Origins and mechanisms of hysteresis in organometal halide perovskites

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Abstract

Inorganic–organic halide organometal perovskites, such as CH\(_3\)NH\(_3\)PbI\(_3\) and CsPbI\(_3\), etc, have been an unprecedented rising star in the field of photovoltaics since 2009, owing to their exceptionally high power conversion efficiency and simple fabrication processability. Despite its relatively short history of development, intensive investigations have been concentrating on this material; these have ranged from crystal structure analysis and photophysical characterization to performance optimization and device integration, etc. Yet, when applied in photovoltaic devices, this material suffers from hysteresis, that is, the difference of the current–voltage (I–V) curve during sweeping in two directions (from short-circuit towards open-circuit and vice versa). This behavior may significantly impede its large-scale commercial application. This Review will focus on the recent theoretical and experimental efforts to reveal the origin and mechanism of hysteresis. The proposed origins include (1) ferroelectric polarization, (2) charge trapping/detrapping, and (3) ion migration. Among them, recent evidence consistently supports the idea that ion migration plays a key role for the hysteretic behavior in perovskite solar cells (PSCs). Hence, this Review will summarize the recent results on ion migration such as the migrating ion species, activation energy measurement, capacitive characterization, and internal electrical field modulation, etc. In addition, this Review will also present the devices with alleviation/elimination of hysteresis by incorporating either large-size grains or phenyl-C61-butyric acid methyl ester molecules. In a different application, the hysteretic property has been utilized in photovoltaic and memristive switching devices. In sum, by examining these three possible mechanisms, it is concluded that the origin of hysteresis in PSCs is associated with a combination of effects, but mainly limited by ion/defect migration. This strong interaction between ion motion and free charge carrier transport can be modulated by the prevalent crystalline structure, chemical passivation, and an external photo/electrical field.

Keywords: organo lead halide perovskites, perovskite solar cells, hysteresis, ion migration, methylammonium lead iodide

(Some figures may appear in colour only in the online journal)
Abbreviation list

| Abbreviation | Description |
|--------------|-------------|
| CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) | Methylammonium lead iodide |
| CsPbI$_3$ | Cesium lead iodide |
| MAI | Methylammonium iodide |
| ITO | Indium tin oxide |
| PEDOT:PSS | Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate |
| TiO$_2$ | Titanium dioxide |
| PSC | Perovskite solar cell |
| PCE | Power conversion efficiency |
| FTO | Fluorine doped tin oxide |
| ETL | Electron transport layer |
| HTL | Hole transport layer |
| Spiro-oMeTAD | 2,2′,7,7′-tetakis-(N,N-dimethylamino)9,9′-spirobifluorene |
| PCBM | Phenyl-C61-butyric acid methyl ester |
| CB | Conduction band |
| VB | Valence band |
| GB | Grain boundary |
| UV–Vis | Ultraviolet–visible light |
| EDX | Energy-dispersive x-ray spectroscopy |
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray diffraction |
| DFT | Density functional theory |
| KPFM | Kelvin probe force microscopy |
| c-AFM | Conducting atomic force microscopy |
| CIGS | Copper indium gallium selenide |
| PFM | Piezoelectric force microscopy |
| EBIC | Electron beam-induced current |
| PTIR | Photothermal induced resonance microscopy |
| V$_{bi}$ | Built-in potential |
| $E_a$ | Activation energy |
| PET | Polyethylene terephthalate |
| PEN | Polyethylene naphthalate |

1. Introduction

A rapidly rising star on the horizon of photovoltaic research, organometal trihalide perovskite solar cells (PSCs), e.g. CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) and CsPbI$_3$, have achieved surprisingly remarkable power conversion efficiencies (PCEs) of up to 22.1% [1] in ≤6 years of intensive investigation. The unique electrical band structure of perovskite materials makes it one of the most promising candidates to replace or complement the current silicon-dominated photovoltaic market, for several reasons: (1) The direct bandgap leads to a higher optical absorption coefficient compared to silicon [2]. (2) The tunability of stoichiometry enables the modulation of its bandgap ranging from 1.4 to 2.3 eV [2–4]. (3) The high dispersion of the conduction band (CB) and valence band (VB) gives rise to a long-range balanced electron and hole transport [5, 6], effectively suppressing the photogenerated charge recombination. And (4) an excellent defect tolerance allows low-temperature solution-processing, e.g. spin-coating, blade coating, or inkjet printing, to realize low-cost, high-efficiency, and even flexible PSCs [7–9].

However, these outstanding properties and the astonishing development of PCEs are accompanied by anomalous hysteretic current–voltage (I–V) characteristics, as shown in figure 1. Hysteresis is still one of the clouds obscuring the pathway towards large-scale commercial applications for PSCs.

Hysteretic I–V characteristics (‘hysteresis’ in this review) mean that the photocurrent response exhibits a discrepancy between two sweeping directions (from short-circuit towards open-circuit and vice versa). In history, this unconventional property has become acquainted in various dissipative devices and systems [12]. As shown in figure 2, a simple Pt/TiO$_2$/Pt two-terminal device exhibits a rich hysteretic I–V characteristic [11]. When the scanning frequency increases by a factor of 10 (i.e. 10$^6$), the hysteresis loop collapses. Out of many examples, another one is the human memory system [13], i.e. synapse-based neural networks which are also related to such a mechanism.

Hysteretic behavior is generally observed in systems that involve a special ‘inertia’ [12], causing a delay between the change of the properties and the external stimulation (electrical or optical field). This temporal behavior can be described as a ‘memory’ effect, meaning that the present properties are determined by past conditions or their history. There are three possible mechanisms suggested for this history-dependent resistance switching [14], viz. (i) formation/rupture of highly conductive filaments, (ii) accumulation of mobile ions or defects at interfaces, or (iii) phase transition. In detail, in (i), inevitable defects exist in the bulk, such as vacancies or interstitial defects, and these can be driven by an external electrical field towards the opposite electrodes, forming conducting filaments. Under high currents, these filaments are melted. As a consequence, the formation and rupture of these conducting pathways lead to low and high resistive states, as shown in figure 3(a). In (ii), rather than forming conducting filaments, ions in this model accumulate at the semiconductor/metal interfaces and cause a modulation of the local interfacial barrier for charge injection/extraction, as shown in figure 3(b). In (iii), figure 3(c) illustrates that the bulk material between two electrodes undergoes a phase change (transition between conducting crystalline and insulating amorphous phases) due to an electrochemical reaction [15].

