

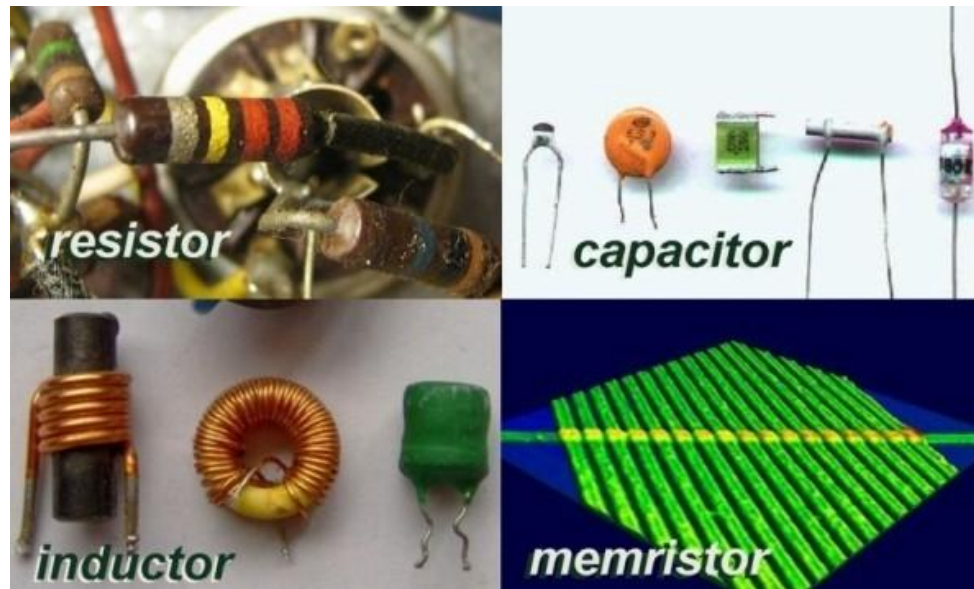
Resistive switch Red-Ox behavior as mechanism behind the operation of polyaniline memristors and neural network elements and PANI-based thermoelectrochemical cells

O.Bogomolova¹, J.Boeva¹, V.Sergeyev¹, D.Godovsky²

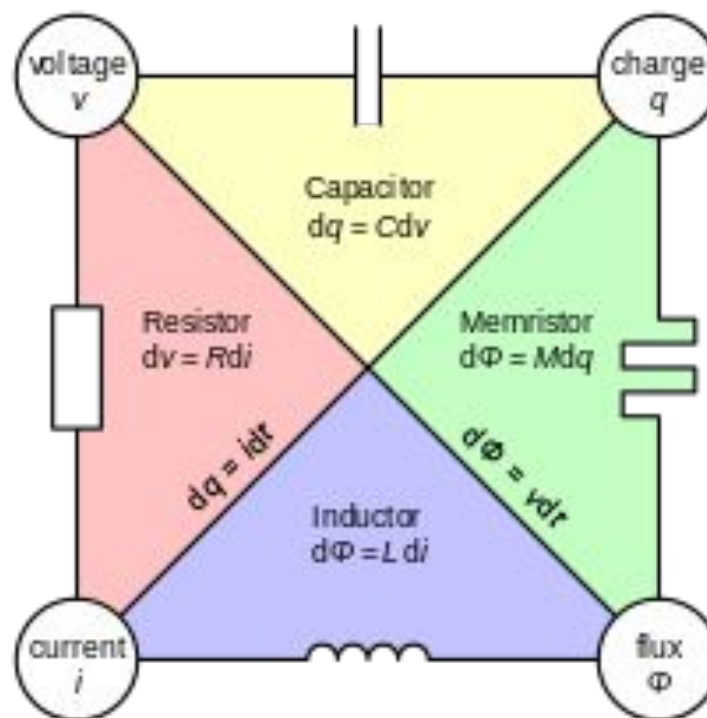
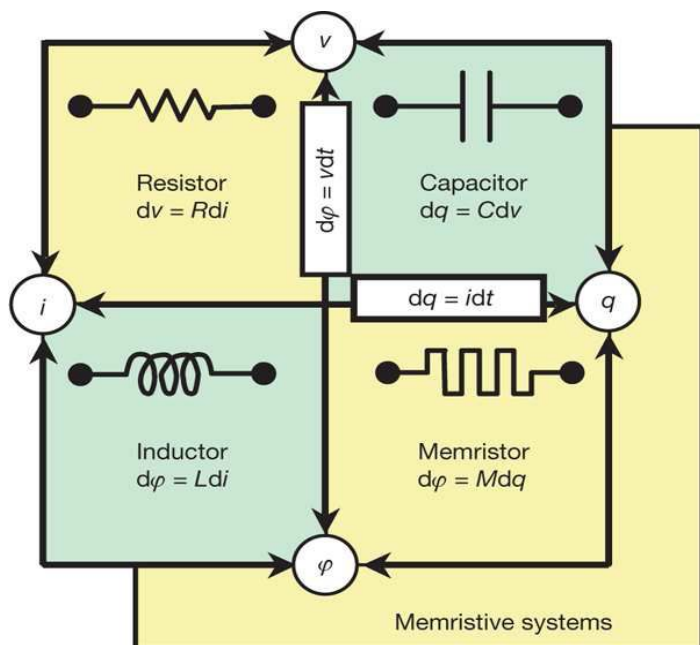
¹ Moscow State University, Chemistry Dept., Vorobievy Gory, 1 Moscow

² INEOS RAS, Vavilova str, 28, Moscow

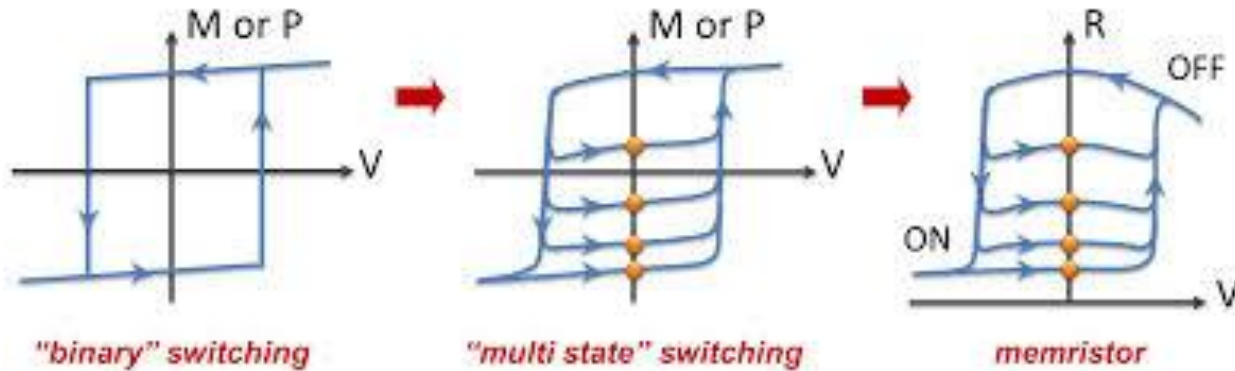
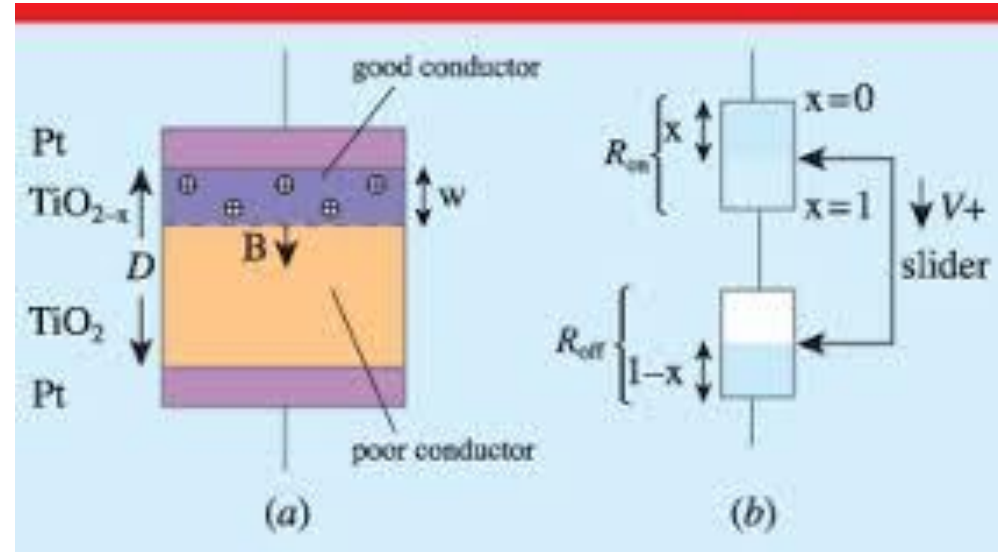
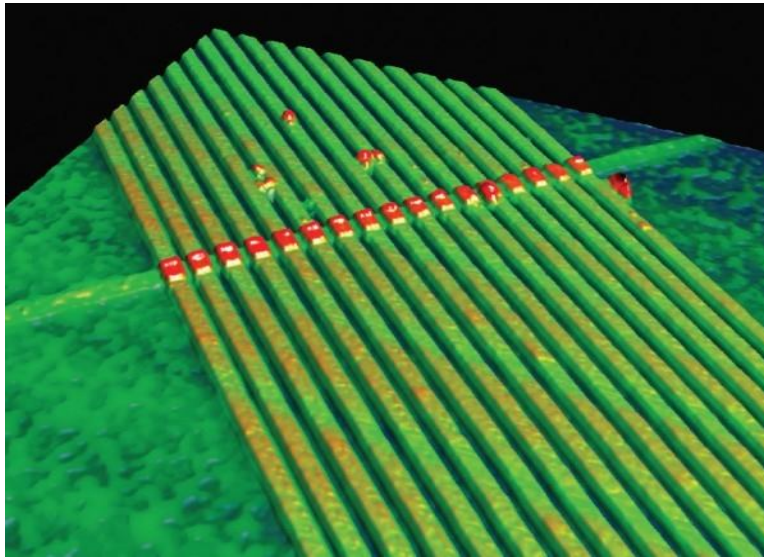
Also at LG TCM, LG Electronics, Moscow, Paveletskaya, 2/3



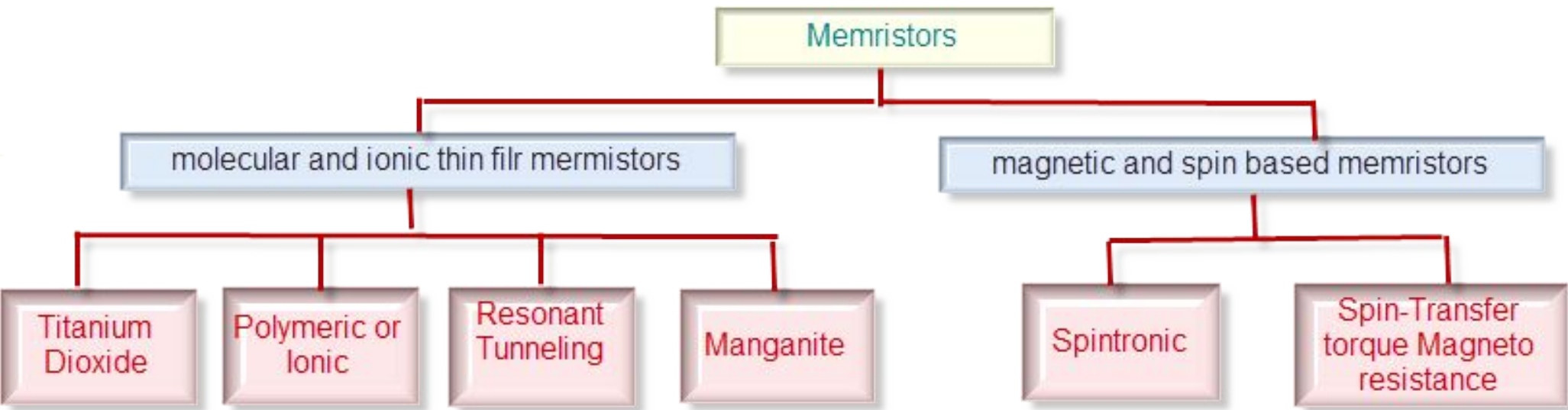
LEON CHUA THEORY BEHIND THE OPERATION OF MEMRISTOR (1971)



