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Physical Model for the Current−Voltage Hysteresis and Impedance of Halide Perovskite Memristors

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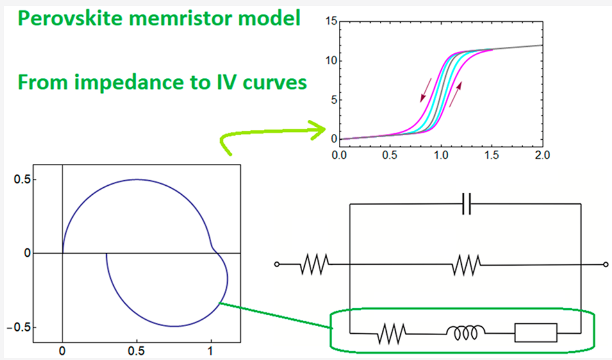
ABSTRACT: An investigation of the kinetic behavior of $MAPbI_3$ memristors shows that the onset voltage to a high conducting state depends strongly on the voltage sweep rate, and the impedance spectra generate complex capacitive and inductive patterns. We develop a dynamic model to describe these features and obtain physical insight into the coupling of ionic and electronic properties that produce the resistive switching behavior. The model separates the memristive response into distinct diffusion and transition-state-formation steps that describe well the experimental current−voltage curves at different scan rates and impedance spectra. The ac impedance analysis shows that the halide perovskite memristor response contains the composition of two inductive processes that provide a huge negative capacitance associated with inverted hysteresis. The results provide a new approach to understand some typical characteristics of halide perovskite devices, such as the inductive behavior and hysteresis effects, according to the time scales of internal processes.



In less than a decade, metal halide perovskite (MHP) materials have established a new photovoltaic (PV) technology that demonstrated very large solar energy conversion efficiencies with low-cost, solution-processed materials.[1−4] The MHP can be described as ABX_3 where A is a monovalent cation such as methylammonium (MA), formamidinium (FA), or cesium (Cs); B is a divalent cation such as lead (Pb) or tin (Sn); and X is a halide anion, including chloride (Cl), bromide (Br), and iodide (I). MHP semiconductors show mixed ionic−electronic conduction in which a significant ionic conductivity due to vacancy displacements exists in addition to the electronic photoconductivity.[5−8] These properties are difficult to measure because of the intersection of very different time scales of ionic and electronic effects that interact with each other. They cause intrinsic memory effects (hysteresis) in current−voltage ($I-V$)[9−14] that lead to substantial differences in the forward and reverse scan currents and permanent resistive changes. These features are highly significant for important new applications in which MHPs are used for nonoptoelectronic applications related to memory storage and brain-like computation. Herein, on the basis of previous understanding of the MHP solar cells,[9,15] we develop a physical model to describe the results of MHP memristors in both voltage cycling and impedance spectroscopy.

A memristor is a two-terminal device whose resistance depends on the history of current and voltage applied to the device. Memristors allow the storage of information by metastable modification of device conductivity.[16−20] Typically, a memristor makes a transition from a high to a low resistance state (HRS−LRS) when a certain threshold forward voltage is passed, which can be restored to the initial state by a reverse voltage sweep.[18,21,22] There has been rapid recent progress in perovskite memristor endurance performance[23] that facilitates application to resistive RAM.[24] Synapsis plasticity, the ability of the connection between neurons to strengthen or weaken by external stimulation, is a central property in the operation of neuronal circuits. The development of spiking neural networks requires a precise control of the functionality of synapses,