This Review specifically aims to discuss the hysteresis in organometal trihalide PSCs, and the origin of this abnormal behavior. First, we will briefly summarize the observation of this hysteretic behavior. Next, we examine the microscopic models, including ferroelectric switching, charge trapping/detrapping, and ion migration. Third, we will present approaches to suppress hysteresis and discuss potential applications in photovoltaic and memory devices.

2. Origin of hysteresis

Snaith et al [16] provided a comprehensive summary of the features: (1) Hysteresis is dominantly associated with the perovskite material itself. (2) Selective contact materials, i.e.
hole and electron transport layers (TLs), play crucial roles in this behavior, including the material and the morphology (mesoporous or planar) of the TLs. (3) The time scale of hysteresis is ~100 s [17, 18], which presents a contrast for the typical charge generation/recombination process (~ns) in PSC [5]. (4) Hysteresis strongly depends on external scanning parameters [19] such as scan rate, amplitude of external electric field, scanning direction, pre-scanning conditions, etc. In the following sections these different mechanisms will be examined in detail.

2.1. Ferroelectricity

Ferroelectricity is a property possessed by a class of materials, in which the spontaneous polarization \( P \) can be modulated by an external electric field. The polarization originates from non-centrosymmetric structures. Though MAPbI\(_3\), the most intensely researched photovoltaic perovskite material, belongs to the centrosymmetric tetragonal space group [2, 20] of \( I4/mcm \) at room temperature, the reorientation of the MA group [21] and the distortion of PbI\(_6\) cages can decrease the crystal lattice symmetry, resulting in a spontaneous polarization [22, 23]. The polarization of organometal perovskite materials has been proved both theoretically and experimentally. Employing density functional theory (DFT), Frost et al [24] and Rappe et al [25, 26] reported the appearance of a strong dipole moment or polarization in the bulk of perovskite materials. In terms of experiments, x-ray diffraction (XRD) has demonstrated a lower symmetry structure at room temperature [27], and Raman spectra confirmed the intrinsic MA vibrational mode which gave rise to the existence of an intrinsic dipole [28]. In addition, electroabsorption spectroscopy or Stark spectroscopy [29] provided unambiguous quantitative evidence of permanent dipoles in the organolead halide perovskite [10, 30].

Two criteria—(1) the existence of polarization and (2) its switchability by an external electrical field—would be required for ferroelectricity. For the second criterion, several groups such as Chen et al [31], Coll et al [32], and Kutes et al [33], demonstrated switching of spontaneous polarizations, resulting in a piezoresponse hysteresis loop in both amplitude and phase using piezoelectric force microscopy (PFM), shown in figure 4. Wei et al [27] also presented ferroelectric properties by employing traditional \( E–P \) measurements on the basis of a classical Sawyer-Tower circuit.

Models based on the ferroelectricity of perovskites [23, 27, 31, 34] are proposed to explain the hysteresis behavior in terms of polarization switching. When applying an electrical field, as shown in figure 5, these dipoles are aligned following the direction of the external field. This dipole alignment process generates a compensating field, i.e. depolarization field. This additional field significantly influences the effective potential dropped in the bulk and increases/decreases the separation of charge carriers. In a first-order approximation we can write

\[
V_{oc+} = V_{bi} + V_p
\]

(1)

\[
V_{oc−} = V_{bi} - V_p
\]

(2)

Where \( V_{oc+} \) and \( V_{oc−} \) are the open circuit voltages under a positive and negative poling field, respectively. \( V_{bi} \) is the built-in potential in the device resulting from the work function difference between two selective electrodes. \( V_p \) arises from the depolarization field due to the alignment of dipoles. This change of \( V_{oc} \) is supposed to agree with the observed shift of \( V_{oc} \) during \( I–V \) curve measurements in figure 1.

In addition, the modulation of the prevalent internal field also gives rise to a change in band bending, influencing the local interfacial barriers and space-charge regions, as shown in figure 5. In a ferroelectric perovskite with multidomain structures, charge carriers move along the domain boundaries. This is depicted as a ‘ferroelectric highway’ proposed by Frost et al [24, 35]. This modulation of the internal electrical field thus results in the hysteresis of the \( I–V \) measurement,

![Figure 1](image-url)  
**Figure 1.** A typical \( I–V \) curve hysteresis behavior in a perovskite solar cell, with scanning speed of ~0.9 V s\(^{-1}\) at room temperature. The arrows exhibit the directions of voltage scanning. Inset indicates the shift of the \( I–V \) curve. The dashed red line is the extension of the \( I–V \) curve below ~0.75 V based on standard single-junction diode equation, and the blue circle indicates the horizon shift of the curves near the flat-band condition. This shift will be discussed in following section. Reprinted with permission from [10]. John Wiley & Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

![Figure 2](image-url)  
**Figure 2.** Hysteresis in an \( I–V \) curve characteristic of a Pt/TiO\(_2)/\) Pt device with frequency of \( \omega_0 \) and \( 10\omega_0 \), respectively. Inset is the schematic structure of the memristive device. Adapted by permission from Macmillan Publishers Ltd: Nature [11], copyright 2008.
which also reflects the change of the effective extraction of photogenerated charge carriers through the TLs [34]. Although this ferroelectricity model has gained some acceptances for the explanation of hysteresis, it still suffers from several arguments.

1. The existence of ferroelectric property in organometal perovskite is under debate. Coll et al [33] obtained the switching behavior of polarization; however, the field decay was very fast. In addition, by using a Sawyer-Tower circuit to characterize the polarization, there appeared a non-standard $P$–$E$ hysteresis loop. Moreover, both Xiao et al [36] and Fan et al [37] claimed that there was no obvious phase contrast during the positive and negative poling process in PFM characterization. Wei et al [27] have obtained some features of ferroelectricity, i.e., ‘s’ shape during the $P$–$E$ measurement. However, this ferroelectric effect was considered too small to be convincing.

2. The time scale of polarization switching does not agree with the one observed in $I$–$V$ curve hysteresis. Based on first-principle simulations (e.g. DFT), the time interval for polarization switching was in the nanosecond region [38]. Leguy et al [36] estimated the time interval within a millisecond range. In contrast, the typical switching behavior observed in PSC is $>10$ s, as pointed out previously.

