Characterization of Planar Lead Halide Perovskite Solar Cells by Impedance Spectroscopy, Open-Circuit Photovoltage Decay, and Intensity-Modulated Photovoltage/Photocurrent Spectroscopy

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INTRODUCTION

The rapid development of organometal halide perovskite solar cells based on CH₃NH₃PbI₃ and its analogs continues to set new records in terms of efficiency. In principle, electron–hole recombination can occur either in the bulk of the perovskite or at the contacts, which are made using materials that are selective for extraction of electrons (e.g., TiO₂) or holes (e.g., spiro-OMeTAD). A number of methods have been used to study electron–hole recombination including transient microwave and terahertz measurements, photoluminescence, transient absorbance, EBIC, photovoltage and photocurrent transients, impedance, and open-circuit voltage decay. Many of these studies have characterized the properties of perovskite cells fabricated using mesoporous oxide substrates of either TiO₂ or Al₂O₃. However, interest is increasingly being focused on planar junction perovskite cells that appear in many instances to operate as p–i–n devices. For this reason we chose to characterize batches of planar perovskite cells using a range of complementary techniques, namely, impedance, intensity-modulated photovoltage spectroscopy (IMVS), intensity-modulated photocurrent spectroscopy (IMPS), open-circuit voltage decay, and intensity-modulated photocurrent spectroscopy (IMPS) with a relaxation time constant in the region of seconds. The high open-circuit voltages (in excess of 1 V) showed AM 1.5 efficiencies of over 15%, suggesting that the mesoporous scaffold used in early types of perovskite solar cells is not essential. We used a variety of techniques to gain a better understanding of thin film perovskite cells prepared by a solution-based method. Twelve cells were studied, which showed AM 1.5 efficiencies of ~11%. The properties of the cells were investigated using impedance spectroscopy, intensity-modulated photovoltage spectroscopy (IMVS), intensity-modulated photocurrent spectroscopy (IMPS), and open-circuit photovoltage decay (OCVD). Despite the fact that all 12 cells were prepared at the same time under nominally identical conditions, their behavior fell into two distinct groups. One half of the cells exhibited ideality factors of m ≈ 2.5, and the other half showed ideality factors of m ≈ 5. Impedance spectroscopy carried out under illumination at open circuit for a range of intensities showed that the cell capacitance was dominated by the geometric capacitance of the perovskite layer rather than the chemical or diffusion capacitance due to photogenerated carriers. The voltage dependence of the recombination resistance gave ideality factors similar to those derived from the intensity dependence of the open-circuit voltage. The IMVS time constant was determined by the product of the geometric capacitance and the recombination resistance. The two types of cells gave very different OCVD responses. The cells with m ≈ 2.5 showed a persistent photovoltage effect that was absent in the case of the cells with higher ideality factors. The IMPS responses provide evidence of minor efficiency losses by recombination under short-circuit conditions.

ABSTRACT: Thin film lead halide perovskite cells, where the perovskite layer is deposited directly onto a flat titania blocking layer, have reached AM 1.5 efficiencies of over 15%, showing that the mesoporous scaffold used in early types of perovskite solar cells is not essential. We used a variety of techniques to gain a better understanding of thin film perovskite cells prepared by a solution-based method. Twelve cells were studied, which showed AM 1.5 efficiencies of ~11%. The properties of the cells were investigated using impedance spectroscopy, intensity-modulated photovoltage spectroscopy (IMVS), intensity-modulated photocurrent spectroscopy (IMPS), and open-circuit photovoltage decay (OCVD). Despite the fact that all 12 cells were prepared at the same time under nominally identical conditions, their behavior fell into two distinct groups. One half of the cells exhibited ideality factors of m ≈ 2.5, and the other half showed ideality factors of m ≈ 5. Impedance spectroscopy carried out under illumination at open circuit for a range of intensities showed that the cell capacitance was dominated by the geometric capacitance of the perovskite layer rather than the chemical or diffusion capacitance due to photogenerated carriers. The voltage dependence of the recombination resistance gave ideality factors similar to those derived from the intensity dependence of the open-circuit voltage. The IMVS time constant was determined by the product of the geometric capacitance and the recombination resistance. The two types of cells gave very different OCVD responses. The cells with m ≈ 2.5 showed a persistent photovoltage effect that was absent in the case of the cells with higher ideality factors. The IMPS responses provide evidence of minor efficiency losses by recombination under short-circuit conditions.
photovoltage decay (OCPVD), and steady-state photovoltage measurements as a function of light intensity. The use of these six techniques on a large number of cells allowed us to assess the consistency of the conclusions.

