Ion Migration in Perovskite Solar Cells

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Abstract

Metal halide perovskite solar cells have significant potential for next-generation solar power production. If not controlled, the migration of mobile ions can hamper the stability of perovskite solar cells. Intensive research efforts have devised ways of supressing ion migration and degradation in perovskite materials, resulting in solar cells that show stability over thousands of hours during accelerated ageing tests. Here, we review the chemical origin of ion migration, its effect on material and device performance and stability, and strategies to mitigate its impact. While ion migration originates in the soft lattice of the halide perovskite framework and its low defect formation energy, the solutions to reduce the effects of ion migration span a multitude of strategies, from compositional engineering of materials and device architecture changes to additives and strain engineering. The field has made great progress in understanding the origin and properties of mobile ions in halide perovskites and has improved operational stability beyond expectations. Yet, there are still ample opportunities to further improve the long-term durability of perovskite solar cells, either by reducing ion migration or its effect on solar cell efficiency.

1. Introduction

Metal halide perovskite solar cells have developed rapidly over the past decade, with power conversion efficiencies exceeding 26%, which are on par with those of conventional photovoltaic technologies.[1] When used in tandem solar cells, they can increase the efficiency beyond the thermodynamic limit of single-junction solar cells, dramatically accelerating the energy transition. Halide perovskites are now known to exhibit ion migration through the lattice, and this transport behavior can lead to stability issues when not controlled or prevented in solar cells and other devices.[2]

Metal halide perovskites are semiconductors with an ABX_3 chemical formula, where A is a monovalent cation (commonly methylammonium (MA), formamidinium (FA) or caesium), B is a divalent metal cation (generally lead or tin), and X is a halide anion (iodide, bromide or chloride; Figure 1a). The soft character of these semiconductors, along with their relatively low formation energies and low migration barriers for ions, makes fabrication straightforward, allows for self-healing,[3,4] and enables applications such as resistive switching memories or memristors.[5] However, the ease of ion migration can harm the performance of perovskite solar cells due to reactions at interfaces or destabilisation of the material. While external stresses like oxygen and water can be prevented by device and module engineering, the increasing density of mobile ions with time, voltage, and light bias is a fundamental feature of the material and one of the main reasons for the degradation of perovskite solar cells.[6]

With the stability of perovskite solar cells often remaining far from the targets needed for commercial viability, ion migration may prove to be the Achilles' heel that needs to be tackled to achieve large-scale commercialisation.[7] However, a comprehensive understanding of the physical chemistry and the effect of ion migration is still lacking, partially because of a lack of suitable experimental characterisation techniques. In addition, controlling or suppressing ion migration remains an ongoing challenge in the field, with efforts ranging from material design to device fabrication.

This review examines ion migration and its implications for metal halide perovskite solar cells. We discuss the chemical origin of ion migration and the ion migration pathways. Thereafter, we evaluate different electrical, optical, and chemical measurement techniques that can be used to investigate ion migration in perovskite solar cells. We further review the effects of ion migration on solar cell performance from a modelling and experimental point of view, followed by a perspective on how ion migration and its adverse effects can be suppressed or controlled through the design of both the perovskite material and the device. Deeper insights gained on ion migration are essential for designing perovskite solar cells with enhanced performance and long-term stability.

2. Chemistry of ion migration in halide perovskites

Hybrid metal halide perovskite materials are unique semiconductors. They show mixed ionic-electronic conduction, distinguishing them from classical semiconductors such as Si, GaAs, and CdTe.[8–12] Defect migration in these semiconductors typically requires a much higher thermal activation compared to perovskites, and is therefore mostly significant under high-temperature annealing.[13] In addition, the defect tolerance seen in perovskites allows them to maintain their optoelectronic performance up to much higher defect levels, leading to mixed electronic-ionic conduction.[14]

The ionic transport character has been apparent through the hysteresis in current-voltage measurements of perovskite solar cells, photo-induced ionic redistribution or phase separation,[15,16] photodegradation,[17] and related phenomena that suggest significant contributions of ion conduction in these materials.[18–20] Solid-state ion migration is mediated by various lattice defects (Figure 1b), including vacancies and interstitials, and their population can be described by equilibrium conditions disturbed by factors such as chemical reactions, temperature changes, electric fields, light, and strain.[10] The contribution of defects to the ion migration process is characterised by the activation energy (E_a) for an ionic jump and the concentration of defects (Info Box 1).[11]

Although central (A) or metal (M) cations may migrate at a slow rate, halide (X^-) or halide vacancy (V_X^+) species are typically assigned as the most mobile on the timescale of lab experiments.[10,11] In vacancy-mediated diffusion, halide anions move through the crystal lattice via adjacent vacancies, driven by electric fields, vacancy concentration gradients, and thermal energy.[18] The halide interstitial forms a characteristic double-bridge structure between two Pb ions and its migration occurs through hopping, where an I-atom moves from one Pb−halide−Pb bridge to a neighboring one, forming a new double bridge.[21] Furthermore, extended defects in the form of surfaces, interfaces, and grain boundaries can influence ion transport by providing alternative migration pathways controlled by the overall microstructure.[10] Consequently, there is an interplay of contributing factors affecting the resulting mixed ionic-electronic conduction in metal halide perovskites.

Halide migration may be the fastest ion migration process in most cases, but also the A-site and metal ions can migrate. A-site migration is sometimes observed on timescales relevant to common measurement techniques, e.g. current-voltage hysteresis,[22] while the metal ion migration is even slower and often not observed within the timescale of lab experiments. This trend was illustrated with perovskite heterostructures, where bilayers of different compositions can be stable for thousands of hours if they differ on the M-site, or differ strongly in size on the A-site, but are not stable if they differ on the X-site.[23]

The complex structure of metal halide perovskites implies that identifying the dominant mobile ion species and their properties is not a simple endeavour. The archetypical perovskite composition, $MAPbI_3$, has been studied early on in this context. Electrical investigations of this perovskite material indicate that halide vacancies are the primary mobile species on the timescale of these measurements,[18,45–47] which was confirmed by measurements of the ionic conductivity as a function of iodine partial pressure.[46] The reduction of iodide vacancies (V_I^+), such as through iodine (I_2) incorporation, enables increasing the hole (h^+) concentration, converting the system into a p-type material according to the reaction (4).[11] Consequently, measurements under various iodine partial pressures demonstrate an increase in electronic and a small decrease in ionic conductivities, indicating iodide vacancies as the main mobile defect, since the ionic conductivity would increase if dominated by iodide interstitials.

$$\frac{1}{2} I_2 + V_I^+ \rightleftharpoons I_I^x + h^+ \tag{4}$$

Iodide vacancies are often considered the most mobile ionic species, but interstitials may be similarly mobile.[48] In particular, interstitials are suggested to be responsible for the electrochemical (redox) reactions at surfaces/interfaces during the operation of devices, leading to the formation and the evaporation of I_2 from the surface of perovskite films.[49] Although either vacancies or interstitials may dominate in the as-synthesised films, a new state-state will be reestablished given external stimuli, changing their concentration.[50] Therefore, it is particularly important to consider the interplay of both types of defects.

Ion migration is affected by external stressors, including temperature changes, electric fields, light, as well as mechanical pressure or related strain (Figure 1c).[10] Ions and charged defects drift when subjected to an electric field, which means that biasing perovskite-based devices leads to a migration of mobile ions through the bulk, and towards or even across the interface. The ionic current adds to the electrical current, and the ionic distribution modifies the electrical field inside the device, which results in a hysteresis in the current-voltage scan (Figure 1d).

In addition to voltage bias, illumination can affect ion migration. Both electronic and ionic conductivities increase upon illumination,[51] which can contribute to photo-induced phase separation.[15,52,53] Halide perovskites have low mechanical toughness, which is related to low cohesive energy (G_c) values (< 1.5 J/m^2).[54] G_c is the energy required to create a crack in the surface, which rarely studied in detail in perovskites. In contrast, the G_c for c-Si solar cells is at least an order of magnitude larger with values of 10 – 200 J/m^2.[55] This softness means that stresses can strain the material, leading to severe ion migration to the extent of phase segregation.[56,57] Strain is often "baked in" during fabrication due to a mismatch of thermal expansion coefficients between the perovskite and the substrate.[58] Physical or chemical pressure can (partially) reverse these effects.[59] Finally, chemical processes that are facilitated by ion migration can induce degradation through reactivity at the interface with selective charge-extraction layers or light-stimulated photoredox transformations, see Section 4.[60] These factors must be considered in the effort to adequately describe ion migration processes and their impact on the material and device during operation.

To this end, it is important to consider that the scales relevant for ion migration range from sub-nanometre to several micrometres, and femtoseconds to hours. Therefore, a multi-scale approach, both in the spatial and time dimension, is needed to study ion migration. Moreover, for computer modelling methods, it is valuable to employ reactive molecular simulations capable of capturing dynamic charge transfer and chemical reactions among diverse species. Recent advancements in foundational machine learning models show promise for this purpose.[61] Coupling these deep machine learning potentials with rare event methods such as meta dynamics[62] or advanced rare event methods such as transition path sampling[63] should be explored to achieve long timescales comparable to experimental observations.[46,64]

Experimentally, we should define a better model system to study the complex chemistry of ion migration. For example, one could start with single crystals and well-defined compositions and then generalise toward polycrystalline thin films of more complex composition. The device should initially be as simple as possible before exploring more complex device architectures.[65] Experiments spanning the large dynamic range in the spatial and time dimensions should combine several techniques to assess and visualise the complexity of ion migration.

