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Hysteresis loop and cross-talk of organic memristive devices

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ABSTRACT

Similarly to inorganic memristors, the organic memristive devices reveal a variation of the hysteresis loop upon the frequency of the applied bias voltage. The on/off ratio of the conductivity increases from 4 to 1000 times for the variation of time delay (equilibration after the application of the voltage increment) from 5 to 60 s. Being implemented in multi-element electrical circuits memristive devices provide a cross-talk, leading to an equilibration trend of the conductivity values. This effect is mainly related to the formation of stable signal pathways.

1. Introduction

Organic memristive devices are nowadays of great interest as they mimic some properties of biological synapses [1–4]. In particular, they allow the realization of junctions with variable conductivity following the Hebbian rule [5], describing synaptic learning and memory in real biosystems. Their applicability in electrical circuits, as key elements with adaptive properties, was already demonstrated [6]. Moreover, these organic memristive devices have been used as artificial synapses in the hardware artificial circuit reproducing a part of a nervous system of the pond snail [7].

We present an organic memristive device carried out as a heterojunction of polyaniline (PANI) conducting polymer and a polyethylene oxide (PEO) solid electrolyte doped with lithium salt. The device's working principle consists in the drastic conductivity difference of PANI in its reduced and oxidized states [8]. The conductivity changes depend on the motion of Li^+ ions in the active zone between PANI and PEO layers, as demonstrated by Raman spectroscopy [9] and X-ray fluorescence measurements [10]. Moreover, there are differences between the theoretically predicted properties of the memristive devices [11] and those observed experimentally on inorganic materials [12,13].

Like synapses, the organic memristive device is an asymmetric system: the conductivity variation strongly depends on the polarity of the applied voltage. The dependence of the device conductivity on the duration or frequency of the applied stimuli corresponds well to the Hebbian rule [5], describing synaptic learning. Indeed, the device has characteristics of “mnemotrix”—an essential element of the V. Braitenberg mental experiment, developed for the explanation of learning in living systems [14]. Moreover, the use of organic materials provides a powerful technological approach for the construction of self-assembled 3D structures. Therefore, organic materials have been successfully applied for the realization of stochastic matrices, possessing properties of adaptation and demonstrating several similarities to the brain learning [15]. The investigation of stochastic system revealed a “cross-talk” between the composing elements. The system, therefore, is in a dynamic equilibrium, when the distribution of the conducting pathways and potential maps depends on the configuration and duration of the applied stimuli. Note that usually cross-talk is considered to be a negative phenomenon in traditional electronic circuits [16,17]. In this particular case, we want to underline the positive aspects of this phenomenon, responsible, similarly to the processes in nervous systems, for the internal processes taking place in the absence of the external stimuli.

Here we address the study of the temporal effect of applied signals on organic memristive devices properties. It means that the actual conductivity of the device depends not only on the value of the applied voltage, but also on the temporal “history” of its application. In addition, we investigate the electrical behavior (cyclic voltage–current characteristics) of a simple serial circuit with two organic memristive devices.

2. Materials and methods

Emeraldine base polyaniline (PANI) was purchased from Sigma (Mn ca. 100,000) and used as purchased. The deposition of the active PANI layer was carried out with a KSV 5000 LB trough, using

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a Langmuir–Schaefer (horizontal lifting) technique. Pure water, purified with a Milli-Q system, serves as the subphase (resistivity 18.2 MΩ cm). Polyethylene oxide (PEO) (average molecular weight 8,000,000) and $LiClO_4$ were purchased from Sigma and used without further purification. A solution of PEO was prepared in 0.1 M $LiClO_4$ and 0.1 M HCl at a concentration of 20 mg/ml.

The device realization, as shown in Fig. 1(a), started from a glass substrate, 9×18 mm^2 with two thermally evaporated chromium electrodes. 48 PANI layers were deposited onto the substrate by the Langmuir–Shaefer technique. Previously performed studies determined the optimal number of layers (48), providing high conductivity of the polymer and, at the same time, effective variation of the device response due to electrochemical reactions, occurring in the active zone (defined as the area of PANI underneath the PEO strip) [1]. The deposited PANI layer was doped by immersion in 1 M HCl for 40 s. This treatment transfers PANI to its conductive form and can be controlled both optically, the color changes from blue to green, and electrically, the resistance arrives up to 100 kΩ. After 40 min, the doping process was repeated to achieve higher stability of PANI layer (generally the resistance reaches a value of 70–150 kΩ). Afterwards a PEO stripe, of about 1–2 mm width, was positioned over the PANI layer crossing it in the central part. Then, a silver wire, 50 μm diameter, was placed over the PEO and was covered by an additional PEO stripe. One end of the Ag wire has been patched with a small indium blob and used as reference (gate) electrode. Finally, the whole structure was doped by exposition to HCl vapor for 30 s. Photograph of the final structure is shown in Fig. 1(b).

