

Effects of Ion Distributions on Charge Collection in Perovskite Solar Cells

Lead halide perovskite solar cells (PSCs) have surged with the outstanding improvement of morphologies, compositional variations, and optoelectronic characteristics that have led to large efficiencies. However, since the discovery of facile ion mobility^{1–4} inside the main lead halide materials, this effect has haunted the photovoltaic research community. Ion migration refers to a hopping displacement of intrinsic or extrinsic ionic species between interstitials or vacancy sites. This is a thermally activated effect heavily dependent on temperature. Added to the usual electronic conductivity that allows for the electro-optical applications, the lead halide becomes a mixed ion-electronic conductor. This property belongs to the realm of solid-state ionics, which is an important traditional field of study.^{5,6} Eventually, effective mixed conduction can yield important applications such as lithium ion batteries.⁷

For the photovoltaic community, however, the main topic of interest is how the reorganization of ions affects the solar cell performance. It has been established that the perovskite solar cell shows slow changes of performance such as a dynamic hysteresis, and these have been often attributed to the redistribution of slowly moving ions that will change the electronic operation of the device when illuminated by sunlight.^{1,4,8–10} Currently, there are two main views of the ionic modifications on the solar cell performance. The first type of effect relates to the accumulation of ions at the interface contacts.¹¹ Such effect is commonly observed in slow charging and capacitive responses¹² that may also have a strong influence on degradation of the contacts.¹³ There is strong evidence that dynamic hysteresis is suppressed by a modification of the contact structure, such as the inclusion of organic layers,^{14,15} which points to a severe influence of the surface polarization on the observed slow dynamic changes.¹⁶

The second important effect refers to the influence of the electrical field distribution on charge collection. This effect exists in those cells in which a substantial part of the built-in potential is distributed over the entire absorber thickness.¹⁷ In a perovskite solar cell, a large built-in voltage could be expected, and this original voltage can be modulated by the ion drift, modifying the charge collection properties.^{4,18–20} Therefore, ions can shield the electrical field and modify the resulting photocurrent.

In either approach, the redistribution of ions in the device due to external or internal forces, such as voltage or photogenerated charges, is a crucial issue for the understanding of its operation. In this Viewpoint, we present a critical discussion of the distributions of ions in operating conditions and their effect on the internal electric field of perovskite solar cells under illumination. This analysis is of critical importance toward establishing an energy diagram of the perovskite solar cell that can be used to obtain operational properties, as well as to predict the modifications by coupling with other semi-

conductor systems in tandem solar cells. Here, we obtain distribution of carriers, band bending, and the internal electric field in illuminated devices at the steady-state. This is achieved by numerically solving the drift-diffusion transport equations in a structure constituted by an electron selective layer (ESL), a perovskite absorber layer, and a hole selective layer (HSL), as described by proper boundary conditions.¹¹ The distributions are determined in short-circuit (Figure 1) and open-circuit (Figure 2) conditions.

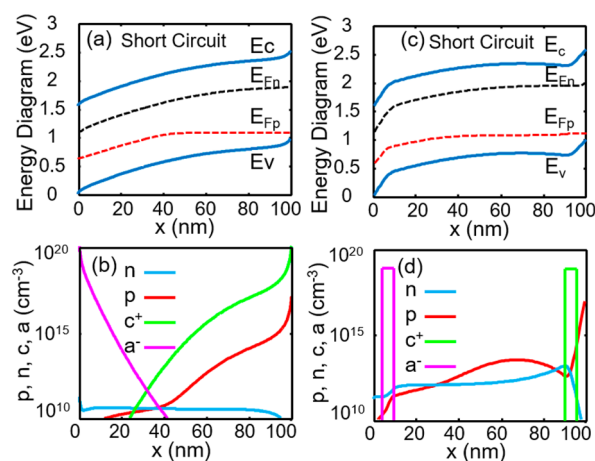


Figure 1. Energy band diagram and distributions of ions, electrons, and holes for a p-doped PSC (with ESC and HSC in the left and right side, respectively) under illumination in short-circuit steady-state, (a, b) including drift-diffusion of ions in the numerical simulation and (c, d) assuming a fixed dipolar-distribution of ions in the numerical simulation.

