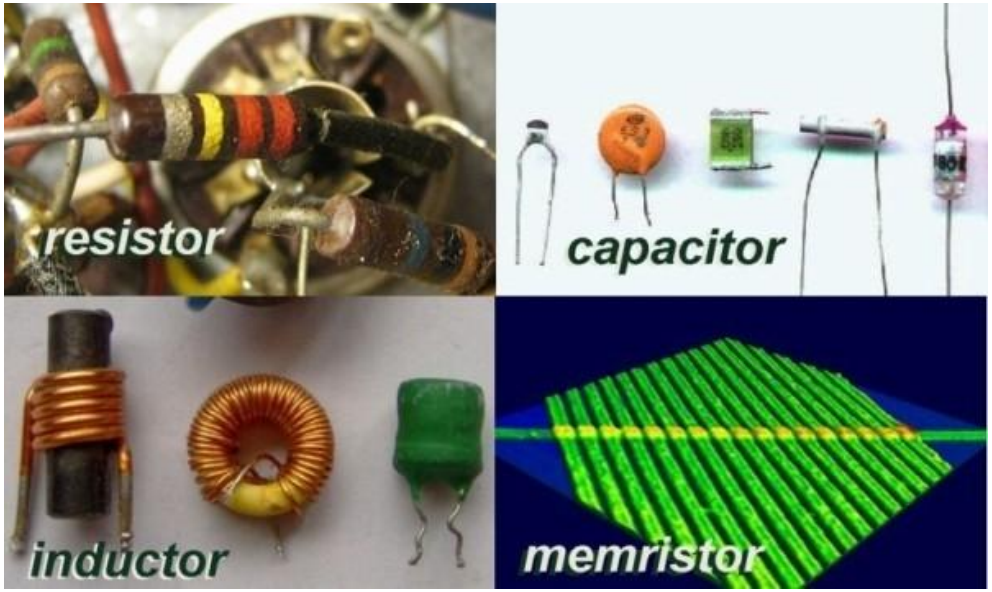
Resistive switch Red-Ox behavior as mechanism behind the operation of polyaniline memristors and neural network elements and PANI-based thermolectrochemical cells

O.Bogomolova[1] , J.Boeva[1], V.Sergeyev[1], D.Godovsky[2]

[1] Moscow State University, Chemistry Dept., Vorobievy Gory, 1 Moscow

[2] INEOS RAS, Vavilova str, 28, Moscow

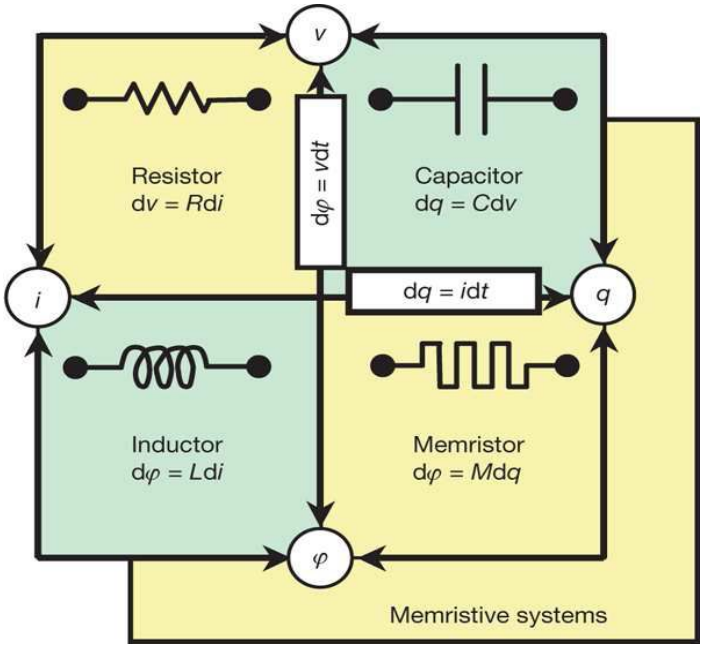
Also at LG TCM, LG Electronics, Moscow, Paveletskaya, 2/3

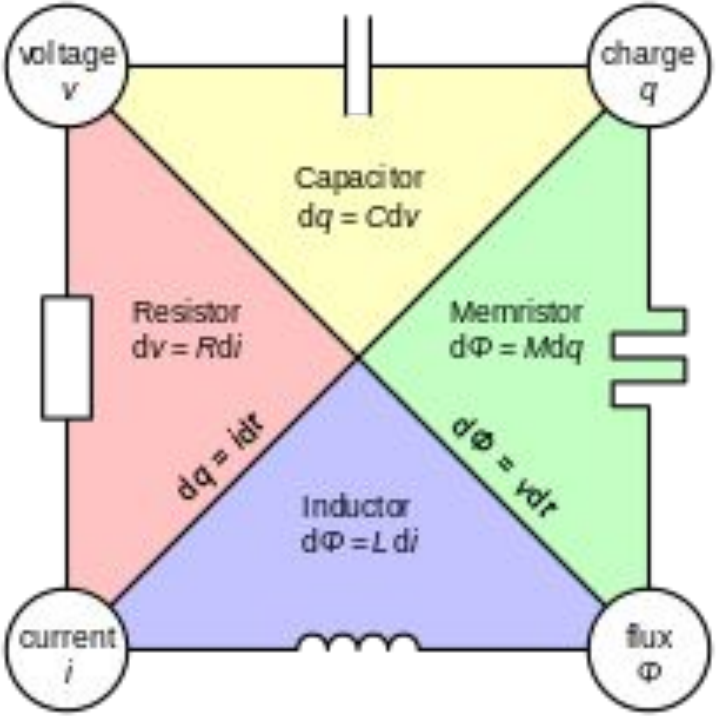


ИПХФ РАН

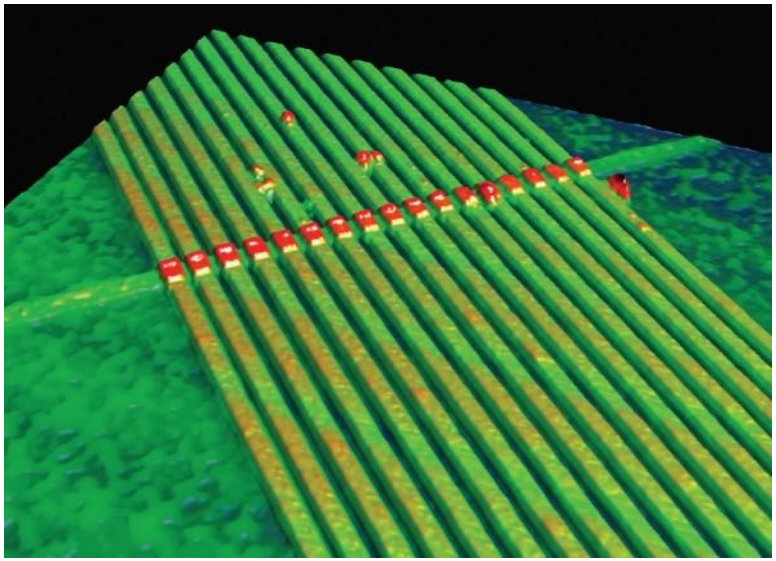
ИНЭОС

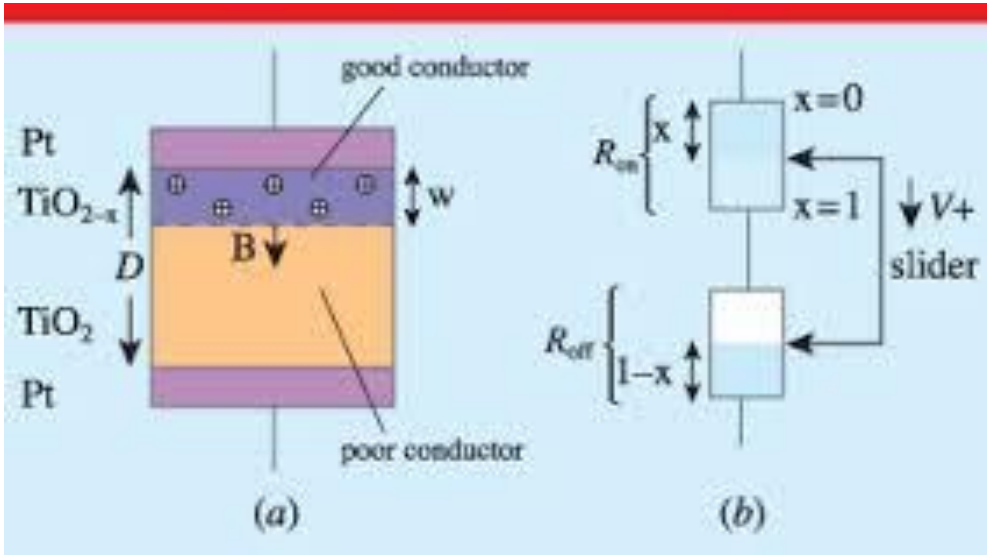
LEON CHUA THEORY BEHIND THE OPERATION OF MEMRISTOR (1971)

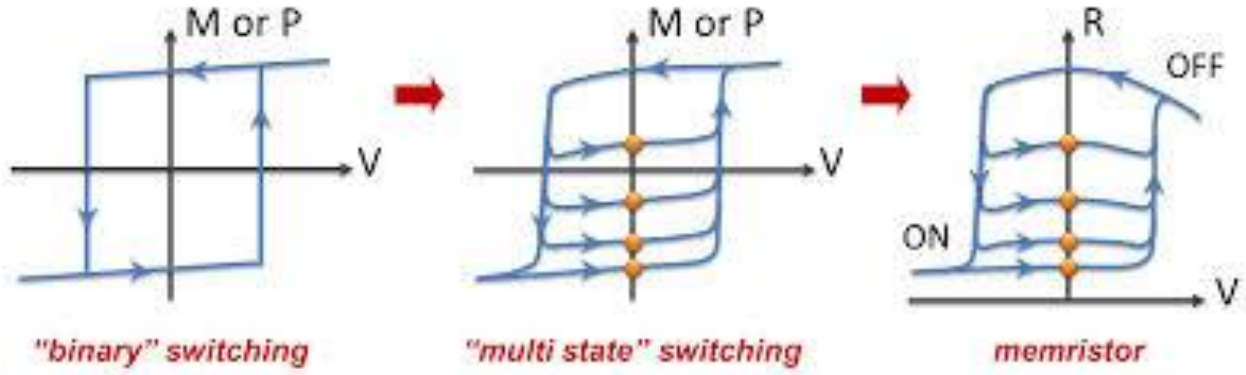




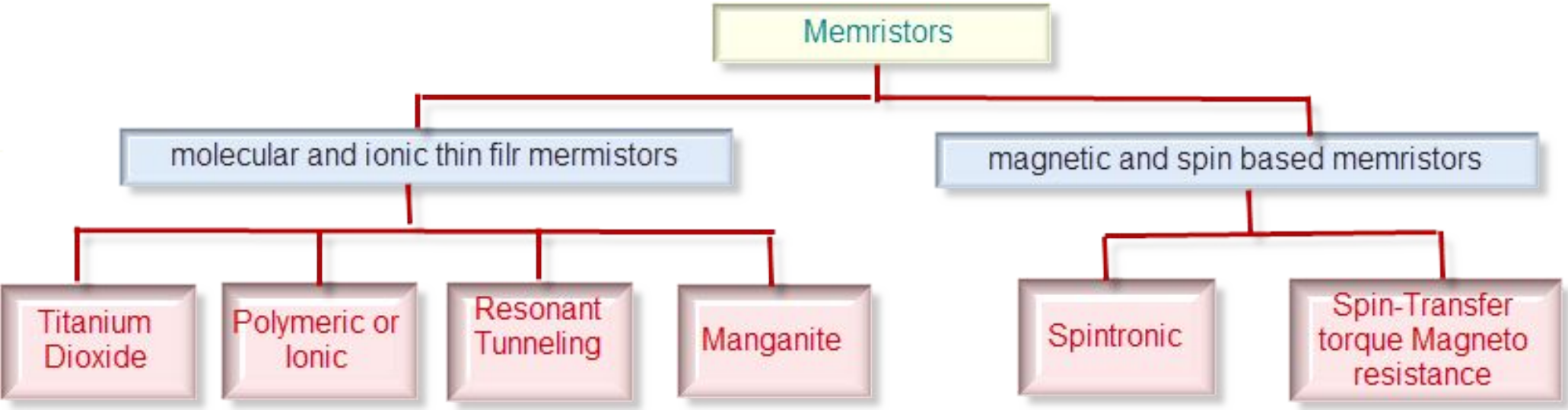
PRINCIPLE OF OPERATION OF TiO_2 MEMRISTOR (STAN WILLIAMS, HP LABS, 2012)







TYPES OF MEMRISTORS

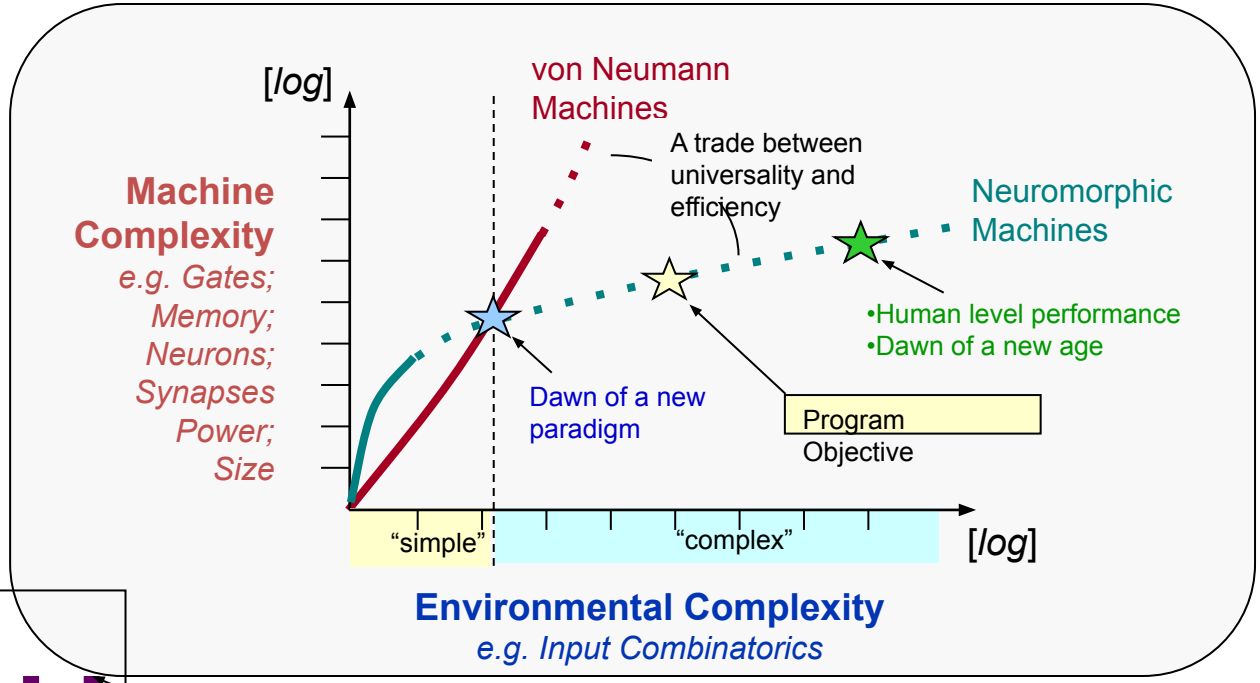


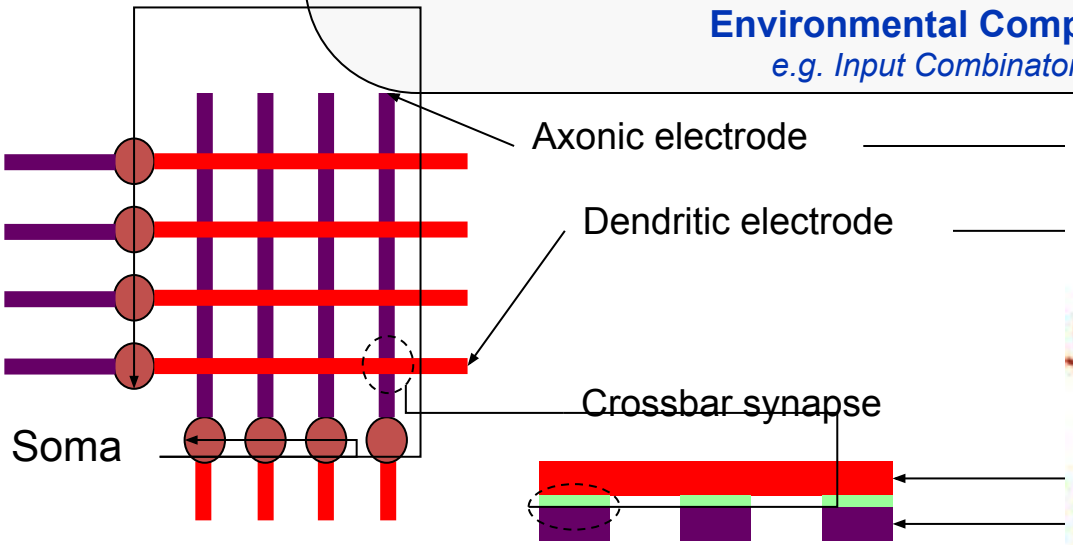
BESIDES MEMRISTORS THERE ARE NOW MEMCAPACITORS AND MEMINDUCTORS!

