TOPICAL REVIEW

Operational stability of perovskite light emitting diodes

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Abstract

Organometal halide perovskite light emitting diodes (LEDs) have attracted a lot of attention in recent years, owing to the rapid progress in device efficiency. However, their short operational lifetime severely impedes the practical uses of these devices. The operating stability of perovskite LEDs are due to degradation due to ambient environment and degradation during operation. The former can be suppressed by encapsulation while the latter one is the intrinsic degradation due to the electrochemical stability of the perovskite materials. In addition, perovskites also suffer from ion migration which is a major degradation mechanism in perovskite LEDs. In this review, we specifically focus on the operational stability of perovskite LEDs. The review is divided into two parts: the first part contains a summary of various degradation mechanisms and some insight on the degradation behavior and the second part is the strategies how to improve the operational stability, especially the strategies to suppress ion migration. Based on the current advances in the literature, we finally present our perspectives to improve the device stability.

1. Introduction

Organometal halide perovskites have been regarded as a promising candidate for the next-generation semiconducting materials for optoelectronics, and considerable progress has been made in the development of light emitting diodes (LEDs) in recent years [1, 2]. Perovskites are a type of semiconducting material with a chemical formula of ABX₃, where A is an organic cation, B is a divalent metal cation (Pb²⁺ and Sn²⁺), and X is halide (Cl⁻, Br⁻ and I⁻). The crystal structure of perovskites can be viewed as a framework of corner-sharing octahedra (PbX₆), where the organic cations fit into the interstitial sites. The crystal system can be cubic, tetragonal or orthorhombic depending on the composition and temperature [3]. In addition to organic cations such as methylammonium (MA) and formamidinium (FA) cations being used as an A site cation, Cs⁺ is also used to synthesize all-inorganic perovskites [4]. For the B site divalent metal cation, due to the toxicity of Pb, Sn has also been used as an alternative to synthesize lead-free perovskites [5]. Each lattice site can be a mixture of different ions (mixed MA⁺, FA⁺ and Cs⁺, mixed Pb²⁺ and Sn²⁺, and mixed halide), providing a large tunability of the electronic and optical properties.

In the last several years, perovskites have been used for photovoltaics application because of their high power conversion efficiencies. More recently, they are also considered for LED applications for the following reasons. First, organometallic halide perovskites are direct bandgap semiconductors whose bandgap can be tuned across the entire visible spectrum by varying the halide composition [6, 7], with the emission wavelength decreasing as the sequence of I, Br and Cl [6, 7]. Second, perovskites have a high defect tolerance [8–11], with most defects introduced during fabrication being shallow defects that do not contribute to non-radiative recombination and charge trapping. In fact, some shallow defects give rise to self-doping, leading to an improved electronic conductivity [12]. Third, the photoluminescence quantum yield (PLQY) of perovskites can be high (up to 90%) [13], which is an important criterion for a high efficiency LED. Forth, the emission linewidth of perovskites is narrow, with a full width at half maximum (FWHM) below 20 nm [14]. This high color purity is a distinct advantage over organic LEDs where the FWHM of the emission spectrum is typically larger than 70 nm. Lastly,
the solution processability of perovskites makes the fabrication process compatible with roll-to-roll processing. Based on these unique properties, research interest on perovskite LEDs has been gaining momentum in recent years. The first perovskite LEDs was demonstrated in 2014 with an external quantum efficiency (EQE) less than 1%\(^{15}\). After that, intense efforts have been devoted to increase the efficiency of perovskite LEDs\(^{16–21}\). More recently, most studies focus on low-dimensional materials such as nanocrystal perovskites\(^{20}\) and quasi-2D perovskites\(^{19,21}\) due to quantum confinement resulting in a large exciton binding energy which promotes bimolecular radiative recombination\(^{22}\). Various strategies have been employed such as compositional engineering\(^{18,19}\), defect passivation\(^{20,21,23,24}\), optimized device structure\(^{17}\) and light extraction\(^{16}\) to improve the device efficiency, leading to an EQE value exceeding 20%\(^{16,17}\).

Despite the high efficiency achieved, the practical use of perovskite LEDs is severely hindered by their poor stability. In fact, it is not uncommon to see perovskite LEDs with an operational lifetime less than a few minutes. Many factors contribute to the degradation of perovskite LEDs\(^{25}\). Degradation that originates from the interactions of perovskite with moisture and oxygen in ambient can be effectively suppressed using standard encapsulation techniques\(^{26}\). On the contrary, the intrinsic degradation induced by electric field during device operation is related to the intrinsic properties of the perovskite materials. Recent studies on the intrinsic degradation mechanisms of perovskite LEDs indicate that ion migration is the first order root cause for their short operational lifetime\(^{25}\). Ion migration also exists in perovskite photovoltaics (PVs). However, due to the low field present during operation, ion migration does not appear to be a severe problem affecting the operational lifetime of perovskite PVs\(^{27}\). On the contrary, it is not uncommon to see a perovskite LED degrades to half of their initial efficiency within hours\(^{16,18,28,29}\) or even minutes\(^{17,30–34}\) due to ion migration under an applied electric field. In addition, perovskite can undergo electrochemical reactions driven by charge injection, leading to interfacial degradation and perovskite decomposition\(^{35}\). In addition to the degradation induced by applied bias, spontaneous interfacial reactions between perovskite and other functional layers is also a mechanism that leads to device degradation\(^{36–40}\). We also noted that photo stability and thermal stability of perovskite materials may play a role in the operational stability of perovskite LEDs. However, we believe these two are secondary factors. For example, the lifetime of perovskite PVs under continuous illumination of AM 1.5 at 60 °C can exceed 1000 h\(^{27}\), indicating that photo stability and thermal stability are not the bottleneck problems for perovskite LEDs. Furthermore, in perovskite LEDs, the Joule heat generated during device operation only raises the temperature to around 40 °C, which is not enough to trigger thermal decomposition of perovskite\(^{34}\). Nevertheless, ion migration can be accelerated due to the increase in temperature, leading to a shorter lifetime. Therefore, ion migration, electrochemical reactions and interfacial reactions are the first order degradation mechanisms in perovskite LEDs, and operational stability is a major obstacle that perovskite LEDs need to overcome. While efforts have been devoted to improving the operational stability through compositional engineering, defect engineering and device architecture engineering\(^{28–33}\), very little progress has been made to date. In order to accelerate this progress, a comprehensive understanding on the degradation mechanisms in the operation of perovskite LEDs is needed.

To date, an in-depth understanding of the degradation mechanisms of perovskite LEDs is still lacking. Different mechanisms have been proposed to describe the degradation of perovskite films under electric field. However, direct studies on the degradation mechanism of LEDs are limited\(^{25}\). Here, we will focus on the operational stability of perovskite LEDs, and the review is divided into two parts. We first begin with a summary of different degradation mechanisms proposed so far and categorize them into ion migration, electrochemical reactions, and interfacial reactions. We will discuss the reversible and irreversible degradation for each mechanism and provide a guideline that helps analyze the results. In the second part, we present the progress made on improving the operational stability, especially the strategies for suppressing ion migration since it is the main reason for device degradation. Lastly, based on the current progress made in the literature, we provide our perspectives for future research to address the stability issue.

