Metal halide perovskites - stability under illumination and bias

Muhammad Umair Ali [a],[1] Hongbo Mo[b],[1] Atta Ur Rehman,[1] Tik Lun Leung,[2] and Aleksandra B. Djurišić[1]

[1]*Dept. of Physics, the University of Hong Kong, Pokfulam Road, Hong Kong*

[2]*School of Physics, The University of Sydney, Sydney, NSW 2006, Australia*

(*Electronic mail: dalek@hku.hk)

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In this short review, we discuss recent progress in developing better understanding of the segregation in mixed composition metal halide perovskite materials, and closely related phenomenon of ion migration (which occurs in both single phase and mixed perovskites). We focus in particular on electrochemical aspects of these phenomena, since they are particularly relevant for operational stability of devices. A short overview of the methods to suppress segregation/ion migration is given, followed by a summary of the stability milestones in perovskite solar cells and perovskite light emitting diodes. Finally, future outlook and challenges are discussed.

Keywords: metal halide perovskite materials, stability, perovskite solar cells, perovskite light emitting diodes, photosegregation, ion migration

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[a] These authors contributed equally

[b] These authors contributed equally

I. INTRODUCTION

Metal halide perovskite materials have attracted intense attention for their applications in various devices, such as perovskite solar cells (PSCs) and perovskite light emitting diodes (PeLEDs). While their efficiencies have mostly reached comparable levels to more mature technologies, their stability still needs substantial improvements. Difficulties in achieving high stability devices are due to the fact that metal halide perovskite materials are ionic crystals (with estimated ion densities of the order of 10^{17} cm^{-3}),[1,2] which exhibit ion migration under illumination, at elevated temperature, and under bias.[2,3] Ion migration and resulting accumulation of charges are responsible for different anomalous behaviors in PSCs, such as light soaking effect, hysteresis and slow open circuit voltage decay, which can be attributed to changes in carrier collection due to ion redistribution (decrease or increase of barriers for charge collection at interfaces),[4] as well as degradation of device performance over time. Degradation due to ion migration is in short term reversible by redistribution of ions (commonly in the dark, or by pulsed reverse bias during maximum power point tracking (MPPT)[5]), but ultimately leads to irreversible degradation.[3] The rate of degradation is dependent on bias voltage, with slower degradation achieved under MPPT compared to open circuit (OC) operation.[6] The degradation can be further exacerbated by elevated temperature[7], exposure to moisture and oxygen,[8] as well as vacuum,[9] possibly due to easier loss of volatile degradation products under vacuum conditions.

The ion migration occurs in all perovskite materials to some extent, while segregation occurs in mixed halide perovskite materials, which in general exhibit tendency to segregate under illumination and remix in the dark.[10] Halide segregation has been listed as one of the causes for open circuit voltage V_{oc} loss in wide band gap PSCs with high Br content. However, it has been recently shown that the major cause of V_{oc} loss is nonradiative recombination, rather than halide segregation.[11] Nevertheless, photoinduced phase segregation is still undesirable for long term stability, as it indicates the existence of anion vacancy defects which facilitate ion migration. Ion migration in mixed halide perovskites was found to have lower activation energy compared to pure halide perovskites, which was attributed to an increased density of vacancy defects.[12] The segregation can occur in both organic-inorganic, as well as purely inorganic lead halide perovskite materials, although there have been conflicting reports on stability of different compositions of $\mathrm{CsPbI_{1-x}Br_x}$.[13] In inorganic perovskites, it typically occurs over a slower timescale, especially in comparison with methylammonium (MA) lead halide $\mathrm{MAPbI_{1-x}Br_x}$. In addition to thin films, segregation also occurs in perovskite nanocrystals.[14,15]

While greater attention has been devoted to halide anion segregation and migration which contribute to the majority of ion migration, cations are also mobile and can exhibit segregation and migration. This applies both to small cations in 3D perovskites,[12,16,17] as well as small cations and bulky spacer cations in quasi-2D/2D perovskites.[18] It was proposed that halides and lead are migrating along (110) reflection in the lattice, while organic cation is migrating along (100) reflection direction.[19] Considering that the ion migration is mediated by vacancies, observations of different orientations for favorable migrations are expected due to different positions of lead and halides (which are forming the octahedra) and a small monovalent cation (which are fitting into the pockets between the octahedra). The cation segregation was found to be exacerbated by initial composition inhomogeneity,[16] and the starting inhomogeneity likely also plays a role in the anion segregation.

