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## **Transition from capacitive to inductive hysteresis: A neuron-style model to correlate I-V curves to impedances of metal halide perovskites**

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### **Abstract**

Metal halide perovskite (MHP) devices often show different types of hysteresis in separate voltage domains. At low voltage the impedance response is capacitive, and the cell gives regular hysteresis. At high voltage the hysteresis is inverted corresponding to an inductive response that causes a negative capacitance feature. We calculate the hysteresis current due to a chemical inductor model, and we show that the current is inversely proportional to the voltage scan rate. We formulate a general dynamical model for the solar cell response in the style of neuronal models for the action potential, based on a few differential equations. The model allows to track the transition from capacitive to inductive properties, both by impedance spectroscopy, and current voltage measurements at different voltage sweep rates. We obtain a correlation of the time constants for the capacitor and the inductor. We interpret the origin of the low frequency features in terms of the ion-controlled surface recombination. This explains the strong correlation of the low frequency capacitance and inductor, as both originate from the same mechanism. The methodology derived in this paper provides great control over the dynamic properties of metal halide perovskite solar cells, even in cases in which there are qualitative changes of the solar cell current-voltage response over a broad voltage range.

## 1. Introduction

Metal halide perovskites (MHP) have established a new photovoltaic (PV) technology for large solar energy conversion efficiencies with low cost, solution processed materials.<sup>1-4</sup> The MHP can be described as  $ABX_3$  where A = monovalent cations (i.e. methyl ammonium – MA, formamidinium, FA), B = divalent cations (i.e.  $Pb_2^+$ ) and X = halide anions (i.e. I). It is possible to use combinations of cations (MA, FA, Cs, and Rb) and anions (I, Br) to modify the band gap, efficiency and stability for different types of applications.<sup>5-7,8</sup> For example,  $MAPbBr_3$  forms a semiconductor with a wide bandgap (2.3 eV) useful for tandem solar cell in combination with Si.<sup>9,10</sup> In addition, the external interfaces play a very important role, and improvement of the charge extraction layers have enhanced the charge external collection and stability of the devices.<sup>11,12</sup>

MHP semiconductors show mixed ionic-electronic conduction in which a significant ionic conductivity exists in addition to the electronic photoconductivity.<sup>13-16</sup> These effects cause intrinsic memory effects (hysteresis) in current–voltage ( $I - V$ )<sup>17-26</sup> that lead to substantial differences in the forward and reverse scan currents and permanent resistive changes. By different empirical methods, it has been possible to minimize hysteresis effects in perovskite solar cells.<sup>27-29</sup> However, hysteresis persists in recent high performance configurations, such as tandem solar cells.<sup>30-33</sup> In addition, hysteresis and memory effects allow the storage of information by modification of device conductivity. This can be exploited in memristors<sup>34-36</sup> and artificial synapse devices<sup>37,38</sup> in which MHPs are used for non-optoelectronic applications related to memory storage and neuromorphic computation.<sup>39-41</sup>

Impedance Spectroscopy (IS) consists of the electrical measurement of the device at a steady state potential  $V$  by a small perturbation of current-to-voltage at varying angular frequency  $\omega$ . It is a central technique for the characterization of PV cells and electrochemical devices.<sup>42,43</sup> The knowledge about the system properties is represented by an equivalent circuit (EC), in which elements change according to the external conditions. Extensive studies of IS of MHP<sup>44-50</sup> have provided a basic picture of shape of spectra and EC models. These results show that the IS description of a MHP measured over a broad voltage range undergoes transformations in which some elements appear and dominate the impedance spectra while others lose relevance. There is a variety of reasons for this, such as that elements show an exponential dependence on bias voltage causing large changes of their values. Another one is that elements may be truly activated at some voltage, as observed in the onset of a large current in memristors.<sup>51, 36</sup>

It has been remarked that hysteresis and impedance are closely related properties, since frequency and time domain response are intimately connected.<sup>25,52</sup> However a quantitative analysis of this assertion in complex cases has not been presented before. This paper uses different tools that have been derived in recent years to provide a more complete methodology that addresses intricate changes of hysteresis and impedance response often found in perovskite solar cells. We aim to make a modelistic description of  $I - V$  curves that change at different scan rates, compatible with the impedance spectroscopy

properties.

There are different studies to this problem based on drift-diffusion simulations and related approaches.<sup>53-61</sup> Here we introduce a different complementary approach, in which the model is formed by a small number of equations, that can describe consistently the different techniques: the  $I - V$  curves at different scan rates, and other large perturbation methods such as the response to large voltage or illumination steps,<sup>62</sup> in the one hand, and in the other hand the small perturbation measurements like IS, IMPS, IMVS.<sup>52</sup> Such a model provides an outstanding tool to correlate the different measurements, and to make predictions of solar cell characteristics based on a few fast measurement characterization.

In particular the model should have the following goals.

- (1) Explain the tendencies of hysteresis in current-voltage and the impedance spectroscopy with a single unified model that contains only a few number of parameters that account for the dominant properties of the device.
- (2) Identify and explain correlations of the impedance parameters.
- (3) Explain why the inductive behaviour (negative capacitance) appears at high voltage in halide perovskite solar cells.
- (4) Explain why it is observed in some cells and not in others.

We use as inspiration the models of neuron theory that describe extraordinarily complex phenomena including spiking, bifurcation and potentiation with just a few nonlinear differential equations (from two to four).<sup>63-65</sup> Recently these models for the time domain responses have been put into correspondence with the impedance spectroscopy properties.<sup>66,67</sup> The same methodology has been applied to halide perovskite memristors.<sup>51,68</sup>

Here we address the much broader problem of hysteresis and impedance properties of halide perovskite solar cells. We show general properties of the transformation of EC elements along the voltage changes in MHP solar cells. In order to summarize the available knowledge and tools we present in the next section a summary of the properties of hysteresis. Then we show the experimental results. Methylammonium lead bromide (MAPbBr<sub>3</sub>) solar cells are selected as they present a manifest transformation from capacitive response at low voltage to a large inductor feature at high voltage.<sup>69</sup> The study in the dark conditions produces highly controlled conditions as compared to under illumination, which facilitates model validation. Furthermore, it avoids the photoinduced effects as the increased ionic conductivity and photo-degradation. Then, we build the model to explain quantitatively the changing properties of hysteresis in relation with the variation of EC properties. We track the evolution of parameters and we find unexpected links between them. We provide a physical interpretation and finish with some conclusions.

## **2. Capacitive and inductive hysteresis in halide perovskites**

### **2.1. Hysteresis and stability**

Hysteresis is obtained when measuring the current of the solar cell under a voltage sweep at a constant velocity. The  $I - V$  curves become separated in the forward and reverse as shown in Fig. 1a and b. Hysteresis of current-voltage is a transient effect.<sup>17-24</sup> By waiting a sufficiently long time the current can be stabilized, and methods are proposed to establish the power conversion efficiency independent of hysteresis effects.<sup>70-73</sup> But in a reasonable dynamic measurement a divergence is often found between forward and reverse curves. It happens when the internal dynamic timescales of the device intersect the time duration of the measurement. Note that the forward photocurrent is smaller in the Fig. 1a than the reverse current (normal hysteresis) and conversely in the Fig. 1b (inverted hysteresis).

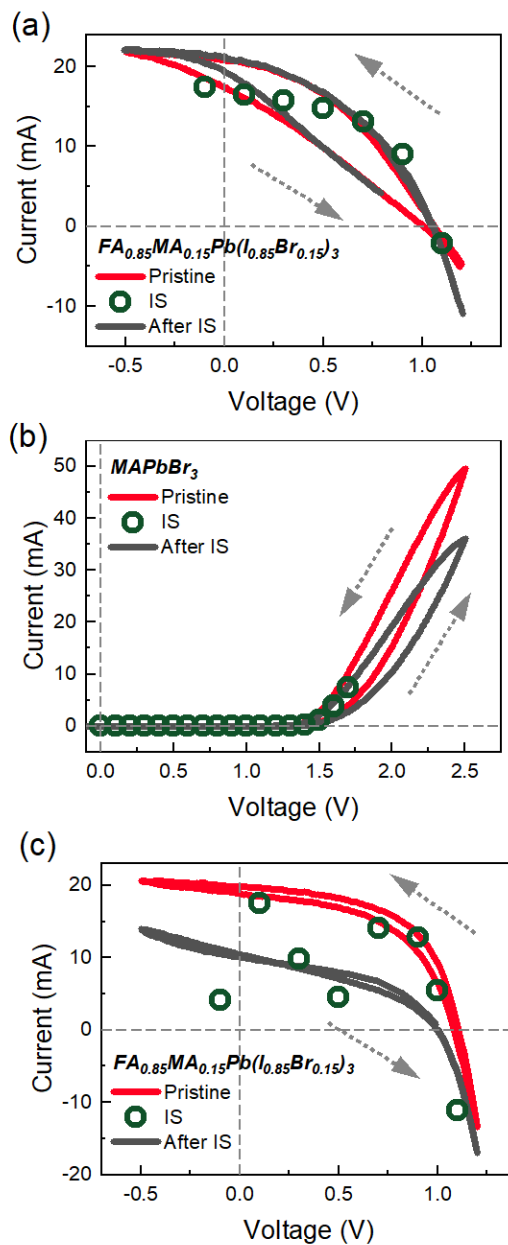


Fig. 1: Representative  $I$ - $V$  response of halide perovskite solar cells measured at 50 mV/s, showing the pristine as-prepared device and after IS measurements. (a) Mixed halide perovskite solar cells under illumination. (b)  $MAPbBr_3$  in the dark. (c) Mixed halide perovskite solar cells under illumination. The current extracted during the IS measurement is shown in circles to determine the correspondence of the electrical measurements  $j$ - $V$  and IS.

It is well known that one has to be cautious in MHP characterization. There are many types of transient phenomena in halide perovskites. These effects may be caused by the sample being away from equilibrium at the beginning of the measurement, or when a fresh

sample is aiming at operation stability.<sup>74</sup> One example is the famous “pretreatment effect” in which one can produce favorable or deleterious effect according to initial biasing.<sup>75</sup> Pockett et al. showed that rapidly changing initial features of a carbon-based perovskite solar cell are captured consistently by TPV and IMVS techniques.<sup>76</sup> An example of a solar cell that is changing the characteristics by voltage cycling in the dark is shown in Fig. 1b, and under illumination in Fig. 1a and 1c. These properties haven been attributed to the slow ion transit effects that create uncompensated electrical fields or modify the interfaces by surface polarization effects.<sup>61,77</sup>

Fig. 1a shows a robust and reproducible solar cell where current-voltage under voltage sweep and the current measured during IS measurement agree. In this paper we are interested in an initial situation that has been stabilized, so that the results of small or large perturbation measurements can be associated entirely to the applied signal and not to hidden memory effects or sample-drift effects. Based on this assumption, we can attribute an EC response to different equilibrated stages of the dynamics, and the full evolution in a voltage excursion can be reasonably treated by parameters that depend on the voltage.