2. Mechanisms of device degradation

The degradation mechanisms of perovskite LEDs are divided into three categories: (i) Ion migration, (ii) electrochemical reactions and (iii) interfacial reactions, as summarized in figure 1. As the first order root cause of device degradation, ion migration inside perovskites can lead to defect migration\(^{41–44}\), annihilation and creation of halide Frenkel defects\(^{45–49}\), modification on charge injection\(^{50–54}\) and distortion of crystal lattice\(^{35,43,49,55}\) (figure 1(a)), while ion migration across the interface can lead to corrosion of electrodes\(^{36,56–61}\) (figure 1(b)). Electrochemical reactions driven by charge injection lead to a decomposition of perovskites into PbI\(_2\) at the anode interface\(^{35,49,62}\) and a formation of deep traps (Pb\(^{\square}\) interstitials) at the cathode interface\(^{63}\) (figure 1(c)). Spontaneous chemical reactions between perovskites and other materials in contact with perovskites including metals\(^{36,37}\), indium-tin oxide (ITO)\(^{38}\), charge transport materials such
as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) \cite{39} and zinc oxide (ZnO) \cite{40} also lead to device degradation (figure 1(d)).

2.1. Ion migration

Halide perovskites possess a mixed electronic and ionic conductivity \cite{50, 64}. To understand the ionic conductivity of perovskites, both experimental \cite{35, 65–67} and theoretical \cite{64, 68–71} studies have been conducted. Yuan et al observed the formation of PbI$_2$ at the anode side in a lateral device structure under an external bias and its propagation towards the cathode has been studied by energy-dispersive x-ray spectroscopy (EDX) mapping, which is a direct experimental evidence for halide ion migration \cite{35}. In another work, the same authors observed an accumulation of methylammonium ions (MA$^+$) at the cathode side by photothermal induced resonance microscopy, showing that MA$^+$ is also mobile \cite{65}. To understand the ion migration mechanisms, various groups have performed computations and found that the activation energies of halide ion and MA$^+$ migration are in the range of 0.1–0.6 eV and 0.5–1.0 eV respectively \cite{64, 68–70}, confirming the possibility of ion migration in perovskites. On the other hand, the activation energy of Pb$^{2+}$ migration has been calculated to be larger than 1.0 eV \cite{64}, which is too large to be mobile. The low activation energy of halide ion migration makes it the most likely mobile ionic species in perovskites, and the main reason for various phenomena reported, including hysteresis in PVs \cite{72}, giant switchable photovoltaic effect \cite{73}, fluorescence intermittency \cite{74}, photo-or-electric-induced enhancement in photoluminescence (PL) \cite{45, 47}, polarity-switchable charge injection \cite{50, 52}, and phase segregation \cite{75, 76}.

Given that ion migration is a thermally activated process, the common approach to determine the activation energy experimentally is to conduct temperature dependent measurements such as impedance spectroscopy \cite{50}, ionic conductivity \cite{77} transient current \cite{78} and transient capacitance \cite{79}. However, the activation energies obtained by different groups show a large discrepancy ranging from 0.1 to 1.0 eV. Meggiolaro et al attributed this discrepancy to the difference in grain size of perovskites fabricated by different groups \cite{70}. Through computation study, they found that defect formation is facilitated at grain boundaries, indicating that smaller grain sizes leads to a lower activation energy due to a larger grain boundary surface area \cite{70}. In other experimental works, ion migration along the grain boundary has also been found to be faster and more prevalent compared to the pathways in the grain interior \cite{66, 80}, supporting the argument of grain-sized-dependent activation energy.

To better understand the role of ion migration on device stability, we classify ion migration in perovskite LEDs into two categories: ion migration inside the perovskite layer and ion migration across the interfaces.
should be noted that these two processes can coexist, complicating the analysis on the degradation mechanism of a perovskite LEDs.

2.1.1. Ion migration inside perovskite

Ion migration inside perovskites can lead to: (i) defect migration [41–44], (ii) annihilation and creation of Frenkel defects [45–49], (iii) modification on charge injection [50–54] and (iv) distortion of crystal lattice [35, 43, 49] (figure 1(a)). In the following discussion, we will show that the first three consequences can give rise to partial reversible changes in device efficiency, while the last one can occur under high driving voltage or prolonged operation, resulting in a completely irreversible degradation. The coexistence of different degradation phenomena induced by ion migration makes the degradation mechanism more complicated.

Ion migration is intrinsically a defect migration. To understand how the migration of defects affects device efficiency, we need to understand the defect chemistry of halide perovskites. From the results of computation study, it has been suggested that most point defects formed in perovskites are shallow defects that do not contribute to non-radiative recombination, except for Pb0 and halide interstitials whose energies are close to the mid-gap energy [9, 11]. As mentioned previously, Pb is not considered to be mobile due to the high activation energy [64]. Therefore, halide ions play the dominant role in affecting the device efficiency through ion migration. The migration of halide interstitials causes a change in the distribution of quenching centers in the perovskite [41–44]. Deng et al reported an electric field induced reversible PL quenching in perovskites under low electric field observed through PL microscopy on a lateral device (figure 2) [43]. They found that the PL efficiency of the perovskite film at the anode decreases with time, which is attributed to the accumulation of halide interstitials at the anode [41, 42, 44]. The decrease in PL efficiency can be recovered by removing the external bias, allowing the halide ions to diffuse back to the original distribution [43]. When the applied electric field was increased to a certain value, irreversible PL quenching was observed, and the formation of PbI2 is an indication of decomposition of perovskites [43]. In this case, distortion of crystal lattice is induced by ion migration under such a high electric field and the degradation becomes irreversible. In addition to the accumulation of halide interstitials, Cheng et al suggested that excess halide vacancies compensated by electrons can reduce Pb0 to Pb2+ which also contributes to PL quenching at the anode side [44]. Although these studies were conducted on a lateral device structure, these phenomena can help visualizing the effects of ion migration on perovskite LEDs. If the recombination zone in a perovskite LED is close to the anode, applying a forward bias can drive halide interstitials toward the recombination zone, resulting in a degradation in the device efficiency. This degradation can also be recovered by either applying a reverse bias to drive the halide interstitials away from the recombination zone, or by removing the bias to allow halide ions to diffuse back to their original distribution. On the contrary, if the recombination zone is close to the cathode interface, applying a forward bias leads to a reversible increase in device efficiency due to the migration of halide interstitials away from the recombination zone. We speculate that this mechanism could be one of the reasons for the dependence of scan rate, scan direction and pre-bias history on device efficiency. However, further study is required to better understand this phenomenon.

Figure 2. PL image of perovskite in a lateral device structure under different electric field. The PL quenching at anode site is reversible at low electric field (<0.9 V μm⁻¹). Reproduced with permission [43]. Copyright 2016, Royal Society of Chemistry.
In addition to the migration of defects, reversible degradation can also be originated from annihilation and creation of halide Frenkel defects [45–49]. Several groups have reported photo-induced PL enhancement in perovskites, and they attributed this phenomenon to annihilation of halide Frenkel defects driven by ion migration (figure 3(a)) [45, 47]. Under photoexcitation, ion migration is promoted by trap-filling-induced electric field such that halide vacancies and halide interstitials can migrate and meet in the perovskite and annihilate to reduce defect density [45]. The reduced defect density through this bimolecular recombination leads to an increase in PL efficiency. When perovskites are stored in the dark for some time, the PL efficiency decreases due to ion back-diffusion [45]. Similar phenomenon has also been observed by applying an electrical stress on perovskite LEDs [46, 48]. Zhao et al reported a reversible increase in device efficiency by applying a short-term electrical stress (figure 3(b)) [46]. The authors found that both the PL efficiency and PL decay lifetime were improved after electrical stress, indicating a decrease in defect density. In this case, the reversible enhancement in efficiency is attributed to annihilation of halide Frenkel defects at grain boundaries. Similar to the photo-induced PL enhancement, when they remove the bias for several days, the device efficiency drops due to a recreation of Frenkel defects driven by ion back-diffusion. The efficiency can be recovered by applying a short-term bias to the device again. However, when the bias is extended up to 15 min, there is an irreversible degradation which could be partially attributed to distortions of crystal lattice under such a prolonged operation.

