskite solar cells [79] and led to improved stability even in conditions of extreme humidity in combination with a graphene/PANI layer [72]. Snailth’s group could keep PCE around 10% for more than 1000 h with an Al₂O₃ scaffold on a TiO₂ base [4]. Avoiding the use of TiO₂, by substituting the scaffold completely by Al₂O₃ nanoparticles, also led to an increment in lifetime up to 1000 h keeping a stable efficiency of 5% (although initial PCE was higher than 10% and an initial drop was produced in the first 100 h [82] (no cut-off UV filters were used)). Other metals have been used as additives, such as Cesium and Rubidium whose role as additives in FAPI/MAPI perovskite solar cells has been recently explored [114, 135].

Also modifications of electron transport layers (ETLs) were accomplished which enhance the performance and stability of PSCs by modifying ZnO-based ETLs with MgO and protonated EA to tune the chemical interactions at the ZnO/perovskite interface [61]; in these devices, the addition of a graphene encapsulating layer on top of the Au electrode led to a large increment in stability (from values around 40 h to more than 500 h storage). Nam Gyu Park’s group used Al-doped ZnO films that act as efficient electron-transporting layers as well as dense passivation layers delivering very stable cells with PCE 18.45% which only reduced to Tₘ₀ after 500 h in constant 1 Sun illumination (with a 420 nm cutoff UV filter) and 85 °C, which is among the best results regarding stability presented so far [94]. ZnO, doped-ZnO and ZnO-based composite layers have been successfully used as cathode in organic polymeric solar cells, improving charge extraction and stability of the devices [133].

Using metal oxide nanoparticles for both ETL (ZnO) and HTL (NiO) layers have provided very good results, a detailed study for MAPI and triple cation methylammonium halides have been carried out by Najafi et al which led to best devices with PCE = 18.6% and more than 1000 h (storage) for Tₘ₀ and since they also used flexible PEN substrates, all the process can be compatible with large scale room temperature roll-to-roll (R2R) fabrication [76].

Finally, a recent strategy has consisted on the formation of a lead oxysalt layer, which increases the carrier recombination lifetime and boosts the efficiency following a passivation strategy for lead halide perovskites by forming a thin compact inorganic lead oxysalt layer thus converting the surfaces of lead halide perovskite to water-insoluble lead (II) oxysalt [109].

3.2.2. Carbon based and other organic interlayers

Organic or carbon based interlayers open several possibilities for easy processing from solution and enhanced encapsulation properties. Carbon has been proposed as the ultimate low cost and low environmental impact back contact with promising stability under long-term (1000 h) light soaking and long-term heat exposure, with PCE = 12.8%, where 5-amino valeric acid (5-AVA) iodide is infiltrated through a porous carbon film [111]. This is so far the best reported result regarding stability. Also inverted (p-i-n) planar device architectures typically use a MAPbI₃-PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester) bilayer junctions. The inorganic layers helped to protect the active layer from degradation by air. The cells achieved PCE > 15%. Furthermore, 90% of the efficiency was maintained after 1000 h of operation [83]. An HTL-free and triple layer-based perovskite solar cell, composed of a simple mesoscopic TiO₂/ZrO₂/Carbon triple layer was reported, where the thick carbon layer (10 µm) provided protection against degradation by moisture [111, 138].

PCBM has also been used as buffer layer to avoid the chemical reactions between the hydroxide groups on the ZnO surface and the active layer, and an increment both in stability and PCE was obtained; polymeric buffer layers such as poly-ethylenimine (PEI) were also used with the same purpose [55]. Modification of PCBM such as [6,6]-phenyl-C₆₁ butyric acid 2-ethylhexyl ester (PC₆₁BEH) increased the electron extraction ability of the ETL as well as increased stability that more than doubled compared with conventional PCBM ETL [71].
Use of carbon nanotubes has been demonstrated, although it did not increase efficiency or lifetime, it reduced environmental impacts when compared with metal-based HTLs, ETLs or electrodes [67, 139]. Sometimes carbon nanotubes are used in mixtures, such as P3HT/SWNT in a PMMA matrix [139] or in a MoOx matrix [106]. Also multiwalled nanotubes have been considered as the most reliable alternative for a stable electrode that may compete with Ag or Au [140]. Graphene has also been used as an interface modifier, for example, GO as an amphiphilic modifier to enhance the interface contact between perovskite and the HTL which lead to additional stability [141], or by doping the mesoporous TiO2 layer with graphene flakes (mTiO2 + G), and improving stability as demonstrated by very detailed study following ISOS protocols [51].