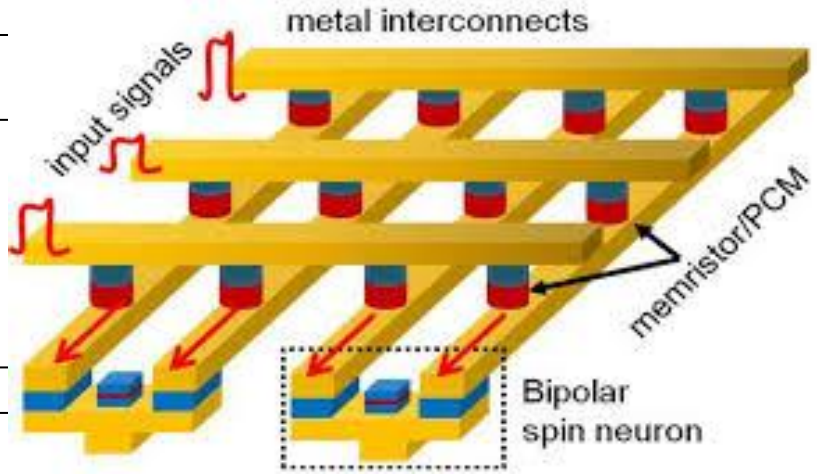
ИПХФ РАН

ИНЭОС

NEUROMORPHIC COMPUTERS – PROJECT SYNAPSE - DARPA







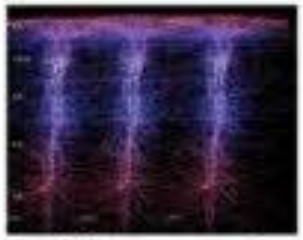
ИПХФ РАН

ИНЭОС

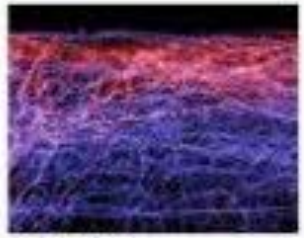
NEUROMORPHIC COMPUTING ROADMAP

~10^{10} synapses/cm^2

~10^{6} neurons/cm^2



~10^{4} neurons/ cortical column

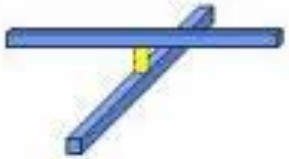


~5X10^{8} long range axons @ 1 Hz

Biological Brain

Synapse | **Neurons** | **Microcircuit** | **Long-range interconnects** | **Brain**

CROSSBAR JUNCTION



~10^{10} intersections/ cm^2 @ 100 nm pitch

CMOS SUBSTRATE

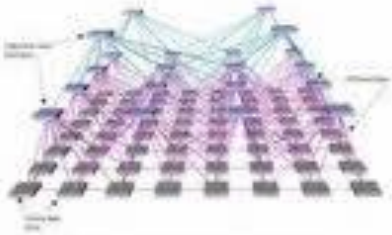
5X10^{8} transistors/ cm^2 @ 500 transistors/ neuron

