ИК РАН

UNIVERSITÀ DEGLI STUDI DI PARMA

Bio-inspired materials: an electrochemically controlled polymeric system which mimics biological learning behavior

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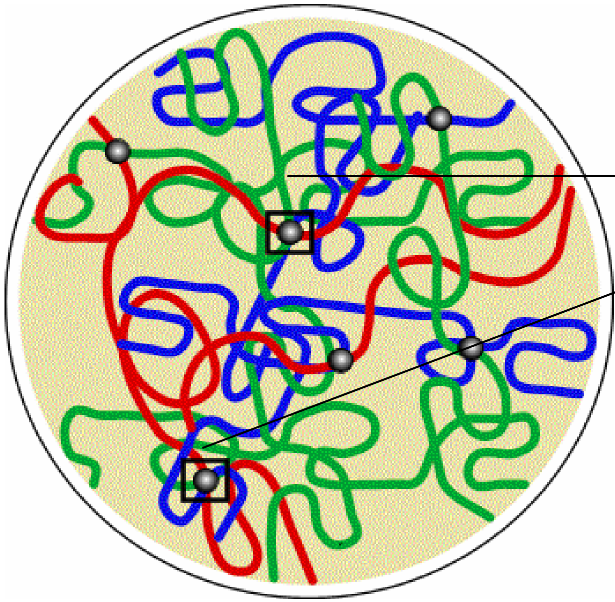
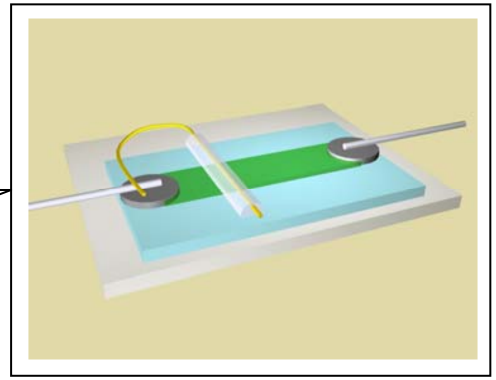
Biologically Inspired Adaptive Organic Networks – BION



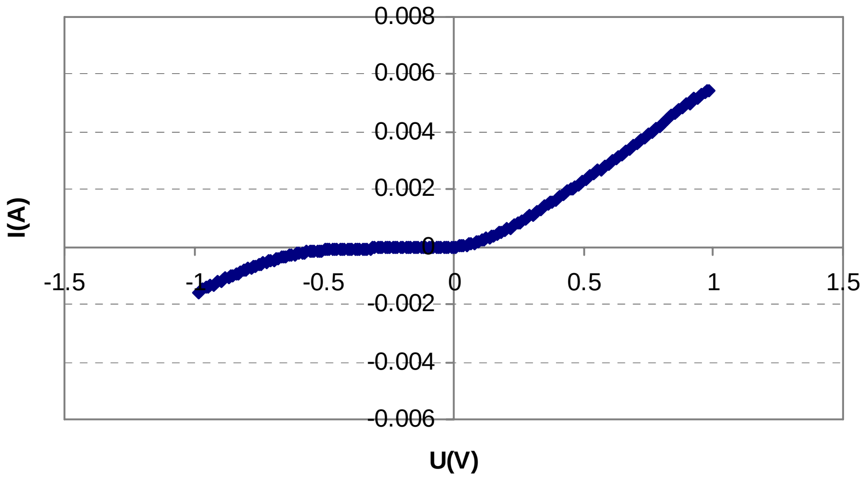


Probability of the pathway involvment into the signal propagation depends on the frequency of its utilization

Training will eliminate occasional connections

NEURON ANALOGS

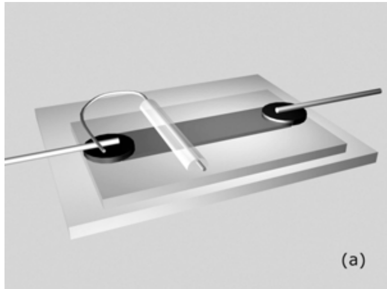
- Schottky barrier

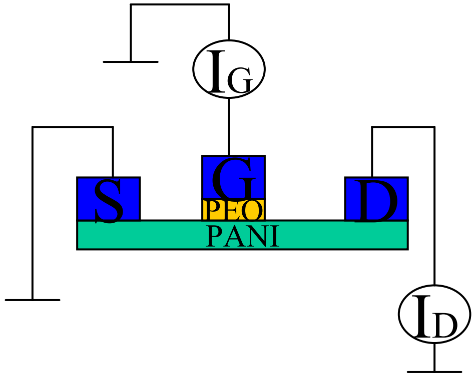


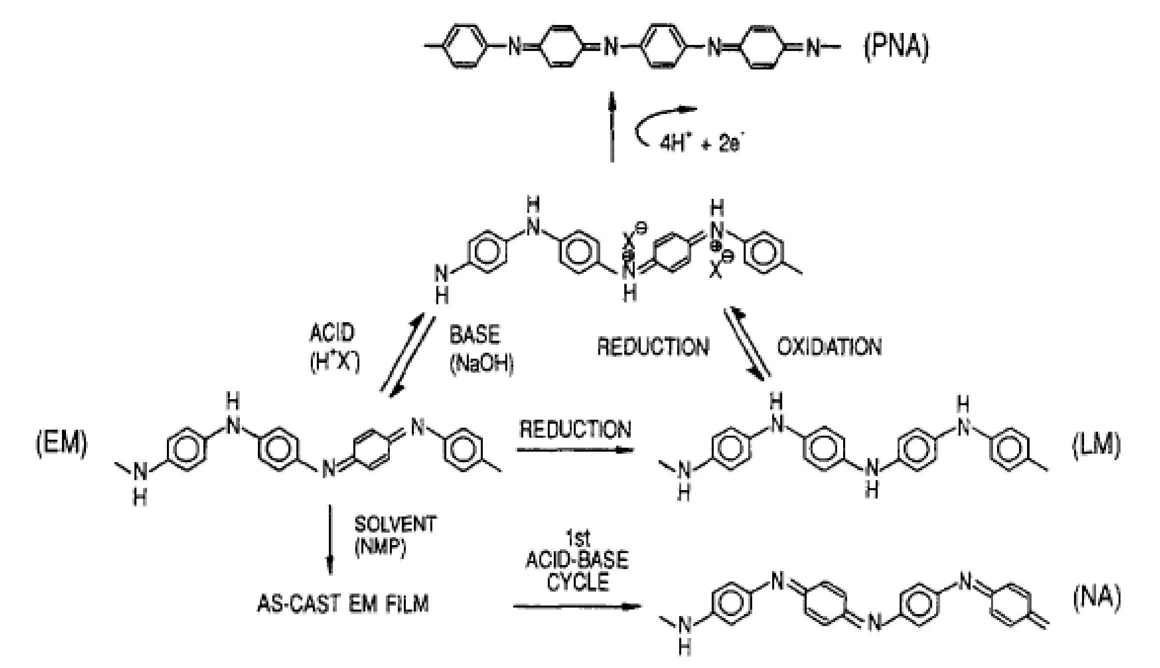
In-PANI-Au structure

Difference in the work functions of Au and PANI results in the rectifying characteristics

SYNAPSIS ANALOG: ELECTROCHEMICAL NONLINEAR ELEMENT (VIEW AND CONNECTION)

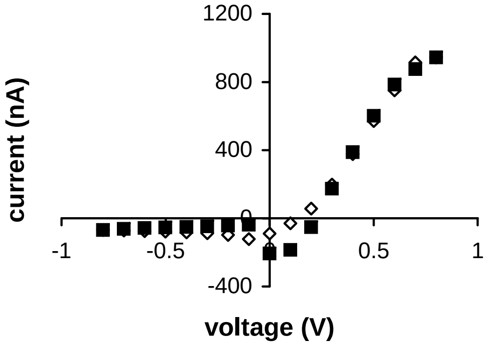




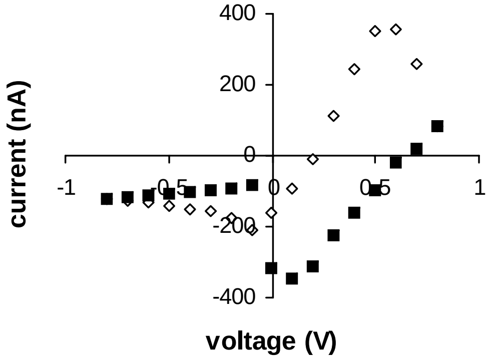


V. Erokhin, T. Berzina and M.P. Fontana, “A polymer based electrochemical device”, *J. Appl. Phys*., 97, 064501 (2005).

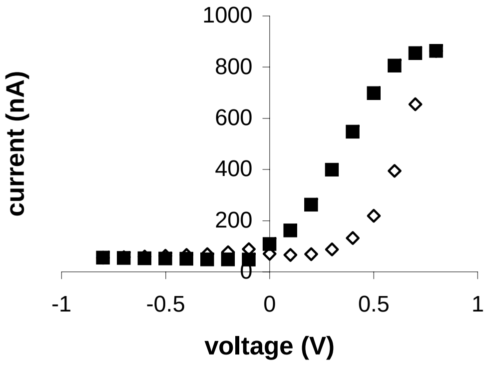
ELECTROCHEMICAL NONLINEAR ELEMENT (V-I characteristics (Ag))