3. Ferroelectric materials require an electrical field inside that is larger than the coercive field to switch ferroelectric domains. This contradicts with the observation of step-wise $I$–$V$ curve measurements, which always exhibit a transition-like behavior [39]. Hence, although the contribution of ferroelectricity to hysteresis is still under debate, this discussion suggests that ferroelectric polarization may not play a dominant role in the $I$–$V$ hysteretic behavior.

2.2. Charge trapping/detrapping

Low-temperature solution processing of perovskite films inevitably involves a certain amount of defect states inside the perovskite films, which show a potential impact on the charge separation/recombination and charge transport [40]. These defects inside are categorized as (1) defects located at the CB/VB band edge following an exponentially decreasing distribution and (2) defects at deep levels within the bandgap following a Gaussian distribution [41]. For the first defect category, evidence illustrates that the energetic width of defect states near the band edge, i.e. Urbach energy, is between 20 and 40 meV depending on the film fabrication method [42]. For the second defect category, the defects reside deep in the bandgap and serve as trap sites for photogenerated charge carriers, playing an important role in Shockley–Read–Hall non-radiative recombination [44, 45]. According to the classical detailed balance model [46], any non-radiative recombination in the open circuit condition leads to a loss of PCE [47]. By filling and releasing charges at these trap sites, the charge transport of photogenerated charges is modulated commensurately, resulting in a hysteretic behavior.

Atomistic simulations, as summarized in figure 7, reveal the energetic distribution of possible defect states, i.e., vacancies, antisites, and interstitials, as shown in figure 6 [48]. With the help of spectroscopic characterization techniques,
it became evident that these traps are dominantly accumulated at the interface or surface, where the periodical crystal-line structure is deformed or where strong electron–phonon coupling takes place (which may be enhanced due to those deformations) [49–51]. Temperature-dependent admittance spectroscopy enables us to further identify the energetic distribution of these defects in the bandgap [52, 53]. It is found that these deep-level defects, which are responsible for non-radiative recombination, require higher formation energies. Detailed values can be found in [54]. This explains the origin of the excellent defect tolerance of these perovskite materials.

Kelvin probe force microscopy (KPFM) [55, 56], employed to investigate the potential distribution on the surface, provides direct evidence of interfacial charging. As shown in figure 8, mapping the charge carrier density distribution along the cross section of a device allows us to track the evolution of accumulated charges after illumination. It has been observed that after turning on the illumination, the accumulation of hole carriers at the interface between perovskite and hole transport layer (HTL) materials results in a reduction of the effective charge extraction through this interface. This observation of charge accumulation and unbalanced charge transport agrees with studies conducted by electron beam–induced current (EBIC) measurements [57, 58].

It is natural to fill or compensate these trap states to improve the device performance and decrease the trap-related hysteresis. Motti et al [59] demonstrated, by means of luminescence characterization, that exposure to a small amount of
O\textsubscript{2} atmosphere led to a significant decrease of trap states in the perovskite material. Noel et al [60] and Dane et al [61] proved that surface treatments with Lewis bases such as pyridine reduced recombination centers, enhancing the photoluminescence (PL) intensities and PL lifetimes of the perovskite films. In addition, it has also widely been observed that the involvement of phenyl-C61-butyric acid methyl ester (PCBM) molecules [62, 63], either as an interlayer or mixed as a bulk heterojunction structure, is able to passivate defects and alleviate/eliminate the hysteresis. The detailed process will be discussed later in this Review.

Although the defect passivation process significantly enhances the performance and decreases the hysteresis, it is found that the time interval for charge trapping and detrapping ranges within milliseconds [64], or even nanoseconds [65], which is much shorter than the typical timescales (>10 s) for hysteretic behavior, vide supra [66]. Therefore, the observed giant switchable photovoltaic effect and slow (~seconds range) increase in photocurrent decay after poling cannot be explained by a charge-trapping mechanism alone [36]. van Reenen et al [64] recently proposed that, rather than a single origin, the hysteresis has to be interpreted in terms of a combination of factors, including (1) charge trapping/detrapping and (2) ionic migration, which will be discussed in detail in following sections.

2.3. Ion migration

Although there are several hysteresis models proposed, ionic migration may be considered the dominant factor, especially taking into account the time scale and recent direct/indirect evidence gained from, e.g. activation energy, band bending, or capacitance measurements. This ionic transport is not only relevant for the I–V curve hysteresis [67] but also a number of other unusual emission (e.g. PL, electroluminescence) and capacitive behaviors [68–72]. Briefly, as illustrated in figure 9(a) and (b), under an external electrical field, ions are driven towards the opposite interfaces (perovskite/ETL and perovskite/HTL, respectively). These accumulated ions result in both a change of the internal field and a modulation of the interfacial barriers, thus giving rise to a hysteretic behavior. So far ion migration has been formulated to be responsible of hysteresis in conjunction with a trapping/detrapping model. In addition, it has also been proposed that ion migration alone can also explain hysteresis in PSCs without the need of a trapping/detrapping model. In this model during the J-V measurement the applied bias induce ion migration towards the external interfaces dramatically modifying the energetic landscape with the voltage at the perovskite/contact interfaces as shown in figure 9(c) and (d) [73]. Indeed, bands can shift towards inversion regime producing a huge accumulation of charge. These accumulated charges are released during the voltage sweeping with the kinetics controlled by ion diffusion, causing extra current over the normal response. The charge shows a retarded dynamics due to the slow relaxation of the accompanying ionic charge, that produces variable shapes depending on the scan rate or poling value and time. In the following sections, aspects of ion migration, i.e. the species of ions, ion migration channels, capacitive studies, the involved thermal activation energy, and the influence on band bending, will be discussed in detail.

2.3.1. Migrating defect species. There are several candidates for the migrating ions prevalent in MAPb\textsubscript{3} PSCs: (i) hydrogen ions, (ii) methylammonium (MA\textsuperscript{+}), or (iii) iodide ions [75, 76]. In detail, these ions originate from defect states during low-temperature fabrication, including vacancies (e.g. V\textsubscript{MA}, V\textsubscript{Pb}, and V\textsubscript{I}) (i.e. Schottky defects), interstitial defects (e.g. MA\textsubscript{i}, Pb\textsubscript{i}, I\textsubscript{i}) (i.e. Frenkel defects), and antisite substitutions (e.g. MA\textsubscript{i}, Pb\textsubscript{i}) [77, 78]. Note that, due to the extremely high activation energy (explained in following section) [77, 79], migration of Pb\textsuperscript{2+} ions can be excluded in this discussion.