Following a different route, in which all charge transport layers are organic and can be grown in a controlled way via sublimation or solvent annealed processes, also led to good efficiencies (12%) with improved stability [64]. The molecular structure and purity of perovskite was highly controlled by a sublimation process in a high vacuum chamber, thus confirming the importance of stable structures for long time stability. Molecule engineered hole transporting materials [142] or the use of small non-hygroscopic molecules as dopant like tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) or Li-bis(trifluoromethane)sulfonyl-imidem(Li-TCI) doped spiro-OMeTAD has been used as HTL with good efficiency (>10%) and improved stability [52]. Crystal crosslinking modification of interface of the MAPI active layer by using phosphonic acid ammonium additives has led to improving resistance to moisture [53].

Finally, polymers have also been used as charge transport layers. The most widely used as HTL has been PEDOT, but it poses a problem due to intrinsic instability (to moisture) and acidic nature which degrades active layers when used in inverted architectures, this is a well know effect in the organic (polymeric) solar cell research community. Replacement of PEDOT is a strategy for extended lifetime in perovskites as Bahr et al demonstrate with a detailed review with focus on HTL materials [143]. Hydrophobic PMMA has been used to avoid degradation by moisture; furthermore, hydrophobicity for long-term stability can be tuned through molecular engineering using a naphthalene diimide (NDI)-based polymer along with dicyanomethine polymer P(NDI2DT-TTCA) instead of PCBM as ETL incremented PCE (17%) and extended lifetime up to 100 h. with better mechanical stability to deformation by bending [77]. Also poly-triarylamine (PTAA) has been used as hole transporting layer in inverted architecture PSCs delivering slower degradation rates than spiro-OMeTAD in similar ageing conditions [142, 144]. In this group, although referring to a different approach for charge transport, the use of ionic liquids in a Cesium containing (FA-MAPI) solar cell has provided a large increase in lifetime to 1800 h under constant illumination at 75 °C, these good results could be extrapolated to more than 5000 h for T80 under normal operating cell conditions [108].

3.2.3. 2D/3D interfaces: a successful approach

A very successful and recent approach is the inclusion of a low dimensional layer on top of the bulk active layer [145]. Thus, hybrid organic–inorganic 2D/3D perovskite interfaces where the functional groups interact through hydrogen-to-halogen bonding or by the interaction of the amine with the surface termination sites of the 3D perovskite have led to impressive results regarding the increment of stability, with solar cells stable for more than 10 000 h, which is above the limit required for a possible commercialization of future modules; these devices have been included in the graphs of figures 2 and 3 with an ‘escaping’ arrow to emphasize that they belong to a different lifetime scale. It has been an important breakthrough regarding stability, while at the same time keeping a good PCE [112, 113].

Early approaches to use meso-superstructured organometals led to large improvement of stability in TiO2-free perovskite solar cells [146]; Tsai et al reported an impressive extension to lifetime by introducing a bidimensional layer in the PSC [147], and a semiconducting 2D (CH3(CH2)NH3)2(CH3NH3)2-PbI2 (n = 1, 2, 3, and 4) perovskite thin film; those thin films of the semi-2D perovskites display an ultrahigh surface coverage as a result of the unusual film self-assembly that orients the [Pb3I6n+1] layers perpendicular to the substrates [148, 149].

The most successful approach to the 2D/3D strategy has been achieved in very recent times by using aminovaleric acid iodide (HOOC(CH2)3NH3, AVAI) to deliver up to T80 = 300 h under 1 Sun illumination and an extended stability test up to 12 000 h in storage [113]; or complemented with a flash annealing technique to reach 720 h lifetime, in this case storage in air [110]. The interface engineering and direct growth of a low dimensional perovskite on a 3D perovskite: a quasi-2D PEA2PbI4 on top of a 3D Cs0.1FA0.74MA0.1PbI3.48Br0.39 delivering and impressive 800 h T80 for constant 1 Sun illumination at 50 °C [102]. Similarly a core/shell structure used a metal-organic-complex monomolecular intermediate, Gallium(III) acetylacetonate ([GaAA3]3) to deliver a 2D/3D structure with improved stability up to 800 h (storage unencapsulated) [104]. There is still no detailed LCA analysis regarding the processing routes for the AVAI approach, this is a work which will put in balance the environmental benefit arising from the extension of lifetime. Ideally, and by similarity with processing routes with MAPI, a large environmental impact is not expected.
Finally, it should be mentioned that perovskite solar cells fabricated by Oxford PV Ltd (the company exploiting the patents from Snaith’s group at Oxford University), reported long term stability data for perovskite devices that were stressed at 60 °C and held at their maximum power point under 1 Sun illumination for more than 3000 h [150]. The detailed structure of these cells has been undisclosed but it seems to benefit from the 2D/3D approach.