## 2.2.Capacitive hysteresis

The first well-identified hysteresis effect in halide perovskite was the description of capacitive current by Garcia-Belmonte and coworkers, see Fig. 2 that shows the results associated to the low frequency capacitance of halide perovskites.<sup>78</sup> Capacitive current effects are very common in electrochemical devices.<sup>79,80</sup> Capacitive hysteresis for diodes in the dark occur with a forward current that is larger than the reverse current as shown in Fig. 2a-b. The capacitive current is proportional to the scan rate, Fig. 2c, and it changes sign when inverting the scan direction, producing the characteristic square shape of Fig. 2d. Capacitive hysteresis was often observed in other types of devices such as dye-sensitized solar cells.<sup>81</sup>

Fig. 3 shows the correlation of the low frequency capacitance with the amount of hysteresis in MHP solar cells with different types of contacts.<sup>21</sup> The huge hysteresis response in Fig. 3a, is due to the large capacitive effect of TiO<sub>2</sub> contact, shown in Fig. 3d and e. In contrast, for the inverted structure the  $I - V$  hysteresis and the equilibration time is decreased, Fig. 3b-c. In the  $I - V$  illuminated characteristic of the solar cell in Fig. 3a, the increasing recombination current at large voltage turns more negative, hence in this representation capacitive hysteresis the forward current becomes smaller than the reverse current.

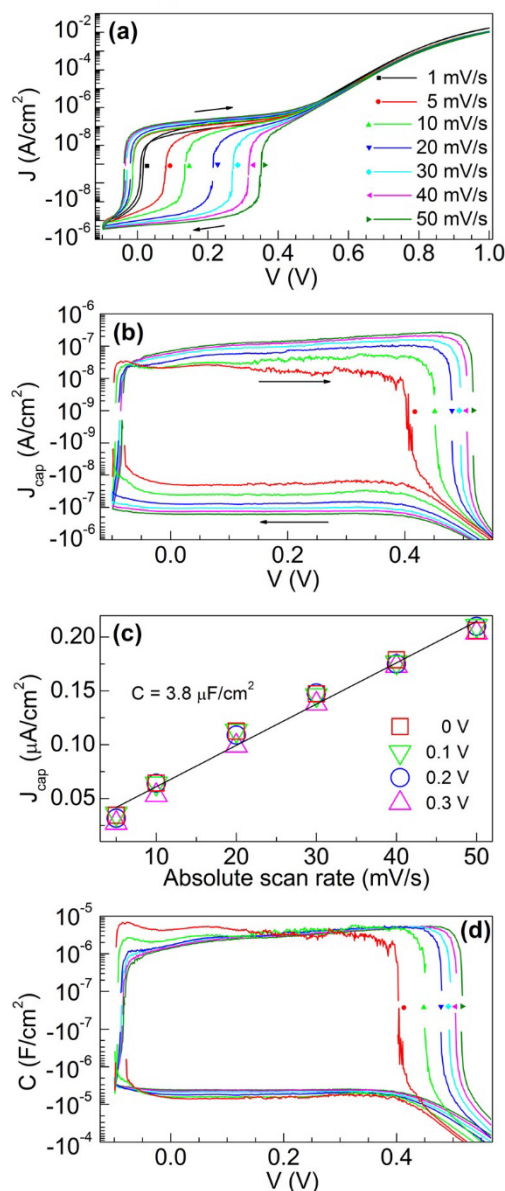


Fig. 2. Measurements of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solar cell in the dark. (a) J–V curves at different scan rates as indicated with logarithmic scaled currents. (b) Capacitive current density  $J_{\text{cap}}$  extracted from J–V curves. (c) Current proportional to the scan rate at different applied voltages. (d) Capacitance calculated from  $J_{\text{cap}}s^{-1}$  at different scan rates as in (a). Reproduced from Ref. <sup>78</sup>. Reproduced from Almora, O.; Zarazua, I.; Mas-Marza, E.; Mora-Sero, I.; Bisquert, J.; Garcia-Belmonte, G. Capacitive dark currents, hysteresis, and electrode polarization in lead halide perovskite solar cells, *J. Phys. Chem. Lett.* **2015**, *6*, 1645-1652. Copyright 2015 American Chemical Society.

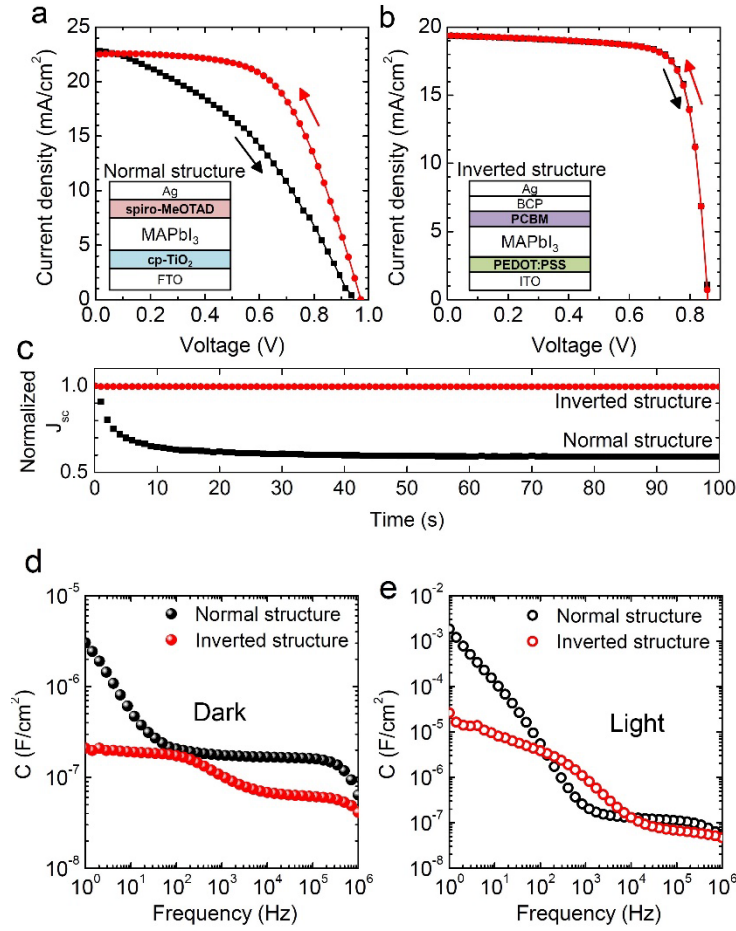


Fig. 3. a)  $J$ - $V$  hysteresis of the cp-TiO<sub>2</sub>/MAPbI<sub>3</sub>/spiro-MeOTAD (normal) structure and b), the PEDOT:PSS/MAPbI<sub>3</sub>/PCBM (inverted) structure. During  $J$ - $V$  scan, the current was acquired for 100 ms after applying a given voltage. c) Normalized time-dependent short-circuit current density ( $J_{sc}$ ) of the normal and the inverted structures. Open-circuit condition under one sun illumination was maintained before measuring  $J_{sc}$ . Capacitance-frequency ( $C$ - $f$ ) curves (d) under dark and (e) one sun illumination at short-circuit condition (bias voltage = 0 V). Reproduced from Kim, H.-S.; Jang, I.-H.; Ahn, N.; Choi, M.; Guerrero, A.; Bisquert, J.; Park, N.-G. Control of I-V Hysteresis in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskite Solar Cell, *J. Phys. Chem. Lett.* **2015**, *6*, 4633–4639. Copyright 2015 American Chemical Society.

For the modeling of capacitive hysteresis we use the following equation

$$I_{tot} = C_m \frac{dV}{dt} + I_b(V) \quad (1)$$

Here,  $I_{tot}$  is the total current,  $V$  is the voltage across the device,  $C_m$  is the capacitance and  $I_b$  is a conduction current that may have different types of values. For an ohmic current with a constant resistance  $R_b$  we have

$$I_b(V) = \frac{V}{R_b} \quad (2)$$



For a recombination current in a solar cell diode at forward bias

$$I_b(V) = I_{b0} e^{qV/m_b k_B T} \quad (3)$$

Here  $I_{b0}$  is a constant prefactor,  $q$  is the elementary charge,  $k_B$  is the Boltzmann's constant,  $T$  the absolute temperature, and  $m_b$  is an ideality factor.<sup>82-84</sup> For practical reasons we define the ideality factor with dimension of voltage

$$V_b = \frac{m_b k_B T}{q} \quad (4)$$

Then Eq. (3) can be expressed

$$I_b(V) = I_{b0} e^{V/V_b} \quad (5)$$

For a voltage sweep measurement at velocity  $v_r$  we have

$$V = V_0 + v_r t \quad (6)$$

Then Eq. (1) becomes

$$I_{tot}(V) = C_m v_r + I_{b0} e^{V/V_b} \quad (7)$$

The capacitive current is proportional to the scan rate, as commented earlier. In a forward scan the capacitive current is added to the diode exponential curve; while subtracted in the reverse scan (negative  $v_r$ ). This is the feature of capacitive hysteresis. The representation of Eq. (7) is shown in Fig. 4a and b. The properties of the current describe very well those reported in Fig. 2.