Although ion transport in perovskite materials under illumination and/or electrical bias is critical for the device performance, it is still not completely understood. This is at least in part due to the complexity of the processes involved. For example, illumination can result in both creation and healing of the defects,[20] as illustrated in Fig. 1, which also shows relevant electrochemical reactions related to various iodide species. Different defects in the perovskite, as illustrated in Fig. 1c,[21] can serve as charge traps and recombination centers (affecting photoluminescence, charge transport, and efficiency) or facilitate ion migration (affecting stability). For example, it has been shown that the passivation of shallow defects with 3-phosphonopropionic acid significantly improves the device stability, while efficiency and nonradiative recombination losses, which are affected by deep defects, do not exhibit a significant change.[22] Among various defects, halide vacancies play a key role in ion migration, in particular along the grain boundaries.[2,23,24] The issue of defects is commonly addressed by passivation with molecules containing relevant functional groups,[25] preferrably multiple groups with different functions, as illustrated in Fig. 1d.

While attempts have been made to understand the reversible and irreversible degradation processes, further work is needed to fully clarify the mechanisms involved and resolve contradictory results and different models reported to date. For example, it has been proposed that exponential decay part of the degradation curve can be attributed to reversible processes, while linear decline can be attributed to irreversible degradation.[6] However, not all PSCs exhibit exponential decay (burn-in) part of the degradation curve, and the performance decline is not necessarily linear. Thus, improved understanding of the device performance degradation is needed to address issues

FIG. 1. (a) Schematic illustration of creation and annihilation of defects under illumination b) Relevant electrochemical reactions involved in iodide defect creation and annihilation summarized from Refs.[27–30]. I_i denotes interstitial iodine, I^- denotes lattice iodide, V_X denotes vacancy of X. (b) Schematic illustration of defect passivation in a 3D perovskite using multifunctional passivating material (generalization of defect management of $FAPbI_3$ surface, illustrated in Ref.[21] and reproduced with permission; Copyright American Chemical Society). (d) Selected examples of common structures of effective functional groups for passivating materials. For a full list and examples of different passivating molecules, see Ref.[25] Different electrochemical reactions occurring under illumination are discussed in more detail in subsections II C and II D.

contributing to these phenomena. For a more detailed review of stability of perovskite materials and devices, which is beyond the scope of this short review, see Refs.[2,6,26] Here we will provide a brief overview of recent advances towards better understanding of ion segregation/ion migration in metal halide perovskite materials, with a focus on electrochemical processes.

II. MECHANISMS RESPONSIBLE FOR PHOTOINDUCED PHASE SEGREGATION-THE ROLE OF CHARGE IMBALANCES

A. Characterizing photoinduced phase segregation and ion migration

The phase segregation, ion migration, and degradation processes in general have been extensively studied for a range of perovskite compositions and stress conditions, using various methods such as optical spectroscopy, X-ray diffraction, electron microscopy, and secondary ion mass spectroscopy (SIMS). In particular, a number of *in situ* investigations has been conducted (for a recent review, see Ref.[31]). For example, *in situ* investigation using multiple techniques has demonstrated long range migration of iodide, extending beyond illuminated region, as well as vertical migration of lead.[32] Thus, despite comprehensive investigations there are still parts of the process which are not fully understood, which is at least in part due to differences in sample preparation and experimental conditions, which can result in different properties of samples with nominally same composition (for example, differences in grain sizes result in different proportion of grain boundaries and consequently different rates of ion migration). Furthermore, it is well known that many common characterisation techniques can result in artefacts when used on the halide perovskite materials due to their unique properties, i.e. ionic and electronic contributions in electrical characterizations, as well as the sensitivity of perovskite to electron beam exposure (low dosages are needed for good imaging), vacuum environment, and ambient air. Among different characterizations, various optical measurements, conducted *in situ* or *ex situ*, are the most commonly used for characterizing photoinduced phase segregation, such as UV-Vis, photoluminescence (PL), and electroluminescence (EL) spectroscopy.[18,31,33–37] Measurement techniques based on light emission[34,35] have the advantage of being very sensitive to the phase segregation, as luminescence preferentially occurs from the lowest bandgap phase present in the film due to charge funneling.[36,37] This can result in an overestimation of degree of segregation,[37] which makes absorption measurements[18,33] preferrable for investigations aiming towards model development and kinetics parameters estimation. However, exceptional sensitivity of PL measurements to phase segregation makes them particularly suitable for confirming suppression of the segregation.

