Oxygen vacancy dynamics in redox-based interfaces: tailoring the memristive response

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Abstract
Redox-based memristive devices are among the alternatives for the next generation of non-volatile memories, but are also candidates for emulating the behavior of synapses in neuromorphic computing devices. Nowadays it is well established that the motion of oxygen vacancies at the nanoscale is the key mechanism for reversible switching of metal/insulator/metal structures from insulating to conducting, i.e. to accomplish the resistive switching effect. The control of oxygen vacancy dynamics has a direct effect on the resistance changes, and therefore on different properties of memristive devices such as switching speed, retention, endurance and energy consumption. Advances in this direction demand not only experimental techniques that allow the measurement of oxygen vacancy profiles but also theoretical studies that shed light on the mechanisms involved. With these goals in mind we analyze the oxygen vacancy dynamics in redox interfaces formed when an oxidizable metallic electrode is in contact with the insulating oxide. We show how the transfer of oxygen vacancies can be manipulated by the use of different electrical stimulus protocols that allow optimization of device figures such as the ON/OFF ratio or writing energy dissipation. Analytical expressions for both high- and low-resistance states are derived in terms of total oxygen vacancies transferred at the interface. Our predictions are validated with experiments performed in Ti/La$_{1/3}$Ca$_{2/3}$MnO$_3$ redox memristive devices.

Keywords: oxygen vacancies dynamic, memristors, redox interfaces

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
trapping and detrapping of charge carriers by interfacial traps [9] and the oxidation/reduction of nanoscale interfacial ultrathin layers, formed when oxidizable metals such as Ta, Ti or Al are used as the electrodes [10, 11]. In the latter case, a thin oxide layer (TaO	extsubscript{x}, TiO	extsubscript{2} or AlO	extsubscript{x}) of a few nanometers is naturally formed at the interface between the metal electrode and the insulating oxide, and its oxidation/reduction upon electrical cycling drives the memristive behavior. Moreover, it was shown that it is possible to engineer memristive devices and improve their performance by introducing additional layers that regulate ionic exchange between the insulator and the electrode [12, 13].

In the case of Ti/LCMO [LCMO (PCMO) being the shorthand notation for La	extsubscript{1−x}Ca	extsubscript{x}MnO	extsubscript{3} (Pr	extsubscript{0.48}Ca	extsubscript{0.52}MnO	extsubscript{3})], the manganite is spontaneously reduced after the deposition of Ti.

The redox reaction is $(La^{3+}Ca^{2+})(Mn^{3+}Mn^{4+})O_2^− + Ti + (La^{3+}Ca^{2+})(Mn^{1+}Mn^{2+}Mn^{3+}Mn^{4+}Mn^{5+})O_2^{−x} + TiO_2$, giving rise to a mixed interface $TiO_x/LCMO_{3−x}$, where the TiO	extsubscript{x} layer behaves as an n-type semiconductor and is in contact with the p-type reduced manganese, forming a p−n diode. In these cases, the RS behavior has been related to a redox process involving the transfer of oxygen ions at the TiO/manganese interface [10, 14], while the other interfaces show ohmic behavior [15, 16].

Moreover, we have recently shown that the redox process is activated after the n−p diode is polarized either in direct mode or in inverse mode above breakdown [17].

The voltage-enhanced oxygen vacancy drift (VEOV) model was originally developed to explain the RS behavior in single manganite samples [8] and it was further extended to analyze binary oxide-based devices [18]. It has been extensively tested in several memristive metal-oxide/metal-2 systems, for oxides ranging from manganites (PCMO, LCMO) and cuprates (YBCO) to binary oxides like TiO	extsubscript{2} and metallic electrodes such as Pt, Au, Cu or Al [8, 18–22].

Recently, the VEOV model has been also adapted to mimic the RS behavior in Ti/LCMO/Pt samples, where the mixed TiO	extsubscript{x}/LCMO	extsubscript{3−x} interface dominates the memristive behavior of the device as a consequence of the already described redox process [17].

With quite a few exceptions [21, 23, 24] most of the theoretical studies disregard the connection between oxygen vacancy dynamics and the manipulation of the attained resistance states. The ability to reversibly control oxygen vacancy profiles should have a straightforward impact on the resistance changes, allowing the improvement of practical device performance. This can lead, for example, to the optimization of switching speeds or to the minimization of energy consumption during the writing process. Advances in this direction demand not only experimental techniques that allow the measurement of oxygen vacancy dynamics [25, 26] but also theoretical studies that shed light on the mechanisms involved. In order to achieve this, we perform a systematic analysis of oxygen vacancy dynamics at redox interfaces and their response to different protocols and stimuli. We show that the simulations indicate how the electrical stimuli can be manipulated to control oxygen vacancy dynamics to optimize memristive figures such as the ON/OFF ratio or the energy consumption linked to the RESET process.

