Universidad Politécnica de Cartagena

REACTIVE CONDUCTING POLYMERS AS ACTUATING SENSORS AND TACTILE MUSCLES

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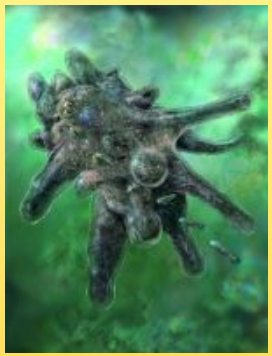
www.upct.es/electroquimica/laboratorio

Full Range of Sizes

Sixty Orders of Magnitude
Life in Middle Region



Planck Length

10^{-35} m

Amoeba
10^{-5} -10^{-4} m

Man
10^{0} m

Radius of Visible Universe

10^{26} m

Good **physical models for very small or very large systems.**
Bad description of the intermediate systems:
complexes molecular interactions and shifts on those interactions (life)

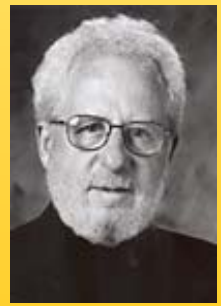
Conducting Polymers

2000 Nobel Award in Chemistry

1977 JCS Chem. Comm. 578-580

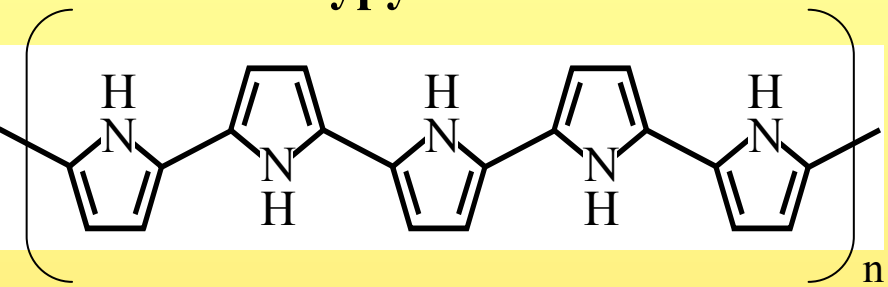
"for the discovery and development of conductive polymers"





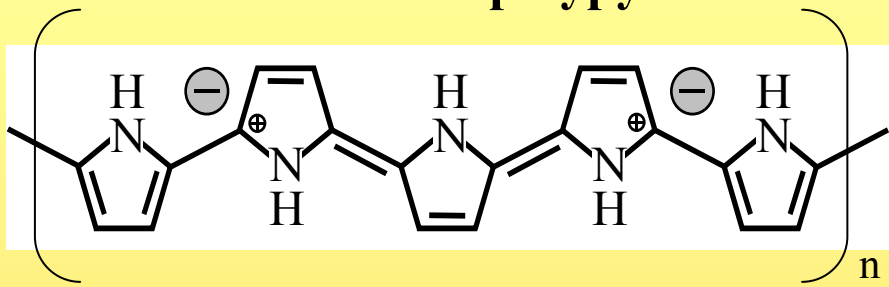
Hideki Shirakawa Alan GMacDiarmid Alan J Heeger

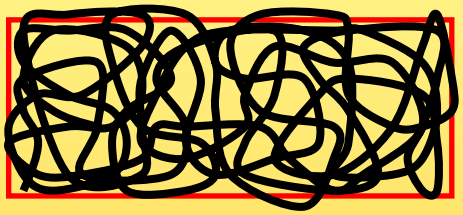
Polypyrrole



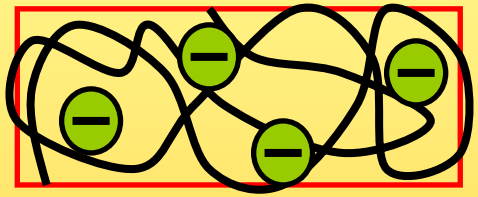
- 2 e⁻

Oxidized polypyrrole





Compacted

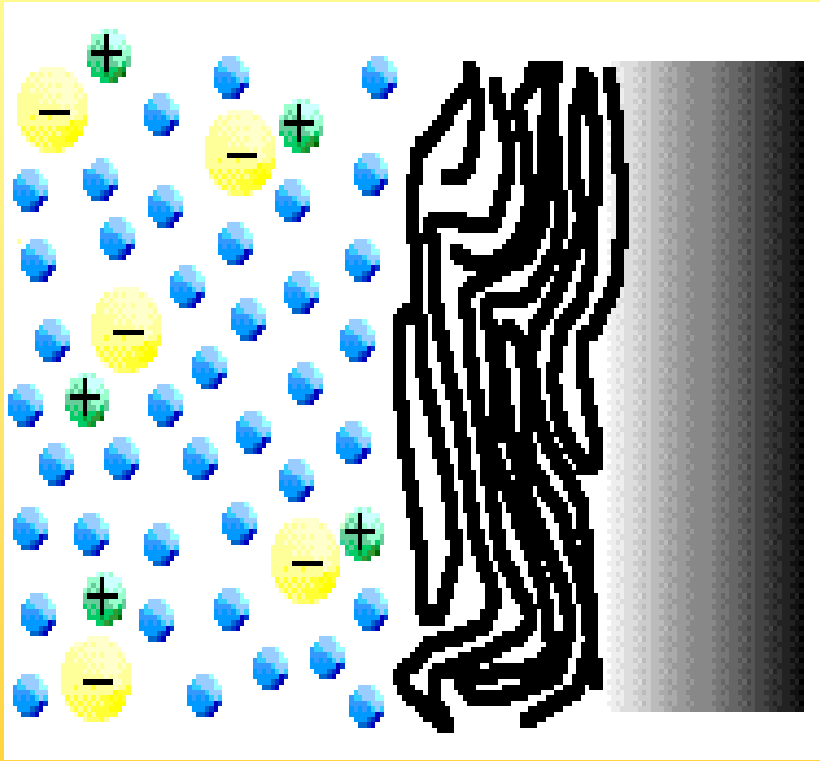


Swelled

THE OXIDATION induces :

- **Breaking of double bonds**
- **Conjugation**
- **New double bonds.**
- **Conformational changes**
- **Soft and back field ionic implantation**

REVERSE ELECTROCHEMICAL OXIDATION/REDUCTION (SWELLIN/SHRINKING) OF A CONDUCTING POLYMER FILM



Polypyrrole film

Aqueous solution

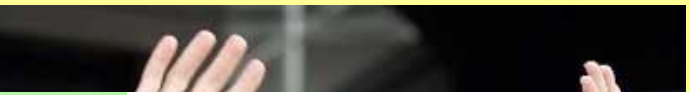
Metal: electric contact

ELECTRO-CHEMO-MECHANICAL DEVICES: SHIFTING ACTUATING MOLECULAR INTERACTIONS DURING THE REACTION.

THE DRIVING ELECTROCHEMICAL REACTION PROMOTES A CHANGE OF THE INTERMOLECULAR INTERACTIONS INSIDE THE FILM:

- -POLYMER-POLYMER
- -POLYMER-COUNTERION
- -POLYMER-SOLVENT
- -SOLVENT-IONS

Universidad Politécnica de Cartagena
Center for Electrochemistry and Intelligent Materials (CEIM) *(CEMI)*
www.upct.es/electroquimica/laboratorio




reduced chains ↔ **neutral chains** ↔ **oxidized chains**
***n* doping** (a) (b) ***p* doping**

THE OXIDATION OF A CHAIN OCCURS THROUGH CONSECUTIVE STEPS

$$CP,\ (CP^{+})A^{-},\ (CP^{2+})A^{-}_{2},\ (CP^{3+})A^{-}_{3},\ (CP^{4+})A^{-}_{4},\ (CP^{5+})A^{-}_{5},\ (CP^{6+})A^{-}_{7},\ldots,\ (CP^{n+})A^{-}_{n}$$

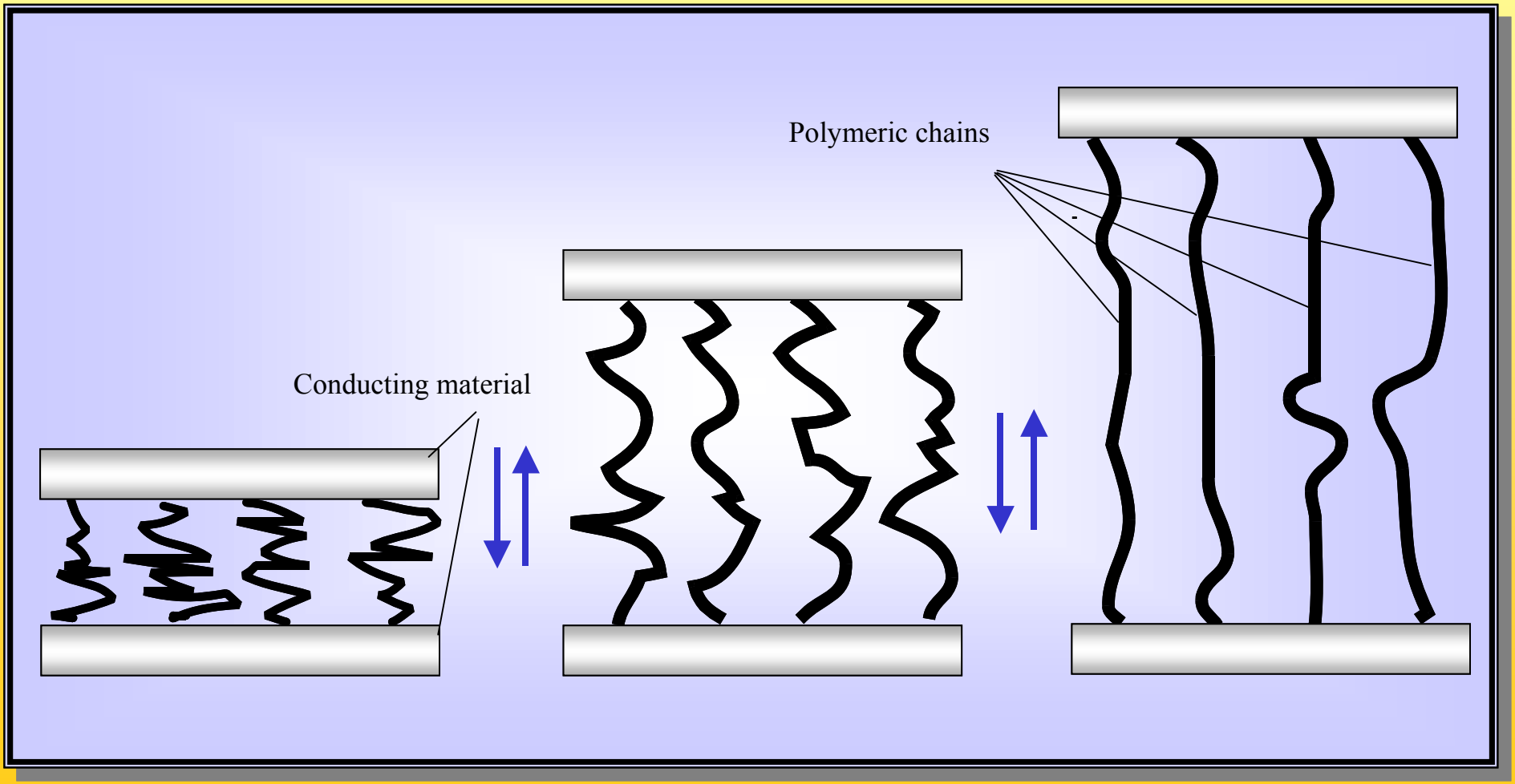
EVERY STEP IS A CHEMICAL EQUILIBRIUM

$$[(pPy^{n+})_s(Cl^-)_n\ (H_2O)_m]_{gel} + (Cl^-)_{aq} + aH_2O \leftrightarrow [(pPy^{(n+1)+})_s(Cl^-)_{n+1}\ (H_2O)_{m+a}]_{gel} + (e^-)_{metal}$$

