Device Physics of Hybrid Perovskite Solar cells: Theory and Experiment

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Perovskite solar cells (PSCs) exhibit a series of distinctive features in their optoelectronic response which have a crucial influence on the performance, particularly for long-time response. Here, a survey of recent advances both in device simulation and optoelectronic and photovoltaic responses is provided, with the aim of comprehensively covering recent advances. Device simulations are included with clarifying discussions about the implications of classical drift–diffusion modeling and the inclusion of ionic charged layers near the outer carrier selective contacts. The outcomes of several transient techniques are summarized, along with the discussion of impedance and capacitive responses upon variation of bias voltage and irradiance level. In relation to the capacitive response, a discussion on the \( J-V \) curve hysteresis is also included. Although alternative models and explanations are included in the discussion, the review relies upon a key mechanism able to yield most of the rich experimental responses. Particularly for state-of-the-art solar cells exhibiting efficiencies around or exceeding 20%, outer interfaces play a determining role on the PSC’s performance. The ionic and electronic kinetics in the vicinity of the interfaces, coupled to surface recombination and carrier extraction mechanisms, should be carefully explored to progress further in performance enhancement.

1. Introduction

Despite the significant advances in power conversion efficiency (PCE), several issues on the characteristic phenomenology of perovskite solar cells (PSCs) are still poorly understood. Among these, one can highlight the diverse time \( t \) domains of different processes, the corresponding dynamic evolution of charge distributions, and the consequent current density–voltage \( \langle J-V \rangle \) curves. About the latter, significant debate has taken place on the anomalous hysteresis phenomenon that currently generates some doubts on the actual PCE reports. The main argument here is that for PSCs, the achievement of a well-defined steady state is quite difficult; thus, for instance, the definition of a reliable short-circuit current density \( (J_{sc}) \) or open-circuit voltage \( (V_{oc}) \) can be problematic in some cases. Accordingly, typical charge extraction evaluation at short-circuit (SC) or the determination of recombination at open-circuit (OC) is also not so evident.

The study of high-efficiency PSCs is accompanied with the analysis of the fundamental physico-chemical mechanisms underpinning their performance. PSCs exhibit dynamic hysteresis in their \( J-V \) curves[1–3] that are strongly dependent on the voltage scan rate, direction (from positive to negative bias, or the opposite way), the bias point before a scan, and preconditioning treatments (in darkness or under illumination at open-circuit or short-circuit).[4,5] They also show a low-frequency giant capacitance response[6,7] and anomalous experimental transient results,[8,9] not observed in classical solar cells. Different possible origins of these phenomena have been proposed: trapping of electrons and holes,[10,11] mobile ions in the perovskite film,[12,13] and chemical or structural changes in the material.[5,14] Recently, the slow changes associated with the dynamic hysteresis in PSCs have been attributed to the redistribution of slowly moving ions.[1,6,15–17] The atomistic study of the motion of the different particles involved in the internal dynamic of the perovskite (electrons, holes, molecules, and ions) also supports this statement.[18] The nature and timescales of these different motions have been quantified with the combination of first-principles and multiscale material modeling and experimental techniques, such as neutron diffraction measurements, quasielastic neutron scattering, and ultrafast vibrational spectroscopy.[18]

Different theoretical models and experimental settings assist the interpretation of the effects of ion migration. Macroscopic...
studies include the analysis of the conductivity, the modeling of dynamic hysteresis, or temporal experimental settings such as photovoltage decays or chronophotocapacitometry. The type of microscopic mechanisms that intervene in the migration, such as vacancy-assisted migration or movement by interstitial ions/defects, and the details of their transport through the perovskite are particular topics of this study. These studies include the determination of the activation energies for these migration mechanisms using density functional theory (DFT) and are compared with kinetic data extracted from the current–voltage response of PSCs. In addition, the direct determination of the ionic diffusion coefficient has been recently addressed. High-computational studies involving electronic structure, molecular dynamics, and Monte Carlo simulation shed light on the chemical bonding of hybrid perovskites.

The peculiar phenomena that turn out to be ubiquitous in PSCs make it necessary to adopt a fresh view on physical modeling and measurement that we attempt to summarize in this review. Many of the well-established tools and techniques come into question, and specific intuition about central features such as band bending needs to be reevaluated. Here, we present a first systematic effort to provide a unified picture of the physical modeling and measurement that has been gathered from the initial years of study of the field. Our analysis is far from complete as we believe that the study still needs years of work ahead, and the definite research directions will depend markedly on the ways that material development of the PSCs occurs. However, the present work provides a general guideline of studies that were absent in the first years of the PSCs studies, causing great confusion about the interpretation of physical measurement.

We begin the study with a summary description of the structure, materials, configurations, and operation of the PSCs. These topics are broadly covered in a variety of review papers and monographies that the reader may consult if more general information is needed. In Section 3, we present a detailed analysis of the physical effects of mobile ions in the solar cell properties. In normal solar cells, it is explicitly assumed that ions form a background-fixed charge density, determining the minority carrier. However, new physical effects happen when several types of ions can slowly flow within the device. The notion of doping becomes problematic; the interfaces can experience strong accumulation effects; and the issue needs a careful discussion by simulation that we have explained by separating many cases in order to provide physically based intuition about the energy diagram for interpreting a wide variety of experimental situations.

After exploring the variety of steady-state band diagrams from simulations tools, we summarize in Section 4 the rich phenomenology observed from experimental transient responses. Contrary to that occurred for other photovoltaic technologies, it is clearly stated for PSCs that operating mechanisms spread in time from nanoseconds up to tens or hundreds of seconds. While photoluminescence (PL) transients exhibit rapid decays for the radiative recombination process in the nanosecond timescale, voltage or current transients present distinct trends with multieponential decays. Particularly illustrative is the dependence of the voltage decay in open-circuit on light-soaking time. The long-time response, in the domain of seconds, is fully altered by pretreatment, signaling the occurrence of dynamically slow ion polarization at the contacts in connection to the charge recombination.

In Section 5, a survey on experimentally gathered impedance and capacitance data is provided. The most intriguing observation, in relation to the solar cell functioning, is the commonly reported light- and voltage-dependent huge values of the low-frequency capacitance (surface capacitance). Its frequency range of observation (seconds) points to the slow transient phenomena treated in Section 4. Again, this is a distinctive feature of PSCs rarely distinguishable in other solar technologies. Dependences of the surface capacitance on perovskite layer thickness and irradiance level allow connecting it to specific ionic or electronic accumulation mechanisms at the outer interfaces.

Finally, the issue of the J–V curve hysteresis is extensively addressed in Section 6. This topic attracts continued interest, due to both the significance of this phenomenon for practical operation of the solar cell and to the variety of phenomena that may act for the delayed and variable response. A summary of the phenomenology on hysteresis and classification of the responses is provided in relation to the variation in control parameters such as scan rate, scan step, temperature, pre-biasing, and light soaking. Models for hysteresis are explained stressing the consistency of the ionic/electronic charge...
accumulation at the electrodes (surface polarization model) with the observed responses and impedance analysis. Strategies of hysteresis suppression are also commented upon. We finish with a few remarking conclusions.

2. Structure of Perovskite Solar Cells

PSCs are basically structured as a light-harvesting perovskite sandwiched between the electron and hole selective layers. The use of numerous materials has been reported,[23] however, the most successful and extensively studied configuration is shown in Figure 1a, where the TiO₂ layer is grown on top of the fluorine-doped tin oxide (FTO)/glass substrate (typically as a mesoporous scaffold on top of a compact layer), then the methylammonium lead iodide CH₃NH₃PbI₃ (referred to as MAPbI₃ in the following) perovskite and subsequently the 2,2′(7,7′)-tetrakis-(N,N-di-p-methoxyphenyl-amine)9,9′-spirobifluorene (spiro-OMeTAD). The metallic electrodes are often made of gold in order to achieve better connections with the load (Rₘₐₜ), even though other nonprecious metals have also been explored.[24] Thus, in this “regular” structure, the light crosses the substrate through the glass and the transparent conducting oxide (TCO), then first through the electron-selective layer (ESL) to be absorbed at the perovskite, leaving the hole-selective layer (HSL) at the end of the light path.

Another important configuration is that of Figure 1c, known as an “inverted” structure. Here, in the same light path direction, the sequence of layers is glass/TCO/HSL/perovskite/ESL/metallic electrode.[26] The selective contacts for these devices are mainly fullerene derivatives and organic compounds, with [6,6]-phenyl-C-61-butryc acid methyl ester (PCBM) and poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) being the most common ESL and HSL, respectively.

However, irrespective of one or other configuration, MAPbI₃ has proved to be the most representative perovskite for photovoltaic applications. As systematically described by Stoumpos et al.[27] in its high-temperature cubic phase, the methyl ammonium organic cation CH₃NH₃⁺ (MA) is A in the perovskite general formula while the lead and the halogen are B and X, respectively, with the crystalline structure that of Figure 1b. Remarkably, MAPbI₃ has an optimum direct bandgap \(E_g \approx 1.6\text{eV}\)[27–30] and the deposition of the material follows easy solution-based fabrication processes, e.g., dip- and spin-coating,[31,32] resulting in layers with good crystalline quality at relatively high reaction rates, even when processed at low temperatures. The estimated theoretical PCE for a 500 nm thick MAPbI₃-based single junction solar cell has been calculated to be around 31% with \(J_{\text{sc}} \approx 26\text{mA cm}^{-2}, V_{\text{oc}} \approx 1.3\text{V}, \) and 91% of fill factor (FF).[33]

Importantly, the electrical intrinsic conductivity of MAPbI₃ can be modified from p-type to n-type by controlling growth conditions, i.e., by managing the concentration of donor or acceptor shallow defects.[34] For example, recent studies have shown that exposure to excess I₂ vapor pressure can create intrinsic p-type conduction in MAPbI₃.[35,36] This tunable conductivity character has produced a significant scattering in the representation of the energy band diagram of PSCs. While several studies have identified or assumed an intrinsic character of the perovskite, meaning a p–i–n heterojunction, some others suggest p⁺–p–n or p–n–n⁺ heterojunctions.[25] The two possible energy band diagram situations are illustrated in Figure 1d.

Figure 1. Basic structure of PSCs in a) regular and c) inverted configurations. b) Crystalline structure of perovskite materials in cubic phase ABX₃, where A, B, and X are CH₃NH₃⁺, Pb²⁺, and I⁻, respectively, for CH₃NH₃PbI₃. General energy band diagram at d) SC and e) OC for different possible perovskite conductivities, as indicated, \(E_F\) being the equilibrium Fermi level and \(E_{\text{Fp}}\) and \(E_{\text{Fn}}\) the quasi-Fermi levels for electrons and holes, respectively. f) Main contributing factors in the degradation processes of PSCs. Most used materials in each case are specified in parentheses. Adapted with permission.[25] Copyright 2017, Sociedad Cubana de Física.
at SC and in Figure 1e for OC condition. It seems that not gross differences are expected at OC, however at SC, the photocurrent (PC) generation is quite sensitive to the nature of minority carriers. Regarding these issues, and including the effects of ions, a more detailed discussion from theoretical modeling by numerical simulations can be found in Sections 3.1–3.3.

Concerning the general performance, the two most characteristic perovskites are the hybrid halide CH3NH3PbI3-xClx and the formamidinium (FA) cation composed HC(NH2)3PbI3. About the former, the chlorine incorporation has been found to mainly improve the carrier transfer across the heterojunction interfaces while in FAPbI3 based devices, a broader absorption toward the infrared region has been obtained.

In addition, one weighty consequence of the PSC structure and involved materials is the occurrence of significant degradation processes. Despite degradation not being the focus of this review, we briefly mention some important points about this issue in order to support subsequent considerations along the varied discussed phenomena where the reactivity influence cannot be ignored. In Sections 5.2 and 6.5, the impact of reactivity mechanisms on capacitance and J–V curves will be noted explicitly. These mechanisms are summarized in Figure 1f, with the moisture being the first to be highlighted. MAPbI3 degradation in humid air proceeds by two competing reactions: (i) the generation of an MAPbI3 hydrate phase by H2O incorporation and (ii) the PbI2 formation by the desorption of CH3NH3I species. Subsequently, loss of CH3NH3+ and I− species and decomposition into PbCO3, Pb(OH)2, and PbO take place. Even if the material is properly encapsulated (or measured in laboratory conditions under inert atmosphere), devices can still be unstable. Particularly, it has been shown that ionic transport induced by the electrical field can lead to the chemical reactivity of the external contacts with iodide ions. In addition, the temperature can induce decomposition at local temperatures around 100 °C and phase transitions around 57 °C. This is a catalytic factor for the other degradation processes.

3. Numerical Simulation of Perovskite Solar Cell Devices

Experimental evidence and theoretical models for simultaneous electron and ion transport in the hybrid perovskite materials show that PSCs exhibit characteristics of mixed ionic–electronic conduction. Electronic conduction is quite common and necessary in photovoltaic materials, but facile ion transport by hopping between favorable lattice sites is a less usual characteristic that appears unexpectedly. This effect causes an enormous impact on the understanding of the PSC device operation, as it implies that general properties like the internal band bending, electric field distribution, and carrier injection characteristics at the boundaries with the contacts can have a dynamic change over different timescales under operation. Then, characteristics that are taken for granted in other well-known semiconductor devices are seen to vary and fluctuate in the PSC. This fact poses a major barrier for understanding and control, as for example, results of many techniques are not reliable, since they depend on details of the measurement protocol. Different distributions of ions inside the perovskite film can alter the electronic operation when illuminated by sunlight. This fact has important implications in terms of the long-term stability as well as the efficiency of the solar cell. For this reason, we begin the section with an analysis of the solar cell device characteristics taking into account the variations caused by the massive displacement of ions.

In perovskite materials, the mobile ion species are associated with vacancies, ions, or interstitial defects. DFT studies at room temperature on MAPbI3 show the existence of high concentrations of iodide vacancies and MA vacancies. Some first-principles studies in MAPbI3 perovskites have shown that the most diffusive species (higher mobility) is the I− anion and suggest the requirement of a long period of time for the migration of Pb and MA vacancies. This was further supported by theoretical calculations that identified Iodide vacancies as the defect with the lowest formation energy (~0.67 eV) in MAPbI3 similar to values reported by Eames et al. However, other experimental studies have confirmed the motion of MA+ with some authors even claiming migration of both I− and MA+ ions. Some studies on MAPbI3 suggest an important equilibrium concentration of iodide (I−), lead (Pb2+), and CH3NH3+ (also denoted as MA+) vacancies, with their respective ions of opposite charge. Other migrating species such as gold or hydrogen have also been detected in perovskite semiconductors.