Lastly, ion migration can modify the charge injection in perovskite LEDs, leading to a reversible change in device efficiency [50–54]. Studies on how ion migration affects charge injection and electroluminescence (EL) of perovskites have been reported by several groups. Zhang et al sandwiched a perovskite layer between two high work function electrodes, where EL can be achieved by injecting electrons or holes from either direction [50]. They attributed this polarity-switchable-EL to ion migration in the perovskite film and regarded the device as light emitting electrochemical cells (LEC). The formation of an LEC is due to ion accumulation at the electrode interface by an applied field, modifying the charge injection barrier, such that charge injection can be facilitated regardless of the energy offset at the electrode/perovskite interface. Similar results have also been reported by Andričević et al where a single crystal perovskite was used as an emitter and vertically aligned carbon nanotubes were used as electrodes [52]. In their study, charge injection can be improved by electrically poing the device, and the change in charge injection is reversible (figures 3(c) and (d)). Bandiello et al directly studied the effects of ion migration on EL efficiency of perovskites [51]. They found that the device efficiency was improved by

![Figure 3.](image-url)
applying a pre-bias and ascribed this phenomenon to the improved charge injection induced by ion migration. However, they cannot rule out the possibility that the enhanced efficiency could also be due to migration of defects or annihilation of Frenkel defects as was discussed previously. More research is needed to differentiate these different processes and understand the interplay of these mechanisms in the operational stability of perovskite LEDs.

2.1.2. Ion migration across interface

Ion migration across the interface in perovskite LEDs can result in irreversible degradation through corrosion of electrode [36, 56–61] (figure 1(b)). Both MA$^+$ and halide ions can migrate through the organic interlayer, allowing the halide ions to react with metal electrodes such as Al and Ag, forming insulating components (AlI$_3$ and AgI) at the electrode interface [56, 60]. This ion migration process has been widely examined by several groups using time-of-flight secondary ion mass spectroscopy (figures 4(a) and (b)) [56, 60] and energy dispersive x-ray spectroscopy [57]. In those experiments, the concentration of halides was found to increase in the electrode as well as the organic interlayer after electric poling. In addition, the formation of silver halide in the silver electrode has also been confirmed by x-ray photoelectron spectroscopy (XPS) (figure 4(c)) [59, 61] and x-ray diffraction (figure 4(d)) [81].

The corrosion of the electrode has several impacts on the device stability. First, the formation of insulating components inhibits charge injection, leading to a failure of EL in some regions, shown as dark spots [56]. Second, the consumption of halide ions at the electrode interface provides a driving force for ion extraction, further facilitating the crossing of ions from the perovskite layer to the metal electrode [60]. Third, since grain boundaries are the main channel of ion migration, the loss of ions starts from grain boundary surfaces and forms a pathway which can grow geometrically and finally evolve into pinholes leading to the formation of shunt paths and hence dark spots [56, 60]. Lastly, the loss of halide ions and MA$^+$ can initiate perovskite crystal decomposition, which affects charge transport and increases defect density, leading to a decrease in device efficiency.

In addition to the corrosion of electrode, halide ions migrating into charge transporting layers can modify their transport properties, thus affecting device efficiency. Lee et al reported a quasi n-doping effect of phenyl-C$_{61}$-butyric acid methyl ester (PCBM) by infiltration of iodine ions in perovskite solar cells [82]. The doping effect is given by a thermodynamically favored formation of PCBM-halide radical. Due to the n-doping effect, the electron transport of PCBM is enhanced. In addition, the molecular packing of the PCBM was also
changed from random to ordered structure through a strong interaction with the infiltrated iodine ions, leading to an increase in the open circuit voltage. Carrillo et al. studied the reaction between iodine ions and 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl) amino]-9,9′-spirobifluorene (spiro-OMeTAD) [83] which is usually used as hole transporting layer (HTL) in perovskite devices. As we know, partial oxidation is required to improve the hole conductivity of spiro-OMeTAD by forming spiro-OMeTAD\(^+\). However, iodine ions can reduce these oxidized molecules into neutral species, leading to a decrease in hole conductivity [83]. In addition to PCBM and spiro-OMeTAD, halide ions can also migrate into other organic layers such as 2, 2′,2″-(1, 3, 5-Benzinetriyl) -tris (1-phenyl-1-H-benzimidazole) (TPBi) [56] which is commonly used as electron transporting layer (ETL) in perovskite LEDs. However, the impact of the interactions of halide ions with TPBi has not been revealed yet. Therefore, further studies are needed to understand its impact on device stability.

### 2.2. Electrochemical reaction

Perovskites can undergo electrochemical reactions under external bias [35, 49, 62, 63], which is another degradation mechanism in perovskite LEDs (figure 1(c)). Electrochemical reactions in perovskites can happen at both the anode and cathode interfaces. At the anode interface, these reactions lead to interfacial degradation and it propagates towards the bulk of perovskite through ion migration [35]. Several studies have shown the formation of PbI\(_2\) at the anode side in a lateral device structure [35, 49, 62] (figure 5). The electrochemical reaction was proposed as follows [35]:

\[
\text{MAPbI}_3 \rightarrow \text{PbI}_2 + \text{MA}^+ + \Gamma, \quad (1)
\]

\[
2\Gamma \rightarrow \text{I}_2 \uparrow + 2e^-. \quad (2)
\]

The escape of iodine gas makes the degradation irreversible. Although a direct study of electrochemical reactions in the degradation of perovskite LEDs is lacking, we speculate that the formation of insulating PbI\(_2\) at the anode interface can impede hole injection, leading to a shift of recombination zone towards the anode and the decomposition of the perovskite film at the anode interface generates defects resulting in EL quenching. However, during device operation the degradation mechanism can be further complicated by ion migration as we discussed in the last section. Therefore, more efforts should be devoted to a comprehensive understanding of the degradation mechanisms of perovskite LEDs.

As for the cathode electrochemical reaction, Birkhold et al. observed a decrease in PL efficiency at the cathode side in a lateral device structure under external bias, and this can be recovered by removing the bias [63]. To understand whether this phenomenon is only due to ion migration, they blocked charge injection by inserting a thin insulating layer between the perovskite and the electrodes, then applying the external bias. In this case, ion
migration still occurred, but PL quenching was not observed. Therefore, the authors proposed that the decrease in PL efficiency at the cathode interface is due to an electrochemical reaction that reduces the Pb$^{2+}$ interstitials into Pb$^0$. According to the computation results, Pb$^{2+}$ interstitials are shallow defects which do not contribute to non-radiative recombination, while Pb$^0$ are deep traps that can quench PL [63]. It should be noted that this electrochemical reaction also requires the help of ion migration since the crossing of halide ions from the cathode side that allows the Pb$^{2+}$ to be reduced. Considering that this process is reversible, it could potentially contribute to a reversible degradation behavior in perovskite LEDs. However, a detailed study is required to differentiate it from other ion migration processes that can also give rise to reversible degradation.

