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PAPER

Multi-component engineering to enable long-term operational stability of perovskite solar cells

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Abstract

With a record efficiency above 25%, the main hurdle for the commercialization of perovskite solar cells (PSCs) is their long-term operational stability. Although different strategies have been applied, the stability of PSCs is still far below the 25 year requirement demonstrated by commercial photovoltaic technologies. To advance in the former, a lab-scale stability analysis should resemble real testing conditions, and this is only possible through the interaction of several stress factors. Here, we briefly introduce the reader to the general degradation mechanisms observed on PSCs and the state-of-the-art strategies applied to realize long-term stable devices. Finally, we highlight the imperative need to engineer multiple components of the PSCs simultaneously and propose a rational design of PSC's constituents to obtain long-term operational solar cells. This perspective article will benefit the progression of PSCs as a reliable photovoltaic technology.

1. Introduction

Hybrid organic-inorganic metal halide perovskites, with a representative perovskite formula of ABX₃ (A = methylammonium (MA), formamidinium (FA), Cs; B = Pb, Sn; X = I, Br), have achieved a certifiedsolar conversion efficiency of 25.2%, approaching the record efficiency of single-crystal silicon solar cells of 26.1% [1]. Nevertheless, their reported lifetime ranges from minutes to around one year [2], which is far from the benchmark of 25 years achieved by silicon solar cells. Commercial photovoltaic cells and modules must comply with several industry-standard qualification tests described in the International Electrotechnical Commission (IEC) standards on terrestrial photovoltaic modules (including the IEC 61215, IEC 61730 and IEC 61646) [3]. These reliability PV standard tests comprise conditions that are currently severe for PSCs, e.g. damp-heat test (85% RH and 85 °C for 1000 h), UV preconditioning test and thermal cycling test (- 40 °C to 85 °C, 200 cycles); however, as PSC technology is still in its early stage of development, it is not ready yet for standardization. For this reason, the international photovoltaic research community has proposed and developed reliability protocols useful to validate and to compare the PSC device lifetime among different laboratories [4-6]. Among them, the ISOS protocols [7], which were recently updated for PSC reliability tests [6], include different stress levels that increase in intricacy comprising from basic lab-scale research to industry device testing. We have observed that the most applied stability tests published for PSCs relate to less stressful conditions, e.g. analysis in the dark, illumination without UV, under inert gas, at room temperature or short testing times. Also rare are stability studies that are comparable to real testing conditions (e.g. outdoor analysis), especially applying more than one stress factor simultaneously (e.g. under continuous light irradiation, temperature over 65 °C and bias voltage). This limits the advancement of the technology towards commercial stable PSCs.

In this perspective article, we highlight the importance of performing stability tests that incorporate multiple stress factors in a single analysis. Most importantly, we show that the path to stable PSCs comprises the simultaneous engineering of multiple constituent materials and interfaces of the device. Thus, we begin by briefly discussing the degradation mechanisms of PSCs under five relevant stress factors: humidity, oxygen, light, heat and bias voltage and their combinations. We also include a concise overview of the

existing strategies currently employed for PSC stability enhancement. Finally, we propose a comprehensive strategy to improve the durability of PSCs based on the engineering of multiple PSC components simultaneously, addressing each of their compositional layers of the device: absorber (perovskite), transporting layers, electrodes and the corresponding interfaces.

2. Degradation mechanisms and stress factors

The aim of this section is not to review the detailed state-of-the-art related to the degradation mechanisms of PSCs. To do so, the reader can be redirected to the extensive work and literature reviews recently published in the area [8–10]. Our objective is to briefly introduce the reader to the main stress factors that affect PSC stability and the related degradation mechanisms, in an attempt to facilitate the subsequent discussions on strategies for stability enhancement. Stress factors referred to here are humidity, oxygen, light irradiation, temperature (heat) and bias voltage. The study of PSC stability by a single stress factor contributes to the understanding of degradation mechanisms occurring specifically in any of the constituent materials; however, the application of multiple stress factors in parallel can closely replicate the real operational conditions of the PSCs and thus can result in a more realistic stability analysis.

2.1. Single stress factors

The testing atmosphere, especially the presence of humidity and oxygen, affects PSC device stability. Due to the hygroscopic nature of the amine groups present in the organic MA and FA cations, humidity can lead to the hydrolysis of the halide metal perovskite into hydrated products, such as $MA_4PbI_6 \cdot 2H_2O$ and PbI_2 [11, 12]. In contrast, the halide perovskite under a pure oxygen atmosphere does not show significant degradation [13]. In commercialized modules, solar cells are well encapsulated to greatly avoid the erosion of humidity and oxygen.

