Organic Memristive Devices and Neuromorphic Circuits

Victor Erokhin

Abstract Bio-inspired computational systems must be based on elements, involved, similarly to the brain, in both memorizing and processing of the information. This paper is dedicated to organic memristive devices—elements that were designed and constructed for mimicking the most important properties of synapses, responsible for Hebbian type of learning. We will consider the architecture of the device and its properties, as well as circuits and networks with adaptive features.

1 Introduction

There is a significant difference in the architecture of the computers and the brain: in the computer the memory and the processor are different devices. The information in this case plays a rather passive role—it can be recorded, accessed, cancelled, but it does not vary connections and properties of the processor. In the brain, instead, the same elements are used for both memorizing and processing of the information. Such architecture is responsible for the possibility of learning of the system at a hardware level. The information plays an active role in this case. It is not only memorized, but it varies connections within processor, what makes it more effective for the resolving of similar tasks in the future.

Nervous system and brain are composed from neurons. Each neuron has several dendrites bringing input signals to the neuron. In addition, for each neuron there is a single axon that provides a further propagation of the signal, when the sum of the inputs overcomes a certain threshold value. Synapse is a very important element of the nervous system. It is a contact point of an axon of one neuron with a dendrite of the other one. An important property of synapses is the possibility to vary the weight function of the signal transmission according to its previous functioning. Such property is a key feature for so-called Hebbian or synaptic learning. The Hebbian rule states [23]:

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> When an axon of cell A is near enough to excite cell B and repeatedly or persistently takes part in firing it, some growth process or metabolic change takes place in one or both cells such that A's efficiency, as one of the cells firing B, is increased.

Considering the electronic circuits, this rule can be considered in the following way. The system must be composed from nonlinear elements connected by a complicated system of wires. The contact points of these wires must increase their conductivity with the frequency and/or duration of their involvement into the formation of signal transfer pathways. In this case learning will mean the formation and the reinforcement of some possible signal pathways and the inhibition of the other ones.

Thus, if our purpose is the realization of a bio-mimicking computational system, we need to have special electronic elements with properties similar to those of synapses.

Even if the properties of neurons and synapses were reproduced with traditional electronic compounds, it seems very perspective to consider another element—memristor, that has recently attracted an explosive attention of numerous research groups. This element was theoretically predicted by Leon Chua in 1971 considering symmetry of electronic [8]. The very important property of the element is the dependence of its resistance on the time integral of the passed current. Later, the term "memristive devices" was introduced [9]. This property is rather similar to that of synapses, described by the Hebbian role: the conductivity depends on the history of the memristor previous functioning. The explosive growth of the activity in the field of memristors started in 2008 after the paper, stating the experimental realization of the memristor [31]. The device was realized from a thin TiO_2 film. The variation of its conductivity was attributed to a drift of oxygen vacancies in the applied external electric field, gradually shifting the relative contributions of the zones with higher and lover conductivities.

The most of the current works in the field of memristors are connected to the metal oxide materials. In this chapter we will not consider these devices. The review of such works can be found in [26].

The aim of this chapter is to describe an organic memristive device that was designed and realized for the artificial reproduction of essential properties of synapse. The device must serve as a key element in circuits allowing Hebbian type of learning [18]. As it was constructed for mimicking synapses, its properties are anisotropic with respect to the applied voltage and the direction of the current flow in a contrary to the "classic" memristors, described by L. Chua and observed in the most of inorganic devices [26] .

2 Architecture and Properties of Organic Memristive Devices

Polyaniline (PANI) is an essential material of the organic memristive devices. Its conductivity can be varied significantly when PANI is in reduced (insulating) and oxidized (conducting) states [25]. Figure 1 illustrates reactions occurring in PANI.

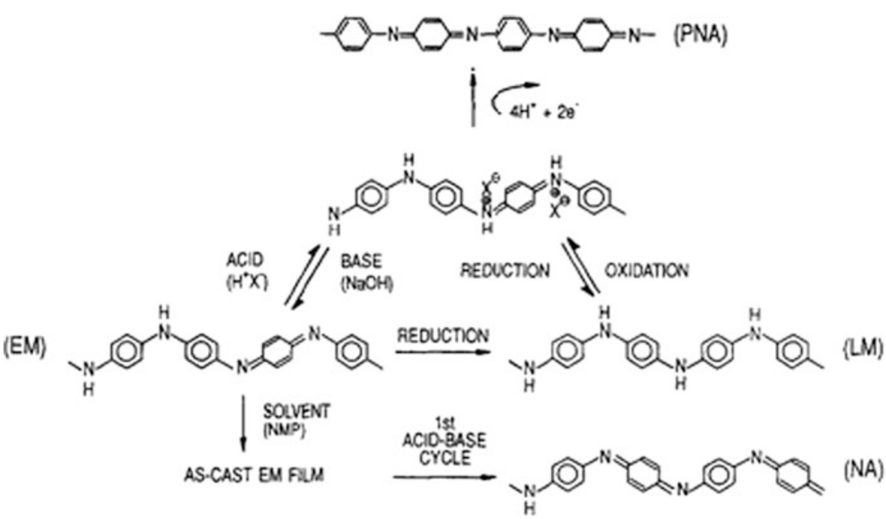


Fig. 1 Interconversions among the various intrinsic oxidation states and protonated/deprotonated states in polyaniline. Reprinted with permission from [25], E.T. Kang et al. in Progr. Polym. Sci. 23:277–324 (1998). Copyright 1998, Elsevier

Emeraldin base form of PANI is an insulator and it becomes conducting (emeraldin salt) after doping (usually by acid treatment). Being doped, PANI varies its conductivity in a reversible way according to the redox state, that can be controlled electrochemically by the application of the external voltage. Right part of the Fig. 1 illustrates these transformations.

The organic memristive devices are prepared in the following way. Thin film of PANI in the emeraldine base form is deposited onto solid insulating substrates with two evaporated metal electrodes by modified Langmuir-Blodgett (LB) technique [13]. LB method allows to form layers with nm resolution what is very important for the organic memristive devices as their working principle implies the diffusion of the metal ions.

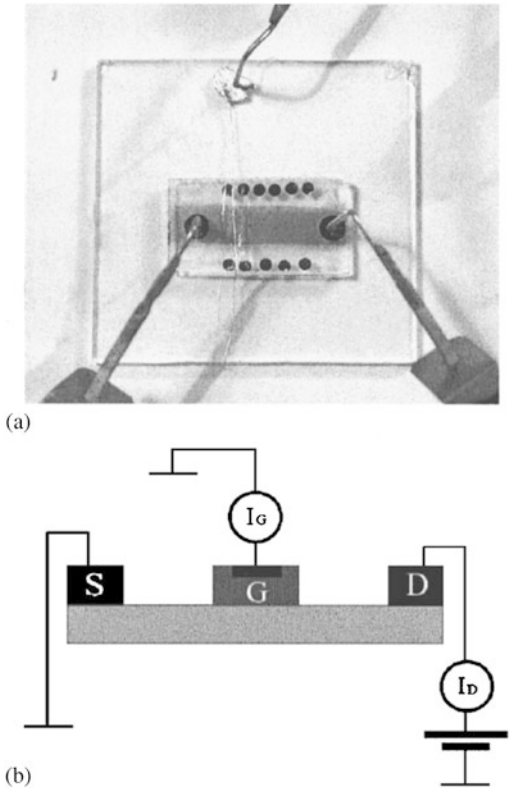
The other important component of the device is the medium suitable for the redox reactions. For these reasons, a narrow line of solid electrolyte is deposited in the central part of PANI layer, as it is shown in Fig. 2.