B. Models of photoinduced phase segregation

Different models have been proposed to date to explain photoinduced phase segregation, such as polaron, thermodynamic, trap-related, and oxidation models.[38] As most of these models, including recent comprehensive thermodynamic band gap model,[38] typically explain only parts of the existing data in the literature, and the majority of the models have been extensively discussed, here we focus on the oxidation model. Oxidation model of photoinduced phase segregation recognises the importance of electrochemical processes in the degradation of perovskite films and devices, and enables explanation of degradation under different conditions using the same principles. The similarity between changes in the perovskite material caused by electrical bias and illumination strongly suggests that the electrical charges play a key role in photosegregation, ion migration, and ultimately perovskite decomposition. It should be noted, however, that segregation and migration phenomena observed under illumination and under bias are not identical. For example, optically stable mixed perovskite composition with low (0.1) bromide content, can still exhibit segregation under bias.[28] In addition, bias thresholds for the observation of halide segregation and perovskite degradation remained constant over a wide range of Br-I ratios, with distinct thresholds observed for segregation (likely anodic reaction of iodide oxidation) and degradation (involving anodic and cathodic electrochemical reactions and the loss of methylammonium halide).[28] The differences between illumination-induced and voltage-induced segregation and degradation could

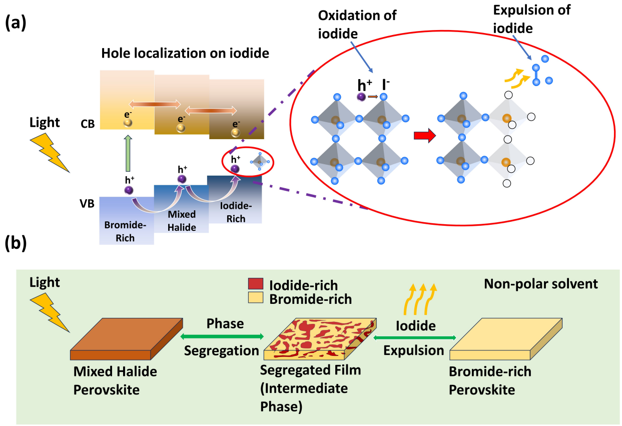

FIG. 2. (a) Schematic Illustration of (a) Hole localization on iodide, oxidation of iodide and expulsion of iodide,(b) Phase segregation and expulsion of iodide in the films. Reproduced with permission from Ref.[29], Copyright American Chemical Society 2022.

originate from fundamental differences between these processes as suggested,[28] or simply from a difference in distribution of excess charge carriers participating in the electrochemical reactions.

C. The role of electrochemical reactions in photoinduced phase segregation

According to the oxidation model, the critical part of the segregation/ion migration process is the oxidation of iodide by photogenerated (illumination stress) or injected (electrical bias stress) holes, as illustrated in Fig. 2.[29] Hole trapping as a starting point of the process was not only identified experimentally,[29] but also in simulations.[39] The oxidation of iodide results in the formation of a neutral iodine interstitial, followed by migration of iodide through vacancy hopping, and ultimately expulsion of iodine species (I_2, I^-, and I_3^-),[40] and irreversible changes due to iodine loss.[13,39] Molecular iodine formed as a result of redox reactions was proposed to readily migrate to the surface,[30] or remain in the film in the form of polyiodides.[41] It also has a key role in the degradation, as it can react with I^- to form triodide I_3^-, which deprotonates organic cation[42] resulting in volatile decomposition products and irreversible degradation.[41,42] Electron microscopy imaging has demonstrated that the loss of MA^+ results in an intermediate structure containing locally ordered vacancies ($MA_{0.5}PbI_3$), followed by the collapse of the perovskite structure into PbI_2.[43] Thus, the oxidation of iodide and deprotonation of organic cation represent basic electrochemical reactions that occur in the presence of excess charges in halide perovskites, although Pb^{2+}/Pb^0 and