Therefore, it has been difficult to identify which ions contribute to the strong ionic conductivity observed. However, recent experiments on ionic conduction in perovskites by Senocate et al. have shed new light on this issue. They first identified that the I− ion is the dominant long-range mobile ionic species (as also corroborated by Li et al. from wide-field PL imaging microscopy) in the perovskite by passing a small current (nA) for 1 week through a Faradaic cell of type +Cu/ MAPbI3/AgI/Ag+, while subsequent X-ray diffraction (XRD) measurements showed the only phase change that occurred was the formation of CuI at the Cu/MA/AgI side. In addition, they determined no long-range diffusion of MA+ ions, through a similar measurement on a +Pb/MAPbI3/AgI/Ag– cell and tracer diffusion experiments on 13C- and 15N-enriched MAPbI3 pellets in contact with each other. The authors then measured the evolution of voltage in a dc galvanostatic configuration of a pure MAPbI3 pellet while varying the I2 partial pressure, allowing for the estimation of the values of ionic and electronic conductivities over a range of partial pressure values. They found that the ionic conductivity reduced with increasing I2 partial pressure, related to the filling of iodide vacancies, hence establishing Iodide vacancy migration as the primary mechanism of ionic movement through the perovskite. However, as a generalization, for the steady-state analysis, we consider only two ionic species, cations and anions, and assume neutrality of ionic charge in the perovskite as a whole.

Currently, there are two main factors that make ion migration alter the solar cell performance. These two effects will have a protagonist role in our paper, since they will be used for the interpretation of hysteresis in the final part of the paper. First, the internal electric field created by any biasing voltage, or by the effect of light-induced photovoltage, produces accumulation of ions at the interface contacts.
charge accumulation has a very strong effect on the measured surface capacitance,[55,56] which is seen to change dramatically depending on the contact material.[2,57–59] This mechanism may have a major impact on degradation of the contacts[42] (highlighted in Figure 1f). This is because, on the one hand, mobile ions inside the perovskite structure show a very slow motion that progressively adjusts to the variations of voltage. This fact points out a severe influence of the surface polarization on the observed slow dynamic changes in measurement. In addition, the ions accumulated at the interfaces may launch slow electrochemical reactions and even penetrate selective contact material producing severe degradation.[42]

The second effect associated with ion migration refers to the influence of the electrical field distribution on charge collection. In a PSCs, a large built-in voltage could be expected, and this original voltage can be modulated by the ion drift, modifying the charge collection properties,[5,6,9,19] see Figure 2. Therefore, the internal electrical field is screened by the ion distribution and the net electric field modifies the value of the PC.

In order to quantify these effects, one needs to address the complex problem of device simulation considering not only usual models combining electrons and holes but additional anionic and cationic species that can be redistributed inside the absorber layer. We will provide a short account of the methods used to deal with these problems, and then we present and discuss the most relevant problems based on a specific solution model.

Accurate modeling and device simulations present significant challenges for describing the mixed ionic–electronic conduction. A well-known simulation tool that supports macroscopic studies in PSCs is drift–diffusion (DD) simulation.[19,47,60] Nevertheless, not all the DD simulations model the distribution of ions in the same way.[61] DD simulation is usually applied to structures such as the one shown in Figure 2a,b or the simplified structure of Figure 2c. In these figures, the cathode in contact with the ESL (hole-blocking layer) and anode close to the HSL (electron-blocking layer) are highlighted. Furthermore, the distance \( x \) from the ESL/perovskite interface is indicated, which will be \( x = L \) at the HSL/perovskite interface for our purposes.

Some DD simulations consider a steady-state ion distribution produced by drift–diffusion mechanisms inside the perovskite, and ion-blocking contacts at the perovskite boundaries.[4,19,47,62] In this approach, the drift and diffusion of anions and cations are

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**Figure 2.** a) Layers of the PSC: cathode–ESL–perovskite–HSL–anode. b) Energy diagram of the different layers before contacting. c) Simplified energy diagram of a p-type solar cell before contacting in which the effect of the ESL and HSL is incorporated as boundary conditions. d) Energy diagram for the solar cell under bias voltage \( V_{\text{app}} \). Only electrons and holes contribute to the electrical current. e) Energy diagram of intrinsic perovskite with a built-in potential as shown, establishing an electrical field through the perovskite that is the difference in work functions between the ESL and HSL. f) The ions (cations and anions are green and red, respectively) drift along this electrical field and establish the equilibrium situation, where the shielding of the electrical field through the bulk occurs. Adapted with permission.[3] Copyright 2017, Royal Society of Chemistry.
coupled with the well-known drift-diffusion model for electrons and holes.\textsuperscript{[8,19,47]} It is worth mentioning the models proposed by van Reenen et al.,\textsuperscript{[62]} Richardson et al.,\textsuperscript{[19]} O’Kane et al.,\textsuperscript{[4]} Calado et al.,\textsuperscript{[47]} Gottesman et al.,\textsuperscript{[8]} and Neukom et al.\textsuperscript{[63]} Their main differences lie in their approaches of the boundary conditions and the inclusion of different physical–chemical mechanisms in their models. In order to obtain quick simulation approaches, the use of approximate distributions of anions and cations is common practice.\textsuperscript{[4,9,19]} Some authors propose that under a net electric field inside the perovskite \( (V_{bi} - V_{app})/L > 0 \) \( (V_{bi} \) is the built-in voltage, given by the difference of contact work functions, and \( V_{app} \) is the external voltage applied between anode and cathode) the positively charged ion vacancies drive into the region of the perovskite adjacent to the HSL. There, they create a narrow positively charged layer. To maintain the neutrality, a negatively charged layer appears, by depletion of the positive vacancies, in the perovskite near the ESL. These regions of opposite charge are termed Debye layers\textsuperscript{[4,19,60,64]} and resemble a dipolar distribution of charge in which the positive and negative charges are confined in thin layers close to the interfaces,\textsuperscript{[9,65]} with ionic Debye length\textsuperscript{[64]}

\[
L_0 = \sqrt{\frac{\varepsilon_\varepsilon k_B T}{q^2N}} \quad (1)
\]

where \( \varepsilon_\varepsilon \) and \( \varepsilon_0 \) are the relative and vacuum permittivity, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( q \) is the elementary charge, and \( N \) is the total density of mobile ions forming the interfacial space charge of the diffuse layer. The band energy structure of the perovskite semiconductor, as seen by charge carriers, is modified electrostatically by the Debye layers, which act to screen the built-in field.\textsuperscript{[4]} At high ion densities, the Debye length is over two orders of magnitude smaller than the perovskite width (a few nanometers compared to hundreds of nanometers). The inclusion of these thin layers in simulations represents a computational challenge. For this reason, Richardson et al.\textsuperscript{[19]} and O’Kane et al.\textsuperscript{[4]} provided a model that adds asymptotic expressions for the charge in the Debye layers to the DD simulations. In this model, exponential voltage drops are associated with the Debye layers, and a constant compensated electric field is assumed in the bulk between these layers. This model needs further discussion, concerning the important feature of charge accumulation at contact interfaces that explains the giant capacitance as described later.

Other DD simulations incorporate qualitative models, including schematic energy diagrams for the distribution of the compensated electric field in the bulk after the migration of ion vacancies.\textsuperscript{[6,9,66]} Authors expect the magnitude of the \( J_{en} \) to be controlled by the extent to which the electric field is screened.\textsuperscript{[5,6]} Tress et al.\textsuperscript{[5]} solved the DD equations modifying the built-in voltage in relation to the electric field compensation amount in the bulk. They suggested that the rate-dependent hysteresis observed in \( J-V \) scans is related to a slow field-induced process that tends to reduce the electric field in the device at each applied voltage, and thus, modify the charge collection efficiencies.\textsuperscript{[9]} In a similar way, Zhang et al.\textsuperscript{[66]} also proposed that the presence of these ions at the interface attracts charge that modifies the energy-band bending. This interface charge affects the value of the PC. In that work, Zhang et al.\textsuperscript{[66]} suggested that the lower the interface charge density, the higher the obtained PC. The aforementioned mechanism suggests that the dynamic change in the interface charge leads to \( J-V \) hysteresis. Despite these efforts, a precise quantification of the screening of the electric field in the bulk of the perovskite is lacking. In this regard, we proposed a numerical simulation of a perovskite structure in which mobile ions are present, as further described below.\textsuperscript{[64]}

Another topic under study concerning the ion migration is related to the specific ions that are transported through the perovskite (a further analysis is provided in Section 3.1). Richardson et al.\textsuperscript{[19]} and Calado et al.\textsuperscript{[47]} distinguished between slow ions with a uniform concentration along the perovskite and fast ions that are allowed to move. This assumption must be considered with care in steady-state studies, as slow ions with non-zero mobility can also migrate after a long period of time. Neukom et al.\textsuperscript{[63]} suggested not employing uniform ion distributions for slow ions. To cope with this problem, they solved the DD equations in two steps. First, the DD equations for the mobile ions are solved at a preconditioning voltage without considering the influence of electrons and holes. In the second place, the DD equations for electrons and holes are solved using the previous steady-state ion distribution as a fixed variable.

In this work, we have systematically analyzed how the distributions of mobile ions and their vacancies affect the distribution of the internal electric field of PSCs under illumination (Figure 2a). Intrinsic and p-doped absorber layers have been analyzed in order to shed light on the nature of the electric field and charge distributions in the perovskite semiconductor.\textsuperscript{[61]} Mechanisms such as capacitive currents, trapping at the interfaces and electron-hole recombination in different layers will be ignored here and discussed in latter sections.

The distributions of ions have been determined in steady state by numerically solving the DD transport equations (Supporting Information). The resulting solution for the distribution of ions is useful to interpret experiments in which the bias and illumination conditions are set constant for a long period of time. A second distribution of ions, considered as a heuristic approximation to the exact steady-state distribution of ions,\textsuperscript{[3,9]} is also studied. This second distribution of ions consists of two layers of opposite charge located close to the interfaces, resembling a dipolar structure similar to Debye layers mentioned previously. All the model equations and detailed description of calculations are presented in the Supporting Information.

### 3.1. Effect of Ionic Species on the Energy Diagram of PSCs

In this section, the effect of the migration of one or two types of ions is analyzed. The starting ion distribution can be different from one to another dynamic experiment, and thus alter the interpretation of the experimental results. In order to study different possible scenarios, the following distributions for the cation \( c(x) \) and anion \( a(x) \) densities are considered.

(i) \( a(x) = c(x) = N_{ion} \): Ions are fixed and uniformly distributed. They are not allowed to move. The net ion charge density is zero. This is equivalent to consider no ions at all.

(ii) \( a(x) = N_{ion} \): The anion concentration is fixed and uniform.
Only cations are allowed to move.

(iii) \( c(x) = N_{\text{ion}} \): The cation concentration is fixed and uniform.

Only anions are allowed to move.

(iv) Both types of ions are allowed to move.

The distributions of carriers, band bending, and internal electric field in steady-state illuminated devices, calculated by the DD method indicated in the Supporting Information, for p-type PSCs at short-circuit condition are shown in Figure 3. The parameters used in the simulation are in Table S1 (Supporting Information). If only one type of ion is allowed to move, the resulting net distribution of ions shows two uniform regions with opposite ionic charge (a positive layer at the anode and a negative one at the cathode) (Figure 3e,h). The net distributions of ions in

![Figure 3](image)

**Figure 3.** Energy diagrams, charge concentration, and net distribution of ions along a p-type PSC with acceptor density \( N_A = 10^{17} \text{ cm}^{-3} \) and average density of ions \( N_{\text{ion}} = 5 \times 10^{17} \text{ cm}^{-3} \), at short-circuit (\( V_{\text{app}} = 0 \text{ V} \)): a–b) case (i) no ions; c–e) case (ii) only cations move and the anion concentration is uniform; f–h) case (iii) only anions move and the cation concentration is uniform; i–k) case (iv) both ions move. The physical parameters used in the simulations are discussed in the Supporting Information.
is combined with an accumulation of free charge of the same sign (holes at the HSL contact). This is an important result in order to explain the experimental observation of accumulation capacitance not only at open-circuit but also at short-circuit (commented later on)[144]. In particular, we have observed that anions and holes accumulate close to the HSL–perovskite contact at short-circuit (Figure 3i) and the same species close to the ESL in open-circuit (Figure S2 in the Supporting Information). In both cases, electronic charge is accompanied by the accumulation of ionic charge of the same sign, which contributes to the slow time response observed.

These different distributions of ions have a clear influence on the distribution of other electrical variables, which are analyzed below. The effect of these three distributions of ions on the energy diagrams is similar to increasing the dopant concentration not only at open-circuit but also at short-circuit (commented later on)[144]. In particular, we have observed that anions and holes accumulate close to the HSL–perovskite contact at short-circuit (Figure 3i) and the same species close to the ESL in open-circuit (Figure S2 in the Supporting Information). In both cases, electronic charge is accompanied by the accumulation of ionic charge of the same sign, which contributes to the slow time response observed.

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open-circuit, as described in detail in the Supporting Information. As mentioned before, we have anions accumulate close to the anode at short-circuit and close to the cathode in open-circuit. Cations accumulate close to the opposite contact.

Here, we study three cases by changing one of the three parameters and keeping the other two of them constant: (i) the thickness of the sheets $b$, (ii) the distance of the layers to their closest interface $d_l$, and (iii) the value of the ion density per unit area $A$.

Figure 6 shows the results of the numerical simulation of a PSC at short-circuit for different values of $b$, $d_l$, and $A$. Two regions within a distance $b + d_l$ to the contacts act as a planar capacitor of thickness $b + d_l$. In each contact region, a voltage $V_{\text{contact}}$ drops. In the central region, a voltage $V_{\text{bulk}}$ drops. The effect of varying the thickness $b$, case (i), can be analyzed after the comparison of Figure 6a,b and Figure 6c,d. We observe that the higher the value of $b$ is, the higher the value of $V_{\text{contact}}$ drops along the contact region and the lower the value of $V_{\text{bulk}}$ drops along the bulk (Figure 6a). The similar electric field close to the contacts in Figure 6a,c is accompanied with no changes in the charge carrier concentrations within a distance $d_l$ next to the contact regions. In Figure 6c, the energy bands are flatter in the bulk, and the carrier concentrations are lower and more uniformly distributed along this central region. Thus, a change in the distance $b + d_l$ (with $A = \text{constant}$) reduces the intensity of the electric field in the bulk, minimizing the effect of the drift mechanism (Figure 6c).

The effect of varying $d_l$ (case (iii)) is seen after the comparison of Figure 6a,b and Figure 6e,f. The bands in the bulk bend in opposite directions in Figure 6a and Figure 6e, respectively. The drifting effect is not only softened but inverted. Cases (i) and (ii) lead to similar conclusions: the displacement of the ionic layers closer to the boundaries is equivalent to making these layers narrower.

Case (iii) analyzes the effect of changing the value of $A$. The energy diagrams and free carrier concentrations of Figure 6g are practically identical to the ones of a perovskite without ions (Figure 3a). A similar study with the parameters $b$, $d_l$, and $A$ of the dipolar distribution for open-circuit is detailed in Figure S5 (Supporting Information).

### 3.4. Comparison of the DD and the Dipolar Distribution of Ions

One of the main differences obtained for the dipolar distribution is the compensation of the internal electric field in the bulk seen at short-circuit. This is observed in Figure 6a,c,e but not in the DD distribution of Figure 3i. The ion density per unit area $A$ in the dipolar distribution must be decreased (Figure 6g,h) in order to achieve similar band diagrams as in Figure 3i. The differences between the DD and dipolar distributions seen at short-circuit can also be observed at reverse voltages. An example is shown in Figure 7 where the DD and dipolar distribution cases are compared at deep reverse bias $V_{\text{app}} = -1 \text{ V}$. At this voltage, the ions tend to accumulate closer to the contacts than at $V_{\text{app}} = 0 \text{ V}$ (Figure 3i).

