Fractional Marcus-Hush-Chidsey-Yakopcic current-voltage model for redox-based resistive memory devices

Georgii Paradezhenko[1], Dmitrii Prodan[1], Anastasiia Pervishko[1], Dmitry Yudin[1], and Anis Allagui[2, 3]

[1]*Skolkovo Institute of Science and Technology, Moscow 121205, Russia*

[2]*Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah, P.O. Box 27272, United Arab Emirates*

[3]*Department of Mechanical and Materials Engineering, Florida International University, Miami, FL33174, United States*

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We propose a circuit-level model combining the Marcus-Hush-Chidsey electron current equation and the Yakopcic equation for the state variable for describing resistive switching memory devices of the structure metal–ionic conductor–metal. We extend the dynamics of the state variable originally described by a first-order time derivative by introducing a fractional derivative with an arbitrary order between zero and one. We show that the extended model fits with great fidelity the current-voltage characteristic data obtained on a Si electrochemical metallization memory device with Ag-Cu alloy

I Introduction

Substantial research efforts have been dedicated to the development of electrically-controlled resistive switching in metal-insulator-metal (MIM) devices or memristors, going from new materials discovery to modelling and simulation, and design and applications. With both memory and logic capabilities combined at the hardware level, in addition to long retention times and high switching rates at relatively low energy consumption, these devices are favorably seen as the next-generation building blocks for nonvolatile memories and neuromorphic computing applications. In a typical memristor, the resistive switching is based on the electrically-stimulated change of cell resistance usually driven by internal ion redistribution, which actually depends not only on the applied excitation but also on the past history of the excitation . Physical mechanisms associated with these reversible transitions have been attributed to different effects including valencechange 16, electrochemical metallization17, and phase change effects18. They can be either abrupt (binary) or gradual (analogue), and evolve at different timescales, leading to rich and complex device behaviors in this seemingly simple device structure of just three layers. Furthermore, with the wide range of diversity in memristors materials and their morphologies, operating mechanisms, and manufacturing technologies there is an urgent need for the development of a general model capable of capturing accurately and effectively their complex nonlinear dynamics. This is crucial not only for the characterization and comparison between different memristor devices, but also for the investigation of larger scale memristorbased circuits and hybrid hardware architectures, and also to explore similar behaviors observed for instance in biological synapse systems

While models at different size scales and thus with different degrees of physical details and computational complexity have been developed for memritors, including but not limited to ab initio, Kinetic Monte Carlo, and finite element method modells, in this work we focus on the circuit-level (compact) current-voltage behavior of the memristors. From this point of view, Memristors are generally described by the systems of coupled equations:

$$i = G(v, x)v, \tag{1}$$

$$\dot{x} = f(x, v), \tag{2}$$

where $i = i(t)$ is the current through the device, $v = v(t)$ is the applied voltage, and $x = x(t)$ corresponds to a state variable or a group of state variables that quantify the internal dynamics of the device. These are, for example, width of doping region, concentration of vacancies in the gap region, and tunneling barrier width. State vairables can not be observed from external electrical behavior. Eq1. (1) follows the $i - v$ curve of the resistive device in the question with $G(v, x)$ being the generalized conductance, whereas Eq. describes the dynamics of the it's internal state x based on it's prehistory. The actual stat of a memristor can only be determined by solving Eqs. (1) and (2) self-consistently. Memristive systems as featured in terms of Eqs. (1) and (2) are known to possess a pinched hysteresis loop at the origin in the i-v plane in the response to any periodic voltage source.

Being versatile and modular enough it is the Yakopcic model 27–29 which is most often used to simulate the nonlinear i-v characteristic of wide range of memristors in response to sinusoidal and repetitive sweeping inputs. The model takes into account electron transmission effects, voltage threshold for state variable motion, and nonlinear velocity function for oxygen vacancies or dopant drift, considered to be the most relevant internal state information29. It follows on the steps of Strukov et al. work30, and describes the memristor as two resistors in series characterized by electron transmission equations so that:

$$i(t) = h_1(v)x + h_2(v)(1 - x). \quad (3)$$

Here, h1 is used to model the behavior in the low resistance state of the device, and h2 captures its behavior in the high-resistance state. The two electron transmission equations are weighted and mixed by the state variable x which is set to take values between zero and one25. In memristive devices, it is the rate of change of the state variable x that is explicitly determined (2), and is given in the Yakopcic memristor model by the product of the two composite functions g(v) and f(x) such that29:

$$\dot{x} = g(v)f(x). \quad (4)$$

An exponential dependency of the state change to the positive and negative regions of the input voltage v is modelled in terms of