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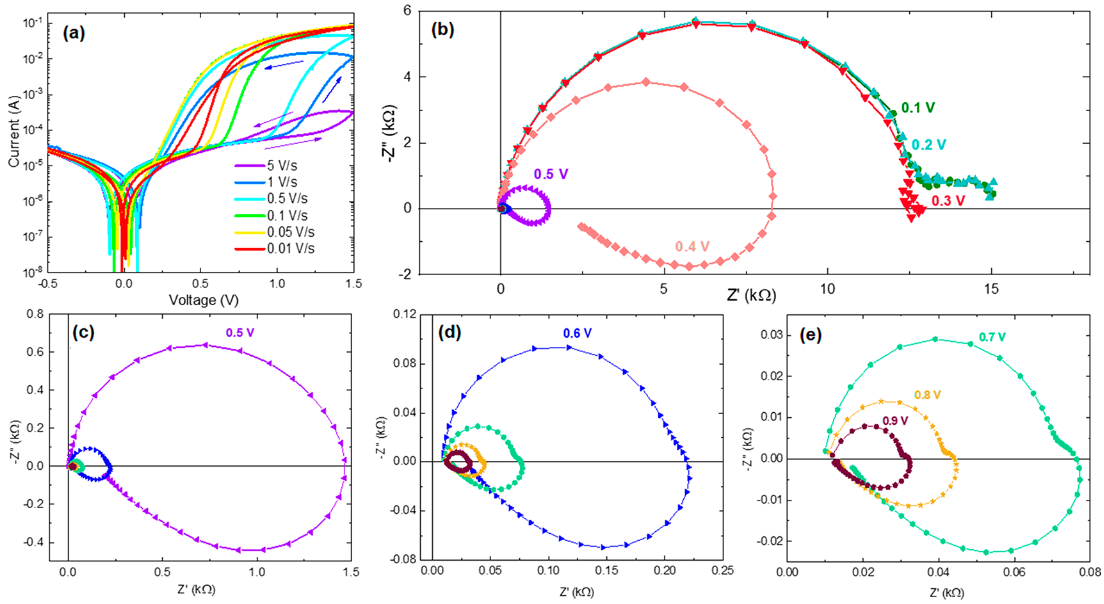

Figure 1. (a) Current−voltage characteristic for an FTO/PEDOT:PSS/MAPI/Au memristor device at 6 different scan rates starting from 5 V/s. Arrows indicate sweep direction. (b−e) Complex plane plot representation of the impedance spectra at different applied dc voltage. Panels c, d, and e correspond to a magnification of the scales.

neurons, and their assemblies by the properties of plasticity, adaptation, spiking, and the synchronization of the temporal dynamics and shapes of repetitive spikes and their integration.[25,26] Currently, there is great interest in developing biorealistic elements that contain no internal circuitry.[27] MHP memristors that undergo a relatively slow transition to HRS take a leading role in the search for emulation of brain functions with assemblies of artificial synapse devices[28−30] in neuromorphic computation.[27,31,32] Furthermore, MHPs provide photoactive synapses suitable to artificial vision devices in which the memory effects can be adapted for preprocessing of image data before transfer to the computing unit eliciting a motor response.[33−35]

In order to design material properties for these applications it is necessary to establish the precise properties of time dynamics of memristors and their response and changes under repetitive stimuli at varying frequency. Impedance spectroscopy (IS) consists of the electrical measurement of current-to-voltage of the device at a steady-state potential V by small perturbation at changing angular frequency ω. It is a central technique for the characterization of PV cells and electrochemical devices.[15,36] We have recently shown that a precise connection can be established between the frequency and time domain in the analysis of hysteresis and time transients of PV devices.[9,37] However, memristors with extreme hysteresis effects have so far not been described with IS models that can predict hysteresis and time transient behavior to determine the physical basis for parameters such as the switching speed and the retention time.

Herein, we take a first step in this direction. We analyze the properties of glass/FTO/PEDOT:PSS/$MAPbI_3$/Au perovskite-based memristor devices.[38,39] The details of device preparation are provided in the Supporting Information. Figure 1 shows the characterization in $I-V$ sweeps of a typical threshold resistive switching device where the switching event is confined to one quadrant only.[40] We note that the effective onset of the transition occurs at higher voltage when the potential sweep is at higher scan rate. The device exhibits ON state retention times of $>10^4$ s at a read voltage of 0.5 V (Figure SI1b), rendering them suitable for volatile memory applications (Figure SI1c). At the beginning, the ON state current exponentially decreases but then stabilizes at 38% of the initial value, maintaining an ON/OFF ratio of ∼1 order of magnitude. Voltage-dependent IS response was performed via a sequence of chronoamperometry (CA) measurement for 10 s, subsequently followed by IS with a frequency range of 0.1 MHz to 0.1 Hz. We note that active areas are very large (0.25 cm^2) for memory applications, but this area helps to maximize the impedance response reducing the noise in the low-frequency region. When devices are scaled to areas of $\sim 10^5$ μm^2, the trends of the $I-V$ curves hold, indicating that the main switching mechanism is maintained but the IS response is noisy (Figure SI2). In any case, the model is still useful to extract different properties of other large-area applications such as solar cells or LEDs.

Figure 1b−e shows the impedance spectra at different applied voltage from 0.1 to 0.9 V. At low voltage the device responds with a double RC arc as is found in solar cell perovskite devices.[15] At 0.3 V and higher voltages a large inductor component at low frequency is formed that is also typical of perovskite solar cells at high voltage, which causes a negative capacitance effect.[9,41−43] This feature has been reported before in perovskite memristors.[39] For 0.5 V and higher the crossing of the real axis of the impedance complex plane shows a strong rightward distortion. This last feature has not been described before, but it is highly reproducible as shown in the Supporting Information with the results of another sample (Figure SI3).