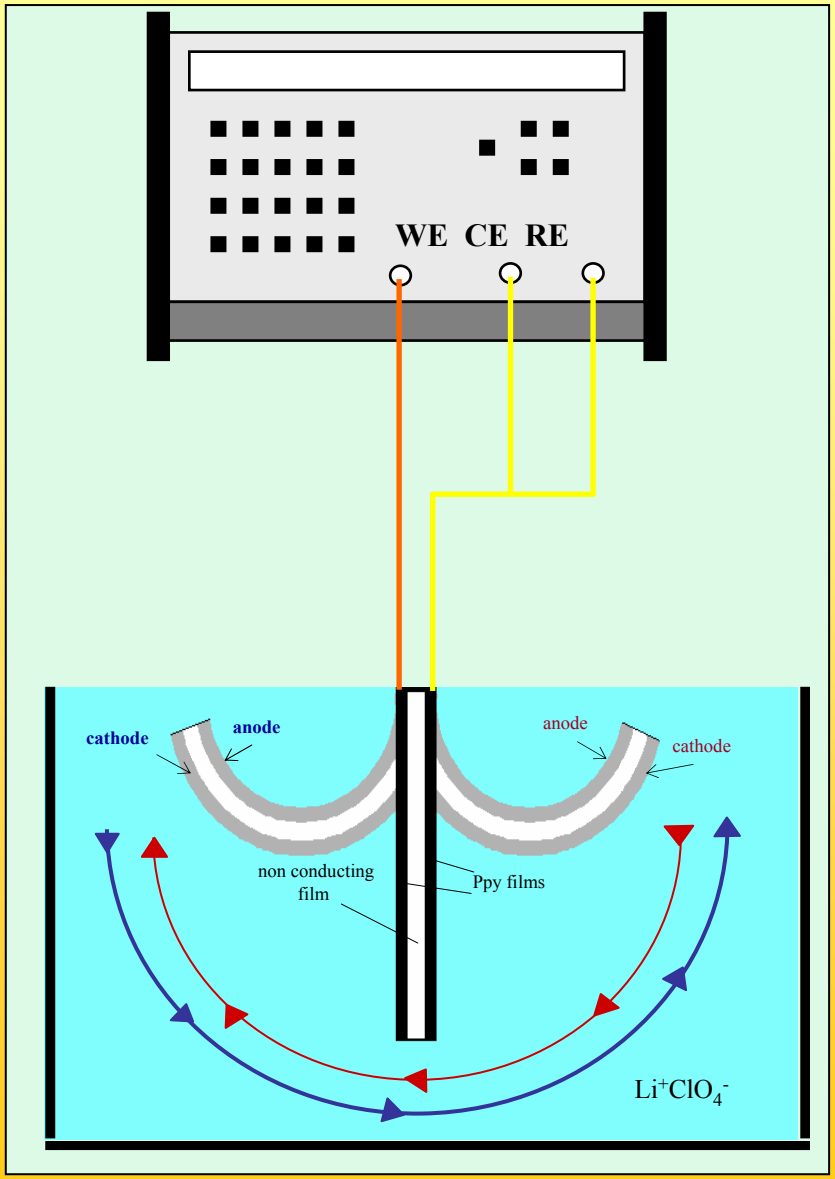
DEFINING AN ELECTRODIC POTENTIAL

$$E = k_1/k_{-1} = E_0 - RT/F\ \ln [(pPy^{(n+1)+})_s(Cl^-)_{n+1}\ (H_2O)_{m+a}]\ /\ [(pPy^{n+})_s(Cl^-)_n\ (H_2O)_m]\ [Cl^-]$$

STRUCTURE FOR AN IDEAL, MIMETIC (ARTIFICIAL) AND NANOMETRIC SARCOMERE



Artificial Muscle for a conscious system



Electric pulses generator

Signals control

Two wires driving signals

Volume variations

Conformational changes

Ionic interchanges

Water interchange

Mechanical stress and work

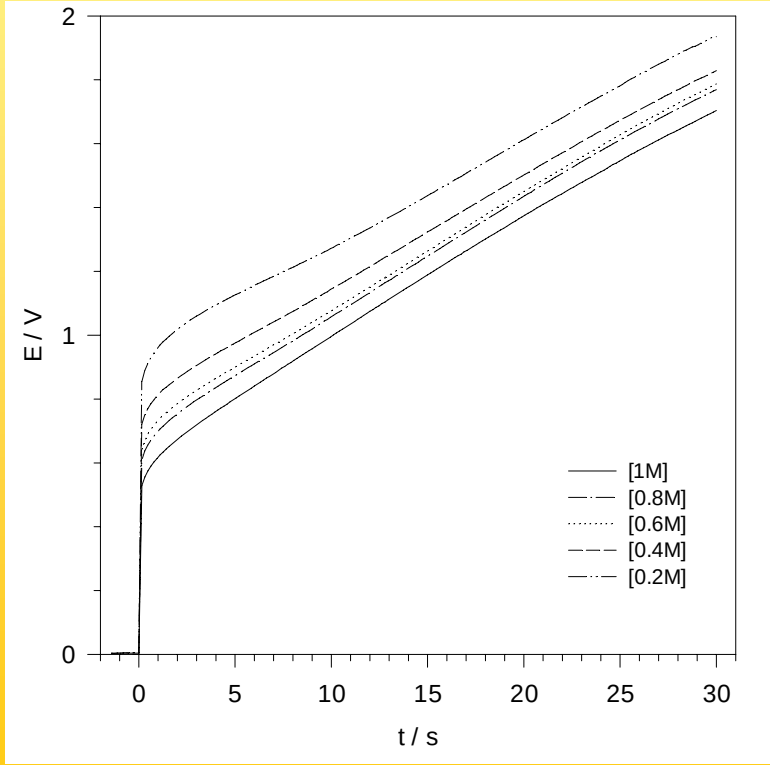
(pPy)s + n(Cl-)aq + mH2O ↔ [(pPyn+)s(Cl-)n (H2O)m]gel + (n e-)metal

(Volume)1 *(conc. and I)* *T* *(Volume)2* *i and E*

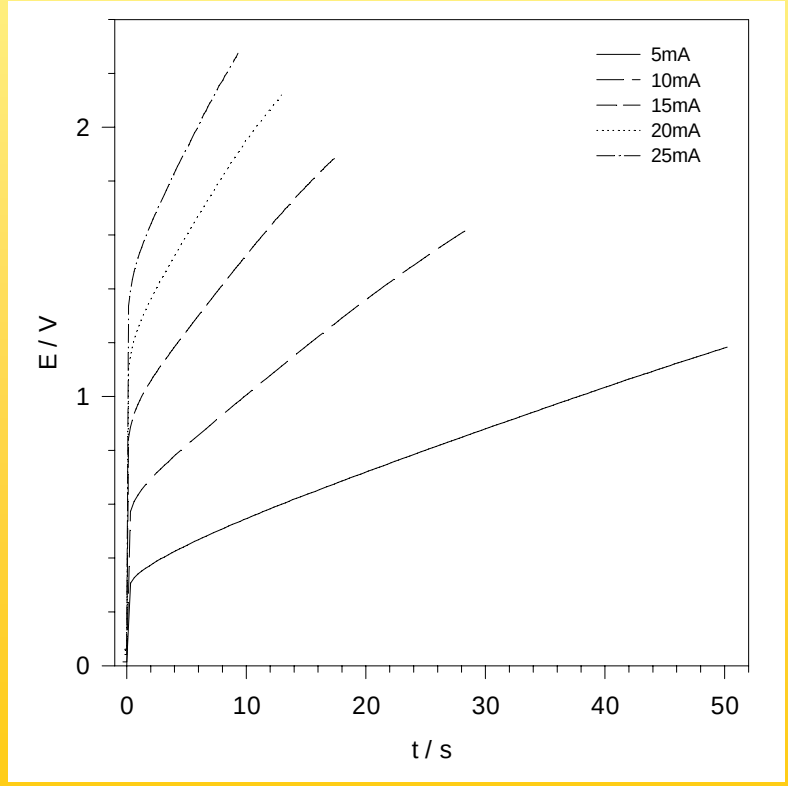
(synthesis contitions)

BIOMIMETICS, 07

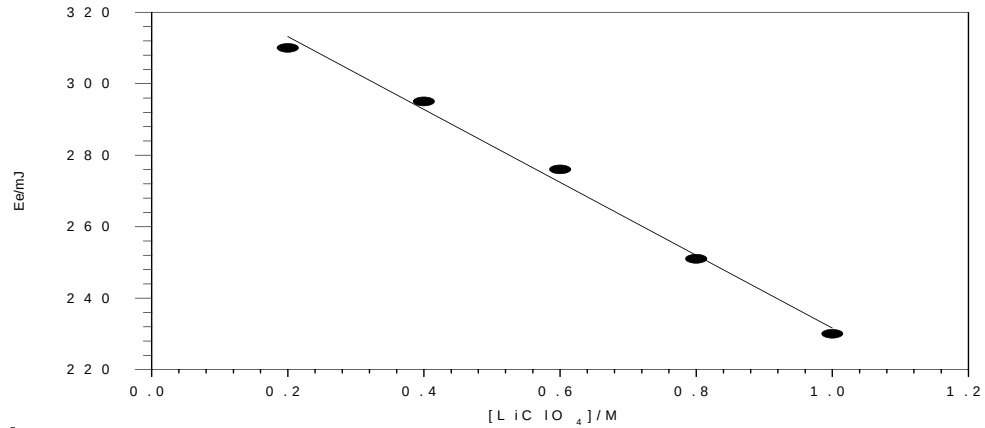
Muscle potential Influence [Electrolyte] i = 10 mA