3. Measurement techniques and visualisation of ion migration

Investigating and characterising ion migration in halide perovskites can be complex. Typical operating conditions (e.g., light, electrical bias, heat) can alter ion migration processes, leading to compositional variations.[15,37,66,67] Many common characterisation probes (e.g. X-rays, electron beams, ion beams, and optical pulses) cause changes in the morphology and composition.[67,68] Adding to the complexity, there can be coupling between different stimuli (e.g. light and heat, light and electron beam, or light and oxygen).[69–71] Perovskite devices also show memory effects (e.g. hysteresis), making it challenging to compare measurements of devices with a different history.[66] Therefore, to characterize ion migration, we need *in-operando* measurements that map out chemical, optical, electrical, and ionic properties with high spatial and temporal resolution and dynamic range, ideally measuring multiple degrees of freedom simultaneously on simple model systems.

Electrical measurements indirectly infer ion motion from the slow response of the electrical signal to external electrical bias, see Figure 2a. While it is often reasonable to assume that signals much slower than typical timescales for charge carrier recombination and transport originate from ion migration, it is not a clean-cut criterion. Signals from deep traps or chemical reactions can also appear on similarly slow timescales, and the fast end of the range of timescales for ion migration might overlap with the slow end of electronic processes.

The most commonly applied method for studying ionic defects in perovskite solar cells is impedance spectroscopy, which measures the complex resistance by determining the current response to an applied alternating current (AC) voltage modulation for a wide range of frequencies. These frequency-resolved measurements are typically interpreted by investigating complex equivalent circuit diagrams[72] to obtain a quantitative description of the loss processes in the device, or simple equivalent circuit diagrams (typically a resistance in series with a parallel resistor and capacitor) to extract only the thermal activation of ion migration.

A variant of impedance spectroscopy called drive-level capacitance profiling[73] is often used to examine electronic traps. It is based on a capacitance-voltage sweep at a fixed AC voltage frequency, but must be applied with caution to defects in perovskite solar cells. The surface charge on the electrodes will lead to an apparent defect density that is a function of thickness and permittivity. For bulk charge to modify the electrostatic potential and thereby the capacitance, the bulk defect density has to exceed the threshold defined by the surface charge.[74] All these modulation-based techniques are relatively easy to apply, and they contain a wealth of information. The challenge lies in the interpretation of the data. For impedance spectroscopy and related techniques, several equivalent circuits are proposed that fit the same dataset, but offer different physical interpretations. To find the most accurate equivalent-circuit description of a device, a combination of impedance spectroscopy with other frequency or time-domain methods, such as intensity-modulated-photocurrent spectroscopy[75] or intensity-modulated-photovoltage spectroscopy[76–78] should be fitted with a single equivalent circuit.[79] Impedance spectra can also be modelled using drift-diffusion models that include both charges and ions.

Complementary to measuring the impedance in the frequency domain, time-domain measurements such as electrical transients are used to characterise ion migration.[18] The basis is deep-level transient spectroscopy, evaluating the decay of capacitance or current after a voltage or light pulse.[80] This method was adapted to measure ion migration under the term transient ion drift.[81] Time-domain techniques yield results consistent with impedance spectroscopy and conductivity from DC galvanostatic polarisation measurements.[22,34] As most capacitance transients do not decay mono-exponentially, an evaluation using the inverse Laplace transform showed that the ion migration rates can be broadly distributed.[31] The formation and migration enthalpies can be determined from temperature-dependent measurements.[29] We note that the resulting values have not been verified independently.[82] Time-domain techniques are less common, but generally span a longer timescale compared to frequency-domain techniques. Supporting the interpretation by device simulations is advisable, as purely analytic evaluation makes the interdependencies in a complete device difficult to account for.[83]

Ion migration is also important to understand when performing other electrical characterisation methods because decoupling of the applied and internal electric fields affects techniques such as current-voltage (I-V) scanning.[84] Many time-resolved techniques do not aim to measure ion migration, yet the ionic signatures still appear. Electrical techniques are not chemically sensitive, but the defect chemistry can, for example, be elucidated by the conductivity as a function of the I_2 partial pressure at a single temperature.[46,85]

Like in other solid electrolytes, the quantification of the properties of ion migration depends on the exact conditions that the ions experience. The ion mobility and charge transport may depend on the concentration and, thus, on the concentration gradient within the device.[86] It may also depend on the local microstructure, including strain and phase differences. In addition, it is not obvious that the same number of ions that contribute to the DC conduction also contribute to the AC conduction. Probing the device in different situations (e.g. different concentration gradients) can elucidate the robustness of the extracted values.

To characterise the ions directly, one would ideally map individual point defects and follow their migration over time. Experimental techniques are very limited in achieving this, but several techniques are able to detect populations of mobile ions, and advanced modelling methods can probe atomic-scale migration mechanisms (chemical characterisation, Figure 2b). To characterize mobile ions, the sensitivity for the chemical composition must be high enough to measure the mobile ion density (ppm range). Historically, the methods to measure chemical composition have been either optimised for organic or inorganic materials, while most perovskite compositions are hybrids of both. The inorganic components are most commonly analysed using the core-level transitions that lead to characteristic spectra in the X-ray energy range using either an electron beam (EDS or EELS) or an X-ray beam (XRF) as the excitation source.[87,88] These probes can be focused down to several (e-beam), several hundreds (synchrotron X-rays) or several thousands (benchtop X-rays) of nanometres, providing mapping possibilities if damage from the probe can be minimised. Many existing systems integrate light and electrical bias to allow for *in-operando* measurements, including at synchrotron facilities.[89–93] In this way, ion migration of dopants or oxygen atoms from the carrier selective transport layers during electrical biasing has been visualised directly.[94] Benchmarking such direct chemical measurements with indirect measurements (e.g. photoluminescence, cathodoluminescence, electrical measurements) makes testing hypotheses based on these (often) more straightforward but indirect measurements possible.

For the organic component, the most common chemical analysis techniques are Fourier Transform Infrared (FTIR), Raman spectroscopy, and Nuclear Magnetic Resonance (NMR) spectroscopy. Recently, the spatial resolution of FTIR and Raman spectroscopy has been brought down to the few-nanometre scale using scanning probe spectroscopy, either detecting light scattered from the tip (for example Scanning Near-field Optical Microscopy, SNOM) or a change in force between the tip and sample (e.g. photothermal infrared (IR) spectroscopy).[95–97] Recently, IR scanning probe measurements have been offered by several SNOM vendors as a standard option.[98,99] The open geometry has already facilitated studies combining infrared spectroscopy mapping with *in-operando* electrical and optical bias.[97,100] NMR has been used extensively to study the bulk composition of halide perovskites, dopant incorporation, and halide and cation mixing. However, its use for investigating ion migration is limited due to the need for migration between sites with different chemical shifts, for example using isotopes.[101] Alternatively, although used much more for the organic component, vibrational spectroscopy (Raman and IR) has sometimes also been applied to inorganic materials. In the case of halide perovskites, the primary difficulty is that the lead halide vibrational modes are at extremely low frequencies (<120 cm^{-1}), inaccessible with most Raman setups and outside the range of commercial nano-IR microscope.[102]

Secondary ion mass spectrometry (SIMS) is used to investigate the composition of both inorganic and organic components. It can provide nanometre-scale spatial resolution via depth profiling or by using a scanning-focused ion beam.[103,104] The excellent mass resolution of SIMS also allows for isotopic labelling studies, for example, to calculate diffusion coefficients by measuring isotope gradients caused by diffusive mixing after making a heterojunction.[105] The major downside of SIMS is that it is a destructive technique, which can change the composition during the measurement, and thus is not easily compatible with *in-operando* or time-resolved measurements.

