ELECTROCHEMICAL DEVICES
PRINCIPLES AND APPLICATIONS
-VOLTAMMETRY-

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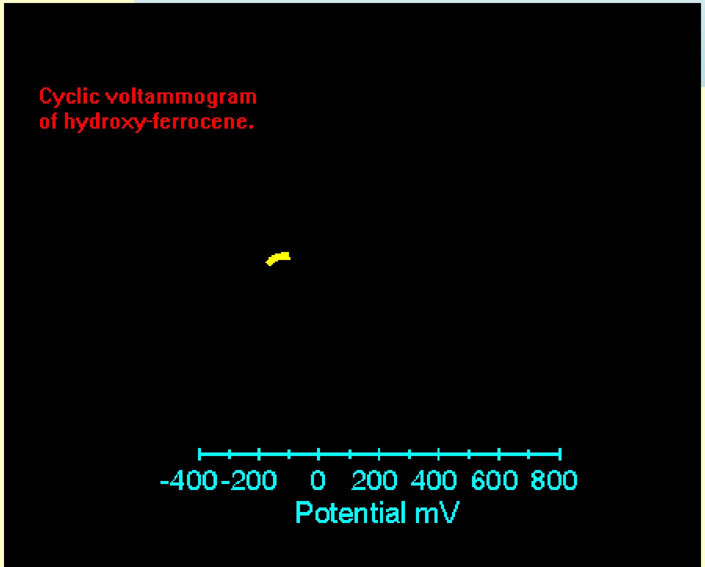
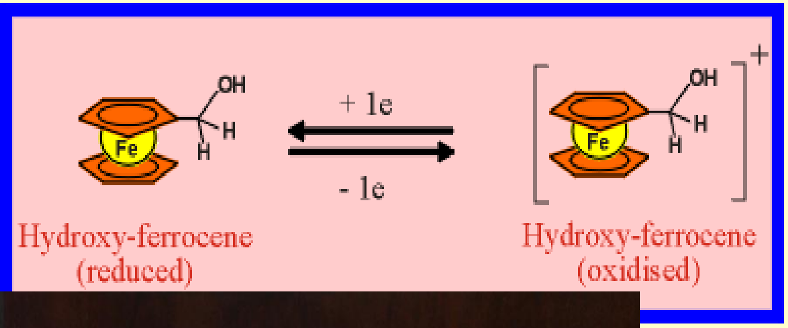
SOE DAAD Ohrid, 2016

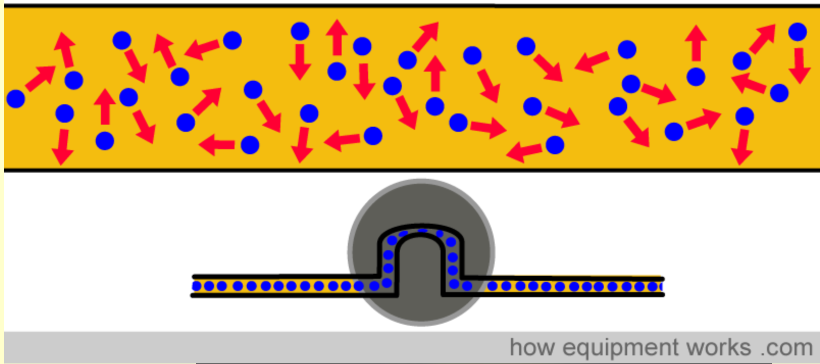


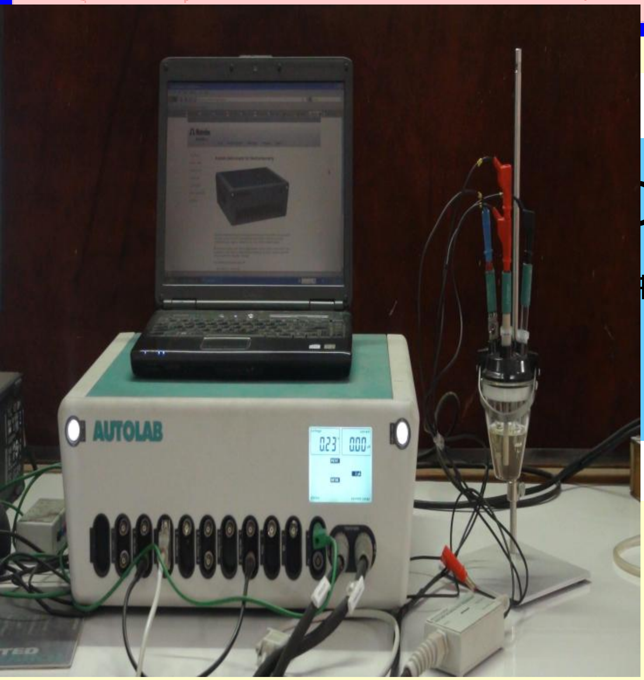
ELECTROCHEMISTRY

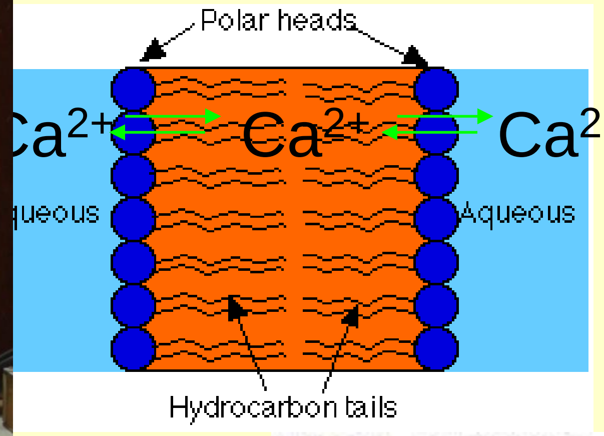
-...is a branch of Physical Chemistry that deals wity the processes of CHARGE transfer between two systems (Charge= electrons or ions)

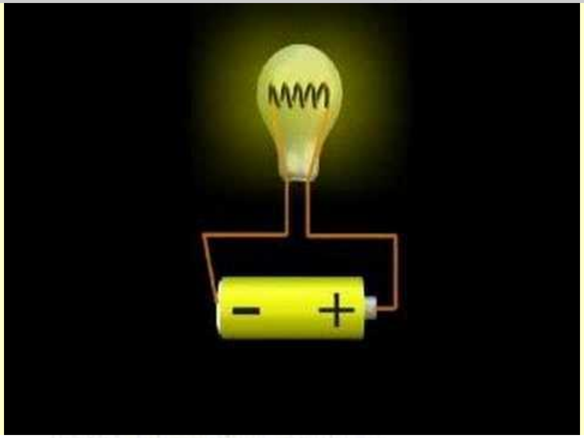
-FLOW of electric charge between two joined systems=CURRENT

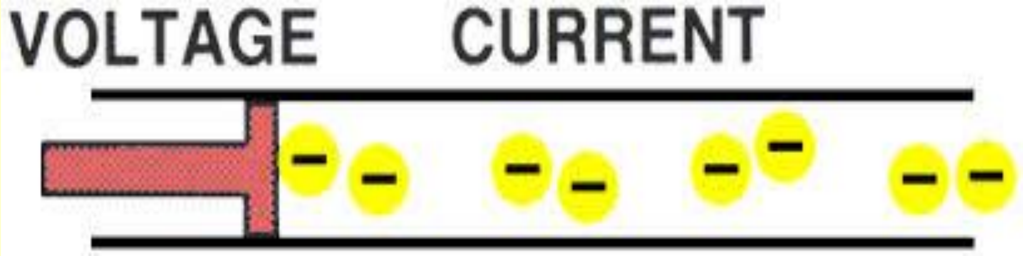




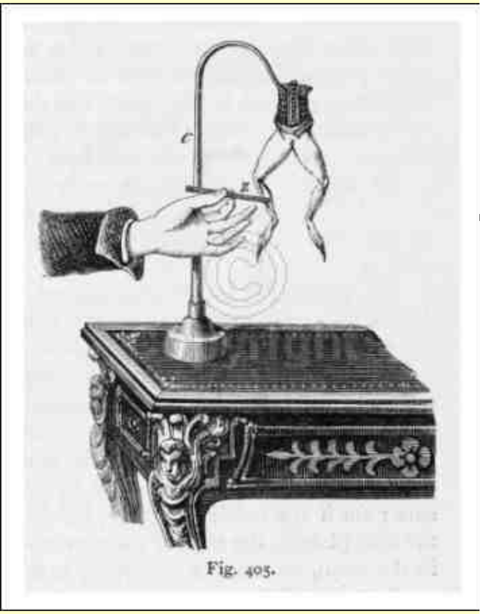


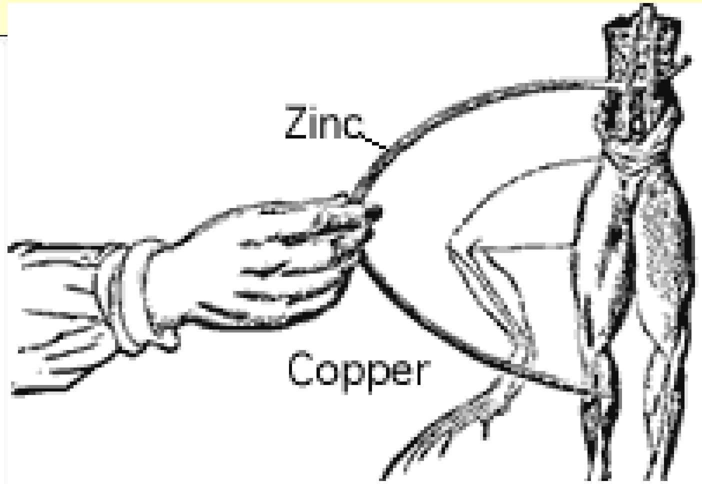


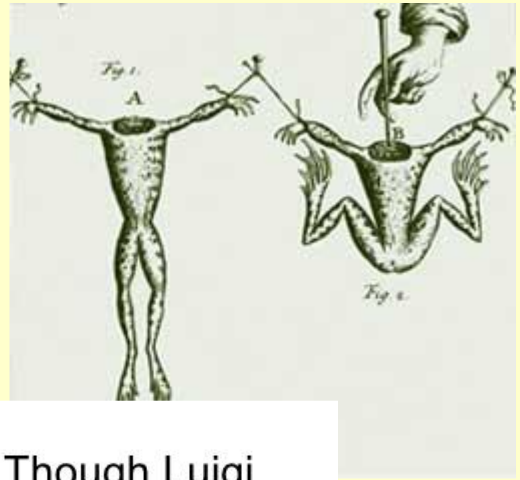




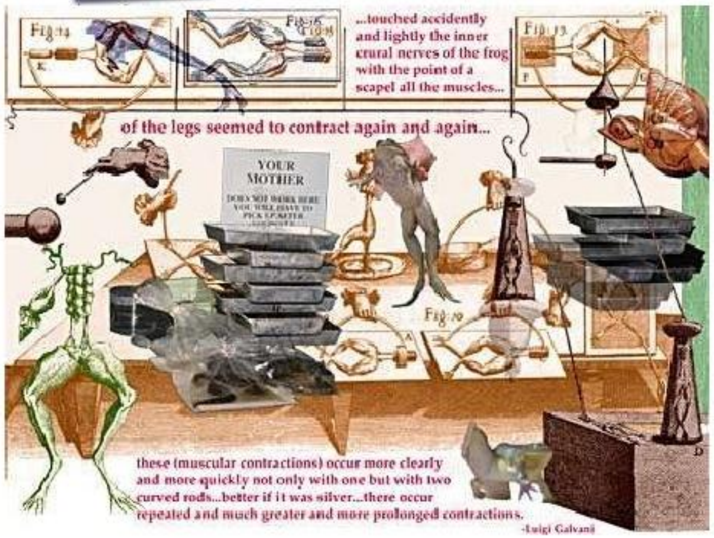
Galvani experiment on frog legs





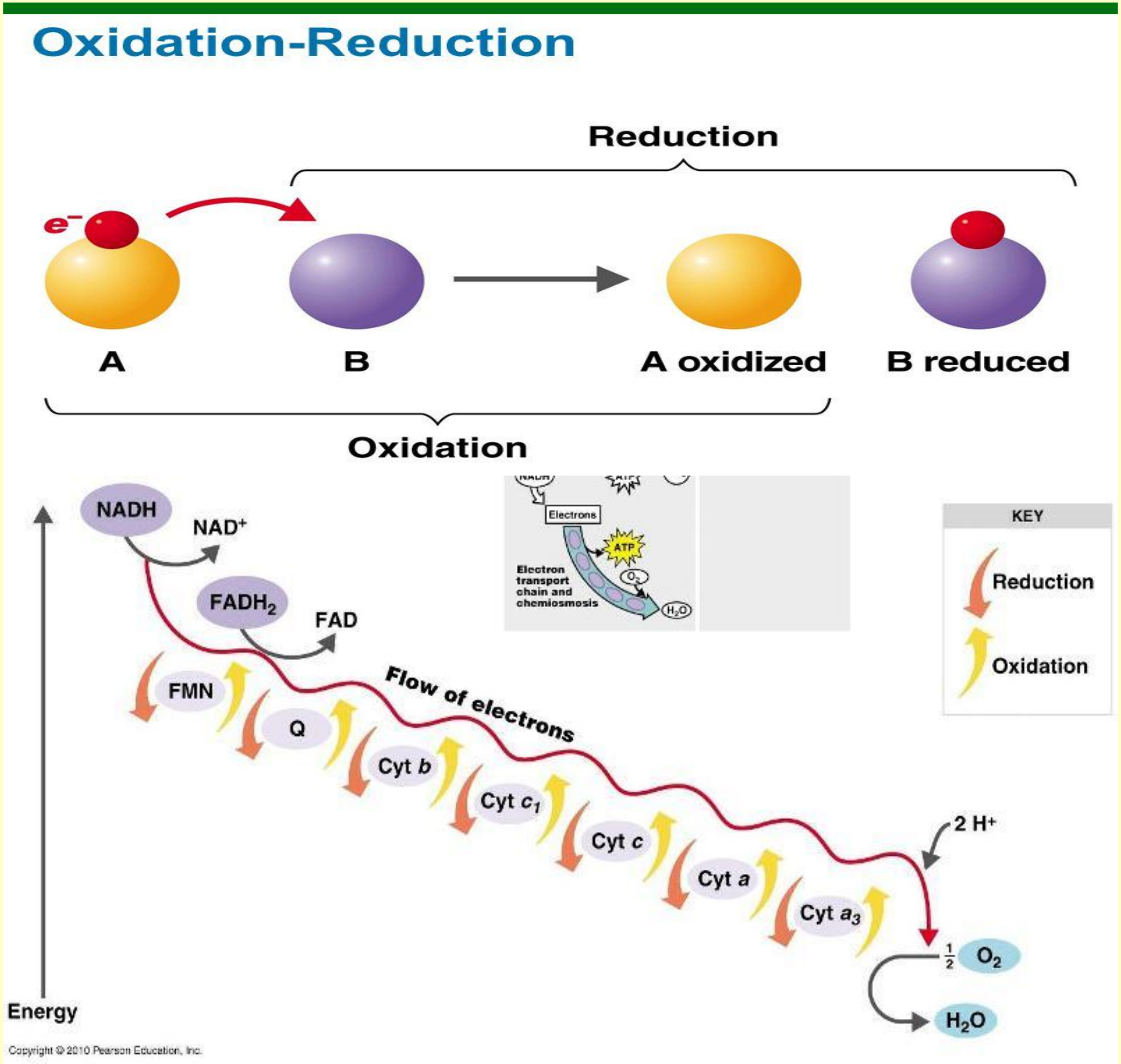


Luigi Galvani



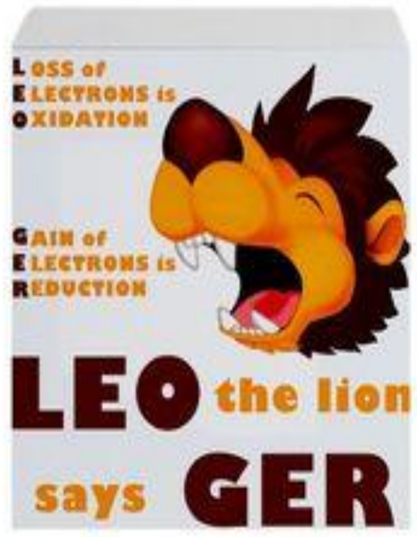
Though Luigi Galvani erroneously concluded that the frog's nervous system generated an electrical charge, his work stimulated much research into the electrical nature of the nervous impulse.

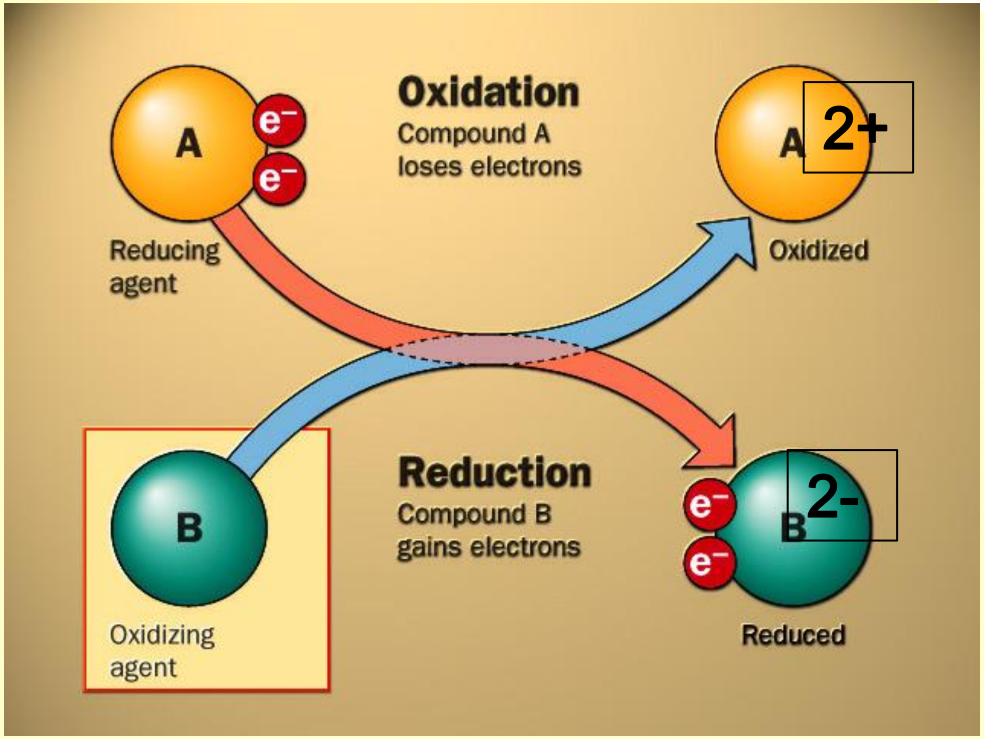
Electrochemistry is ***mainly*** dedicated to study the OXIDATION-REDUCTION Processes

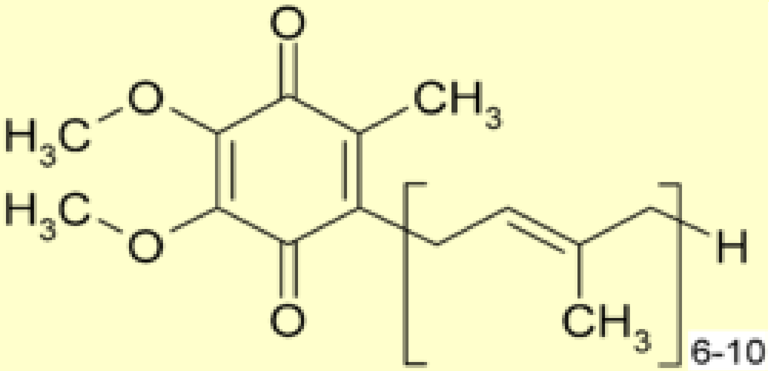


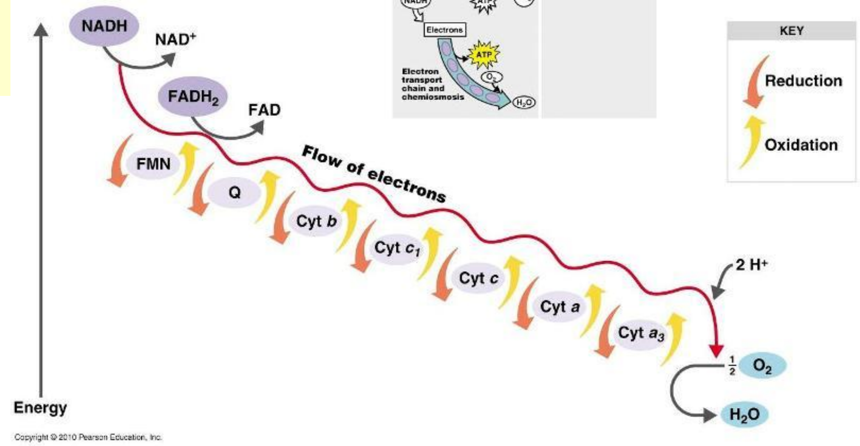
DEFINITIONS

- Oxidation: **Loss of electrons**.
- Reduction: **Gain of electro**ns.
- Reductant: Species that loses electrons.
- Oxidant: Species that gains electrons.