Evolution of the muscle potential Under different current flow

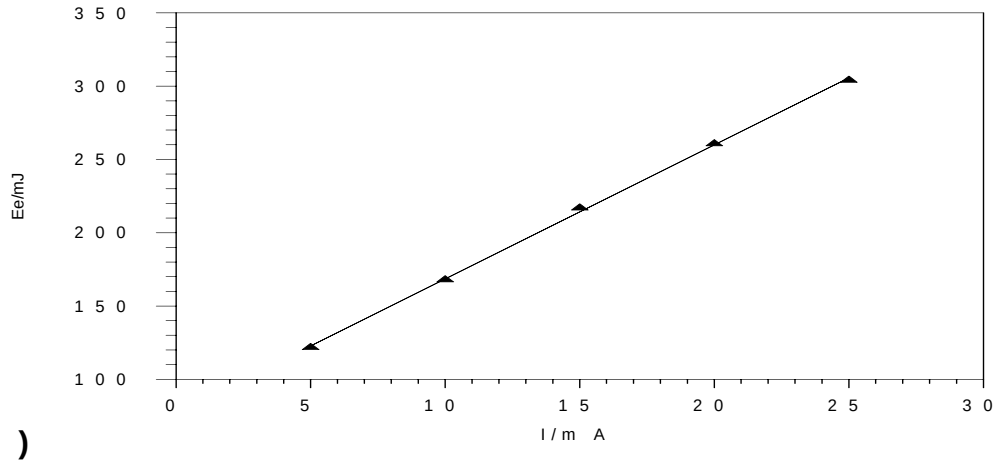


ACTUATORS AND SENSORS



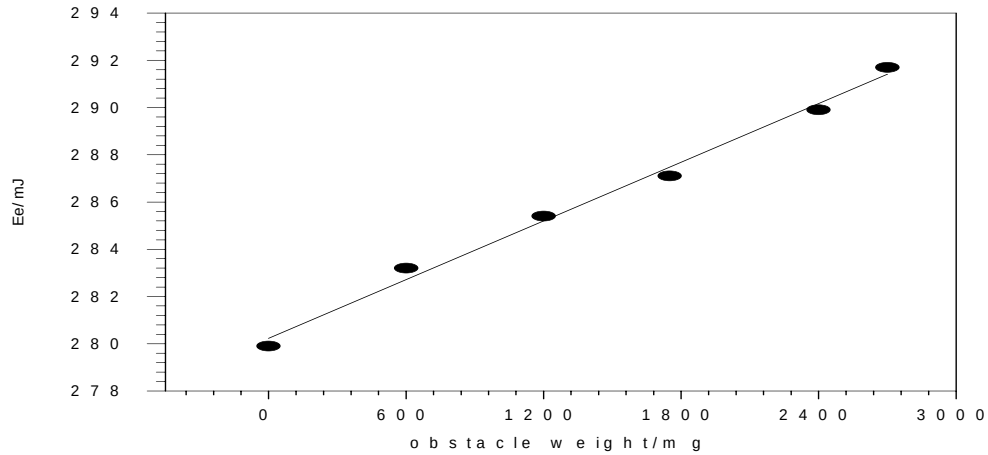
[Electrolyte]

b)



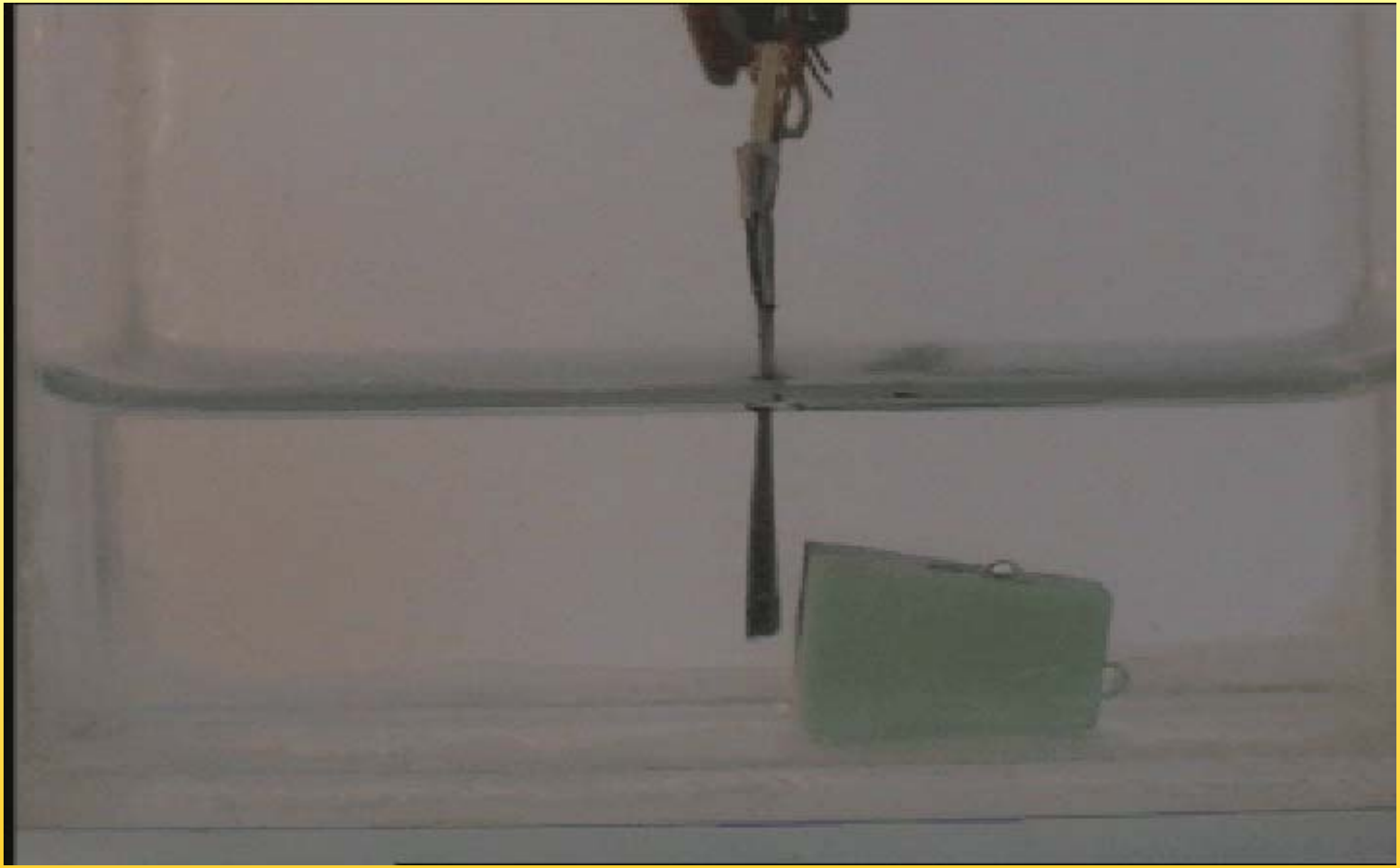
Current

c)



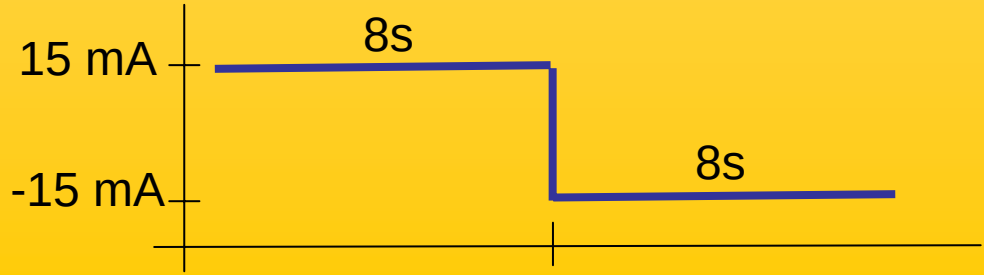
Trailed weight

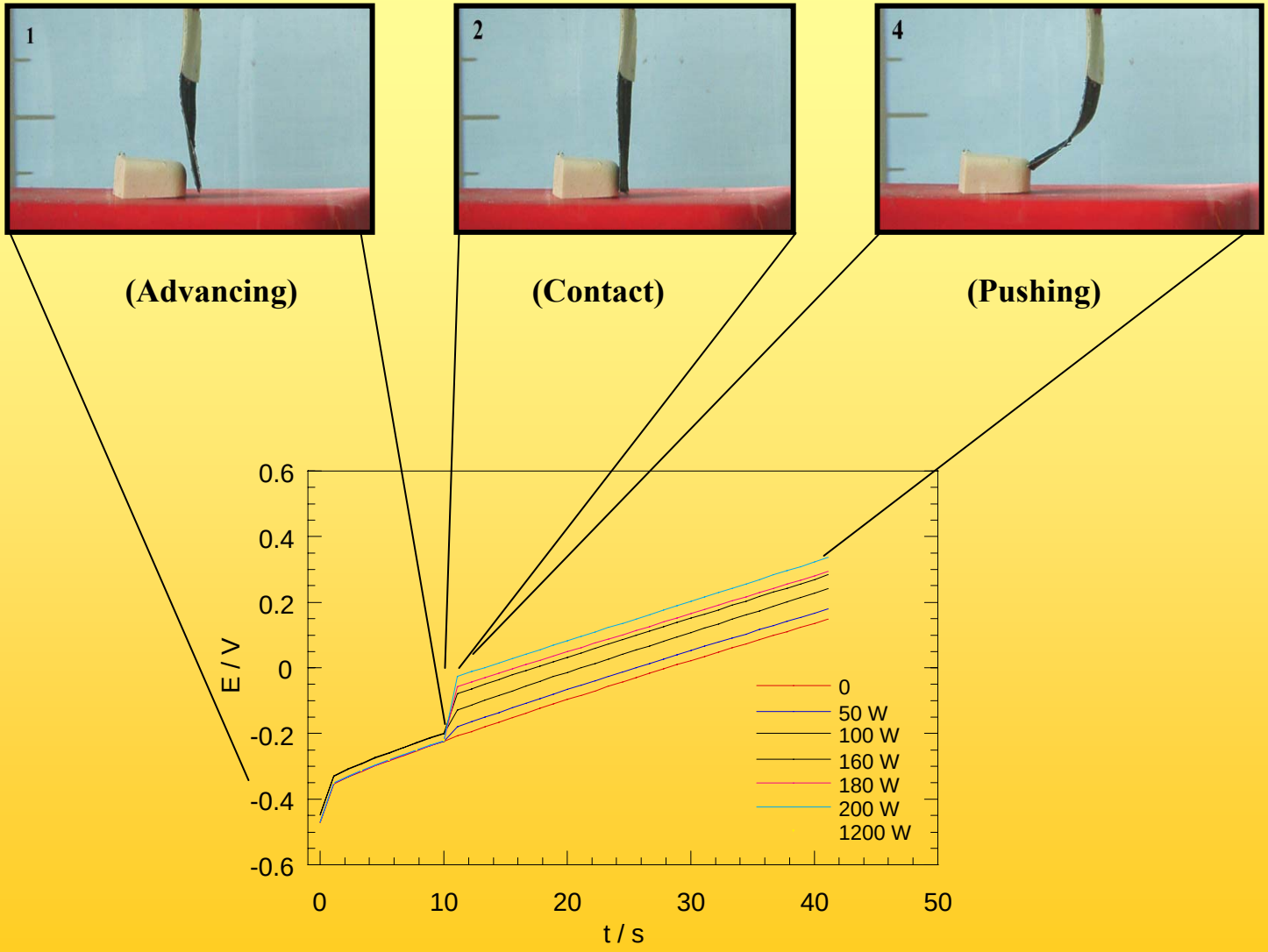
TOUCHING, PUSHING, AND SENSING MUSCLE



Device: 2 x 1 cm²

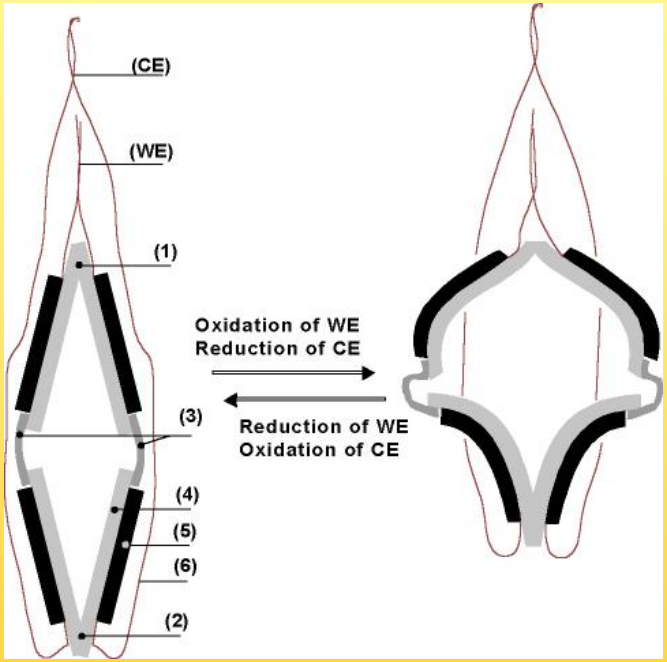
Adv. Mat. 15, 279-282 (2003)