3.3. Encapsulation

Encapsulation has probed to increase stability in many cases, and some cheap commercial barriers have been successfully employed even for flexible cells on PET since some time ago. An example is the use of 467 MP 3M™ Adhesive Transfer Tape used as sealant and Viewbarriers® (Mitsubishi Plastic, Inc.) was used as the plastic barrier encapsulant [62]. For conventional MAPI/Spiro-OMeTAD cells, the lifetime was incremented from 20 h to more than 500 h (storage in ambient conditions). Therefore, encapsulation is a good strategy to provide an effective barrier for moisture and oxygen degradation, and it is already compatible with cheap and marketable alternatives. Nevertheless, many approaches have been failing when ambient tests are carried out at elevated temperatures (T > 85 °C) [151]; although this temperature is not reached in normal operating conditions, it is a recommendation that high temperature tests should be carried out.

Also, encapsulation strategies should be established to avoid the leak of toxic substances in the environment, especially lead, during the lifetime of the device or at the end of life (recycling or landfilling). Lead is, according to the International Lead Association (ILA), one of the most recycled elements, reaching 80% of recovery. This recommendation is based on the lack of publications considering encapsulation strategies oriented to their capability to capture degradation subproducts at the end of life of devices, which is specially important for lead capture and will facilitate future recycling strategies.

4. Life cycle environmental and economic cost: making the manufacturing process more sustainable

This section is devoted to the analysis of processing routes and its possibilities for improvement with a focus on the reduction of its environmental impacts and economic costs. The discussion is related to the previous section,
since the selection of materials and device architectures with the purpose of stability improvement have a direct consequence on processing routes.

4.1. Indium replacement or recycling

Indium has been suggested as the most unsustainable metal for large scale deployment of organic electronic devices using transparent conducting oxides. It is a scarce and very expensive metal. Nevertheless, indium-tin-oxide (ITO) conducting substrates have been replaced by fluor-doped tin oxide (FTO), which is now used as an almost universal substrate with simple industrial processing and good performance [152]. Most of the devices in table 2 now use FTO substrates with no apparent PCE or stability reduction when compared with ITO-based similar devices, and the trend shows that most recent devices tend to use FTO instead of ITO substrates. Additionally, FTO has a higher temperature stability and nowadays surface roughness is similar to ITO thus reducing the advantages that ITO showed for solar cells in the early years of development.

On the other hand, ITO recovery through recycling and reuse process has produced fresh cells with only a 0.85% reduction in PCE when compared with devices using pristine ITO, this result is promising since glass is an important contributor to embedded energy during production process, and indium as a scarce metal is the main drawback for massive commercialization [153]. The procedures can be extended to recycling of FTO substrates.

4.2. Improving processing routes

In general, solution processable routes have lower environmental impact than evaporation based routes, due to reduced use of electricity. In many cases, evaporation of metals and oxides have been substituted successfully by solvent processing. ZnO ETL was suppressed without important loss of PCE in CH$_3$NH$_3$PbI$_3$ inverted cells using either P3HT or spiro-OMeTAD [56]; thus providing a significant gain in stability, with a $T_{80}$ increase of 40% (although from low initial values). P3HT was also being used in very efficient perovskite solar cells as ETL delivering PCE = 9.3% [154]. A sequential two step deposition method delivered PCE = 15% [8]; the two-step deposition technique can be used for preparing CH$_3$NH$_3$PbI$_3$ perovskite solar cells using ZrO$_2$ and TiO$_2$ as a mesoporous layer [155] or for controlling the size of CH$_3$NH$_3$PbI$_3$ crystalline cuboids [49]. The use of a polymeric hole conductor (such as poly-triarylamine) creates new opportunities for the development of low-cost, solution-process solar cells with improved stability [70], since the triarylamine copolymer has shown good stability in air [156]. Co-deposition of a combined Al$_2$O$_3$-perovskite layer at a low temperature (T < 110 °C, PCE = 7.2%) reduces processing steps [87].

