

# Mechanistic and Kinetic Analysis of Perovskite Memristors with Buffer Layers: The Case of a Two-Step Set Process

Cedric Gonzales and Antonio Guerrero\*

**Cite This:** J. Phys. Chem. Lett. 2023, 14, 1395–1402



Article Recommendations

ACCESS

III Metrics & More

**ABSTRACT:** With the increasing demand for artificially intelligent hardware systems for brain-inspired in-memory and neuromorphic computing, understanding the underlying mechanisms in the resistive switching of memristor devices is of paramount importance. Here, we demonstrate a two-step resistive switching set process involving a complex interplay among mobile halide ions/vacancies  $(I^-/V_I^+)$  and silver ions  $(Ag^+)$  in perovskite-based memristors with thin undoped buffer layers. The resistive switching involves an initial gradual increase in current associated with a drift-related halide migration within the perovskite bulk layer followed by an abrupt resistive switching associated with diffusion of mobile  $Ag^+$  conductive filamentary formation. Furthermore, we develop a dynamical model that explains the characteristic I-V curve that helps to untangle and quantify the switching regimes consistent with the experimental memristive response. This further insight into the two-step set process provides another degree of freedom in device design for versatile applications with varying levels of complexity.



Supporting Information

rtificially intelligent devices have recently been attracting A considerable attention due to the increasing hardware demands of neural network configurations with varying levels of computational complexity.<sup>1-3</sup> Resistive random-access memory (ReRAM) based on memristor devices is widely considered as the most promising candidate for nextgeneration computational frameworks owing to their inmemory and neuromorphic computing capabilities.<sup>3-5</sup> This includes their simple device structure, high device density, low power consumption, fast switching speed, and monolithic integration compatibility with existing complementary metal/ oxide/semiconductor (CMOS) systems.4,6,7 Resistive switching has been demonstrated in a diverse range of devices such as metal/oxide/metal structures,<sup>8-10</sup> organic semiconductors,<sup>11-13</sup> CMOS-compatible silicon-based devices,<sup>14-16</sup> and numerous halide perovskite formulations.<sup>17–19</sup>

Different neuromorphic computing schemes require specific switching properties from artificial neuromorphic hardware. These characteristics range from nonvolatile binary switching for digital in-memory computing and spiking neural networks<sup>1,3</sup> to volatile analog switching for artificial neural network configurations and brain-inspired computing.<sup>4,20–22</sup> The device application is intimately associated with the switching mechanism. In this respect, proposed resistive switching mechanisms range from drift-related nonfilamentary oxygen vacancy migration and redistribution in metal and titanium oxide-based devices<sup>23,24</sup> and diffusive formation and rupture of metallic conductive filaments in silicon oxide-based devices<sup>15,16</sup> to halide filamentary formation followed by electrochemical interactions with contacts that promote switching in perovskite-based devices.<sup>25,26</sup> Despite the rapid

development of material systems and configurations exhibiting distinct memristive switching properties, understanding the precise mechanisms is essential for tailoring device design for a wider range of applications in more advanced computational frameworks.

Metal halide perovskite materials are versatile candidates for memory applications as they benefit from mixed ionicelectronic conduction due to ionic halide defect displacement resulting in intrinsic memory effects.<sup>27-29</sup> Metal halide perovskites have a chemical structure of ABX<sub>3</sub>, where A is a monovalent cation (i.e., MA =  $CH_3NH_3^+$ ), B is a divalent cation (i.e., Pb<sup>2+</sup>), and X is a halide anion (i.e., I<sup>-</sup>). With the flexibility of the perovskite structure as the material platform, it possesses a broad range of switching physics suitable for a wide variety of neuromorphic computing achitectures.<sup>30</sup> Perovskitebased memristive devices have been demonstrated to function as artificial synapses exhibiting essential synaptic behaviors for neuromuscular systems, pupil reflex, and light-sensitive optogenetic applications.<sup>31–34</sup> Additionally, integration of two-dimensional structures,<sup>35,36</sup> mixed formulations,<sup>37,38</sup> and nanocrystals<sup>21,39</sup> further increases the already vast degrees of freedom or state variables in perovskite-based memristors allowing tunability and versatility specific to the desired

Received:December 2, 2022Accepted:January 18, 2023Published:February 4, 2023





implementation. However, with the inclusion of various intermediate buffers,<sup>40,41</sup> a complete picture of the resistive switching mechanism is imperative for tailoring the design of reliable memristive devices for more versatile applications.

Here, we present a two-step resistive switching (RS) SET process in methylammonium lead iodide (MAPbI<sub>3</sub>) memristors with various thin undoped buffer layers. The MAPbI<sub>3</sub> perovskite formulation is selected to gain a simple and wellestablished understanding of the electronic and ionic dynamics with a low activation energy. The two different buffer layers used are (6,6)-phenyl C61 butyric acid methyl ester (PCBM), typically used as an electron selective layer,<sup>42</sup> and the insulator poly(methyl methacrylate) (PMMA), typically used as a protective layer for the perovskite.<sup>43-45</sup> On the basis of the switching characteristics of the memristor devices, in conjuction with a direct comparison to a device configuration without a buffer layer, two distinct switching regimes are untangled: (1) an initial gradual increase in current associated with drift-related I<sup>-</sup> ion and V<sub>I</sub><sup>+</sup> defect migration and redistribution within the perovskite bulk layer followed by (2) an abrupt resistive switching associated with diffusionrelated Ag<sup>+</sup> filamentary formation irrespective of the buffer layer. The two-step SET process exhibits both drift and diffusive mechanisms, depending on the applied field, allowing memristor device designs specifically tailored for targeted neural network configurations.

The cross-sectional scanning electron microscopy (SEM) micrographs of the fabricated memristor devices with PCBM and PMMA layers are shown in panels a and b of Figure 1, respectively, with the device configuration indicating the layers. Both devices have MAPbI<sub>3</sub> perovskite layers with comparable thicknesses (~400 nm) and similar crystal morphologies. The buffer layers are substantially thin with thicknesses ranging from  $\sim 5$  to  $\sim 10$  nm to have a minimal voltage drop within these layers. The characteristic I-V curves of a representative memristor device with the PCBM buffer layer is shown in Figure 1c, and RS activation and deactivation involve migration of  $I^-/V_I^+$  and Ag<sup>+</sup>. The memristive response requires initial conditioning of the fresh device (electroforming process) at relatively high voltages, which produces a significant change in the device conductance.<sup>46–50</sup> From the fresh state of the device, a positive voltage sweep is applied to promote the electroforming process (Figure 1d). As the applied voltage approaches  $\sim 0.9$  V, the current gradually increases and the continued voltage sweep abruptly increases the device current at ~1.45 V. A cutoff current of 50 mA is imposed on the measurement to avoid the irreversible processes that can lead to complete device breakdown. This cutoff current is reached at  $\sim$ 1.6 V, where the scan direction is immediately reversed back to 0 V. Another scan toward positive bias reveals a new stabilized high-resistance state (HRS). A positive voltage sweep gradually increases in current at a first threshold voltage of  $V_{\rm Th1} \sim 0.25$  V [SET1 process (Table 1)] and then abruptly switches ON to the lowresistance state (LRS) at a second threshold voltage of  $V_{\rm Th2} \sim$ 0.56 V (SET2 process) with an ON/OFF ratio of ~21.3. This two-step SET process indicates two distinct switching regimes in the different voltage ranges as illustrated in Figure 1d, which will be discussed in detail below. The memristor device, then, stays at the LRS on the reverse scan direction and finally switches OFF to the HRS (RESET process) at  $V_{\rm RESET} \sim -0.59$ V. Once electroforming has taken place, the I-V curve is stabilized and the curves of multiple cycles overlay as shown in