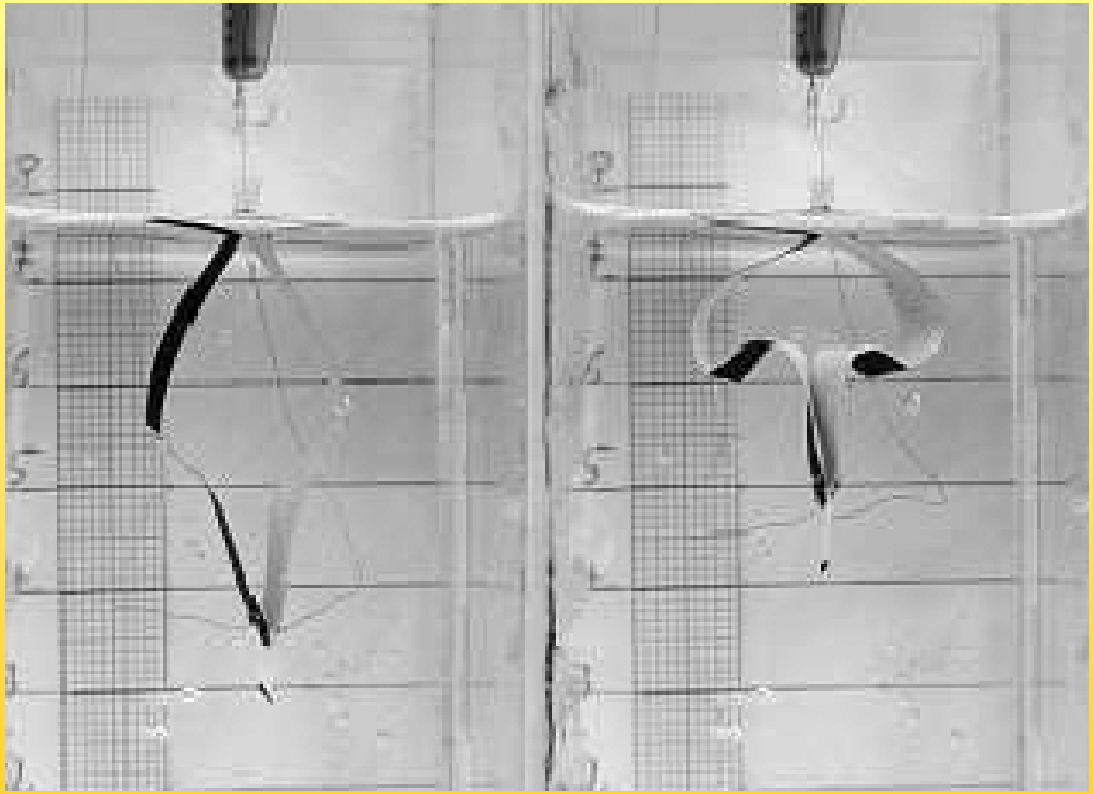



1
2
4
(Advancing)
(Contact)
(Pushing)
E / V
t / s
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
10
20
30
40
50
0
50 W
100 W
160 W
180 W
200 W
1200 W

COMPLEXES STRUCTURES KEEP SIMULTANEOUS ACTUATING-SENSING RPOPERTIES: ROMBIC DEVICE BY COMBINATION OF BILAYERS

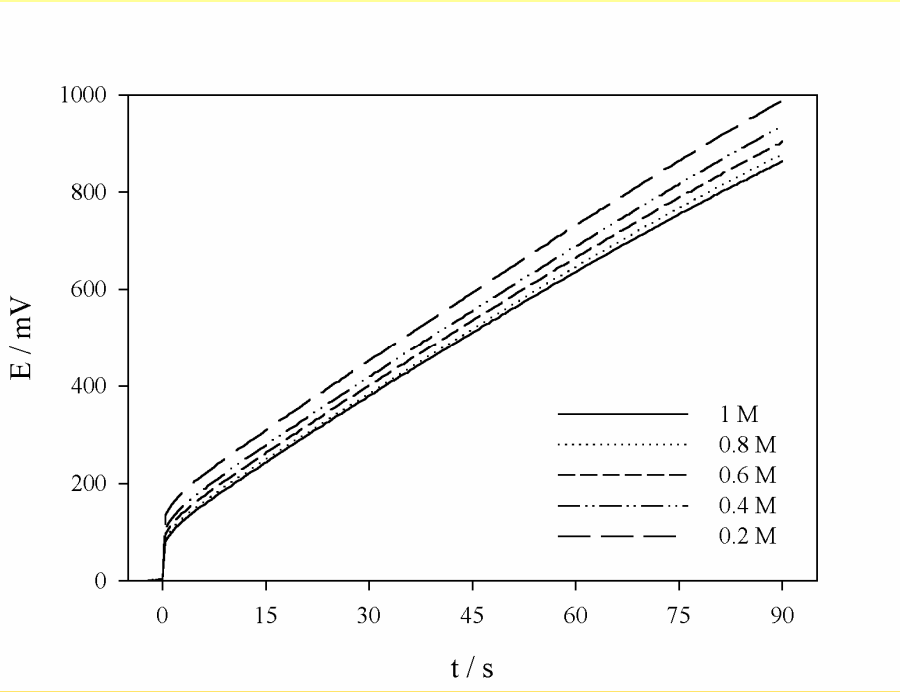
INCLUDING: WE, RE and CE

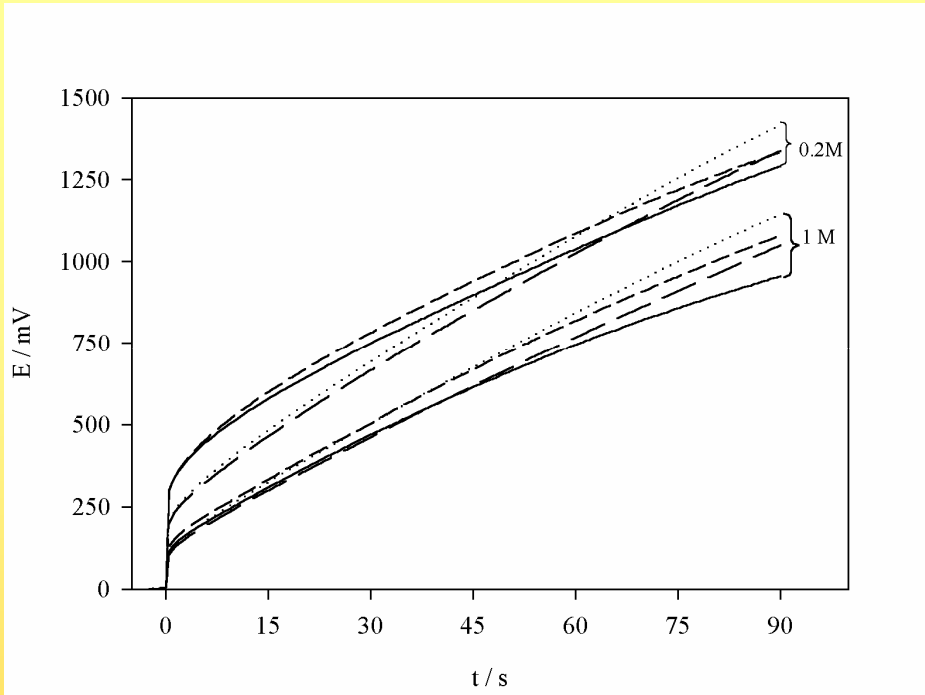


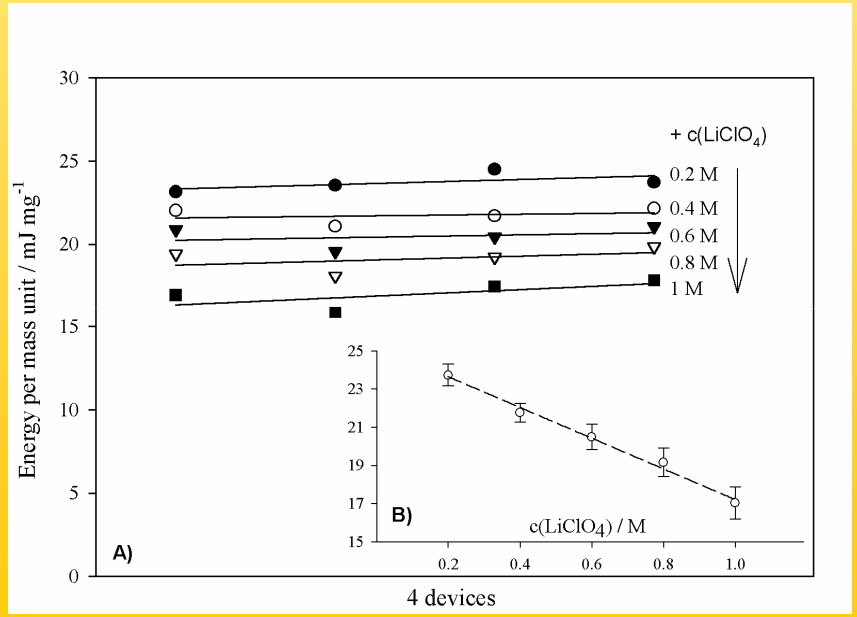


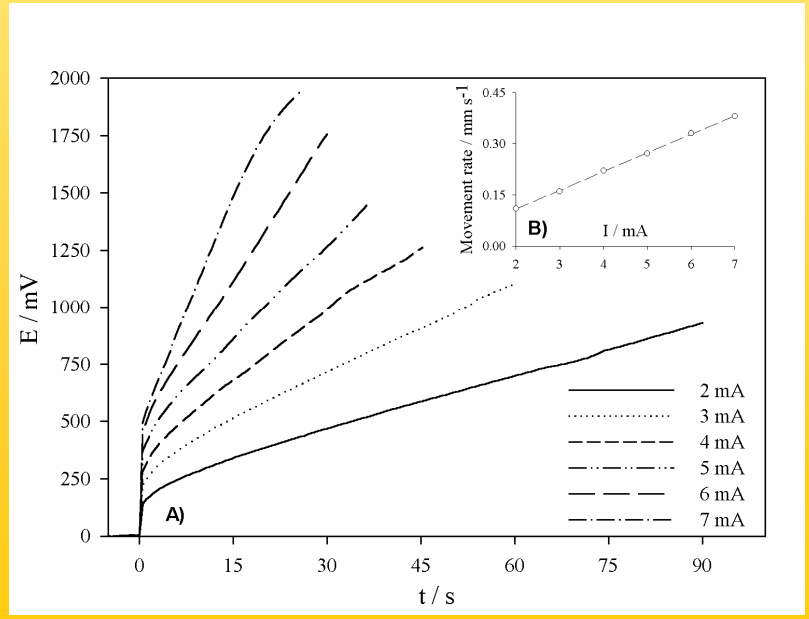
J. Bioelectrochem. Bioenerg., **38,** 411-414 **(1995)**
J. Bioelectrochem. Bioenerg., **42,** 117 - 122 **(1997)**