We aim to establish the simplest models that can explain the observed properties of IS and current voltage curves at different scan rates, accounting qualitatively for the strong memory effect and resistive switching phenomena. Our model is adapted to those perovskite memristors that show a gradual transition in current−voltage scans so that the change of conductance can be regulated by the voltage amplitude and operation time.[32] These properties allow us to faithfully replicate the nature of plasticity in synapses.[28] We adopt a method related to the dynamic systems of neurons,[44,45] of the class of fast−slow dynamic models,[46] that describes rather complex phenomena with a relatively simple number of differential equations, like the two-dimensional FitzHugh−Nagumo neuron model.[47] Another famous model of this type is the Hodgkin−Huxley (HH) model.[48] It is four dimensional with a fast variable (the voltage across the cell membrane) and several slow variables that describe the conduction state of a particular voltage-gated ion channel, which can be open or closed according to the value of the membrane voltage. In the HH model the channel state is described by a continuous function that varies from 0 to 1 and obeys a first-order kinetic equation for the evolution to the voltage-driven equilibrium state.[44,49] We will utilize this type of state variable in our model as well. In the following paragraphs, we develop the main model and several simplified cases. The expressions and properties are listed in Tables 1, 2, and 3.

Table 1. Main Equations of This Work

equation
$I_{tot} = C_m \frac{du}{dt} + \frac{u}{R_b} + i_c \quad (1)$
$\tau_d \frac{di_c}{dt} = i_{c0} f - i_c \quad (2)$
$\frac{df}{dt} = k_0(1-f) - k_1 f \quad (3)$
$f(u) = \frac{1}{1 + e^{-(u-V_T)/V_m}} \quad (4)$
$\tau_k \frac{df}{dt} = e^{\alpha(u-V_T)/V_m}(1-f) - e^{(\alpha-1)(u-V_T)/V_m} f \quad (5)$
$\tau_d \frac{di_c}{dt} = i_{c0} \frac{1}{1 + e^{-(u-V_T)/V_m}} - i_c \quad (6)$
$I_{tot} = C_m \frac{du}{dt} + \frac{u}{R_b} + i_{c0} f \quad (7)$
$I_{tot} = C_m \frac{du}{dt} + qN\frac{df}{dt} + \frac{u}{R_b} + i_{c0} f \quad (8)$
$I_{tot} = C_m \frac{du}{dt} + qN\frac{df}{dt} + \frac{u}{R_b} + i_c \quad (9)$

Table 2. Impedance Spectroscopy Models of This Work

equation	figure
$Z(s) = \left[C_m s + R_b^{-1} + \frac{1}{Z_c}\right]^{-1} \quad (10)$	3e
$Z_c(s) = (1 + s\tau_d)(R_a + L_a^k s) \quad (11)$	
$R_a^{-1} = \frac{di_c}{du} = \frac{i_{c0}}{V_m} f(1-f) \quad (12)$	
$L_a^k = f\tau_k R_a \quad (13)$	
$L_a^d = \tau_d R_a \quad (14)$	
$Z_c(\omega) = R_a + i\omega L_a^k + i\omega L_a^d + R_c(\omega) \quad (15)$	
$R_c(\omega) = -\frac{L_a^k L_a^d}{R_a}\omega^2 \quad (16)$	
$Z(s) = \left[C_m s + R_b^{-1} + \frac{1}{R_a + L_a s}\right]^{-1} \quad (17)$	3a
$Z(s) = \left[C_m s + R_b^{-1} + \frac{1}{R_a + L_a^k s} + \frac{1}{R_2 + \frac{1}{C_2 s}}\right]^{-1} \quad (18)$	3c
$R_2 = \frac{L_a^k i_{c0}}{Q_m} \quad (19)$	
$C_2 = \frac{Q_m}{R_a i_{c0}} \quad (20)$	
$Z(s) = \left[C_m s + R_b^{-1} + \frac{1}{R_2 + \frac{1}{C_2 s}} + \frac{1}{Z_c}\right]^{-1} \quad (21)$	SI8