Processing routes of perovskite active layers (including raw material processing) is relatively simple, while the route for spiro-OMeTAD is very complex, involving toxic solvents, and therefore a straightforward recommendation for a simple processing route that could be up-scaled to industrial levels, is to develop alternatives for spiroOMeTAD as HTL. The concern about spiro-OMeTAD has been extended also to environmental issues, where the impact in several categories, such as Human Toxicity and Freshwater Ecotoxicity (ILCD methodology), is very large [17, 157]. Strategies oriented to the replacement of spiro-OMeTAD or to HTL-free architectures for the perovskite solar cell have been developed; an example of this exploration is the substitution of spiro-OMeTAD by a carbon layer, with only a small reduction in PCE (from 13.24% to 10.29%), which enables a potentially strong reduction in economic cost, and furthermore, addition of NiO nanoparticles (1:20, NiO:C in weight) to the carbon electrode boosts efficiency to 13.26%, thus demonstrating the viability of the HTL free solar cell with stability of 800 h in storage [54]. Jeon et al achieved longer stability (up to 320 h under 1 Sun illumination) by replacing spiro-OMeTAD with N2,N2,N7,N7′-tetakis(9,9-dimethyl-9H-fluoren-2-yl)-N2,N2,N7,N7′—tetakis(4-methoxyphenyl)-9,9′-spirobi[fluorene]-2,2′,7,7′-tetramine (that can be summarized as DM); the problem with this approach is that DM also has a complex processing route making it difficult to achieve cost reductions and its environmental impact has not been estimated so far [100].

Towards large scale industrial production, low temperature (70 °C) sequential slot die coating scalable procedures with good PCE (10%) have been used for all layers except the electrode [74]; the same group points out that ink-jet printing will help to save material during processing, which was demonstrated with efficiencies >12% [158]. This method, with the important reduction in the use (and waste) of materials, opens the door to further reductions in environmental impacts, and an additional advantage was the low processing temperature of the best cells (50 °C). The use of a PbI$_2$ passivation phase in the perovskite layer has enabled low temperature (<150 °C) process and therefore a reduction of costs and environmental impact in the PSC large scale production [41]. Roll-to-roll (R2R) slot die coating and screen printed back electrodes under ambient conditions were successfully applied in an up-scaling effort by Krebs’ group to fabricate large size modules [159], the efficiencies were 4.9%, with a significant reduction in comparison to small size spin-coated devices with same structure (9.4%).
Still very few publications are devoted to improvement of processing routes for large modules which require interconnections between serially connected cells; nevertheless, a proof-of-concept at laboratory scale has demonstrated the viability of module interconnections avoiding metals with the use of EH44 9-(2-Ethylhexyl)-N,N,N,N-tetrais(4-methoxyphenyl)-9H-carbazole-2,7-diamine) [105, 106]. A successful fabrication of large size modules were demonstrated by Hu et al by optimizing the components of the cell and its method of interconnection for ten cells serially connected to fabricate a $10 \times 10$ cm$^2$ module (with active area of 49 cm$^2$), which shows a 10.4% PCE (down from 14.02% of the individual cells) and a larger 7 m$^2$ panel printed on an up-scaled production line (no data for PCE available); the $10 \times 10$ cm$^2$ module shows good stability under continuous illumination over 1000 h in a local outdoor environment for 1 month, and in the dark over 1 year [135].

Post processing treatments to increase stability have also been demonstrated, for example, a post-device ligand (diethylenetriamine (DETA)) treatment to significantly improve the PCE of a completely fabricated CH$_3$NH$_3$PbI$_3$ solar cells from 18.7% to 20.13% and at the same time extending lifetime to more than 500 h under constant 1 Sun illumination, this approach also contributes to the reduction of lead waste [75]. This procedure of post-processing ligands resembles the strategy of 2D/3D structures mentioned in section 3.2.3.

4.3. Tandem perovskite solar cells

For organic polymeric solar cells, the tandem option has been a step forward for possible commercialization; the inclusion of additional processing steps to fabricate a tandem cell is compensated by the superior performance in terms of efficiency and stability. As early as 2013, organic polymeric tandem solar cells were reported to have PCE $= 12\%$ (Heliatek), with superior performance for vacuum evaporated cells over solution processed cells and the main recommendation of an extensive review was that the intermediate layer should be stable, and the best option was a solution-processed thin layer based Ag nanostructure to remove the recombination restrictions at the interface between the ETL and HTL [160]. The analysis of losses in the interconnection and optimization of processing has pushed up efficiencies [161], but only reaching PCE $= 13.8\%$ [162], which is still far from the maximum PCE $= 21\%$ predicted for organic tandem cells [163].