Finally, Transmission Electron Microscopy (TEM) is one of the most powerful techniques for directly visualising ion migration in halide perovskites. This is the only technique that can simultaneously provide crystallographic and chemical information at the atomic scale.[106,107] TEM can be used to analyse both the bulk material and interfaces with electrodes and, for example, provided the first visualisation of oxygen extraction from TiO_2 transport layers into the perovskite absorber during electrical biasing.[94] One major challenge in applying TEM to halide perovskites is beam-induced damage.[108] Fully inorganic halide perovskites are relatively tolerant to the electron beam, showing even atomic-resolution EDS maps in STEM, but compositions containing organic cations are more sensitive. TEM techniques optimised for beam-sensitive organic and biological samples, such as 4D STEM and cryo-TEM are emerging as useful approaches for hybrid halide perovskites.[109]

Optical techniques are often used to study the properties of semiconductors. The variation in bandgap with composition makes optical techniques particularly well suited for studying ion migration in multi-component halide perovskites (see Figure 2c). Absorption, reflection, photoluminescence (PL), and cathodoluminescence have all been used extensively for ion migration studies.[110] Some of the earliest ion migration studies examined shifts in photoluminescence wavelength upon illumination, for example due to photosegregation.[15] Later, lateral contact devices were used to visualise the movement of ions under electrical bias.[66] Absorption, reflection, and PL are limited to a spatial resolution of several hundreds of nanometres, and very often, the probe itself (typically laser excitation) substantially perturbs the measured properties. However, the signal-to-noise ratio is typically large, such that time resolution in the millisecond (or even faster) range can be achieved, allowing for an analysis of the effect of the probe. Cathodoluminescence can have a much higher spatial resolution of several tens of nanometres, showing great promise for future studies.[111]

Scanning probe techniques, particularly Kelvin probe force microscopy (KPFM), have been extensively applied to visualise halide migration.[112] In KPFM, the surface potential is mapped, which can depend on the mobile ion distribution. For establishing compositional correlations, corroborating experimental methods or first-principles calculations may be used.

Key issues persist regarding the characterisation of mobile ions in metal halide perovskites. Owing to the nature of this phenomenon, ion migration is fluent and easily perturbed. Therefore, probes or measurement regimes that do not perturb ion migration or local composition during the measurement are crucial. Furthermore, identifying and separating contributions from different mobile ionic species observed in electrical measurements and separating the contributions of mobile ions from other changes in the perovskite material properties remains a significant challenge. In general, combining multiple methods can overcome these issues and the limitations of individual techniques to ultimately obtain a more complete (in space and time), coherent, and quantitative picture.

4. Effects of ion migration on solar cell performance

The influence of mobile ions on the performance of perovskite solar cells can generally be divided into two categories. On the one hand, mobile ions moving as charged species through the perovskite layer can impact device performance by changing the electric field distribution. On the other hand, mobile ions can lead to a performance decay caused by chemical and material degradation, which can result in reduced carrier lifetimes, increased carrier recombination at interfaces, and more resistive charge transport layers, affecting the charge extraction efficiency.

Most halide perovskites are intrinsic semiconductors,[114] which means that the charge redistribution by mobile ions can significantly alter or even dominate the distribution of the electric field across the device. All efficient solar cell technologies use workfunction differences between different layers inside the solar cell stack to generate a built-in electrostatic potential difference, V_{bi}. In thermodynamic equilibrium, this electrostatic potential difference does not lead to a detectable voltage. It is balanced by an equal difference in the chemical potential, leading to zero electrochemical potential differences, that is, no Fermi level splittings or gradients.[115] In non-equilibrium situations, such as under illumination or applied bias, this balance between chemical and electrostatic potentials is modified, leading to net current flow.

In solar cells under illumination and at the maximum power point, the voltage V_{mpp} generated by the solar cell is measurable over the load resistance. It reduces the electrostatic potential difference within the device to $\Delta\varphi_{\mathrm{mpp}} = V_{\mathrm{bi}} - V_{\mathrm{mpp}}$. For the efficient operation of a solar cell, particularly in case of limited mobilities, this electrostatic potential difference $\Delta\varphi_{\mathrm{mpp}}$ should remain positive. Ideally, the electric field in the absorber and charge transport layers of the device should not change its sign to prevent charge-collection losses. The consequence of a change in the sign of the electric field throughout the device is typically an increased series resistance followed by an S-shaped current-voltage curve.[116]

In the case of halide perovskites, the movement of ions may modify the electric field sufficiently so that charge collection is impeded, even with a sufficiently high V_{bi} in place (see Figure 3a).[117–120] The modified electric field distribution can slow charge-carrier transport. Therefore, the impact of ionic movement on the current-voltage curve is often most evident in situations where extraction and recombination are competing. Thus, for instance, in fast hysteresis measurements (see Figure 3b), the strongest effects of hysteresis are often observed for the fill factor.[6]

Increased hysteresis is often observed upon degradation of devices,[121] with devices that show a lower initial hysteresis often being more stable. The presence of mobile cations, moving at very slow (up to 10^2 seconds) timescales, has been linked to the occurrence of fully reversible losses during day/night cycling.[122] The rate-dependency of current-voltage curves has been shown to change over time with ageing, with increased screening of the electric field giving rise to a drop in current output and a change in the hysteresis of perovskite solar cells.[123]

Because of the ion-induced hysteresis, the measured efficiency of a solar cell will depend on the scan rate of the voltage sweep as well as the sweep direction (short circuit to open circuit or *vice versa*). An important step towards quantifying ionic performance losses was the development of the fast hysteresis measurement based on the idea of measuring current-voltage curves as a function of scan speed and direction over a wide range of speeds. Figure 3b illustrates fast hysteresis measurements of $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ perovskite solar cells. At slow scan rates, when ions can follow the voltage sweep, they screen the electrostatic potential within the active layer, reducing the photocurrent. Upon ageing, ion migration becomes more severe, increasing both the hysteresis and the effect of field screening. This process is affected by chemical reactions, photoinduced transformations, as well as redox processes. Additionally, ionic field screening may result in spectral changes in the External Quantum Efficiency (EQE), depending on the device and the dominant recombination processes. For carbon-based PSCs, it was found that the EQE drops in the longer wavelengths upon ionic screening, indicating that the photocurrent loss originates predominantly from charges generated deeper in the absorber.[124]

The field screening is widely seen as the most significant aspect of ion migration reducing device performance. However, chemical reactions and reduced charge carrier mobility also play an important role.

Chemical reactions significantly affect the performance and stability of perovskite solar cells. An electrical field induced by light or voltage can lead to electrochemical reactions coupled with the migration of ions (vacancies or interstitials), which could further accelerate decomposition reactions, see Figure 3c.

Chemical reactions at the interfaces may increase surface recombination, thereby decreasing the device voltage. The degradation of transport layers may cause a reduction in mobility, leading to losses in the fill factor and overall efficiency. In extreme cases, ions can form conductive filaments, shunting the solar cell.

Recent computational work suggests that the change of charge state of defects by ion migration may reduce overall charge transport in both the bulk and at interfaces, particularly if ions become trapped at interfaces.[21]

For example, methylammonium (MA^+) cations penetrate 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) and induce deep traps.[6,125] At higher temperatures, iodine (I^-) anions can prevent oxidation of Spiro-OMeTAD, thereby degrading its electrical properties.[126] In addition, mobile ions have been found to diffuse to the metal electrodes, where they can react, thereby degrading the metal contacts.[127–129] Conversely, metal ions from the contacts can diffuse into the perovskite layer and degrade it.[130] This reaction can be monitored during cyclic voltammetry measurements where the oxidation of Ag to Ag^+ leads to a depletion of mobile I^- and generation of Pb(0) in the perovskite.[131]

Decomposition reactions, where the perovskite layer breaks down into its basic components, are commonly triggered by external stress, including heat, light, and moisture. For example, methylammonium lead iodide ($MAPbI_3$) decomposes into lead iodide (PbI_2) and methylammonium iodide (MAI) under the influence of moisture. Hydration and hydrolysis reactions add complexity as water molecules interact with the perovskite material, forming hydrated phases that progressively degrade into PbI_2 and other byproducts.[132,133] Similar factors can cause phase instability, especially for $CsPbI_3$ and $FAPbI_3$ perovskites.[134] Here, the phase transition from the photoactive black phase to the photoinactive yellow phase is likely linked to ion mobility, leading to irreversible phase transitions and loss of photoactivity.

Photoexcitation increases ion mobility and may change the defect charge states. Photogenerated charge carriers change the electrostatic potential, modify the chemical potential, and lead to different defect types and concentrations in the lattice, changing their activity.[50,135] Even for the same defect type, their charge states and local atomic structures can be altered by photoexcitation, thereby changing ion migration rates and reactions/interactions with their surroundings. All these factors can influence recombination rates and, thereby, device efficiency.

Photoinduced reactions present another challenge: photogenerated electric fields and local heating change the defect content (types and concentrations) and may accelerate ion migration within the perovskite lattice. These reactions form new recombination centres for the charge carriers, alter the perovskite composition, and induce phase segregation in mixed halide compositions.[136–138] Photoinduced phase segregation in mixed-halide perovskites is often attributed to the photo-generated holes that localise on the iodide sites, promoting the formation of neutral iodine interstitials that ultimately trigger photodecomposition via iodine excorporation in iodide-based perovskites.[44]

Redox reactions contribute to the degradation of halide perovskites. A wide variety of electrochemical reactions can occur and typically involve most of the materials in contact with the ions. These reactions can be divided into those occurring in the bulk of the perovskite materials and those occurring at the interfaces with the contacts. For example, in the bulk of the perovskite, the photooxidation of I^- to I_2 and I_3^- has been detected.[139] This reaction is coupled with the reduction of metal or oxygen species. This conversion introduces iodine vacancies, which act as recombination centres. Combined experimental and modelling studies have provided mechanistic insights into oxygen-induced photodegradation. Oxygen diffusion into $MAPbI_3$ films is accompanied by the photo-induced formation of highly reactive superoxide species, and mobile iodide vacancies are the preferred defect sites in mediating the photo-induced formation of oxygen species.[90] In addition, iodide vacancies further increase the density of mobile ions in the bulk, facilitating other degradation channels. Redox reactions occurring at the charge transport layers and contacts are common with selective layers made from metal oxides, e.g. TiO_2[140] (electron transport layer) or MoO_3[141] (hole transport layer), which can catalyse reactions, especially under light exposure and electrical bias conditions where the photocatalytic properties of these oxides play a role.