Table 3. Different Models of This Work

denomination	variables	time constants	dynamic equations	impedance function
(1) full transition model	u, i_c, f	τ_m, τ_d, $f\tau_k$	1, 2, 5	9
(2) diffusion-limited	u, i_c	τ_m, τ_d	1, 6	16, $L_a = L_a^d$
(3) formation-limited	u, f	τ_m, $f\tau_k$	7, 5	16, $L_a = L_a^k$
(4) formation and capacitance	u, f	τ_m, $f\tau_k$, τ_2	8, 5	17
(5) inductors and capacitance	u, i_c, f	τ_m, τ_d, $f\tau_k$, τ_2	9, 2, 5	21

The models we propose describe the evolution of the external variables of the MHP memristor, namely, the total current I_{tot} and the voltage across the internal contacts, u, under a certain stimulus out of equilibrium, influenced by two internal variables, i_c and f, that obey the set of dynamic equations (eqs 1−3) indicated in Table 1. These equations define model 1 in Table 3. In this model, we adopt a number of premises to describe the experimental observations. The conduction current I_{tot} has three components, as indicated in eq 1: a capacitive charging of the interfaces with capacitance C_m, a small ohmic current of constant resistance R_b, and a slow-responding current i_c, with a large saturation value i_{c0}. Very different mechanisms for the formation of the LRS have been suggested in the literature, according to different materials and configurations: (1) formation of a filamentary conductive pathway,[18] (2) decrease of a surface barrier by ion-assisted electrochemical interactions between the perovskite and contacts,[38,50] and (3) decrease of the surface barrier by formation of ion-assisted self-doped regions in the vicinity of interfaces.[27] These physical transformations are often associated with general ion migration effects. In this work, we do not attempt to clarify the mechanism of the investigated memristor, which requires an in-depth investigation of materials and contact properties that will be presented elsewhere. However, in order to describe the complex dynamic properties that have been observed by voltammetry and IS, we will separate clearly two features in the transition to the LRS:

(a) The onset of conduction in quasi-equilibrium depends on a threshold voltage V_T connected to the material properties (bulk and interface). The activation of the high current component i_c occurs by the change of an occupation function $0 \le f \le 1$ that is controlled by the voltage. Similar to the ion channel behavior in neurons, the variable f indicates the state of the mechanism that establishes the high-conductivity state up to the limiting current i_{c0}. Equation 3 is a reaction equation with rate constants k_0 and k_1 that describes the voltage-controlled activation of the high-conduction configuration.

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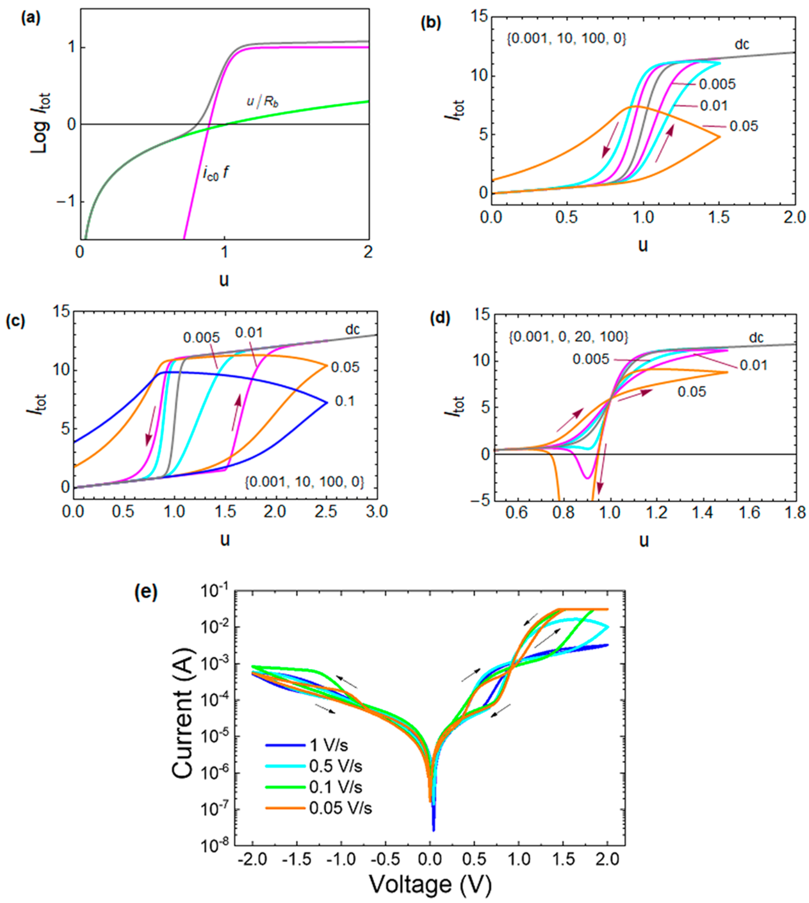

