Negative Capacitance and Inverted Hysteresis: Matching Features in Perovskite Solar Cells

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Abstract

Negative capacitance at low frequency domain and inverted hysteresis are familiar features in perovskite solar cells, which origin is still under discussion. Here we use Impedance Spectroscopy to analyse the evolution of these features in methylammonium lead bromide cells (MAPbBr₃) treated with extrinsic cations at the cathode/perovskite interface and in iodide devices (MAPbI₃) exposed under different relative humidity (%RH) conditions. To process the impedance spectra, an equivalent circuit based on the Surface Polarization Model (SPM) is implemented, obtaining the same result for all sample, i.e. large kinetic relaxation times and high recombination values correspond to those samples exhibiting strong inverted hysteresis and negative capacitance. A scan rate analysis of the cyclic voltammetry curves confirms the recombinant nature of both features and the direct relationship between them, providing experimental evidence of the recombination activated by ionic surface interaction as the main origin of inverted hysteresis and negative capacitance responses.
The benefits of lead halide perovskite solar cells (PSCs) in the photovoltaic field are indisputable. However, the current impressive power conversion efficiency (PCE) approaching 26% in the lab scale, is accompanied by a wide-range of features during device operation that still need to be solved. Hysteretic behaviour is one of them, representing a bottle-neck in the reporting of PSCs performance for high efficiency values, slowing down the race of the scalable horizon. This feature consists of a delay between the change of the properties of the system under variation of an external electric field. The consequence is a difference in the J-V curves during the sweeping in the two directions: from short-circuit towards open-circuit (Reverse scan, RS) and vice versa (Forward scan, FS). A remarkable presence of this phenomenon depends on the external parameters affecting the J-V curve: i.e. temperature, light intensity, scan-rate, pre-biasing voltage and external contacts. These perturbations lead to a wide range of hysteresis responses including: capacitive hysteresis, bump close to V_{oc}, decay of photocurrent in RS and apparent V_{oc} shift on FS. The hysteretic behaviour most commonly observed in PSCs is the normal hysteresis (NH) which performs with an improved fill factor (FF) and photovoltage (V_{oc}) for the FS, while the RS brings lower values. In this process the cell behaves as a capacitor. During the RS, an accumulation of charge occurs (“capacitor filling”), while in the FS this charge is realised (“capacitor emptying”) leading to an excess of current in the external circuit. On the other hand, an inverted hysteresis (IH) can also be present in certain samples and/or under specific pre-conditions. In this case, the FS displays lower photovoltage and FF values. Several mechanisms have been proposed for the different hysteretic features, including charge trapping and de-trapping, ferroelectric polarization, ion migration, capacitive effects, charge accumulation at the interfaces and unbalanced distribution of electrons and holes. All of them are deeply connected with the mixed ionic-electronic nature of PSCs, bringing out the perovskite/selective contact interfaces as the critical factor controlling charge extraction capability, accumulation and recombination mechanisms. The accumulation mechanisms reported for the IH involve unfavourable energy level alignment, ionic accumulation and space-charge buildup.