In addition, we derive analytical expressions for the attained resistance values in terms of both the total number of oxygen vacancies transferred along the interface and the applied voltage, which allows reconstruction of the $R$ versus $V$ resistance hysteresis switching loops (HSL).

Our predictions are validated with experiments performed on the Ti/LCMO interface, demonstrating the capability of this kind of simulation to understand the physics related to redox memristive processes, paving the way to optimize the electrical response of practical devices.

2. The VEOV model revisited for mixed redox interfaces

In order to be self-contained and to clarify notation, we describe here the main assumptions and equations of the VEOV [8, 18] migration model adapted for the study of RS in the mixed TiO	extsubscript{x}/LCMO	extsubscript{3−x} interface (see the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia for details).

The interface is the active region for the RS behavior, and it is modeled as a one-dimensional chain of $N = N_l + N_r$ total sites, where $N_l$ and $N_r$ sites are associated with TiO	extsubscript{x} and LCMO	extsubscript{3−x} layers, respectively. The sites physically represent small domains of nanoscopic dimensions in both sub-oxides with an initial oxygen vacancy concentration corresponding to the pristine state (PS).

We characterize each domain $i$ along the chain by its resistivity $\rho_i$ which is a function of the local oxygen vacancy density, $\delta_i$. A universal feature of oxides is that their resistivity is dramatically affected by the precise oxygen stoichiometry. LCMO is a complex oxide that behaves as a p-type semiconductor in which oxygen vacancies disrupt Mn–O–Mn bonds with an increase of resistivity. On the other hand, TiO	extsubscript{2} behaves as an n-type semiconductor in which oxygen vacancies increase the conductivity. As a consequence, we adopt for the first $N_l$ domains associated with TiO	extsubscript{x} the (simplest) relation between resistivity and oxygen vacancy density:

$$\rho_i' = \rho_0 - A_i \delta_i,$$

where we define $\rho_0'$ as the residual resistivity of the left layer for negligible oxygen vacancy concentration ($\delta_i = 0$) and the coefficient $A_i$ is constant, specific to the TiO	extsubscript{2} layer.

As the model description is given in terms of oxygen vacancies, we conceive the TiO	extsubscript{x} as oxygen vacancy-doped TiO	extsubscript{2} and therefore $\rho_0'$ corresponds to the resistivity of TiO	extsubscript{2} (i.e. $x \sim 2$).

On the contrary, as the resistivity of the LCMO	extsubscript{3−x} layer increases with the presence of oxygen vacancies [27] we define for sites $i = N_l + 1, N$:

$$\rho_i' = \rho_0' + B_i \delta_i,$$

where $\rho_0''$ is the residual resistivity of stoichiometric LCMO and $B_i$ is a constant, characteristic of the manganite layer. We notice that both $A_i$ and $B_i$ can also be taken as smoothly
dependent on the site position without affecting the qualitative behavior of the simulated results. The total resistance along the interface is computed as \( R = c \sum_{i=1}^{N} \rho_i \), with the scale factor here taken as \( c = 1 \) for simplicity (see the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia for details). Following equations (1) and (2) we obtain

\[
R = \sum_{i=1}^{N_l} \rho_i^l + \sum_{i=N_l+1}^{N} \rho_i^j,
\]

\[
= R_s - \sum_{i=1}^{N_l} A_i \delta_i + \sum_{i=N_l+1}^{N} B_i \delta_i,
\]

with \( R_s \equiv N_l \rho_0^l + N_r \rho_0^j \) being the residual resistance of the interface.

Given an external stimulus (either current \( I(t) \) or voltage \( V(t) \)) applied to the interface at time \( t \), the oxygen vacancy density at site \( i \) is updated for each simulation step according to the probability of transfer from site \( i \) to a nearest neighbor site \( j = i \pm 1 \) given by \( p_{ij} = \delta_i(1 - \delta_j) \exp(-V_{ij} + \Delta V_i) \). Notice that \( p_{ij} \) is not constant upon electrical cycling. This assumption is valid in real devices if the topmost device layer in contact with the atmosphere behaves as a blocking barrier to both oxygen and moisture. As stated in [28], capping the top electrode with Au is a suitable strategy for this purpose.

According to standard RS experiments, we chose the stimulus \( V(t) \) as a linear ramp following the cycle \( 0 \rightarrow V_{m_1} \rightarrow -V_{m_2} \rightarrow 0 \). At each simulation time step \( t_k \) we compute the local voltage profile \( V_i(t_k) \) and the local voltage drops \( \Delta V_i(t_k) \). Employing the probability rates \( p_{ij} \), we compute oxygen vacancy transfer between the (low-resistance) initial state of the complete interface (see figure 1(b)).