Solid electrolyte line was formed from a polyethylene oxide (PEO) doped with lithium salt. The choice of lithium is determined by the necessity to have its diffusion in a solid state phase. Usually, LiClO4 was used for doping.

Two electrodes, connected to the PANI film are called “source” and “drain”, similarly to the field effect transistor. In order to have a reference potential, a silver wire was connected to the solid electrolyte. This electrode is called “gate” or “reference electrode”. For mimicking synapse properties, the element must have only two terminals. Therefore, the reference electrode is directly connected to the source electrode, that is usually maintained at a ground potential level.

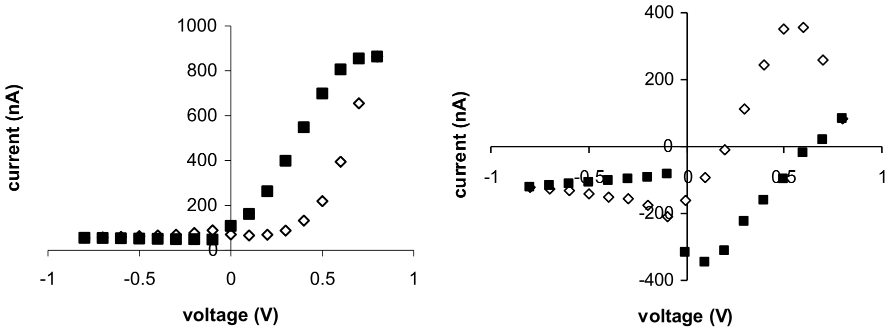
It is possible to distinguish two types of current that give their contribution to the total current passing through the device. We can measure experimentally the ionic

Fig. 2 Photo (**a**) and simplified scheme (**b**) of the organic memristive device. Reprinted with permission from [13], V. Erokhin et al. in J. Appl. Phys. 97:064501 (2005). Copyright 2005. American Institute of Physics



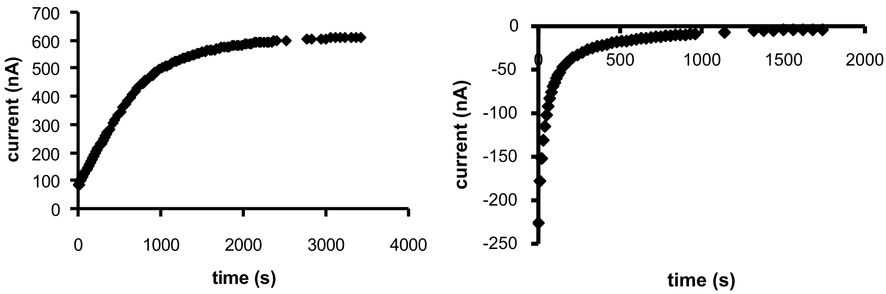
current in the circuit of reference electrode, and the total current, that is a sum of ionic current, mentioned above, and electronic current in PANI active layer, that is measured in the circuit of the drain electrode. However, in order to understand better the device working principle, it is more convenient to consider dependences of ionic and electronic (total minus ionic) currents on the cyclically applied voltage. Cyclic voltage-current characteristics for electronic (a) and ionic (b) currents are shown in Fig. 3. The measurements are usually performed in the following way. Measurements were started at 0 V applied voltage. Then, it is increased with a fixed step in the voltage (usually 0.1 V). After the application of the voltage, the system was equilibrated for fixed time interval (usually—one minute) before readout of the current value. Variation of this time interval results in the variation of the shape of the hysteresis loop [22], as it was also observed for inorganic memristors [26]. Maximum applied voltage must not exceed 1.5 V in order to prevent irreversible overoxidation of PANI.

As it was mentioned above, the measurements start from 0 V. Initial increase of the applied voltage result in the low current values—PANI is in the reduced insulating state. At about +0.5 V we can see a significant increase of the electronic conductivity, what is also accompanied by the appearance of the positive peak in the characteristics for the ionic current. PANI is transferred into oxidized conduct-



(a) (b)

Fig. 3 Cyclic voltage-current characteristics for electronic (**a**) and ionic (**b**) currents of organic memristive device (*empty rhombuses*—increase of the voltage, *filled squares*—decrease of the voltage). Reprinted with permission from [13], V. Erokhin et al. in J. Appl. Phys. 97:064501 (2005). Copyright 2005. American Institute of Physics



(a) (b)

Fig. 4 Temporal variation of the current in organic memristive device at fixed applied voltage of +0.6 V (**a**) and −0.2 V (**b**). Reprinted with permission from [13], V. Erokhin et al. in J. Appl. Phys. 97:064501 (2005). Copyright 2005. American Institute of Physics

ing state. In the most of experiments the max applied positive voltage was +1.2 V in order to avoid the overoxidation, mentioned above. After reaching this value, the voltage was decreased with the same step. The device remains in a conducting state before the applied voltage is diminished till +0.1 V. At this value, PANI is transferred into reduced insulating state, what is also confirmed by the presence of the negative peak in the characteristics for the ionic current. The whole negative branch of the characteristics corresponds to the low conductivity of the device.

However, for the realization of bio-inspired systems capable to learning, it seems even more important the behaviour of the device at a constant bias voltage. These dependences for positive (a) and negative (b) voltages are shown in Fig. 4. In the case of positive bias, the applied potential must be higher than the oxidation one. Usually, it is significantly higher than the oxidizing potential, as the applied voltage is distributed on the whole PANI channel length, while the active zone (PANI-PEO contact) is in the centre of the organic memristor. In the case of the negative bias any potential will result in the diminishing of the conductivity as the reduction potential has a small positive value.

The curve in Fig. 4b makes directly a basis for the possibility to Hebbian type of unsupervised learning. Let us consider the system composed from such devices. Preferential signal pathways will be established by elements, the strength of which will increase with the frequency and/or the duration of their involvement into the signal transfer process. The dependence shown in Fig. 4b is also very important. On the one hand, if the system composed from organic memristive devices will operate at a positive bias for a rather long time, all components of the circuit will reach their saturated conducting state. No learning will be possible anymore. However, if we will provide a periodic short-term application of negative voltage between all input-output pairs of electrodes, we will be able to prevent the system from the saturation. On the other hand, this dependence establishes a basis for the possibility of so-called supervised learning. It implies the external action of a "teacher". In fact, if the system, during unsupervised learning, will establish some connections between inputs and outputs, that are a priori wrong, it will be enough just to apply negative voltage between chosen pairs of electrodes and the signal pathway between them will be suppressed.

