

# Light-Induced Space-Charge Accumulation Zone as Photovoltaic Mechanism in Perovskite Solar Cells

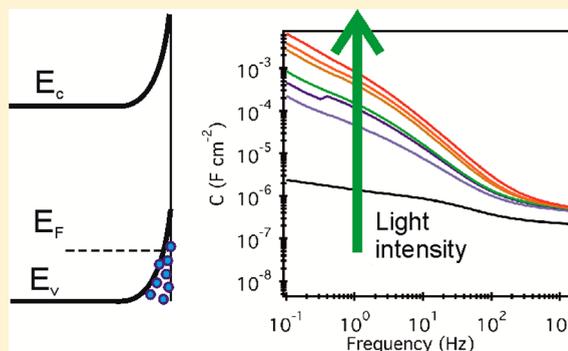
Isaac Zarazua,<sup>†</sup> Juan Bisquert,<sup>\*,†,‡</sup> and Germà Garcia-Belmonte<sup>\*,†</sup>

<sup>†</sup>Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain

<sup>‡</sup>Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

## Supporting Information

**ABSTRACT:** We fabricated formamidinium lead iodide perovskite solar cell for analysis of the photovoltaic mechanism based on the interpretation of the capacitance variation under illumination. It was shown that the low-frequency capacitance increases proportional to incident light intensity, and in addition it increases proportional to absorber thickness. Furthermore, the voltage dependence of capacitance is exponential with slope 1/2 (thermal energy). We conclude that the large photovoltage and capacitance are associated with electronic accumulation zone at the interface with the metal oxide contact. While this type of accumulation capacitance is common in many devices as transistors, the perovskite solar cell shows a singular behavior in that under light the electronic carrier accumulation grows unlimited by another series capacitance, reaching values as large as  $10 \text{ mF cm}^{-2}$  at one sun illumination.



Lead halide organic–inorganic perovskite solar cells have demonstrated a rapid raise of solar energy conversion efficiency that so far exceeded 20%<sup>1–4</sup> and is expected to further increase. The hybrid perovskites also show exceptional optoelectronic properties that promise the development of new applications;<sup>5,6</sup> however, the emergence and widespread observations of peculiar phenomena, including acute hysteresis in current density–voltage ( $J$ – $V$ ) curve and switchability by voltage pretreatment,<sup>7</sup> indicate that the mechanisms that determine the performance of hybrid perovskite solar cells have not yet been understood. Here we report the interpretation of the large capacitance under illumination<sup>8,9</sup> that reveals the origin of this feature. We suggest a large accumulation of majority carrier at the contact that indicates an unprecedented photovoltaic mechanism in the family of high-performance solar cells.

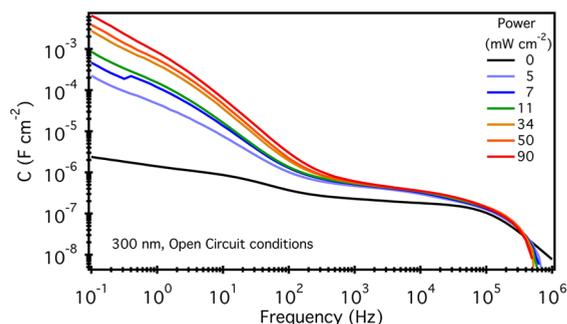
Previous studies of impedance spectroscopy pointed out the significance of contacts to understand capacitive features of the solar cell device;<sup>10,11</sup> however, it has now been recognized that hybrid perovskite solar cells contain different kinds of charge carriers: ionic and electronic. Ionic defects can easily drift under internal electrical field, and they accumulate to the interfaces.<sup>12</sup> A large low-frequency capacitance observed under dark conditions has been attributed to ionic electrode polarization,<sup>13</sup> and this effect has emerged as a dominant factor for time-dependent and hysteresis behavior of the lead halide perovskite solar cell.<sup>9,14</sup> In addition to the capacitive properties in dark, the low-frequency capacitance increases rapidly under photo-generation of carriers.<sup>8</sup> It is therefore reasonable to assume that such capacitance is enhanced by electronic phenomena,

requiring a different explanation from the ionic polarization observed under dark conditions. Overall, the large low-frequency capacitance observed to rise under illumination is believed to play a major role in performance via contact modification,<sup>15</sup> but a detailed understanding of the mechanism, whereby the capacitance displays such extraordinary rise in a solar cell, has not been previously stated.