Drain current



Gate current

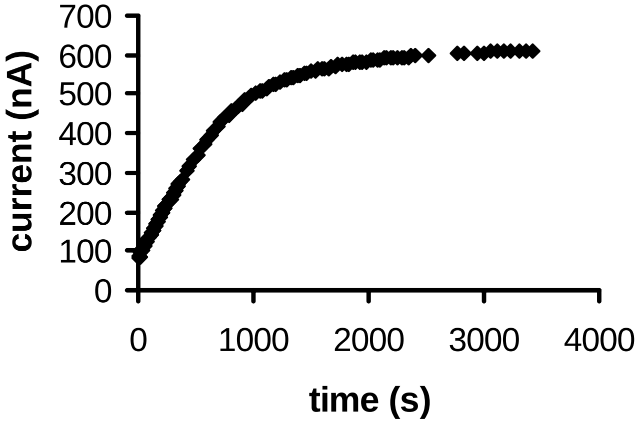


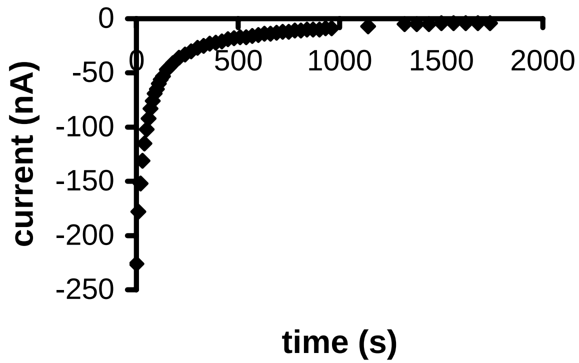
Differential current

Empty squares – increasing V

Filled squares – decreasing V

ELECTROCHEMICAL NONLINEAR ELEMENT (adaptive behavior)

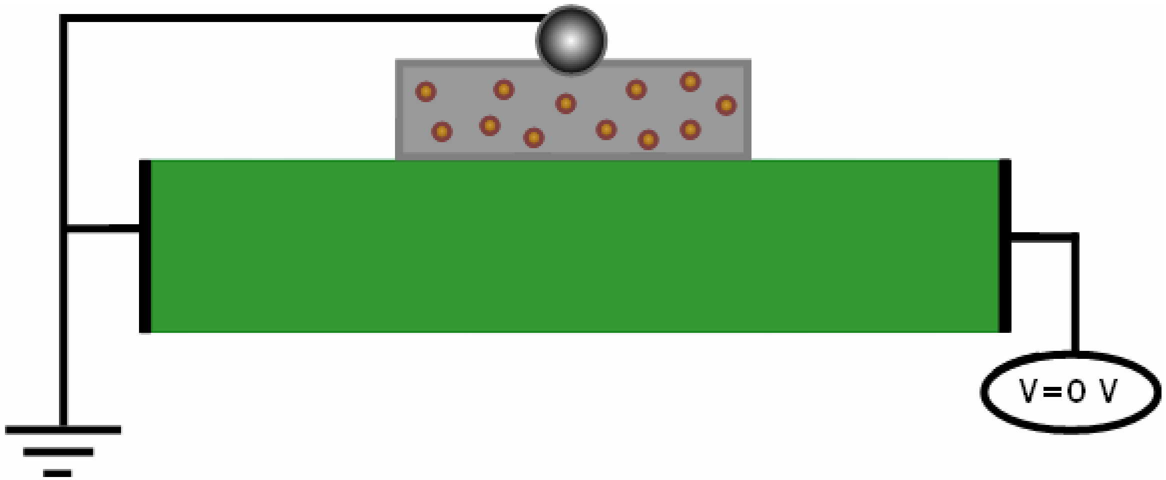




Kinetics of drain current variation at positive (+0.6 V) bias

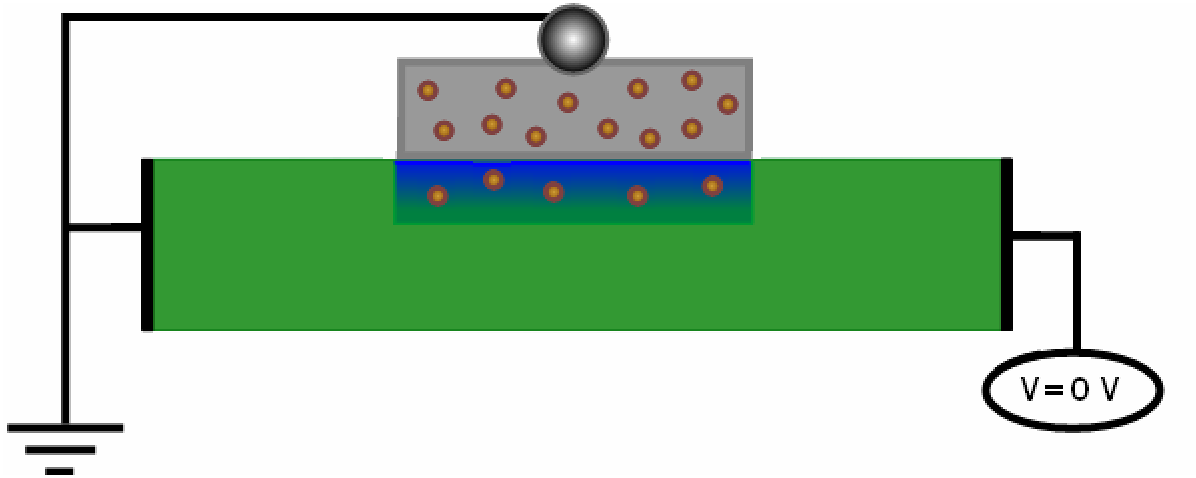
Kinetics of drain current variation at positive (-0.1 V) bias

WORKING PRINCIPLE



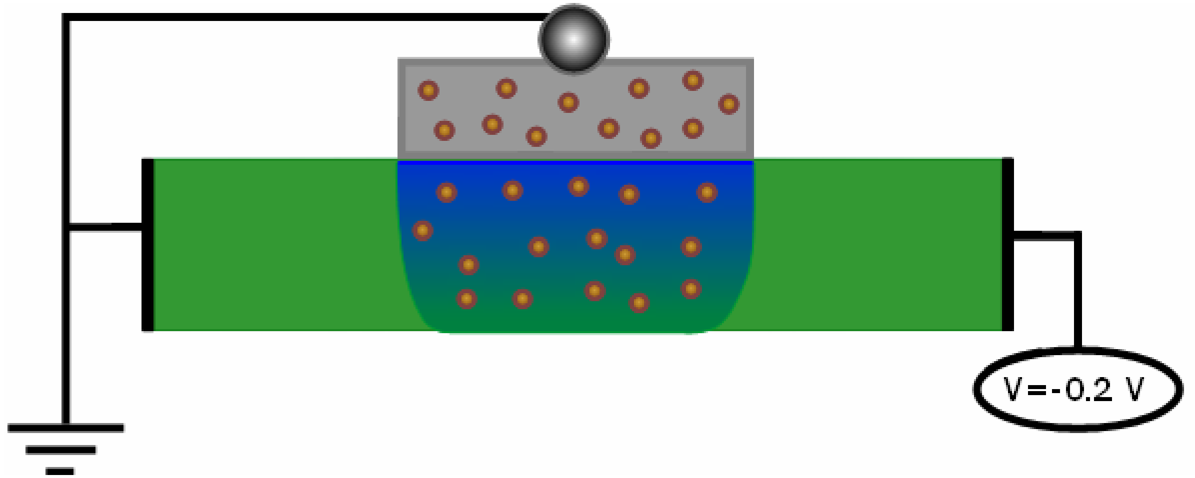
(blue dot)	electrons;	(brown dot)	Li^+ ions;
(blue square)	insulating PANI;	(green square)	conducting PANI;
(grey square)	solid electrolyte ($LiClO_4$ doped PEO);		

WORKING PRINCIPLE



Li+ ions penetrate PANI active layer decreasing its conductivity before application of voltage (partial reduction)

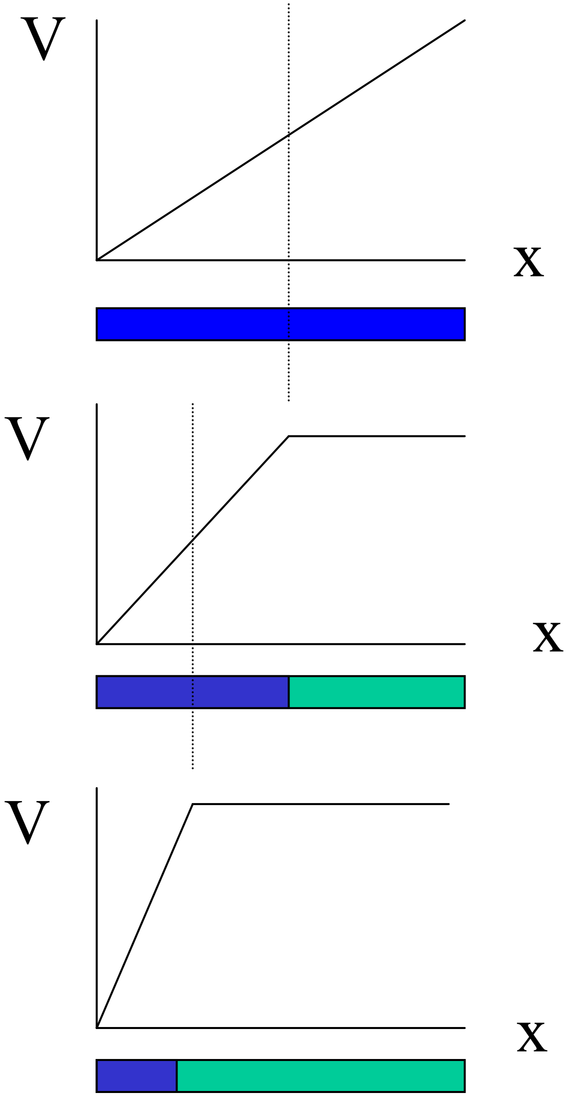
WORKING PRINCIPLE



When biased negatively, Li+ ions penetrate on practically whole depth of active PANI layer, transferring it into insulator (reduction)