For perovskite solar cells this approach has proved to be effective for tandems, where the main challenge to reach theoretical efficiencies in tandem is to optimize the interconnection layers [20]. Manufacturing two terminal tandem cells reduces up to 30% of the environmental impacts equivalent to two single junction devices, mainly because of the reduced use of glass. Different tandem options have been fabricated and analysed: perovskite (with Pb) on top of inorganic Si, CIGS and CZTS bottom cell and a full perovskite tandem (SnPb/Pb), with extrapolated energy pay back time (EPBT) of 13, 7, 2, and 1 months, respectively, and the full perovskite (SnPb/Pb) structure has the potential to be the most environmentally friendly technology, but can only compete with Si technology if efficiencies of 30% and 16 year lifetime are reached [27]. For now the perovskite on top of Si is the technological option which is being rapidly developed, including a company (Oxford PV Ltd) which may commercialize modules very soon [164].

4.4. Recycling

If perovskite solar modules reach a commercialization stage and perovskite photovoltaic systems are deployed in a large scale, it is envisaged that in a short period of time, large amounts of encapsulated or unencapsulated panels will be stored and processed at the end of its operational lifetime, which will be relatively short compared to other PV technologies already in the market. This perspective requires the design of effective recycling routes leading to industrial recycling facilities or waste management sites; with a special focus on lead recovery, since lead from the methylammonium halide active layer is at risk of being accidentally released into the environment [165].

Recycling is progressing fast in PV technologies [166], and this is also the case for perovskite technology. Several approaches have been proposed to recycle and reuse materials from PSCs, in some cases with demonstration of recycling routes allowing the recovery of all major components, saving raw materials and using them to prepare ‘second generation’ cells without significant loss of PCE in comparison to the original device [167].

Furthermore, Chen et al demonstrated the successful fabrication of perovskite solar cells using the lead from recycled batteries, obtaining PCE $= 9.37\%$, almost the same as PCE obtained using a commercial supplier of PbI$_3$ with the lead recovered from a single lead-acid car battery $\sim 700$ m$^2$ of PSCs can be fabricated [168]. This result was commented on by Li et al who pointed out that the experiments were carried out with a new battery and that a spent electrode will pose major difficulties toward the effective realization of this interesting recycling route [169], a comment that was replied to by Chen et al [170]. This discussion about the possibility of Pb recycling and its application to PSC fabrication deserves a future detailed Life Cycle Assessment based on the existing and eventually additional experimental evidence. An alternative method to conventional smelting in the
recovery and recycling of different lead-based energy materials has been demonstrated using a deep eutectic solvent to recover up to 99.8% of lead in a recycled perovskite solar cell [171], and more recently in situ recycled PbI_2 scaffolds was shown to be a possible route in manipulating the morphology of the perovskite active layer [172]. Pre-industrial fabrication processes for lead-based perovskites confirmed the conclusion of section 2: lead is not among the main current concerns for the use of PSCs, contrary to the most extended assumption that the lead contained in the perovskite is the main responsible of the impacts of PSC [157].

By isolating the toxic lead iodide in high yield, it has been shown that PbI_2 can be reused for the preparation of new solar cells with comparable performance to the first generation and in this way avoid lead waste [173]; furthermore, the most expensive part of the solar cell, the conductive glass (ITO or FTO), can be reused several times. Under standard AM1.5 illumination, the fresh device shows a promising power conversion efficiency of 13.6%, and an efficiency of 12.1% is obtained in the reused devices. In other cases the device scaffold can be reused by washing away the perovskites and reloading, the reuse process is realized in such perovskite solar cell devices by repeated loading of the perovskite material [174]. LCA studies have recommended reduction of TiO_2 use because of its contribution to human toxicity impact category and higher production costs, but recycling strategies for ETL can make solar cells based on TiO_2 two-step production methods competitive, from the environmental point of view, with other cells [157].

5. A difficult balance from a Life Cycle Assessment perspective

Life Cycle Assessment (LCA) is a well established methodology, regulated by standardization (ISO14040 family) and therefore provides useful information about the environmental impacts of any material, product or service. The possibility of comparison between alternatives for the same service is one strength of the LCA approach. The clear definition of a ‘functional unit’ used to make the calculations allows researchers a fair comparison between different processes.

