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PERSPECTIVE

Taking Control of Ion Transport in Halide Perovskite Solar Cells

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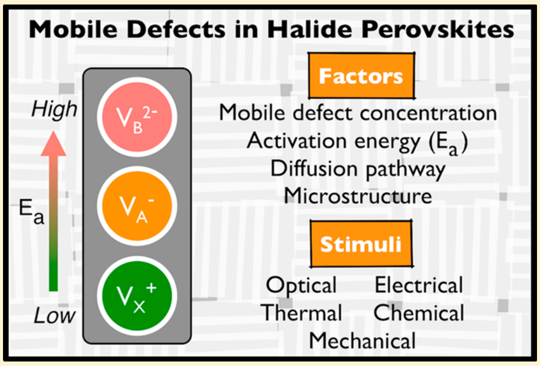
ABSTRACT: Lead halide perovskites are mixed electron−ion conductors that support high rates of solid-state ion transport at room temperature, in addition to conventional electron and hole conduction. Mass transport mediated by charged defects is responsible for unusual phenomena such as current−voltage hysteresis in photovoltaic devices, anomalous above-bandgap photovoltages, light-induced lattice expansion and phase separation, self-healing, and rapid chemical conversion between halides. We outline the principles that govern ion transport in perovskite solar cells including intrinsic (point and extended defects) and extrinsic (light, heat, electrical fields, and chemical gradients) factors. These microscopic processes underpin a wide range of reported observations, including photoionic conductivity, and offer valuable directions for both limiting ion transport, where required, and harnessing it to enable new functionality.



Mass transport in solids is an important topic with a rich history.[1−3] Most chemical reactions involving crystalline materials are limited by the rate of diffusion of ions through a solid matrix (diffusion-controlled), ranging from grain growth to corrosion. For a cubic crystal, as found for the high-temperature phase of many perovskites, the ion flux (J_{ion}) can generally be written as

$$J_{\text{ion}} = -D_{\text{ion}} \frac{\partial C_{\text{ion}}}{\partial x} \quad (1)$$

where C_{ion} is the ion concentration and D_{ion} is the characteristic diffusion coefficient. Equation 1 describes Fickian diffusion down a concentration gradient. Diffusion coefficients can be measured (e.g., using radioactive tracers) or predicted using computer simulations (e.g., using quantum chemical approaches). It is common to separate the component of the diffusion coefficient that describes local atomic motion (jumping from site to site) by an Arrhenius relationship

$$D_{\text{ion}} = D_0 \exp\left(\frac{-\Delta G_{\text{ion}}}{k_B T}\right) \quad (2)$$

where D_0 is a temperature-independent prefactor (containing an attempt frequency ω) and the second term represents the probability of overcoming the activation energy for solid-state diffusion (ΔG_{ion}; T is temperature and k_B is the Boltzmann constant). Note that eq 2 describes the random walk of mobile ion diffusion; therefore, D_{ion} is only equal to that in eq 1 for the case of ideal, dilute ensembles of mobile defects. For example, in Cu metal, an activation energy of 0.489 eV and a prefactor of 0.468 cm^2/s lead to a self-diffusion coefficient of 10^{-12} cm^2/s at 1000 K.[4] The diffusivity of extrinsic impurities in Si spans from below 10^{-20} (Ge) up to 10^{-5} cm^2/s (H) at high temperatures.[5] In the family of halide perovskites studied in solar cells, values for ion diffusivity as high as 10^{-7} cm^2/s have been measured at around room temperature,[6] and this value is likely to be further enhanced in highly defective samples.

Solid-state diffusion is often mediated by lattice defects, including site vacancies and interstitials. The population of defects can be described by equilibrium thermodynamics but is also influenced by the history of a sample, including annealing temperature, environment, and chemical treatments. A range of elementary diffusion processes are shown in Figure 1. The importance of each mechanism is determined by the activation energy (eq 2) and the concentration of available lattice defects. For example, interstitial diffusion may have a low activation energy, but if the concentration of interstitial species is low, they will not contribute appreciably to the overall ion transport. Beyond bulk processes, extended defects, including dislocations (pipe diffusion), surfaces, interfaces, and grain boundaries, can influence mass transport in several ways. They act as "sinks" for high concentrations of charged defects and can also provide alternative low-energy diffusion pathways.