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

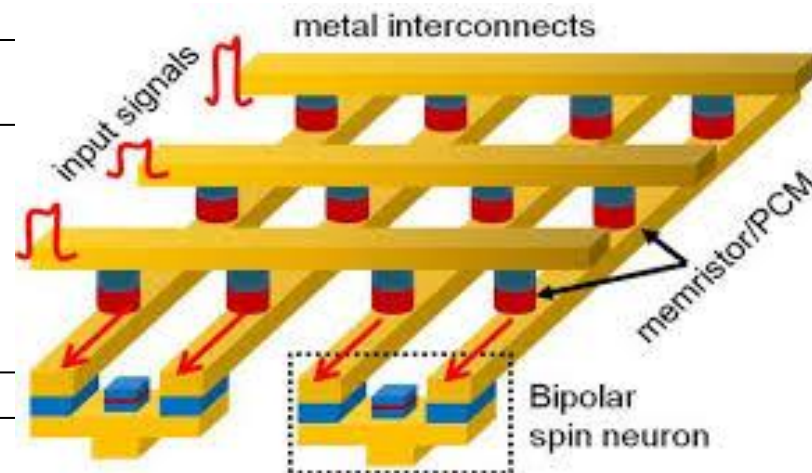
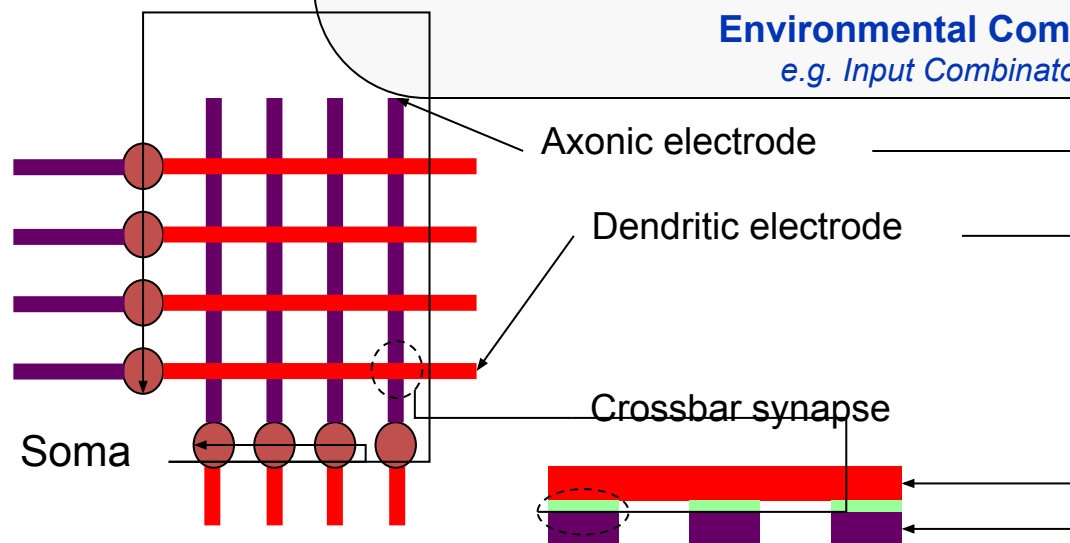
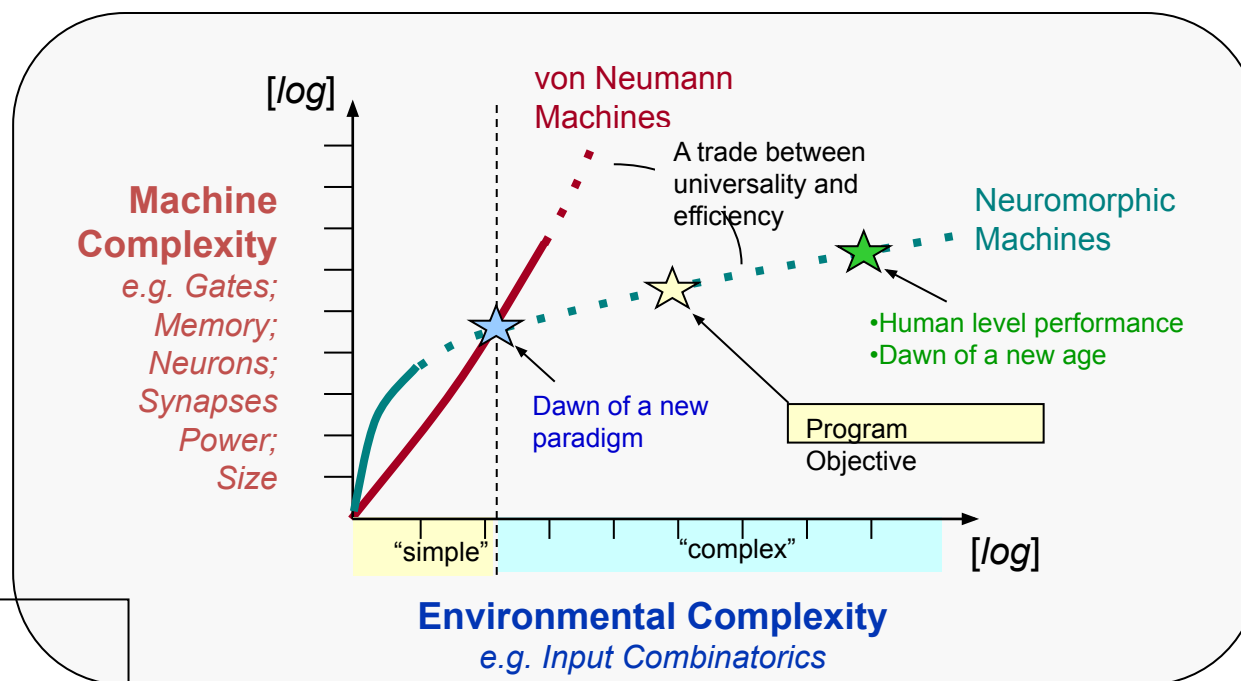


TYPES OF MEMRISTORS

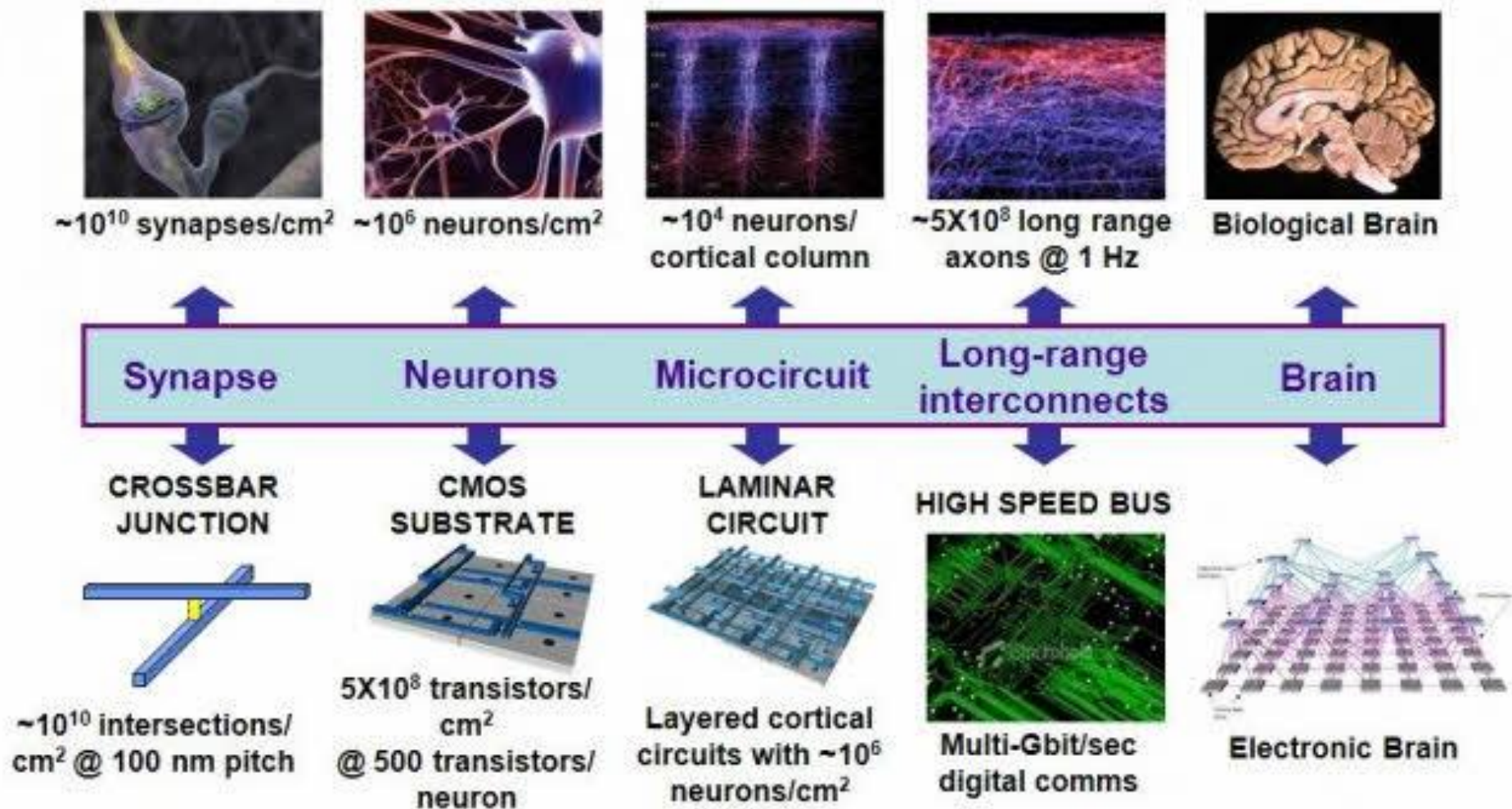


BESIDES MEMRISTORS THERE ARE NOW MEMCAPACITORS AND MEMINDUCTORS!

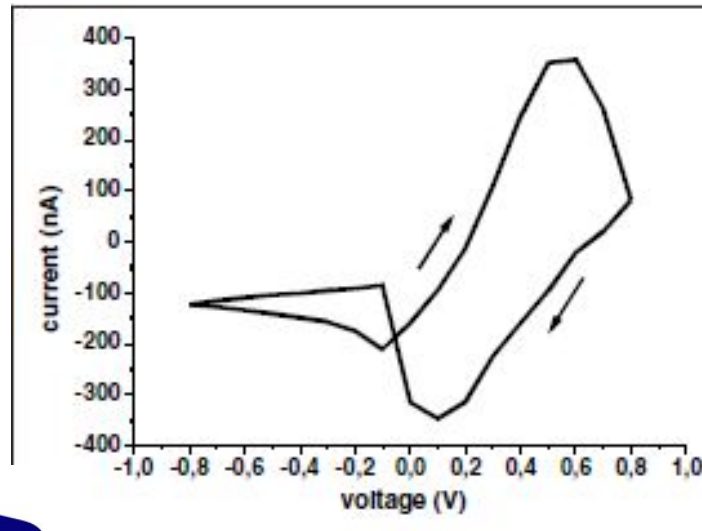
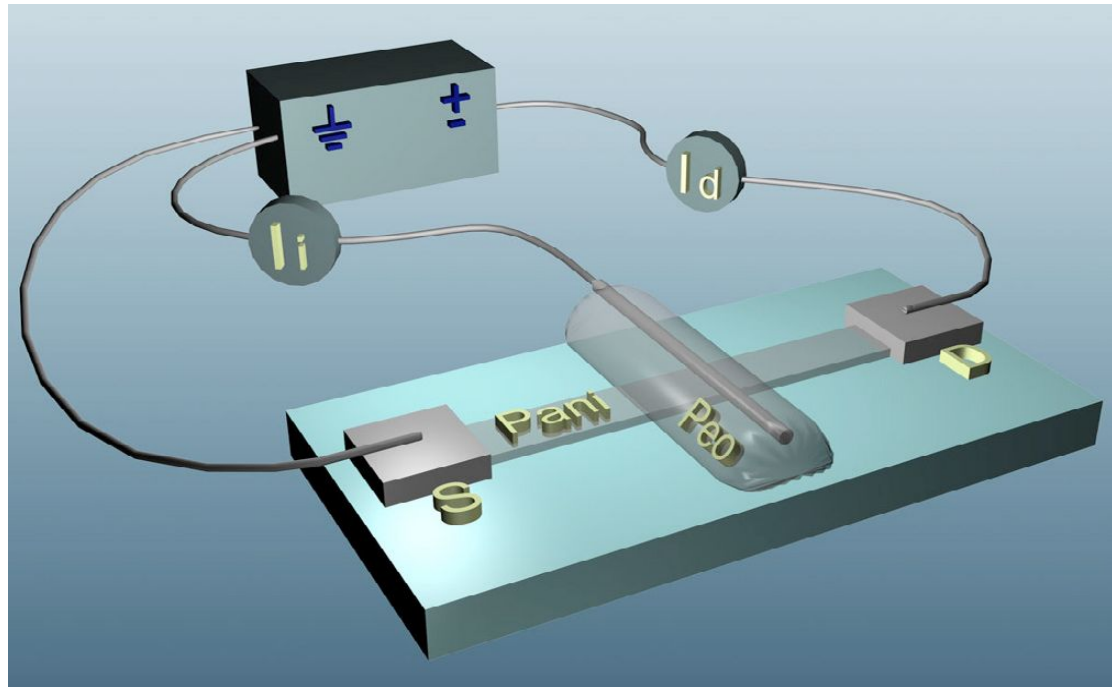
NEUROMORPHIC COMPUTERS – PROJECT SYNAPSE - DARPA



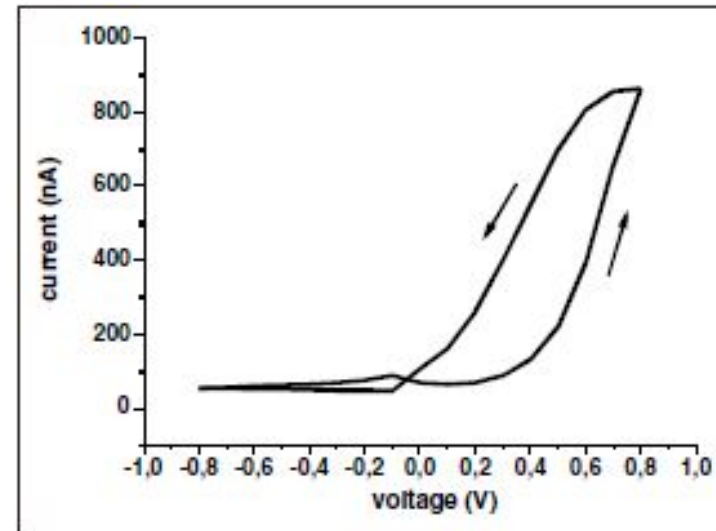
NEUROMORPHIC COMPUTING ROADMAP



PANi BASED MEMRISTOR – EROKHIN, FONTANA - 2008

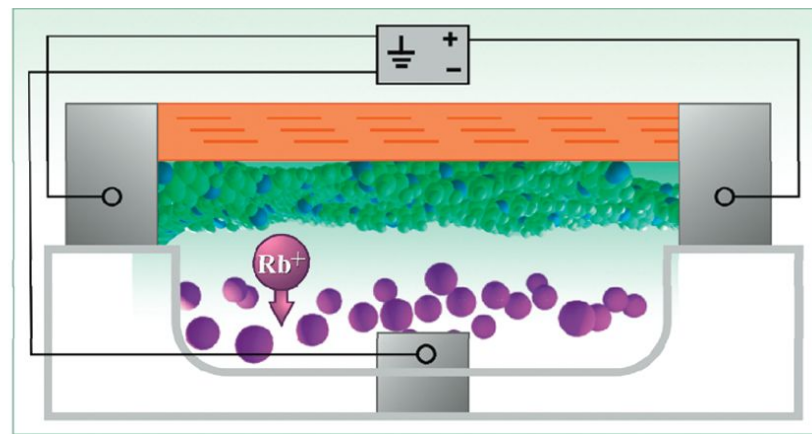
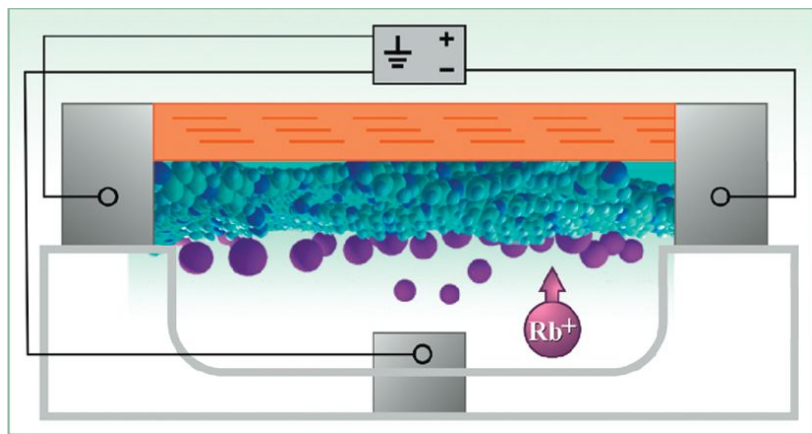
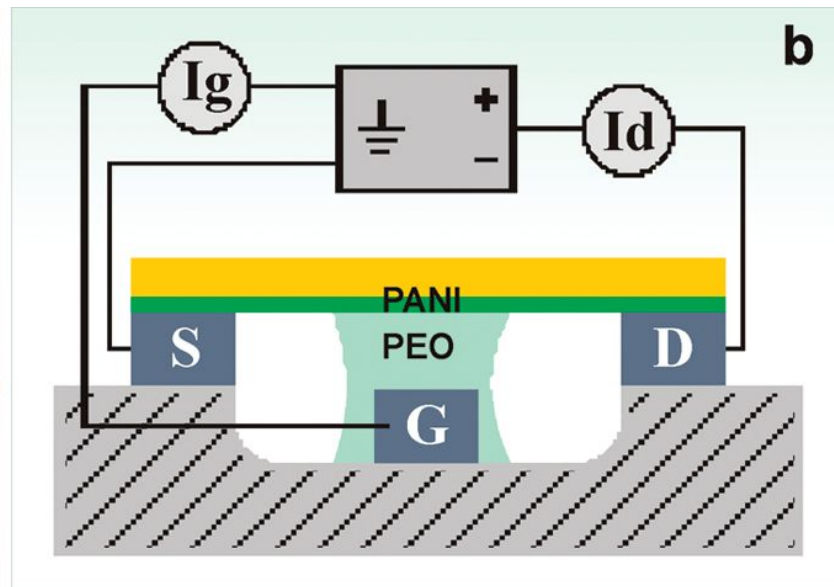
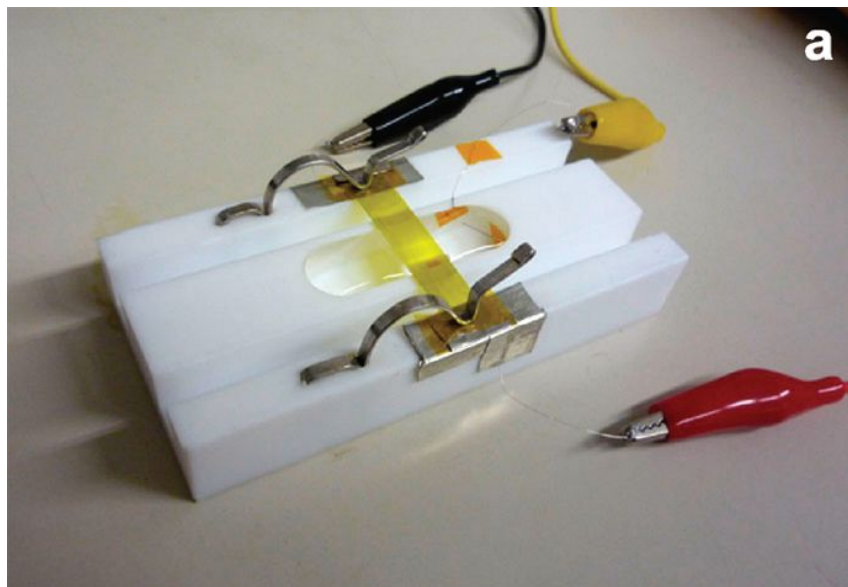