The other interesting feature for the dipolar distribution is the existence of an electric field located in the bulk of the absorber layer that opposes the internal electric field at short-circuit (Figure 6a,c,e) and not existing in Figure 6g. The electric field seen in the bulk of Figure 6a,c,e facilitates the collection of charge at the electrodes, thus increasing the PC close to the short-circuit region. As mentioned before, some authors suggest that ionic charge accumulates at the edges of the perovskite in the Debye layers. From this comparative analysis, (Figures 3 and 6 for short-circuit, Figure 7 at $V_{\text{app}} = -1 \text{ V}$, and Supporting Information for open-circuit) the surface band

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Figure 6. a,c,e,g) Energy diagrams and b,d,f,h) charge concentration of electrons, holes, anions, and cations at short-circuit with the physical parameter values depicted above the figures.
bending associated with Debye layers is detected only in the dipolar distribution of ions (Figures 6 and 7c). For the DD distributions of ions, the bands bend very slightly close to the perovskite interfaces (Figure 3i and 7a), not showing this Debye layer.

It is immediately apparent that the distribution of the ions and carriers for the DD and dipolar distributions will have a strong impact on the device performance. The large neutral region in the bulk of Figure 6a,c,e shows that the photo-generated carriers in the bulk will be separated mainly by diffusion to the contacts, as opposed to Figure 3i where the ions create their own electrical field through the device, which facilitates charge separation similar to the case without ions. The charge extraction at the contacts in both cases (DD and dipolar distributions) should also be different. In the case of the dipolar distribution, steep potential drops at the contacts 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.[3]

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.

Overall, 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 changes in the parameters that determine the dipolar distribution of ions affect the net distribution of electric field in the perovskite semiconductor significantly.

Another important conclusion is about the discussion of the general doping character of the hybrid perovskite and the basic energy diagram model, i.e., whether the barrier is close to one interface, or the built-in voltage produces a slanted band as in a p–i–n solar cell. Our calculations show that so far as the moving ion density is significant and close to the native doping density, the moving ions determine the barrier and field distribution irrespective of the conductivity nature of the perovskite, such as p-type or intrinsic semiconductor. Therefore, one needs be aware that pretreatments of the device may produce important and sometimes irreversible changes in the operation of the solar cell, as shown experimentally.[67]

4. Transient Response Measurements

The physical phenomena occurring in a PSCs span an impressive range of diverse timescales, from the phonon response for charge shielding and cooling of photogenerated carriers in picoseconds time to the slow relaxation at room temperature that may take seconds. In the following sections of this review, we will describe a variety of techniques which are used to probe the different phenomena that occur in the slow side of the general timescale, i.e., from microseconds to seconds. Time transient experiments as well as frequency domain techniques are surveyed. Here, we aim to bridge the gap between fundamental properties and device operation. Therefore, we
need to measure full devices with contacts and determine the observations corresponding to different relevant phenomena such as transport, recombination, charge injection, and ion drift, identifying, if possible, the locus of the physical signal, i.e., the bulk of the absorber, grain boundaries, or outer interfaces. We present a selection of important descriptions and explanatory experiments approaching central aspects of the unique phenomenology of PSCs. With this purpose, we first comment on methods of transient time measurements at different timescales, as well as the consideration on recombination. Subsequently, in Section 5, our attention will be focused on the charge accumulation by discussing the capacitance ($C$) with the associated resistance ($R$). In our program to cover the main aspects of the device operation for practical purposes, the hysteresis of $J$–$V$ curves plays a dominant role and this issue will be approached in Section 6.

4.1. Characteristic Response Times and Basic Transient Behavior

For characterizing the response time domains and transient behavior of PSCs, several techniques and particular experiments have been reported in the literature. In general, given the significant variety among device designs (e.g., materials and structure of layers) and fabrication procedures (e.g., composition and variables during processing), certain scattering is often found for most measurements on these devices. However, general features can be highlighted as typical and even unique, especially when samples of large quality and efficiency become available.

Obviously, in the focus of our approach, the electron–hole recombination mechanisms play a fundamental role. These are (i) the radiative recombination, (ii) the nonradiative Shockley–Read–Hall (SRH), and (iii) Auger recombinations. While in the first case a photon is emitted, in the SRH recombination, the electron relaxation is assisted by midgap states (traps) and the energy is dissipated as lattice vibrations. In the other case, the Auger recombination occurs when the energy is given to a third carrier, which accesses a different kinetic energy in the same band and then is often thermally relaxed.

It should be noticed that the absorption coefficient $\alpha$ of MAPbI$_3$ is quite remarkable for having an unusually sharp shoulder near $E_g$ with higher values than most other comparable semiconductors, which can be observed in Figure 8a. This abrupt optical band edge exhibits a clear exponential law $\alpha \propto \exp \left( \frac{h \nu}{E_U} \right)$ with the photon energy $h \nu$. The resulting Urbach tail energy $E_U = 15$ meV is far lesser than a-Si and CuInGaSe$_2$ (CIGS) solar cells. Actually, it approaches those of other successful direct-band-gap materials such as GaAs and CdTe.$^{68,69}$ Therefore, contrasting indirect-band-gap materials like a-Si, the low $E_U$ of MAPbI$_3$ suggests a very low degree of structural disorder and the purely exponential Urbach tail means that no optically detectable deep states are present in the MAPbI$_3$ material. This is a key element for explaining the large achieved $V_{oc}$ values.

![Figure 8. a) Absorption coefficient spectra of high-quality semiconductors in photovoltaic technologies, as indicated. Adapted with permission.$^{[68]}$ Copyright 2014, American Chemical Society. b) PL spectrum and corresponding absorbance (in Tauc plot representation for direct bandgap recombination) of a TiO$_2$/MAPbI$_3$ layer showing virtual absence of Stokes shift around the bandgap: 1.6 eV (775 nm). Data courtesy of Thi Tuyen Ngo (INAM). c) PL decays from different pulsed fluences in a MAPbI$_3$-based device. Adapted with permission.$^{[71]}$ Copyright 2017, American Chemical Society. d) Evolution of normalized PL intensity under continuous excitation for three different devices of distinct perovskite and fabrication procedure. Reproduced with permission.$^{[17]}$ Copyright 2014, American Chemical Society. e) Evolution of the normalized EL signal of a working device under air and nitrogen atmosphere at constant voltage (1.5 V). The inset shows the evolution of the signal at a shorter timescale window. Reproduced with permission.$^{[72]}$ Copyright 2015, American Chemical Society.](image-url)
around 1.1 V, whose nonradiative losses have been estimated around 230 mV from the radiative $V_{oc}$ limit of 1.33 V.[76]

The radiative recombination in MAPbI$_3$ is basically due to band-edge electrons and holes, as is evident from the nearly absent difference (at most 10 meV) between the absorption onset and the PL peak, i.e., the Stokes shift.[30,70,73,74] This is illustrated in Figure 8b where PL and absorbance (in Tauc plot representation) spectra are compared. In contrast, some singularities in alternative perovskites can be mentioned. For instance, in the work by Wright et al.[75] the Stokes shift in FAPbI$_3$ was found to be temperature dependent and larger when the excitation fluence was reduced. Moreover, for CsPbBr$_3$ nanocrystals, it is enhanced to hundreds of meV as the nanocrystals' edge length is reduced to a few nanometers[76] and even anti-Stokes shift has been found in MAPbI$_{3-x}$Br.[77]

As a basic practice for testing radiative recombination, the samples are typically pulsed with a nearly monochromatic light source, and the PL decay is recorded in order to estimate the PL lifetime. For PSCs, these measurements report values from tens to, unusually, hundreds of nanoseconds, extracted from the fitting to a monoeXponential law that characterizes the dominant radiative recombination path. Nevertheless, in some studies, a two-time constant PL decay has been found[78–81] with the consequent consideration of competing recombination mechanisms. In this context, the work by Kanemitsu[30] particularly showed that PL decay curves are sensitive to the excitation fluence, as in Figure 8c, and that the PL decay dynamics are well explained by the free-carrier band-to-band recombination rather than the exciton recombination. The latter was concluded from the absence of Stokes shift (lack of nonradiative recombination increase) at larger excitation fluences, when the PL decays are faster and two time constants appear. In addition, they also proposed that photon recycling could be responsible for the unusual slow PL decay.[10]

On the other hand, other singular behaviors were reported by Sánchez et al.[17] who measured the evolution of the PL intensity under continuous excitation for different device structures and fabrication procedures. Two decaying intensities (Sing-MA/I−Cl and Seq-MA/I in Figure 8d) and an increasing one (Seq-FA/I in Figure 8a) were noticed. The PL intensity drop was attributed to the increase of the nonradiative losses and the increase of charge separation rate toward regions such as grain boundaries, abrupt changes in the absorption spectrum of the perovskite upon illumination as a consequence of the dielectric polarization, or anisotropic absorption of the different light polarization angles. The latter explanation, upon reaching the dielectric polarization of the device, would be compatible with the slight PL enhancement for the Seq-FA/I sample. Complementary to the reversible PL responses of Figure 8a, a subsequent study[21] also showed the electroluminescence (EL) evolution with time at a constant applied bias. It was shown that the EL presents a mostly irreversible increase followed by a quenching in different timescales depending on the atmosphere composition.

Returning to the PL decays from different pulsed excitation intensities, Handa et al.[71] made an interesting combination of these results (fluence dependence of time constants) with PC measurements, proving a significant reduction of the external quantum efficiency (EQE) above a certain level of illumination.

The direct implication here is that the carrier-injection rate is sensitive to the photogenerated carrier density, meaning that a carrier-injection bottleneck strongly enhances recombination losses of photocarriers in the perovskite layer at high excitation conditions. Moreover, they discarded the influence of Auger recombination for photocarrier densities below $10^{17}$ cm$^{-3}$.

Additional irregularities were noticed by Unger et al.[15] from their study of full EQE spectrum evolution with time and corresponding $f_{sc}$ change. As displayed in Figure 9a, after half an hour, the spectral shape of the EQE did not change substantially between repeated scans, but a vertical shift appeared in correspondence to the current reduction by that time in Figure 9b. This suggests that the PC decay results from a reduction in the charge extraction efficiency rather than optical changes to the absorber or contact layer. Consequently, a direct macroscopic implication arises here from these slow transients; a serious unreliability can be found with the matching between integrated EQE values and PC densities determined from $J$–$V$ measurements, mainly at long delay times or steady-state PC measurements. Furthermore, the evaluation of complementary important parameters can be similarly affected for these anomalous behaviors. This is the case, for instance, of the yielded open-circuit voltage radiative limit obtained from EL and EQE, as presented by Tvingstedt et al.[70] and Tress et al.[82]

At this point, it is already clear that the competition of several factors affecting the charge extraction, also evidenced in the radiative recombination, produces a noteworthy time change in recombination, and thus current. Here is precisely where several studies have been focused on, e.g., dealing with the evolution of PC and open-circuit voltage ($V_{oc}$) under different configurations, perturbation types, and device characteristics. As in Figure 10b–d, one basic approach is to apply a light perturbation and record the subsequent response. For instance, in the simplest case, when the sample behaves nearly as an RC circuit (Figure 10a), the current at SC should decay exponentially with an extraction time constant $\tau_{ext} = R_{ext} \cdot C_{ext}$ and the voltage at OC with a recombination time $\tau_{rec} = R_{rec} \cdot C_{oc}$. However, as we will comment in the following section, for PSCs it can be quite challenging to actually obtain such “textbook” experimental relaxations.
Among the most common practices one can find in the reports from several groups are those of photoinduced (PI) transient PCs (TPC) and transient photovoltage (TPV), where typically the signal produced by a small light pulse perturbation is recorded in SC and OC conditions, respectively.[83,84] The main aim of acquiring TPV is to evaluate the lifetime of the charge carriers as a measure of the recombination in the sample, while the TPC provides a quantification of the amount of charge produced by the device given a certain illumination, being evidently the TPC transient decays, or e–g) by impedance spectroscopy. In each case, the perturbation (above) and the response (below) with time are displayed. Additionally, for the IS, the corresponding complex plane plot is shown in panel (f).

A two-time constant decay process was first identified in this context by Sánchez et al.[17] by measuring PI-TPV on several configurations. Subsequently, O’Regan et al.[86] conducted a broader description during their studies on PI-TPV, PI-TPC, and PI-CE. Illustratively, PI-CE measurements at 1 sun showed a transient PC decay of 180 mA cm$^{-2}$ in about 50 μs (inset of Figure 11a) while the remaining 50 μA cm$^{-2}$ needed seconds to relax (Figure 11a, bottom axis). Importantly, the integrated charge collected for the slow decay ($\approx$3.6 $\times$ 10$^{-5}$ C cm$^{-2}$) was about 50 times higher. Similarly, the PI-TPV decays at 1 sun were found to present a fast component of 1–2 μs and a slow part around 5–10 μs, as observed in Figure 11b. Subsequently, further reasoning[87] associated the fastest lifetime from the PI-TPV with recombination processes. They also suggested that reorganization of dipoles could explain the slowest relaxations.

Interestingly, current interrupt voltage measurements were also shown to evolve in the domain of milliseconds, as shown in Figure 11c. By switching from illuminated SC to dark OC, the sample voltage rises during $\approx$2 ms up to a peak while charge is transported toward the contact electrodes, and hence it decays during tens of milliseconds due to recombination.[86] Importantly, the time of SC illumination enhances the $V_{oc}$ peak, possibly indicating that it increases the band offset at the voltage generating interface(s) in the cell. Subsequently, Palomares and co-workers[88] compared the two-time constant TPV decays between devices with and without mesoporous TiO$_2$ and also looked at the transient absorption spectroscopy[84] patterns. The results showed apparent differences only for the slowest recombination time, and therefore, they assigned the fastest component to recombination between electrons in the MAPbI$_3$ and holes in the HSL.

### 4.2. Slower than Second Relaxation Processes

Beyond double exponential decays, the work of Baumann et al.[89] identified three distinct time regimes during the $V_{oc}$ decay at OC under several pulsed illumination intensities ranging from 1 to 100 mW cm$^{-2}$. Importantly, while the two first characteristic time constants were of 10–100 μs and 1–100 ms, respectively, the third phase of the decay was as slow as 10 s. As illustrated in Figure 12, this behavior is different from that of organic solar cells (OSCs) whose decays can be fitted to a single exponential along almost the complete transient. In all the cases, the slowest process was associated with shunting and the apparent illumination-dependent recombination once more became a target of further discussion keeping in the core of debate the influence of the interface. About the latter, Nagaoka et al.[90] also found similar decays but specifically pointed to the sensitivity of the nature of the perovskite/ESL interface.