For PSCs, UV light (< 400 nm) is by far the most detrimental wavelength range of the entire AM 1.5 G solar spectrum. The degradation mechanisms taking place are mainly related to the degradation of transporting layers and their interfaces with perovskite. TiO₂ based PSCs experience instability under UV illumination due to the deep trapping of electrons caused by light-induced desorption of surface-adsorbed oxygen or the decomposition of perovskite caused by the photocatalytic effect of TiO₂ at the interfaces [14, 15]. This light-induced degradation is characteristic of many other metal oxides under UV light, such as ZnO electron transporting layers (ETL) [16]. Recent studies suggest the application of materials that are insensitive to UV light to mitigate this issue [17, 18].

Heat-induced instability occurs due to the degradation of the halide perovskite itself or the degradation of any other constituent layer of the device, including the transporting layers and the electrode. The halide perovskite MAPbI₃ is prone to decompose into methyl iodide (CH₃I), ammonia (NH₃) and lead iodide (PbI₂) under elevated temperatures applied as long-term treatment [19]. This decomposition process is proved to be a surface-initiated layer-by-layer degradation [20]. The low formation energy of MAPbI₃ of 0.11-0.14 eV, close to the thermal energy of 85 °C, is an inherent cause [13]. High temperatures (e.g. > 70 °C) can also greatly accelerate the inter-diffusion of elements in component layers, e.g. iodine from perovskite to transporting layers, or electrode diffusion to the perovskite layer, leading to the severe degradation of the transporting properties of PSCs [21].

Briefly, there are four modes of bias voltage applied on solar cell modules in the field, including maximum power point (MPP) voltage (normal operation), reverse bias voltage (shaded modules), open circuit (disconnected) and short circuit (shunting). The degradation caused by bias voltage is mainly ascribed to the migration of ions present in the halide perovskite (e.g. I^- and MA^+) [22]. As a result, the accumulated charges at the interfaces lead to the formation of radicals and the observation of hysteresis in IV curves. Moreover, the induced external ion diffusion into the transporting layers and metal contacts provoke the formation of carrier traps and detrimental reactions [22–24]. In particular, it is reported that a reverse bias voltage of merely -1 to -4 V can cause the breakdown of perovskite solar cells, while the breakdown value for silicon solar cells is around -15 V [24]. The mechanism is considered to be the shunt path formation or the electrochemical reaction of defects in the contacts [24].

2.2. Combination of stress factors

In general, the combination of stress factors results in more severe degradation to PSCs due to the synergetic effects and interactions between different failure mechanisms [25]. For instance, elevated temperature accelerates all involved chemical reactions, ion migration and diffusion due to the increased thermal energy of atoms. Light excites electrons and holes in the perovskite thin films, leading to further reactions with neighbouring materials and the interaction with point defects.

Light coupled with humidity can further catalyse perovskite to form I₂, resulting in irreversible reactions and trapped charge-driven degradation [26, 27]. Compared to conditions under a single stress factor, MA⁺ based halide perovskites decompose faster in the presence of light and oxygen or under bias voltage and oxygen. This is ascribed to the reaction of MA⁺ with the superoxide O₂⁻, which originates from the reaction of photo-excited electrons in perovskite and molecular oxygen [28, 29]. Light coupled with oxygen and bias voltage is likely to cause accelerated irreversible degradation starting from defective grain boundaries [30]. When PSCs are aged under one sun with MPP tracking, at room temperature and under inert gas, stability depends mainly on ion and defect migration taking place at the constituent materials and interfaces [31, 32]. Interestingly, PSCs have already passed the damp-heat standard stability test for 1000 h by several groups [33, 34], but it is still challenging to overcome tests under continuous light irradiation at elevated temperatures. Stable PSCs under 85 °C and one sun illumination for 1000 h have not been reported yet, though promising results for 500 h have been demonstrated [35, 36]. Moreover, under constant light and heat, PSCs perform worse if analysed under open circuit voltage conditions than under the MPP tracking mode, indicating that ion migration and charge accumulation are critical for the stability of PSCs [37, 38]. Therefore, the long-term stability of PSCs analysed under the combination of light, elevated temperature and bias voltage is significantly important and can be considered as a prerequisite towards commercialization. An important challenge originates from I₂-induced degradation [38, 39], thermal decomposition, ion migration, interface deterioration and their coupling with defects, leading to accelerated degradation processes. Particularly, the generation of I₂ vapour, which originates from either the oxidation of I⁻ by photo-generated holes [40] or decomposition of the halide perovskite through the presence of defects in the bulk, is a self-catalysed reaction, and thus urgent innovative solutions are necessary to address this problem [38].