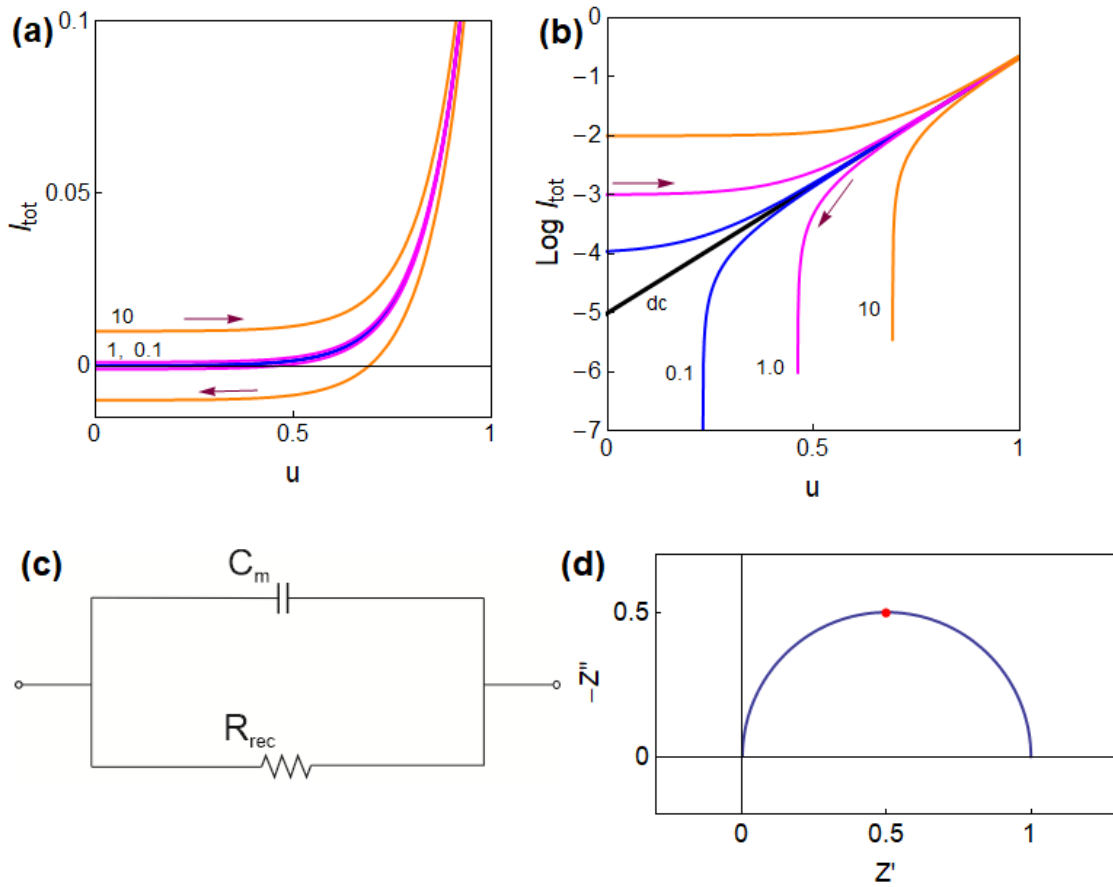


Fig. 4. Simulation of hysteresis for a diode characteristic in the dark with a constant capacitor in (a) linear and (b) logarithmic current  $I_{tot}$  (in  $A cm^{-2}$ ) as a function of voltage  $u$  (in V). In (b) only positive values of current are shown. Parameters  $C_m = 0.001 F cm^{-2}$ ,  $i_{b0} = 10^{-5} A cm^{-2}$ ,  $V_b = 0.10 V$ . The scan rate  $v_r$  for each curve is indicated in  $V s^{-1}$ . The dc line of equilibrium is marked by a black line. (c) Equivalent circuit for small ac impedance. (d) Complex plane impedance spectrum for the parameters  $C_m = 0.001 F cm^{-2}$ ,  $R_{rec} = \Omega cm^2$ . The red point is at the characteristic frequency  $\omega_m = 1/\tau_m = 1/R_{rec}C_m$ .

### 2.3. Capacitive impedance

In the impedance spectroscopy measurement we use a sinusoidal small perturbation  $\hat{V}(t)$  over a steady state  $\bar{V}$ ,  $V = \bar{V} + \hat{V}(t)$ . For the small perturbation components Eq. (1) becomes

$$\hat{I}_{tot} = C_m \frac{d\hat{V}}{dt} + \frac{1}{R_{rec}} \hat{V} \quad (8)$$

where the recombination resistance is, by Eq. (3),

$$R_{rec} = \left( \frac{\partial I_b}{\partial V} \right)^{-1} = \frac{V_b}{I_{b0}} e^{-V/V_b} \quad (9)$$

Taking the Laplace transformation of Eq. (8) we obtain

$$\hat{I}_{tot} = \left( C_m i\omega + \frac{1}{R_{rec}} \right) \hat{V} \quad (10)$$

Therefore the impedance is

$$Z = \frac{\hat{V}}{\hat{I}_{tot}} = \left( C_m i\omega + \frac{1}{R_{rec}} \right)^{-1} \quad (11)$$

This last result is a parallel RC connection EC, Fig. 4c, that forms a semiarch in the complex impedance plot, Fig. 4d. The associated time constant is  $\tau_m = R_{rec}C_m$ . The elementary EC of a solar cell<sup>43,85</sup> has the same structure as Eq. (11) but  $C_m$  is interpreted as a chemical capacitance that depends exponentially on the potential.<sup>86</sup>

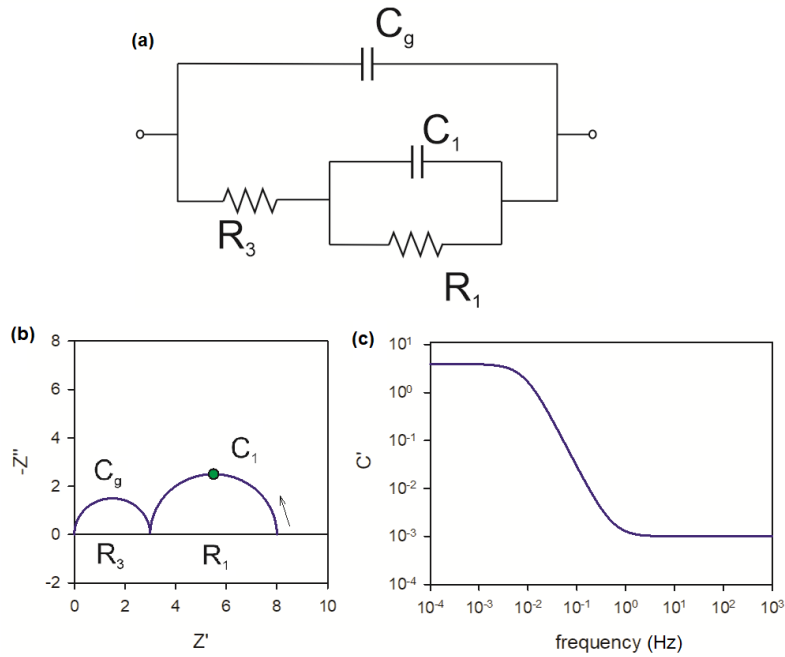


Fig. 5. (a) Equivalent circuit and (b) complex plane impedance spectrum (impedances in  $\Omega$ ). The arrow indicates the direction of increasing frequency. The point indicates the angular frequency  $1/\tau_1 = 1/R_1C_1$  (c) Real part of the capacitance vs. frequency. Parameters  $R_1 = 5 \Omega$ ,  $R_3 = 3 \Omega$ ,  $C_1 = 10 \text{ F}$ ,  $C_g = 10^{-3} \text{ F}$ .

The characteristic impedance patterns of halide perovskites have been recently summarized.<sup>43</sup> The simplest behaviour found experimentally is given by two arcs as shown in Fig. 5b and the related capacitance step in the frequency plot of Fig. 5c. It is described by an EC formed by two resistances and two capacitors, Fig. 5a. We denote the low frequency arc resistance as  $R_1$  and the high frequency resistance as  $R_3$ .<sup>87</sup> The meaning of the resistances depends on the illumination conditions, but the low frequency arc usually relates to the perovskite/contacts interface (ion migration, accumulation and recombination).<sup>88</sup> hence, the capacitance  $C_1$  is a surface capacitance related to ionic-electronic phenomena, and  $C_g$  is a dielectric geometrical capacitance. The parallel connection of  $R_1$  to  $C_1$  generates the low frequency arc. Typical experimental parameters

as a function voltage are shown in Fig. 6.

It should be noted that Fig. 5a cannot be obtained with a simple extension of Eq. (1). At least two voltages in series need to be used.<sup>25</sup> Such generalization will be described below.

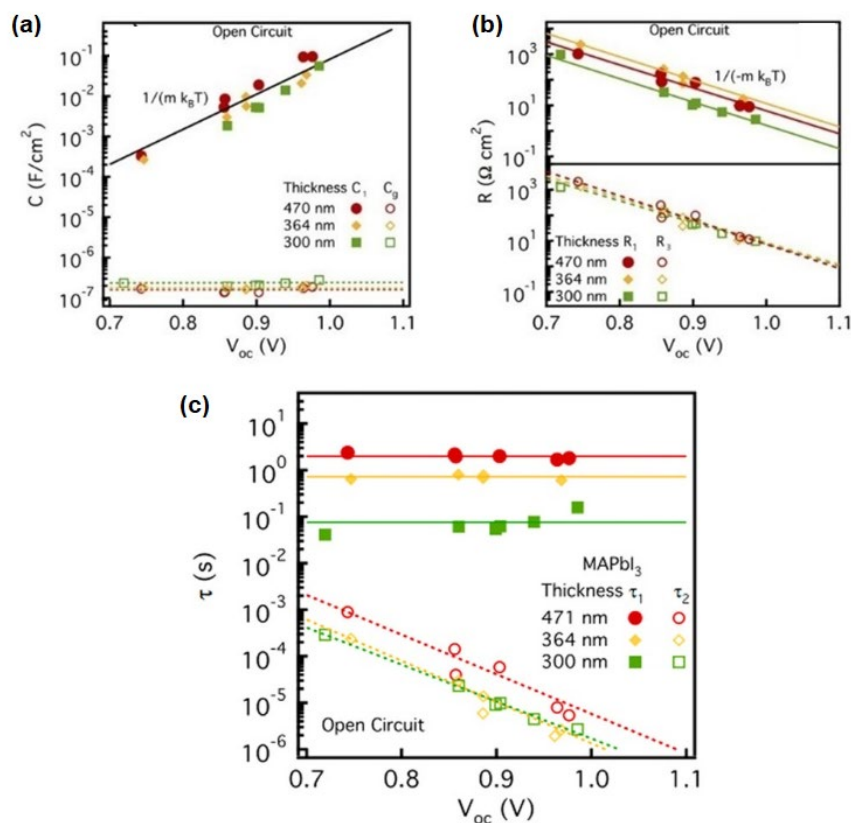


Fig. 6. Impedance spectroscopy results of a planar structure FTO/TiO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro-OMeTAD/Au solar cell under open-circuit conditions. Solid lines correspond to fits using the simplified EC of Fig. 5a. (a) Capacitances  $C_1$  (solid circles) and  $C_g$  (empty circles) and (b) resistances  $R_1$  (solid circles) and  $R_3$  (empty circles). Solid lines (low-frequency arc) and dashed lines (high-frequency arc) correspond to linear fits. In panel a,  $m = 1.90 \pm 0.17$ , and in panel b,  $m = 1.94 \pm 0.08$ . (c) Characteristic response time calculated from the RC product, for different cell thickness. Solid circles  $R_1C_1$ , empty circles  $R_3C_g$ . Reproduced from Zarazua, I.; Han, G.; Boix, P. P.; Mhaisalkar, S.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; Garcia-Belmonte, G. Surface Recombination and Collection Efficiency in Perovskite Solar Cells from Impedance Analysis, *J. Phys. Chem. Lett.* **2016**, *7*, 5105-5113. Copyright 2016 American Chemical Society.

Fig. 6 shows characteristic results of the fitted parameters of the model of Fig. 5a under open-circuit conditions. The geometric capacitance  $C_g$  is basically constant, but the other three parameters in the EC show an exponential dependence with the voltage,<sup>83,89</sup> and they

may be expressed as

$$R_1(V) = R_{10}e^{-qV/m_1k_B T} \quad (12)$$

$$R_3(V) = R_{30}e^{-qV/m_3k_B T} \quad (13)$$

$$C_1(V) = C_{10}e^{qV/m_C k_B T} \quad (14)$$

Here  $m_i$  ( $i = 1, 3$ ) is an ideality factor for each resistance parameter and  $m_C$  for the low frequency capacitance. In the case of band-to-band recombination it is  $m_i = 1$ .<sup>90</sup> In Fig. 6 it is obtained  $m_i \approx 2$  in all the cases, indicating a recombination resistance. On the other hand  $C_1$  cannot be suitably interpreted as a chemical capacitance.<sup>91</sup>

A strong correlation occurs in the low frequency elements,  $m_C \approx m_1$ , so that the response time for the slow relaxation phenomenon is a constant independent of the voltage,<sup>88,89,92</sup>

$$\tau_1 = R_1 C_1 \quad (15)$$

Eqs. (12)-(15) provide a suitable reference for the construction of a more general model later in this work.