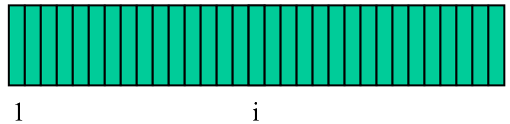
$$PANI^{+} : Cl^{-} + Li^{+} + e^{-} \Leftrightarrow PANI + LiCl$$

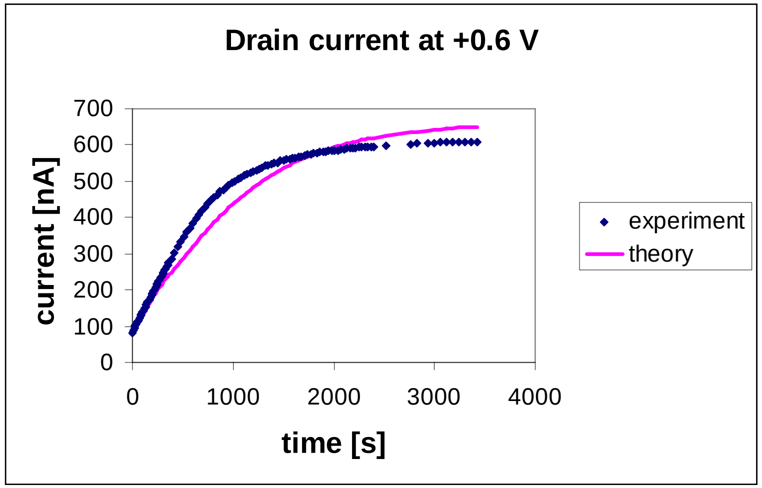
GRADUAL SHIFT OF THE INSULATING AREA BOUNDARY IN THE DIRECTION OF SOURCE AT POSITIVE BIAS



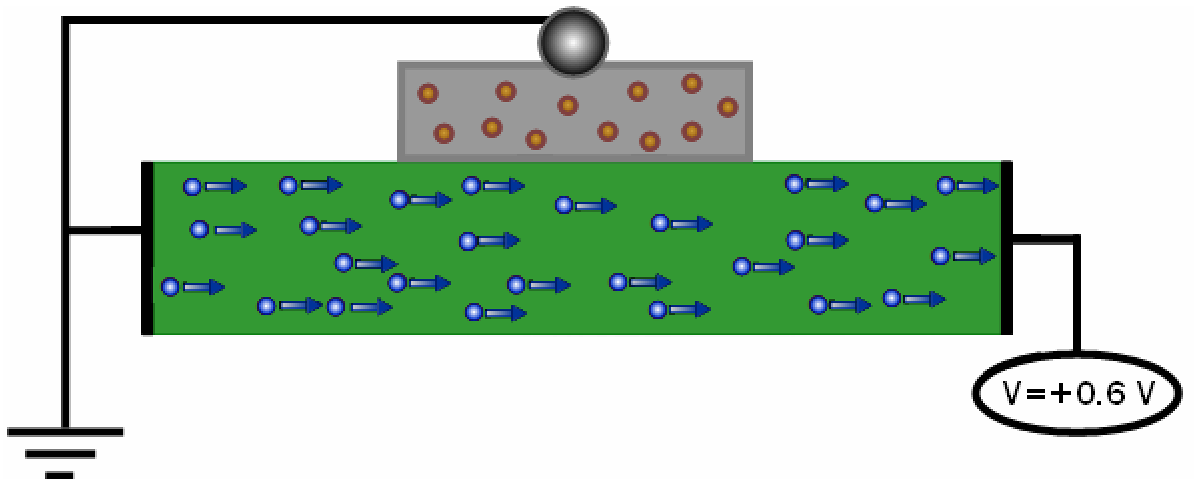
$R_i = R^{ins}$ if $V_i < V_{ox}$

$R_i = R(t)$ if $V_i > V_{ox}$



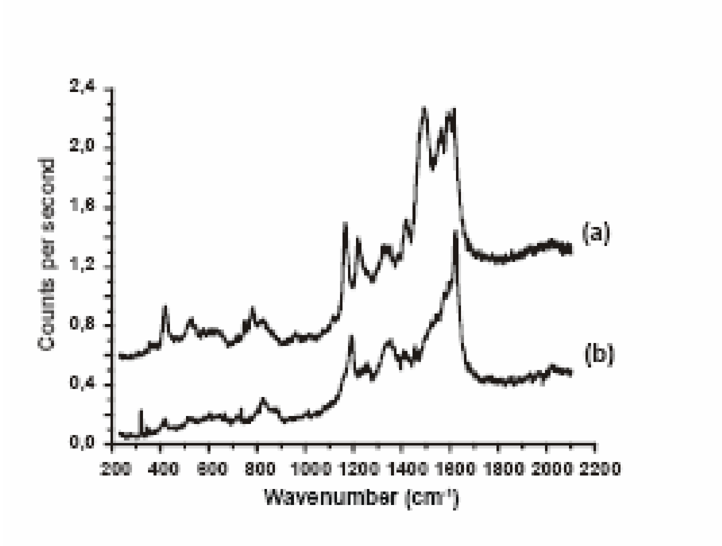


WORKING PRINCIPLE



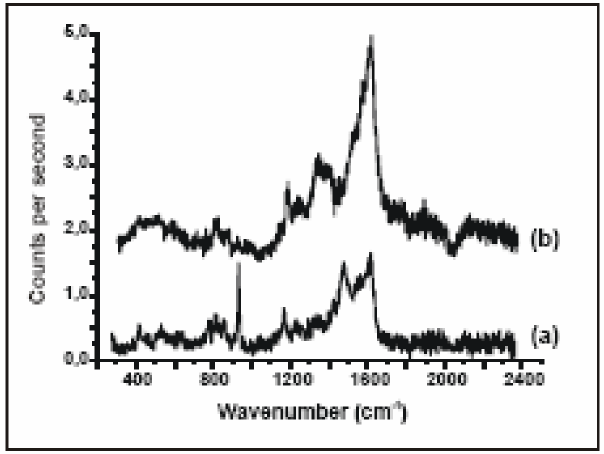
When biased positively, Li+ ions are shifted into solid electrolyte layer (PEO); PANI layer is highly conducting (oxidation)

RAMAN SPECTROSCOPY CHARACTERIZATION



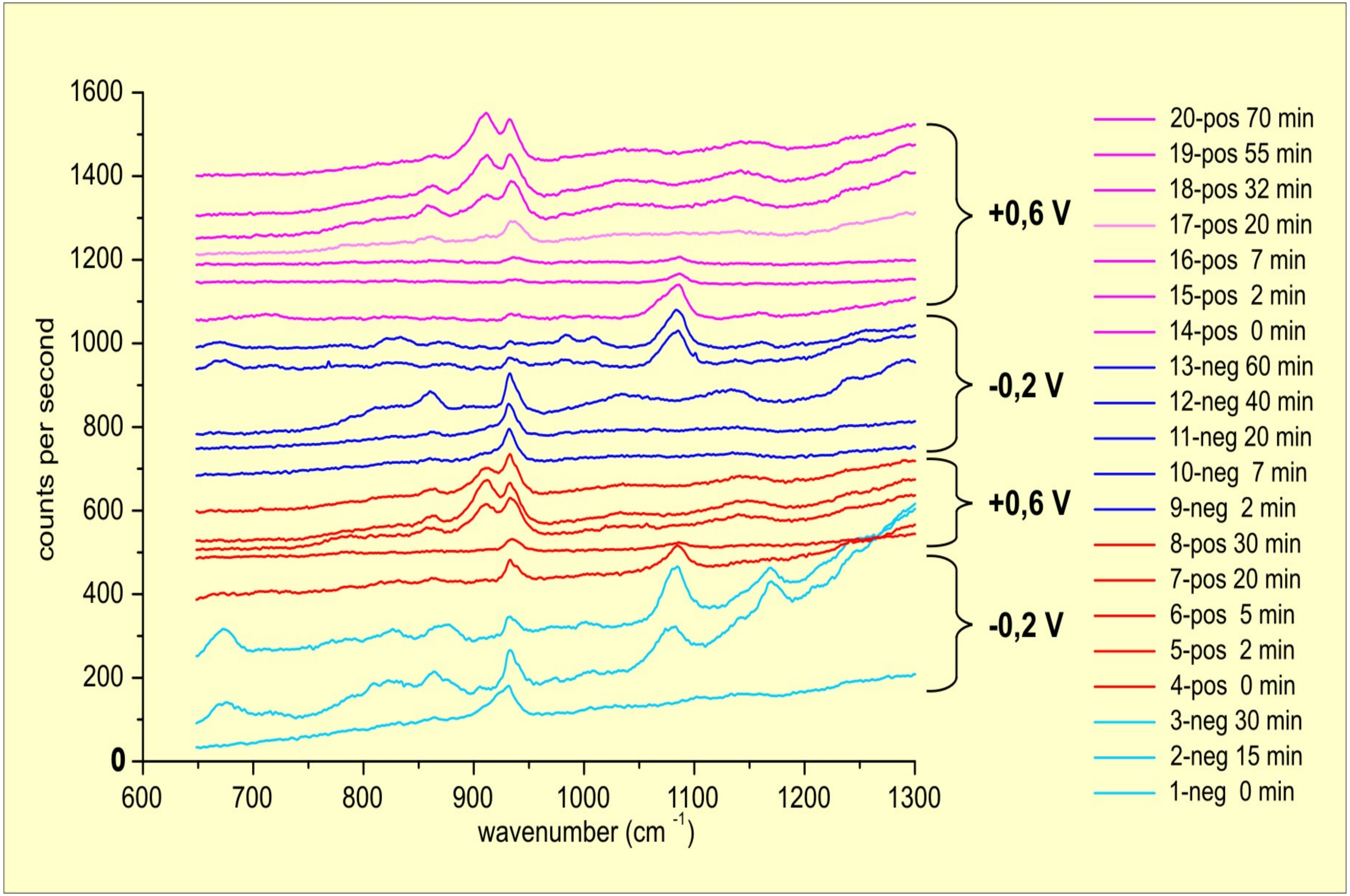
Raman spectra of non conducting (a) and conducting (b) PANI LS film upon excitation at 488 nm.