6-10


NADH
NAD+
FADH2
FAD
Flow of electrons
FMN
Q
Cyt b
Cyt c1
Cyt c
Cyt a
Cyt a3
2 H+
½ O2
H2O
Energy
KEY
Reduction
Oxidation
Electrons
Electron transport chain and chemiosmosis
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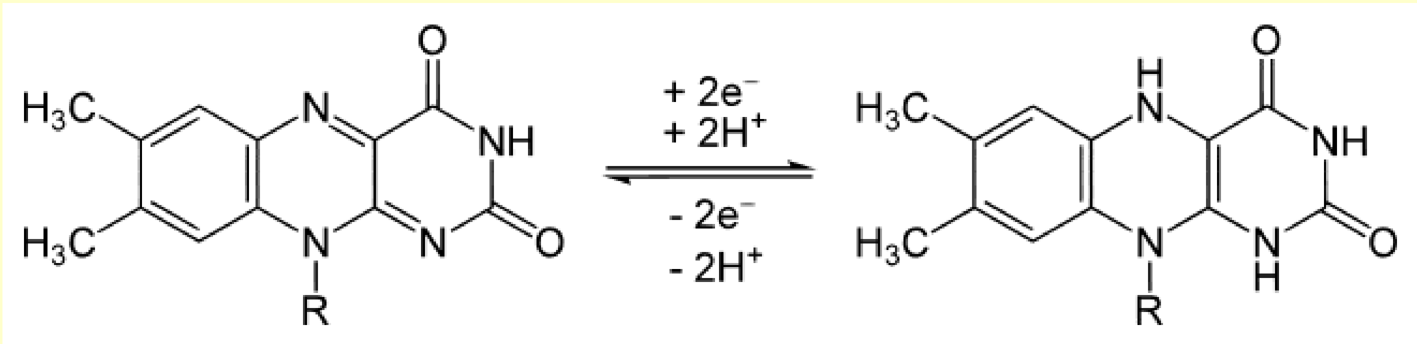
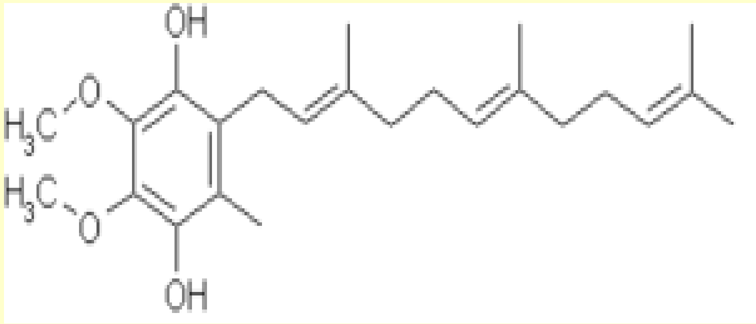
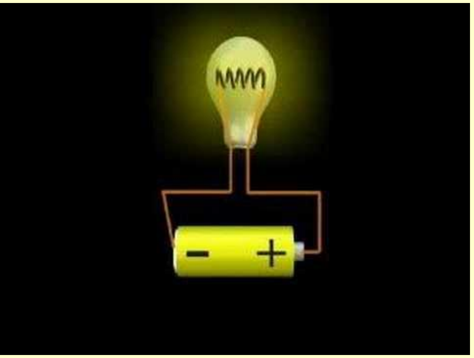
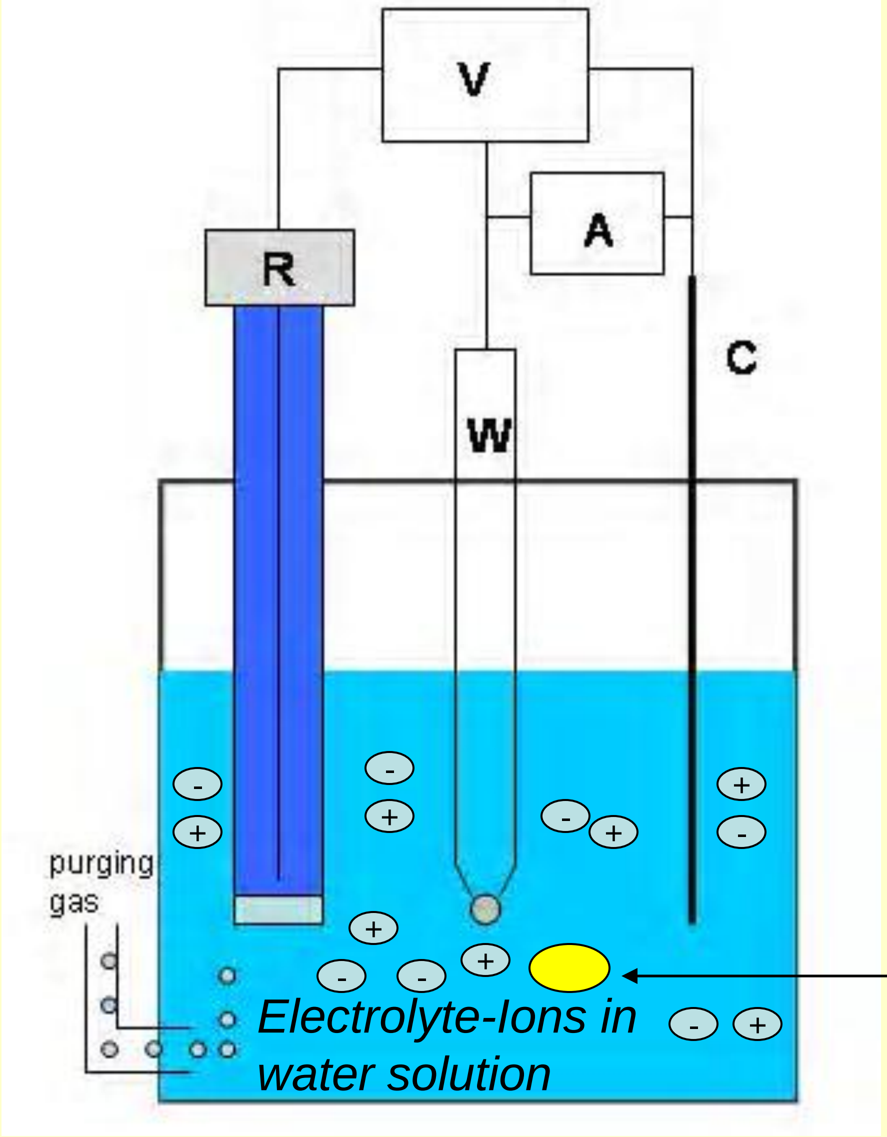