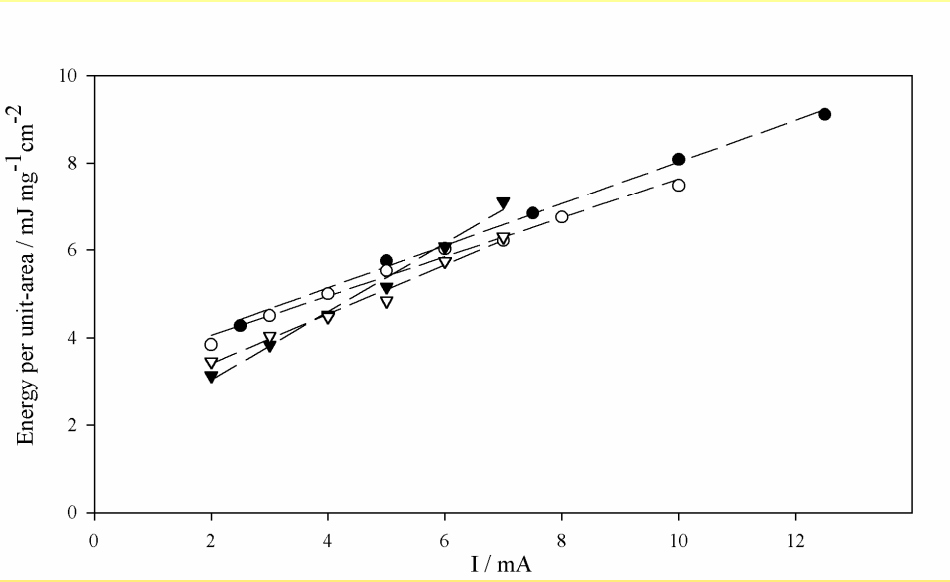
J. Appl. Electrochem., 36, 205–214 (2006)

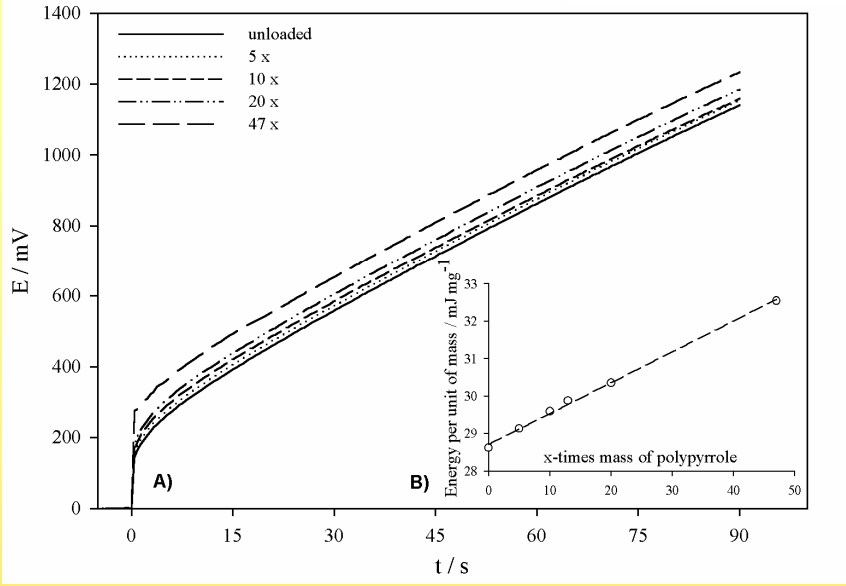

E / mV
t / s
1 M
0.8 M
0.6 M
0.4 M
0.2 M

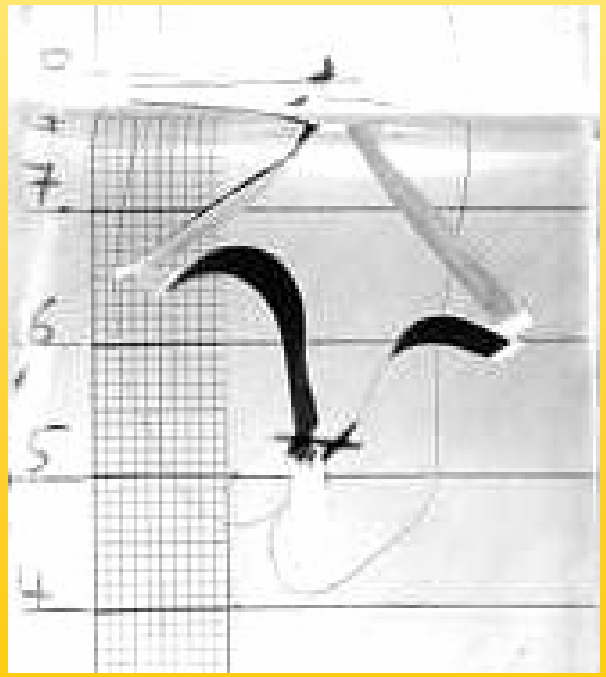

E / mV
t / s
0.2M
1 M

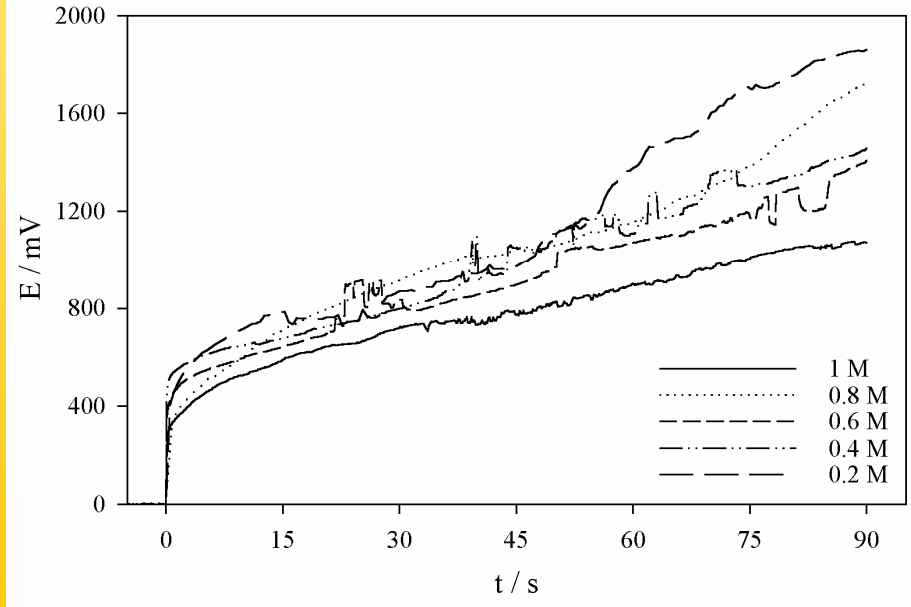

Energy per mass unit / mJ mg-1
+ c(LiClO4)
0.2 M
0.4 M
0.6 M
0.8 M
1 M
A)
B)
c(LiClO4) / M
4 devices


E / mV
t / s
A)
B)
Movement rate / mm s-1
I / mA
2 mA
3 mA
4 mA
5 mA
6 mA
7 mA


Energy per unit-area / mJ mg-1cm-2
I / mA


unloaded
5 x
10 x
20 x
47 x
E / mV
t / s
A)
B)
Energy per unit of mass / mJ mg-1
x-times mass of polypyrrole




E / mV
t / s
1 M
0.8 M
0.6 M
0.4 M
0.2 M

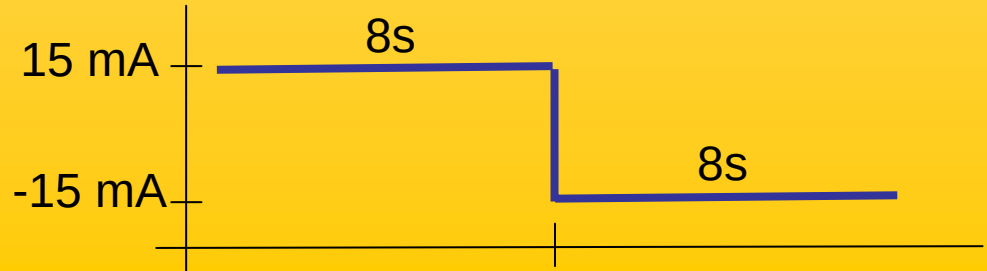
LARGE (40%) LONGITUDINAL MOVEMENT

PATENT:P200300800

40% ΔI

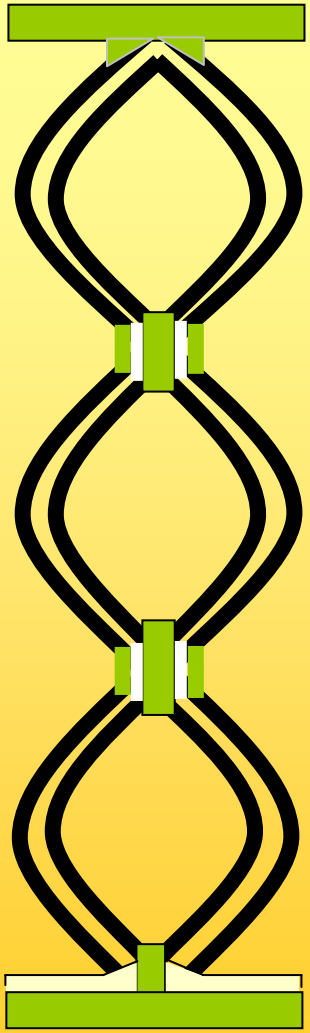
Devices: 2 x 1,5 cm²

Electrochim. Acta (2007)



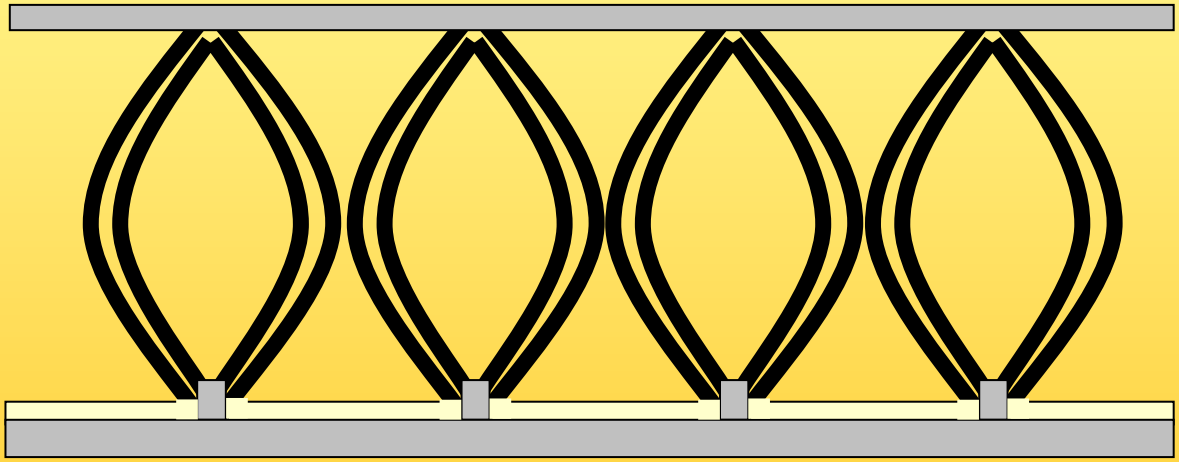
Monodimensional combination of devices

(In progress)