I^-/I_3^- redox reactions were also proposed to drive photoinduced phase segregation.[13] Similarly, in mixed halides the iodide gets preferentially oxidized by the photogenerated holes since it has lower oxidation potential compared to bromide,[13,30] which can then result in phase segregation due to higher mobility of iodide compared to bromide.[2] The differences in diffusion rates/ion transport occur due to preferential oxidation of iodide by trapped holes, since smaller bromide ions should diffuse faster.[13]

D. The role of hole accumulation

Different types of experiments on thin films and devices have been performed to investigate this issue and provide evidence on the critical role of holes in photoinduced phase segregation and ion migration. For example, the relatedness between the two phenomena (segregation and ion migration) has been illustrated by the fact that the rate of iodide expulsion in the solvent was found to be strongly dependent on the rate of photoinduced segregation.[40] Furthermore, the applied bias was found to modulate photoinduced iodide expulsion from mixed metal halide perovskite, which was attributed to the control over hole accumulation.[44] Iodine expulsion is also observed under illumination, and the rate of the expulsion was dependent on the perovskite composition.[40] In other words, expulsion was observed for MA-based perovskite, while no expulsion is observed for Cs-based perovskite,[40] as illustrated in Fig. 3. It was also found that excess charge carriers and elevated temperatures accelerated perovskite degradation under illumination,[7] and that hole injection accelerated iodine diffusion.[45]

Additional evidence on the critical role of accumulated charge carriers and resulting electrochemical reactions in segregation/migration has been obtained from characterizing partial or full devices, i.e. examining the photostability in presence of one or more charge transport layers, hole transport layer (HTL) and/or electron transport layer (ETL). For example, more pronounced segregation is observed for perovskite on titania compared to zirconia, which has been attributed to the transfer of photogenerated electrons to titania, leaving behind excess photogenerated holes which lead to iodide oxidation and halide segregation.[46] The critical role of holes in this process is confirmed by the suppression of segregation by hole extraction,[46,47] perovskite stability dependence on HTL material used,[48] device degradation under nitrogen and in the dark,[49] different rates of degradation of hole-rich and electron-rich perovskites upon exposure to different atmospheres,[50] and observation of degradation at different interface between perovskite and charge transport layer,

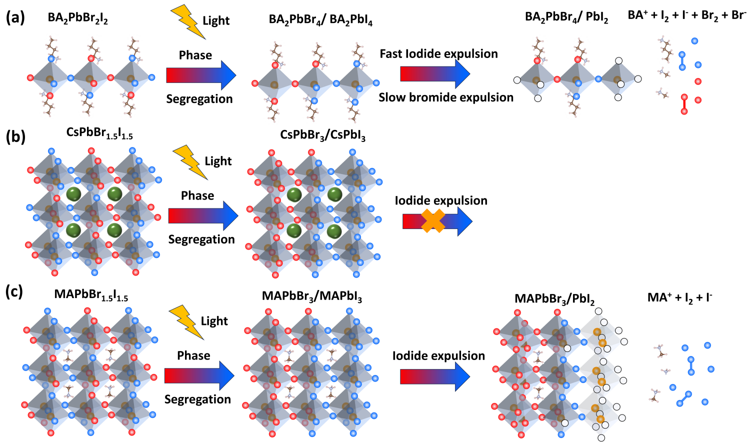

FIG. 3. Schematic illustration of A-Site cation effect on the iodide expulsion following photoirradiation of mixed halide perovskite films in dichloromethane (DCM), (a) BA, (b) Cs, and (c) MA. (a) is reproduced with permission from Ref.[52], Copyright American Chemical Society 2022. (b) and (c) are Reproduced with permission from Ref.[40] Copyright American Chemical Society 2020.