LAMINAR CIRCUIT

Layered cortical circuits with ~10^{6} neurons/cm^2

HIGH SPEED BUS

Multi-Gbit/sec digital comms

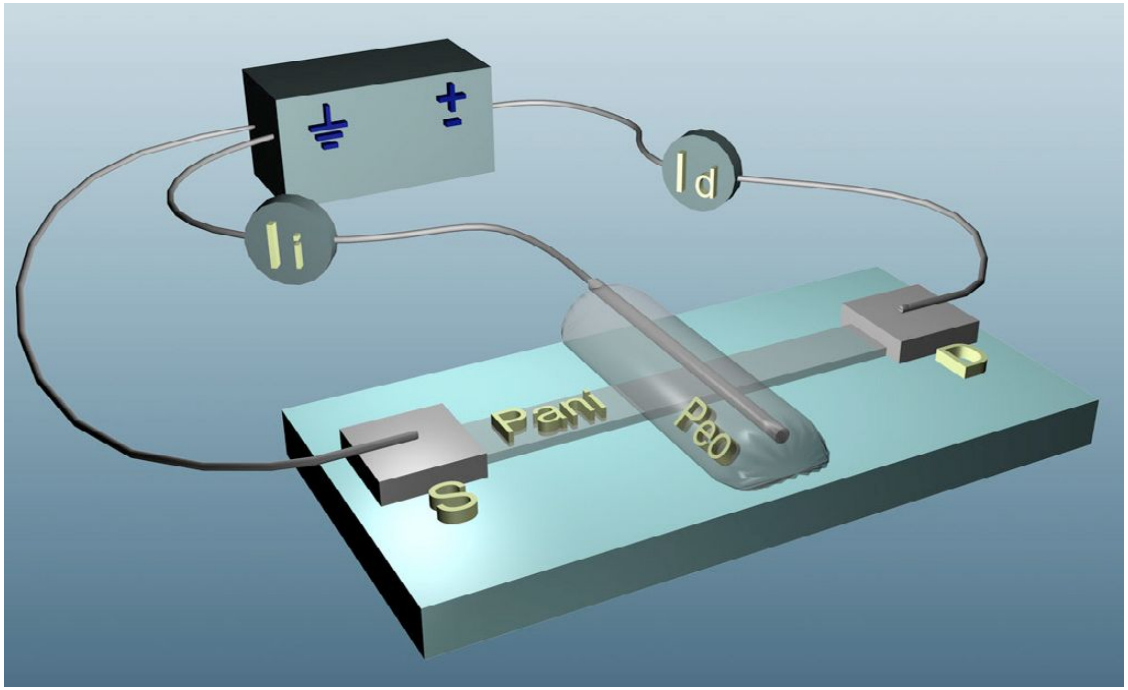


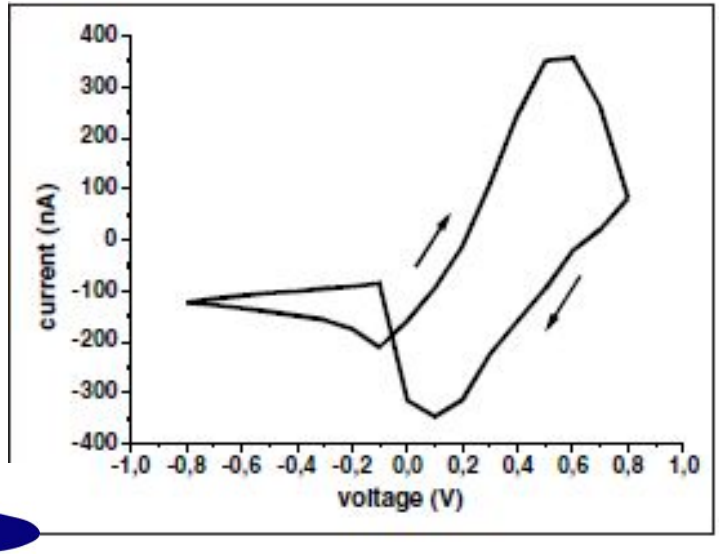
Electronic Brain

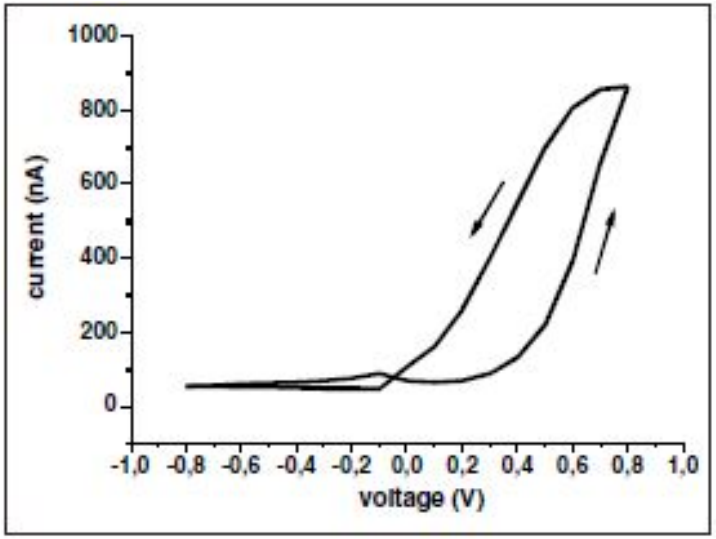
ИПХФ РАН

ИНЭОС

PANi BASED MEMRISTOR – EROKHIN, FONTANA - 2008



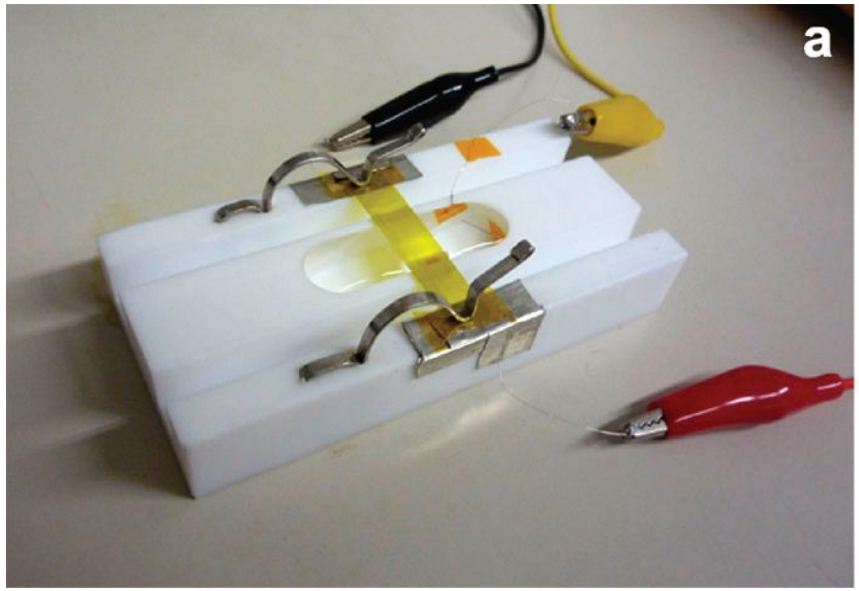


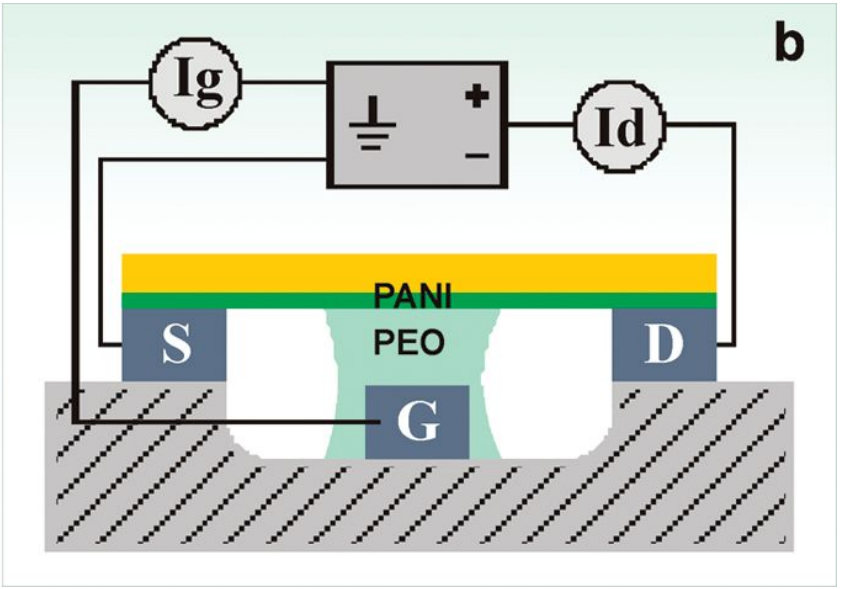


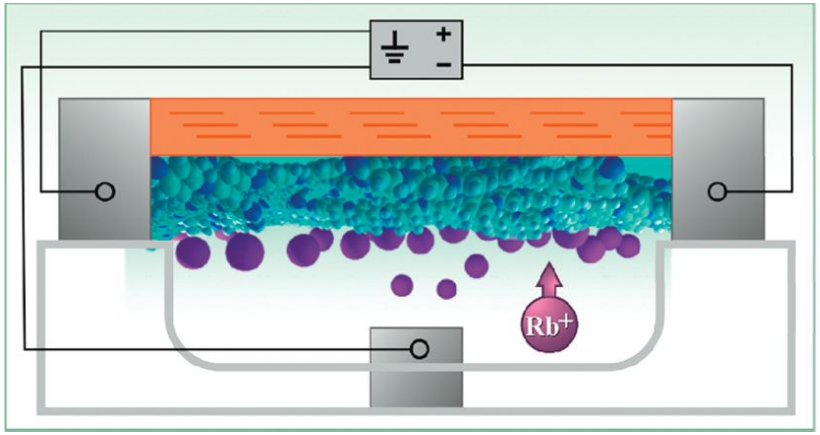
Ionic current

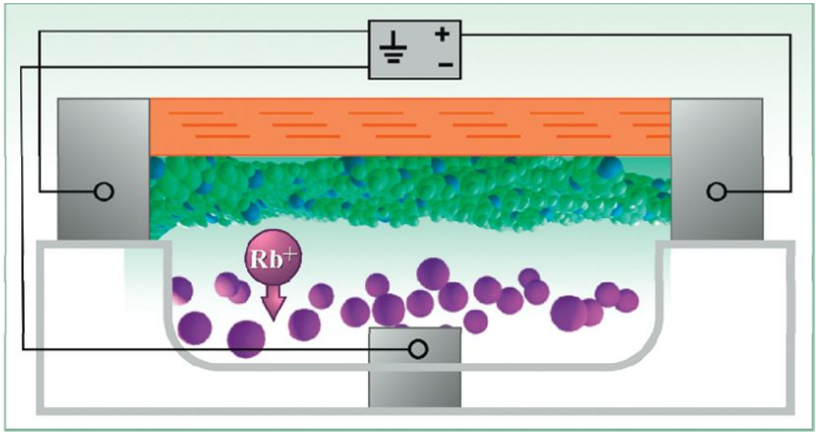
Electronic current

FIRST ATTEMPTS TO INTERPRET PANi MEMRISTOR OPERATION MECHANISM – EROKHIN, 2013





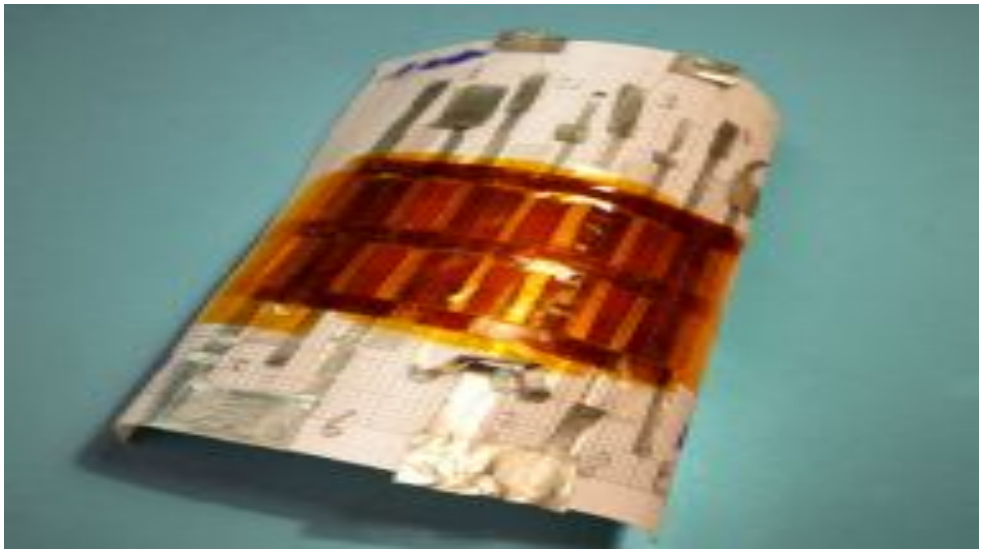


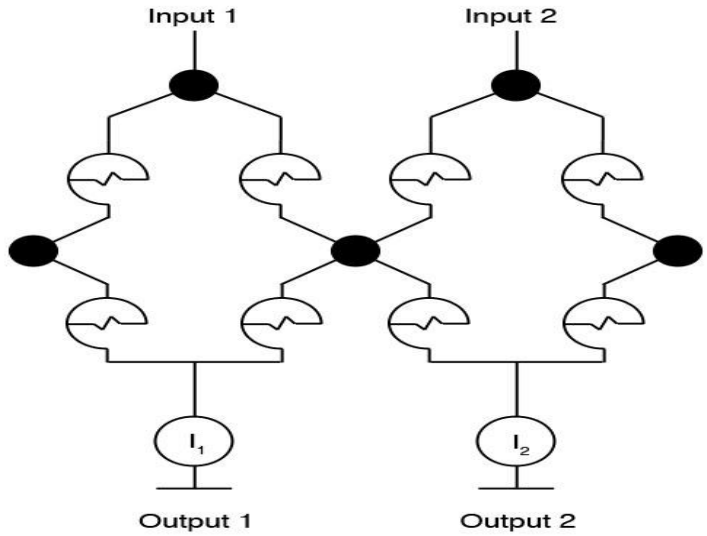


ИПХФ РАН

ИНЭОС

SET OF 8 PANi BASED MEMRISTORS ON FLEXIBLE SUBSTRATE

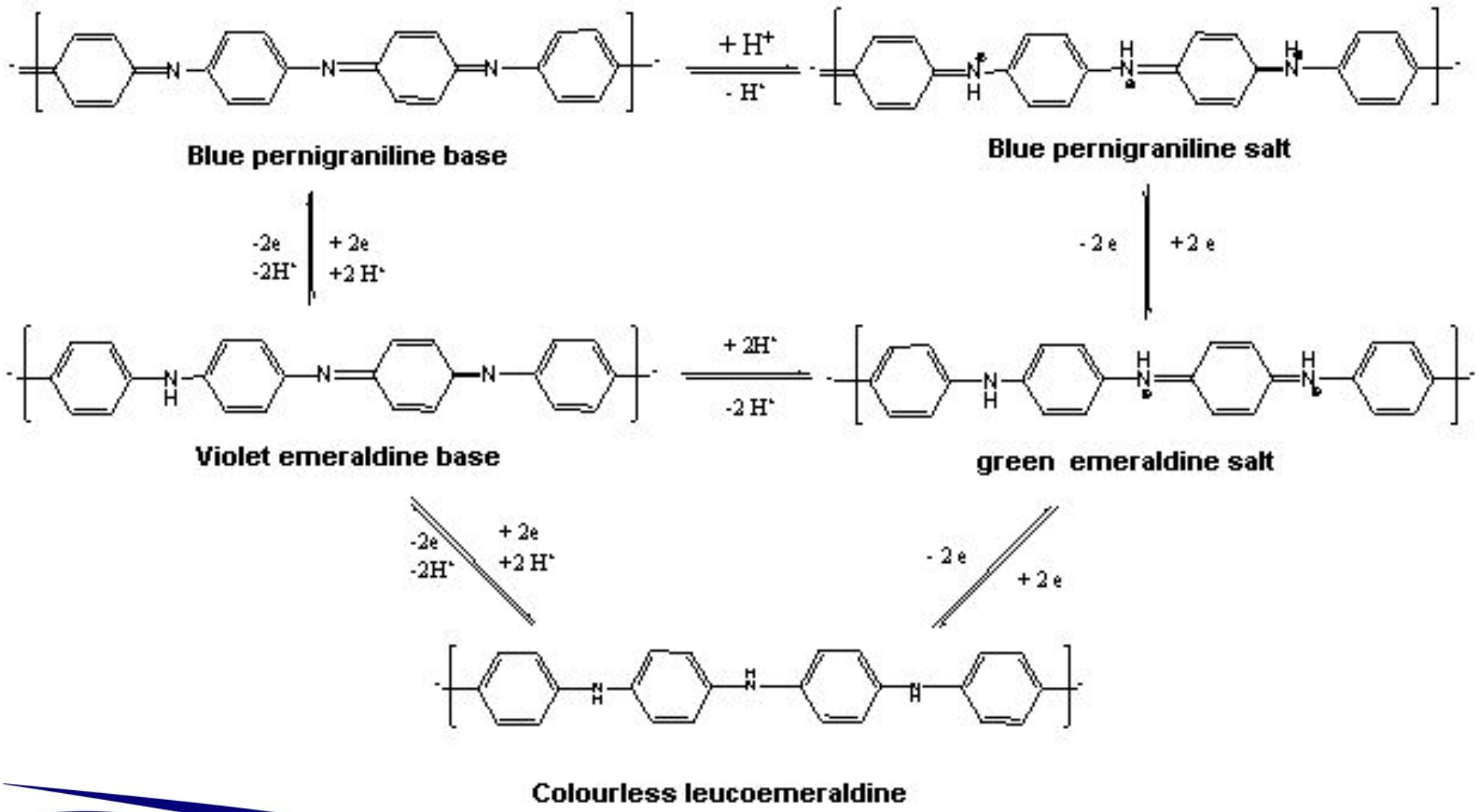




Simple learning procedure

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

RED-OX STATES OF PANi AND ELECTROCHEMICAL TRANSITIONS BETWEEN THEM

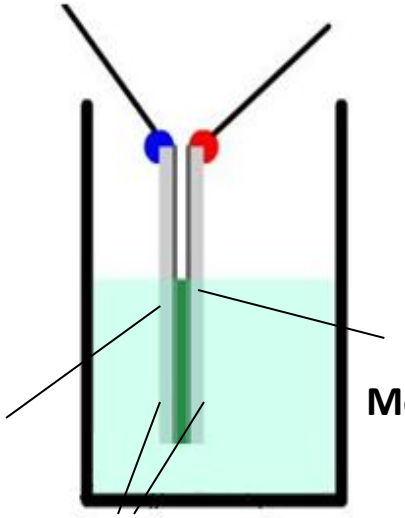


ИПХФ РАН

ИНЭОС