Moreover, Bertoluzzi et al.[91] attempted to separately inspect the fast and slow components by measuring short lifetimes with typical PI-TPV (pulsed constant small perturbation with different background illuminations) and the large time constant from $V_{oc}$ decays (switch from light to dark at OC) at different illumination intensities, also known as open-circuit voltage decay (OCVD). Their results corroborated 100 μs and 1 ms for the faster components whose meaning was ascribed to discharge and recombination of photogenerated electrons and holes, respectively. However, the third and slowest component, with an estimated characteristic time up to 100 s, was found to behave as a power law decay relaxation. Ionic–electronic polarization and depolarization kinetics depending on internal voltage were proposed as explanation. Importantly, they introduced the useful concept of instantaneous relaxation time defined as

$$\tau_{ir} = \left(\frac{1}{V \frac{dV}{dt}}\right)^{-1}$$

(2)

This parameter straightforwardly gives a criterion on the presence or not of exponential relaxation decays and it also illustrates the characteristic time constants or domain.
Furthermore, the effect of prior light soaking was found to be determinant on the shape of the OCVD, as described in the contribution of Gottesman et al.\[8\] The two types of OCVD response are shown in Figure 13a and the related \( \tau \) are presented in Figure 13b, where the differences are evident after the initial fast decay (\( \approx 1.0–0.8 \) V) that is out of the resolution of this experiment. Initially, or when dark recovery is set before the pulse, a slow decay of seconds takes place when \( V_{oc} \) goes from 0.8 to 0.2 V with the competition between exponential (plateaus in Figure 13b) and power law (monotone regions in Figure 13b) relaxation decays. Subsequently, an even slower power law relaxation occurs during more than 10 s. Differently, when light soaking is set before the pulse, a faster exponential decay reduces \( V_{oc} \) from 0.8 to 0.2 V with a time constant of 10 ms, and the slowest power law relaxation takes at least an hour to remove the remaining electrostatic internal potential \( \Delta V_{elec} \). In other words, light soaking (i) makes the initial \( V_{oc} \) decay faster but (ii) slows down the final part of the decay where an extra \( \Delta V_{elec} \) takes considerably more time to relax.

Regarding the first issue, the light-soaking condition of fast recombination was stated in terms of major changes in the contact region deduced from physical simulations. Likewise, other modeling results illustrated that \( \Delta V_{elec} \) is possibly sustained by the charge accumulation of slow, mobile positive ion charges and electronic holes in a double layer at the perovskite/ESL interface, as shown in Figure S2 (Supporting Information). These results were subsequently corroborated by Hu et al.\[92\] on diverse device configurations. Additionally, they measured the \( V_{oc} \) as a function of the illumination intensity with and without light soaking preconditioning. They observed a clear \( V_{oc} \) reduction after light soaking above a given illumination level, which they attributed to large surface recombination of accumulated electronic carriers at the perovskite/ESL interface upon light soaking.

However, besides light soaking, the polarization history, or prepoling has been found to directly modify the internal processes behind the slow mechanisms too. Figure 14 shows the \( J_{sc} \) after switching from OC to SC under constant 1 sun illumination for two preceding reverse applied voltages measured by Chen et al.\[93\] Once more, the separation between faster and slower responses takes place. Independent of poling, a quicker decay occurs in all cases in a timescale from milliseconds to seconds presumably associated with capacitive effects due to electrode polarization. Afterward, for the transient without poling, the \( J_{sc} \) reaches its constant equilibrium level, which is the general shape of the response, although in some reports\[6,90\] the possibly capacitive transient can last tens of seconds. In contrast, as the reverse poling increases, a larger reduction of \( J_{sc} \) happens that relaxes toward the equilibrium level during about 100 s. This second process could be explained in terms of contact barrier modification due to

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**Figure 11.** Different transient behaviors showing two time regimes. a) Current decay from Pt-CE set up with the first 60 s of SC (fast transient) in the inset. b) Experimental Pt-TPV and theoretical fitting with mono- or double-exponential relaxation laws. c) Dark \( V_{oc} \) decay following current interrupt from illuminated SC with similar \( J_{sc} \) but during different times, as indicated. Adapted with permission.\[86\] Copyright 2015, American Chemical Society.
to interface ionic charges. Illustrative of the ionic nature of charge balance at the interfaces, measurements by Almora et al. [64] on MAPbI$_3$ showed a typical Guoy–Chapman diffuse layer performance.

5. Impedance and Capacitance Features of Perovskite Solar Cell Devices

So far, the evaluation of time domains during the electrical responses has been reviewed aiming to illustrate how the current and voltage evolve under different conditions. An alternative and very useful method uses a small perturbation signal in the frequency domain. As there are different alternative approaches, we provide a short introduction of impedance spectroscopy (IS), centered on capacitance, and evaluation of similar quantities by the small perturbation time transits.

5.1. Definitions

For convenience, here we first introduce a set of important clarifying concepts as well as experimental set-up descriptions which will be systematically alluded to in the subsequent sections.

Interpretation of Measurements and Measured Quantities: The IS [94] analysis has been widely used for the characterization of solar cells. [95] In general, the impedance is the measurement of small perturbation voltage ($\tilde{V}$) to current ($\tilde{I}$).

In the potentiostatic variant, the IS basically consists of applying an ac potential small perturbation $\tilde{V} = V_0 \exp[i\omega t]$ at a given frequency $f = \omega/2\pi$ (using the complex numbers representation where $i$ is the imaginary unit) with respect to the angular frequency $\omega$ as in Figure 10e. Subsequently, the ac current response $\tilde{I} = I_0 \exp[-(\omega t - \phi)]$ of the sample (Figure 10f) is detected, $\phi$ being the phase shift between perturbation and response. The impedance is defined as

$$Z = \frac{\tilde{V}}{\tilde{I}}$$

Figure 12. Photovoltage decay of a MAPbI$_3$-based solar cell (green) and two OSCs (red and blue) for different illumination intensities, as indicated. Differently to OSCs, the PSC decay is divided in three time regimens. Reproduced with permission.[89] Copyright 2014, AIP Publishing, in accordance with the CC BY 3.0 license.

Figure 13. Effect of light soaking in the $V_{oc}$ of PSCs. a) Dark transient $V_{oc}$ after long-term storage in dark (Reference), light soaking (6 min), and again dark recovery (1 h). Reproduced with permission.[8] Copyright 2016, Elsevier. b) Instantaneous relaxation time from OCVDs similar to those of panel (a) for PSCs with different ESL and with prior light or dark soaking times, as indicated. During light soaking, at least three time regimens are identified and from dark recovery, the relaxation can be possibly divided in four stages, as indicated. Adapted with permission.[91] Copyright 2015, Royal Society of Chemistry.

Figure 14. Dynamic $J_{sc}$ transient behavior when switching from OC to SC for unpoled and reverse poled conditions. Reproduced with permission.[93] Copyright 2015, American Chemical Society.
Z(ω) = \frac{\hat{V}(ω)}{\hat{I}(ω)} \quad (3)

The real and imaginary parts of the impedance, Z′ and Z″ respectively, are obtained as

Z(ω) = Z′ + iZ″ \quad (4)

For an Ohmic process, the impedance is a constant, Z = R, the resistance that is a positive and real quantity. Under modulation of any system, the kinetic processes produce a frequency-dependent response that includes imaginary values.

For the simplest case of an RC circuit, shown in Figure 10a, the complex plane plot representation, −Z″(Z′) in Figure 10g, exhibits a semicircle. The characteristic time is

τ = \omega_{c}^{-1} = RC \quad (5)

with respect to the angular frequency \( \omega_{c} \), that marks the top of the arc. Note that the characteristic resistance R is obtained at zero frequency, \( Z(0) = R \). The value \( \omega = 0 \) in parenthesis indicates that the displacement is infinitely slow, i.e., \( \hat{V}(0) \) and \( \hat{I}(0) \) attain a value that is independent of time. For a solar cell with area A, the quotient of the small quantities gives

\[ Z(0) = \frac{\hat{V}(0)}{\hat{A}J(0)} = \left( A\frac{d\hat{J}}{d\hat{V}} \right)^{-1} = R_{dc} \quad (6) \]

That is, the small quantities give a derivative of voltage with respect to current. This is the reciprocal of the slope of the J−V curve, which is in turn the dc resistance of the solar cell \( R_{dc} \) (per area) in those particular conditions.

In real systems, there is at least a series resistance element that shifts the arc toward the right in Figure 10g, and multiple pairs of capacitive and resistive elements can add and/or deform arcs in the complex plane plot. In addition, inductive and/or nonlinear elements can also complicate the IS spectra. Concerning the PSCs, a more detailed discussion on the general characteristics of the impedance spectra is provided in Section 5.5. However, at this point, it is instructive to highlight that no less than two arcs are often presented in the complex plane plots for these devices, at low and high frequencies, respectively. Therefore, each arc may correspond to an individual mechanism with its own time constant. In this context, several IS studies have reported lifetimes in good agreement with the transient photoinduced measurements at least with one of the RC constants.

In a discharge experiment, in the time domain decay method, we apply a small step of the voltage \( \hat{V}(t) = \Delta V \cdot u(t) \), \( u(t) \) being the unit step function at \( t = 0 \), and we observe the consequent evolution of the charge \( \hat{Q}(t) \) that passes to the system. However, it is not usually feasible to measure a charge transient; thus, we need to observe the current transient \( \hat{I}(t) \) and perform an integration

\[ \hat{Q}(t) = \int_{0}^{t} \hat{I}(t') \, dt' \quad (7) \]

Let us look at this process in the frequency domain. We use the variable \( s = i\omega \), with \( i = \sqrt{-1} \). The Laplace transformation of a function \( f(t) \) to the frequency domain is defined as

\[ F(s) = \int_{0}^{\infty} e^{-st} f(t) \, dt \quad (8) \]

Application of the transform to Equation (7) gives

\[ \hat{Q}(s) = \frac{\hat{I}(s)}{s} \quad (9) \]

Now we introduce a frequency-dependent capacitance that indicates the modulation of charge with respect to voltage

\[ C^*(\omega) = \frac{\hat{Q}(\omega)}{\hat{V}(\omega)} \quad (10) \]

\( C^*(\omega) \) is a function of the frequency that coincides with the static differential capacitance \( C \) at \( \omega = 0 \), as follows

\[ C = \frac{\hat{Q}(0)}{\hat{V}(0)} \quad (11) \]

where

\[ C = \frac{d\hat{Q}}{d\hat{V}} \quad (12) \]

We now remark that representing either impedance or capacitance is a matter of choice. Both functions correspond to the same measurement, since they are connected by Equation (9), indeed

\[ C^*(\omega) = \frac{\hat{I}(\omega)}{i\omega \hat{V}(\omega)} = \frac{1}{i\omega Z(\omega)} \quad (13) \]

or more explicitly

\[ C^*(\omega) = \frac{Z′(\omega) + iZ″(\omega)}{\omega(Z″(\omega)^2 + Z′(\omega)^2)} \quad (14) \]

However, with respect to graphical presentation, both magnitudes show different information. For a resistive/conductive/recombination process, the arcs in the complex impedance plane show immediately the different components of resistance, while the capacitance is hidden. On the other hand, a plot of the real part of the capacitance versus frequency reveals very clearly the charge storage modes of the system that we describe in detail in the following sections.

Here, we also note that the usual normalization convention considers capacitance in units of Farads per unit area (e.g., F cm⁻²). Accordingly, analogous definitions to Equations (10)–(12) should be used, but with the charge expressed in Coulomb per unit area (e.g., C cm⁻²). Similarly, impedances and resistances like in Equations (13) and (14) may be presented in Ohms at unit area (e.g., Ω cm⁻²).

Physical Interpretation of the Capacitance: The most basic capacitive response from a solar cell is that of the geometrical
Capacitance $C_g$, which only accounts for the sum of the dielectric contribution of each layer between the metallic electrodes. For the typical case of thin-film heterostructures, where the classic parallel-plate capacitor is a suitable model, the geometric capacitance per unit area of a device of $m$ different layers in series can be obtained as

$$[C_g]^{-1} = \sum_{m} \left[ \frac{\varepsilon_0 \varepsilon_m}{d_m} \right]^{-1}$$

(15)

where $d_m$ is the thickness of the $m$th layer and $\varepsilon_{m}$ its relative dielectric constant towards the limit $\omega \rightarrow \infty$. Obviously, from Equation (15) it is clear that $C_g$ can be dominated by the layer whose dielectric capacitance is lower in comparison with the rest. Actually, $C_g$ is in general the smallest characteristic capacitance of a sample, thus frequencies above 1 MHz are often needed to determine it.[96]

A second capacitive response to mention is that of the accumulated charge at the edge of the depletion layer in p-n junction-based devices. In the one-side abrupt charge density profile approximation[97] (same as used in Section 3), the depletion layer capacitance per unit area can be expressed as

$$C_{dl} = \frac{\varepsilon_0 \varepsilon_r N_{eff}}{w} \sqrt{\frac{q}{2(V_{bi} - V)}}$$

(16)

where $q$ is the elementary charge, $w$ is the space charge width, $\varepsilon_r$ and $N_{eff}$ are the relative dielectric constant and the effective concentration of fixed ionized species (approaching $N_A$ or $N_D$ depending on the case) respectively of the layer where the depletion zone is placed and $V_{bi}$ is the built-in voltage, also known as flat-band potential. From Equation (16), a few observations can be remarked. First, at equilibrium, $C_{dl} \geq C_g$, since $w \leq d$ for any layer between the metallic electrodes. Therefore, in general $C_{dl}$ dominates the dielectric polarization capacitance in an intermediate frequency range, typically between 1 kHz and 1 MHz. For the latter, $C_{g}$ shunted by $C_{dl}$ may be considered due to nearly negligible resistive or inductive losses in the bulk and interfaces beyond the space charge, i.e., $V$ between the metallic electrodes matches that between the edges of the depletion region. Second, as reverse bias increase, $C_{dl}$ decreases toward $C_g$ following an inverse square root law $C_{dl} \propto V^{-1/2}$ as the depletion layer is enhanced. In the opposite sense, when the bias is increased toward $V_{bi}$, $C_{dl}$ grows as the width of the depletion layer is shrunk. And last but not least, the well-known Mott–Schottky plot is obtained from $C_{dl}^{-1} = 2(V_{bi} - V)/q\varepsilon_0 \varepsilon_r N_{eff}$ for $V < V_{bi}$ allowing to estimate $V_{bi}$ and $N_{eff}$ from the linear trend.

Notably, the regimen of evaluation for $C_g$ and $C_{dl}$ is that where the displacement currents related to the charging and discharging of the capacitors are around or above the order of the continuous currents through the device. This is the case of low leakage currents (large shunt resistance $R_{sh}$) and reverse or low forward bias.