(either ETL/perovskite or perovskite/HTL interface, depending on ETL material used).[51] The electrochemical nature of the process was confirmed by the fact that the voltage thresholds for degradation (Au electrode oxidation at 0.8 V, MA reduction at 1.2 V) were independent on the perovskite film thickness and the choice of conductive oxide electrode and hole transport material.[49] Similar experiments on mixed halide perovskite films have confirmed that in mixed perovskites more easily oxidized halide species, i.e. iodide in I-Br mixed halide films, is preferrentially oxidized at the anode.[27] This results in iodide interstitials flux towards the cathode, while both bromide and iodide ions can move through the sublattice (vacancy mediated transport) towards the opposite electrode.[27] Consequently, unbalanced Br and I fluxes result in halide segregation.[27]

III. APPROACHES TO SUPPRESS PHASE SEGREGATION AND/OR ION MIGRATION

Since the ion migration is defect mediated, minimizing concentrations of native defects reduces ion migration. Perovskite quality can be improved and defect concentration reduced by adjusting processing conditions, composition, morphology, and crystallization, or by directly targeting defects using bulk additives, interface passivations, and/or interfacial layers, as illustrated in Fig. 4. Generally, larger grain sizes, fewer grain boundaries, and increased fraction of stable terminated

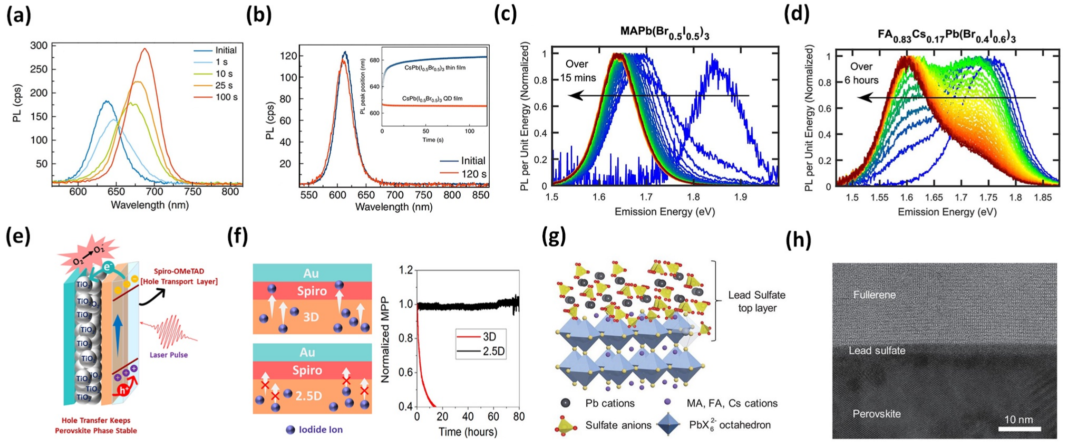

FIG. 4. Factors affecting photoinduced halide segregation and photostability. Effect of film morphology: (bulk film *vs*. nanocrystal film): Timeevolution of $CsPb(I_{0.5}Br_{0.5})_3$ (a) thin film and b) nanocrystal-based film emission spectra (PL, photoluminescence) under 405 nm continuous wave (CW) excitation (I_{exc} = 60 mW cm^{-2}). Inset in (b) displays $CsPb(I_{0.5}Br_{0.5})_3$ thin film and nanocrystal-based film emission peak position during illumination. Reproduced with permission from Ref.[53] Effect of erovskite composition: Normalized PL spectra for perovskite thin film coated with PMMA under a light of intensity of 190 mW cm^{-2}, wavelength 470 nm for (c) $MAPb(Br_{0.5}I_{0.5})_3$, 15 min. and (d) $FA_{0.83}Cs_{0.17}Pb(Br_{0.4}I_{0.6})_3$, 6h. Reproduced with permission from Ref.[54]. Copyright American Chemical Society 2021. (e) Illustration of the effect of hole extraction on the perovskite degradation (f) Illustration of the effect of interfacial layer on the perovskite degradation.