For large displacements

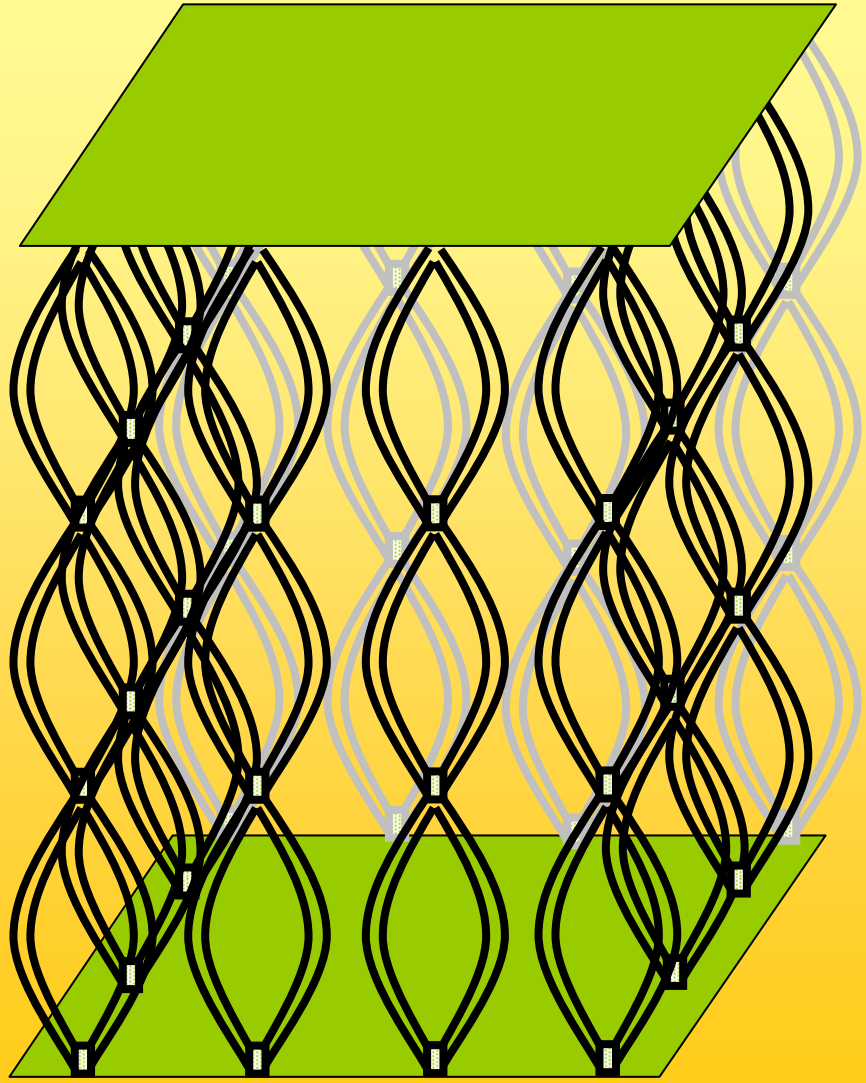
For strong mechanical developments



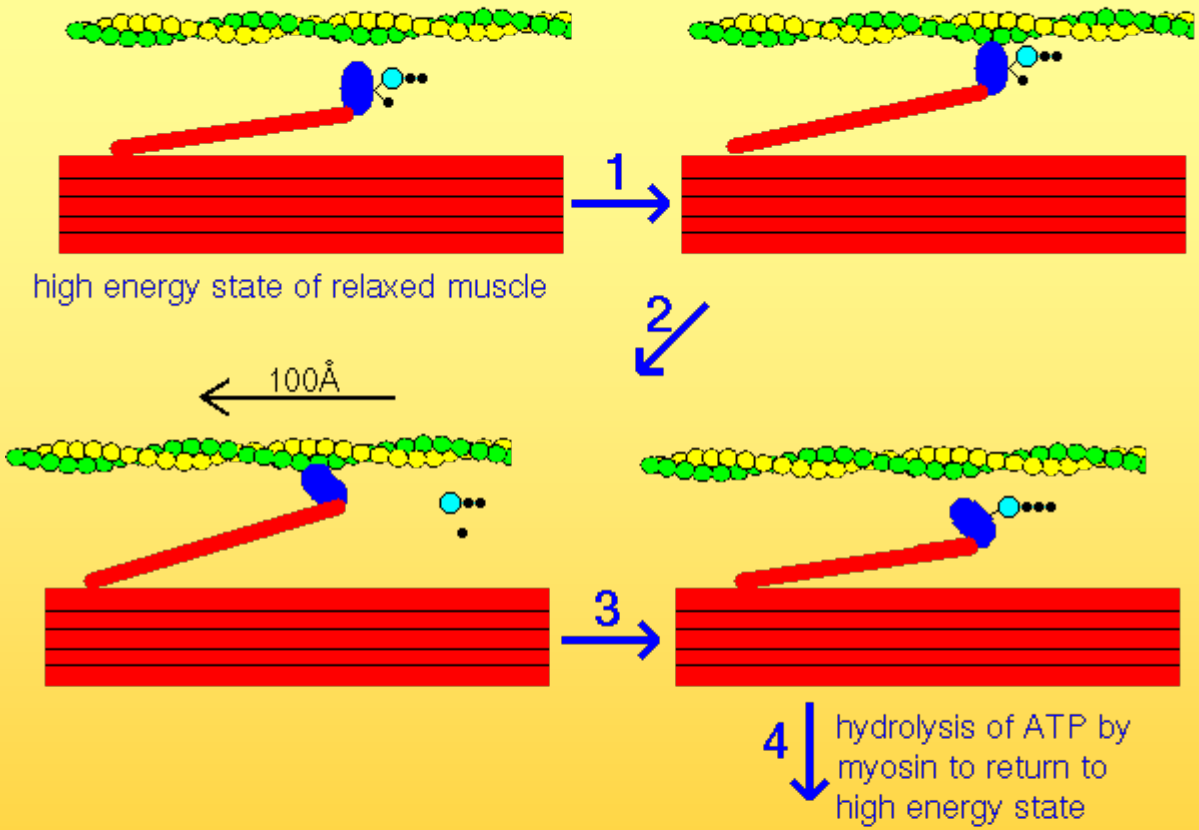
MUSCLE ELEMENT IN THREE DIMENSIONS

(In progress)