The accumulation of ions at the interface has been reported in a previous paper as the origin of capacitive response;<sup>13</sup> however, a large rise of ionic space charge capacitance is limited by the Helmholtz capacitance situated in series, so that one does not expect values substantially higher than  $\mu\text{F cm}^{-2}$ . We fabricated  $\text{CH}(\text{NH}_2)_2\text{PbI}_{3-x}\text{Cl}_x$  (FAPbI<sub>3-x</sub>Cl<sub>x</sub>) perovskite solar cells of planar structure by the method described in the [Experimental Section](#). The values of capacitance versus frequency shown in [Figure 1](#) have been measured under open-circuit conditions at different illumination intensities and room temperature. This experimental procedure maximizes charge accumulation as dc currents are suppressed. The high-frequency part is dominated by dielectric and series resistance contributions (see [Figure S1](#)). The low-frequency capacitance increase greatly exceeds the mentioned Helmholtz capacitance limit, as already previously established.<sup>8</sup> Therefore, we need to turn to another explanation, in which electronic carriers form a large interfacial capacitance. It is well known that huge electronic interfacial capacitance is possible in the domains of

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**Figure 1.** Capacitance spectra measured in open-circuit conditions for different illumination intensities of 300 nm thick  $\text{CH}(\text{NH}_2)_2\text{PbI}_{3-x}\text{Cl}_x$ -based solar cells between 100 mHz and 1 MHz. Dark response at zero bias is also shown.

accumulation and inversion at semiconductor surfaces, as there is no limit to the packing of electrons in a short distance at the vicinity of the contact. Accumulation capacitance is, in fact, very common in transistor and MIS devices,<sup>16</sup> although the measured capacitance is limited by the series connection of the oxide dielectric capacitance. In contrast with this, we suggest that an accumulation capacitance is observed in the perovskite solar cell, which is unlimited by any complementary constant capacitance (as the oxide layer is a conductor). Accumulation capacitance is, however, quite uncommon in solar cell devices. This new phenomenon explains the giant capacitance that has been previously reported.<sup>8</sup>

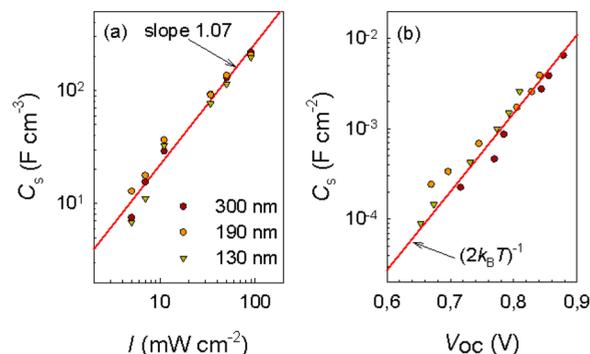
To summarize the physical basis of accumulation capacitance, in the p-type semiconductor surface, the conduction band bends upward at the surface and penetrates the Fermi level, as shown in Figure 2c. The charge per unit surface is  $Q = qp_b L_D F_s$ ,<sup>17</sup> where  $q$  is electron charge,  $p_b$  is the bulk carrier density corresponding to dopant density, and  $F_s \approx \sqrt{2} e^{qV/2k_B T}$ , where  $k_B T$  is thermal energy and  $qV$  corresponds to local separation of vacuum level (VL) from bulk value.  $V_{oc}$  is the voltage at the contact, as indicated in Figure 2. The Debye length is given by  $L_D^2 = \epsilon_r \epsilon_0 k_B T / q^2 p_b$  in terms of relative dielectric constant  $\epsilon_r$  and vacuum permittivity  $\epsilon_0$ . For the capacitance we find the expression

$$C_s = \frac{dQ}{dV} = \frac{qp_b^{1/2}}{\sqrt{2}} \left( \frac{\epsilon_r \epsilon_0}{k_B T} \right)^{1/2} e^{qV/2k_B T} \quad (1)$$

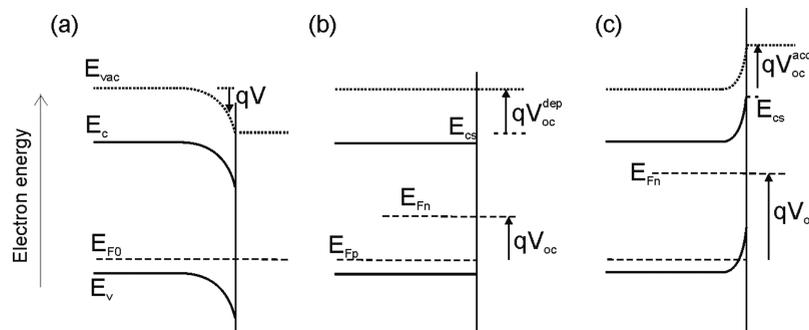
In the planar perovskite solar cell, we assume, as shown in Figure 2, that voltage drop corresponding to the photovoltage

is established at the  $\text{TiO}_2$ /perovskite interface (equivalent to the potential at the cathode metal), while the *spiro*-OMeTAD/perovskite hole extraction contact is considered ohmic. This is in agreement with the main charge accumulation interface, as observed in transient decays.<sup>18</sup> In dark equilibrium, a depletion layer is observed at this interface as revealed by Mott–Schottky plot and direct measurement of VL.<sup>19</sup> The increase in minority carriers first removes the depletion region, up to flatband condition (Figure 2b), and then is followed by the creation of accumulation region (Figure 2c). The accumulation capacitance can grow to very large values; see Figure S3.