facets are expected to result in lower segregation/ion migration.[24] However, opposite trends have also been reported, for example in nanocrystal-based films,[53] as illustrated in Fig. 4a&b, which is likely due to passivated surfaces of nanocrystals. Other approaches to minimize defects include strain manipulation,[55–57] and composition optimization[17,54,58–60] These approaches can result in a reduced formation of halide vacancy defects,[23] increased activation energy for ion migration,[57,59] control of lattice distortion[58] and superior crystallinity resulting in the lack of fast ionic migration pathways.[54] An example of the effect of composition on photoinduced segregation is shown in Fig. 4c&d.[54] Photostability can also be improved by inclusion of a small amount of chloride[61–63] and by adjusting I:Br ratio.[64] The choice of charge transport layers can also affect the stability due to variations in charge extraction capability and charge accumulation. Efficient extraction of holes, and thus suppression of iodide oxidation, is expected to contribute to improved photostability, as illustrated in Fig. 4e.

A. Defect passivation

Defect passivation can be achieved by incorporating additives directly into perovskite precursor solution, incorporating additives into antisolvent, or applying other post-treatments of perovskite surface (such as spin-coating passivating agent on top of annealed perovskite film). For a detailed review of passivation molecules and strategies beyond the scope of this short review, see Ref.[25] Different additives can be used to control the crystallization of the perovskite film, improve homogeneity of the starting composition, and increase fractions of more stable grain terminating facets.[16,65,66] Additives capable of passivating both cationic and anionic defects[67,68] are of particular interest since multiple types of defects typically exist, and this type of additives has been shown to significantly suppress the segregation/ion migration and improve photostability of wide band gap perovskites. The additives reported to date include both organic and inorganic materials, which have a strong interaction either with defect sites or with different ions forming the perovskite, and thus accomplish one or more of previously outlined features (mediation of crystallization, passivation of defects, and/or adjusting energy level alignment at the interface).[69] For example, additives such as NaF have been proposed to suppress the formation of anion and cation vacancies by strengthening the chemical bonding in the perovskite.[70] Similarly, polyvinylpyrrolidone suppressed photoinduced segregation in an inorganic perovskite by passivating cationic and anionic vacancies.[67] In addition, the use of bis-diazirine molecules to immobilize organic cations by covalent bonding has also been reported.[71] The suppression of loss of volatile degradation products by immobilizing organic cations has resulted in significant improvement in PSC stability.[71] Another type of additives useful for stability improvement are redox additives, such as Eu^{3+}-Eu^{2+} redox shuttle that can oxidise reduced lead and reduce oxidized iodide defects at the same time.[72] As the electrochemical redox reactions are significant contributors to perovskite degradation, this approach to improve stability is particularly promising. The potential of redox additives to suppress undesirable electrochemical reactions is also illustrated by differences observed in devices with inert and "active" (more easily oxidized than iodide) metal electrodes, namely the suppression of segregation when "active" anode is used.[27]

B. Surface/interface modification

Passivation/modification of interfaces is particularly important at metal oxide/ perovskite interfaces, and suitably selected interface modifications typically lead to both improved device efficiency as well as improved stability, with reduced photosegregation and/or ion migration,[42,73,74] as illustrated in Fig. 4f. Various interface modifications/interfacial layers have been reported for suppressing the ion migration and improving stability, such as lead sulfate,[75] organometallic compounds,[76], thiols,[42] etc. The interface modifications are of critical importance to ensure long term stability, since the oxidation of iodide by photogenerated holes is only reversible if iodide stays within the perovskite film.[2] However, it should also be noted that interface passivation can also potentially have detrimental effects to the device stability if it results in unfavorable change in energy level alignment, causing charge accumulation and degradation of performance.[77] Thus, the molecules used need to be carefully optimised for a specific perovskite composition and device architecture to ensure not only interfacial defect passivation but also achieve more efficient charge collection and avoid charge accumulation.

