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Adaptive polymeric system for Hebbian type learning

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Abstract

We present the experimental realization of an adaptive polymeric system displaying a “learning behaviour”. The system consists on a statistically organized networks of memristive elements (memory-resistors) based on polyaniline. In a such network the path followed by the current increments its conductivity, a property which makes the system able to mimic Hebbian type learning and have application in hardware neural networks.

After discussing the working principle of single memristive element developed in our lab we present realization and the relative experimental results a statistically organized polymeric adaptive network.

Introduction

Artificial neural networks have been intensively studied in the last decades due to their great performances in complex tasks like for example pattern recognition or parallel information processing [1]. Neural networks are inspired by biological systems and in analogy with the brain are composed of interconnections artificial neurons (or nodes) evolving their organization as a functions of input stimuli (neuroplasticity). As first hypothesized by Hebb such modification can be connected to the strengthening or inhibition of synaptic connections occurring respectively in the more and less excited networks path (Hebbian rule [2-3]). Neural networks based on Hebb’s principle has been so far mostly software developed with only few exceptions of hardware realization [4] due to the difficulties in producing smart “hebbian-type” material elements. The software approach in spite its versatility however is limited by the computation power of computers and cannot handle networks with a very large number of elements. The synthesis of material adaptive systems able to mimic neuroplasticity would allow to overcome this limitation and lead to the realization of higher performance neural networks.

Possible candidates for the task are the so called “memristive” systems which have attracted great interest in the last years [5]. A memristive device is a two terminal element with “memory”, to be more precise, using definition [6]: it displays a resistance $R(w)$ function of an internal state variable w whose derivative is a function of the passing current i , as summarized by the two equations:

$$R(w) = \frac{V}{i}$$

$$\frac{dw}{dt} = f(i)$$

Equation 1

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3 Several memristive systems have been recently proposed, mainly based on hard materials, like
4 metal oxide materials, such as Gd_2O_3 [7], VO_2 [8], or silicon [9] while in our lab an organic system
5 has been developed [10].

6
7 The organic device is based on the heterojunction of a thin doped polyaniline (PANI) layer acting as
8 conducting element with an electrical resistance variable through redox reactions, and a thick film
9 of the solid electrolyte PEO: Li^+ . The PANI polymer actually may be switched electrochemically
10 between an insulating and a conductive form, namely: Leucomeraldine (reduced form) and
11 Emeraldine salt (oxidized one) [11]. In order to induce such reaction, the part of the PANI film
12 must be in a contact with an ions reservoir provided by a poly(ethylene oxide) gel doped with
13 lithium salt kept at ground potential. As previously reported [10], in this system the electrically
14 induced exchange of Li^+ ions between PEO and PANI is involved in processes responsible for the
15 modulation of the element conductivity; when both ions reservoir and conductive layer are at the
16 same potential the ions migrate spontaneously inside the film reducing the polymer to the insulating
17 form, while on other hand when a positive voltage is applied, the opposite effect takes place
18 resulting in an oxidation of PANI and recovery of its conductive state.

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20 The element exhibits therefore a rectifying behavior: when a positive voltage higher than the
21 oxidation potential is applied the conductivity increases while for zero or negative voltage the
22 material is insulating. For both polarities, the element presents a gradual variation of the
23 conductivity in time till the saturation level. For the best organic memristors, the ratio in the
24 conductivity can reach 4 orders of magnitude. Such characteristic is the electrical analog of Hebbian
25 synaptic plasticity and therefore such device may be used as weighting element (synapse) in
26 hardware neural networks.

27
28 Realization of an artificial system mimicking to some extent processes occurring in brain, demands
29 the use of millions of nodes and synapses. Of course, it is possible to apply modern powerful
30 electronics technologies, based mainly on high-resolution lithography, for miniaturization of the
31 memristor sizes and for the increase of the integration level. However, it will not solve completely
32 the problem, as it is very difficult to form multiple connections between elements in 2 D structures.
33 Therefore, our current activity is directed to the realization of statistical 3 D networks using
34 properties of organic materials for self-organization. In this work, we report data on the networks
35 based on porous/fibrillar PEO matrix with incorporated PANI additions. At the level of single
36 discrete elements, the approach was shown to be adequate. In this study, we aim to demonstrate its
37 adaptivity properties for more complicated systems with multiple electrodes.
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43 **Materials and methods**

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46 The synthesized statistical structure consists of a porous PEO matrix filled with PANI forming a
47 network of statistically connected conductive channels. The PEO matrix contains also the Li^+ ions
48 responsible for the redox reactions and the conductivity modulation of the PANI.