**Figure 1.** Cross-sectional SEM micrographs of memristors with thin undoped (a) PCBM and (b) PMMA buffer layers with a schematic diagram of the device configuration. (c) Representative characteristic I-V curves of the initial conditioning step of the FRESH device and the stabilized two-step SET process and RESET process with the arrows indicating the scan direction. (d) Schematic diagram of the electroforming and two-step SET process mechanism under the applied voltage of the memristive devices with buffer layers. The colors of the device configuration indicate the layers in the schematic diagram.

Table 1. Summary of Threshold Voltages  $V_{Th1}$ ,  $V_{Th2}$ , and  $V_{RESET}$  Corresponding to the SET1, SET2, and RESET Processes, Respectively, and ON/OFF Ratios for All Memristor Devices

device	$V_{\mathrm{Th1}}$ (V)	$V_{\mathrm{Th2}}$ (V)	$V_{\text{RESET}}$ (V)	ON/OFF ratio
PCBM	+0.25	+0.56	-0.59	21.3
PMMA	+0.26	+0.60	-0.59	39.3
MAPbI <sub>3</sub> /Au	+0.57	-	+0.29	21.0

Figure S1. Both devices exhibit ON state retention times approcaching  $10^5$  s at a read voltage ( $V_{read}$ ) of 0.2 V with an endurance of >50 cycles (Figure S2), and we note some performance degradation is observed during the initial 50 cycles. It is worth noting that the memristor device configuration is designed to emphasize the kinetics and dynamics of the resistive switching mechanism. Incorporation of a large cation dopant, such as ethylenediammonium (en), has been proven to substatially improve the device stability to record endurances of  $1.2 \times 10^4$  cycles.<sup>30</sup>

To investigate the effect of the buffer layer on the switching properties, the performance of memristors containing either PCBM or PMMA as the buffer layer is compared with that of devices that contain no buffer layer. PCBM and PMMA are materials very different from the point of view of their



**Figure 2.** Characteristic I-V curves on the semilog scale of the memristor devices with thin undoped (a) PCBM and (b) PMMA buffer layers exhibiting nonvolatile bipolar resistive switching and (c) the MAPbI<sub>3</sub>/Au device exhibiting volatile unipolar resistive switching. The arrows indicate the scan direction and the corresponding SET and RESET processes with their respective threshold voltages. Corresponding SET processes on the log–log scale of the (d) PCBM, (e) PMMA, and (f) MAPbI<sub>3</sub>/Au devices with the slopes calculated via piecewise linear fitting.

electronic properties, which will help to rule out any effects of energy level aligments that affect charge extraction. Indeed, while PCBM is a semiconductor that is often used a an electron selective layer, PMMA is an insulating material. The representative stabilized responses of their memristors are shown in panels a and b of Figure 2, respectively. Both memristors feature a resistive switching with the two-step SET process as described above with similar threshold values and current levels (Table 1). Therefore, effects related to energy level alignemnt at the perovskite interfaces do not appear to be related to the switching mechanims, and the resistive switching mechanism is of a different nature as explained below. The resistive switching with the SET and RESET processes occurring at opposite polarities of the applied voltage indicates a nonvolatile bipolar resistive switching characteristic of the memristor device.<sup>40,45,51</sup> Alternatively, Figure 2c shows the characteristic I-V response of a memristor without any buffer layer and a nonreactive contact (MAPbI<sub>3</sub>/Au). Interestingly, this device exhibits only the gradual SET1 process but without the abrupt SET2 process at the positive polarity. In addition, a gradual RESET process to the HRS in the reverse scan direction is observed. The SET and RESET processes occur at the same polarity, indicating that the device works as a volatile unipolar resistive switch.<sup>21,51</sup> Therefore, a volatile memory device is transformed into a nonvolatile device by adding a buffer layer, indicating that the buffer layer acts not only as a physical barrier to ions but also as a "pool" of ions that become trapped when the external electrical field is removed.

With regard to the activation mechanims, different authors have established that for devices that do not contain a buffer layer in the presence of a nonreactive contact (i.e., Au), the gradual increase in current is attributed to the mobile I<sup>-</sup> ions migrating toward the Ag contact, consequently doping the intermediate buffer layer (Figure 1d).<sup>26,27,52,53</sup> Correspondingly, the iodine vacancies (V<sub>I</sub><sup>+</sup>) migrate toward the inert PEDOT:PSS, leaving behind a doped perovskite material.<sup>25,54</sup>

In addition, the chemical interactions of migrating ions with the external contact can also lead to a reduction of the extraction barriers. Note that if the external contact is a reactive metal (i.e., Ag), a fast electrochemical reaction masks the memristive response as shown for the MAPbI<sub>3</sub>/Ag/Au interfaces in Figure S3. Alternatively, when buffer layers are used, we propose that the electroforming process at high applied voltages pushes the I<sup>-</sup> ions to cross the nonconductive buffer layer, accumulating at the Ag contact leading to the formation of AgI (Figure 1d).<sup>25,26</sup> The electrochemical reaction generates mobile Ag<sup>+</sup> ions that migrate toward the bottom contact under the influence of the applied field. Note that neutral Ag does not have a driving force to follow the electrical field. The migration and accumulation of mobile Ag<sup>+</sup>,  $I^-$ , and  $V_I^+$  eventually switch the device abruptly to the LRS or ON state. Once the applied voltage returns to 0 V, the mobile  $Ag^+$ , I<sup>-</sup>, and V<sub>I</sub><sup>+</sup> relax and a new stabilized HRS or OFF state is established. In addition, the thin Ag/Au contact is used to control and modulate the interactivity of the mobile I<sup>+</sup> ions with Ag to prevent the formation of an excessively thick AgI structure with a low ionic conductivity.<sup>55</sup> In general, the presence of the buffer layer in conjuction with the reactive Ag contact is responsible for the abrupt SET2 process by controlling the formation of a pool of slow-moving ions within the buffer layer and the perovskite and by regulating the reactivity of migrating ions with Ag.