The series of 12 planar perovskite devices could be divided clearly into two groups on the basis of the intensity dependencies of the open-circuit voltage, which corresponded to diode ideality factors that clustered either around ~2.5 or around ~5.0. The high-frequency impedance and intensity-modulated photovoltage (IMVS) responses of the cells were modeled satisfactorily using a simple lumped RC circuit. At low frequencies an additional feature was observed which Juárez-Pérez et al.13 attributed to a photoinduced giant dielectric effect. The influence of the GDE on the low-frequency impedance response has been modeled by Bisquert et al.,26 but in this paper the low-frequency feature has not been included in modeling. Substantial information about the cell was extracted using the simple lumped model at mid and high frequencies, and we are currently measuring and modeling the low-frequency feature separately. The results obtained at open circuit by impedance and IMVS are in good agreement, both indicating that for open-circuit voltages below 0.9 V, the geometric capacitance associated with charge in the contacting phases (TiO2 and spiro-OMeTAD) is larger than the chemical (or diffusion) capacitance associated with the buildup of electrons and holes in the perovskite absorber, even at the highest light intensities used here (equivalent to 0.1 Sun). The voltage dependence of the recombination resistance gave nonideality factors close to those derived from the intensity dependence of the open-circuit voltage. OCVD also reveals that some cells exhibit a persistent photovoltage that extends the decay time into the region of seconds when the voltage falls below 0.4 V.

EXPERIMENTAL SECTION

Perovskite Precursor Preparation. Methylamine iodide (MAI) was prepared by reacting methylamine, 33 wt % in ethanol (Sigma-Aldrich), with hydroiodic acid (HI), 57 wt % in water (Sigma-Aldrich), at room temperature. HI was added dropwise while stirring. Upon drying at 100 °C, a white powder was formed, which was washed with ethanol and dried overnight in a vacuum oven before use.

To form the nonstoichiometric CH3NH3PbI3−xClx precursor solution, methylammonium iodide and lead(II) chloride (98%, Sigma-Aldrich) were dissolved in anhydrous N,N-dimethylformamide (DMF) at a 3:1 molar ratio of MAI to PbCl2, with final concentrations of 0.88 M lead chloride and 2.64 M methylammonium iodide. This solution is stored under a dry nitrogen atmosphere.

Substrate Preparation. Devices were fabricated on fluorine-doped tin oxide (FTO) coated glass (Pilkington, 7 Ω  cm). To prevent shunting upon contact with measurement pins, FTO was removed from regions under the anode contact by etching with 2 M HCl and zinc powder. Substrates were then cleaned sequentially in 2% Hellmanex detergent, acetone, propan-2-ol, and oxygen plasma. A hole-blocking layer of compact TiO2 was deposited by spin coating a mildly acidic solution of titanium isopropoxide in anhydrous ethanol (350 μL in 5 mL of ethanol with 0.013 M HCl) and annealed at 500 °C for 30 min. Spin coating was carried out at 2000 rpm for 60 s.

Perovskite Solar Cell Fabrication. A total of 12 cells was fabricated in groups of 3 cells on one substrate, each with a pixel area of 0.15 cm2. To form the perovskite layer, the nonstoichiometric precursor was spin coated on the substrate in a nitrogen-filled glovebox at 2000 rpm for 45 s. After spin coating, the films were left to dry at room temperature in the glovebox for 30 min to allow slow solvent evaporation. They were then annealed on a hot plate in the glovebox at 90 °C for 180 min and subsequently at 120 °C for 15 min.

A hole-transporting layer was then deposited via spin coating a 0.79 M solution of 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spiropentfluorene (spiro-OMeTAD) in chlorobenzene, with additives of lithium bis(trifluoromethanesulfonyl)-imide (0.0184 M) and 4-tert-butylpyridine (0.0659 M). Spin coating was carried out at 2000 rpm for 45 s. Devices were then left overnight in air for the spiro-OMeTAD to dope via oxidation. Finally, gold electrodes were thermally evaporated under a vacuum of ∼10−6 Torr at a rate of ∼0.1 nm s−1 to complete the devices.

Solar Cell Characterization. The current density–voltage (J–V) curves were measured (2400 Series SourceMeter, Keithley Instruments) under simulated AM 1.5 sunlight at 100 mW cm−2 irradiance generated by an Abet Class AAB sun 2000 simulator, with the intensity calibrated with an NREL calibrated KG5-filtered Si reference cell. The mismatch factor was calculated to be 1.2% between 400 and 1100 nm. The solar cells were masked with a metal aperture to define the active area, typically 0.0625 cm2, and measured in a light-tight sample holder to minimize any edge effects.