49 All the chemicals: $LiBF_4$ salt, Emeraldine base polyaniline PANI and poly(ethylene oxide) PEO
50 were purchased from Sigma Aldrich. The polymers PANI and PEO had an average molecular
51 weight M_n respectively 100000 and 8000000.

52
53 The starting materials have been characterized by Fourier Transform Infrared Spectroscopy (FTIR)
54 in Attenuated Total Reflection (ATR) geometry using a Jasco 420 FTIR spectrometer equipped
55 with a ZnSe ATR crystal. Both PEO and PANI polymer have been deposited on the ATR crystal
56 by cast solution, (respectively from a water and methylpyrrolidone both at 1 mg/ml
57 concentration). The conductive form of PANI (Emeraldine salt) has been obtained with doping
58 the film with a 0.1 M $LiBF_4$ water solution and then also characterized with FTIR spectroscopy.
59 The spectra of polymers which have been acquired in the fingerprint region ($600-200\text{ cm}^{-1}$) are
60 reported in figure 1. The absorption peaks have been assigned according to literature [12-14] are
reported in table I.

	PEAK cm^{-1}	ASSIGNMENT
PEO	842	CH_2 asymm. rocking
	957	CH_2 rocking sym., C–O–C
	1100	C–O–C (sym. + asymm.) stretching
	1236	CH_2 twisting sym.
	1280	CH_2 twisting (asymm. + sym.)
	1344	CH_2 asymm. wagging
	1357	CH_2 sym. wagging, CC stretching
PANI	1160	Quinoid= N^+H -benzenoid (doped)
	1280	C–N stretching
	1495	C=C stretching of benzenoid ring
	1580	C=C stretching of quinoid ring

We note, as we have already reported [15], that in the LiBF_4 doped form of PANI a strengthening of the 1150 cm^{-1} peak takes place which is associated with high electrical conductivity and a high degree of electron delocalization [14].

The matrix has been prepared starting from a highly concentrated PEO gel, which dried in a vacuum chamber, forms a sponge-like structure subsequently filled with a PANI solution. In detail the preparation procedure consisted of making a 20 mg/ml PEO solution with LiBF_4 salt at 0.1 M concentration; the compounds have been mixed and vigorously stirred to obtain a complete solution in water and then left to rest 12 hour in order to allow the gelification process. About 0.5 ml of gel has been then placed on the middle of 16 electrodes in a radial configuration (see fig 2) and left for 2 hours in the mechanically pumped vacuum chamber. The formed PEO sponge has been then filled at various times with a PANI solution in n-methyl-2-pyrrolidone (NMP) 1 mg/ml concentrated. Before the injection of PANI a silver wire was inserted in the structure to provide the reference electrode.

In order to induce and measure changes of conductivity in the prepared matrix a special multiplexing circuit has been developed. Such circuit is able to select any couple of pins among the 16 terminals and apply a voltage with the relative current measurement. The developed electronics is based on two analog, bidirectional, 16 to 1 channels, multiplexers (Intersil DG4006), where the 16 “input” channels are connected one to one while the two single “output” are connected to two electrometers. The terms “input” and “output” are used to distinguish to which side of the multiplexer the channels belong, however we remark that such term maybe is not appropriate since the device is bidirectional. The two electrometers employed for voltage application and current measurement consist on two homemade devices based on an ultra low noise operational amplifier (Burr Brown OPA128) set up in a voltage clamp configuration. The currents acquisition and the applied voltages control is done by a computer acquisition board (National Instrument USB 6002) which control also the selected pins with 8 digital output (4 bit per multiplexer). Finally a special software has been developed to select serially or randomly any couple of pins and apply a voltage.