3. Current strategies for stability improvement

Several strategies have been proposed and applied to improve the long-term stability of PSCs. Some of them aim to prevent the permeation of humidity and oxygen and to block the out-diffusion of ions and volatile species from the perovskite layer. This has been achieved by interface engineering or by the application of stable transporting layers, electrodes and interlayers [41–45]. Further strategies focus on the perovskite layer itself, which can be compositional and additive engineered, to enhance its robustness under stress factors [32, 36, 46, 47]. This is realized by the replacement of cations or anions shaping more stable perovskite structures or by the decrease and passivation of detrimental defects. Based on different published strategies, ongoing representative routes are discussed in the following sections.

3.1. Triple-layer carbon based mesoscopic PSCs

The carbon-based mesoscopic PSCs fabricated by screen printing have demonstrated the best long-term operational stability of over 10 000 h [2], representing a promising low-cost technology route for PSC marketization. The devices feature a hole-conductor-free printable triple-layer architecture made of mesoporous TiO₂ (mp-TiO₂) as the ETL, mesoporous ZrO₂ (mp-ZrO₂) as the scaffold and mesoporous carbon as the back electrode [48]. Perovskite applied here is mainly MAPbI₃. The superior stability stems from the special mesoporous structure of thermally-stable inorganic metal oxide, the hydrophobic carbon electrode and the 2D/3D mixed composition realized by the addition of 5-ammonium valeric acid iodide (5-AVAI) [2, 48]. Specifically, the mp-TiO₂ protects the perovskite from external degradation factors like humidity, vapours and impurity diffusions [31]; the mp-ZrO₂ prevents the electrons from flowing into back contact recombining with the holes in the perovskite/carbon interface, as well as acting as another protective layer surrounding perovskite [48]; the thick carbon back electrode (around 10 μ m) effectively serves as a water-retaining layer avoiding the moisture attack on perovskite [48]; the additive 5-AVAI can form a template for crystal nucleation and growth of perovskite and can cross-link the perovskite crystals facilitating defects passivation and carrier transport, as well as increasing the loading of perovskite inside the mp-TiO2 [48, 49]. The advantage of the triple-layer carbon based mesoscopic PSCs is their lost-cost process avoiding the use of hole transporting layer and noble metals like Au and Ag, together with the exceptional long-term stability. Nevertheless, the efficiency of this type of PSC still falls far behind the hybrid PSCs (<17%) [50], which is mainly due to the poor contact at the perovskite/carbon interface, and the relatively high resistance of bulk carbon [51]. A good interface contact is depending on the porosity and wettability of carbon, which enables the diffusion and loading of perovskite into the porous structure. Various strategies have been performed to mitigate these issues, by using malleable ultrathin graphite [52], pore forming agent [53], post-treatments [54], and interlayers [55].

3.2. Inorganic PSCs

An emerging approach to stable PSCs is the application of all inorganic perovskite compositions, which avoids the use of unstable organic cations. Recently, CsPbI₃ PSCs have achieved over 18% certified efficiency, marking a record in all types of inorganic halide PSCs [50]. The devices have demonstrated 500 h under continuous illumination at room temperature [56], which is a huge step forward in terms of stability. Although inorganic halide PSCs are intrinsically and thermodynamically more stable than organic-inorganic counterparts, the phase stability at operating temperature still requires further investigation, e.g. through additive and defect engineering [57–59].

3.3. 2D PSCs

Another concept is the use of bulkier hydrophobic organic cations to replace the hygroscopic MA and FA organic ions. Due to tolerance factors, the use of a large bulkier organic cation results in the transformation of the 3D perovskites into the 2D layered perovskite structure, which is environmentally more stable [60, 61]. Although more efforts to enhance device efficiency are required [62], the adoption of 2D/3D hybrid structures or 2D interlayers is promising routes to explore the advantages of both types of perovskites. For instance, hybrid 2D/3D PSCs have achieved the longest reported operational stability, currently at 10 000 h (around 1 year), by introducing the 5-AVAI molecule within the halide perovskite absorber [2]. The application of the n-butylammonium additive resulted in 2D/3D PSCs above 17% efficiency, showing 1680 h stability under continuous illumination and open circuit voltage conditions [63]. In addition, the employment of an ultrahydrophobic 2D perovskite interlayer of (FEA)₂PbI₄ (FEA = henylethylammonium) onto the 3D perovskites surface, led to a 2D/3D PSCs. This type of PSCs with over 22% can retain 90% of the initial efficiency during continuous operation for 1000 h in humid air under simulated sunlight (unsealed device) [64].