2.3. Interfacial reaction
Spontaneous interfacial reactions in perovskite LEDs are another reason for irreversible device degradation [36–40] (figure 1(d)). Unlike ion migration and electrochemical reactions, this process does not require an external bias. As mentioned in the previous section, halide ions can react with metal electrodes (Al and Ag) through migration across the organic interlayer. Therefore, a spontaneous chemical reaction occurs when perovskite is in direct contact with these metals [36]. Reactions between perovskite and noble metal Au have also been reported [36, 37]. In this case, a type of reduction/oxidation reaction termed underpotential deposition is involved, wherein Au functions as a catalyst leading to decomposition of perovskite [37]. In addition to metals, perovskites can also react with an ITO electrode. Kerner et al found that ITO can be readily etched by perovskite, releasing In$^{3+}$ ions into the perovskite layer [38]. The authors observed In$\text{I}_3$ by XPS at the top surface of the perovskite film deposited on ITO after thermal annealing.

PEDOT: PSS is a commonly used hole injection layer in perovskite LEDs. However, the acidic nature of PEDOT: PSS can etch ITO electrode [84], releasing In and Sn metallic species that diffuse into perovskite layer. These metallic impurities of In and Sn in perovskites act as non-radiative recombination centers, leading to a decrease in device efficiency. In addition, PEDOT: PSS can also react with perovskite through adsorption of moisture during fabrication process [39]. The water molecules in PEDOT: PSS can initiate the decomposition of perovskite [85], leading to interfacial degradation.

Perovskites can also decompose in to PbI$_2$ at elevated temperatures when in direct contact with ZnO [40]. This interfacial reaction can happen during the fabrication process where thermal annealing is required to facilitate crystallization and during the device operation where carrier recombination generates Joule heat. Two mechanisms have been proposed for such a reaction: one is the residual hydroxide on the ZnO surface leading to the decomposition of the perovskite; another is the deprotonation of methylammonium cation by the surface oxygen of ZnO [40].

In summary, the degradation mechanism of perovskite LEDs is complex, involving different processes (ion migration, electrochemical reactions and interfacial reactions) which are not independent and can interplay leading to device degradation. As we can see, ion migration not only is the main reason of device degradation, but also plays an important role in the other two processes. The continuous progress of the electrochemical and interfacial reactions requires mass transport via ion migration. The contribution of each process can vary with different device structures, charge balance, perovskite compositions and driving conditions, leading to different degradation behaviors. In stability studies, some devices show a continuous degradation while others show an initial increase in efficiency followed by a decrease when subjected to prolonged operation; some degradations are reversible while some are not. To clarify the origin of the difference, we summarize the degradation behavior of different processes in table 1. This table provides a basic guideline that can help analyze the diverse degradation behaviors in the stability test of perovskite LEDs.

3. Strategies to improve operational stability
Given that ion migration is the main reason for device degradation, suppressing ion migration has become the main strategy to improve the operational stability. According to the pathways of ion migration, we divide the strategies into three categories: suppressing bulk ion migration, suppressing grain boundary ion migration and suppressing interlayer ion migration. The first two strategies tackle ion migration inside the perovskite film, while the third one tackles ion migration across the interface. It should be noted that the electrochemical reactions can also be suppressed by suppressing ion migration inside perovskite, and the interfacial reactions can be eliminated by incorporating ion blocking layers that are used to suppress interlayer ion migration.

3.1. Suppressing bulk ion migration
Ion migration in the bulk of perovskite is mainly through point defects such as vacancies and interstitials. Two approaches can be employed to suppress bulk ion migration: one is to reduce the bulk defect density, and another is to increase the ion migration barrier. They can be realized through A-site and B-site compositional
engineering, and through forming quasi-2D perovskite. It is important to note that halide segregation in mixed-halide films is induced by bulk ion migration as experimentally shown by Barker et al [86]. Therefore, suppressing bulk ion migration not only improves the device lifetime, but also enhance spectral stability in a mixed halide perovskite LEDs.

### 3.1.1. A-site engineering

The A-site composition in Perovskite LEDs can affect the ease at which ion migration occurs within the bulk material [87–89]. Many studies have been conducted to shed light on the influence of organic (MA+ and FA+) [87, 88, 90] and inorganic (Cs+ and Rb+) [91–93] cations in pristine and mixed conditions for perovskite materials. Devices with different single-cation and mixed-cation perovskites are compared to highlight the impact of the A-site composition on the operational stability.

Despite FA+ being 23% larger than MA+, the unit cell volume for FAPbBr3 is only 4% bigger than that of MAPbBr3 [87]. The higher density of the former structure already suggests there is less available space for ions to migrate within the lattice. Oranskaia et al conducted a comprehensive study on the influence of these organic cations on ion migration and halogen vacancy using density functional theory (DFT) calculations [87]. Their study revealed that the formation energies for bromide vacancies and bromide interstitials are lower for MAPbBr3 than that of FAPbBr3, resulting in a higher defect density in MAPbBr3. The computation results are also supported by the experimental results reported by Zhukekenov et al where the trap density in MAPbBr3 is about 3 times higher than that of FAPbBr3 [88]. The authors conducted space-charge-limited current (SCLC) measurements on single crystal perovskites (MAPbBr3 and FAPbBr3) and extracted the trap density of each through fitting on the trap-filling region of the SCLC curves. A lower trap density is significant since ion migration is essentially defect migration. Furthermore, the ion migration barrier when using FA+ is larger than that of MA+, which was attributed to its stronger H-bonding between H and Br [87]. Therefore, using FA+ in perovskite LEDs is expected to give a better operational stability. Additionally, using Cs+ can also suppress bulk ion migration. Zhou et al reported that the ion migration barrier of MAPbI3 (0.07 eV) was much smaller than that of CsPbI2Br (0.45 eV) under illumination [94]. This resulted in an improved operational stability in CsPbI2Br solar cells having an operating lifetime 30X better than MAPbI3 cells.