#### 2.4. Inductive hysteresis

Fig. 7b shows the typical capacitive current in a dark perovskite diode, already discussed before. A different type of behaviour that produces non-capacitive currents as shown in Fig. 7c was identified by Garcia-Belmonte and coworkers.<sup>22</sup> In the region of separation of the current-voltage curves the forward current is smaller than the reverse current. In consequence the current in a voltage sweep changes in the opposite way to the capacitive variation. Fig. 7a provides a summary of the different types of currents.<sup>93</sup> This behaviour was observed in illuminated solar cells,<sup>26</sup> as shown in Fig. 8, and termed Inverted hysteresis.<sup>24,26,54,55</sup> This feature is found in many perovskite devices, including solar cells and memristors.<sup>36</sup>

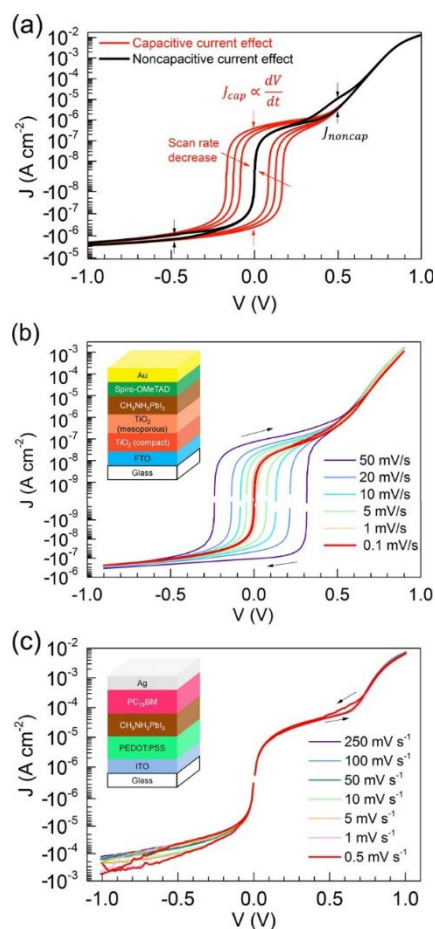


Fig. 7. Dark J–V curves at room temperature in logarithm scaled current representation: (a) simulation illustrating different hysteretic effects as a function of the scan rate during the bias sweep in both senses; experimental data from (b) RegularMeso (FTO/cTiO<sub>2</sub>/mTiO<sub>2</sub>/MAPbI<sub>3</sub>/spiro-OMeTAD/Au) and (c) Inverted (ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/Ag) perovskite solar cells at different scan rates with corresponding structures sketched in the insets. Reproduced from Almora, O.; Aranda, C.; Zarazua, I.; Guerrero, A.; Garcia-Belmonte, G. Noncapacitive Hysteresis in Perovskite Solar Cells at Room Temperature, *ACS Energy Lett.* **2016**, *1*, 209-215. Copyright 2016 American Chemical Society.

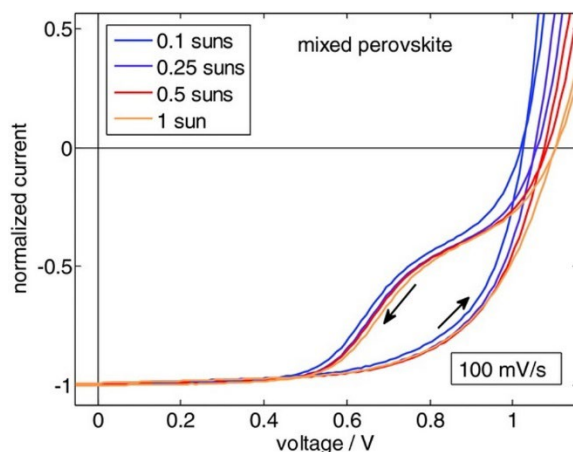


Fig. 8. Normalized (at  $-0.2$  V) current–voltage curves of a mixed perovskite device measured at different illumination intensities indicating that the S-shape hysteresis is independent of photogenerated charges. Reproduced by permission from Tress, W.; Correa Baena, J. P.; Saliba, M.; Abate, A.; Graetzel, M. Inverted Current–Voltage Hysteresis in Mixed Perovskite Solar Cells: Polarization, Energy Barriers, and Defect Recombination, *Adv. Energy Mater.* **2016**, *6*, 1600396. Copyright 2016 Wiley.

For the description of inverted hysteresis we formulate a model that has been denoted a “chemical inductor”.<sup>94</sup> Chemical inductor is a general denomination for a class of dynamical models that occur in different types of systems (corrosion, batteries, neurons, electrocatalysis, memristors). These dynamical models produce a formal inductive response in impedance and transients *without* the occurrence of an electromagnetic (induction) effect. The chemical inductor is *not* related to the previously mentioned chemical capacitance, that describes a charge accumulation by the increase of the chemical potential.<sup>14</sup>

Here we apply the chemical inductor to the solar cell.<sup>94</sup> We modify Eq. (1) as follows

$$I_{tot} = C_m \frac{dV}{dt} + i_d \quad (16)$$

Here,  $i_d$  is a new variable, a current across the solar cell device that does not respond instantaneously to the applied voltage  $V$ . It is regulated by the equation

$$\tau_d \frac{di_d}{dt} = I_a(V) - i_d \quad (17)$$

$\tau_d$  is a time constant parameter for the delay of the current.  $I_a(V)$  in Eq. (17) is the dc current that gives the steady-state dependence. Indeed, in equilibrium condition we have from the Eqs. (16) and (17)

$$I_{tot}(V) = i_d = I_a(V) \quad (18)$$

Throughout this paper the uppercase currents as  $I_a(V)$  are closed expressions of current-voltage, while the lowercase  $i_d$  is a variable current determined by the set of differential equations.

To complete the solar cell model we use for  $I_a(V)$  the diode recombination current of Eq. (5). The current for a constant sweep rate is given by the equations

$$I_{tot} = C_m v_r + i_d \quad (19)$$

$$V_R \frac{di_d}{dV} + i_d - I_{b0} e^{V/V_b} = 0 \quad (20)$$

where we have defined the sweep velocity parameter as

$$V_R = \tau_d v_r \quad (21)$$

The differential equation (20) is expressed as a function of voltage and can be integrated. For the initial condition  $i_d(V = V_0) = i_{d0}$  we obtain

$$i_d(V) = \frac{V_b}{V_b + V_R} I_{b0} e^{V/V_b} + \left( i_{d0} - \frac{V_b}{V_b + V_R} I_{b0} e^{V_0/V_b} \right) e^{(V_0 - V)/V_R} \quad (22)$$

Consider the evolution of the first term in the right side (the second term is a transient related to the initial conditions). If the scan rate is slow  $V_R < V_b$  the equilibrium curve is not affected and there is not hysteresis. If the scan rate is fast  $V_R > V_b$  we obtain

$$i_d(V) = \frac{V_b}{V_R} I_{b0} e^{V/V_b} \quad (23)$$

We conclude that the current in inductive hysteresis is inversely proportional to the scan rate.

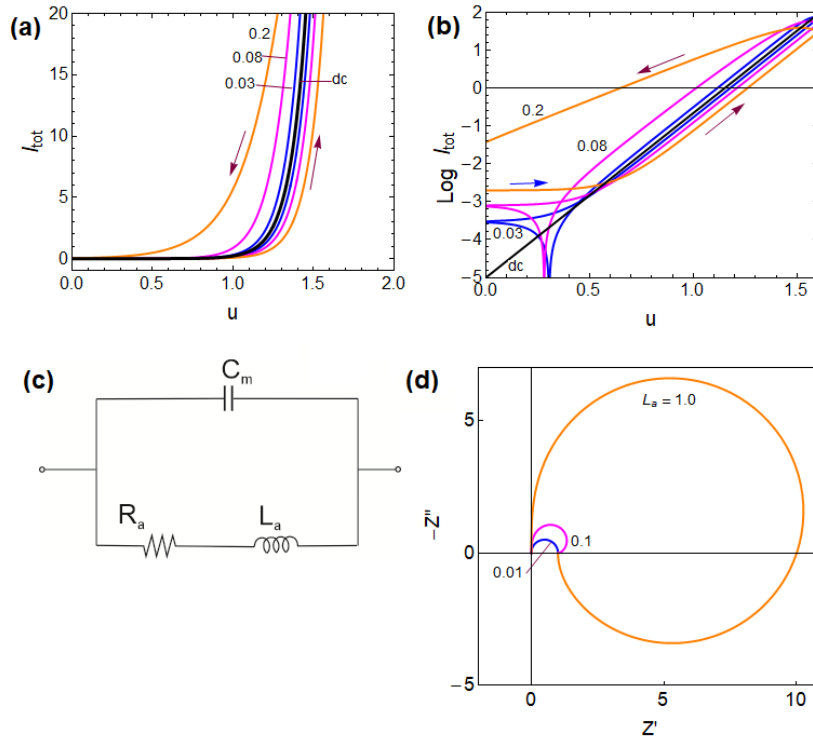


Fig. 9. Simulation of hysteresis for a diode characteristic in the dark with a constant capacitor and a chemical inductor in (a) linear and (b) logarithmic current  $I_{tot}$  (in  $\text{A cm}^{-2}$ ) as a function of voltage  $u$  (in V). In (b) the absolute values of current are shown. Parameters  $C_m = 0.01 \text{ F cm}^{-2}$ ,  $i_{b0} = 10^{-5} \text{ A cm}^{-2}$ ,  $V_b = 0.10 \text{ V}$ ,  $\tau_d = 1 \text{ s}$ . The scan rate  $v_r$  is indicated in  $\text{V s}^{-1}$ . The dc line of equilibrium is indicated by a black line. The blue arrow in (b) indicates a capacitive hysteresis region. (c) Equivalent circuit and (d) Impedance spectra for  $C_m = 0.1 \text{ F cm}^{-2}$ ,  $R_a = 1 \Omega$ ,  $L_a$  as indicated (H).



The total current due to the model of Eqs. (16)-(17) is obtained inserting Eq. (22) into Eq. (19). We observe in Eq. (23) that the transient inductive current is smaller than the equilibrium current on the forward scan, as shown in Fig. 9a and b. We conclude that the Eqs. (16)-(17) for the chemical inductor applied to the solar cell describe well the inverted hysteresis features.

In Fig. 9b we observe that the capacitive current of Eq. (19) dominates at low voltage. There is a crossing from capacitive to inductive current. We will describe this phenomenon more completely later based on the experimental results.

