On the Interpretation of Hysteresis Loop for Electronic and Ionic Currents in Organic Memristive Devices

On the Interpretation of Hysteresis Loop for Electronic and Ionic Currents in Organic Memristive Devices

Silvia Battistoni[*,1], Alessio Verna[2], Simone Luigi Marasso[1,2], Matteo Cocuzza[1,2], Victor Erokhin[*,1]

[1] Consiglio Nazionale delle Ricerche, Institute of Materials for Electronics and Magnetism (CNR-IMEM), Parma, Italy
[2] Chilab—Materials and Microsystems Laboratory, DISAT, Politecnico di Torino, Chivasso (Turin), Italy

Key words: Organic Memristive devices, Electrochemical reactions, working principle

[*] Corresponding author: e-mail victor.erokhin@imem.cnr.it

Being promising elements for neuromorphic computation, memristive devices have been often described as crucial elements for the mimicking important synapse properties, such as memory and learning. Among them, Organic memristive devices (OMDs) can claim low cost fabrication processes and the easy tunability of their electrical properties. Up to now, the major bottleneck for their larger uses in neuromorphic computation are low rate of the resistance switching and stability. Here we report a new approach, based on the use of a liquid electrolyte, leading to the manufacturing of OMD with higher stability and faster resistive switching.

1 Introduction Memristive devices are considered as very promising elements for the implementation of artificial neuron networks (perceptrons) [1,2] and neuromorphic circuits, mimicking properties of nervous system [3–5]. The most of reported memristive devices include thin metal oxide layers, and their working principle is based on the growth of conducting filaments with successive variation of their conductivity [6,7]. Such mechanism is rather random and not well controlled, resulting in the uncertainty of ON and OFF voltage values not only from one device to the other, but also for different cycles of the same device [8]. This is the main limitation of the use of these devices for neuromorphic applications. Organic memristive devices (OMDs) [9,10], specially designed for mimicking important synapse properties, such as memory and rectification, do not show this disadvantage. Moreover, their effective use as weight function switching elements in perceptrons has been demonstrated [11–13]. In addition, it was demonstrated the possibility of their utilization as synapse analogs in neuromorphic systems, mimicking parts of nervous system of simple animals (pond snail *Lymnaea Stagnalis*) [14]; in systems with frequency dependent plasticity [15]; circuits, allowing STDP (spike-timing dependent plasticity) [16] and in circuits, providing synaptic connection between two nervous cells of the rat cortex [17]. However, limiting factors of the organic memristive devices are low rate of the resistance switching and stability. It has been shown that down-scaling of the devices sizes results in the increase of the ON/OFF switching rate as well as endurance [18,19]. Despite this result, obtained using a solid polymeric electrolyte, can be considered as an important step forward for the use of OMD in complex circuits, it could be further improved increasing the switching speed. In this work we want to improve further these parameters by using other types of electrolytes (ion motion in electrolyte is an important factor responsible for the speed of the device operation). As already pointed in [9], analyzing the electrodes distribution I_g cyclic characteristic should be considered a direct expression of the redox activity of the polyaniline (PANI). However, there is still a marked difference between the ideal PANI cyclic voltammetry and OMDs' I_g in anodic and cathodic voltage peaks, scan speed response and reaction time. These discrepancies have been attributed to voltage distribution and relative potential drop along the polymeric thin film [9]. Although the mechanism involving the switching between ON and

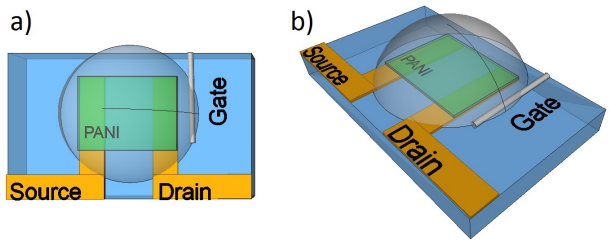

Figure 1 Scheme of the device: top (panel a) and perspective (panel b)view.

OFF conductivity states has never been under discussion (since strongly supported by spectrophotometric analysis), a clear quantitative analysis of the mechanism at the basis of the working principle of these devices is still missing due to variability affecting OMDs' characteristics. This information is crucial for the understanding of device performances and possible integrative applications but it requires a significant decrease of variation of OMD properties.

Here we report a significant improvement of organic memrstive devices performance in terms of stability, reproducibility, switching speed. These results, in agreement with what reported in Ref [19] allow us to reach a quasi perfect overlapping of PANI cyclic voltammetry and OMDs' I_g and to conduct a systematic and parallel study of the optimization of the working condition of the device.

