VOLTAMMETRY-100 YEARS ON

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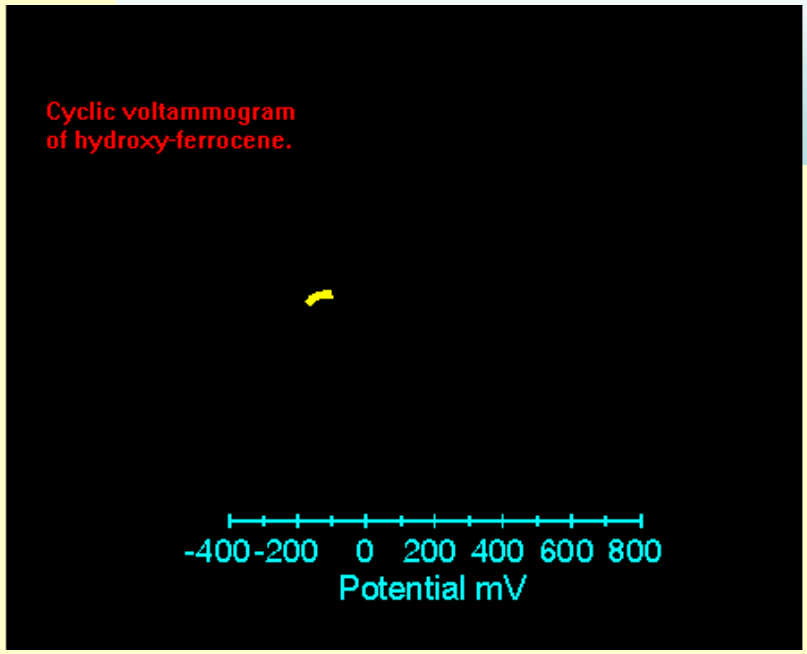


15th Congress of the Students of Chemistry and Technology of MACEDONIA

FIRST Paper reporting on Polarography as a new electroanalytical technique
Published exactly 100 years ago.
(*Polarography is recognized as a predecessor of all voltammetric techniques*)

J. Heyrovský, *Chemické Listy* 1922, *16*, 256–264

537.33

RESEARCHES WITH THE DROPPING MERCURY CATHODE.

PART I.

General introduction

BY

J. HEYROVSKÝ.

The electrolysis with the dropping cathode [1]), as applied to the study of electrolytic processes by the present author, uses the mercury cell arrangement of B. Kučera, which is a modification of Lippmann's capillary electrometer method for the determination of the change of surface tension of polarised mercury.

If the solution in this cell be freed from air, and the current due to the polarising E. M. F. be measured, the initial "residual current" is found to be very small (of the order of 10^{-8} to 10^{-7} amp.) and the beginning of the electrolytic deposition is well marked.

Moreover, owing to certain favorable circumstances, such as the continuous renewal of the surface in the mercury drop at the cathode, the high over-potential on pure mercury and the constancy of the anodic potential of the large mercury layer, this electrolysis has been found to be highly "reversible" i. e. the potentials of polarised drops are in just as simple equilibrium with the ions of the solutions as electrodes of concentration cells are. This is evident from the shifts of the "current-voltage" curves proceeding with the dilution of the electrolyte, which shifts closely agree with those calculated from the ionic concentrations.

Since the apparatus and experimental arrangements have already

cathode, which may consist in the depo
their valency, or in general in the redu
of being chemically reduced.

If the process proceeds reversibly in
at each potential acquired by the pola
established between the reducible substa
ion products arising at the cathode — t
the potential of the drop.

Consider first the case of the electro
Me, represented as

$$Me^{n(+)} + n(-)$$

If the drop is polarised to the poten
onto mercury, accumulating there to
expression

$$\pi = -\frac{RT}{nF}\log.$$

must hold, where K_{Me} is a specific co
on the "solution tension" of its amalga

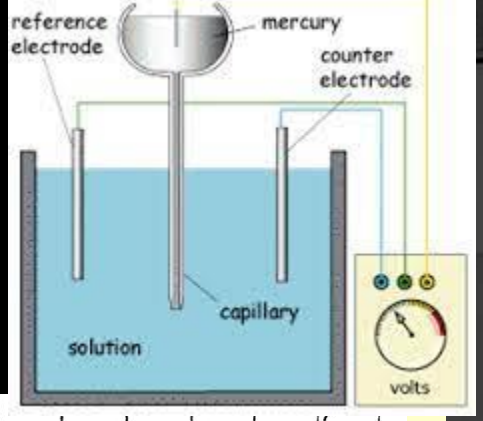
Secondly let us consider the electr
reaction

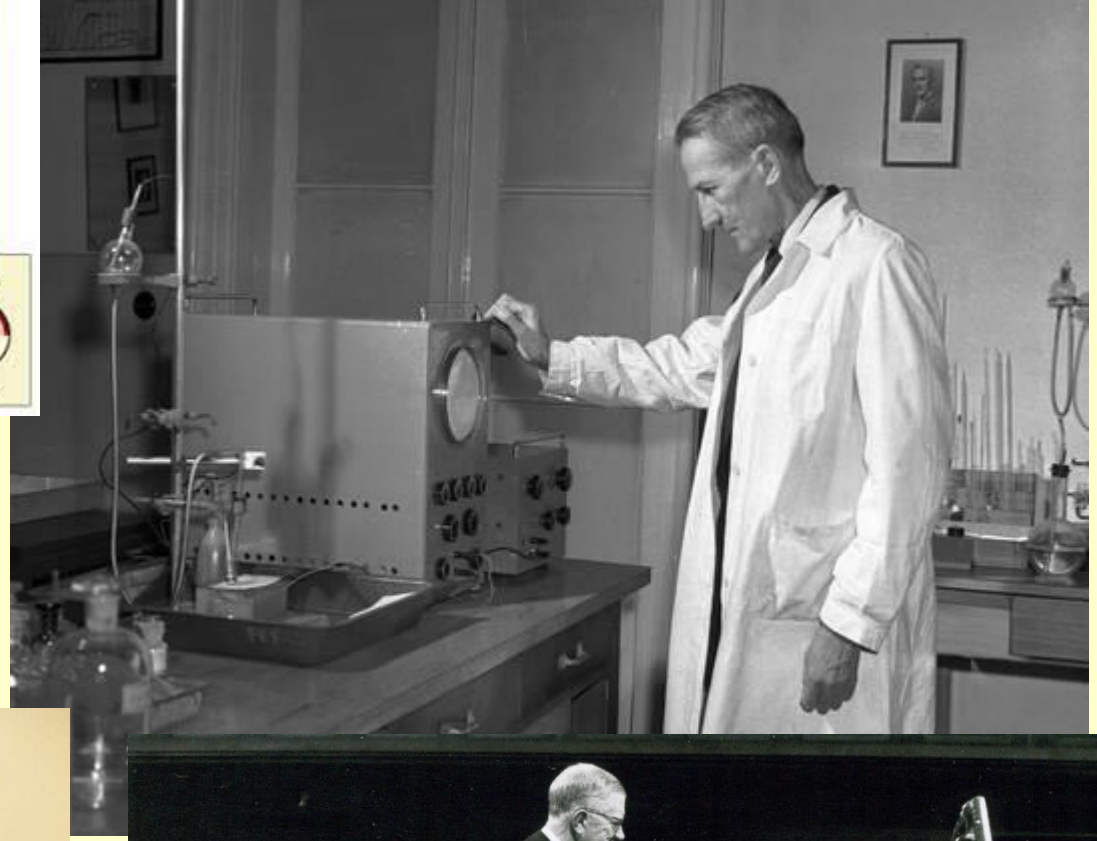
$$M^{n(+)} + r(-) \rightarrow M$$

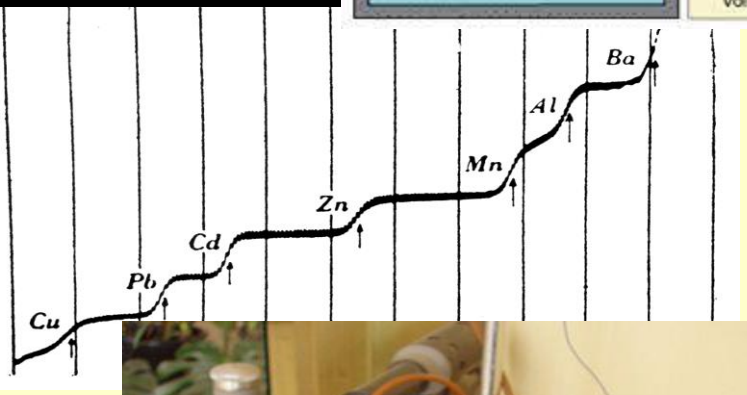
Denoting by $[M^{(n-r)+}]$ the con
accumulated at the mercury drop surfa
ion surrounding the drop, we must hav
the ionic electrode equilibrium accordi

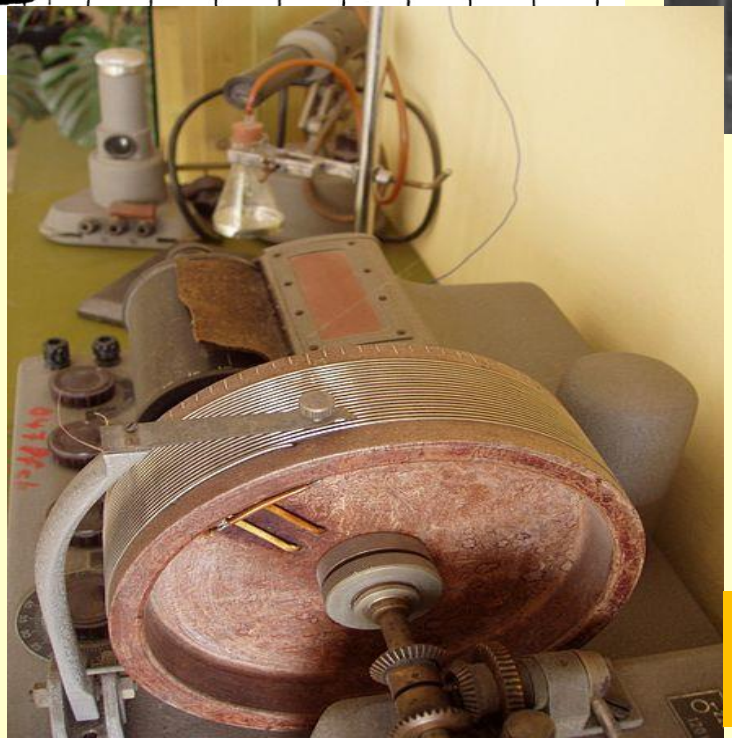
$$\pi = -\frac{RT}{r.F}\log.$$

if the process proceeds rapidly enou
instantly. This is possible with very
amp.), which pass through the dropp

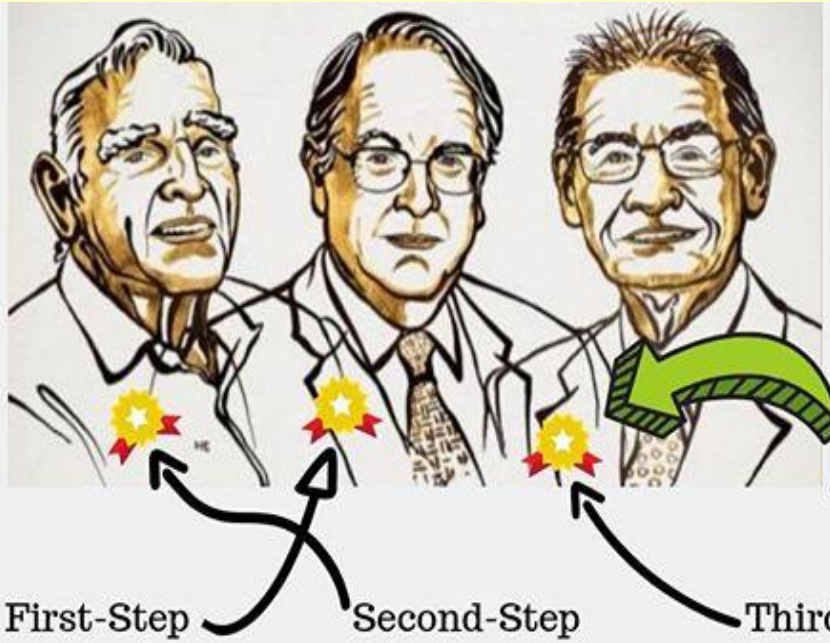


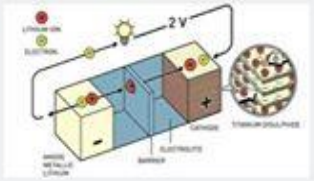




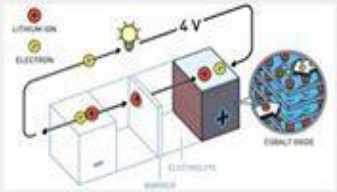


For the development of Polarography, Heyrovsky was awarded to Nobel Prize in Chemistry 1959

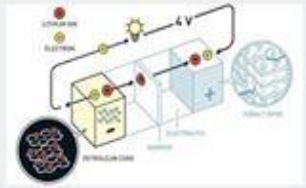




Whittingham's Li-ion battery

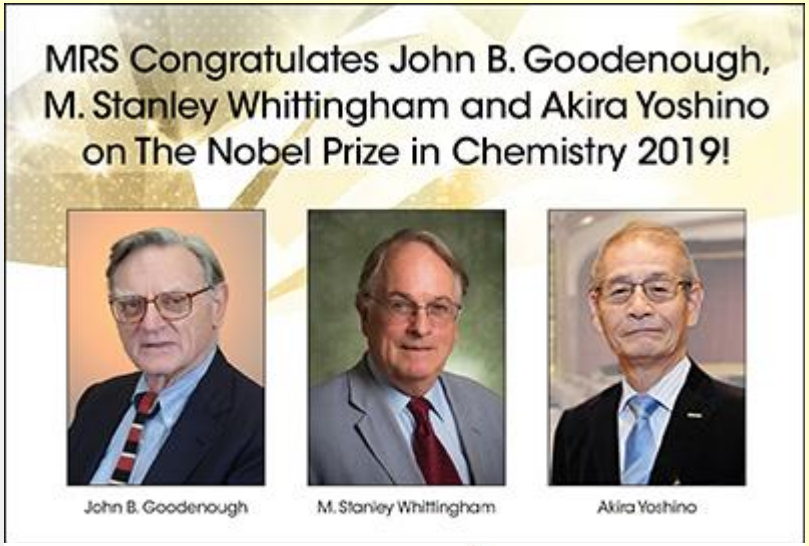


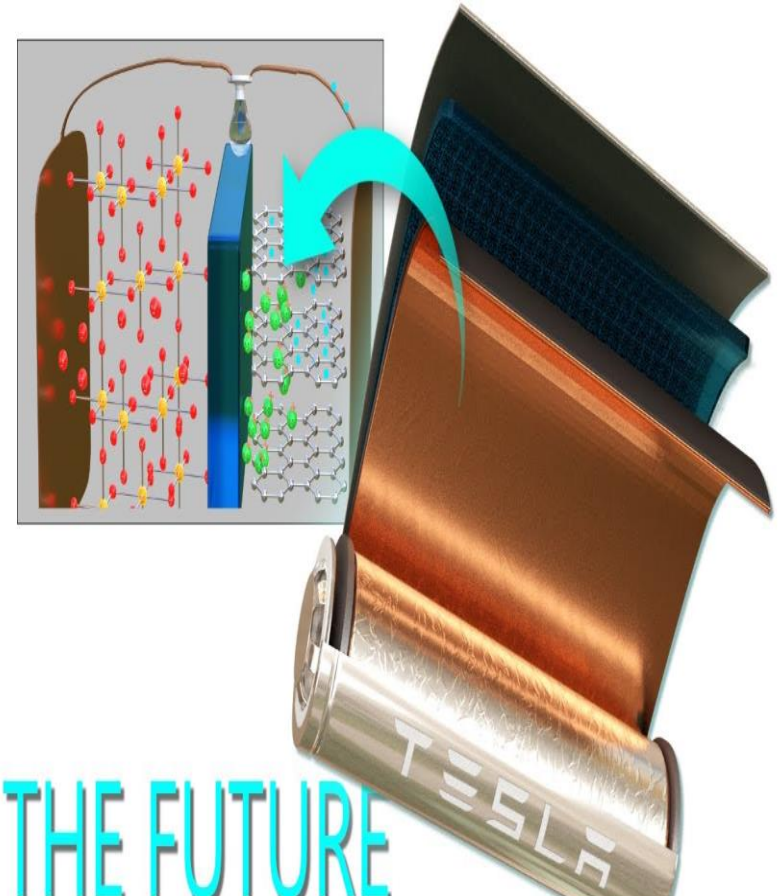
Goodenough's Li-ion battery



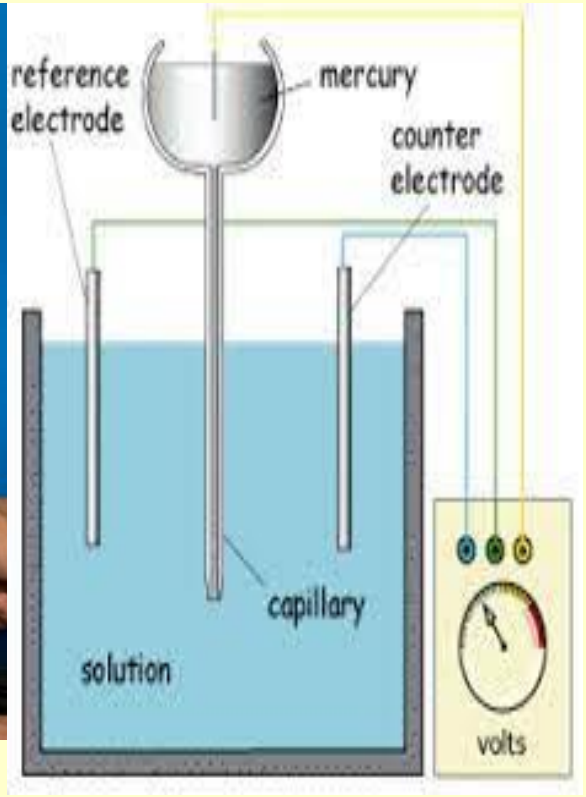
Yoshino's Li-ion battery

The Nobel Prize in Chemistry 2019 rewards the development of the Lithium-ion Battery - Part 1

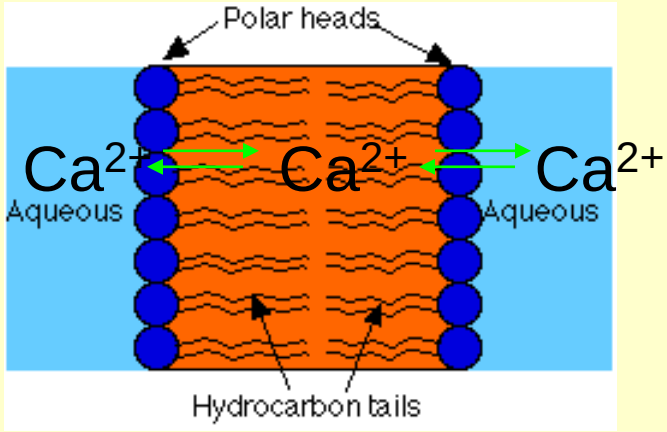




VOLTAMMETRY is a succesor of Polarography
(branch of *ELECTROCHEMISTRY)*
-deals wity the processes of CHARGE transfer between two conjoined systems
-FLOW of electric charge=CURRENT

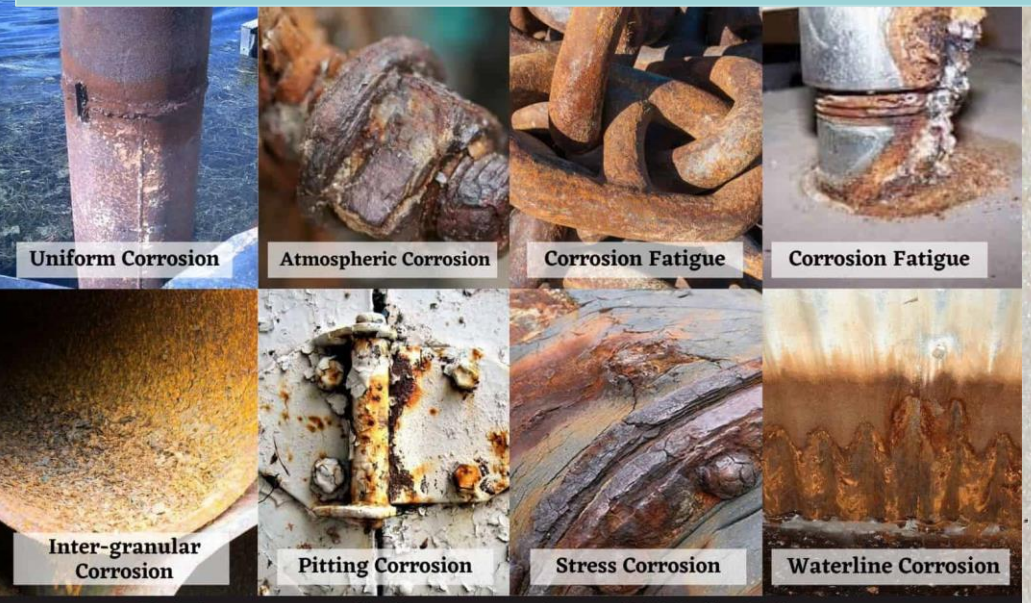


Plunge Battery

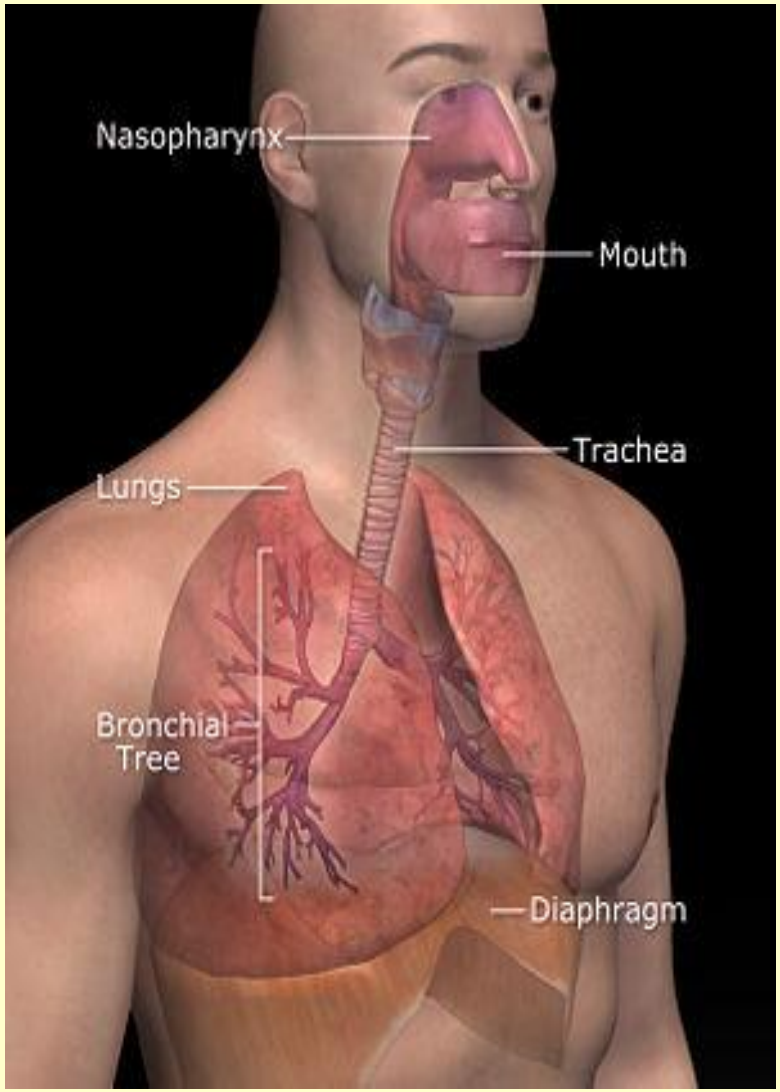


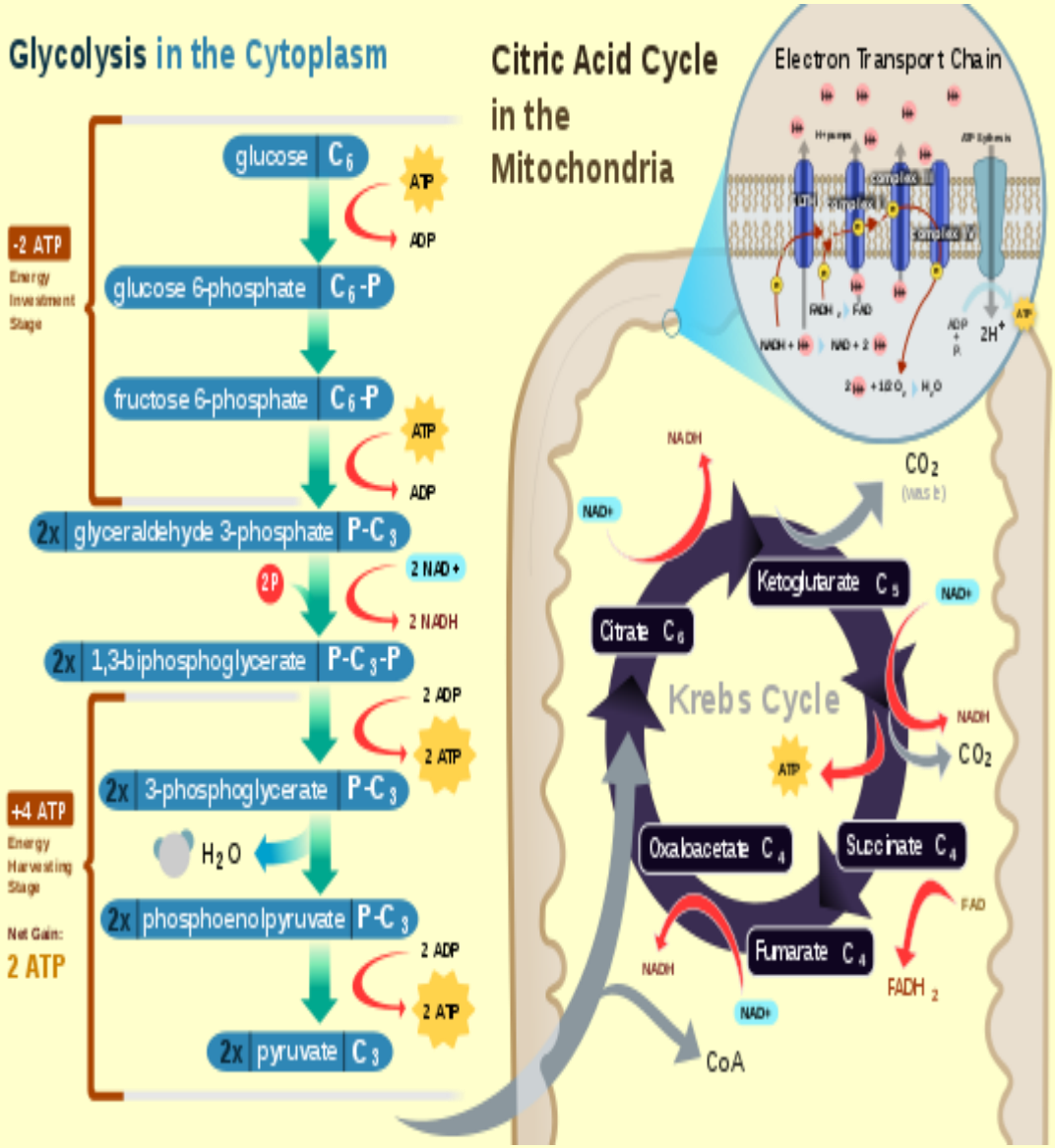
Voltammetry considers MAINLY the Processes of oxidation and reduction