Able to save internal electrical interruptions

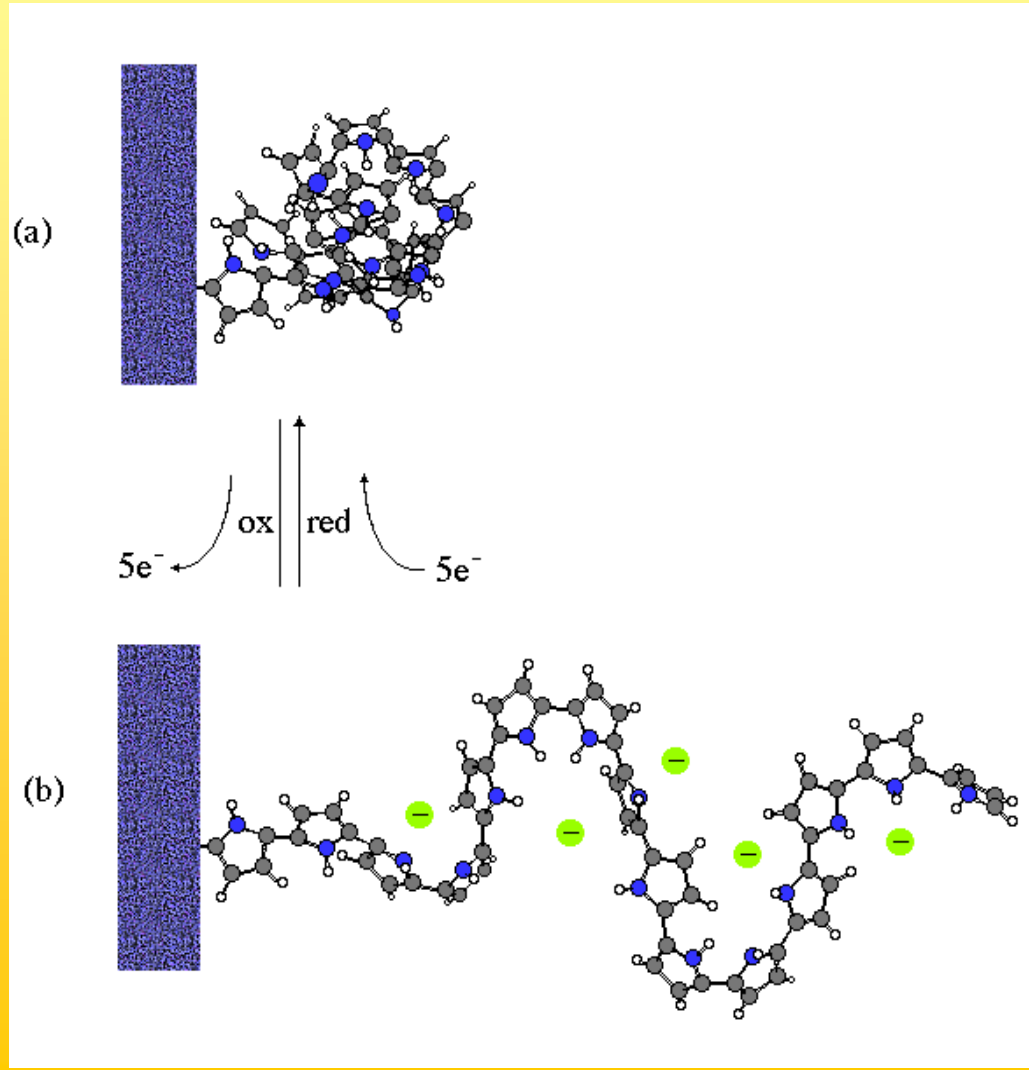


Skeletal Muscle Fibre Contraction Cycle



MOLECULAR MOTOR: IDEAL, LINEAL CHAIN OF A CP GRAFTED TO AN ELECTRODE

METAL SOLUTION

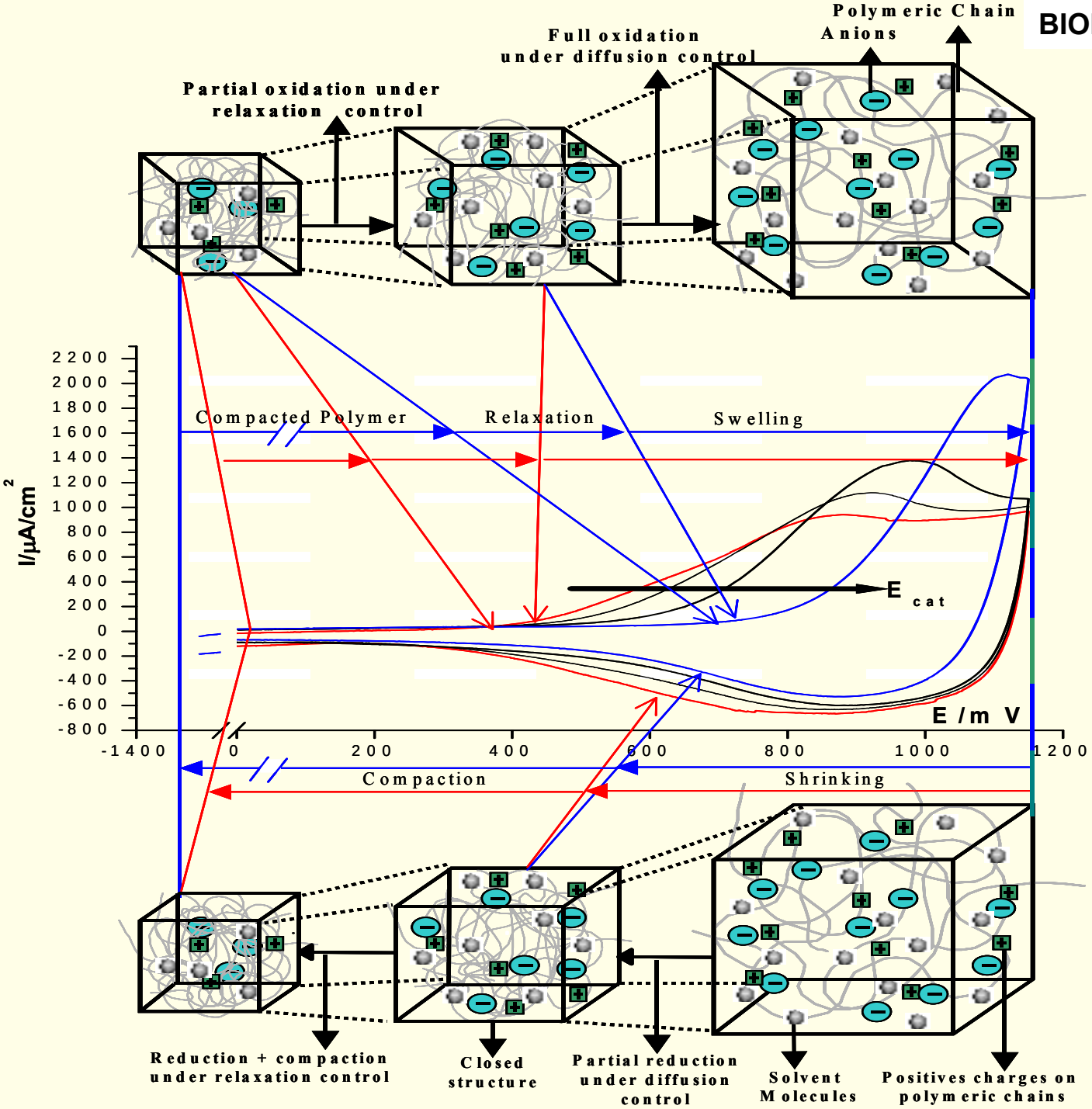


CONFORMATIONAL MOVEMENTS
ORIGIN OF
ACTUATING AND SENSING
PROPERTIES

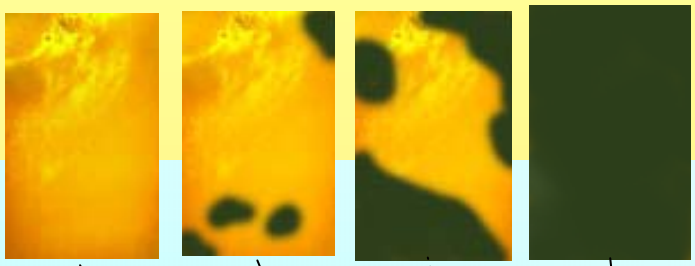
PROBLEM:
CHARACTERIZATION???

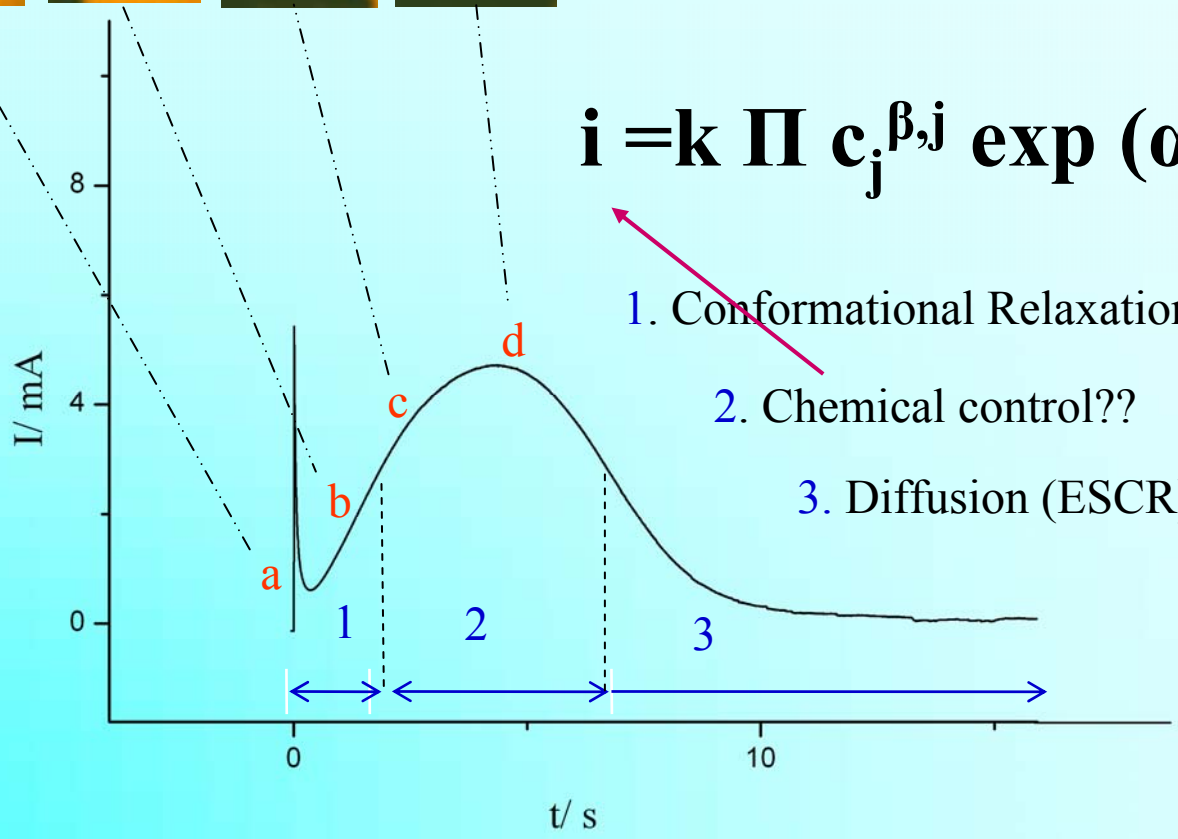
SOLUTION:
THE CONFORMATIONAL ENERGY !!!

QUESTION:
IS THIS ENERGY AN
ACTIVATION ENERGY ??
OF THE STIMULATING
ELECTROCHEMICAL REACTION


Polymeric Chain Anions
Full oxidation under diffusion control
Partial oxidation under relaxation control
Compacted Polymer
Relaxation
Swelling
E cat
I/µA/cm 2
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1400
0
200
400
600
800
1000
1200
E /m V
Compaction
Shrinking
Reduction + compaction under relaxation control
Closed structure
Partial reduction under diffusion control
Solvent Molecules
Positives charges on polymeric chains

Kinetic Control





$$i = k \Pi c_j^{\beta,j} \exp(\alpha z F \eta / RT)$$

1. Conformational Relaxation (ESCR)
2. Chemical control??
3. Diffusion (ESCR)

ELECTROCHEMICAL REACTIONS OF POLYTHIOPHENE
IN PRESENCE OF THE SOLVENT **S** CONTAINING THE ANION **A**

$$(pTh)_s + n(A^-)_{solv} + m(S) \leftrightarrow [(pTh^{n+})(A^-)_n\,(S)_m]_{gel} + (n\,e^-)_{metal}$$

neutral chains **oxidized chains**

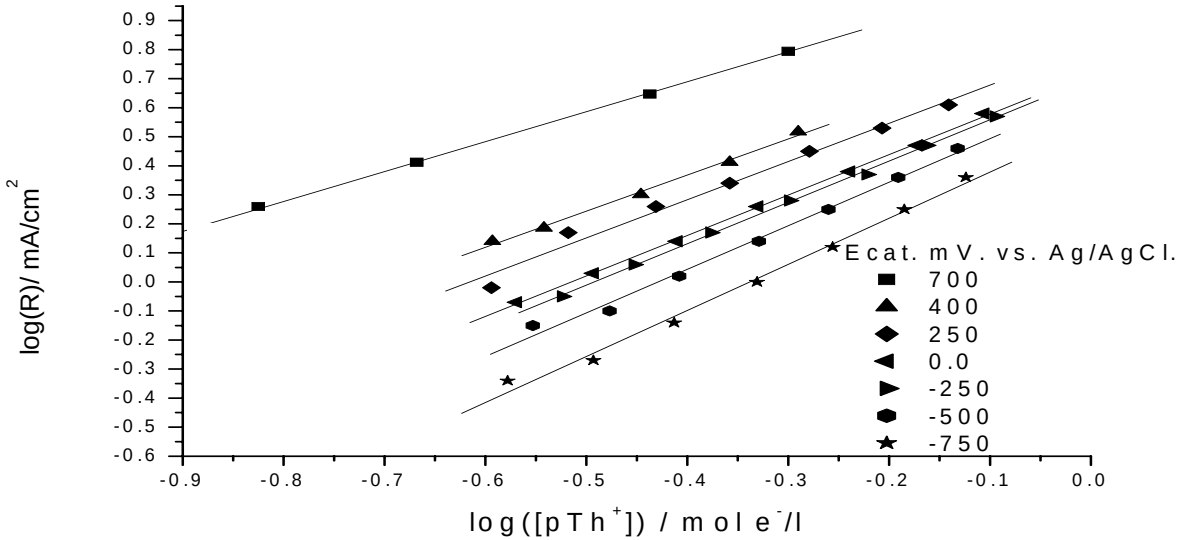
OXIDATION EMPRICAL KINETIKS

$$R = A \exp(-E_a/RT)\,[ClO_4^-]^{\alpha}\,[pTh^+]^{\beta}$$

$$\text{Log } R = dQ/dt = i$$

$$Log\ i = log[A\ exp(-E_a/RT)] + \alpha\ log\ [C10_4^-] + \beta\ log\ [pTh^{n+}]$$

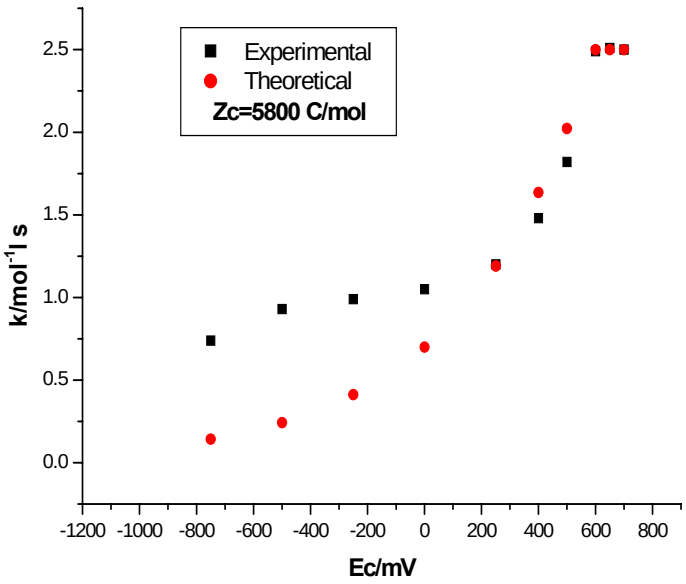
This equation states the experimental procedure required to obtain: k, $E_{a,,}$ α and β.