Figure 2. (a) Logarithmic current−voltage curve for model 1 memristor. The gray line is the total equilibrium dc current. (b) Current at forward and backward scan of model 1 at different rates as indicated, $\alpha = 0$, $V_m = 0.05$, and (c) $\alpha = 0.1$, $V_m = 0.025$. Parameters $R_b = 1$; $i_{c0} = 10$, $V_T = 1$, $[\tau_m, \tau_d, \tau_k, Q_m]$. (d) Current at forward and backward scan for model 4 at different rates as indicated, $\alpha = 0$, $V_m = 0.05$. (e) Current−voltage characteristic for an FTO/PEDOT:PSS/MAPI/Spiro-MeOTAD/Au device at 4 different scan rates.

(b) The observations indicate that the increase of f is also determined by the rate of ion transport. We introduce in eq 2 a delay of i_c with the characteristic time τ_d (eq 2). Typically, this temporal parameter represents a diffusion or migration time of ions, necessary to establish the configuration of high f that produces the large electronic current i_{c0}.

This model is an extension of the two-dimensional models that have been recently proposed to describe inductive behavior and inverted hysteresis in MHP and in neurons,[9,15,45,51] and it is also an extension of the standard set of equations for a voltage-controlled memristor.[19,52] Model 1 of eqs 1−3 is three-dimensional and displays additional kinetic complexity that is necessary to account for the observed experimental behaviors of the memristor. We remark that eq 2 is a rather simplified transport equation, and one may use drift-diffusion approaches in a more sophisticated treatment. In addition, the form of eq 3 is not unique but may depend strongly on the kinetics mechanisms and material properties, e.g., with higher-order reaction kinetics. Here we adopt eqs 2 and 3 as the simplest reasonable assumption that illustrates the coupling of different steps in the overall model.

Let us analyze in more detail the properties of the dynamic model. It is important to find, first of all, the steady-state characteristics represented by current−voltage curves. By suppressing the time derivatives in eqs 1−3, we obtain the following conditions for a stationary state:

$$I_{tot} = \frac{u}{R_b} + i_c \tag{22}$$

$$i_c = i_{c0} f \tag{23}$$

$$k_0(1 - f) = k_1 f \tag{24}$$

The last equation can be stated

$$f(u) = \frac{1}{1 + \frac{k_1}{k_0}} \tag{25}$$

By the detailed balance principle, this last equation corresponds to the equilibrium occupancy given by the Fermi−Dirac or Nernst equilibrium distribution function, eq 4, where V_T is the redox potential of the activation state so that in the equilibrium line $f(V_T) = 0.5$. V_m in eq 4 is a constant with dimension of voltage, with a diode ideality factor m with respect to the thermal voltage $k_B T/q$, where T is the absolute temperature, k_B the Boltzmann constant, and q the elementary charge, so that $V_m = m k_B T/q$. Therefore, we obtain

$$\frac{k_0}{k_1} = e^{(u - V_T)/V_m} \tag{26}$$

We introduce the kinetic time of the formation process τ_k. Then the reaction kinetic constants are expressed by a partition that satisfies eq 26:[53]