### 2.5. Impedance properties and inductive hysteresis

We analyze the small ac impedance of the chemical inductor model of Eqs. (16) and (17). We obtain the equations

$$\hat{I}_{tot} = C_m i\omega \hat{V} + \hat{i}_d \quad (24)$$

$$\tau_d i\omega \hat{i}_d = \frac{1}{R_a} \hat{V} - \hat{i}_d \quad (25)$$

where the resistance is

$$R_a = \left( \frac{\partial I_a}{\partial V} \right)^{-1} \quad (26)$$

We also introduce the chemical inductance

$$L_a = R_a \tau_d \quad (27)$$

and we obtain the impedance function

$$Z = \left( C_m i\omega + \frac{1}{R_a + L_a i\omega} \right)^{-1} \quad (28)$$

This analysis shows that the introduction of the delayed current  $i_d$  in Eq. (17) generates an inductor in series with the resistance in Eq. (28), cf. Eq. (11), so that the EC takes the form shown in Fig. 9c. The impedance of the inductor element is  $Z(\omega) = L_a i\omega$ . If the inductance is small it corresponds to a short circuit and barely changes the  $RC$  arc, as shown in the blue spectrum in Fig. 9d. But when the inductor is large it creates a big negative loop passing through the fourth quadrant, in the orange line of Fig. 9d, until it closes at the real axis of the complex impedance plane to the value of the dc resistance.

Based on the previous results we can establish a direct connection between the existence of an inductive branch in the EC of the impedance results, and the presence of inverted hysteresis in  $I - V$  curves. This has been exposed by Fabregat-Santiago and coworkers<sup>95</sup> and it has been explained in general terms by the chemical inductor model.<sup>25,94</sup> The inductor branch in the EC has a large impact in the solar cell performance as it reduces the recombination resistance and diminishes the power conversion efficiency.<sup>95,96</sup>

By the relation that we have established of noncapacitive currents (Figs. 7, 8, 9) with the inductor element, we may classify hysteresis in two distinct types: *capacitive hysteresis* (regular) and *inductive hysteresis* (inverted).

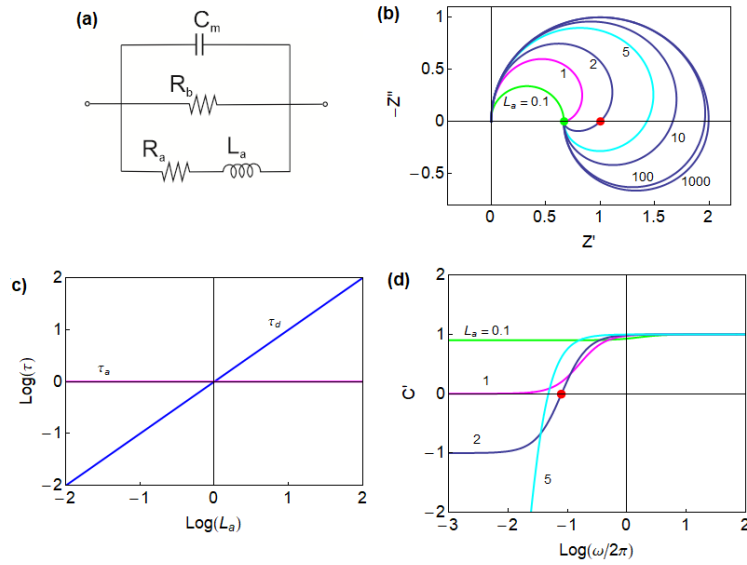


Fig. 10. (a) Equivalent circuit of the chemical inductor with capacitance and additional conductance. (b) Impedance spectra generated for  $C_m = 1 \text{ F}$ ,  $R_a = 1 \text{ } \Omega$ ,  $R_b = 2 \text{ } \Omega$  and  $L_a$  as indicated (H). The green dot is the dc resistance at  $\omega = 0$ , and the red dot is the resistance at the intercept when the spectrum crosses the real axis  $Z'$ . (c) The time constants  $\tau_a = R_a C_m$  and  $\tau_d = L_a/R_a$  for a varying inductance. The negative loop in the complex plane occurs when  $\tau_d > \tau_a$  is satisfied. (d) Representation of the real part of the capacitance as a function of frequency. The red point indicates the crossing of the horizontal axis.

## 2.6. Interpretation of inductive current and the negative capacitance

The chemical inductor is normally found in conjunction with additional conduction pathways, leading to an extended model. If the ohmic conduction Eq. (2) is included in the model of Eqs. (16) and (17), then Eq. (24) will take the form

$$\hat{I}_{tot} = C_m i \omega \hat{V} + \frac{\hat{V}}{R_b} + \hat{i}_d \quad (29)$$

When combined with Eq. (17), this more general model leads to the EC of Fig. 10a, which displays a variety of spectra shown in Fig. 10b. Again, the negative loop is observed for the larger values of the inductor parameter. Fig. 10c indicates that the crossing to the fourth quadrant occurs when the condition

$$\tau_d = \frac{L_a}{R_a} > \tau_a = R_a C_a \quad (30)$$

is satisfied.<sup>94</sup> In Eq. (29) the decrease of the current of the chemical inductor at increasing scan rate is limited by the parallel branch  $R_b$ .<sup>25</sup>

The complex capacitance  $C(\omega)$  is defined from the impedance as

$$C(\omega) = \frac{1}{i\omega Z(\omega)} \quad (31)$$

The real part of the capacitance is denoted  $C'(\omega) = \text{Re}[C(\omega)]$ . In the capacitive model of Fig. 5 the total capacitance is strictly positive, Fig. 5c. Fig. 10d shows an interesting phenomenon. When the loop in the fourth quadrant occurs in the complex plane impedance spectrum, the complex capacitance becomes negative. We arrive at the conclusion that the chemical inductor generates the feature of a negative capacitance at low frequency that has been extensively reported in halide perovskite solar cells.<sup>46,48,85,97-101</sup> The negative capacitance can be described by a *positive* chemical inductor that arises from the model of Eqs. (16) and (17). A truly *negative* capacitance parameter is not necessary.

The chemical inductor is generally obtained from the delay equation (17), as shown above.<sup>102</sup> But what is the interpretation of this delay effect in halide perovskites? Since the observation of the negative capacitance is widespread, many different explanations are provided. Some examples are the physical surface polarization model,<sup>77,103</sup> the changing environment of ions when their occupation at the double layer is modified by the photovoltage or polarization,<sup>92,104,105</sup> and the modulation of electronic conduction or recombination currents.<sup>53,97,99,100,106-111</sup> Most of these models have in common that a slow step of ionic displacement determines a faster step of electronic current recombination or transfer at the contact. These different models presented for negative capacitances and inductive hysteresis are compatible with the general operation principle of the chemical inductor. In fact the model of a chemical inductor originates from a voltage-gated ion channel in the neuron membrane originally described by Hodgkin and Huxley.<sup>63,64</sup> It describes well a voltage gated electronic current at the bulk of surface of the solar cell.<sup>53,98,108,109</sup> However, the molecular mechanism of this behavior has not been determined yet in perovskite solar cells.

### 3. Methods

#### 3.1. MAPBr solar cell fabrication

The fluorine-doped tin oxide (FTO) substrates were partially etched with zinc powder and 2 M HCl solution. The etched samples were brushed to mechanically remove the remaining residues of the etching procedure, then, were sonicated for 15 minutes each in deionized water with Hellmanex detergent solution, acetone, and isopropyl alcohol, respectively. The cleaned substrates are then dried using a nitrogen gun.

In preparation for the electron selective titanium dioxide (TiO<sub>2</sub>) compact layer deposition, the cleaned substrates were subjected to ultraviolet (UV) ozone treatment for 15 minutes to further remove organic contaminants on the substrate surface. The TiO<sub>2</sub> compact layer was then deposited via spray pyrolysis of 1:9 titanium (IV) diisopropoxide bis (acetylacetonate) (75% solution in 2-propanol, Sigma Aldrich) (60 % in acetylacetone):ultrapure ethanol at 450 °C with oxygen as carrier gas. The TiO<sub>2</sub> compact layer is then kept at 450 °C for 35 minutes before letting the samples cool down to room temperature. Another UV ozone treatment for 15 minutes was conducted to samples with

the TiO<sub>2</sub> compact layer to ensure ultraclean surface prior to the deposition of TiO<sub>2</sub> mesoporous layer. A 100  $\mu$ L diluted TiO<sub>2</sub> paste (Dyesol) (150 mg: 1 mL ultrapure ethanol) was then spin-coated onto the TiO<sub>2</sub> compact layer at a speed of 2000 RPM, acceleration of 2000 RPM/s with a duration of 10 s. The deposited TiO<sub>2</sub> mesoporous layer was annealed under ambient conditions at the following temperature, ramp time and dwell time: 370 °C with 40 minutes ramp for 20 minutes, 470 °C with 25 minutes ramp for 10 minutes, and 500 °C with 10 minutes ramp for 30 minutes.

Once the annealing treatment of the TiO<sub>2</sub> mesoporous layer was completed, the samples were cooled down to 150 °C and were immediately transferred inside a glove box in preparation for the MAPBr deposition. A 1.4 M MAPBr precursor solution is prepared using PbBr<sub>2</sub> (>98 %, TCI) and MABr (>99.99 %, Greatcell Solar) in 1:4 dimethylsulfoxide (DMSO) ( $\geq$ 99.9 %, Sigma Aldrich):N,N-dimethylformamide (DMF) (99.8 %, Sigma Aldrich) solution. A 50  $\mu$ L MAPBr perovskite solution was statically spin-coated onto the TiO<sub>2</sub> mesoporous layer via a two-step anti-solvent method: 1000 RPM for 10 s then 4000 RPM for 40 s. A 100  $\mu$ L toluene (99.8 %, Sigma Aldrich) anti-solvent was injected 22 seconds before spin coating ends. The samples were then annealed at 100 °C for 30 minutes.

The hole selective lithium-doped 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was deposited on top of the annealed perovskite layer. A 72.3 mg Spiro-OMeTAD in 1 mL chlorobenzene (99.8 %, Sigma Aldrich), 28.8  $\mu$ L 4-tert-butylpyridine (98 %, Sigma Aldrich) and 17.5  $\mu$ L of a stock solution of 520 mg lithium bis-(trifluoromethyl sulfonyl) imide (99.95 %, Sigma Aldrich) in 1 mL acetonitrile (99.8 %, Sigma Aldrich) was prepared. A 50  $\mu$ L lithium-doped Spiro-OMeTAD solution was dynamically spin-coated at 4000 RPM, 800 RPM/s for 30 s. Finally, an 85 nm gold contact was thermally evaporated using a commercial Oerlikon Leybold Univex 250.

### 3.2. MAPBr solar cell characteristic $J - V$ curves and statistics

The characteristic  $J - V$  curves of the MAPBr solar cells were measured with a mask aperture area of 0.120 cm<sup>2</sup> using a computer controlled Keithley 2400 under a simulated AM1.5 solar spectrum from an ABET Technologies Sun 2000 solar simulator. The MAPBr solar cells had total active areas of  $\sim$ 0.257 cm<sup>2</sup>.

### 3.3. Impedance Spectroscopy Measurement

All electrical measurements were conducted inside a nitrogen-controlled glove box under dark conditions using Autolab PGSTAT204. The voltage-dependent IS response was measured via a sequence of chronoamperometry (CA) for 5 s, subsequently followed by IS with a frequency range of 1 MHz to 0.02 Hz and a perturbation amplitude of 0.01 V. The CA-IS sequence was carried out at varying applied voltages ( $V_{app}$ ) from 0 to 2 V at 0.1 V increments.