Results

In order to create some conductive channels inside the matrix inhibiting at the same time the other possible current pathways, a special signal sequence has been applied to the sample electrodes. The “training protocol” aimed to increase the conductivity between two selected couples of pins and decrease it for the others. More specifically, a positive voltage was applied respect to the reference potential on one terminal of the selected couple in order to induce the PANI oxidation on the connecting path and thereby decrease the electrical resistance, while the negative potential was applied in the other cases to obtain the opposite effect (PANI reduction and increase of resistance).

The applied voltage sequence and its effects are described in figure 3: the first multiplexed device selects one fixed terminal labelled “0” while the second open serially the other 15 (labelled “1” to

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3 “15”). During the 15 channels scan, a positive voltage is applied when the terminals 2 and 10 are
4 selected while negative in the other cases. In other words the aim of the protocol is to create two
5 conductive paths between the couple of pins 0-2 and 0-10 while inhibiting the current flows for the
6 other 13 connections. The top graph of figure 3 shows the six initial cycles of the measurement
7 reporting the relative measured currents for the second terminal selected (the first is fixed on 0
8 channel) which are referred respectively to the left and right axis. The voltage between 0-10 has
9 been switched to positive starting from cycle 3, as it can be deduced by the top plot, while the path
10 0-2 has been “open” after 15 cycles. The trend of the absolute value of the currents in the 15
11 selected paths is shown in the bottom graph of figure 3 as a function of time (or cycles number).
12 The two selected paths 0-10 and 0-2 increase their conductivity after voltage reversal (cycle 3 and
13 15) till reaching the highest value around the 90th cycle, while the inhibited channels show an
14 opposite increase of the resistance. After achieving the maximum currents in the “open” paths,
15 however, the resistance increases in all channels. During the experiment the dynamics of the
16 currents shows therefore two processes: a “training” and an “aging”; after 90 cycles the “training”
17 protocol has the highest effect, setting the conductivity in open channels about 16 times greater than
18 in the closed ones, while afterwards the conductivity decrease in all channels is probably due to an
19 aging effect. The increase of resistance is ascribable to a deterioration of the structure since the
20 trends of the channels seem to be correlated and in particular the conductivity decrease with the
21 same time constant in both opening and closing channels. The aging effect may be due to several
22 causes, which are currently under investigation; the increase of resistance of polyaniline may be due
23 to dedoping (deprotonation) [16], overoxidation [14], to thermal degradation or ambient effects .
24 The deprotonation of polyaniline increases the resistance since it reduces the number of carriers;
25 such effect depends strongly on the doping agents [16] which may be selected in order to increase
26 the stability of the device. The overoxidation instead consists on the irreversible oxidation of
27 polyaniline to the insulating pernigraniline form which normally takes place at a higher potential
28 with respect to emeraldine salt while thermal degradation could simply arise from the Joule effects
29 due to the flow of current in the device. The relative contribution of the possible causes of aging
30 process would be the subject of future investigation: it could be evaluated for example by
31 changing the doping agent and sealing the device, changing temperature and the applied potential
32 respectively to separate respectively the effects due to dedoping, thermal degradation and
33 overoxidation (electric induced aging) .
34 However in spite the aging effects the structure maintains memory of the training protocol with a
35 final average conductivity ratio between open/close channels about 10.
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45 **Conclusions**

46 The presented results have demonstrated the applicability of the statistic network formation
47 approach for the realization of multichannel adaptive systems, capable of learning. Reinforcement
48 of the connection between selected input-output pairs simultaneously with the inhibition of all
49 others demonstrates directly a formation of multiple signal pathways, operating rather
50 independently. As a result, this random statistical network can be trained externally to establish
51 desirable electrical properties. During the network operation, these properties can be modified as a
52 result of the action of external stimuli. Further development of the work will be in the direction of
53 minimizing the aging effect and reaching higher ratio in the conductivity between opened and
54 closed channels.
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59 **References**

- 60 [1] Principe, J.C. "Artificial Neural Networks" The Electrical Engineering Handbook Ed. Richard C. Dorf