The cells were stored in a nitrogen glovebox between measurements to minimize degradation. Open-circuit voltages were measured as a function of light intensity using a 625 nm light-emitting diode (LED) (Thorlabs MRLED). The incident photon flux was controlled using neutral density filters (Edmund Optics) and measured using a calibrated silicon photodiode (Newport 818-SL with OD3 neutral density filter). All modulated techniques were also carried out with illumination from a 625 nm LED where appropriate (Thorlabs MRLED). Impedance measurements for different illumination intensities were made at the corresponding open-circuit voltage using an Autolab PGSTAT30. Impedance measurements were also made in the dark as a function of applied voltage. Impedance data were fitted using ZView software (Scribner Associates). IMVS and IMPS measurements were made using a Solartron 1260 frequency response analyzer (FRA) combined with a Thorlabs DC2100 controller (bandwidth 100 kHz) driven by the dc and sine wave output of the FRA. The modulation depth was set to be 10% of the dc level. The illumination intensity was varied using calibrated neutral density filters. To ensure long-term stability, cells were illuminated with a single wavelength at intensities of 0.1 Sun and lower. By measuring trends with respect to illumination intensity we were able to derive significant amounts of information on cell behavior. In the environment solar cells need to operate at illumination intensities below 1 Sun; therefore, tests of cell performance at 0.1 Sun can still be considered as the working environment for a cell. To correct for attenuation and phase lag in the modulated light output at higher frequencies, a glass microscope slide was used as a beam splitter enabling provision of a reference signal for the frequency response analyzer from a fast p–i–n photodiode. For IMPS, the cell current was measured using a current amplifier (Femto DLPCA-200). A high-impedance (>1012 ohm) voltage follower was used for IMVS. The bandwidth of the system was checked using a fast p–i–n photodiode in place.
of the solar cell. OCVD measurements were made using step
function illumination of the cells (625 nm LED; on period 60 s). The voltage decay after switching the light off was measured using the high-impedance voltage follower amplifier and a
digital storage oscilloscope. Care was taken to totally exclude stray light.

THEORY

Diode Ideality Factor. The diode ideality factor, \( n \), is
normally defined in terms of the Shockley diode equation,
which describes the dependence of the diode current density, \( j \), on the applied voltage \( V \). Here, \( j_{sat} \) is the reverse saturation current

\[
j = j_{sat} \left( e^{qV / n k_B T} - 1 \right)
\]

(1)

In theory, \( n \) can take different values between 1 and 3,
depending on the recombination mechanism\(^2\) (Hall Shockley
Read, Sah Noyce Shockley, Auger, etc.), although in some cases
anomalously high experimental values of \( n \) may point to the
existence of several junctions in a device.\(^2\) Here, we are mainly
concerned with the behavior of perovskite cells under
illumination, and so we define a diode ideality factor \( m \) using the
intensity dependence of the open-circuit voltage, which
takes the form

\[
\frac{\partial V_{oc}}{\partial \ln I_0} = \frac{mk_B T}{q}
\]

(2)

The ideality factors \( n \) and \( m \) are not identical for perovskite
cells since the dark and light current voltage plots cross at
forward bias (see Supporting Information).

Impedance. A simple equivalent circuit for a planar thin
film p–i–n solar cell is shown in Figure 1. Here, the
capacitance \( C_{total} \) reflects the overall charge storage in the
device. This is the sum of (a) the charge in the contacts (related
linearly to the voltage by the geometric or junction capacitance,
\( C_{geo} \)) and (b) the charge associated with photogenerated
electrons and holes in the perovskite layer (usually related
exponentially to the voltage by the chemical capacitance, \( C_p \)).
The relationship between \( C_{geo} \) and \( C_p \) is discussed in more
detail in the main text and also in the Supporting Information.