Ionic current

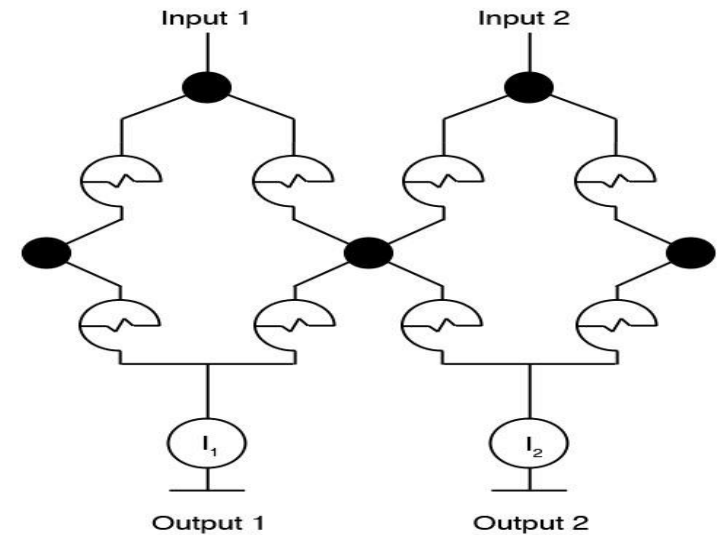
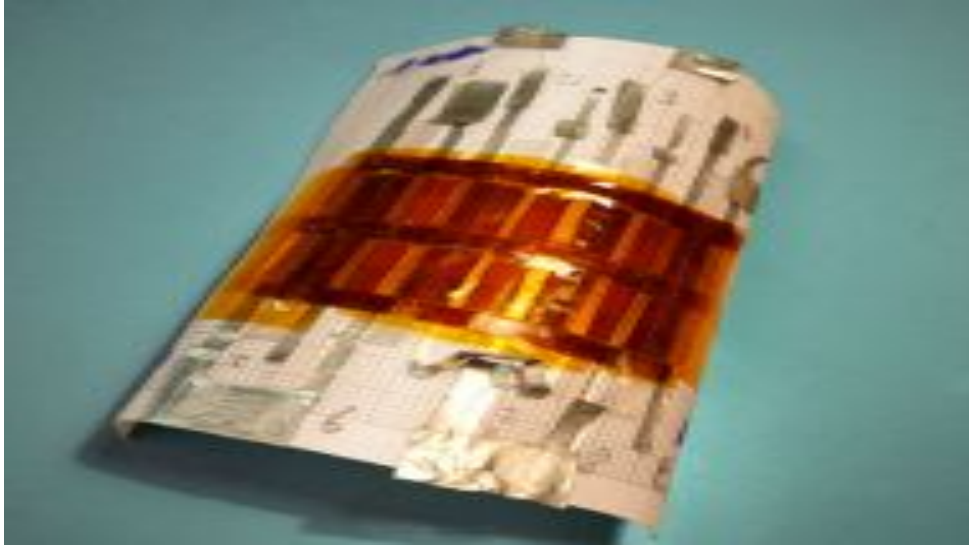


Electronic current

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



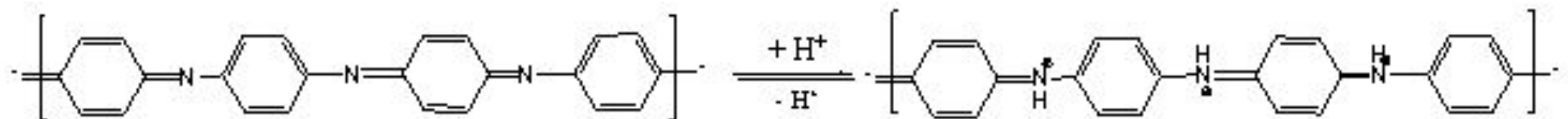
SET OF 8 PANi BASED MEMRISTORS ON FLEXIBLE SUBSTRATE



Simple learning procedure

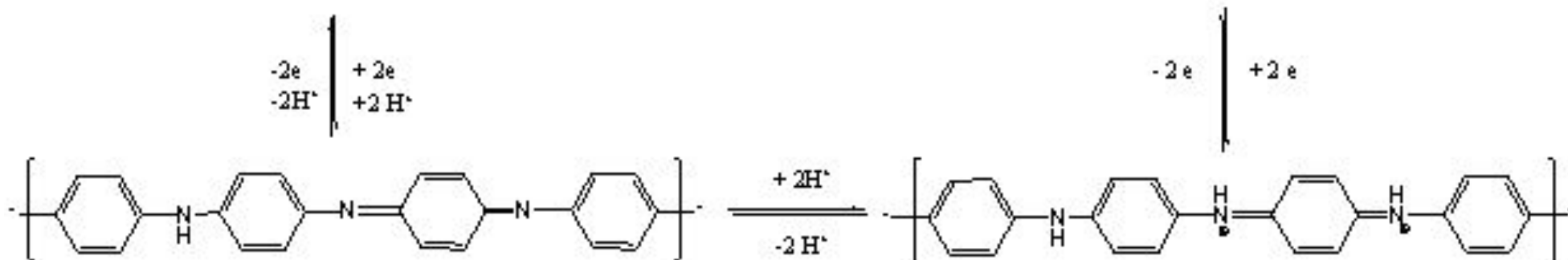
	Out 1 (nA)	Out 2 (nA)
Before training	120	32
After training	65	124