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2
3 [2] Boca Raton: CRC Press LLC, 2000 D. O. Hebb, *The Organization of Behavior. A*
4 *Neurophysiological Theory*. Second Edition. Wiley and Sons, New York (1961).
5
6 [3] C. H. Bailey, M. Giustetto, Y.-Y. Huang, R. D. Hawkins, and E. R. Kandel, *Is*
7 *Heterosynaptic Modulation Essential for Stabilizing Hebbian Plasticity and Memory?* *Natur*
8 *Rev. Neurosci.*, **1**, 11 (2000).
9
10 [4] C. Mead, *Analog VLSI and Neural Systems*, Addison Wesley, Menlo Park, Ca. 1989.
11 [5] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, *The Missing Memristor*
12 *Found*, *Nature*, **453**, 80 (2008).
13 [6] L. Chua, *Memristor – The Missing Circuit Element*. *IEEE Trans. Circuit Theory*, **18**, 507
14 (1971).
15 [7] X. Cao, X. Li, X. Gao, W. Yu, X. Liu, Y. Zhang, L. Chen, and X. Cheng, *Forming-Free*
16 *Colossal Resistive Switching Effect in Rare-Earth-oxide Gd₂O₃ Films for Memristor*
17 *Applications*, *J. Appl. Phys.*, **106**, 073723 (2009).
18 [8] T. Driscoll, H.-T. Kim, B.-G. Chae, M. Di ventra, and D. N. Basov, *Phase-Transition*
19 *Driven Memristive System*, *Appl. Phys. Lett.*, **95**, 043503 (2009).
20 [9] T. H. Kim, E. Y. Jang, N. J. Lee, D. J. Choi, K.-J. Lee, J. Jang, J. Choi, S. H. Moon, and J.
21 *Cheon, Nanoparticle Assemblies as Memristors*, *Nano Lett.*, **9**, 2229 (2009).
22 [10] V. Erokhin, T. Berzina, and M. P. Fontana, *Hybrid Electronic Device Based on*
23 *Polyaniline-Polyethylene Oxide Junction*, *J. Appl. Phys.*, **97**, 064501 (2005).
24 [11] S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, and
25 *A. G. MacDiarmid, Polaron Lattice in Highly Conducting Polyaniline: Theoretical and*
26 *Optical Studies*, *Phys. Rev. Lett.*, **59**, 1464 (1987).
27 [12] Wang, W.; Li, L.; Xi, S. *J. Colloid Interface Sci.* **1993**, *155*, 369–373
28 [13] Kimura, N.; Umemura, J.; Hayashi, S. *J. Colloid Interface Sci.* **1996**, *182*, 356–364.
29 [14] Kang, E. T. *Polyaniline: A polymer with many interesting intrinsic redox states*
30 *Progress in Polymer Science* **2** 277 1998
31 [15] Berzina, A. Smerieri, G. Ruggeri, M. Bernabo', V. Erokhin and M.P. Fontana, ,
32 *Mater. Sci. Engineer. C* **30** (2010), pp. 407–411
33 [16] Sedenkova, I; Trchova, M; Stejskal, J *Thermal degradation of polyaniline films*
34 *prepared in solutions of strong and weak acids and in water - FTIR and Raman*
35 *spectroscopic studies POLYMER DEGRADATION AND STABILITY*, **93** (12): 2147-2157
36 *DEC 2008*
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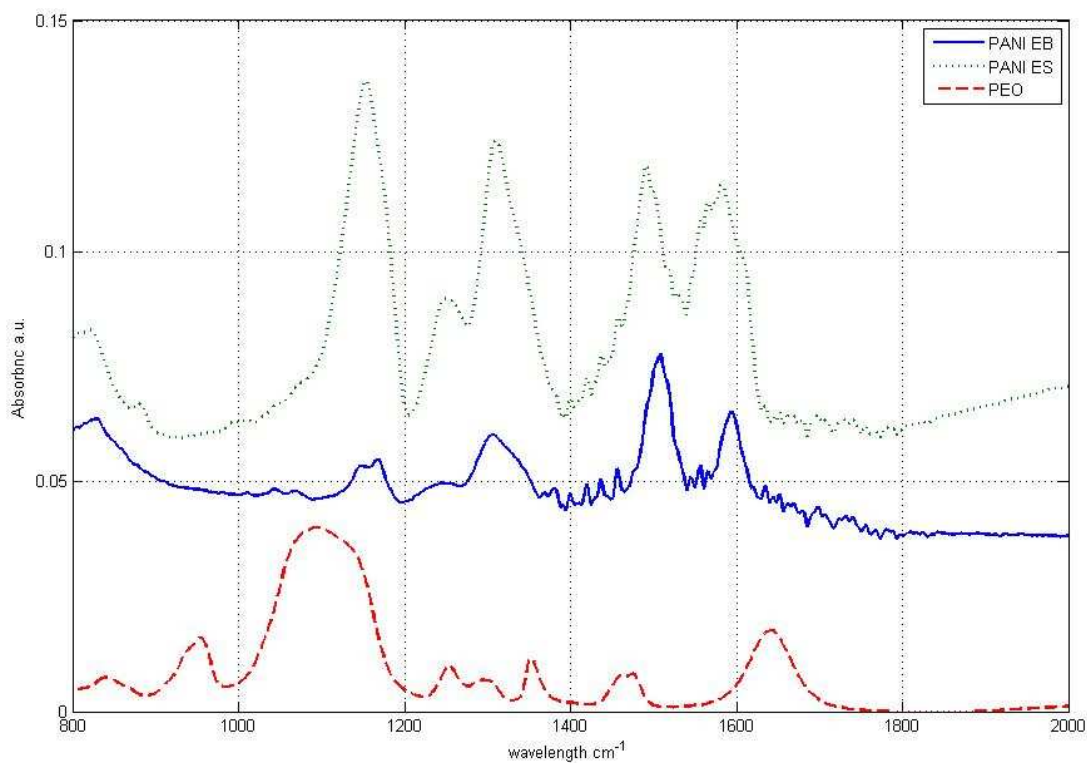