MEASUREMENT SET UP AND EXPERIMENTAL PROCEDURE

Electrochemical potentiostat



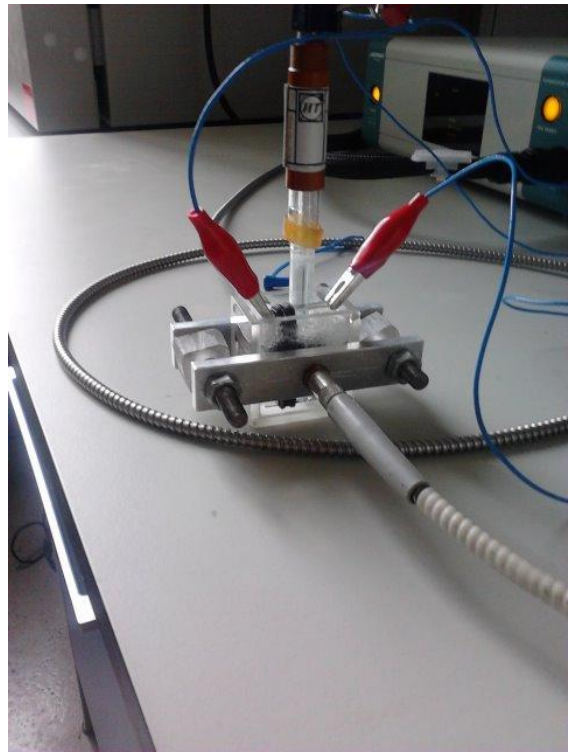
Measured film

Solution $HCl/LiClO_4$

acetonytile,

water

ITO glasses

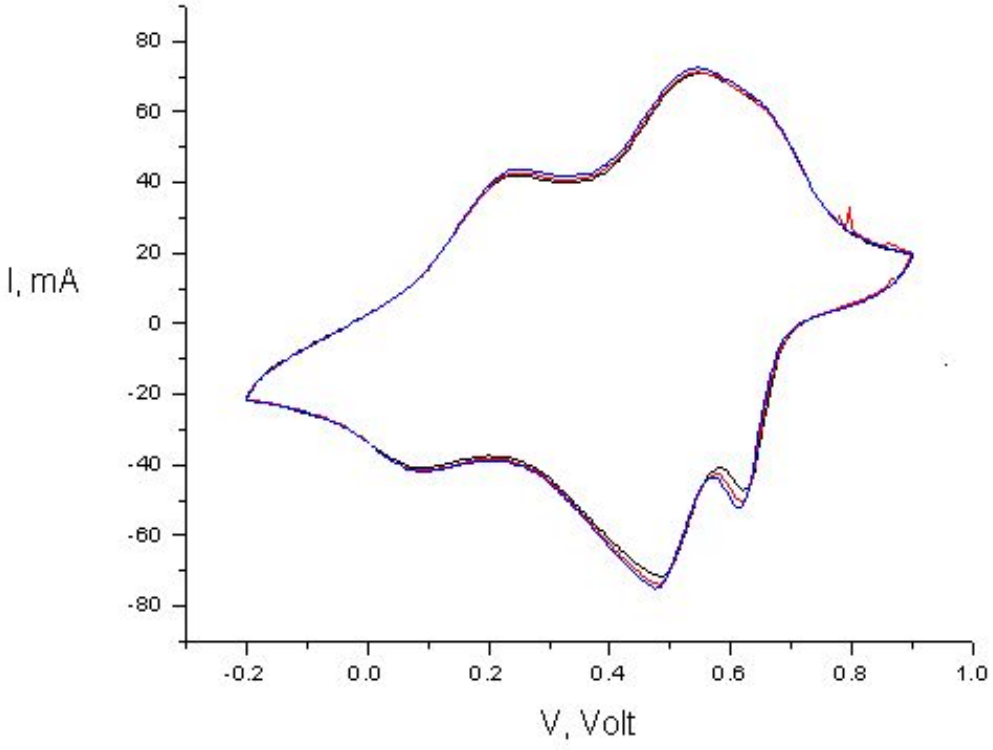


ИПХФ РАН

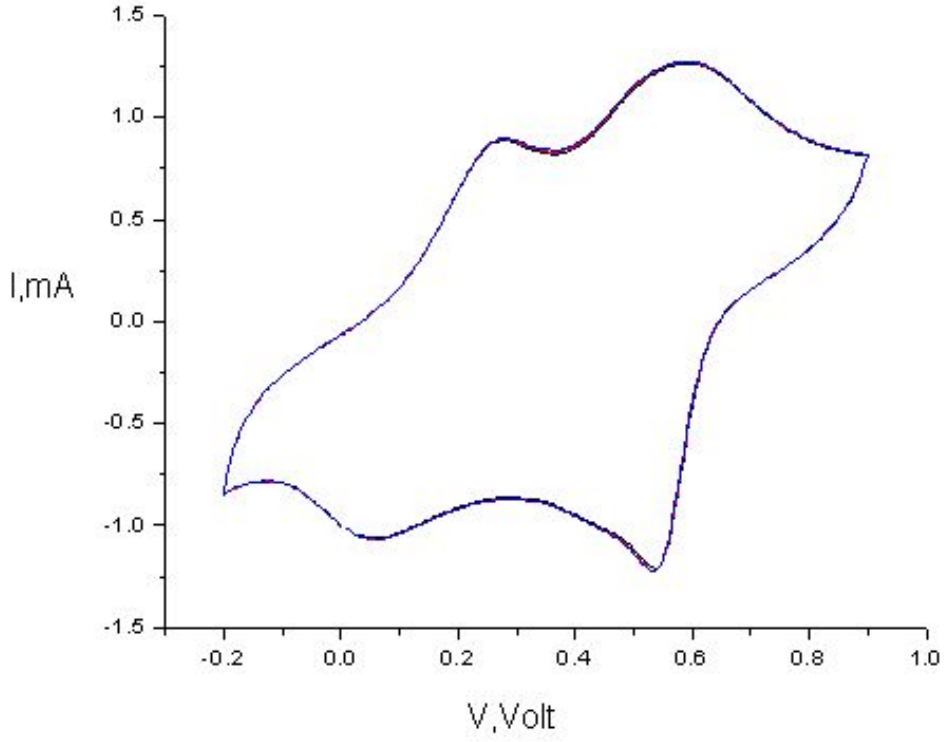
ИНЭОС

PANi IN SOLUTION OF $LiClO_4$/HCl CYCLOVOLTAMMETRY

Red – Ox peaks are very broad, it is important



Cyclovoltammogramm in 0.1 M HCl in water



Cyclovoltammogramm in 0.1 M $LiClO_4$ in acetonytrile

ИПХФ РАН

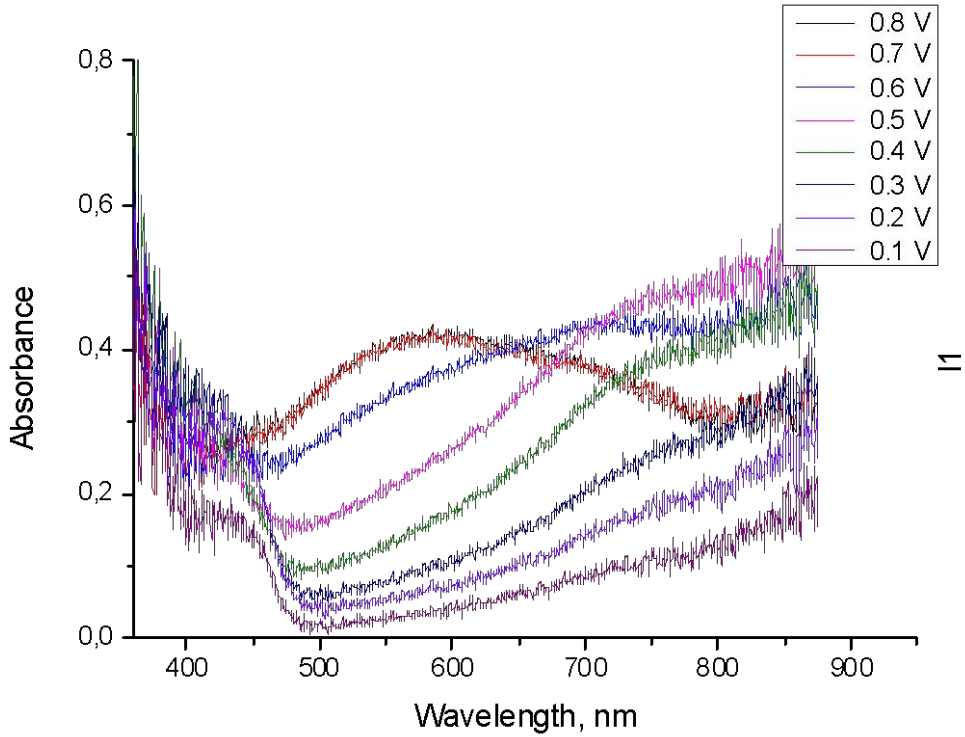
ИНЭОС

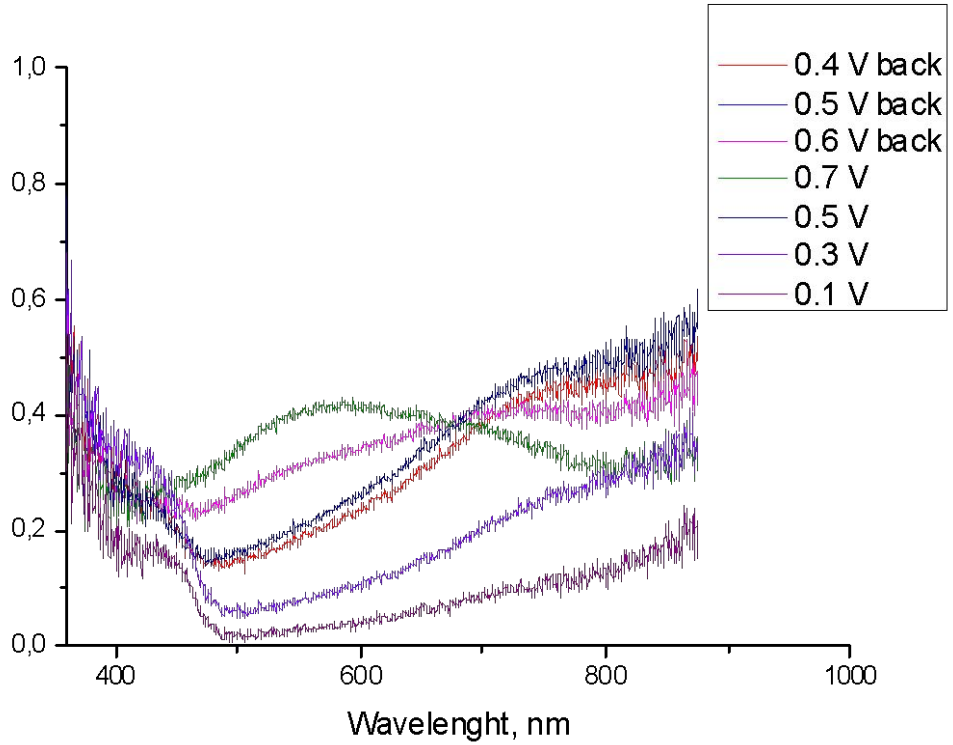
ELECTROCHROMIC CYCLOVOLTAMMOGRAMM

ИПХФ РАН

ИНЭОС

SPECTROELECTROCHEMISTRY MEASUREMENTS





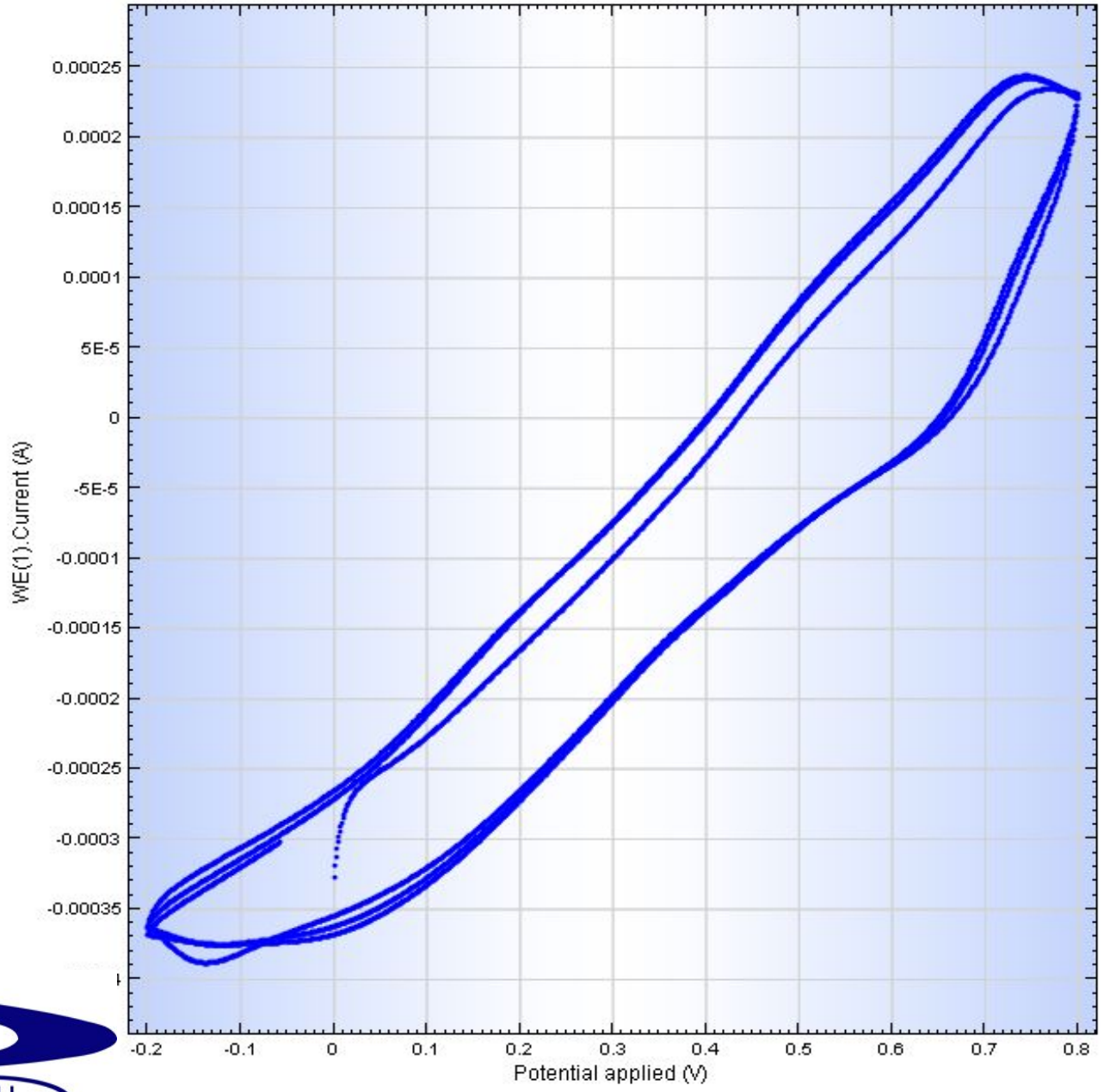
PANi film versus Ag/AgCl, 0.1 M HCl Water

Backwards, with memristive effect on absorbance spectra

ИПХФ РАН

ИНЭОС

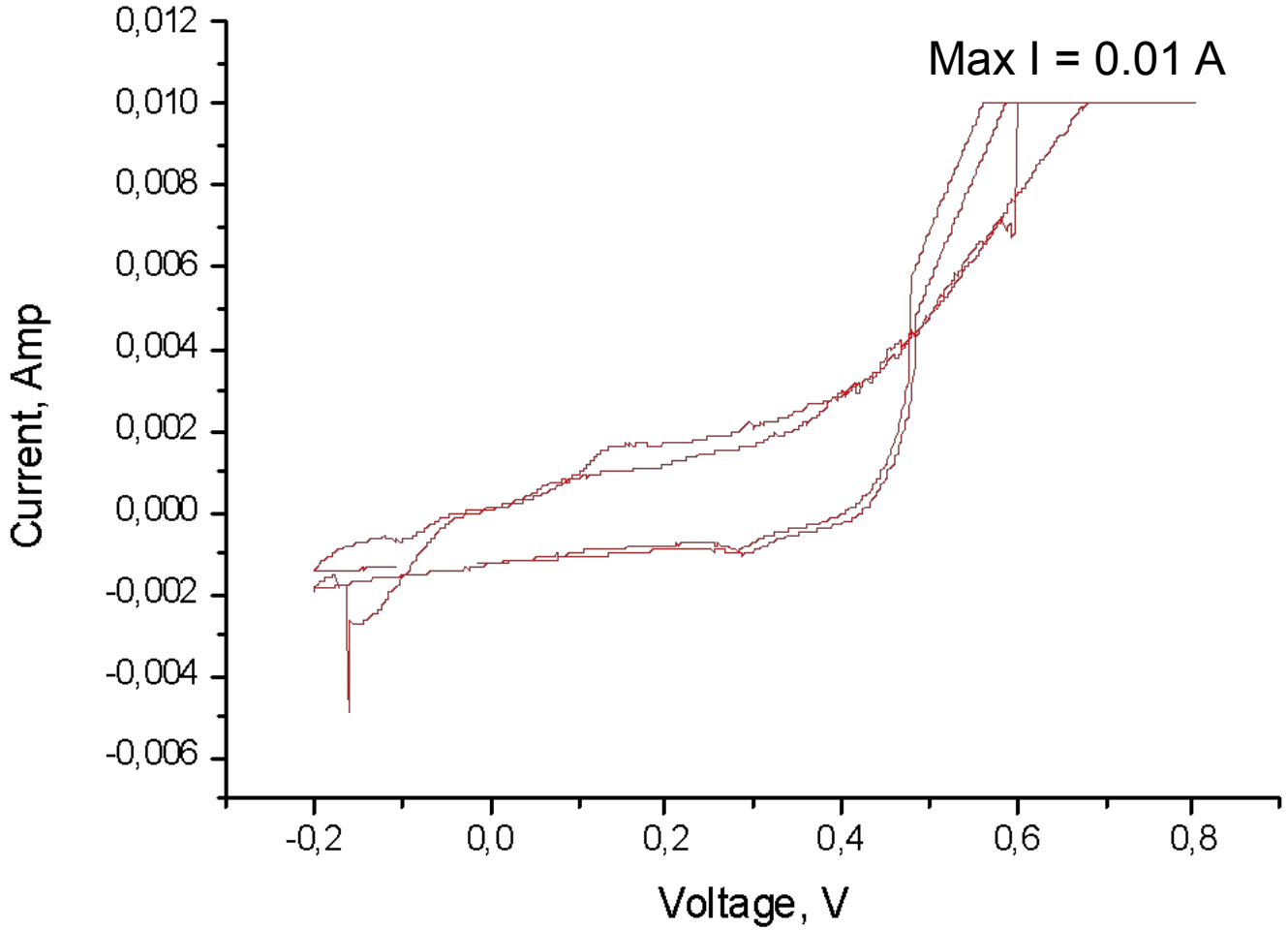
MEMRISTIVE EFFECT IN_PLANE CONDUCTANCE (I-V CURVES)



ИПХФ РАН

ИНЭОС

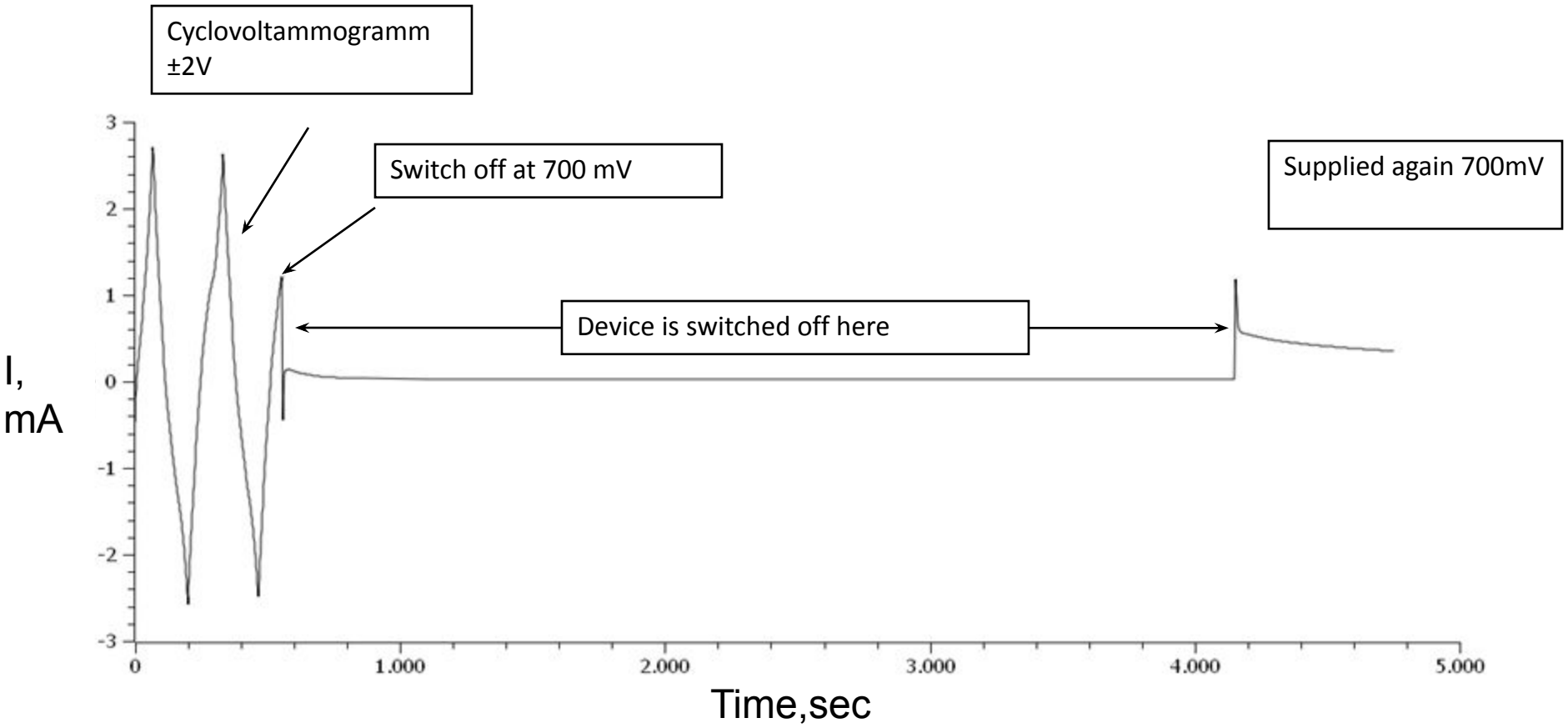
PANI FILM-THROUGH CONDUCTIVITY MEASUREMENT