Qualitatively, the observed difference in the kinetics for the conductivity variation for positive and negative applied voltages can be explained considering that in the case of the negative bias the whole active zone is under the reduction potential, while in the case on the positive bias only the part of the active zone, closer to the drain electrode, is at a oxidation potential. Thus, in a case of negative potential PANI in the active zone is reduced in the same time, while in a case of positive potential we have a gradual displacement of the conducting zone boundary in the direction from drain to source. Quantitatively, the experimental data were explained by the developed model, calculating temporal behaviour of the potential distribution profiles along the length of the active zone, where PANI is in a contact with solid electrolyte [30].

The conductivity variation in the organic memristive device can be described by the following formula:

$$\mathrm{PANI}^{+} : \mathrm{Cl}^{-} + \mathrm{Li}^{+} + e^{-} \leftrightarrow \mathrm{PANI} + \mathrm{LiCl}$$

When conducting, PANI chain is protonated (positive) what demands the presence of the counter-ion (Cl-) for the maintaining of the electrical neutrality of the molecule. When reduced, lithium enters the PANI and associates with chlorine. Direct detection of the Li ions motion between the PANI active layer and the solid electrolyte was first demonstrated using microRaman spectroscopy [2] and, then, confirmed by X-ray fluorescence measurements using synchrotron radiation for the excitation [3]. These measurements allowed to state that the conductivity of the organic memristive device is a function of the passed ionic charge (time integral of the ionic current).

From this point of view, the suggested device has also some similarities with a memistor—an element introduced by Widrow [32] for construction of adaptive

Fig. 5 Association of the object with the presence of two properties (shape and color)

circuits with memory. According to the definition: Like the transistor, the memistor is a 3-terminal element. *The conductance between two of the terminals is controlled by the time integral of the current in the third, rather than its instantaneous value as in the transistor.*

Finally, our device is also similar to a mnemotrix—an essential element of Valentino Braitenberg mental experiment, developed for the explanation of learning in the brain [7]

> …we buy a role of special wire, called Mnemotrix, which has the following interesting property: its resistance is at first very high and stays high unless the two components that it connects are at the same time traversed by an electric current. When this happens, the resistance of Mnemotrix decreases and remains low for a while …

3 Logic Elements with Memory

Brain does not use Boolean logic. The same must be done also for bio-inspired computational systems. The output of logic gates must depend not only on the actual configurations of input signals, but also on the history of their utilization.

For the illustration let us consider AND element with memory (MAND). Other logic gates with memory, such as MOR (OR with memory) and MNOT (NOT with memory) were also realized and their properties can be described similarly to the MAND gate [21]. In the case of living beings, the function of the AND element can be considered as the association of an object with the presence of two important properties. For example: the orange (fruit) can be associated with a color (orange) and a shape (spherical) as it is shown in Fig. 5.

However, for living beings the presence of these two stimuli will not immediately result in such association. The individual must learn that the association is correct. As more frequently these properties are present with the confirmation of correctness by the taste, for example, as the output signal value will be increased from 0 to 1 value. Moreover, if it will happen a wrong association, the value of the output signal will be decreased (if the system is equipped with adequate feedback, similar to taste in nature).

The architecture of the MAND element, based on the organic memristive device is shown in Fig. 6a.

The MAND element contains two inputs, one output and an organic memristive devices as a key basic element, allowing memory. External voltages are used as

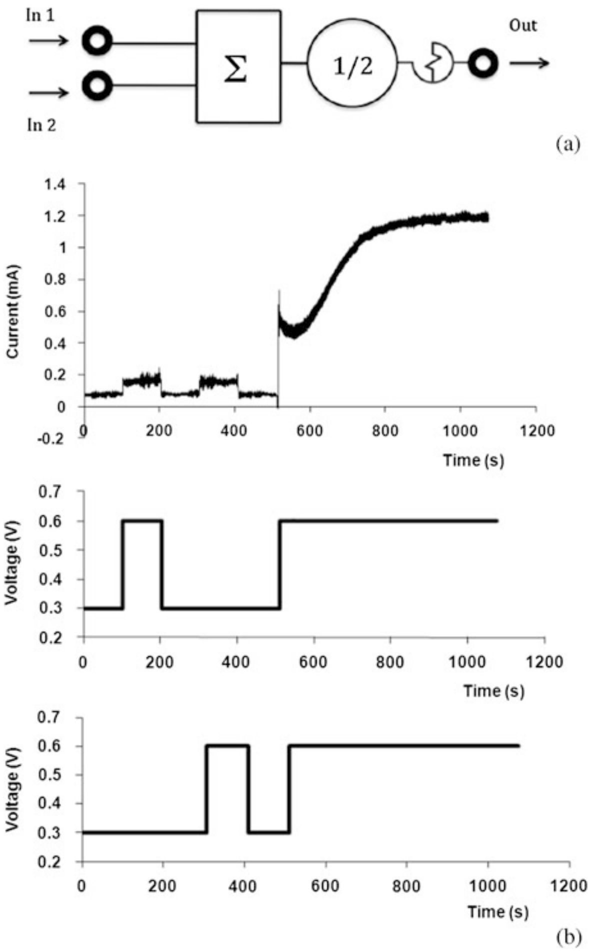


Fig. 6 Scheme of the MAND element (**a**). Temporal dependence of the output current of MAND element (*upper*) and voltages applied to the first and second inputs (**b**). Reprinted with permission from [21] V. Erokhin et al. in Int. J. Bifurc. Chaos 22:1250283 (2012). Copyright 2012, World Scientific Publishing Company

input signals, while the output is a current value. The other two elements in the circuit in Fig. 6a are: a summator, that provides a sum of the applied voltages; and a divider—this element divide the resultant voltage by a factor of 2. Thus, when only one input voltage is applied, after the division it will be not enough to vary the conductivity of the memristive device.

In order to have similar values of input and output signals, comparable also with those applicable to MOR and MNOT elements, the values of input voltages were chosen to be enough for transferring the organic memristive device into the conducting state (+0.6 V).

Experimental results of the variation of MAND conductivity in time together with dependences of the voltages, applied to the first and second input electrodes, are shown in Fig. 6b.