Tress and co-workers observed a NH for MAPbI\textsubscript{3} while an IH for mixed-cation perovskite devices. After including an isolating layer onto the mesoporous titanium dioxide (m-TiO\textsubscript{2}) in the simple perovskite device, they concluded that the process responsible for the IH was an energetic extraction barrier at the TiO\textsubscript{2} interface. On the other hand, Nemnes et. al showed that pre-poling bias (in particular negative pre-poling) can produce the switching from the normal to IH for the same structure device. They also analysed by a dynamic electrical model (DEM) the influence of the scan rate in terms of the time evolution of electronic and ionic charge accumulated at the interfaces. This DEM model includes a capacitor accounting for nonlinear polarization effects in the equivalent circuit. This theory is in perfect agreement with the Surface Polarization Model (SPM) proposed by Ravishankar et.al. This model is based on the formation of a surface potential, V_s, at the ESL/perovskite interface due to the arrival of positively charged ions
under large injection or illumination conditions, creating a massive accumulated density of both ionic and electronic holes, increasing recombination dynamics. An experimental work reported by Bisquert and co-workers, provided evidences of the surface polarization of the ESL/perovskite interface. In their work, a switching from NH to IH is shown when the thickness of the c-TiO$_2$ material is diminished, attributing this evolution to an interaction between charge accumulation and recombination mechanisms. The charge accumulation at the TiO$_2$/perovskite interface has been related with an abnormally high capacitive features (mFcm$^{-2}$) in the low frequency domain (LF) ($< 1$ Hz), measured using Impedance Spectroscopy (IS) and being also present under dark conditions, which brings out the strong influence of slow ionic dynamic on the hysteretic behaviour. This relation was clearly demonstrated in the work of Park and co-workers. They systematically compared the hysteretic behaviour between a regular perovskite configuration, using TiO$_2$ as ESL, and an inverted configuration, with PCBM as ESL. In the case of inverted structure, a hysteresis-free performance of the J-V curve was observed, together with a much lower value of capacitive response in the LF domain. They established the origin of this reduction as a decreased polarization of the device electrode.

Beyond the giant capacitive response, even in dark conditions, a negative capacitance has been also measured under a wide range of external conditions and in many different perovskite devices, becoming one of the hardest features to decode. The only thing in which there seems to be some agreement in literature, is the unfavourable effect on the optoelectronic response of the cells. An electron injection through interfacial states was attributed to the origin of negative capacitance in light emitting diodes (LEDs), being assigned as well as the main cause in PSCs by Anaya et. al. Bisquert and co-workers analysed the IS response of samples with negative capacitance by SPM, matching the negative capacitance to an inductive element included in their equivalent circuit (EC). This negative capacitance was attributed to a delay of the surface voltage which depends on a certain kinetic relaxation time, controlling the equilibration of the cathode/perovskite interface governed by ionic dynamic. The value of that kinetic constant depends on the process governing the slow response. To this respect, a recent review summarizes the kinetic values for halide vacancy diffusion and the response of ions accumulated at the perovskite surface; being in the range of $10^{-1}$ s and $10^{0} – 10^{2}$ s, respectively.

The next question lies then if there is any relation between the negative capacitance and hysteresis response. A recent work reported by Tress and co-workers correlate the negative capacitance with a stronger scan rate dependence of hysteresis behaviour, considering a change in the charge injection as the cause of this effect. Contrary, Jacobs et.al reported an ion-drift-diffusion (IDD) theory to simulate the negative capacitive processes and its relation with the scan rate dependence, pointing to a phase-delayed recombination mechanisms due to mobile ions as the main origin. In this work we demonstrate experimentally how negative capacitance is related specifically to inverted hysteresis, being both features caused by the same origin. We
apply the SPM to a batch of MAPbBr$_3$ devices with lithium treatment at the ESL and MAPbI$_3$ devices exposed to moisture. Matching results are obtained for all the cells. Samples with IH and strong negative capacitive response present higher kinetic constant and lower recombination resistance values than the ones with lower IH or NH and low negative capacitances. We correlate these results with a surface ionic interaction, leading to a phase-delayed recombination mechanism. These insights provide an overwhelming explanation about the origin of these two features, confirming the direct relationship between them and steeping forward to a deeper knowledge about PSCs dynamics.

We performed an exhaustive analysis of the impedance response and the hysteretic behaviour of well-known methylammonium lead bromide perovskite solar cells (MAPbBr$_3$) with and without lithium treatment at the ESL (Li and No-Li samples). This Li$^+$ treatment lead to a photovoltage enhancing as well as increased electroluminescence (EL) emission of the perovskite layer, due to a reduction of undesired non-radiative and surface recombination mechanisms. The samples analysed presented moderate power conversion efficiency (PCE), as the negative capacitance feature has been considered as deleterious effect of the optoelectronic performance of perovskite cells.