Upon illumination in open circuit photogenerated holes are collected at the accumulation zone to build up the measured photovoltage. The absorption depth of formamidinium perovskite is a few hundred nanometers,<sup>20</sup> greater than the film thickness range (130–300 nm) used here. Consequently, thicker films generate larger amounts of carriers, which are eventually collected at the accumulation zone. The electronic accumulation model therefore predicts an increase in the surface capacitance as a function of the perovskite absorber layer thickness. This is in accordance with the higher open-circuit voltage exhibited by thicker perovskite layers, as observed in the  $J$ – $V$  curves (Figure S4). To check such a hole-accumulation mechanism, we plotted capacitance per unit length as a function of the light intensity in Figure 3a for



**Figure 3.** Accumulation capacitance of  $\text{FAPbI}_{3-x}\text{Cl}_x$ -based solar cells extracted from the low-frequency values in Figure 1. (a) Normalized to the absorber film thickness as a function of the light intensity showing a proportional dependence with the perovskite layer thickness and light intensity and (b) per unit surface as a function of the open-circuit voltage. Solid line accounts for the fitting using eq 1 with exponential dependence on voltage with slope  $1/2k_B T$  (room temperature) as indicated. Fitting parameters are  $p_b = 2 \times 10^{17} \text{ cm}^{-3}$  and  $\epsilon_r = 26$ .



**Figure 2.** Energy diagram for electron selective contact to the semiconductor absorber layer at open-circuit conditions. (a) Depletion layer at equilibrium. Generation of minority carriers produces flatband condition (b) and further accumulation (c) of majority carrier. The total open-circuit voltage is the increase in minority carrier Fermi level that corresponds to total change of surface vacuum level as  $V_{oc} = V_{oc}^{dep} + V_{oc}^{acc}$ .

different layer thickness. Low-frequency capacitance values increase proportionally with the light intensity, as reported previously,<sup>8</sup> and are also proportional to the perovskite layer thickness. The observation of these two proportionalities (light intensity and film thickness) constitutes a direct proof that the surface capacitance charging is made up of photogenerated carriers coming from the absorber bulk.

Experimental capacitance data in Figure 3b show the characteristic slope of  $1/2k_{\text{B}}T$  for solar cells with different absorber perovskite thickness, in agreement with the accumulation capacitance expression (eq 1). The fitting assumes  $p_{\text{b}} = N_{\text{A}} = 2 \times 10^{17} \text{ cm}^{-3}$  as derived from previous works,<sup>19</sup> and  $\epsilon_{\text{r}} = 26$  extracted from fitting of the capacitance spectra (see Figure S2). The resulting Debye length is  $L_{\text{D}} = 14 \text{ nm}$ , a value non-negligible in relation to the absorber thickness. From a fit (Figure 2b) the voltage needed to reach flat-band potential under illumination can be estimated, which amounts 0.44 V. This value situates  $E_{\text{Fp}}$  at  $\sim 0.25 \text{ eV}$  from the perovskite valence band, consistent with a doping level around  $10^{17} \text{ cm}^{-3}$ . We note that this voltage does not correspond to the built-in usually encountered through Mott–Schottky analysis performed in the dark,  $V_{\text{bi}} \approx 1 \text{ V}$ .<sup>19</sup>

Finally, an important additional feature should be discussed. Depletion capacitance or accumulation capacitance are different types of dielectric capacitances that respond in short time and high frequency. The typical large low frequency observed in perovskite solar cells is onset on “slow” time scales with frequencies below 100 Hz; see Figure 1. This type of low-frequency accumulation capacitance is quite unexpected and indicates that polarization is dominated by an additional factor that regulates the formation of electronic space charge. Clearly, the large accumulation capacitance is facilitated by large doping density  $p_{\text{b}}$ , as indicated in eq 1. We suggest that local doping at the interface is controlled by ionic defects, so that the capacitance needs charge compensation ion formation for the accumulation capacitance to take place. This is a self-doping mechanism that obviously depends on the details of contact materials and surface morphology. Such dependence is in agreement with the rather varied phenomenology of contact capacitance and hysteresis.<sup>15,21,22</sup> We previously connected the low-frequency capacitance excess measured under dark conditions to the electrode polarization caused by ionic defect pile-up.<sup>13</sup> This mechanism predicts similar capacitive values independently of the absorber layer thickness, as seen in experiments (see Figure S1). The interplay between ionic and electronic effects suggests the occurrence of an electronic interfacial accumulation with a kinetics controlled by ionic defects. A discussion of the difference types of contacts and bulk perovskite materials lies beyond the scope of this report and will be presented in future work.