PANi film conductivity, 0.1M HCl water, Ag/AgCl

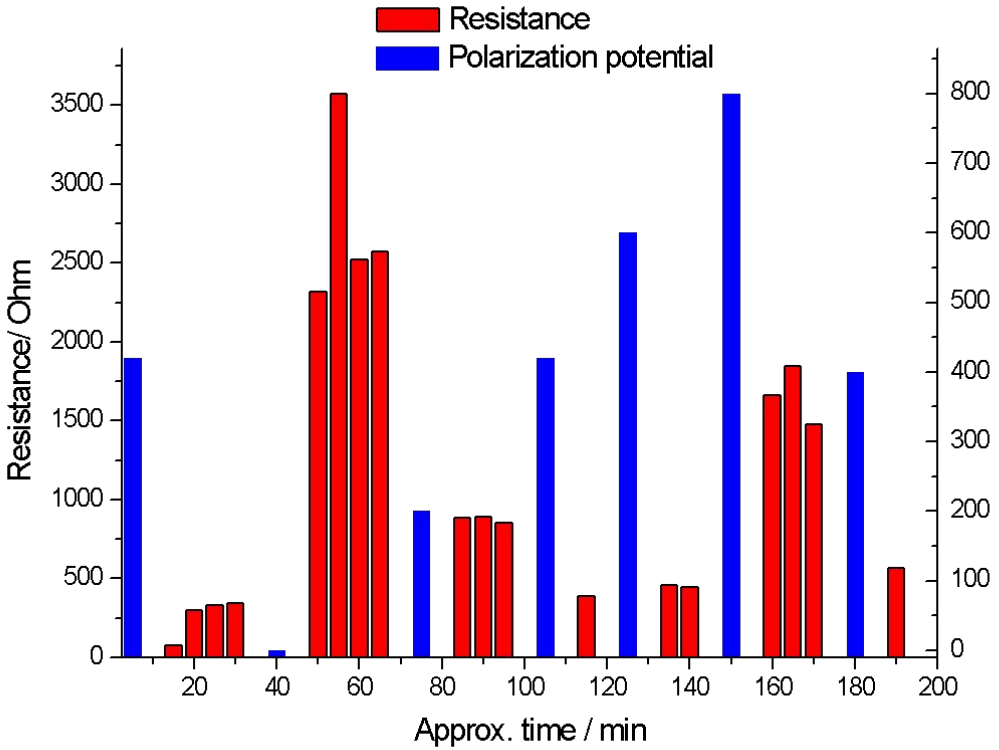
ИПХФ РАН

MEMRISTIVITY: RESISTANCE AFTER SWITCH OFF VOLTAGE

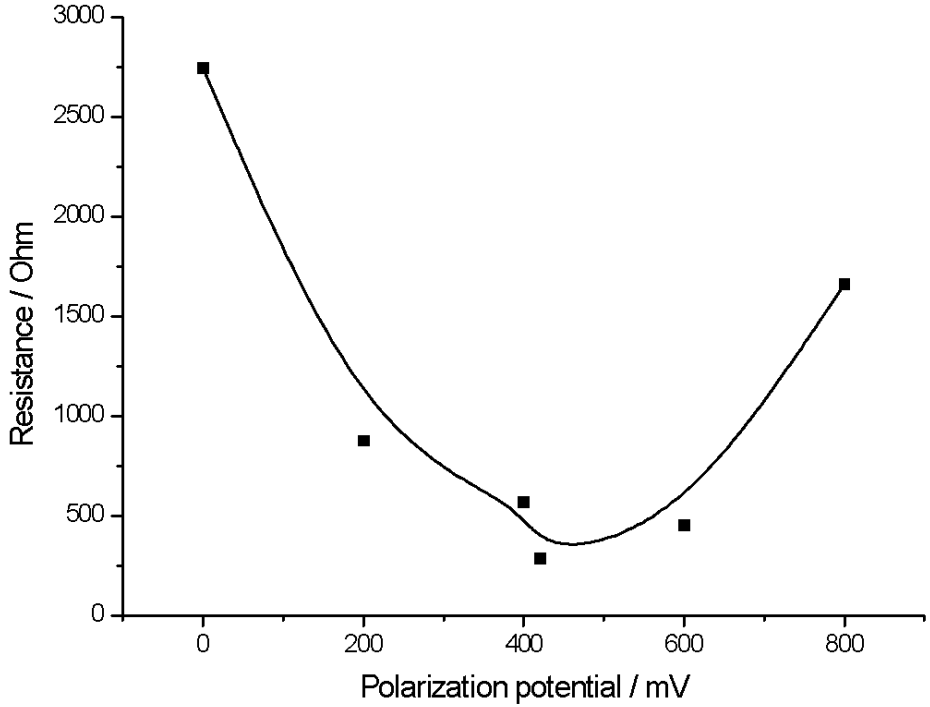


Memristive effect as from voltage switch off/ switch on.