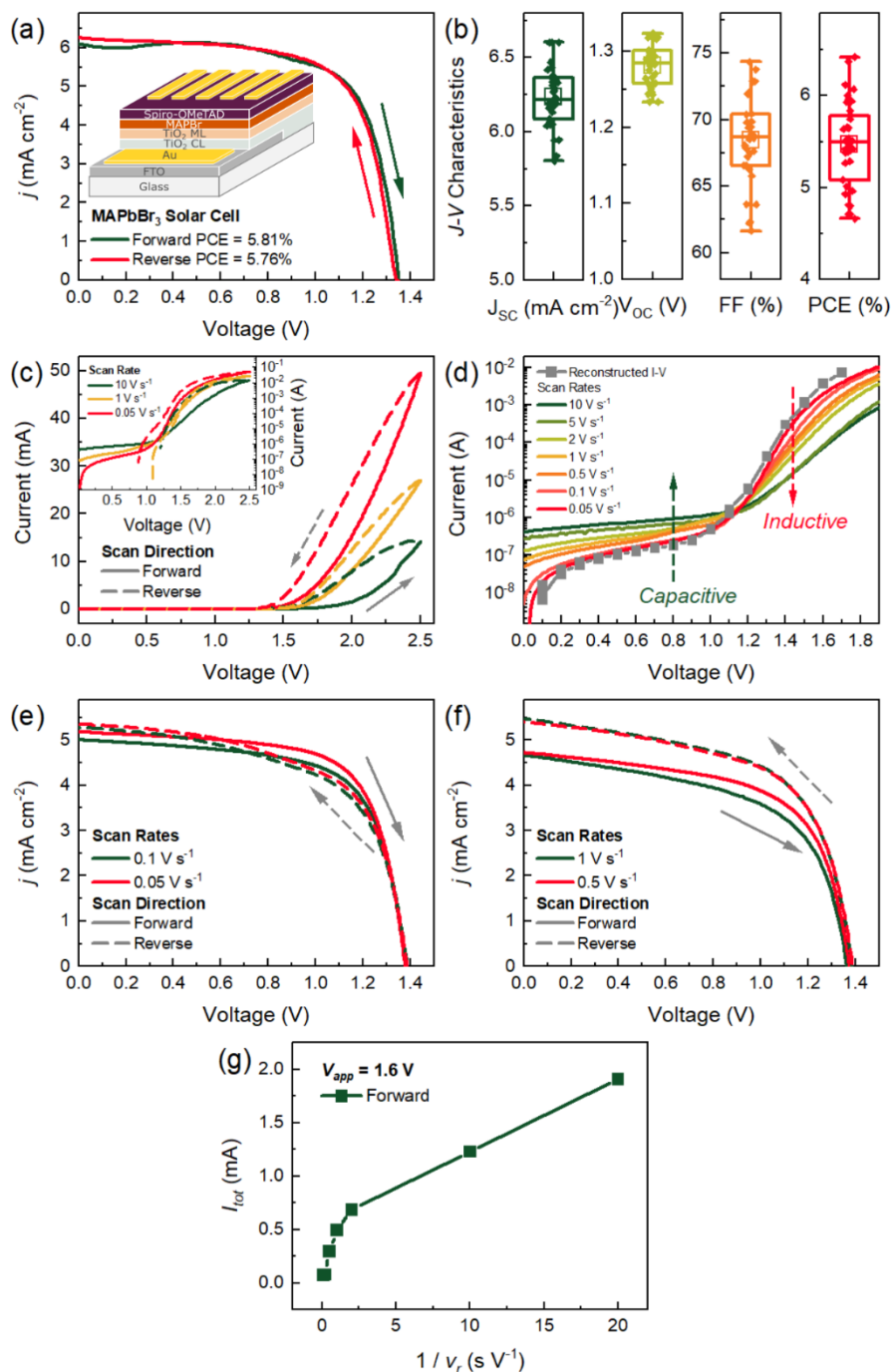


Fig. 11. The (a) characteristic  $I - V$  curve of the MAPBr solar cell under 1 sun illumination exhibiting inverted hysteresis with the inset showing the schematic diagram of the device configuration. (b) The  $I - V$  characteristic parameter statistics of 34 devices measured in the reverse scan direction. (c) The forward and reverse  $I - V$  scans with varying scan rates exhibiting inverted hysteresis measured inside a nitrogen-controlled glove box under dark conditions. (d) Evolution of hysteresis in the forward direction in log vertical scale in dark. (e)-(f) Hysteresis under illumination conditions. (g). The current in forward for inverted hysteresis in the dark at 1.6 V, vs. reciprocal scan rate.

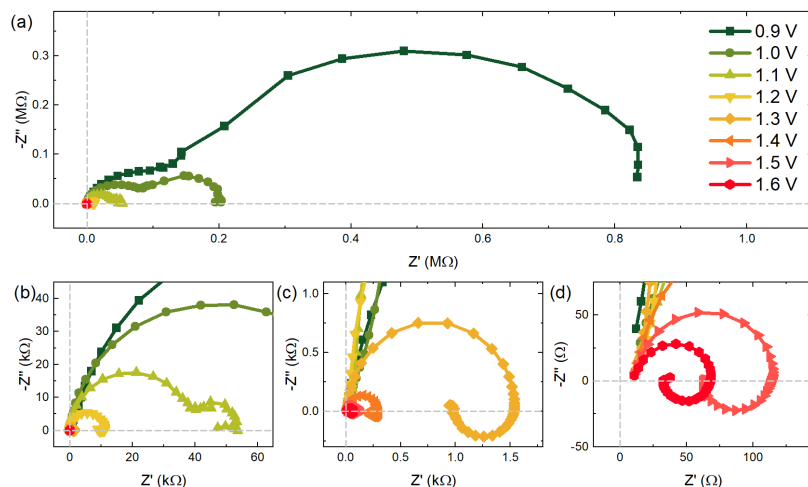


Fig. 12. (a) Representative IS spectral evolution of the the MAPBr solar cell at  $V_{app} = 0.9$  to 1.6 V under dark conditions. (b)-(d) shows different magnifications around the origin.

#### 4. Results and Discussion

Fig. 11 shows the electrical characterization of the fabricated MAPbBr<sub>3</sub> solar cells.  $I - V$  characteristics and device statistics are presented in Fig. 11a-b. The power conversion efficiencies approaching 6 % in the forward and reverse scan direction, are within the normal values reported for this formulation.<sup>69</sup> Devices with optimized contacts can show still higher efficiency.<sup>112,113</sup>

The current-voltage curves in the dark at different scan rates in Fig. 11c show intense inverted hysteresis and correspondingly exhibit decreasing current levels with increasing scan rates, as indicated in Fig. 11d.<sup>25,53</sup> The log scale representation of Fig. 11d reveals a region of capacitive hysteresis at low voltage as announced in Fig. 9 before. A crossing point is observed in which a transition from regular to inverted hysteresis occurs. This transition has been applied recently to explain the negative spikes observed in transient time measurements.<sup>102</sup> Fig. 11g shows that the forward current is inversely proportional to the scan rate for the slow voltage sweeps, as predicted in Eq. (23) for the chemical inductor. For faster scan rates the current tends to reach a minimum due to parallel pathways, as discussed before in Eq. (29). A similar behavior is observed in the current-voltage curves under illumination at different scan rates. However, the crossing point under light is not fixed. It shifts from values close to 0 V at low scan rates (Fig. 11e) to higher values with an increase in the sweep rate. At fast scan rates (Fig. 11f) the crossing point is not observed and the hysteresis is only inductive. Since this additional effect complicates the analysis in the following only data in the dark will be discussed.

These properties can be put in correspondence with the stabilized impedance spectra shown in Fig. 12. The fully capacitive spectra, consisting on several arcs in the low voltage

region (Fig. 12a-b), correspond to the regular hysteresis domain. In the high voltage region, a large inductive feature appears (Fig. 12c-d) that causes a negative transient current resulting to an inverted hysteresis. These separate features have been explained in the Section 2. As described earlier, ionic charges can modulate the carrier extraction rate or recombination current. As the ionic motion is much slower than electronic response, a delay of the electrical current is observed that causes capacitive and inductive components.

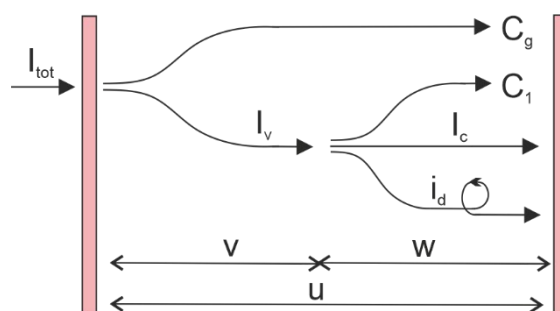


Fig. 13. Scheme of the dynamical model showing total current  $I_{tot}$  and voltage  $u$ , internal voltages  $u = v + w$ , conduction ( $I_v, I_c, i_d$ ) and capacitive ( $C_g, C_1$ ) currents between the current collector plates. The lines arriving to the right contact indicate the dc current.

#### 4.1. The dynamical model

We present here an advanced dynamical model that enables to correlate both the results of impedance and current-voltage curves, and obtain a physical interpretation of the evolution of parameters with the voltage. The model is formulated as a set of dynamical equations valid for any type of perturbation. These equations contain the minimal components to describe all the features shown in Fig. 11 and 12, based on the experience in different capacitive and inductive components and series and parallel elements that has been summarized in Section 2. This model goes further than combining the component parts as it needs to account for the data across the whole voltage range and especially it must explain the emergence of the inductor and the disappearance of the low frequency impedance arc in Fig. 12. The model is the first of its kind that introduces a voltage divisor in order to deal with two impedance arcs.<sup>51</sup>

The physical basis for the model is shown in Fig. 13. The total current flowing through the device is divided into the following components:

- (1) A part of  $I_{tot}$  is a displacement current that charges the geometrical capacitance of the perovskite material ( $C_g$ ).  
The remaining current  $I_v$  will be divided in three branches:
- (2) Charging the surface capacitance  $C_1$ .
- (3) Extracting rapid current  $I_c$  at the contact.

(4) Extracting current slowly *via* an ion modulated current  $i_d$ .

Therefore, the model equations are

$$I_{tot} = C_g \frac{du}{dt} + I_v(v) \quad (32)$$

$$I_v(v) = \frac{dQ_s(w)}{dt} + I_c(w) + i_d \quad (33)$$

$$\tau_d \frac{di_d}{dt} = I_d(w) - i_d \quad (34)$$

The external variables are the total current  $I_{tot}$  and voltage  $u$ . The voltage is divided in two internal parts  $v, w$ , that correspond to bulk and surface potential differences, respectively, and satisfy

$$u = v + w \quad (35)$$

The internal currents  $I_v(v), I_c(w)$  are instantaneous functions of the respective voltage, while  $i_d$  is a variable current that is delayed by a characteristic time  $\tau_d$  due to ionic effects, as described in Section 2.4.<sup>94</sup> Hence Eq. (34) is the standard form of the chemical inductor introduced in (17). The model also includes a surface charge function  $Q_s(w)$ , and the stationary value of the delayed current,  $I_d(w)$ .<sup>51</sup>

We have noted in Eq. (12)-(14) that the resistances and capacitance in perovskite solar cells have exponential dependencies on voltage, and some of them are correlated. Based on these observations, we assume the exponential dependence in the currents

$$I_v(v) = I_{v0} e^{v/V_b} \quad (36)$$

$$I_c(w) = I_{c0} e^{w/V_b} \quad (37)$$

$$I_d(w) = I e^{w/V_d} \quad (38)$$

Here  $I_{v0}, I_{c0}, I_{d0}$  are prefactors and  $V_b, V_d$  are ideality factors<sup>82</sup> with dimension of voltage.