3.4. 3D hybrid organic-inorganic PSCs

The 3D hybrid organic-inorganic PSCs hold the world record in efficiency among all types of PSCs and thin film photovoltaic technologies [1]. If the stability issues can be solved, it will definitely become the next commercialized photovoltaic technology. Enormous efforts have been made to improve the stability as well as the efficiency of hybrid PSCs. Recently, hybrid PSCs with an efficiency higher than 20% have demonstrated excellent stability of over 1000 h under one sun at temperatures above 60 °C. This is achieved by using ionic liquid additives [46], or via interface engineering with wide band gap PbSO₄ salts [43] or chlorinated graphene oxide [42], or through the replacement of unstable N2,N2,N2',N7',N7,N7,N7'-octakis(4-methoxyphenyl)-9,9'-spirobi[9 H-fluorene]-2,2',7,7'-tetramine (Spiro-OMeTAD) hole transporting layer (HTL) by the inorganic CuSCN [44]. The estimated T₈₀ (time at a performance loss of 20%) of high efficiency hybrid PSCs at 70 °C–75 °C is less than 6000 h [46], indicating a huge improvement, although there is still considerable research required before realizing practical applications.

Table 1 summarises the most stable PSCs reported in the literature to date following real stability test conditions, meaning analyses under outdoor conditions or under indoor conditions exposed to a combination of light, heat and bias voltage. We have included only those PSC devices able to stand for more than 500 h under one sun at temperatures above 50 °C and retaining more than 80% of their initial efficiency.

4. Multi-component engineering for enhanced stability

In general, halide perovskite with a Cs-containing composition has been proven to be more stable than the sole use of MAPbI₃ due to the intrinsically stable structure and enhanced chemical bonds [65–67]. Moreover, MA-free perovskite has higher thermal stability [31]. The 2D perovskite degrades much more slowly under humidity in comparison with 3D perovskite due to its superior hydrophobic nature [61, 64]. Inorganic transporting layers are thermally more stable than organic counterparts. For HTLs working at temperatures > 60 °C, the poly-[bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) outperforms the most commonly used HTL Spiro-OMeTAD in stability, due to its lower permeation of the Au metal electrode [36, 37].

Table 1 shows that the long-term operational stability of PSCs can be achieved regardless of the type of device: inverted or normal configuration, planar or mesoporous structure, or carbon-based architecture. The most important aspect is the robustness of each of the constituent materials of the device: the halide perovskite, the transporting layers (HTLs and ETLs), the electrodes and their interfaces. It can also be observed that when the stress temperature is below 70 °C, the application of a single strategy, such as the modification of one component of the device, can lead to stable PSCs. Some of these strategies include the use of inorganic transporting layers or interlayers [42, 68], the engineering of perovskite composition [63, 69], or the encapsulation with highly hydrophobic photocurable fluoropolymers [70]. Above 70 °C,

| Device structure | | | Stability | | | | |
|--|-------------------------------------|------------------------|-----------|---------------|-------------------------|--|---------|
| Front contact | Testing time (h) Initial | | Stre | Stress factor | | | |
| Perovskite Back Configuration contact | eff. (% Relative eff. retaining (%) | Light source | T (°C) | Bias voltage | RH (%) and Oxygen | Strategy employed to enhance stability | Ref |
| Inverted planar NiO (FA _{0.83} MA _{0.17}) _{0.95} CS _{0.05} Pb(L _{0.9} Br _{0.1}) ₃ | 1885 ~18 | Xenon Lamp with UV | 70–75 | Open circuit | Sealed, 40–50 | (1)Interlayer: Cr(Cr ₂ O ₃); (2)Additive: Ionic liquid BMIMBF ₄ ; | 46 |
| :BMIMBF ₄ PCBM/ BCP/Cr(Cr_2O_3)/ Au | ~85 ~ | | | | aır | (3) Composition engineering: Cs containing. | |
| $\begin{array}{c} PTAA \ Cs_{0.05}FA_{0.81}MA_{0.14} \\ PbI_{2.55}Br_{0.45} \end{array}$ | 1200 19.44 | Plasma lamp with UV | 65 | MPP | Sealed $\sim 60 \pm 10$ | (1)Interface engineering: PbSO ₄ layer; (2)Encapsulation: CYTOP fluoropolymers; | 43 |
| PbSO ₄ /C ₆₀ /BCP/Cu | 96.8 | Yough lamp | r, | Mpp | air Heesslad | (3) Composition engineering Cs containing. | ς, L |
| PbI ₃ PCBM/BCP/ | 16.5 | No UV | 6 | 1,11,1 | 20–60 | (1) Outer layer Passivation: 72203; (2) Interlayer: AZO; | C) |
| AZO/Ag/Al ₂ O ₃ | 86.7 | | | | air | (3) Composition engineering: Cs containing. | |
| NiMg(Li)O | 1000 | Solar simulator | 45-50 | Short circuit | Sealed air | (1)Inorganic HTL and ETL: Metal oxide | 89 |
| $MAPbI_3$ | I | No UV | | | | NiMg(Li)O and Ti(Nb)Ox | |
| PCBM/ | 06 | | | | | | |
| Ti(Nb)Ox/Ag | | | | | | | |