Figure 6b demonstrates that the application of individual signals to the first or the second input does not vary the state of the output current (small linear increase of

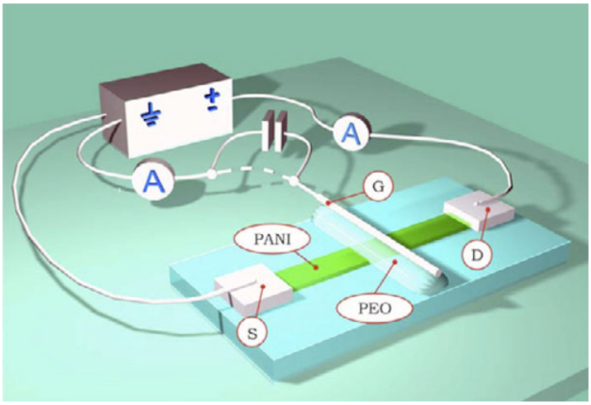


Fig. 7 Scheme of the modified organic memristor device for its use as an oscillator. Reprinted with permission from [15], V. Erokhin et al. in J. Phys. Condens. Matter 19:205111 (2007). Copyright 2007, IOP Publishing Ltd

the value). The application of both input signals results in the gradual increase of the memristive device conductivity. If necessary, the MAND element can be easily reset to the initial sate by the application of a negative potential to any input electrode.

4 Oscillating Element

An essential property of any living being is a capacity to produce rhythmic oscillations of signals even in not variable environmental conditions, as it was stated by E. Schrödinger: "Living matter evades the decay to equilibrium" [27].

Each living system contains in its neural system a neurone (or group of neurones) that, once been activated, produces rather long sequences of spikes.

For the bio-inspired computational systems we also need to foresee such kind of elements. These elements will act, for example, as clock generator analogs, providing a frequency references for all computations.

Memristors were considered as perspective candidates for the oscillator realization [24]. It is interesting to note that the organic memristive device can be easily transferred into an oscillator. For this reason it is enough just to insert an element, capable for the charge accumulation, into the circuit of the reference electrode, as it is schematically shown in Fig. 7 [15].

The simplest realization of such configuration can be done by attaching an external capacitor in the circuit of the reference electrode. If one wants to avoid the utilization of the external elements, it is possible to make a reference electrode from the material, capable to the charge accumulation. Experimentally observed temporal dependences of the output current at fixed applied voltages are shown in Fig. 8 [15].

It is to note that the phases of ionic and total currents in the organic memristive devices are shifted in phase.

If one does not want to connect additional external devices to the system, there is the other possibility to have current oscillations. In this case, the reference electrode must be realized from a special material, capable for charge accumulation

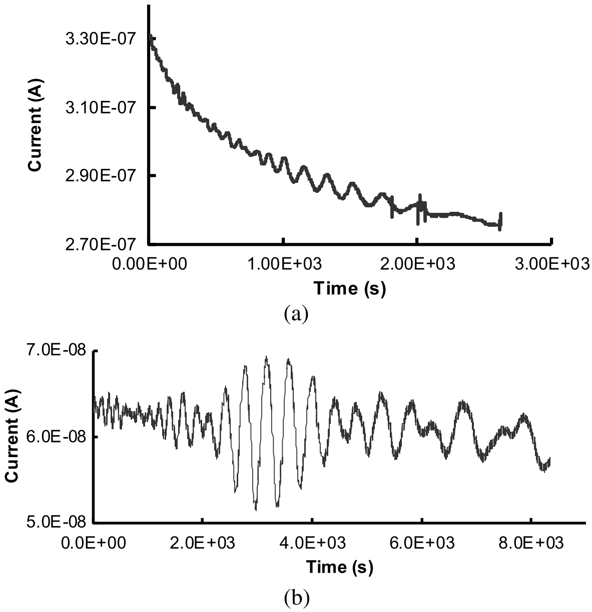


Fig. 8 Temporal dependences of the output current at fixed applied voltage for the organic memristive device, when the reference electrode was realized from highly oriented pyrolytic graphite (**a**) and where an external capacitor was connected into the reference electrode circuit (**b**). Reprinted with permission from [15], V. Erokhin et al. in J. Phys. Condens. Matter 19:205111 (2007). Copyright 2007, IOP Publishing Ltd

[16]. In our experiments, we have taken highly oriented pyrolytic graphite, as it is well known its capability to accumulate Li^+ ions due to the possibility of their intercalation between the planes of the crystal lattice of this material.

The observed characteristics were explained qualitatively using the already mentioned model, taking into account kinetics of all processes occurring in the device [30]. It is interesting to note that the observed phenomenon cab be also qualitatively explained using the approach, describing Belousov-Zhabotinsky reaction [33], mentioned also in [15].

5 Circuits with Adaptive and Neuromorphic Properties

Supervised [10, 16] and unsupervised learning [28] have been demonstrated in artificial systems by realizing several deterministic circuits, based on organic memristive devices. Even if we present here mainly the results obtained in the DC mode, similar results were obtained when the input signals were performed in a pulse mode [29].

The simplest neuromorphic circuit was realized with one organic memristive device [28], and it has demonstrated the possibility of unsupervised learning. The circuit for supervised learning was composed from 8 memristive devices [16]. Application of the appropriate training procedure resulted in the formation of electrical connections between pre-determined pairs of input-output electrodes. Let us consider now one example of memristive device-based neuromorphic circuits that demonstrates directly the possibility to mimic artificially synapse properties of living be-

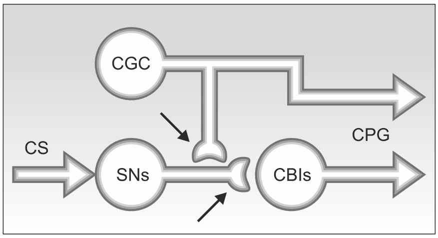


Fig. 9 Model of the part of the nervous system of pond snail Lymnaea stagnalis responsible for learning during feeding. Arrows indicate the position of synapses. Reprinted with permission from [19], V. Erokhin et al. in BioNanoScience 1:24 (2011). Copyright 2011, Springer Science+Business Media, LLC

ings. This example illustrates the electronic reproduction of a part of the nervous system of a simple animal, responsible for its learning.

The model of the part of the nervous system of the Pond snail *Lymnaea stagnalis*, responsible for learning of the animal during its feeding that was developed basing on the experimental data obtained with a system of implanted microelectrodes, was already available [1]. Therefore, it was taken as a biological benchmark for our experiments. Learning in this case means the association of an initially neutral stimulus with the presence of food (similarly to the famous Pavlov's dog; however, the snail is much easy to reproduce artificially (even at the level of the architecture), as the model already exists). In this case of learning of the snail, two stimuli must be applied to the system: initially neutral stimulus (mechanical touching of its lips) and the presence of food (sugar). Touching the lips with the sugar result in the fact that after the successive touching without sugar, the animal begins to open its mouth and start the digesting process.

The scheme of the part of the nervous system, responsible for such learning, is shown in Fig. 9 [19].

As it is clear from the Fig. 9, the architecture of the model is rather simple and it allows the direct reproduction using organic memristive devices in positions of synapses [19].

Therefore, the architecture, presented in Fig. 9 was taken as the starting point for the artificial reproduction with memristive devices. Scheme of the electronic circuit, reproducing the model and results of its experimental testing are shown in Fig. 10.