RESISTANCE IN PLANE, DRY FILM – AC CONDUCTIVITY



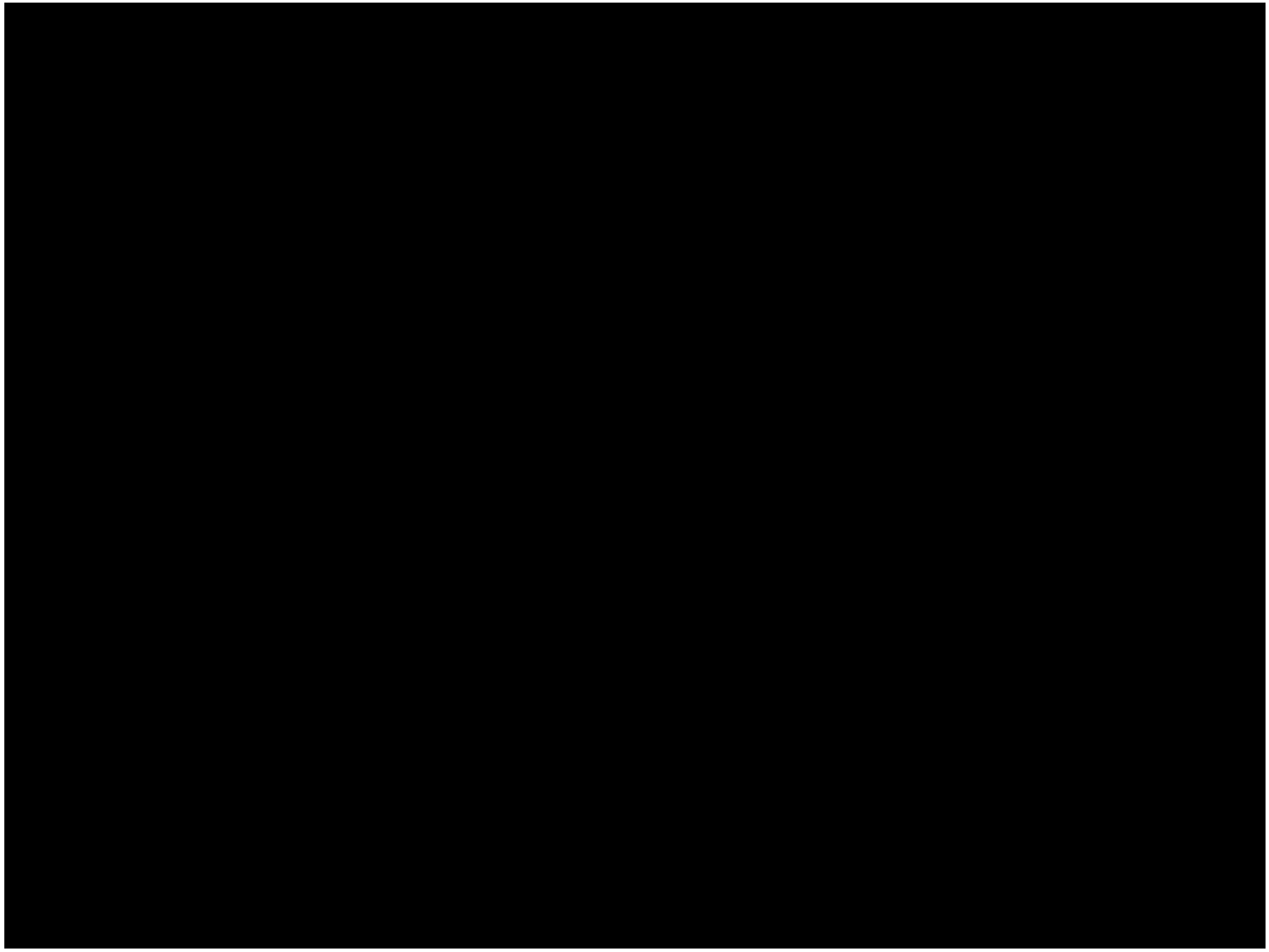
Bias voltage – 0, amplitude – 5 mV



ИПХФ РАН

ИНЭОС

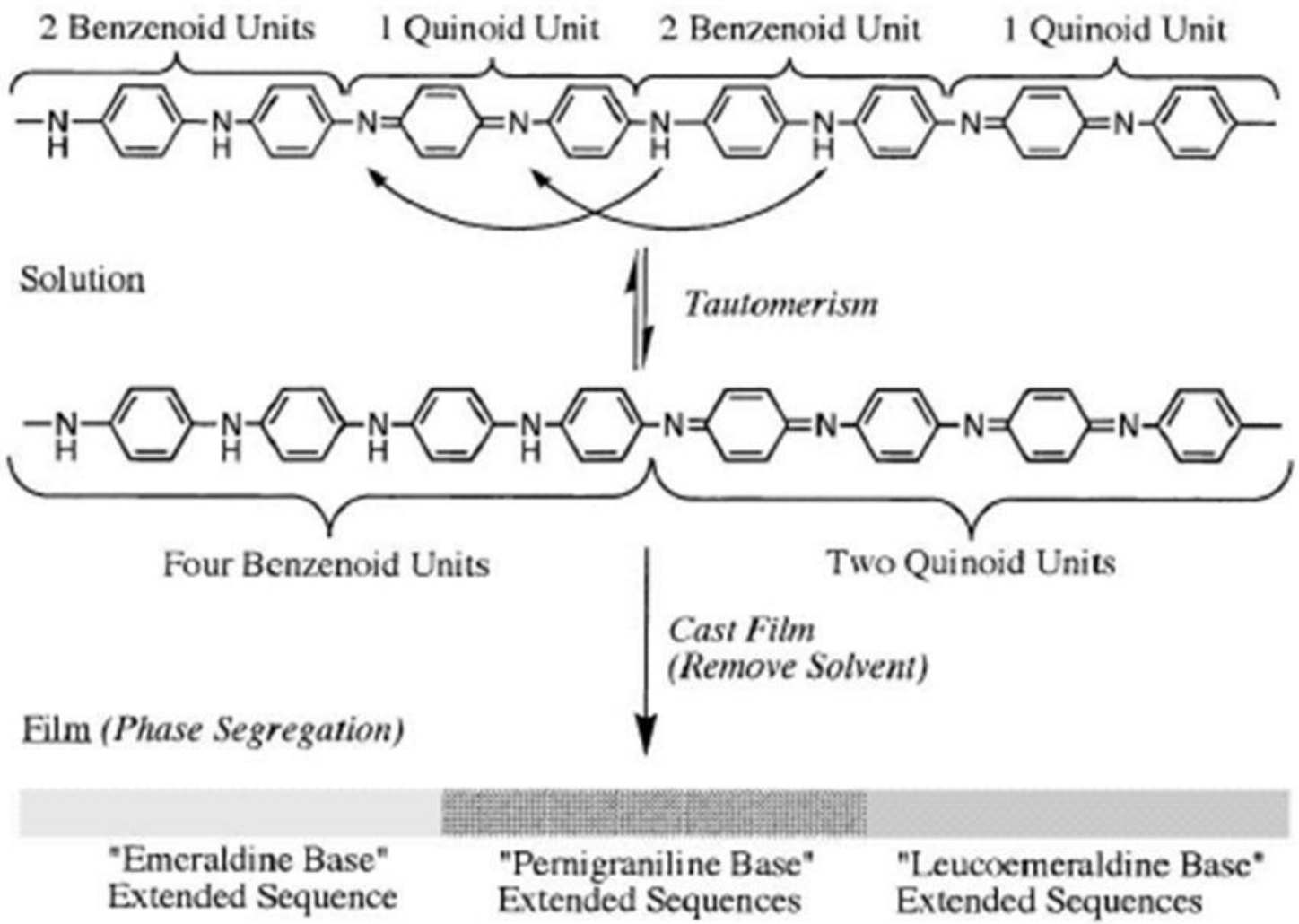
MEMRISTIVE EFFECT MOVIE



ИПХФ РАН

ИНЭОС

BLOCK NATURE OF CONDUCTIVITY IN PANi – EXPLANATION OF MEMRISTANCE



ИПХФ РАН

ИНЭОС

PROPAGATION OF RED-OX FRONTS IN PANi AS A BASIS FOR NEURAL NETWORKS

ИПХФ РАН

ИНЭОС

USE OF PANi NEURAL NETWORK FOR IMAGE PROCESSING

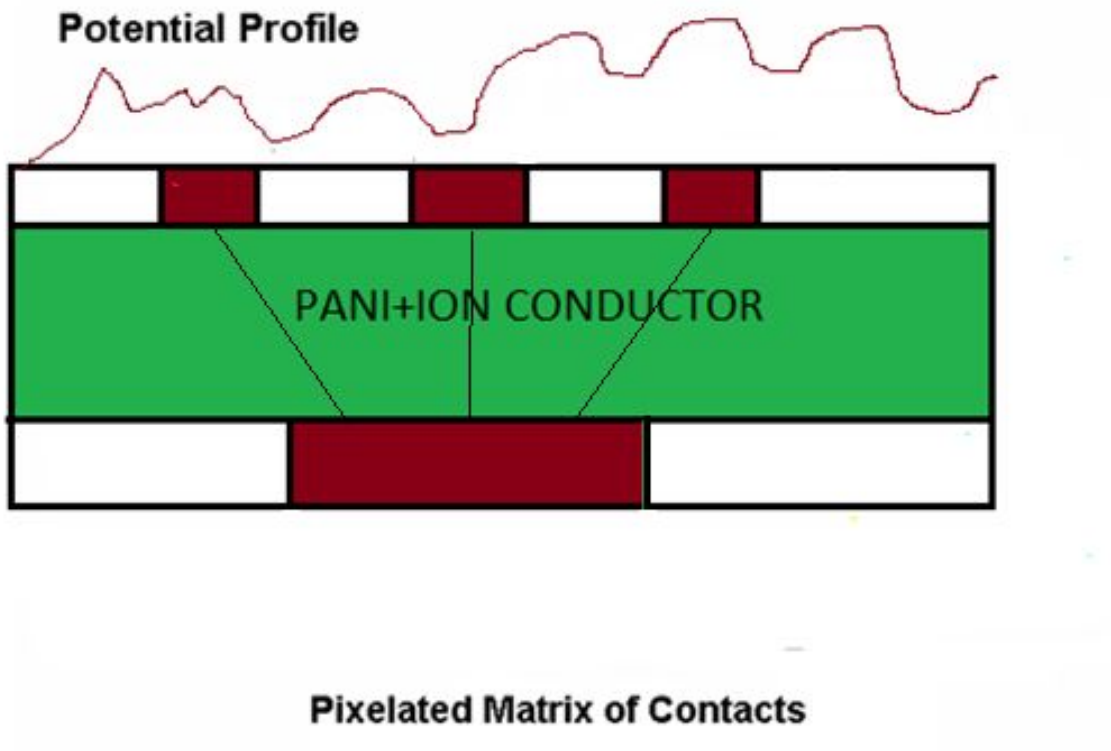


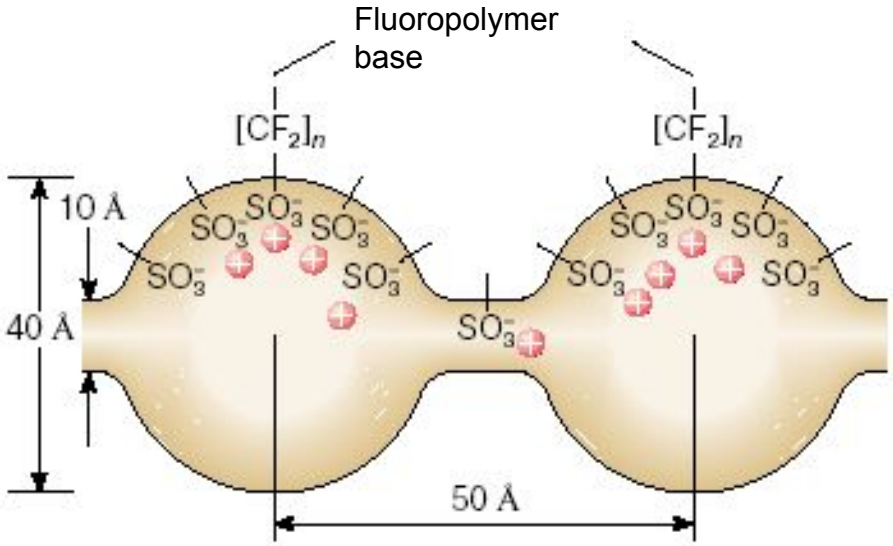
Image processing operations possible:

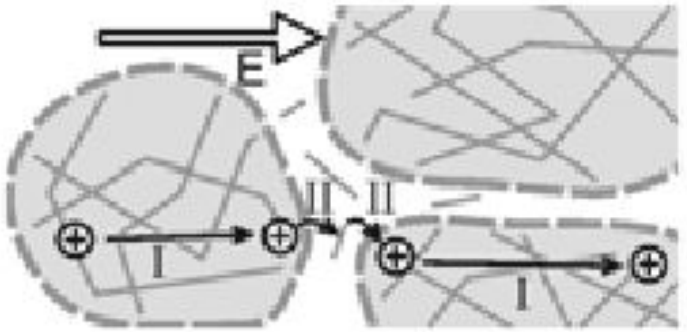
1.Image segmentation
2.Contrasting
3.Simple object recognition

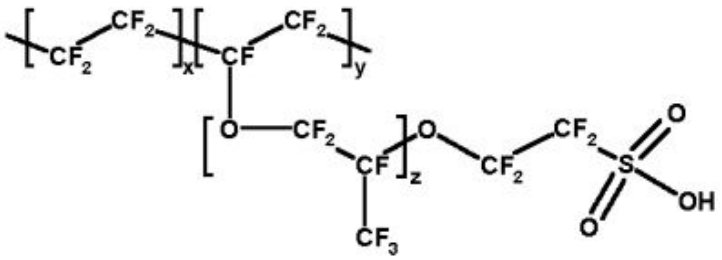
ИПХФ РАН

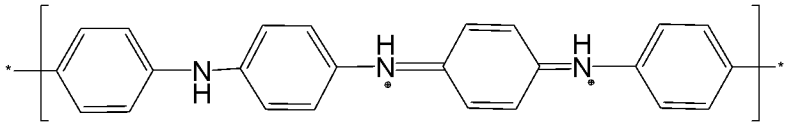
ИНЭОС

PANi-NAFION INTERPOLYELECTROLYTE COMPLEXES



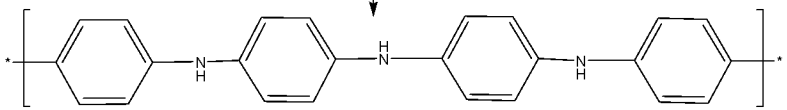






Green emeraldine salt

+ 2 e

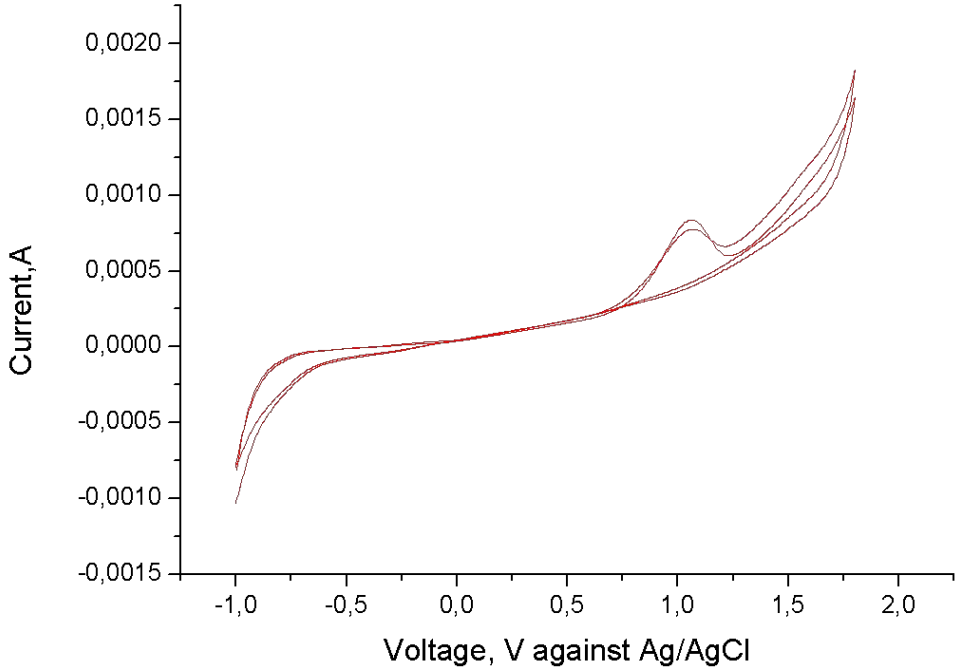


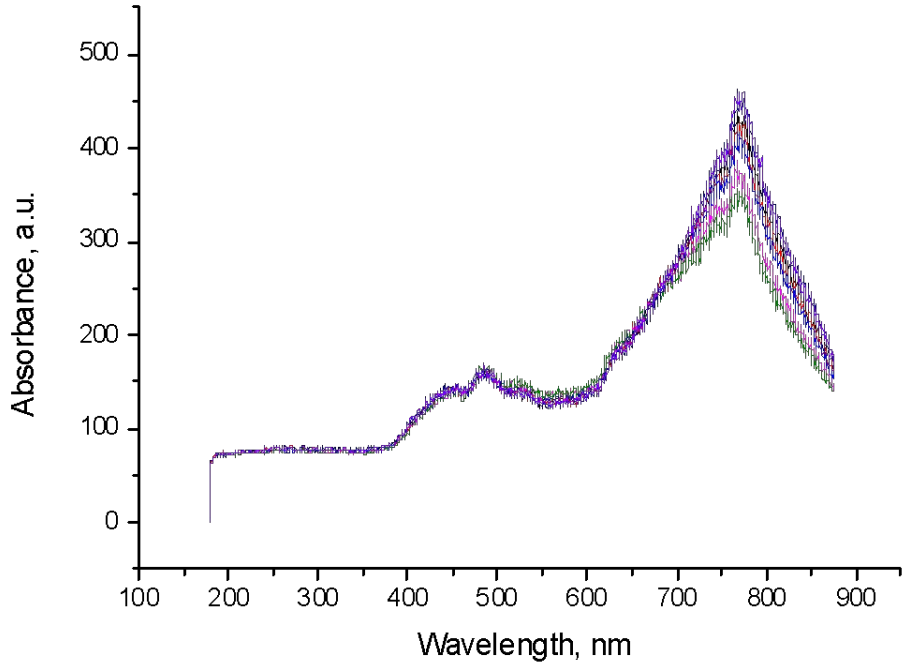
Colourless leucoemeraldine

ИПХФ РАН

ИНЭОС

PANi-NAFION IN SOLUTIONS OF $LiClO_4$, Acetonytrile





Cyclovoltammogramm in 0.1MLiClO4, acetonytrile, versus Ag/AgCl

Absorbance spectra of films during cyclovoltammetry

ИПХФ РАН

ИНЭОС

CONCLUSIONS

- *Polymer electrochemistry is a complicated matter*
- *Polyaniline-based memristor operating mechanism is determined by change of Red-Ox states of PANi*
- *Probably TiO_2, VO_x memristors operation is similar.*
- *It is not clear why PANi-Nafion films do not change Red-Ox states*
- *It is possible to make simple neural networks based on PANi*

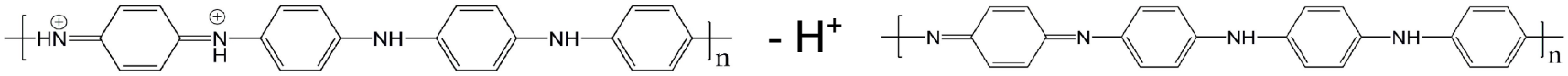
ИПХФ РАН

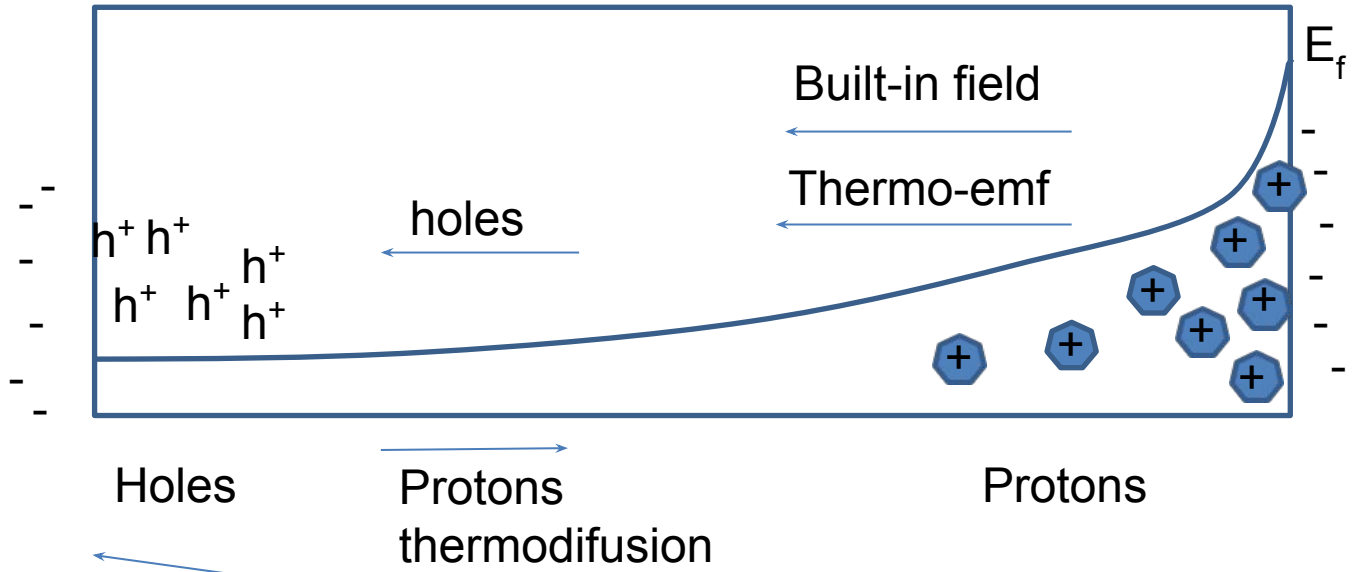
ИНЭОС

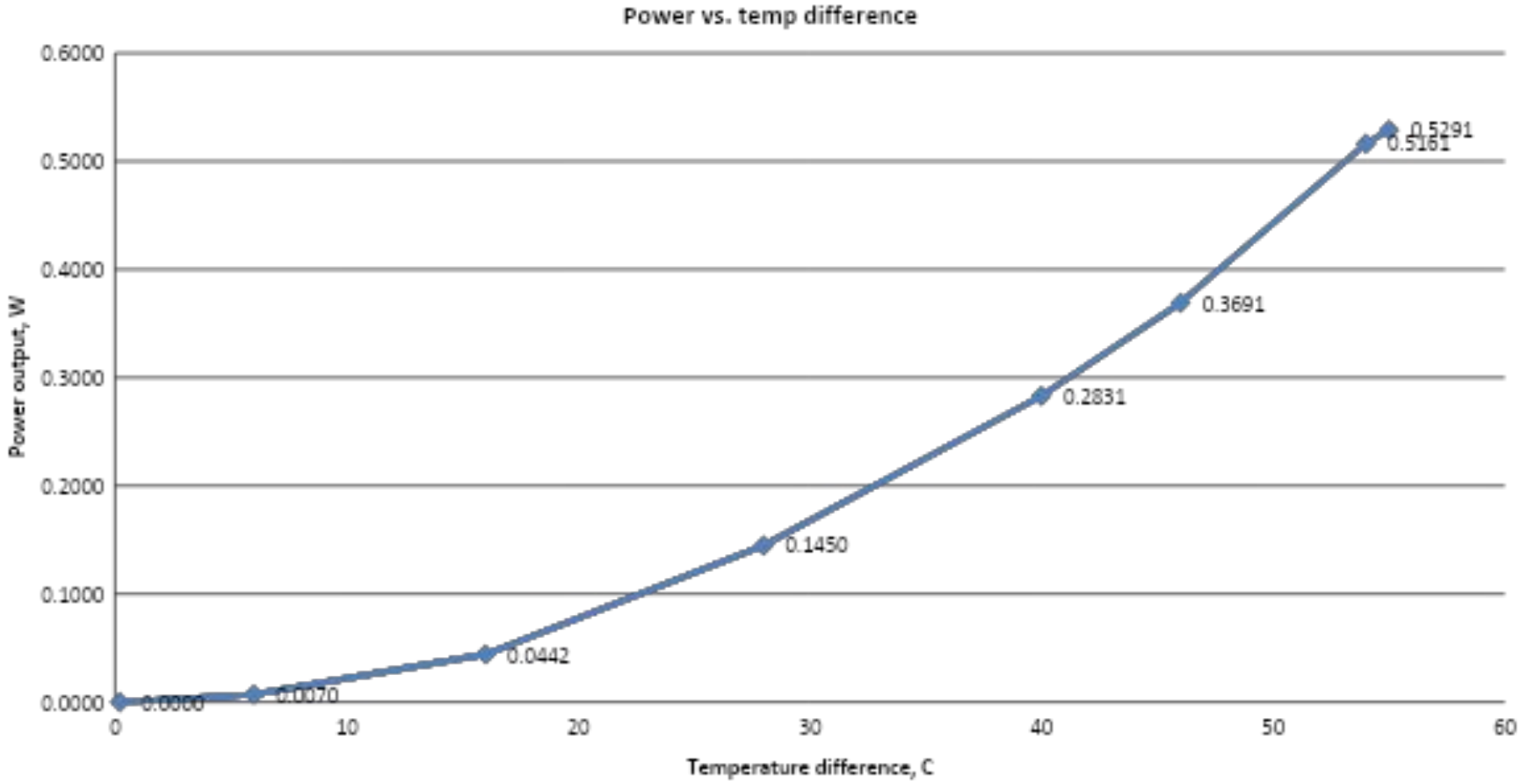
$$E_{red} = E^{\ominus}_{red} - \frac{RT}{zF} \ln \mathbb{Q} = E^{\ominus}_{red} - \frac{RT}{zF} \ln \frac{a_{Red}}{a_{Ox}}$$