2 Materials and Methods

2.1 Devices' preparation Electrodes were fabricated by e-beam evaporation (ULVAC EBX-14D) of Ti/Au film (thickness 10nm/100nm) on Si wafer (100) finished with 1 μm of thermal oxide, patterned by standard photolithography and wet etching.The preparation of the solution to be deposited has been reported in several papers[5,20]. Briefly, a solution (0.1mg*mL1) of emeraldine base form of Polyaniline (Sigma Aldrich, Mw100.000) in 1-methyl-2-pyrrolidinone (Sigma Aldrich ACS reagent 99.0%) with the addition of 10% of Toluene (AnalaR NORMAPUR® ACS) is deposited by means of the Langmuir-Schaefer technique onto a masked substrate.

We prepared 3 sets of samples having different numbers of deposited monolayers (60, 40 and 20 layers) and we applied 150 μL - 200μL of HCl (1 M) on top of the channel, covering all the PANI interface with the electrolyte.In this configuration, a silver gate electrode is used as reference electrode and it's simply inserted in the liquid electrolyte. A scheme of the device configuration is reported in Figure 1.

2.2 Devices' characterization Prepared samples (deposited with 40 monolayers of PANI) were characterized following the standard characterization procedure by sweeping the voltage value V_{SD} between 1V and -0.3V, with steps of 0.01 V varying the scan rate of the measurement between 200mV/s and 1mV/s.

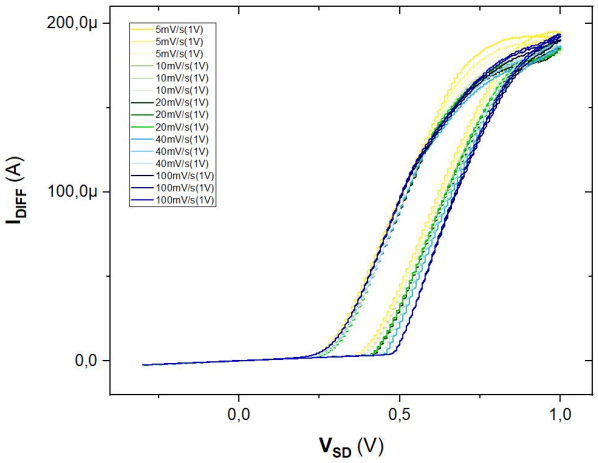

Figure 2 60l OMD's hysteresis: response of the I_{DIFF} current to V_{SD} sweeps.

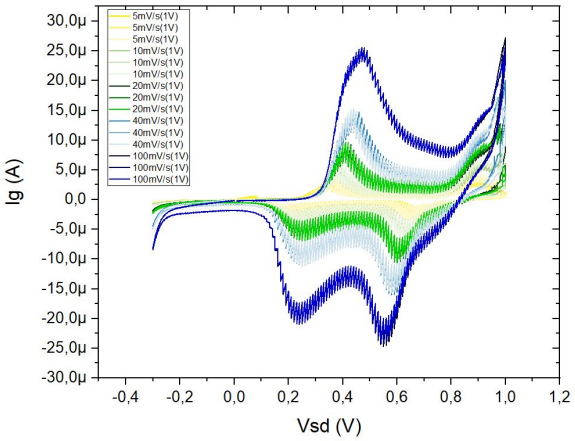

Figure 3 60l OMD's hysteresis: response of the I_G current to V_{SD} sweeps.

3 Results and Discussion As a preliminary characterization, we explored the device's response to this new configuration in which the electrolyte is not confined in a narrow area but spread in direct contact with the entire polymeric channel. Thus we started our measurements characterizing the device whose channel has the thickness of our standard OMDs (60 PANI monolayers).