The cyclic voltammetry performed at 50 mV s$^{-1}$ of the two devices (Li and No-Li) are shown in Fig. 1a. As it can be observed, both of them respond with an inverted hysteretic behaviour, but clearly this effect is much stronger in the case of the un-doped device (no lithium additive at the ESL).

![Figure 1](image.png)

**Figure 1.** Black and red colours correspond to the Li and No-Li devices. (a) CV measures
of both configurations. Dashed line corresponds to forward scan, while solid line represents the reverse one. (b) EC used in the fitting of experimental impedance response. \( R_s \) is the series resistance, \( C_d \) is de dielectric capacitance, \( R_{rec} \) is the recombination resistance, \( R_C \) is the series resistance with inductance \( L \) and \( R_C \) is the series resistance with the surface charging capacitance \( C_1 \). (c) Impedance plot and (d) corresponding capacitance spectra, measured under dark conditions and at 1.1V. Solid lines corresponds to fits using the equivalent circuit showed in panel b.

As previously reported, the beneficial effect of lithium cation at the ESL/perovskite interface lies in the decrease of the density of majority carriers at the charge accumulation zone (holes in a p-type absorber material), and the surface recombination mechanisms. The accumulated charge at this interface, under light, is mainly ionic represented by the \( \text{Li}^+ \) creating the upward bending of the conduction band at the surface, improving the photovoltage.\(^{31}\) Due to the crucial role of the ionic dynamic in these devices and focusing on the fact that both, capacitance and hysteretic phenomena have been correlated with slow transients, specifically to ionic electrode polarization, we performed IS analysis at forwarding bias and under dark conditions to prevent further complexity due to photogeneration mechanisms.\(^{12}\) The accumulation of charge at the cathode implies the formation of a surface voltage, and this build-up of band energy and the recovery of the equilibrium distribution is severally delayed by the rapidity of ion displacement.\(^{32}\) The SPM proposed by Ravishankar and co-workers agrees to this premise, giving rise to an inductance element in the EC represented in Fig.1b. We use this EC to depth analyse the impedance response in dark conditions.

In Fig. 1c it is shown the fitting of the impedance spectra measured at 1.1 V in a wide range of frequencies from 1 MHz to 10 mHz, to ensure the low frequency ionic contribution. As it can be observed, pronounced differences in the recombination resistance are presented comparing both samples. This is in complete agreement with our previous results, confirming that lithium decreases the surface recombination dynamics. Together with that, the appearance of a negative feature, represented by the inductive element in the EC, is traduced in a negative capacitance (Fig. 1d) for both samples.

The negative capacitance feature was attributed in the model to a delay in the surface voltage \( (V_s) \) depending on a certain kinetic relaxation time \( (\tau_{\text{kin}}) \). This surface voltage cannot follow immediately the external voltage \( V \) imposed, but in a slower rate mode is determined by the speed of ions movement. The relaxation equation defining this behaviour has been previously described by the SPM as follows:

\[
\frac{dV_s}{dt} = - \frac{V_s - (V - V_{bi})}{\tau_{\text{kin}}} \tag{1}
\]

where \( V_{bi} \) is the built-in potential (see SI for the definition of the EC elements corresponding to the model). The extracted parameters from the impedance spectra corresponding to both samples are detailed in Table 1 (See table S1 for the complete
fitting parameters).