As a result of ion migration, perovskite solar cells show both degradation and self-healing under operation. The rate of defect formation or annihilation under light and electric fields could cause a nonlinear reduction in device performance,[142] possibly temporarily enhancing properties such as photocurrent generation before leading to a deterioration of these properties.[143] Ion migration is often measured on small-scale solar cells. Since ions can migrate long distances (100s of µm), edge effects can lead to an overestimation of the effect of ion migration.[144] In upscaled devices, edge-effects should be reduced but might still be relevant.

Linking individual defect types, their concentrations, reaction and migration mechanisms, and rates to the various degradation mechanisms is challenging. Simulations using density functional theory (DFT) and beyond DFT-methods can predict the thermodynamics of defects, including defect types, concentrations, and their affinity for capturing charges (electron and holes).

Reactive molecular dynamics (MD) offer insights into the dynamics of these defects, such as diffusion and reaction mechanisms, rates, and coefficients. Advanced techniques, as described in Section 3, offer empirical data on defect types, concentrations, and reactivity. Additionally, device-level simulations that solve drift-diffusion equations for charge carriers and ionic defects can re-create the electrical measurements *in silico* and thereby elucidate the complex effects chemical reactions have on device performance.[24]

Addressing the aforementioned complexities underscores the need for a multiscale approach. Drift-diffusion simulations typically model the whole device,[145–147] while atomistic models consider a single ionic jump.[18] A multiscale model can reveal how changes at the atomic scale, such as a new defect type, a new charge state, or a slightly altered crystal structure, might impact overall device performance. This challenge requires advanced data management systems and machine learning to accelerate calculations.[48] Crucially, the predictive power of these simulations must be iteratively validated and refined through systematic experimentation.

In addition to theoretical efforts, improving the reproducibility of device data, together with standardised data collection, will enormously increase the value and predictive power of the understanding of ion migration. Currently, most research groups rely on their individual (interpretation of) solar cell fabrication recipes, and only the most common measurement techniques (e.g. power conversion efficiency measurement) are standardised. Ion migration is tightly linked to the history and fabrication conditions of a device, which means that any effort towards a better quantitative understanding of ion migration would benefit from more standardised fabrication and measurement procedures. The rise of automation in device fabrication is a promising step in the right direction.[148] At the same time, more standardisation of the measurement techniques and data structure would enable the use of big data models across laboratories to further direct research efforts.

5. Suppression of ion migration effects in materials and solar cell devices

To make perovskite solar cells commercially viable, ion migration must be suppressed or controlled such that it does not lead to degradation.[149] This control can refer to two aspects (i) reduction in ion migration, in magnitude or diffusion rate, such that it does not negatively influence the long-term stability of solar cells (a stable solar cell), or (ii) it can involve the development of strategies to reduce the effect of ion migration, such that a solar cell is dynamically stable despite ion migration still taking place (a durable solar cell).

It is interesting to start with a thought experiment and ask 'what would an ideal perovskite solar cell material look like'? (see also Info Box 2.) An ideal perovskite solar cell must be stable over tens of years at the maximum power point under 24-hour light/dark cycles. Considerable effort goes into preparing cells that are stable and 'hysteresis free' during initial I-V measurements and other short-term dynamic measurements, but given enough time, the ions will migrate.[6,150–154] This migration can degrade the cell (Section 4), which may be exacerbated if degradation increases the mobile ion density.[152]

There are two limiting cases for ideal materials (Figure 4a). The first case is a metal halide perovskite where the activation energy for ion migration is so high that the ions do not diffuse over the lifetime of the solar cell. Considering a stable ionic environment, for example, when less than 0.1% of the ions will move over the 25-year lifetime of a solar cell at temperatures of 60 °C. Using a reasonable pre-exponential factor of 10^{11} s^{-1},[18,155] this would translate to an activation energy for ion migration of >1.5 eV, well above activation energies measured for all currently used compositions (<1 eV[22]). Alternatively, one could reduce the mobile ion density by 3-5 orders of magnitude to reduce the pre-exponential factor.[156]

Over the last ten years, many studies have shown that material engineering can be used to slow iodide ion migration (see Figure 4b).[41,157–165] A- and B-site cation mixing distorts the crystal lattice, making the halide migration pathway more tortuous and increasing the activation energy for ion migration. Activation energies for iodide migration of 0.5 – 0.8 eV have been measured for triple cation perovskites.[166] The substitution of very large A-site cations (such as guanidinium in $MAPbI_3$ or phenyl-ethyl-ammonium to form quasi-2D perovskites) can shift the iodide migration out of the measurement window of impedance measurements.[41,109,167–170] A more elaborate design using (supra)molecular modulators and partial A-site doping also suppresses ion migration.[41,171–

[173] More recently, B-site mixing (Sn and Pb) has also been shown to slow ion migration, possibly due to the influence of Sn vacancies.[162] Introducing two metal atoms of alternating valency (e.g. Ag^{+1} and Bi^{+3}) to form double perovskites could have a similar effect, but ion migration is under-explored in these compositions.[174–176] An alternative approach is using larger organic A-site cations to induce the formation of low-dimensional or layered (2D) perovskite at the interface between the 3D perovskite and the charge transport layers (see Figure 4b). Activation energies of 0.75 eV have been measured for halide ions in low-dimensional and 2D perovskites.[177,178] The thin 2D (over)layers at the interface can confine ion migration to the bulk of the film and increase the Debye layer thickness away from the electron- and hole-transport layer interfaces, modifying their effect on the rate of interfacial recombination. A similar approach using steric hindrance via strain, either externally applied or using smaller cations, has been shown to increase the activation energy by roughly 50%.[179]

A third approach is using molecular overlayers at perovskite surfaces which provide a barrier to ion migration and/or eliminate surface defects, thereby inhibiting non-radiative charge-carrier recombination, see Figure 4c. Such surface passivators have included molecular Lewis acids/bases, ammonium halide salts and amino-silanes, among others.[157,165,180–187] In many cases, it is not clear where in the device the passivators distribute and how, mechanistically, they reduce the physical and electrical defect density. Recent reports also show that surface passivation suppresses local ion migration, possibly due to reduced halide vacancy concentrations.[188–190]

Ion migration can be enhanced at grain boundaries, which may also act as a source or sink of mobile defects.[191,192] Consequently, single-crystal perovskites are more stable than polycrystalline films,[193] but a direct comparison in solar cells is lacking.[194] Additives in the active perovskite layer, which influence the crystallisation of the perovskite and act as passivation agents at grain boundaries, have been used to reduce the mobile ion density.[195] For example, the formation of interstitial iodide has been suppressed by adding different zinc salts to the precursor solution, such as zinc trifluoromethane sulfonate.[196] Here, the Zn^{2+} cation may act as a trap for migrating interstitial iodides. A slightly different approach is to add reducing agents like mercaptoethylammonium iodide, which provide continuous reduction of the I_2 that forms during operation.[197] In this way, I_2 is reduced to I^-, preventing the volatile I_2 from leaving the device, thereby decreasing the iodide vacancy density.[198]

The second limiting case is to accept that mobile ions are an intrinsic part of lead halide perovskites and to engineer materials in which ion migration is fast but fully reversible. It may be benign as long as ion migration does not lead to degradation. For example, phase segregation, an effect driven by ion migration, is benign even in the presence of mobile ions, if the material conditions ensure that the segregated phase is similar enough to the mixed phase.[199] There are even suggestions from simulations that, in specific cases, mobile ions can be beneficial to perovskite solar cells.[149,200–202] For example, in cells with a non-ideal band offset between the perovskite and the interface, mobile halide ions act to improve charge extraction.[200] The major challenge is to engineer the perovskite material where ion migration does not cause performance losses.

Device design offers many opportunities to mitigate the effects of ion migration. Ideally, the dynamic processes in all the layers are reversible, i.e. promoting back transfer and potentially self-healing[203]. Layers adjacent to the perovskite should not promote irreversible chemical reactions but block intrinsic ionic species from leaving the device and extrinsic ions (dopants, metal ions) and potential external reactants (oxygen, water) from entering the active layer. Additionally, the device should be designed such that displaced ions do not negatively affect the performance when screening the field[204,205] and do not affect the reverse-bias stability.[206] Such design includes transport layers with sufficiently high conductivity to avoid charge accumulation which would further decrease the field gradient. Passivated interfaces are also required to avoid surface recombination both for ion distributions expected at the maximum power point and under open circuit conditions. Considering that mobile ions can induce deep and/or shallow electronic defects responsible for non-radiative recombination, adjacent layers or additives could play a beneficial role, for example, by providing steric hindrance to ion migration.