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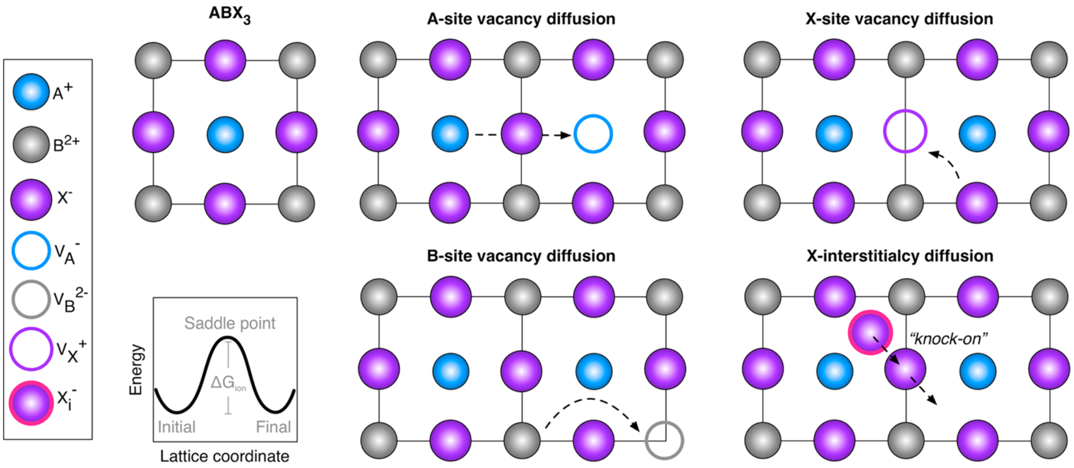

Figure 1. Illustration of possible elementary microscopic mechanisms for ion transport mediated by the activated diffusion of charged point defects in ABX_3 halide perovskites. In common ABX_3 halide perovskite materials, A = Cs, CH_3NH_3, $HC(NH_2)_2$); B = Pb, Sn; X = I, Br, Cl. The filled circles represent regular lattice sites containing charged ions, the empty circles represent charged vacancies (empty lattice sites), and the halide interstitial is highlighted by a pink halo.

Changes in microstructure are one reason why different samples of the same material may exhibit very different conductivity behavior and photophysical response.[7]

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The focus of our Perspective is ion transport in halide perovskite solar cells. The literature on this topic consists of many studies with conflicting results and models. By placing these computational and experimental reports in the context of the physical chemistry of mass transport in solids, we explain the behavior of these materials and indicate factors that can be used to control ion transport in halide perovskite technologies.

There is now overwhelming evidence supporting the macroscopic transport of ions within halide perovskite solar cells,[6,8,9] and it has been suggested that ionic conductivity has the potential to be *higher* than electronic conductivity in $CH_3NH_3PbI_3$.[6] The circumstantial evidence for ion mobility includes observations of current−voltage hysteresis in operating devices depending on the starting condition of the solar cell,[10] a reversible (p−i−n to n−i−p) photovoltaic effect,[11] anomalous above-bandgap photovoltages following a large applied bias,[12] light-induced ionic redistribution[13] and phase separation in mixed-halide compounds,[14] as well as rapid chemical conversion between different metals and halides.[15,16] In addition, there have been direct ionic conductivity measurements of the cesium lead halides dating back to the 1980s.[17,18] What factors govern ion transport and can lead to variation in behavior between different samples and devices?

Intrinsic Factors. In a semiconducting compound, it is important to distinguish between carrier concentrations (excess electrons and holes), point defect concentrations (deviations from ideal lattice site occupancy), and recombination centers (defects that acts as efficient carrier traps). In lead halide perovskites, carrier concentrations are generally measured to be below $10^{15} cm^{-3}$ in the dark, point defect concentrations have been predicted to exceed $10^{18} cm^{-3}$,[19] while the population of recombination centers has been measured in the 10^{13}−$10^{15} cm^{-3}$ range.[20] Concerning ion transport, the point defect concentration is the primary quantity of interest, as discussed below.