**Table 1.** Extracted parameters from IS for the samples with and without Li$^+$ at the ESL.

| Cells | $R_{\text{rec}}$ (Ω·cm$^2$) | L (H·cm$^2$) | $R_L$ (Ω·cm$^2$) | $\tau_{\text{kin}}$=L/R$_L$ (s) |
|-------|----------------|----------|----------------|---------------|
| Li    | 2.2 x 10$^3$  | 2.1 x 10$^4$ | 2.9 x 10$^4$ | 0.7           |
| No Li | 1.2 x 10$^3$  | 4.9 x 10$^4$ | 7.7 x 10$^3$ | 6.4           |

The recombination resistance value ($R_{\text{rec}}$), in the case of lithium doped device is almost the double of the un-doped one, confirming a reduction of recombination processes due to lithium effect as previously mentioned. According to the model, $R_L$ is similar to $R_{\text{rec}}$, both are inversely proportional to $f_{\text{rec}}$ (see eq. S2 and S3). In the EC they are in parallel, consequently $R_L$ reduces the total low frequencies recombination resistance. The smaller $R_L$ is, the smaller total recombination resistance will be, and the IV-quadrant arc becomes bigger. In Table 1 can be noted that $R_L$ is smaller in the case of the No-Li sample, related to a bigger IV-quadrant arc in Fig. 1c.

From eq. S4 the kinetic constant ($\tau_{\text{kin}}$) is the characteristic time (L/ $R_L$) of the LF-arc. As can be seen in Table 1, the $\tau_{\text{kin}}$ value in the No-Li sample is one order of magnitude bigger. Larger values of the kinetic constant are attributed to a slower ionic delay to the equilibrium state after an external voltage is applied (V). For the No-Li device, the kinetic value is in the order of $10^0$ - $10^2$ s, which agrees with a response of accumulated and binding ions at the perovskite surface. Contrary, the sample with Li shows a kinetic value in the range of $10^1$ s, which agrees with halide vacancy diffusion time.$^{27}$ The reactivity of migrating ions with TiO$_2$ defects (Ti$^{3+}$) have been discreetly reported in literature as other aspects to consider in order to avoid instability and hysteretic responses.$^{33,34,35}$ A great intrinsic ionic accumulation at the ESL/perovskite interface could facilitate ionic interactions at the surface, having larger kinetic constants associated, increasing as well surface recombination processes. Attending to our results, the presence of lithium at that interface could reduce the accumulation of the intrinsic ions, and especially avoid that interactions, reducing the density of holes, the surface recombination processes and the kinetic times. The fact that the kinetic times corresponding to lithium sample agrees to ionic diffusion and not to an accumulation process, endorse this theory. Besides, it has been recently reported the effect of the ion drift-diffusion in the photoluminescence (PL) quenching.$^{36}$ The origin of this phenomenon is attributed to the creation of non-radiative recombination centres in the perovskite bulk. Potassium doping of the perovskite material seems to reduce this non-radiative recombination mechanisms, avoiding the ionic attachment to the surface.$^{37}$ This phenomenon could explain the recombination feature at the characteristic time of vacancy diffusion obtained for the Li sample. In fact, the lithium cation at the ESL generates an additional effect enhancing the PL and electroluminescence (EL) response of the MAPbBr$_3$ bulk material, as previously demonstrated.$^{30}$

To check that the negative capacitance and the IH are not features corresponding just
to a bad solar cell performance, we analyse two representative champion cells with the same characteristic of the previous ones, evaluating the influence of the scan rate in the hysteretic behaviour. We developed cyclic voltammetry (CV) measurements at different scan rates, from 10 mV s$^{-1}$ to 500 mV s$^{-1}$ under illumination conditions in order to force the ionic effect into the electronic photogenerated carriers.

![Figure 2](image)

**Figure 2.** Cyclic voltammetry of Li (a) and No-Li devices performed at different scan rates from 10 mV s$^{-1}$ to 500 mV s$^{-1}$. (c) Hysteresis index and (d) photovoltage versus scan rate comparing both samples: black dots for doped and red dots for un-doped samples.