Following these requirements, two main strategies have been devised in the literature to control ion migration and mitigate its detrimental effects on device performance. On the one hand, the perovskite formulation has been modified to suppress ion migration, as discussed above. On the other hand, contacts have been designed to withstand the supply of ions under operating conditions. Figure 4c displays the stability performance T_{80} values, i.e. the time required to decay 20% of the initial efficiency, as a function of the ion diffusion coefficient (D_{ion}).[207] The stability of the devices is similar in formulations with highly activated ion migration (i.e. mixed halide formulations) and begins to increase once the ion migration is suppressed beyond $D_{ion} < 10^{-11}$ cm^2/s, with an increase of up to two orders of magnitude when moving from 3D perovskites to lower dimensionality perovskites. The large guanidinium cations (GA) act as a spacer in the crystalline structure, reducing the ion diffusion coefficient and the kinetics for ions to reach the contacts. Alternatively, a careful design of the contacts can increase the T_{80} values by three orders of magnitude, as can be seen in the stability results of mixed halide cation formulations. Some of the latest approaches will be discussed next.

Interlayers used in perovskite solar cells typically have a double function concerning ion migration. First, they provide adequate energy levels for efficient and selective extraction of charge, and second, they act as a physical barrier for migrating ions to avoid ions reaching the metal electrode. Some recent examples of ion-blocking layers between perovskite and the most common hole-transport layer, Spiro-OMeTAD, in high-performance devices include a thin 4-methanesulfonyl-benzamidine hydrochloride barrier layer for ions external to the perovskite, such as Li^+.[208] Another example is a dimethylphenethylsulfonium iodide treatment of the perovskite surface that reduces both iodine and Au migration and enabled 4,500 hours of continuous operation with just 1% performance loss.[209] A further recent example of inhibiting I^- migration constitutes a perovskite surface treatment with phenylpropylammonium iodide.[210] Alternatively, capping layers with reduced dimensionality on top of the perovskite suppress ion migration at the interfacial level, leading to improved stability.[211] For example, for devices with two-dimensional $Cs_2PbI_2Cl_2$, degradation could only be observed at elevated temperatures (20% power conversion efficiency loss after 2,100 hours at 110°C), potentially because of the increased activation energy discussed above.[212] Often, steric hindrance of ions by the bulky organic cations in 2D perovskite interlayers is considered necessary for increased stability.

Beyond introducing physical blocking layers, electric-field-induced blocking has been used to prevent ions from reaching the contacts. In a recent study, a depletion layer close to the hole-transport layer interface was introduced by dopants such as aspartame. The resulting electric field is supposed to retard iodide migration towards the hole-transport layer enabling stable devices in air.[213] Similarly, the concept of fixed charges at the interface has been realised by metal oxides (AlO_x) between the NiO_x hole-transport layer and the perovskite. While reduced surface recombination and 2,000 hours of operational stability at 85 °C come along with a suppression of volatile products, the role of the fixed charge on mobile ions is not fully clear yet.[214]

The metals selected as charge-collecting electrodes also play an essential role in the degradation of devices. Depending on the work function, an electrochemical reaction may occur between metals and migrating ions (see Section 4). For example, devices fabricated with Ag typically show AgI forming during degradation experiments.[215] This is why most stable devices use noble metals, mostly Au, where the electrochemical reactions occur under more demanding conditions. These electrochemical reactions will lead to a perovskite formulation deficient in iodide and/or can be coupled with a reduction of Pb^{2+} to Pb(0), a recombination centre. Transparent conductive oxides[216] or metallic interlayers like those fabricated with Cr/Cr_2O_3 are useful to block the electrochemical reactions and to act as a physical barrier for ions to reach the contact[127] or metal ions penetrating the perovskite. Figure 4d presents an overview of the strategies to reduce the effect of ion migration on perovskite solar cells.

Several challenges need to be overcome toward full control or mitigation of ion migration. If ion migration under typical operating conditions is an intrinsic property of the perovskites used in solar cells, then we must design approaches that decouple ion migration from degradation. Any contact layers must be able to chemically or physically interact with the migrating ions to immobilise them at the interface and provide an adequate energy level alignment to extract the charge. Also, any migration in the perovskite needs to be reversible, even after thousands of day-night cycles. Suppose we can find a solar cell design where the thermodynamically most stable state is the most operationally efficient. In that case, solar cells can be even more durable than traditional ones. They would self-heal and reform their operational state whenever environmental perturbations disturbed them, making them ideal solar cells in challenging environments.

6. Summary and Outlook

Ion migration in perovskite solar cells remains a longstanding Achilles heel limiting operational stability of devices. This review has highlighted the progress being made in the detailed characterization and deeper understanding of its effects. Future studies are likely to address key challenges of ion migration in perovskites and will encompass the following areas:

Technique development. Continued developments in characterization, testing and modelling techniques to directly probe ion migration and interfacial processes are crucial. Methods that feature chemical resolution are often optimally sensitive for organic or inorganic materials, while most perovskites are hybrid. Combining several experimental techniques will provide a greater quantitative view of ion migration. For example, correlative microscopy combining optical methods (e.g. PL, cathodoluminescence) with methods that resolve the composition and structure (e.g. SIMS, EBSD, nano-IR) and in-situ electrical biasing could provide a powerful tool to investigate materials and interfaces under dynamic conditions. Significant computational technique developments include the growing use of multi-scale modelling and machine learning methods to facilitate the study of larger realistic systems.

Materials design. The use of compositional engineering, including chemical doping and novel low-dimensional structures, will continue to help develop new candidate materials. Perovskites with high migration energies and low defect densities might lead to negligible ion migration, for example, by employing A- and B-site cation substitution to distort the perovskite lattice and increase the migration barrier. Surface passivation strategies (e.g., molecular compounds, physical barriers, strain engineering) will also play important roles in reducing the density of mobile ions and minimising the adverse effects mobile ionic and vacancy defects can have on device performance due to defect-mediated charge recombination. Physical barriers to ion diffusion out of the active perovskite layer are needed at the device interfaces to prevent interfacial reactions. Currently, a systematic and complete overview of the effects of materials design (composition, structure, additives), external effects (chemical environment, light intensity) and the effect of a combination of several design strategies on ion migration is missing but would form a great basis for further materials optimization.

Device recovery. A fascinating aspect of perovskite solar cells is the apparent recovery of some devices during dark periods of light cycling, often referred to as self-healing.[137] Further insights into the mechanisms and timescales behind this recovery process and the role mobile ions play will be crucial for improving the operational stability of these devices. The question remains whether we can design a durable device that keeps its performance despite its dynamically changing components or that recovers its performance during the night.

Tandem cells and non-photovoltaic devices. One of the most promising ways to improve solar cell efficiency with perovskites is their application in perovskite-silicon tandems or all-perovskite multi-junction tandems. Like single junctions, perovskite-based tandem cells are also significantly impacted by ion migration.[218] While many challenges described above remain the same for tandem solar cells, additional tandem-specific issues can be faced because of the voltage bias that the other subcell might induce under different operating conditions onto the perovskite subcell. If the other subcell is silicon-based, the morphological structure of the silicon surface, often micrometre-sized pyramids, might affect the growth conditions and, thereby, the density of mobile ions. In all-perovskite tandems, the possible interdiffusion of ions between different sub-cells presents an additional challenge, potentially changing the bandgap and other properties of the different sub-cells.

Perovskites are used in many different optoelectronic devices, where ion migration may play a crucial role.[207] In LEDS, for example, the migration of ions might change the emission wavelength and efficiency, or shift the emission zone. For transistors and other logical devices, ion migration can lead to memory effects, at which point it could be exploited as a blessing and not a curse. Similarly, for radiation detection, ion migration might help with the long-term device stability by self-healing the damage encountered by high-energy particles.

To conclude, it is clear that there is a critical need to advance our understanding of ion migration in halide perovskites. We hope this focused review inspires new directions for mitigating ion transport effects with important implications for enhancing solar cell performance and long-term durability that are crucial for fundamental understanding and for technological applications.

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Competing interests

The authors declare no competing interests.