We next set out to further analyze the characteristic I-V response to understand if the kinetics of the SET processes can be correlated between different samples, providing further insight into the mechanisms governing the switching processes. The SET processes from the HRS to the LRS for all memristor devices are represented in the log–log scale as shown in Figure 2b. At applied voltages below  $V_{Th1}$ , the memristor devices are in the HRS with the current exhibiting a linear dependence on the applied voltage. Correspondingly, the calculated HRS slopes via piecewise linear fitting result in  $m_{HRS}$  values of ~1

for all memristor devices, indicating an ohmic conduction mechanism.  $^{45,49,56}$  Beyond  $V_{\rm Th1}$ , the current gradually increases (SET1) with  $m_{\text{SET1}}$  values of ~4.20 and ~4.83 for the memristors with PCBM and PMMA buffer layers, respectively.  $m_{\text{SET1}}$  values of >1 are attributed to a drift-related switching mechanism due to halide ion migration and redistribution within the perovskite material.<sup>57,58</sup> Once the applied voltage reaches  $V_{Th2}$ , the memristor devices with buffer layers abruptly switch (SET2) to the LRS, which is indicative of diffusionrelated conductive filament formation across the buffer layer.  $^{22,59-61}$  In the reverse scan direction, the samples with the buffer layers maintain an ohmic conduction response during the reverse scan with an  $m_{LRS}$  of ~1. On the contrary, the MAPbI<sub>3</sub>/Au device exhibits an ohmic HRS with a slope of  $m_{\rm i} \sim 0.98$  for applied voltages below  $V_{\rm Th1}$ . As the applied voltage is further increased, the SET1 process exhibits a higher  $m_{ii}$  of ~12.78. This higher  $m_{ii}$  of MAPbI<sub>3</sub>/Au could be attributed the reduced series resistance of the devices, as compared to those with buffer layers. Thus, at a given applied external voltage, the electrical field present at the perovskite layer is higher than that of the devices with the buffer layers, promoting a fast migration of ions and more current injection. Once switched ON, the device then stays in the LRS with an  $m_{\rm iii}$  of ~2.66 in the reverse scan direction followed by a gradual decrease in current with an  $m_{iv}$  of ~7.08 and eventually switching the device OFF back to the ohmic HRS with an  $m_{\rm y}$ of ~1.13.

As the characteristic I-V response of the memristor devices is carried out under dark and controlled conditions inside a glovebox, the measurement protocol is identical to that of the space-charge-limited conduction (SCLC) characterization.<sup>22,45,49,62</sup> In SCLC analysis, the conduction mechanism at different voltage ranges is interpreted from the obtained slopes via piecewise linear fitting. However, the SCLC characterization considers only the carrier transport and injection properties of the device. In lieu of the SCLC analysis, we present a dynamical model for elucidating the experimental observations and provide a clearer understanding of the complex features of the characteristic I-V resistive switching response of the memristor devices with buffer layers. Our model takes into account interfacial reactions and charge accumulation and is not solely based on carrier transport mechanisms. This general model lends an alternative analysis pathway to various approaches such as SCLC,<sup>22,62</sup> drift-diffusion simulations,<sup>16,63</sup> and SPICE modeling.<sup>64-67</sup>

The dynamical model consists of a system of equations describing the characteristic I-V response given by  $^{68,69}$ 

$$I_{\text{tot}} = \frac{u}{R_{\text{b}}} + i_{c_1}f + i_{c_2}g + C_{\text{m}}\frac{\mathrm{d}u}{\mathrm{d}t}$$
(1)

$$\tau_{k_1} \frac{\mathrm{d}f}{\mathrm{d}t} = (1 - f) - \mathrm{e}^{(u - V_{T_1})f/V_{m_1}} \tag{2}$$

$$\tau_{k_2} \frac{\mathrm{d}g}{\mathrm{d}t} = (1 - g) - \mathrm{e}^{(u - V_{T_2})g/V_{m_2}} \tag{3}$$

The model considers four contributions for the extracted current  $(I_{tot})$  under the applied electrical field.  $u/R_b$  is the ohmic conduction response term with a constant resistance  $R_b$ .  $i_{c_b}f$  is the gradual injection current term with a saturation value of  $i_{c_1}$  controlled by an occupation function f ( $0 \le f \le 1$ ) associated with the SET1 process.  $i_{c_2}g$  is the subsequent current

transition term with a saturation value of  $i_{c_2}$  controlled by a different occupation function g ( $0 \le g \le 1$ ) associated with the SET2 process, and the capacitive charging of the interfaces term with a capacitance  $C_{\rm m}$ .<sup>68–70</sup> The four independent variables contribute to the total current  $I_{\rm tot}$  the applied voltage (u), and occupation functions f and g. Both eqs 2 and 3 represent the diffusion or migration time of ions introducing a delayed response that lags behind the applied voltage with characteristic times  $\tau_{k_1}$  and  $\tau_{k_2}$ , respectively. The delay equations are controlled by onset potentials  $V_{T_1}$  and  $V_{T_2}$ , and ideality factors  $m_1 = q \frac{V_{m1}}{k_b T}$  and  $m_2 = q \frac{V_{m2}}{k_b T}$  for eqs 2 and 3, respectively, where q is the electron charge,  $k_b$  is the Boltzmann constant, and T is room temperature. When the time derivative is suppressed, the steady state solutions become

$$f_{\rm ss}(u) = \frac{1}{1 + e^{-(u - V_{T_1})/V_{m_1}}}$$
(4)

$$g_{ss}(u) = \frac{1}{1 + e^{-(u - V_{T_2})/V_{m_2}}}$$
(5)

Hence, the steady state current is then expressed as

$$I_{\rm tot} = \frac{u}{R_{\rm b}} + i_{c_{\rm f}} f_{\rm ss}(u) + i_{c_{\rm g}} g_{\rm ss}(u)$$
(6)

Applying the dynamical model (eq 6) to the experimental results provides valuable information about the resistive switching of the memristor devices with buffer layers. The fitted SET process characteristic I-V responses of the memristor devices on the linear, semilog, and log–log scales are presented in Figure 3. The detailed fitting method is



**Figure 3.** The characteristic I-V SET process with the corresponding fitted curves using the dynamical model for both memristor devices in the (a and b) linear, (c and d) semilog, and (e and f) log–log scales.