RED-OX STATES OF PANi AND ELECTROCHEMICAL TRANSITIONS BETWEEN THEM



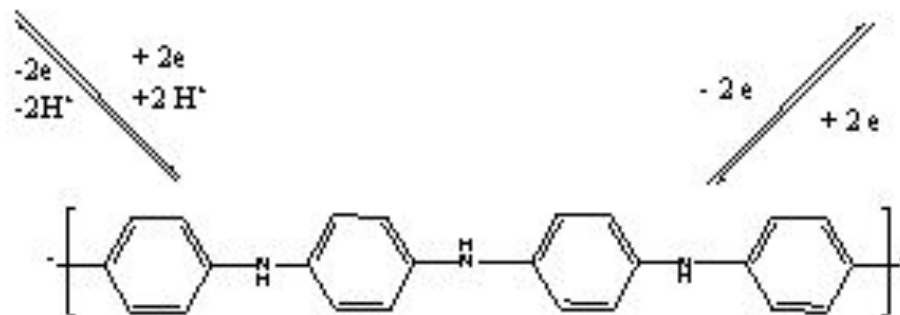
Blue pernigraniline base

Blue pernigraniline salt



Violet emeraldine base

green emeraldine salt

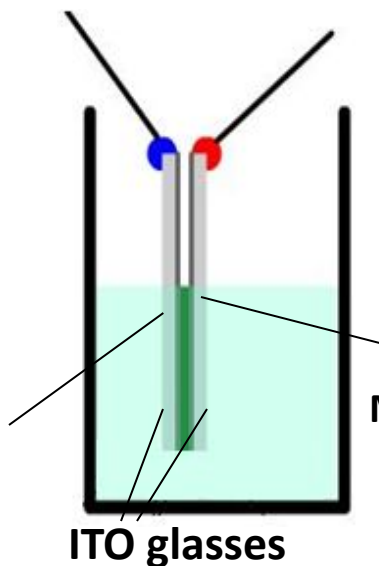


Colourless leucoemeraldine

MEASUREMENT SET UP AND EXPERIMENTAL PROCEDURE



Electrochemical
potentiostat

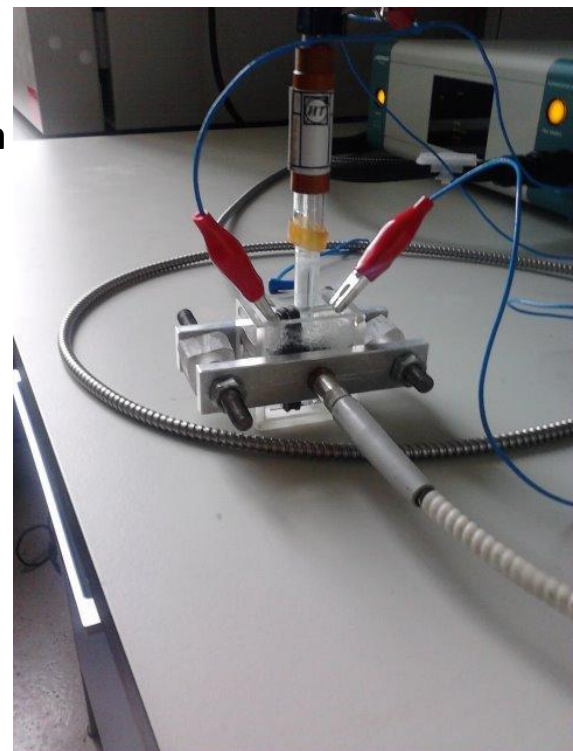


Solution
 HCl/LiClO_4

ITO glasses

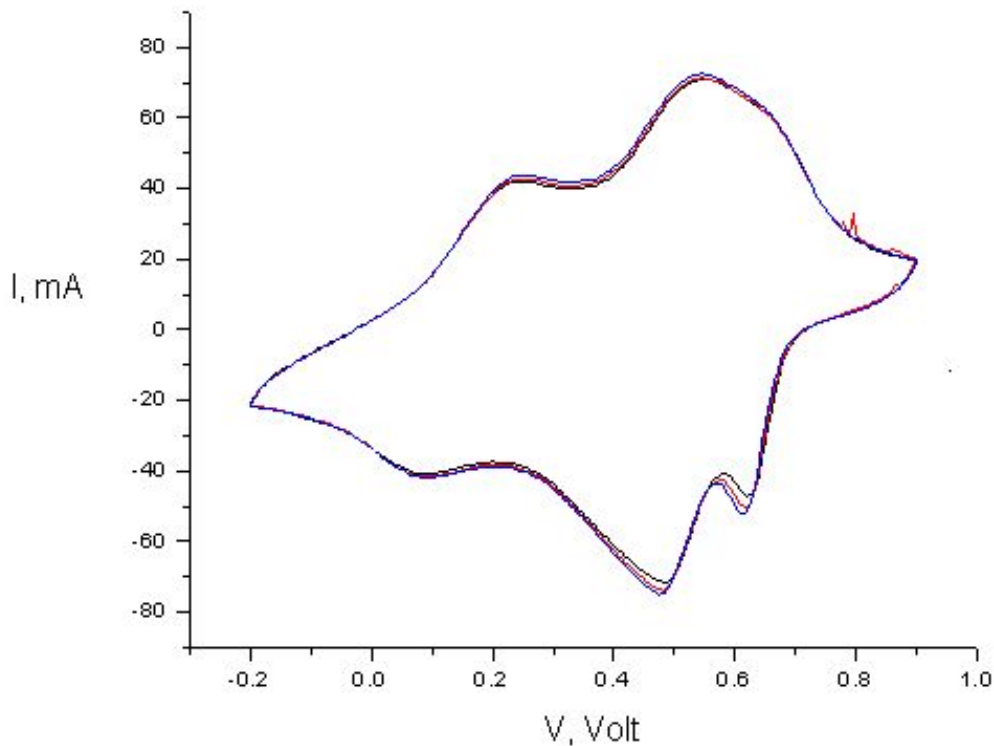
acetonytile,
water

Measured film

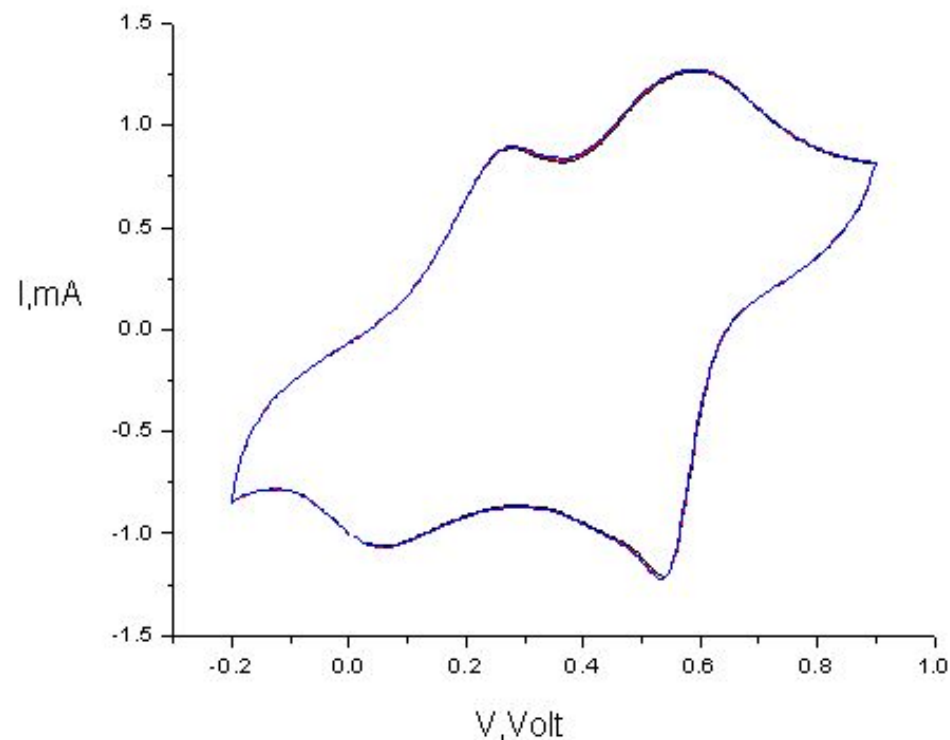


PANi IN SOLUTION OF $\text{LiClO}_4/\text{HCl}$ CYCLOVOLTAMMETRY

Red – Ox peaks are very broad, it is important

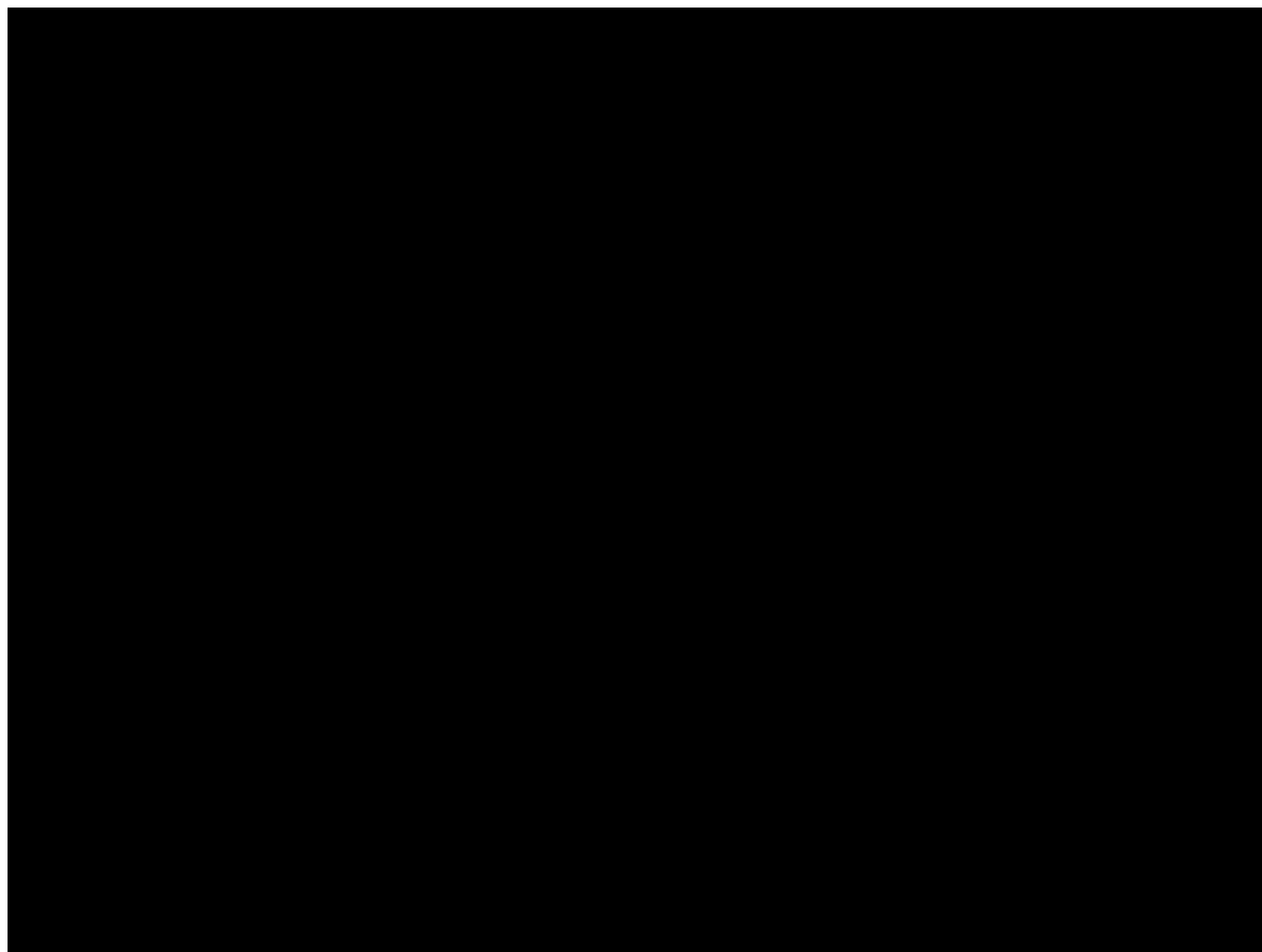


Cyclicvoltammogramm in 0.1 M
HCl in water

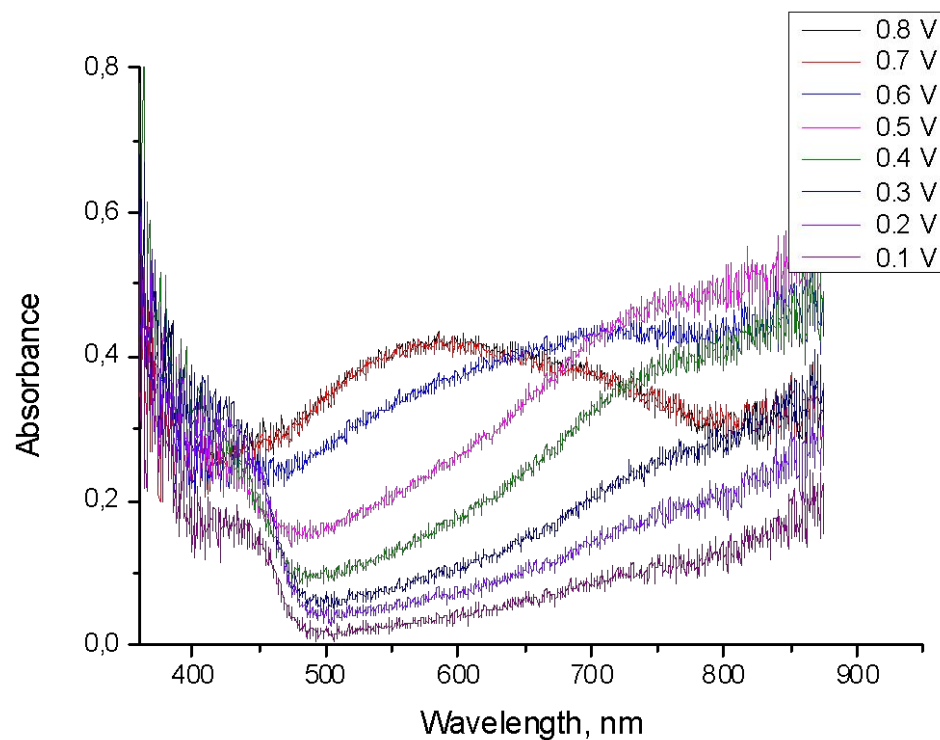


Cyclicvoltammogramm in 0.1 M
 LiClO_4 in acetonitrile

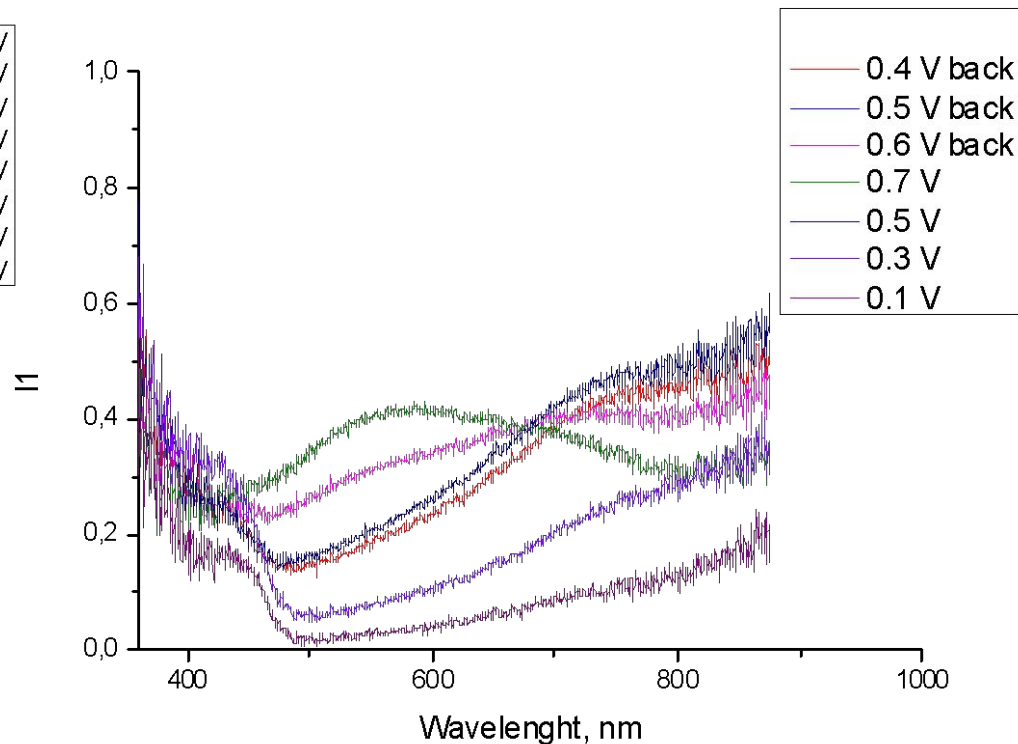
ELECTROCHROMIC CYCLOVOLTAMMOGRAMM



SPECTROELECTROCHEMISTRY MEASUREMENTS



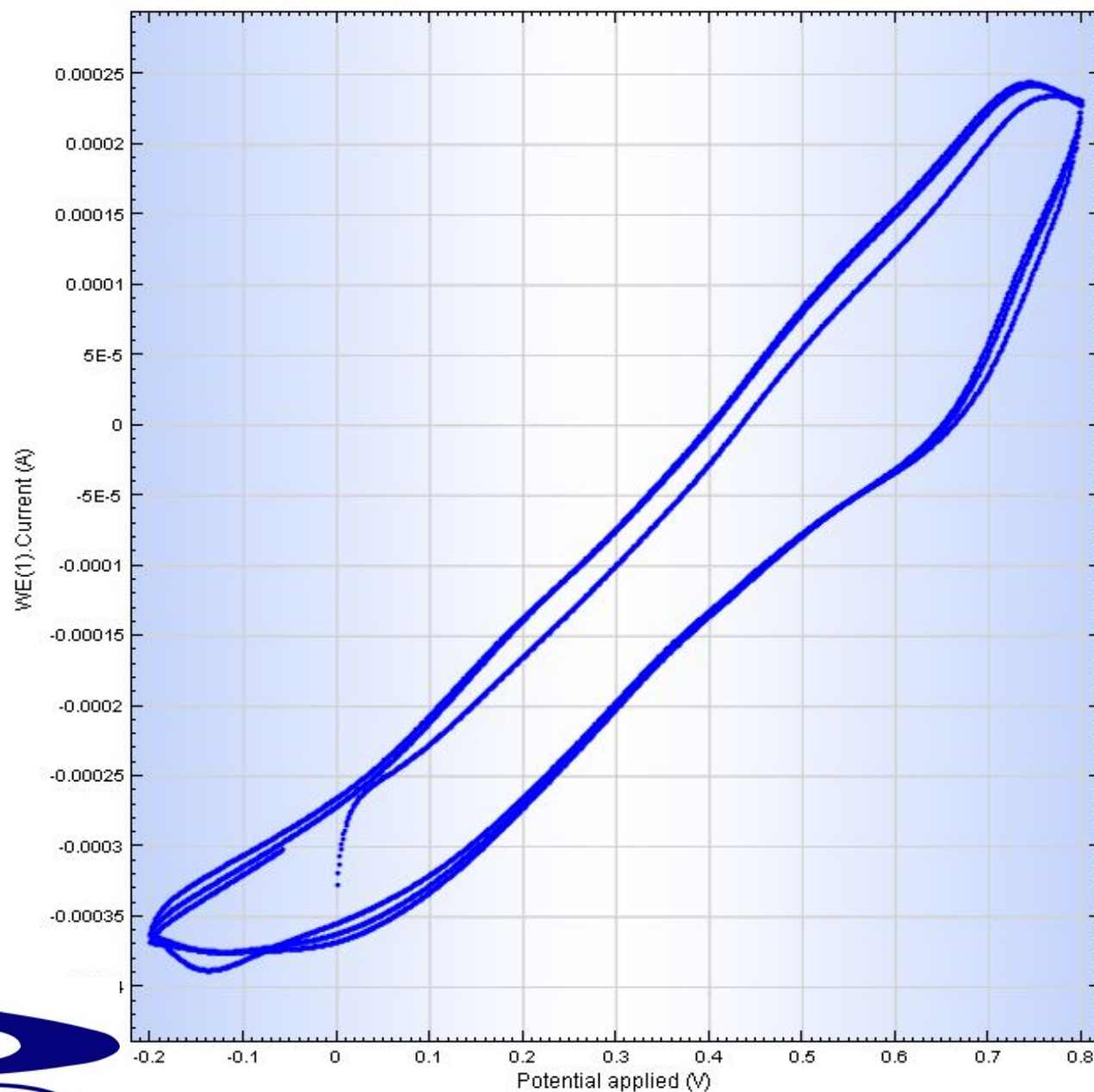
PANi film versus Ag/AgCl, 0.1 M HCl Water