What comes first to our mind when we talk about electrochemistry

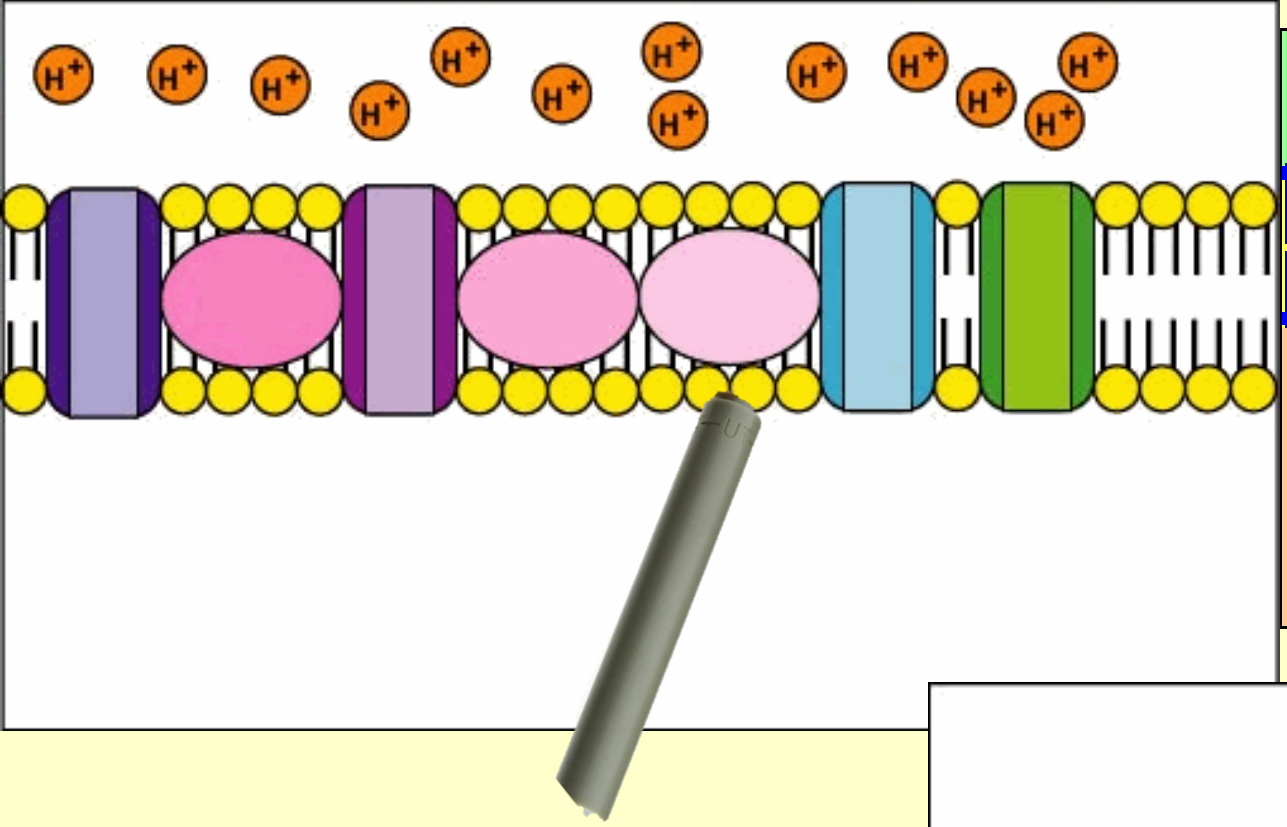


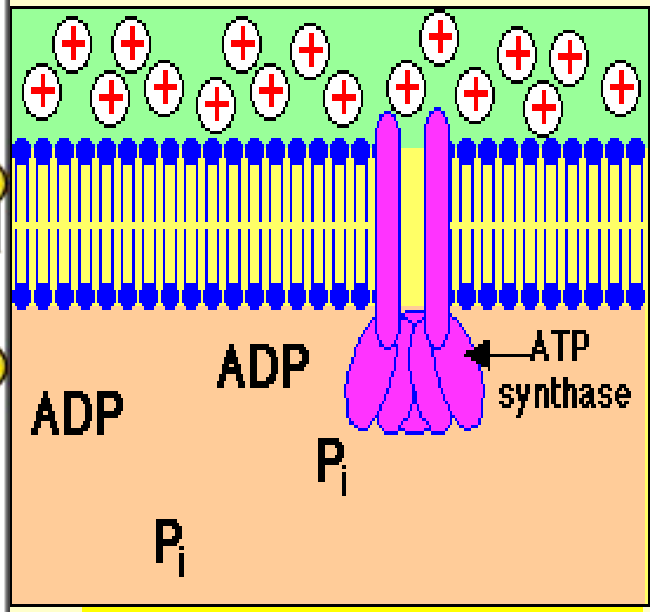
Breathing is a pure electrochemical process, for example



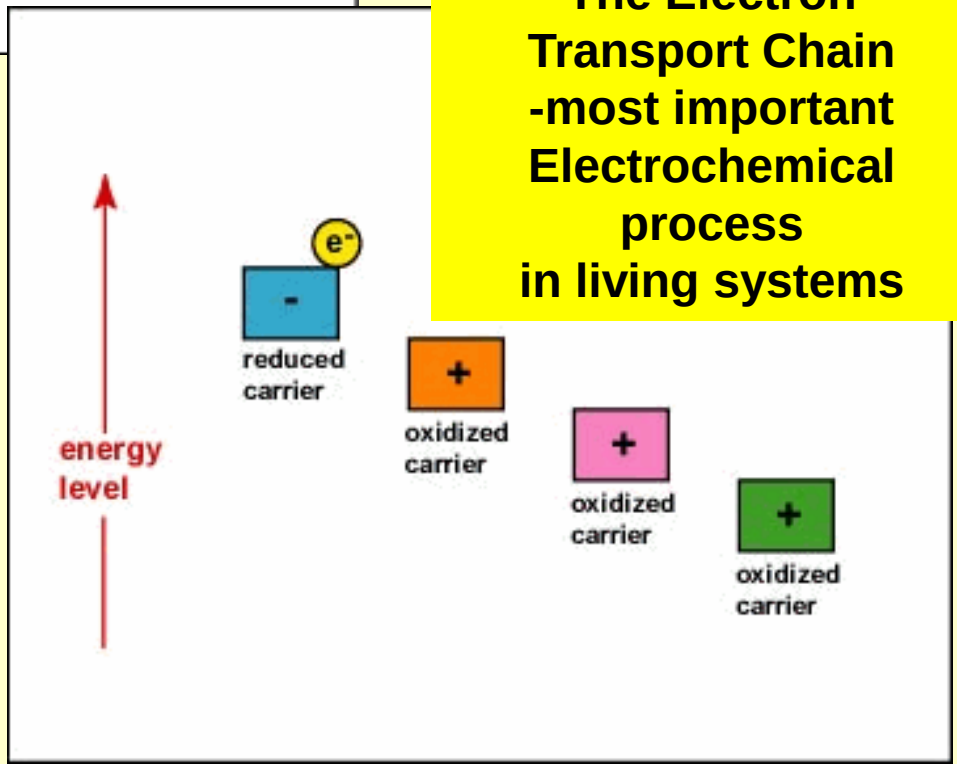


$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2880$ kJ/mol



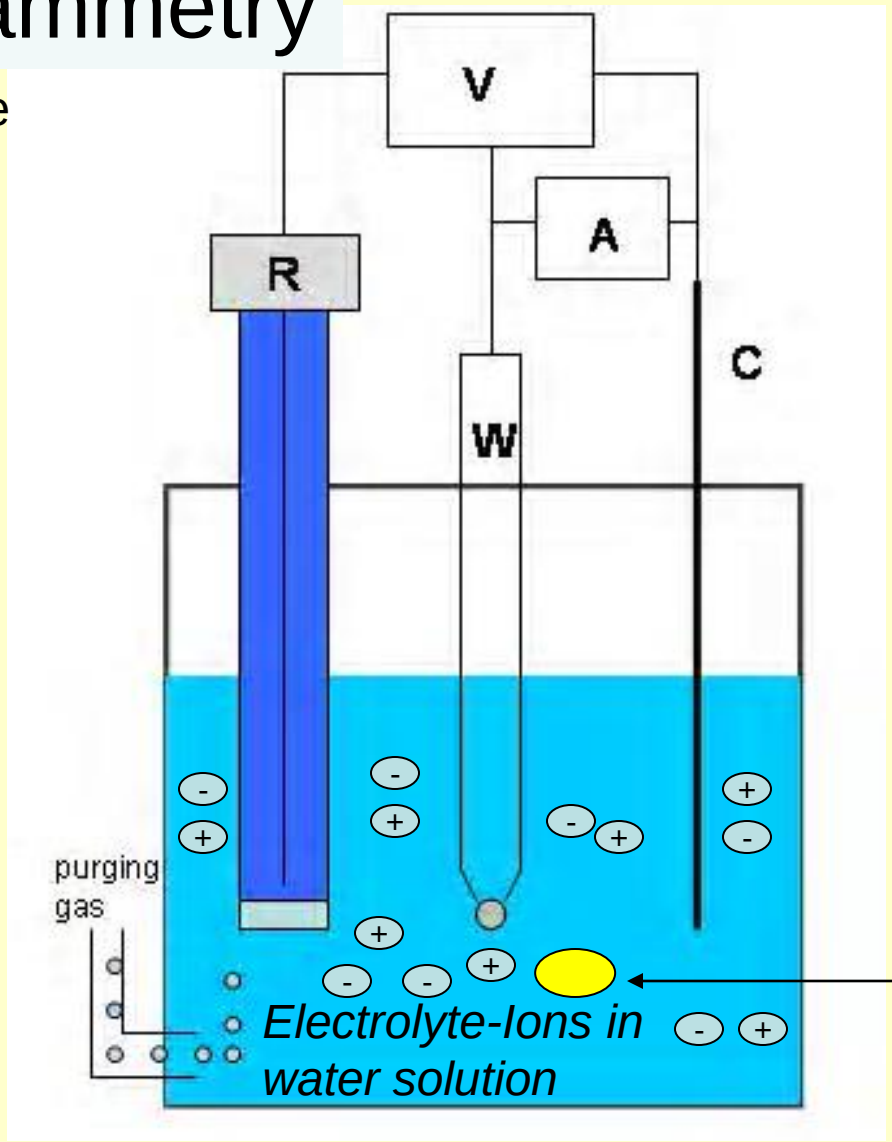


The Electron Transport Chain -most important Electrochemical process in living systems



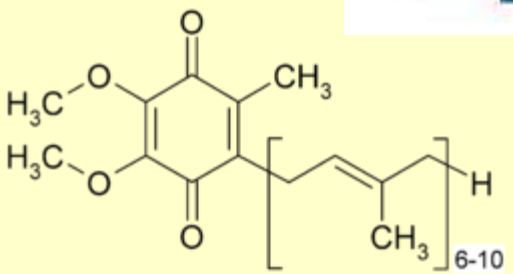
Voltammetry

W-working electrode

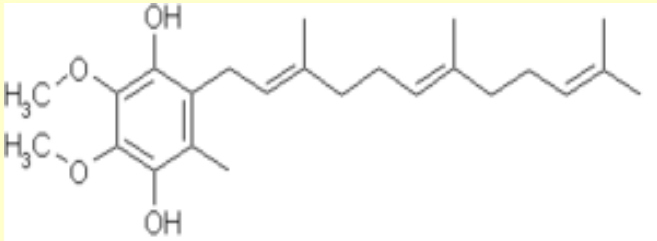


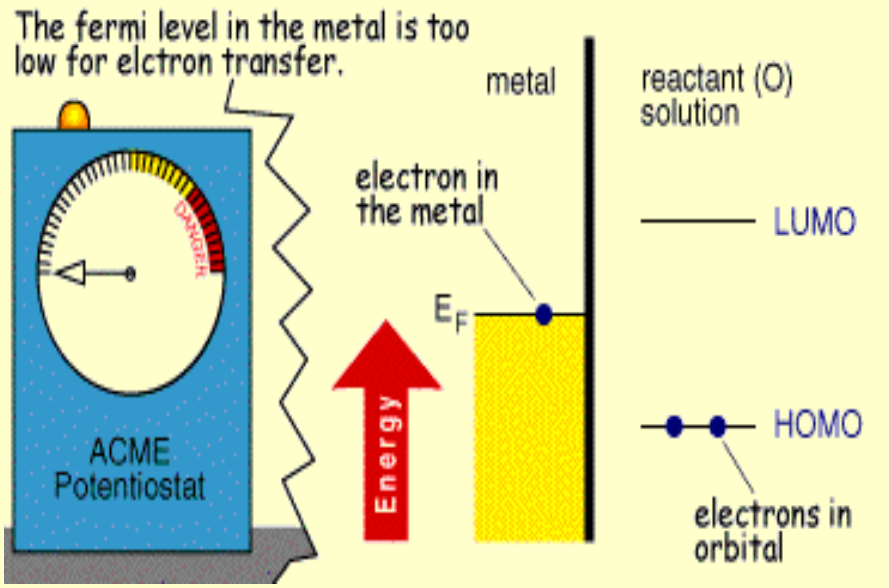
R-reference electrode

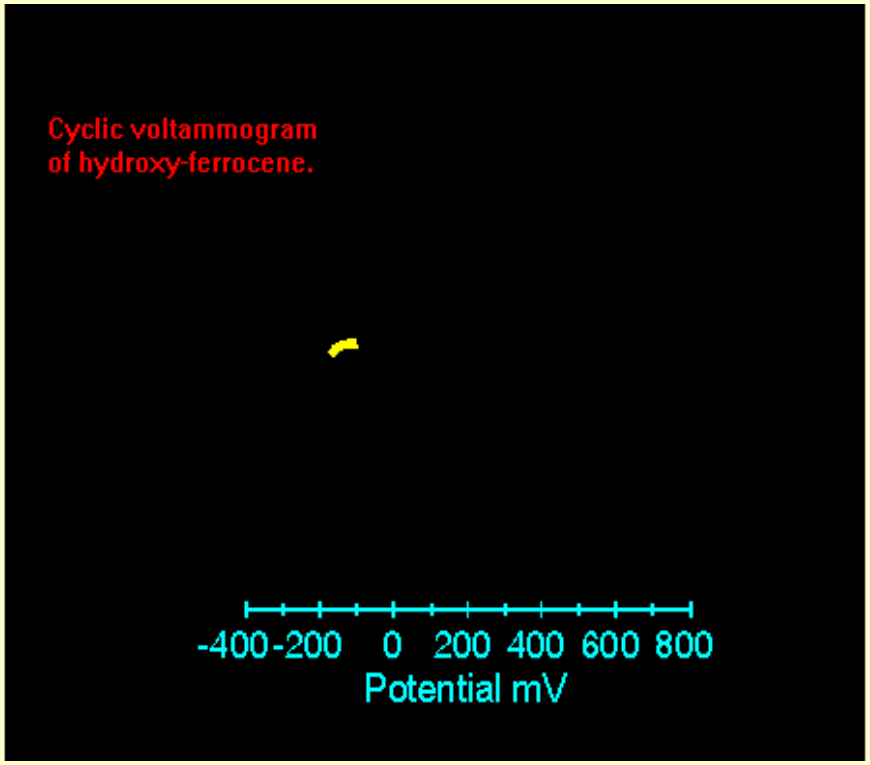
Redox probe



+2 H+ + 2e- ⇌




The fermi level in the metal is too low for elctron transfer.
metal
reactant (O) solution
electron in the metal
LUMO
E_F
Energy
HOMO
ACME Potentiostat
electrons in orbital


Cyclic voltammogram of hydroxy-ferrocene.
-400 -200 0 200 400 600 800
Potential mV

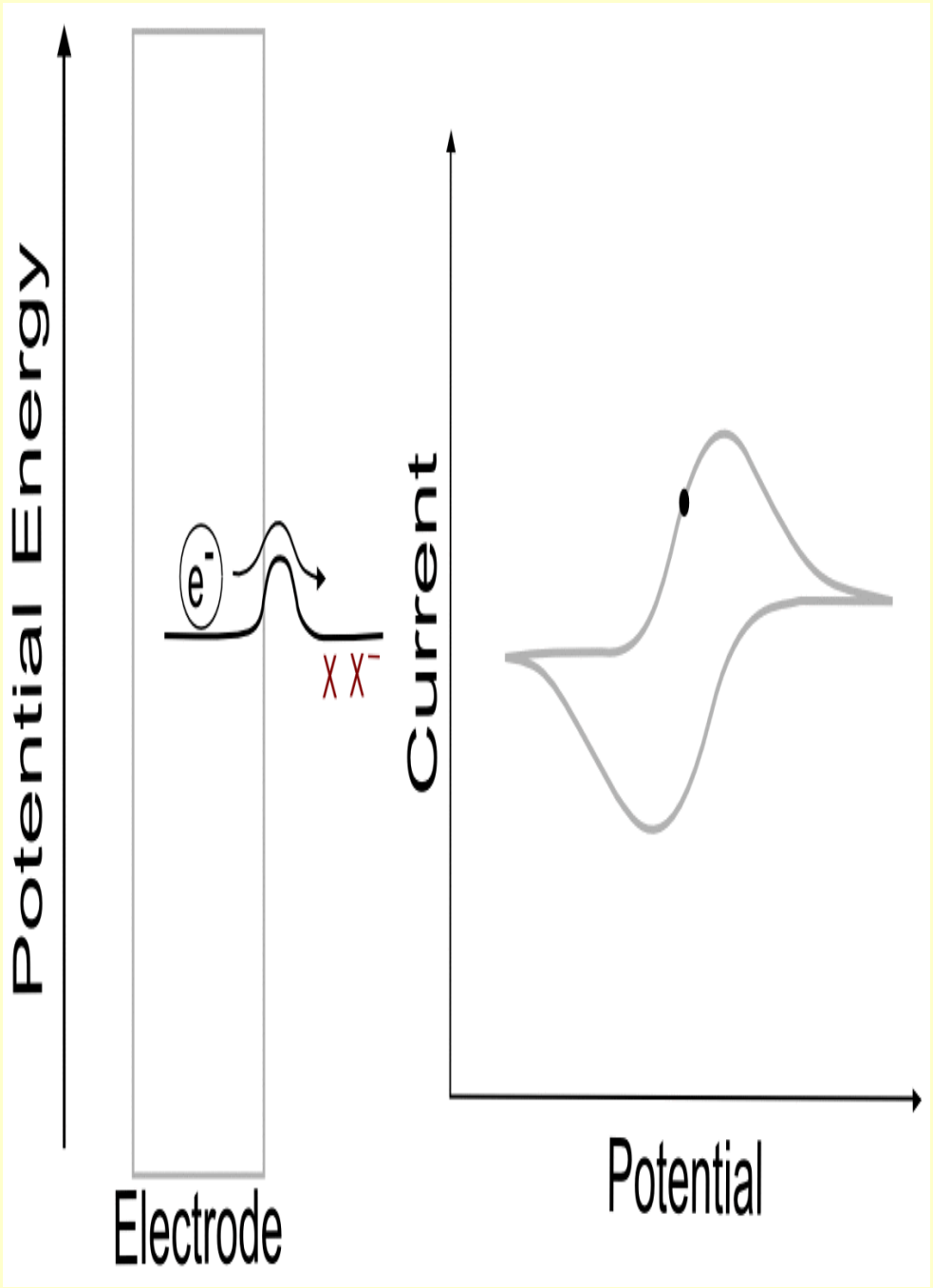
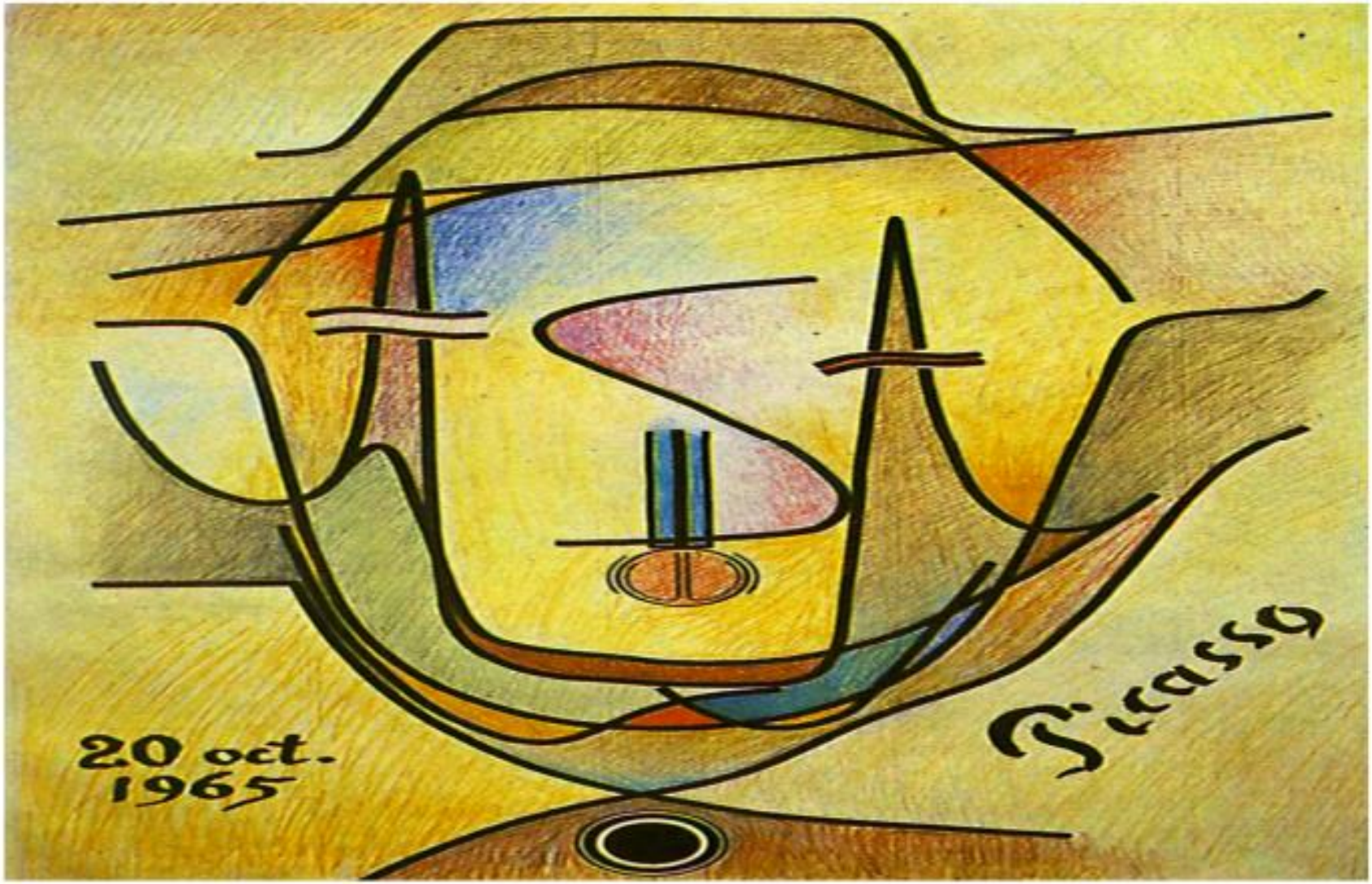

Potential Energy
e-
X X⁻
Electrode
Current
Potential

Image of electrochemistry by Picasso

http://www.elch.chem.msu.ru/wp3/wpcontent/uploads/2016/02/portret.pdf

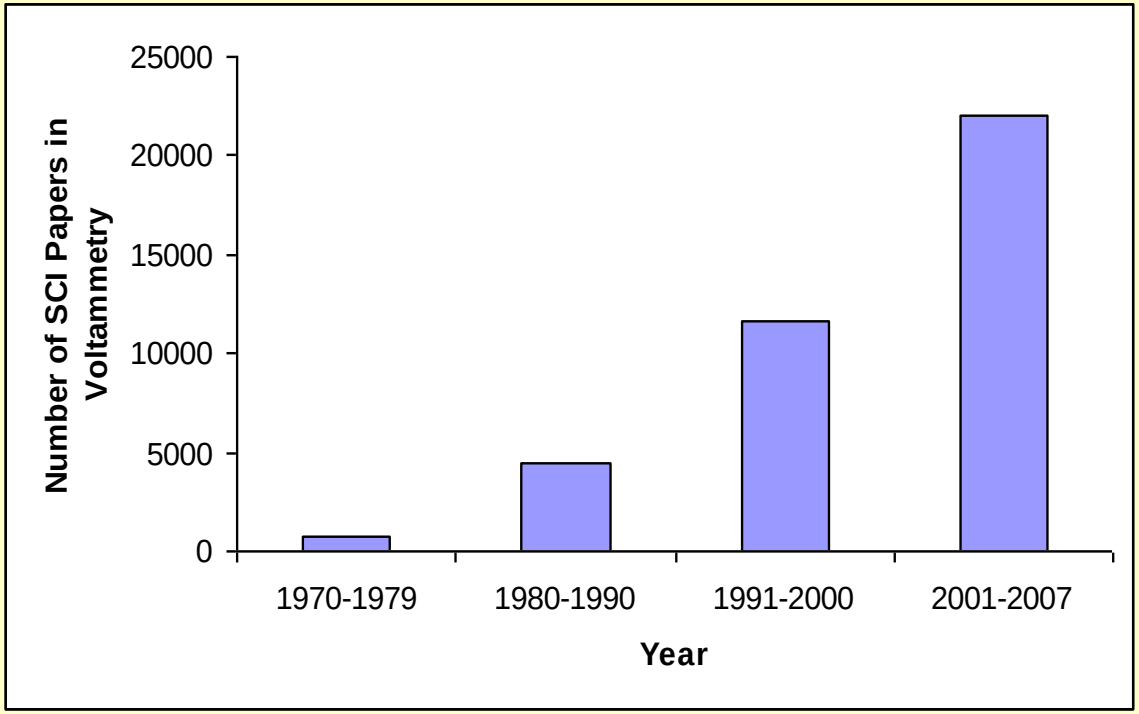


Application of the Voltammetry

-In Chemistry, Physics and Engineering

-In Biology and Biochemistry (biosensors)

-In Pharmacy



-In Medicine

-detection of reactive radicals nitroxides, superoxides,...