+ 2e−
+ 2H+
- 2e−
- 2H+



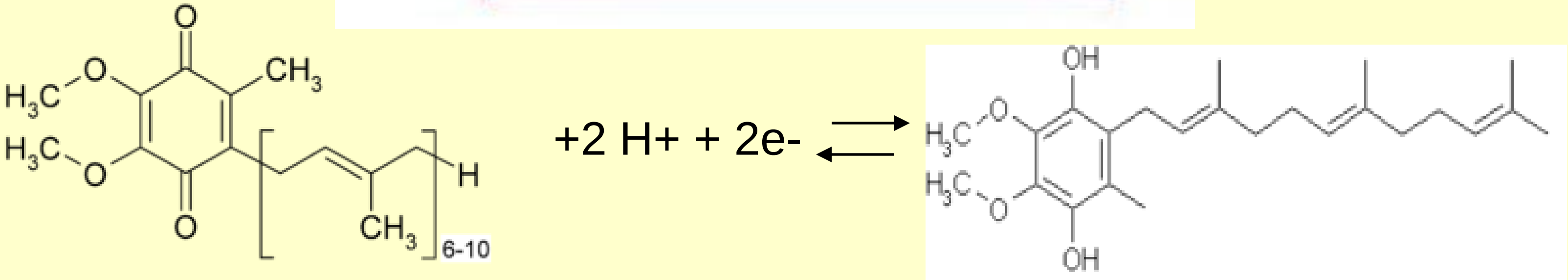
W-working electrode



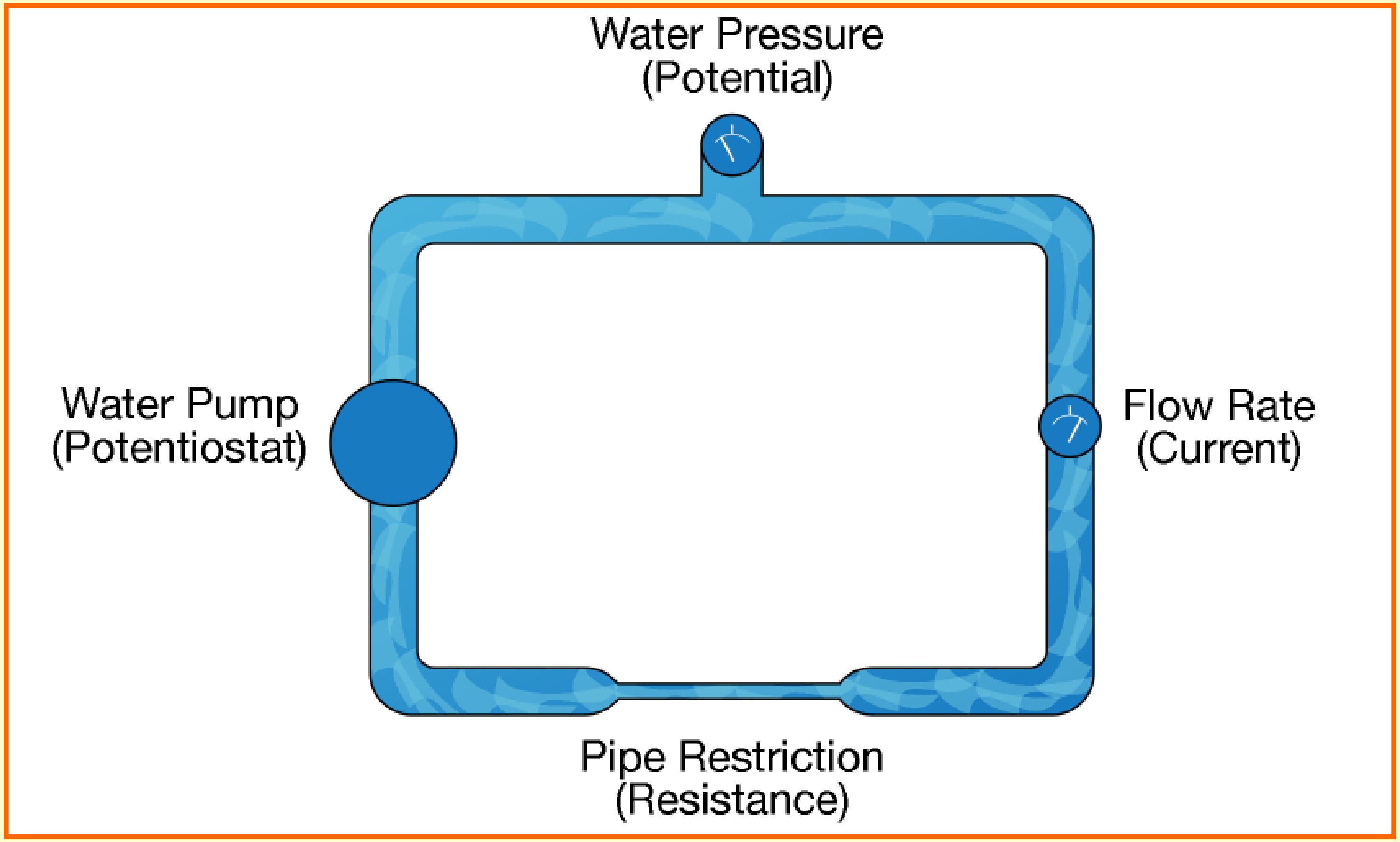


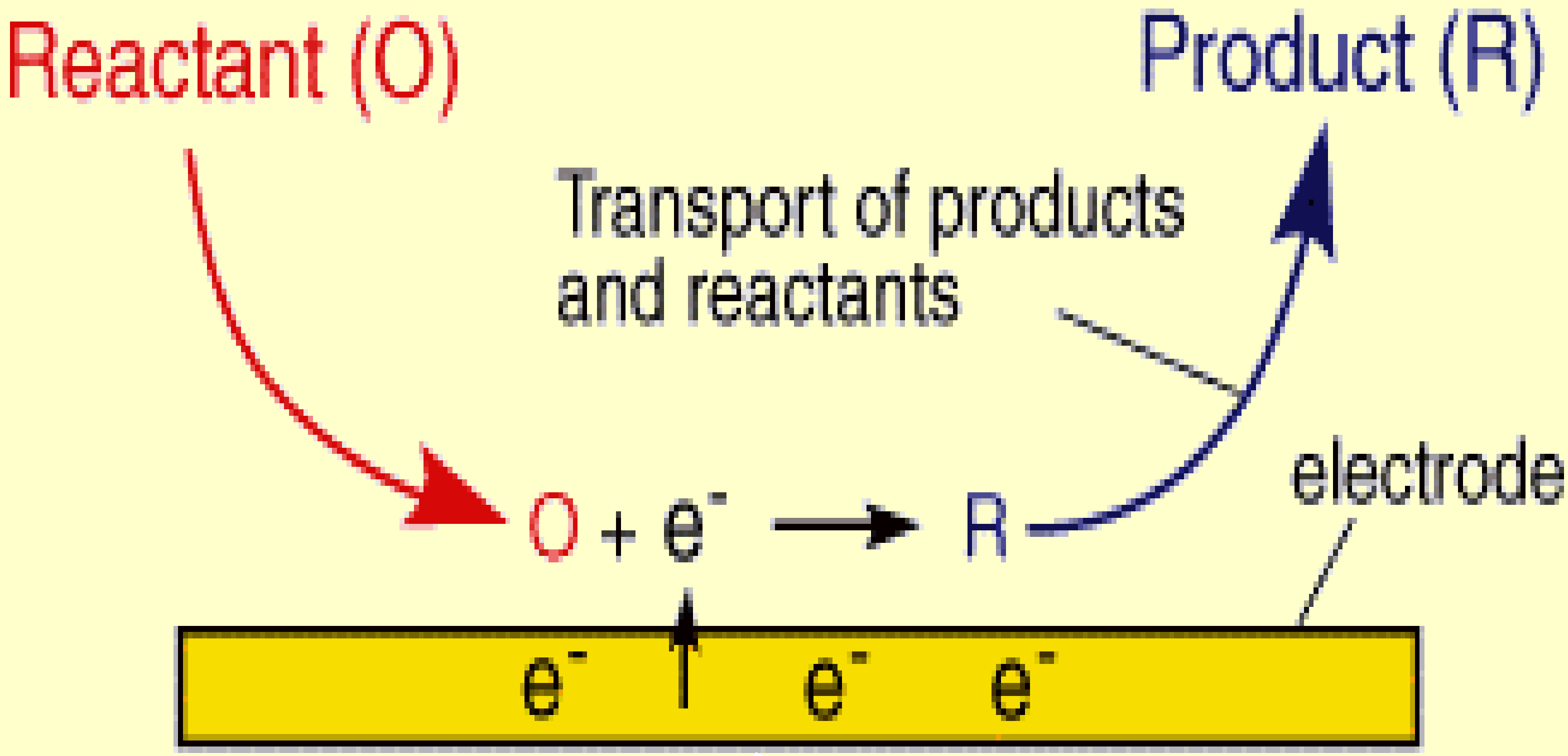
Redox probe

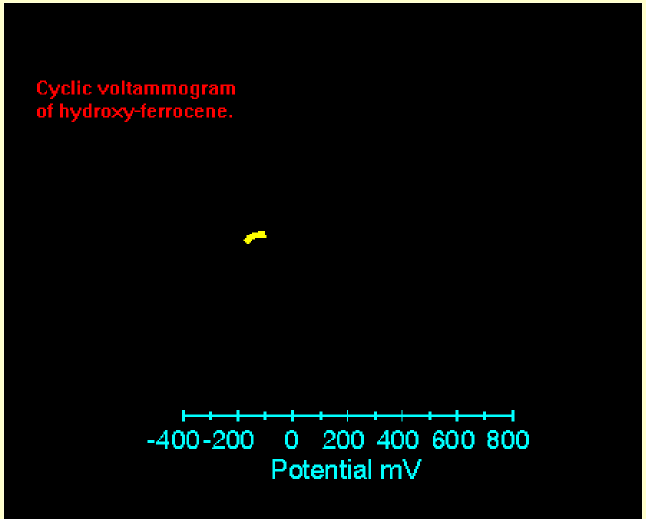
R-reference electrode



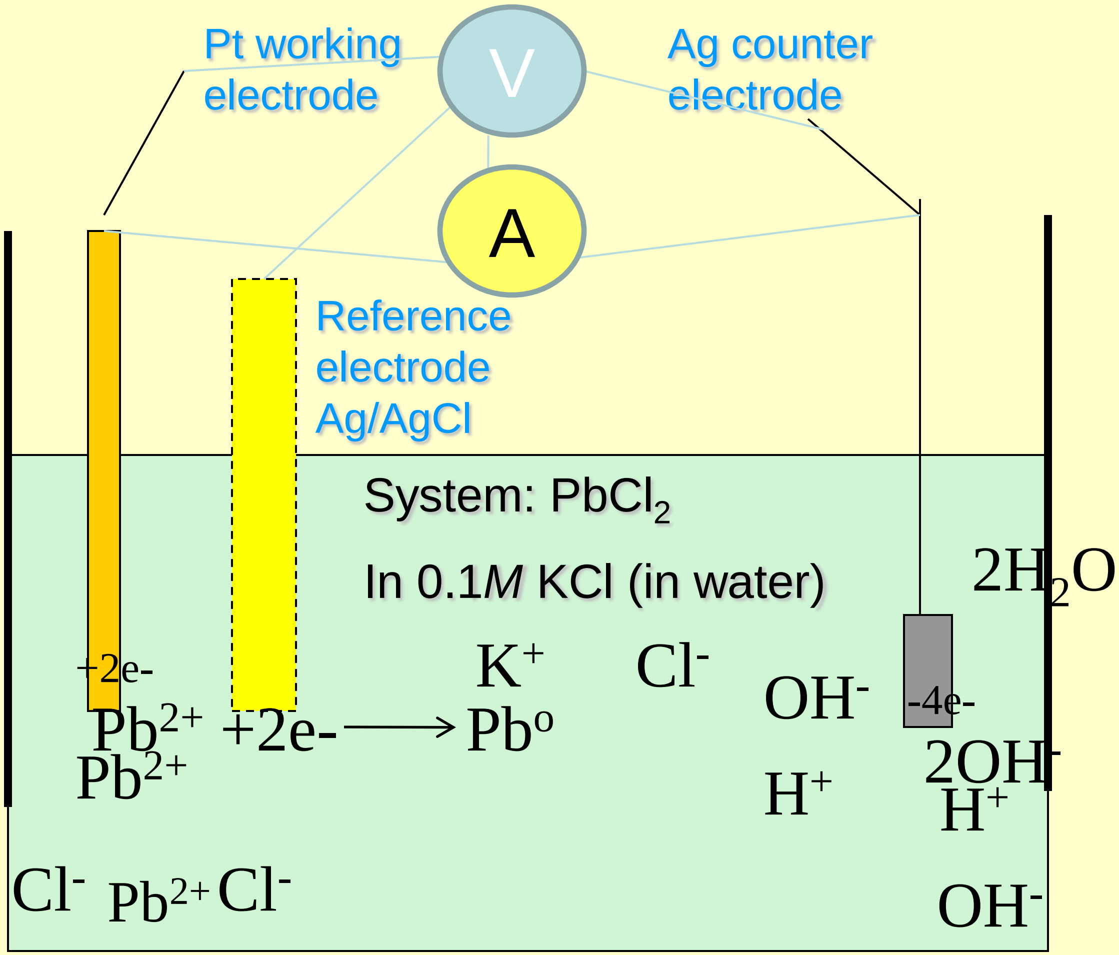
An Analogy of Potential and Current as a Flowing Water Circuit



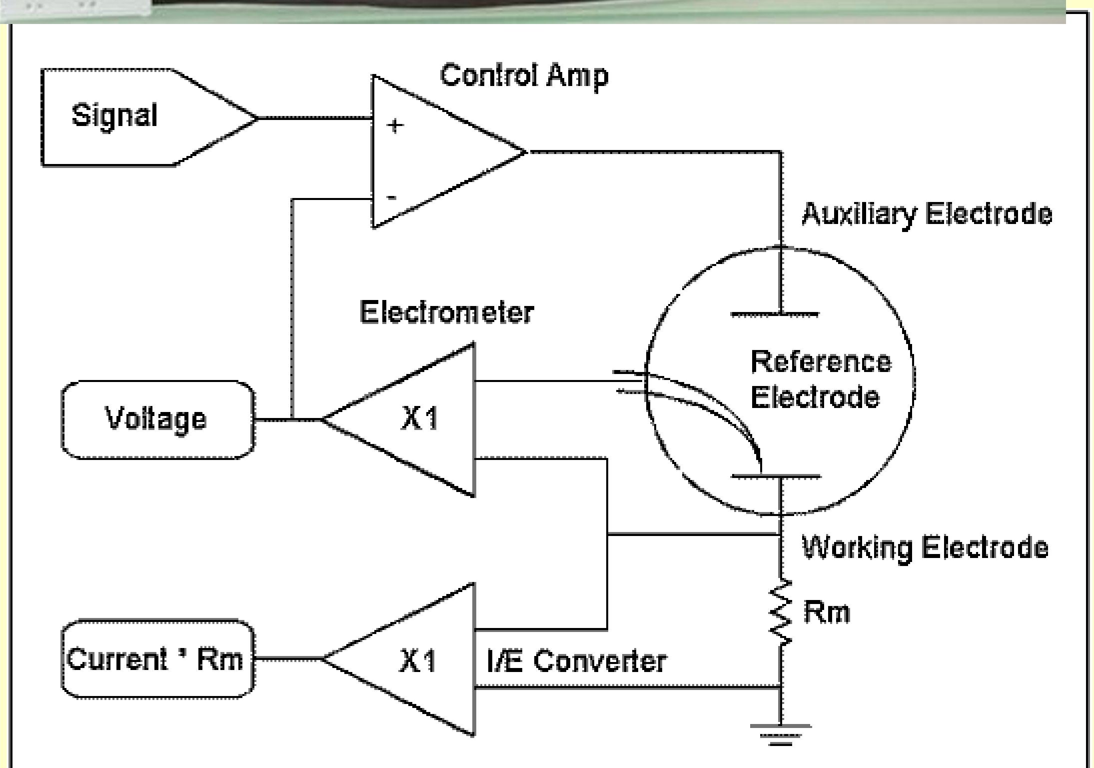

Reactant (O)
Product (R)
Transport of products and reactants
electrode
O + e⁻ → R
e⁻ e⁻ e⁻

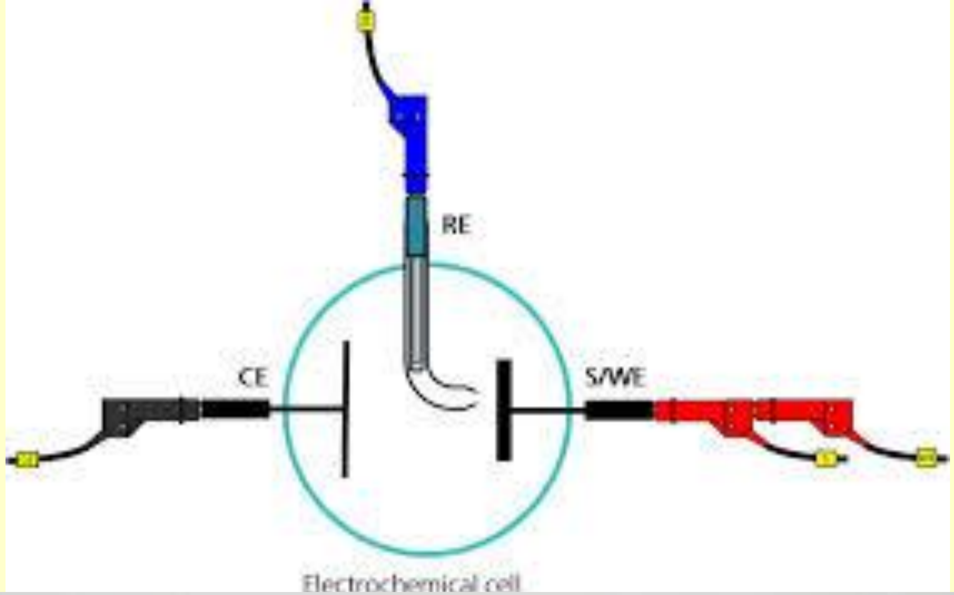

Cyclic voltammogram of hydroxy-ferrocene.
-400 -200 0 200 400 600 800
Potential mV

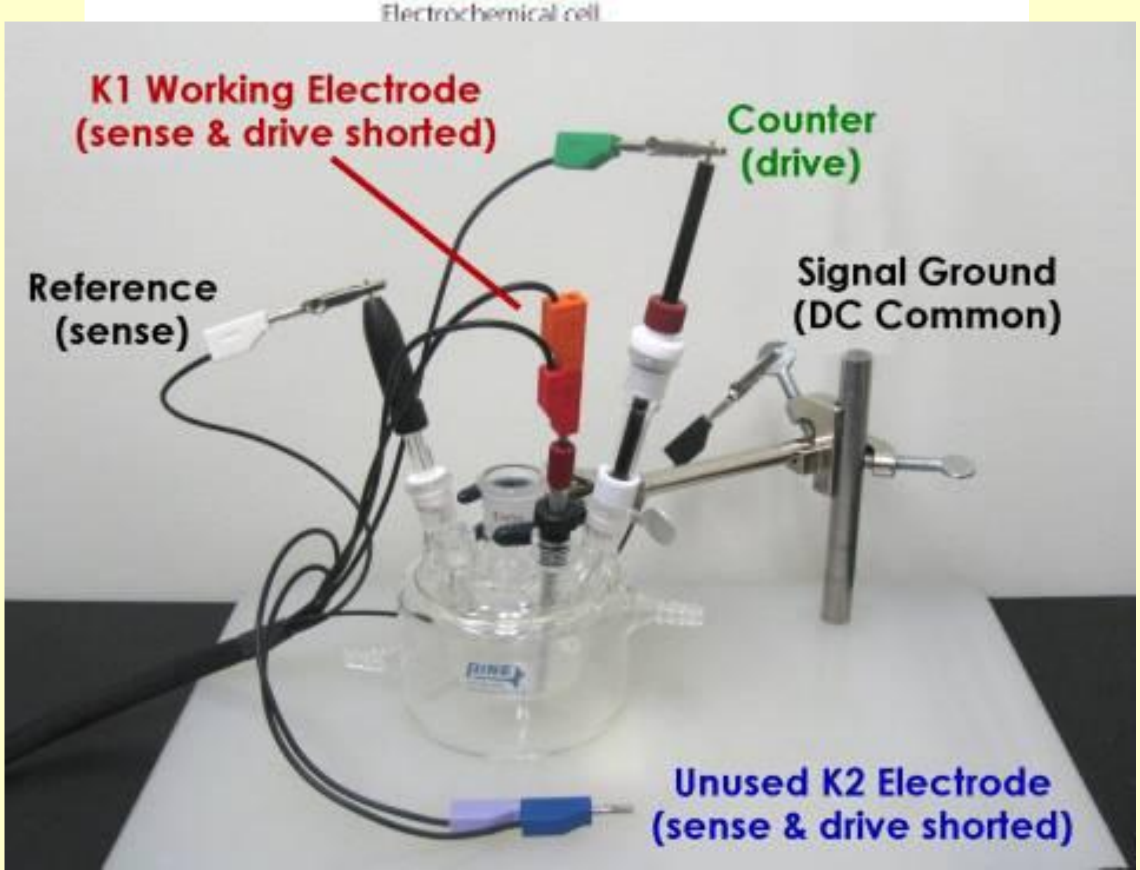
System: $PbCl_2$ in KCl




AUTOLAB


Signal
Control Amp
+
-
Auxiliary Electrode
Electrometer
Voltage
X1
Reference
Electrode
Working Electrode
Rm
Current * Rm
X1
I/E Converter


RE
CE
S/WE
Electrochemical cell


K1 Working Electrode
(sense & drive shorted)
Counter
(drive)
Reference
(sense)
Signal Ground
(DC Common)
Unused K2 Electrode
(sense & drive shorted)

What's a Potentiostat?

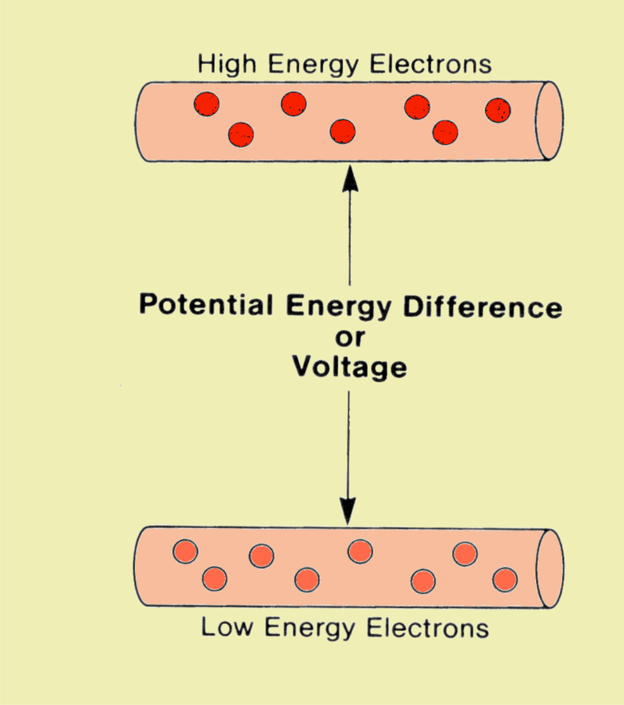
- Potentiostat
  - An electronic instrument that measures and controls the voltage difference between a Working Electrode and a Reference Electrode.
  - It measures the current flow between the Working and Counter Electrodes.

What is Potential?

Potential or Voltage (E, sometimes V):

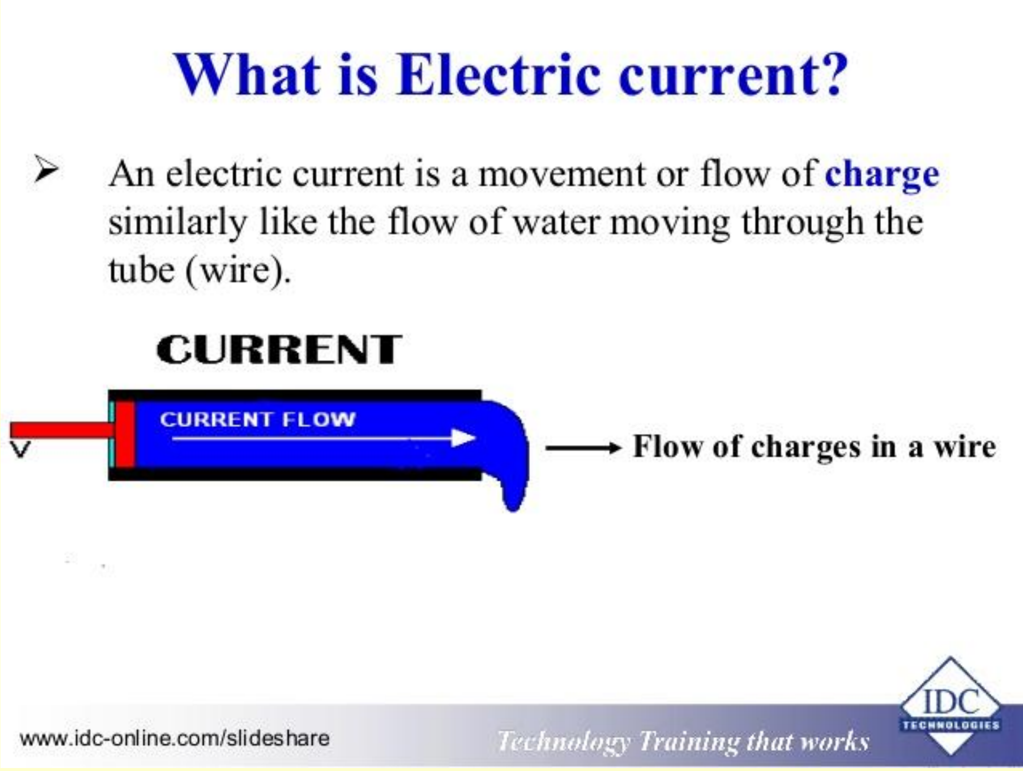
- Unit: **Volt**
- The **Potential** is the **driving force for the redox reaction.**
- IT IS RELATED TO THE ENERGY OF THE "EXCHANGABLE" ELECTRONS IN THE WORKING ELECTRODE CONDUCTOR
- The potential is related to the thermodynamics of the system:

  $\Delta G = -n \mathbf{F} \Delta E$ (negative ΔG is spontaneous)
- Potential is always measured versus a Reference Electrode.
- A positive voltage is oxidative and a negative voltage reductive.
- 0 Volts is not nothing! Redox reactions happen at 0 v that do not happen at +1 volt.



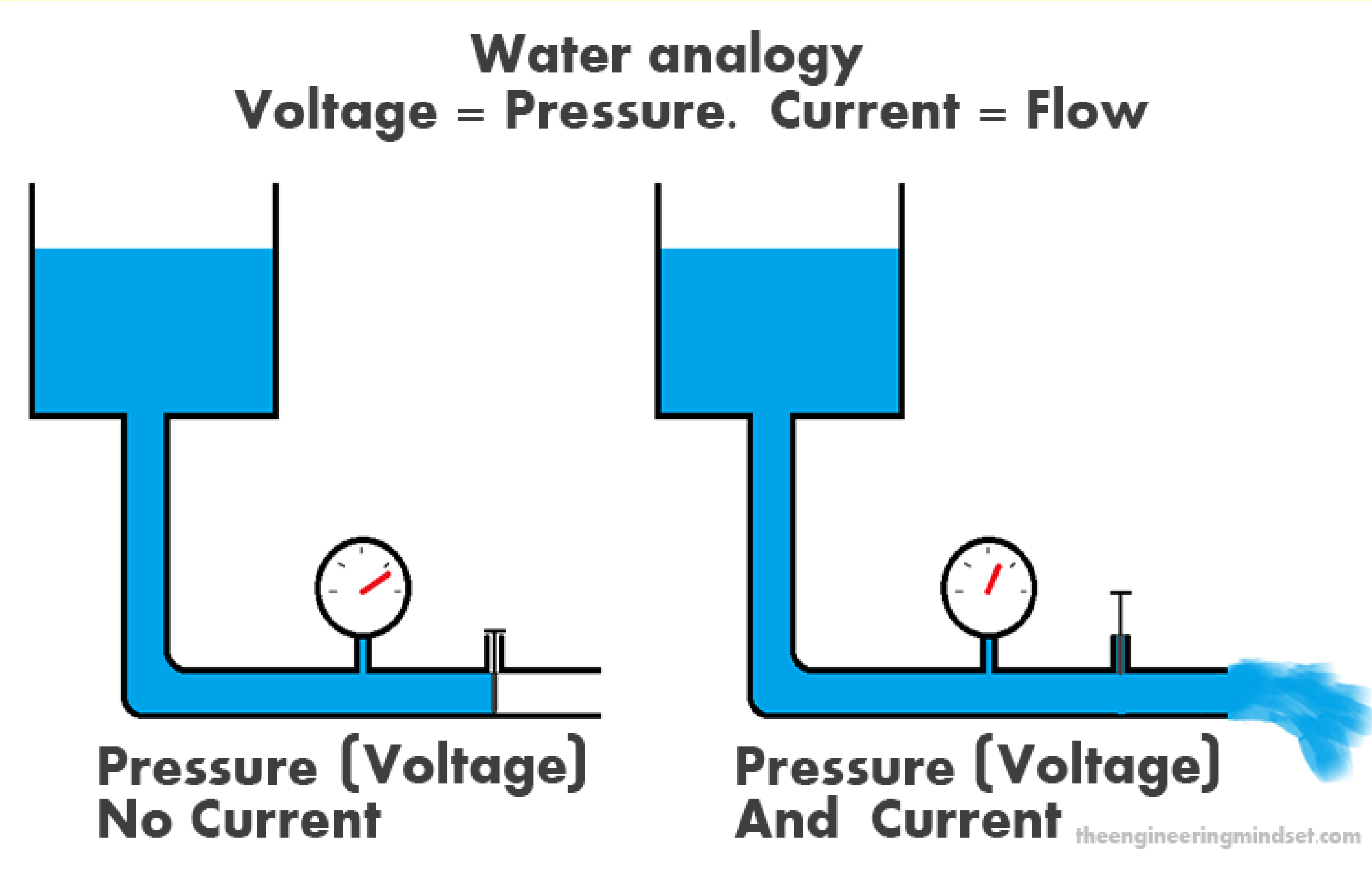
There is no correlation between the thermodynamics of the chemical system and the kinetics (rate) of the reaction.