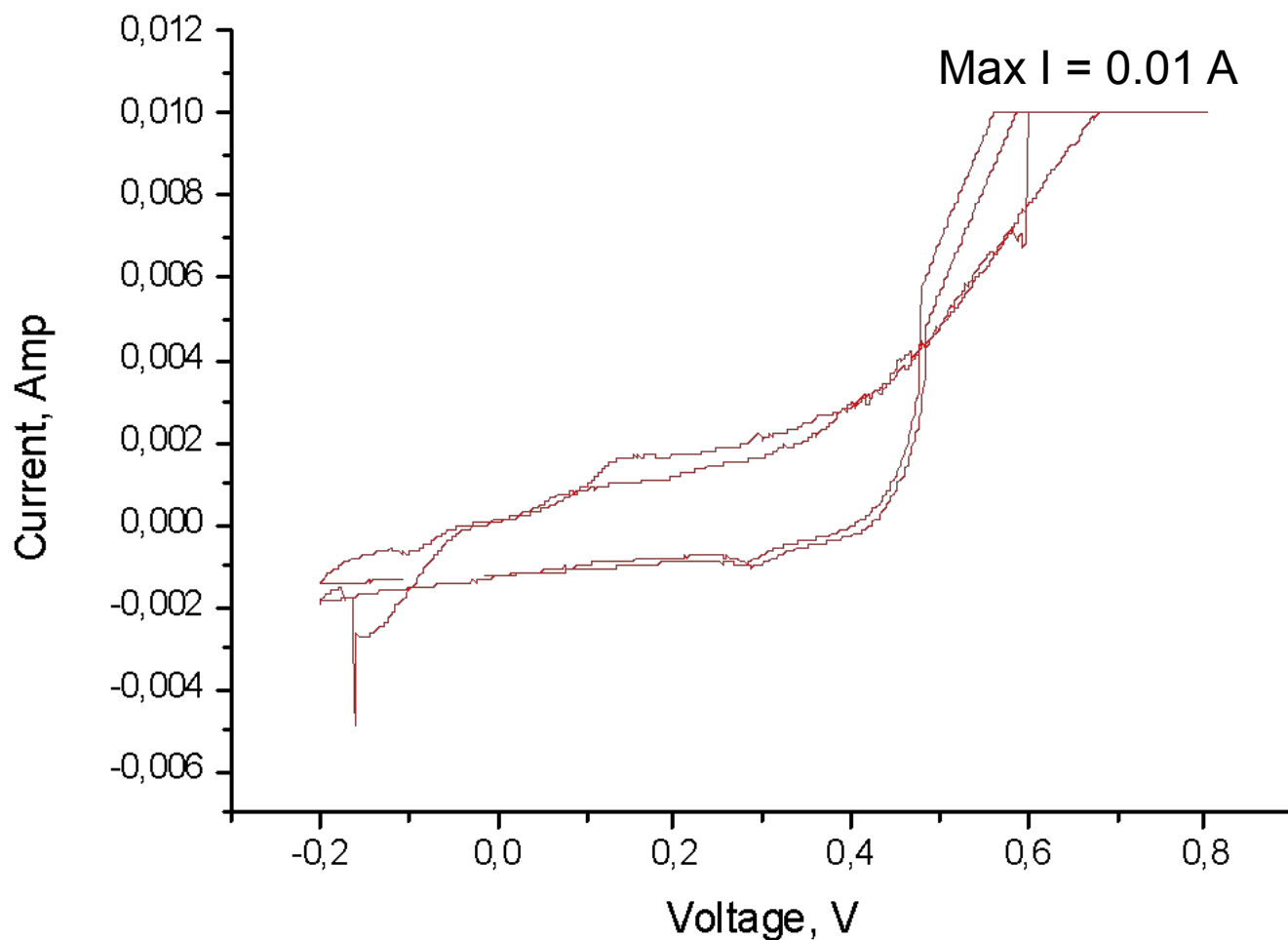
Backwards, with memristive effect on absorbance spectra



MEMRISTIVE EFFECT IN_PLANE CONDUCTANCE (I-V CURVES)



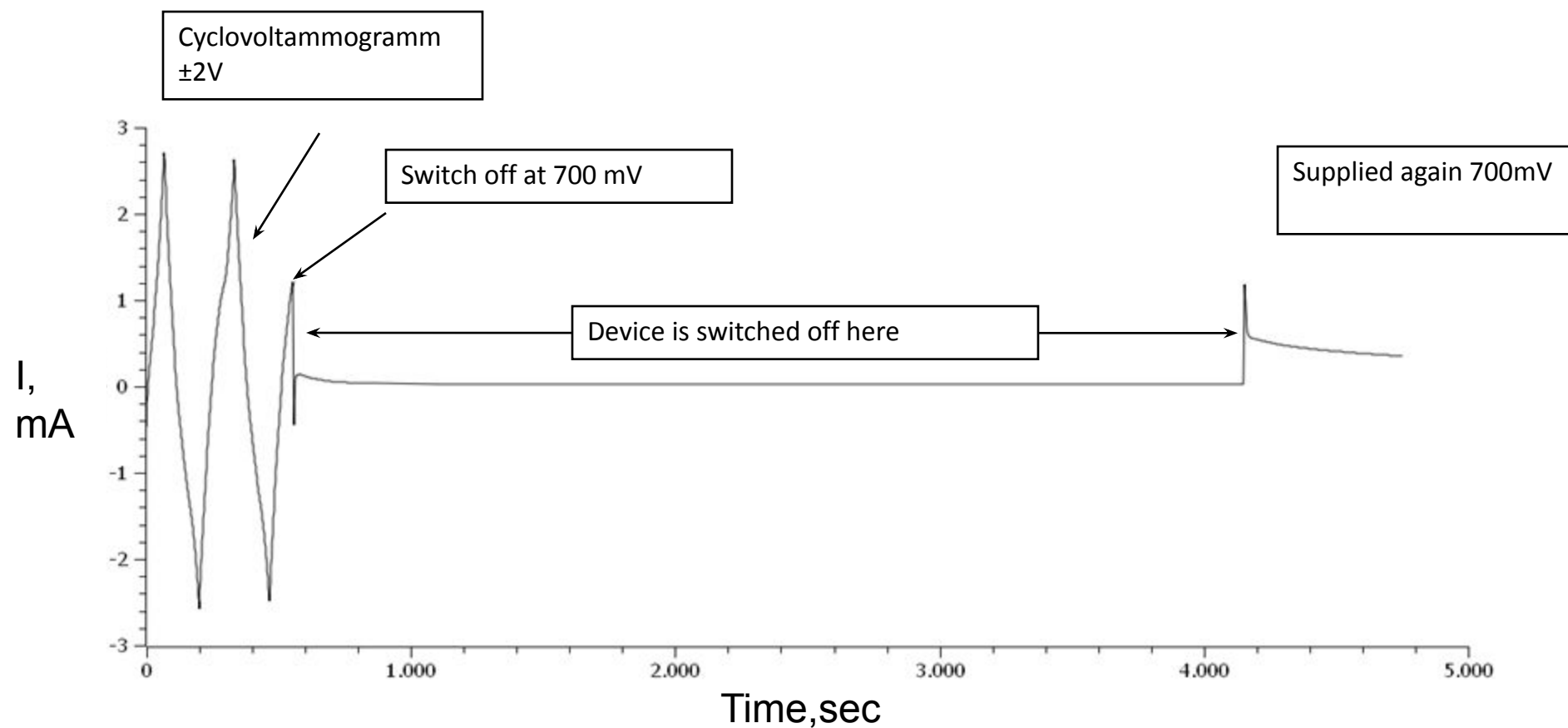
PANI FILM-THROUGH CONDUCTIVITY MEASUREMENT



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



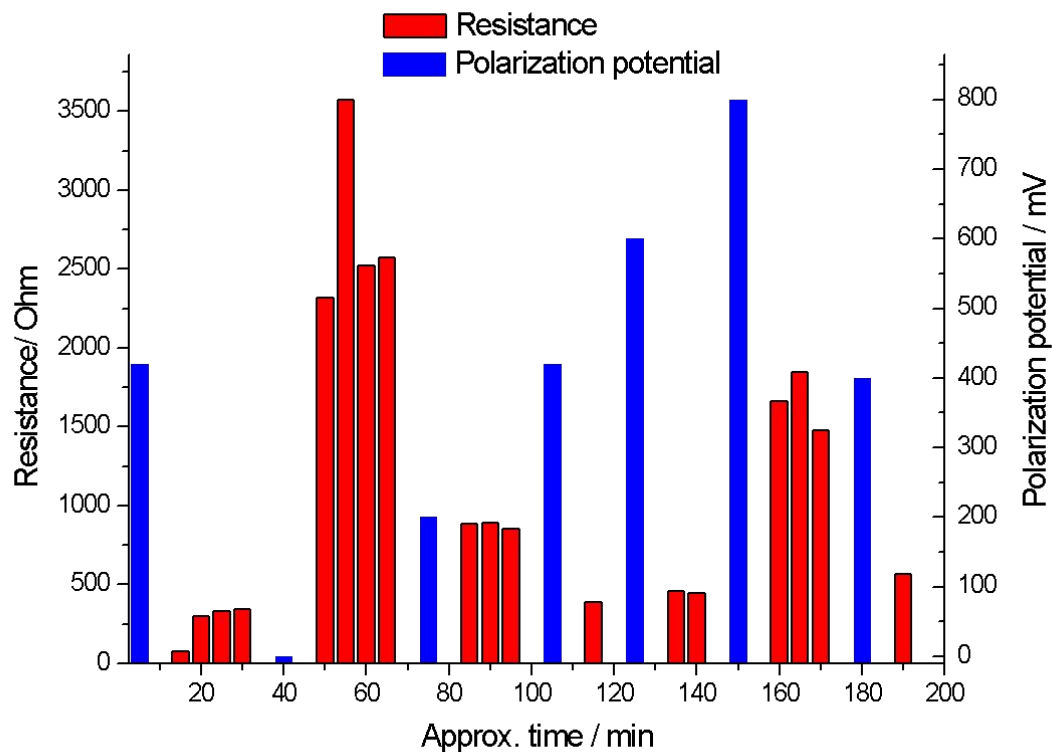
MEMRISTIVITY: RESISTANCE AFTER SWITCH OFF VOLTAGE



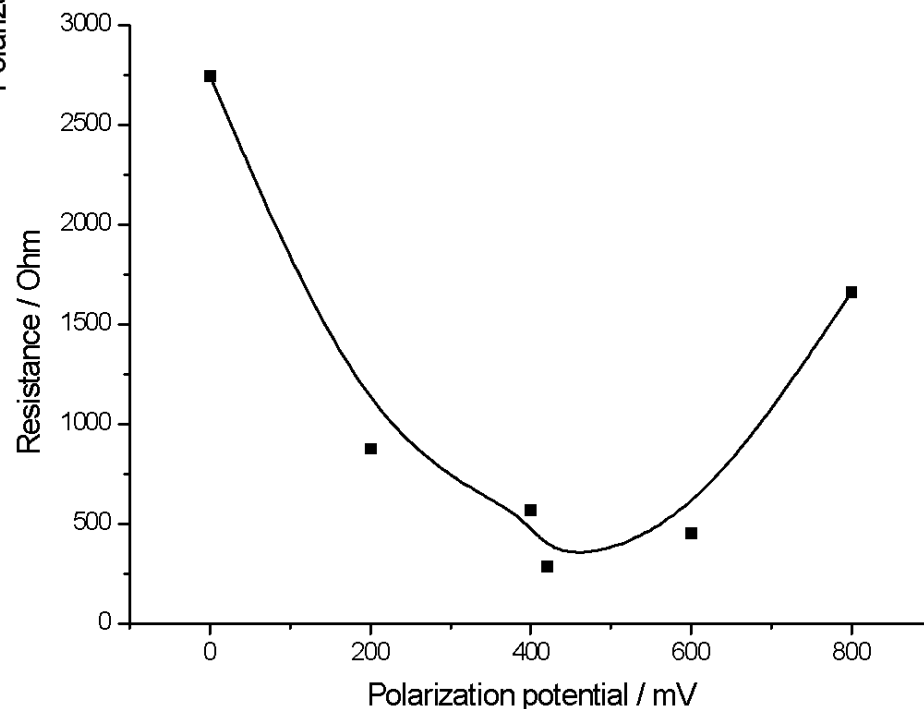
Memristive effect as from voltage switch off/ switch on.



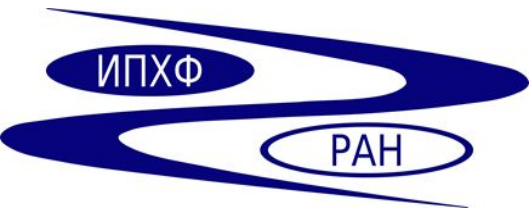
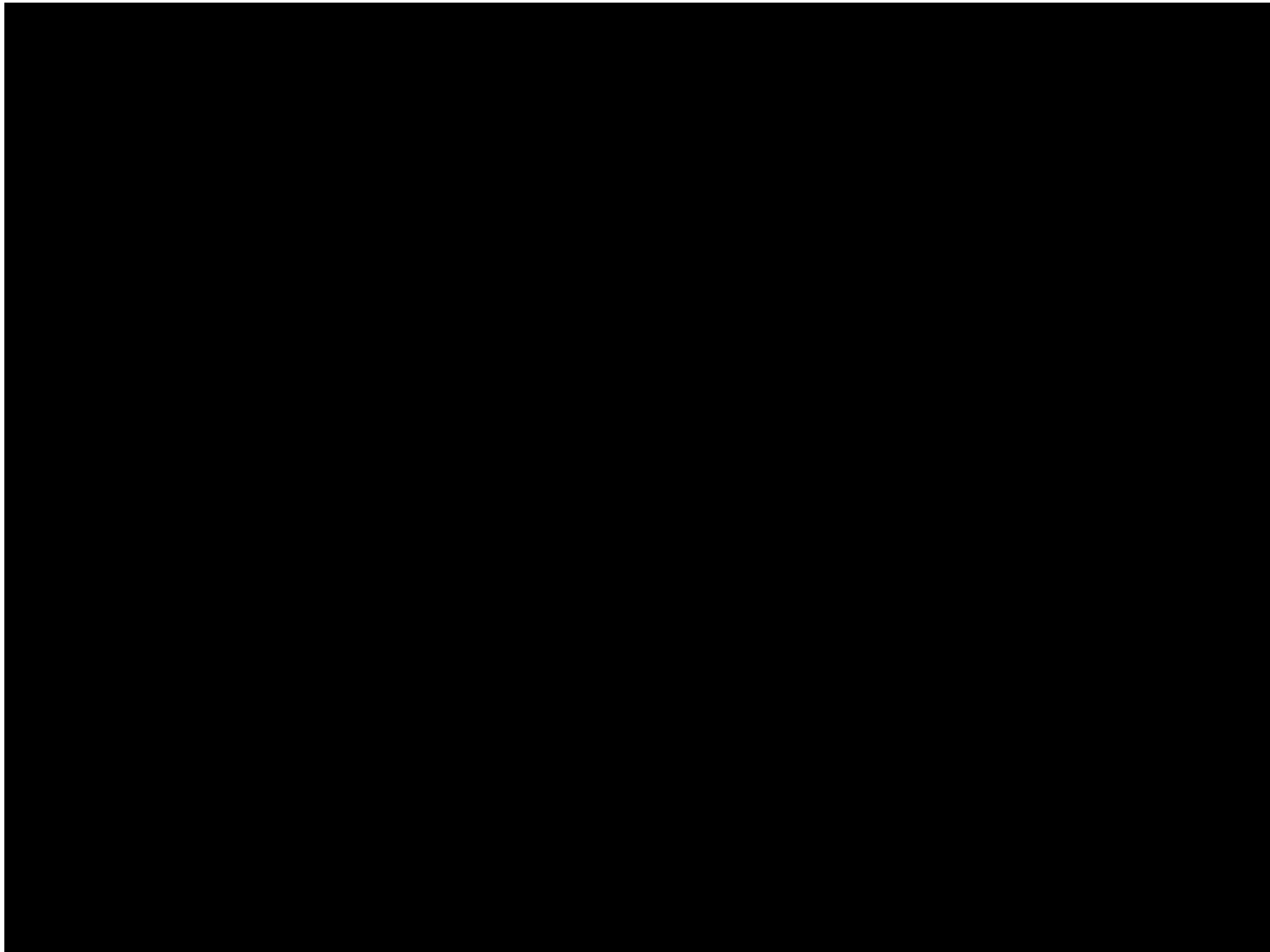
RESISTANCE IN PLANE, DRY FILM – AC CONDUCTIVITY