In contrast to the reciprocal dependency of dielectric capacitance with the film thickness, under forward bias around and above $V_{bi}$, another type of capacitive effect dominates, increasing directly proportional to the film volume. This is due to the bulk charging and discharging during continuous current at a given voltage, and it is the chemical capacitance[98] (or diffusion capacitance in older textbooks[97]). This capacitance per unit volume can be normalized with the layer thickness $L_g$ and hence the capacitance per unit area is given by

$$C_g = \frac{q^2 L_g N_{eff}}{k_B T} \text{exp} \left[ -\frac{qV}{\beta k_B T} \right]$$

(17)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $\beta$ is a statistic parameter, and $N_{eff}$ is the effective total equilibrium charge density that contributes to $C_g$. The nature of $N_{eff}$, for instance, can be related to minority holes/electrons or traps, depending on the case. Note that Equation (17) describes $C_g$ for systems where the use of the Boltzmann statistics is reasonable; however, for other systems, it can be approximated by $C_g = q^2 L_g \cdot dN/dE$, with $dN/dE$ being the total density of states.[44]

Capacitance from Small Perturbation Transient Methods: A capacitance measurement is also acquirable from the transient response to small light perturbations, like in the case of the photoinduced differential charging (PI-DC).[83,84] In this case, PI-TPC and PI-TPV are performed under the same light pulse, at SC and OC respectively, as introduced in Section 4.1. From PI-TPC, the extracted charge per unit area is obtained by calculating the integral of the current density, which results in $\Delta Q = \Delta J_{oc} \tau_{oc}$ in the case of a monoeponential current decay $\Delta J_{oc} \text{exp} \left[ -1/\tau_{oc} \right]$. Subsequently, from PI-TPV, the amplitude $\Delta V_{oc}$ is taken and then Equation (12) is approximated to

$$C = \frac{\Delta Q_{oc}}{\Delta V_{oc}} = \frac{\Delta J_{oc} \tau_{oc}}{\Delta V_{oc}}$$

(18)

Here, two assumptions should be considered: (i) the charge losses at SC in the solar cell under illumination are negligible and (ii) the solar cell PC value is linear with the increase of simulated light intensity and is bias independent. In addition, note that the measurements of $\Delta V_{oc}$ and $\Delta V_{sc}$ in Equation (18) are made under different operation conditions, SC and OC, respectively, thus implying different resistances. Therefore, it is commonly found that capacitance from PI-DC differs in amount from that of IS.

Regarding the characteristic time $\tau_{oc}$, it should not be mistaken with other magnitudes (e.g., recombination lifetime) given that it may account for the charge extraction processes, which are expected to depend on the resistive features of the sample (e.g., bulk, contacts, and interfaces). It is also expected that $\tau_{oc}$ will be a faster time than that required for the recombination at OC. However, it is often found that non- or multieponential $J_{sc}$ decays occur, which makes the interpretation of these transient responses difficult, e.g., due to the competition between majority and minority carrier processes or in more challenging systems like PSCs.

More importantly, the chemical capacitance character of $C$ in Equation (18) must be ensured given that PI-DC is habitually performed at forward bias, i.e., with different intensities of background illumination. If not, and without clarifying considerations of such capacitive nature, the ratio of Equation (18) could be reported on phenomena different from that of the rearrangement of charges due to the change in the chemical potentials of the carriers.
As well, from the PI-CE, also introduced in Section 4.1, different $V_{o.c.}$ values can be estimated by changing the light intensity and the corresponding charge can be integrated after switching from OC to SC. Thus, the capacitance behavior with $V_{o.c.}$ can be obtained as

$$C = \frac{dQ}{dV_{o.c.}} = \frac{d\left(\int J_{sc} \, dr\right)}{dV_{o.c.}}$$  \hfill (19)

However, care should be taken with the interpretation of this charge extraction PI-CE capacitance, since the charge extracted from the decay does not account for a small perturbation process, unlike the IS and PI-DC methods.

**Capacitance in Voltage Sweep:** For the evaluation of capacitive responses, apart from IS and photoinduced transient measurements, cyclic voltammetry (CV) is often employed. CV basically consists of the continuous bias sweep from an initial voltage $V_0$ to a different $V_1$ and then back to $V_0$ at a given scan rate $s = dV/dt$, whose sign depends on the direction of sweeping. In contrast to Equation (10) that defines the small amplitude measurement, the CV and related voltage sweep techniques produce a continuous measurement and large amplitude response signal.

If we assume that the measured current is capacitive, then the current is calculated as

$$J_{cap} = \frac{dQ}{dt} = C \frac{dV}{dt} = sC$$  \hfill (20)

and the capacitance can be obtained as $C = J_{cap}/s$ from the measured current.

### 5.2. Dark Capacitance and Dielectric Components

By using IS, the capacitance spectra of PSCs can be obtained as in Figure 15. In dark equilibrium, two main plateaus can be identified in the capacitance–frequency plot at frequencies below those where the series resistive and inductive effects are present. Accordingly, at least two characteristic capacitances should be identified with their respective characteristic resistances and, hence, two arcs are expected from the complex plane plot, as in the inset of Figure 15. This general trend is not exclusive of solar cell structures, taking into account the fact that symmetrically contacted bulk perovskite layers can deliver the same features.

Regarding the high-frequency (Figure 15) behavior, a dielectric polarization domain takes place, whose corresponding capacitance approaches $C_{eff}$. Guerrero and co-workers\textsuperscript{[64,99]} corroborated this plateau to fulfill Equation (15) at room temperature and reported dielectric constant values around 22–24 for MAPbI$_3$. The latter was in good agreement with previous calculations (23.3) of Onoda-Yamamuro et al.\textsuperscript{[100]} who fitted the Kirkwood–Fröhlich equation and also agreed with predictions (24.1) of Brivio et al.\textsuperscript{[101]} from DFT simulations with quasiparticle corrections.

Importantly, several phase transitions occur even in the operational temperature range, e.g., MAPbI$_3$ changes from orthorhombic to tetragonal structure around $\approx 150$ K (space applications) and from tetragonal to cubic around $\approx 57$ °C, which produce gaps in the dielectric constant. The latter is illustrated in the literature,\textsuperscript{[13,27,28,100,102,103]} as well as the complete dark capacitance spectra below\textsuperscript{[13]} and above\textsuperscript{[104]} room temperature.

Another important effect on the dark high-frequency capacitance is that of applied voltage, which critically depends on the bias range and device charge density. At reverse bias, the capacitance often saturates toward $C_{fr}$ as illustrated in Figure 16, meaning full depletion of the space charge zone. However, care must be taken when interpreting the capacitance in the Mott–Schottky plot representation at forward bias because at least two different capacitances compete below and around $V_{th}$. Like in the experimental data in Figure 16a, some devices actually present a nearly constant charge density profile $\rho(x) = qN_{eff}$ (negative, if $N_{eff} = N_0$, $x$ being the distance from the junction. Hence, the Mott–Schottky analysis is meaningful and the fitting of the linear region of low forward bias gives $N_{eff}$ and $V_{th}$. However, in most cases, the quasi-intrinsic character of the perovskite and variable doping by vacancy displacement prevents the use of this technique, which is the situation of Figure 16b. For such samples, the fitting of the nearly linear region around equilibrium (Figure 16b, dashed red line) would deliver a meaningless $V_{th}$ value, and the fitting of the apparently linear abrupt step around the expected $V_{th}$ (Figure 16b, solid red line) is that the transition to a dominant exponential capacitance that appears as flat-band potential is approached and exceeded (see Figure 16, right axes). Consequently, Mott–Schottky analysis is not useful here. Actually, for some devices, the shape of the charge density can be approximated to a power law $\rho(x) = q\eta x^\gamma$ ($\eta$ is a constant with units of cm$^{-\gamma-1}$) and $\gamma$ is an integer. Thus, by integrating the Poisson equation (analogously to Section S1.1 in the Supporting Information) along a depletion layer of width $w$, it is easy to obtain after some calculations\textsuperscript{[97,106]} such that

$$C_d \approx \frac{(V_{th} - V)}{\eta}$$  \hfill (21)

For instance, the capacitance of Figure 16b gives a clear linear trend around equilibrium when represented as $C^{-16}(V)$.
in Figure 16c. This suggests that a depletion layer capacitance from a charge density profile like \( \rho(x) = q\eta x^7 \) can dominate the capacitive response if \( V_{bi} \approx 1 \text{V} \). Note that this assumption is considered as a correction of \( N_A \) (assuming p-type perovskite) in Equation (S8) of Section S1.1 in the Supporting Information; thus, it cannot be mistaken as an effect of mobile ions like Equation (S15) in Section S1.2.1 in the Supporting Information. Additionally, once the dc current becomes substantial, at high enough forward bias, an exponential capacitance \( C_e \) arises as in Figure 16, right axes. This can also be roughly appreciated from Figure 15 between 0.5 and 0.75 \text{ V} around a few tens of kilohertz. Regarding the nature of this \( C_e \), a chemical component (Equation (17)) could be expected; however, an overlapping occurs with slow mechanisms that presumably rules the low-frequency capacitance \( C_d \). The effect of the sluggish processes on high-frequency capacitance can be straightforwardly appreciated from capacitance–voltage curves at different scan rates and directions showing a hysteresis similar to that of \( J-V \) curves.\(^{[105,107]} \) In contrast to the argument on Figure 16c, this effect could be related to the features discussed earlier in relation with mobile ion distributions which are introduced in the Poisson equation (see Equation S15) in Section S1.2.1 in the Supporting Information. In addition, for inverted cells with organic selective contacts, where nearly negligible hysteresis is obtained from \( J-V \) curves (see Section 6.6), Faradaic current peaks can affect the \( C(V) \) measurements even at frequencies as high as 10 kHz.\(^{[107]} \) The dc polarization may be responsible for the drift of ions toward the interphases where the charge accumulation could be a catalytic factor for reactivity in a reversible or irreversible way (degradation), as shown in Figure 1f.

Importantly, calculations by Garcia-Belmonte and coworkers\(^{[108]} \) have shown \( C_p \) of MAPbI\(_3\) to be far below \( C_e \). This was done considering (i) the MAPbI\(_3\) low intrinsic density of defects (\( \approx 10^6 \text{ cm}^{-3} \), similar to CdTe but 5 orders below silicon) and (ii) the condition when generated carriers exceed majority carriers around 1 \text{ V} forward bias (\( \beta = 2 \) in Equation (17)). Consequently, in practice, it would not be possible to measure \( C_p \) unless (i) larger intrinsic density of states actually occurs or (ii) minority carriers do not surpass majorities at 1 \text{ V} (\( \beta \rightarrow 1 \) in Equation (17)).

Last but not least, at low frequency, there is a remarkable enlargement of the capacitance which is exponentially magnified as the electronic charge is injected (Figure 15) or generated (see Figure 19). In this regime, there is no clear distinction between forward bias below or above the flat-band potential and the capacitance systematically grows. This can be seen in the capacitance–frequency plot of Figure 15 around a few fractions of hertz, while in the complex plane representation (inset of Figure 15), it results in a deviation from the high-frequency arc whose extrapolation can show resistances up to megaOhm. Notably, experiments by Almora et al.\(^{[11]} \) on cells with different thicknesses in perovskite layers showed no clear correlation between MAPbI\(_3\) and Cl\(_x\) thickness and the low-frequency capacitance, so they proposed that electrode polarization and surface processes should be behind this effect. In addition, they calculated a characteristic dark capacitance by subtracting the \( J_{cap} \) from the current density–voltage curves at different scan rates, as in Equation (21), whose results are illustrated in Figure 17, showing magnitudes in the range of \( \mu \text{F cm}^{-2} \). Moreover, despite the dark \( J_{cap} \) being less than \( \mu \text{A cm}^{-2} \), below flat-band condition, they grow exponentially as carrier injection rises and reach larger than \( \text{mA cm}^{-2} \) values under light, irrespective of the bias regime.

### 5.3. Capacitance from Light-Induced Transients

Figure 18 illustrates some typical results for PI-CE and differential charging PI-DC for PSCs, which in general reproduce

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**Figure 16.** Mott–Schottky plots (left axes) and corresponding capacitance–voltage curves (right axes) at 10 kHz for two devices of different perovskite a) with and b) without constant charge density profile. c) The capacitance of panel (b) as \( C^2(V) \) is presented; thus, a 14th power law charge density profile results in a more suitable condition when assumed \( V_{bi} = 1 \text{V} \). The inset in each graph is the respective absolute charge density. Adapted with permission.\(^{[109]} \) Copyright 2016, AIP Publishing.
an exponential trend as approaching $V_O$, like in Figure 16. As introduced in Section 4.1, differently to other cell types, the transient decays from PI-TPV, PI-TPC, and PI-CE present at least two characteristic times during relaxations. This was interpreted by O’Regan et al.\textsuperscript{[86]} as evidence of multiple mechanisms of charge storage within the cell. Additionally, they point out that for PSCs, the capacitance from PI-DC results are significantly lesser than that from PI-CE, as a consequence of the differences in the current relaxation timescales. This has been subsequently checked by Palomares and co-workers in several studies,\textsuperscript{[87,88,109,110]} in which they also realized a crucial effect due to the composition and morphology of the selective contacts.

A slower charge extraction at SC in PI-CE than charge recombination at OC in PI-TPV is meaningless without considering the influence of extra phenomena. The core of the discussion here lies on the doubts regarding the chemical nature of the capacitance measured by these means. For example, feasibly during the PI-CE charging at 1 sun illumination, besides charge accumulation as $C_{\mu}$, surface polarization at the electrodes create extra concentration of charge whose ulterior relaxation time is considerably slower. This is a big ionic–electronic accumulation effect, whose occurrence has been concluded several times in the literature\textsuperscript{[82,85]} and it is explained here by simulations in Figure 3 and Figure S2 (Supporting Information). Contrarily, for PI-DC, a steady state is secured prior to the small perturbation, that is possibly too fast for the slow mechanisms. All of these can be related to the above-mentioned (see also the following sections) low-frequency capacitance; in other organic solar cells and dye-sensitized solar cells (where there is no $C_{\mu}$), the capacitances from PI-CE and PI-DC coincide. Actually, a recent work\textsuperscript{[111]} showed comparable charge carrier densities both from PI-CE and PI-DC on MAPbI$_3$-based cells with organic selective contacts, also known as inverted configuration. These devices have been shown to have significantly lower $C_s$ in comparison with those that typically include TiO$_2$ and spiro-OMeTAD as selective contacts.\textsuperscript{[57,107]} Figure 18 shows the clear difference between PI-CE and PI-DC for devices with multienveloped decays (typically those with TiO$_2$/MAPbI$_3$ interface) while for monoexpanding decays, both techniques deliver not so distinct values. Among cells with monoexpanding decays, those with organic selective contacts are a good example, despite some optimized regular devices also showing this feature.

5.4. The Low-Frequency Capacitance under Steady-State Illumination

The appearance of an anomalously large $C_s$ under illumination is one of the clearest evidences of the presence of slow dynamic charge mechanisms in PSCs. This feature has been reported by several research groups\textsuperscript{[7,55,56,112–114]} mainly with the aim of illustrating its dependence with the composition and morphology of the selective contacts as well as the close relation with the widely discussed hysteresis behavior in the $J$–$V$ curves (see Section 6).