Results of the hysteresis, as a function of the scan rate, are reported in Figure 2 and Figure 3. The reduction of the channel dimension in combination with the new configuration of the interface between PANI and electrolyte seems to preserve memristive properties and indeed to stabilize the OMD performance and to allow a faster working routine. Successive scan with the same scan rate, produce a very stable and reproducible device's I_{SD} output. The relative I_G output (Figure 3) presents, even in this case, a high stabil-

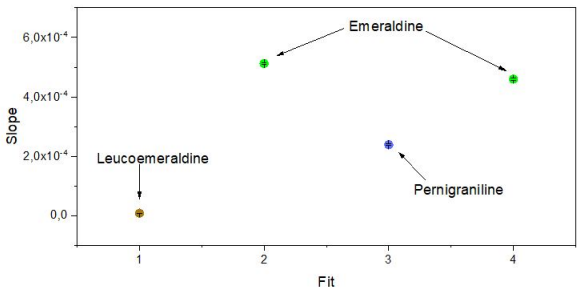

Figure 4 OMD's hysteresis: Slope of the linear fit performed on Figure 2 in different ranges: between 0 and 0.45V (1), 0.55 V to 0.7 V (2), 0.8 V to 0.6 V (3) and 0.5V to 0.3 V (4)

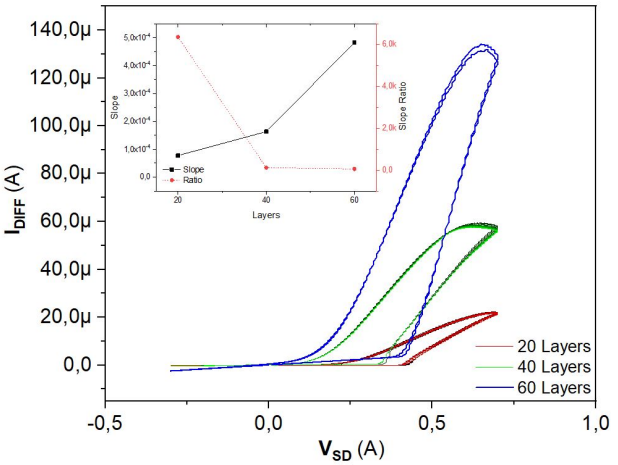

Figure 5 Effect of different thicknesses: OMD's hysteresis for 20 (red), 40 (green) and 60 layers (blue) acquired at 100mV/s. In inset: slope and slope ratio for all samples.

ity at a fixed scan speed. All scan speeds present a marked anodic peak localized between 0.3 V and 0.4 V and a successive positive peak starting at 0.8 V. These two can be attributed to the oxidation of leucoemeraldine in emeraldine and, successively, in pernigraniline[21]. Cathodic peaks corresponding to the respective reductions occur between 0.55 V and 0.7 V (for the formation of the emeraldine) and 0.1 V and 0.25 V (for the leucoemeraldine) [21–24]. Despite the slight shift in cathodic and anodic peaks voltages, these latter results are agreement with ones predicted in literature, specially if considering the non-ideal measurement configuration. Moreover, the attribution of peaks in Figure 3 is furthermore supported by the conductivity variations reported in Figure 2. Among all states, PANI form having the highest conductivity is emeraldine [25,24] and in fact, after the partially oxidation in this form, OMD's I_{SD} shows an abrupt decrease of the resistivity that remains mostly stable until reaching the end of the voltage positive range, where only a slight bending could be appreciated. This transition or *switching* between low and high conductivity regimes, due to the emeraldine formation, could be considered as a benchmark for OMDs.

During the back scan, 2 important conductivity variations are present in correspondence of the two cathodic peaks (0.6 V and 0.2 V). To quantify these variations, we extracted the slope of linear fits (that is directly proportional to the conductivity) of 4 voltage ranges of the hysteresis reported in Figure 2: between 0 and 0.45V (leucoemeraldine region), 0.55 V to 0.7 V (emeraldine), 0.8 V to 0.6 V (pernigraniline) and 0.5V to 0.3 V (emeraldine) (Figure 4). It's to be noted that the slope of the two emeraldine regions (in the direct and back scan) are perfectly comparable confirming the stability of the reversible reaction at the basis of the OMD switching mechanism. This trend is preserved even reducing the scan speed of the measurement with the only effect of shifting the switching point to smaller voltage values (in agreement with the shift reported in Figure 3) and a marked rectification in the higher positive voltage range. This latter is more prominent for slowest measurements and could be attributed to a higher ratio of pernigraniline formed during the scan.

Since the working principle of an OMD involves only the transition between leucoemeraldine and emeraldine, it's possible to reduce the voltage window explored in this measurement to 0.7V, without losing any information and avoiding possible electrodes interaction [26,27].