C. 2D/quasi-2D perovskites

A variety of organic ammonium bulky cations, as well as preparation methods, have been reported for passivation/interface modifications using 2D /quasi-2D perovskite materials.[26] In these materials, n octahedral layers are separated by organic cations, where n=1 for 2D and $n > 1$ for quasi-2D materials (for large n values material properties approach those of 3D perovskites, and those cases are sometimes referred to as quasi-3D). In general, 2D perovskites can be used as additives to passivate defects,[78] and the spontaneous formation of 2D perovskite at grain boundaries suppresses ion migration,[79] or they can be used as interfacial layers. Interface modifications using 2D/quasi-2D perovskites can be used at either top or bottom interfaces between the perovskite and charge transport layers (depending on the device architecture for the optimal energy level alignment). Bottom interface modification has potential benefits of improved charge collection, defect passivation and improved perovskite crystal quality. However, to achieve full benefits of suppressed ion migration the use of 2D perovskite at the top interface is preferred to utilize lower rate of ion migration through the capping 2D/quasi-2D layer. In addition, it should be noted that for the most significant performance improvements, interface modification is necessary at both perovskite interfaces.[80] Such modifications not only can improve the device performance, but also significantly suppress ion migration[80] and improve device stability.[81] Ion migration in quasi-2D perovskites can be further suppressed using additives,[82] similar to the case of 3D perovskites.

There have been number of reports indicating that lower photoinduced segregation, lower ion migration, and lower density of mobile ions is observed in 2D and quasi-2D materials compared to 3D materials,[81,83–86]. The observed suppression was attributed to lower formation of vacancy-type defects[84] (similar to the case of over-stoichiometric cesium lead halide perovskite.[13]) and higher activation energies for halide migration.[87] As these materials typically have non-random halide distribution unlike 3D perovskites,[85] distribution of I and Br at preferred lattice sites was also proposed to contribute to the suppression of photosegregation.[88] Despite the observation of suppressed[83,89] or very slow photosegregation (over hours instead of minutes),[90] 2D/quasi-2D materials are still susceptible to photoinduced phase segregation and/or ion migration,[18,33,89,90] and remixing at room temperature can be inhibited due to increased energy barriers for ion migration.[85] The segregation is dependent on the spacer cation chemical structure,[91] due to the differences in the interactions between spacer cations, as well as lattice stiffness.[89,91] Butylammonium (BA)-based 2D materials in particular exhibit poor photostability, as the expulsion of not only iodide (fast), but also bromide (slow) is observed,[52] as illustrated in Fig. 3. In addition to spacer cation, stability in these materials is also dependent on the number of perovskite octahedral layers between the bulky spacer cations n.[83,92] As n increases, diffusion coefficients and halide mobility increase,[92,93] while the activation energy for halide migration decreases.[92]

Finally, while 2D and quasi-2D perovskites offer a possibility of lower ion migration (at least for some material compositions), the existence of multiple n phases (n is the number of octahedral perovskite layers separated by bulky cations) in thin films makes these type of materials complex and challenging due to competing phenomena affecting device efficiency and stability. The ideal quasi-2D mixed halide perovskite would exhibit uniform anion distribution with narrow n distribution, while in reality other combinations (one or both present: non-uniform halide distribution, wide n distribution) are common.[94] The simultaneous achievement of uniform halide and narrow n distribution is possible, but it requires careful spacer cation design to suppress phase separations.[94]

IV. STABILITY MILESTONES

While improved understanding of the photoinduced phase segregation and ion migration, as well as the interplay of different reversible and irreversible degradation processes under illumination, elevated temperature, and/or electrical bias, is still needed, huge advances in the stability have been achieved for PSCs. Although the stability testing in the dark still remains very common, the number of reports on operational stability under illumination, as well as outdoor testing following International Summit on Organic and Hybrid Photovoltaics Stability (ISOS) protocols has been increasing, and some of highly promising results have been achieved, such as T_{90}=1000 h, with initial PCE of 24.6% under ISOS-L-1 protocol and stability test up to 10000 h (ISOS-LC1 protocol).[2] In addition, there are examples of solar cells successfully passing damp heat and temperature cycling (International Electrotechnical Commission (IEC) standard: IEC61215:2016 standard tests), with 95% of initial efficiency retained after 1000 h of damp heat and 85% of initial efficiency retained after 200 cycles (-45°C, 85°C), respectively.[76] Most importantly, the number of reports on outdoor testing has been increasing. Outdoor testing milestones include 10 months under ISOS-O3 protocol with no measurable decay,[2] with testing times of working devices up to 8760 h (one year) reported.[95] Outdoor tests have been reported for individual cells (both $n-i-p$ and $p-i-n$ configurations), as well as tandem solar cells (up to 2000 h) and modules (up to 6552 h).[95] These these advances, there is a recognised need for further advances in the area of wide bandgap PSCs which are particularly affected by photoinduced segregation due to their high Br content, as well as narrow bandgap PSCs where the stability is negatively affected by the presence of Sn which is susceptible to oxidation.[2]