(i) On the basis of first-principle calculations (DFT method), Egger et al [80] proposed that hydrogen ions formed through the displacement of iodide ions and hydrogen bonds cause an impact on observed mobile charged defects. However, due to the weak acidity of methylammonium, it is difficult to maintain a high concentration of H\textsuperscript{+} in PSCs [76]. Hence, even though there exist H\textsuperscript{+} ions, they should play a minor role compared with other defects.

(ii) MA\textsuperscript{+} ions are proposed as one of the major reasons for the observed and demonstrated giant field-switchable photovoltaic effect in PSCs [74]. Employing the recently invented technique of photothermal-induced resonance microscopy, Yuan et al [81] observed a MA\textsuperscript{+} ion concentration contrast between before and after poling the device. This redistribution of MA\textsuperscript{+} ions induced by an external electrical field clearly indicated the migration of MA\textsuperscript{+} ions. Also, Azpiroz et al [77] proposed that, on the basis of computational studies, MA\textsuperscript{+} ions were driven...
and aligned by an external field to accumulate at the TL/
perovskite interface, thus hindering/enhancing the effec-
tive charge transport and extraction process.

However, the extent of the contribution of MA$^+$ ions to the hysteresis is still under debate. van Reenen et al [64] estimated the diffusion coefficient of mobile ions, responsible for the measured hysteresis with around $2 \times 10^{-11}$ cm$^2$ s$^{-1}$. Eames et al [79] estimated the diffusion of I$^-$ ions with a coefficient of $10^{-12}$ cm$^2$ s$^{-1}$. Their estimated value for MA$^+$ ions, however, was $10^{-16}$ cm$^2$ s$^{-1}$ [79], which was four to five orders of magnitude lower than the coefficient of I$^-$ ions. Therefore, iodide ions may play a more important role in the hysteresis compared to MA$^+$ ions [79].

(iii) Recent evidence consistently suggests that the migration of iodide ions is the main reason for the hysteretic behavior. Xiao et al [74] proposed that positively charged iodide vacancies $V_I$ were responsible for the $n$-type doping in PSC under an external electrical field. Furthermore, long-time (110 min) electrical biasing (1.2 V $\mu$m$^{-1}$) in devices with lateral configured elec-

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**Figure 9.** Schematic diagram of ionic migration under different external electrical fields in a PSC. (a) Positive and (b) negative ions drift towards to opposite electrodes and accumulate at these interfaces. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications [74], copyright 2015. (c), D) Schematic representation of the energy diagram of a perovskite solar cell with electron-selective contact at the left and holes elector contact at the right side. (c) Equilibrium in the dark. (d) Open-circuit under illumination. $E_c$ and $E_v$, edges of conduction and valence band, respectively; $E_F$, Fermi level; $E_{Fp}$ and $E_{Fp}$, quasi-Fermi level of electrons and holes, respectively; $V$, external voltage of the contacts; $V_{bi}$, constant built-in voltage; $V_s$, variable surface polarization voltage. Indicated in panel b are the accumulation of holes and cations and the tunnelling of electrons across the surface barrier. Note that electrons at the contact side of the interface that contribute to charge compensation are not shown. Reprinted with permission from [73]. Copyright ©2017 American Chemical Society.

**Figure 10.** XPS result of a CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ device with lateral electrodes. (a) and (b) are XPS spectra of Pb and I elements, respectively, near the ground electrode. (d) and (e) are the XPS spectra of Pb and I elements, respectively, near the positive electrode. (c) Schematic illustration of the setup for the measurement of element distribution. The applied DC voltage is 1 V for 30 min. The lateral electrode distance is 200 $\mu$m. (f) Ratio of I/Pb distribution across the channel after applying bias between two lateral electrodes. The dashed line shows the stoichiometry of perovskite, I/Pb ~ 3. Reprinted with permission from [10]. John Wiley & Sons. Copyright ©2016 by John Wiley & Sons, Inc.
trodes led to an obvious degradation at the anode side. To elucidate the species of ions, Yang et al. [82] conducted long-term (one week) high-temperature (50 °C) electrical biasing (DC current of 10 nA) experiments using a Pb/MAPbI3/AgI/Ag device structure. The formation of PbI2, which was characterized by energy dispersive x-ray spectroscopy (EDX) and XRD, indicated that iodide ions resulted in the observed stoichiometric change. Similarly, by using XRD and EDX, Yuan et al. [83] directly observed the migration of iodide ions at higher temperatures (330 K) under an electrical field of 3 V µm−1 for 20–60 s. During the experiment, MAPbI3 first decomposed into a small thread of PbI2, which could be driven by the external field from the positive to the negative electrode. Furthermore, Li et al. [10] carried out the x-ray photoemission spectroscopy (XPS) characterization of long-term (30 min) biased perovskite films with laterally configured electrodes at room temperature. After 30 min biasing (1 V), this perovskite film was measured by XPS, which quantitatively characterized the element distribution across the channel. As shown in figure 10(f), it demonstrated that the I/Pb ratio was 5.57 at the positive electrode, while the ratio at the ground electrode was only 2.59. This result showed the significant iodine element redistribution away from its initial stoichiometric ratio I/Pb of ~3 in the pristine device. In addition, as shown in figure 10(a), analyzing the binding energy of Pb in the XPS signal revealed the decomposition of MAPbI3 at the negative electrode, which was consistent with the observed degradation characterized by Xiao et al. [74].

2.3.2. Detailed migration process and migration channels. The detailed migration process of ions in PSCs can be treated considering dynamics of defect states. Due to the difficulty of directly characterizing the ionic movement, most of the descriptions are based on theoretical DFT calculations [38, 79, 84].

Figure 11. Schematic diagram for the ionic migration, especially I−, Pb2+, and MA+ ions, respectively. (a) Iodide ions move along the octahedron edge, Pb2+ ions move along the diagonal direction. (b) MA+ ions move via neighboring vacancy sites. Reprinted with permission from [79] CC BY 4.0 (c) Detailed process of iodide ion migration. (i) Bulk structure is a perfect periodical crystalline structure. (ii) Distance between iodide vacancies and ions increases, denoted as TS states. (iii) Two intimate defect states, with a distance of 4.5 Å, equatorial V1I and apical I−, respectively. (iv) Two intimate defect states consequently with a distance of 6.5 Å, both V1I and I−, at the apical sites. Reproduced from [84] with permission of The Royal Society of Chemistry.