The operational stability of perovskite LEDs can be improved by mixing A-site cations, which helps decrease trap densities [31, 95], as shown by Lee et al [96] using admittance spectroscopy to determine the trap densities of FAPbI3 and FA0.45Cs0.17PbI3. Xie et al demonstrated that the addition of FA+ into CsPbBr3 resulted in an enhanced operational lifetime in perovskite LEDs, which was attributed to a reduced trap density [31]. Yang et al achieved a more significant operational stability improvement with a partial substitution of Cs+ in a FA+ based perovskite LED [28]. The mixed-cation perovskite LED had a lifetime of ~31 h in contrast to ~1 h for the device without Cs+ addition under a constant current density of 10 mA cm⁻². The suppressed ion migration in this mixed halide device was evident from its constant PL intensity under cyclic voltages as compared to the device without Cs+ that demonstrated a slower recovery of PL, reflecting the influence of ion migration. In addition, mixing Cs+ with MA+ or FA+ also causes a lattice contraction due to its smaller radius of 1.81 Å [93]. This, in turn, enhances the interaction of the A-site cation because of the lattice contraction [97]. Tennyson et al compared the Voc of MAPbBr3 and mixed-cation mixed-halide Cs0.06(MA0.83FA0.17)0.94Pb(I0.83Br0.17)3 solar cells [98]. It was shown that for MAPbBr3, the ion migration of the Br ions resulted in hysteresis whereas this was

| Degradation behavior                      | Reversible/Initial increase | Irreversible               |
|------------------------------------------|----------------------------|-----------------------------|
| Ion migration inside perovskite           | · Defect migration          | · Distortion of crystal lattice |
| · Annihilation and creation of Frenkel defects |
| · Modification on charge injection        |                           |                             |
| Ion migration across interface            |                           | · Corrosion of electrode     |
| · Interaction with charge transporting layer|
| Electrochemical reaction                  | · Cathode reaction         | · Anode reaction             |
| Interfacial reaction                      |                           | · Metals, ITO, PEDOT: PSS, ZnO |

Table 1. Summary of the degradation behavior of different processes.
not the case for the mixed A-site solar cell. The suppressed ion migration was attributed to the lattice strain induced by the smaller radius of the Cs cation. The mixing of Rb cations with other A-site cations have also been reported to decrease the defect density in the perovskite films [91, 99]. Kanwat et al reported the formation of large defect-free crystals with the addition of Rb⁺ in a MAPbBr₃ solution [91]. It was also shown that when adding 5% of Rb⁺ to (FA)₉.75(MA₀.₁₈Cs₀.₈₂)₀.₃₅Pb₁₂Br, the defect density decreased due to an enhanced crystallinity, resulting in reduced hysteresis in a solar cell [99]. The reduction in trap densities in these mixed A-site cations can hinder ion migration, which in turn, can enhance the operational stability in perovskite LEDs.

### 3.1.2. B-site engineering

Compared to the A-site engineering, less attempts of B-site engineering have been used to suppress bulk ion migration. The B-site cations are coordinated by six X-site anions, hence forming a [BX₆]⁴⁻ octahedron. Partial doping of B-site ions has been investigated with metal ions such as Mn²⁺ [30, 100–102], Zn²⁺ [101], Ni²⁺ [103], Bi³⁺ [104–106], and Nb⁵⁺ [103].

Introduction of Mn²⁺ can reduce the defect density in perovskites, thus suppressing ion migration and hence leading to an improved operational stability [30, 102, 106]. Gangishetty et al reported enhanced operational stability and spectral stability in red and sky-blue mixed-halide perovskite LEDs through the partial doping of Mn²⁺ ions [30]. The PLQY and time-resolved PL data suggest that the introduction of Mn²⁺ decreased the trap density, results in reduced ion migration. As a result, a 15% addition of Mn²⁺ in the red perovskite LED increased the operational lifetime ($T_{50}$) from less than a minute to over 5 h under a constant current density of 3 mA cm⁻². Under the same conditions, a 30% addition of Mn²⁺ in the sky-blue device increased the operational time from a few seconds to 24 min. Additionally, mixing Mn and Zn ions in CsPb₂Br₃ can also reduce the trap density [101]. Defects in this same crystal structure were also suppressed with the proper doping ratio of Nb⁵⁺, as the solar cell using this perovskite had a reduced hysteresis [103]. Other metals such as Ni²⁺ can have the same effect as demonstrated by Yong et al from the increase in the PLQY of perovskite nanocrystals from 2.4% to near unity with the introduction of 11.9% of Ni²⁺ in CsPbCl₃ [107]. Their DFT calculations revealed that the introduction of Ni²⁺ increases the defect formation energy of all the constituents. Furthermore, at low Bi³⁺ concentrations, lower trap densities were also reported for CsPb₀.₃₆Bi₀.₆₄I₃ films [105] and CsPbCl₃ nanocrystals (0.6% Bi³⁺) [106].

### 3.1.3. Quasi-2D perovskite

Adding bulky organic cations in the precursor to form quasi-2D perovskites has become an important strategy not only to fabricate high efficiency perovskite LEDs, but also to improve the device stability. The bulky organic cation layers that separate inorganic octahedra sheets in the quasi-2D perovskites function as an ion migration barrier along the out-of-plane direction such that ion migration is suppressed [108]. Results of theoretical calculation indicate that ion migration along the in-plane direction is also suppressed due to an increase in the defect formation energy compared to that of 3D perovskites [109]. Therefore, ion migration can be suppressed in quasi-2D perovskite, leading to an improved operational stability [110].

Lin et al experimentally demonstrated that ion migration is suppressed along the out-of-plane direction both in the dark and under illumination in quasi-2D perovskite films as compared to 3D perovskite films [108]. The comparison of the temperature dependent conductivity was done for the quasi-2D perovskite film (BA)$_n$(MA)$_{3-n}$PbI$_3$ ($n = 4$) and the 3D film MAPbI₃, and the results show that as the temperature increases, the 3D film displays a clear transition of electron dominated conductivity to ion dominated conductivity, whereas for the 2D layered perovskite film this transition was not observed, indicating an increased activation energy of ion migration in quasi-2D perovskites. For ion migration along the in-plane direction, Xiao et al conducted similar measurements on a single crystalline quasi-2D perovskite BA₂MA₂PbI₆ film ($n = 3$) grown by cooling-induced supersaturation, with the external bias along the in-plane direction [109]. They found that the transition from electronic conductivity to ionic conductivity was also not observed up to 350 K both in the dark and under illumination, indicating a suppressed ion migration along the in-plane direction. To understand the origin, they used DFT calculations to demonstrate that the formation energies of defects (iodide vacancy and MA⁺ vacancy) in the quasi-2D perovskite are higher than that in 3D perovskite, leading to a reduced defect density in the former. Based on these results, it is evident that ion migration in quasi-2D perovskites can be suppressed along all directions due to the ion blocking effect and the increased defect formation energy.

The operational stability of quasi-2D perovskite LEDs has also shown to be greater than that of its 3D counterpart as demonstrated by Wang et al [111]. The device lifetime of the lower dimensional perovskite LED stood for almost two hours with a final EQE of half of its initial value, whereas the 3D perovskite LED only lasted for 1 min. Both devices were driven under a constant current density of 10 mA cm⁻². Tian et al has reported one of the most stable red quasi-2D perovskite LED with the EL intensity remained almost unchanged for 4 h due to a decrease in ion migration from the quasi-2D structure [112].
3.2. Suppressing grain boundary ion migration

As mentioned previously, grain boundary ion migration is more significant compared to the pathways in the bulk of the grain due to the low formation energy of surface defects [70]. In addition, to have efficient radiative recombination through exciton confinement, the grain size of the perovskites in LEDs is usually made to be small (less than 20 nm) [20], leading to a large grain boundary surface area. Therefore, suppressing grain boundary ion migration is very critical to the operational stability of perovskite LEDs, and defect passivation is the most effective approach. The commonly used passivation materials for perovskite are Lewis bases [29, 81, 113]. In perovskites, Pb$^{2+}$ is considered as Lewis acid containing an empty orbital that can accept the unbonded electron pair of a Lewis base, resulting in Lewis acid-base reaction [114]. Therefore, the defects such as undercoordinated Pb at the surface can be passivated by Lewis bases [114]. In the literature, Lewis bases such as amine (−NH$_2$) [81], hydroxyl (−OH) [47, 112, 115], carboxyl (−COOH) [29] and phosphine oxide (P=O) [21, 47] derivatives are widely used as passivation agents for perovskites. More recently, except for the essential passivating functional groups, it was found that the hydrogen-bonding ability between the passivation agents and the organic cations in perovskites also played an important role on the effectiveness of passivation. The weaker the hydrogen-bonding ability, the stronger interaction between the functional group and the perovskite defect site, resulting in more effective passivation [116].