We have realized and tested two circuits. The first one was based on one organic memristive device, while the other one, similarly to the described model, included two memristive devices. Both circuits have two inputs: one of the inputs corresponds to the initially neutral touching stimulus and the other one corresponds to the stimulus, representing the presence of the food. The system has also one output electrode. If we consider that the learning procedure was successful when the system will be able to perform some execution function (supplying the power to the motor, representing the mouth opening, for example), the value of the output signal must be higher than a certain threshold level (the value of the threshold can be varied and

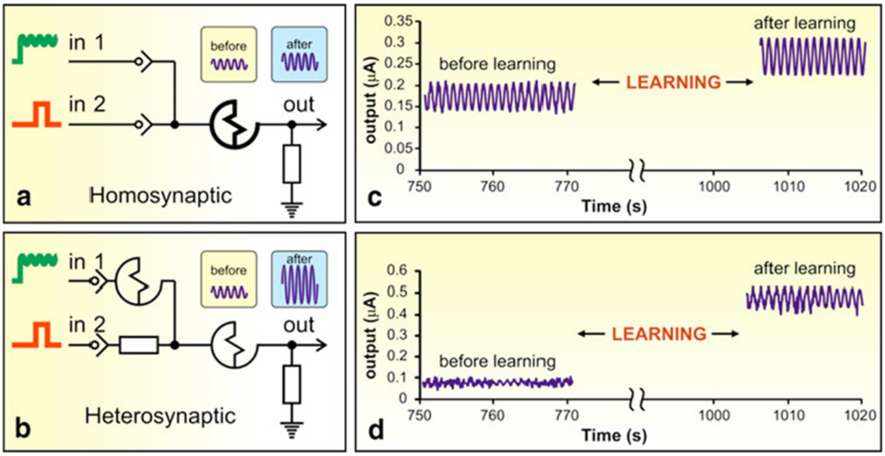


Fig. 10 Scheme of one- (**a**) and two- (**c**) memristor-based circuits, mimicking learning of the pond snail; (**c**) and (**d**) are experimental results, measured on these schemes. Reprinted with permission from [19], V. Erokhin et al. in BioNanoScience 1:24 (2011). Copyright 2011, Springer Science+Business Media, LLC

pre-defined). Thus, if the learning was successful, the mouth of the snail will be opened even in the presence of the touching-mimicking stimulus only.

Let us first consider a one-memristor device circuit shown in Fig. 10a. Touching-mimicking (neutral) signal is applied to the input 1. Initially, it results in the rather low value of the output current, shown in Fig. 10c. The signal, mimicking the presence of the food, is applied to the second input. During the "LEARNING" period (Fig. 10), both signals are applied to the circuit. We have chosen their values in such a way, that only their sum can result in the variation of the memristive device conductivity. After the end of the "LEARNING" phase, we have applied again only one input signal, corresponding to the touching (neutral) stimulus. As it is clear from Fig. 10c, the learning in this configuration was successful. After the simultaneous application of "touching" and "presence of food" stimuli, the resultant current for the successive application of the "touching" stimulus only was increase for about 50 %.

In the second phase of the experiment, we have realized a circuit based on two memristive devices (Fig. 10b) The architecture of this circuit was very similar to that of the model, represented in Fig. 9. Organic memristive devices are exactly in the position of synapses. Input and output signals are rather similar to the previous case, shown in Fig. 10a. However, the values of the input voltages (about +0.6 V) were chosen in such a way, that they are enough to transfer only one organic memristive device into a conducting state. Similarly to the previously described case of the one organic memristive device circuit, we have applied initially only a signal to a input 1, corresponding to a neutral touching-mimicking stimulus. In this case, the applied voltage is distributed between both memristive devices and, therefore, is not enough to transfer any of them into the oxidized conducting state. As a result, we can observe a rather low value of the output current (Fig. 10d). During the "LEARNING" phase, both signals ("touching" and "food presence") are applied. The situation in this case is very different: the input 2 voltage is applied to the one memristive device only. Thus, its value is enough now for the transferring it into a conducting oxidized state. When the transformation was done, the input 1 voltage is mainly distributed onto the second memristive device and can transfer it into the conducting oxidized state. After the finishing of the "LEARNING" phase, the successive application of an input 1 only (neutral "touching-mimicking" stimulus) results in the 5-times increase of the output current (both of DC off-set and AC amplitude), as it is shown in Fig. 10d.

The described experiments have successfully demonstrated that the organic memristive device can be really considered as an artificial electronic analog, mimicking main properties of biological synapses. Reproduction of the architecture of the part of the simple animal nervous system has resulted in the mimicking of learning capabilities at the level of hardware adaptations.

6 Stochastic Fibrillar and Self-assembled Networks

Even if, as it was shown above, the approach, connected to the fabrication of deterministic electrical circuits, based on organic memristive devices, allow to mimic some properties of elements of the nervous system [18], it does not permit high level of the integration of synapse analogs (about 10 in power of 14 in the brain). Therefore, further motion in the direction of mimicking of other simple brain properties will demand the consideration of alternative approaches. In particular, the brain has 3D organization with the existence of connections between rather distant neurones. Current planar technology cannot provide the possibilities for making it. Thus, it is necessary to develop other approaches based on bio-inspired bottom-up technologies, including self-assembling and phase separation.

The first attempt was done by performing the architectures, where the stochastic 3D networks were based on the statistically distributed connections of conducting and ionic elements using polymer fibers [14], forming free-standing networks.

In our case, the attempt to form fibers by electro-spinning turned out to be not very successful: it was possible to form PEO fibers, but not those of PANI. Therefore, the alternative approach was developed, using the capability of PEO to form fibrillar structures in vacuum chamber. Initially, fibers of polyethylene oxide were formed by vacuum treatment of its concentrated viscous solution. Then, these fiber structures were used as templates for the formation of PANI fibrillar systems over it, done by placing the solution of PANI over PEO fibers with the successive vacuum treatment. The optical microscopy image of the resultant structure is shown in Fig. 11.

As we already know from the consideration of the single discrete device, it is necessary to have a junction of the conducting polymer (PANI) and solid electrolyte (PEO) in order to realize the architecture of the organic memristive device.