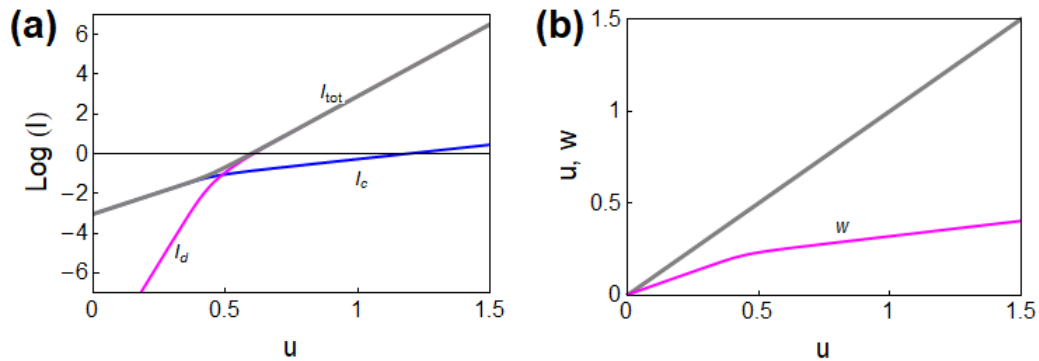


Fig. 14. Model simulation. (a) Stationary current-voltage curve and the component currents, (b) distribution of internal voltage. Parameters:  $I_{v0} = 10^{-3}$ ;  $I_{c0} = 0.9 \times 10^{-3}$ ;  $I_{d0} = 10^{-11}$ ;  $V_b = 0.05$ ;  $V_d = 0.01$ . Currents in A and voltages in V.



According to Fig. 13 the partial currents satisfy the following equation in dc conditions

$$I_v(u - w) = I_c(w) + I_d(w) \quad (39)$$

By Eq. (39) the relation of external voltage  $u$  to internal potential is

$$u = V_b \ln \left( \frac{I_{c0}}{I_{v0}} e^{2w/V_b} + \frac{I_{d0}}{I_{v0}} e^{w/V_c} \right) \quad (40)$$

where

$$V_c^{-1} = V_d^{-1} + V_b^{-1} \quad (41)$$

The total current is shown in Fig. 14a and the distribution of the internal voltages in Fig. 14b. Since  $V_d < V_c$ , the delayed current  $I_d$ , that starts at a low value in Fig. 14a, overcomes the direct recombination current  $I_c$  at the internal voltage value given by the parameter

$$w_T = \left( \frac{1}{V_d} - \frac{1}{V_b} \right)^{-1} \ln \left( \frac{I_{c0}}{I_{d0}} \right) \quad (42)$$

#### 4.2. The ac impedance model

For the interpretation of impedance spectroscopy of our experimental results, we develop (32-34) into the small perturbation equations, that become

$$\hat{I}_{tot} = C_g \frac{d\hat{u}}{dt} + \frac{1}{R_3} \hat{v} \quad (43)$$

$$\frac{1}{R_3} \hat{v} = C_1 \frac{d\hat{w}}{dt} + \frac{1}{R_1} \hat{w} + \hat{i}_d \quad (44)$$

$$L_a \frac{d\hat{i}_d}{dt} = \hat{w} - R_a \hat{i}_d \quad (45)$$

Here the new circuit elements have the form

$$C_1 = \frac{dQ_s}{dw} \quad (46)$$

$$R_1 = \left( \frac{dI_c}{dw} \right)^{-1} \quad (47)$$

$$R_3 = \left( \frac{dI_v}{dv} \right)^{-1} \quad (48)$$

$$R_a = \left( \frac{dI_d}{dw} \right)^{-1} \quad (49)$$

$$L_a = \tau_d \left( \frac{dI_d}{dw} \right)^{-1} \quad (50)$$

$C_1$  is a capacitance related to the surface charging,<sup>86,114</sup>  $R_1, R_3, R_a$  are variable resistances connected to the currents of Eqs. (36-38), and  $L_a$  is an inductor associated to the delayed current of Eq. (34). Now the different resistances can be calculated as a function of voltage.

$$R_1 = \frac{V_b}{I_{c0}} e^{-w/V_b} \quad (51)$$

$$R_a = \frac{V_d}{I_{d0}} e^{-w/V_d} \quad (52)$$

$$R_3 = \frac{V_b}{I_{v0}} e^{-v/V_b} \quad (53)$$

Noting the correlations of  $C_1$  and  $R_1$  commented in Fig. 6 we write

$$C_1 = C_{10} e^{w/V_b} \quad (54)$$

We have the characteristic times

$$\tau_1 = R_1 C_1 \quad (55)$$

$$\tau_a = R_a C_1 \quad (56)$$

$$\tau_d = \frac{L_a}{R_a} \quad (57)$$

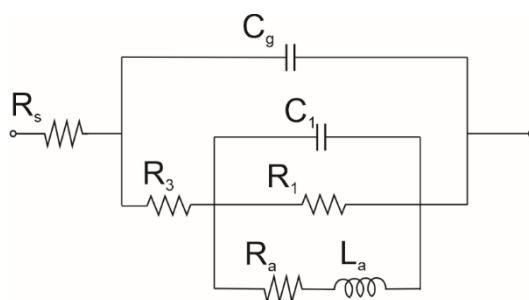


Fig. 15. The schematic diagram of the general equivalent circuit model.

By taking the Laplace transform of (43-45) in terms of the variable  $s = i\omega$ , the calculation of the impedance  $Z = \hat{u}/\hat{I}_{tot}$  gives the result

$$Z(s) = \left[ C_g s + \frac{1}{R_3 + \frac{1}{C_1 s + \frac{1}{R_1 + \frac{1}{R_a + L_a s}}}} \right]^{-1} \quad (58)$$

The impedance in Eq. (58) becomes that of the EC of Fig. 15, with the addition of a constant series resistance  $R_s$ . The branch formed by  $R_a$  and  $L_a$  is the arrangement of the chemical inductor that describes delayed surface controlled recombination as in Section 2.5.

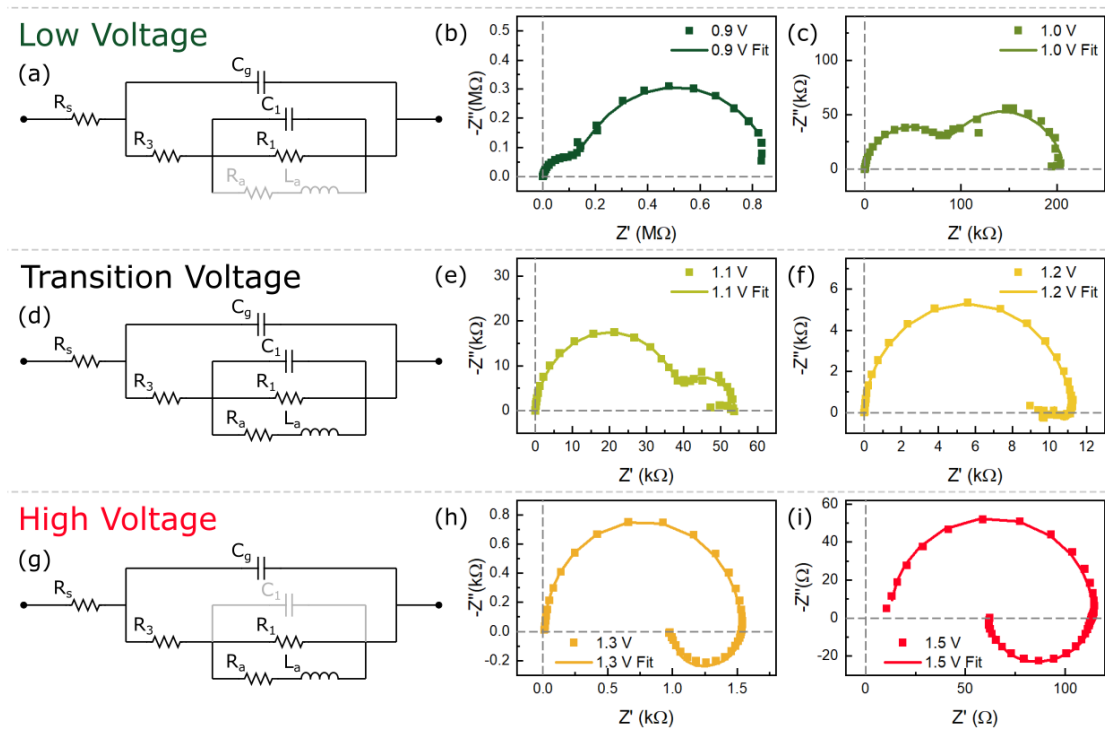


Figure 16. Individual representative IS spectral evolution of the MAPBr solar cell at varying applied voltages ( $V_{app}$ ) under dark conditions exhibiting (b-c) the fully capacitive regime at low voltages ( $V_{app} < 1.1$  V), (e-f) the region of transformation ( $1.1$  V  $\leq V_{app} \leq 1.2$  V), and (h-i) the inductive regime at high voltages ( $V_{app} > 1.2$  V) with the corresponding equivalent circuits (a, d, and g), respectively.

### 4.3. Obtaining the impedance parameters

The analysis of the spectra of Fig. 12 cannot be done by direct fitting of the full equivalent circuit of Fig. 15, since the elements of the circuit are not present in the entire voltage range. Different simplifications of Fig. 15 are used as EC in separate voltage ranges as shown in Fig. 16, that displays the EC adopted in the various domains for the spectral analysis of IS data in Fig. 12.

At low voltages in Fig. 16a the inductor impedance is large, and we obtain the double RC feature of Fig. 16a that was shown previously in Fig. 5, see the spectra Fig. 16b-c. The intermediate region of voltages in Fig. 16d is a transition region where all the elements in the EC are present. The spectra in Fig. 16e-f show the replacement of the low frequency arc by an incipient inductive feature. At high voltages in Fig. 16g the capacitive arc associated to  $C_1$  is not observed, and it is replaced by the chemical inductor feature of Fig. 10. Now the inductive arc is well developed in the experimental spectra in Fig. 16h-i. An additional parallel shunt resistance of constant value  $R_{sh}$  is used in the fitting as described in the Supporting Information. The fits capture well the features of the impedance spectra as shown in Fig. 16 with the resulting EC parameters summarized in Fig. 17: resistances (Fig. 17a), effective capacitances (Fig. 17b), effective inductance (Fig. 17c) and the

corresponding time constants (Fig. 17d).