Electrical measurements of cyclic voltage–current (*V–I*) characteristics were performed by applying the voltage to the drain electrode (source and gate (reference) were maintained at the ground level) and successive measuring of two current values: the total current in the circuit and its ionic component of the reference electrodes. Application of the voltage started from zero value and increased with a step of 0.1 V until its maximum value. The voltage was decreased, with the same step, down to the minimum (negative maximum), and finally, increased again until zero. At each voltage step, a delay of 5, 10, 20, and 60 s has been used to equilibrate the transient processes in the devices. For *V–I* characteristics, the current values at the end of such time intervals were plotted. Application of the voltage and measurement of the total current through the device were done with 236 Source Measure Unit (Keithley). Ionic current was measured with 6514 System Electrometer (Keithley). Electrical connections for the measurements of *V–I* characteristics of single organic memristive devices are shown in Fig. 1(a). As outlined above, one of the two metal electrodes, the source in particular, and the silver wire inside PEO (acting as a gate or reference electrode) are short-circuited and connected to the ground potential level. However, external voltage units bias the second metal electrode, the drain. Therefore, all redox reactions occur according the potential of the active area with respect to the zero potential applied to the gate. However, even if this device is apparently a transistor because of the three electrodes, such configuration turns the element into a two terminal device.

To study the “cross-talk” between organic memristive devices, the following measurements were performed. A Source Meter Keithley 2400 drove the electrical characterization of two devices, connected in series. The configuration of the samples was as two-terminal devices: the gate (reference) electrodes were short-circuited with the corresponding source electrode of the same device. Applied bias voltage increased from 0 V to +1.5 V. Subsequently it was decreased from +1.5 V to −1.5 V, and, finally, again increased from −1.5 V to 0 V without interruption and by steps of 0.1 V. A delay time of 60 s has been used between the voltage application and the acquisition of the current flowing in the circuit. The time delay is an essential parameter to equilibrate the transient processes in the organic memristive devices, as demonstrated in our previous work [18]. The samples under test were kept in air and the room conditions (temperature, humidity, and lighting) were guaranteed to be constant during the whole experiment. Scheme of the connections is shown in Fig. 2.

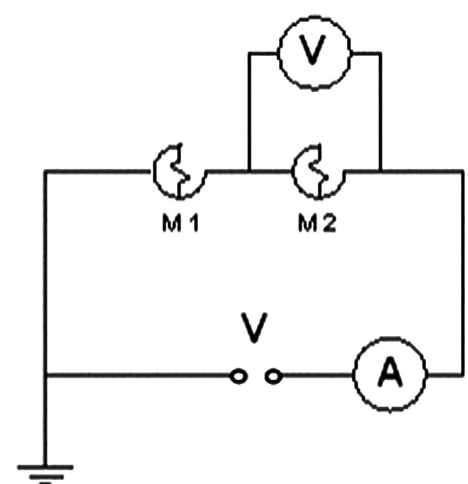

Fig. 2. Experimental scheme of the circuit with two organic memristive devices for electrical measurements.

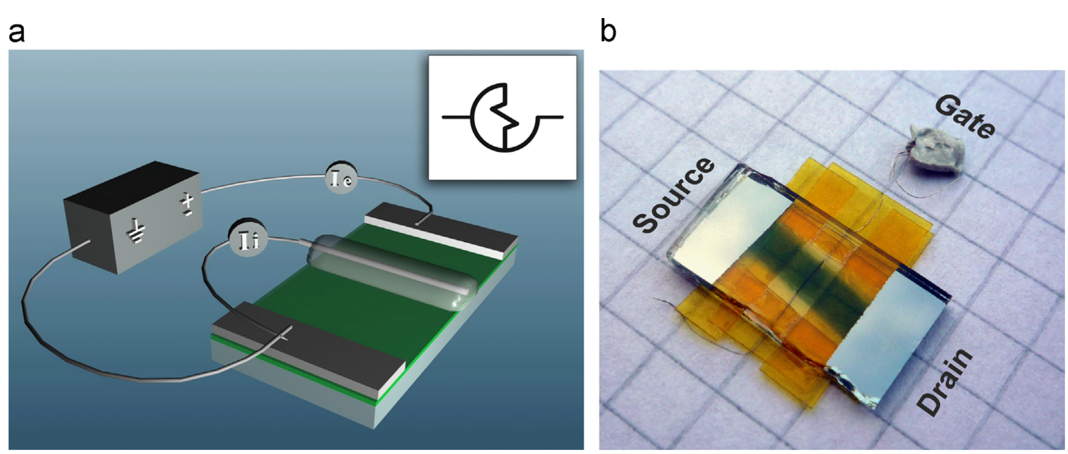

Fig. 1. Experimental scheme of a single organic memristive device (a) and photograph of an organic memristive device: kapton film protects the PANI layer from degradation (b).