As shown in Figure 19, the general trend of the spectra is not so different from that created by charge injection throughout forward bias at dark (Figure 15), meaning that the explanation behind such an effect is directly related to the increase of electronic charge density either by injection or photogeneration. As summarized by Bisquert et al.,\textsuperscript{[109]} explanatory proposals include (i) change of electrode polarization,\textsuperscript{[11]} (ii) change of bulk polarizability,\textsuperscript{[115]} or (iii) change of chemical capacitance\textsuperscript{[104]}

The first argument, where ionic species pile up at the interface, can explain equilibrium dark $C_s$ in the order of µF cm$^{-2}$. This situation of dipolar distribution of ions toward the anode and the cathode has already been presented in Section 3.3 with related profiles and band diagrams. Almora et al.\textsuperscript{[64]} found evidence that shows a combination of Helmholtz capacitance $C_{\text{HL}}$ and diffusion layer capacitance

$$C_{\text{diff}} = \frac{\kappa \varepsilon_0}{L_0} \cosh \left[ \frac{qV}{2k_BT} \right]$$

(22)
in a Debye length as in Equation (1) for conditions where $C_{\text{HL}} > C_{\text{diff}}$. Note that these capacitances are connected serially; thus, the nearly constant $C_{\text{HL}}$ prevents the total capacitance to achieve values larger than tens of μF cm$^{-2}$; thus, the enhancement of $C_s$ under larger charge densities cannot be explained in terms of $C_{\text{diff}}$ increase due to the series configuration.

Therefore, $C_{\text{HL}}$ should no longer be significant under light or forward bias in order to achieve capacitances as large as mF cm$^{-2}$. This can happen as a consequence of a large concentration of carriers forming a large interfacial capacitance$^{[115]}$. Similarly, it is possible that there are $C_{\mu}$ effects; however, an important role from native defects could also be expected, as suggested by Li et al.$^{[112]}$

Following the idea of a large surface capacitance due to accumulation of electronic carriers, the works by Zarazua et al.$^{[55,114]}$ showed a clear experimental $C_s \propto [qV/(2k_BT)]$ dependency. This will be a consequence of a band bending induced by light that is contrary to the equilibrium Schottky barrier, with the majority carriers entering an accumulation regime. Assuming a p-type semiconductor at the MAPbI$_3$-TiO$_2$ interface, the accumulation capacitance has the expression

$$C_s = \sqrt{p_b \frac{q^2 \epsilon \epsilon_0}{2k_BT} \exp \left( \frac{qV}{2k_BT} \right)} \tag{23}$$

where $p_b$ is the bulk carrier density corresponding to native defects. Interestingly, Equation (23) resembles the exponentially growing term of $C_{\text{diff}}$ from Equation (22), but considering $N = 2p_b$ in Equation (1). This could mean that the general mechanism is not so different in nature; hence, strongly linked ionic-electronic features possibly govern the slow processes. However, in contrast to the ions being blocked at the interface, the electronic accumulation does not find a series limitation and can rise to very high values. For instance, the experiments with the perovskite thickness $d$ are illustrative of the regimens where each charge type is of most importance. In dark equilibrium, $C_s$ is almost $d$ independent or nearly inversely proportional$^{[113]}$, while upon increasing electronic charge density, $C_s$ grows proportionally with $d^{[113,114]}$ indicating the dependence of surface capacitance on charge collection length. Importantly, the exact linear behavior $C_s \propto d^{-1}$ in the dark has not been clearly obtained, which discards the idea of its origin as purely bulk dielectric in nature. Neither exact $C_s \propto d$ in light/forward bias has been plainly reported, thus the pure bulk chemical capacitance mechanisms can be ruled out.

### 5.5. Negative Capacitance and the Equivalent Circuit

As commented above in Section 5.2 with respect to Figure 15, the most typical impedance response from PSCs may include two capacitances with their respective resistances that generate two arcs in the complex plane representation of impedance and two plateaus in the capacitance–frequency representation of capacitance. Subsequent discussion stated the nature of the low-frequency region as corresponding to slow mechanisms possibly associated with ionic/electronic interface processes ($C_s, R_s$), while the high-frequency branch of spectra are in principle related to dielectric bulk polarization ($C_{\text{bulk}}, R_{\text{bulk}}$). Additionally, further phenomena can also occur, generating intermediate arcs/plateaus in the IS spectra. However, in some cases, even inductive loops can be found in the impedance plots whose corresponding capacitances result in negative values, as reported initially by Sánchez et al.$^{[17]}$

Special attention to these patterns was paid by Guerrero et al.$^{[99]}$ who studied the IS spectra from diverse configurations. For example, Figure 20a illustrates the loops in the complex plane plots for different ESL thicknesses, showing a critical dependency. Particularly for the loop in the middle (15 nm ESL), a portion of the spectrum lies below the level of zero imaginary impedance ($Z'' > 0$) which implies a negative capacitance, like in Figure 20b.

A proper model for the IS response is provided by the equivalent circuit of Figure 20c, which successfully reproduces the experimental patterns as indicated by the solid lines in Figure 20a,b. In addition to the series resistance $R_{\text{series}}$, the low-frequency circuit ($C_s, R_s$) is set in series with the high-frequency resistance $R_{\text{bulk}}$ and all of these are shunted by the high-frequency capacitance $C_{\text{bulk}}$. Notably, in this configuration, $R_{\text{bulk}}$ accounts for bulk resistive contributions, and possibly also contact related impedance, in regions different from that of the voltage drop associated with $R_s$; e.g., if $R_s$ corresponds to a $L_D$ region toward the ESL contact, $R_{\text{bulk}}$ would include remaining resistive effects within the device. By only using these five elements ($R_{\text{series}}, C_{\text{bulk}}, R_{\text{bulk}}, C_s, R_s$), most of the IS spectra can be effectively modeled toward the high- and low-frequency limits in PSCs$^{[114]}$. This configuration (without the elements in red of Figure 20) is also known as Matyoshka equivalent circuit.

Nevertheless, sometimes there is a need for the inclusion of a third pair $C_L$ and $R_L$ in series with the low-frequency components ($C_s, R_s$) that often modifies the transition between the two arcs/plateaus. For instance, in the complex plane plot, the characteristic intermediate frequency $f_3 = (2\pi C_1 \cdot R_3)^{-1}$ will determine if a distortion is apparent on the high-frequency arc or toward low frequencies. For the capacitance spectra of Figure 20b, $f_3$ is in the order of hundreds of hertz which modifies the transition between $C_{\text{bulk}}$ and $C_s$ that seems to be ESL-thickness independent. In addition, the appearance of loops can be understood as the effect of an inductive element $L$ shunting
C1 and R1. These three elements are highlighted (red) in the equivalent circuit of Figure 20c, although they are not always present or not measurable in practice. The physical meaning of C1, R1, and L, whose effects are not always measurable in practice. Adapted with permission. Copyright 2016, American Chemical Society. d) Alternative equivalent circuit as proposed by Bisquert and co-workers. 

Remarkably, in a subsequent work, a family of theoretical IS spectrum patterns with the inclusion of inductive loops was provided based on a previously developed surface polarization model (see Section 6.4). In that study, an approach different from that of the equivalent circuit of Figure 20c was proposed, with the advantageous direct identification of recombination resistance \( R_{\text{rec}} \) and surface charging capacitance \( C_1 \). This equivalent circuit is observable in Figure 20d, where \( C_3 \) is the dielectric capacitance and \( R_L \) is the series resistance with \( L \). In addition, a characteristic relaxation kinetic constant was straightforwardly associated with the inductive element \( L \). Also, Anta and co-workers summarized on further possible alternatives of equivalent circuits. Furthermore, they provided a handy methodology for avoiding mistaken processing of IS measurements.

6. Current–Voltage Curve Hysteresis

The phenomenon of hysteresis in PSCs has been plaguing the scientific community for several years now. It has been known that PSCs are highly sensitive to several experimental parameters such as prebiasing voltage and time, scan rate, and light intensity. This promotes large anomalies in the current–voltage characteristics based on specific measurement protocols as dynamic hysteresis (hereafter, alternatively referred to as hysteresis). For convenience, we also define the scan from the starting forward (F) voltage to the final reverse (R) voltage as the FR scan, and vice versa as the RF scan. While a number of different types of dynamic hysteresis have been reported in literature (even in cases where not noticed or virtually neglected) and therefore, an adequate resolution of the problem of dynamic hysteresis remains a very important and relevant question that needs to be solved.

We formally define the distortions in current–voltage characteristics based on specific measurement protocols as dynamic hysteresis (hereafter, alternatively referred to as hysteresis). For convenience, we also define the scan from the starting forward (F) voltage to the final reverse (R) voltage as the FR scan, and vice versa as the RF scan. While a number of different types of dynamic hysteresis have been reported in literature, in the work by Ravishankar et al., a summary of the general observed features was shown as in Figure 21 whose description is listed as follows:

(a) Capacitive Hysteresis: This typically shows a symmetric current above and below the apparent steady-state PC value depending on the direction of the voltage scan in a manner identical to a capacitive discharge. This capacitive current increases linearly with the scan rate (inset of Figure 17) and has been observed in dark measurements as well (Figure 22a).

(b) “Bump” Close to \( V_{oc} \): When the scan goes from \( F \) to \( R \), there
occurs a maximum in the current close to $V_{oc}$ which is actually larger than the SC PC. This behavior has a strong dependence on the applied bias before the scan.$^{[15,120,121]}$

(c) **Apparent PC Enhancement in FR Direction:** This behavior is usually observed at large scan rates, where the PC value is enhanced compared to the steady-state case while the $V_{oc}$ and forward bias resistance are unaltered.$^{[5,15,121-123]}$

(d) **Strong Decay of PC in RF Direction:** This phenomenon is highly dependent on the scan routine and is also accentuated at large reverse pre-bias values.$^{[5,19,124]}$

(e) **Apparent $V_{oc}$ Shift for RF Scan:** This behavior is the most commonly observed for PSCs where the RF scan delivers a reduced $V_{oc}$ compared to the FR scan.$^{[119,124-126]}$ $J_{sc}$ and low forward bias resistance are not modified. Subsequently, a mismatch between the initial and the final current after a loop may occur.$^{[107]}$ The combination of Figure 21d and Figure 21e patterns is generally referred to as “normal hysteresis” (NHys).

(f) **Inverted Hysteresis (IHys):** Here the RF curve exceeds the FR within some region between SC and OC$^{[125,126]}$ unlike all previous patterns where the absolute current is always lower in RF direction than in FR. For less-efficient cells, the crossing is accentuated and can occur at low forward or even reverse bias.$^{[127]}$ This phenomenon is sensitive to initial bias before the scan$^{[126]}$ and will be more widely discussed in Section 6.5.

It must be noted that the majority of the diverse hysteretic trends shown in Figure 21 involve strong variations in the PC, which is symptomatic of low-efficiency PSCs. For high quality, state-of-the-art PSCs, the PC values are very stable and the dominant factor governing the type of hysteresis is variations in $V_{oc}$, akin to Figure 21f. The rapid improvement in the quality of the perovskite layer in laboratories all over the world will eliminate any transport limitations in the perovskite, leading to hysteresis that is dependent only on contact properties and/or specific recombination mechanisms at a given state of the solar cell. This distinction will have a significant impact on the modeling of high-efficiency PSCs, which is tackled in subsequent sections.

### 6.1. Dark $J$–$V$ Curve Hysteresis

O’Regan et al.$^{[86]}$ showed early on that hysteresis is not necessarily a light-driven process from their studies of dark current evolution under bias. Dark hysteresis in PSCs has been broadly reported in the literature.$^{[13,25,43,107,126,128]}$ In general, signifying that, similar to Figure 21, dark patterns can be obtained, and

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Figure 21. Summary of dynamic hysteresis trends in PSCs. The arrows show the direction of the sweep. a,c) Dashed lines indicate the steady-state curve, and b,d) $J_{sc}$ and zero bias, respectively. Adapted with permission.$^{[2]}$ Copyright 2017, American Chemical Society.
only that under illumination, the effect is enhanced by the augmentation of generated electronic charge density.

Particularly, several works by Almora and co-workers\textsuperscript{[13,43,107,128]} have illustrated dark hysteresis in the useful representation of logarithm-scaled currents, as in Figure 22. In these works, constant capacitance-related current $J_{\text{cap}}$ at different scan rates, like Equation (20), was added to typical diode curves resulting in apparent $J_{\text{sc}}$ and $V_{\text{oc}}$ values for faster bias sweeps. Note that the log vertical scale increases for either positive or negative currents to show clearly the opening of capacitive properties of the device. Instead of the scan rate, a better metric would be using a delay time between consecutive voltage steps, which shows the timescale of recovery of the current to a new steady state upon a voltage step.

The representation of Figure 22a can serve as a comparison tool among samples with different hysteresis degrees. This is due to the advantage of measuring in a less stressful configuration (dark), so effects like degradation are fewer. Furthermore, it could be thought that the commonly used empirical hysteresis index\textsuperscript{[17,128]} does not have validity in dark. This quite intuitive parameter is defined as

$$HI = 1 - \frac{J_{\text{RF}}(V_{\text{hyst}})}{J_{\text{FR}}(V_{\text{hyst}})}$$

where $J_{\text{RF}}$ and $J_{\text{FR}}$ are the currents at RF and FR scan directions, respectively, and $V_{\text{hyst}}$ is a convenient bias (e.g., $V_{\text{hyst}} = V_{\text{oc}}/2$\textsuperscript{[17]}, $V_{\text{hyst}} = 4V_{\text{oc}}/5$\textsuperscript{[113]}) resulting in $HI \rightarrow 1$ when more hysteresis and $HI \rightarrow 0$ when less. However, it is precisely within the bias range between 0.5 and 0.6 V (approximately $V_{\text{oc}}/2$ at 1 sun) where the dark hysteretic currents are more prominent, as evident from Figures 17, 22a, and clearly in Figure 22b. Actually, $HI$ can straightforwardly account for the presence of NHys ($HI < 1$) or even IHys ($HI < 0$) at a given voltage. The latter graphic advantage can be appreciated in a recent work\textsuperscript{[129]} on tunable hysteretic features (see Section 6.5) where an analog parameterization to Equation (15) was used.

Interestingly, as presented in Figure 21b, the origins of this characteristic current maximum above the corresponding $J_{\text{sc}}$ or bump, has been argued to be due to either capacitive currents or to changed quasi-steady-state PC generation.\textsuperscript{[5]} The first explanation is related to the discussion on $C_{\text{c}}$ from Section 5 and its effect on the $J$–$V$ curve. About this, Figure 23 in Section 6.2 illustrates that these capacitive currents can be as high as 5 mA cm$^{-2}$, thus the needed asymmetry for the bump of Figure 21b pattern should be an effect of a given preconditioning. On the other hand, from the second possibility, it would be expected that the current maximum (bump) will never exceed the actual or steady state $J_{\text{sc}}$ since only modifications in the recombination and/or charge extraction are considered. In any case, a combination or overlapping of both effects could be happening, but it should be noticed that $J$–$V$ curves in Figure 22b expose the same bump pattern in dark (where $J_{\text{sc}} = 0$). Despite capacitive currents in Figure 22b being within the order of µA cm$^{-2}$, the asymmetric form of the capacitive dark bump favors the explanatory hypothesis of the charge-accumulation mechanisms upon prior biasing. Nevertheless, extra confirmation is still lacking since no bump has been reported for devices with $J_{\text{sc}}$ close to the theoretical PC limit (around 22 mA cm$^{-2}$ for a 200 nm thick MAPbI$_3$ layer).\textsuperscript{[33]}

### 6.2. Capacitive Hysteresis and Step Voltage Scans under Illumination

The analysis of $J$–$V$ curves, while useful, does not easily provide in-depth information regarding transport, recombination, and capacitive properties of the device. Instead of the scan rate, a better metric would be using a delay time between consecutive voltage steps, which shows the timescale of recovery of the current to a new steady state upon a voltage step.