In Fig. 2a and 2b we show the corresponding hysteretic behaviour for champion cells with a without lithium at the ESL, respectively. The clear differences between them are clear determining the hysteresis index following eq.2:\textsuperscript{18}

$$HI = 1 - \frac{PCE_{FS}}{PCE_{RS}}$$\textsuperscript{(2)}

As it can be observed, in this case the Li device presents NH independently of the scan rate applied. However, in the case of No-Li device, large values of IH are detected at higher scan rate, and also at the lowest scan rate of 10 mV s$^{-1}$ a clear inverted hysteretic behaviour appears (Fig. 2c). The variation of the photovoltage with the scan rate is also notorious (Fig. 2d). Regarding the open circuit potential, Li sample keeps $V_{\infty}$ almost...
constant independently of the scan rate. However, in the absence of lithium, the photovoltage increases sharply from 10 to 50 mV s\(^{-1}\) and then remains nearly stable. This effect can be explained as follows: the slow scan rate allows the intrinsic ions to pile up and interact with the cathode/perovskite interface, increasing the surface recombination and consequently, reduces the open-circuit potential. Furthermore, the photovoltage value is lower for the No-Li device at any scan-rate, due to the major surface recombination, as previously reported. These results evidence that the appearance of these features, even being deleterious for the solar cells, can also be found in a good cells, just letting the intrinsic ions to accumulate and interact with the surface, recording the CV at a scan rate slowly enough to allow it.

To check that these results are not only a consequence of the specific conditions of interfacial doping in bromide cells, we decide to perform the same analysis in the most widely used MAPbI\(_3\) perovskite. In these standard cells under normal working conditions, there is no presence of IH or negative capacitance, thus a controlled deleterious effect has to be involved. Moisture is one of the main degradation factors in PSCs, closely related with hysteretic behaviours. Thus, a number of IS and CVs measurements were performed on MAPbI\(_3\) cells under different %RH (see Fig. 3 and SI for the experimental part of the procedure).

**Figure 3.** Measurements of regular MAPbI\(_3\) solar cells (FTO/TiO\(_2\)/m-TiO\(_2\)/MAPbI\(_3\)/spiro-OMeTAD/Au) at different relative humidity (0, 30, 45 and 60 %), under dark conditions. (a) Cyclic voltammetry with their (d) hysteresis index defined by eqn. (1), calculated at 0.75 V. (c) Impedance plots with (d) the corresponding capacitance
spectra, at 0.95 applied voltage. Solid lines correspond to fits using the equivalent circuit detailed in Fig 1c.

In Fig. 3a we show the cyclic voltammetry corresponding to the different %RH exposure. From Fig. 3a the evolution of hysteretic behaviour is clear: a switching from NH to IH is produced when moving from dry conditions to high humidity. For the best of our knowledge, there is not an equivalent definition of hysteretic index for dark conditions in literature, at least in the perovskite field. Then, an approach has been made following the eq. 3 for dark hysteresis index (DHI):

$$DHI(V_R) = \frac{I_{RS(V_R)}}{I_{FS(V_R)}} - 1$$

(3)

were $I_{RS}$ and $I_{FS}$ are the current-density at the reference voltage $V_R$, established in 0.75 V as representative voltage, which is close to the maximum power point voltage under 1 sun (See Fig. S11). As it can be observed in Fig. 3b, a sequentially decrease in the DHI takes place, from high positive values corresponding to a big NH, reducing the positive hysteresis while the %RH is increased, and finally reaching a negative value at 60% RH corresponding to an IH response.