able 1. (Continued)

| | | Ref | 34 | | 87 | | | 44 | | | | 47 | | | |
|------------------|--------------------------|--|---|------------------------------------|---------------------------------------|------------------------------|-------------------------------|--------------------------|----------------------|--|---------------|---|---------------------------------------|--|--------------|
| | | Strategy employed to enhance stability | (1) Interface engineering: 2D iodide diffusion blocking barrier: graphitic carbon nitride | $(g-C_3N_4)$ | (1) Interface engineering: Trimethyl- | olpropane triacrylate (TMTA) | (2) Additive: TMTA | (1)Inorganic HTL: CuSCN; | (2)Interlayer: r-GO; | (3) Composition engineering: Cs contain- | ing. | (1)Interface engineering: SN surface layer; | (2) Additive: SN molecular modulator; | (3) Composition engineering: Cs containing | and MA-free. |
| | | RH (%) and Oxygen | Sealed air | | Unsealed | Glove box | | Unsealed | \mathbf{N}_2 | | | Unsealed | Ar | | |
| | Stress factor | Bias voltage | MPP | | MPP | | | MPP | | | | MPP | | | |
| Stability | Stre | T (°C) | 09 | | 09 | | | 09 | | | | 55–60 | | | |
| | | Light source | Solar simulator No UV | | White LED | No UV | | White LED | No UV | | | Whtie | LED | No UV | |
| | Testing time (h) Initial | eff. (% Relative eff. retaining (%) | 1000 ~15 | 91 | 1000 | I | 80 | 1000 | ~ 20 | 95 | | 1000 | 20.9 | 98.1 | |
| Device structure | Front contact | Perovskite Back contact | NiO FA _{0.85} MA _{0.15} Pb(I _{0.85} | $ m Br_{0.15})_3$ G-PCBM/BCP/Ag | P3CT-N | $(FA,MA)Pb(I,Br)_3$ | PCBM/C ₆₀ /TPBi/Cu | $c-TiO_2/$ | $mp-TiO_2$ | $(Cs,FA,MA)Pb(I,Br)_3$ | CuSCN/r-GO/Au | $c-TiO_2/$ | $mp-TiO_2$ | $FA_{0.9}Cs_{0.1}PbI_3:SN^*$ | SN/Spiro/Au |
| Ď | | Perovsk Configuration contact | | | | | | | | | | Normal | mesoporous | | |

Table 1. (Continued)