The numerical implementation starts with the input of an initial oxygen vacancy profile at the interface, \( \delta_i(0), \forall i = 1..N \). We recall that the total number of oxygen vacancies is assumed to be constant upon electrical cycling. This assumption is valid in real devices if the topmost device layer in contact with the atmosphere behaves as a blocking barrier to both oxygen and moisture. As stated in [28], capping the top electrode with Au is a suitable strategy for this purpose.

In the experiments reported in [10, 17], the RESET process takes place for a positive stimulus and it is related to the transfer of oxygen vacancies (positive defects) from the TiO\(_2\) layer to the LCMO\(_{3-x}\) layer, the first becoming nearly stoichiometric (\( x < 2 \)) and thus highly resistive. At the same time, oxygen vacancies at the LCMO\(_{3-x}\) layer also contribute to increasing the interface resistance. In figure 1(b), the oxygen vacancy profile associated with the HR state linked to the first HSL is shown, and is in complete agreement with the described behavior.

5 Au capping is the strategy we have followed for the devices presented in this work to experimentally validate the simulation results. See the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia for details on the device geometry and fabrication procedure.
The SET transition takes place for a negative stimulus, when the interface returns to the LR state. The associated oxygen vacancy profile, shown in figure 1(b), corresponds to the LR state after the completion of the first HSL. In this case oxygen vacancies accumulate at the left side of the interface, in contrast to the initial PS (which has a higher resistance value), where the vacancy density is constant. We notice that the difference between PS and LR states is small, and both resistance values remain much lower than the HR state. The resistance of the device is dominated by the contribution of the \( LCMO_{-1} \) layer [17], which displays similar oxygen vacancy profiles for both PS and LR states.

Besides the initial behavior of the first HSL, the HR and LR states associated with the following cycles are highly repetitive and stable. We notice that the first RESET event can be identified as a forming process, consistent with the work of Herpers et al [15] on Ti/PCMO interfaces. Thus the erratic behavior of the first HSL—also exhibited in the first experimental HSL [17]—can be attributed to an initial metastable distribution of oxygen vacancies which is washed out during the first electrical cycle, leading upon further cycling to the switching between states with more stable oxygen vacancy configurations. As an example, we show in figure 1(b) the oxygen vacancy configuration corresponding to the HR state during the second HSL.

The inset of figure 1(a) shows an experimental HSL recorded for the Ti/LCMO interface for a complete voltage-stimulated cycle (see the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia for details about the device geometry and fabrication procedure). The similarity between the simulated and experimental HSL is remarkable, demonstrating the ability of the VEOV model to represent the physics of the memristive effect. Notice that as the number of transferred oxygen vacancies is controlled by the amplitude of the electrical stimuli, different experimental HSLs can be obtained by tuning the voltage (or current) excursions, as already discussed in [17].

We also notice that our modeling neglects the presence of self-heating (Joule) effects, which are known to be less relevant in area-dependent memristive effects, as in our case (evidence about area-dependent memristive behavior is given in the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia). In addition, in the experiments presented in this work possible self-heating effects are minimized by using a writing protocol consisting of consecutive single pulses (typical time-widths of 1–10 ms) separated by times with no stimuli of (at least) similar magnitude, instead of using continuous voltage ramps. This allows the heat produced by the Joule effect to be drained and avoids a significant temperature rise in the active zone of the device. In [30], significant Joule heating effects follow the application of a continuous triangular voltage ramp with a duration of 100 ms, which is at least one order of magnitude longer that our single pulses. We have also previously shown [31] that for manganite memristive systems at temperatures close to room temperature, the diffusive contribution to oxygen vacancy migration is a higher-order correction to electric field-driven drift of vacancies. These facts indicate that for our system and writing protocol, neglecting self-heating and diffusive effects is a good approximation.

3. Resistance in terms of transferred oxygen vacancies

In this section we go a step further and derive analytical expressions for the resistance values cast in terms of the transferred oxygen vacancies as a function of the applied stimulus.

As in typical experiments, the external electrical stress can be either voltage \( V(t) \) or current \( I(t) \). For the sake of simplicity we consider voltage-controlled experiments following the aforementioned protocol, but the following reasoning will be also valid when the stimulus is \( I(t) \).

We start from the initial state, corresponding to the configuration depicted in figure 1(b), and consistent with the PS. Taking into account equation (3) we write

\[
R(0) = R_s - A a_0 + B a r_0,
\]

where \( R_s \) has been previously defined. We denote the left and right initial areas (total number of oxygen vacancies), as \( a_0 = \sum_{i=1}^{N_l} \delta_{i,0} \) and \( a r_0 = \sum_{i=N_l+1}^{N} \delta_{i,0} \), respectively, with \( \delta_{i,0} \equiv \delta_{i,0} \), being the oxygen vacancy density at site \( i \) for the initial state.