Recombination is represented by the voltage-dependent
recombination resistance, \( R_{rec} \), defined by

\[
R_{rec} = \frac{\partial V}{\partial \ln j_{rec}}
\]

(3)

where \( j_{rec} \) is the recombination current density. Generally, the
variation of the recombination resistance with voltage is related
to the ideality factor \( m \) by

\[
\frac{\partial \log R_{rec}}{\partial V} = \frac{q}{2.303mk_B T}
\]

(4)

\( R_{rec} \) is the series resistance of the cell, which in the present
case is largely associated with the FTO substrate. \( C_{total} \)
represents the total capacitance of the cell, \( C_{geo} + C_p \). If
necessary, it can be replaced by constant phase shift elements
(CPE) to reflect effects such as those arising from heterogeneity (see
Supporting Information for a discussion of \( \text{CPE behavior} \))\(^2\). In the case where \( C_{total} \) is dominated by the
buildup of photogenerated charge (as in the DSC and in silicon
p–n devices),\(^31,32 \) the recombination lifetime is given by the
product of the chemical capacitance \( C_p \) and the recombination
resistance \( R_{rec} \). In the case where the geometric capacitance,
\( C_{geo} \) dominates the recombination lifetime is not obtained and
the time constant for the process is \( R_{rec} C_{geo} \).

The circuit shown in Figure 1 neglects complications that
arise in the case of perovskite cells from low-frequency effects.
These have been discussed recently by Bisquert et al.,\(^26 \) who
attribute the low-frequency response to the GDE. Discussion of
the low-frequency response of the planar cells is deferred to a
forthcoming paper. In general, the circuit model in Figure 1
gives a satisfactory fit of the impedance data for the planar
perovskite cells at frequencies above 100 Hz. The low-
frequency feature only becomes an issue at low light intensities
(low open-circuit voltages), where the \( RC \) time constant of the
solar cell becomes comparable with the time constant for the
process.\(^29 \)

The circuit in Figure 1 differs from the transmission line
model that has been used for mesoporous perovskite solar
cells.\(^10,21 \) As shown below, the planar perovskite cells
investigated here do not show transmission line behavior
even in the highest frequency part of the impedance responses,
indicating that transport of charge carriers by drift/diffusion is
very fast in the thin (600 nm) perovskite absorber layer.

IMVS AND OCVD

Intensity-modulated photovoltage spectroscopy (IMVS) has
been widely used to study recombination in dye-sensitized solar
cells (DSC). It has also been used to investigate mesostructured
perovskite cells.\(^33–35 \) To the best of our knowledge, this is the
first time IMVS has been used to characterize planar perovskite
cells. The method involves using a small sinusoidal modulation
of the illumination intensity to perturb the Fermi level splitting
around a steady state at open circuit. Generally, the IMVS
response is a semicircle with a characteristic radial frequency at
its maximum that is the inverse of the photovoltage decay time
constant, \( \tau_{IMVS} \). In the case where the effects of the geometric
or junction capacitance can be neglected, \( \tau_{IMVS} \) is given by the
product of the recombination resistance and the chemical
capacitance, which corresponds to the ambipolar carrier
lifetime. However, in the case where \( C_{geo} \) is dominant, we expect
\( \tau_{IMVS} \) to be determined by the product \( R_{rec} C_{geo} \).

For open-circuit photovoltage decay (OCVD) measure-
ments, the cell is illuminated at open circuit to establish a
photostationary state. The light is then switched off, and the
decay in \( V_{oc} \) is monitored as a function of time. The
photovoltage decay lifetime, \( \tau_{OCVD} \), is then obtained using eq
\( S \) (see Supporting Information).

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\[ \tau_{\text{OCVD}} = -\frac{2k_BT}{q} \left( \frac{dV_{\text{OC}}}{dt} \right)^{-1} - \frac{dV_{\text{OC}}}{dt} \left( \frac{d^2V_{\text{OC}}}{dt^2} \right)^{-1} \] (5)

Equation 5 is derived using an approach similar to that of Zaban et al.\textsuperscript{35} but for the two carrier case where the excess carrier densities are higher than the doping density of the material (see Supporting Information). The second term in eq 5 is often omitted, and a satisfactory approximation of the lifetime can be obtained by the first term (see ref 31 for more details).

If the chemical capacitance of the cell is larger than the geometric capacitance obtained from eq 5, the decay lifetime corresponds to the ambipolar carrier lifetime. However, in the case where the geometric/junction capacitance dominates, we expect \( \tau_{\text{OCVD}} \) to correspond to the RC time constant \( R_{\text{ser}}C_{\text{geo}} \).