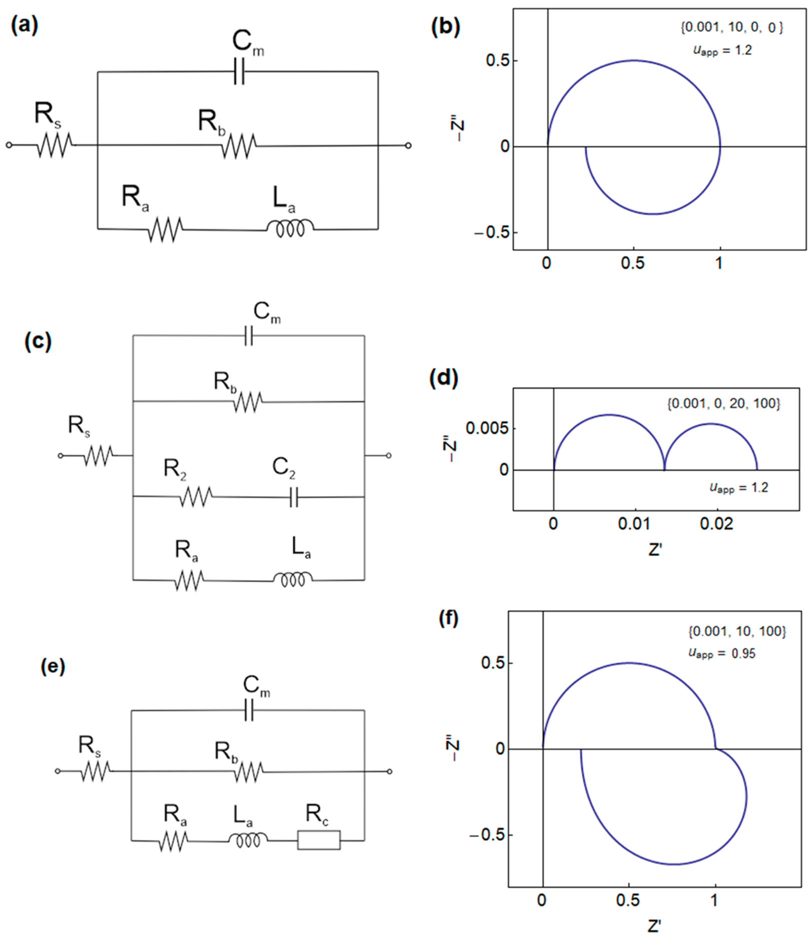

Figure 3. (a) Equivalent circuit model for diffusion-limited model 2 and formation-limited model 3. (b) Impedance spectrum of model 2 for parameters $R_b = 1$; $i_{c0} = 10$; $V_T = 1$; $\alpha = 0$; $V_m = 0.05$; $[\tau_m, \tau_d, \tau_k, Q_m]$. (c) Equivalent circuit model for surface capacitive model 4. (d) Impedance spectrum of model 4. (e) Equivalent circuit model for model 1. (f) Impedance spectrum of model 1.

$$k_0 = \tau_k^{-1} e^{\alpha(u-V_T)/V_m} \tag{27}$$

$$k_1 = \tau_k^{-1} e^{(\alpha-1)(u-V_T)/V_m} \tag{28}$$

The constant and $0 \leq \alpha \leq 1$ is a Tafel coefficient. We can write the dynamic eq 3 in the final form (eq 5). In the simulations the unit of time is s, voltage is V, current is A, and resistance is Ω. The steady-state current–voltage equation is

$$I_{app} = \frac{u_{app}}{R_b} + \frac{1}{1 + e^{-(u_{app}-V_T)/V_m}} i_{c0} \tag{29}$$

This is shown in Figure 2a. As stated before, the dc current is formed by two components: an ohmic baseline (green) and a large current that is onset at voltage V_T (magenta). This is the typical form of MHP memristors[27] as shown in Figure 1a.

Memristor dynamics are characterized by a rich variety of transient phenomena that our model is intended to describe. These will be determined by the three time parameters of model 1: $\tau_m = R_b C_m$, τ_d, and τ_k, which we assume to be constants. To analyze these questions, we present the results of CV, in which the current is measured under voltage sweep at scan rate v_r according to the expression

$$V(t) = V_0 + v_r t \tag{30}$$

This method reveals the famous hysteresis effects in current−voltage curves of solar cells.[9,54−57] When we apply eq 30, the model eqs 1, 2, and 5 become

$$I_{tot} = \frac{u}{R_b} + i_c + C_m v_r \tag{31}$$

$$\tau_d v_r \frac{di_c}{du} = i_{c0} f - i_c \tag{32}$$

$$\tau_k v_r \frac{df}{du} = e^{\alpha(u-V_T)/V_m}(1-f) - e^{(\alpha-1)(u-V_T)/V_m} f \tag{33}$$

The two differential equations (32 and 33) can be solved with the chosen boundary conditions. In this case we take $f(u = 0) = 0$ and $i_c(u = 0) = 0$. The voltage-dependent $i_c(u)$ is inserted into eq 29. A set of simulation results of model 1 are presented in Figures 2b,c and SI4. The transition to high conduction happens at higher voltage for fast scan rates, as observed experimentally in Figure 1a. Figure 2c shows a wider separation between forward and backward scans due to a modification of α coefficient. Figure SI4g shows the distinctive conductivity levels that provide the synaptic property of the perovskite memristors by gradual analog switching.[32] The model is valid for both volatile and nonvolatile memories as noted in Figure SI4.