-determination of various active compounds

-studying of protein-protein interactions

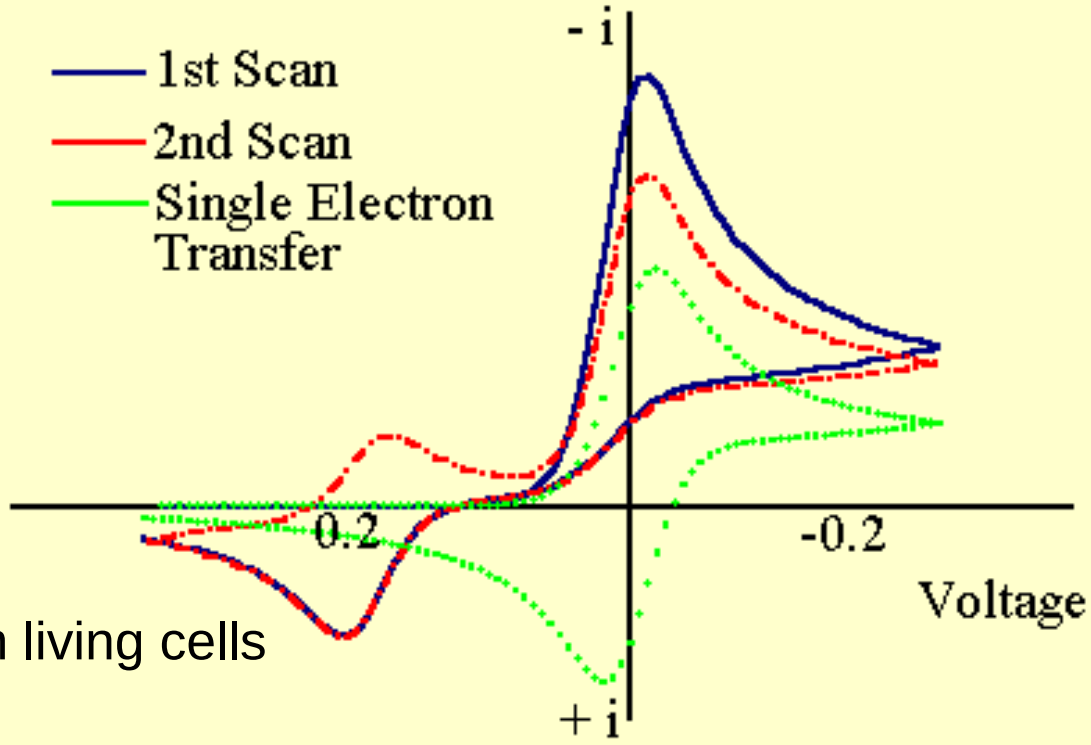
-medical sensors for various electron cariers and neurotransmiters

And in 2021 alone, more than <u>15000</u> Papers have been published In which voltammetry was explored

What kind of information can provide Voltammetry?

-Mechanistic pathway

-detection of the **intermediates** and final products of the redox reactions



Peroxyde nitrite oxidation in living cells

ONO_2^- - e- = $ONO_2^{\cdot}$...NO_2^-

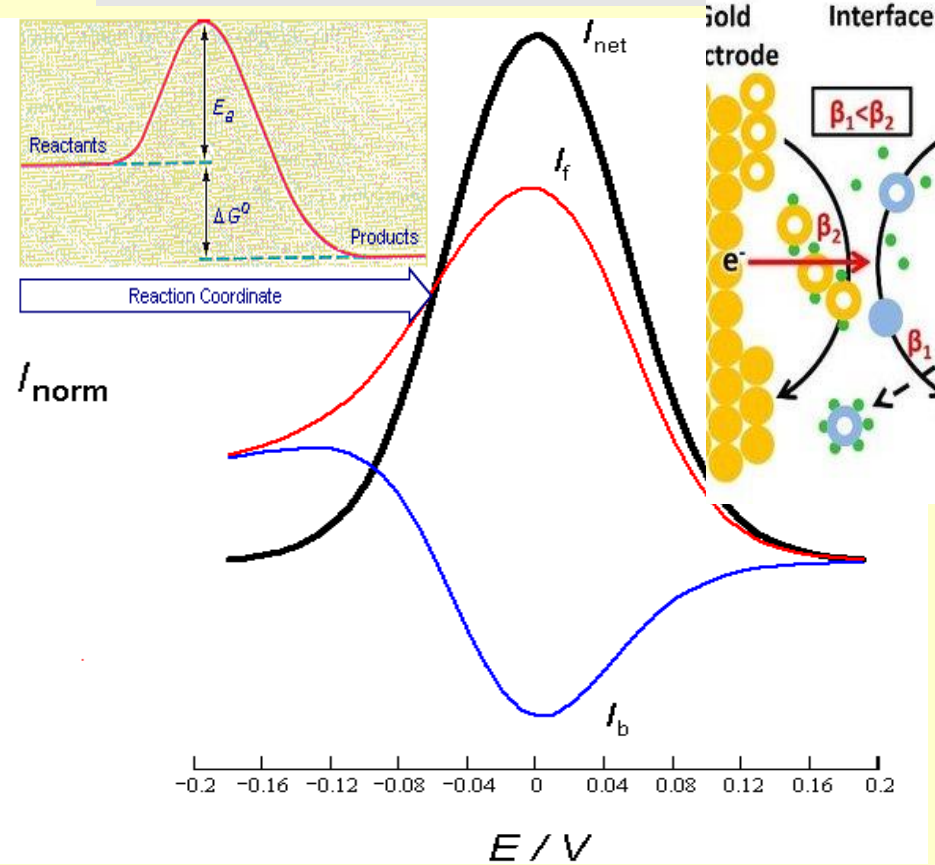
NO_2^- + 2OH- -2e- = NO_3^- + H_2O

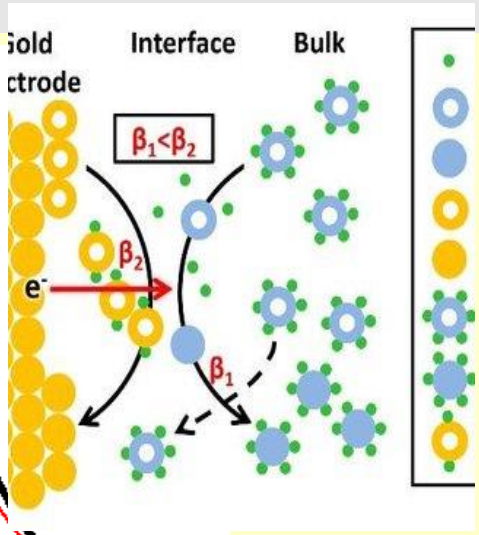
-Thermodynamic Parameters of Redox Reactions

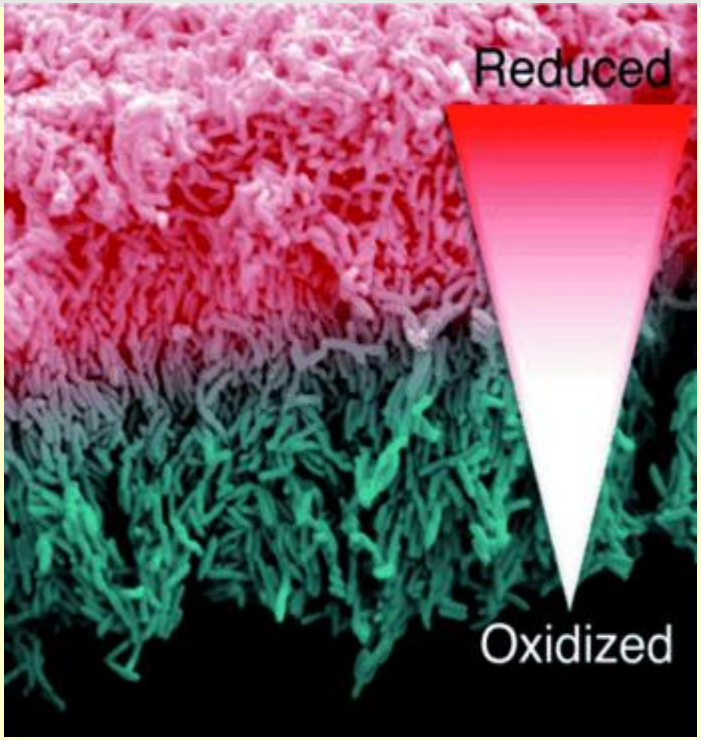
***Standard Redox Potential**-Energy of Activation*., Enthalpy, **Complexation Constants**...

-Kinetic Parameters

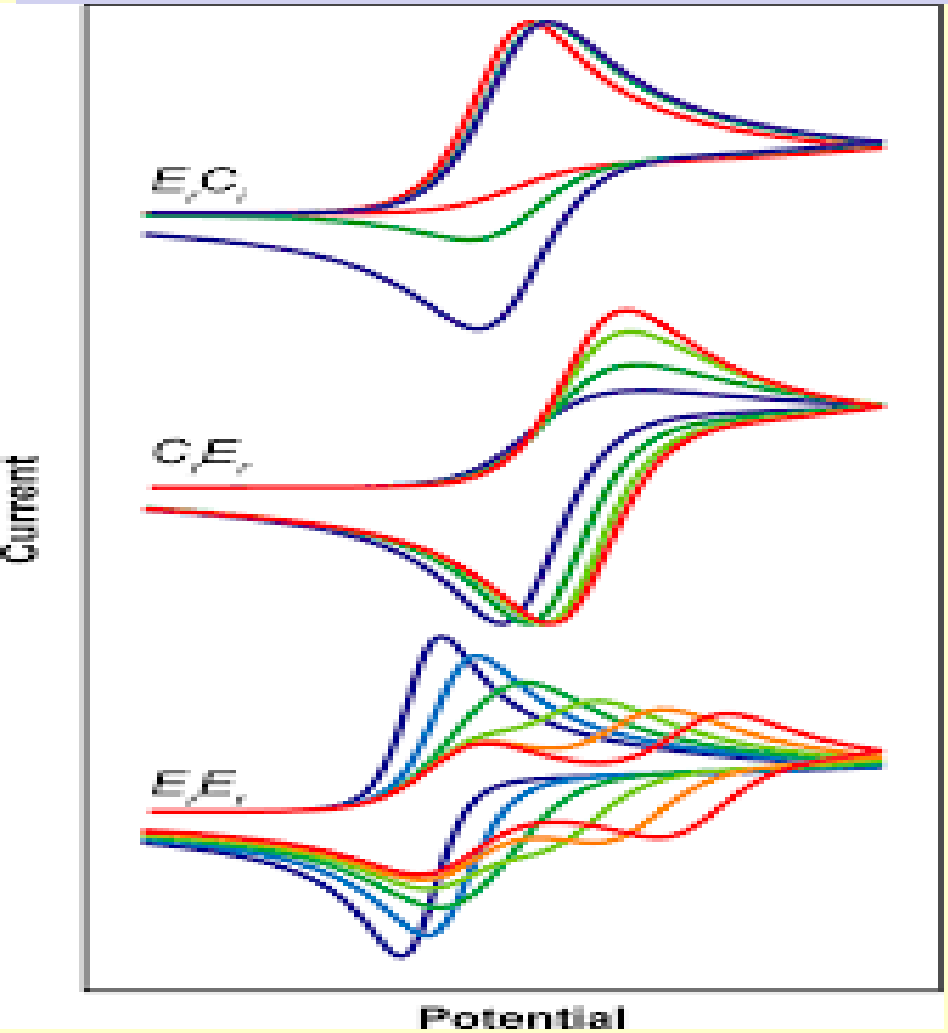
-standar rate constants of electron/ion transfers***; kinetics of enzymatic reactions***; kinetics of chemical reactions; ***pharmakokinetic parameters...***

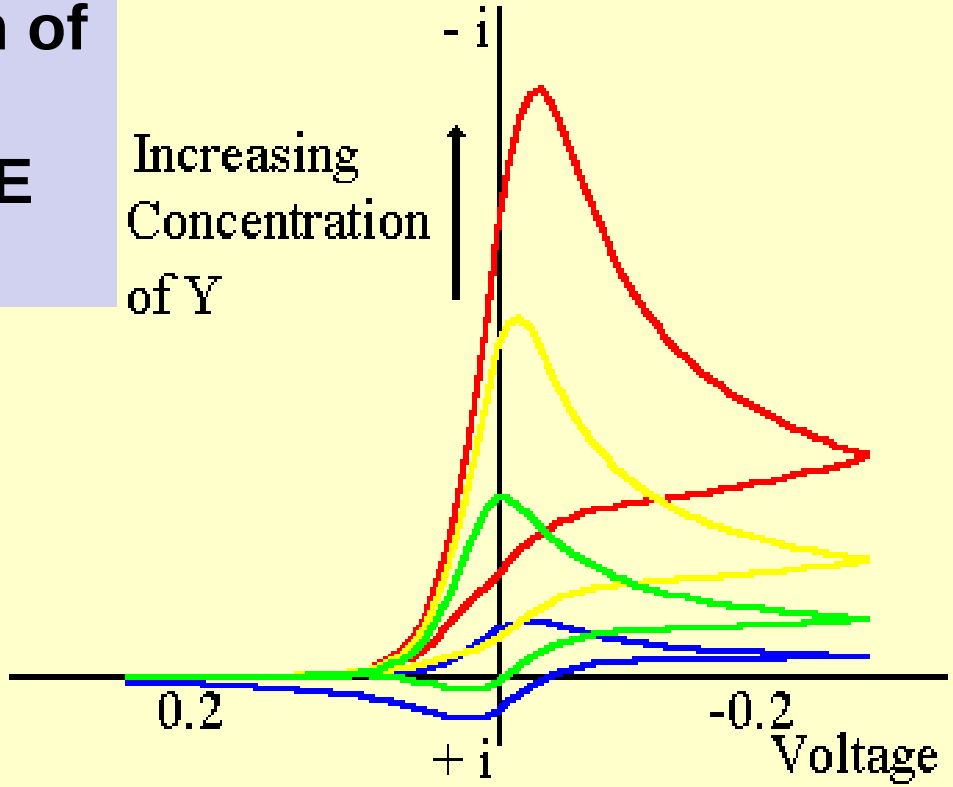


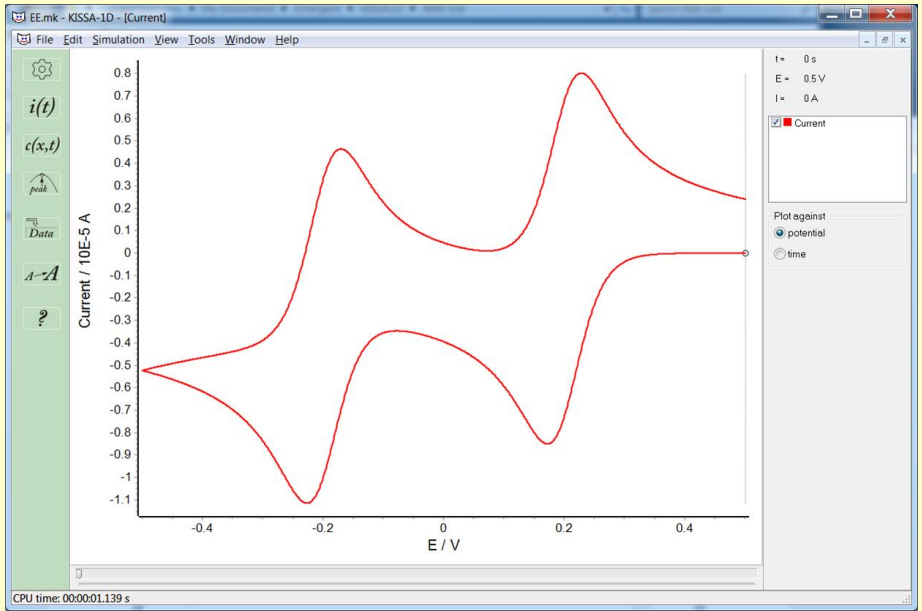




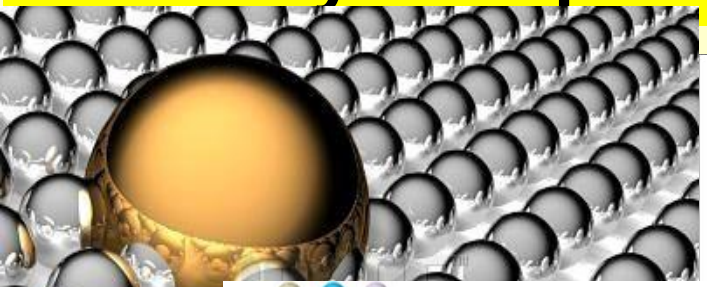
Information on the mechanism of transformation of given Analyte is hidden in the SHAPE of the Voltammograms!!

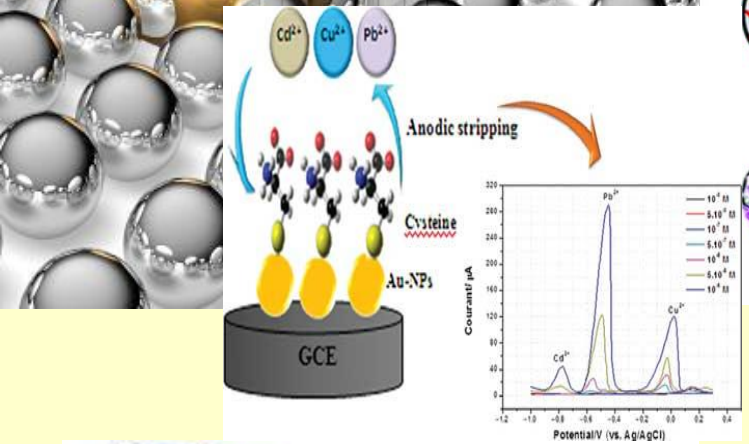


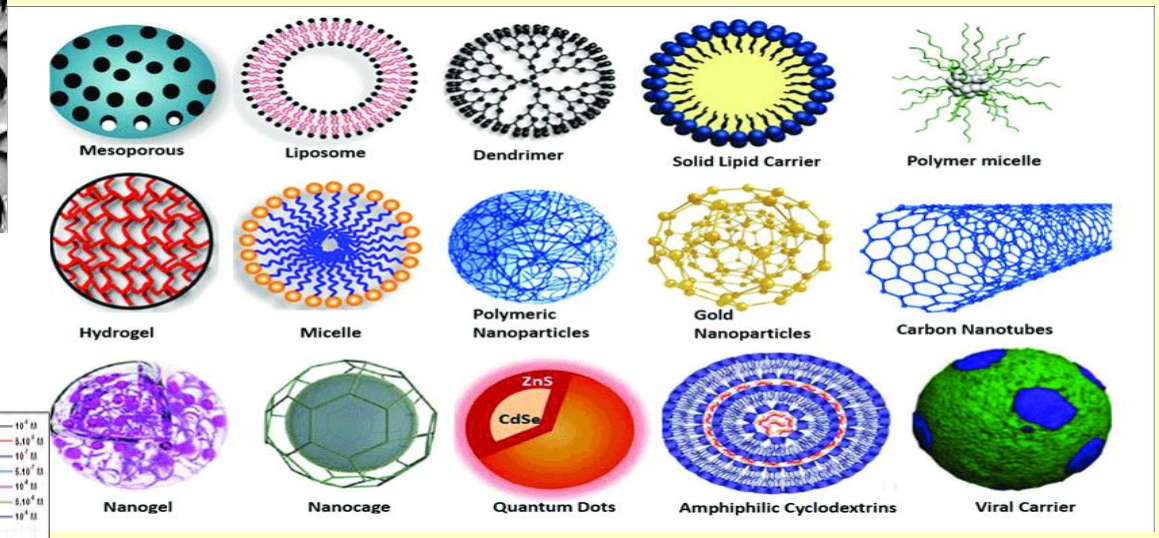


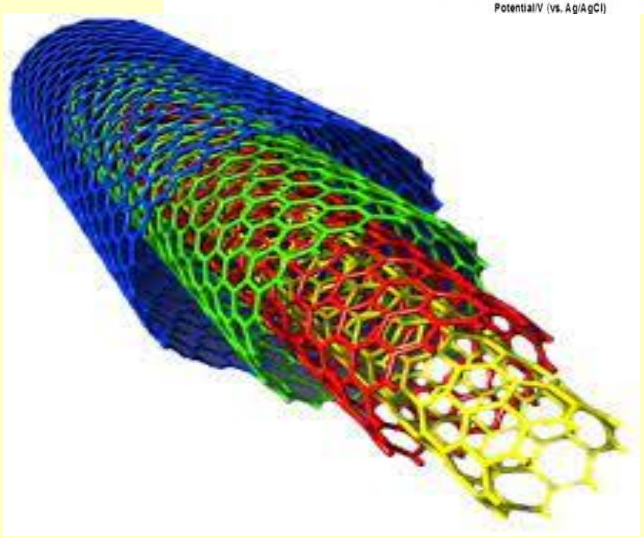


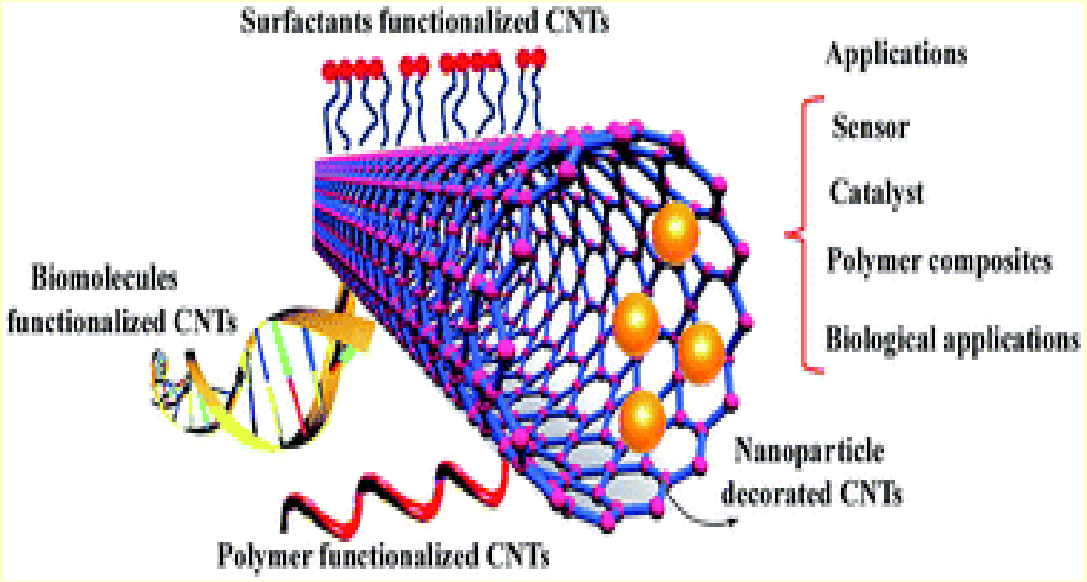
Voltammetry-NANOPARTICLES MODFICATION -new way of improving electrochemical responses