Graphical Abstract

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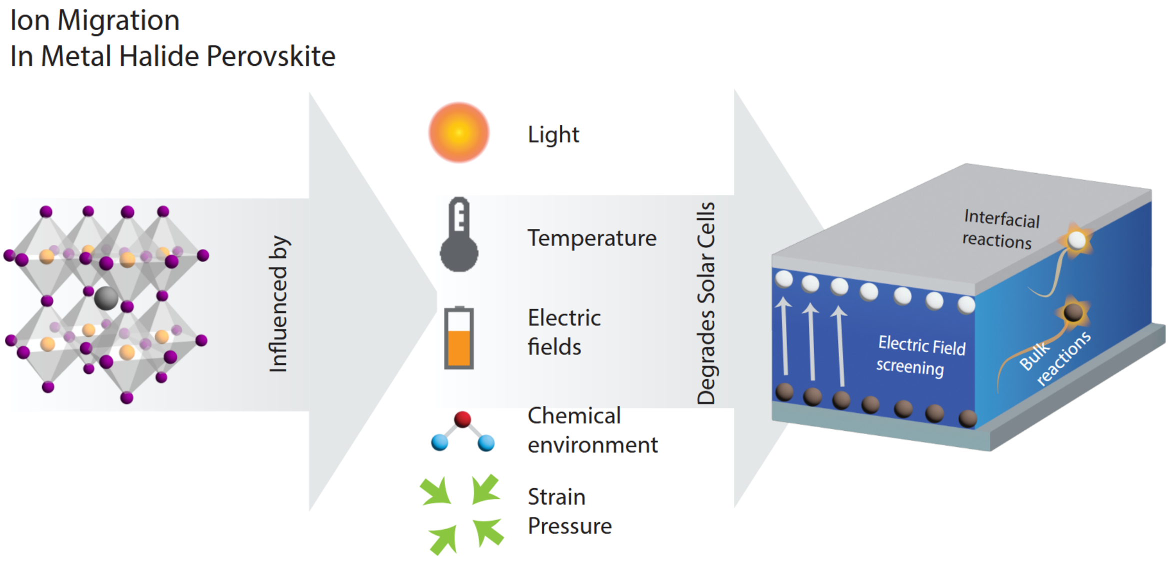
Graphical Abstrac



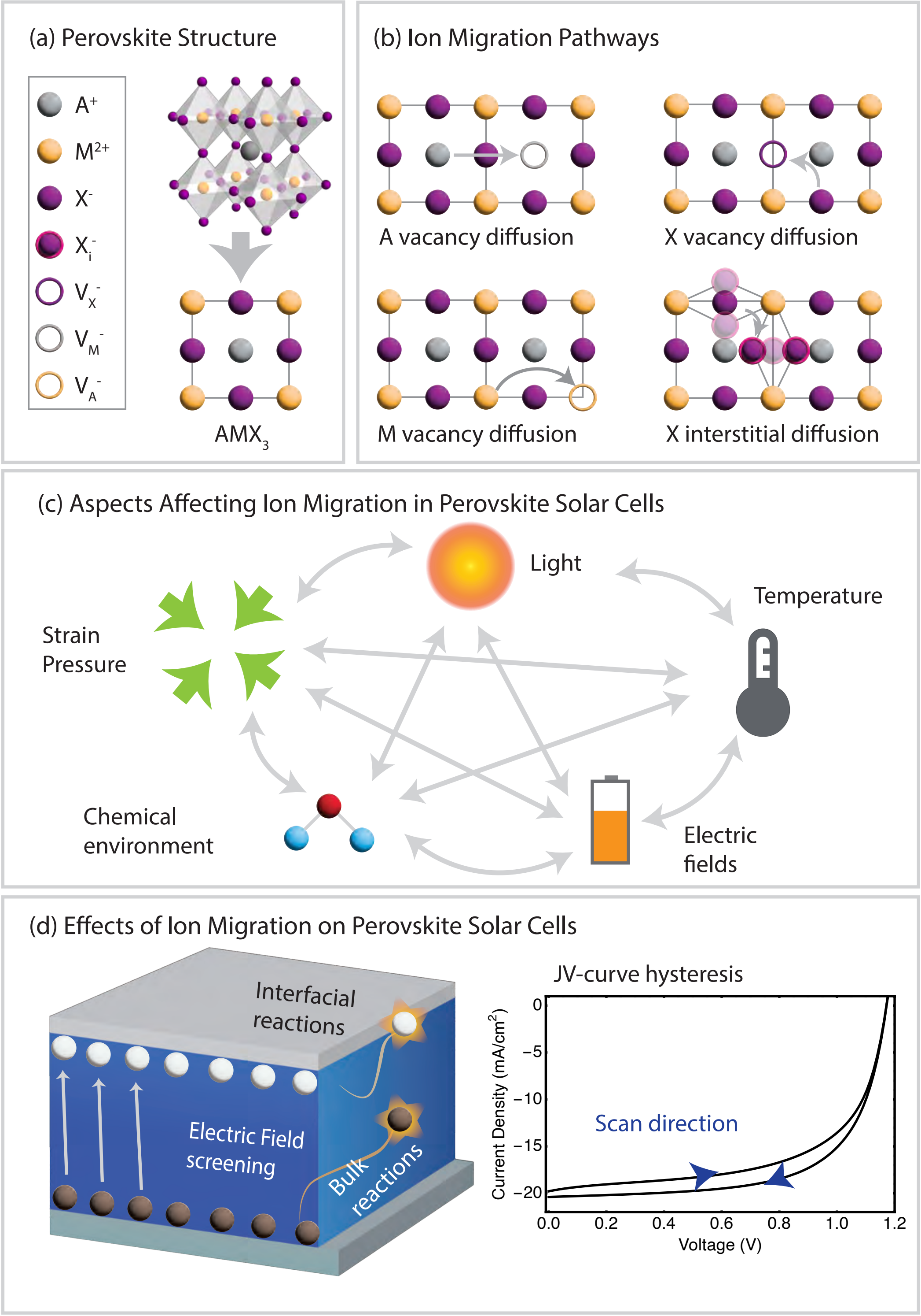


Figure 1. (a) Schematic representation of the AMX_3 metal halide perovskite structure and (b) the mechanisms for ion transport. Adapted with permission based on ref. [10] *Defects are represented by the A_L^C notation, where A is the defect type (V stands for a vacancy and i for interstitial), L represents a regular site in a crystal (A, M, X), and C effective charge. (c) Illustration of the various external and internal factors that affect ion migration. (d) Illustration of the electric field screening and the chemical reactions caused by ion migration. Depending on the scan rate, these effects can lead to a current-voltage (IV) hysteresis. The IV curve is calculated with a drift-diffusion simulation using SIMsalabim*[24] *using the parameter set found at* [25].