| IMPS |

In cases where carrier transport is slow, the IMPS response can be used to measure the delay in collecting carriers at the contacts. IMPS has been used extensively to study trap-limited electron transport in dye-sensitized solar cells.\textsuperscript{37,38} It has also been used to study mesostructured perovskite solar cells.\textsuperscript{33} However, in the case of normal p–n or p–i–n solar cells without deep trap states, carrier separation is so fast that it is much more difficult to measure by IMPS. The high-frequency IMPS response is dominated in this case by the attenuation arising from the time constant of the solar cell, which corresponds to \( R_{\text{ser}}C_{\text{total}} \) in Figure 1. By contrast, in the case of mesostructured perovskite solar cells, IMPS may give both the RC time constant and a time constant due to electron transport in the mesoporous titania scaffold. IMPS has also been used to characterize charge transfer and recombination in semiconductor–electron contacts.\textsuperscript{39} In this case, the modulated illumination generates a flux of minority carriers into the surface (e.g., at the semiconductor–solution interface). Once there, the carriers either can be involved in a charge transfer reaction or may combine with majority carriers. The relaxation of the minority carrier concentration at the surface by charge transfer and recombination gives rise to a semicircle in the complex plane IMPS plot with a radial frequency at the maximum that is equal to the inverse of the relaxation lifetime \( \tau_{\text{IMPS}}^{-1} = k_{\text{trans}} + k_{\text{rec}}^{-1} \). The normalized low-frequency intercept of the IMPS plot corresponds to the dc response, and it depends on the fraction of the minority carriers that make it across the interface. This charge transfer efficiency, \( \eta_{\text{trans}} \), is given simply by the ratio \( k_{\text{trans}}/(k_{\text{trans}} + k_{\text{rec}}) \).\textsuperscript{39} Here, \( k_{\text{trans}} \) and \( k_{\text{rec}} \) are first-order (or pseudo-first-order) rate constants for charge transfer and recombination at short circuit, respectively.

| RESULTS AND DISCUSSION |

Cell Efficiencies. Representative IV curves (Figures S1 and S2) and a summary of the efficiencies of all the cells used in this study are given in the Supporting Information. Five devices were studied, each of which contained three pixels, making a total of 15 solar cells. The cells showed an average efficiency of 11.05% at 1 Sun and AM1.5 with a standard deviation of 1.02% (number of samples, \( n = 14 \)). The two cells presented in most detail below had efficiencies of 11.98% (FS43_1) and 9.60% (FB06_1). One of the pixels gave an anomalously low efficiency and was disregarded, two further pixels degraded during transport, and the data from them was also not included in the study.

Intensity Dependence of \( V_{\text{oc}} \). All of the cells were made at the same time using identical techniques and annealed together on the same hot plate. Figure 2 illustrates the two types of intensity dependence of the open-circuit voltage observed when the cells were illuminated with monochromatic light (\( \lambda = 625 \text{ nm} \)). Interestingly, the cells fell into two groups. One pixel from each of the two groups showed different types of intensity dependence of the open-circuit voltage (Figures S1 and S2). The open-circuit voltage is given by the equation

\[ V_{\text{oc}} = k_{\text{trans}}/(k_{\text{trans}} + k_{\text{rec}}) \]

where \( k_{\text{trans}} \) and \( k_{\text{rec}} \) are the charge transfer and recombination rates, respectively.

Figure 2. Intensity dependence of the open-circuit voltages for two different cells/pixels illustrating the difference in ideality factor between the two groups.

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that the cell with \( m = 2.6 \) in Figure 2 exhibits a remarkably slow decay of \( V_{oc} \); the voltage is still 0.4 V after 1 s, and the decay is not complete even at 10 s. By contrast, the open-circuit voltage of the cell with \( m = 5.3 \) decays much more rapidly, falling below 0.1 V in only 10 ms. Similar anomalously slow OCVD behavior has been reported by Baumann et al.\(^{25} \) for vapor-deposited perovskite cells in which the TiO\(_2\) and MeOTAD contacts were replaced by PC\(_{70}\)PCBM and PEDOT:PSS/polyTPD, respectively. The authors interpreted the decay in terms of the kinetics of electron–hole recombination and found that the recombination order was between 2 and 3 and that it varied depending on the illumination intensity the cell was exposed to prior to the decay.

The IMVS responses (Figure S8, Supporting Information, shows representative IMVS data) of the cells measured over two decades of light intensity were well-defined semicircles in the complex plane, and \( \tau_{IMVS} \) was derived from the inverse of the radial frequency corresponding to the maximum of the imaginary component.