Bias voltage – 0, amplitude – 5 mV

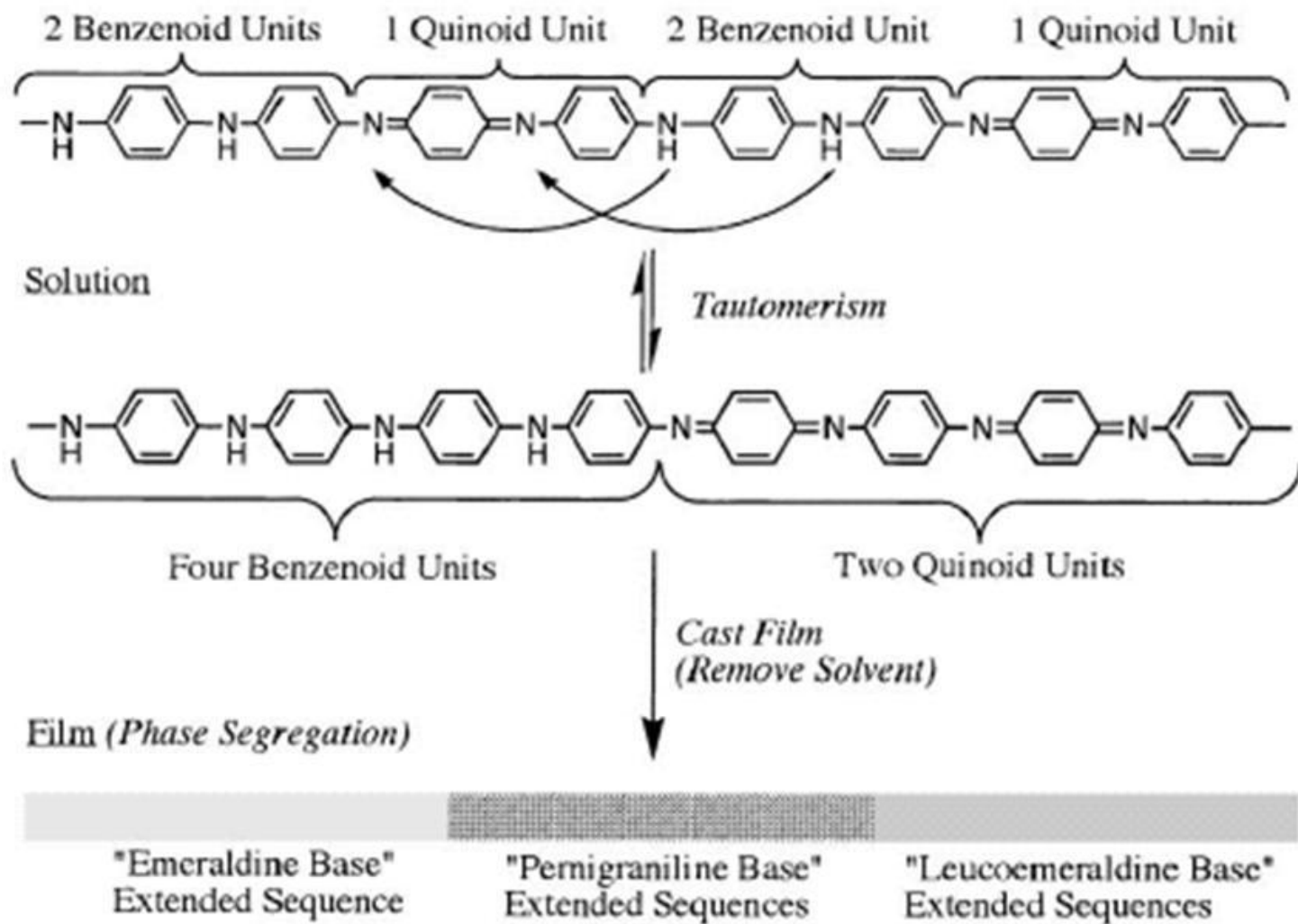


MEMRISTIVE EFFECT MOVIE



BLOCK NATURE OF CONDUCTIVITY IN PANi

– EXPLANATION OF MEMRISTANCE



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



USE OF PANi NEURAL NETWORK FOR IMAGE PROCESSING

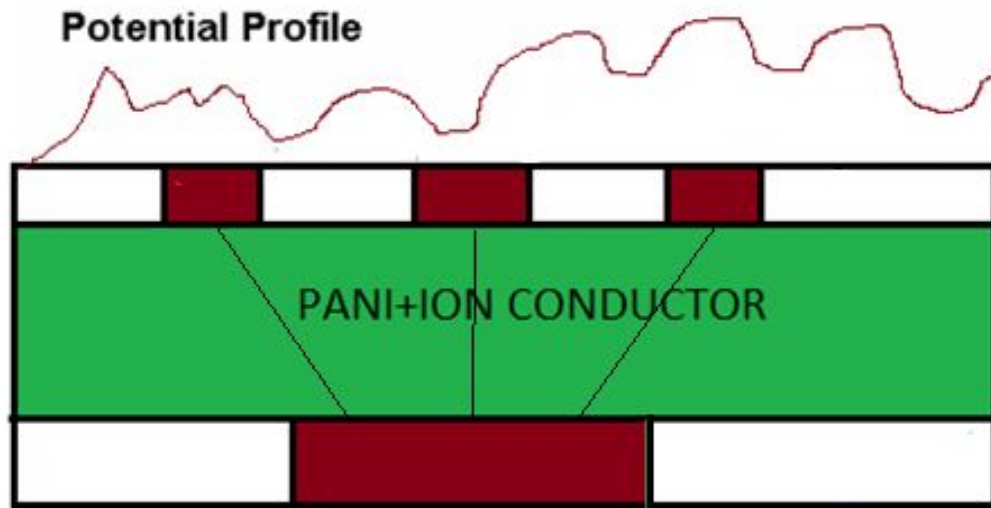
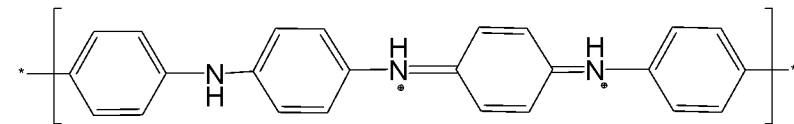
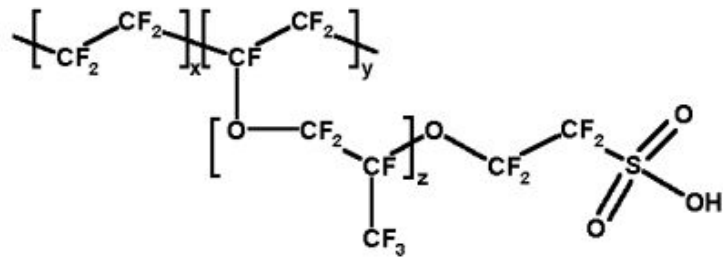
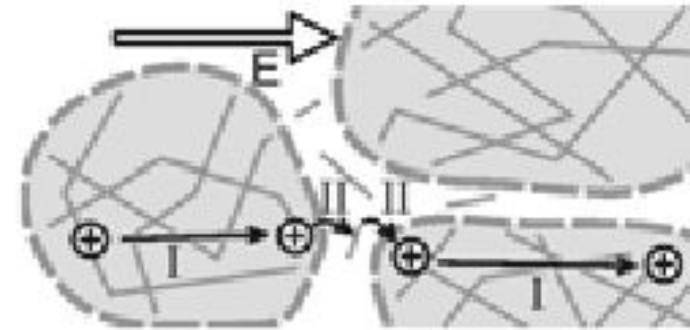
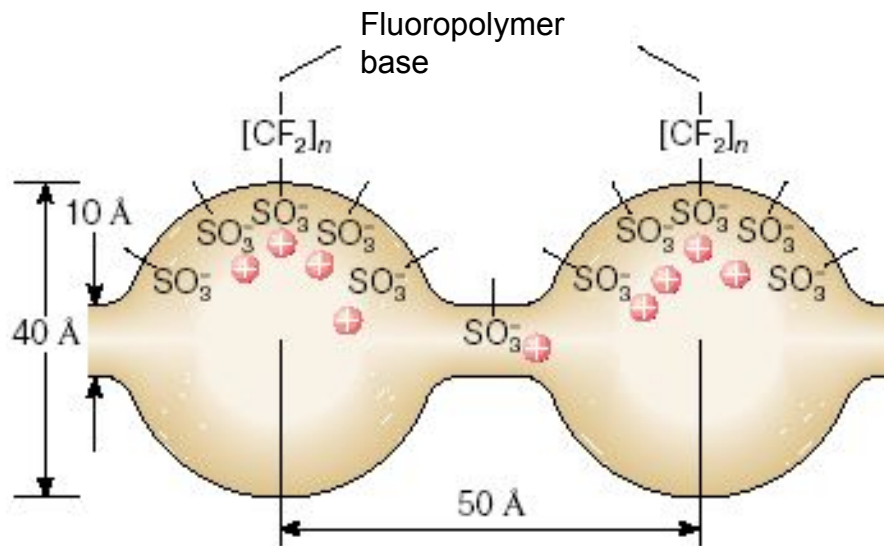


Image processing operations possible:

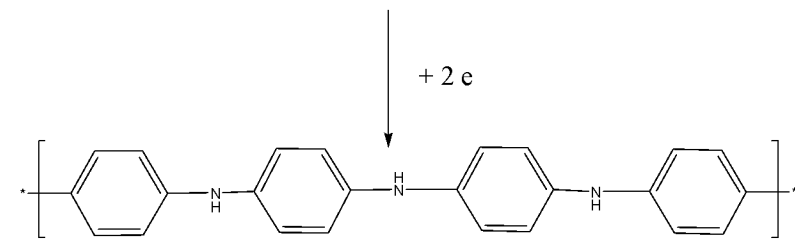
1. Image segmentation
2. Contrasting
3. Simple object recognition

Pixelated Matrix of Contacts

PANI-NAFION INTERPOLYELECTROLYTE COMPLEXES



Green emeraldine salt



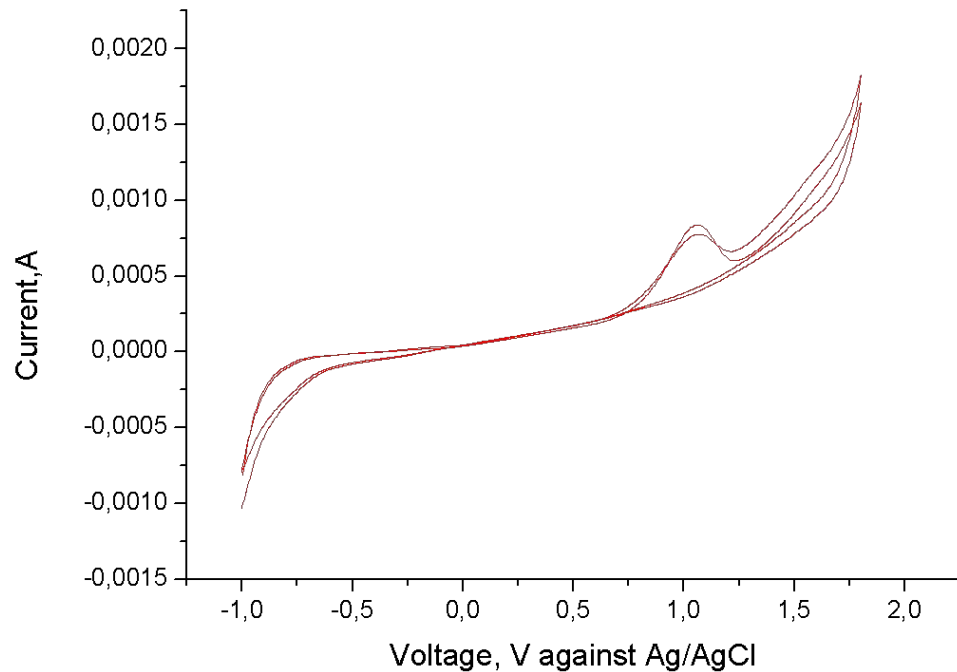
Colourless leucoemeraldine

ИПХФ

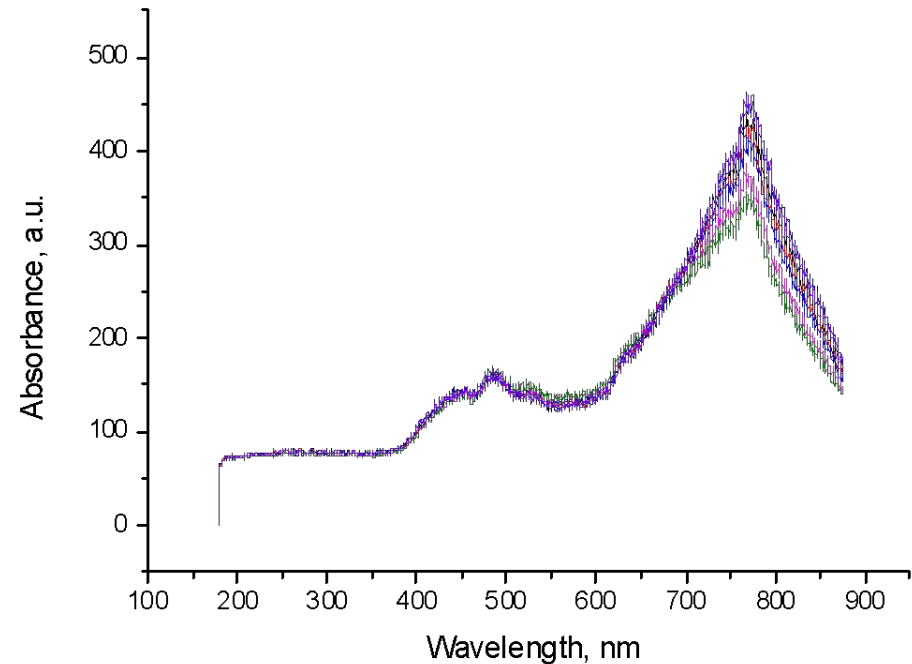
РАН

ИИЭОС

PANi-NAFION IN SOLUTIONS OF LiClO_4 , Acetonytrile



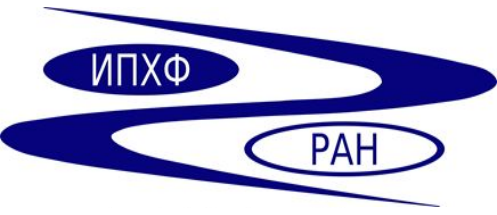
Cyclicvoltammogramm in 0.1M LiClO_4 , acetonytrile, versus Ag/AgCl