(1) Nature of Mobile Defects. The first consideration is the nature of point defects present in a perovskite sample that have the potential to act as *mobile* species.[21] First-principles calculations unanimously agree that there are a large number of low-energy point defects in halide perovskites, which should lead to high equilibrium ("unavoidable") concentrations.[19,22,23] Site vacancies favor an ionized charge state (e.g., V_I^+ for the singly positively charged iodine vacancy in $CH_3NH_3PbI_3$) and have very low energy when formed in charge-neutral combinations in the form of Schottky ionic disorder.[19] Under illumination, in an operating solar cell, other metastable charge states could be formed with long lifetimes due to trapping of photogenerated electrons and holes. Interstitial defects can also form (e.g., Frenkel disorder),[24,25] leading to a complex defect chemistry that will be sensitive to the chemical potentials of the constituent elements present during crystal growth. While there is a lack of quantitative data, based on current understanding, we expect there to be a sufficient supply of charged defect centers to support ion transport under standard growth conditions.

(2) Point Defect Migration Energy. Vacancy-mediated anion diffusion is common in perovskite structured materials and is well characterized in metal oxides.[26] The corner-sharing network of metal halide octahedra supports high anion mobility: a given halide vacancy has eight nearest-neighbors in three dimensions and the individual jump distance is $\frac{a}{\sqrt{2}}$, where a is the cubic lattice constant. There is evidence that vacancy-mediated iodide diffusion is the dominant diffusion mechanism in iodide perovskites, with calculated activation energies of 0.6 eV[27] or below[28,29] that are consistent with experimental reports of halide diffusion at around room temperature.[6,9,13−15,17,30] However, additional contributions from $CH_3NH_3^+$ diffusion under "device-like" conditions cannot be ruled out as the activation energy is also reasonably small (0.8 eV) compared to that of Pb^{2+} diffusion (2.3 eV) and A-site diffusion in other perovskites (e.g., 3.7 eV for Sr migration in $SrTiO_3$).[31] In hybrid halide perovskites, the

orientation of the organic molecule can influence the local diffusion barriers due to electrostatic interactions;[32] however, at around room temperature, the high levels of dynamic orientational disorder of the molecules (with characteristic time constants of several picoseconds[33]) would result in an averaging effect. To put these numbers in context, the activation energies for diffusion of oxygen in fast-ion metal oxide conductors is around 0.5 eV.[34]

(3) Extended Defects. While bulk diffusion is the dominant process in single crystals, for polycrystalline thin films (10s to 100s of nanometers thick) used in optoelectronic devices, extended defects can be a source of rapid diffusion paths. Indeed, grain boundaries have been found to support fast iodine diffusion in $CH_3NH_3PbI_3$ using conductive atomic force microscopy.[35] Further measurements performed using Kelvin probe microscopy found a shorter recovery time from the application of a bias voltage at grain boundaries compared to the bulk.[36] The presence of grain boundaries has been observed to reduce the effective activation energy for iodine diffusion from 0.50 to 0.27 eV in the dark,[37] which transitions these materials from fast-ion transport toward the regime of superionic conductivity. The measured activation energy here is *effective* as ionic transport may be the result of a range of diffusing species and pathways rather than a single process. It is likely that grain boundaries accommodate high concentrations of charged point defects, which are extruded to the boundaries and surfaces during grain growth; this is consistent with some observations of enhanced charge carrier recombination at these sites.[38,39]

Extrinsic Factors. The free energy of a closed system is minimized when the constituent chemical potentials are constant and the sum of their products is zero. The application of an external perturbation will trigger a response from the system to remove any gradients in potential (e.g., chemical or electrochemical). We now discuss external perturbations relevant to perovskite solar cells.

(1) Applied Electric Field. The origin of current−voltage hysteresis in halide perovskite solar cells has been attributed to the slow motion of ions and associated long-lived interface polarization effects that depend on the state of the solar cell and the applied electric field (ϕ). Contributions due to spontaneous electric polarization (ferroelectricity) have also been suggested but are no longer considered to be the dominant mechanism.[40−42] There have been several observations of ion migration in the presence of an electric field, for example, through poling of device structures.[43] These structures can be selectively designed to either prevent or promote the injection of charge carriers in order to modulate whether electronic and/or ionic conductivity are present. Recent work suggests that the combination of field-induced ion migration and injected charge carriers leads to trap formation.[44] In extreme cases, such poling leads to degradation of the perovskite material.[11,43]