The lifetimes derived from the OCVD plots in Figure 3 and from the corresponding IMVS measurements on the two representative cells are presented in Figure 4. Details of the smoothing and fitting procedures used to obtain \( \tau_{OCVD} \) are given in the Supporting Information. The reasonable agreement between the lifetimes derived by the transient and small sinusoidal modulation methods indicates that the open-circuit decays through a set of quasistatic states, at least in the voltage range preceding the steeper rise in lifetime that can be seen in the \( \tau \) plots for both cells. The slopes of the regression fits of the IMVS plots for the two types of cell correspond to \( m \) values, which are similar to those derived from the intensity dependence of the \( V_{oc} \) (see Figure 2).

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The lifetimes measured by IMVS for the two cells were found to be inversely proportional to the incident light intensity as shown in Figure 5. Remarkably, the lifetimes of the two cells at the same light intensity are very similar, in spite of the fact that the open-circuit voltages (and presumably therefore the excess electron and hole concentrations) are quite different. As shown below, the recombination resistances of the two cells measured by impedance spectroscopy were also very similar.
when measured at the same illumination intensity (cf. Figure 8). The recombination resistance is expected to vary linearly with the inverse of light intensity, providing the dark and light responses from the cell are additive (see Supporting Information). As the lifetime $t_{IMVS}/t_{OCVD}$ equals $R_{rec}C_{geo}$ in the case of the cells measured here, it follows that $t_{IMVS}/t_{OCVD}$ should also vary linearly with light intensity provided that $C_{geo}$ is effectively constant across the full range of light intensities measured. This contrasts strongly with the case of normal $p$–$n$ junctions, where the chemical capacitance is dominant and increases with light intensity due to the increase in electron and hole concentrations.

**Impedance.** Impedance measurements were carried out at open circuit under illumination (and also in the dark as a function of voltage bias, see Supporting Information). Figure 6a

![Image](image.png)

**Figure 6.** (a) Example of the impedance response measured at open circuit at the highest light intensity ($\lambda = 625$ nm, $3.17 \times 10^{-16}$ cm$^{-2}$ s$^{-1}$). Points are the experimental, line fitting to the circuit shown in Figure 1. (b) Bode plot (symbols) and fit (lines) to the circuit shown in Figure 1 with $C_{num}$ replaced by a constant phase shift element for the impedance response.

and 6b illustrates the impedance response observed at an intensity corresponding to $\sim 0.1$ Sun. At all intensities three typical features were seen in the Nyquist plots. A mid-frequency semicircle was attributed to $C_{total}$ and $R_{rec}$. The semicircle was distorted at the highest frequencies by another process which we attributed the effect of stray capacitance (e.g., from the connectors); however, it could also be due to the impedance of the titania blocking layer. A third low-frequency feature was always observed below $\sim 100$ Hz, as illustrated in Figure 6a. Each of the features is discussed in more detail below.

Impedance measurements have been used extensively to characterize mesostructured lead halide perovskite solar cells.$^{10,22,24}$ In the case of the mesostructured cells, the analysis has been based on transmission line models developed for dye-sensitized solar cells that consider electron transport and recombination.$^{10,13,21,24,43}$ In the case of the planar perovskite cells studied here, we did not observe transmission line behavior, even at the highest frequencies (1.5 MHz). It is likely therefore that for these planar cells the transport of carriers through the perovskite films is too fast to be measured by impedance spectroscopy. This result suggests that the response of these planar cells is much simpler than that of mesostructured cells, and it is possible that the transmission line seen in mesostructured cells is a result of the electrons in the titania scaffold rather than in the perovskite itself.

The time constant for the semicircle obtained in the impedance of all the planar cells, at all illumination intensities, was much shorter than the relaxation time reported for the giant dielectric effect.$^{12,36,13,26}$ The response can be fitted to the simple circuit shown in Figure 1 if the total capacitance is replaced by a constant phase shift element. When this was done the $P$ values for the CPE representing $C_{total}$ were all between 0.87 and 1 (see Supporting Information for further discussion). It should also be noted that fitting the mid-frequency range of the semicircle to a simple model containing only $R_{rec}$, $R_{ser}$ and $C_{total}$ without a CPE gave a reasonable fit and showed identical trends in the recombination resistance. When the simple $R_{ser}(R_{rec}C_{total})$ model was used, $C_{total}$ (e.g., reported here for FS43_1) had values of between 20 and 32 nF over the entire intensity (and hence voltage) range. The geometric capacitance for a perfectly smooth device can be calculated to be $\sim 5.3$ nF ($C = \varepsilon_0\varepsilon_r A/d$; $A = 0.15$ cm$^2$, $d = 600$ nm, $\varepsilon_r = 24^{12,44}$). The experimentally derived values of the capacitance are approximately 4 times larger than the calculated geometric capacitance for the cell using a relative permittivity of 24. This suggests either a perfectly flat perovskite film with a relative permittivity of 100 or a film with a relative permittivity of 24 and a roughness factor of 4. A roughness factor of 4 is entirely reasonable for a multicrystalline perovskite film; mechanically polished gold films have roughness factors of between 3 and 5, for example.$^{45}$ However, the difference in calculated and measured capacitance could also be due to an increase in dielectric constant under illumination as reported by Juarez-Perez et al.$^{13}$