Absorbance spectra of films during cyclicvoltammetry

CONCLUSIONS

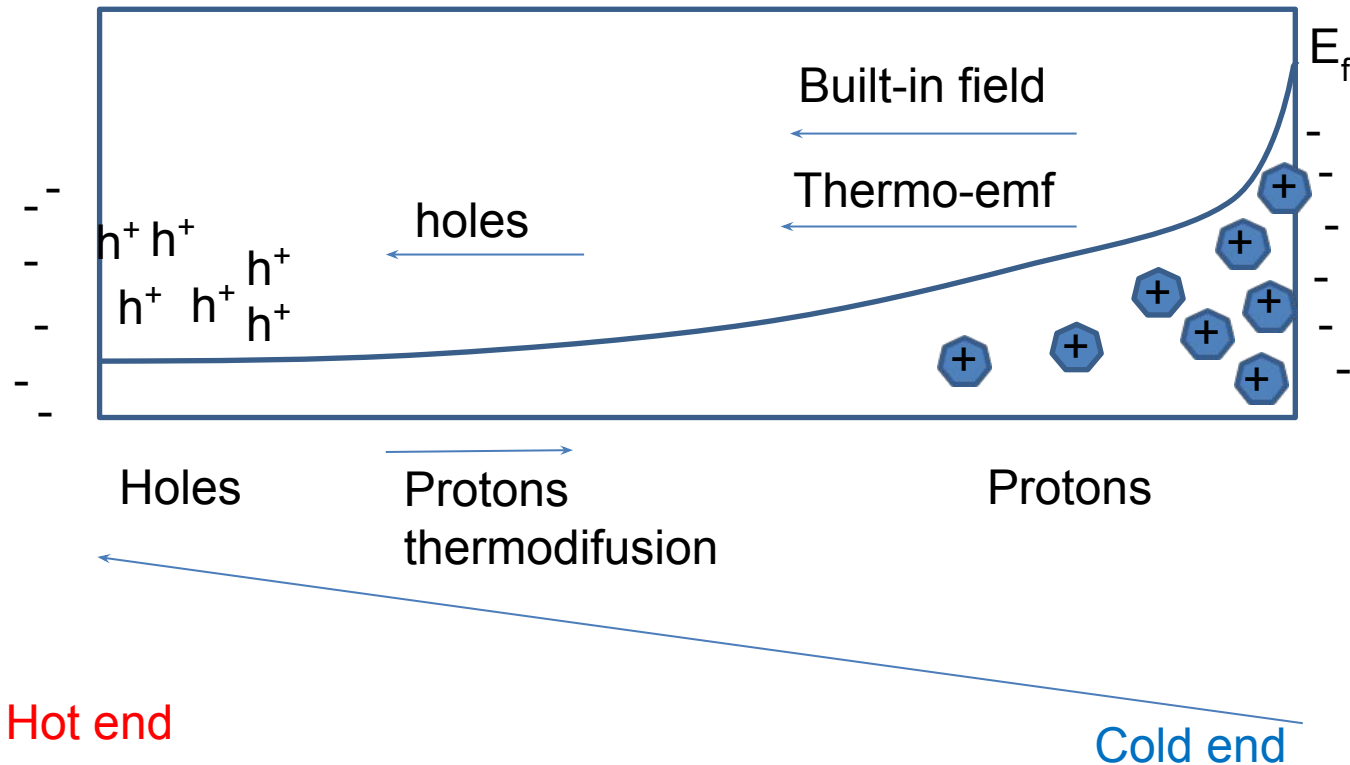
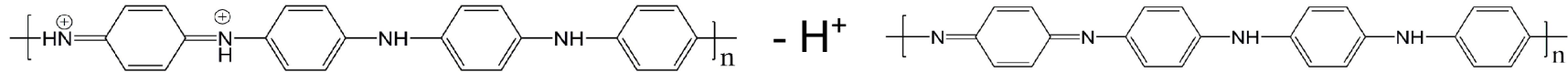
- *Polymer electrochemistry is a complicated matter*
- *Polyaniline-based memristor operating mechanism is determined by change of Red-Ox states of PANi*
- *Probably TiO_2 , VO_x memristors operation is similar.*
- *It is not clear why PANi-Nafion films do not change Red-Ox states*
- *It is possible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

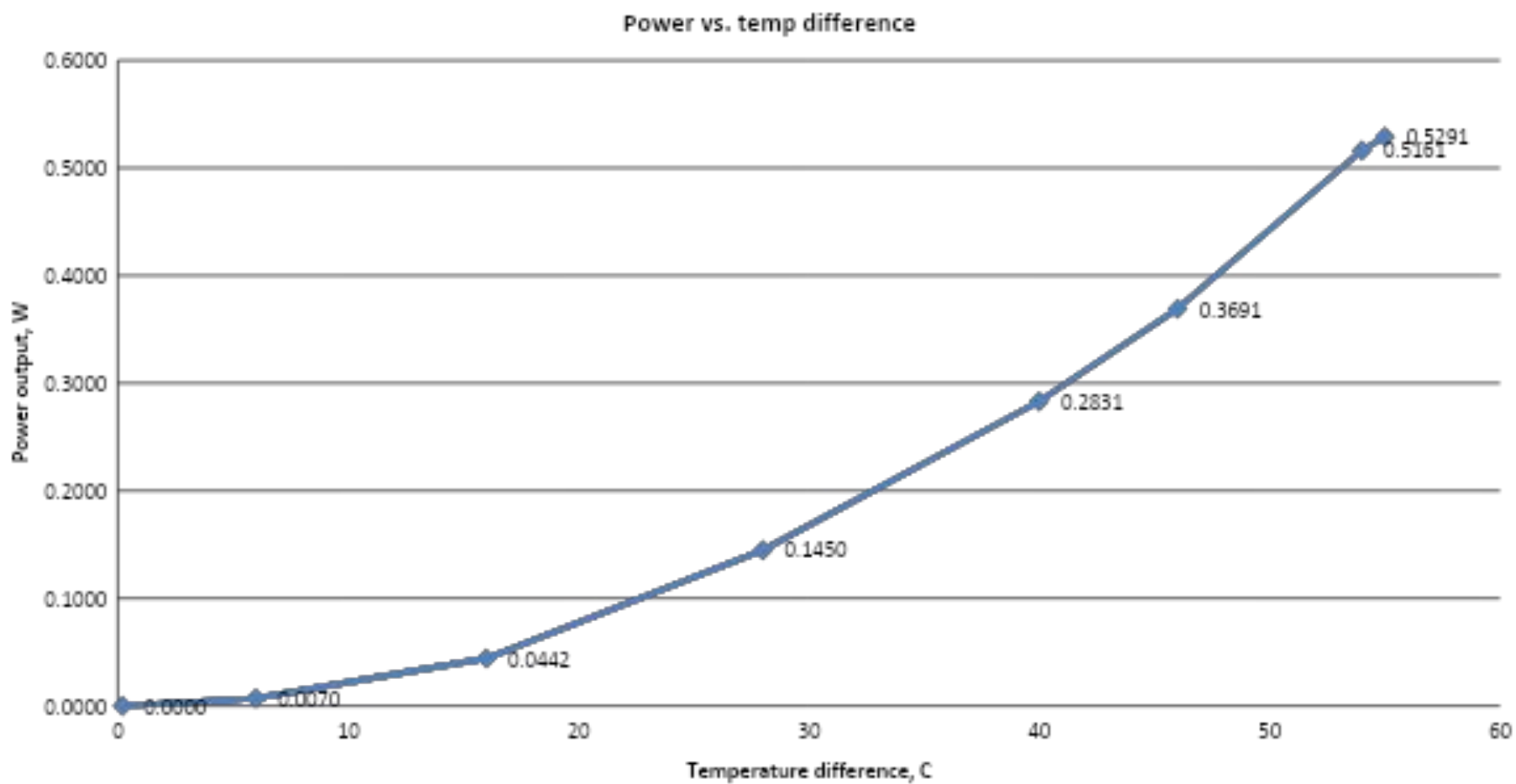


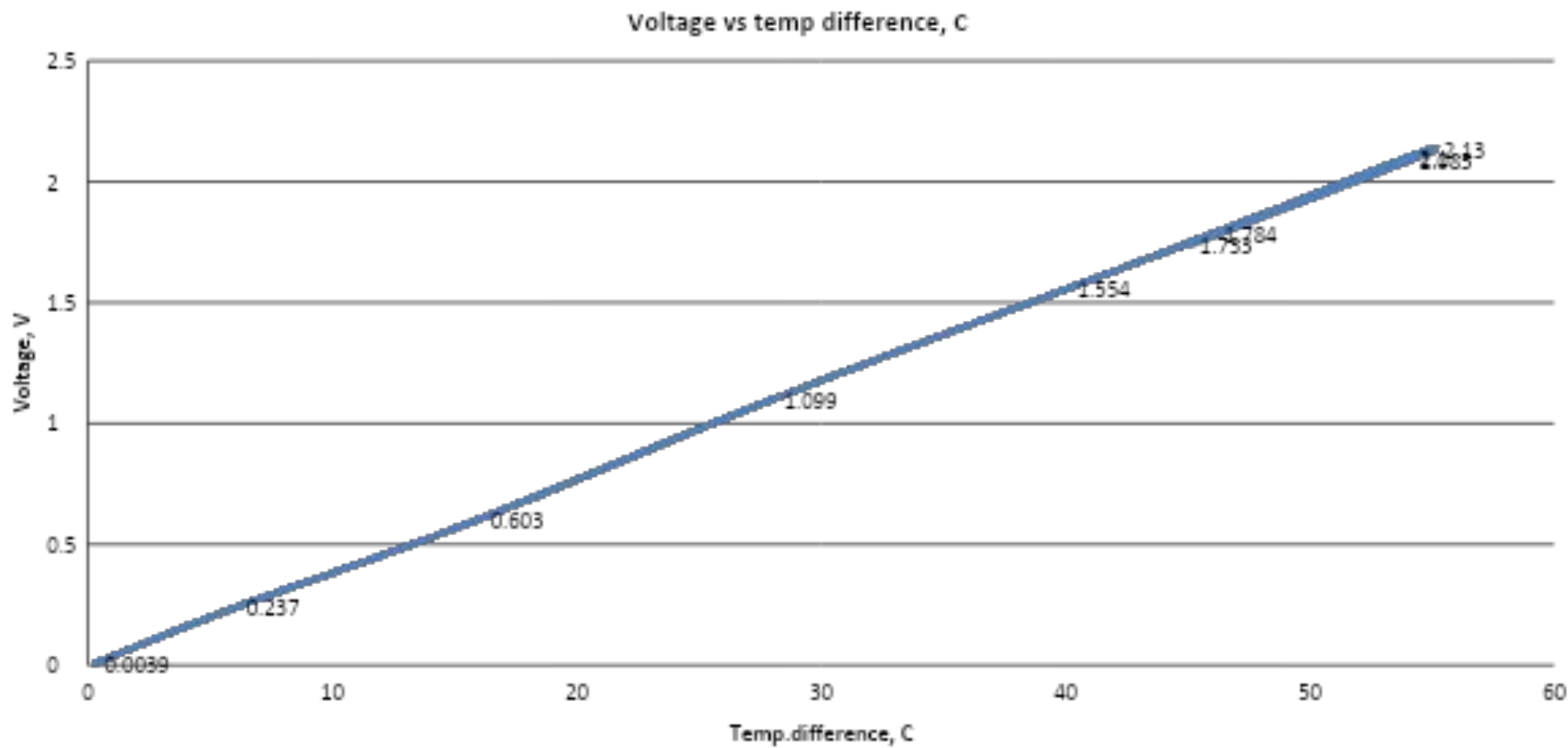
$$E_{\text{red}} = E_{\text{red}}^{\ominus} - \frac{RT}{zF} \ln Q = E_{\text{red}}^{\ominus} - \frac{RT}{zF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}}$$