From electrostatic considerations, a defect in charge state q will be subject to an additional force $|q|\phi$, which can drive ion motion (drift). However, in mixed conductors, a more general expression is

$$F = |q|\phi Z \tag{3}$$

where Z represents the strength of electromigration, i.e., momentum transfer between the moving electron current and the diffusing ion, which depends on the carrier concentration and the cross section for collisions. The inelastic scattering between ions and electrons can be described as an "electron wind" that may have a significant effect on ion diffusion in mixed ionic−electronic conductors.[1] While the electron and hole concentrations are generally low for halide perovskites in the dark, under solar illumination and particularly following laser irradiation, contributions from electromigration could be significant. There are no quantitative investigations of these effects in halide perovskites to our knowledge.

(2) Chemical Gradient. If an initially homogeneous material (e.g., $CH_3NH_3PbI_3$) is placed in a chemical gradient (e.g., Br vapor), then exchange of ions will take place until a new equilibrium is reached. The solid-state ion exchange in $CH_3NH_3PbX_3$ (X = Cl, Br, I) occurs within seconds or minutes after contact with a different halide solution.[30] Here the chemical kinetics can be tracked spectroscopically by the change in bandgap and the corresponding light absorption or emission wavelengths. Perhaps even more remarkably, dynamic A-site exchange of methylammonium for formamidinium has also been observed,[45] followed by reports on B-site exchange of Pb for Sn.[16] These studies provide strong evidence that *all* sublattices in the perovskite structure are mobile. In contrast to rapid halide exchange, cation exchange proceeds over several hours, which is consistent with the higher activation energies for diffusion discussed earlier. Beyond deliberate chemical treatments, the environment that a material is processed in can have profound consequences, including water, oxygen, and iodine vapors;[46−48] discussion of these chemical processes is beyond the scope of this Perspective.

(3) Thermal Gradient. A significant fraction of energy in a single-junction solar cell is lost to heat, as contained within the Shockley−Queisser limit.[49] The excess energy of photons with wavelengths shorter than the bandgap of the semiconductor generates hot carriers, which cool by multiphonon emission.[50] In addition, nonradiative electron−hole recombination is responsible for significant local heating, which in some materials can directly activate defect formation and transport.[51] For halide perovskites, early attempts at vibrational measurements showed decomposition (e.g., $CH_3NH_3PbI_3 \rightarrow PbI_2 + CH_3NH_3I$) triggered by a Raman laser.[52]

While characterization of thermal stress is currently limited, an operating perovskite solar cell is likely to feature significant local gradients in temperature, in particular, due to the exceptionally low thermal conductivity of these materials.[53−55] In this case, the flux of ions described by eq 1 would be changed to

$$J_{\text{ion}} = -D_{\text{ion}}\frac{\partial C_{\text{ion}}}{\partial x} - S_{\text{ion}}\frac{\partial T}{\partial x} \tag{4}$$

where S_{ion} represents the thermal diffusion coefficient. In a closed-system with ion-blocking electrodes ($J_{\text{ion}} = 0$), this relationship implies that a temperature gradient can establish a concentration gradient, which is the well-known Soret effect (or thermophoresis)

$$\frac{\partial C_{\text{ion}}}{\partial x} = -\left(\frac{S_{\text{ion}}}{D_{\text{ion}}}\right)\left(\frac{\partial T}{\partial x}\right) \tag{5}$$

One implication of the Soret effect could be on multicomponent perovskite compounds (e.g., Cs/FA, Sn/Pb, Br/I systems), where the thermodynamic balance between order and disorder is small.[56] A homogeneous solid solution that is subjected to a thermal gradient will unmix until the variation in local ion concentrations cancels out the thermodynamic activity caused by the variation in temperature. Therefore, the distribution of ions within a mixed perovskite crystal may change due to thermal stress, which could result in spatial fluctuations in bandgap and electron−hole recombination rates.

