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# Spectrophotometric characterization of organic memristive devices

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ABSTRACT

Realizing element able to mimic some features of the human brain is a challenging perspective. The concept of organic devices, based on conductive polymers, is attracting significant interest being generally bio-compatible, able to work in liquid phase, with low bias voltage ranges. Organic memri-stive devices have demonstrated the capability of mimicking some properties of biological synapsis. Moreover, memristive devices based on polyaniline (PANI) have been used as artificial synapsis in the hardware of a single layer perceptron. In the perspective of a multi-layered perceptron, a fundamental step is the knowledge of the conductive state of each single memristor. The electrochromicity of PANI endows us to developed a non-invasive and precise method to solve this problem; in fact, PANI memristor's state (induced by the voltage biasing) can be monitored measuring its optical features variation by means of a spectrophotometer. The latter, thanks to its high accuracy, allows distinguishing minimal color variation at a micrometric distance and, without lowering its precision, can measure areas of 7 × 60 $cm^2$ in a single scan and reach, in several scans, a total area of 120 × 140 $cm^2$. Therefore, in future works we will extend the here proposed method in order to get, in a single scan, contact-less measurement and information about the state of each single PANI memristor belonging to a multi-layered perceptron.

## 1. Introduction

Since 2008 [1], year of the first report on the realized memristor, we can observe a growing interest to this element that can be considered as a synapse analogue in electronic circuits. By definition the latter can vary its resistance depending on the charge passed through it and can keep memory of its previous conductive states [2]. Thanks to these features memristors can be used as non-volatile memories and as logic gate, being capable of performing logical operations [3,4]. The most of reported memristive devices use metal oxides as an active layers [5]. However, there are several works, where organic memristors were reported [6].

Organic memristors have several advantages, with respect to devices based on inorganic materials, such as higher flexibility, easy and low costs deposition methods and a low voltage working range. In particular, memristors based on polyaniline (PANI), designed and realized specifically for adaptive networks, stood out among others, demonstrating classical memristive features, such as hysteresis loop in current vs voltage characteristic and also synapse mimicking [7] properties and learning capabilities [8]. Finally, using PANI based memristors, it was constructed a single layer (or elementary) perceptron [9]. The latter is the simplest form of a complex artificial neural network (ANN), based on adaptive links [10]. Similar results were also reported on cross-bar system, based on inorganic memristive devices [5]. Single layer perceptron can solve elementary anthropomorphic tasks such as: input classification, image and speech recognition. In such system, memristive devices work as synapsis, capable to vary their weight functions. Output signals are summed in a neuron, realized by a simple circuit based on operational amplifiers. In particular, the realized perceptron was trained in a way that, after learning, it was able to perform NAND or NOR logic functions. The training (correction of the weight functions, performed by memristors) was done analysing the actual output signal value at a certain combination of inputs and comparing it with a theoretical value of the output for a particular logic element. When the error was equal to zero, no action was required while, if the error was negative, the link was reinforced by external action or inhibited, if the error was positive. It is important to note that, in the case of a single layer perceptron, we need to know only the configuration of the inputs and corresponding

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output signal for making the adequate learning procedure. It is not the case if the perceptron is made from two or more layers. For the successful application of the back error propagation algorithm we need to know the conductivity state of each memristor after each learning epoch, whose signals are summed in a neuron, represented by a small circuit based on Operational Amplifiers. In other words, during the working procedure, the output value of the network depends both on the input used and on the conductivity of each single memristive device (belonging to the perceptron). Therefore, one of the most important parameters to monitor is the conductivity [11,12] (or *memconductance*) of all the devices and, in case of a complex network, like a multi-layer perceptron [13], this step can be tricky and time consuming. One option is the acquisition of memconductances by means of an additional circuit, capable of characterizing each node individually, detaching it from the circuit (when performing this measurement). However, this approach increases the electronic complexity of the whole system and negatively affects the main network and measurements.

Therefore, it seems very useful to achieve this control by means of a different method. In this work, we address the study of a new, and non invasive, way to detect the variation of PANI memristor conductivity during its functioning. This switching is, in fact, the basis of the working principle of the organic memristive devices and is always accompanied by the phenomenon of electrochromism that is the reversibly variation of the color of the polymer, in response to electrochemical redox reactions. We take advantage of the electrochromic features of PANI to detect the memristor's switching, without any additional electronics. More in details, the polyaniline's redox reaction from non-conductive leucoemeraldine form to the conductive emeraldine form (and vice-versa) is always accompanied by the chromic variation from yellow to green (and vice-versa) [14]. This transition occurs in the device's active zone [15], that is in contact with the electrolyte, upon the application of a proper voltage. By means of a spectrophotometer, acquiring the reflectance spectra of the memristor at different bias, we provide evidence of the conductivity states variations in the analysed element. The here proposed method can be a simple technique to measure the conductivity states of each memristor in complex networks, such as PANI memristor based multi-layer perceptrons without the addition of noise nor perturbation being avoided any kind of contact.