The use of large-voltage steps compared to the values used in standard $J$–$V$ measurements allows the visualization of the timescale of the slow transients quite clearly. We refer to such measurements as step voltage scans or step scans. The step scans are generally reported with PC as a function of time or by plotting the PC at the end of each delay time sequence versus applied voltage.

Figure 8a shows the general trends observed for step scans on PSCs.\textsuperscript{[15,93,113,130]} The PC transients are seen to change
direction depending upon the sign of the applied voltage step, where in the case of the FR scan, upon stepping the voltage to a lower forward bias value, a sharp increase in the PC occurs followed by a slow decay to the steady-state value. This trend is reversed in the RF scan, where there is a sharp transient PC in the direction of recombination followed by a slow increase in current until it reaches steady state. For the FR scan, the magnitude of the non-steady-state PCs shows a strong dependence on the applied bias with a maximum close to $V_{oc}$ followed by a drop-off in either direction. The decay lifetimes of these nonsteady-state PCs were observed to be in the range of a few hundred milliseconds to a few seconds.[15,93,120]

The trends of the PC plotted versus voltage for step scans are shown in Figure 23b,c. For the FR scan, the SC PC value increases for shorter delay times, similar to the case of Figure 21c. In certain cases, as in Figure 23b, a “bump” is observed close to $V_{oc}$ similar to Figure 21b. The shape of the FR scan can also take the patterns of Figure 21e, as shown in Figure 23c. In general, the $V_{oc}$ for FR scans at different delay times is the same or slightly increases for shorter delay times. For the RF scans, the $V_{oc}$ consistently reduces for shorter delay times.

However, there exists a variability in the trends of the SC current values for the RF scan, wherein it increases for shorter delay times,[15] as seen from Figure 23b,c, while others[113,120] have observed that the SC current decreases for shorter delay times. While a consistent interpretation unifying the observed trends has not been achieved, several broad mechanisms have been correlated with the trends of the step voltage scans. The capacitive discharge upon voltage stepping has been attributed to electronic and/or ionic accumulation at the contacts,[93] or ferroelectric depolarization,[15] correlated with the large low-frequency capacitance observed from IS.[93] The slow component following the capacitive discharge is interpreted as arising from the slow migration of ions through the device,[15,93] which can modify the efficacy of extraction of photogenerated carriers or from the reorientation of ferroelectric domains in the device.[120]

6.3. Effect of Preconditioning on J–V Curves

From Section 4, it has been clear that the transient evolution of PSCs is critically dependent on the history of the sample. For instance, Figure 14 showed effects of different prior biasing on current while Figure 13 summarized on studies on voltage decays after light or dark conditions. Evidently, these effects are also appreciable when performing J–V curves.

Voltage preconditioning has a significant impact on the FF and PCE of the PSCs. Figure 24a shows the effect of large forward bias preconditioning before making the J–V measurement. Large forward preconditioning bias improves the $V_{oc}$ and the FF.[5,15,123,131] The “bump” in the PC as shown in Figure 21b is also observed during FR scans with forward bias preconditioning.

Figure 24b shows the effect of reverse bias preconditioning. In this case, the FR scan generally shows higher $J_{sc}$ and FF compared to the RF scan. For large reverse biases, this loss in $J_{sc}$ and FF for the RF scan is pronounced, similar to Figure 21d.[123,124] In some cases, the $V_{oc}$ is severely deteriorated depending on the value of the preconditioning bias.[19] In addition, extra effects such as IHys can be obtained when prior bias is applied, as subsequently discussed in Section 6.5.
The effect of illumination time and intensity on the performance of PSCs is shown in Figure 24c and Figure 24d, respectively. Prolonged light soaking gradually improves the device performance metrics of efficiency, FF and $V_{oc}$.[15,132,133] The SC current has not been seen to vary significantly. The effect of changing light intensity does not affect the shape of the hysteresis. Note the “bump” scales with the light intensity as shown in the normalized curves of Figure 24d.[5]

In addition to hysteresis in J–V curves, the effects of light soaking manifest themselves in several other experiments as well and provide strong insights into the operation of the PSCs. Hu et al.[92] observed that the magnitude of the $V_{oc}$ for a given light intensity was reduced for a light-soaked MAPbI$_3$–xCl$_x$ solar cell compared to when it was in dark storage. This reduction was minimized for cells with an Al$_2$O$_3$ scaffold. Zhang et al.[134] identified that the evolution toward a steady-state $V_{oc}$ was much faster in the case of light-soaked cells compared to cells that were not kept in dark storage. These light-soaking effects have been found to be reversible, with the cells regaining their original presoaking behavior upon extended dark storage. Similar trends have been observed from EQE measurements,[135] where 30 min of light soaking yielded a 50% drop from the EQE of an unsoaked device, followed by a recovery to 90% of the initial value upon extended dark storage. Furthermore, Shao et al.[136] (subsequently by Zhang et al.[137]) identified that replacing PCBM with PTEG-1 as the electron selective contact in inverted MAPbI$_3$–xCl$_x$ cells eliminates the light-soaking effect, indicating the importance of the external contacts for this effect. These observations in addition to the remnant $V_{oc}$ observed over long timescales (see Figure 13) and light intensity-dependent low-frequency capacitance (see Figure 19) have been interpreted as the accumulation of electronic carriers at the perovskite/ESL contact, where surface recombination could explain the observed trends, as proposed by Bisquert and co-workers. This model is further discussed in Section 6.4.

Hysteresis in J–V curves is also strongly dependent on temperature. For instance, it has been observed to increase for temperatures below room temperature,[14,120,137] as shown in Figure 25. Bryant et al.[138] also observed a similar trend for fullerene top cathode MAPbI$_3$ cells which are virtually hysteresis-free at room temperature. They observed an increase in the timescale of the slow relaxation process as the temperature decreased, with hysteresis disappearing at 77 K. From chronoamperometry measurements, they calculated an Arrhenius behavior for the PC decay half-times, yielding an activation energy of 0.12 eV for this process. Both Bryant et al.[138] and Zou and Holmes[139] identified that the performance of the cell was maximized under prebiasing at a large forward bias at low temperatures, where the low temperature “freezes” the favorable condition of the prebiasing. In general, the hysteresis is maximized when the timescale of the slow relaxation process is similar to the timescale of the J–V measurement. By correlating the slow, temperature-activated process to the low-frequency time constant observed in IS measurements...
at different temperatures, Contreras et al.\textsuperscript{[14]} were also able to estimate activation energies of the slow process based on an Arrhenius-type equation, which they attributed to the ionic diffusion process.

Another unique and extreme case of the hysteretic phenomena described in the previous section is that of the switchable photovoltaic effect. This effect was observed by Xiao et al.\textsuperscript{[16]} for inverted configuration perovskite samples consisting of ITO/PEDOT/\text{MAPbI$_3$}/Au. They observed that depending on the poling bias, the sign of the photovoltage and PC could be switched to either positive or negative, allowing photovoltaic operation in either bias direction, which is an extreme case of the pattern of Figure 21d.

6.4. Hysteresis Interpretation: Two Main Models

Due to the complex nature and range of dynamic hysteresis trends and their sensitivity to materials and methods, a general all-encompassing model that accounts for these trends has been very difficult to achieve. Several general mechanisms have been proposed to explain the dynamic hysteresis in PSCs, such as ionic motion, ferroelectric effects,\textsuperscript{[17,124,130]} displacement currents due to depolarization of ionic accumulation\textsuperscript{[126]} and unbalanced electron and hole fluxes\textsuperscript{[140]} due to inefficient charge extraction and subsequent transport in the TiO$_2$ layer.\textsuperscript{[141–144]}

We can summarize two models in the current literature that systematically capture several dynamic hysteresis trends based on the specific experimental routines. These models are shown in Figures 2e and 26, and described in the subsequent paragraphs.

The first model,\textsuperscript{[5,9]} as has also been described in Section 3, is based on variations in the charge collection efficiency of the PSCs throughout a $J$–$V$ scan. This model considers the device as a p–i–n solar cell with a built-in electrical field through the device that is the difference in the work functions between the two contacts. This electrical field controls the transport of the photogenerated carriers to the respective selective contacts and their recombination, depending upon the applied voltage, which modifies the electrical field. The mobile cations and anions in the perovskite cell drift along the built-in potential, forming space charge layers at the contacts that effectively shield or screen the net electric field, creating a bulk field-free region with sharp potential drops at the contacts in the dark at equilibrium, as shown in Figure 2e. From this situation, depending on the scanning direction, charge collection is either favored (FR) or deterred (RF). Under applied forward bias, the bands tilt, creating an electrical field that is unfavorable for extracting photogenerated electrons and holes at ESL and HSL, respectively, causing recombination of electron–hole pairs. Upon moving from equilibrium, the amount of screening or compensation of the bulk electrical field under applied bias is modulated by the slow drift of the ions toward the respective contacts due to the applied voltage.

Simulations based on this model capture the capacitive behavior with respect to scan rate as shown in Figure 21a, with the bulk electrical field compensated through the scan at very low scan rates, leading to low hysteresis, intermediate scan rates showing large hysteresis, and high scan rates not giving enough time for redistribution of the ions and hence...
low hysteresis.\textsuperscript{[19]} This model also obtains the “bump” in the PC of Figure 21b and the strong decay of PC (Figure 21d) and $V_{oc}$ in the RF direction.

Further support for the charge collection effect in the measurements of dynamic hysteresis can be introduced by combining step voltage measurements with transient PC decay measurements. This was carried out by Calado et al.\textsuperscript{[47]} and Belisle et al.\textsuperscript{[9]} in the form of step-dwell-probe (SDP) and step-dwell-step-probe (SDSP) measurements. The SDP measurement (Figure 27a) involves a voltage step ($V_d$) from equilibrium, followed by a waiting period (dwell time), upon which a square wave pulse is applied and the PC decay is measured. The SDSP measurement (Figure 27b) involves another voltage step termed the probe voltage ($V_{pr}$). The authors observed currents opposite to extracted PC for forward voltages (0.3 V) much smaller than the built-in potential of the perovskite, see Figure 27c, indicating the compensation of the bulk field. The role of the slow migration of ions in the shielding is reinforced by the shift in the onset of the extracted PC density for larger dwell times in an SDSP experiment, Figure 27d.

The second model, which, in our opinion, is a more relevant model that captures the hysteretic trends of the PSCs, is based on interfacial polarization and recombination, starting from a surface polarization model.\textsuperscript{[9]} The central support for this approach comes from the well-known fact that the dynamic hysteresis is closely related to the nature of the contacts used.\textsuperscript{[145,146]} This information was apparent from the fact that inverted perovskite structures showed much lower hysteresis compared to regular planar or mesoporous scaffold configurations. In addition, depending on the nature of the contact, the hysteresis trends and their characteristic times are also observed to be altered,\textsuperscript{[15]} indicating a strong dependence of hysteresis on the interfacial properties of the device. A deeper study into the contact properties of the PSCs from IS measurements revealed a strong connection between the low-frequency capacitance under illumination and the degree of hysteresis observed, where the low-frequency capacitance in the dark and under illumination was reduced substantially upon replacing c-TiO$_2$ with a PCBM layer.\textsuperscript{[56]} The capacitive nature of the TiO$_2$/perovskite interface has been attributed to the reversible accumulation of I$^-$ ions at this interface due to weak Ti=I=Pb bonds, where measurements on symmetric TiO$_2$/MAPbI$_3$/TiO$_2$ and Spiro-OMeTAD/MAPbI$_3$/Spiro-OMeTAD samples clearly showed reversible capacitive currents only for the symmetric TiO$_2$/MAPbI$_3$/TiO$_2$ device.\textsuperscript{[43]} Therefore, the chemical and capacitive properties of the interfaces in a PSCs, specifically the TiO$_2$/perovskite interface, have been deemed critical for the hysteresis in the device.

The surface polarization model considers a p-type perovskite with respective selective contacts as shown in Figure 26. Note that the transport of carriers in the perovskite is predominantly diffusive and are considered to be excellent, and hence, the Fermi levels are flat throughout the perovskite.

Under applied forward bias, an accumulation layer of cations and holes is created at the TiO$_2$/perovskite interface, creating an upward band bending with an excess surface potential. Upon voltage cycling, this surface potential relaxes, causing a capacitive discharge of the accumulated holes in the form of an extracted PC. However, this capacitive discharge is delayed by the slow transport of the accumulated ions away from the interface. This model reproduces several of the observed features of dynamic hysteresis in the FR direction such as the “bump”
of Figure 21b, the PC trends of Figure 21c and the apparent shunt resistance effect observed in some cases. The validity of the formation of an accumulation layer at the TiO₂/perovskite interface is based on detailed drift–diffusion simulations[8] and strong experimental evidence, including a large low-frequency capacitance of the order of mF cm⁻² that scales with light intensity as detailed earlier, and an unbalanced distribution of charge in the perovskite with an excess density of positive charge at the TiO₂/perovskite interface under illumination, from kelvin probe force microscopy (KPFM).[147] The slow discharge of the accumulated holes is also consistent with the observation of a remnant Vₘₐₓ over large timescales as commented earlier. This model successfully reproduces several of the anomalous spectra observed from IS, including the observation of a negative capacitance (Figure 20) at intermediate to low frequencies.[117]

The origin of the collection model is related to the initial stages of development of the PSCs, where the hysteretic trends were dominated by variations in the PC density, as shown in Figure 21. This allowed simply modeling the PSCs with transport limitations similar to an organic solar cell, with an electric field through the bulk. However, state-of-the-art PSCs with high efficiencies show excellent charge transport features, as will be detailed in Section 6.6. Therefore, the influence of an electrical field that facilitates transport should be minor, unless working in large reverse bias conditions. The strong correlation between the contact capacitance and the hysteretic trends indicates that variations in Vₘₐₓ governed by specific recombination mechanisms will be the distinguishing factor for hysteresis in high quality, state-of-the-art PSCs.

Furthermore, the charge collection model does not account for some global observations of the properties of the PSCs.

The first is the strong dependence on contacts mentioned before; the effect of the contacts in this model actuates only through the work function and built-in voltage, and a correlation between these and hysteresis is not demonstrated. The dynamic hysteresis correlates with the surface capacitance rather than the energetic properties of the contact. Second, the approximation of sheets of ionic charge at the contacts[3,9,66] in narrow Debye layers close to the interfaces that compensate the electrical field is erroneous as this distribution does not produce a flat electrochemical potential of the ions. Allowing for this consideration leads to a partially compensated electrical field, rather than a complete compensation[61] as seen from Figure 5 and discussed extensively in Section 3. Moreover, the distinct recombination features observed from OC voltage decays, where a remnant Vₘₐₓ was observed over a timescale of seconds,[8,89,91] unison with the observation of a large low-frequency capacitance from IS measurements that scales with light intensity[55] (Figure 19), much higher than the limit of an ionic Helmholtz double layer capacitance,[7] are unaccounted for in this model.