What is Current?



Current (i):

- Unit: **Ampere**
- Electron flow is the result of a redox reaction.
- Current measures the **rate** of the reaction (electrons *per* second).
- Zero current is nothing, i.e., if the current is zero, no redox reactions are occurring (that’s not quite true in corrosion!).
- Anodic (oxidation) and cathodic (reduction) currents have different polarity (signs).
- Current may be expressed as current or current density.


Water analogy
Voltage = Pressure. Current = Flow
Pressure (Voltage)
No Current
Pressure (Voltage)
And Current
theengineeringmindset.com

Electrodes

–A Potentiostat works (in most of the cases) with three electrodes immersed in a conductive electrolyte.

- **Working Electrode**

  A sample of the corroding metal being tested.

- **Reference Electrode**

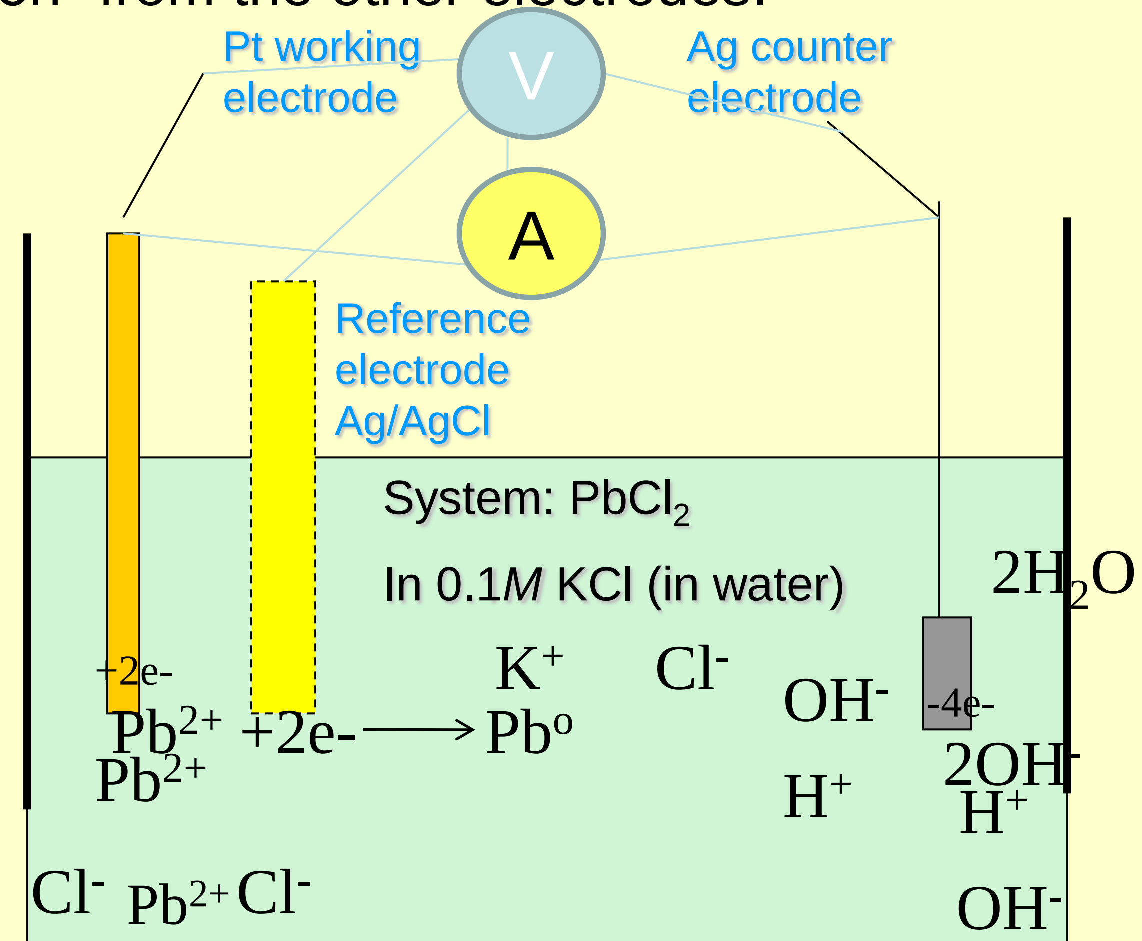
  An electrode with a constant electrochemical potential.

- **Counter Electrode**

  A current-carrying electrode that completes the cell circuit ■

Why does a Potentiostat have three electrodes?

We would like to study the electrochemical events taking place at one specific electrode…the Working Electrode. The use of a three-electrode potentiostat with a separate Reference and Counter Electrode allows the potential at the WE and the current at the WE to be measured with little or no “interference” or “contribution” from the other electrodes.



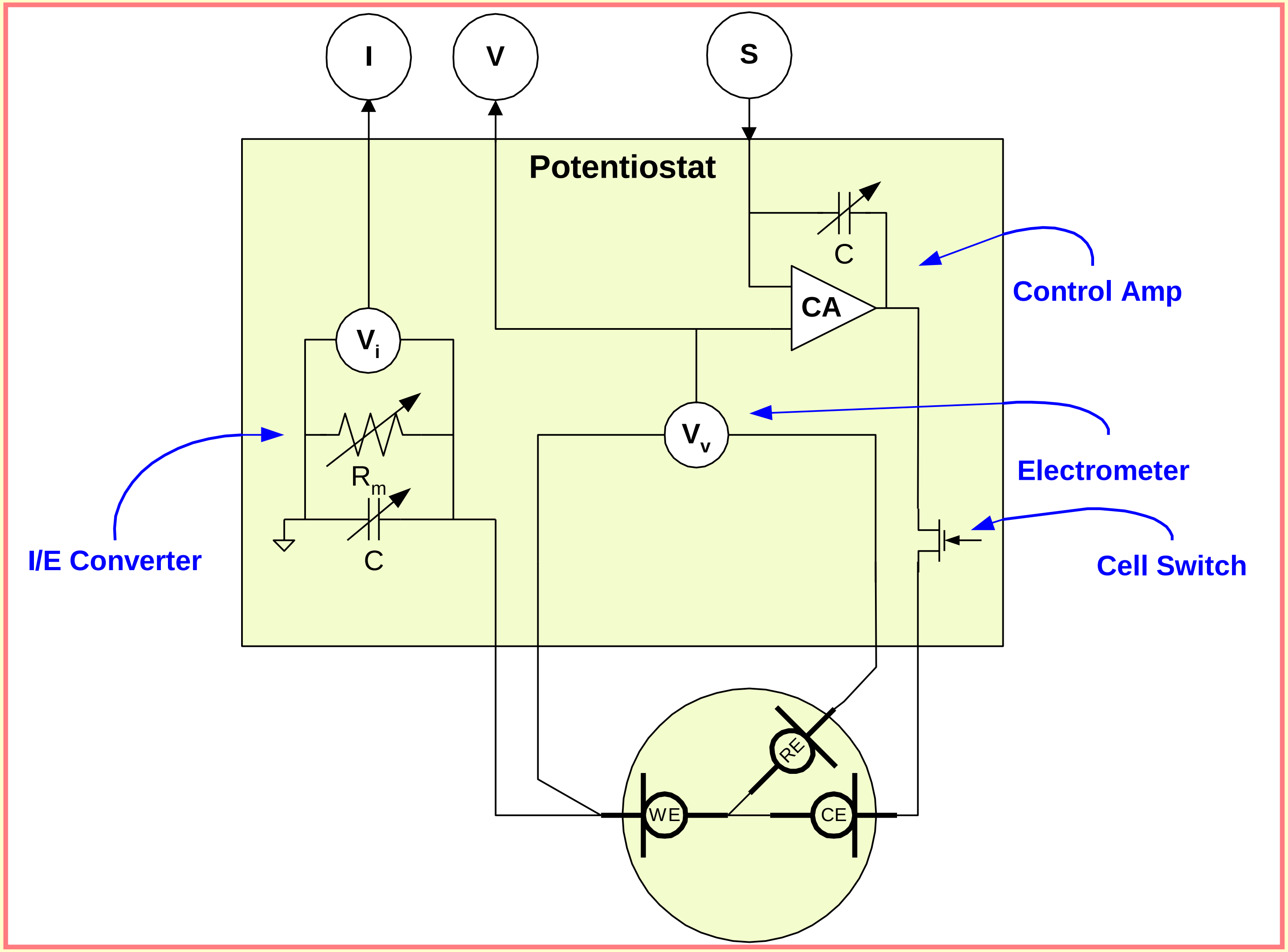
Pay Special Attention to the Reference Electrode!

– A Potentiostat needs a low impedance Reference Electrode!
  - Use large junction reference electrodes
  - Replace isolation frits regularly
  - Avoid narrow Luggin Capillaries

– Potentiostats are less forgiving of high-impedance Reference Electrodes than pH Meters!

– If there's an problem with the cell, it's almost always the Reference Electrode!

The Analog Potentiostat



Three Primary Components of a Potentiostat

- **Control Amplifier**: Supplies the power to maintain the controlled potential between the Working and Reference Electrodes.

- **Electrometer**: Measures the potential difference between the Reference and Working Electrodes.

- **Current-to-Voltage Converter**: Measures the current between the Working and Counter Electrodes.

- **Do you need to know how a Potentiostat works?**
- **No.**

- **Do you need to be able to recognize when something is wrong?**
- **Yes!**

- **Why would something go wrong?**
- **Because the performance of the Potentiostat is affected by the electrical characteristics of the sample…or something in the cell is causing a problem…or the Potentiostat is busted!**

To Evaluate Your Electrochemical Data… Look At It!

- Electrochemical data is always a collection of individual data points…one followed smoothly by another.
- Noisy data is bad.
- Flat-lined data is bad.
- Overloads are bad.
- It is very rare to collect bad data that looks good.

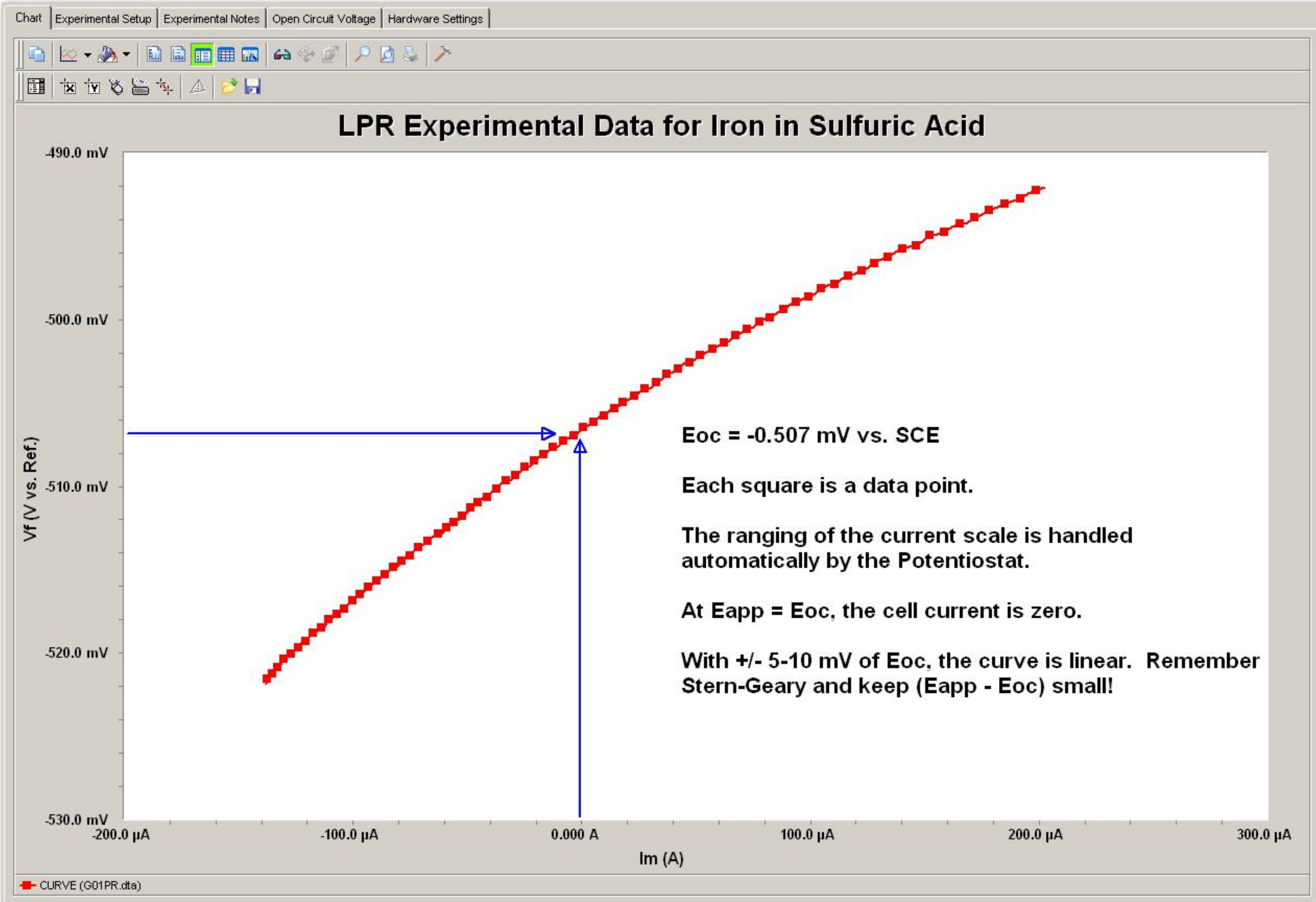


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
LPR Experimental Data for Iron in Sulfuric Acid
-490.0 mV
-500.0 mV
-510.0 mV
-520.0 mV
-530.0 mV
Vf (V vs. Ref.)
-200.0 µA
-100.0 µA
0.000 A
100.0 µA
200.0 µA
300.0 µA
Im (A)
Eoc = -0.507 mV vs. SCE
Each square is a data point.
The ranging of the current scale is handled automatically by the Potentiostat.
At Eapp = Eoc, the cell current is zero.
With +/- 5-10 mV of Eoc, the curve is linear. Remember Stern-Geary and keep (Eapp - Eoc) small!
CURVE (G01PR.dta)

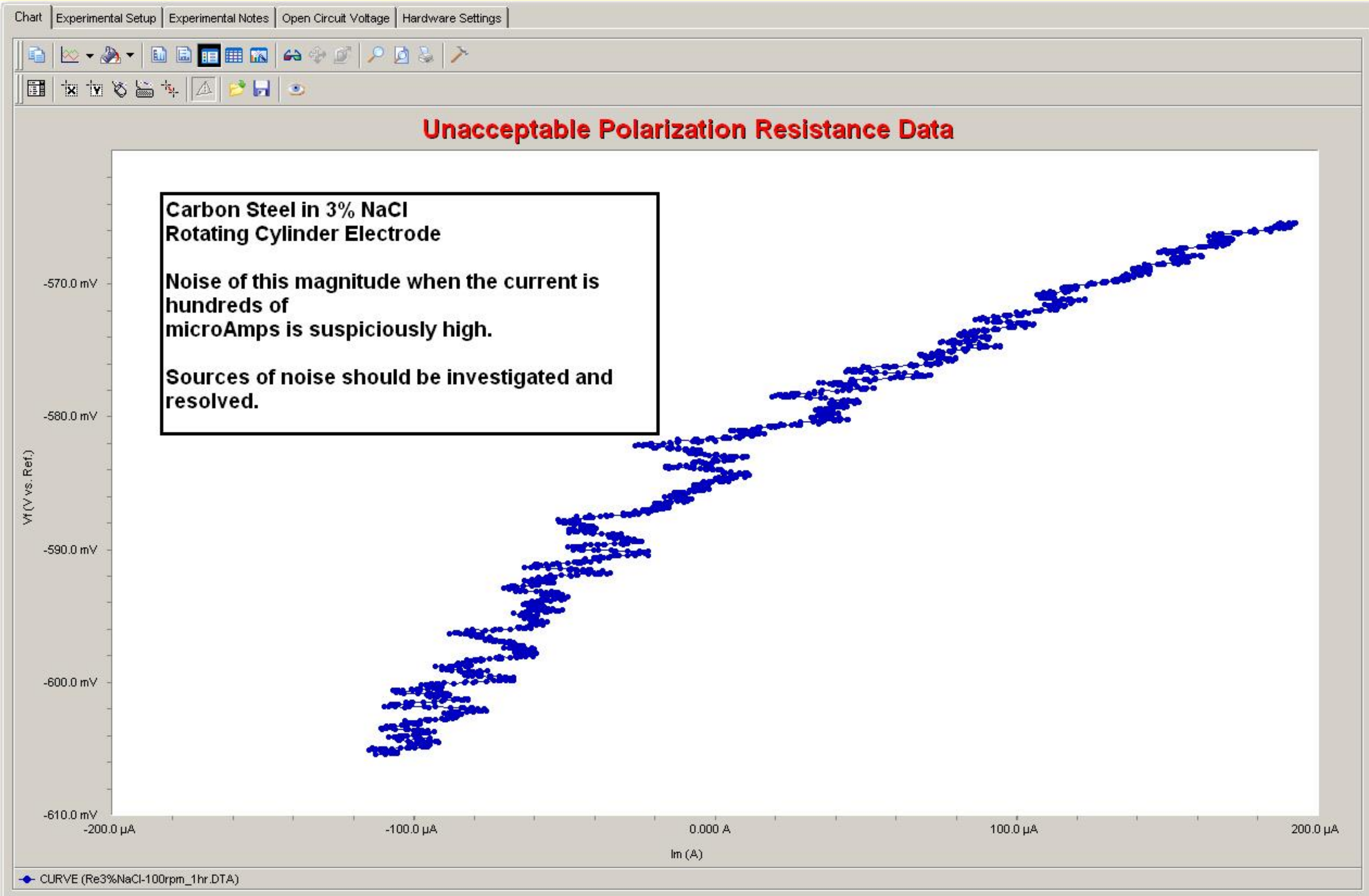


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
Unacceptable Polarization Resistance Data
Carbon Steel in 3% NaCl
Rotating Cylinder Electrode
Noise of this magnitude when the current is hundreds of
microAmps is suspiciously high.
Sources of noise should be investigated and resolved.
Vf (V vs. Ref.)
-570.0 mV
-580.0 mV
-590.0 mV
-600.0 mV
-610.0 mV
-200.0 µA
-100.0 µA
0.000 A
100.0 µA
200.0 µA
Im (A)
CURVE (Re3%NaCl-100rpm_1hr.DTA)