(4) Light. Photoinduced phase separation in mixed-halide samples has been one of the most studied phenomena related to ion transport in perovskites. The attention is due to the clear spectroscopic fingerprint for halide separation that occurs in $CH_3NH_3Pb(I,Br)_3$ solid solutions[14,57] and the importance of this mixture for producing wider-bandgap perovskites for tandem photovoltaic applications. The stimulation of ion mobility by light is not unique to alloys and also occurs in single-halide $CH_3NH_3PbI_3$ samples.[8,9,13,37] A key observation is that the direction of ion migration in each case is down the illumination gradient, i.e., ions migrate away from the illuminated surface and further into the bulk.[13,58]

The coupling of light absorption and ion motion is challenging to describe microscopically.

The coupling of light absorption and ion motion (photoionic transport) is challenging to describe microscopically. Electronic and ionic processes are commonly assumed to be decoupled in standard transport models due to differences in time scale.[59] There are a range of possible direct and indirect effects that could be active. Illumination of a solar cell will result in electrical and thermal changes, thereby influencing the factors previously discussed. There have also been suggestions of direct photochemistry including conversion of methylammonium to methylamine,[60,61] which could enhance the predicted proton mobility that has an activation energy of 0.3 eV.[62] Illumination can also access metastable charge states of defects due to the trapping of electrons or holes, for example, the production of mobile iodine (I_n) complexes including the I_2^--based H and V centers.[25] The large polaron nature (band carriers coupled to the optical phonon modes of the lattice[41,63,64]) of charge carriers in lead halide perovskites has been used to propose an electronic driving force for alloy separation through the formation of small-bandgap regions.[65,66] There have been further reports of macroscopic effects including photostriction (light-induced lattice expansion) in both single-crystal and thin-film samples.[67] It was recently proposed that illumination could also cause strain relief in perovskite crystals;[68] although ion migration was discounted, ionic rearrangement is necessary to alleviate such strained interfaces. A range of possible processes underpinning photoionic transport are summarized in Figure 2.

Controlling Ion Migration. In an optoelectronic device such as a solar cell, ion migration is an unwanted process that causes hysteresis because the distribution of charged ions can inhibit electron and hole collection at the electrical contact interfaces.[10] In addition, there is evidence suggesting that the mobile ions and defects associated with ion migration are also