Therefore, we can conclude that under extreme forcing by external bias, major reorganization of ions can produce a severe electrical field which may cause effects of variation of PC and even IHys, as discussed in the following section. This is especially the case for low-quality PSCs, where charge collection properties are poor and can be modified significantly by the ions.

However, under normal operation of high-performance PSCs, the charge collection properties are excellent; hence, the observed dynamic hysteresis is dominated by the effect of the contacts by a combination of two factors: (a) the charge accumulation at contacts governed by surface capacitance that depends on state of illumination and bias and (b) the slow reorganization response governed by the interplay of charge accumulation and recombination.

6.5. Inverted Hysteresis and Noncapacitive Currents

So far, as noted earlier, most of the J–V curve hysteric patterns evidence a clear advantage in reporting the FR scan direction in which, generally, larger Jₘₐₓ and/or FF and hence PCE are attained, in comparison with the RF bias sweep. Without considering further specific features, this has been known as “normal” hysteresis.

However, just the opposite behavior was reported by Tress et al.[125] from J–V curves of mixed perovskite-based cells after 1.2 V forward biasing for 10 s. As illustrated in Figure 28, an S-shaped significant reduction of the current around the operation voltage region diminishes FF, and hence PCE, during the FR scan with respect to RF. Note that here, H₁ < 0 around the operation voltage (Equation (24)), differently to NHys where 0 < H₁ < 1. This behavior was subsequently termed as “inverted” hysteresis, and their effects were proved to persist at different scan rates, scan loops, prebiasing and illumination intensities. Regarding these latter experiments, Figure 28 shows the light-independent character of the current kink during a FR sweep, which was interpreted as discarding the relation between IHys and charge extraction barriers due to photogenerated charges. In addition, they also found IHys in MAPbI₃ devices with a mesoporous TiO₂ scaffold covered with a thin insulating Al₂O₃ shell. They attributed this observation to the existence of a barrier for electron extraction at the TiO₂/perovskite interface in their cells, where charge extraction is favored at 0 V (SC) instead of at large forward bias due to negative accumulated ionic charge at the TiO₂/perovskite interface at SC, which creates a dipole that allows for band alignment.

Figure 28. IHys in J–V curves of mixed perovskite-based devices at different illumination intensities. Reproduced with permission.[125] Copyright 2016, Wiley-VCH.
Interestingly, subsequent reports on IHys\[^{107,126,148,149}\] focused on less exotic perovskites that did not include the S-shape of the measurements by Tress and co-workers.\[^{125}\] Shen et al.\[^{148}\] defined IHys predominantly in the form of variations in the $J_{sc}$ of their cells upon strong F poling, where the $J_{sc}$ of the FR scan changed from being higher to lower than that of the RF scan when moving from slow to fast scan rates. Moreover, the effect was apparently dependent on the fabrication procedure, which was understood as an effect of different MAPbI$_3$ electron affinities. In this sense, they suggested that in some devices, ion accumulation occurs at large forward biases, producing a temporary and localized increase in recombination at the MAPbI$_3$/TiO$_2$ interface, leading to IHys at fast scan rates. Such a hypothesis was also supported by numerical semiconductor models including ion accumulation where two possible origins for these localized recombination losses were proposed: one based on band bending and the other on an accumulation of ionic charge in the perovskite bulk.

Recently, an analysis of hole-conductor-free printable cells with a triple-layer architecture of TiO$_2$/ZrO$_2$/carbon\[^{129}\] has shown new features of the dynamic hysteresis in robust and stable PSCs, as presented in Figure 29. The changes of hysteresis patterns are caused exclusively by a tuning of the TiO$_2$ compact layer, which speaks of the dominant role of charge accumulation at this interface. Furthermore, the appearance of NHys, hysteresis-free and IHys, affects only the voltage, as mentioned before in connection with Figure 25, while charge collection at SC is virtually the same in all cases. These physical features have been explained by an extension of the original surface polarization model\[^{[2]}\] that considers in addition the rate of surface recombination that is modified by the quality of the TiO$_2$ blocking layer.

An approach more focused on the influence of prebiasing, also known as prepoling, was made by Nemnes et al.\[^{126}\] who measured TiO$_2$/MAPbI$_3$-$\chi$Cl$_x$/spiro-OMeTAD based devices in the continuous sequence FR–RF–FR after bias pretreatment. They verified that NHys typically appears at prepoling biases larger than $V_{oc}$, while pronounced IHys occurs for adequate negative bias prepoling. These observations are in close relation to the $J_{sc}$ response of Figure 14. Interestingly, they also showed dark $J$–$V$ curves with the occurrence of these trends.

Contrastingly, dark IHys as defined above were found by Almora and co-workers\[^{107,128}\] at slow scan rates without prebiasing in several device configurations (see Figure 22a). The appearance of this feature when approximating quasi-steady-state measurements suggested additional noncapacitive charge extraction mechanisms, possibly due to reversible reactivity. As shown in Figure 1f, the drift of ions due to polarization catalyzes reactivity processes, which act similarly to prebiasing during slow voltage sweeps. Importantly, it was remarkably noticeable in devices with organic selective contacts. The latter was also supported by Erdenebileg et al.\[^{149}\] who found very small IHys under illumination at slow scan rates in other cells with organic materials comprising the perovskite. They however attributed this feature to a build-up of a space charge region at the ESL–perovskite interface.

### 6.6. Other Factors Affecting Hysteresis and Its Suppression

Another prominent interpretation of the dynamic hysteresis involves trapping and detrapping effects. As in other solar cells, the presence of traps can affect the PSC performance, modifying the magnitude of the current density and the shape of $J$–$V$ curves.\[^{[150–152]}\] Minemoto and Murata\[^{[153]}\] identified the contribution of the defect density at the front interface to the hysteresis as much stronger than that at the back interface for large absorption coefficient materials (such as PSCs) without considering ion migration, though they did not implement dynamic scans. Other authors include both charge trapping and ion migration in numerical modeling,\[^{[6,62,63]}\] where the distribution of ions can significantly alter the collection properties of the device. In fact, van Reenen et al.\[^{[62]}\] suggested that the relatively high rate of recombination at the interface is sustained by large electron and hole densities due to (i) electronic compensation of ionic space charge and (ii) electronic traps. Neukom et al.\[^{[61]}\] reproduced NHys trends by considering variations in surface recombination and diffusion lengths of the carriers in addition to ionic migration. Similar conclusions have been reported by Sherkar et al.\[^{[154,155]}\] in their study of recombination employing drift–diffusion simulations, who suggested that there is a direct correlation between the density of trap states, the density of mobile ions, and the degree of hysteresis observed in the current–voltage curves.

While the effects of trapping–detrapping cannot be ruled out, the magnitude of the low-frequency capacitance observed
from IS measurements, where the response from traps is generally observed, is extremely large and is known to scale exponentially with light intensity and large forward bias, as seen from Figures 15 and 19, respectively, and therefore cannot be ascribed to a density of traps. Furthermore, the slow transients in the timescale of seconds indicate detrapping rates at the same timescale, which is unrealistic, casting further doubt on the validity of trapping–detrapping effects having a significant impact on the dynamic hysteresis trends.

Another important aspect contributing to the dynamic hysteresis is the modification of injection/extraction barriers at the perovskite interface due to reorganization of mobile ions, as described earlier. These modifications can cause large changes in the extraction capability of the cell (see Figure 14), which can lead to dynamic hysteresis. It is well known that the use of organic contacts such as PCBM suppresses the dynamic hysteresis. Several authors also correlate the reduced hysteresis with the improved charge transport and extraction properties of fullerene-incorporated perovskite devices\[58,59\] as compared to TiO$_2$-based perovskite cells. As will be seen subsequently, these injection/extraction barriers are highly dependent on the nature of the contacts used and strongly affect the hysteretic trends.

**Figure 30.** $J$–$V$ curves of high-efficiency bulk heterojunction perovskite-PCBM device, which is hysteresis-free under different scan speeds and direction. The fullerene is incorporated either as a planar layer or is mixed into the perovskite layer in a bulk heterojunction form.\[156,157\] Xu et al.\[157\] tested several ratios of perovskite:PCBM hybrid devices and observed a monotonic increase in the transient PL quenching efficiency with increasing perovskite:PCBM ratio, as shown in Figure 30c, which was attributed to the increased carrier extraction efficiency for the hybrid devices. However, for extremely high concentrations of PCBM, the quenching reduced greatly (Figure 30c, black line). In addition, thermal admittance spectroscopy measurements on perovskite and perovskite:PCBM samples showed a large reduction in the shallow trap density for perovskite:PCBM samples as shown in Figure 30d, which was further corroborated by a blueshift in PL emission for perovskite:PCBM samples.\[10\]

Several other studies have also shown the improved carrier transport and extraction properties for perovskite cells with PCBM layers as ESL and perovskite:PCBM hybrid devices from intensity-modulated photovoltage spectroscopy measurements,\[144\] transient PC measurements,\[10,156\] and PL decay measurements.\[59,144,158\] The faster decays of PC and quenching of PL in fullerene-incorporated devices in these cases have clearly shown that charge transfer/extraction at the PCBM/perovskite interface is significantly faster than that of the TiO$_2$/perovskite interface. The use of C$_{60}$-PCBM as the ESL in planar cells has also been observed to increase the efficiency of charge extraction from transient absorption measurements.\[159\] These results indicate that charge extraction at interfaces can be a significant factor in the hysteretic properties of a PSCs, and subsequent models must take this into account to develop a holistic model.
While the mechanisms of dynamic hysteresis are being strongly debated, it is well known that the origin of the hysteresis is strongly linked to the migration of ions through the perovskite lattice. Therefore, strategies to suppress hysteresis have been mainly focused on blocking ion migration channels, namely bulk point defects and grain boundaries,[160] in addition to trap passivation. The most successful and prominent ones are the incorporation of fullerene in contacts/blend form, and improvement of crystalline quality of the perovskite absorber. We discuss these two strategies in detail in the subsequent paragraphs, while touching on several related hysteresis suppression techniques.

The beneficial effect with respect to minimizing hysteresis by the incorporation of fullerenes such as PCBM in the PSCs has generally been attributed to passivation of traps in the bulk or at the surfaces.[10,156,157] Furthermore, it has been proposed that PCBM can tie up iodide-rich surface sites or simply iodide anions, preventing the migration of anions through the perovskite,[157] or more generally, filling defects at grain boundaries that allow the migration of ions through the device.[161]

The role of grain boundaries in facilitating the migration of ionic species within the perovskite has in fact been confirmed from sophisticated conductive-atomic force microscopy measurements that allow evaluation of hysteretic currents at regions close to and far from grain boundaries.[161] In order to reduce the bulk defect density and to minimize the effect of grain boundaries on the hysteretic properties of the device, several attempts have also been made to improve the quality of the perovskite absorber by increasing the grain size of the crystals. To this end, high-performance cells with micrometer-sized grains have been reported.[162–164] Xiao et al.[163] observed that inverted MAPbI₃ cells obtained from a solvent-annealing (SA) procedure yielded large grain sizes of the order of micrometers. These cells showed higher performance and negligible hysteresis at room temperature compared to samples obtained from thermal annealing (TA), with average grain sizes of a few hundred nanometers. The authors also carried out thermal admittance spectroscopy measurements which showed a much lowered defect density for SA samples compared to TA samples, resulting in rapid charge extraction and larger lifetimes observed from PC and photovoltage decay measurements respectively.

The effect of annealing also appears to lower the density of deep trap states as shown in Figure 30d. Shao et al.[161] also observed similar results, with SA samples showing reduced dark hysteresis properties. A systematic study by Kim and Park[113] with different crystal grain sizes for planar MAPbI₃ cells also identified that the hysteresis reduced strongly with increasing grain size of the absorber.

In an extreme scenario, Nie et al.[166] showed the absence of hysteresis (Figure 31a,b) in high-efficiency inverted PSCs with the grain size of the absorber in the range of millimeters. From Hall measurements, they observed that the mobility showed a fourfold improvement when the grain size was increased from 100 to 170 µm, see Figure 31c. They also identified that the dominant recombination pathway was band-to-band bimolecular recombination, as can be seen from the slope of the evolution of Voc versus light intensity in Figure 31d and also from time-resolved PL measurements on small and large grains, typical of high-quality devices. Therefore, the reduced hysteresis has been generally linked with the improved carrier transport properties for high crystallinity devices.

However, a recent study by Peng et al.[167] has strongly questioned the influence of grain boundaries in the observed hysteresis. The authors prepared high efficiency, monocrystalline MAPbBr₃ devices with and without ESL and HSL. They observed strong hysteresis in cells without an ESL and HSL, which was significantly reduced upon addition of TiO₂ as the ESL. Since the monocrystalline absorber has an ultralow bulk trap density and is devoid of grain boundaries by definition, it is apparent that there exist further factors that contribute to the hysteretic behavior such as bulk ion migration, which could consequently create a need to alter the chemical structure of the perovskite itself. Increasing valence charges of the ions and codoping cations with higher and lower valence ions have been proposed in this regard.[168]

Recent strategies to minimize dynamic hysteresis involve the modification or treatment of the TiO₂ layer, which has been deemed critical for the operation of the PSCs. A novel strategy to eliminate dynamic hysteresis involves the use of Cl-capped TiO₂ nanoparticles at the ESL. These cells showed extremely high performance and stability, coupled with the absence of dynamic hysteresis trends. The Cl-capped TiO₂ nanoparticles were shown to double the charge carrier recombination lifetime of ordinary TiO₂ based cells, thereby connecting the reduction in dynamic hysteresis to the passivation of surface traps at the TiO₂/perovskite contact.[169] Based on similar reasoning, PSCs based on Li-treated mesoscopic TiO₂ have been shown to be hysteresis-free, attributed to the improved charge extraction properties observed from photoluminescence decays upon Li treatment compared to untreated TiO₂.[170]

7. Conclusions

The emergence and consolidation of PSCs has opened a wide new field of study in photovoltaics. PSCs are distinguished by a very broad set of peculiar physical properties with respect to former kinds of solar cells. In this review, we have addressed the connection between fundamental properties and device models that allow us for the interpretation of macroscopic measurements in the time and frequency domain. It is widely recognized that the perovskite cells display a rich and very complex phenomenology. Two major factors have contributed to the improved understanding, one is the enhancement of quality of materials and devices, which now allows focusing on the characterization of specific phenomena, and the second is the already very big size of a cooperative community that has given rise to emerging regularities. However, the presence of many morphologies, mixed ionic–electronic conduction and organic components of the device, makes the problems yet very open. Despite the great deal of advances in characterization methods and understanding of basic properties, there is a long way to go yet.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest
The authors declare no conflict of interest.

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Figure 31. J–V curves for different a) scan direction and b) scan rate for inverted PSCs with millimeter-sized grain size for the absorber. c) The calculated mobility from Hall measurements and d) the trend of $V_{oc}$ versus light intensity for two grain sizes in terms of their annealing temperature (larger temperature has the larger grain size), with corresponding linear fits and their respective slope $k$. Adapted with permission.[166] Copyright 2015, American Association for the Advancement of Science.

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