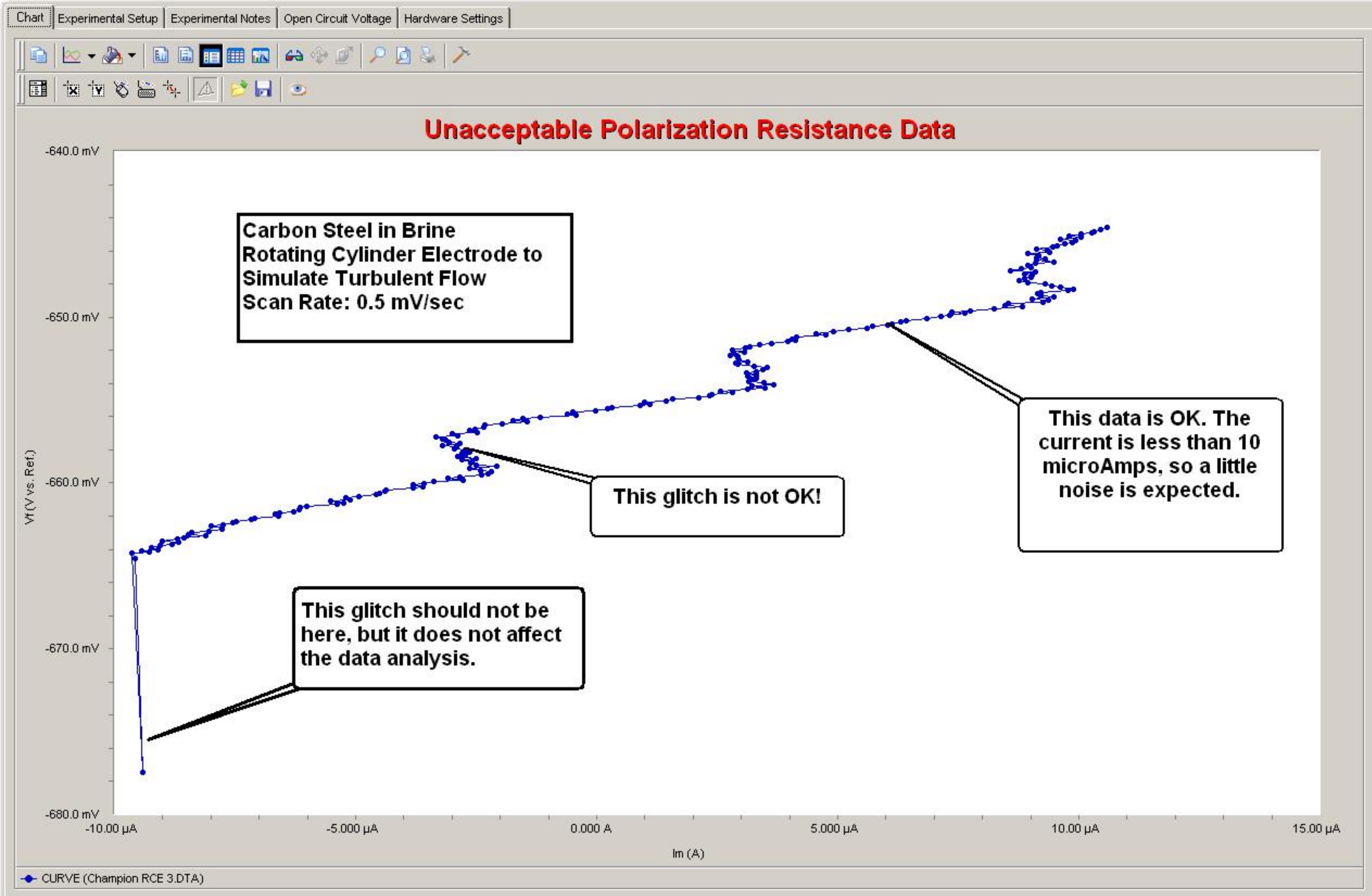


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
Unacceptable Polarization Resistance Data
Carbon Steel in Brine
Rotating Cylinder Electrode to
Simulate Turbulent Flow
Scan Rate: 0.5 mV/sec
This data is OK. The current is less than 10 microAmps, so a little noise is expected.
This glitch is not OK!
This glitch should not be here, but it does not affect the data analysis.
-640.0 mV
-650.0 mV
-660.0 mV
-670.0 mV
-680.0 mV
Vf (V vs. Ref.)
-10.00 µA
-5.000 µA
0.000 A
5.000 µA
10.00 µA
15.00 µA
Im (A)
CURVE (Champion RCE 3.DTA)

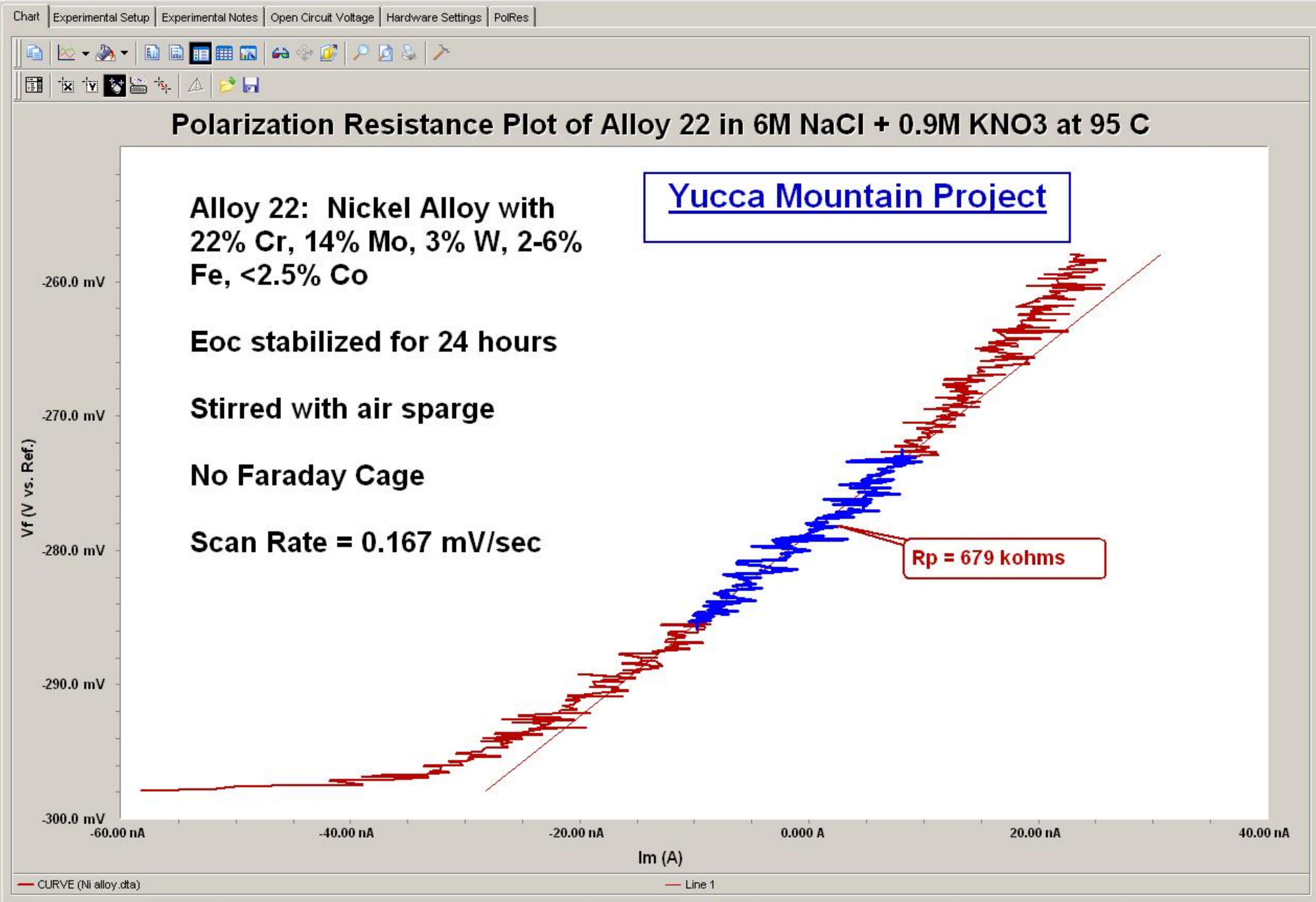


Chart
Experimental Setup
Experimental Notes
Open Circuit Voltage
Hardware Settings
PolRes
Polarization Resistance Plot of Alloy 22 in 6M NaCl + 0.9M KNO3 at 95 C
Yucca Mountain Project
Alloy 22: Nickel Alloy with 22% Cr, 14% Mo, 3% W, 2-6% Fe, <2.5% Co
Eoc stabilized for 24 hours
Stirred with air sparge
No Faraday Cage
Scan Rate = 0.167 mV/sec
Rp = 679 kohms
Vf (V vs. Ref.)
-260.0 mV
-270.0 mV
-280.0 mV
-290.0 mV
-300.0 mV
-60.00 nA
-40.00 nA
-20.00 nA
0.000 A
20.00 nA
40.00 nA
Im (A)
CURVE (Ni alloy.dta)
Line 1

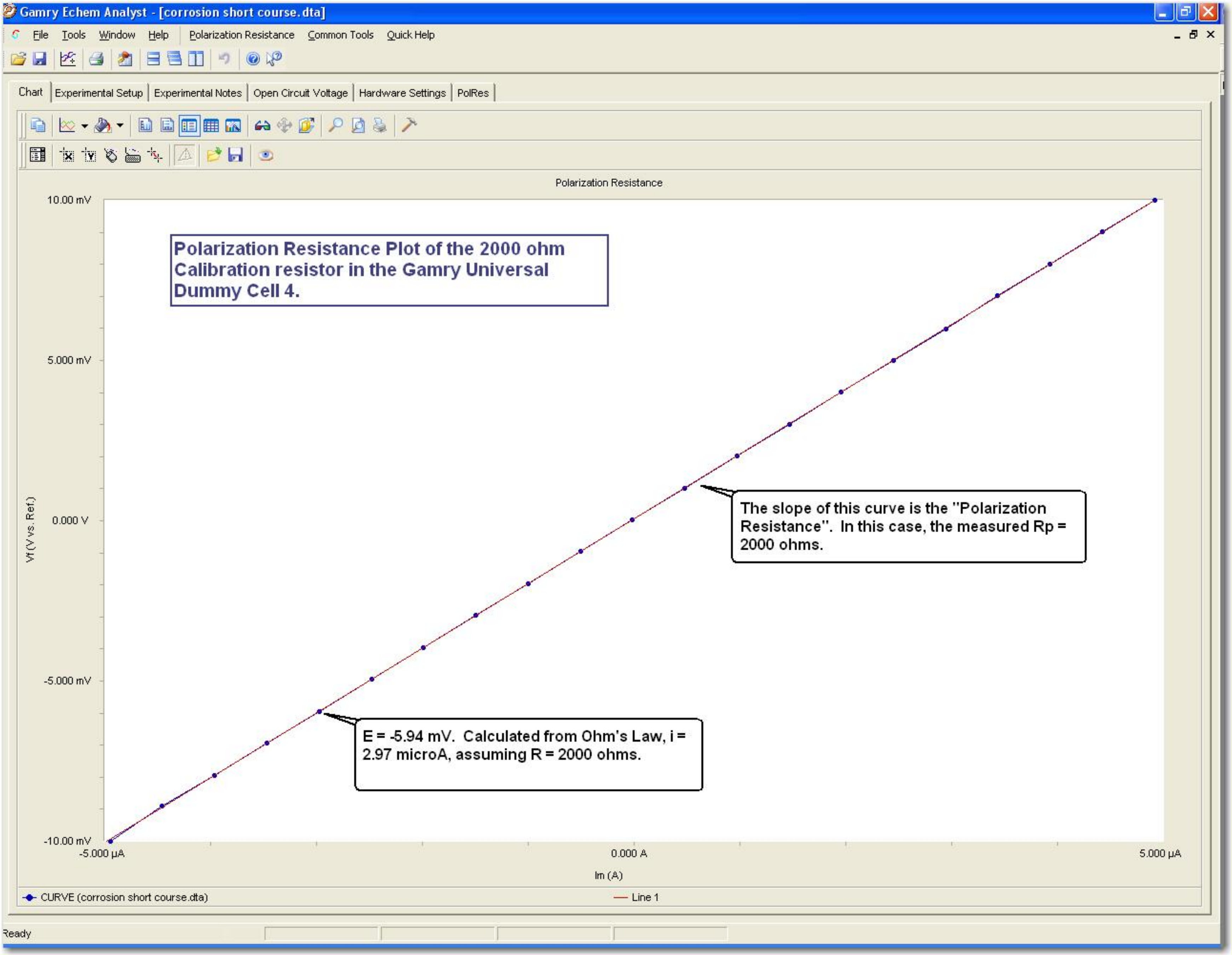
My Data Is Bad. Now What Do I Do?

1. Calibrate the Potentiostat.
2. If calibration is successful, check the Potentiostat by running a dummy cell (a network of resistors/capacitors that give a known result).
3. If the instrument is OK, then check the cell. Check the Reference Electrode first!
4. If the cell is OK, then it's something in your sample chemistry. Do you need a Faraday Cage?
5. At some point, you should contact your Potentiostat supplier for technical support

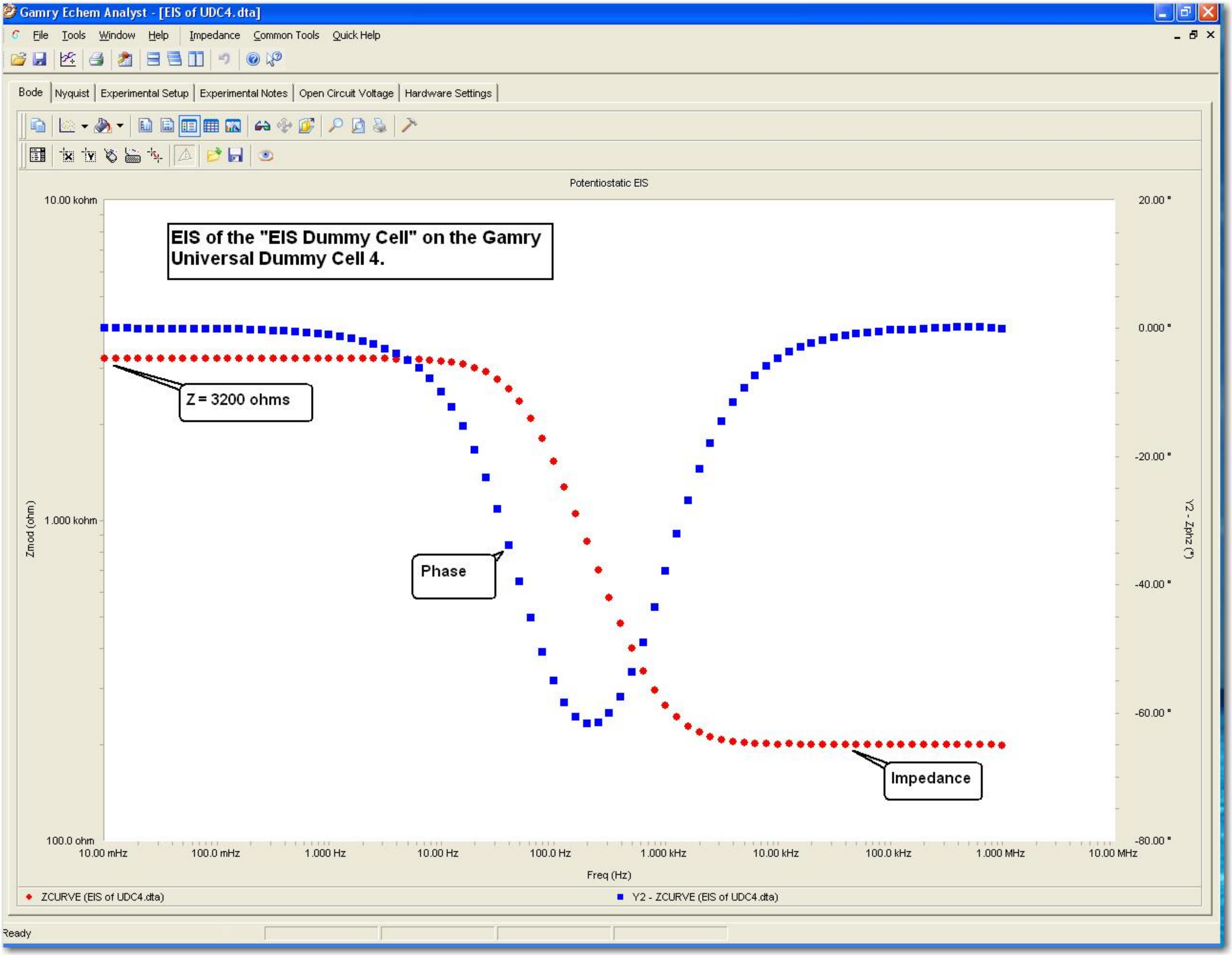
The One Equation You Need to Know

- Ohm's Law
- $E = iR$
- If I apply 100 mV to a 1000 ohm resistor, I should measure a current of…
- 100 µA

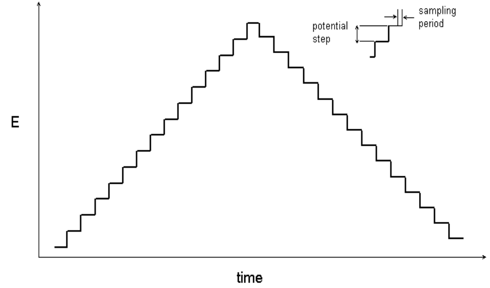
Pstat Check-Out: PolRes on a 2000 Ohm Resistor