T. Berzina, V. Erokhin, and M.P. Fontana, J. Appl. Phys., in press



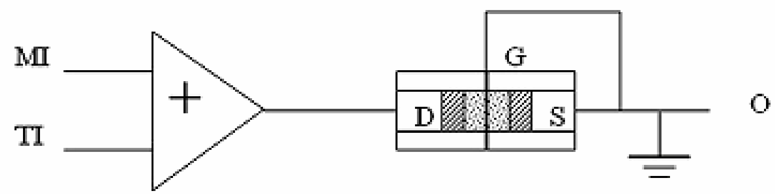
Raman spectra taken for the PANI-PEO junction before the final doping with HCl . The spectra were taken focussing near the silver electrode (a) and in the PANI-only area (b).

Sequence of Raman spectra upon application of positive and negative voltage cycles



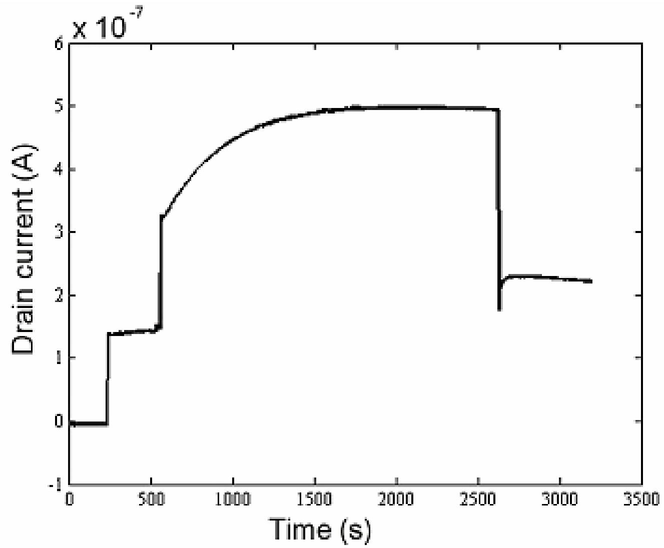
IMITATING THE SNAIL LEARNING PROCESS

After several simultaneous applications of "taste" and "touch" actions, feeding pattern begins to start, when only "touch" action is applied.



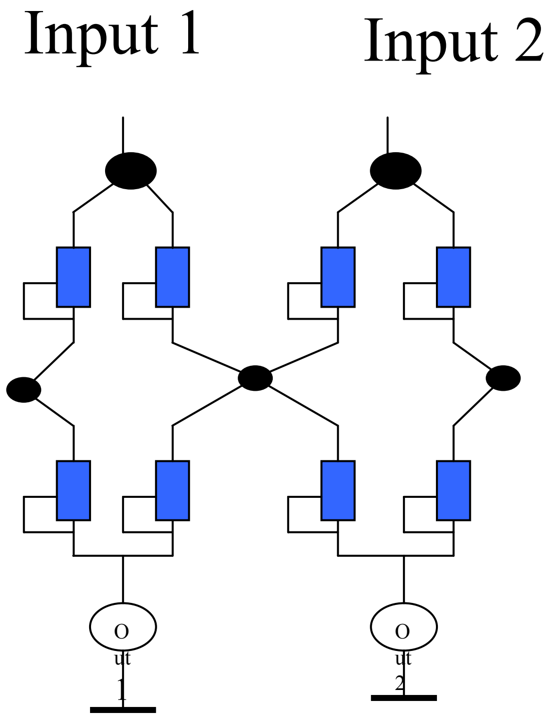
Main input (MI) corresponds to the "touch"action
Teaching input (TI) corresponds to the "taste" action

A. Smerieri, T. Berzina, V. Erokhin, and M.P. Fontana, Mater. Sci. Engineer. C, submitted.



After learning the output signal was twice higher at the same input conditions

MODEL ADAPTIVE NETWORK



Teaching by applying –0.5V between 1 input and 1 output

	Out 1 (nA)	Out 2 (nA)
Before teaching	120	32
After teaching	65	124

V. Erokhin, T. Berzina, and M.P. Fontana, Crystallogr. Rep. In press.

"Living matter evades the decay to equilibrium"

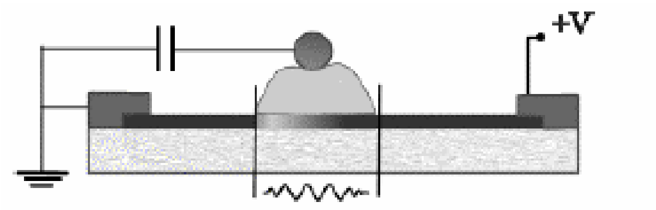
Schrödinger E. // What is Life? Physical Aspect of the Living Cell. Cambridge University Press, 1944

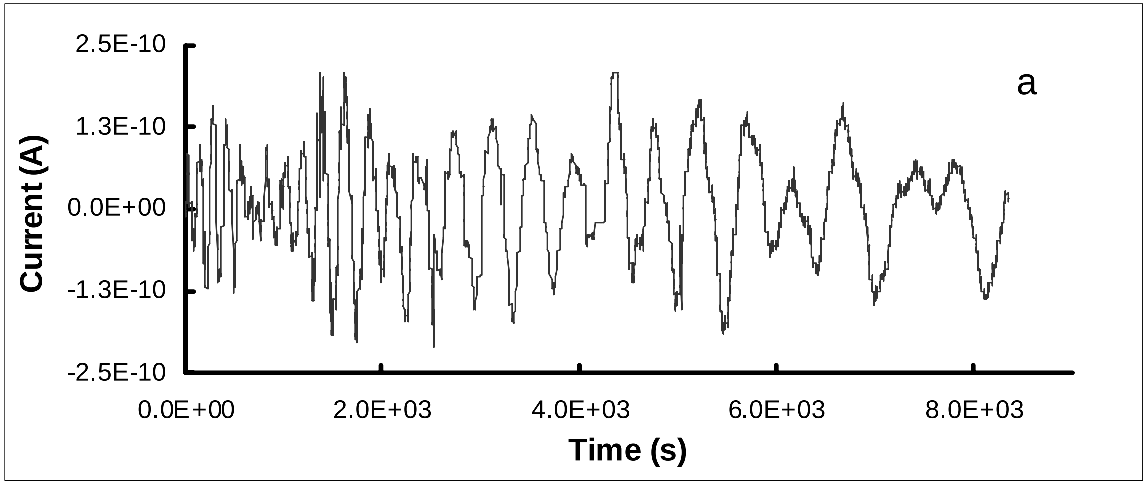
If we take the example of the pond snail, we can recognize one neuron, whose behavior is different from all the others, namely, the N1M neuron. Being activated once, it produces a rather long sequence of potential pulses. These pulses, then, interfere with nervous system treated signals from sensory elements providing learning and performing commands to executive organs.

Straub V.A., Staras K., Kemenes G., Benjamin P.R. // J. Neurophysiol. 2002. V. 88. P. 1569.

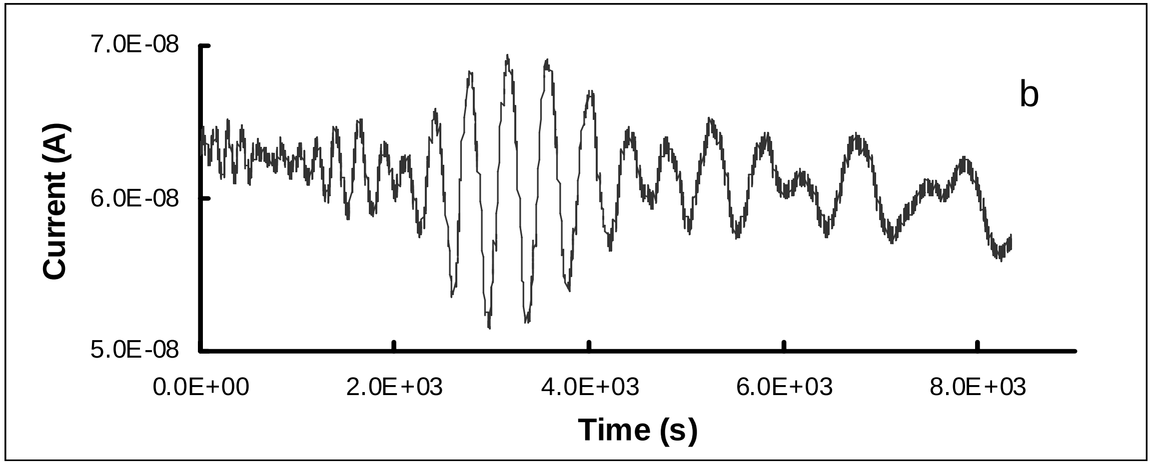
Our electrochemical element can be modified in order to perform similar tasks.