Figure 12. Ionic migration pathways of different defects states, including (a) V1I, (b) VMA, (c) VPb, and (d) I− defects. Solid lines refer to the ion migration, while dashed lines refer to migrating vacancies. H are atoms depicted in white, C in brown, I in purple, N in blue, and Pb in black. Adapted with permission from [77]. Copyright ©2015 Royal Society of Chemistry.
Herein, the ionic transport is described as a hopping mechanism, i.e. jumping between neighboring sites [85]. As shown in figure 11, (i) MA$^+$ ions migrate into nearby vacant cages, (ii) Pb$^{2+}$ ions migrate via the diagonal direction, while (iii) iodide ions move along an octahedron in the Pb–I plane [79]. The migration of these ions requires energy to open the PbX$_3$ framework, which acts as a barrier for the ionic migration. This barrier results in an activation energy $E_a$ that will be discussed in detail in the following section. For the mobile ions, e.g. iodide ions, Mosconi et al [84] provided a detailed description on the basis of DFT simulations. Accompanying the reorientation of the MA$^+$ group, an iodide interstitial ($I_i$) forms, leaving iodide vacancies ($V_I$) at its original location. Then, $V_I$ and $I_i$ form $V_I/I_i$ pairs, denoted as a transition state (TS) in figure 11(c). Next, by overcoming the activation energy, $V_I$ and $I_i$ separate by a distance of 4.5 and 6.5 Å, respectively (figure 11(c)), generating distinct defects by migrating in opposite directions within the electrical field. In addition, Azpiroz et al [77] provide detailed migrating pathways for each defect using DFT calculations, including iodide vacancies, MA vacancies, Pb vacancies, and iodide interstitials, as shown in figure 12. The migration paths of individual ions/defects are consistent with the one proposed by Eames et al [79].

Apart from hopping through point defects (Schottky and Frenkel defects) ascribed from the thermodynamic equilibrium in the crystal lattice [85] (shown in figures 13(a) and (b)) there exist other possible ion migration channels. For instance, local lattice distortions, originating from charge accumulations or additional impurity atoms, light illumination, or piezoelectric effects, provide additional migration channels as shown in figures 13(d)–(f) [75]. Moreover, recent evidence emphasizes the impact of grain boundaries (GBs), which possess a large density of defects, illustrated in figure 13(c), on the ionic migration. Xiao et al [74] found that compared with large-crystal-size (between 600 and 1000 nm) devices, in films composed of smaller-sized grains (around 300 nm), the polarization can be switched more easily under an external electrical field. By carrying out conducting atomic force microscopy (c-AFM), EDX, and SEM, Shao et al [86] indicated that the devices with GBs where these defects resided was the fast-moving channel for ion migration after poling of 0.5 V µm$^{-1}$ for ~120 s at 330 K. Moreover, Yun et al [87] conducted Kelvin probe force microscopy to reveal that ion migration near GBs was much faster than inside the grains at

![Figure 13. Schematic diagrams illustrating the ionic migration channels. (a) Schottky defects, or vacancies; (b) Frenkel defects, or interstitial defects. (c) Ion migration at the grain boundaries. Distortion of lattice due to (d) accumulation of charges, (e) impurities, (g) light-illumination-induced lattice softening, and (f) piezoelectric effect. Reprinted with permission from [75]. Copyright ©2016 American Chemical Society.](image)

![Figure 14. Illustration of ion migration and the energy diagram for the migrating positive and negative ions, via periodical barriers, denoted as activation energy $E_a$ here. L is the distance between the neighboring sites. Red and blue circles represent MA and iodide ions, respectively. Reprinted from [77] with permission of The Royal Society of Chemistry.](image)
room temperature under ambient conditions. At the GBs, ions exhibited higher diffusivity and supported a more effective charge separation. Xing et al. [88] also observed that devices with larger crystal sizes (~1 µm) exhibited higher activation energies than smaller crystal sizes (~300 nm), i.e., ions had to overcome higher barriers to migrate. MacDonald et al. [89] revealed that GBs demonstrated a depth-dependent resistivity and this inhomogeneity was one of the limits for the improvement of PSC efficiency. The aforementioned studies show that GBs play a decisive role in perovskite-based devices, and further work will still be required towards their detailed understanding.

### 2.3.3. Activation energy characterization

The ionic migration/transport within the bulk of solids [85], especially in traditional perovskite materials (ABO₃), has been intensively investigated. The movement of ions is facilitated by a hopping mechanism between the atomic lattices via defect states (i.e., Table 1.