The impedance results strongly suggests that $C_{total}$ is dominated by the value of the geometric capacitance and that the charge stored in the contacts is significantly larger than the charge due to photogenerated electrons and holes in the perovskite. In contrast to measurements on mesostructured cells with titania scaffolds, we do not appear to measure the chemical capacitance and do not see large amounts of charge stored in the bulk of the perovskite.$^{13,33}$ Previous measurements on planar perovskite cells (300 nm active layer) also showed a large capacitance which was attributed to a high intrinsic density of states in perovskite films.$^{21}$ We did not observe such a large capacitance in our measurements, and the devices studied here show a capacitance which does not vary strongly with intensity. It is possible that the capacitance behavior depends on the methods used to prepare the perovskite cells, as several recent papers have shown large differences in cell properties for small differences in preparation.
The fact that $C_g$ dominates $C_μ$ over the frequency range is consistent with a $p$–$i$–$n$ device, although other authors have suggested that perovskite solar cells may function as $p$–$n$ devices.

The parallel resistance that accompanies $C_{geo}$ is attributed to the recombination resistance. The lifetimes calculated from the product of $C_{geo}$ and $R_{rec}$ agree well with the values measured by IMVS and OCVD (Figure 4 and Figure S9, Supporting Information). We therefore conclude that the perovskite can be considered as essentially intrinsic. This is consistent with the very low doping density ($\sim$10$^9$ cm$^{-3}$) calculated from the transition to first-order decay seen in Figure 4. The variations of the recombination resistance with $V_{oc}$ and with intensity are shown in Figures 7 and 8. The semilogarithmic plots of $R_{rec}$ vs $V_{oc}$ for the two types of cells have different slopes as shown in Figure 7, reflecting the different ideality factors of the cells. The ideality factors of 2.7 and 4.8 are very similar to those obtained from the intensity dependence of the open-circuit voltage (cf. Figure 2). By contrast, the intensity dependence of $R_{rec}$ is almost identical for both types of cells, with a slope close to $−1$, mirroring the intensity dependence of $τ_{IMVS}$ measured by IMVS (cf. Figure 5).

The low-frequency feature that appears in the impedance plots below 100 Hz has not been studied in detail, as we were concerned that the cells could degrade on the time scale of the very slow low-frequency measurements. Juarez-Perez et al. attribute the low-frequency feature to the GDE in the perovskite.\textsuperscript{13} We are currently looking at the low-frequency feature in more detail, but the conclusion of this paper is that a simple circuit gives a good fit to all data above 100 Hz.

**IMPS**

IMPS has been extensively used to investigate carrier transport in DSC. It has also been used to study recombination and interfacial transfer of minority carriers in illuminated semiconductor electrodes.\textsuperscript{39,40,50} IMPS was recently used by Guillén et al. to study mesostructured perovskite cells; two time constants were observed in one quadrant of the complex plane plot. Figure 9 shows a representative IMPS plot for FS43_1 at 0.1 Sun equivalent illumination. The high-frequency semicircle is incomplete as the LED could not be modulated satisfactorily at frequencies higher than 200 kHz. The IMPS response for DSC is usually a semicircle trending to a 45$^\circ$ line toward the origin at high frequencies. The characteristic frequency of the semicircle is related to the electron transport time, which ranges from milliseconds to seconds, depending on the illumination intensity. By contrast, in the case of the planar perovskite solar cell...
cells studied here, the high-frequency semicircle is dominated by the time constant \( R_{ser}C_{geo} \) of the cell, and it is difficult to deconvolute the effect of carrier transport because the carrier transit times are similar to or shorter than the RC time constant. However, we believe that the distortion of the semicircle at high frequencies may not be an instrumental artifact but could be due to an additional phase lag associated with transport. The values of the series resistance measured by impedance spectroscopy were used to estimate the capacitance from the relaxation time for the high-frequency semicircle. The series resistance for FB06_1, for example, was \( \sim 40 \, \Omega \) which gave capacitance values of between 26 and 36 nF. These values are consistent with the values of \( C_{total} \) obtained from both IMVS and impedance spectroscopy.