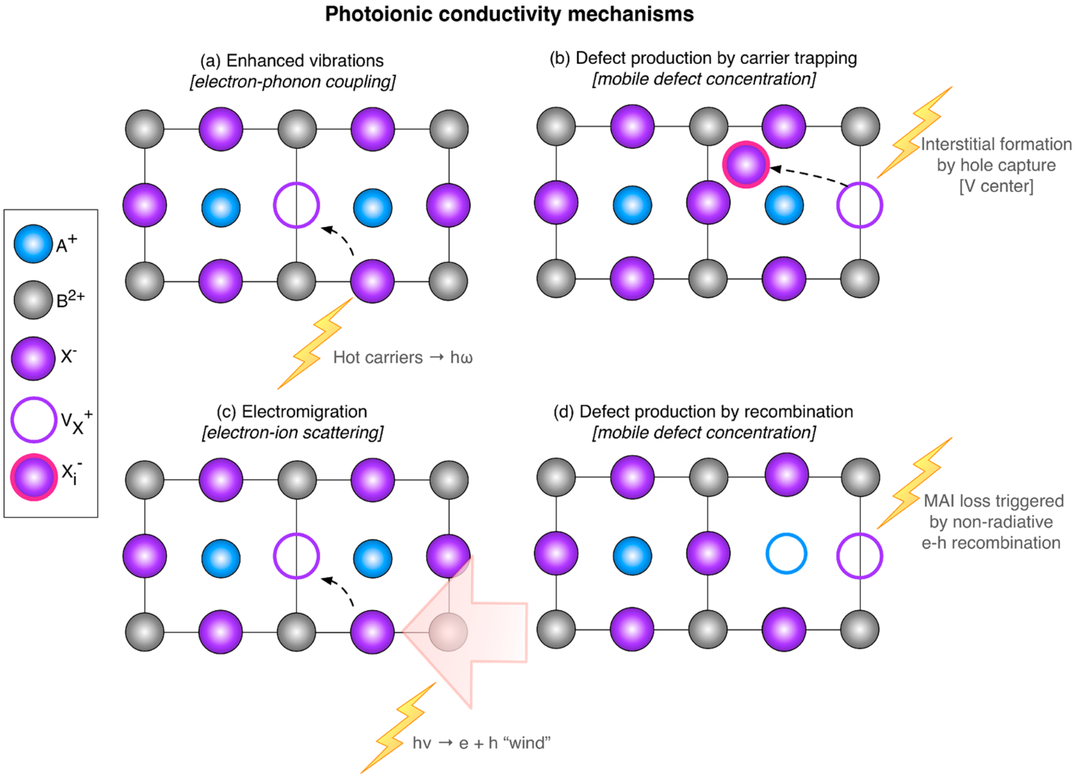

Figure 2. Enhanced mobility of ions upon illumination in halide perovskites can be caused by a range of processes, which differ in the way that the photon energy is converted to a driving force for diffusion. Beyond changes in electric fields and thermal stresses, these include the following: (a) Absorption of light results in hot carriers with excess energy (0−2 eV), which cool to the lattice temperature by phonon emission that could enhance the rate of ion migration; (b) electrons or holes are trapped at lattice sites where the gain in potential energy (0−1.5 eV) offsets the cost of defect formation; (c) carrier concentrations are enhanced upon illumination, and the transfer of momentum between electrons and ions can occur in mixed conductors; (d) recombination of electrons and holes has sufficient energy (up to 1.5 eV) to stimulate the formation of enhanced mobile defect concentrations such as the loss of MAI from $MAPbI_3$ ($MA = CH_3NH_3^+$).

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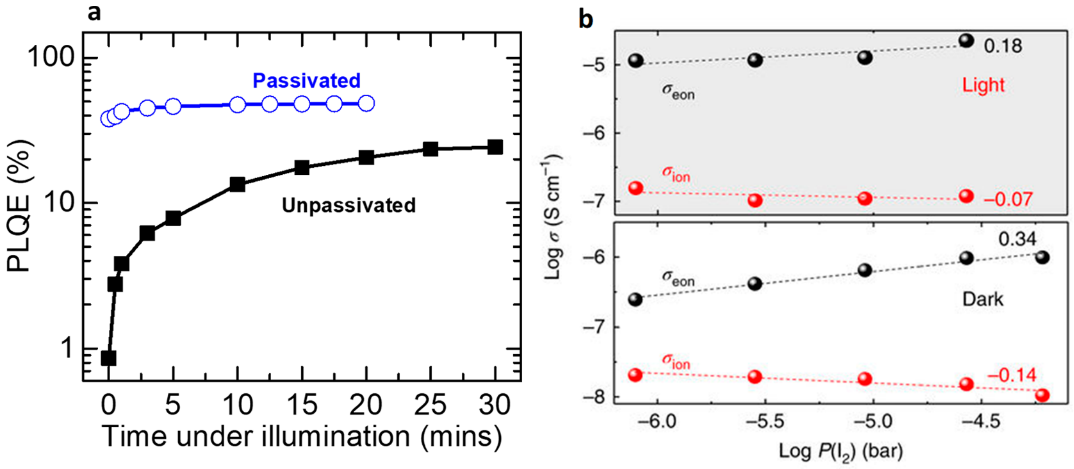

Figure 3. Importance of ion transport for optoelectronic applications of halide perovskites: (a) Suppression of ion transport improves performance, as shown by the photoluminescence quantum efficiency (PLQE) time course for (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films passivated with potassium (10% relative to the A-site cations), illuminated with a 532 nm laser at an excitation intensity equivalent to 1 sun (60 mW cm^{-2}) in an ambient atmosphere. Removal of the transient effects with K treatment is consistent with inhibition of photoinduced ion migration. Data extracted from ref 73 with permission from Nature, Copyright 2018. (b) Effect of light on charge transport through the comparison of electronic conductivity (σ_{eon}) and ionic conductivity (σ_{ion}) as a function of iodine partial pressure (Ar as the carrier gas) in the dark (bottom panel) and under weak 1 mW cm^{-2} illumination (top panel). Reproduced from ref 9 with permission from Nature, Copyright 2018.

directly associated with parasitic nonradiative charge-carrier recombination centers;[20] at least some of these centers form in the presence of both mobile ions and charge carriers.[44] Thus, these ionic migration processes must be suppressed in such device structures.