Adding passivation agents into perovskite precursors is one way to passivate grain boundary defects thus suppressing ion migrations [29, 115, 117]. By adding polyoxyethylene sorbitan monolaurate (Tweeen 20) into CsPbBr$_3$ perovskite precursor [115], the undercoordinated Pb at the grain boundaries can be passivated, as confirmed by Fourier transform infrared spectroscopy. The C−O−C stretching peak at 951 cm$^{-1}$ in pure Tween 20 red-shifted to 935 cm$^{-1}$ in Tween 20:CsPbBr$_3$ owing to the reduced stretching force caused by the Lewis acid−base interaction. Also, compared to the neat CsPbBr$_3$ film, a more uniform and stronger PL emission was observed in Tween 20:CsPbBr$_3$ by PL mapping, indicating an overall reduction of defects (figures 6(a) and (b)) [115]. As a result, the operational lifetime ($T_{30\%} L_0 = 100$ cd m$^{-2}$) of the passivated perovskite LEDs has been improved from several minutes to several hours (figure 6(c)) [115]. 5-aminovaleric acid (5AVA) has also been used to passivate the grain boundary defects in FA$_{0.47}$Cs$_{0.53}$Pb$_{(0.87)\text{Br}_{0.13}}$ perovskite, in which the NH$_3^+$ group and the COO$^-$ group of 5AVA can form Lewis acid-base adduct with the FA/Cs vacancies and...
undercoordinated Pb at the grain boundary [29]. Due to the suppressed nonradiative recombination and ion migration, the passivated perovskite LEDs showed an improved efficiency and operational stability. In addition, hydroxyl additives such as polyethylene glycol (PEG) [117], methoxypolyethylene glycol (mPEG) [118], and polyethylene oxide (PEO) [112, 113] have also been added into perovskite precursors to improve the efficiency and the stability of perovskite LEDs. More recently, additives having a weaker hydrogen-bonding ability by introducing O atom is considered as an effective passivation agent, such as 2,2′-oxybis (ethylenoxy)] diethylamine (ODEA) [116]. By adding ODEA into FAPbI₃ precursors, the perovskite LEDs showed an improved lifetime ($T_{50} = 20$ h) at 20 mA cm⁻² compared with the control devices ($T_{50} = 1.5$ h), which was attributed to reduced Joule heating and the suppression of ion migration due to a low trap density [116].

Another way to passivate grain boundary defects is to add passivation agents into anti-solvents [119, 120]. Anti-solvent dripping is a commonly used technique to fabricate smooth and pin-hole free perovskite films [20]. By adding phenylmethylamine (PMA) into chlorobenzene (CB) antisolvent which is drop-casted onto a precursor coated substrate during spin coating, the operational lifetime of the resulting device has been improved significantly to 135 min compared with the device without PMA which has a lifetime of 22 min (figure 5(d)) [119]. Moreover, EL-blinking was not observed in the PMA-passivated devices indicating a suppressed charge trapping and ion migration [119]. In addition, 9,9-spirobifluoren-2-yl-diphenylphosphine oxide (SPPO1) has also been added into chloroform antisolvent, resulting in a high PLQY through defect passivation [120].

### 3.3. Suppressing interlayer ion migration

As mentioned in section 2.1.2, the escape of ions from the perovskite layer not only can create defects, but also can corrode the electrodes leading to an irreversible degradation. Therefore, suppressing ion migration across the interface is critical to the operational stability of perovskite LEDs. The approaches of suppressing interlayer ion migration include adding a passivation layer, incorporating an ion blocking layer and using a non-reacting stable electrode.

Defect passivation layer can impede ion migration across the interface. For example, Lee et al deposited a thin layer of ethylenediamine (EDA) on the top surface of MAPbBr₃ perovskite [81]. On one hand, the amine group in EDA can effectively passivate the surface defects, resulting in a higher PL intensity and longer PL lifetime. On the other hand, a better corrosion resistance was observed for perovskites in direct contact with Ag, and there is no change in the electrode even after 30 d. Through XPS and XRD analysis, the authors showed the formation of AgBr in the sample without the EDA passivation layer, while AgBr was not observed in the sample with the passivation layer, indicating that ion migration from the perovskite layer to the electrode is suppressed by the EDA passivation. As a result, the operational stability of the perovskite LEDs has been significantly improved with the EDA passivation (figure 7(a)) [81].

Metal oxides can be used as ion blocking layer which also impedes the leaving of mobile ions from perovskite to other layers. For example, ZnO has been used to replace the organic electron transporting layer [121, 122], such that the mobile ions are blocked at the perovskite/ZnO interface, leading to no corrosion on the Al electrode after storage for 10 d [121]. However, as mentioned previously, direct contact between perovskite and ZnO can lead to thermal instability. Therefore, other n-type metal oxides such as TiOₓ has been used as an alternative. Amin-mediated TiOₓ interlayer has been inserted between Ag cathode and PCBM to suppress halide ions migration from the perovskite film to the Ag cathode (figure 7(b)) [58], leading to solar cells with long-term stability. Sanehira et al studied the critical role of MoOₓ interlayer between Al and HTL on the stability of perovskite solar cells [123]. They suggested that Al can react with the underlying MoOₓ, forming a thin layer of Al₂O₃ which slows down the iodonization of Al electrode. In addition, metal oxide can also effectively avoid interfacial reaction. The etching issue of ITO by acidic PEDOT: PSS can be suppressed by using NiOₓ as the hole transporting layer [32, 121, 122], which significantly increases the operational lifetime of perovskite LEDs [32, 121].

Lastly, the selection of electrode materials also plays an important role in the electrode corrosion. Al and Ag are the most commonly used metal electrodes in perovskite LEDs, and they can be corroded by halide ion migration [81]. Even noble metals such as Au can diffuse across the organic interlayer into perovskites, leading to a decrease in device efficiency [124]. Recently, Cr has been considered as a good candidate for the electrode of perovskite optoelectronic devices [125]. By directly depositing Cr and Au metals on single crystalline MAPbBr₃, it was found that Cr greatly reduced the amount of hysteresis at the metal/perovskite interface by reducing interfacial recombination and polarization, compared to the large hysteresis observed in the device with Au contact (figures 7(c), (d)) [125]. A faster response in pulse voltage measurement is observed in Cr/perovskite contact indicating a less contribution of charge trapping and ion migration compared to the device with just the Au contact [125]. In addition, the Au diffusion can be hindered by inserting a Cr layer, which has been confirmed by inductively coupled plasma mass spectrometry [124]. Furthermore, using Cr₂O₃/Cr as a cathode...
can enhance the stability of perovskite solar cells, owing to the prevention of electrode reacting with iodide ions [36]. In addition, copper has also been shown to be a stable electrode in perovskite PVs operated in air [126]. No diffusion of Cu into MAPbI3 or formation of CuI has been observed under thermal annealing (80 °C) for over 22 h, as shown by EDX measurement (figure 7(e)) [127]. The chemically inert graphene anode has also been used to replace ITO to fabricate stable and flexible perovskite LEDs [128]. In this case, the degradation caused by diffusion of In and Sn from ITO into perovskite layer can be avoided.