In conclusion, we have described a charge accumulation mechanism that explains a peculiar type of voltage built-in via electronic carrier accumulation at the interface. This observation is suggested as a distinctive photovoltaic operating principle of hybrid organic–inorganic perovskite solar cells.

## EXPERIMENTAL SECTION

In this study,  $\text{CH}(\text{NH}_2)_2\text{PbI}_{3-x}\text{Cl}_x$  perovskite is used in a planar structure of the type: FTO/TiO<sub>2</sub>/FAPbI<sub>3-x</sub>Cl<sub>x</sub>/spiro-OMeTAD/Au. All studied cells were prepared over FTO glasses (25 × 25 mm, Pilkington TEC15,  $\sim 15 \Omega/\text{sq}$  resistance), which were partially etched with zinc powder and HCl (2 M) to avoid short circuits, obtaining 0.25 cm<sup>2</sup> of active electrode

area. The substrates were cleaned with soap (Hellmanex) and rinsed with Milli-Q water and ethanol. Then, the sheets were sonicated for 15 min in a solution of acetone/isopropanol (1:1 v/v), rinsed with ethanol, and dried with compressed air. The substrates were treated in a UV–O<sub>3</sub> chamber for 20 min. The TiO<sub>2</sub> layer was deposited onto the substrates by spray pyrolysis at 480 °C using a titanium diisopropoxidebis(acetylacetonate) (75% in isopropanol, Sigma-Aldrich) solution diluted in ethanol (1:39 v/v), with oxygen as carrier gas. The spray was performed in four steps of 12 s, spraying each time 10 mL (approx.), and waiting 1 min between steps. After the spraying process, the films were kept at 480 °C for 5 min. Subsequently, a UV–O<sub>3</sub> treatment was performed for 20 min. The thickness determined by scanning electron microscopy was  $\sim 200 \text{ nm}$ , as observed in Figure S1 (Supporting Information).

The perovskite precursor solution was prepared by reacting 2.64 mmol of  $\text{CH}(\text{NH}_2)_2\text{I}$  and 0.88 mmol of  $\text{PbCl}_2$  (3:1 molar ratio) in 1 mL of DMF. 100  $\mu\text{L}$  of this solution was spin-coated inside a glovebox, spin-coating speeds were 1500, 2500, and 3500 rpm, producing perovskite films of 130, 190, and 300 nm (see Figure S1) After the deposition, the substrate was kept at 100 °C for 10 min. Next, the substrates were heated to 100 °C during 90 min in an oven under air stream. Then, the perovskite films were covered with the hole-transporting material (HTM,  $\sim 300 \text{ nm}$  thick) by spin coating at 4000 rpm for 30 s under air conditions using 100  $\mu\text{L}$  of spiro-OMeTAD solution. The spiro-OMeTAD solution was prepared by dissolving in 1 mL of chlorobenzene 72.3 mg of (2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene), 28.8  $\mu\text{L}$  of 4-*tert*-butylpyridine, and 17.5  $\mu\text{L}$  of a stock solution of 520 mg/mL of lithium bis-(trifluoromethylsulfonyl)imide in acetonitrile. Finally, 60 nm of gold was thermally evaporated on top of the device to form the electrode contacts using a commercial Univex 250 chamber from Oerlikon Leybold Vacuum. Before beginning the evaporation, the chamber was evacuated until pressure of  $2 \times 10^{-6}$  mbar. The active electrode area of 0.25 cm<sup>2</sup> per pixel is defined by the FTO and the Au contacts. Current density–voltage  $J$ – $V$  curves were recorded under AM 1.5 100 mW/cm<sup>2</sup> simulated sunlight (ABET Technologies Sun 2000) previously calibrated with an NREL-calibrated Si solar cell. For the measurement of capacitance spectra as a function of the light power intensity, a Gambry 3000 potentiostat was used. The AC voltage perturbation was 10 mV under open-circuit conditions. Each frequency spectrum was measured ranging between 0.1 Hz and 1 MHz at a given constant incident power, which was changed between 0 and 90 mW/cm<sup>2</sup>.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.5b02810.

Calculation of permittivity, calculation of accumulation capacitance, current–voltage curves analysis, SEM analysis, and photovoltaic parameters. (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

\*J.B.: E-mail: bisquert@uji.es.

\*G.G.-B.: E-mail: garciag@uji.es.

### Notes

The authors declare no competing financial interest.

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