Positive voltages \( 0 < V \leq V_{nl} \) move vacancies (as positive defects) from the left layer of the interface (TiO\(_2\)) to the right layer (LCMO\(_{-1}\)), as we have already described. For each value of \( V(t) > 0 \) it is possible to compute the transferred area of the oxygen vacancy profiles \( a^+ (V(t)) \). Taking into account conservation of the total number of vacancies, we define \( a^+ (V) = a_0 - a^- (V) \) and \( a^- (V) = a r_0 + a^+ (V) \). In this way we can write

\[
R^+ (V) = R_s - A a^- (V) + B a r^+ (V) = R(0) + (A + B) a^+ (V),
\]

showing that the resistance \( R^+ (V) \) for positive voltages \( V(t) \) is determined by the transferred area \( a^+ (V) \) and sample-specific parameters. As \( a^+ \) increases, \( R^+ \) attains higher values and thus it might be expected that for a sufficiently strong voltage \( V_F < V_{nl} \), the RESET transition to the HR state takes place, i.e. \( R^+ (V_F) \equiv HR \). In the next section we will study the oxygen vacancy transfer process in order to analyze different scenarios for the RESET transition. An important issue that will be addressed is whether the RESET takes place for \( a^+ (V_F) = a_0 \) (complete transfer of the initial number of oxygen vacancies) or alternatively for \( a^+ (V_F) < a_0 \).

For negative voltages, oxygen vacancies move from the right to the left side of the interface. Defining \( a^- (V) \) as the net transferred area for a (negative) voltage \( |V| \leq V_{a2} \), we can write \( a^- (V) = a_0 - a^- (V_F) + a^- (V) \) and \( a^- (V) = a r_0 + a^- (V_F) - a^- (V) \), for the left and right interfaces, respectively. For simplicity we have assumed that once the RESET transition takes place for positive polarities, and until the reversal of the voltage polarity, the transfer of
vacancies from the right to the left interface is inhibited. This assumption is consistent with the (almost) flat shape of the HSL observed experimentally for this range of voltages (see the inset of figure 1(a)). Thus, we write for \( |V| \leq V_{\text{m}} \),

\[
R^{-}(V) = R_{0} - A a^{+}(V) + B a^{-}(V)
\]

\[
= R_{0} + (A + B) \left\{ a^{+}(V_{R}) - a^{-}(V) \right\} . \tag{6}
\]

By analogy with the previous description, we define the SET transition for a negative voltage \( |V| \leq V_{\text{m}} \) with an associated transferred area \( a^{-}(V_{S}) \). Therefore, from equation (6), the LR state is \( R^{-}(V_{S}) = R_{0} + (A + B) \left\{ a^{+}(V_{R}) - a^{-}(V_{S}) \right\} \equiv LR \).

We can repeat the described procedure for additional cycles of the applied voltage protocol, but as the systematics is essentially the same as the one already detailed, we restrict the explicit description to a single cycle.

From equations (5) and (6) it is possible to reconstruct \( R \) for a complete cycle of \( V(t) \), i.e. the HSL, once the transferred areas are determined.

Depending on the relation between \( a^{+}(V_{R}) \) and \( a^{-}(V_{S}) \) different scenarios emerge for the LR state. In those cases where \( a^{+}(V_{S}) = a^{-}(V_{S}) \), the attained LR state is identical to the initial one (see equation (6)). However, in cases where \( a^{+}(V_{R}) \equiv a^{-}(V_{S}) \), LR \( \equiv R_{0} \). These responses have been already observed in the experiments in [17] and generate either close or open HSLs after a complete cycle of the voltage excursion.

Besides the formal simplicity of equations (5) and (6), the analytical determination of \( a^{+}(V) \) and \( a^{-}(V) \) is not a trivial task. In the following we summarize the main steps of a procedure we have adopted that allows us to obtain \( a^{+} \), and refer readers to the appendix for further details. As \( V(t) \) is a known function of the (discretized) elapsed time \( t \equiv \sum_{k} t_{k} \), the total transferred area can be written as \( a^{+}(t) = \sum_{k} a^{+}(t_{k}) \). To simplify the notation, we denote \( a_{k}^{+} \equiv a^{+}(t_{k}) \). After a lengthy calculation, we can write (see the appendix)

\[
a_{k}^{+} = a_{k}^{NL} + a_{k}^{NL}, \tag{7}
\]

where we define the linear and non-linear contributions, respectively, as:

\[
a_{k}^{NL} = C_{N_{L}} \delta(N_{L}) \exp(I(k)\rho_{NL}(k)) - C_{N_{L}+1} \delta(N_{L}+1)(k) \exp(-I(k)\rho_{NL+1}(k)),
\]

\[
ah_{k}^{NL} = -\delta_{NL}(k)\delta(N_{L}+1)(k)\{-C_{N_{L}} \exp(-I(k)\rho_{NL+1}(k))
\]

\[
+ C_{N_{L}} \exp(I(k)\rho_{NL}(k))\},
\]

with \( I(k) = V(k)/R(k) \), following the adopted convention.