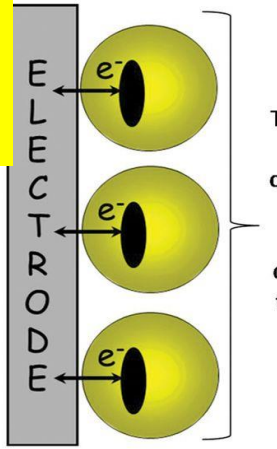




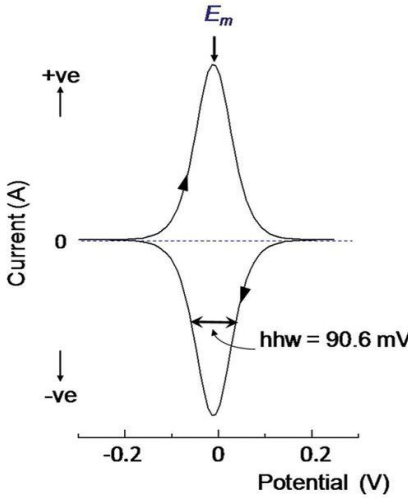


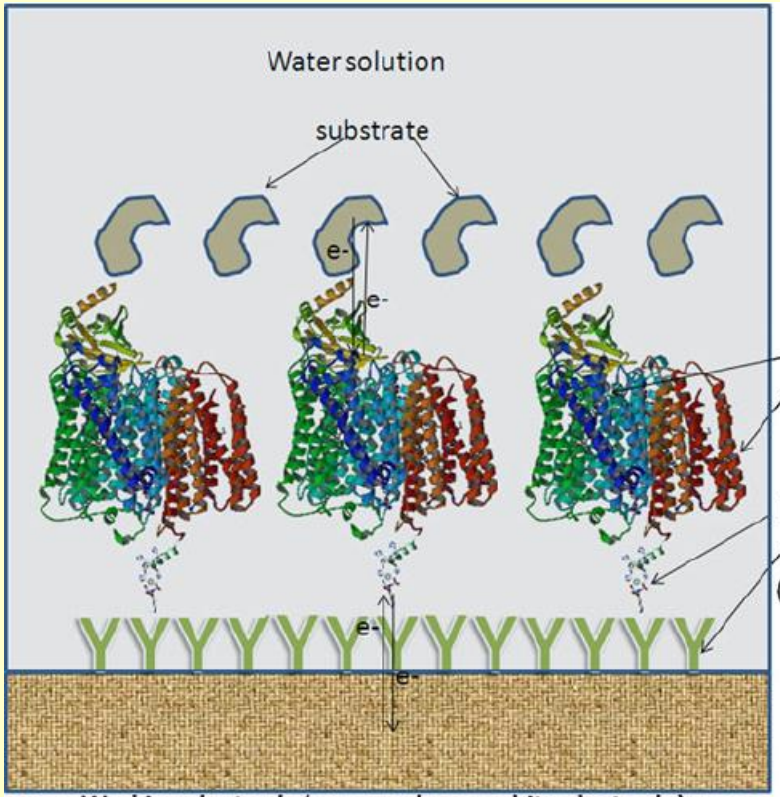


PROTEIN-FILM VOLTAMMETRY
Enzymes-Redox Chemistry



The adsorbed protein film can be placed in solutions of different composition, temperature etc.



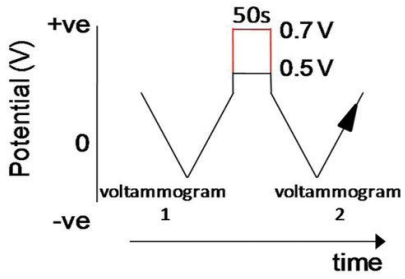


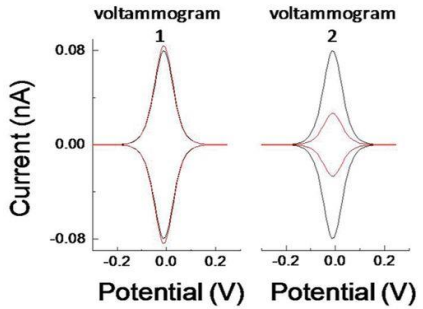
insulating parts of the protein

Protein redox active site

Modifiers of the electrode surface (nano particles, conducting polymers)

B





Stabilitätspakt für Südosteuropa
Gefördert durch Deutschland
Stability Pact for South Eastern Eu
Sponsored by Germany

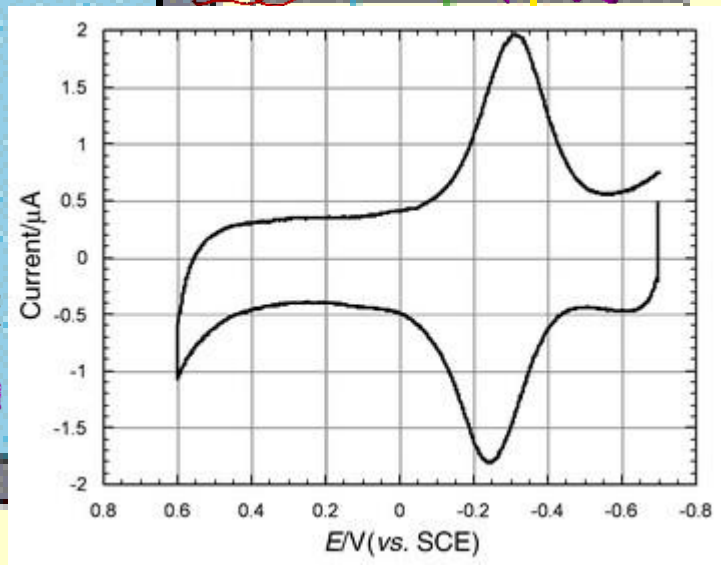
reference electrode

Working electrode

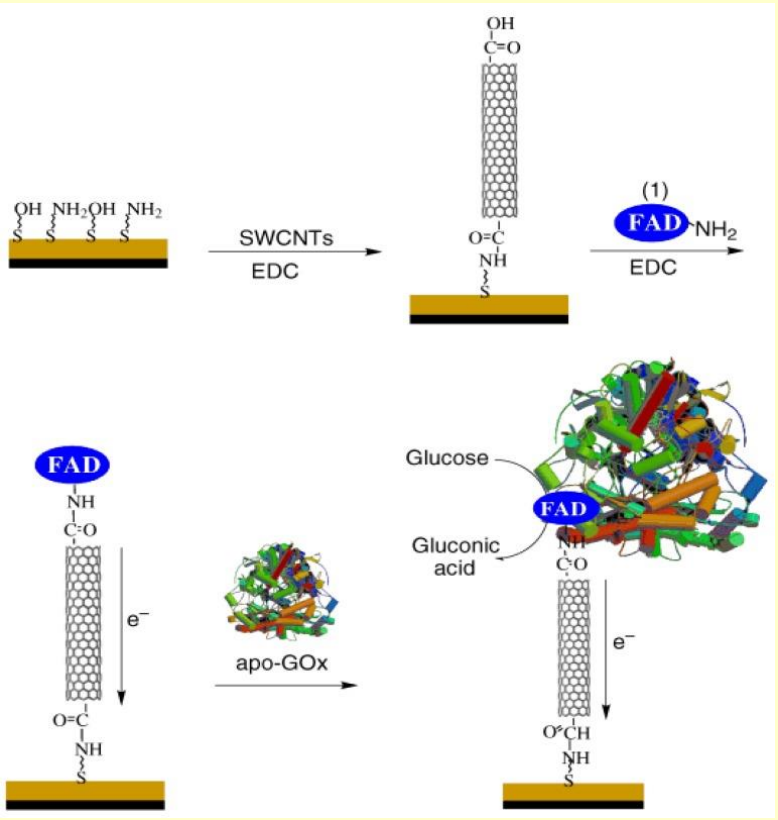
Counter electrode

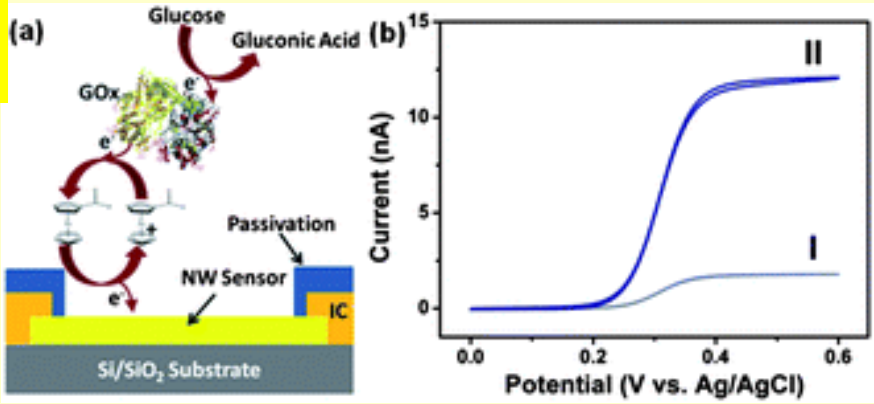
e- e- e- e-

solution



Voltammetry is a tool for Designing BIOSENSORS





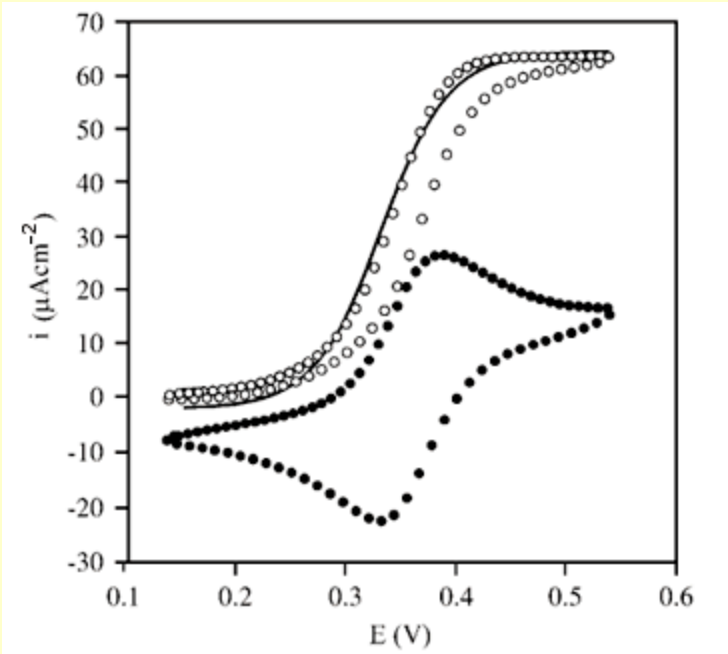
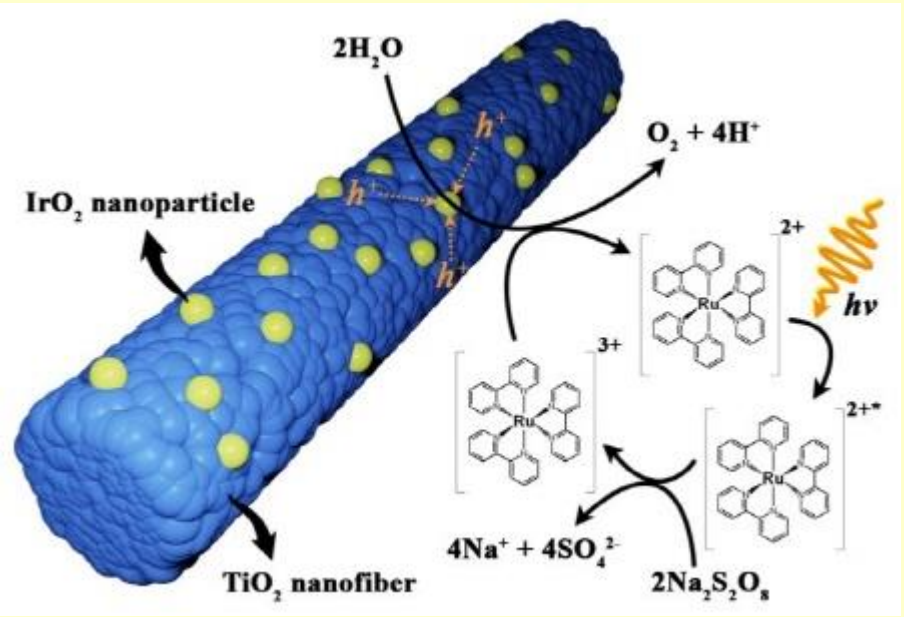
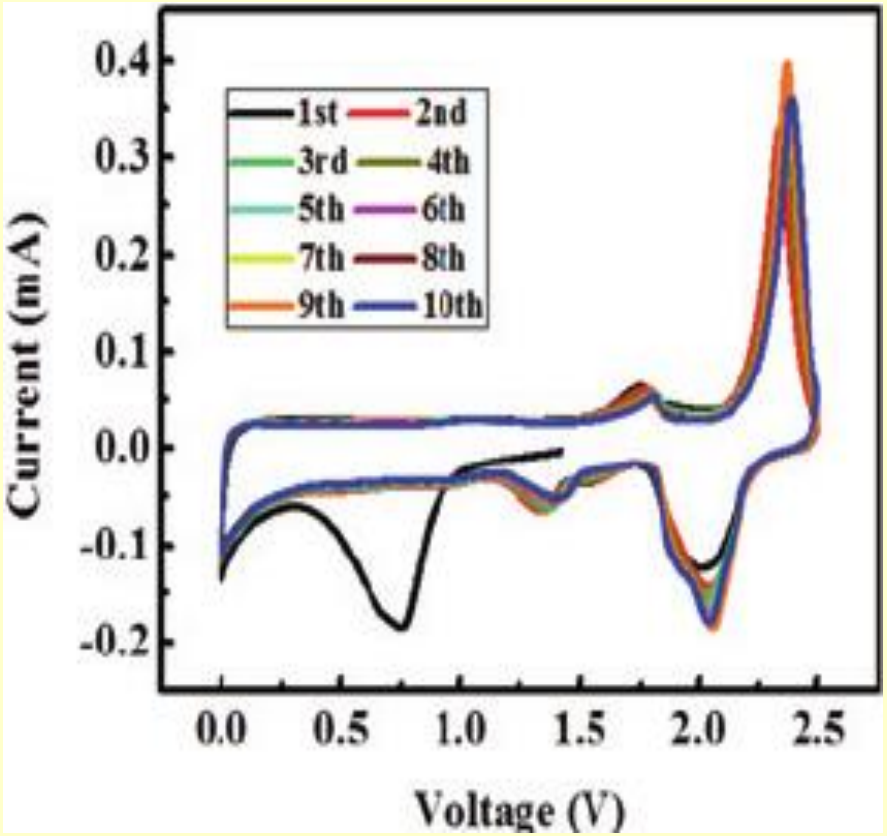
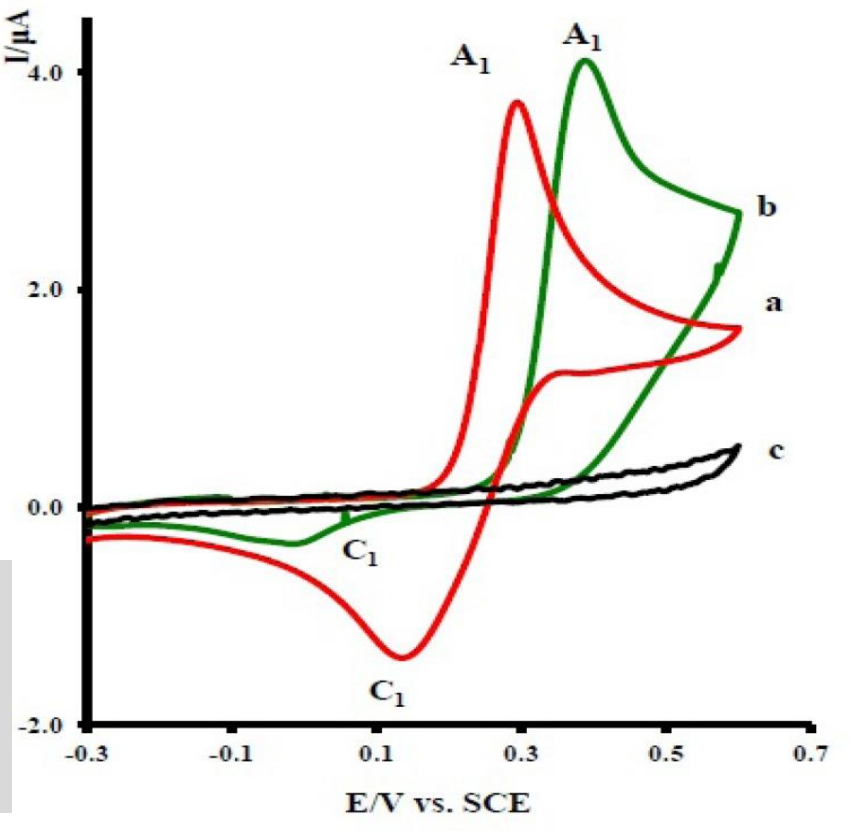


Figure 5. Catalytic wave for glucose oxidation in 50 mM phosphate buffer pH 7.1 and 0.1 M KNO_3 at a Fc-PAA-GOx hydrogel modified electrode (•) glucose free solution 10 mV s^{-1} and (o) 0.1 M glucose solution 5 mV s^{-1}. Solid line corresponds to best fit to Eq. 8. (see text).

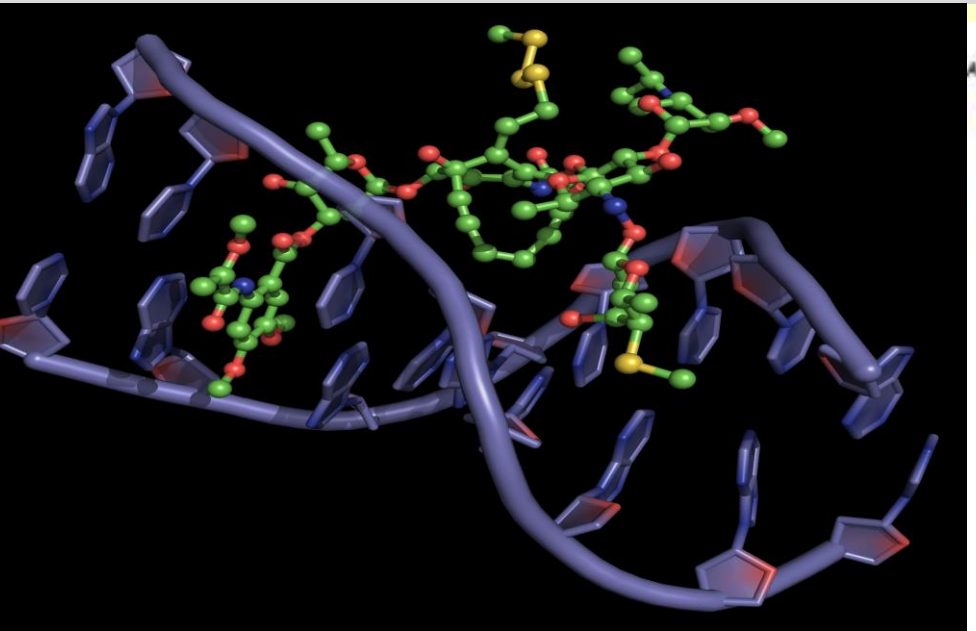
Voltammetry of BIOMATERIALS

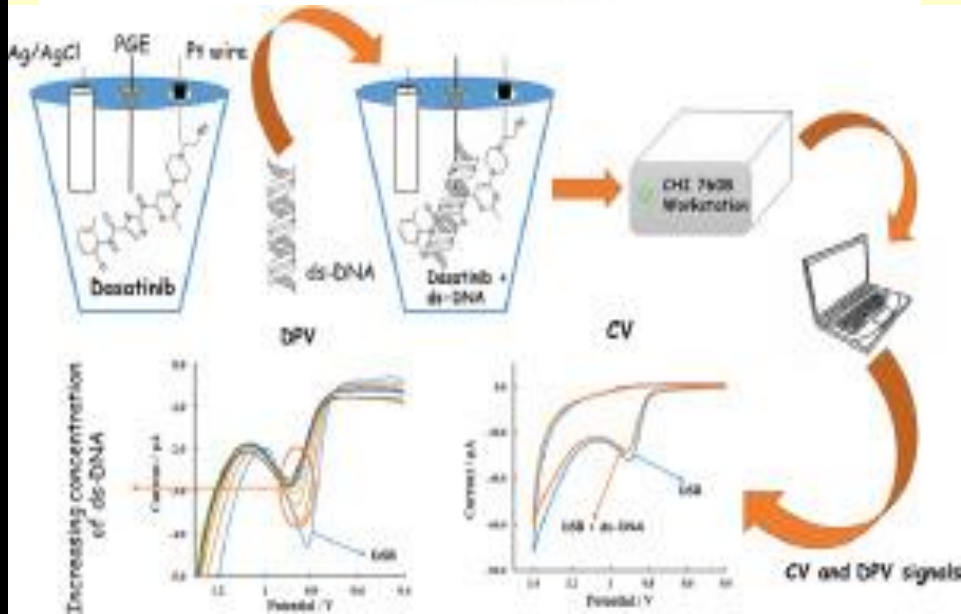




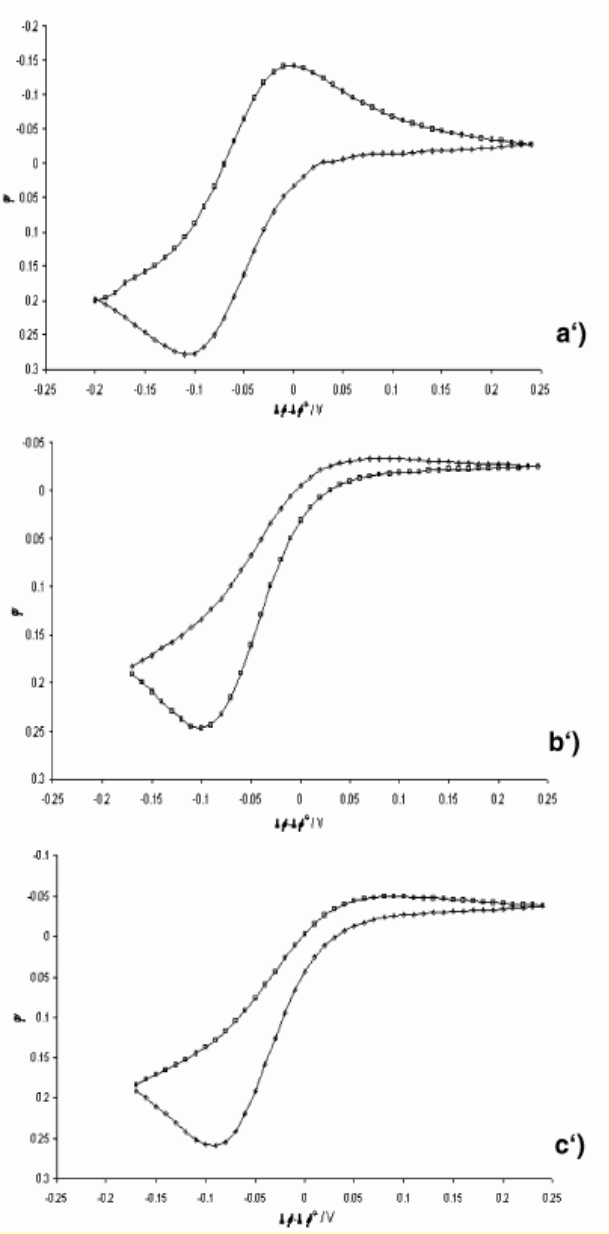


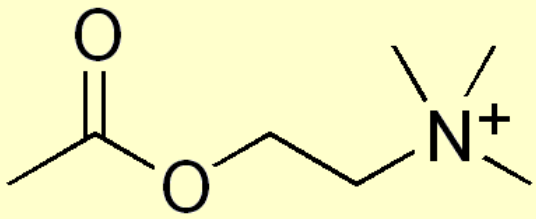
Voltammetry can get insight into
Drug-Drug
or Drug-DNA interactions