pubs.acs.org/JPCL

Letter

Table 2. Summary of the Fitted Parameters with the Corresponding Ideality Factors *m* Given by the Equation  $V_m = mk_bT/q$ Using the Dynamical Model for All Memristor Devices

device	$R_{\rm b}~(\Omega)$	$V_{T_1}$ (V)	$V_{m_1}$ (V)	$m_1$	$i_{c_1}$ (A)	$V_{T_2}$ (V)	$V_{m_2}$ (V)	$m_2$	$i_{c_2}$ (A)
РСВМ	$6.39 \times 10^{2}$	$6.36 \times 10^{-1}$	$6.81 \times 10^{-2}$	2.619	$2.22 \times 10^{-2}$	$5.69 \times 10^{-1}$	$5.77 \times 10^{-4}$	0.010	$8.69 \times 10^{-3}$
PMMA	$2.77 \times 10^{3}$	$6.92 \times 10^{-1}$	$8.65 \times 10^{-2}$	3.327	$2.53 \times 10^{-2}$	$6.04 \times 10^{-1}$	$1.89 \times 10^{-3}$	0.032	$1.05 \times 10^{-2}$

described in the Supporting Information to determine the relevant parameters as summarized in Table 2. The fitted curves capture the pertinent features of ohmic LRS and the two-step SET process of the memristor devices from the linear to the log-log scales. From the extracted parameters of the fitting, the memristor devices have different  $R_{\rm b}$  parameters. The  $R_{\rm b}$  values can be attributed to the differences in buffer layer intrinsic resistivity and slight variations in layer thicknesses. In addition, SET1 onset potential  $V_1$  and saturation current  $i_{c_1}$  of the PCBM and PMMA devices have similar values. Moreover, both devices have comparable  $m_1$ ideality factor values of  $\sim$ 2.6 and  $\sim$ 3.3 for the memristor with PCBM and PMMA buffer layers, respectively. These ideality factor values can be attributed to the slow and gradual migration and reaction of  $ions^{18,70}$  or the decrease in the surface barrier at the perovskite/contact interface.<sup>70-72</sup> Similarly, SET2 onset potential  $V_2$  and saturation current  $i_{c_2}$ of the PCBM and PMMA devices also have similar values. Notably, ideality factors  $m_2$  of the memristor devices are significantly lower than their corresponding  $m_1$  values with values of ~0.01 and ~0.03 for the devices with PCBM and PMMA buffer layers, respectively. The lower  $m_2$  values capture the abrupt resistive switching and the continued current increase after the SET process, suggesting that the conductive filamentary formation is an avalanche effect. The high correlation of the fitted SET1 parameters indicates that the mechanism during the gradual current increase is general in both devices regardless of the type of buffer layer. On the contrary, the differences in the  $m_2$  parameters suggest that the avalanche SET2 process is affected by the slight variations in the intrinsic properties and layer thicknesses of the buffer layers.

On the basis of these results, a two-step resistive switching SET process is proposed involving the complex interplay among mobile Ag<sup>+</sup>, I<sup>-</sup> ,and V<sub>I</sub><sup>+</sup> ions as schematically presented in Figure 1d. In the initial device state (FRESH state), (i) the mobile I<sup>-</sup> ions and V<sub>I</sub><sup>+</sup> defects are uniformly distributed throughout the perovskite bulk layer. During the electroforming process, migrating I<sup>-</sup> ions and V<sub>I</sub><sup>+</sup> defects accumulate at the top and bottom contacts, respectively, (ii) switching the device to the LRS. The implemented cutoff current prevents device breakdown and the irreversible conductive filamentary formation that can permanently keep the device in the LRS state. The immediate reverse scan direction back to 0 V relaxes the ion and defect migration, resulting in the rupture of conductive filaments and (iii) maintaining a stabilized HRS lower than that of the equilibrium FRESH state. From the new lower stabilized HRS with an ohmic resistance  $R_{\rm b}$ , a positive scan allows mobile I<sup>-</sup> ions to migrate toward the Ag contact, consequently doping the intermediate buffer layer.<sup>26,52</sup> Correspondingly, the VI+ defects migrate toward the inert PEDOT:PSS and FTO bottom contacts.<sup>25,54</sup> As the device is already at a less resistive HRS, a lower applied voltage  $(V_{\mathrm{Th1}})$  is required for the migrating I<sup>-</sup> ions and V<sub>I</sub><sup>+</sup> defects to accumulate at the contacts, (iv) gradually switching the

resistance state of the device (SET1). Subsequently, the accumulated I<sup>-</sup> ions promote the oxidation of the Ag contact, resulting in the formation of a AgI layer at the contact interface allowing activated Ag ions to migrate toward the bottom contact through the buffer layer.<sup>25,41,52</sup> The combination of activated migrating ions and defects at a specific applied voltage  $(V_{Th2})$  favor the conductive filamentary formation through the buffer layers (v) abruptly switching the device to the LRS (SET2). The memristor devices, then, remain in the LRS in the reverse scan direction, necessitating a negative  $V_{\text{RESET}}$  (vi) to stably rupture the conductive filaments and to return back to the stabilized HRS. It is noted that the RESET process does not exhibit the two-step process. As observed in the two-step SET process, the diffusion of migrating  $I^-$  and  $V_I^+$ (SET1) occurs prior to the formation of the Ag<sup>+</sup> conductive filaments (SET2). Hence, during the reverse scan toward the negative voltages, the migrating I<sup>-</sup> ions and V<sub>I</sub><sup>+</sup> defects already approach their relaxed state prior to the complete rupture of the conductive Ag<sup>+</sup> filaments. Therefore, the single-step RESET process can be attributed to the difference in the time scales between the faster diffusion of ions and defects and the slower diffusion of the Ag ions.

In summary, we have demonstrated that a two-step resistive switching SET can be induced by the introduction of a buffer layer between the perovskite and the top contact. This additional layer turns a device that shows a volatile memory response into a nonvolatile memory. The buffer layer in conjuction with the reactive Ag contact is responsible for the abrupt SET2 process by controlling the formation of a "pool" of slow-moving ions within the buffer layer and the perovskite and by regulating the reactivity of migrating ions with Ag. Furthermore, we present a dynamical model that distinctly describes the two different switching mechamism regimes indicated by the extracted ideality factors. The experiments reveal that the current control is due to accumulated charges and interfacial reactions. Moreover, the high correlation of the model parameters suggests that the two-step SET process is governed by the same mechanism irrespective of the buffer layer. This insight into the mechanisms governing the switching response would be relevant for memristor configurations specifically tailored for targeted neural network applications with varying levels of complexity. These devices exhibit both drift and diffusive switching responses and can be utilized for adaptable implementation of versatile device designs in more diverse computational frameworks.

#### METHODS

The fabricated memristor device configuration consists of a fluorine-doped tin oxide (FTO)/poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS)/MAPbI<sub>3</sub>/buffer layer/Ag/Au structure. The two different buffer layers used are (6,6)-phenyl C61 butyric acid methyl ester (PCBM) and poly(methyl methacrylate) (PMMA). The thin buffer layers are prepared by spin coating without any additional dopants and with similar thicknesses. The fabrication method is further discussed in detail in the Supporting Information.