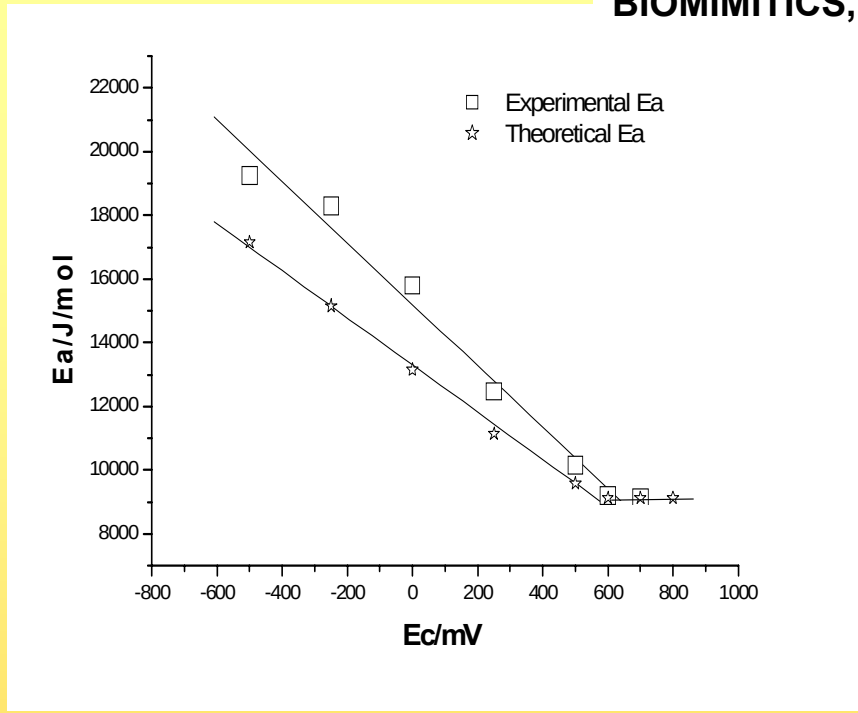


Double logarithmic plot: oxidation rates of a polythiophene-coated platinum electrode versus **[pTh+]**.
The film was submitted to potential steps between different cathodic potentials (**kept for 30 s every time**) and different (700, 750, 800, 850, 900 and 950 mV) anodic potentials.
The **[pTh+]** in the polymer film is obtained from the overall oxidation charge consumed at the end of the potential step, the polymer weight **0.23 mg** and the polymer density.

E_{cat} (mV)	700	400	250	0	-250	-500	-750	-1000
R_0/mA cm^{-2}	1.098	0.87	0.78	0.72	0.695	0.668	0.571	0.15
β	1	1.24	1.2	1.4	1.4	1.6	1.71	1.85
k/mol l^{-1}s^{-1}	39.6	23.4	19.1	16.6	15.7	14.7	11.8	5.4

Slopes from the figure are the reaction orders β. By extrapolation of the lineal variations to **[pTh+]=0**, the limit oxidation rates **R0 (mA cm-2)** were obtained. Values of the rate coefficients, **k,** were calculated).

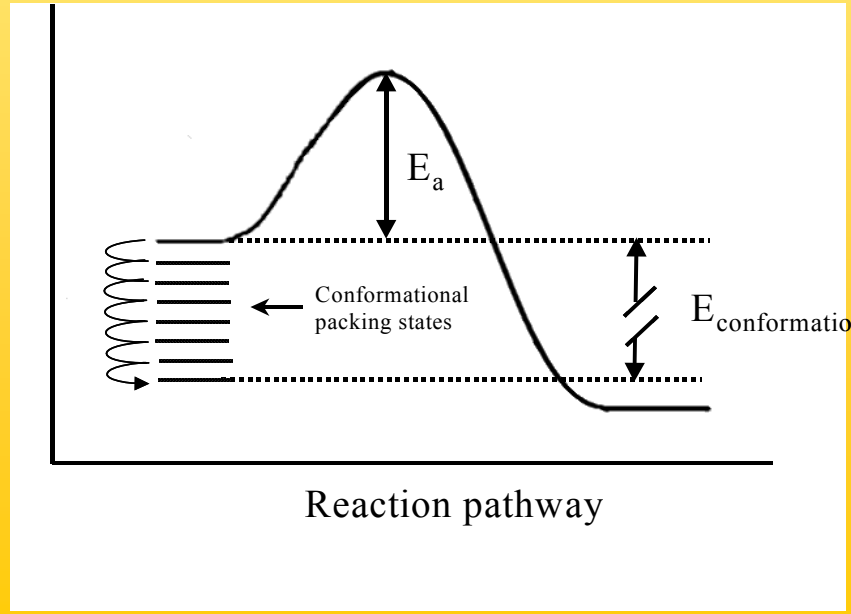


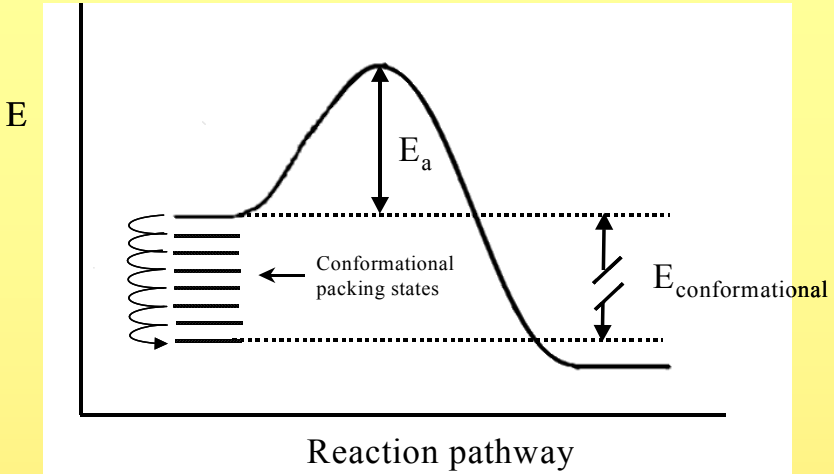


$$\ln k = \ln k_0 + (\Delta H^* + z_r\eta)/RT - z_c\eta_c/RT = \ln k' - z_c\eta_c/RT$$

$$E_a = RT + \Delta H = RT + \Delta H^* - z_c\eta_c + z_r\eta$$

J. Electroanal Chem. (In press)
Electrochim. Acta (In press)



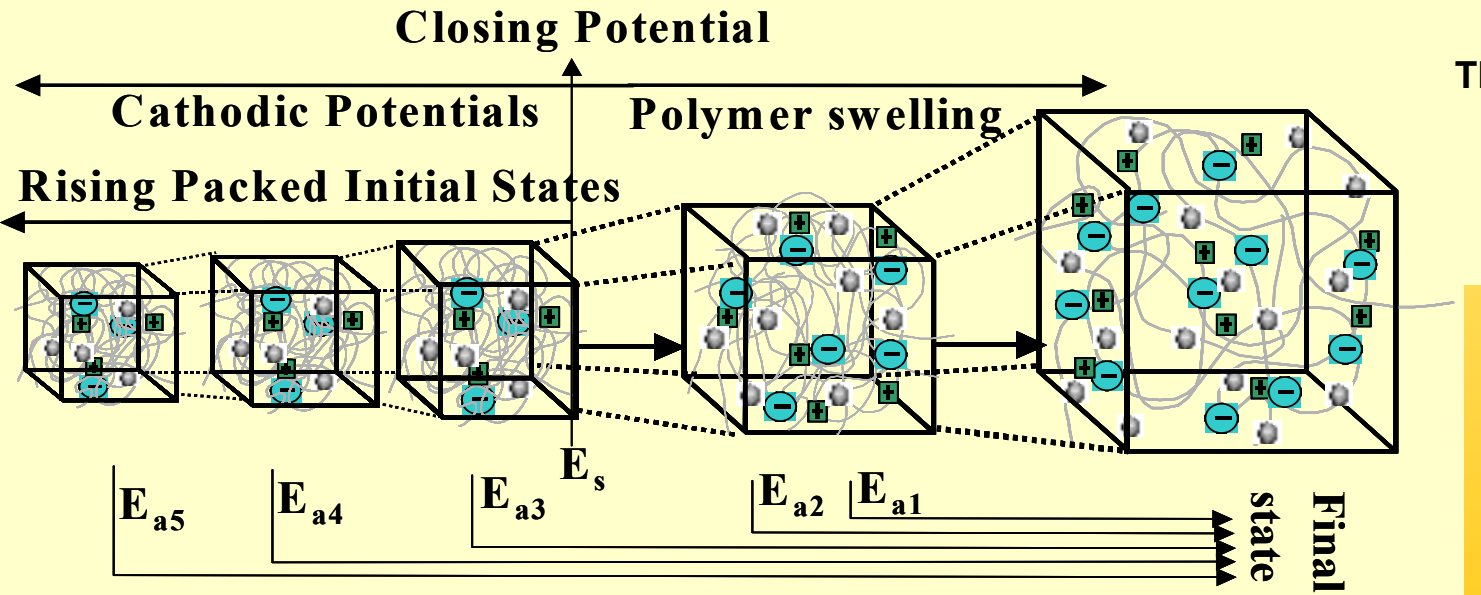


The experimental activation energy includes two component:

- the constant chemical activation energy ($E_{a)}$)

- and the energy required to relax the initial packed structure of folded chains.

(E_{relax} or $E_{conformational}$)



ACTIVATION ENERGIES QUANTIFFY THE CONFORMATIONAL PACKING STATE, This is a CONFORMATIONAL MEMORY

$$E_{a1} = E_{a2} < E_{a3} < E_{a4} < E_{a5}$$

$$(p\text{-}Th)_s + n(A^-)_{aq} + mH_2O \rightarrow [(p\text{-}Th^{n+})(A^-)_n (H_2O)_m]_{gel} + (n\ e^-)_{metal}$$

MEMORY:
ERASABLE
PERMAENT

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Dedicated to the memory of Prof. A. MacDiarmid,

how had accepted our invitation as a plenary lecturer

and his nomination as Honorary Doctor of the Polytechnic Univ. of Cartagena.

Universidad Politécnica de Cartagena

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