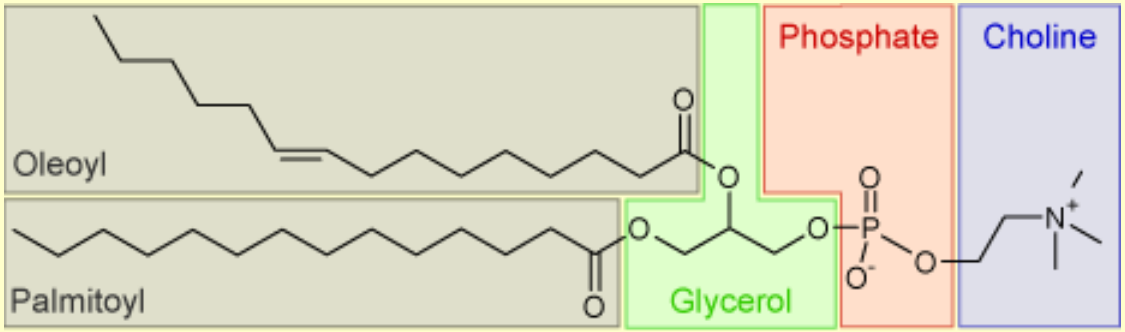


-Strenght of interactions between various substances





Acetylcholine



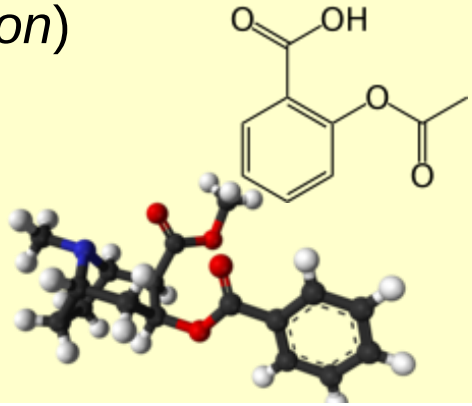
Phospholipids

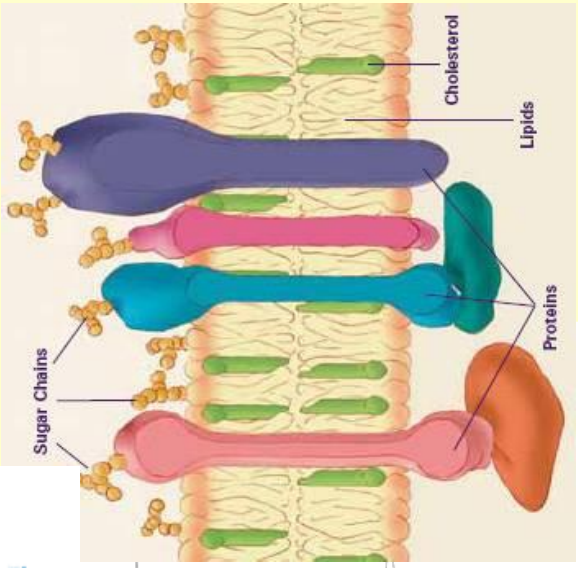
TABLE 1: Determined Kinetic Parameters of the Ion Transfer of AcH^+ from Water to DCE (k_s and α) and for the Interactions between AcH^+ and DOPC (K, ϵ, k_f, and k_b)

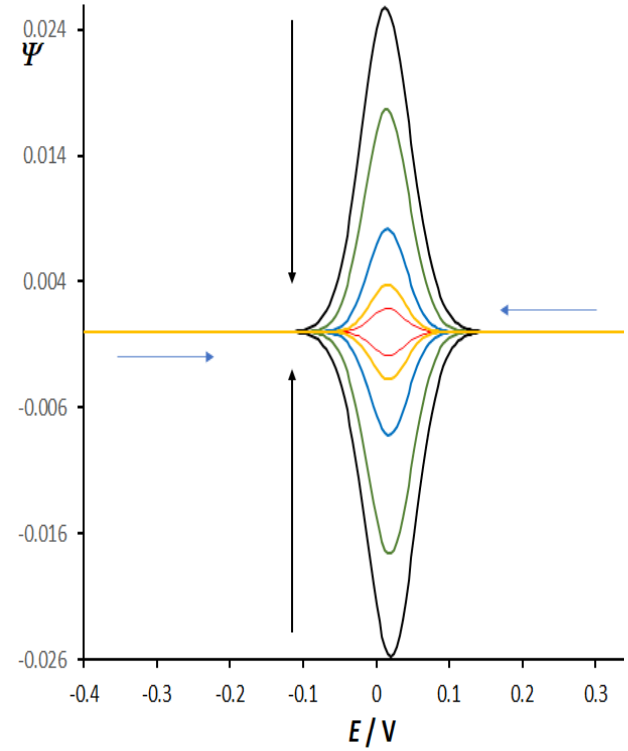
measuring technique	k_s/cm s^{-1}	α	K	ϵ/s^{-1}	k_f/s^{-1}	k_b/s^{-1}
SWV	0.0030	0.50	0.44	13.10	4.00	9.10
EIS	0.0033	0.53	0.80	13.30	5.90	7.40

-***physical phenomena taking place in the system***
(*adsorption, phase transformation*)

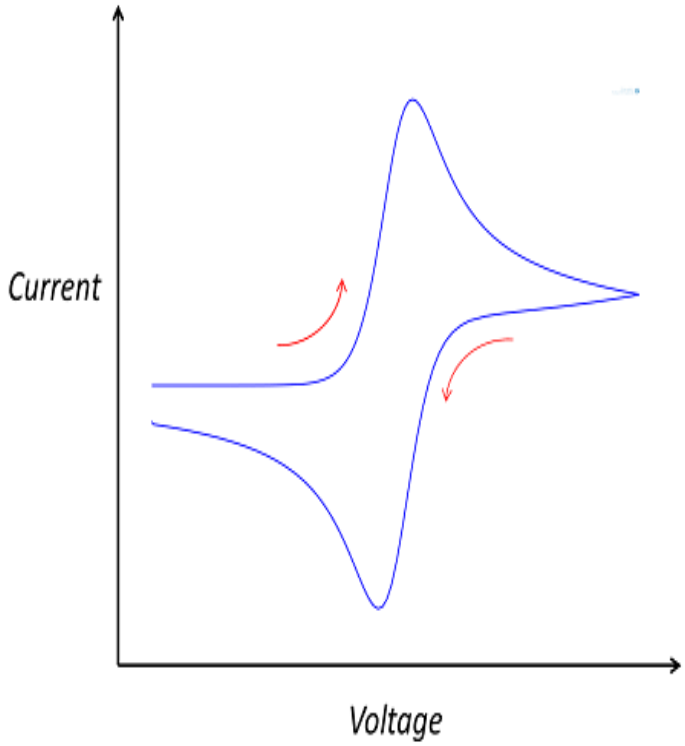
-nature of mass transfer



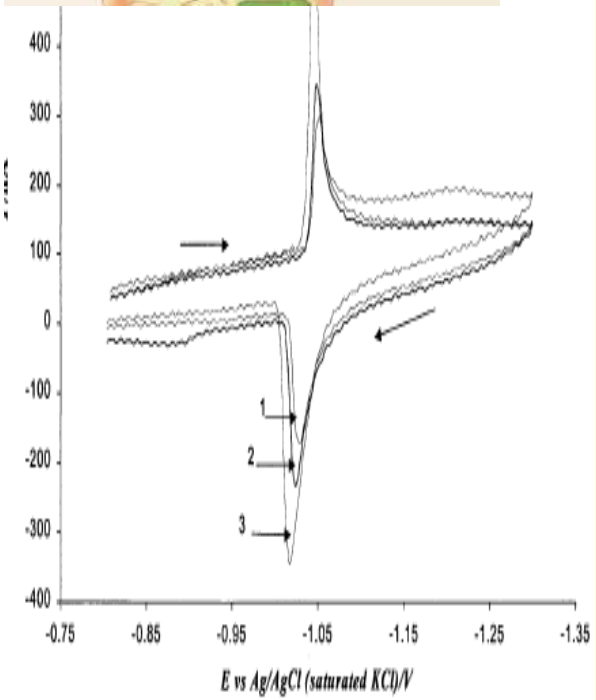




adsorption



diffusion

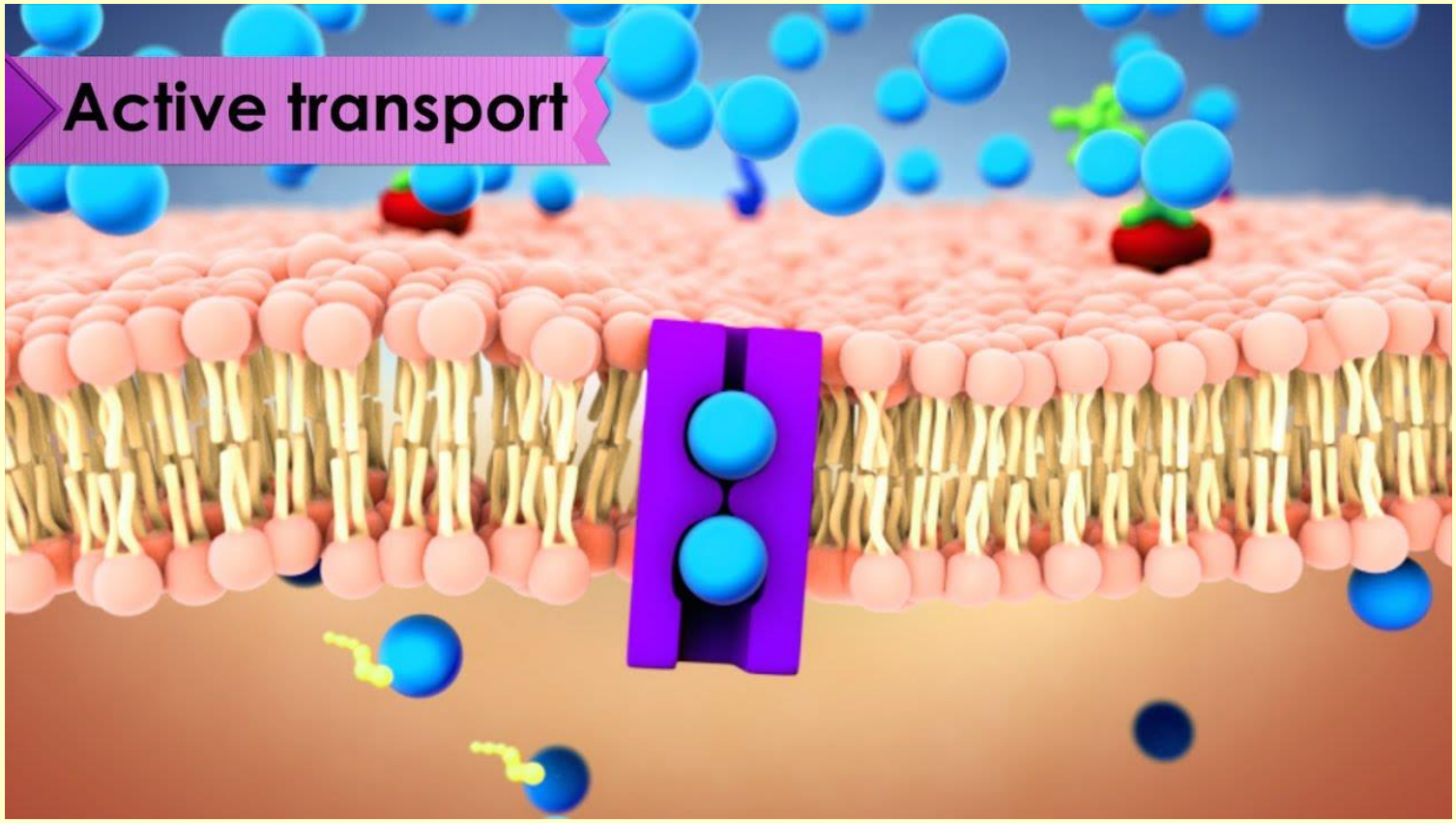


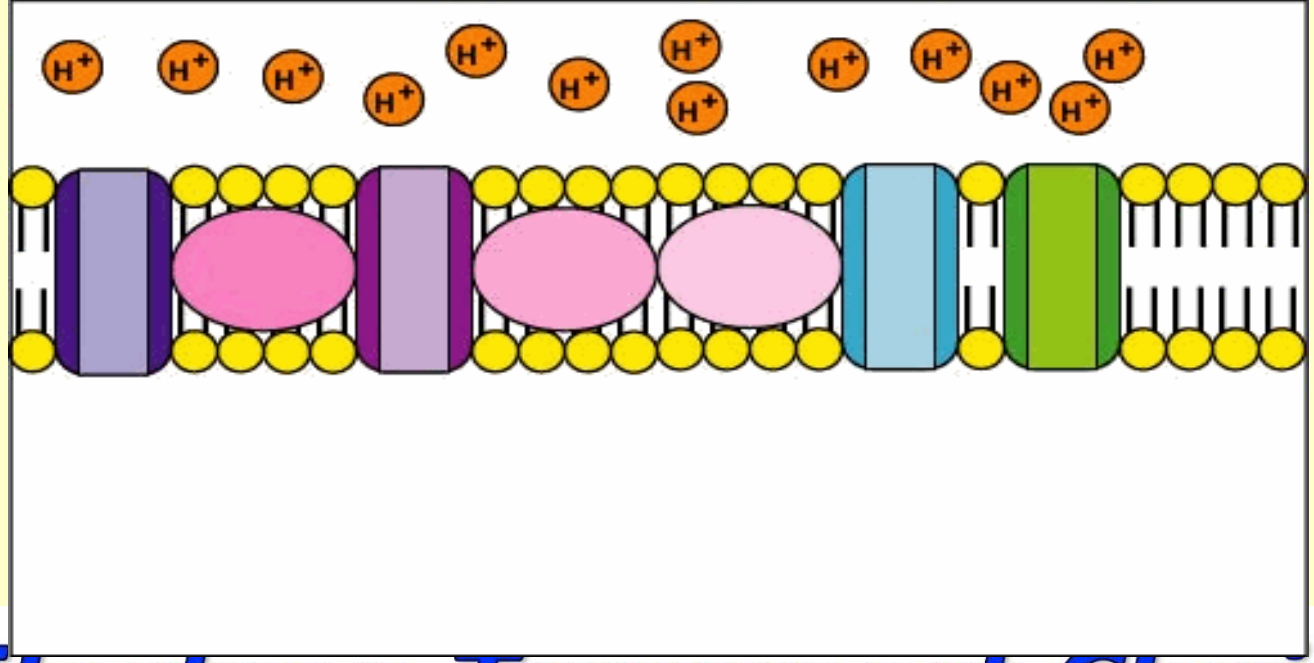
Phase-transformation

-thermodynamic and kinetic parameters related to the physical phenomena

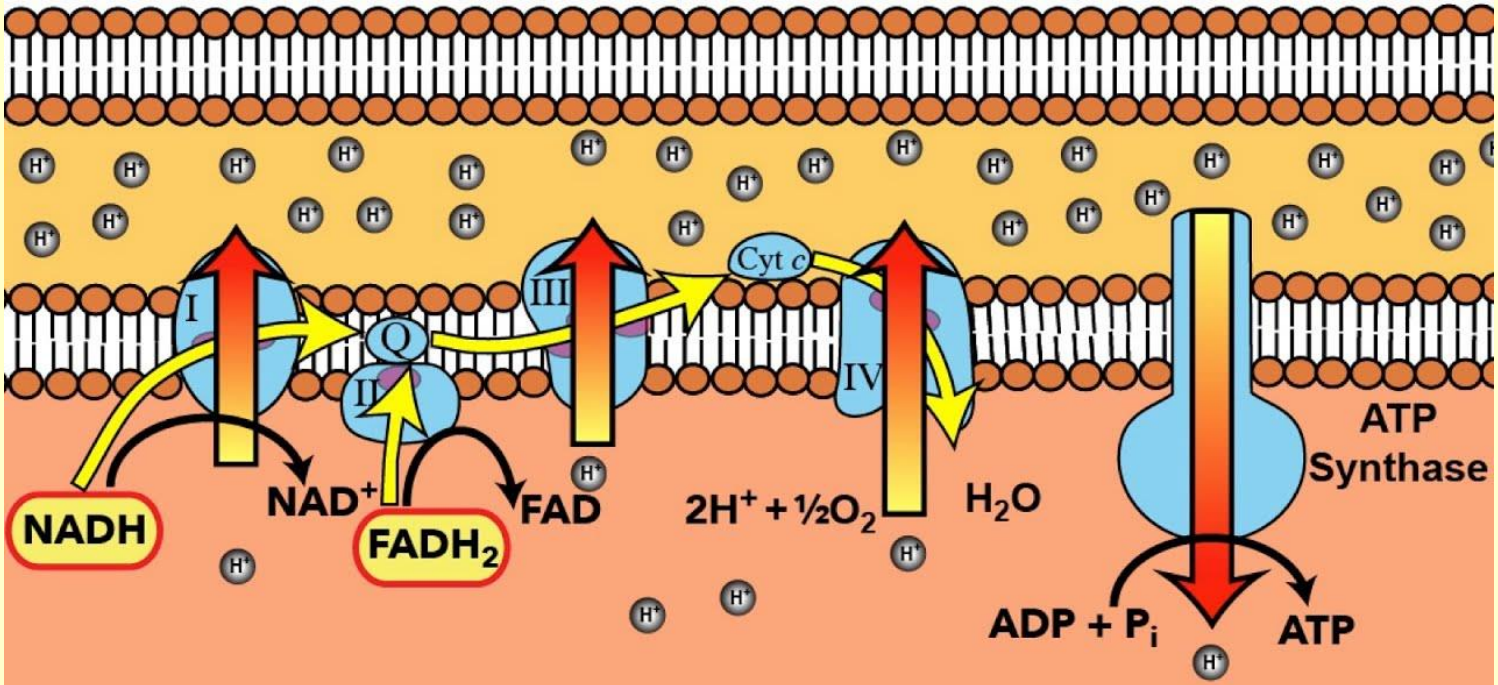
Is it possible to investigate only the "electron" transfer reactions with Voltammetry?

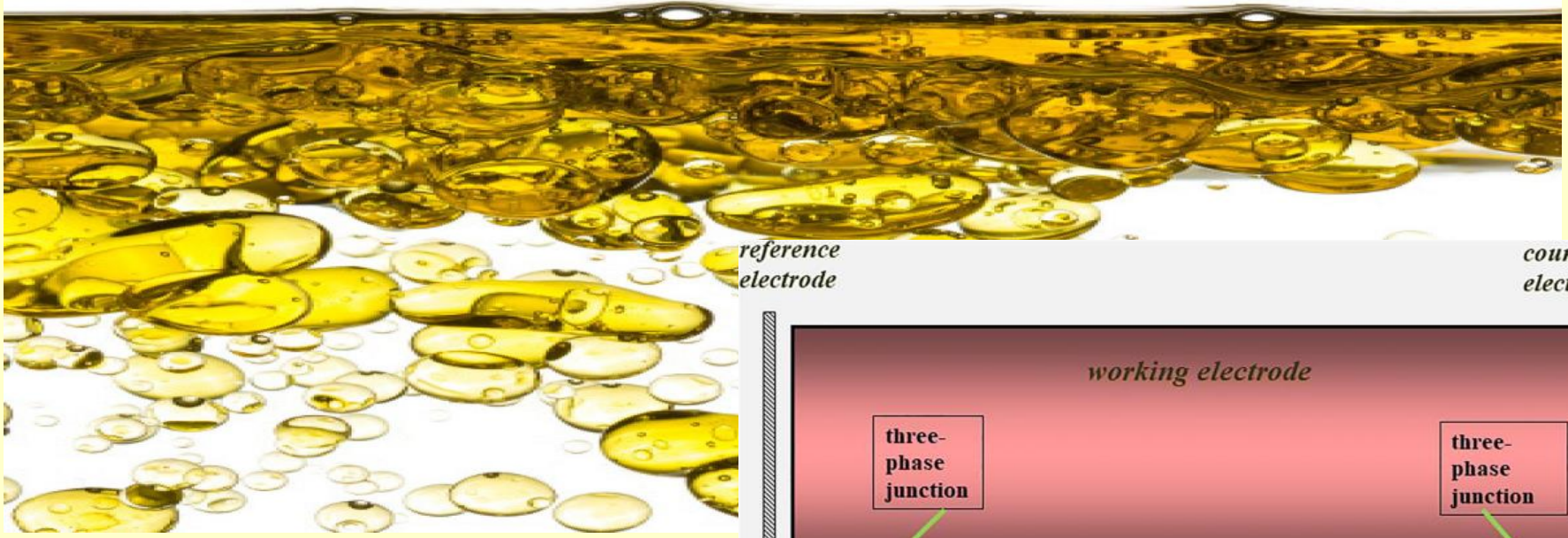
NO, it is possible to follow voltammetrically also reactions comprising only ION transfer,
or COUPLED ELECTRON-ION transfer