Interestingly, a second semicircle in the lower quadrant is seen at lower frequencies. As discussed above, a similar response is observed for illuminated semiconductor/electrolyte junctions, where the second semicircle is due to the relaxation of the minority carrier concentration at short circuit by charge transfer (with rate \( k_{trans} \)) and recombination (with rate \( k_{rec} \)) at the solution–electrode interface. The high-frequency intercept corresponds to the instantaneous photocurrent and the low-frequency limit to the steady-state photocurrent. In this case, the semicircle has a radial frequency at the minimum that is equal to the inverse of the relaxation lifetime, \( \tau_{IMPS} = k_{trans} + k_{rec} \) and a normalized low-frequency intercept that depends on the charge transfer efficiency, \( \eta_{trans} = k_{trans}/(k_{trans} + k_{rec}) \). It should be noted that the “relaxation lifetime” measured using IMPS is quite separate from the “recombination lifetime”, which is measured at open circuit. The open-circuit recombination lifetime is the product of the chemical capacitance and the recombination resistance. In contrast, the relaxation lifetime from IMPS is measured at short circuit. The IMPS lifetime is not influenced by the geometric capacitance which, as outlined above, is observed in the high-frequency semicircle in the upper quadrant of the IMPS plot. IMPS can therefore give useful information about interfacial charge transport and recombination in perovskite solar cells at short circuit.

In view of the similarity mentioned above, we attribute the low-frequency IMPS response for the perovskite cells to relaxation of photogenerated carriers due to interfacial recombination and transport at short circuit. Values for \( k_{trans}, k_{rec}, \tau_{IMPS} \), and \( \eta_{trans} \) were extracted from the maximum frequency and normalized low-frequency intercepts of the IMPS plots recorded as a function of light intensity. Figure 10 shows the collection efficiency, \( \eta_{trans} \) for the two cells studied in detail in this paper. It can be seen that \( \eta_{trans} \) for FS43_1 is higher than that of FB06_1 at all intensities. This result is consistent with the higher global efficiency measured for this cell.

Figure 11 shows the short-circuit relaxation lifetime calculated from the maximum of the low-frequency IMPS semicircles. A linear variation with intensity is seen for \( \tau_{IMPS} \) and its values are higher than the values of \( \tau_{IMVS} \) measured at the same light intensities. The calculated rate constants are shown in Figure 12. At all intensities \( k_{trans} \) is approximately an order of magnitude greater than \( k_{rec} \) which is consistent with the high external quantum efficiencies typically measured for perovskite solar cells under short-circuit conditions. Cell FB06_1 showed a higher recombination rate than cell FS43_1 \((3.43 \times 10^3 \, \text{s}^{-1} \) compared to \(3.18 \times 10^3 \, \text{s}^{-1} \) at 0.1 Sun); the rate constant for interfacial transport was also slower

![Figure 10. Collection efficiency, \( \eta_{trans} \) for FB06_1 and FS43_1 calculated from the intercept of the low-frequency semicircle in the IMPS.](image1)

![Figure 11. \( \tau_{IMPS} \) from IMPS measurements of FB06_1 and FS43_1.](image2)

### CONCLUSIONS

IMVS, OCVD, impedance, and IMPS have been used to study planar perovskite solar cells. Despite the fact that all cells were made at the same time, two distinct sets of behaviors were seen. One half of the cells had ideality factors of \( \sim 2.6 \), and the other
half showed ideality factors of ~5.2. The difference in behavior was also seen in the OCVD: the cells with the lower ideality factors showed a persistent photovoltage. Lifetimes from IMVS were in good agreement with those calculated from OCVD. IMVS and impedance spectroscopy showed time constants that were dominated by the geometric capacitance rather than the chemical capacitance, meaning that the ambipolar recombination lifetime could not be extracted. IMPS showed two semicircles, one at high frequency attributed to the RC time constant of the cells and a second at lower frequency attributed to interfacial transport and recombination at short circuit. Analysis of the IMPS response suggests that the collection of photogenerated carriers is very efficient under short-circuit conditions in these planar perovskite cells.

ASSOCIATED CONTENT

Supporting Information
IV characteristics and cell efficiencies, IMVS results, analysis of constant phase shift elements, dark impedance, OCVD fitting and theory, and modeling of the geometric and chemical capacitance for a planar p-i-n cell. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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