| | | | Stability | | | | |
|--|-------------------------------------|------------------------------|-----------|---------------|-----------------------------|--|---------------|
| | Testing time (h) Initial | | Str | Stress factor | | | |
| | eff. (% Relative eff. retaining (%) | Light source | (°C) | Bias voltage | RH (%) and Oxygen | Strategy employed to enhance stability | Ref |
| c-TiO ₂ / mp-TiO ₂ (Rb,Cs,FA,MA)Pb(I,Br) ₃ | 500 ~14 95 | Whtie LED No UV | 85 | MPP | Unsealed N ₂ | (1)HTL: PTAA; (2)Composition engineering: Rb, Cs containing. | 36 |
| r.t.av/Au c-TiO ₂ / mp-TiO ₂ (EAI) _{0.81} (PbI ₂) _{0.85} (MABr) _{0.15} (PbBr ₂) _{0.15} : BrPh-ThR*:bis-PCBM | 1500 - 90 | Whtie LED No UV | 55 | MPP | Unsealed $ m N_2$ | (1)Additive engineering: Lewis base and acid: BrPh-ThR and bis-PCBM | 88 |
| | 2208 - 95 | Outdoor, In Turin, Sun | -3-27 | Open circuit | Unsealed, 27 Rainy days | (1)Encapsulation: photocurable fluoropolymers protective layer | 70 |
| optro/Au/nuoropolymers c-TiO ₂ / mp-TiO ₂ MAPbI ₃ | 500-85 | White LED, No UV | 95 | MPP | Unsealed, N ₂ | (1)HTL: PTAA | 37 |
| c-TiO ₂ / mp-TiO ₂ MA _{0.75} GUA _{0.25} PbI ₃ | 1100 17.14 80 | Indoor, one sun | 09 | MPP | Unsealed, Ar | (1)Composition engineering: Guanidinium mixing69 | 69 8 1 |

| | | | Table 1. (Continued) | nued) | | |
|-------------------------------------|--------------------------|--------------|----------------------|---------------|------------|---|
| Device structure | | | Stability | | | |
| Front contact | Testing time (h) Initial | | Str | Stress factor | | |
| Perovskite Back | eff. (% Relative eff. | | | | RH (%) and | RH (%) and Strategy employed to |
| onfiguration contact | retaining (%) | Light source | T (°C) | Bias voltage | Oxygen | enhance stability |
| ormal Planar SnO ₂ /PCBM | 1680 | xenon lamp | 50–60 | Open circuit | Sealed, | (1) Composition engineering: 2D/3D mixt |

| | | Ref | 63 | 42 | 89 i- | 68 | 2 |
|------------------|--------------------------|--|--|--|--|------------------------------|--------------------------|
| | | Strategy employed to enhance stability | (1)Composition engineering: 2D/3D mixture and Cs containing MA-free. | (1)Interface engineering: Cl-GO interlayer; (2)HTL: PTAA. | (1)Mesoporous metal oxide; (2)Hydrophobic carbon layer; (3)Additive:5-AVAI leading to 2D/3D composition. | | |
| | | RH (%) and Oxygen | Sealed, 40–50, air | Sealed, air | Unsealed, 54, air | Sealed module, 80, air | Sealed module, air |
| | Stress factor | Bias voltage | Open circuit | MPP | MPP | MPP | Short circuit |
| Stability | Str | (°C) | 50–60 | 09 | 50 | 30 | 55 |
| | | Light source | xenon lamp With UV | AM 1.5G, one sun | Solar simulator, With UV | Outdoor, In Wuhan, Sun | Solar simulator No UV |
| | Testing time (h) Initial | eff. (% Relative eff. retaining (%) | 1680 | 1000 21.4 90 | 1000 8 100 | 720 8 100 | $10000 \ \sim 10 \ 100$ |
| Device structure | Front contact | Perovskite Back contact | SnO ₂ /PCBM BA _{0.09} (FA _{0.83} CS _{0.17}) _{0.91} Pb(I _{0.6} Br _{0.4}) ₃ Spiro/Au | SnO ₂ (FA,MA)PbI ₃ Cl-GO/PTAA/Au | c-TiO ₂ / mp-TiO ₂ / mp-ZrO ₂ MAPbI ₃ : 5-AVAI mp-carbon | • | |
| Dev | 1 | Perovsk Configuration contact | Normal Planar SnO ₂ /PCBM BA _{0.09} (FA _{0.83} Pb(I _{0.6} Br _{0.4}) ₃ | <i>y,</i> — <i>O</i> | Carbon c based r | | |

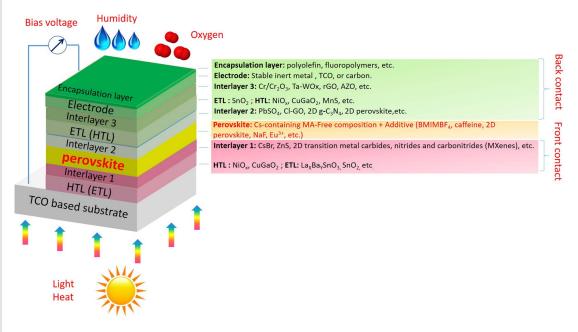


Figure 1. Schematic representation of the proposed device design for highly efficient PSCs with long-term operational stability.