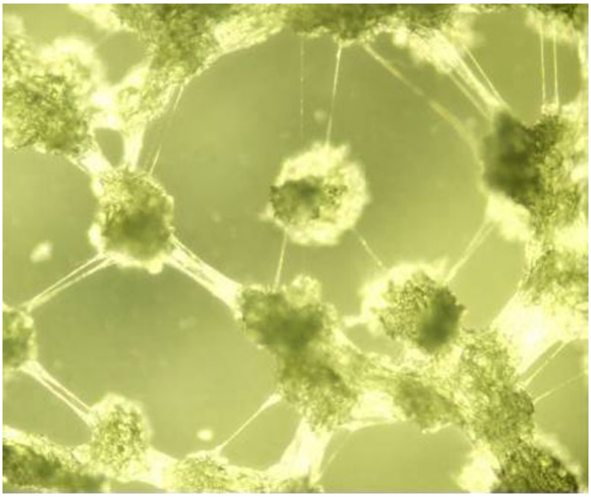


Fig. 11 Optical image of PEO-PANI fiber structure. Reprinted with permission from [14], V. Erokhin et al. in Soft Matter 2:870 (2006). Copyright 2006, The Royal Society of Chemistry

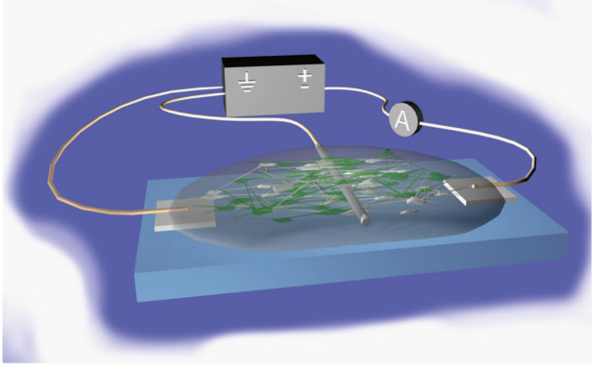


Fig. 12 Organic memristor based on statistically distributed structure of PANI and PEO fibers. Reprinted with permission from [12], V. Erokhin et al. in J. Comput. Theor. Nanosci. 8:313–330 (2011). Copyright 2011, American Scientific Publishers

Therefore, the main idea of the formation of the fibrillar structure was to organize a stochastic crossing between PEO and PANI fibers that form structures, similar to the architecture of the deterministically formed devices. In order to check whether this hypothesis works, the fibrillar structure was deposited between two planar metal electrodes, and a silver wire was placed in it before the vacuum treatment. Scheme of the realized structure and its electrical connection to the power supply and measuring devices is shown in Fig. 12.

Cyclic voltage-current characteristics, measured on these structures in the way, similar to that used for the deterministic stand-along organic memristive devices, revealed rectifying behaviour, that confirm the formation of desired crossing of fibers of two different materials.

Unfortunately, the properties of such structures were found to be very unstable. Only few cycles of voltage-current characteristics turned out to be possible to measure. Then, we have observed a significant decrease of the device conductivity. Finally, in about 40–60 minutes the device stopped working. However, this behaviour

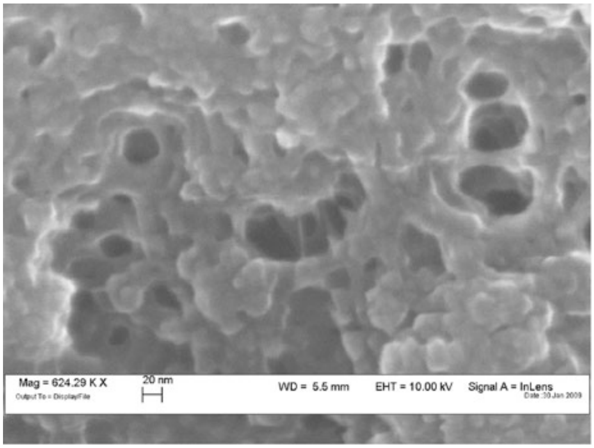


Fig. 13 SEM image of the polymer fibers formed on porous support SEM image of the polymer fibers formed on porous support. Reprinted with permission from [17], V. Erokhin et al. in Nano Commun. Netw. 1:108–117 (2010). Copyright 2010, Elsevier

is not strange for the sample of such type. The degradation of the sample was attributed to the free-standing nature of these structures. Passed current resulted in heating of fibers, their deformation and, finally, complete destruction. Several approaches were carried out for improving the stability. In particular, porous materials were used as supports for making a rigid "skeleton" for these soft structures [17]—the approach that is widely used in the nature. SEM image of the fibrillar structure, formed on porous matrix, is shown in the Fig. 13.

The mentioned approach turned out to be perspective and has allowed to improve the stability of the stochastic systems, based on the fibers of required polymers. However, our efforts were re-distributed because the other approach was found to be even better. This second approach was based on self-assembling of specially synthesized copolymers, allowing phase separation that were then used for the formation PANI layers with associated gold nanoparticle.

The mentioned approach had demanded a synthesis of several specially designed compounds and methods of their assembling into networks, having structure and properties similar to those of the fibrillar systems. In this case the active layer was more complicated with respect to the devices, reported above. Gold nanoparticles were added to the PANI films. The reason of the adding of these particles was to perform a threshold function, somehow similar to the function of the neuron body: to allow the entrance of the signal but to perform a certain barrier for its exit [10]. Such property was realized due to a significant difference of work functions of gold and PANI.

Several types of gold nanoparticles with different terminal-groups used for their stabilization were tested. The best results were obtained when gold nanoparticles were stabilized by 2-mercaptoethanesulfonic acid. The end-group not only stabilizes the structure of the particles, but it acts also as an additional doping agent, stabilizing the conductivity properties of PANI [5]. SEM images of networks of such gold nanoparticles wires are shown in Fig. 14.

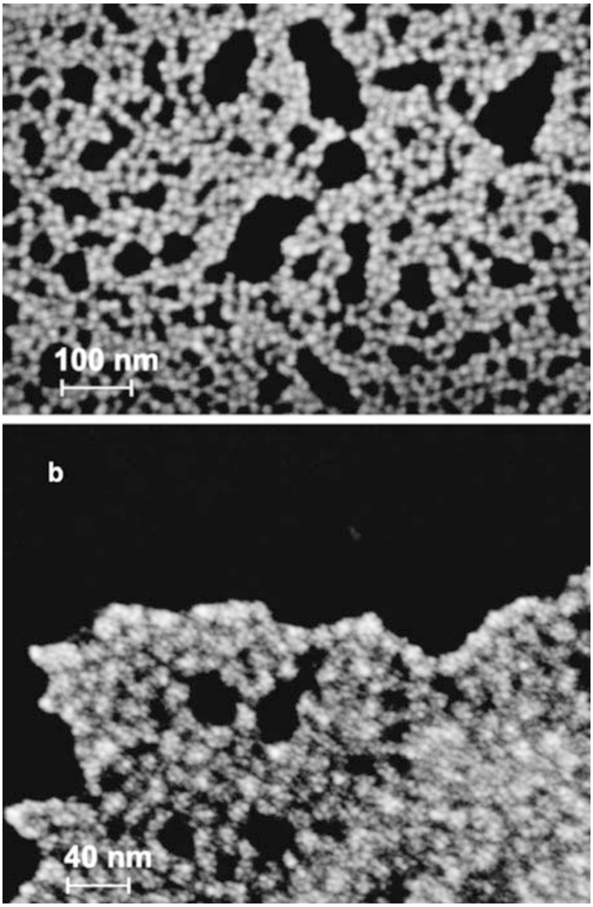


Fig. 14 SEM images of 2-mercaptoethanesulfonic acid stabilized gold nanoparticles. Reprinted with permission from [5], T. Berzina et al. in Synth. Met. 161:1408–1413 (2011). Copyright 2011, Elsevier

Deposition of the PANI/gold nanoparticles composite layers was done using modified Langmuir-Blodgett technique [4]. As it was already mentioned, LB films provide nm resolution in the thickness.