| No | Characterization method | Bulk material | Particle type | Activation energy (eV) |
|----|-------------------------|---------------|---------------|------------------------|
| 1  | Theoretical calculation | MAPbI₃ film   | V⁺, MA, Pb⁺   | 0.08                   |
|    |                         |               |               | 0.46                   |
|    |                         |               |               | 0.8                    |
|    |                         |               |               | 0.09                   |
|    |                         |               |               | 0.56                   |
| 2  | Theoretical calculation | MAPbI₃ film   | V⁺, MA, Pb⁺   | 0.58                   |
|    |                         |               |               | 0.84                   |
|    |                         |               |               | 2.31                   |
|    | Short-circuit photocurrent relaxation | MAPbI₃ film | V⁺, MA, Pb⁺   | 0.60-0.68 |
| 3  | First-principle calculation | MAPbI₃ film | V⁺, MA, Pb⁺   | 0.44                   |
|    |                         |               |               | 0.57                   |
|    |                         |               |               | 0.48                   |
|    |                         |               |               | 0.61                   |
| 4  | Minimum-energy-path calculation | MAPbI₃ film | H⁺           | 0.29                   |
| 5  | Impedance spectra at different temperatures | MAPbI₃ film | MA⁺ ion      | 0.58 (<320 K)          |
|    |                         |               | MA⁺ ion      | 0.23 (>320 K)          |
|    |                         |               | MA⁺ ion/F⁺ ion | 0.63              |
|    |                         |               | MA⁺ ion/F⁺ ion | 0.22 (<330 K) |
|    |                         |               | MA⁺ ion/F⁺ ion | 0.79 (>330 K) |
| 6  | Temperature-dependent stepwise-stabilized current responses | MAPbI₃ film | V⁺           | 0.10-0.18 (1 sun) |
| 7  | Temperature-dependent current density in dark | MAPbI₃ ClₓIₓ film | I⁻ ion | 0.23-0.31 |
| 8  | Temperature-dependent bulk conductivity | MAPbI₃ film | Mobile ions | 0.43                   |
| 9  | Theoretical calculation | MAPbI₃ film | Mobile ions | 0.5                    |
| 10 | Temperature-dependent conductivity | MAPbI₃ film | MA⁺ ion | 0.36                   |
| 11 | Growth rate of PL peak at different temperature | MAPbBr₃Iₓ | Br⁻ and I⁻ ion | 0.27                   |
| 12 | Rate of PL rise at different temperatures | MAPbI₃ film | V⁺    | 0.137                  |
| 13 | Rate of PL rise at different temperatures | MAPbI₃ film | V⁺    | 0.19                   |
| 14 | Grain growth exponent at different temperature | MAPbI₃/PbI₃Clₓ film | Mobile ion | 0.3                    |
| 15 | Temperature-dependent conductivity | MAPbI₃ film | Mobile ion | 0.08-0.14 (0.25 sun) |
|    |                         |               | Mobile ion | 0.27-0.50 (dark)     |
|    |                         |               | Mobile ion | 0.47 (0.25 sun)      |
|    |                         |               | Mobile ion | 1.05 (dark)          |
| 16 | Current difference between forward and reverse voltage scan at different temperatures | MAPbI₃ film | Mobile ion | 0.314-0.341 (1 sun) |
|    |                         |               | Mobile ion | 0.168 (1 sun)        |
|    |                         |               | V⁺    | 0.28-0.45            |
|    |                         |               | V⁺    | 0.7-1.12             |
|    |                         |               | V⁺    | 1.39-1.78            |
|    |                         |               | V⁺    | 0.27-0.29            |
|    |                         |               | V⁺    | 0.7-1.2              |
|    |                         |               | V⁺    | 0.94-1.22            |
| 17 | Temperature shift in the capacitance derivative peak | MAPbI₃ ClₓIₓ film | Electrode polarization | 0.45 (low temperature) |
|    |                         |               | Electrode polarization | 0.25 (high temperature) |
| 18 | Molecular dynamics simulation | MAPbI₃ crystal | V⁺    | 0.1                    |
|    |                         |               | V⁺    | 0.24                   |

2.3.3. Activation energy characterization. The ionic migration/transport within the bulk of solids [85], especially in traditional perovskite materials (ABO₃), has been intensively investigated. The movement of ions is facilitated by a hopping mechanism between the atomic lattices via defect states (i.e.,...
vacancies, interstitials, etc) [90]. This hopping process to the neighboring sites requires energy, i.e. an activation energy $E_a$, to overcome the barriers, as shown in figure 14.

This hopping process highly depends on the temperature and is described as a thermally activated point defect movement. The migration ratio, $r_m$ is expressed empirically in form of an Arrhenius relation [10, 38, 77, 91]:

$$r_m \propto \exp \left( -\frac{E_a}{k_BT} \right)$$

(3)

where $k_B$ and $T$ are the Boltzmann constant and absolute temperature, respectively. By fitting the slope in temperature-dependent measurements, the respective activation energy can be obtained. Since $E_a$ strongly relies on the ionic species, determining the value of $E_a$ enables us to identify which ions are moving. Taking into account the different phenomena related to ionic migration, it is feasible to obtain and compare $E_a$ in different measurements, as summarized in table 1. For instance, Meloni et al [38], Eames et al [79], Li et al [10], and Yu et al [91] extracted $E_a$ by fitting temperature-dependent transient $I$–$V$ curve measurements. Yang et al [82] obtained the $E_a$ by carrying out temperature-dependent transient $I$–$V$ curve measurements. Yang et al [82] observed that, under 0.25 Sun light illumination conditions, the activation energy decreased from 0.27 to 0.08 eV in polycrystalline and from 1.05 to 0.47 eV in a single crystal compared with dark conditions. In addition, giant PL blinking in perovskite films and nanoparticles is widely observed at room temperature [68, 72, 98, 99]. This is ascribed to light-driven ion migration and subsequent accumulation, which can act as non-radiative recombination centers in the film.

Apart from the impact of the chemical structure or stoichiometry [91] of the perovskite, an external optical field can also significantly influence the activation energy. It is found that illumination can decrease the barrier of hopping and facilitate the migration. As shown in figure 15, Xing et al [88] observed that, under 0.25 Sun light illumination conditions, the activation energy decreased from 0.27 to 0.08 eV in polycrystalline and from 1.05 to 0.47 eV in a single crystal compared with dark conditions. In addition, giant PL blinking in perovskite films and nanoparticles is widely observed at room temperature [68, 72, 98, 99]. This is ascribed to light-driven ion migration and subsequent accumulation, which can act as non-radiative recombination centers in the film.

Here, it is necessary to mention that, by characterizing the temperature-dependent properties, perovskite materials show a strong sensitivity to the external optical/electrical fields and temperature due to thermally activated ion migration. In presence of an external electrical field (~3 V µm$^{-1}$ for 1 min) and temperatures as low as 330 K, perovskite (MAPbI$_3$) films can exhibit significant degradation (leading to PbI$_2$ formation) [83]. Therefore, to fulfill the requirement of practical photovoltaic applications, it is essential to further improve the device stability under high temperature and external optical/electrical fields [100–102].

2.3.4. Capacitive studies. Capacitance is the ability of a material to store an electric charge by different mechanisms. The time domain in which different capacitive processes occur in a solid can be divided into fast processes such as electronic movement ($\approx 10^{15}$ Hz), atomic vibrations ($\approx 10^{12}$ Hz), or dipolar displacements ($\approx 10^{8}$ Hz) and slow processes like ion migration ($<10^{3}$ Hz) or slow photo/electrochemical reactions [103, 104]. The interpretation of capacitance in PSCs is complex due to
the richness of physical phenomena occurring simultaneously during device operation. These capacitive processes include (1) dielectric capacitance, (2) chemical capacitance, (3) depletion layer at contact barrier, and (4) electrode polarization [97, 105, 106]. A complete discussion of the different processes is beyond the scope of this Review, and hence only processes related to ion migration will be discussed here. In an ideal scenario, these processes occur at different characteristic time domains (frequency), and impedance spectroscopy (IS) can be a useful tool to understand the working principles of PSCs, as the technique can resolve signals in the frequency domain.