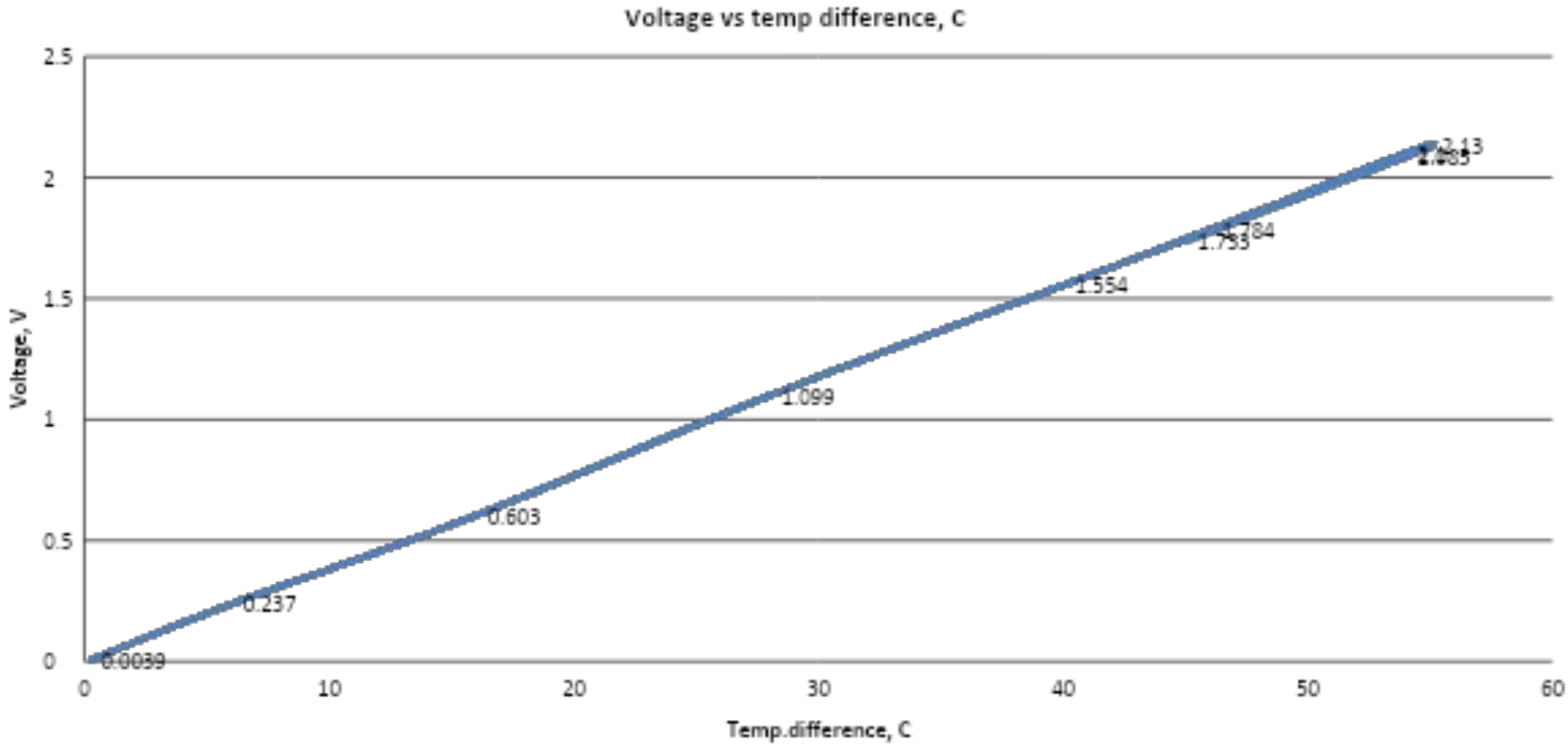
Protonated PANi

Deprotonated PANi

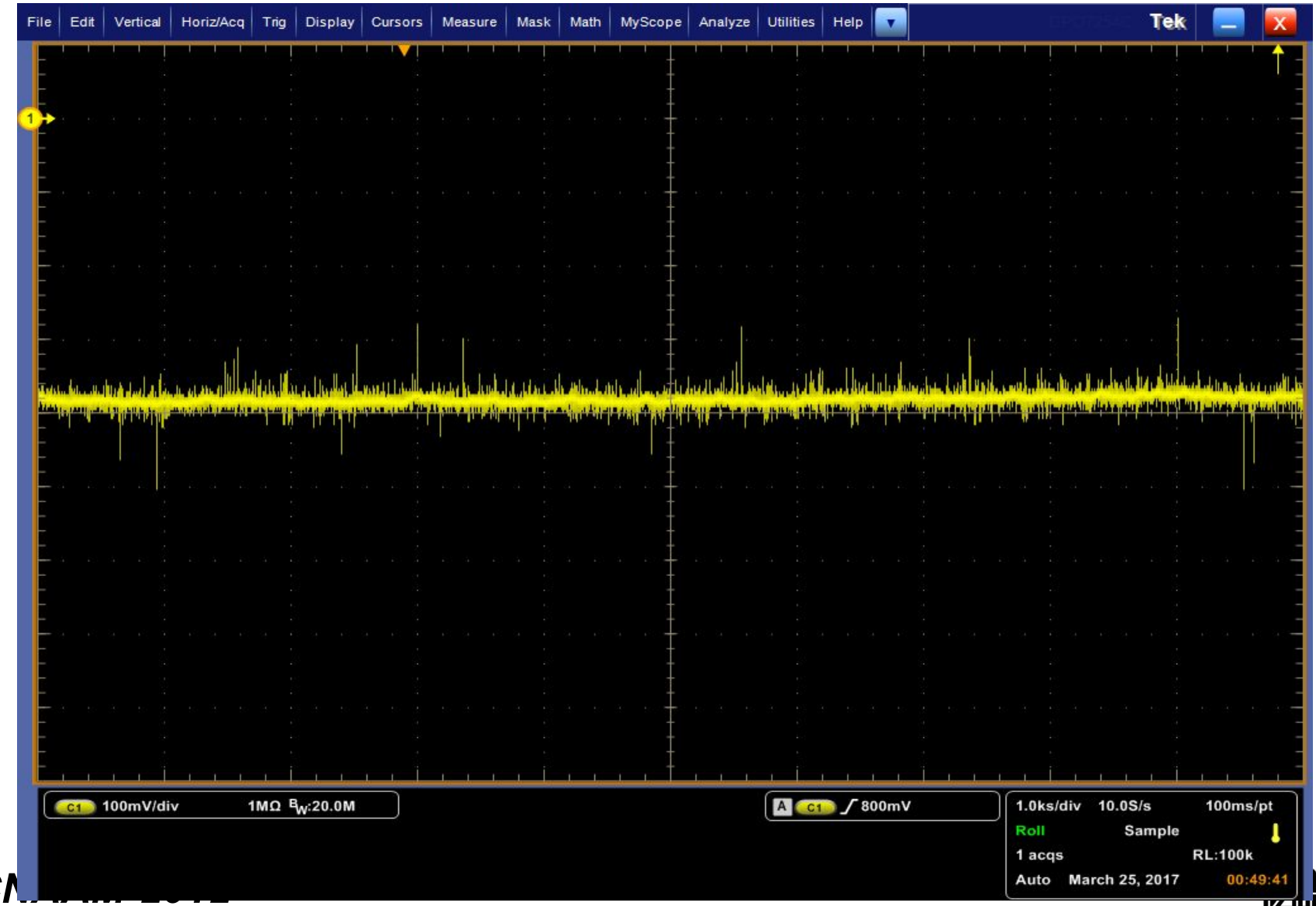




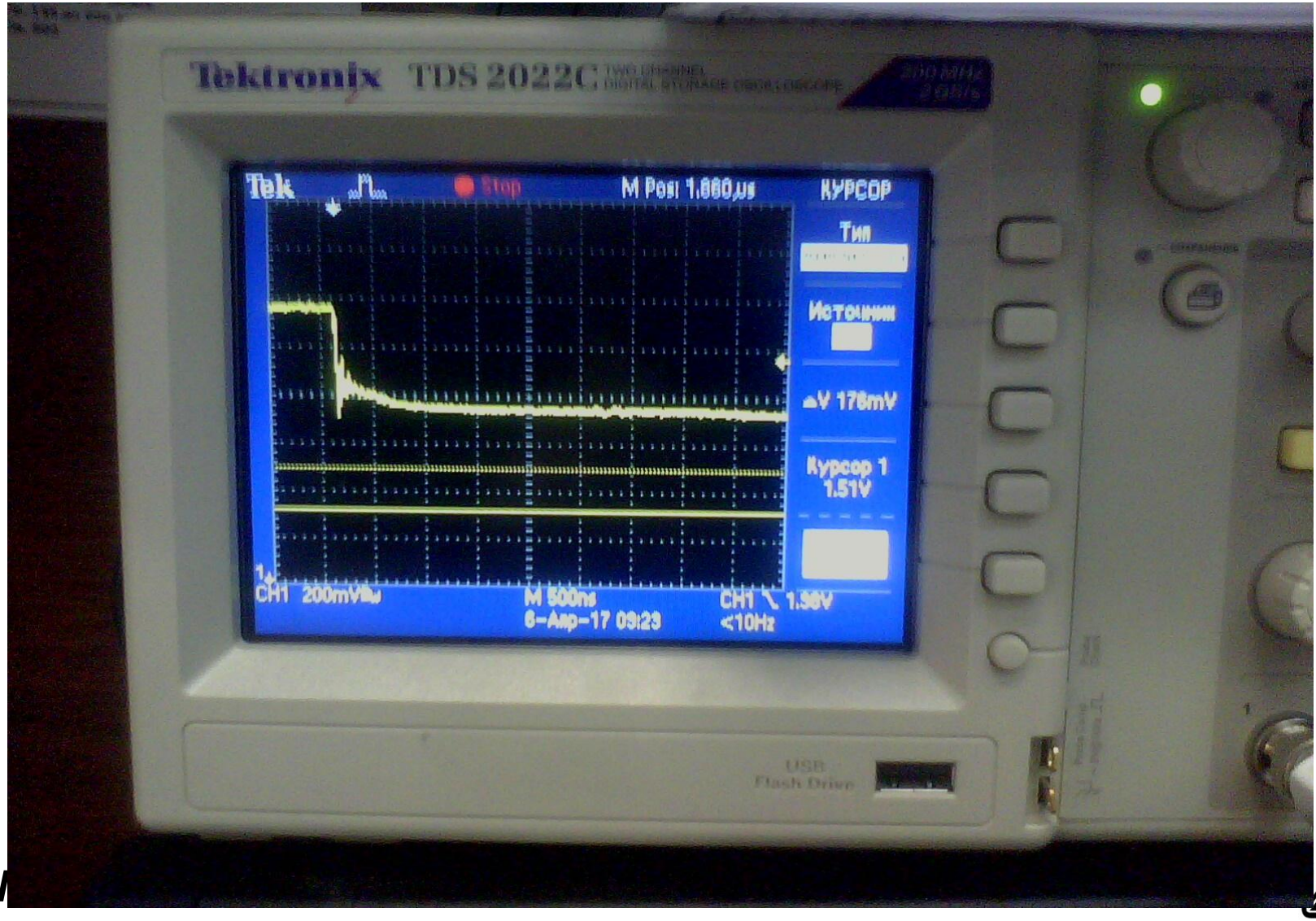

Power vs. temp difference
Power output, W
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
0.0000
0.0070
0.0442
0.1450
0.2831
0.3691
0.5161
0.5291
0
10
20
30
40
50
60
Temperature difference, C


Voltage vs temp difference, C
Voltage, V
Temp.difference, C
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
60
0.0039
0.237
0.603
1.099
1.554
1.733
1.784
2.13