The film morphology of the memristor devices is inspected via cross-sectional SEM (JEOL JSM-7001F). The electrical characterizations of the memristor devices are performed inside a nitrogen-controlled glovebox in the dark using an Autolab PGSTAT204 potentiostat to minimize moisturerelated degradation effects and to improve reproducibility.

The electroforming step is initiated via a voltage sweep from 0 V to 2.5 V to 0 V with a cutoff current of 50 mA, which immediately reverses the scan direction once it is reached to avoid complete device breakdown. Instead of current compliance, which limits the maximum operating current but continues the voltage scan direction, the cutoff current is implemented to observe the full switching response without a loss of information. The characteristic I-V responses of the devices are then measured via a voltage sweep from 0 V to  $+V_u$  to  $-V_l$  to 0 V, where the upper  $(V_u)$  and lower  $(V_l)$  voltage vertices are selected for stable, reproducible resistive switching from a HRS or OFF state to a LRS or ON state.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c03669.

Memristor device fabrication, stabilized characteristic *I*– *V* switching response, ON state retention and endurance measurements, redox reaction of the MAPbI<sub>3</sub>/Ag/Au device, and dynamical model fitting resources (PDF)

Raw current-voltage data of device containing PCBM buffer layer (TXT)

Transparent Peer Review report available (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

Antonio Guerrero – Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain; orcid.org/0000-0001-8602-1248; Email: aguerrer@ uji.es

#### Author

Cedric Gonzales – Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain; Orcid.org/ 0000-0002-6550-2007

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.2c03669

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors are thankful for the financial support from the Generalitat Valenciana for the Grisolia Grant (GRISOLIAP/ 2019/048) and the Ministerio de Ciencia e Innovación of Spain (MICINN) (PID2019-107348GB-100).

#### REFERENCES

(1) Ielmini, D.; Wong, H. S. P. In-Memory Computing with Resistive Switching Devices. *Nat. Electron.* **2018**, *1* (6), 333–343. (2) John, R. A.; Shah, N.; Vishwanath, S. K.; Ng, S. E.; Febriansyah, B.; Jagadeeswararao, M.; Chang, C. H.; Basu, A.; Mathews, N. Halide Perovskite Memristors as Flexible and Reconfigurable Physical Unclonable Functions. *Nat. Commun.* **2021**, *12* (1), 3681.

(3) Zidan, M. A.; Strachan, J. P.; Lu, W. D. The Future of Electronics Based on Memristive Systems. *Nat. Electron.* **2018**, *1* (1), 22–29.

(4) Ielmini, D.; Wang, Z.; Liu, Y. Brain-Inspired Computing Via Memory Device Physics. *APL Mater.* **2021**, *9* (5), 050702.

(5) Park, Y.; Lee, J.-s. Metal Halide Perovskite-Based Memristors for Emerging Memory Applications. *J. Phys. Chem. Lett.* **2022**, *13*, 5638–5647.

(6) Prezioso, M.; Merrikh-Bayat, F.; Hoskins, B. D.; Adam, G. C.; Likharev, K. K.; Strukov, D. B. Training and Operation of an Integrated Neuromorphic Network Based on Metal-Oxide Memristors. *Nature* **2015**, *521* (7550), 61–64.

(7) Zhao, M.; Gao, B.; Tang, J.; Qian, H.; Wu, H. Reliability of Analog Resistive Switching Memory for Neuromorphic Computing. *Appl. Phys. Rev.* 2020, 7 (1), 011301.

(8) Lee, A. R.; Bae, Y. C.; Baek, G. H.; Chung, J. B.; Lee, S. H.; Im, H. S.; Hong, J. P. Multifunctional Resistive Switching Behaviors Employing Various Electroforming Steps. J. Mater. Chem. C 2016, 4 (4), 823–830.

(9) Strukov, D. B.; Snider, G. S.; Stewart, D. R.; Williams, R. S. The Missing Memristor Found. *Nature* 2008, 453 (7191), 80–83.

(10) Huang, H. M.; Yang, R.; Tan, Z. H.; He, H. K.; Zhou, W.; Xiong, J.; Guo, X. Quasi-Hodgkin–Huxley Neurons with Leaky Integrate-and-Fire Functions Physically Realized with Memristive Devices. *Adv. Mater.* **2019**, *31* (3), 1803849–1803849.

(11) Gerasimov, J. Y.; Gabrielsson, R.; Forchheimer, R.; Stavrinidou, E.; Simon, D. T.; Berggren, M.; Fabiano, S. An Evolvable Organic Electrochemical Transistor for Neuromorphic Applications. *Adv. Sci.* **2019**, *6* (7), 1801339.

(12) Melianas, A.; Quill, T. J.; LeCroy, G.; Tuchman, Y.; Loo, H. v.; Keene, S. T.; Giovannitti, A.; Lee, H. R.; Maria, I. P.; McCulloch, I.; Salleo, A. Temperature-Resilient Solid-State Organic Artificial Synapses for Neuromorphic Computing. *Sci. Adv.* **2020**, *6* (27), abb2958.

(13) Van De Burgt, Y.; Lubberman, E.; Fuller, E. J.; Keene, S. T.; Faria, G. C.; Agarwal, S.; Marinella, M. J.; Alec Talin, A.; Salleo, A. A Non-Volatile Organic Electrochemical Device as a Low-Voltage Artificial Synapse for Neuromorphic Computing. *Nat. Mater.* **2017**, *16* (4), 414–418.

(14) Covi, E.; Wang, W.; Lin, Y. H.; Farronato, M.; Ambrosi, E.; Ielmini, D. Switching Dynamics of Ag-Based Filamentary Volatile Resistive Switching Devices - Part I: Experimental Characterization. *IEEE T. Electron Dev.* **2021**, 68 (9), 4335–4341.

(15) Ilyas, N.; Li, C.; Wang, J.; Jiang, X.; Fu, H.; Liu, F.; Gu, D.; Jiang, Y.; Li, W. A Modified Sio 2 -Based Memristor with Reliable Switching and Multifunctional Synaptic Behaviors. *J. Phys. Chem. Lett.* **2022**, *13*, 884–893.

(16) Wang, W.; Covi, E.; Lin, Y. H.; Ambrosi, E.; Milozzi, A.; Sbandati, C.; Farronato, M.; Ielmini, D. Switching Dynamics of Ag-Based Filamentary Volatile Resistive Switching Devices - Part Ii: Mechanism and Modeling. *IEEE T. Electron Dev.* **2021**, *68* (9), 4342– 4349.

(17) Beom, K.; Fan, Z.; Li, D.; Newman, N. Halide Perovskite Based Synaptic Devices for Neuromorphic Systems. *Mater. Today Phys.* **2022**, 24, 100667–100667.

(18) Fang, Y.; Zhai, S.; Chu, L.; Zhong, J. Advances in Halide Perovskite Memristor from Lead-Based to Lead-Free Materials. *ACS Appl. Mater. Interfaces* **2021**, *13* (15), 17141–17157.