$$g(v) = \begin{cases} a_p \cdot (1 - e^{U_p - v}) \cdot e^v, & u - u_p > 0, \\ a_n \cdot (e^{u_n + v} - 1) \cdot e^{-v}, & u + u_n < 0, \\ 0, & \text{otherwise} \end{cases} \quad (5)$$

including programming voltage thresholds up and un. The magnitude of state change for a voltage potential is defined with ap and an. The second function f(x) is determined by

$$f(x) = \begin{cases} w_p(x, x_p) \cdot e^{-(x - x_p)}, & x \geq x_p, \\ 1 & x < x_p, \end{cases} \quad (6)$$

for $v > 0$, while $v < 0$, it is defined as

$$f(x) = \begin{cases} w_n(x, x_n) \cdot e^{x + x_n - 1)}, & x \leq x_n, \\ 1 & x > x_n, \end{cases} \quad (7)$$

Effectively, this function introduces the nonlinear ion motion, as it becomes harder to change the state of the devices when the state variable approaches the boundaries. In Eq. (6), $w_p(x, x_p)$ is a windowing function that ensures $f(x)$ equals zero when $x(t) = 1$, and in (7), $w_n(x, x_n)$ keeps $x(t)$ from becoming less than 0 when the current flow is reversed. These two functions can explicitly be written as $w_p(x, x_p) = 1+(x_p-x)/(1-x_p)$ and $w_n(x, x_n) = x/(1 - x_n)$.

Clearly, in (3), the functions h1 and h2 are dependent on the structure and type of memristor under study. Several types of resistive switching memory devices can be classified as nanoionic-based electrochemical systems, wherein an ion conductor in the form of electron insulator layer is placed between two electrodes31,32. For the case of cation-migration-based electrochemical metallization memory cells, Ag or Cu are typically used as active electrodes, Pt or W as counter electrodes, and a variety of oxides or chalcogenides thin films as solid electrolytes. When a positive voltage is applied, the active electrode material is oxidized at the electrode–electrolyte interface leading to the release of metallic ions in the adjacent electrolyte, followed by drift and diffusion of these ions across the electrolyte, and then their deposition in filamentarylike metal structures at the counter electrode surface. Short-circuit occurs when the filament has grown sufficiently far to make an electronic contact with the opposite electrode, which defines the low-resistance state of the cell. When a negative voltage is applied, the cell returns back, in principle reversibly, to the high-resistance state31. Anion-migration-based valence change cells, on the other hand, are formed by placing a metal oxide between for example Pt or TiN electrodes and another oxygen-affine, lower work function electrode. The lowresistance and high-resistance states are defined based on the electrochemical formation of oxygen-deficient, mixed ionic–electronic conducting filaments, and the nanoionic modification of the potential barrier between the tip of the filament and the electrode it faces31. For these types of redox-based resistive memory cells, it is more appropriate to consider electron transfer theory associated with the kinetics of redox reactions to better describe their i-v characteristics. Furthermore, because the formation and rupture of the metallic filaments follow random paths, the possibility of charge trapping from one operation sequence to another, charge leakage, the dynamics of an internal state variable associated with these cells cannot be defined solely based on its immediate past, in other words via integer-order derivative as in (2). Taking into account the integral past is believed to be more representative for a proper mathematical description of the complexity and dissipative nature of these cells.

Motivated by these observations, we herein propose a circuit-level model for redox-based resistive memory devices, where the current equation (1) is taken from the Marcus-Hush-Chidsey (MHC) theory33–35 of heterogeneous electron transfer, while the state variable equation (2) is taken from the Yakopcic generalized memristive model27. We consider the dynamics of the state variable with respect to time to be of fractional, non-integer, order. Mathematically, this adds an extra degree of freedom to the model that can be generically correlated to the non-perfect reversibility of the device when looking at it from one cycle to another. We fit the extended model to the experimental data obtained on a Si memristor with Ag-Cu alloy as reported in36. A close inspection of numerical results unambiguously reveals that switching to the fractional derivative allows one to significantly improve the agreement between the theory and experimental data.

II Memristor model

The generalized i-v relationship, as specified by Eq. (1), for the proposed memristor model reads

$$i = \gamma_1 x h(\delta_1 v) + \gamma_2 (1-x) h(\delta_2 v), \tag{8}$$

where $\delta_1, \delta_2, \gamma_1, \gamma_2 > 0$ are model parameters, and the function

$$h(v) = h_+(v) - h_-(v), \tag{9}$$

is based on the MHC model for electron transfer described by the Gauss-

Fermi integral,

$$h_{\pm}(v) = \beta \int_{-\infty}^{\infty} = \exp\left\{-\frac{(z-\lambda \pm v)^2}{4\lambda}\right\}\frac{dz}{1+e^z}. \tag{10}$$