Protonated PANi

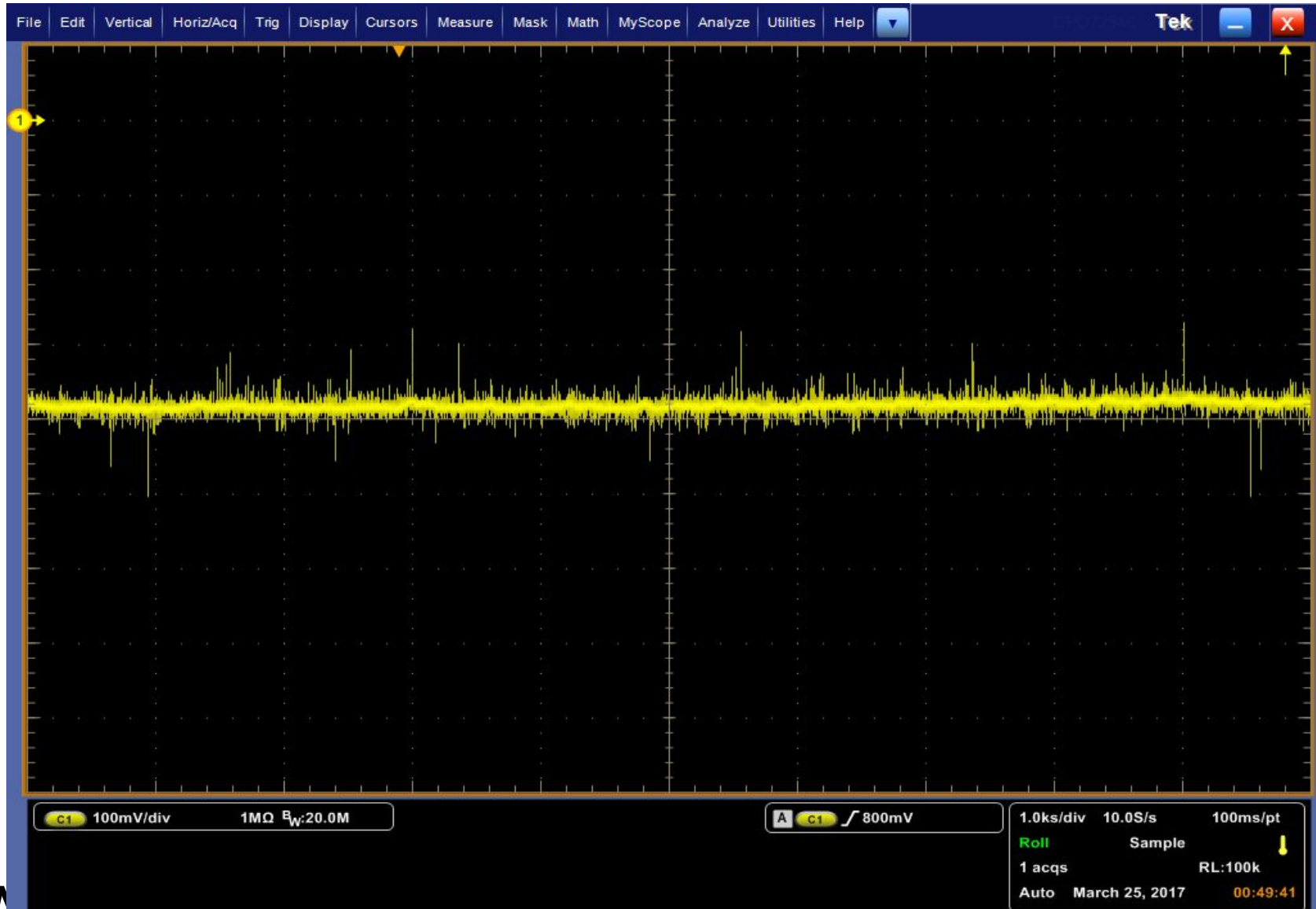
Deprotonated PANi



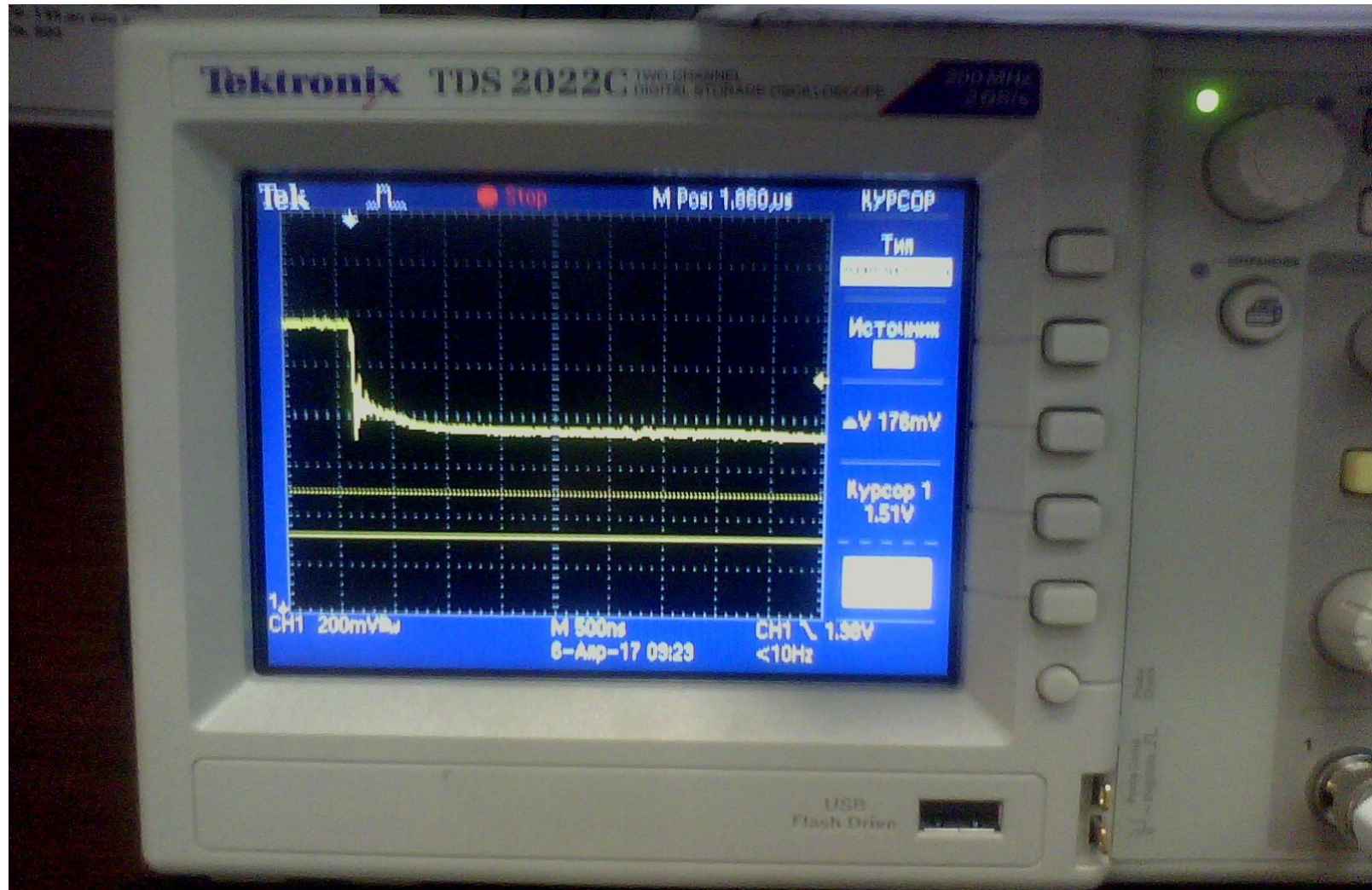




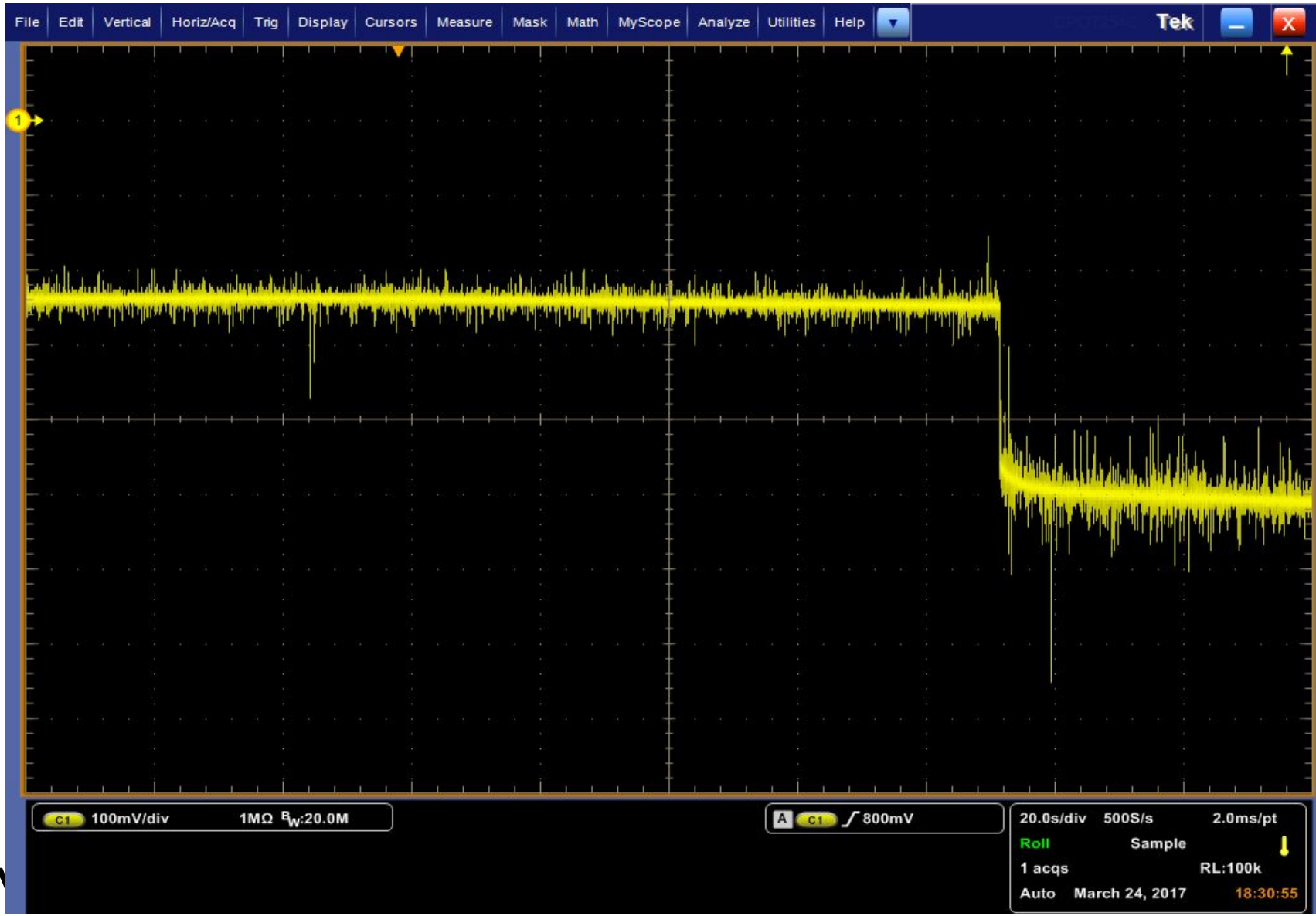
Stability at 55°C



Discharge to short circuit



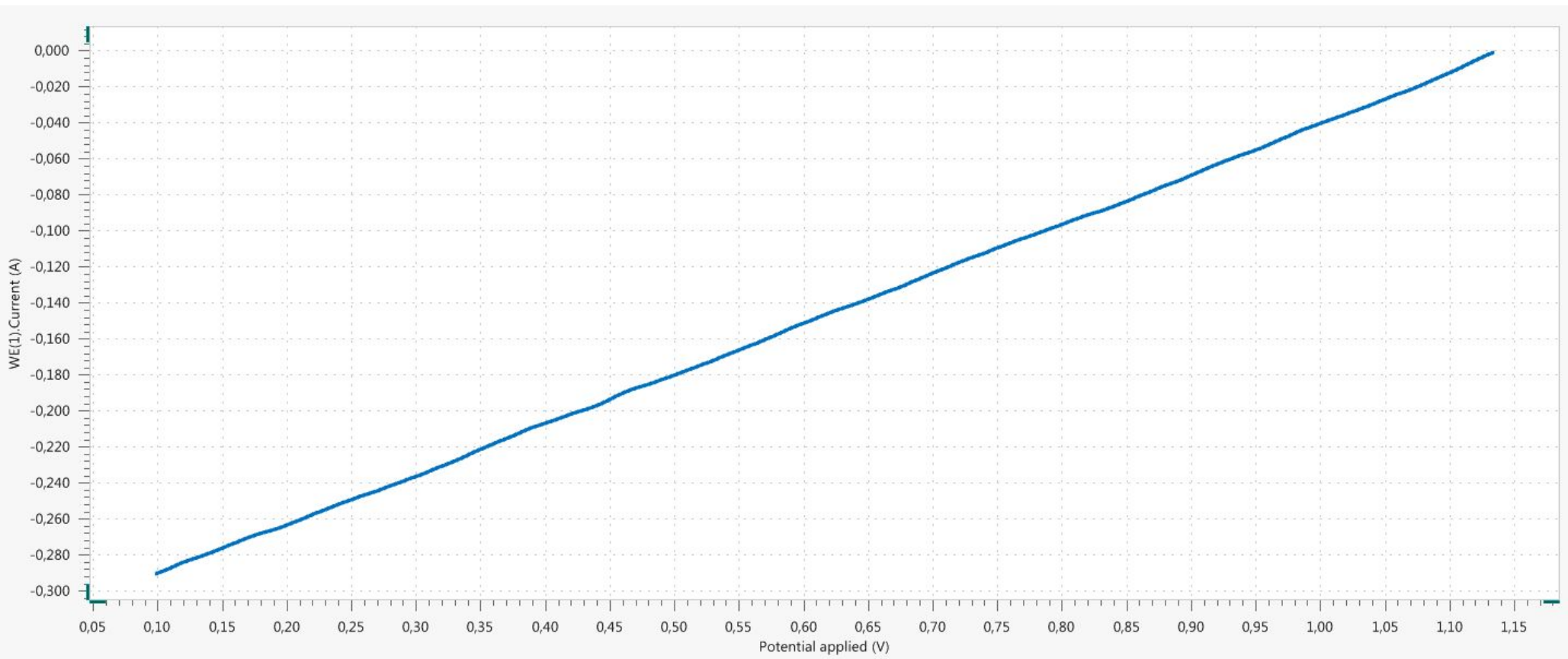
Discharge to 3 Ohm



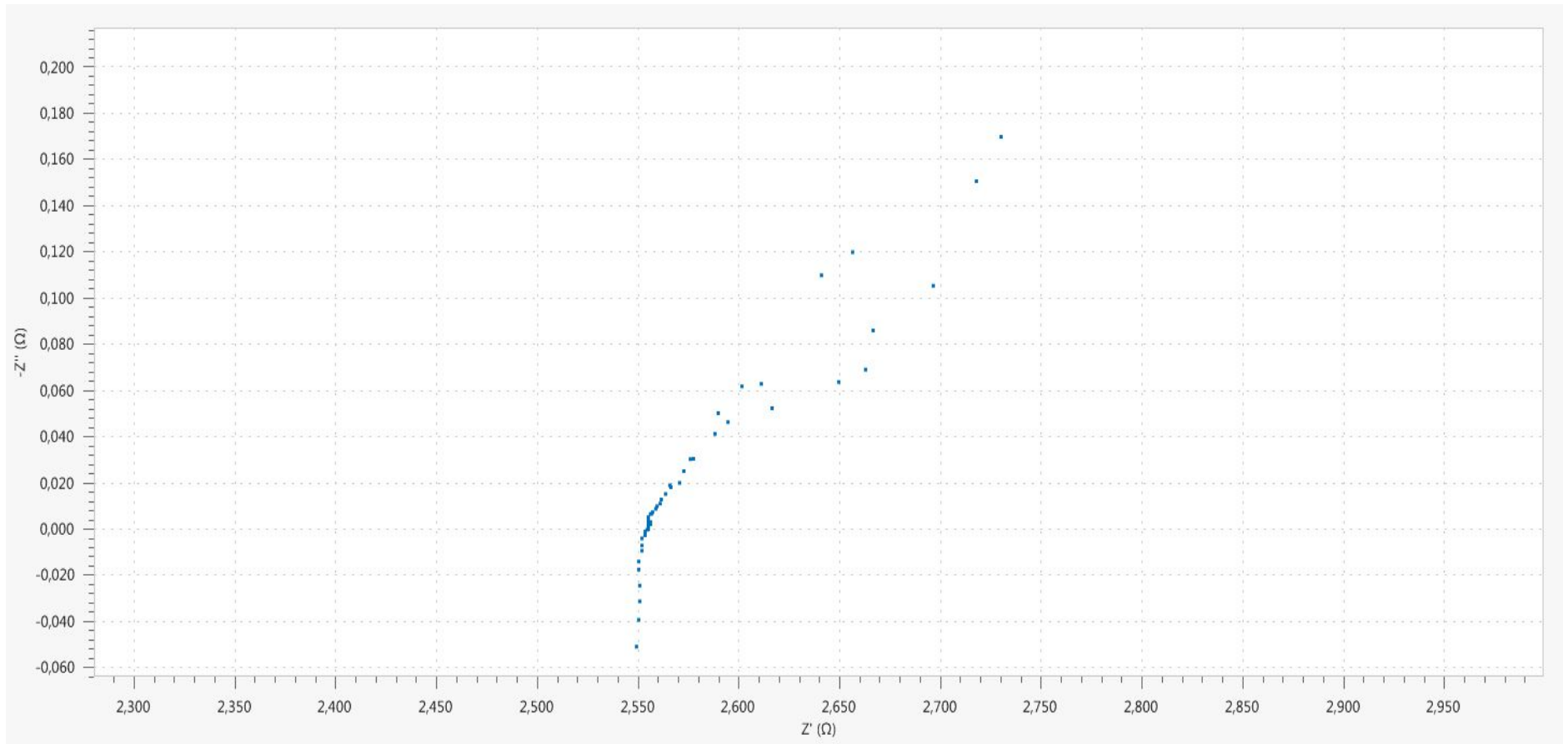
ICM

BOC

I-V curve at 40 C



Impedance at 40 C



Results of approximation of equivalent circuit