Notice that in the case of current-controlled experiments, in which \( I(k) \) is known, the above equations indicate that the transferred area \( a_{k}^{+} \) for the time interval \( t_{k} \) is determined in terms of the density of oxygen vacancies at the sites at each side of the interface i.e. \( \delta_{NL} \) and \( \delta_{NL+1} \), respectively. This is a non-trivial result that could be experimentally tested using oxygen vacancy imaging techniques [25, 32] in current-controlled experiments, and should contribute to the design of optimized interfaces for RS experiments.

Figure 2. The a-dimensional transferred area \( a^{+} (a^{-}) \) for a protocol \( I(t) = 0 \rightarrow I_{m1} \rightarrow 0 (0 \rightarrow -I_{m2} \rightarrow 0) \). The circles (squares) were obtained following the analytical estimates from equations (7) and (8) (equation (A.17)) normalized in terms of the total density of oxygen vacancies, \( b_{0} \). The diamond and triangle symbols correspond to the numerical calculations employing the VEOV model simulations.

Equation (8) can be further simplified taking into account that the activation energies satisfy \( V_{S} < V_{B} \), which implies \( C_{N_{L}} \gg C_{N_{L}+1} \). Considering this approximation, the obtained analytical estimates for \( a_{k}^{+} \) (see equation (A.12)) enable the determination of the transferred areas as a function of the applied stimulus.

In the appendix, we also derived estimates for \( a_{k}^{-} \) (see equation (A.17)) to compute the transferred area \( a^{-} = \sum_{k} a_{k}^{-} \) for the case of a negative applied stimulus.

To give a concrete example, we consider current-controlled protocols for which the expressions for \( a^{+}(I) \) and \( a^{-}(I) \) acquire their simplest form, due to the fact that \( I(k) \), the current at each time step \( t_{k} \), is known. Figure 2 shows the analytical estimates for \( a^{+}(I) \) and \( a^{-}(I) \) obtained from equations (7), (8) and (A.17) for a current loop \( I(t) = 0 \rightarrow I_{m1} \rightarrow -I_{m2} \rightarrow 0 \). Notice that in this case the conversion from transferred areas to resistance values is trivial following equations analogous to equations (5) and (6). Thus, the analytical reconstruction of the HSL, \( R \) versus \( I \), in terms of the applied stimulus is fully accomplished. The analytical estimates, which only consider oxygen vacancies at sites \( N_{L} \) and \( N_{L} + 1 \), are almost indistinguishable from the numerical values (see figure 2) obtained with the VEOV model. In this last case the complete oxygen vacancy profile along the whole interface has to be updated at each simulation step \( t_{k} \), which demands an appreciable computational effort.

An important figure of merit is the HR/LR ratio which, from equations (5) and (6), can be expressed as:

\[
\frac{RL - R_{0}}{RH - R_{0}} = \frac{a^{+}(V_{R}) - a^{-}(V_{S})}{a^{+}(V_{R})}, \tag{9}
\]

taking \( R_{0} \) as a reference value.

To give further insight into the area transfer process, in the next section we will analyze the oxygen vacancy dynamics for different electrical protocols. This will allow us to determine
optimal stimuli protocols, which will be confirmed with experiments performed on the Ti/LCMO interface.

4. Dynamics of oxygen vacancies

Given the fact that the HR and LR states are essentially determined by areas transferred during RESET and SET transitions, respectively, an interesting and quite unexplored aspect is related to the sensitivity of these processes to the peculiarities of the voltage protocol. With this in mind, in this section we analyze the oxygen vacancy dynamics for different applied stimuli. We concentrate on the RESET process that takes place for positive stimulus $V(t)$, but the same analysis can be performed for the SET process.