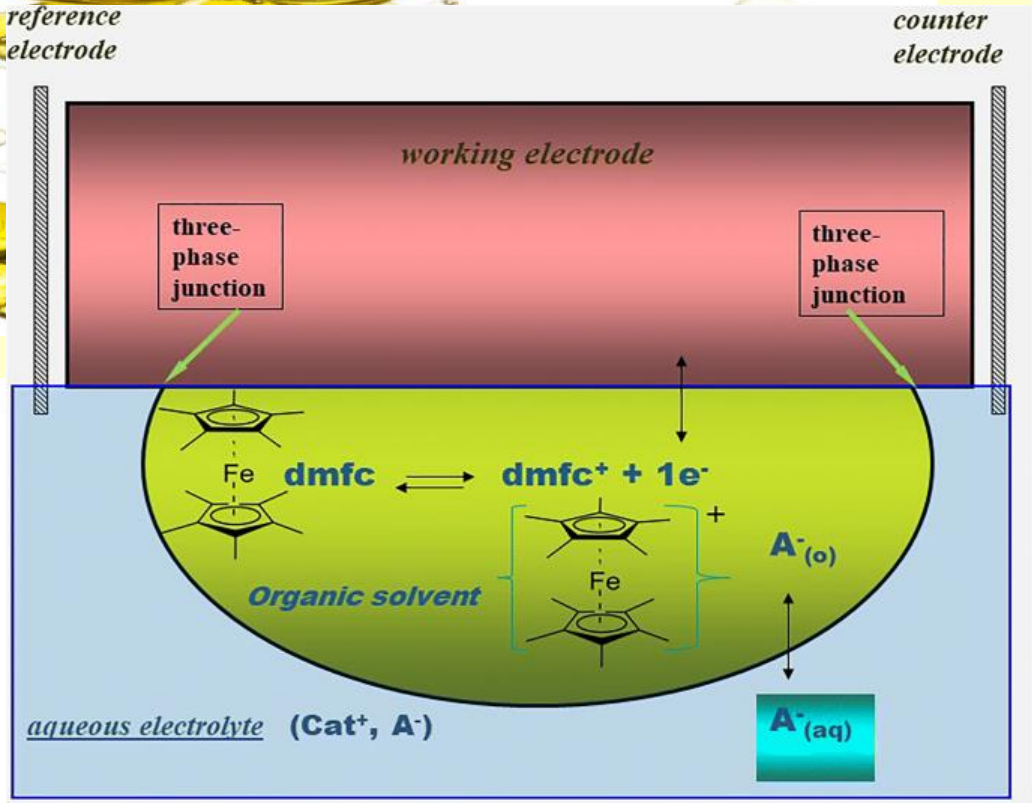


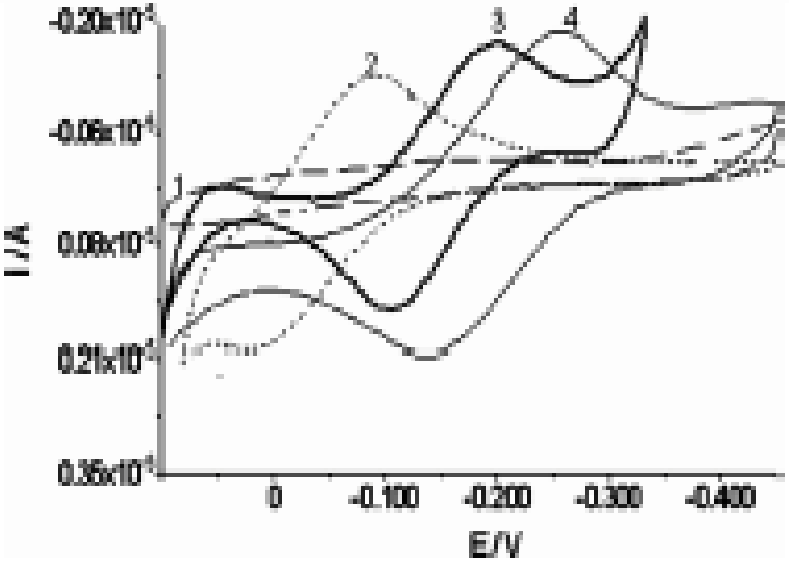


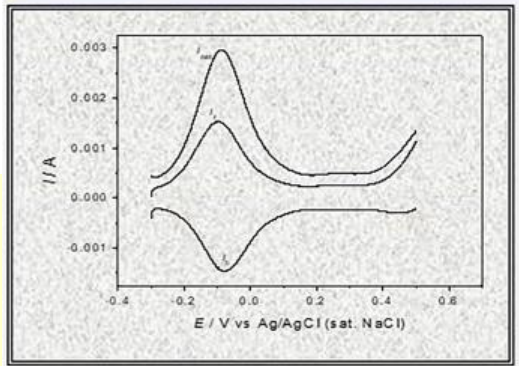
Electron Transport Chain

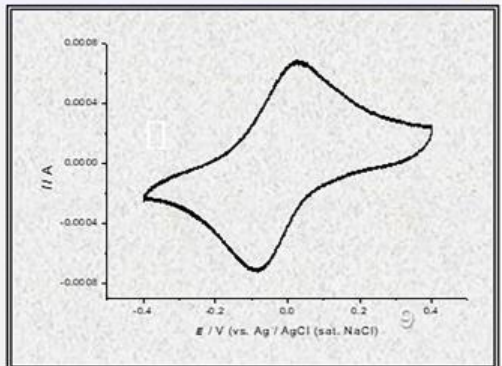






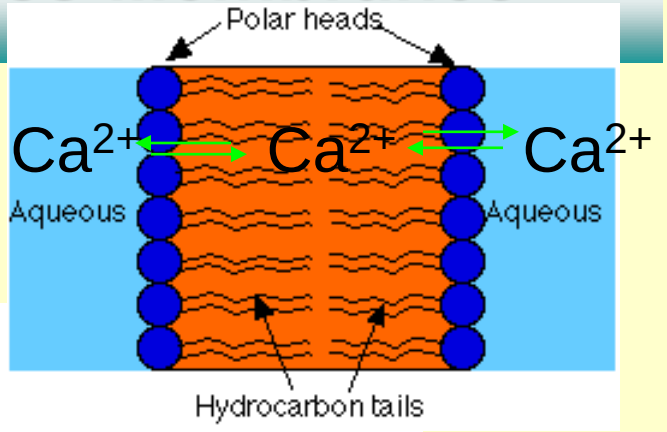


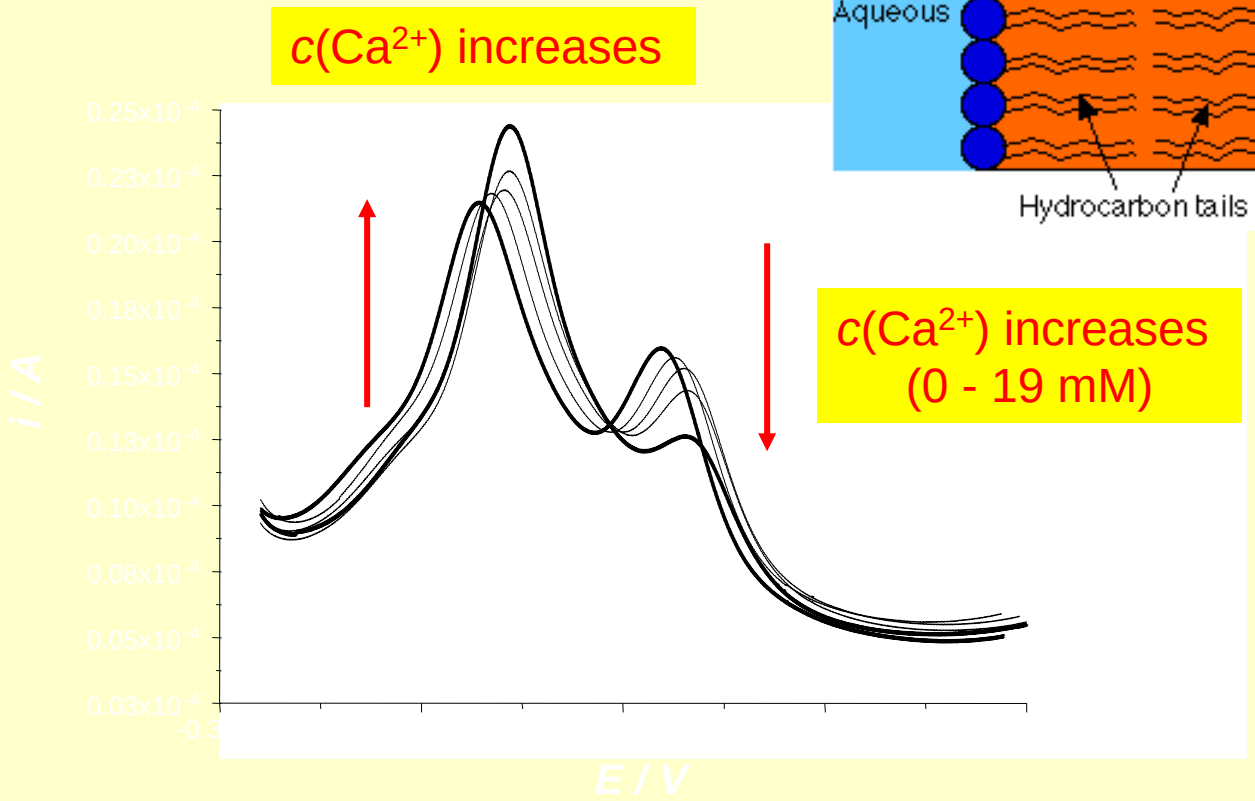




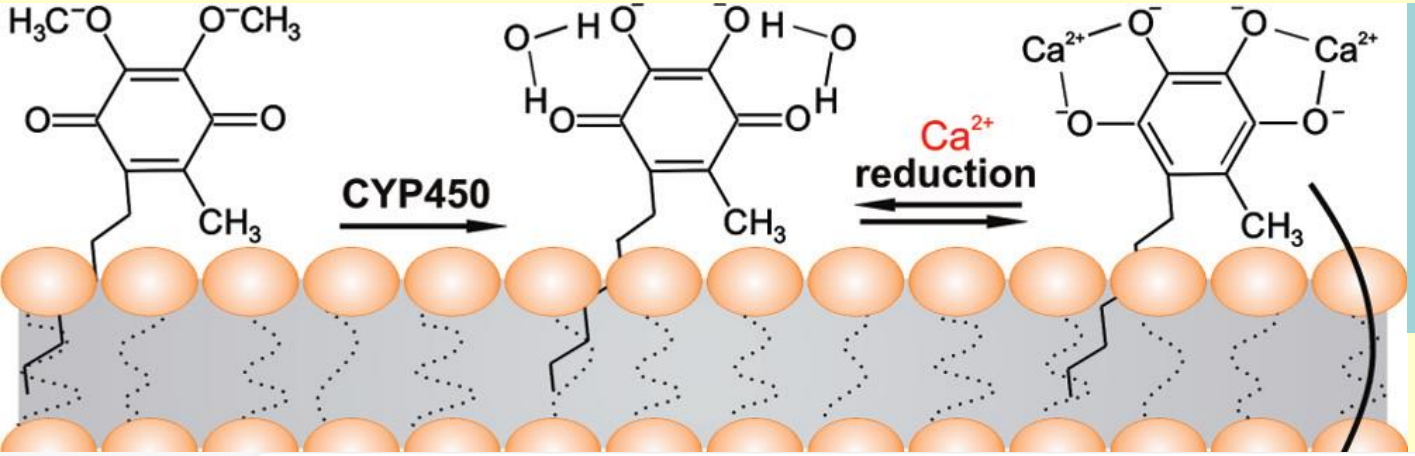
Transfer of Ionized Drugs-
heroin, cocaine and codeine
across biomimetic membranes

Transfer of Ca^{2+} Ions Across Membranes





Cyclic voltammograms showing complexation of PalmytoilQuinone with Ca^{2+}



Novel Function of CoQ10 in transfer of Ca^{2+}

https://pubs.acs.org/doi/10.1021/ja110190t

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Calcium Binding and Transport by Coenzyme Q

Ivan Bogeski[†], Rubin Gulaboski[*†‡§], Reinhard Kappl[†], Valentin Mirceski[§], Marina Stefova[§], Jasmina Petreska[§], and Markus Hoth[*†]

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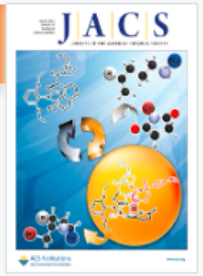

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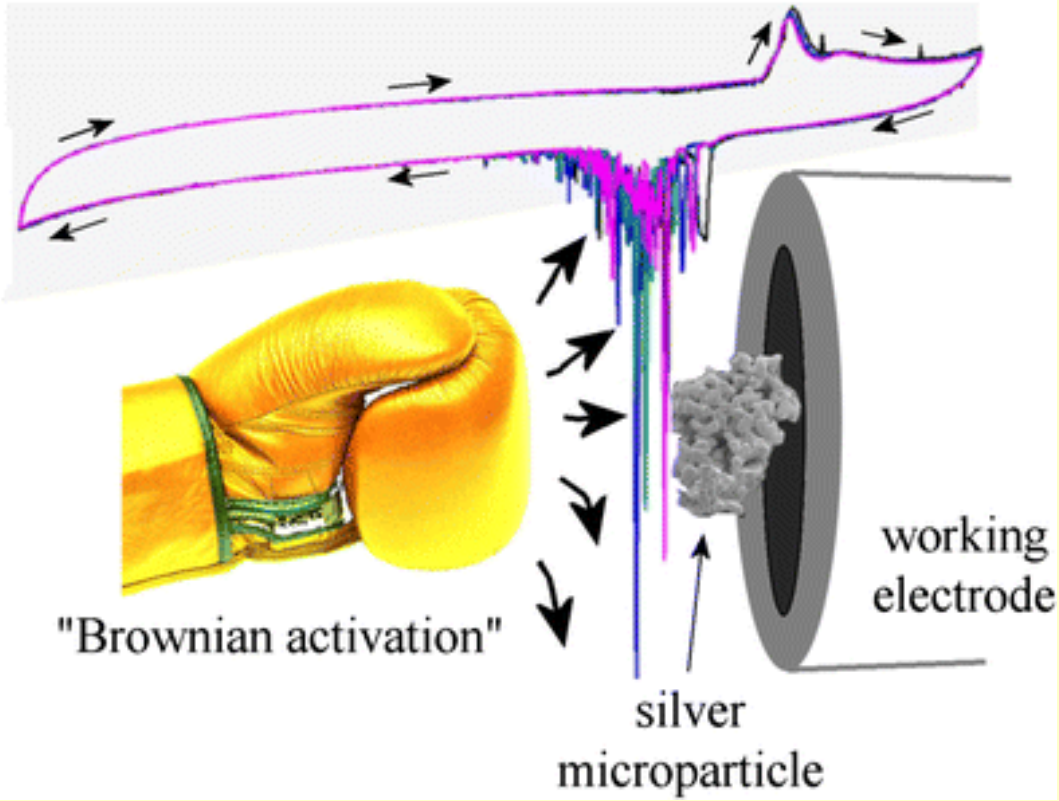
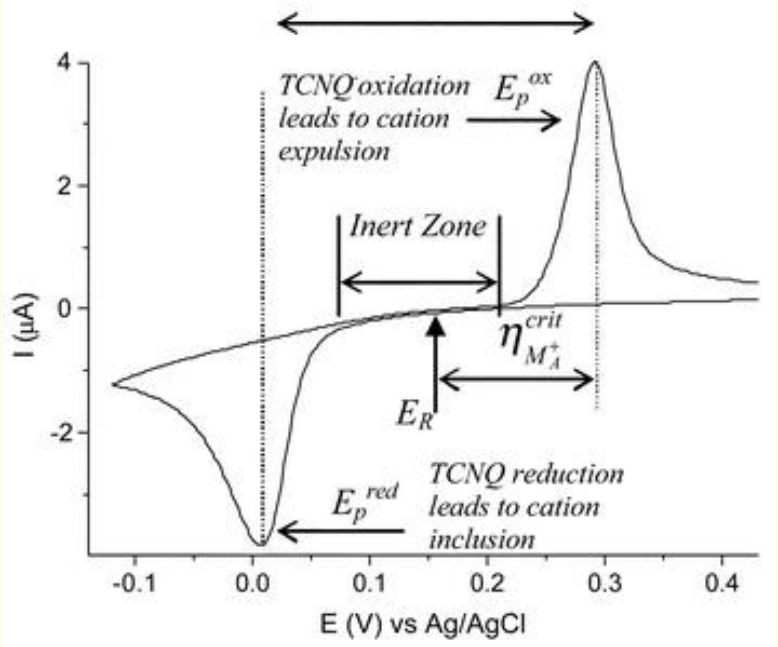
SUBJECTS: Hydroxyls, Ions,

Abstract

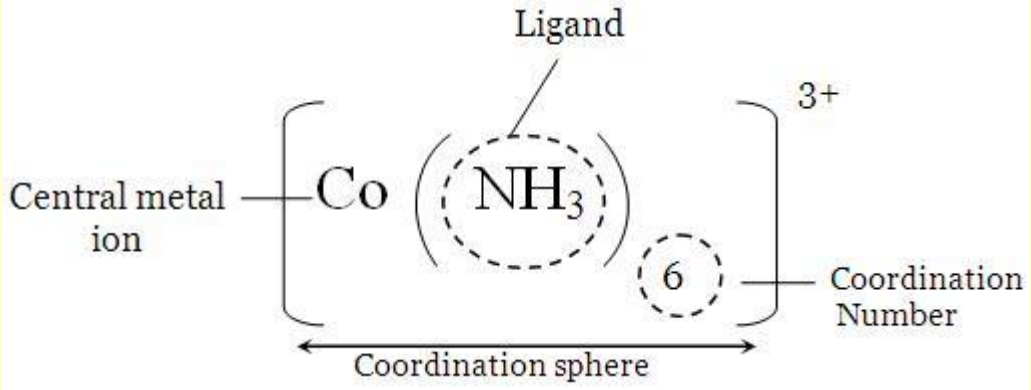
Voltammetry from Solid State





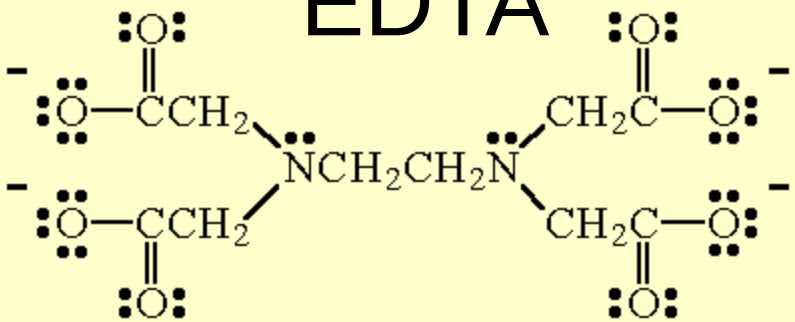
Pioneered by prof F Scholz

VOLTAMMETRY is Extremely efficient and powerfull toll in characterizing Coordination complexes

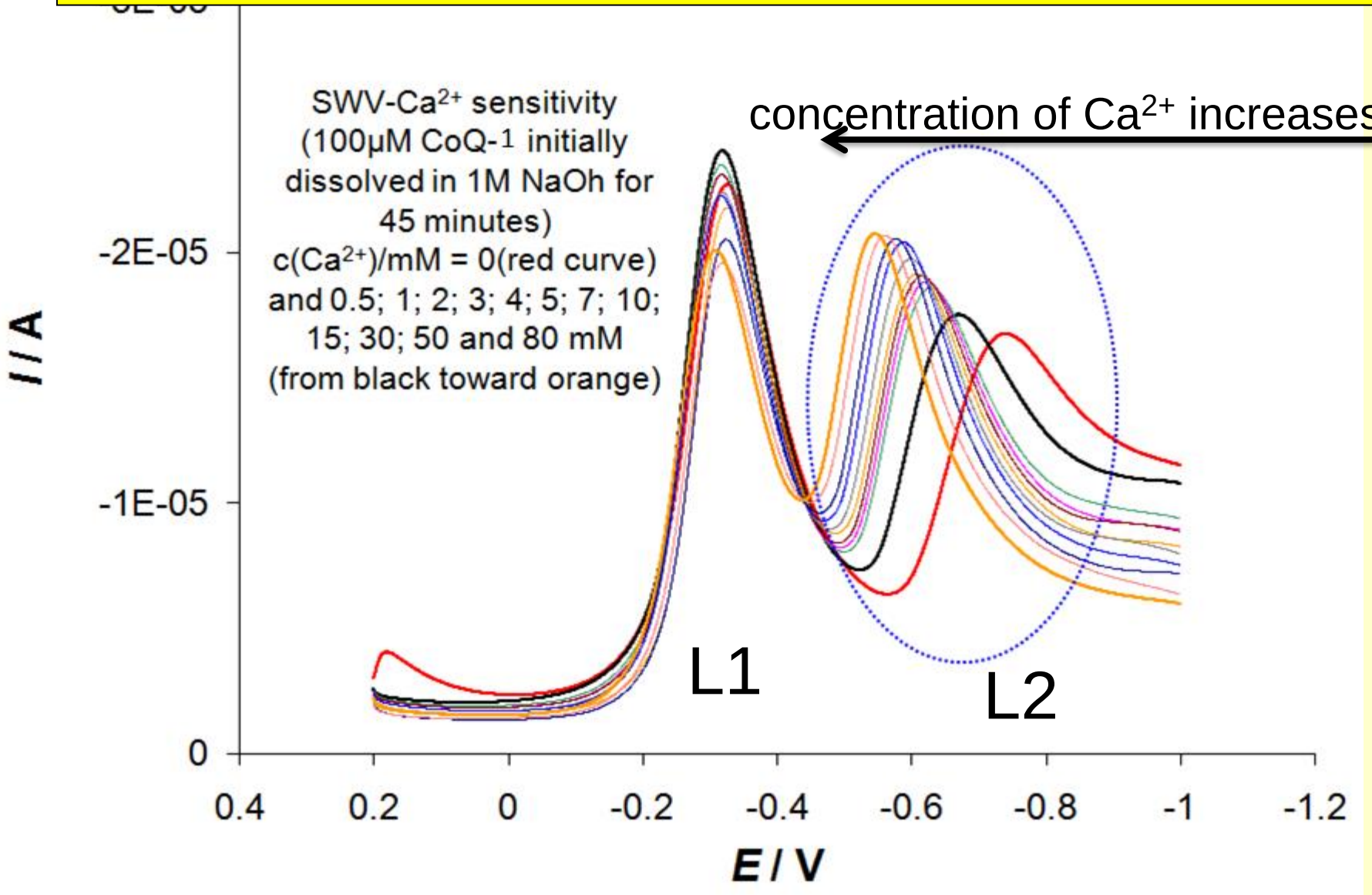


EDTA

Kstab

Lu^{3+} +  ⇌ Lu-(EDTA)x

TWO LIGANDS L1 and L2-One (L2) is able to bind Ca^{2+} ions in stochiometric ratio 1:2 ($L:M^{2+}$), while the other (L1) NOT

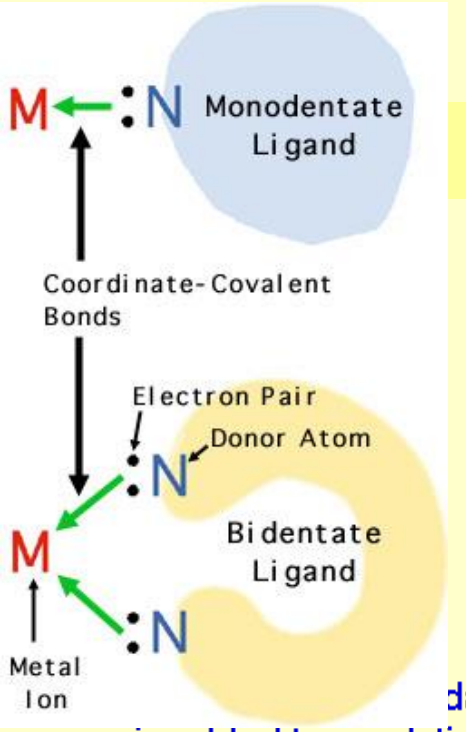


What can we evaluate from voltammetric Experiments?

Kst → Stability constant value

$$M^{X+} + yL = [MLy]^{X+}$$

→ Stochiometry of the complexes



dark blue tetraammine copper(II) ion when ammonia is added to a solution of copper(II) sulfate.

$$Cu^{2+}(aq) + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

$$K_f = \frac{[Cu(NH_3)_4^{2+}(aq)]}{[Cu^{2+}(aq)][NH_3]^4}$$

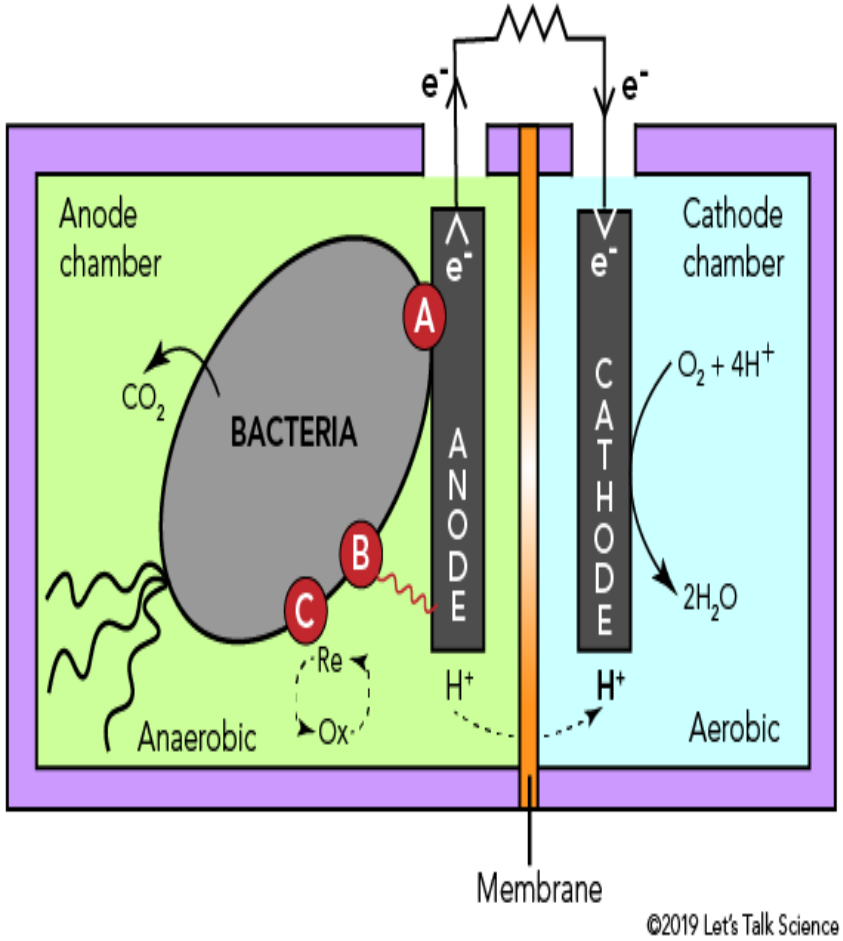
Stability constant / Formation constant

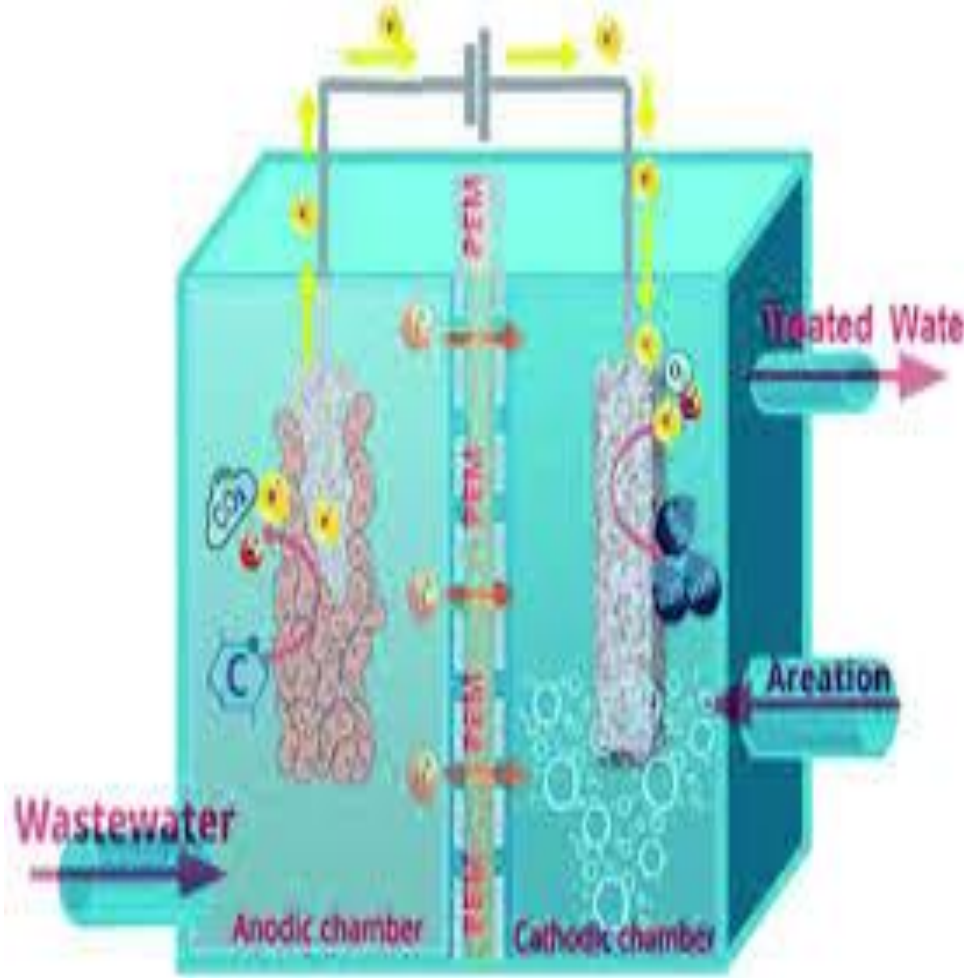
- According to Bjerrum formation of a complex in aqueous solution proceeds through a stepwise fashion with corresponding equilibrium constants