## 2. Material and methods

Emeraldine base polyaniline (PANI) was purchased from Sigma Aldrich (Mw ca. 100,000) and used as arrived. The memristive devices were made using an established routine [16,17]: as a starting point, two chromium electrodes have been evaporated at the sides of a 13 × 8 mm rectangular glass substrate. Langmuir films of PANI were spread in a KSV 5000 LB trough and deposited by means of Langmuir Schaefer (horizontal lifting) technique as in Ref. [7]. Water purified with a Milli-Rho-Milli-Q system was used as a subphase (resistivity 18.2 MΩcm). Our devices contained 60 PANI layers, which provide both rather high conductivity and fast response to electrochemical changes [18]. The PANI film was successively twice doped by 1.0 M HCl treatment. Polyethylene oxide (PEO) (average molecular weight 8,000,000) and $LiClO_4$ were purchased from Sigma Aldrich and used without further purification. A water solution of PEO, with a concentration of $20 mg/ml$, was prepared adding lithium salts until the concentration of 0.1 M $LiClO_4$. A PEO strip, about 1–2 mm wide, was cast across the PANI channel, approximately in the center between the two electrodes. A thin silver wire (purchased from Good-fellow) was placed over the PEO strip and then covered with another PEO strip; a small indium patch was attached at one end of the silver wire to provide a stable electrical contact. Finally, the assembled structure was doped with HCl vapors. We used a spectrophotometric scanner to collect reflectance spectra of the memristor and a 236 Source Measure Unit (Keithley) to apply the voltage and measure the current. The spectrophotometer [19,20] is made up of a transmission spectrometer (Imspector V8 manufactured by Specim, Finland) designed for a 2/3 inch CCD sensor equipped with a 25$\mu$ m entrance slit and covering the 400–780 nm spectral range with a spectral resolution of about 2 nm. The spectrometer is coupled to monochrome 2/3 inch CCD matrix chill digital camera (Hamamatsu C4742-12 bit, 1280 × 1024 pixels, 9 f/s) while a collecting lens (Computar TEC-M55 designed for a 2/3 inch sensor) focuses the sample on the plane of the entrance slit. Two 150 W halogen lamps provide the illumination. The optical parts are firmly mounted on a rigid and massive platform and move rigidly during the scan. The digital camera is interfaced to a PC by means of a 12 bit frame grabber (Mutech *MV*1000). A software program drives the scanner, acquires data and allows to save them as a spectral image (as a standard BMP or TIFF image) or as an ASCII file, after calculation of the CIE color coordinates based on the CMFs and illuminant, previously selected.

## 3. Results

Spectrophotometric device has been already used by authors in Ref. [20] to discriminate PANI layers conductive states. Here, we make a step further acquiring the real time electrochromic variation of a PANI memristor under oxidation and reduction bias potential. The PANI bulk reduction potential is +0.1 V, while the oxidation one is +0.3 V [21]. However, our case is slightly different because redox processes take place in a small area, defined as active zone. Thus, we need to consider the voltage distribution along the whole memristive channel. The process dynamics have been analysed in detail in Ref. [15] where different kinetics for reduction and oxidation reactions were defined and the explanation was suggested. According to this explanation, we can say that the reduction occurs simultaneously in the whole active zone (when any negative potential is applied to the device), while the oxidation takes place gradually with a progressive displacement of the conductive parts in the active zone from the drain to the source electrodes.

The time of the resistance switching in the organic memristive device, $t_{switch}$, depends strongly on the area of the active zone [22], following the relationship: $t = switch\ 0.47\ s/mm^2$. Thus, in case of sub-micrometer size of the active zone, it can be very fast (about 0.5 ps if the active zone is 1 $nm^2$). However, in this study we used a macroscopic configuration of the device (active area about 50 $mm^2$) to have a better temporal resolution of the conductivity switching and respective spectroscopic variations.

Initially, the memristor was characterized by recording the current vs time, (shown in Fig. 1), applying DC voltage of +0.8 V for 22 min to induce oxidation of PANI and, after, −0.1 V for 16 min to induce reduction. These measurements, defined as current kinetics, have been performed sampling a current value each second.

As it is clear from Fig. 1, during the negative bias (blue curve), the process reaches saturation after only 180 s, while, in case of positive polarity (black curve), the conductivity increases slowly and reaches the saturation after 400 s, confirming the above-mentioned explanation. The Spectrophotometric analysis has been performed while biasing the device by means of a source-meter. In this case, a single measurement requires 1 min and we recorded one spectrophotometer image each 120 s. We started with a first spectrophotometric image on a just prepared sample as a reference, then we applied +0.8 V to induce the oxidation process. Keeping the bias for 22 min, we recorded 11 spectrophotometric images; on the other hand, the reduction potential, the duration of which was