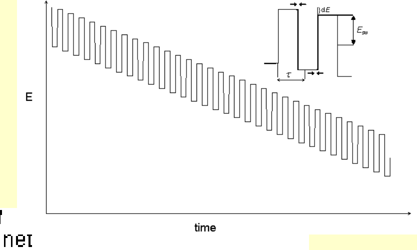


Pstat Check-Out: EIS on a Dummy Cell

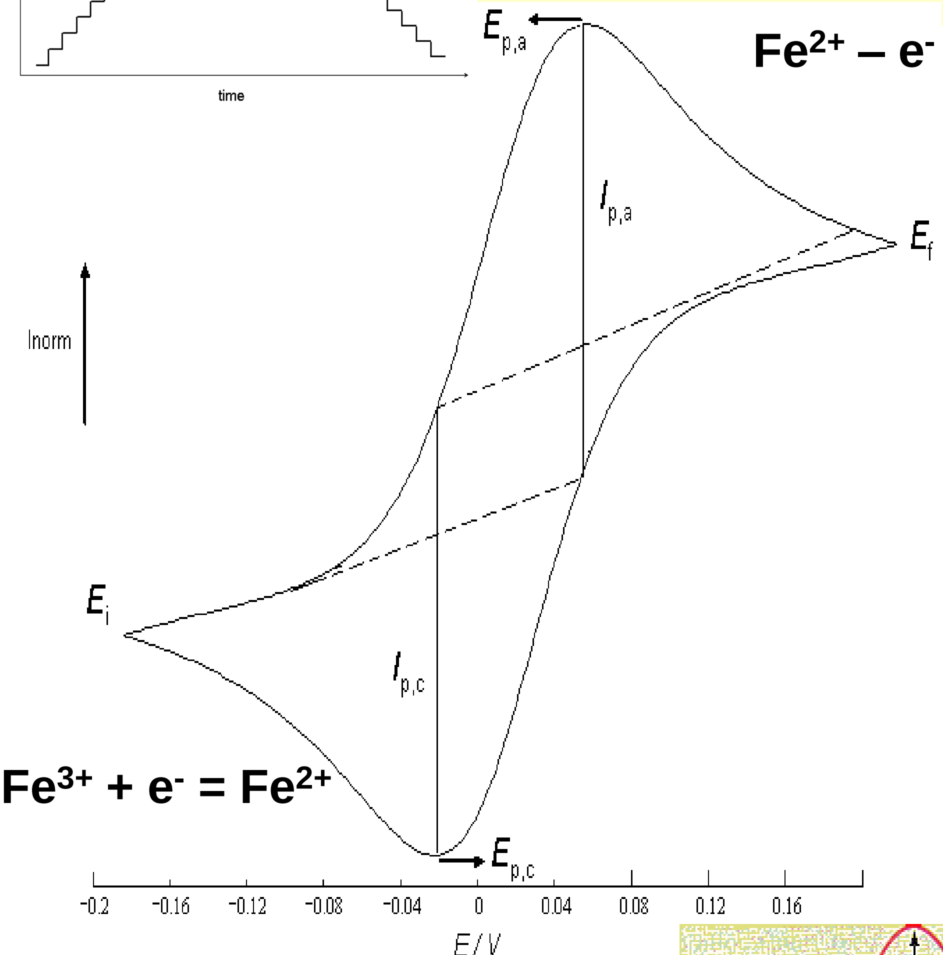


$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$$

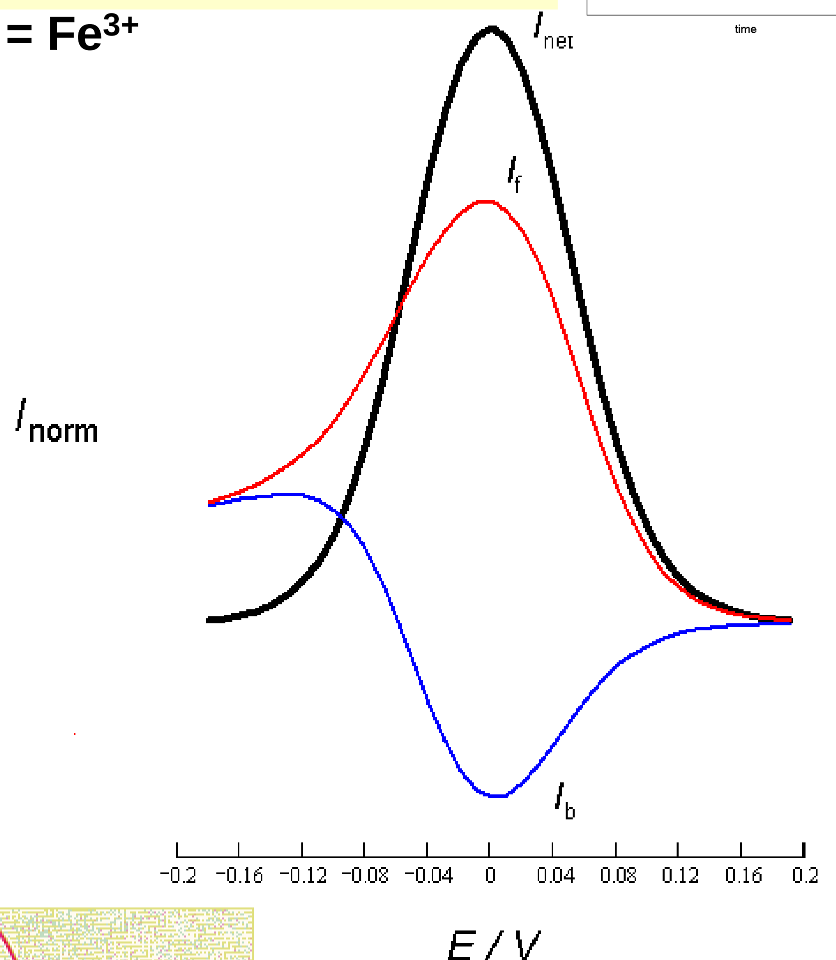




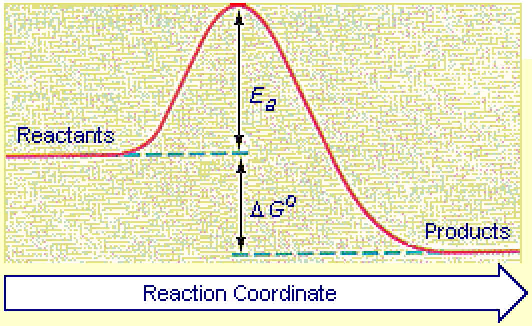
$Fe^{2+} – e^{-} = Fe^{3+}$



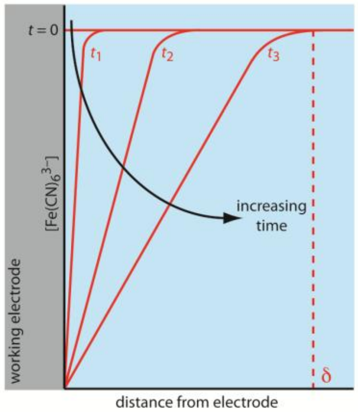
$Fe^{3+} + e^{-} = Fe^{2+}$



Cyclic voltammogram

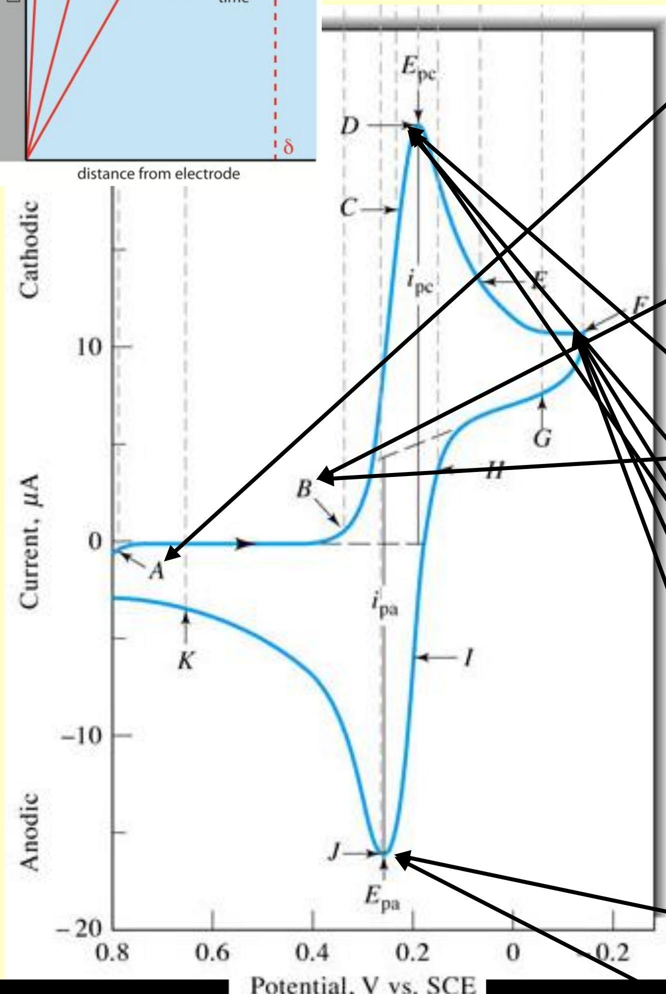


Square-Wave Voltammogram



SYSTEM: $Fe(CN)_6^{3-}$ Working electrode Pt & reference electrode SCE

CN)$_6$ & 1 M KNO_3



Small current at the beginning, mainly due to oxidation of H_2O to O_2

ALMOST NO current flow between A & B (+0.7 to +0.4V) since no particles can be oxiudized or reduced in this potential region

B. At 0.4V, current starts rising as a result of the following reaction at the working electrode:

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

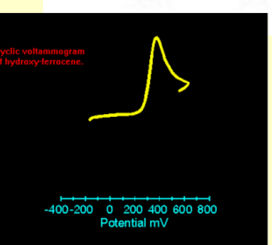
B.-D. Sudden increase of the current as a result of the diminishing of the surface concentration of $Fe(CN)_6^{3-}$

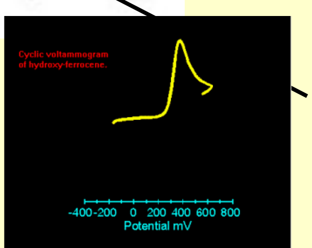
D. Cathodic peak potential (E_{pc}) and cathodic peak current (i_{pc})

D.-F. Current starts to diminish intensively since the diffusion layer exapnds towards the bulk of the solution

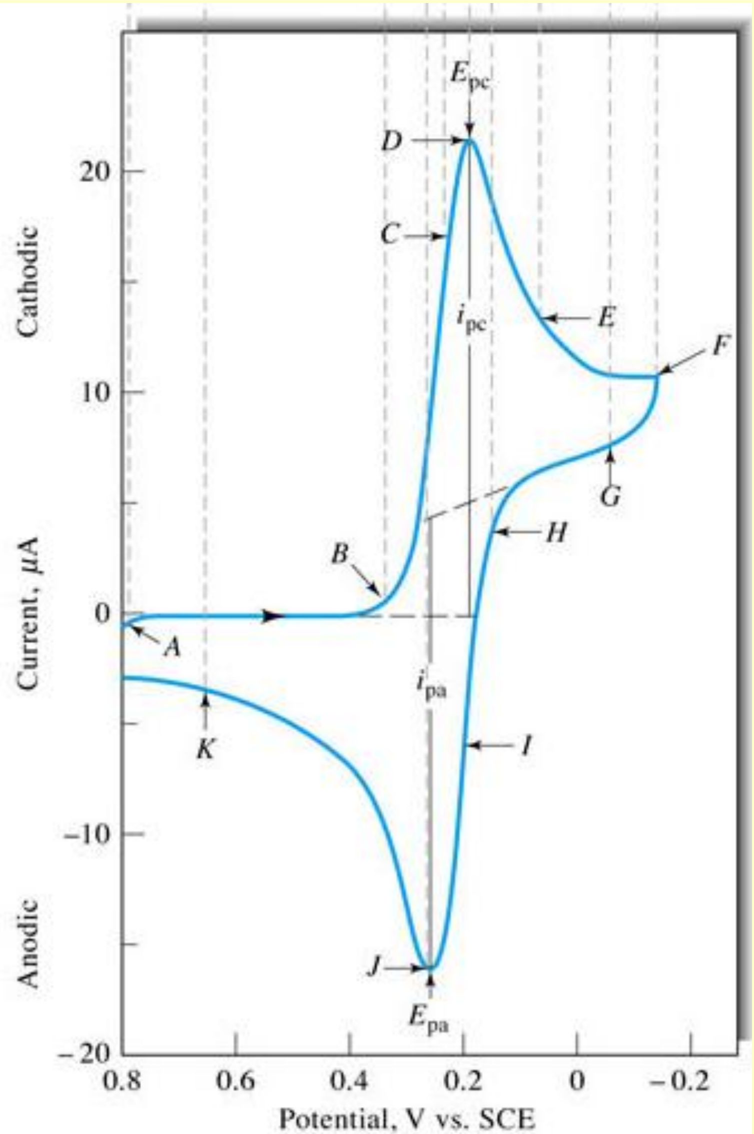
F. Potential swift at (-0.15V), at this potential intensive reduc´tion of $Fe(CN)_6^{3-}$ happens

F.-J. Between H and J oxidation of $Fe(CN)_6^{4-}$ happens





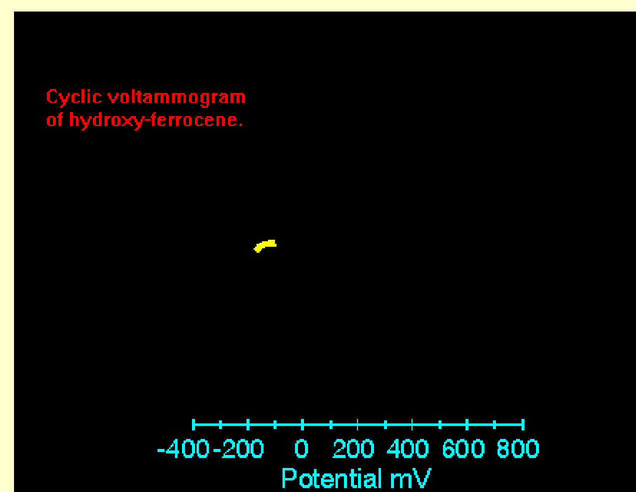
J. Anodic peak potential (E_{pa}) and anodic peak current (i_{pa})



Important quantitative information got from the Cyclic voltammogram

- i_{pc} i_{pa}
- $\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$,
n = number of electrons
- E_{mid} = mid peak potential between $E_{pa} \rightarrow E_{pc}$
- $i_p = 2.686\text{x}10^5 n^{3/2} A c D^{1/2} v^{1/2}$

  - ***A*: electrode surface**
  - ***c*: concentration of electroactive compound**
  - **v: scan rate**
  - ***D*: diffusion coefficients**

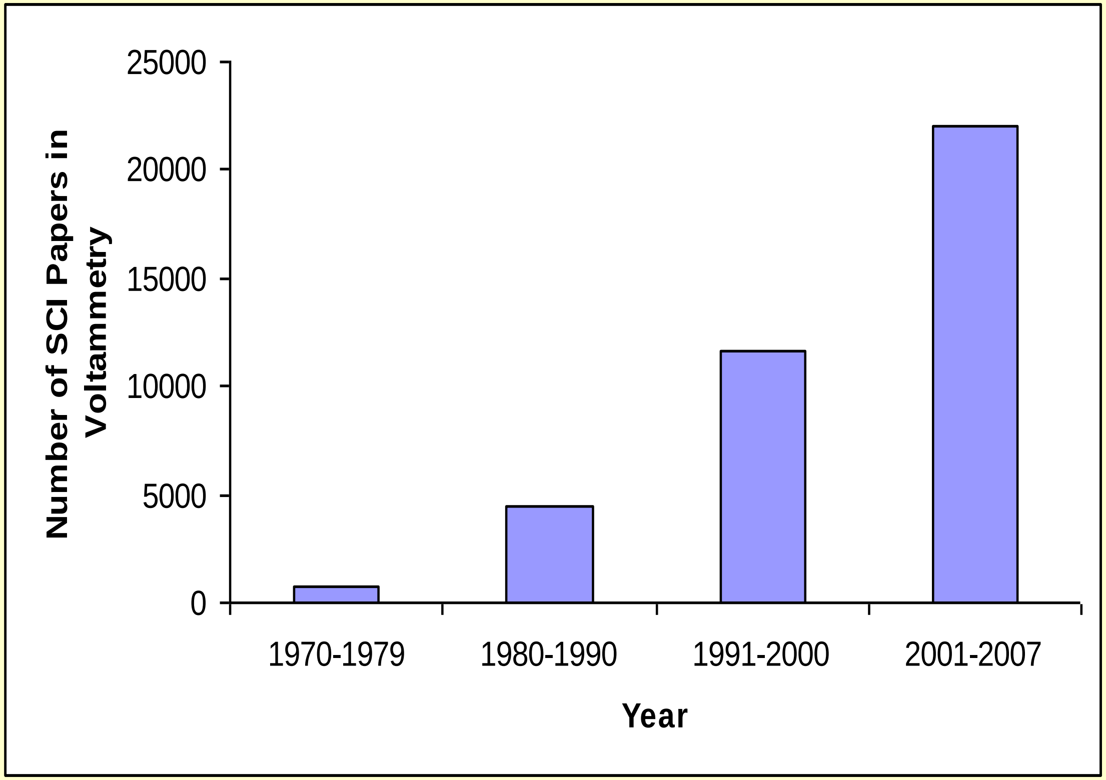


Application of the Voltammetry

-In Chemistry, Physics and Engineering

-In Biology and Biochemistry (biosensors)

-In Pharmacy



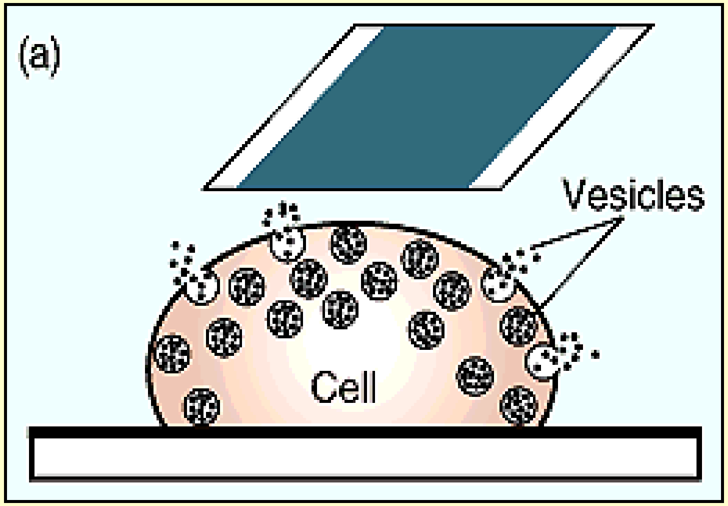
-In Medicine

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

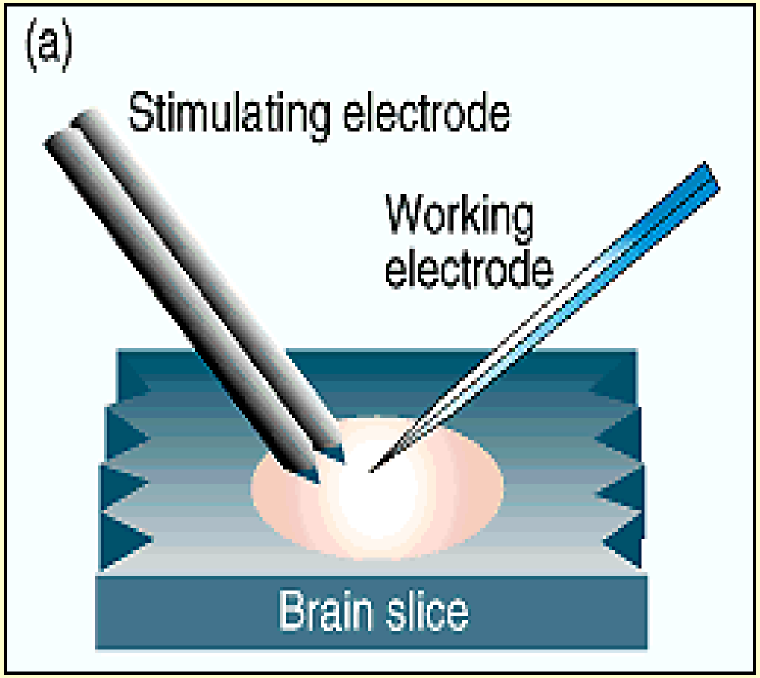
-determination of various active compounds