EXTERNAL CAPACITOR



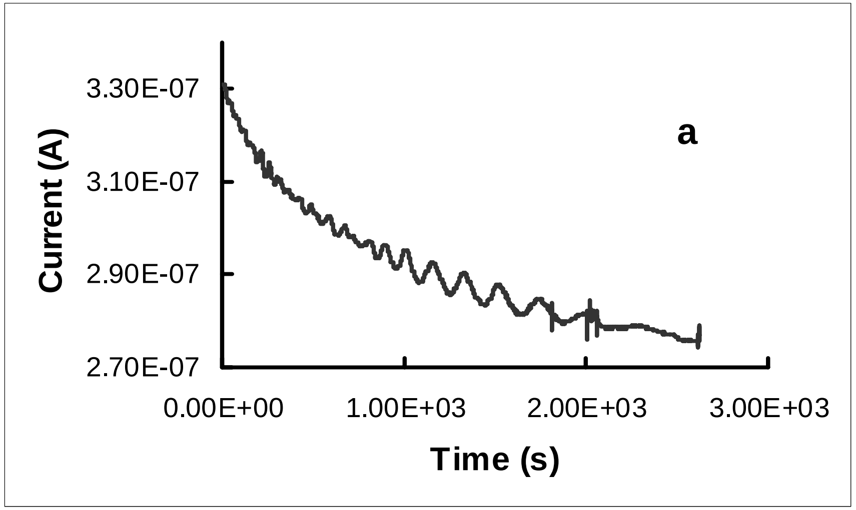


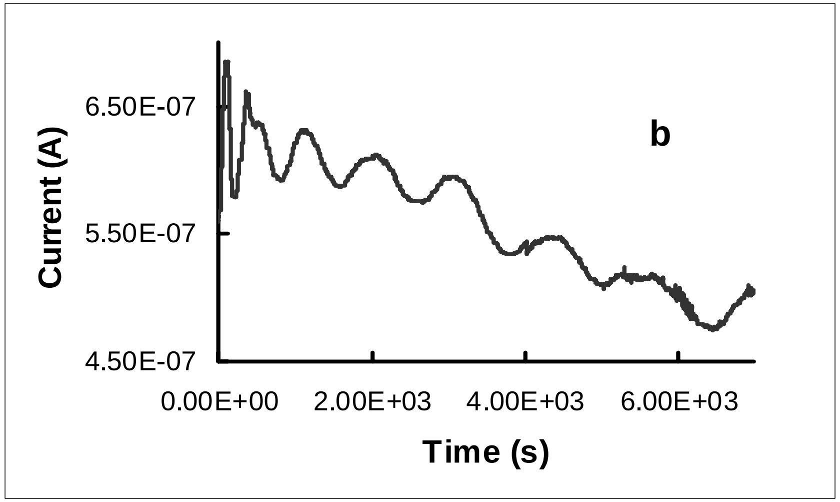
Current oscillations are caused by periodic conductivity variations due to the ionic flow after the potential redistribution: a highly non linear situation



V. Erokhin, T. Berzina, P. Camorani, and M.P. Fontana, J. Phys. Condens. Mat., submitted.

GRAPHITE STRIPE AS GATE





Current oscillations were also observed when graphite stripe, capable to accumulate charges by intercalation, was used as gate electrode.

A - positive bias

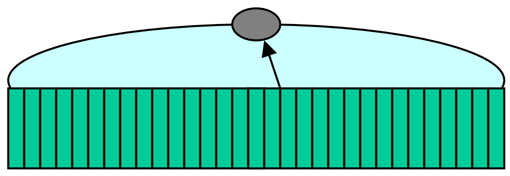
B - negative bias

The oscillations lasted at least 24 hrs, when our observation was stopped

⇓

Non-equilibrium reactions must be considered for the explanation of observed phenomenon

MODEL



$$I_g = \sum_{i=1}^{N} i_i^g \qquad i_i^g = i_{pas} + i_{act}$$

$$I_d = \frac{V_d}{\sum_i R_i} + I_g$$

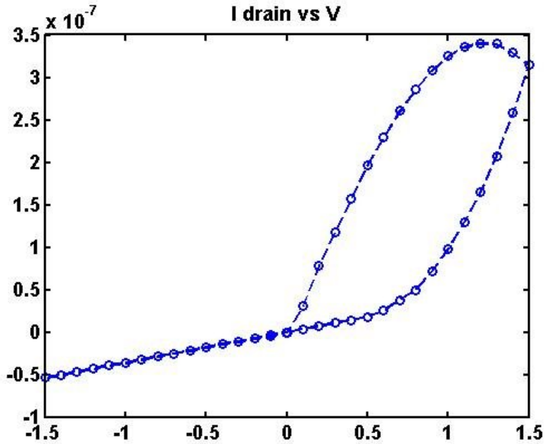
$$i_{pas} = \frac{(V_g - V_i)}{R_i^{el}}$$

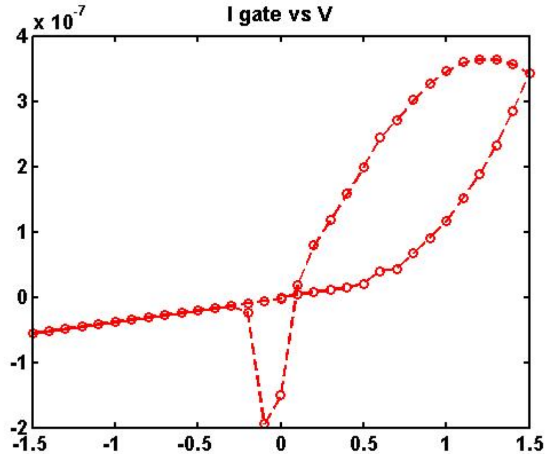
$$i_{act} = f(t)$$

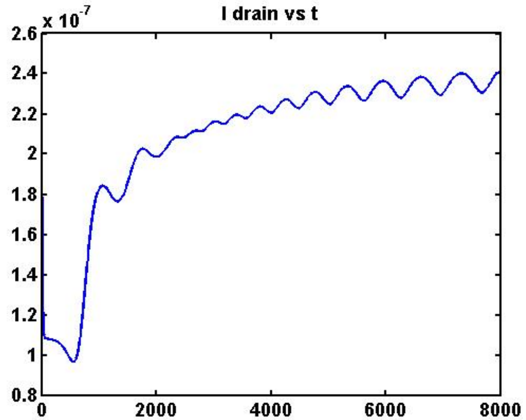
When ΔV pass oxidation or reduction potential value

Active area is devided into 100 zones. Conductivity variation is due according actual potential of the zone with respect to the G potential.

CALCULATION RESULTS

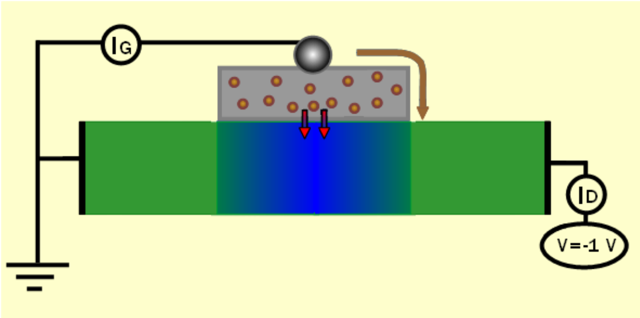




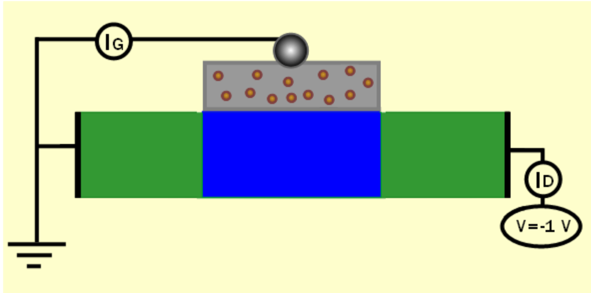


- Variation of capacitor value
- Variation of drain voltage
- Variation of resistances

SCHEME OF THE PROCESS

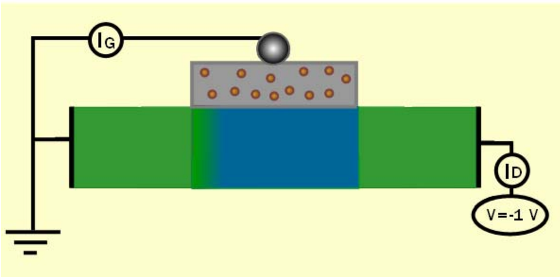


Transfer to insulating state + charging of the capacitor

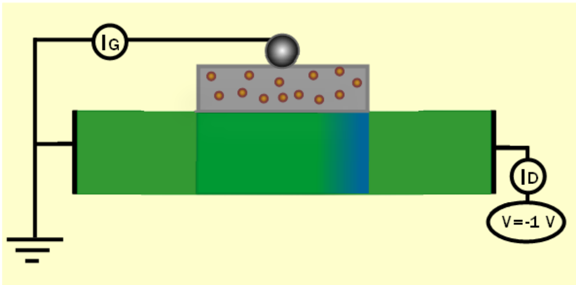


Capacitor is charged (negatively).

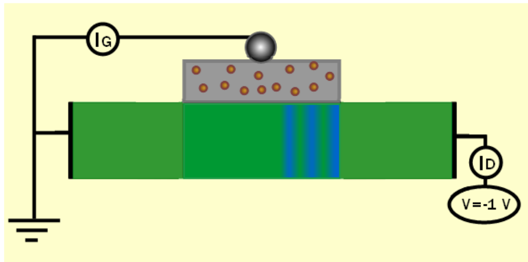
Channel is insulating



Discharge of the capacitor. Areas at potential more then oxidizing one become conducting.



Redistribution of the potential profile. Enlargement of the conducting area.