The nature of the semiconductor has been modeled in various ways in the literature. Some authors assume the perovskite to be intrinsic,^{9,18,21} while others question the intrinsic nature of the perovskite semiconductor or question that the electrical field is not distributed uniformly.¹¹ We have checked that the distributions of ions cause the same effect on the electrical field in intrinsic or p-doped perovskites. This is due to the fact that, under illumination, electronic and ionic charges become determinant rather than the initial dark equilibrium picture. For the sake of simplicity, we consider the last case. On the other hand, the migration of ions is often modeled under different assumptions. Actually, there is no general agreement about the chemical origin of the perovskite ion transport. It is not clear yet whether only one type of ion moves^{4,18} or both anions and cations move at the same

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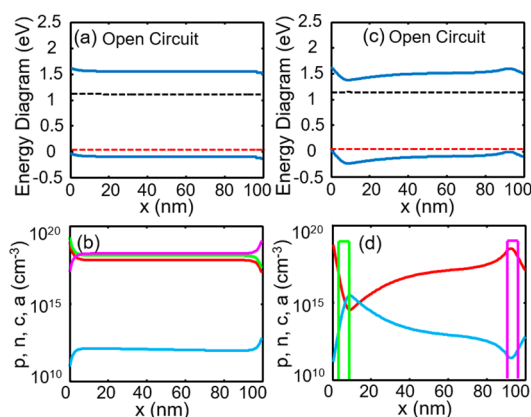


Figure 2. Energy band diagram and distributions of ions, electrons, and holes for a p-doped PSC under illumination in open-circuit steady-state, (a, b) including drift-diffusion of ions in the numerical simulation and (c, d) assuming a fixed dipolar-distribution of ions in the numerical simulation. The color code is the same as that in Figure 1.

time.^{21,22} Regarding the distribution of the electrical field, we have checked that all these situations produce analogous results. We show the results in which both kinds of ions are allowed to move.

We discuss here two main approaches regarding the problem of the ionic distribution that use somewhat different assumptions. The first one is a steady-state ion redistribution produced by drift-diffusion movements inside the perovskite and ion blocking contacts at the perovskite boundaries, shown in the left columns of Figures 1 and 2. This ion redistribution is regulated by the property that the electrochemical potential of ions is constant across the perovskite layer,⁵ and this method is based on sound physicochemical principles. In this approach, the drift-diffusion movement of anions and cations is coupled with the well-known drift-diffusion model for electrons and holes.^{18,23} Such movement of ions has been suggested by several authors.^{18,22–24} The distributions of ions and electric field are simultaneous solutions of these coupled transport equations.^{11,25} A steady-state case is reached when ions have enough time to distribute along the perovskite after the device is biased with a constant voltage, either open-circuit or short-circuit voltage. A common feature in our results of the perovskite solar cell in steady states is the accumulation of anions at the cathode and cations close to the anode in short circuit and the accumulation of cations at the cathode and anions close to the anode at open circuit. Transient mechanisms such as capacitive currents, trapping at the interfaces, recombination between electrons and holes between different layers, or chemical phenomena have not been considered as we intend to focus the study on a single mechanism: the effect of the distribution of ions in the perovskite semiconductor.