$M + L \overset{K_1}{\rightleftharpoons} ML$	ML	$K1 = [ML] / [M][L]$
$ML + L \overset{K_2}{\rightleftharpoons} ML_2$	ML_2	$K_2 = [ML_2] / [ML][L]$
$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3$	ML_3	$K_3 = [ML_2] / [ML2][L]$
.....		
.....		
$ML_{n-1} + L \overset{K_n}{\rightleftharpoons} ML_n$	ML_n	$K_n = [ML_n] / [ML_{n-1}][L]$

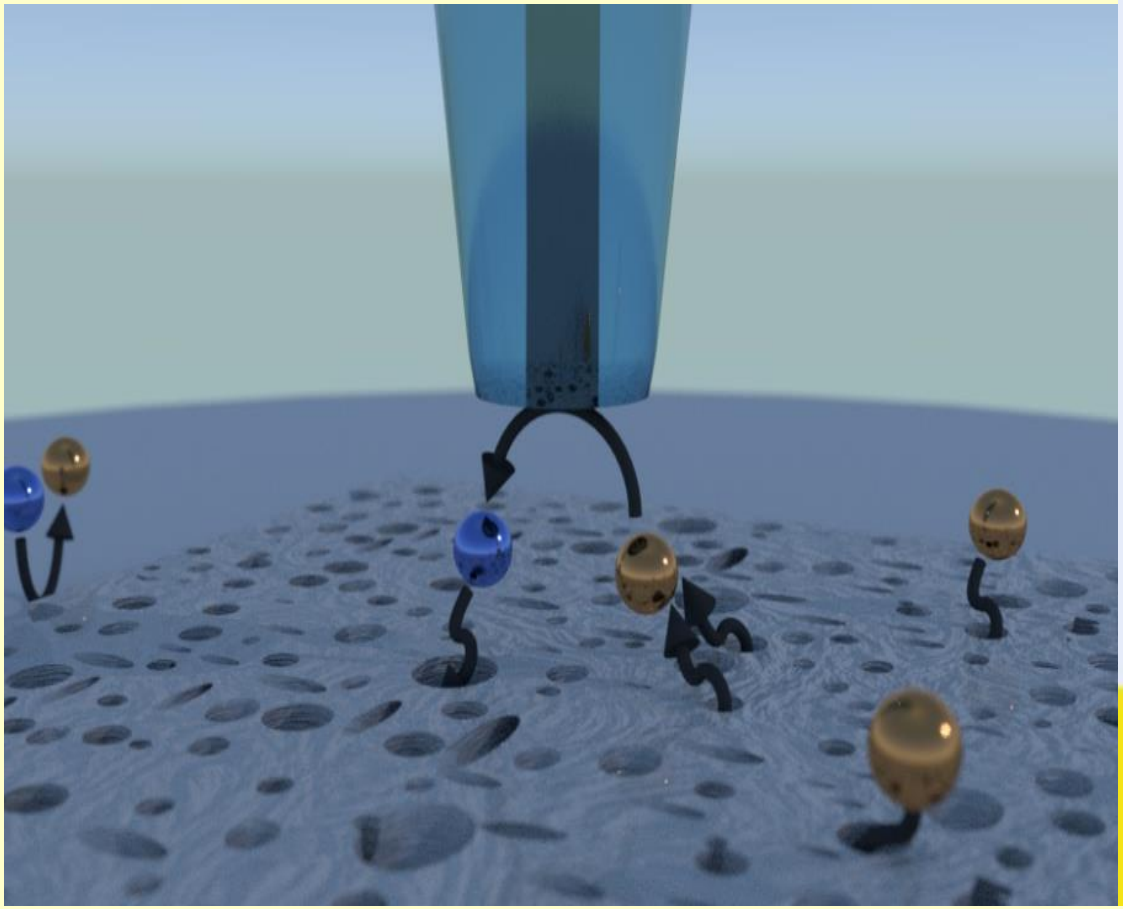
These $K_1, K_2, K_3 \ldots K_n$ are called stepwise formation constants

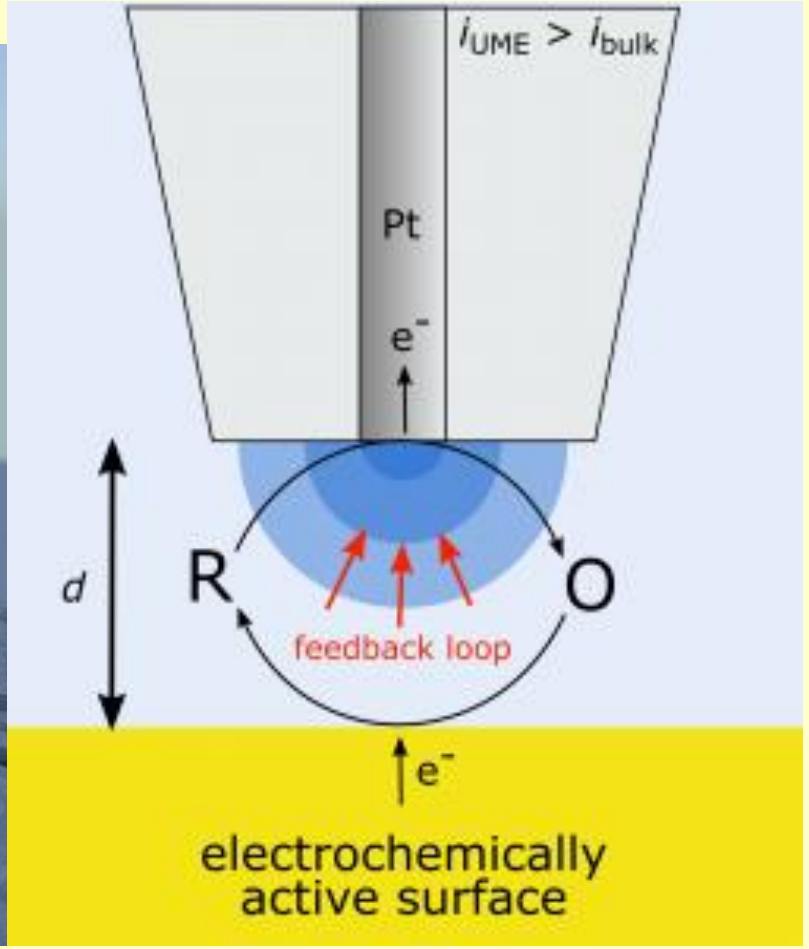
Voltammetry application in biofuel cells

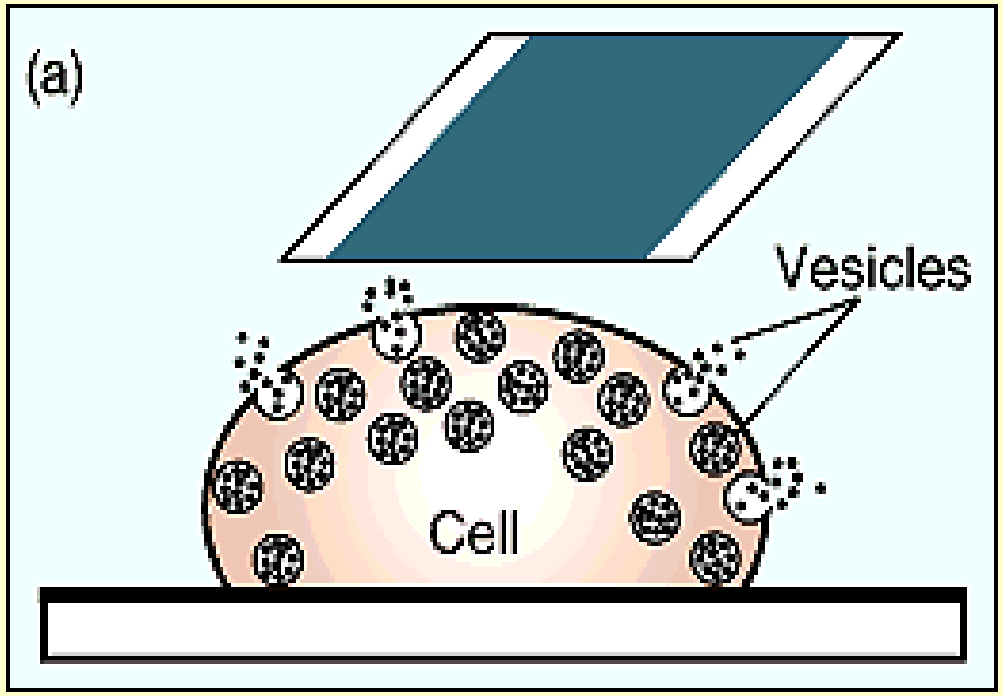




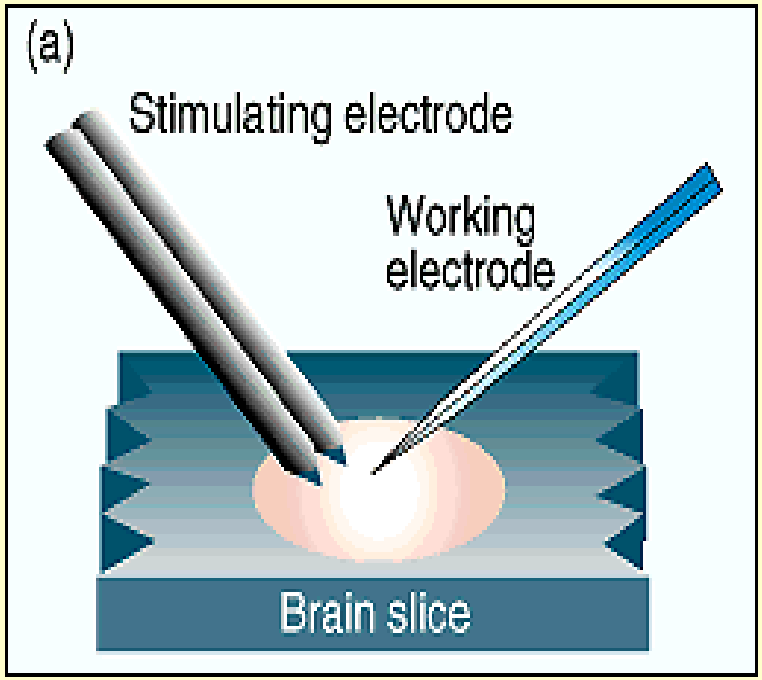
Scanning Electrochemical Microscopy-the Most Sophisticated Electrochemical Technique-Able to be Applied With help of microelectrodes even in SINGLE CELLS!

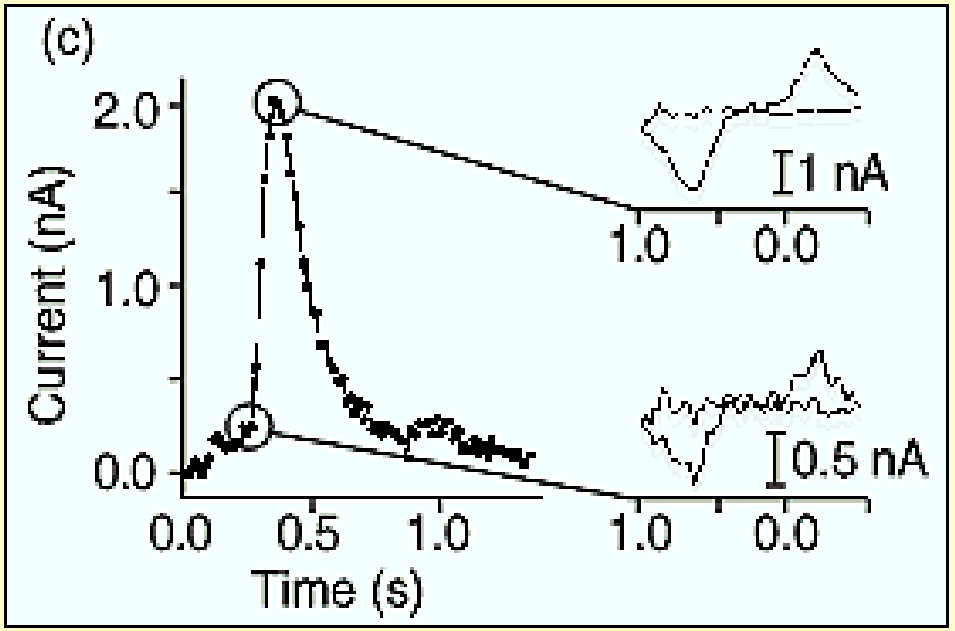


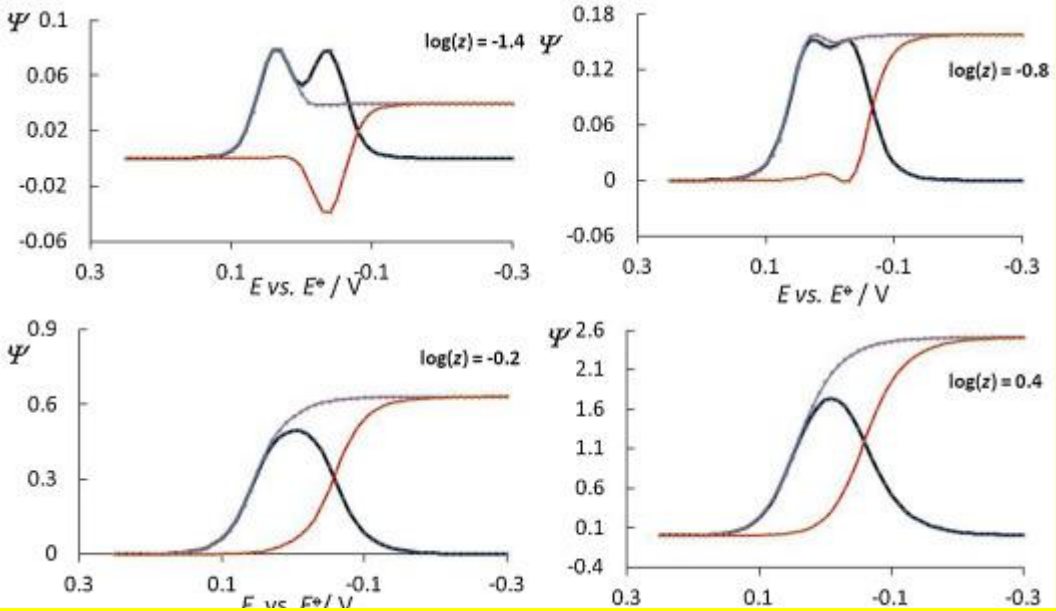


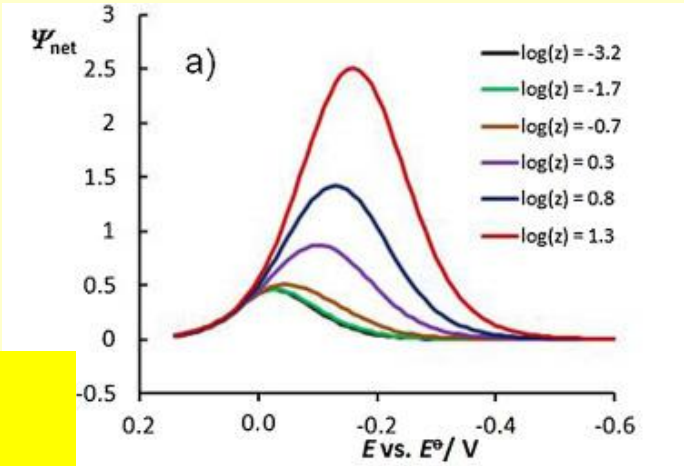


IN-VIVO voltammetric determination of dopamine







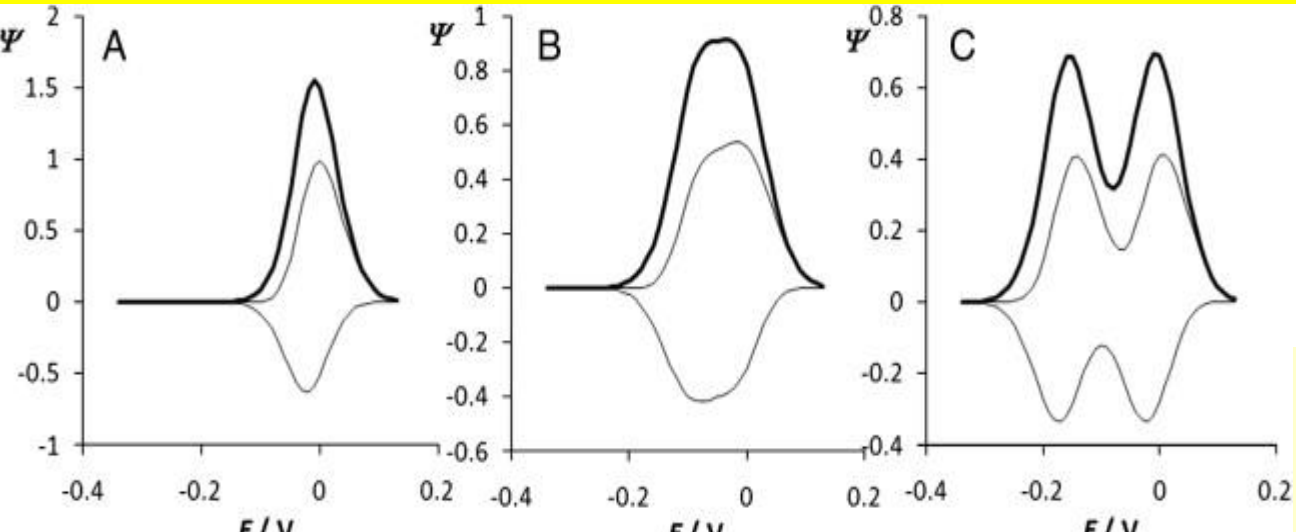


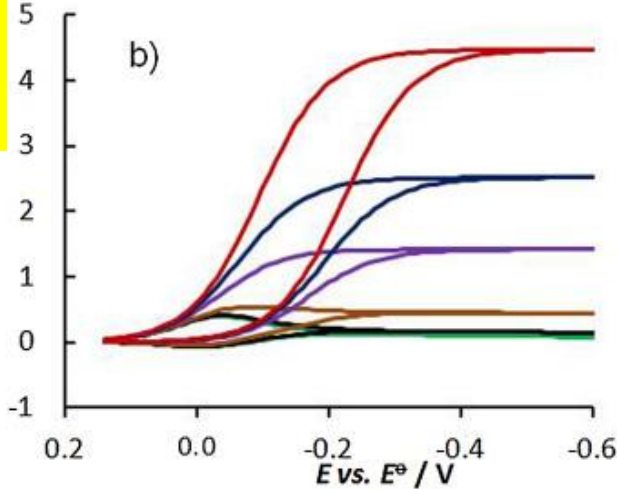
Well-Developed Theories in Voltammetry but

….**but???**

Miscommunication exists between

Theoretical and experimental electrochemists





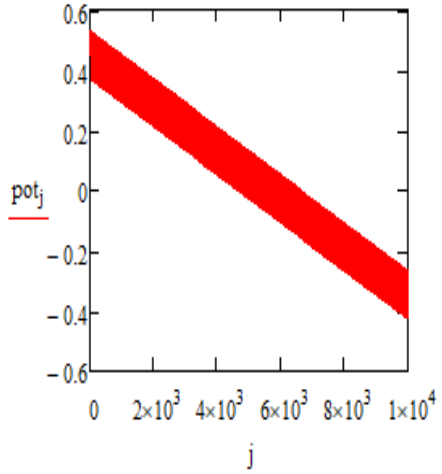
$Es := 0.45 \quad \Delta E := 0.8 \quad dE := 0.004 \quad Esw := 0.08$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

$j := 1 .. \frac{\Delta E}{dE} \cdot 50$

$\alpha := 0.5$

$$pot_j := Es + Esw - \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw \right) - dE \right]$$



$k := 1 .. \frac{\Delta E}{dE} \cdot 50$

$$S_k := e^{\frac{Kchem}{50} \cdot (-k)} - e^{\frac{Kchem}{50} \cdot (-k+1)}$$

$\Phi_j := n \cdot \frac{F}{R \cdot T} \cdot pot_j \qquad Ket := 0.032$

$kc := 1000.00$

$f := 10$

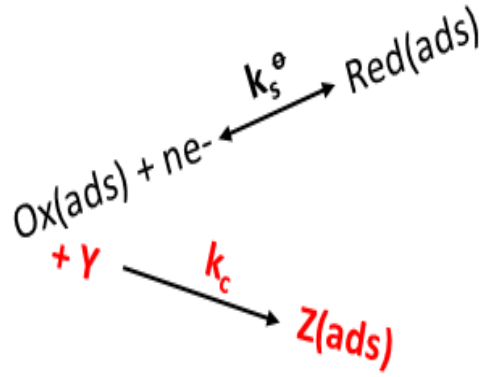
$ks := 10^{-0.5}$

Model of Surface Electrode Mechanism with Irreversible Chemical Reaction Coupled to Initial Redox Form in Protein-Film Voltammetry

$Ket := \frac{ks}{f}$

$kc := 10^3$

$Kchem := \frac{kc}{f}$



Definitions and Meanins of the Symbols

f is the SW frequency
ks is standard rate constant of electron transfer
α is electron transfer coefficient
n is number of exchanged electrons
dE is potential step
Esw is square-wave amplitude
T is thermidynamic teperature
R is universal gas constant
kc is rate constant of irreversible chemical rection
Ket is dimensionless kinetic electrode parameter
Kchem is dimensionless kinetic chemical parameter
Sk is numerical integration factor
Es is starting potential
Φ is dimensionless potentials
F is the Faraday constant
Ψ is dimensionless current

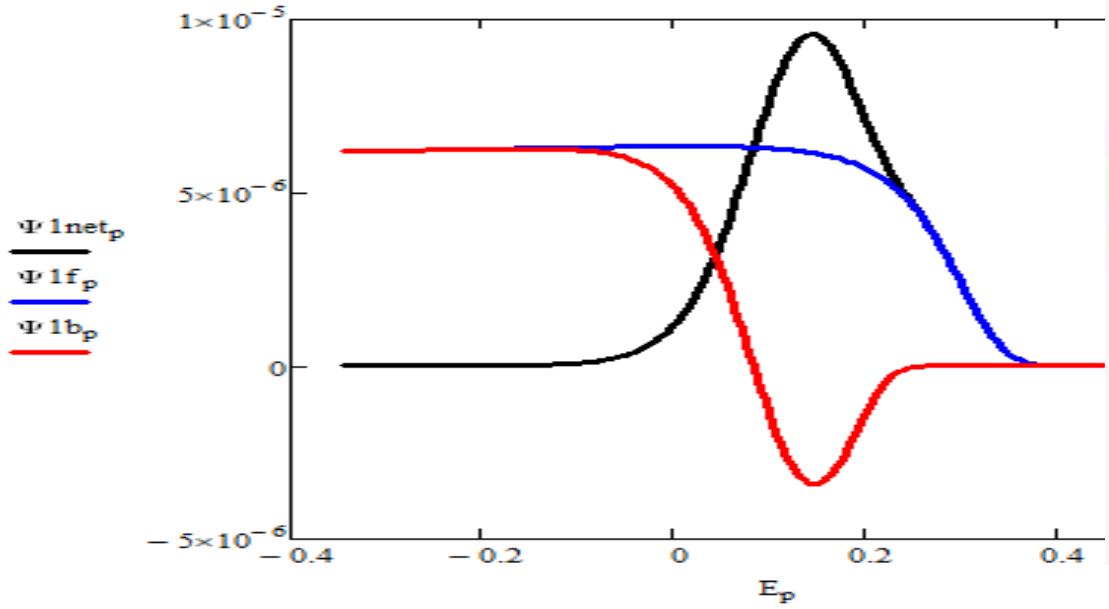
$$\Psi 1_1 := \frac{\frac{Ket}{50}\cdot e^{-\alpha\cdot\Phi_1} - \left[Ket\cdot e^{-\alpha\cdot\Phi_1}\cdot\frac{\left(1+e^{\Phi_1}\right)}{50}\cdot 0 + \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_1}\cdot 1\cdot S_1}{1}\right]}{1+\frac{Ket\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)}{50} - \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_1}\cdot 1\cdot S_1}{1}}$$

$$\Psi 1_k := \frac{\frac{Ket}{50}\cdot e^{-\alpha\cdot\Phi_k} + \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_k}\cdot 1}{1}\cdot\sum_{j=1}^{k-1}\left(\Psi 1_j\cdot S_{k-j+1}\right) - Ket\cdot e^{-\alpha\cdot\Phi_k}\cdot\frac{\left(1+e^{\Phi_k}\right)}{50}\cdot\sum_{j=1}^{k-1}\Psi 1_j}{1+\frac{Ket\cdot e^{-\alpha\cdot\Phi_k}\cdot\left(1+e^{\Phi_k}\right)}{50} - \frac{Kchem^1\cdot e^{-\alpha\cdot\Phi_k}\cdot 1\cdot S_1}{1}}$$

$$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$$

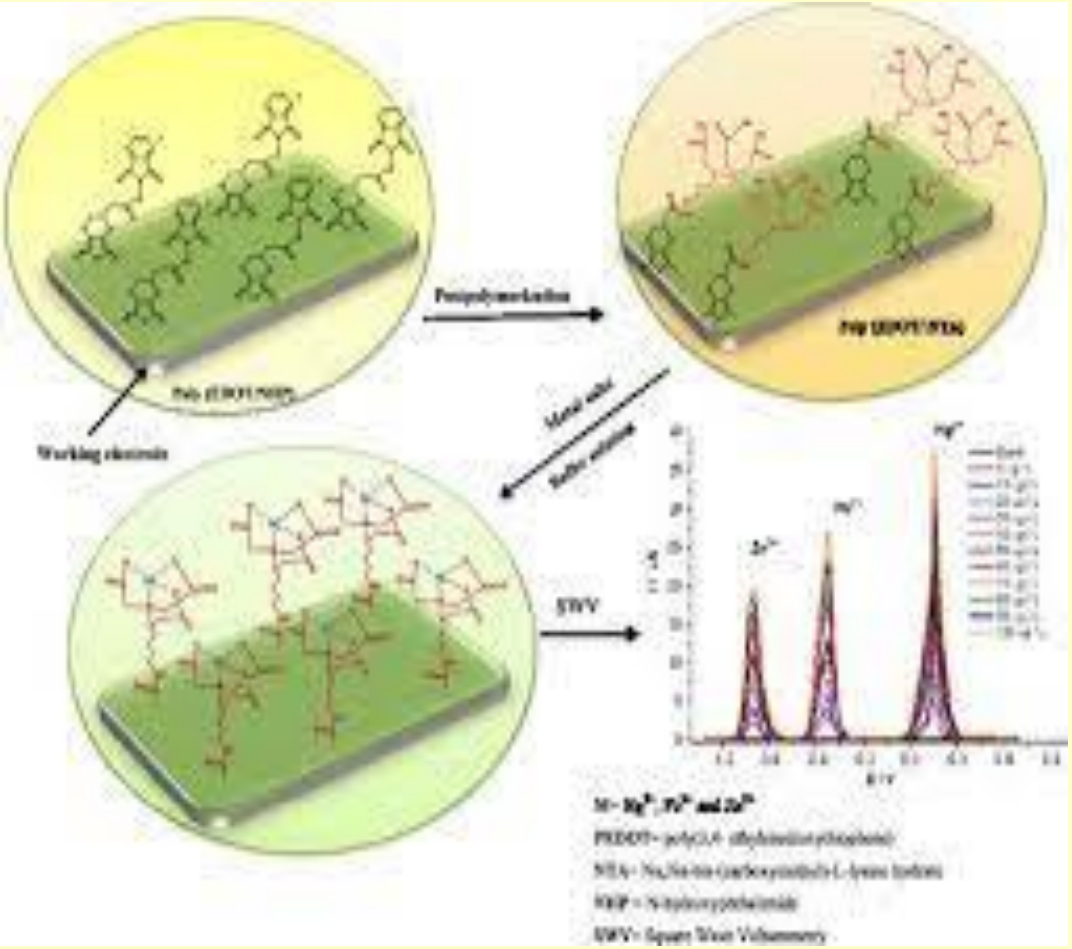
$$\Psi 1f_p := \Psi 1_{(p+1)\cdot 50} \qquad \Psi 1b_p := \Psi 1_{50\cdot p+25} \qquad \Psi 1net_p := \Psi 1f_p - \Psi 1b_p$$