Repetition of the process
⇒ space periodicity
⇒"conductivity waves"

BELOUSOV-ZHABOTINSKY REACTION

Cyclic reaction (often redox reactions) far from the equillibrium of the reagents concentration.

$BrO_3^- + Br^- \Rightarrow HBrO_2 + HOBr$ Rate = $k_1[BrO_3^-][Br^-]$

$HBrO_2 + Br^- \Rightarrow 2HOBr$ Rate = $k_2[HBrO_2][Br^-]$

$BrO_3^- + HBrO_2 \Rightarrow 2HBrO_2 + 2Ce^{4+}$ Rate = $k_3[BrO_3^-][HBrO_2]$

$2HBrO_2 \Rightarrow BrO_3^- + HOBr$ Rate = $k_4[HBrO_2]^2$

$B + Ce^{4+} \Rightarrow 1/2fBr^-$ Rate = $k_c[Z][Ce^{4+}]$

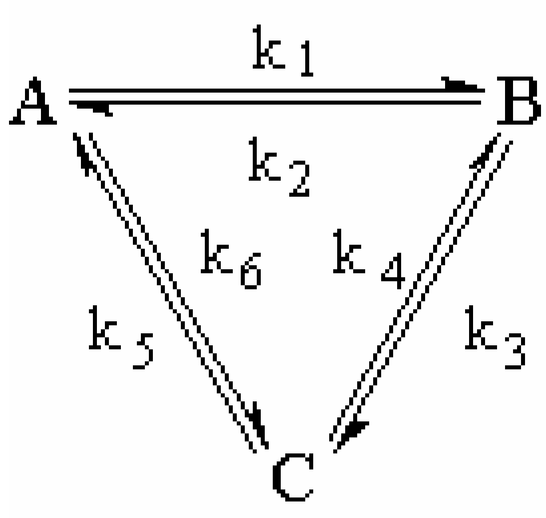
Zaikin AN and Zhabotinsky AM 1970 *Nature* **225** 535

PROCESSES IN THE ELECTROCHEMICAL ELEMENT WITH CAPACITOR:

•Process A: Oxidation (increase of the conductivity)

•Process B: Reduction (decrease of the conductivity)

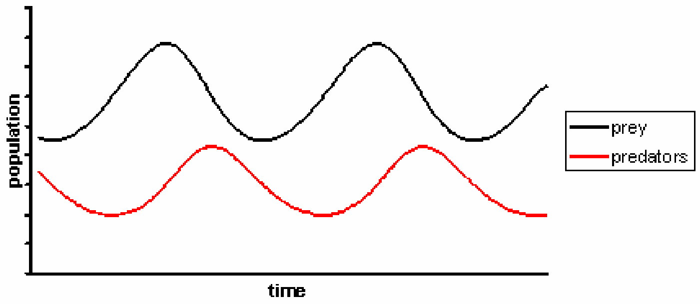
•Process C: Variation of the gate potential due to the charge accumulation and Redistribution of the potential profile along the channel due to the conductivity variation



BZ REACTION CAN BE DESCRIBED BY LOTKA-VOLTERRA EQUATIONS:

$$\frac{dX}{dt} = aX - bXY$$

$$\frac{dY}{dt} = -dY + hXY$$



$$\frac{dX}{dt} = k_3AY - k_2XY + k_5AX - 2k_4X^2$$

$$\frac{dY}{dt} = -k_3AY - k_2XY + 0.5k_6BZ$$

$$\frac{dZ}{dt} = 2k_5AX - k_6BZ$$

IN OUR CASE :

$$\frac{dA}{dt} = k_1 I_g B - k_2 A$$

$$\frac{dB}{dt} = -k_3 I_g A - k_4 B$$

$$\frac{dV_g}{dt} = \frac{I_g}{C}$$

$$I_g = k_5 (V_g - V_{act})$$

$$V_{act} = k_6 B + k_7$$

$$\frac{dI_g}{dt} + \frac{dB}{dt} = \frac{k_8 I_g}{C}$$

A – amount of oxidized PANI;

B – amount of reduced PANI;

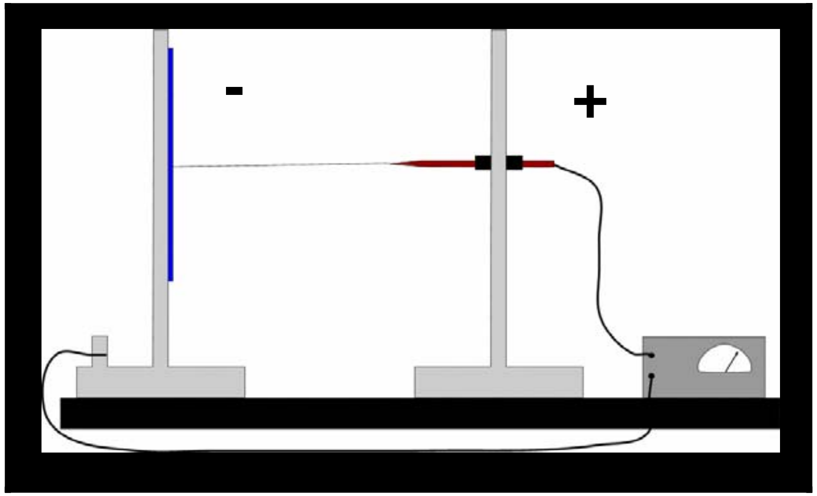
Ig – gate current

ALTERNATIVE APPROACH

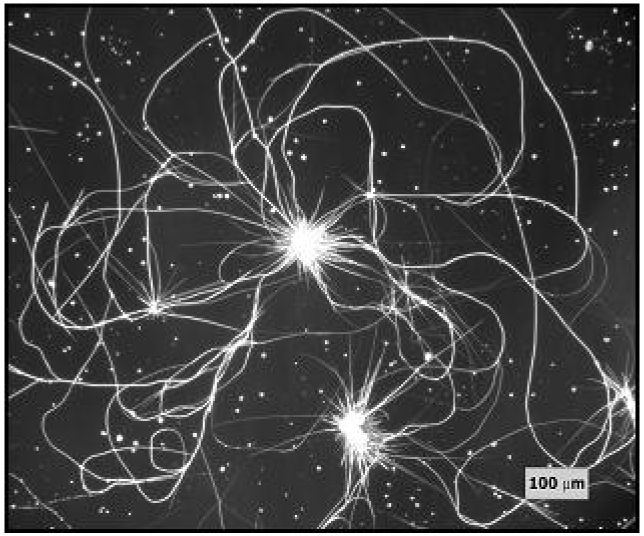
Formation of the network by statistical assembling of electrochemical junctions

Realization of fibrillar structures

Electric field assisted polymer fiber formation



4 kV bias



PEO fibrillar matrix fabricated by vacuum treatment of PEO solution

PEO solution (0.1-0.5 ml) on the substrate (glass or glass with Cr electrodes) was placed into the vacuum chamber and pumped with mechanical pump at 10-2 Torr for 15-20 min.

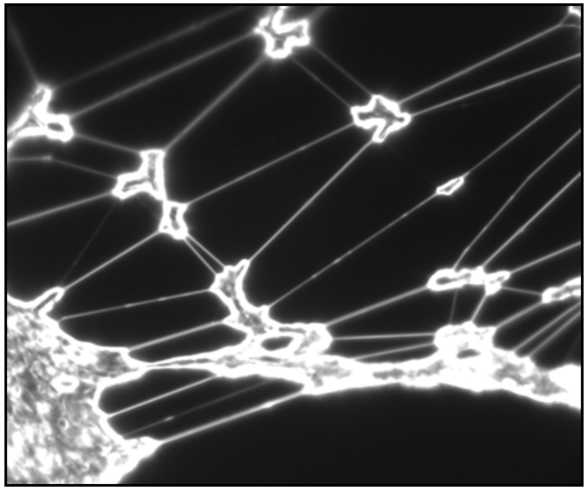
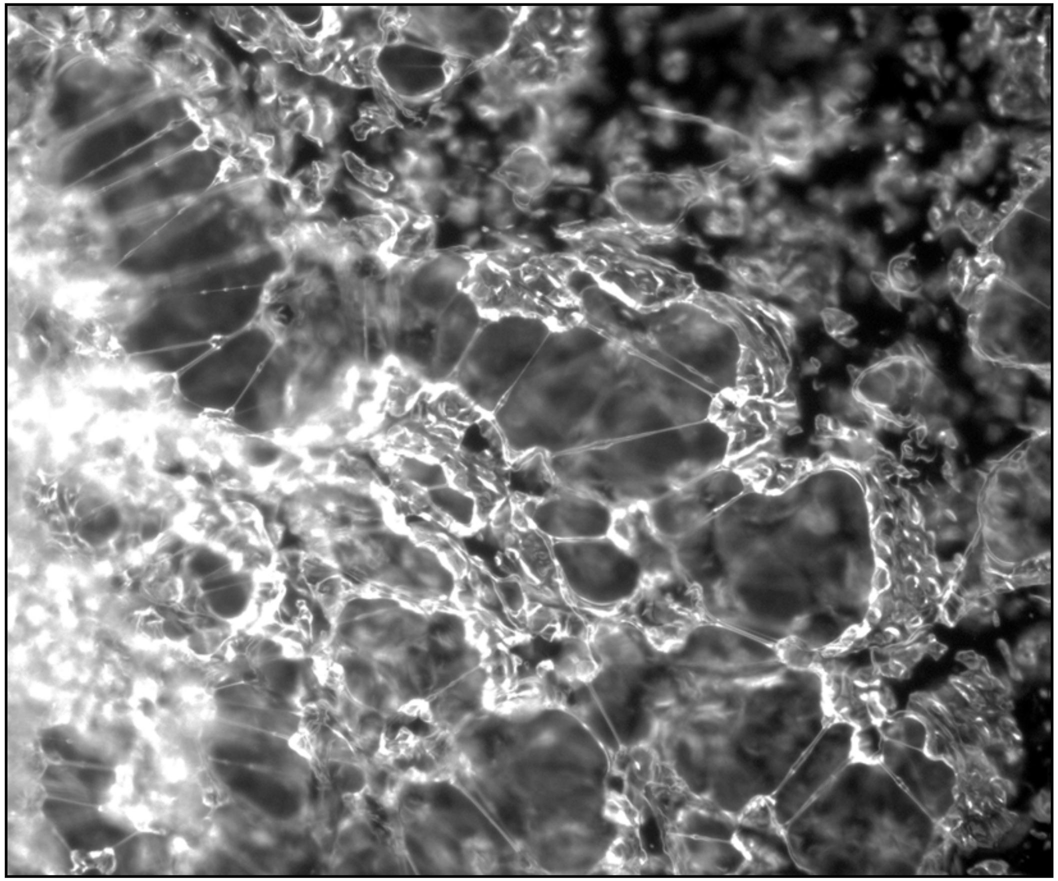