During IS measurements, a DC voltage is applied in an operating device and an AC voltage perturbation is overimposed. The differential current output offers capacitance information from the operating device under different conditions (i.e. light or dark).

Figure 16(a) shows a representative capacitance frequency plot of a device in the configuration FTO/TiO2/MAPbI3/Spiro-oMeTAD/Au. In the dark at an applied bias of 0 V, two plateaus in capacitance are observed. In the low-frequency domain ($<10^2$ Hz), a capacitance due to surface space charge of ions accumulating is observed [97]. As the applied bias is increased, the capacitance increases as a result of the ion migration induced by the applied bias, providing higher ion concentration at the contacts shown in figure 16(b). This process is known as electrode polarization and electroneutrality maintained by the contact that provides an electron or hole leading to a capacitive current [107]. This capacitive current, characterized by a slow kinetics limited by ion diffusion, has been shown to be one of the major factors affecting the hysteresis in the $I$–$V$ curves of perovskite devices [108, 109]. Due to the soft nature of the perovskite material, the Gouy–Chapman theory typically described for liquid solutions has been successfully used for PSCs, illustrated in figure 16(b) [110]. Alternatively, at high frequencies ($10^3$–$10^6$ Hz), the dielectric properties of the perovskite layer were probed [111, 112]. For perovskite devices containing a significantly high defect density ($\geq 10^{17}$ cm$^3$), the depletion layer width can be modulated by modifying the applied bias without much effect from electrode polarization [111, 112]. In these cases, and selecting an adequate frequency, classical Mott–Schottky analysis can be applied to extract the perovskite acceptor defect density and the built-in potential (figure 16(c)) [113]. This defect density is clearly related to hysteresis, as it offers access to the concentration of ions present in the bulk of the perovskite prone to provide migration towards the contacts [114]. In addition, it is known that the contacts play a very important role in the hysteresis observed during the measurement of the $I$–$V$, i.e. TiO$_2$ reversibly reacts with iodide ions modulating the observed capacitive current [108]. Particularly useful is the Mott–Schottky analysis where the chemical reactivity of the external contacts can be a real problem, i.e. MAPbI$_3$/PCBM/Al. In this case, the measured $V_{bi}$ can also provide information on light-induced dipole generation that leads to a shift in the $C(V)$ curve (figure 16(c)), acting as an impediment for charge extraction.
2.3.5. Energy band bending. To fully understand the influence of ionic migration on the device performance, an energy level diagram is a useful schematic approach depicting not only the field distribution inside, but also the interfacial barriers. Several groups have made efforts towards the construction of a band diagram based on indirect evidence, such as transient photocurrent measurements \cite{79}, surface potential characterization \cite{87}, etc. Techniques such as electroabsorption spectroscopy \cite{115–117} have proven to be a powerful approach to studying the internal electrical field, enabling us to directly characterize the field of device and interfacial barrier modulation in working condition \cite{118}. Li et al \cite{10} found that there is a shift of the built-in potential during the device scanning, as shown in figure 17. In addition, the shift of the potential $\xi$ is equivalent to the change of open circuit voltage, $V_{oc}$. This indicates that the modulation of $V_{oc}$ is ascribed to a change in the internal field, caused by ion migration.

Based on the aforementioned evidence, a band diagram influenced by ionic migration is presented in figure 18 \cite{79}. To simplify the discussion, the work functions of both electrodes are considered the same. Without an external electrical field and according to a classical metal–insulator–metal model, the voltage drops across the whole film, as shown in figure 18(a). When a field is applied to the device, ions (i.e. positive and negative defects) are driven towards the opposite electrodes \cite{74}. These ions accumulate at the selective contacts, causing (1) a change of the internal field within the device due to screening of the external field, and (2) a modulation of the perovskite/electrode interfacial barriers. In the first case (figure 18(b)) accumulated charges, (i.e. positive and negative ones) are driven to the opposite electrodes, generating an additional electrical field. This field can either enhance or decrease the original field. Consequently, the separation of photogenerated charges can be improved or deteriorated \cite{79}. (2) Apart from the influence of the internal field, accumulated charges can also modulate the interfacial barriers. The drifted ions located at the interface between the perovskite and the selective electrode result in a manipulation of the charge injection/extraction barriers. In this respect, the effective charge-transfer process through these interfaces can be changed by the redistribution of ions, which are driven by the external electrical field \cite{119}.

3. Suppression of hysteresis

Looking at the origin of the hysteresis as a consequence of ionic migration combined with charge trapping/detrapping as reasoned previously, it seems useful to suppress the hysteresis via three approaches: (1) reducing the amount of defects/ions, (2) hindering the motion of these ions, and (3) promoting the interfacial charge transfer process.
3.1. Larger crystal size

It is found that devices with larger crystal size exhibit less hysteretic behavior. Exploiting a hot-casting method, PSCs with millimeter-scale perovskite grains were achieved by Nie et al [122], exhibiting no significant hysteresis. PSCs, fabricated by certain solvent engineering techniques to obtain uniform and densely packed large grains on mesoporous TiO₂ layers, also achieved negligible hysteresis during I–V curve scanning [123]. In a different study, the hysteresis was reduced by increasing and controlling the atmospheric humidity during the growth of perovskite crystal films [124]. The authors attributed this significantly decreased hysteresis to the realization of large-sized crystal grains that possess (1) much less defects, which is the source of ions; (2) less grain boundaries, which serve as the fast channel of ionic migration; and (3) better charge transfer at the interface.

Recently Xing et al [88] found that, with increasing grain size in the device, the activation energy of ionic migration also increases. For a single crystal, the activation energy increases to as high as 1.05 eV in dark conditions. This increased activation energy suggests a higher energy barrier for the ionic migration, leading to no observable ion migration on the surface of a single crystal.