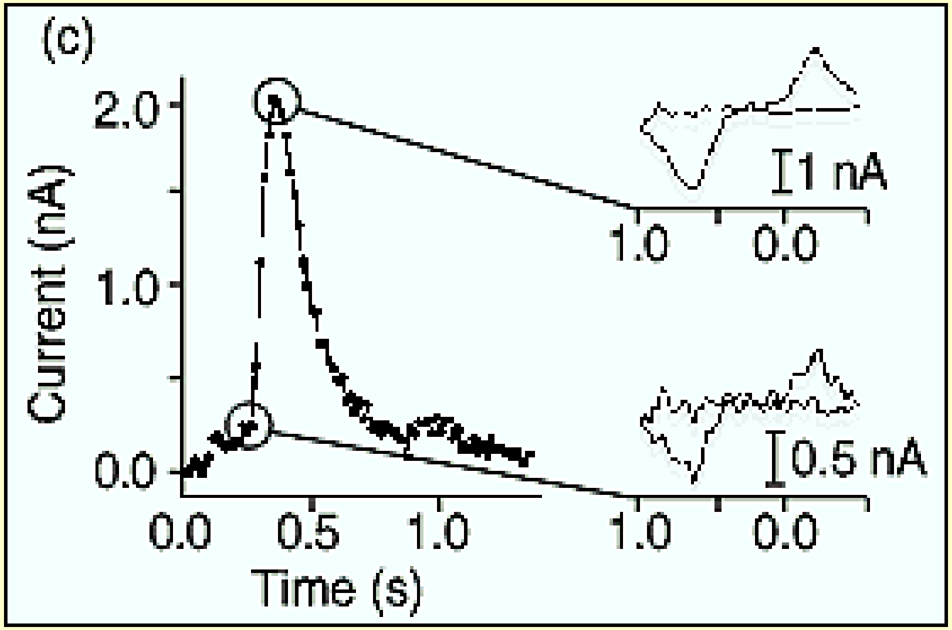
-following of protein-protein interactions

-medical sensors for various electron cariers and neurotransmiters



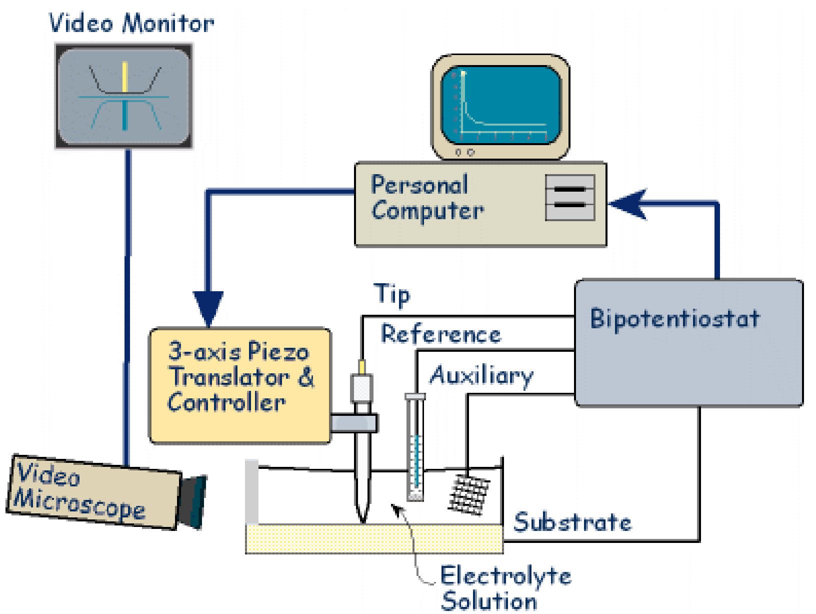
IN-VIVO voltammetric determination of catecholamine

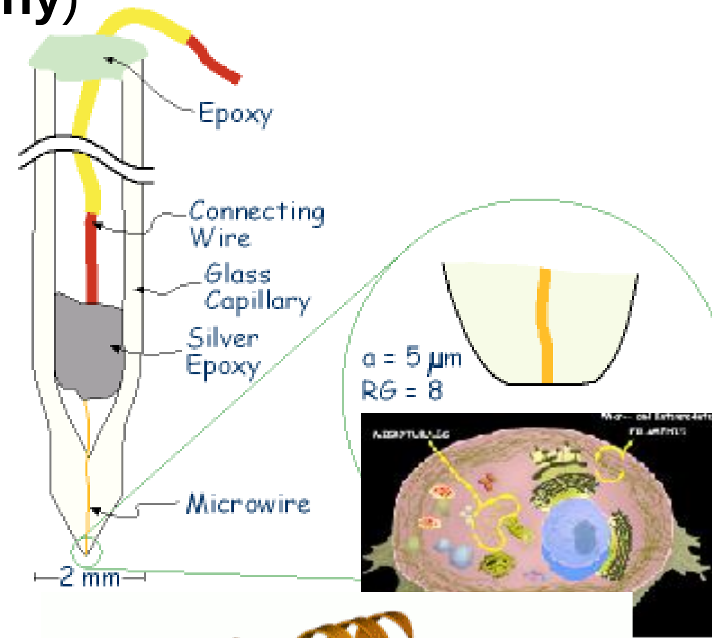




Voltammetry in service of the Scanning Electrochemical Microscopy

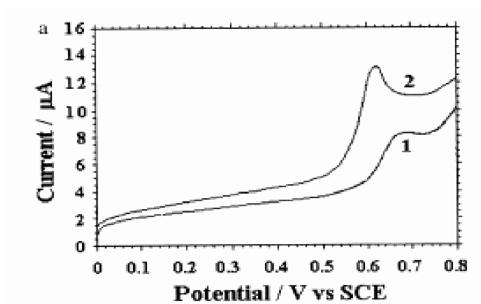
-Powerfull tool for probing the electrochemical activity of single living cells at different spots (**cell topography**)





-Detection of **active sites of Enzymes**

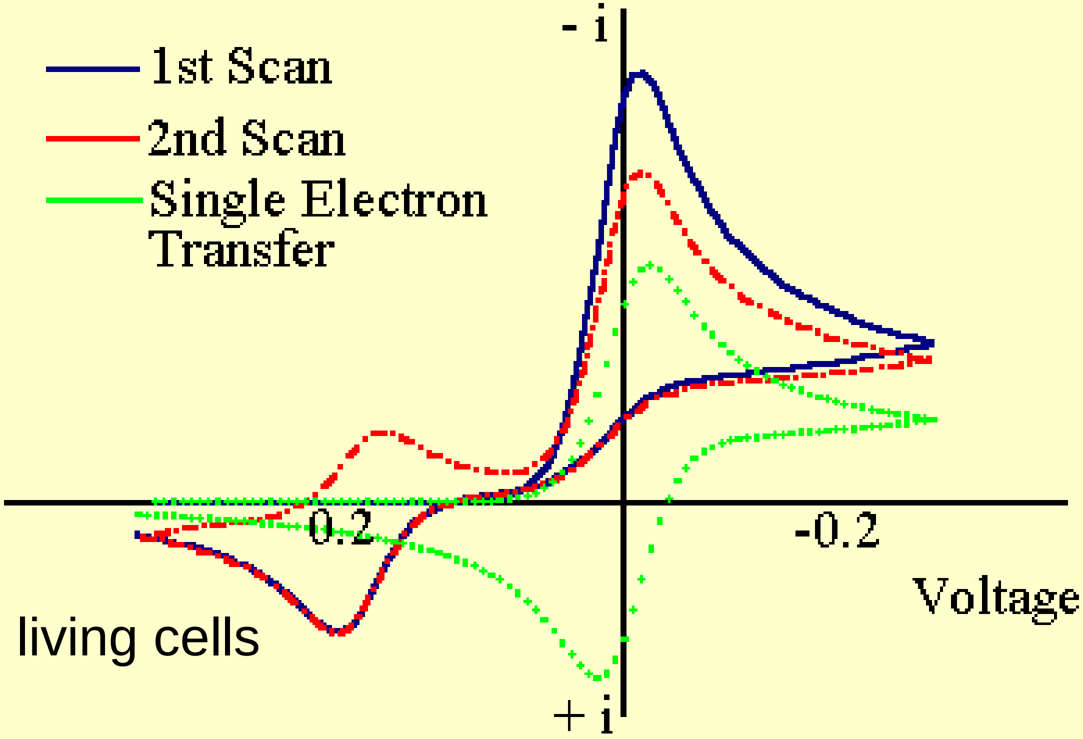
-Detection of **human breast cancer cells**



What kind of information can provide Voltammetry?

-Mechanism 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-

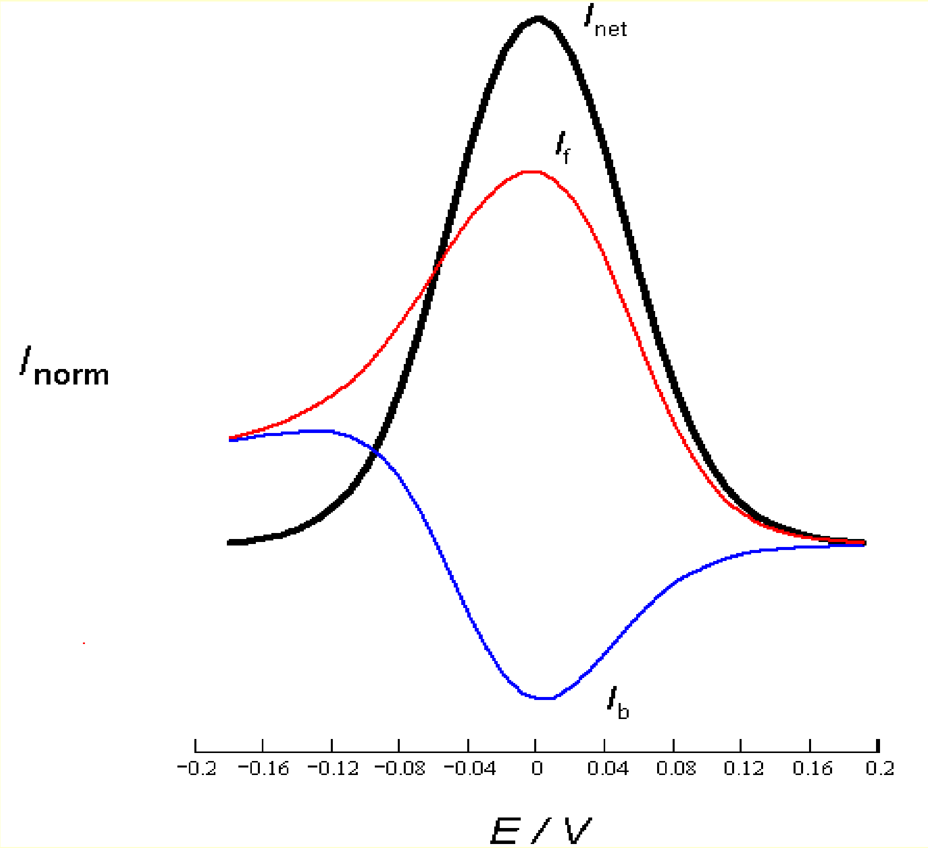
NO_2- + 2OH- -2e- = NO_3- + H_2O

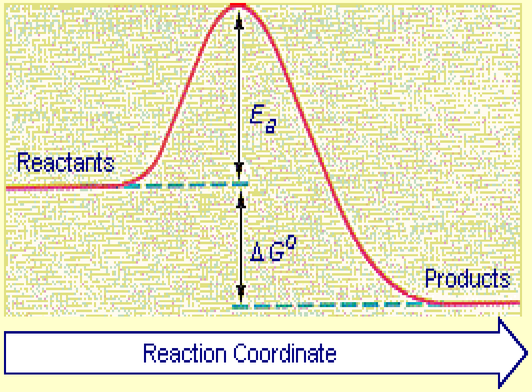
-Thermodynamic Parameters of Redox Reactions

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

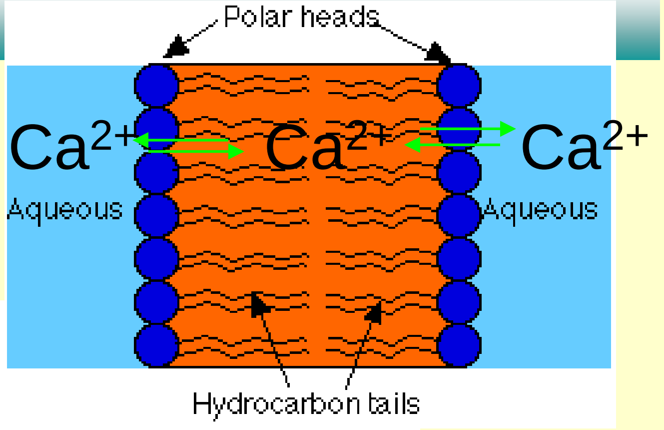
-Kinetic Parameters

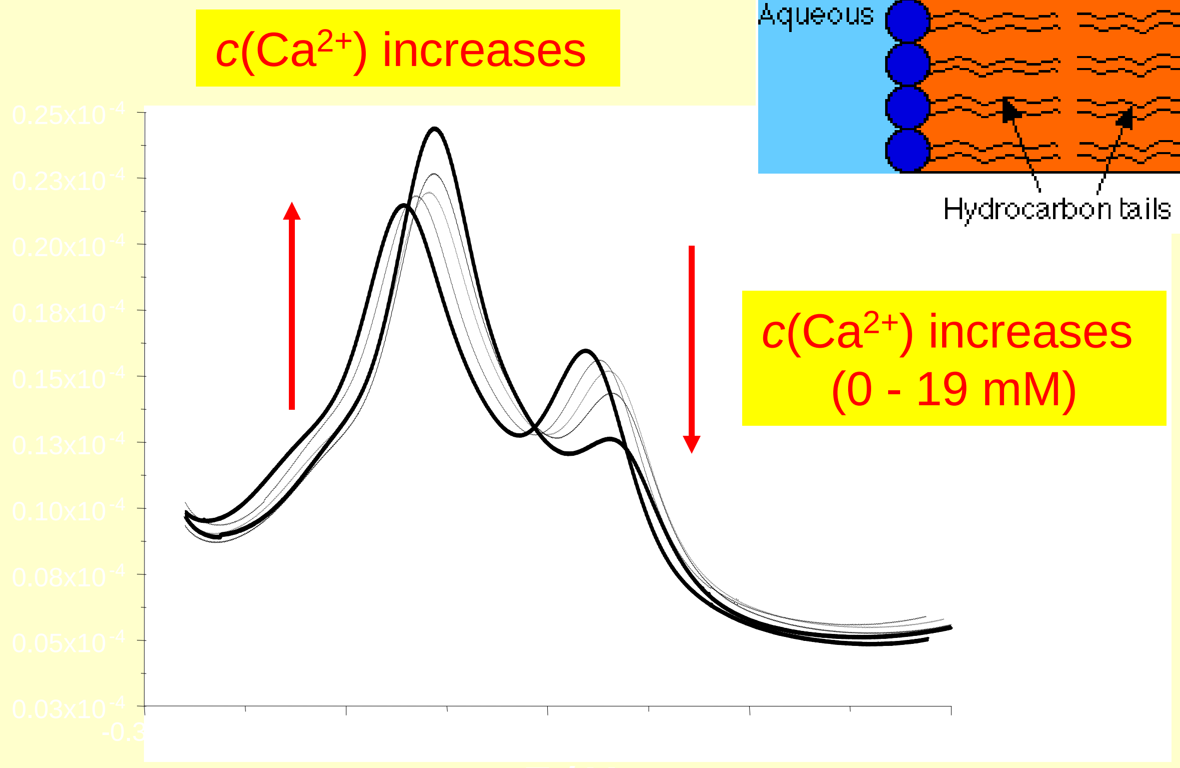
-standar rate constants of electron/ion transfers; kinetics of enzymatic reactions; kinetics of chemical reactions; ***pharmakokinetic parameters...***





Complexation of Quinone-like compounds and Ca^{2+} ions

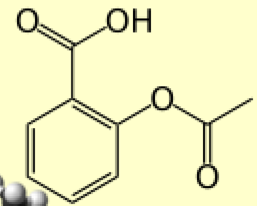


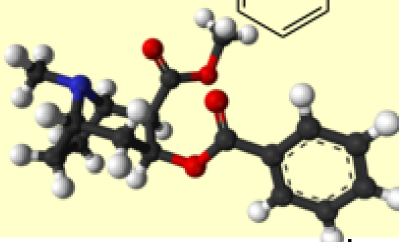


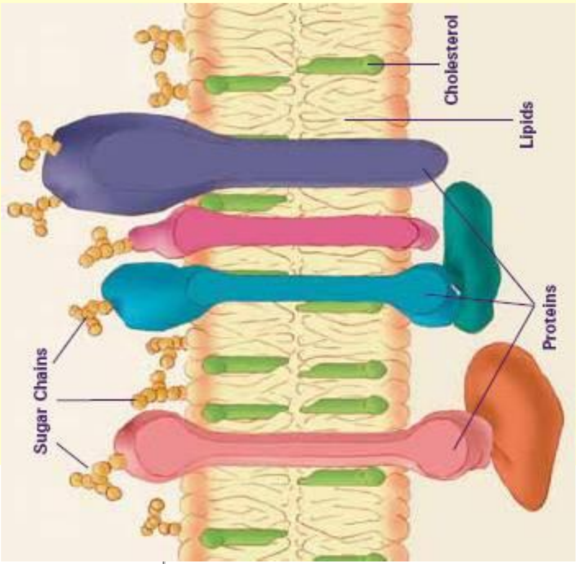
Cyclic voltammograms showing complexation of PalmytoilQuinone with Ca^{2+}