image size 0.6 x 0.5 mm

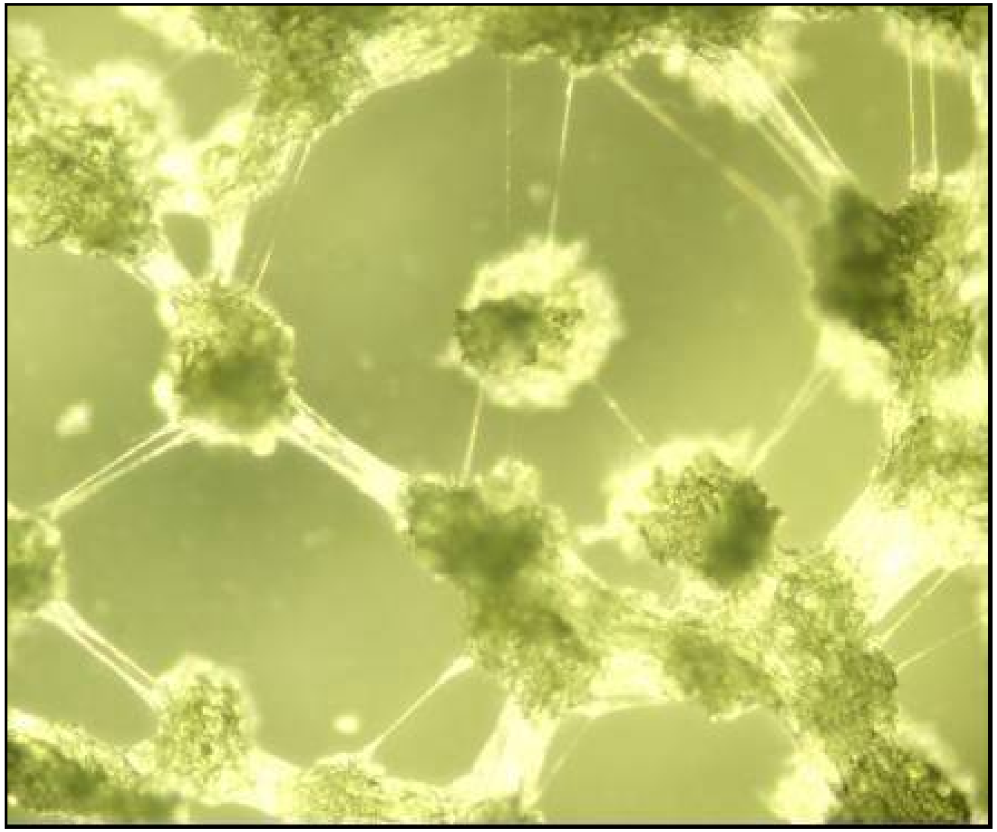


Optical microscopy image of PEO fibrillar network

PEO –PANI fibrillar networks after vacuum treatment

- PANI fibers were formed on PEO fibrillar matrix by dropping 0.1-0.2 ml of PANI solution on it, placing the structure into the vacuum chamber, and pumping again for 15-20 min till 10-2 Torr.

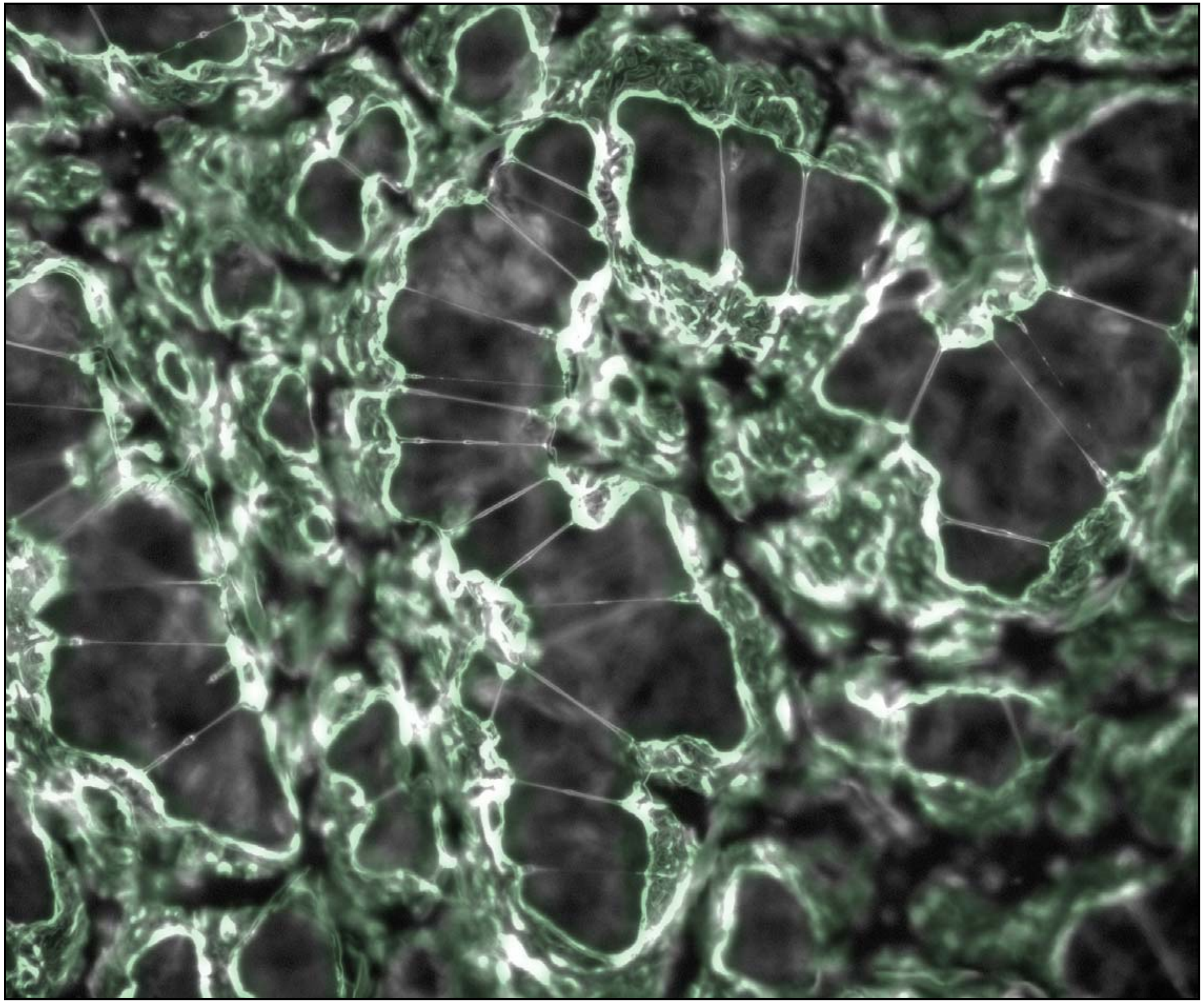
- The formed fibers of different diameter of both PEO and PANI (from less than one micron up to tens of microns) and length (up to some millimeters) are clearly visible, as well as the 3D morphology.