For energy applications, and particularly when evaluating photovoltaic technologies, two Functional Units (FU), have been most commonly used: 1kWh of produced electricity [17, 21], or 1 m² of solar module [16, 18], or 1 cm² of film used to fabricate a solar cell [15]. Complementary to standard LCA studies, different approaches for energy analysis of PV technologies require additional harmonization of the definition of energy-related parameters such as embedded energy in materials or devices (also called cumulative energy demand, CED), energy pay back time (EPBT), levelized cost of electricity (LCOE) or energy return on energy investment (EROI).

In this article, the most standard approach has been used to select references and if necessary to convert to units (FU or energy-related) which allows for a fair comparison of results [175]. Several LCA studies have been published recently, starting with the historical review of perovskite solar cell technology by Jung et al. This review included some information about environmental impacts [23], some focused on a specific process or device architecture [15, 17], others on comparison between lead or lead-free alternatives [18], and more recently with a focus on tandem devices [20, 21, 27].

The relationship between both functional units, 1 kWh of generated electricity or 1 m² of module area is provided by equation (1):

\[
A = \frac{E}{PCE \cdot I \cdot \gamma \cdot PR}
\]

where \(A\) (m²) is the area of the module, \(E\) is the energy generated (electricity, kWh), \(PCE\) is the power conversion efficiency (%), \(\gamma\) is lifetime (years), \(I\) is solar irradiation or insolation (kWh/m²/year) and \(PR\) is the performance ratio of the photovoltaic system. Some authors also include an extra factor called net extra conversion efficiency (around 4%–5%) [20], but it is not common practice and it is not considered here to compare FUs. The energy output and solar radiation can be promediated for a determined span of time, one day, one month, and most usually, one year. The results of these calculations will depend on technical parameters (in principle well known from experimental measurements, such as PCE or lifetime, but in some cases assumed for different scenarios), others depend on the geographical locations where the system will operate, such as solar irradiation or PR (which includes thermal losses and other system-related losses). The EPBT time is easily calculated by dividing the cumulative energy demand for fabrication and use of the solar module (provided by the LCA study) and the annual energy produced by the system under study. For the LCOE and EROI calculations, a lifetime for the device must be considered.

Therefore, the global LCA results depend on the selection of parameters or scenarios and a sensitivity analysis must be carried out, since it has been demonstrated that variations on PR has a strong influence on results of EPBT and CO₂ emission factors (g CO₂-eq per kWh), with around 1:1 linear variations in percentage (i.e. 10% PR variation produces a 10% EPBT or CO₂-eq variation) (Gong 16), while for other technical parameters, EPBT shows a robust behaviour with results with >95% confidence under sensitivity analysis. Another LCA uncertainty arises from the different impact category calculation method, the most common ones
are TRACI, ReCiPe and ILCD, and they allow researchers to perform an easy comparison of studies if the processes are clearly defined [85, 176].

The main results of the LCA studies published for perovskite solar cells can be summarized as follows: first, for Freshwater Ecotoxicity, identified as the main environmental impact category, the contributions for a process where the perovskite layer is vapour deposited comes from FTO for Freshwater Ecotoxicity, identified with an EPBT around 5 years and considering a minimum lifetime of 5 years and PR. Also a detailed accelerated degradation study was carried out under concentrated sunlight and the degradation under light exposure is very dependant on composition since MAPbBr$_3$ films showed photobleaching [179].

Environmental impacts of the use of Au or Ag metals for electrodes is high when calculated by the Life Cycle Assessment either in perovskite solar cells [177], or in silicon/perovskite tandem solar cells [21] in the Global Warming Potential, Human Toxicity and Freshwater Ecotoxicity categories. This adds to the main recommendation about avoiding spiro–OMeTAD, mentioned in the previous section. The use of Al instead of Au or Ag and spiro–OMeTA- free cells are recommended for the reduction of its environmental impact. Using titanium nanotubes (TNT) as anodes, the PSCs total embodied energy 0.27 kWh to produce a 1 cm$^2$ active area, and the manufacturing energy used in the process to fabricate the solar cell is calculated to be 0.01 kWh cm$^{-2}$ with an EPBT around 5 years [15].

For a detailed EPBT calculation, information about in situ outdoor operation of perovskite solar cells or modules are required.