To better understand the dynamic properties, we develop the method of IS. We apply a small perturbation procedure to

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the dynamic equations and Laplace-transform the time derivative to $s = i\omega$. The small amplitudes of the variables are denoted $\hat{x}$. The resulting equations have the form

$$\hat{I}_{\mathrm{tot}} = \frac{\hat{u}}{R_{\mathrm{b}}} + \hat{i}_{\mathrm{c}} + C_m s\hat{u} \tag{34}$$

$$\tau_{\mathrm{d}} s\hat{i}_{\mathrm{c}} = i_{\mathrm{c0}}\hat{f} - \hat{i}_{\mathrm{c}} \tag{35}$$

$$\tau_{\mathrm{k}} s\hat{f} = -\frac{\hat{f}}{f} - \frac{f(1-f)}{V_m}\hat{u} \tag{36}$$

We calculate the impedance $Z(s) = \hat{u}(s)/\hat{I}_{\mathrm{tot}}(s)$ and we obtain eqs 10 and 11 where R_{a} in eq 12 is a resistance and $L_{\mathrm{a}}^{\mathrm{k}}$ and $L_{\mathrm{a}}^{\mathrm{d}}$ are inductors (eqs 13 and 14). These elements have been explained in two-dimensional models in previous publications[15,51] in relation with negative capacitance and hysteresis in MHP. However, model 1 is three-dimensional and contains two inductive processes that are combined in eq 11. This impedance introduces the two inductor elements in the expression of eq 15 and furthermore introduces a negative and frequency-dependent resistance $R_{\mathrm{c}}(\omega)$, eq 16, not previously reported in the literature, to our knowledge. As the standard time constant of the *RL* elements is R/L, the effective time constants of the model-determining transient behaviors are τ_m, τ_{d}, $L_{\mathrm{a}}^{\mathrm{k}}/R_{\mathrm{a}} = f\tau_{\mathrm{k}}$. Note that $L_{\mathrm{a}}^{\mathrm{k}}/R_{\mathrm{a}} = \tau_{\mathrm{k}}$ occurs only when $f \approx 1$. The circuit elements and time constants are shown in Figure SI5.

To facilitate a physical interpretation of model 1 we consider simplified cases. We can define conditions in which the reaction time $\tau_{\mathrm{k}} \approx 0$ so that f takes the equilibrium value of eq 4 at any moment. Then eq 2 can be simplified to eq 6 and the dynamic system becomes two-dimensional, with the variables u, i_c, formed by eqs 1 and 6. This can be termed *diffusion-limited transition*, model 2 in Table 3, by analogy to classical electrochemistry terminology.[58] Another limiting situation is when $\tau_{\mathrm{d}} \approx 0$ so that eq 1 can be written as eq 7. Then the dynamic system is two-dimensional also, formed by eqs 7 and 5 with the variables u and f. This is a *formation-limited transition* mechanism, model 3.

By suppressing either τ_{d} or τ_{k} in the general impedance of eq 10, the impedance in eq 10 reduces to eq 17 that contains an inductor−resistor branch, as shown in the EC of Figure 3a. This circuit has been well-described before in relation to inverted hysteresis in perovskite solar cells.[9,15,59] The shape of the spectra are shown in Figures 3b and SI6. In the CV behavior we obtain that all models 1, 2, and 3 show inductive or "inverted" hysteresis[10−14] (see Figures 2b,c and SI4c−f). The diffusion-limited model 2 produces a separation of forward and voltage curves right at the onset of the transition, leading to a shift of the effective onset voltage (Figure SI4e). On the other hand, for the formation-limited model 3 in Figure 3d the hysteresis effect occurs only when the current takes a large value (Figure SI4f).

While the large inverted hysteresis is the ordinary behavior of CV of memristors, there are also cases of perovskite memristors with regular hysteresis corresponding to capacitive response.[60,61] To account for such behavior we introduce in eq 1 the capacitive current of the interfacial transition mechanism, $qN\,\mathrm{d}f/\mathrm{d}t$, where N is the total number of surface sites for ions, and the total possible surface charge is $Q_m = Nq$. The resulting equation is indicated in eq 8, and the impedance response is given by eq 18. The EC is presented in Figure 3c. The C_2 in eq 20 is the surface capacitance associated with the activation of interface sites, in addition to the background capacitance C_m, and R_2 in eq 19 is the associated series resistance. The time constant is $\tau_2 = R_2C_2 = L_{\mathrm{a}}^{\mathrm{k}}/R_{\mathrm{a}}$. When $f = 1$, it is $\tau_2 = \tau_{\mathrm{k}}$ by eq 13. This type of serial process at intermediate frequencies has been previously observed unambiguously by Ravishankar et al. in IMPS measurements of $MAPbBr_3$ solar cells,[62] and it was interpreted as an ion accumulation process. The impedance spectra show a regime of two capacitive arcs, Figure 3d, and the inductive element becomes active at large voltage. Consequently, the hysteresis under voltage sweep changes from normal to inverted as shown in Figure 2d. Here we obtain this feature experimentally by introduction of a Spiro-MeOTAD layer as shown in Figure 2e. The crossing of the line in the CV is also observed in the slow scan of Figure 1, indicating the significance of the capacitive contribution at low voltage. Finally, when the Q_m is large the CV becomes fully regular (capacitive) as seen in Figure SI4h. A related two-capacitor circuit is shown in Figure SI10 with the spectra in Figure SI11.