3.2. Incorporation of PCBM molecules

It is widely observed that devices incorporating PCBM molecules, either using them as a selective ETL [126] or intermixed as a bulk heterojunction [127], show much less hysteresis and better stability. As previously discussed, these ions are driven by the external field and accumulate at the perovskite/TL interfaces. This accumulation leads to (1) a locally high p and n doping, effectively enhancing/decreasing the built-in potential. Meanwhile, (2) these ions also change the interfacial barrier in the device. Hence, this significant reduction of hysteresis is interpreted in terms of these two origins.
Furthermore, in PSCs incorporating a layer of PCBM or a mixed perovskite/PCBM layer, PCBM molecules distribute within the bulk of perovskite film. As shown in figure 18(a), when absorbed at perovskite defective sites, these PCBM molecules passivate defect states, e.g. iodide interstitials or iodide vacancies, giving rise to the decrease or even halting of ion migration. Xu et al [125] have demonstrated the formation of PCBM–halide radicals in perovskite–PCBM solutions using UV–Vis absorption spectroscopy. In detail, by direct electron transfer from anions (iodide ions here) to PCBM or C60, iodide ions form strong bonds with PCBM molecules as shown in figure 20(b) [128]. This production of anionic fullerene derivatives originates from the reaction between PCBM and the $I_3^-$ trimer, associated with the Pb-I antisite defects [75]. As a consequence, the iodide ions/defects are immobilized by combining with the PCBM molecules in the bulk of the perovskite film so that they will not reach the perovskite/TL interfaces.

In the meantime, PCBM is able to passivate surface states, promoting the charge transfer process through the perovskite/ETL interface. Wojciechowski et al [130] provided spectroscopic evidence that the C60 buckyballs formed a self-assembled monolayer and passivated or inhabited the trap states at the interface between TiO$_2$ and the perovskite layer. Xing et al [129] observed an obvious reduction of the perovskite/TiO$_2$ interfacial barrier by inserting a PCBM layer on top of the TiO$_2$ layer, illustrated in figure 21. Shao et al [53] attributed the elimination of hysteresis to the passivation of charge trap states in the bulk of perovskite film during the thermal annealing process. These thermodynamically activated PCBM molecules diffused into the perovskite, passivating traps at the surface and at GBs, thus enhancing the charge transport and charge extraction. Therefore, the suppressed hysteresis is associated with both the reduction of ionic motion and the improvement of the interfacial charge-transfer process.

4. Application in devices

4.1. Photovoltaic device

It has been demonstrated that long-time biasing leads to the redistribution of ions [10]. The designed ionic distribution can enhance the internal field inside and decrease the interfacial barriers, thus improving the device performance. This is the main reason for the pre-biasing procedure before the standard $I$–$V$ curve characterization to achieve higher performance values (PCEs) [39, 119]. In addition, by driving ions to the perovskite/TL interfaces, Zhang et al [131] realized efficient charge injection through high work function electrodes with low voltages. In this case, the accumulation of ions decreased the interfacial charge-injection barriers.

In a next step, these ions can be immobilized at the proper position, which is beneficial for an improved PCE. In this respect, controlled $p$ and $n$ doping induced by an external
electrical field [79] allows us to further modulate the properties in the PSC. With this approach, it is possible to improve the performance by enhancing the internal field and reducing the charge-extraction barrier at interfaces through adjusted ionic motion.

4.2. Memory devices

Memristors, or memory + resistors, are defined as two-terminal devices with resistive switching [132] and have been attracting interest in recent decades towards their potential for next-generation, non-volatile memory applications. Traditionally, ABO₃ perovskite materials and metal oxides have intensively been investigated for such purposes [11, 15]. However, most of these materials require high processing temperatures in order to achieve the desired crystallinities, which guarantee a reliable and reproducible performance. This high-temperature treatment strongly restricts the fabrication on flexible polymer substrates such as polyethylene terephthalate, polyethylene naphthalate, etc. In this aspect, organometal trihalide perovskites demonstrate their advantages in low-temperature processing with an excellent defect tolerance.

Xiao et al [74] realized perovskite-switchable photovoltaic devices based on an ITO/PEDOT:PSS/perovskite/Au structure (figure 22), in which different resistive states were switched by different poling directions. This demonstrated their possible applications in memory devices. Similarly, Yoo et al [133] fabricated bipolar resistive switching devices on the basis of an Au/perovskite/FTO structure, which demonstrated stable endurance (>100 times) and long retention time (10⁴ s). This resistive switching was achieved by modulating between traps (defects) trapping and detrapping, which resulted in different conduction mechanisms such as Ohmic conduction, trap-controlled space charge limit current, or Poole–Frenkel conduction. By utilizing a structure of Ag/perovskite/Pt, Choi et al [134] realized ultralow voltage (as small as 0.15 V), multilevel resistive switching devices with high ON/OFF ratios as shown in figure 23. This low-voltage-driven resistive switching was attributed to the low activation energy of iodide ion migration. Furthermore, Gu et al [135] achieved flexible perovskite memory devices by depositing a perovskite precursor solution on transparent plastic substrates coated with ITO. It was proposed that this reliable resistive switching stemmed from the alignment of iodide vacancies, which caused the formation of conducting filaments. This schematic mechanism has been presented earlier in figure 3(a). In summary, it seems possible to apply and take usage out of these resistive switching properties, opening a pathway to the fabrication of low-cost flexible memory devices.

5. Conclusion

In this Review, we first summarized the features of hysteresis behavior in PSCs. Then the possible mechanisms for this behavior were examined in detail, including ferroelectricity, charge trapping/detrapping, as well as ionic migration under an external electrical field. Recent experimental and theoretical results consistently support the idea that, rather than a single origin, the combined influence of ion migration and charge trapping/detrapping are responsible for the hysteresis. Hereby, considering the timescales for each of the processes, a major part will be attributed to the migration of ions. This was discussed in detail, including the species of ions, migration channels, activation energies, capacitive studies, and influence on the band structure. To eliminate or alleviate hysteresis, we presented different approaches, including increasing crystalline size, improving crystal quality, and involving PCBM molecules for passivation. Furthermore, we gave two examples for the potential application of hysteresis, such as the enhancement of PCE in PSCs by externally induced fields and in memristive switching devices. Although there are still unsolved issues as to the origin of hysteresis, we can attribute this behavior to the strong interaction between ionic migration and free charge carrier transport. This interaction can be modulated by (1) external optical/electrical fields, (2) the crystalline structure, and (3) chemical passivation giving rise to the optimization of PSCs in several directions.

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