Initial reports for perovskite solar cells, based on assumptions of PCE and lifetime, delivered an EPBT between 0.2 to 10 years [16, 17]; in other detailed estimations comparing different routes, the EPBT were estimated as 1.0–1.5 years [26], and the most recent reviews limits the range to 0.2–5.4 years [131]. When the analysis is focused on climate change mitigation potential, the amount of avoided emissions ranges from 100 g CO$_2$eq per kWh (Gong [16]) for processing from solution using ZnO and TiO$_2$ transport layers, to intermediate values around 200–400 g CO$_2$eq per kWh for vacuum, HTL free or solution process [15, 26], and a maximum of 1000 g CO$_2$eq per kWh similarly for vacuum or solution process [17] with a peak up to 1800 g CO$_2$eq per kWh when lead-free, Sn-based perovskites are considered [18].

Outdoor studies of PSCs are scarce; the first report of outdoor tests was performed for a desert climate (7 days) and complemented with indoor long-term light soaking as well as heat exposure over 3 months at $80–85\,^\circ\mathrm{C}$ for a CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunction using ZrO$_2$ as HTL and carbon as counter electrode [178]. Also a detailed accelerated degradation study was carried out under concentrated sunlight (100×), showing that degradation under light exposure is very dependant on composition since MAPbBr films were not degraded (at 25 °C), while MAPbI films showed photobleaching [179].

Because of the importance of industrial approaches to Si/perovskite tandem (record efficiencies and possible commercialization by Oxford PV Ltd) the LCA analysis by Monteiro et al should be emphasized, and can be summarized by the EPBT data and comments that PCE assumed for the tandem >20% in all scenarios, with PR = 0.75 and insolation assumed to be 1700 kWh m$^{-2}$ per year, with EPBT values ranging between 1.3 years for perovskite/Si(p-n) tandem (scenario 1) and 1.7 years for perovskite/Si (HTT) (scenario 2) with the following assumptions: perovskite 1 year lifetime, scenario 1: becomes opaque not allowing Si to work, scenario 2 becomes transparent and conductive allowing Si to work efficiently [21]. These results are very similar to the EPBT calculated by Espinosa et al [17], between 1.1 and 1.5 years for the productions routes using solution phase deposition described by You et al [176] and vapour phase deposition described by Liu et al [85], respectively, for a single junction perovskite solar cell, assuming a PCE = 10% at module level, although the published PCE for small devices are larger (11.5% and 15.4%), with PR = 0.8 and insolation 1700 kWh m$^{-2}$ per year.

Technoeconomic analysis with detailed assumptions about unit prices for materials calculates a unit cost of 0.41 USD/W$_p$ for a perovskite solar cells, which assuming PCE = 16% (module), delivers an EPBT of 0.25 years and considering a minimum lifetime of 5 years and PR = 0.75, delivers an average LCOE = 6.45 USD cent/kWh with a minimum of 4.93 USD cent/kWh for Alamosa (CO, USA), the value depending on insolation and temperature conditions in different USA cities [22]. All calculated LCOEs are competitive with grid cost of electricity with the exception of Alaska, but the main criticism to this study is the excessive lifetime assumed (30 years, with a PCE degradation rate of 0.541% per year) which is too optimistic for a real commercialization of perovskite solar cells (at least for the initial stages of market penetration). Other estimations considering a 30USD/m$^2$ module cost, with PCE = 12% and lifetime of 15 years respectively deliver a LCOE of 3.5–4.9 USD
cents/kWh, a very low value but that does not take into account some costs of balance-of-module production stages [180]. A more realistic calculation delivers a cost of 102 to 90USD/m² of perovskite solar modules fabricated in China that could be competitive if PCE = 18% and lifetime of 20 years, with LCOE around 9–18 USDcents/kWh [181]. For perovskite on Si-tandem to be economically competitive a required lifetime of 24 years must be achieved as has been recently reported [182].

Interestingly, all economic studies point to glass as one of the main contributors to module cost, with a share between 41% and 58%, and therefore a road to reduce cost is moving towards flexible substrates, followed by the economic impact of electrodes, where moving from expensive Au or Ag to cheaper Al or other alternatives is critical. Nevertheless, there is still a large uncertainty related to any cost calculation for module manufacture, which is strongly dependant on assumptions about costs of certain process steps which still have not been implemented at large scale.

The balance between progress in PCE and stability can be visualized in figures 2 and 3, including its historical evolution. PCE has surpassed 20% since 2016 and lifetimes (in storage) are well above 1000 h, with two breakthrough results in 2017 pushing the limits to 8760 h [112] and 10 000 h [113], with devices based on the 2D/3D approach, as indicated by arrows in figures 2(A) and 3(B). The progress toward better PCE and larger stability is clear, but there are a large variation of results for all materials and device structures. The lead-free devices are not providing the most promising results, but lead is not seen as posing an environmental risk, while all LCA studies point to spiro-OMeTAD as a material that should be replaced and this is being accomplished with success, delivering better results with stabilities approaching 1500 h (storage) and efficiencies above 15%, thus opening the door to future commercialization with low environmental impact devices.