Table 2 summarizes the operational lifetime of representative perovskite LEDs reported by various groups in 2018 and 2019. From the table, it should be noticed that the progress of improving the stability of perovskite LEDs is still far behind the requirements of practical applications. Therefore, more research effort should be dedicated to addressing this critical issue.

4. Summary and outlook

In this review, we have summarized different degradation mechanisms of perovskite LEDs as well as the strategies to improve the operational stability. The degradation mechanisms are categorized into ion migration (inside perovskite and across interface), electrochemical reactions (anode and cathode) and interfacial reactions (perovskite reacts with metal, ITO, PEDOT: PSS, and ZnO), among which ion migration is the first order problem, and it plays also an important role in the other two mechanisms. Ion migration inside the perovskite crystalline grains leads to defect migration, annihilation and creation of Frenkel defects, modification on charge injection and distortion of crystal lattice, while ion migration across the interface can lead to electrode corrosion and interaction of halide ions with organic interlayer. The electrochemical reaction at the anode interface leads to formation of PbI2 that can propagate towards the bulk through ion migration, while the electrochemical reaction at the cathode interface reduces ion-migration-induced Pb2+ interstitials to Pb0 interstitials that act as non-radiative recombination centers. The degradation mechanism of perovskite LEDs is complicated due to the involvement of many processes, presenting a challenge in analyzing the degradation mechanisms of a perovskite LED. Through analyzing the basic degradation mechanisms and their degradation behaviors, we provide a comprehensive guide on how to solve the degradation problem of perovskite LEDs in the future research.

Given that ion migration is the main reason for device degradation, suppressing ion migration is the number one task to address the operational stability problem. Three strategies are important to suppress ion migration to improve the lifetime: (i) suppressing bulk ion migration through compositional engineering (A-site, B-site and quasi-2D perovskite); (ii) suppressing grain boundary ion migration by defect passivation; (iii) suppressing...
| Authors and references | Year/Month | Device structure | Operational lifetime | Measurement conditions |
|------------------------|------------|------------------|----------------------|------------------------|
| Shan and co-workers [134] | 2018/01 | ITO/Al:ZnO|CsPbBr3 QDs/|ZnO NPs/Ag | $L_0 = 12$ h | At 8 V under ambient condition (30%–40% humidity) |
| Sun and co-workers [135] | 2018/01 | ITO/PEDOT:|PSS/PolY-TDP/|OPA-CsPbBr3 QDs/|TPBi/LiF/Al | $L_0 \approx 30$ min | At 2.5 mA cm$^{-2}$ |
| Zhu and co-workers [133] | 2018/01 | ITO/PEDOT:|PSS/Cs/PbBr3|Ag/Bhpen | $L_0 = 10$ min | At 6 V |
| Park and co-workers [136] | 2018/02 | ITO/ZnO/PEI:|α-|Cs/PbBr3|PEO/|Poly-TDP/WO3/Al | $L_0 = 5$ h | $L_0 = 5$ cd m$^{-2}$ at 5.71 mA cm$^{-2}$ (5 V) |
| Wang and co-workers [137] | 2018/02 | ITO/ZnO/PEI/|NMAF:|FAI:|PbI2(2.1-9.2)/|TPBi/MoO3/Au | $L_0 = 30$ min | At 100 mA cm$^{-2}$ |
| You and co-workers [21] | 2018/02 | ITO/PEDOT:|PSS/PEA2|FAPbBr3|Tri|TOP/|TPBi/LiF/Al | $L_0 = 60$ min | $L_0 = 300$ cd m$^{-2}$ at 0.5 mA cm$^{-2}$ |
| Wu and co-workers [138] | 2018/02 | ITO/PEDOT:|PSS/Rb-doped|FAPbBr3|Ag/|TPBi/LiF/Al | $L_0 = 50$ s | $L_0 = 600$ cd m$^{-2}$ at 5 mA cm$^{-2}$ |
| Song and co-workers [119] | 2018/03 | ITO/PEDOT:|PSS/|MAPbBr3|0.5|vol%|PMA/|TPBi/LiF/Al | $L_0 = 135$ min | At 5 mA cm$^{-2}$ |
| Ma and co-workers [112] | 2018/03 | ITO/PEDOT:|PSS/|Poly-TDP/|PECOAE|CsPb|Br3|BCP/|LiF/Al | $L_0 = 4$ h | At 3.5 V |
| Lee and co-workers [139] | 2018/03 | ITO/SOCp/|FA|Cs/Pb|Br3|TPBi/LiF/Al | $L_0 = 38$ min | $L_0 = 100$ cd m$^{-2}$ |
| Wang and co-workers [28] | 2018/04 | ITO/ZnO/PEI/|NMAF:|Cs/Pb|Br3|TPBi/MoO3/Au | $L_0 = 30$ h | At 10 mA cm$^{-2}$ |
| Ning and co-workers [140] | 2018/04 | ITO/PEDOT:|PSS/FPI|FAPbI3|Ag/|LiF | $L_0 = 60$ min | At 10 mA cm$^{-2}$ |
| Sun and co-workers [141] | 2018/06 | ITO/poly-TDP/|PEA2|FAPbBr3|Ag/|TPBi/LiF/Al | $L_0 = 25$ min | At 3.5 V |
| Sargent and co-workers [142] | 2018/08 | ITO/PEDOT:|PSS/|PEA2|CsPb|Br3|Ag|TPBi/MoO3/Au | $L_0 = 0.5$ min | At 210 cd m$^{-2}$ |
| Sun and co-workers [143] | 2018/09 | ITO/poly-TDP/|CdsPb|Br3|40%|PEA+|crown|TPBi/LiF/Al | $L_0 = 90$ min | At 2 mA cm$^{-2}$ |
| Xu and co-workers [144] | 2018/09 | Au|MgO/CsPb|Br3|n-MgZnO|n+|GaN | $L_0 > 18$ h | At 10 V under ambient condition 25 °C, 30%–45% humidity |
| Song and co-workers [32] | 2018/10 | ITO/|NiO|BA|FA|Pb|Br3|TPBi/LiF/Al | $L_0 = 102$ min | $L_0 = 100$ cd m$^{-2}$ |
| Kido and co-workers [145] | 2018/10 | ITO/PEDOT:|PSS/|Poly-TDP/|CsPb|Br3|QDs/TPBi/LiQ/Al | $L_0 = 180$ min | $L_0 = 100$ cd m$^{-2}$ at 1.25 mA cm$^{-2}$ |
| Wang and co-workers [16] | 2018/10 | ITO/ZnO/PEI/|SVA|FA|PbI2(0.7:2.4:1)/|TPBi/MoOx/Au | $L_0 = 20$ h | At 100 mA cm$^{-2}$ |
| Wei and co-workers [17] | 2018/10 | ITO/PEDOT:|PSS/|Cs/Pb|Br3|MABr(1:1)/|PMMA|BPYMPM/LiF/Al | $L_0 = 10$ min | $L_0 = 7130$ cd m$^{-2}$ at 166.7 mA cm$^{-2}$ |
| Liu and co-workers [115] | 2018/10 | ITO/SDBS-dopped|PEDOT:|PSS/Tween20:|CsPb|Br3|TPBi/LiF/Al | $L_0 = 6$ h | $L_0 = 100$ cd m$^{-2}$ |
| Zeng and co-workers [146] | 2018/10 | ITO/PEDOT:|PSS/|PVK|NEA:|α-CsPbI3/|TPBi/LiF/Al | $L_0 = 6$ h | At 5 mA cm$^{-2}$ |
| Land and co-workers [18] | 2018/11 | ITO/MZO-PEI/|NMAF:|FA|PbI2:|poly-HEMA|5:8:4)/|TFB-PFO/MoO3/Au | $L_0 = 46$ h | At 0.1 mA cm$^{-2}$ |
| Wei and co-workers [118] | 2018/11 | ITO/m PEDOT:|PSS/mPEG-doped|CsPb|Br3|Ag/|TPBi/LiF/Ag | $L > L_0$ for 24 h | $L_0 = 100$ cd m$^{-2}$ |
| Rand and co-workers [34] | 2018/11 | ITO/poly-TDP/|MAPbI3|TPBi/LiF/Al | $L_0 = 280$ min | At 10 mA cm$^{-2}$ |
| Yip and co-workers [147] | 2018/11 | ITO/Poly-TDP/|CsPb|Br3|Ag/|TPBi/LiF/Al | $L_0 = 190$ min | At 10 mA cm$^{-2}$ |
| Zhang and co-workers [148] | 2019/01 | ITO/PEDOT:|PSS/|Poly-TDP/|MoO3/|Ag | $L_0 = 60$ s | At 10 mA cm$^{-2}$ |
| Liu and co-workers [149] | 2019/02 | ITO/PEDOT:|PSS/|Poly-TDP/|α-|Cs/Pb|Br3|QDs/TPBi/LiF/Al | $L_0 = 5$ min | At 10 mA cm$^{-2}$ |
| Rogach and co-workers [150] | 2019/02 | ITO/PEDOT:|PSS/|Cs/Pb|Br3|Ag/|TPBi/LiF/Al | $L_0 = 0.5$ h | $L_0 = 300$ cd m$^{-2}$ |
| Chang and co-workers [151] | 2019/02 | ITO/PEDOT:|PSS/|Cs/Pb|Br3|Ag/|TPBi/LiF/Al | $L_0 = 120$ min | 0.5 h |
| | | | | | $L_0 = 10$ min | 6 V |
| | | | | | $L_0 = 142$ min | 6V |
| | | | | | $L_0 = 250$ h | 10 mA cm$^{-2}$ |
| | | | | | $L_0 = 3$ h | 10 mA cm$^{-2}$ |
| Authors and references          | Year/Month | Device structure                                                                 | Operational lifetime | Measurement conditions |
|--------------------------------|------------|-----------------------------------------------------------------------------------|----------------------|------------------------|
| Chen and co-workers [152]      | 2019/05    | ITO/ZnMgO/(EDBE)(FA)$_3$Pb$_3$I$_{12}$/TFB/MoO$_x$/Al                             | $L_{50} = 78$ min    | At 10 mA cm$^{-2}$     |
| Chen and co-workers [153]      | 2019/05    | ITO/PEDOT: PSS/PVK/MAPbBr$_3$ QDs/TPBi/LiF/Al                                     | $L_{50} = 7$ min     | Under ambient condition (50% RH) |
| Peng and co-workers [154]      | 2019/08    | ITO/PEDOT: PSS/C$_{30.8}$FA$_{0.2}$Pb$_3$I$_{12}$/TPBi/LiF/Al                     | $L_{50} = 30$ min    | At 3 V                 |
| Wang and co-workers [155]      | 2019/08    | ITO/NiO$_x$/PVK/CdPbBr$_3$ NPs/TPBi/LiF/Al                                       | $L_{50} = 40$ min    | At 0.33 mA cm$^{-2}$   |
| Huang and co-workers [156]     | 2019/08    | ITO/ZnO/PEIE/FAPbI$_3$/TFB/MoO$_x$/Au                                            | $L_{50} = 23.7$ h    | At 100 mA cm$^{-2}$    |
interlayer ion migration by optimal device structure (passivation interlayer, ion-blocking layer and stable electrode). The first two categories are related to the properties of perovskite materials, while the third one is related to the device architecture. We give our perspectives and suggestions in the subsequent discussions.