The starting point is the initial oxygen vacancy configuration, which is shown in both top panels of figure 3 labeled by $V=0$ V. This distribution defines an initial (a-dimensional) area $a_{0}=1$ on the left side of the interface, which we recall corresponds to the TiO$_x$ layer ($N_l=50$ which gives $W_l=11.1$ nm; see the online supplementary material at stacks.iop.org/TDM/53/015302/mmedia). To analyze the time evolution of this initial density profile, we consider two positive voltage excursions (ramp1 and ramp2) of a linear ramp $0 < V \leq V_{sat}$, with $V_{sat}=2.9$ V and rise times $T_1=0.1$ s (ramp1) and $T_2=2.5$ s (ramp 2), respectively. The dashed black line shows the initial OV profile for $t=0$, $V=0$, which gives an a-dimensional area $a_{0}=1$. Lower panels: a-dimensional transferred area $a^+$ for different voltage values shown in the upper panel legends. The RESET voltages $V_R$ are estimated following the criteria explained in the text.

In the top panels of figure 3, we show representative snapshots of the density profiles for selected voltages. The associated transferred areas $a^+(V)$ are shown in the lower panels. An important outcome is that the duration of the ramp controls whether the transfer is complete or not. Notice that for ramp 1 the transferred area seems to saturate at a value $a^+_{sat} \sim 0.65 < a_{0}=1$ before the completion of the voltage excursion. In addition, a finite number of vacancies remain in the TiO$_x$ region, consistent with the fact that complete transfer is not achieved. On the other hand, for ramp 2 (right top panel of figure 3) the initial area is fully transferred, i.e. $a^+_{sat}=a_{0}=1$. Indeed this is attained for voltage values lower than $V_{ml}$ (see the oxygen vacancy profile in the right top panel). From the plateau in each plot of $a^+$ (lower panels) we can define a saturated area value, $a^+_{sat}$. By doing this we define a plausible criterion for estimating the reset voltage $V_R$, as the voltage obtained at the intersection between the horizontal line corresponding to null transfer area with the tangent line at the value $a^+_{sat}/2$. This is explicitly sketched in both lower panels of figure 3. The obtained values of $V_R$ are in excellent agreement with those extracted from the HSL in the VEOV model simulations.

In the present example complete transfer of vacancies is attained for ramp 2, with $T_2 > T_1$. We therefore can conclude that, for linear continuous ramps, lower slopes favor complete transfer from the left to the right side of the interface once the amplitude of the ramp $V_{ml}$ exceeds the critical voltage necessary to activate the transfer. From the above analysis, the onset of the RESET transition is clearly identified with the ‘first arrival’ of the oxygen vacancy front at the right-hand side of the interface (LCMO$_{3-x}$).
Next, we analyze the case of the RESET process driven by pulsed voltage ramps, which consist of a series of pulses of increasing amplitude and time-width $\Delta T$. Consecutive pulses are separated by intervals $\Delta T$ with no applied voltage, as shown in the inset of figure 4(b). This type of voltage protocol is extensively used in RS experiments.

We systematically vary $\Delta T$, leaving the total duration of the ramp constant. In this way, a shorter $\Delta T$ is associated with ramps with a greater number of pulses. Figures 4(a) and (b) display the corresponding $R$ versus time and $R$ versus $V$ associated with the RESET process, for different $\Delta T$ values shown in the legend.

We recall that larger transferred area $a^+(V)$ implies a larger remnant resistance, as deduced in equation (5). It can be observed from the figure that the transferred area is maximized for the shortest pulses, indicating that the OFF/ON (HR/LR) ratio is optimized by accumulating a greater number of short pulses rather than a smaller number of wider ones. This non-trivial result is experimentally confirmed for the Ti/LCMO interface, as shown in figures 4(c) and (d), which display several RESET processes for voltage pulsed ramps with a fixed total duration of 2.88 s and different $\Delta T$, ranging between 2 and 10 ms. It is evident that a higher HR final state is achieved for shorter (2 ms) pulses, confirming the prediction derived from the simulations. In addition, the qualitative and quantitative agreement with the numerical predictions is remarkable.

Finally, we address the study of the RESET process for trains of rectangular pulses differing in their time-widths $\Delta T$ and amplitudes $V_0$, but keeping the product $V_0 \times \Delta T = \text{constant}$. We start with an oxygen vacancy profile defining an initial area $a_0 = 1$. The RESET process is considered as completed when the initial area is fully transferred (we choose the amplitude $V_0$ in order to satisfy this requirement).