Similar to PSCs, stability of PeLEDs has improved significantly since early reports, and the mechanisms of degradation have been extensively studied (for a recent review of PeLED stability, see Ref.[96]). However, the achieved lifetimes are still much shorter compared to other light emitting diode (LED) technologies. While record lifetimes of the order of tens of thousands of hours have been reported for infrared[68] and green[97] PeLEDs, typical reported lifetimes (usually reported for 100 cd/m^2) range in hundreds of hours for the green, thousands of hours for the red, and tens of hours for the blue.[98,99] The lifetimes are even shorter at higher luminance, with reported figures below 1 h for blue, 11 h for green and 112 h for red, which is much shorter compared to organic LEDs at similar brightness.[100] This is significantly shorter than the requirement for commercialisation, i.e. half-lifetime T_{50} exceeding 10000-400000 h at luminance of 1000 cd/m^2.[99]

The operational stability is thus a more complex problem in LEDs, as they require charge injection and higher operating voltages compared to PSCs, which results in significant Joule heating as well as exacerbated ion migration.[100] Similar to other perovskite devices, some of the performance degradation can be reversible if mobile ions remain confined within perovskite layer and do not react with other components of the device, namely charge transport layers and electrodes.[100] Balanced charge injection is expected to be really critical not only for high efficiency but also for high operational stability, since charge accumulation would lead to electrochemical reactions in the perovskite. Improving perovskite layer quality and minimizing grain boundaries would also likely be beneficial, considering significant improvement in lifetime for single crystal green PeLEDs.[97]

V. CONCLUDING REMARKS AND FUTURE PERSPECTIVES

While great progress has been achieved in stability of perovskite thin films and devices, challenges in further stability improvements remain, in particular for PeLEDs and wide- and narrow-gap PSCs. The electrochemical reactions (oxidation of halide anions, reduction of cations) under illumination and bias are a fundamental feature of metal halide perovskite materials. Mitigating negative impact of these reactions is thus a significant challenge, as the bias, as well as illumination for PSCs, are unavoidable during device operation. Device architecture thus needs to be carefully optimized in order to avoid charge accumulation due to mismatch in transport of electrons and holes in the devices. Considering that devices commonly contain one inorganic charge transport layer and one organic charge transport layer, this is not a trivial problem due to vastly different conductivity of these types of materials. An ideal case would likely be the use of inorganic charge transport layers below and above the perovskite with similar charge transport properties, but this can be challenging due to deposition process constraints. Interface passivation for both interfaces would also be necessary considering that interfaces with inorganic (commonly metal oxide) charge transport layers often contain high concentrations of defects. In addition, bulk defect passivation and the use of redox additives to suppress undesirable electrochemical reactions is also highly desirable. The perovskite layer composition should also be optimized, to contain high fraction of Cs, and possibly small amount of Cl. This would require careful optimization of not only perovskite film composition but also the deposition conditions to obtain desired morphology and crystallinity. in terms of the stability milestone challenges, it should be noted that PSCs are closer to meeting the requirements, with increased demonstration of long term stability. In contrast, PeLED lifetimes are still typically orders of magnitude behind the requirement for commercialization and will be far more challenging to improve, due to operating voltages typically above thresholds for electrochemical reactions. Significant breakthrough in defect passivation, redox additives, and the use of blocking layers preventing the loss of volatile reaction products, combined with improvements in charge transport layers used, are needed to achieve significant lifetime improvements in PeLEDs based on polycrystalline films.

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