3.1 Different polymer thicknesses The thickness of a polymeric thin film is a crucial parameter able to modify the conductivity and the time constant of redox reactions [28]. For practical applications, it's necessary to estimate the optimal number of PANI monolayers necessary to ensure on the one hand a good conductivity, on the other hand high switching rate. Our findings (reported in Figure 5) suggest that a lower number of PANI monolayers leads to higher maximum resistivity while increasing the thickness of the PANI channel, OMDs could experiment a higher current, as expected (black squares in inset of Figure 5). However, calculating the ratio between the slope in leucoemeraldine and emeraldine form (i.e. high and low resistance states), the highest value is reached in the case of the thinnest sample (red circles inset of Figure 5). This suggests the possibility of further reducing the thickness of the polymeric channel, without affecting the memorization capabilities and the possible uses of this new organic memristor devices' configuration.

3.2 Endurance test After the evaluation of the thickness contribution, we tested the endurance response in both hysteresis cycling. We selected the sample with 40 PANI layers since it represents a good compromise between conductivity, speed of the reaction and ON/OFF ratio and we acquired its hysteresis for 250 consecutive cycles. Results, reported in Figure 6 and Figure 7, confirm once more the good stability already discussed in previous section extending this latter to a more sever measurement routine. OMD

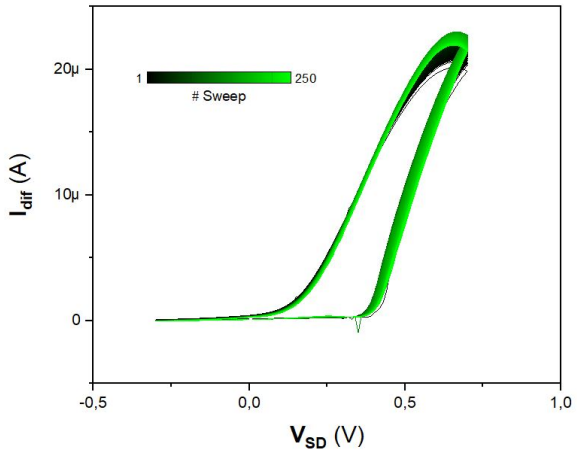

Figure 6 OMD's hysteresis: response of the I_{Dif} current to 250 consecutive V_{SD} sweeps.

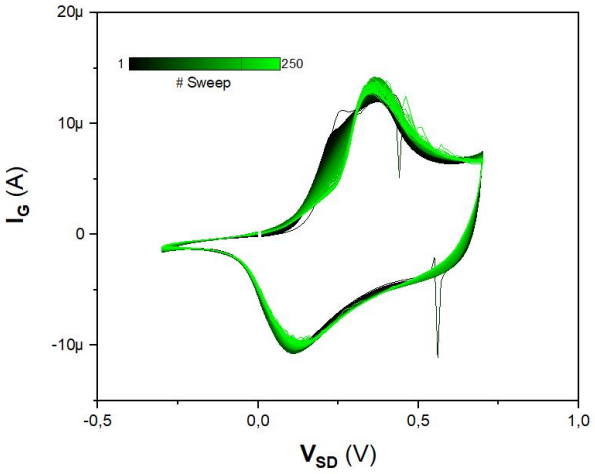

Figure 7 OMD's hysteresis: response of the I_G current to 250 consecutive V_{SD} sweeps.

hysteresis remains stable practically for all the sweeps as well as the switching voltage. In the case of OMD I_G instead is possible to notice the initial presence of a second anodic peak, localized at 0.2 V, that progressively merges with the most intense positive peak. This one could be due to the formation of protoemeraldine [21] or to possible changes of the layer structure during continuous potential cycling [29].

4 Conclusions Here we report a new OMD configuration in which the electrolyte used (1M HCl) is in contact with the entire active area of the polymeric channel. The so obtained devices present a marked memristive behaviour that remains stable even if it undergoes to sever endurance test. Moreover we evaluated the effect of the thickness of the PANI channel, demonstrating that the optimal ratio between high and low resistance belongs to the device with thinnest channel. These results, combined with an extremely fast response of the memristors, is rather promising and suggest a possible use of this new configuration in applications in which the stability and the high resistive switching are necessary.

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Graphical Table of Contents

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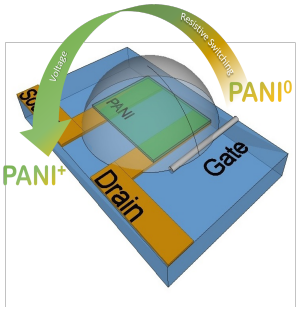

In organic memristive devices, the fast and stable resistive switching is due to variation of the oxidation state of the polymer (Polyaniline) caused by the application of a specific voltage value.