(19) Xiao, X.; Hu, J.; Tang, S.; Yan, K.; Gao, B.; Chen, H.; Zou, D. Recent Advances in Halide Perovskite Memristors: Materials, Structures, Mechanisms, and Applications. *Adv. Mater. Technol.* **2020**, 5 (6), 1900914.

(20) Christensen, D. V.; Dittmann, R.; Linares-Barranco, B.; Sebastian, A.; Le Gallo, M.; Redaelli, A.; Slesazeck, S.; Mikolajick, T.; Spiga, S.; Menzel, S.; Valov, I.; Milano, G.; Ricciardi, C.; Liang, S.-J.; Miao, F.; Lanza, M.; Quill, T. J.; Keene, S. T.; Salleo, A.; Grollier, J.; Markovic, D.; Mizrahi, A.; Yao, P.; Yang, J. J.; Indiveri, G.; Strachan, J. P.; Datta, S.; Vianello, E.; Valentian, A.; Feldmann, J.; Li, X.; Pernice, W. H. P.; Bhaskaran, H.; Furber, S.; Neftci, E.; Scherr, F.; Maass, W.; Ramaswamy, S.; Tapson, J.; Panda, P.; Kim, Y.; Tanaka, G.; Thorpe, S.; Bartolozzi, C.; Cleland, T. A.; Posch, C.; Liu, S.; Panuccio, G.; Mahmud, M.; Mazumder, A. N.; Hosseini, M.; Mohsenin, T.; Donati, E.; Tolu, S.; Galeazzi, R.; Christensen, M. E.; Holm, S.; Ielmini, D.; Pryds, N. 2022 Roadmap on Neuromorphic Computing and Engineering **2022**, *2*, 022501.

(21) John, R. A.; Demirağ, Y.; Shynkarenko, Y.; Berezovska, Y.; Ohannessian, N.; Payvand, M.; Zeng, P.; Bodnarchuk, M. I.; Krumeich, F.; Kara, G.; Shorubalko, I.; Nair, M. V.; Cooke, G. A.; Lippert, T.; Indiveri, G.; Kovalenko, M. V. Reconfigurable Halide Perovskite Nanocrystal Memristors for Neuromorphic Computing. *Nat. Commun.* **2022**, *13* (1), 2074.

(22) Zhu, J.; Zhang, T.; Yang, Y.; Huang, R. A Comprehensive Review on Emerging Artificial Neuromorphic Devices. *Appl. Phys. Rev.* **2020**, 7 (1), 011312.

(23) Pickett, M. D.; Strukov, D. B.; Borghetti, J. L.; Yang, J. J.; Snider, G. S.; Stewart, D. R.; Williams, R. S. Switching Dynamics in Titanium Dioxide Memristive Devices. *J. Appl. Phys.* **2009**, *106* (7), 074508.

(24) Prezioso, M.; Merrikh Bayat, F.; Hoskins, B.; Likharev, K.; Strukov, D. Self-Adaptive Spike-Time-Dependent Plasticity of Metal-Oxide Memristors. *Sci. Rep.* **2016**, *6*, 21331.

(25) Solanki, A.; Guerrero, A.; Zhang, Q.; Bisquert, J.; Sum, T. C. Interfacial Mechanism for Efficient Resistive Switching in Ruddlesden-Popper Perovskites for Non-Volatile Memories. *J. Phys. Chem. Lett.* **2020**, *11* (2), 463–470.

(26) Zhu, X.; Lee, J.; Lu, W. D. Iodine Vacancy Redistribution in Organic–Inorganic Halide Perovskite Films and Resistive Switching Effects. *Adv. Mater.* **2017**, *29* (29), 1700527.

(27) Azpiroz, J. M.; Mosconi, E.; Bisquert, J.; De Angelis, F. Defect Migration in Methylammonium Lead Iodide and Its Role in Perovskite Solar Cell Operation. *Energy Environ. Sci.* **2015**, *8* (7), 2118–2127.

(28) Lopez-Varo, P.; Jiménez-Tejada, J. A.; García-Rosell, M.; Ravishankar, S.; Garcia-Belmonte, G.; Bisquert, J.; Almora, O. Device Physics of Hybrid Perovskite Solar Cells: Theory and Experiment. *Adv. Energy Mater.* **2018**, 8 (14), 1702772.

(29) Senocrate, A.; Maier, J. Solid-State Ionics of Hybrid Halide Perovskites. J. Am. Chem. Soc. 2019, 141 (21), 8382-8396.

(30) Sakhatskyi, K.; John, R. A.; Guerrero, A.; Tsarev, S.; Sabisch, S.; Das, T.; Matt, G. J.; Yakunin, S.; Cherniukh, I.; Kotyrba, M.; Berezovska, Y.; Bodnarchuk, M. I.; Chakraborty, S.; Bisquert, J.; Kovalenko, M. V. Assessing the Drawbacks and Benefits of Ion Migration in Lead Halide Perovskites. *ACS Energy Lett.* **2022**, *7*, 3401–3414.

(31) Gong, J.; Wei, H.; Liu, J.; Sun, L.; Xu, Z.; Huang, H.; Xu, W. An Artificial Visual Nerve for Mimicking Pupil Reflex. *Matter* **2022**, *5* (5), 1578–1589.

(32) Gong, J.; Yu, H.; Zhou, X.; Wei, H.; Ma, M.; Han, H.; Zhang, S.; Ni, Y.; Li, Y.; Xu, W. Lateral Artificial Synapses on Hybrid Perovskite Platelets with Modulated Neuroplasticity. *Adv. Funct. Mater.* **2020**, *30* (46), 2005413.

(33) Liu, J.; Gong, J.; Wei, H.; Li, Y.; Wu, H.; Jiang, C.; Li, Y.; Xu, W. A Bioinspired Flexible Neuromuscular System Based Thermal-Annealing-Free Perovskite with Passivation. *Nat. Commun.* **2022**, *13* (1), 7427.

(34) Zhu, X.; Lu, W. D. Optogenetics-Inspired Tunable Synaptic Functions in Memristors. ACS Nano 2018, 12 (2), 1242–1249.

(35) Gedda, M.; Yengel, E.; Faber, H.; Paulus, F.; Kreß, J. A.; Tang, M. C.; Zhang, S.; Hacker, C. A.; Kumar, P.; Naphade, D. R.; Vaynzof, Y.; Volonakis, G.; Giustino, F.; Anthopoulos, T. D. Ruddlesden–Popper-Phase Hybrid Halide Perovskite/Small-Molecule Organic Blend Memory Transistors. *Adv. Mater.* **2021**, *33* (7), 2003137.