different strategies are combined to achieve exceptional long-term stability [35, 36, 46]. In particular, when aging for over 1000 h at 70 °C–75 °C under continuous light irradiation and open circuit conditions, the simultaneous engineering of perovskite composition, additive content and interlayers is employed [46]. An increase in testing temperature of only 10 °C could result in the acceleration of PSC degradation by a factor of two

[4, 46], suggesting that more sophisticated methods must be employed to overcome instability. We should highlight that the current most stable PSCs (the Carbon-based PSCs) also involve the strategy of multi-component engineering. It adopts a 2D/3D perovskite composition, uses a mixture of mesoporous oxides (as transport and scaffold layers) and applies hydrophobic carbon electrodes simultaneously [2, 48]. We note that in table 1, MAPbI₃-based PSCs with a simple strategy applying PTAA HTL retained 85% of their initial efficiency at 95 °C under MPP tracking for 500 h [37]; however, under similar aging conditions at 65 °C, PSCs based on CsFAMA triple-cation composition retained 97% performance versus 90% remaining efficiency of MAPbI₃-based PSCs [37]. This again demonstrates that the Cs-containing composition is superior to pure MAPbI₃ counterparts, and even more enhanced stability can be expected if multi-component engineering is applied.

In summary, composition and additive engineering are necessary to improve the inherent photo-thermal stability of perovskite at 85 °C under one sun, while other strategies, including the application of inorganic transporting layers and barrier interlayers, stable electrodes and interface engineering, are crucial to prevent humidity and oxygen incursion into the device. Many of these strategies play an important role in passivating defects at the grain boundaries and interfaces, mitigating the migration of ions. Equally important is the engineering of PSCs considering an economic perspective. Expensive transporting materials, such as PTAA and [6]-phenyl-C⁶¹ -butyric acid methyl ester (PCBM), may not be favourable for large-scale production. Because the ultimate aim is to achieve a levelized cost of electricity (LCOE) value comparable with other energy resources for future commercialization, low cost, high efficiency and long-term stability should be considered comprehensively [71].

Therefore, the long-term operational stability of PSCs requires a rational design of each of the constituent materials of the device; however, most importantly, a robust device can only be developed through the simultaneous engineering of the different constituent materials and interfaces of the PSCs.

Table 2 summarises (a) the main stress factors and (b) the failure modes that affect the stability of PSCs. We have also shown (c) the methods currently applied to engineer the different components of a PSC to enhance its efficiency and stability.

Thus, in an attempt to achieve highly efficient PSCs with long-term operational stability, we highlight the strategy of multi-component engineering based on a device configuration shown in figure 1. In addition to the common constituents of a PSC, this configuration also includes an encapsulation layer and the introduction of three interlayers, two of which are placed between perovskite and transporting layers and a

Table 2. Summary of (a) main stress factors and (b) failure modes observed in PSCs analyzed under continuous light irradiation for more than 500 h at temperatures above 50 °C, and (c) the strategies proposed for the engineering of each of the constituents of PSCs to reduce degradation. To fabricate stable PSCs we propose a multi-component engineering strategy which implies the simultaneous application of several of the strategies described in (c).

| | | (a) Mair | (a) Main stress factors | ş | (b) Main failure | | | (c) Strategies for stability improvement | bility improvemen | t | |
|------------------------|-------|----------|-------------------------|------------|---|---|--|---|---|------------|---------------|
| Device | | | Bias | Humidity | modes | Halide p | Halide perovskite | Transport | | | |
| structure | Light | Heat | voltage | and Oxygen | | Composition | Additive | Layer | Interfaces | Electrodes | Encapsulation |
| Front Contacts | 7 | 7 | > | 1 | UV instability, interface photochemical reaction, detrimental ion diffusion to perovskite | <u> </u> | | Apply thermally stable materials: Metal oxides (e.g. NiO _x , SnO ₂ , CuGaO ₂), complex oxides (e.g. LaxBaySnO ₃ , PbZrTiO ₃), Metal sulfides (e.g. MnS), cuSCN, or their | Application of UV and thermally stable Interlayers for interface passivation and band alignment optimization. (e.g. CsBr, ZnS, 2D transition metal carbides, nitrides and carbonitrides (MXenes)) | I | |
| Halide per- ovskite | 7 | 7 | 7 | 7 | defects and ion migration, thermal decomposition, hydrated reaction, light and oxygen induced superoxide, I ₂ induced degradation under light and heat | Improve photo-thermal stability and environmental stability by applying Cs-containing and MA-free halide perovskites (e.g. (Cs,EA) Pb(I,Br) ₃ , (Rb,Cs,EA)Pb (I,Br) ₃) | Enhance photo-thermal stability, passivation of defects and immobilize ion migration by the use of additives (e.g. NaF,Eu³+,Ionic liquid BMIMBF4, Caffeine, 2D perovskite) (Continued) | I | 1 | I | I |