The other essential component of the 3D stochastic network is a block-copolymer, allowing phase separation during self-assembling. In our experiments we have synthetized and used a new block copolymer - poly(styrene sulfonic acid)-b-poly-(ethylene oxide)-b-poly(styrene sulfonic acid) (PSS-b-PEO-b-PSS) [20].

The schematic representation of the experimental sample is shown in Fig. 15a.

Four Cr electrodes were deposited onto a glass (or any other insulating material) support by thermal evaporation. Films of the composite material, containing alternating layers of PANI/gold nanoparticles composite and block copolymer, were deposited on this support and patterned in order to make connections between two pairs of diagonal electrodes in a crossed configuration. A ring made from adhesive Kapton layer (36 microns thick) was placed over the crossed area and PEO gel containing Li^+ and H^+ ions was deposited within the area restricted by the ring. Three

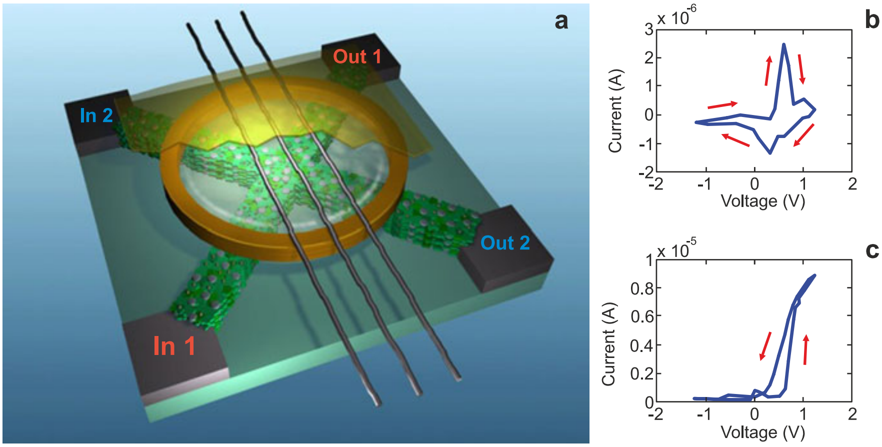


Fig. 15 Scheme of the system used for the learning experiments (**a**) and typical cyclic voltage–current characteristics for ionic (**b**) and electronic (**c**) conductivity measured between each input–output pair. Maximum (at about +0.5 V) and minimum (at about +0.1 V) of the ionic current correspond to the oxidation and reduction potentials of PANI, respectively. As a result, the increase or decrease of electronic conductivity is observed. The presence of hysteresis indicates the memory effect in the system. Reprinted with permission from [20], V. Erokhin et al. in J. Mater. Chem. 22:22881–22887 (2012). Copyright 2012, The Royal Society of Chemistry

silver wires, acting as reference electrodes, were placed in a contact with the PEO gel, whereas the latter in-turn isolated the wires from the active layer. The area was protected by Kapton film in order to prevent the system from the degradation.

The formation of the phase-separated structure was confirmed by optical microscopy and SEM imaging. The images are shown in Figs. 16a and 16b respectively.

Before studying the performance of the network as a whole, we have done the tests whether the conductivity variations between each pairs of input-output electrodes are similar to those, observed for deterministically fabricated organic memristive devices. The typical cyclic voltage-current characteristics for the ionic and electronic currents are shown in Figs. 15b and 15c respectively with the indication of the voltage variation direction.

Such phase-separated architecture of the realized network was expected to provide the formation of multiple possible signal pathways between both pairs of metal electrodes, realized by the stochastic connections of PANI areas with solid electrolyte zones that are also separated by the insulator areas. Conductivity variation will occur in the junctions of the contact of PANI chains with areas of solid electrolyte after the application of the appropriate voltage values. In particular, if PANI in the contact with electrolyte is in the conducting state and a negative potential is applied, it will be transferred into the reduced insulating state. Instead, if it was in the insulating state and a positive potential, higher than the oxidation potential is applied, we will observe a gradual transformation of PANI into the oxidized conducting state.

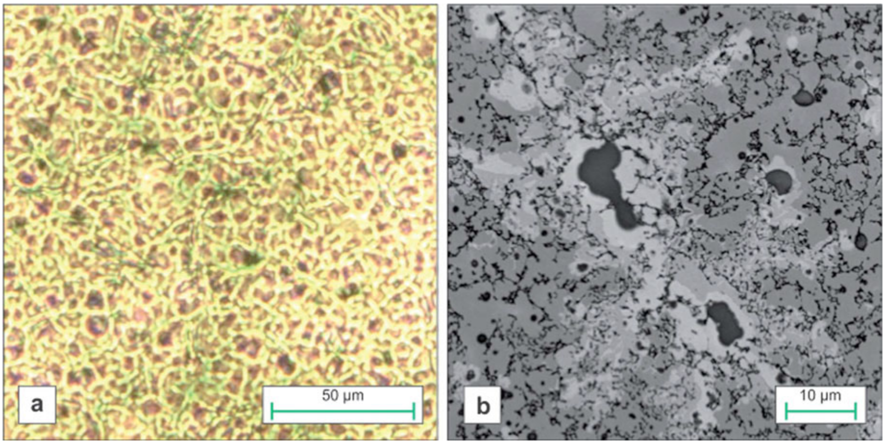


Fig. 16 Optical (**a**) and SEM (**b**) images of the cast film prepared from the composite material. Reprinted with permission from [20], V. Erokhin et al. in J. Mater. Chem. 22:22881–22887 (2012). Copyright 2012, The Royal Society of Chemistry

The aim of the performed experiments was to induce a high conductivity between one pair of input-output electrodes, on the one hand, and to suppress the conductivity between the other pair of electrodes, on the other hand.

We have applied two types of training algorithms to the system shown in Fig. 15a: simultaneous and sequential ones.

In the first case (simultaneous training of both pairs of electrodes), reinforcing and inhibiting voltages were applied simultaneously to the two different pairs of electrodes. After the training, the state of the conductivity between different pairs of electrodes was checked applying a positive voltage with the value that cannot vary the state of the conductivity of the induced signal pathways (+0.3 V). As a result, it was observed that the ratio of the conductivity between pairs of electrodes where the reinforcing and inhibiting potentials were applied was about one order of magnitude. During the second stage of the simultaneous training, the situation was inverted: the reinforcing potential was applied between the pair of electrodes with previously inhibited conductivity and the inhibiting potential was applied between the pair where the conductivity was reinforced. The test measurements, performed similarly to the measurements during the first stage, revealed that the second training was also successful. It was possible to invert the conductivity state between the electrode pairs. The final ratio of the conductivities was also about one order of magnitude.

In the case of the sequential training the procedure was the following one. Initially, the reinforcing voltage was applied between one pair of electrodes, while no voltage was applied between the other one. Then, the inhibiting voltage was applied between the second pair of electrodes, while no voltage was applied to the first one. Test measurements, performed as in the case of simultaneous training, revealed that the conductivity ratio between reinforced and inhibited signal pathways was about two orders of magnitude in this case.