(36) Park, Y.; Lee, J.-s. Controlling the Grain Size of Dion–Jacobson-Phase Two-Dimensional Layered Perovskite for Memory Application. ACS Appl. Mater. Interfaces **2022**, 14 (3), 4371–4377.

(37) Huang, L.; Wu, L.; Sun, Q.; Jin, C.; Wang, J.; Fu, S.; Wu, Z.; Liu, X.; Hu, Z.; Zhang, J.; Sun, J.; Zhu, X.; Zhu, Y. All in One: A Versatile N-Perovskite/P-Spiro-Meotad P–N Heterojunction Diode as a Photovoltaic Cell, Photodetector, and Memristive Photosynapse. *J. Phys. Chem. Lett.* **2021**, *12*, 12098–12106.

(38) Tang, L.; Huang, Y.; Wang, C.; Zhao, Z.; Yang, Y.; Bian, J.; Wu, H.; Zhang, Z.; Zhang, D. W. Flexible Threshold Switching Selectors with Ultrahigh Endurance Based on Halide Perovskites. *Adv. Electron. Mater.* **2022**, *8* (2), 2270009.

(39) Zhang, X.; Yang, H.; Jiang, Z.; Zhang, Y.; Wu, S.; Pan, H.; Khisro, N.; Chen, X. Photoresponse of Nonvolatile Resistive Memory Device Based on All-Inorganic Perovskite Cspbbr3 Nanocrystals. *J. Phys. D: Appl. Phys.* **2019**, *52* (12), 125103.

(40) Gogoi, H. J.; Mallajosyula, A. T. Multifunctional Bipolar and Complementary Resistive Switching in Hoip Memristors by the Control of Compliance Current. ACS Appl. Electron. Mater. **2022**, 4 (3), 1039–1046.

(41) Gonzales, C.; Guerrero, A.; Bisquert, J. Spectral Properties of the Dynamic State Transition in Metal Halide Perovskite-Based Memristor Exhibiting Negative Capacitance. *Appl. Phys. Lett.* **2021**, *118*, 073501.

(42) Kim, H. S.; Jang, I. H.; Ahn, N.; Choi, M.; Guerrero, A.; Bisquert, J.; Park, N. G. Control of I-V Hysteresis in Ch3nh3pbi3 Perovskite Solar Cell. J. Phys. Chem. Lett. **2015**, 6 (22), 4633–4639. (43) Han, J. S.; Le, Q. V.; Choi, J.; Kim, H.; Kim, S. G.; Hong, K.; Moon, C. W.; Kim, T. L.; Kim, S. Y.; Jang, H. W. Lead-Free All-Inorganic Cesium Tin Iodide Perovskite for Filamentary and Interface-Type Resistive Switching toward Environment-Friendly and Temperature-Tolerant Nonvolatile Memories. ACS Appl. Mater. Interfaces **2019**, 11 (8), 8155–8163.

(44) Kim, S. Y.; Yang, J. M.; Choi, E. S.; Park, N. G. Layered  $(C_6H_5CH_2NH_3)_2CuBr_4$  Perovskite for Multilevel Storage Resistive Switching Memory. *Adv. Funct. Mater.* **2020**, 30 (27), 2002653.

(45) Zeng, F.; Guo, Y.; Hu, W.; Tan, Y.; Zhang, X.; Feng, J.; Tang, X. Opportunity of the Lead-Free All-Inorganic Cs3cu2i5 Perovskite Film for Memristor and Neuromorphic Computing Applications. *ACS Appl. Mater. Interfaces* **2020**, *12* (20), 23094–23101.

(46) Lee, M. H.; Kim, K. M.; Kim, G. H.; Seok, J. Y.; Song, S. J.; Yoon, J. H.; Hwang, C. S. Study on the Electrical Conduction Mechanism of Bipolar Resistive Switching Tio2 Thin Films Using Impedance Spectroscopy. *Appl. Phys. Lett.* **2010**, *96* (21), 219901.

(47) Bory, B. F.; Meskers, S. C. J.; Janssen, R. A. J.; Gomes, H. L.; De Leeuw, D. M. Trapping of Electrons in Metal Oxide-Polymer Memory Diodes in the Initial Stage of Electroforming. *Appl. Phys. Lett.* **2010**, 97 (22), 222106.

(48) Waser, R.; Dittmann, R.; Staikov, C.; Szot, K. Redox-Based Resistive Switching Memories Nanoionic Mechanisms, Prospects, and Challenges. *Adv. Mater.* **2009**, *21* (25–26), 2632–2663.

(49) Liu, D.; Lin, Q.; Zang, Z.; Wang, M.; Wangyang, P.; Tang, X.; Zhou, M.; Hu, W. Flexible All-Inorganic Perovskite Cspbbr3 Nonvolatile Memory Device. ACS Appl. Mater. Interfaces 2017, 9 (7), 6171–6176.

(50) Joshua Yang, J.; Miao, F.; Pickett, M. D.; Ohlberg, D. A. A.; Stewart, D. R.; Lau, C. N.; Williams, R. S. The Mechanism of Electroforming of Metal Oxide Memristive Switches. *Nanotechnology* **2009**, *20* (21), 215201.

(51) Lanza, M.; Wong, H. S. P.; Pop, E.; Ielmini, D.; Strukov, D.; Regan, B. C.; Larcher, L.; Villena, M. A.; Yang, J. J.; Goux, L.; Belmonte, A.; Yang, Y.; Puglisi, F. M.; Kang, J.; Magyari-Köpe, B.; Yalon, E.; Kenyon, A.; Buckwell, M.; Mehonic, A.; Shluger, A.; Li, H.; Hou, T. H.; Hudec, B.; Akinwande, D.; Ge, R.; Ambrogio, S.; Roldan, J. B.; Miranda, E.; Suñe, J.; Pey, K. L.; Wu, X.; Raghavan, N.; Wu, E.; Lu, W. D.; Navarro, G.; Zhang, W.; Wu, H.; Li, R.; Holleitner, A.; Wurstbauer, U.; Lemme, M. C.; Liu, M.; Long, S.; Liu, Q.; Lv, H.; Padovani, A.; Pavan, P.; Valov, I.; Jing, X.; Han, T.; Zhu, K.; Chen, S.; Hui, F.; Shi, Y. Recommended Methods to Study Resistive Switching Devices. *Adv. Electron. Mater.* **2019**, 5 (1), 1800143.

(52) Kerner, R. A.; Zhao, L.; Harvey, S. P.; Berry, J. J.; Schwartz, J.; Rand, B. P. Low Threshold Voltages Electrochemically Drive Gold Migration in Halide Perovskite Devices. *ACS Energy Lett.* **2020**, 5 (11), 3352–3356. (53) Jacobs, D. A.; Wu, Y.; Shen, H.; Barugkin, C.; Beck, F. J.; White, T. P.; Weber, K.; Catchpole, K. R. Hysteresis Phenomena in Perovskite Solar Cells: The Many and Varied Effects of Ionic Accumulation. *Phys. Chem. Chem. Phys.* **2017**, *19* (4), 3094–3103.