In order to obtain quick simulation approaches, it is common to find in the literature the use of approximate distributions of anions and cations.^{18,19,24} The second distribution we consider here consists of sheets of charge at the interfaces, as shown in the right columns of Figures 1 and 2.^{19,21,24,26,27} These approximations resemble a dipolar distribution of charge where the positive and negative charges are located in thin layers close to the interfaces.²⁵ The two sheets of charge create a macroscopic dipole across the full thickness of the sample, similar to a standard parallel plate capacitor. This distribution

can be considered as a heuristic approximation to the previous one,²¹ based on the previously commented fact that the ions accumulate at the interfaces. However, this dipolar distribution of ions leads to a nonconstant quasi-Fermi level (electrochemical potential) of ions. A dipolar distribution formed by anions at the cathode and cations at the anode is studied in Figure 1c,d. The opposite case, cations at the cathode and anions at the anode, is studied in Figure 2c,d. The distributions of ions shown in Figures 1d and 2d are fixed and not allowed to change. Some experimental results suggest that cations are trapped close to the surfaces of PSCs because of chemical interactions.²⁸ This trapped charge could also be modeled by a fixed sheet of charge.

For the realistic distribution at short circuit (Figure 1b), a net accumulation of ions is observed close to the interfaces (positive at the anode and negative at the cathode). This is accompanied by the confinement of holes into a thin region at the perovskite–anode interface. No compensation of the internal electric field is seen in any region of the perovskite, unlike the normal picture of ions shielding the electric field often found in the literature.^{4,19–21} In the open-circuit case, negative mobile ions accumulate at the anode and positive mobile ions at the cathode. The distribution of ions modifies the band bending only close to the perovskite–contact interface and not in the bulk.

One of the main differences obtained for the dipolar distribution is the compensation of the internal electric field seen in short circuit. This is observed in Figure 1c with the existence of a neutral region in the bulk that does not appear in Figure 1a. The other interesting feature for the dipolar distribution is the existence of an electric field in open circuit located in the bulk of the absorber layer (Figure 2c) and not existing in Figure 2a. The electric field seen in the bulk of Figure 2c facilitates the collection of charge at the electrodes, thus increasing the photocurrent close to the open-circuit region. Some authors^{18,24} suggest that ionic charge accumulates at the edges of the perovskite under the influence of the built-in electric field in what is known as Debye layers (also termed double layers). From the analysis of Figures 1 and 2, the surface band bending associated with double layers is detected in Figures 1c and 2c for the dipolar distribution ions. For the simulations in which ions are allowed to move, the bands bend very slightly close to the perovskite interfaces (Figures 1a and 2a), not showing this Debye layer.

It is immediately apparent that the distribution of the ions and carriers in both cases will have a strong impact on the device performance. The large neutral region in the bulk of Figure 1c shows that the photogenerated carriers in the bulk will be separated mainly by diffusion to the contacts, as opposed to Figure 1a where the ions create their own electrical field through the device, which facilitates charge separation. The charge extraction at the contacts in both cases should also be markedly different. In the case of the dipolar distribution, the Debye layers create sharp potential drops at the contacts, creating the “valleys” and “humps” in the band profile often referred to in the literature.¹⁹ These can serve as preferential recombination sites for photogenerated carriers (surface recombination), and indeed this is often used to explain the large reduction in open-circuit potential when scanning from short circuit to open circuit.²¹

It must also be noted that these Debye layers provide large injection–extraction barriers for the carriers, and consequently, the device performance is mostly controlled by the efficacy of

charge extraction and recombination at the contacts itself rather than any transport considerations. In the case of the flat Fermi level of the ions, the potential gradients are much less sharp and the barriers at the contacts are minimized. Therefore, bulk transport and recombination considerations should play a bigger role in the device operation in this case, in addition to surface recombination.

To conclude, the approximation of the exact steady-state ion distributions by means of dipolar distributions is a reasonable starting model, but it must be used carefully because it introduces some unphysical features. Consequently, dynamic hysteresis often attributed to the redistribution of slowly moving ions would be explained very differently under the two distributions studied in this work. In any case, the dipolar distribution can be useful to model other effects such as the existence of a large and concentrated amount of charge created by other mechanisms, such as traps, interfacial effects, or chemical phenomena.

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

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