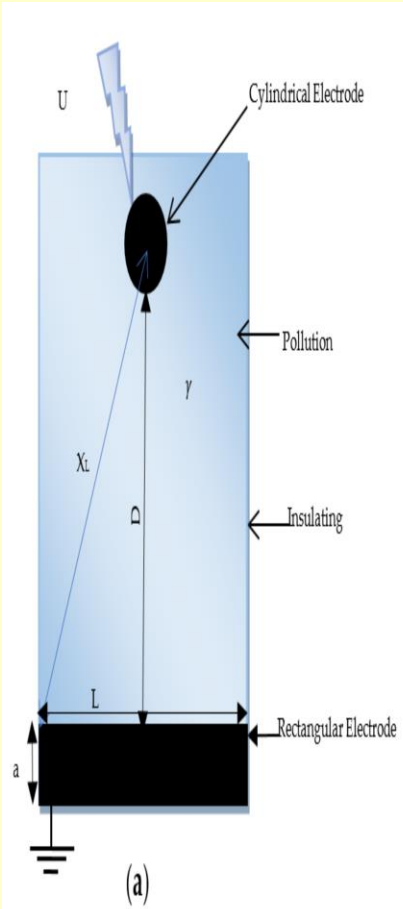
$$E_p := Es - p\cdot dE$$



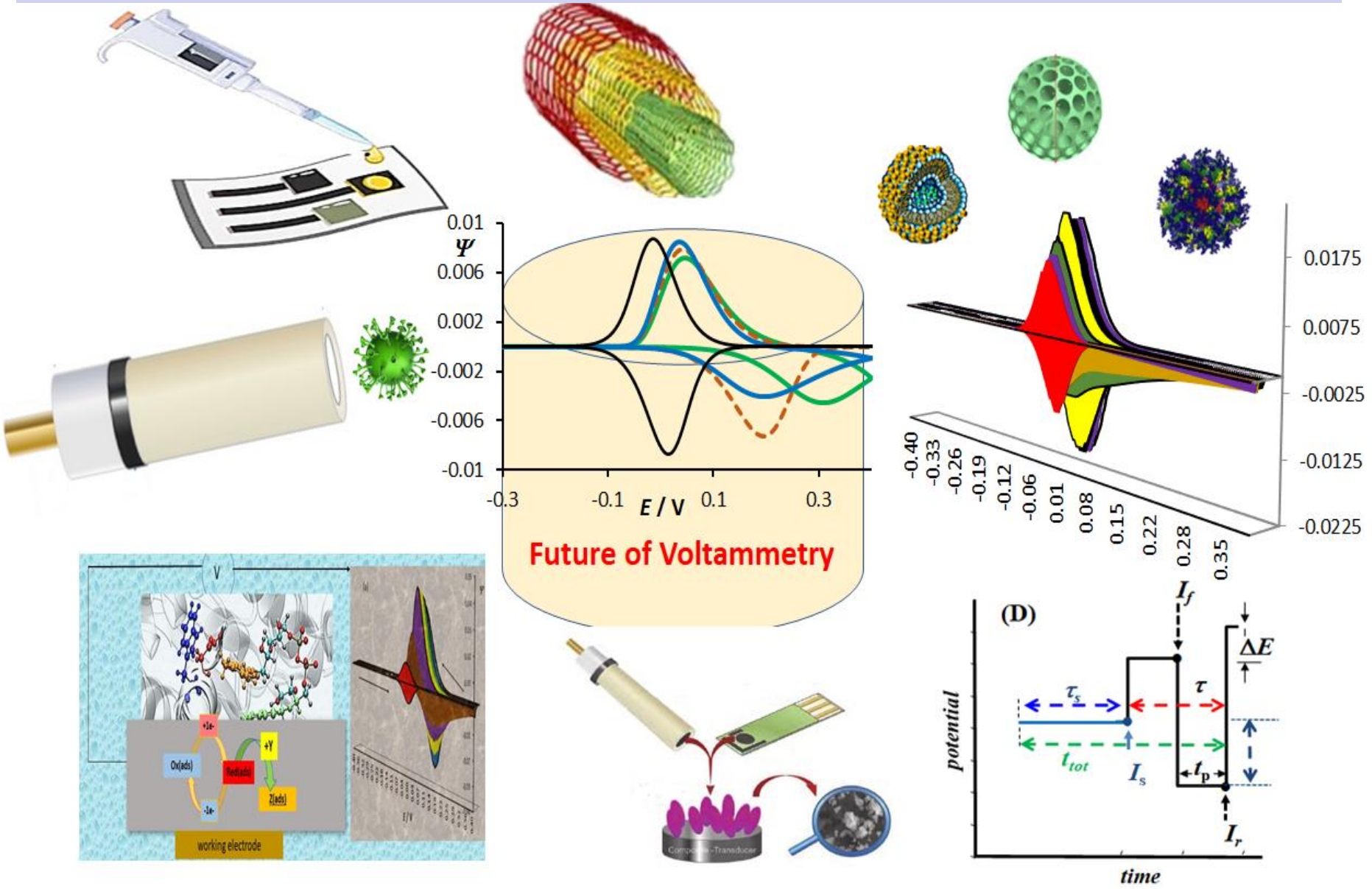
Are there some limitations?

Biggest problem in Voltammetry is the ***CONTAMINATION*** of the **working electrodes**, especially those made of carbon or Gold





Where Voltammetry Will Go in the Next 50 Years? (MJCCE 2022)



Concluding remarks

...ADVANTAGES of using Voltammetry

-fast înstrumental technique-experiments performed is couple of seconds

-extremely cheap instrumentation

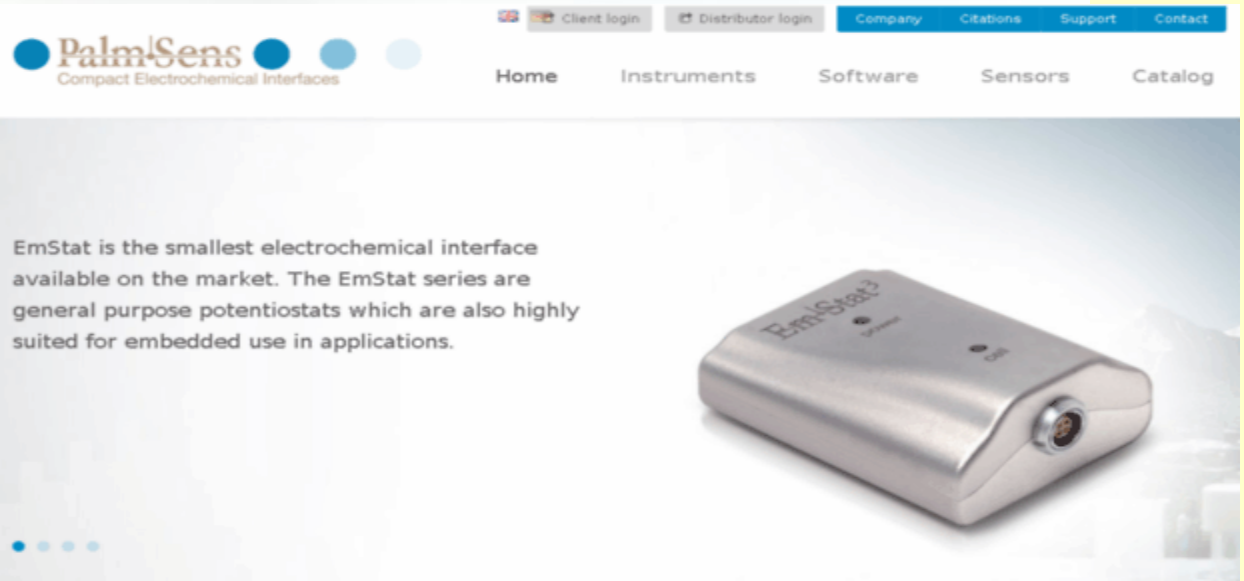
-common chemicals are used available in every Lab

-...suitable for qualitative, quantitative studies, mechanistic studies, kinetic and thermodynamic measurements

Total costs for the voltammetric instrumentation

3-4000 Euros!!!!

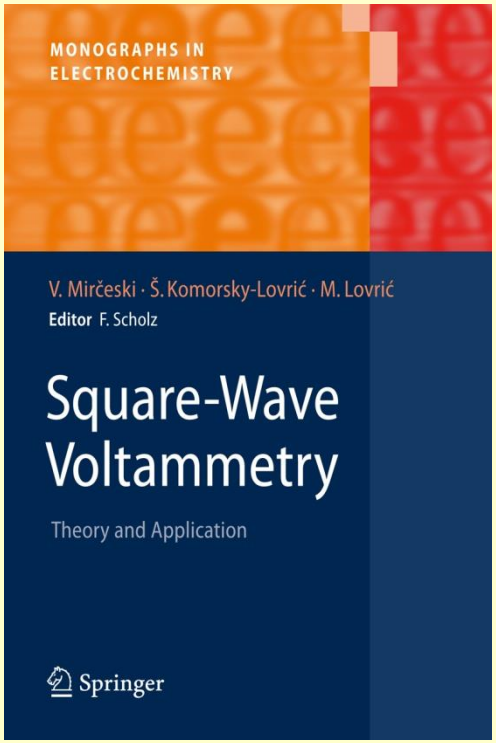
Making a great science for small money!!!
Amazing!!!

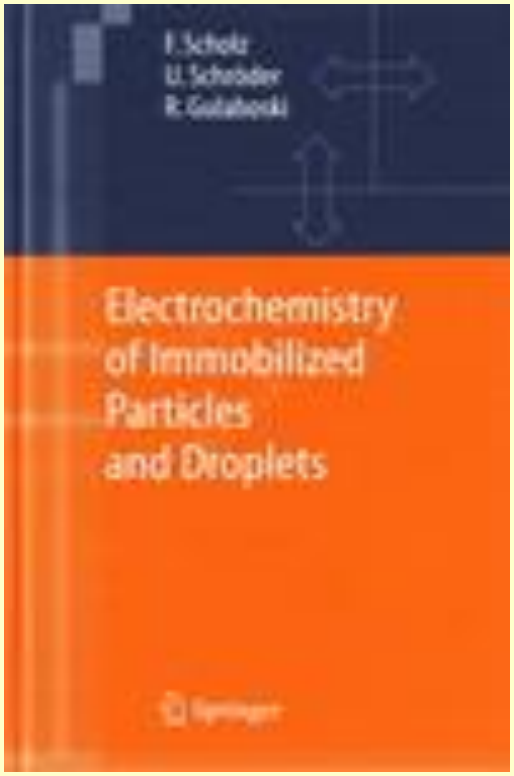


…and AFTER ALL THESE YEARS…
MY QUESTION IS:
WAS IT WORTH DOING SCIENCE?

This is the Lab where we started…

The chemicals we used in our experiments…

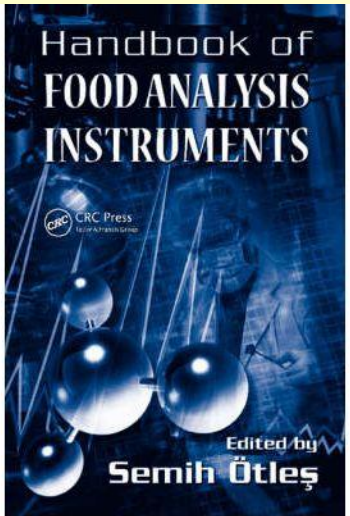




ELECTROCHEMICAL DICTIONARY (2008)
A. J. Bard, G. Inzelt, F. Scholz (editors)

F. Scholz, U. Schroeder, **R. Gulaboski**

R. Gulaboski, C. M. Pereira in
Handbook of Food Analysis Instruments (2008)
Semih Otles (Ed.)



Six Macedonian scientists among the most influential scientists in the world on the Stanford list

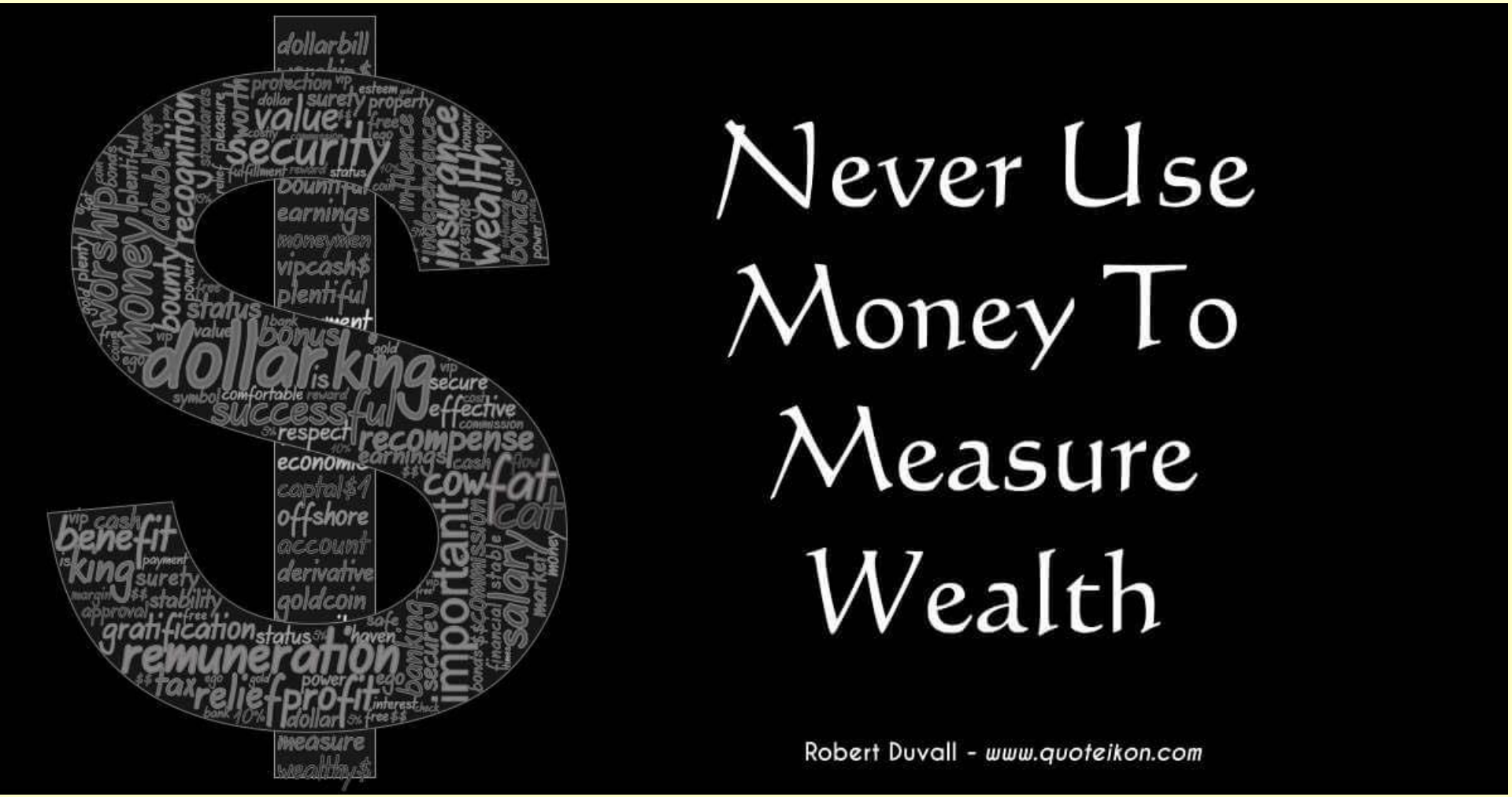
Six Macedonian scientists are ranked in the top two percent of the world's most influential scientists on the Stanford list / Photo: MIA

Six Macedonian scientists are ranked in the top two percent of the world's most influential scientists on the list of the prestigious American Stanford University for 2021. Ljupco Kocarev (MANU), Leonid Grcev (MANU) Valentin Mirceski (Institute of Chemistry, Faculty of Natural Sciences, UKIM, Skopje), Rubin Gulaboski (Faculty of Medicine) are ranked on the cumulative list for the best top two percent of scientists of all times (from all fields). sciences, UGD Stip) and two retired professors, Trajche Stafilov (Institute of Chemistry, Faculty of Natural Sciences, UKIM, Skopje) and Ivan Grozdanov (Institute of Chemistry, Faculty of Natural Sciences, Skopje).

→First DAAD Scholarship Holder from MACEDONIA in 2001

-One of few Alexander von Humboldt Fellows from MKD-Postdoc in Germany
-PostDoc stay in Porto-Portugal
-Patent published in Germany
-**Meeting with Nobel Laurates Lindau 2002**
-Ten best scientists under the age of 35 Barcelona 2006
-among six MACEDONIANS on the list of Stanford University in 2020, 2021…
-Meeting with Nobel Laurates…

We made a piece of GOOD Science FROM NOTHING
…and we worked for NOTHING!!!
Money is not the measure of real wealth!!
Doing Science---it is about the WILL!!!



F. Scholz-Germany
M. Hoth-Germany
R.Kappl-Germany
M. Bozem-Germany
I. Bogeski-Germany
K. Kumerow-Germany
H. Haeri-Iran
B. Hoth-Germany
A. Kretzchmar-Germ
Maurice L Her-France
Zbigniew Stojek-Poland
C. Pereira-Porto
N. Cordeiro-Porto
M. Chirea-Romania
F. Borges-Portugal
E. Fereira-Portugal
E. Mazanes-Spain
R. Compton-UK
Tim Anders-USA
M. Randjelovic-Serbia

V**. Mirceski-Macedonia**
M. Lovric-Croatia
S. Lovric-Croatia
D. Jadresko-Croatia
S. Mitrev-Macedonia
I. F. Dan-Hungary
Yihe Zhu-China
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Z. Stojek-Poland
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For doing Science-
YOU MUST FIND SOMEONE
WHO WILL GIVE YOU INSPIRATION, Motivation….

Happy 50th Anniversary

Acknowledgments

Prof. Fritz Scholz
Greifswald Universi

Prof. Markus Hot
Saarland Univers

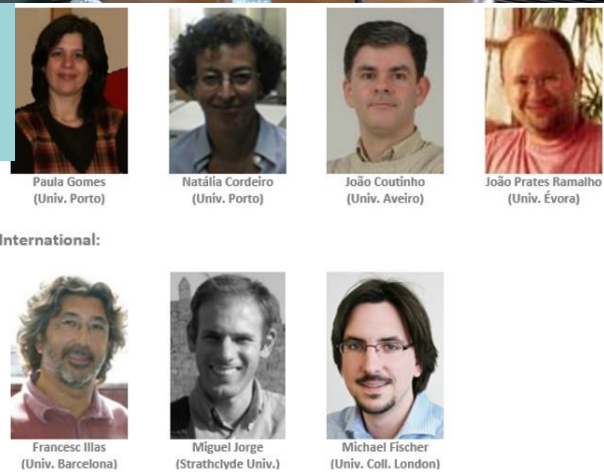
Prof. Carlos Pere
Porto Universit

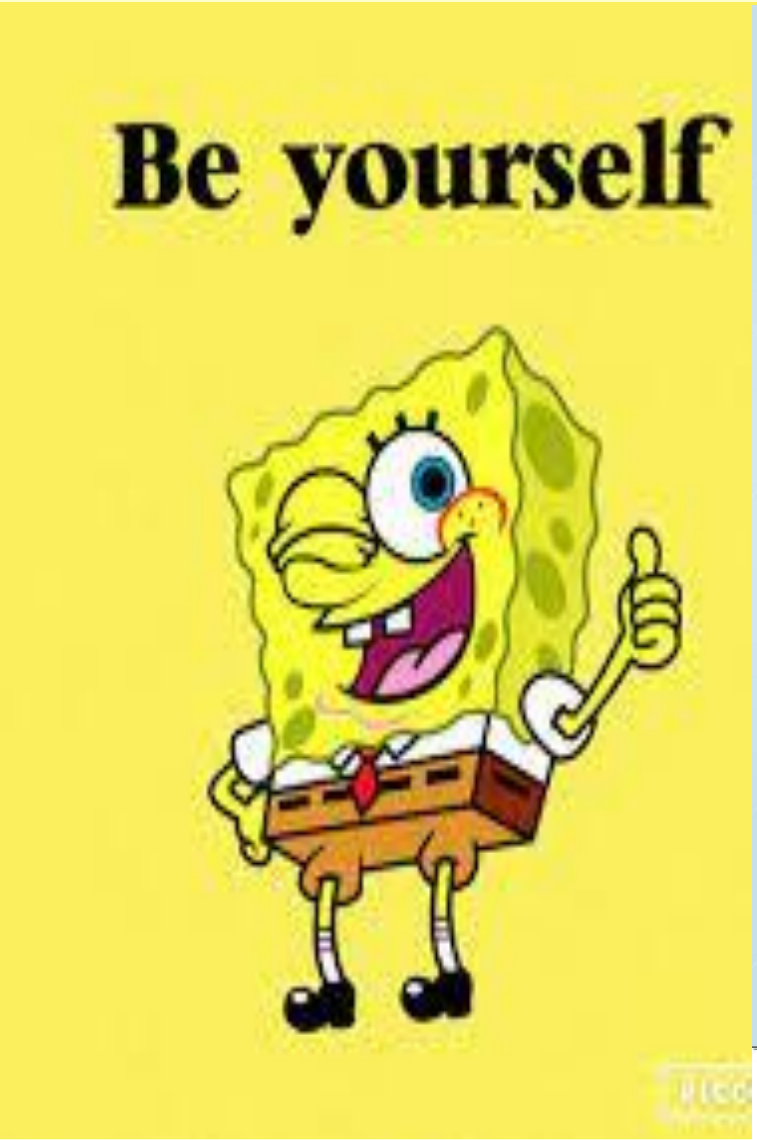
Prof. Reinhard Kappl
Saarland University

Prof. Valentin Mirceski
Macedonia

Prof. Milivoj and Sebojka Lovric
Croatia

Prof Ivan Bogeski,
Goettingen UNI





THANKS FOR YOUR ATTENTION

…and thanks for all you have done RF…

The speaker's attendance at this conference was sponsored by the Alexander von Humboldt Foundation.

- http://www.humboldt-foundation.de