In Fig. 3c it is shown the impedance response of the different cells measured at 0.95V. The imaginary part of the impedance ($Z''$) spectres corresponding to 0 and 30% RH do not become negative at any frequency. But when we increase the humidity up to 45% RH positive values of $Z''$ appear at low frequencies, leading to an arc below the $Z'$ axis. Furthermore, when the humidity reaches 60% RH, this arc become bigger, evidencing the negative capacitance trend (Fig. 3d). The quantification of these results applying the EC of Fig. 1b is shown in Table 2 (See table S1 for the complete fitting parameters).

| Cells      | $R_{rec}$ ($\Omega \cdot \text{cm}^2$) | $L$ ($\text{H} \cdot \text{cm}^2$) | $R_L$ ($\Omega \cdot \text{cm}^2$) | $\tau_{kin}=L/R_L$ (s) |
|------------|---------------------------------------|-----------------------------------|-----------------------------------|------------------------|
| 45% RH     | 38                                    | $2.1 \times 10^4$                | 860                               | 24                     |
| 60% RH     | 29                                    | $3.0 \times 10^3$                | 69                                | 44                     |

Table 2. Extracted parameters from IS for the samples under moisture conditions showing negative capacitance.

For both moisture conditions, the $R_{rec}$ and $R_L$ parameters show clear differences. The lower values correspond to the higher %RH, which agrees with higher recombination rates. This aggravate the degradation of the cells, leading to a worst optoelectronic performance. On the other hand, the kinetic constant for both conditions present similar values in the range of $10^0$ – $10^2$ s, which agrees with large interactions between accumulated ions and the surface. The differences in the recombination resistances with similar kinetic values associated, indicate that the mechanism responsible for the increased recombination rates is the same: ionic-surface interaction. The chemical degradation of perovskite material and TiO$_2$ by %RH, leads to a major density of defects,
which can interact with the accumulated ions at the ESL/perovskite interface. This interaction leads to an additional recombination process, represented by $R_L$, produced between the TiO$_2$ and the perovskite material. The total low frequency resistance is reduced, bringing negative capacitance and IH behaviours as consequence. Then, a straight forward relation between the %RH and the appearance of negative capacitance and IH is demonstrate.

In Fig. 4a and 4b the kinetic time and recombination resistance associated to it are represented for all samples with respect to the applied bias. The kinetic times are in the same range for No-Li and moisture exposed devices, indicating that in both cases accumulated ions have strong interactions at the ESL/perovskite interface dominating the response of the CV. For Li devices, $\tau_{\text{kin}}$ is one order of magnitude lower, yielding to a behaviour dominated by ionic diffusion.

**Figure 4.** Kinetic constants (a) and recombination values (b) versus applied bias corresponding to all samples analysed. It is shown how the kinetic values and recombination resistances decrease with the applied voltage. Black circles and red triangles correspond to Li and No-Li samples, respectively; green squares and yellow diamonds to iodide samples under 45 %RH 65 %RH, respectively. (c) Schematic diagram of the mechanisms occurring at times lower than $\tau_{\text{kin}}$. Black and white spheres represent electron and holes, respectively. Blue spheres represent ionic vacancies migrating...
towards the ESL/perovskite interface. (d) Shows the surface accumulation and binding of ions responsible of the large $\tau_{\text{kin}}$, favouring interfacial electronic recombination processes as well.

The origin of the negative capacitance and IH is explained in Figs. 4c and 4d. At times lower than the kinetic constant, the intrinsic ions can migrate towards the ESL/perovskite interface and accumulate, but not interact. This brings normal hysteresis and positive capacitive responses (Fig. 4c). However, at times higher than $\tau_{\text{kin}}$, the accumulated ions are allowed to interact with the surface and their movement to follow changes in the applied potential becomes delayed.

In summary, we have demonstrated experimentally the specific relationship between negative capacitance and IH. The validity confirmation of the SPM brings the opportunity to reveal the same microscopic origin for both behaviours. The ionic accumulation and interaction with surface defects at the ESL, entails a recombination process between the metal oxide and perovskite material with an associated kinetic constant in the range of $10^0$ – $10^3$ s. This slow kinetic correlates with the appearance of inverted hysteresis at slow scan rates with lower photovoltages associated, consequence of an increased recombination process. Our findings reveal that the correlation between the frequency and time domain constants governing the IS and cyclic voltammetry response respectively, can be used to detect the recombination processes consequence of the slower dynamics affecting the PSCs.

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