The first reports of $CH_3NH_3PbI_3$-based n−i−p solar cells exhibited substantial ion-migration effects, but these were somewhat mitigated through use of different contacts (e.g., in a p−i−n structure) in which the ion distribution toward the interfaces was less problematic for charge collection.[69] In addition, mesoporous charge-collecting scaffolds continue to exhibit reduced hysteresis, likely due to increased surface area for charge collection, with the state-of-the-art solar cells currently containing perovskite infiltrated into a thin mesoporous scaffold with a thick capping layer.[70] Recently, alloyed configurations such as the triple cation ($Cs_{0.05}FA_{0.80}MA_{0.15}$)Pb($I_{0.85}Br_{0.15}$)$_3$ composition have been shown to exhibit substantially reduced ion migration activity, consistent with either lower defect concentrations or kinetic barriers to ion diffusion. Similarly, ion diffusion appears to be suppressed in 2D perovskites as the interlayer spacing acts as an ion-blocking layer.[71]

Recent approaches have provided additional levers for reducing ionic migration effects. One route to modify the native defect concentrations is by postsynthetic annealing, for example, treating in low partial pressures of iodine vapor can reduce the iodine vacancy concentration.[72] Recently, the addition of K and Rb halides to precursor solutions has led to improved solar cell performance and suppressed photoinduced ion migration and hysteresis[73,74] (see Figure 3a). This behavior has been attributed to a reduced vacancy concentration due to the increase in halide chemical potential, where the alkali metal acts as a halide-sequestering species to manage the defect and vacancy concentrations.[73] Photobrightening effects in the presence of oxygen and water molecules have also been shown to inhibit photoinduced ion migration while increasing the luminescence quantum yield.[75−77] These observations have been attributed to a strong interaction between oxygen-related species and defects in the presence of light.[78] The connection between ion migration and nonradiative decay is a topic of growing interest,[20,44] which could suggest common sources and therefore common solutions.

On the other hand, one may want to utilize ionic migration and the dual electronic−ionic conductivity phenomena for novel device structures such as light-induced energy storage devices or switches. One emerging application area is resistive-switching solid-state memory.[79,80] Perovskites could be particularly well suited to these customizable applications based on a recent report suggesting that light excitation enhances by several orders of magnitude the ionic conductivity of $CH_3NH_3PbI_3$ (Figure 3b). A recent demonstration of a "photobattery" is an excellent example of a useful device where a halide perovskite is used to simultaneously achieve photocharging and Li-ion migration/storage.[81] Another example is the field of light-emitting electrochemical cells containing an electron-transporting semiconductor that also exhibits ionic conductivity and two ion-blocking electrodes, allowing a p−n junction diode to be created in situ through ionic doping. An initial demonstration of a perovskite-based electrochemical LED device has been recently shown.[82]

The connection between ion migration and nonradiative decay is a topic of growing interest, which could suggest common sources and therefore common solutions.

The factors influencing the transport of ions in halide perovskites outlined in this Perspective will invariably be coupled in operating optotelectronic devices such as solar cells. For example, a gradient in the concentration of one species could contribute to the flux of another. Fully separating the roles of charge carriers, light, heat, and electric fields is a major challenge that will require further developments in theory and experiment. However, key principles can be extracted concerning the use of materials processing to tune the mobile defect concentrations, the role of external stimuli in driving ion transport, and, most critically, the connections between ion diffusion and device phenomena such as hysteresis, recombination, and chemical degradation in metal halide perovskite solar cells.

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The authors declare no competing financial interest.

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Aron Walsh is a Royal Society University Research Fellow and leads the Materials Design Group at Imperial College London. He first became interested in solid-state ion diffusion during undergraduate lectures given by J. Corish in the Department of Chemistry at Trinity College Dublin but has since been distracted by other topics including electronic structure theory, lattice dynamics, and materials informatics.

Samuel D. Stranks is a Royal Society University Research Fellow and Group Leader in the Cavendish Laboratory at the University of Cambridge. He completed his Ph.D. at the University of Oxford, investigating organic solar cells. He turned his focus to the physics of halide perovskites as a Junior Research Fellow at Oxford and then as a Marie Curie Fellow at MIT. His group investigates the optical and electronic properties of emerging semiconductors.

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