Table 2. (Continued)

| | | (a) Main | (a) Main stress factors | s | (b) Main failure | | | (c) Strategies for sta | (c) Strategies for stability improvement | t l | |
|-----------|-------|----------|-------------------------|------------|------------------|-------------|-------------------|------------------------|--|------------------|-------------------|
| Device | | | Bias | Humidity | modes | Halide I | Halide perovskite | Transport | | | |
| structure | Light | Heat | voltage | and Oxygen | | Composition | Additive | Layer | Interfaces | Electrodes | Encapsulation |
| Back | | 7 | 7 | 7 | Heat induced | I | Ī | Employ Metal | Use of thermally | | Use of thermal, |
| Contacts | | | | | structure | | | oxides (e.g. | stable | ical stable con- | photo and air- |
| | | | | | transformation, | | | NiO_x , SnO_2 , | Interlayers to | ductors (e.g. | stable encapsu- |
| | | | | | electric bias | | | $Ti(Nb)O_x$, | block ion | Carbon, TCO) | lation materials. |
| | | | | | induced ion | | | $CuGaO_2$), | migration, | | (e.g. |
| | | | | | diffusion from | | | complex oxides | humidity and | | polyolefin, |
| | | | | | perovskite, | | | (e.g. | oxygen | | fluoropolymers, |
| | | | | | humidity and | | | $La_XBa_YSnO_3$, | incursion. | | epoxy resin, |
| | | | | | oxygen | | | PbZrTiO $_3$), | $(e.g. PbSO_4,$ | | (ER)-based |
| | | | | | penetration | | | Metal sulfides | Al_2O_3 , rGO, | | polymers) |
| | | | | | | | | (e.g. MnS), | Cl-GO, MnO ₃ , | | |
| | | | | | | | | CuSCN, | Ta-WOx, | | |
| | | | | | | | | Or their | $Cr/Cr_2O_3,2D$ | | |
| | | | | | | | | combinations | \mathbf{g} -C ₃ N ₄ , 2D | | |
| | | | | | | | | | perovskite) | | |

third between the back electrode and transporting layers. The strategy of multi-component engineering consists of the simultaneous application of several of the strategies described in table 2, section (c), such as:

- Perovskite layer: the use of an MA-free and Cs-containing composition along with additives (e.g. BMIMBF₄, Caffeine, NaF, SN, Eu³⁺, etc) to enhance the PSC photo-thermal stability, to passivate defects, to minimize I₂ vapor generation and to immobilize ion migration of perovskite layer [31, 32, 46, 47, 69, 72, 73].
- Transporting layers: to apply thermal, photo and air-stable materials, such as metal oxides and metal sulphides [17, 18, 68, 74–80].
- Interlayers: to consider the engineering of interfaces applying thermally stable materials, which will minimize ion diffusion, interface recombination and air ingress. For example, the use of PbSO₄, Cl-GO, 2D materials, metal oxides or sulphides, among others [42–44, 46, 64, 81, 82]. In particular, Interlayer 1 is for the minimization of interfacial reactions due to the photocatalytic effect, Interlayer 2 is for blocking ion diffusion from perovskite and Interlayer 3 is for preventing humidity and oxygen incursion and electrode diffusion. All the interlayers can also play an important role in interfacial defect passivation and band alignment optimization.
- Electrodes: to select chemical stable conductors (e.g. carbon, transparent conductive oxides (TCO)) [33, 48, 83].
- Encapsulation: to apply water and oxygen resistant materials, e.g. polyolefin, fluoropolymers or 2D materials [70, 84–86].

5. Outlook

Given the high efficiency of hybrid organic-inorganic PSCs, the research focus should be shifted to long-term stability under more realistic operational conditions, and specifically under a combination of light, heat and bias voltage. More innovative solutions and strategies are still urgently needed to tackle the I_2 -induced degradation in the bulk and to improve the long-term photo-thermal stability at 85 °C and under one sun. To achieve a lifetime of 25 years for PSCs, multi-component engineering is an option worthy of attention. The application of this multi-component engineering strategy may encourage researchers to develop PSC devices with enhanced stability under more stressful but practical operational conditions. This can guarantee a competitive technology that can realize commercialization more rapidly.

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