Figure 1 (color online version only) FTIR spectra of pristine PANI (solid line), doped PANI (dotted line) and PEO (dashed lines) polymers . The baselines have been shifted for better readability.

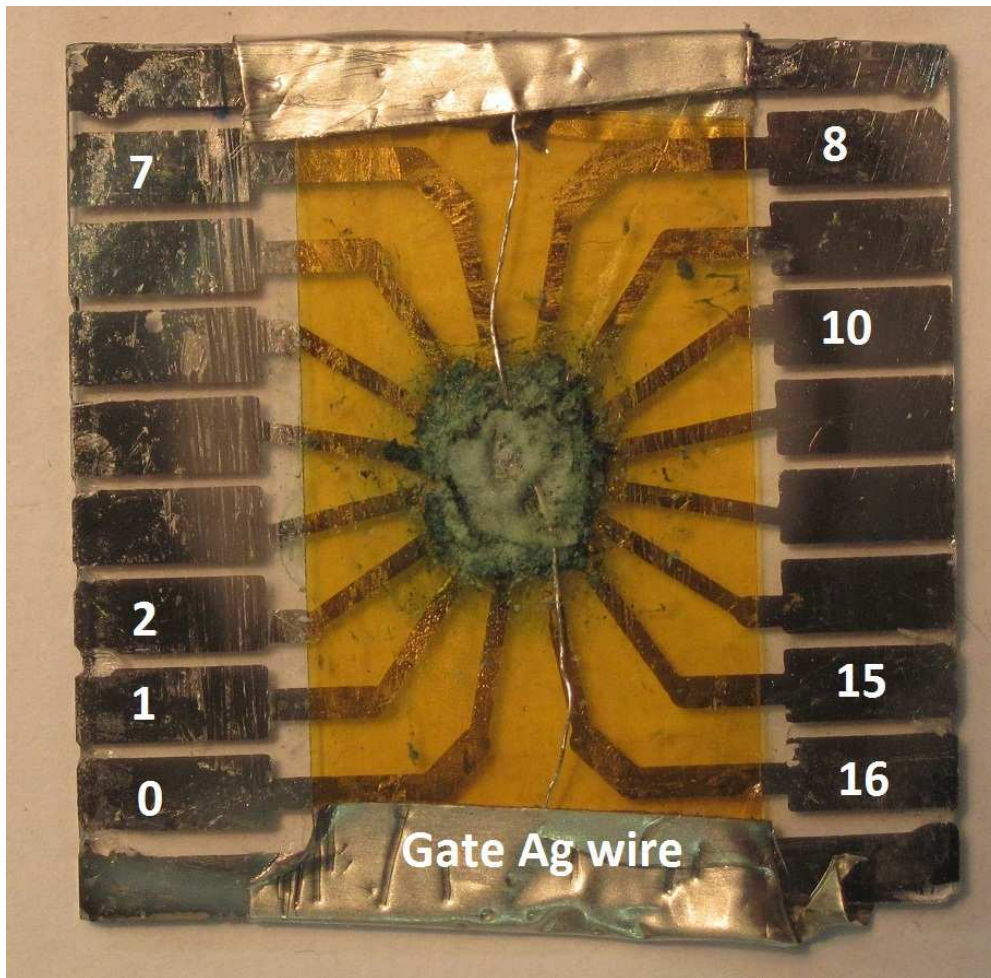


Figure 2 (color online version only) Sample and Electrodes scheme

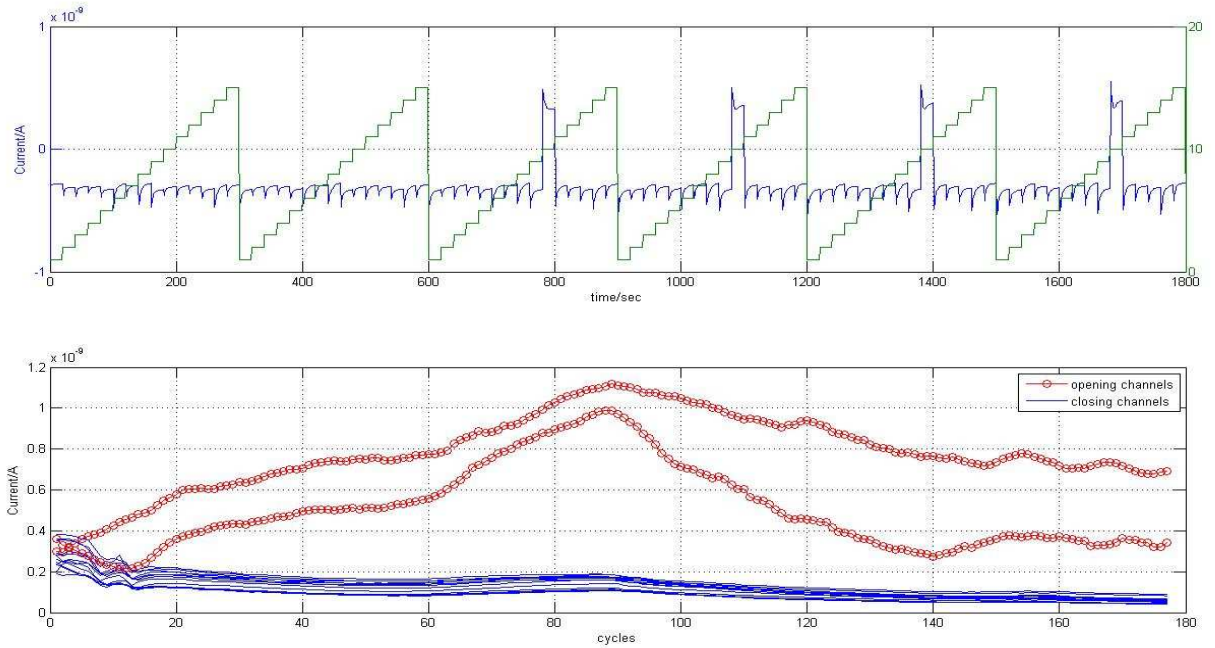


Figure 3 (color online version only) (Top graph) Electrical currents in the selected path as a function of time. The blue curve relative to the right Y axis displays the measured current while the green curve relative to the left axis indicates the selected channel. The figure reports the first 6 cycles of the measurement, with one cycle consisting of a scan from channel 1 to 15 for 20 sec per channel. (Bottom graph) Absolute value of electrical currents as a function of time (1 cycle=300 sec) relative to the reinforced channels 2×10^9 (circles) and to the inhibited channels (solid line)