Since ion migration is related to the intrinsic properties of perovskites, the selection of perovskite materials is fundamentally critical. The published data strongly suggest that quasi-2D perovskite is the most promising candidate to achieve stabled device and efficient perovskite LEDs. In general, 3D perovskites contain a large amount of grain boundary defects which not only facilitate ion migration leading to device degradation, but also contribute to non-radiative recombination leading to low device efficiencies. In addition, the small exciton binding energy in 3D perovskites results in a slow bimolecular radiative recombination rate which further facilitates the pathways of non-radiative recombination [22]. Therefore, both grain boundary passivation and exciton confinement are needed for device efficiency and stability, and they can be achieved using quasi-2D perovskites: the amine groups of the bulky organic cations in quasi-2D perovskites not only passivate defects [23], but also contribute to the formation of perovskite nanocrystals [20]. In addition, the bulky organic cations function as an ion migration barrier [108]. However, the morphology (phase distribution and orientation) of quasi-2D perovskite film is difficult to control during processing. Ion migration can be affected by the orientation of the texture of the 2D phases. For example, ion migration can be more effectively suppressed if the 2D platelets are normal to the direction of the applied electric field. Therefore, further studies are needed to resolve two issues: (i) developing a process to control the film texture; (ii) correlating the film texture with ion migration for better device stability and efficiency. In addition, the molecular structure of the bulky organic cations probably impacts ion migration, which requires further study.

In addition to the perovskite material itself, the device architecture is also important to stability. Since ions can migrate across the organic interlayer and reach the metal electrode, metal oxides instead of organic materials are a better choice for charge transporting materials. However, two issues arise from this approach: (i) the processability of metal oxide on perovskite; (ii) EL quenching at the perovskite/metal oxide interface due to interfacial defects. Processing of metal oxide thin films typically requires a high annealing temperature which will damage the underlying perovskite film. In addition, the solvent used for the metal oxide film should not dissolve the underlying perovskite film. Therefore, compatible fabrication processes of metal oxides need to be developed, and metal oxide nanoparticles dispersed in a non-polar solvent might be a preferred strategy. Related to EL quenching at the metal oxide interfaces, the interfacial defects can be suppressed by inserting a passivation interlayer, which not only improves the device efficiency, but also suppresses ion migration and improves the device stability.

It should be noted that each individual strategy cannot prohibit all the degradation processes as we summarized previously. Therefore, we suggest that different strategies should be combined to fabricate stable perovskite LEDs. For example, using quasi-2D perovskite as the emitting layer and metal oxides as the charge transporting layers not only suppress ion migration in perovskites, but also eliminate ion migration across the interface. As we emphasized throughout this review, ion migration is the number one problem to the operating stability of perovskite LEDs. To date, the best operating lifetime is on the order of tens of hours and ion migration is probably the limiting factor. Therefore, we do not know the intrinsic stability of perovskite films even though the ion migration problem is solved. Studying the photoluminescence stability might shed some light on the intrinsic stability of perovskites while the research community is addressing the ion migration problem.

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