(54) John, R. A.; Yantara, N.; Ng, S. E.; Patdillah, M. I. B.; Kulkarni, M. R.; Jamaludin, N. F.; Basu, J.; Ankit, A.; Mhaisalkar, S. G.; Basu, A.; Mathews, N. Diffusive and Drift Halide Perovskite Memristive Barristors as Nociceptive and Synaptic Emulators for Neuromorphic Computing. *Adv. Mater.* **2021**, *33*, 2007851.

(55) Teymourinia, H.; Gonzales, C.; Gallardo, J. J.; Salavati-Niasari, M.; Bisquert, J.; Navas, J.; Guerrero, A. Interfacial Passivation of Perovskite Solar Cells by Reactive Ion Scavengers. *ACS Applied Energy Materials* **2021**, *4* (2), 1078–1084.

(56) Zhang, J. J.; Sun, H. J.; Li, Y.; Wang, Q.; Xu, X. H.; Miao, X. S. AgInSbTe Memristor with Gradual Resistance Tuning. *Appl. Phys. Lett.* **2013**, *102* (18), 183513.

(57) Gu, C.; Lee, J. S. Flexible Hybrid Organic-Inorganic Perovskite Memory. ACS Nano 2016, 10 (5), 5413–5418.

(58) Guan, X.; Hu, W.; Haque, M. A.; Wei, N.; Liu, Z.; Chen, A.; Wu, T. Light-Responsive Ion-Redistribution-Induced Resistive Switching in Hybrid Perovskite Schottky Junctions. *Adv. Funct. Mater.* **2018**, *28* (3), 1704665.

(59) Tress, W. Metal Halide Perovskites as Mixed Electronic-Ionic Conductors: Challenges and Opportunities - from Hysteresis to Memristivity. J. Phys. Chem. Lett. 2017, 8 (13), 3106–3114.

(60) He, Y.; Ma, G.; Zhou, X.; Cai, H.; Liu, C.; Zhang, J.; Wang, H. Impact of Chemical Doping on Resistive Switching Behavior in Zirconium-Doped Ch3nh3pbi3 Based Rram. *Org. Electron.* **2019**, 68 (2019), 230–235.

(61) Ge, S.; Huang, Y.; Chen, X.; Zhang, X.; Xiang, Z.; Zhang, R.; Li, W.; Cui, Y. Silver Iodide Induced Resistive Switching in Cspbi 3 Perovskite-Based Memory Device. *Adv. Mater. Interfaces* **2019**, *6* (7), 1802071.

(62) Duijnstee, E. A.; Ball, J. M.; Le Corre, V. M.; Koster, L. J. A.; Snaith, H. J.; Lim, J. Toward Understanding Space-Charge Limited Current Measurements on Metal Halide Perovskites. *ACS Energy Lett.* **2020**, 5 (2), 376–384.

(63) Strukov, D. B.; Borghetti, J. L.; Williams, R. S. Coupled Ionic and Electronic Transport Model of Thin-Film Semiconductor Memristive Behavior. *Small* **2009**, *5* (9), 1058–1063.

(64) Khadar Basha, N.; Ramashri, T. Spice Model of Memristor with Threshold Switching Characteristics. *ARPN J. Eng. Appl. Sci.* **2018**, *13* (7), 2581–2587.

(65) Garcia-Redondo, F.; Gowers, R. P.; Crespo-Yepes, A.; Lopez-Vallejo, M.; Jiang, L. Spice Compact Modeling of Bipolar/Unipolar Memristor Switching Governed by Electrical Thresholds. *IEEE T. Circuits Syst. I: Regul. Pap.* **2016**, *63* (8), 1255–1264.

(66) Yakopcic, C.; Taha, T. M.; Subramanyam, G.; Pino, R. E. Memristor Spice Model and Crossbar Simulation Based on Devices with Nanosecond Switching Time. *The 2013 International Joint Conference on Neural Networks (IJCNN)* **2013**, DOI: 10.1109/IJCNN.2013.6706773.

(67) Yakopcic, C.; Taha, T. M.; Subramanyam, G.; Pino, R. E.; Rogers, S. A Memristor Device Model. *IEEE Electr. Device L.* 2011, 32 (10), 1436–1438.

(68) Berruet, M.; Pérez-Martínez, J. C.; Romero, B.; Gonzales, C.; Al-Mayouf, A. M.; Guerrero, A.; Bisquert, J. Physical Model for the Current–Voltage Hysteresis and Impedance of Halide Perovskite Memristors. *ACS Energy Lett.* **2022**, *7*, 1214–1222.

(69) Munoz-Diaz, L.; Rosa, A.; Bou, A.; Sánchez, R. S.; Romero, B.; John, R. A.; Kovalenko, M. V.; Guerrero, A.; Bisquert, J. Inductive and Capacitive Hysteresis of Halide Perovskite Solar Cells and Memristors under Illumination. *Front. Energy Res.* **2022**, *10*, 911.

(70) Bisquert, J.; Guerrero, A. Dynamic Instability and Time Domain Response of a Model Halide Perovskite Memristor for Artificial Neurons. J. Phys. Chem. Lett. **2022**, *13*, 3789–3795.

(71) Yang, J. J.; Pickett, M. D.; Li, X.; Ohlberg, D. A. A.; Stewart, D. R.; Williams, R. S. Memristive Switching Mechanism for Metal/ Oxide/Metal Nanodevices. *Nat. Nanotechnol.* **2008**, *3* (7), 429–433. (72) Yang, J. J.; Strukov, D. B.; Stewart, D. R. Memristive Devices for Computing. *Nat. Nanotechnol.* **2013**, *8* (1), 13–24.

## **Recommended by ACS**

Quantitative Determination of Charge Accumulation and Recombination in Operational Quantum Dots Light Emitting Diodes via Time-Resolved Electroluminescence Spectroscopy

Hui Bao, Haizheng Zhong, et al. FEBRUARY 10, 2023 THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS

READ 🗹

Rapid and Reversible Sensing Performance of Hydrogen-Substituted Graphdiyne

Yoon Tae Nam, Hee-Tae Jung, et al. FEBRUARY 17, 2023 ACS SENSORS

READ 🗹

#### Coherent Loading–Deloading Mechanism in Polymeric Nanohybrid Network Structures

Sudeepa Devi, Mayank Dwivedi, et al. JANUARY 30, 2023 LANGMUIR

READ 🗹

RFAD

#### Versatile Use of 1,12-Diaminododecane as an Efficient Charge Balancer for High-Performance Quantum-Dot Light-Emitting Diodes

Seunghyun Rhee, Jeongkyun Roh, *et al.* JANUARY 27, 2023 ACS PHOTONICS

Get More Suggestions >