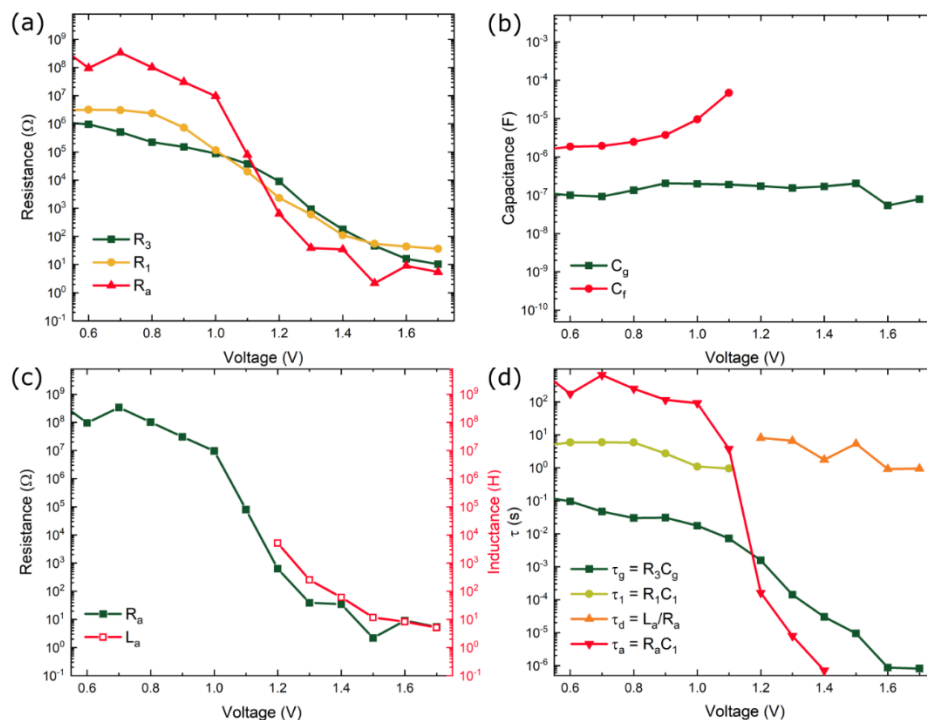


Fig. 17. The voltage-dependent evolution of the (a) resistances, (b) capacitances, (c) inductance at high voltage, and (d) the corresponding time constants resulting from the fitting using Eq. (12) with a consistent shunt resistance of  $\sim 1.24 \times 10^9 \Omega$  throughout the voltage range.

In Fig. 17, we find well established features of the impedance parameters of the low voltage region, by comparison to Fig. 6. The  $R_1$  and  $R_3$  decrease exponentially with voltage, with similar slopes, as in Fig. 6b. The  $R_a$  also decreases with voltage but with a different slope, and it is correlated to  $L_a$ , which makes  $\tau_d$  a constant as assumed in the model. The  $C_1$  increases exponentially as in Fig. 6a, inversely correlated to  $R_1$ , hence the characteristic time  $\tau_1$  in Fig. 17d is a constant as in Fig. 6c.

#### 4.4. Transition from capacitor to inductor

We now discuss the properties of the chemical inductor observed in Fig. 17. The change from capacitor to inductor is controlled by the relation of the time constants as explained in Fig. 10. When  $\tau_d > \tau_a$ , there is a transition of the spectra in the low frequency range, with the appearance of the inductor in the fourth quadrant (producing a negative capacitance feature).

Let us write the time constant  $\tau_1$  using Eqs. (46,47,55)

$$\tau_1 = \frac{dQ_s}{dw} \frac{1}{\frac{dI_c}{dw}} = \frac{dQ_s}{dI_c} \quad (59)$$

We obtain that the ionic charging of the interface occurs with the time constant  $\tau_1$  as

follows

$$Q_s \approx \tau_1 I_c \quad (60)$$

We note the property of nearly continuity of characteristic times obtained in Fig. 17d

$$\tau_1 \approx \tau_d \quad (61)$$

We have remarked before that the capacitor  $C_1$  vanishes when the inductive process appears. The match of time constants in Eq. (61) explains the relation between them. According to the proposed interpretations,<sup>53,59,88,89</sup> the current  $I_c$  in Fig. 13 is a surface recombination process observed at low voltages, influenced by ionic changing from the bulk via the ionic-electronic capacitance  $C_1$ . The delayed current  $i_d$  in Fig. 13 dominant at high voltage is a recombination current influenced by ionic transport to the interface. Hence  $L_a$  and  $C_1$  are not completely independent processes: they both relate to the ionic influence on recombination. Both correspond to a similar ionic-controlled recombination, one is capacitive, the other inductive. Therefore, they are represented by different branches in Fig. 13 and Fig. 15. The connection between capacitive and inductive time constants is also found in a surface polarization model in which the slow variable that produces the chemical inductor is a surface voltage.<sup>103</sup>

By the Eqs. (60) and (61), we write the prefactor of the capacitor in (54) as

$$C_{10} = \frac{I_{c0} \tau_d}{V_b} \quad (62)$$

and we get the charging function as

$$Q_s = I_{c0} \tau_d e^{w/V_b} \quad (63)$$

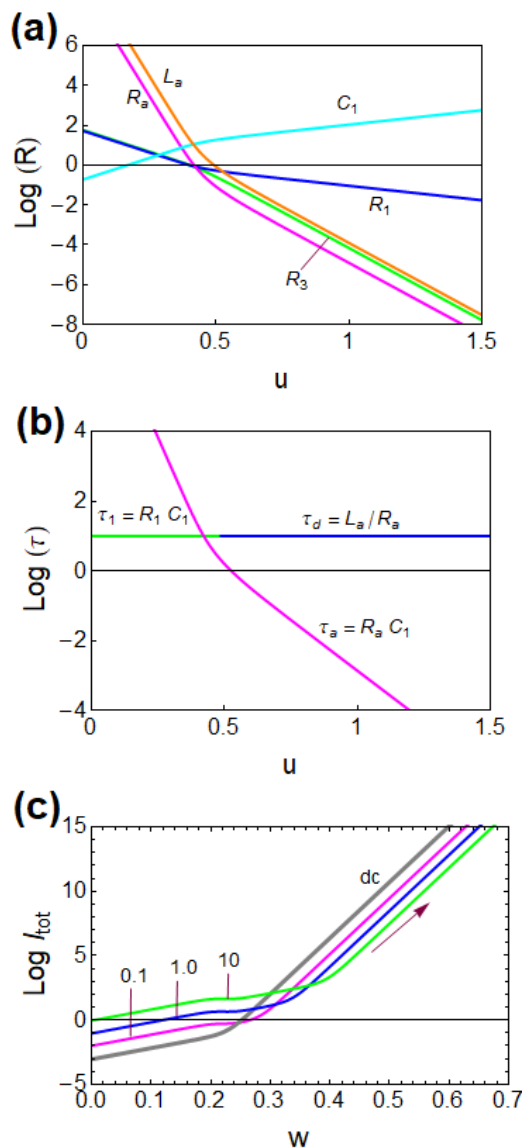


Fig. 18. Simulation of the model. (a) Impedance parameters,  $C$  in F,  $R$  in  $\Omega$ ,  $L$  in H, current in A, voltages in V. (b) Characteristic times (s), and (c) current-voltage curves at different scan rates  $v_r = 0.1, 1.0, 10$  ( $\text{V s}^{-1}$ ) as indicated. The grey line is the dc stationary current. Parameters:  $I_{v0} = 10^{-3}$ ;  $I_{c0} = 0.9 \times 10^{-3}$ ;  $I_{d0} = 10^{-11}$ ;  $V_b = 0.05$ ;  $V_d = 0.01$ ;  $\tau_d = 10$  s. Currents in A and voltages in V.

The EC elements are then plotted in Fig. 18a and reproduce the tendencies of the experimental features observed in Fig. 17. The model accounts successfully for the voltage variation of the impedance parameters.

In addition, the model shows that the correlation<sup>83,89,92</sup> often observed on  $R_1$  and  $R_3$  is based on Eq. (39) and occurs when there are no alternative pathways to the current, e.g., while  $I_d(w)$  is small and the shunt resistance is large.

The characteristic times are shown in Fig. 18b. As already discussed, there is a continuity of  $\tau_1 = \tau_d$  in the transition from capacitive to inductive impedance spectra. It

can be stated that

$$\tau_a = R_a C_1 = \tau_d \frac{I_{c0} V_d}{I_{d0} V_b} e^{\left(\frac{1}{V_b} - \frac{1}{V_d}\right) w} \quad (64)$$

As already mentioned, the transition where the impedance enters the fourth quadrant, occurs when the time  $\tau_a < \tau_d$ .<sup>67</sup> However, if  $\tau_a > \tau_d$  at all voltages, there will not be a domain of negative capacitance effect. The condition (64) therefore explains in which cases there will be an observation of inductive or negative capacitance features.

#### 4.5. Change of type of hysteresis

Finally, we aim to explain the transition from regular to inverted hysteresis observed in the current-voltage curves of Fig. 11d, corresponding to the change of the impedance from capacitive to inductive response. We formulate the dynamical equations for the stimulus of a voltage sweep as in Eq. (6)

$$u = v_r t \quad (65)$$

Hence, we obtain

$$I_{tot} = C_g v_r + C_1(w) v_r \frac{dw}{du} + I_c(w) + I_v(v) \quad (66)$$

$$\tau_d v_r \frac{dw}{du} \frac{dI_d}{dw} = I_d(w) - I_d \quad (67)$$

where

$$\frac{dw}{du} = \frac{I_{c0} e^{2w/V_b} + I_{d0} e^{w/V_c}}{2I_{c0} e^{2w/V_b} + \frac{V_b}{V_c} I_{d0} e^{w/V_c}} \quad (68)$$

The differential equation (67) can be solved for the given  $v_r$  and inserted into Eq. (66) to provide the total current. The resulting current-voltage curves at forward scan are shown in Fig. 18c and reproduce the crossing due to change of hysteresis type observed in Fig. 11d.

## Conclusion

We formulated a dynamical model for the external current, the voltage, and a few internal variables of a solar cell, to describe impedance spectroscopy and hysteresis in current-voltage curves of halide perovskite solar cells that show a transition from a capacitive domain at low voltage to an inductive domain at high applied voltage. The model reproduces the main experimental characteristics of impedance, steady state current-voltage, and the curves under different sweep rates.

It is well known that the capacitive excess current is proportional to the scan rate; we showed that the inductive current is inversely proportional to the scan rate.

The application of the model provides a great degree of control over the kinetic properties of halide perovskite solar cells, including the amount and type of hysteresis that may be expected from the measurement of impedance spectroscopy at different voltages. By determining a few parameters in an impedance spectroscopy measurement it is now possible to predict the amount and type of hysteresis that the perovskite solar cell device

will have. Furthermore one can correlate the hysteresis response with the device materials properties via the impedance parameters that are obtained in the equivalent circuit.

The general model can track a transformation of the low frequency capacitor into a chemical inductor, both related to ionic-controlled surface recombination process. The different kinetic properties are regulated by the variation of certain time constants that determine the dominant impedance response. This explains why the inductive feature may not produce a negative capacitance, so that hysteresis will remain regular in the whole voltage range.

### **Supporting Information**

Mathematica program for calculations, data fitting program.

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