The simulated evolution of $R$ versus time for the different trains is displayed in figure 5(a) for $V_0 \times \Delta T = 3$ V ms. It is found that the number of pulses needed to achieve the RESET changes in a non-monotonic way with the amplitude $V_0$. This information is indexed in figure 5(b), which also displays the electrical energy necessary to complete the RESET process, as a function of $V_0$. These energies were calculated as $U = V_0^2 \sum_i \Delta T_i / R_i$, with $R_i$ being the resistance value attained after application of the $i$th pulse of duration $\Delta T_i$. From this analysis we conclude that there is a pair $\{\Delta T, V_0\}$ which minimizes the RESET energy. This was indeed verified experimentally for the Ti/LCMO interface, as shown in figures 5(c) and (d). Pulse trains with $V_0$ and $\Delta T$ ranging between 1.8–3 V and 1–1.75 ms were tested with the product $\Delta T \times V_0 = 3$ V ms. In the experiment we consider the RESET process as completed when the relative resistance change after the last applied pulse is below 5%. Again, the number of pulses necessary to complete the RESET process displays a non-monotonic dependence with $V_0$. To estimate the injected energy...
During each pulse, we assumed that the resistance increases linearly to its final value during the application of the pulse. Under this approximation, the trend shown in figure 5(d) is in good (qualitative) agreement with the simulated data of figure 5(b). An exact determination of experimental RESET energies requires measurement of the current transients during the RESET process, which allows the tracking of non-linear contributions to oxygen vacancy dynamics [33].

The present analysis clearly shows that the VEOV simulations appear to be a powerful tool for analyzing the dynamics of oxygen vacancies in redox memristive systems and predict optimum writing protocols to increase the efficiency of practical devices.

5. Conclusions

In summary, we have thoroughly addressed the oxygen vacancy dynamics in redox p–n interfaces by using an updated version of the VEOV model. The simulations allow us to predict the optimum write protocol to control and enlarge the ON/OFF ratio. Our results are relevant not only for memory optimization but also for neuromorphic computing applications, as the presence of multilevel resistance states allows mimicking of the adaptable synaptic weight of brain synapses [34].

In addition we found the optimum stimulus protocol that minimizes the energy consumption linked to the RESET process. This is also important for the optimization of neuromorphic computing devices aimed at emulating the highly efficient energy consumption of biological systems [35].

The numerical predictions were fully validated with experiments on the Ti/LCMO memristive interface, demonstrating the power of this type of phenomenological modeling to predict and optimize the behavior of practical memristive devices. We finally notice that the stimulus time-scale (i.e. the time-width of pulses) was chosen to be in the millisecond range to facilitate experimental verification of the simulation predictions. However, we recall that the modeling is not constrained to this time-scale and can also describe and predict oxygen vacancy dynamics at shorter time-scales (down to nanoseconds; see, e.g., how figure 5(a) describes the evolution of the transient simulated resistances after the application of voltage pulses), which is a key issue in simulating the electrical response of high-speed applications.

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Appendix. Analytical estimates for the transferred areas

In this appendix we derive the expressions for the transferred area $a^+_i$ from the left to the right side of the interface, in terms of the linear and non-linear contributions (equation (8)).

We start by defining the rate of variation of oxygen vacancies between neighboring sites $i-1$, $i$ and $i+1$ as

$$\Delta_i (k) = (p_{i-1,i}(k) + p_{i,i+1}(k)) - (p_{i-1,i}(k) + p_{i,i+1}(k)),$$  \hspace{1cm} (A.1)

with

$$p_{i,j}(k) = C_i \delta_i(k)(1 - \delta_j(k)) \exp(I(k)\rho_i(k))$$ \hspace{1cm} (A.2)

and $C_i = \exp(-V_A)$, already introduced in section 2 of the main text. In the following we consider $C_N = \exp(-V_A)$ and $C_{N+1} = \exp(-V_B)$.

Employing equation (A.1), we write the transferred area (total number of transferred vacancies) $a^+_i$ as

$$a^+_i \equiv \sum_{i=N+1}^{N} \Delta_i (k) = \sum_{i=N+1}^{N} \Delta^L_i (k) + \sum_{i=N+1}^{N} \Delta^NL_i (k)$$

\hspace{1cm} (A.3)

where we have defined

$$\Delta^L_i (k) = C_{i-1} \delta_{i-1}(k) \exp(I(k)\rho_{i-1})$$

$$+ C_{i+1} \delta_{i+1}(k) \exp(-I(k)\rho_{i+1}) - C_i [\delta_i(k) \exp(-I(k)\rho_i) + \delta_i(k) \exp(I(k)\rho_i)].$$  \hspace{1cm} (A.4)

and

$$\Delta^NL_i (k) = -C_{i-1} \delta_{i-1}(k) \delta_i \exp(I(k)\rho_{i-1})$$

$$- C_{i+1} \delta_{i+1}(k) \delta_i \exp(-I(k)\rho_{i+1}) + C_i [\delta_i(k) \delta_{i-1}(k) \exp(-I(k)\rho_i)$$

$$+ \delta_i(k) \delta_{i+1}(k) \exp(I(k)\rho_i)].$$  \hspace{1cm} (A.5)