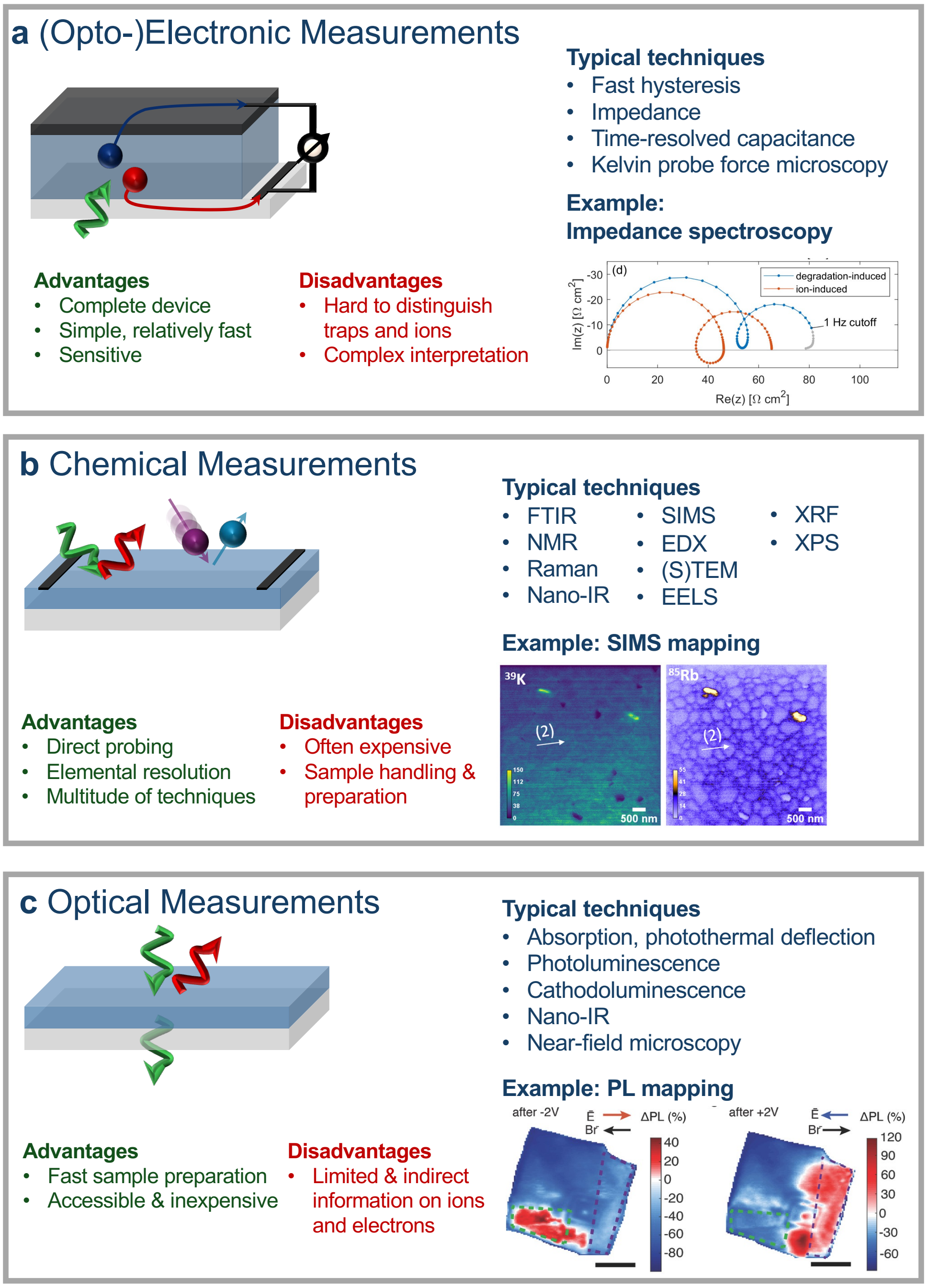
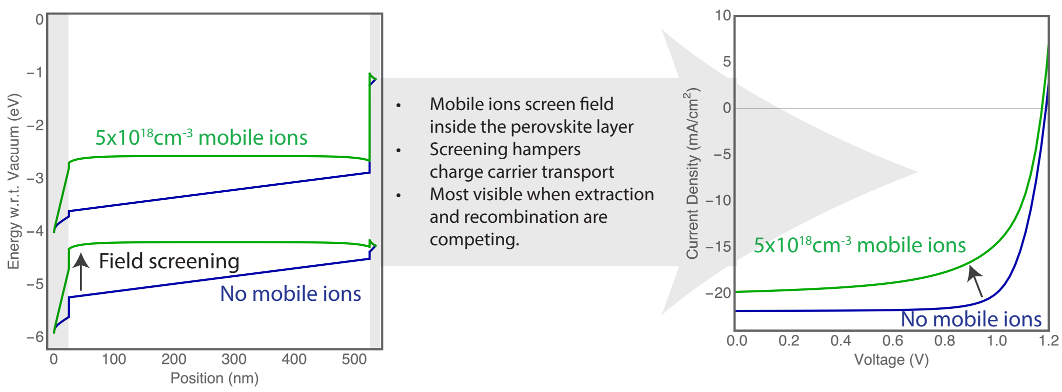
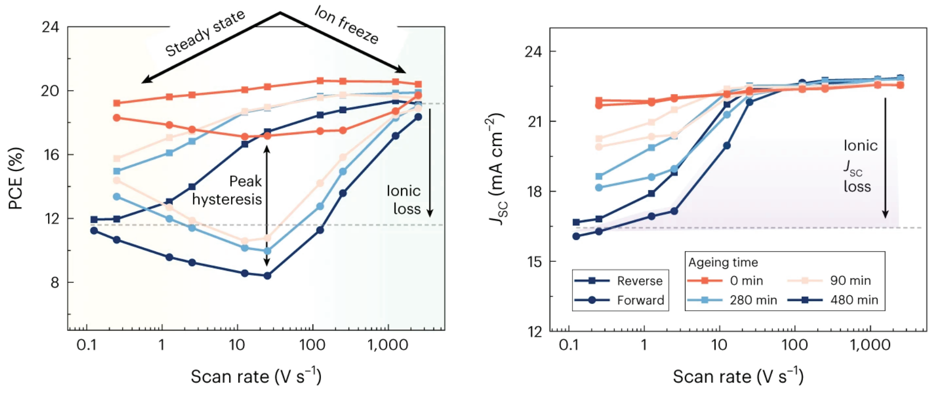


Figure 2. Schematic overview of different measurement techniques to study ion migration in metal halide perovskites. (a) Electronic measurements with impedance spectroscopy as an example showing the different effects degradation and ionic motion have on the spectrum (reproduced with permission from ref. [113]) (b) Chemical measurements. The example shows SIMS mapping of a $[RbPbI_3]_{0.05}[CsPbI_3]_{0.05}[(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}]_{0.9}$, perovskite visualizing the distribution of potassium and rubidium ions (reproduced with permission from ref. [103]). (c) Optical methods. The inset shows the PL map of a $MAPbBr_3$ single crystal on lateral contacts after application of electrical bias which moved bromide ions (reproduced with permission from ref. [66]). Several methods need to be combined to achieve a full understanding of ion migration.

(a) Field screening reduces charge carrier transport



(b) Fast hysteresis measurements reveal ion-induced degradation



(c) Mobile ion induced chemical reactions

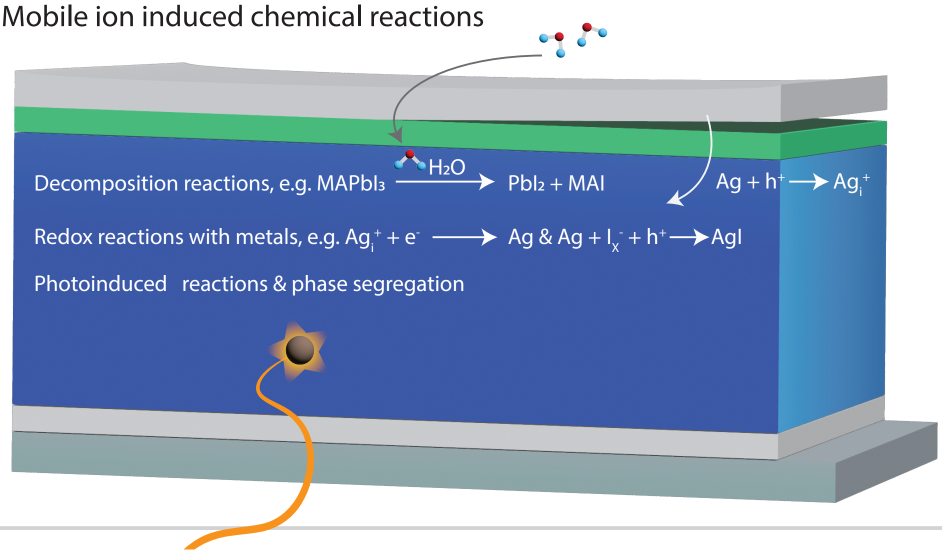
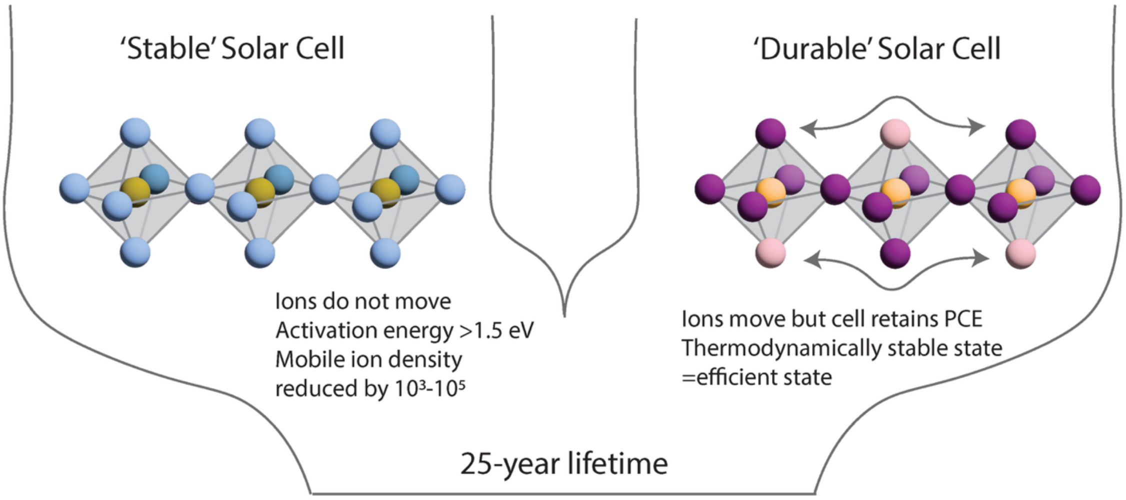


Figure 3. (a) Distribution of the conduction band (CB) and valence band (VB) of a simulated solar cell with and without mobile ions at 0V (J_{SC}) under 1 sun illumination and with a relatively low ETL mobility (10^{-4} cm^2/Vs). Corresponding IV curve of simulated solar cells without mobile ions (blue) and with a significant mobile ion density. Simulations were performed using drift-diffusion simulator SIMsalabim[24] with the parameters found at [25].(b) Fast hysteresis measurements of perovskite solar cells showing that hysteresis appears on timescales comparable to ion drift. At slow scanning speed, where ions screen the electric field in the device, photocurrent is reduced. Figure reproduced from ref. [6], © by the authors under CC-BY 4.0. (c) Overview of possible reactions facilitated by ion migration in perovskite solar cells.