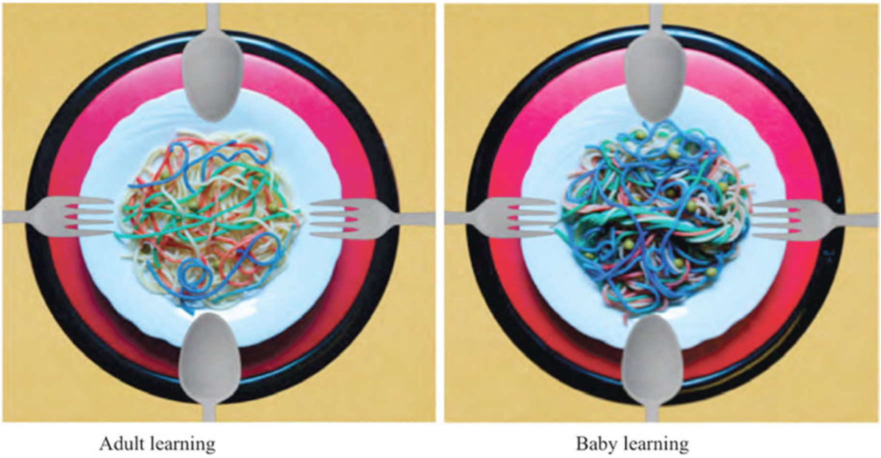


Fig. 17 Schematic representation of the stochastic network after "adult" (*left*) and "baby" (*right*) learning. Reprinted with permission from [11] V. Erokhin et al. in Int. J. Unconv. Comput. 22:1250283 (2013). Copyright 2013, Old Sity Publishing, Inc.

Similarly to the case of simultaneous training experiment, second sequential training was applied to the stochastic system, tending to invert the conductivity state of the already formed signal pathways. However, in this case it was found to be impossible: we have observed only small variation of the conductivity for both channels. Moreover, if the system was leaved without the application of the external potentials, it relaxed itself to the conductivity state reached after the application of the first training.

Making the comparison with the behaviour of living beings, we can conclude that the two observed situations were rather similar to the so-called "adult" and "baby" learning (the last one can be also called—imprinting). In the first case several external stimuli were simultaneously applied to the network. Such algorithm results in the dynamic equilibrium between the formation and the inhibition of signal pathways. There is a "cross-talk" of stochastically distributed memristive devices [6]. In the second case, instead, when single long-term stimulus is applied to a stochastic network, it results in the formation of stable configurations of signal pathways (channels) and potential distribution maps due to the charge trapping in gold nanoparticles. Such stable configuration is acting against successive action of external stimuli and is responsible for the long-term memory. Qualitative explanation of the observed behaviours can be found in [11]. The formation of the connections within the stochastic network was explained by the variation of the "spaghetti" color, representing the areas of PANI in a contact with solid electrolyte. The scheme, illustrating the difference between the states of the system after the "adult" and "baby" learning is shown in Fig. 17.

The reinforcing of the signal pathways in this case was done between two electrodes, shown as forks (only forks are used in Italy for eating spaghetti), while the signal pathways between "spoon" electrodes were inhibited.

"Adult" learning results in the formation of few single preferential pathways between "fork" electrodes, while there is a partial suppression of the conductivity near the "spoon" electrodes. Instead, in the case of "baby" learning (imprinting), stable channels, including multiple signal pathways, are formed between "fork" electrodes.

In other words, the "adult" learning can be compared with the behaviour of foreigners in Italy: looking around they begin to eat spaghetti with forks. However, if their stay was rather short, they will begin to eat spaghetti with spoons when they will come back to their countries. The formed connections within the brain are not stable and can be easily varied in the varied environmental conditions.

In the case of "baby" learning (imprinting) the situation is very different. Italian children in the childhood learn that spaghetti can be eaten with forks only and not with spoons. Application of the training algorithms to the fresh stochastic network without already formed connections result in the formation of stable configurations that are preserved for the practically whole life period and tending to relax to the pre-formed configuration of the connections even if the environmental stimuli are changed.

7 Conclusion

Bio-inspired computing systems must integrate processing and memorizing of the information within the same devices. It demands the utilization of new types of electronic compounds: their electrical properties must depend on the history of their involvement into the formation of signal transfer pathways.

We have considered in this chapter the organic memristive device. This element was designed and constructed for mimicking synapse properties for its successive utilization in circuits allowing Hebbian (or synaptic) type of learning. Some properties of the organic memristive devices, such as hysteresis loop and dependence of the conductivity on the ionic compound of the passed charge, are rather similar to the "classic" memristors. However, it has also some differences, such as anisotropy of the conductivity upon the polarity of the applied voltage. This last feature is very important for mimicking the synapse properties as there is a strong anisotropy of the signal propagation in the nervous system. On the other hand, the described device has properties of the mnemotrix of V. Braitenberg,—key element of the mental experiment, describing learning processes in the nervous system.

Several important characteristics of the device, presented in this chapter, have demonstrated the possibility of the realization of artificial electronic circuits, mimicking some functions of the parts of nervous system of real animals (pond snail). The possibility of the utilization of organic memristive as key elements for the realization of variable logic gates (fuzzy logic) has been also demonstrated. Such logic gates work in such a way that the output signal depends not only on the actual configuration of the input signal values but also on the "history" of its involvement into the information processing.

Just small variations of the device architecture are required for the possibility of the generation of auto-oscillations in the fixed environmental conditions (biased voltage). Such property is a characteristic feature of the living beings and it is very important for all types of the computational systems.

Very interesting properties were registered by the construction and study of the stochastic networks, fabricated by self-assembling of polymeric and nanoparticulate compounds. These features are somehow similar to the learning of the living beings. Application of different training algorithms can result in the long-term (imprinting) associations or in the short-term (every day learning) formation of the preferential signal pathways. In addition, we have observed a "cross-talk" of elements in the network even in the absence of the external stimuli [6, 20]. We can predict at least two possible applications of the deterministic and/or stochastic systems, described in this chapter.

On the one hand, they can constitute a key part of the "brain" of robotic systems: being adequately combined with traditional electronic devices, transferring the signals form sensors (optical, acoustic, mechanical, etc.) to adequate values for application to the network and providing necessary offset and feedback values, it will be possible to attribute "personal features" to each robot for working along or in the group. It will also allow "learning" and adaptations of properties as the reaction to the variable environmental conditions.

On the other hand, the stochastic network can be considered as a very useful tool for making model hardware experiments for the study of processes in the brain. In fact, it will be possible to study the reaction of the system to the variations of the external stimuli at different stages of the system learning. In this respect, it seems important the fact that the variation of the conductivity results also in the variation of color of signal pathways composed from PANI. This property will be used for studying not only the final state of the conductivity between input and output electrodes, but also reinforcement and inhibition of the signal pathways inside the network.

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