Performing the summations in equation (A.3) and accounting for the boundary condition $C_{N+1} = 0$, we get

$$\sum_{i=N+1}^{N} \Delta^L_i (k) = C_{N} \delta_N(k) \exp(I(k)\rho_N)$$

$$- C_{N+1} \delta_{N+1}(k) \exp(-I(k)\rho_{N+1})$$  \hspace{1cm} (A.6)

and

$$\sum_{i=N+1}^{N} \Delta^NL_i (k) = -\delta_N(k) \delta_{N+1}(k) [C_N \exp(I(k)\rho_N)$$

$$- C_{N+1} \exp(-I(k)\rho_{N+1})].$$  \hspace{1cm} (A.7)

The linear term $a^+_i^L$ has been written as the sum of two contributions,

$$a^+_i^L \equiv P(k) - Q(k),$$ \hspace{1cm} (A.8)

defined as

$$P(k) = C_N \delta_N(k) \exp(I(k)\rho_N(k)),$$

$$Q(k) = C_{N+1} \delta_{N+1}(k) \exp(-I(k)\rho_{N+1}(k)).$$ \hspace{1cm} (A.9)

Analogously, we write the non-linear term as

$$a^+_i^{NL} \equiv S(k) - T(k),$$ \hspace{1cm} (A.10)

with

$$S(k) = C_{N+1} \delta_{N+1}(k) \exp(-I(k)\rho_{N+1}(k)),$$

$$T(k) = C_N \delta_N(k) \exp(I(k)\rho_N(k)).$$ \hspace{1cm} (A.11)

Notice that for current controlled experiments in which the current $I(k)$ is known by input, the transferred areas at each time interval $t_i$ only depend on vacancy densities and resistivities at the sites $NI$ and $NI + 1$, respectively.

As already mentioned in section 2, the activation energies for oxygen vacancy diffusion satisfy $V_A < V_B$ and thus $C_{N+1} \ll C_N$. Therefore, we can safely approximate

$$a^+_i = a^+_i^L + a^+_i^{NL} \approx P(k) - T(k).$$ \hspace{1cm} (A.12)

This equation can be updated for the next time interval $t_{i+1}$ employing

$$\delta_i(k + 1) = \delta_i(k) + \Delta_i (k),$$ \hspace{1cm} (A.13)

for $i = NI - 1, NI$ and $NI + 1$, respectively.

From equations (A.2) and (A.1) we write, after straightforward algebra

$$\Delta_Ni(k) = C_N \delta_N(k)[-2 \cosh(I(k)\rho_N)]$$

$$\exp[I(k) + 1] \rho_0 - A(\delta_N(k) + \Delta_Ni(k)).$$ \hspace{1cm} (A.14)

Performing the substitution $k \rightarrow k + 1$, replacing equation (A.13) in $P(k)$ (equation (A.9)), and taking into account equation (1) in the main text, we obtain

$$P(k + 1) = C_N[\delta_N(k) + \Delta_Ni(k)]$$

$$\exp[I(k + 1)] \rho_0 - A(\delta_N(k) + \Delta_Ni(k)).$$ \hspace{1cm} (A.15)

In a similar way we derive, after updating $T(k)$ in equation (A.11),

$$T(k + 1) = C_N[\delta_N(k) + \Delta_Ni(k)][\delta_{N+1}(k) + \Delta_{N+1}(k)]$$

$$\exp[I(k + 1)] \rho_0 - A(\delta_N(k) + \Delta_Ni(k)).$$ \hspace{1cm} (A.16)

Employing these last two equations we compute

$$a^+_i \approx P(k + 1) - T(k + 1).$$

Following the described prescription iteratively, the total transferred area $a^+$ after an elapsed time $t_e = \sum t_i$, can be computed under the present assumptions.

The same procedure can be applied to compute $a^-$ for a negative electrical stimulus. Assuming that the current protocol $0 \rightarrow I_{n1} \rightarrow 0$ is completed for a time $T_d = \sum t_i$, the initial condition for the negative current protocol $0 \rightarrow I_{n2} \rightarrow 0$ should be taken as the oxygen vacancy profile at time $T_d^+$, i.e. $\delta_i(K)$. 

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To avoid repetition we give below the final expression, valid for $k > K_c$:

$$a_k^* = C_N \delta_N(k) \exp(I(k) \rho_{N_k})$$

$$- C_{N+1} \delta_{N+1}(k) \exp(-I(k) \rho_{N_{k+1}})$$

$$+ \delta_N(k) \delta_{N+1}(k) (C_{N+1} \exp(-I(k) \rho_{N_{k+1}}))$$

$$- C_N \exp(I(k)) \rho_{N_k}). \quad \text{(A.17)}$$

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