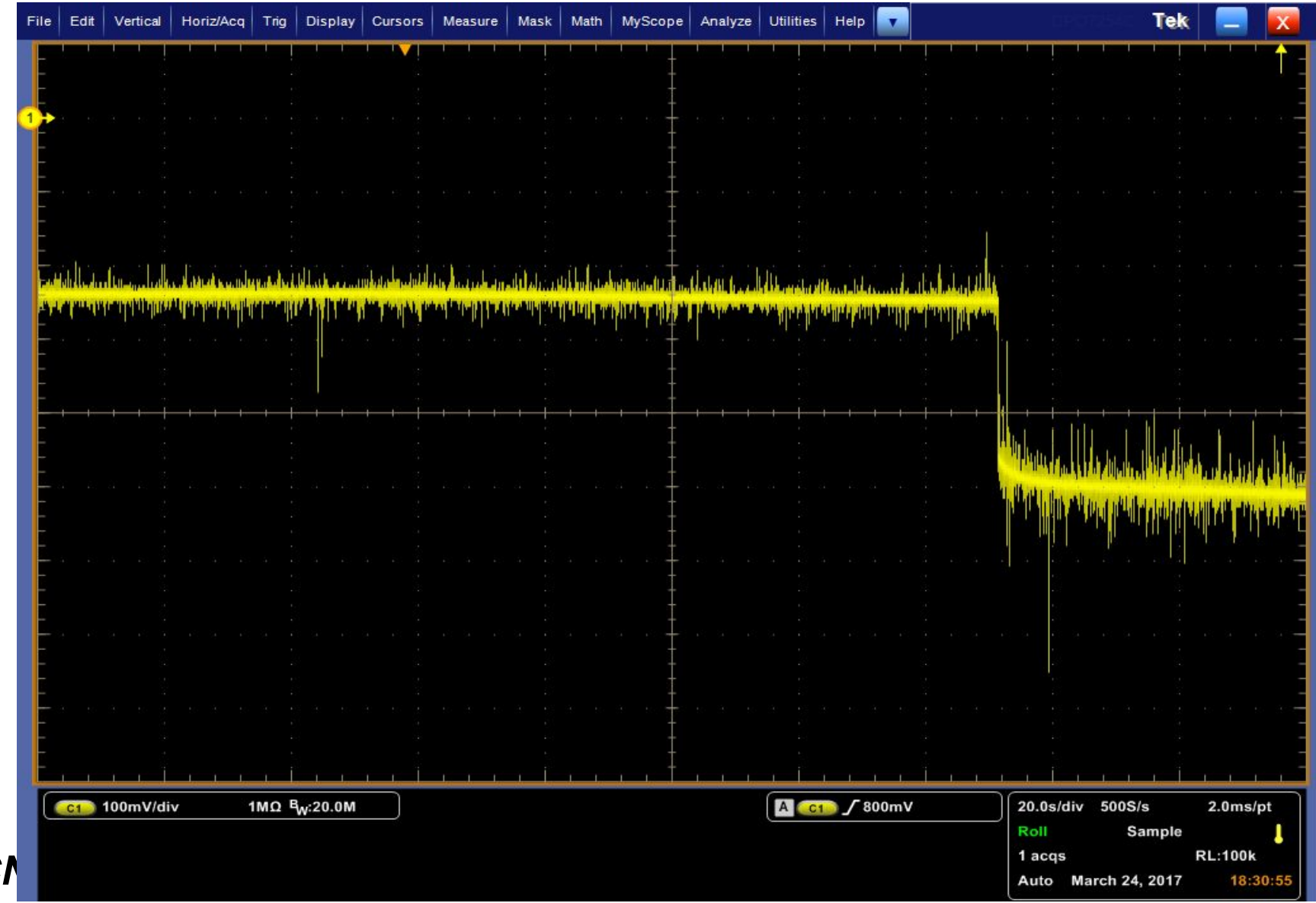
Stability at 55°C



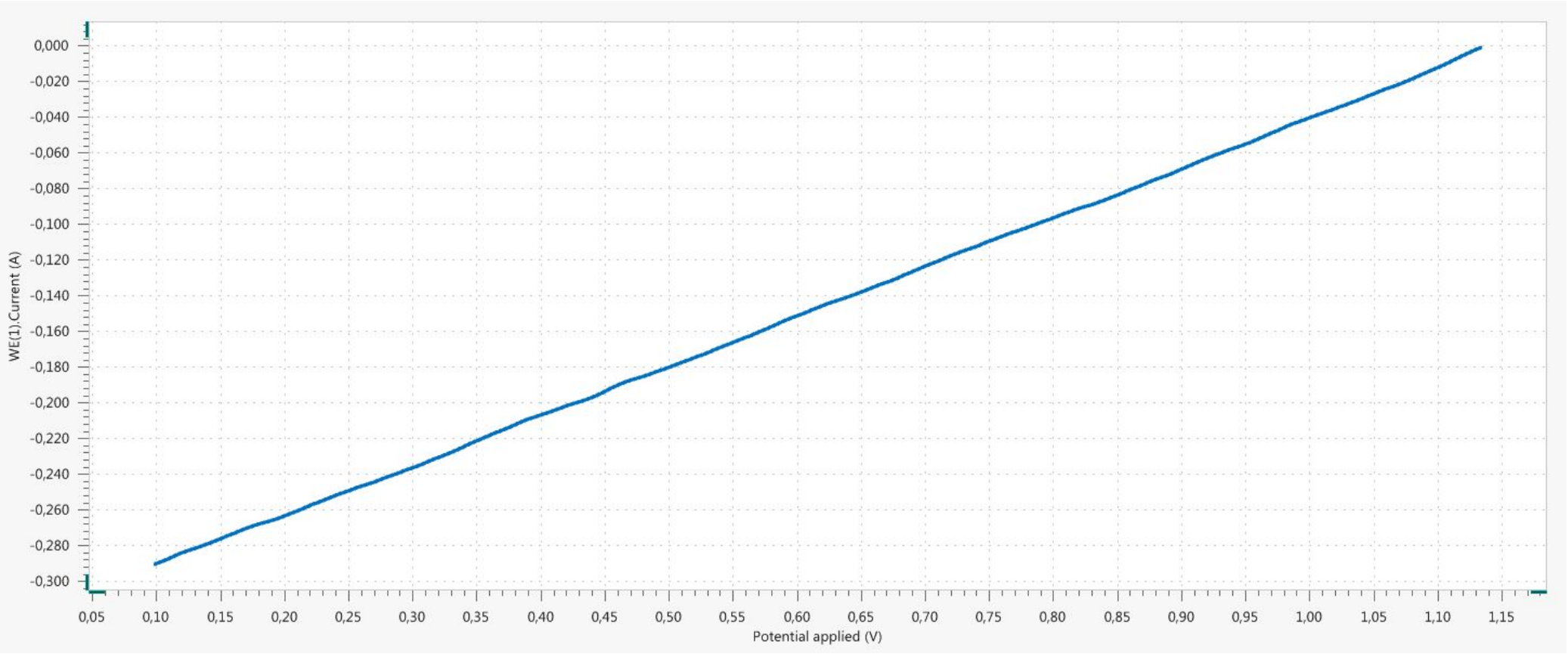
Discharge to short circuit



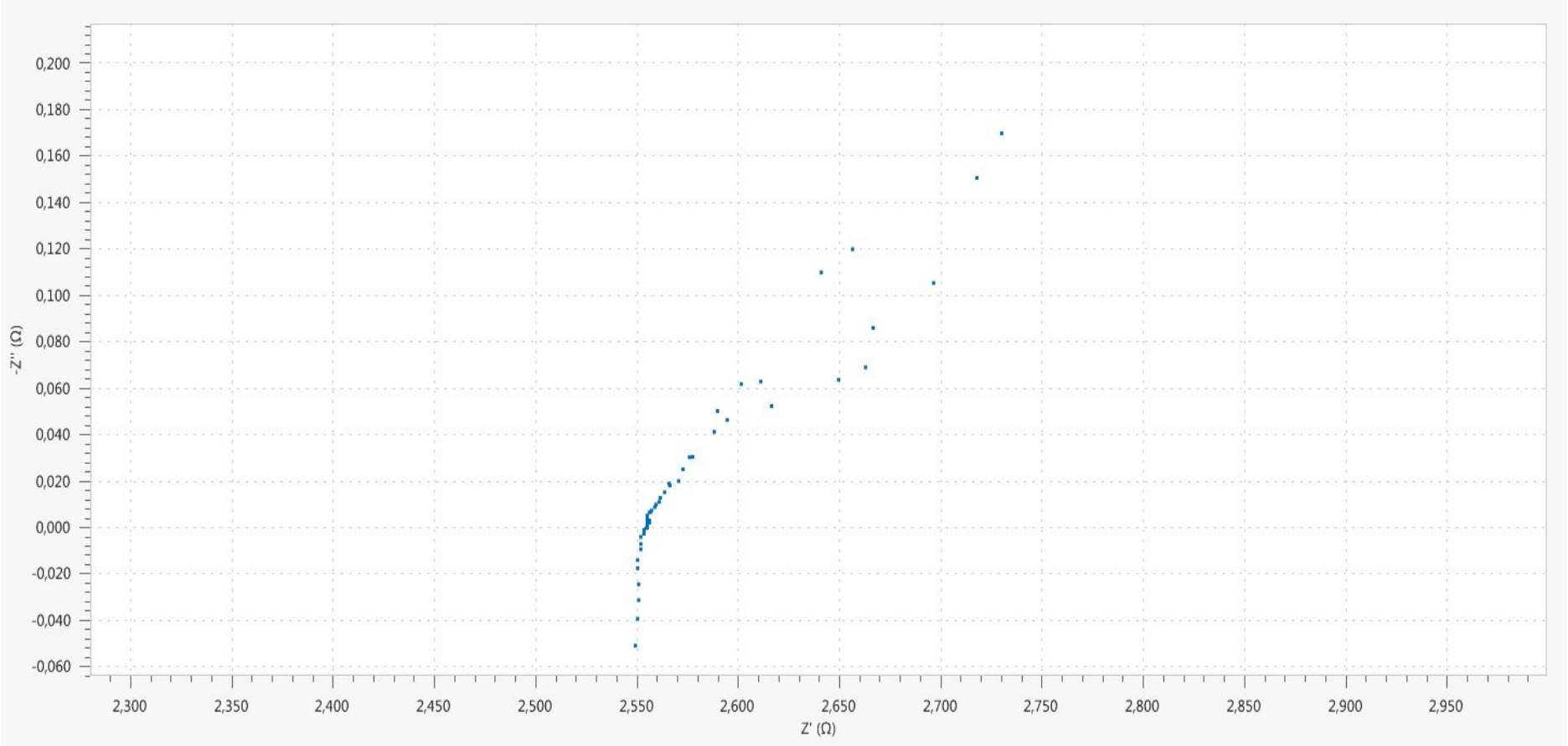
Discharge to 3 Ohm



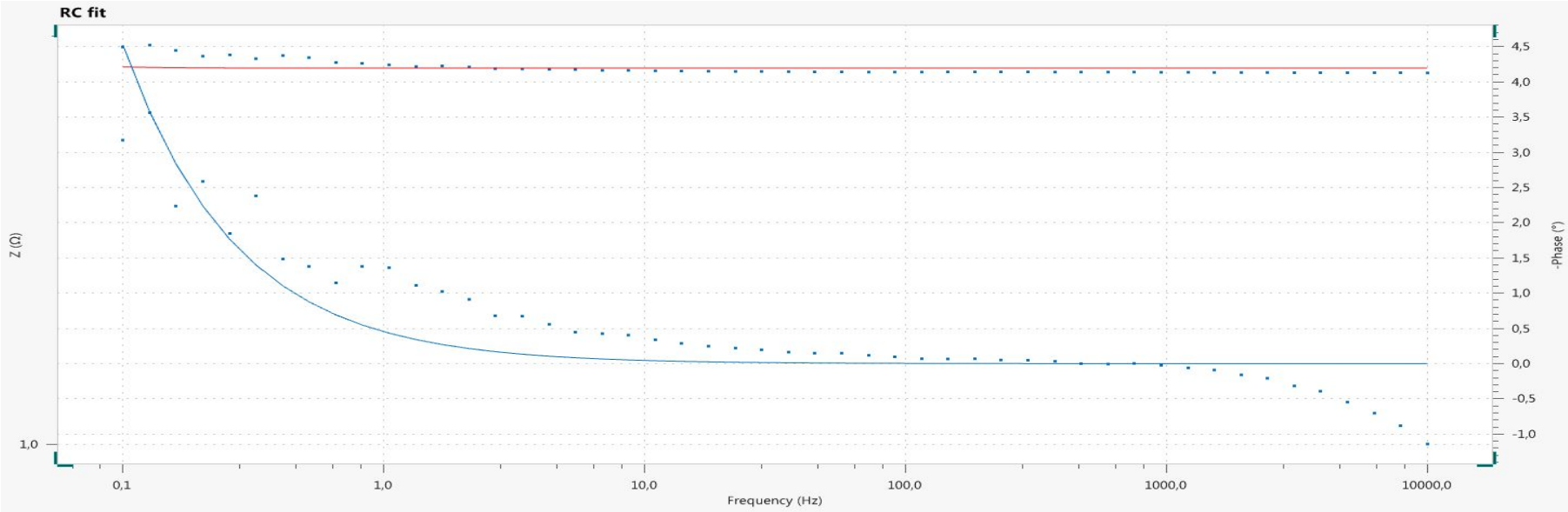
I-V curve at 40 C

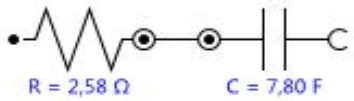


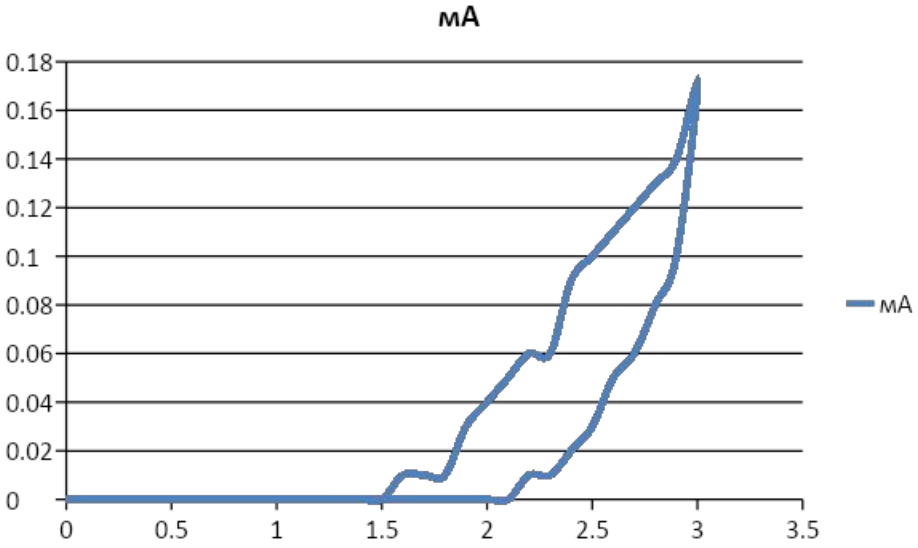
Impedance at 40 C

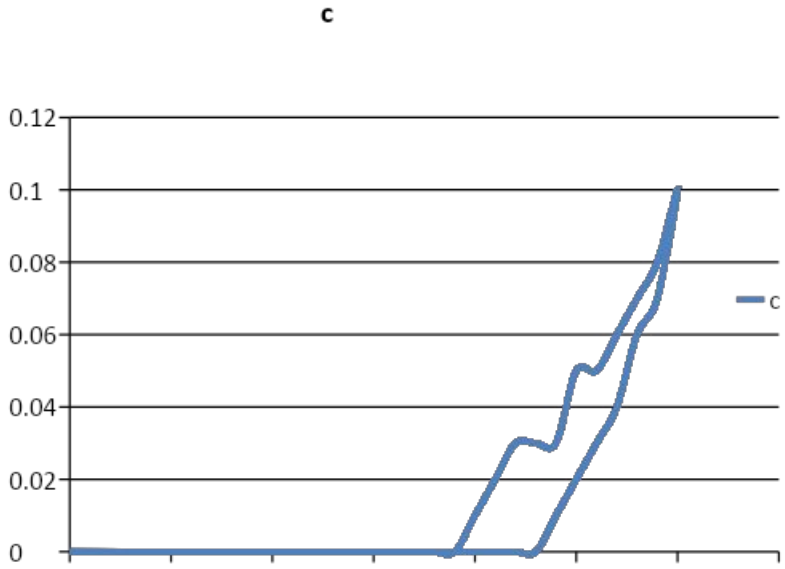


Results of approximation of equivalent circuit






мА
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
2.5
3
3.5
мА


с
0.12
0.1
0.08
0.06
0.04
0.02
0
с