The dominance of *RC* elements at low voltage and the inductive response at higher voltage can be explained by the increase of the inductive time constant $f\tau_{\mathrm{k}}$ after the transition region, when f increases. However, the simplified models do not accurately describe the impedance spectra at high voltage. We therefore analyze the impedance of model 1 without simplifications. The novelty in this model with respect to the standard circuit of Figure 3a is the product of two $R-L$ impedances in Z_{c} (eq 11). The full EC is shown in Figure 3e. The simulations of the impedance spectra are shown in Figures 3f and SI7. These and other spectra for different combinations of parameters can be visualized with a Mathematica program presented in the Supporting Information. In the low-voltage region of Figure SI7b the impedance is a single *RC* arc. As we approach the transition region of the $I-u$ curve, in Figure SI5c the impedance develops the inductive loop already described in Figure 3b. But Figure 3f shows a new type of spectrum not found in the previous models. The behavior caused by the impedance Z_{c} in the inductive branch increases the real part of the impedance before entering the fourth quadrant. This property corresponds to the high-voltage experimental spectra in Figure 1.

If we turn to the experimental results of Figures 1 and SI2, we note that they show a capacitive response with one of two arcs at low voltage and the generation of an inductive component close to the onset of the current rise. Therefore, we combine all the previous models into model 5 (Table 3) that contains two inductive and two capacitive processes, as shown in Figure SI8, as the minimal model needed for the measured memristors (see the predicted spectral shapes in Figure SI9). A full analysis of the spectral data shows that the impedance model fits well the experimental spectra (Figure SI12) and provides the required parameters (Figures SI13 and SI14). The fitting method is described in the Supporting Information, and it includes the use of constant phase element exponents to account for nonperfect semicircles.[63] An important property of the model is the description of a saturation current in agreement with the experimental results. By the shape of CVs, it is expected that the resistance R_{a} decreases to a minimum value when $f \approx 1/2$ as indicated in Figure SI5. This is confirmed by the impedance parameters, because the measured R_{a} decreases exponentially with a diode factor $m = 3.6$ and then undergoes a saturation at large voltage (Figure SI13). The

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effective time constants resulting from the impedance spectra fittings are shown in Figure SI15. In the current transition region they are reasonably constant, as assumed in the model. We observe that the longest time is for the kinetic formation of the high conduction effect; hence, the system is predominantly formation-limited, while the ion supply is rather fast in comparison.

The models presented in this work are designed to account for the combination of internal processes in MHP memristors. Our $MAPbI_3$ memristors are admittedly slow, with characteristic times of 10 ms−1 s. The model, however, can be applied to much faster time scales with adequate experimental tools and the specific functions for diffusion and formation characteristics that each case may require. Recently, perovskite memristors for high switching speed with times of 20 ns have been reported by Park et al.[64] From the measurement at different duration pulses, we observe that the resistance for Park et al. is larger for the larger duration pulse, in agreement with our model. Therefore, we believe that the model has a general significance for the analysis of the behavior of memristors, even though we do not claim a universal model because there is a wide variety of materials and systems, and a larger investigation is needed.

In conclusion, we presented the results of kinetic measurements of $MAPbI_3$-based memristors, and we developed a three-dimensional dynamic model that describes well the observed properties of voltage cycling and impedance spectroscopy. The different couplings of ionic and electronic phenomena are characterized by capacitive and inductive features that generate new impedance functions in agreement with the experimental measurements. We also describe well the changes from regular to inverted hysteresis by the dominance of capacitive or inductive elements, respectively. It is not possible to know the formation of diffusion mechanisms a priori, but the essential progress we provide here is the need to separate them, finding the consequences of their compositions on experimental measurements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c00121.

> Materials and device preparation; details of models; impedance spectra fitting resources and results; Mathematica program to represent current−voltage curves and impedance spectra (PDF)

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Notes

The authors declare no competing financial interest.

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