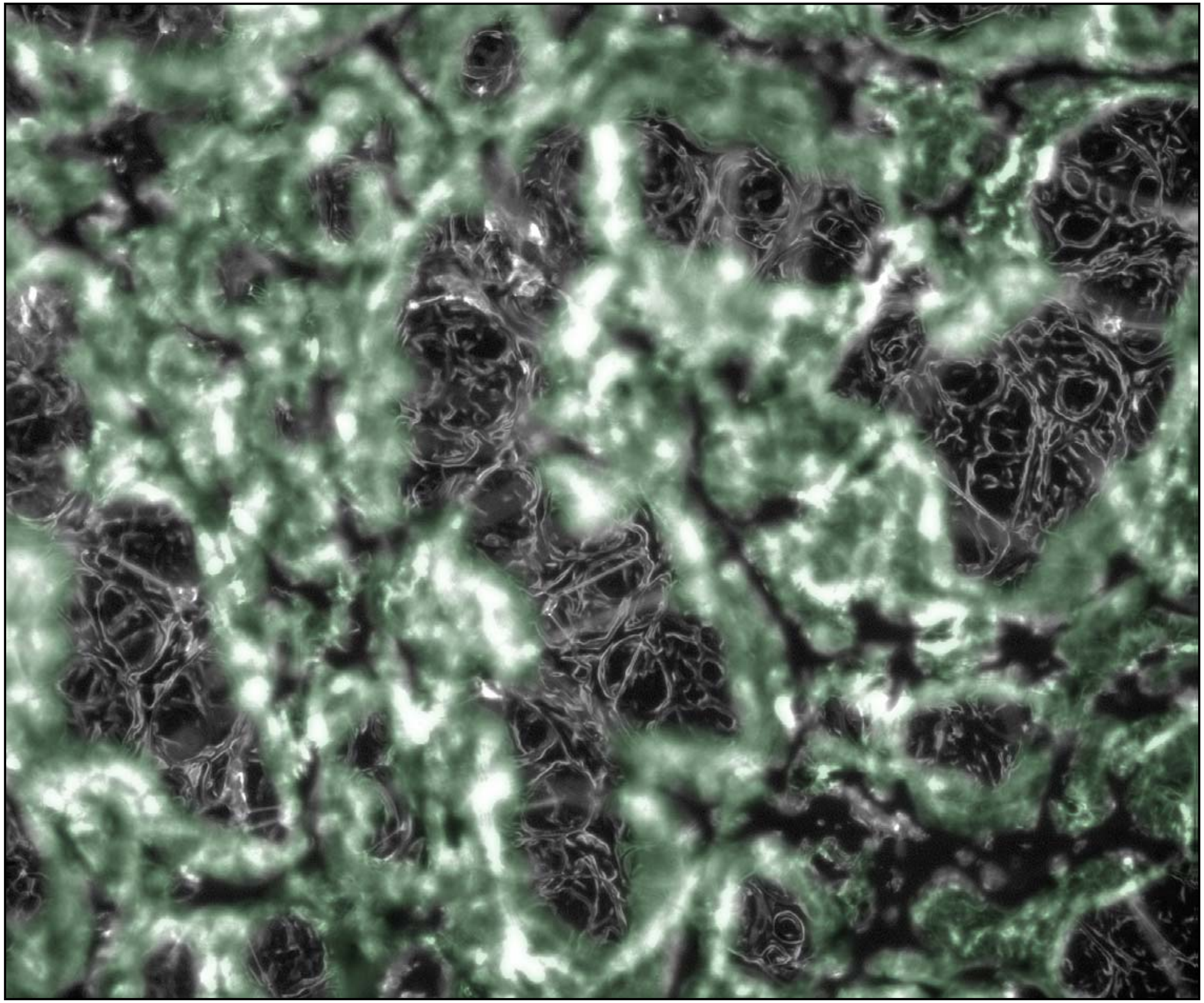
Optical microphotograph (image size 0.6 x 0.5 mm).

V. Erokhin, T. Berzina, P. Camorani, and M.P. Fontana, *Soft Matter*., **2**, 870 (2006).

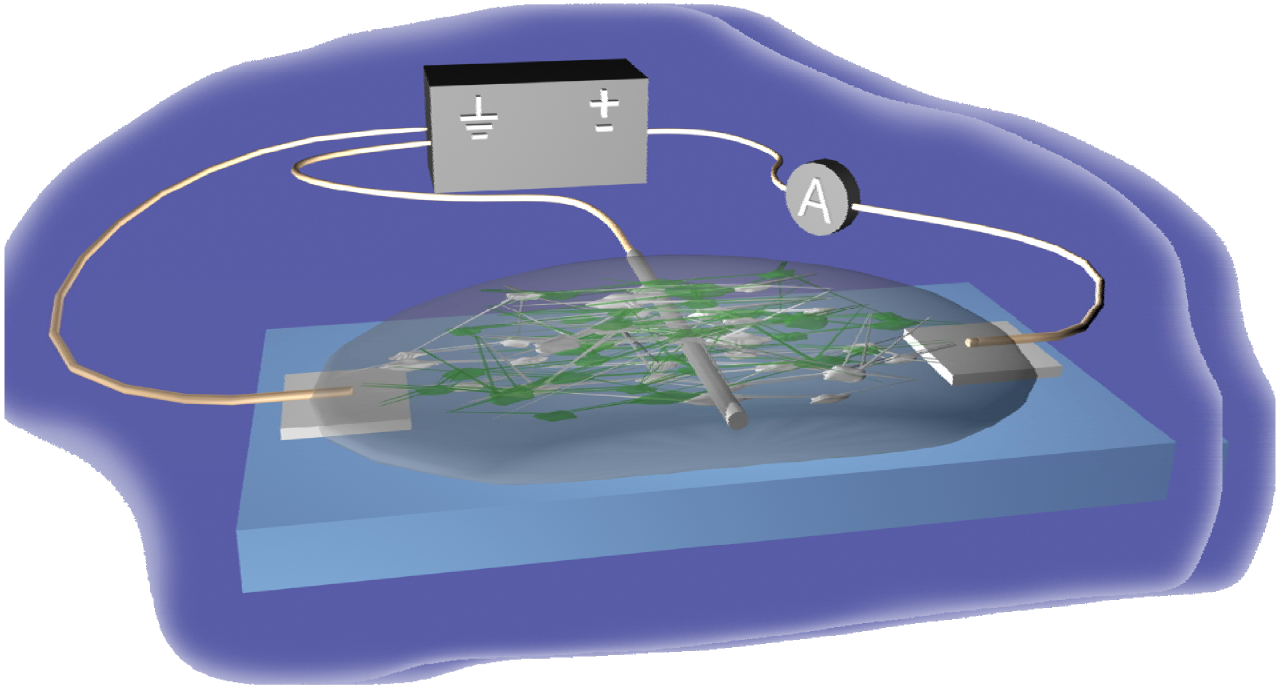
Statistical network of mixed PEO-PANI fibers



Statistical network of mixed PEO-PANI fibers



FIBRILLAR STRUCTURE WITH 3 ELECTRODES



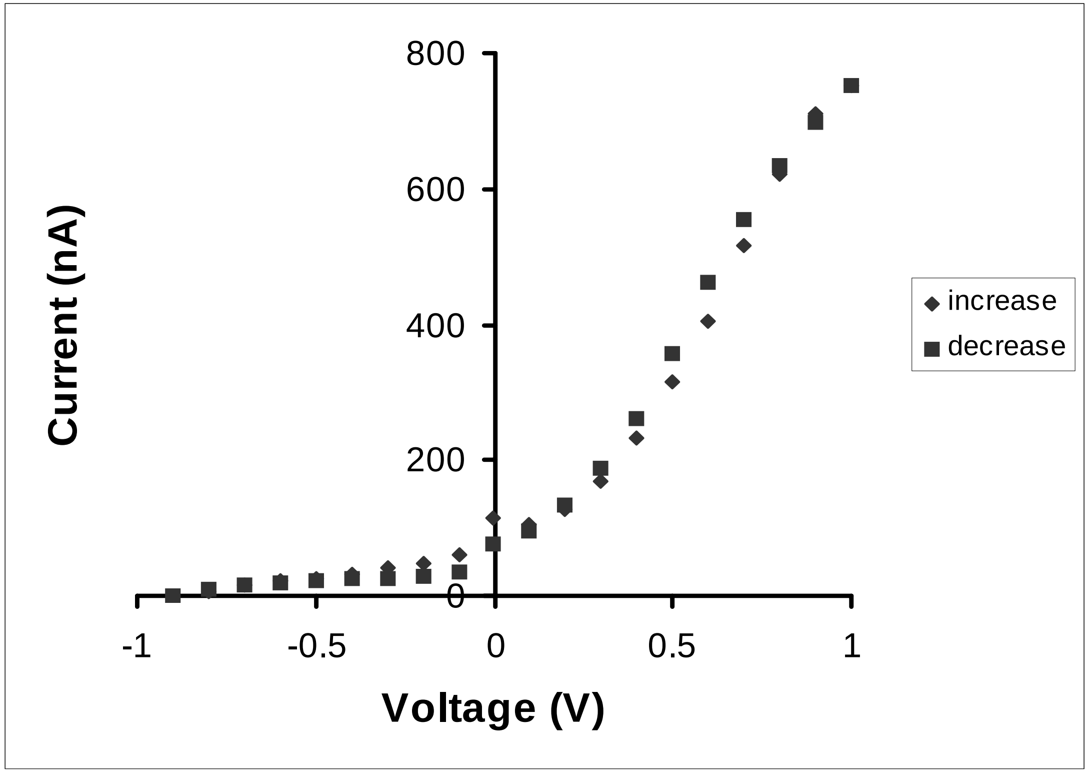
The third electrode (Ag wire) was inserted into the drop of PEO before vacuum evaporation. Thus, after the formation of PEO and PANI fibers, the wire would be retained in the middle of the fibrillar structure to maintain ground potential level in PEO-PANI junctions in the central part of the structure.

Question:

Is the formed structure complex enough in order to provide by the statistically distributed PANI-PEO fiber interconnections the pathways similar to those directly fabricated in the discrete deterministic device?

In other words, whether some parts of the structure have Ag wire – PEO – PANI heterojunctions?

Non linear electrical characteristics were found, implying the substantial presence of nodes similar to the fabricated device



V/I characteristics measured in on the drain electrode in 3 electrode circuit.

Clearly visible rectifying behavior of the curve confirms the success of the realization of the desirable heterojunctions in some areas of the formed fibrillar network

CONCLUSIONS

- Demonstration of the possibility to realize adaptive network based on electrochemically controlled polymeric structures.
- Observation of non-equilibrium rhythmic electrical behavior at fixed external conditions.
- Possible interpretation of the observed phenomena in terms of Belousov-Zhabotinsky reaction.
- Justification of the connection to biological systems

COLLABORATORS

- Prof. Marco P. Fontana
- Dr. Tatiana Berzina
- Dr. Paolo Camorani
- Dr. Svetlana Erokhina
- Anteo Smerieri

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