(a) Two ways to achieve long lifetime in solar cells

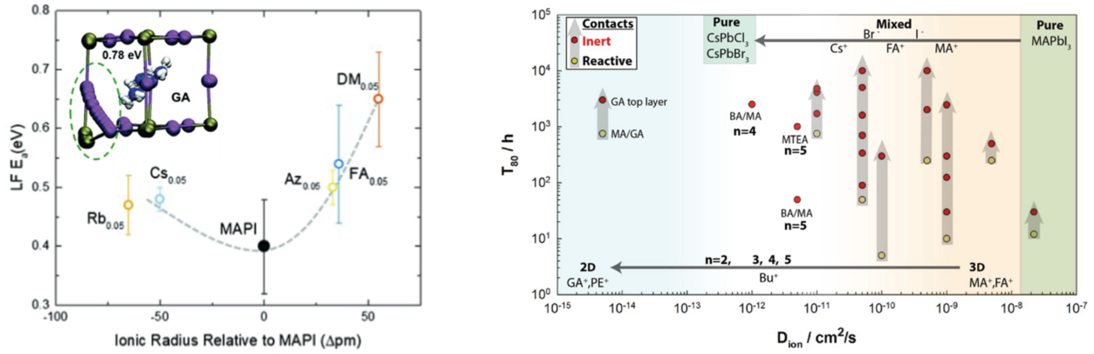


Ions do not move
Activation energy >1.5 eV
Mobile ion density
reduced by 10^3-10^5

Ions move but cell retains PCE
Thermodynamically stable state
=efficient state

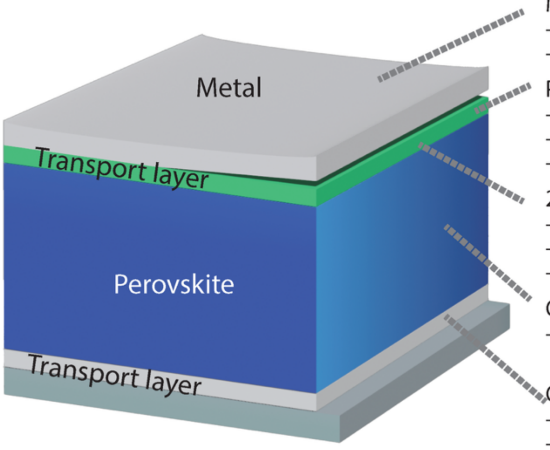
25-year lifetime

Examples of reduced ion migration leading to enahnced stability

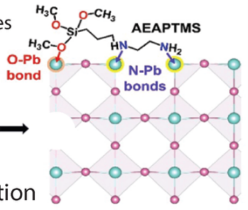

(b) Composition engineering

(c) Enhanced T_{80} lifetimes

(d) Device design to reduce the effect of ion migration



Metal contacts with low reactivity
- reduce the formation of metal halides
- increase breakdown voltage



Passivation layers
- prevent ions from crossing interface
- increase breakdown voltage
- increase Voc

2D perovskites to block ion migration
- self assemble near the interface
- block ions from reaching the interface
- prevent ingress external molecules

Composition engineering
- perovskite compositions with fewer mobile ions or higher activation barrier for ion transport

Conductive and inert transport layer
- prevents chemical reactions at the interfaces
- prevents charge build-up at the interfaces, thereby reduces effect of ion accumulation

Figure 4. (a) Schematic illustration of the two pathways to achieve a long lifetime in solar cells despite the presence of ion migration: either slow down ion migration until it is irrelevant for degradation or build a solar cell that achieves high efficiency despite mobile ions. (b) Activation energy measured by impedance spectroscopy against the A-cation ionic radius relative to methylammonium, MA. There are no activation energies for GA or Ac as ion transport was too slow to be measured in the impedance spectra (the dashed line is a guide to the eye). Adapted with permission from ref. [41]*. The inset shows ab-initio simulations of the ion transport path and activation energy in* $MA_{0.75}GA_{0.25}PbI_3$ *(key: Pb, green; I, purple). Local lattice relaxation is highlighted with displacement of the adjacent Pb ion of 0.6 Å. (c) Increased* T_{80} *timescales using various strategies to improve solar cell stability. Increasing the size of the organic cations and forming quasi-2D perovskites can improve stability by reducing the ion diffusion, as indicated by the horizontal arrow on the bottom. Compositional engineering, for example, by changing the cation or halide (horizontal arrow on the top), can also increase the stability compared to pure* $MAPbI_3$*. Finally, device design by, for example, adding inert contacts (red dots) drastically improves the stability. Adapted with permission from ref.* [207]*. (d) Illustration of the various methods used to reduce the effect of ion migration on solar cell performance and degradation. As an example, the schematic illustrates the molecular passivation of* $FAPbI_3$ *using an amino-silane. Adapted with permission from ref* [185]*.*

Info Box 1: Solid-state Ion Transport in Perovskites

Ionic conductivity (σ_{ion}) is a function of elementary charge (q), concentration (n_{ion}), and mobility of mobile ions (μ_{ion}) in accordance with equation (1).[12]

$$\sigma_{ion} = q n_{ion} \mu_{ion} \tag{1}$$

Mobility can be expressed by using the Nernst-Einstein relation following the equation (2)[12]

$$\mu_{ion} = \frac{q}{k_B T} D_{ion} \tag{2}$$

where k_B is the Boltzmann constant, *T* the temperature, and D_{ion} the ionic diffusion coefficient. The *diffusion coefficient* depends on the probability of an ion to overcome the energy barrier for an ionic jump by following the Arrhenius relationship, with a temperature-independent pre-factor D_0 (a function of the attempt frequency of ionic jump, ν_0, and the jump distance, *d*) and the change in Gibbs free energy of the jump (*ΔG*) defining *activation energy* E_A by equation (3)[26–29]

$$D = \frac{\nu_0 d^2}{6} \exp\left(-\frac{\Delta G}{k_B T}\right) = D_0 \exp\left(-\frac{E_A}{k_B T}\right) \tag{3}$$

Quantitatively, in lead halide perovskites, carrier concentrations (excess electrons and holes) are estimated to be below 10^{15} cm^{-3}, whereas point defect concentrations (deviations from ideal lattice site occupancy) are predicted to exceed 10^{18} cm^{-3} and the recombination centres (defects acting as efficient traps for charge carriers) reach 10^{13}–10^{15} cm^{-3} concentration.[10] The concentration of mobile ions is critical for device operation, and for the understanding of ionic motion, yet wide ranges of mobile ion densities are measured, between 10^{15} – 10^{19} cm^{-3}, possibly in part because their density may depend on the preparation methods, precursor ratios[30], sample morphology, composition, and structure.[31–33] Diffusion coefficients for halide anions range between 10^{-11} and 10^{-6} cm^2/s at room temperature,[34] which is faster than mobile A cations (e.g., MA$^+$) with diffusion coefficients between 10^{-10} and 10^{-12} cm^2/s.[22,35] Consequently, mobile halide anions require a few to hundreds of milliseconds to migrate through the perovskite bulk with thicknesses of several hundred nanometres, while other ions migrate on much longer timescales, which has implications on the measurement techniques.[12,36,37] The techniques that are commonly used for quantifying diffusion coefficients and the density of mobile ions are impedance spectroscopy and transient current and capacitance measurements.[22,38–40] For $MAPbI_3$, the activation energy for vacancy-mediated iodide diffusion at room temperature is around 0.4-0.6 eV,[19,41] with higher activation energies for the A-cation (i.e. MA^+, 0.8 eV)[11,41] and metal cation (i.e. Pb^{2+}, 2.3 eV).[10,18] There are variations in the values of reported E_a for different experimental methods and some reports find a broad distribution of values.[31] DFT studies can also find a variation of values due to symmetry issues in the calculations.[42] Grain boundaries can further reduce E_a. Consequently, differences may emerge due to variations in sample fabrication, leading to inconsistencies across the reports.[41,43,44]

Info Box 2: What makes a good solar cell?

For a solar cell to convert electromagnetic radiation into electricity, three conditions must be fulfilled. (1) The incoming photons must be efficiently absorbed if their energy exceeds the band gap of the photovoltaic absorber material. (2) The photogenerated electron-hole pairs must be separated such that the electrons and holes are transported to different contacts. (3) The solar cell needs to be able to generate a photovoltage such that each electron collected carries some free energy that can do work in the external circuit. For these processes to be efficient, the absorber material and contacts must have properties that define if a material is suitable for use in photovoltaics. An absorber material should have a suitable band gap (for single-junction solar cells 1.10 eV to 1.45 eV is best), a high absorption coefficient ideally already directly above the band gap, a sufficiently high mobility, a long charge carrier lifetime which is related to a high luminescence quantum efficiency, and low interface recombination velocities. Even if all these conditions are met, also the contact layers of a solar cell need to fulfil certain properties as these are usually relevant to meet condition (2), namely, to generate charge selectivity in the device. The contact layers therefore usually have different work functions, whereby the contact with the lower work function is collecting the electrons and the contact with the higher work function collects the holes. This work function difference creates an electrostatic selectivity of the device which implies that the electron contact will have a high conductivity for electrons and a much lower one for holes and *vice versa*. This difference is decisive to generate a net photocurrent. The electrostatics of any solar cell, however, can be further affected by space charge originating from either free carriers, trapped carriers, or ionic species. These space charges may for instance reduce the electric field in some parts of the solar cell and increase it in others, which will affect the efficiency of charge collection.

Summary

Ion migration plays a crucial role in perovskite solar cells. This review covers its mechanisms, impact on device performance and degradation, measurement techniques and emerging strategies towards controlling ion migration.