6. Conclusions

An extensive review on the evolution of perovskite solar cell development has been carried out with an environmental impact and economic cost perspective. The stability of the devices is the most important parameter to be improved in order to reach a succesful commercialization of the perovskite photovoltaic technology in the near future, and has a direct impact on both the environmental and economic cost calculations.

Power conversion efficiency is a parameter that it is well defined and can be certified according to standards, this is not the case for stability-related parameters, such as lifetime (Tₘ₀) or degradation rates. There are recommended protocols for organic solar cell stability tests (ISOS), but they are mostly not used for perovskite solar cell stability studies. This fact creates additional difficulties for a comparative analysis of stability. Nevertheless, it is clear that lead-free solar cells cannot compete with lead containing alternatives, which have already achieved PCE above 20% with lifetimes of 10 000 h in storage and more than 1000 h under constant illumination; it is easier to reduce the environmental impact of the solar cells by replacing other materials such as spiro-OMeTAD. The alternatives of spiro-free perovskite solar cells can approach to benchmark devices achieving record efficiencies (FAPI-based approaches) with good stabilities. The best architectures with good efficiency and good lifetimes are those cell using ternary or quaternary cations in (FA-MA)PBI active layers and the 2D/3D approach which introduces an amino-valeric acid iodide layer next to the active layer in devices improving the lifetime to impressive values of more than 8000 h.

Regarding the environmental impact studies using Life Cycle Assessment methodology, there is a large consensus about two main conclusions. The first one: lead, although a toxic material, does not pose a barrier towards commercialization of lead-containing perovskite solar cells, since the reduced amount of lead in the devices creates lower environmental impacts in all categories than other materials present in the cell (in particular in Human Health or Freshwater Ecotoxicity). The second one: spiro-OMeTAD is identified as an important source of environmental impacts because of the difficulty for its complex processing route involving toxic solvents and also because it is a limiting factor for cheap perovskite solar cells; therefore using inorganic metal oxides, or carbon derivatives (carbon, PCBM, carbon nanotubes or graphene), or other organic layers (polymers, such as P3HT or small molecules) as a replacement of this HTL is critical and it has been succesful, as demonstrated by alternatives keeping good PCEs and in some cases extending stability. Additionally, indium (in ITO) has been replaced by the use of FTO substrates without loss of efficiency or stability.

In different scenarios with realistic assumptions regarding future perovskite modules in photovoltaic system, several studies show that a levelized cost of electricity in the range of 5–10 USD cents per kWh can be achieved by perovskite solar cells in order to compete with other photovoltaic technologies and to grid supplied electricity. This result depends strongly on technical assumptions such as PCE or lifetime and environmental assumptions such as irradiation and temperature of the geographical location where the system is deployed, in both cases sensitivity analysis shows that the results are robust and that perovskite solar cells can provide cheap electricity with a reasonable extension to lifetime.
Finally, two recommendations: (1) stability protocols such as ISOS should be used to report stability in perovskite solar cell research, this will allow fair comparison between materials and device architectures and also clarify the research roadmap towards longer lifetimes, and (2) recycling should be considered as part of a research strategy for perovskite solar cells; in particular the design and fabrication of embedded layers or encapsulation materials that may act as lead (or other metals)-capturing traps to avoid the release of toxic components at the end of life and at the same time facilitating the recovery of these materials for its use in a new generation of cells.

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| Chen H et al | Planar perovskite solar cells with superior reproducibility and stability | Sci. Rep. | 2014 |
| Jeon N J et al | Highly efficient perovskite solar cells for inverted planar structures | J. Phys.: Energy | 2018 |
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| Christians J A et al | An inorganic hole conductor for organolead halide perovskite solar cells | Nat. Mater. | 2014 |
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**Notes:**
- The table includes publications from 2014 to 2018 relevant to the research on perovskite solar cells.
- The authors, titles, journals, and years are listed in a structured format for easy reference.
- The research covers various aspects such as material properties, device performance, and stability improvements.

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**Additional Notes:**

- The research on perovskite solar cells has seen significant advancements in material and device optimization.
- The focus has been on improving stability, efficiency, and reproducibility of perovskite solar cells.
- The table provides a snapshot of the progress made in this field over the years.
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