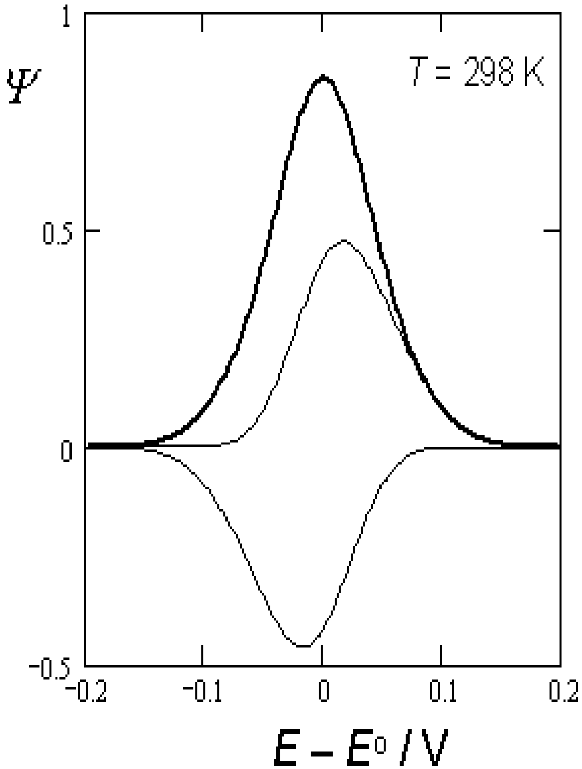
-***physical phenomena taking place in the system*** (*absorption, phase transformation*)

-way of mass transfer

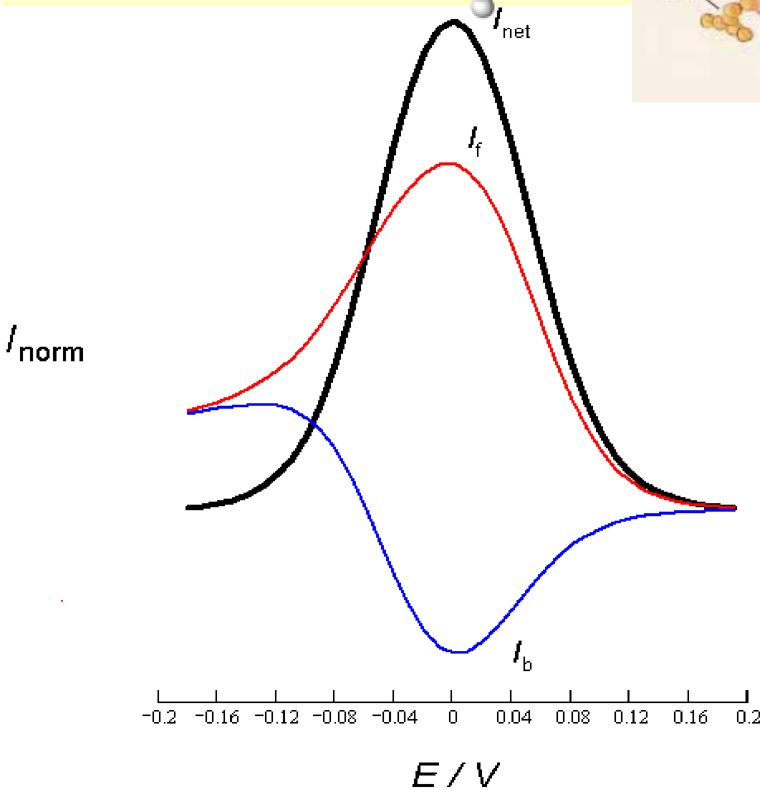




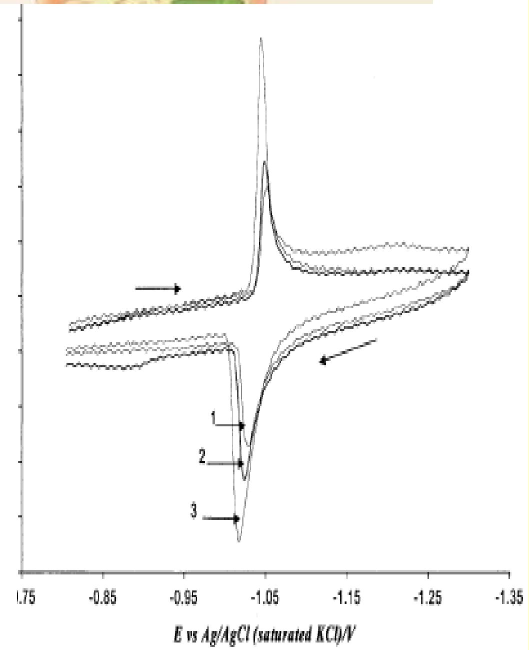




absorption



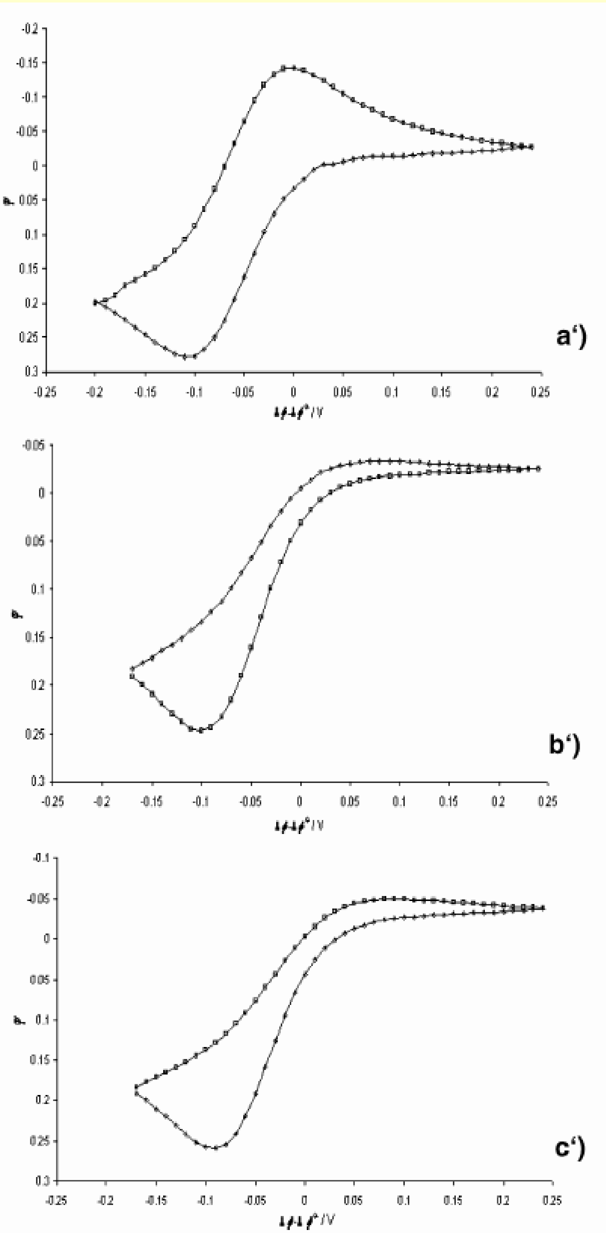
diffusion

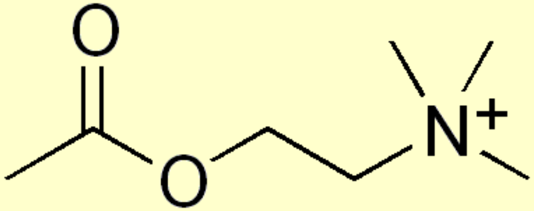


Phase-transformation

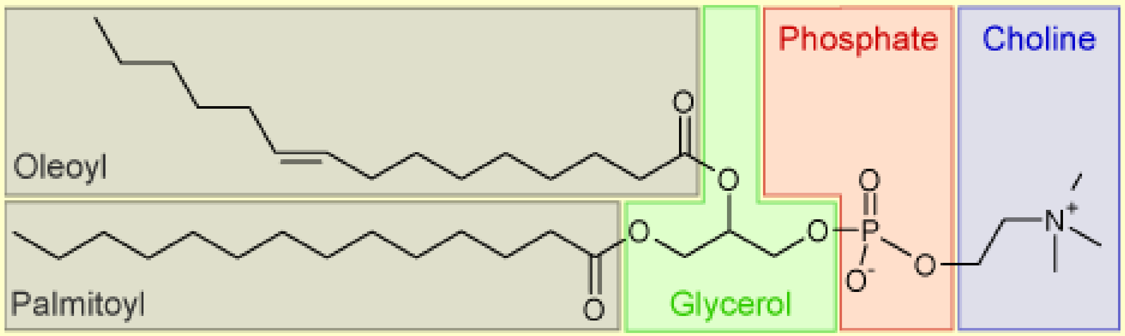
-thermodynamic and kinetic parameters related to the physical phenomena

-type and strenghts of interactions between various compounds





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

Which compounds can be investigated by Voltammetry?

Inorganic compounds, metals, alloys,

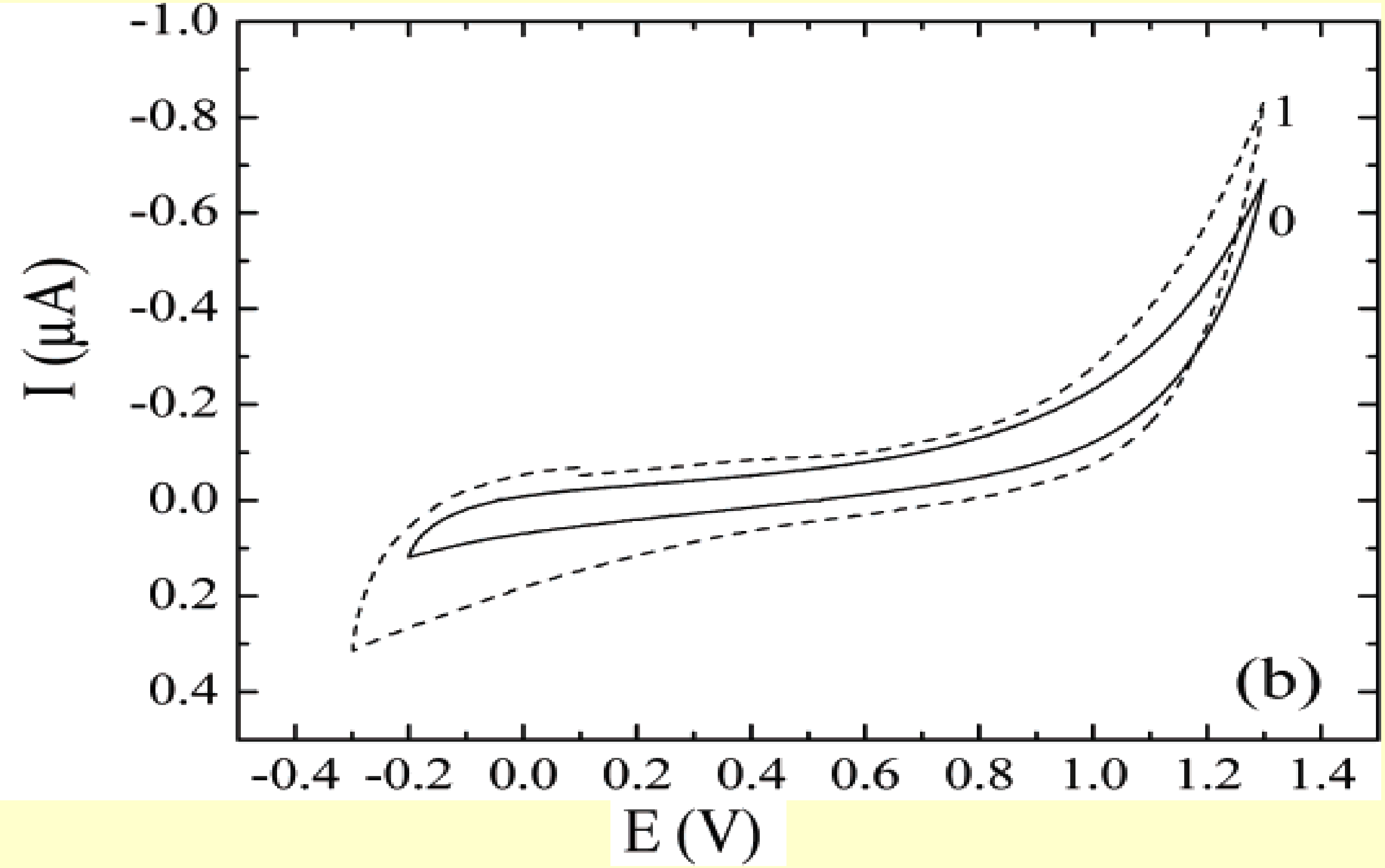
Organic compounds containing redox active groups:
C=O;Ar=O; N-R; “=“; N=N; S-H; Ar-OH: Ar-NO_2

Organic compounds containing incorporated metal ions (various **redox enzymes**

All medicaments and drugs containing “redox active” sites.

neurotransmitters dopamine, noradrenaline, adrenaline, serotonin…

Are there some limitations?

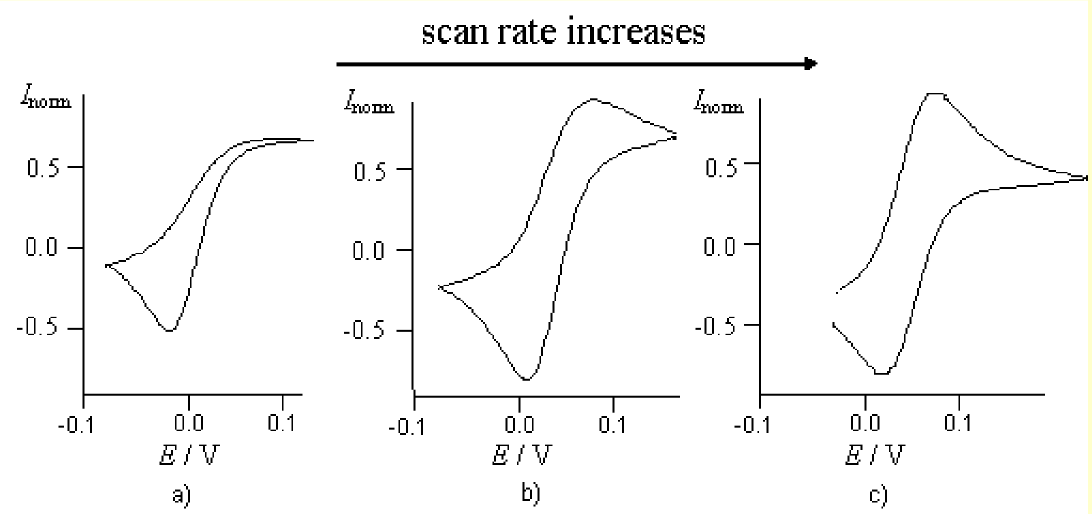


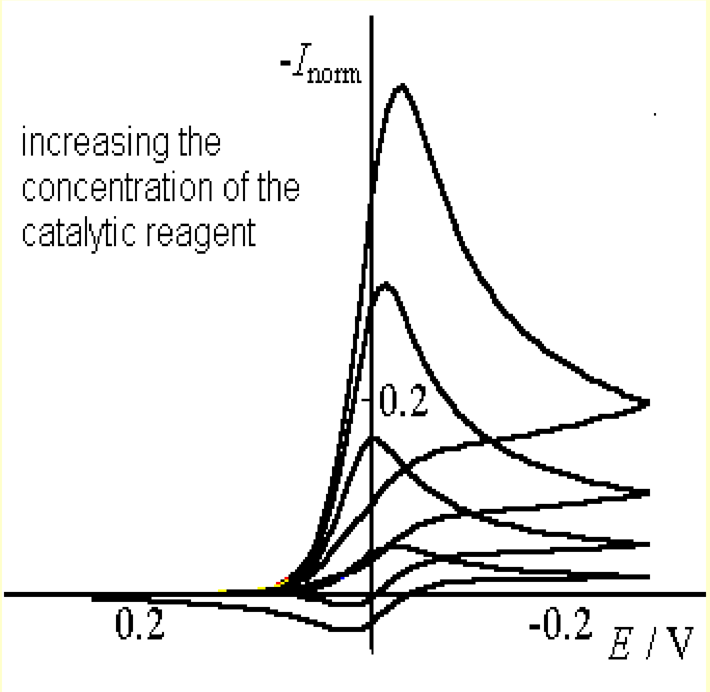
BLANK Cyclic voltammogram

-What can we make in the case if our compound does not show “electrochemical activity”?

transmitters such as GABA, glycine and glutamate are NOT electroactive

-to make coupled CHEMICAL reactions with redox active compounds

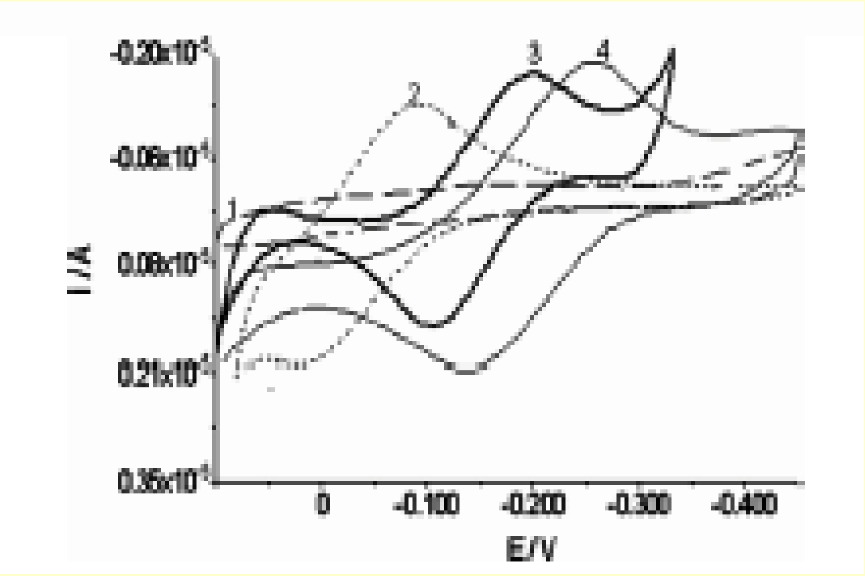




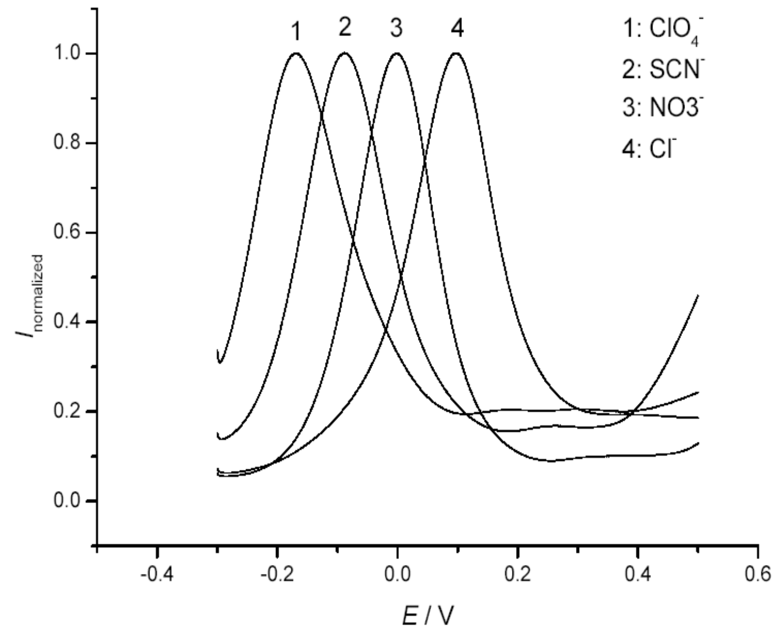
-to probe whether our compound can react with the material of the electrode

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

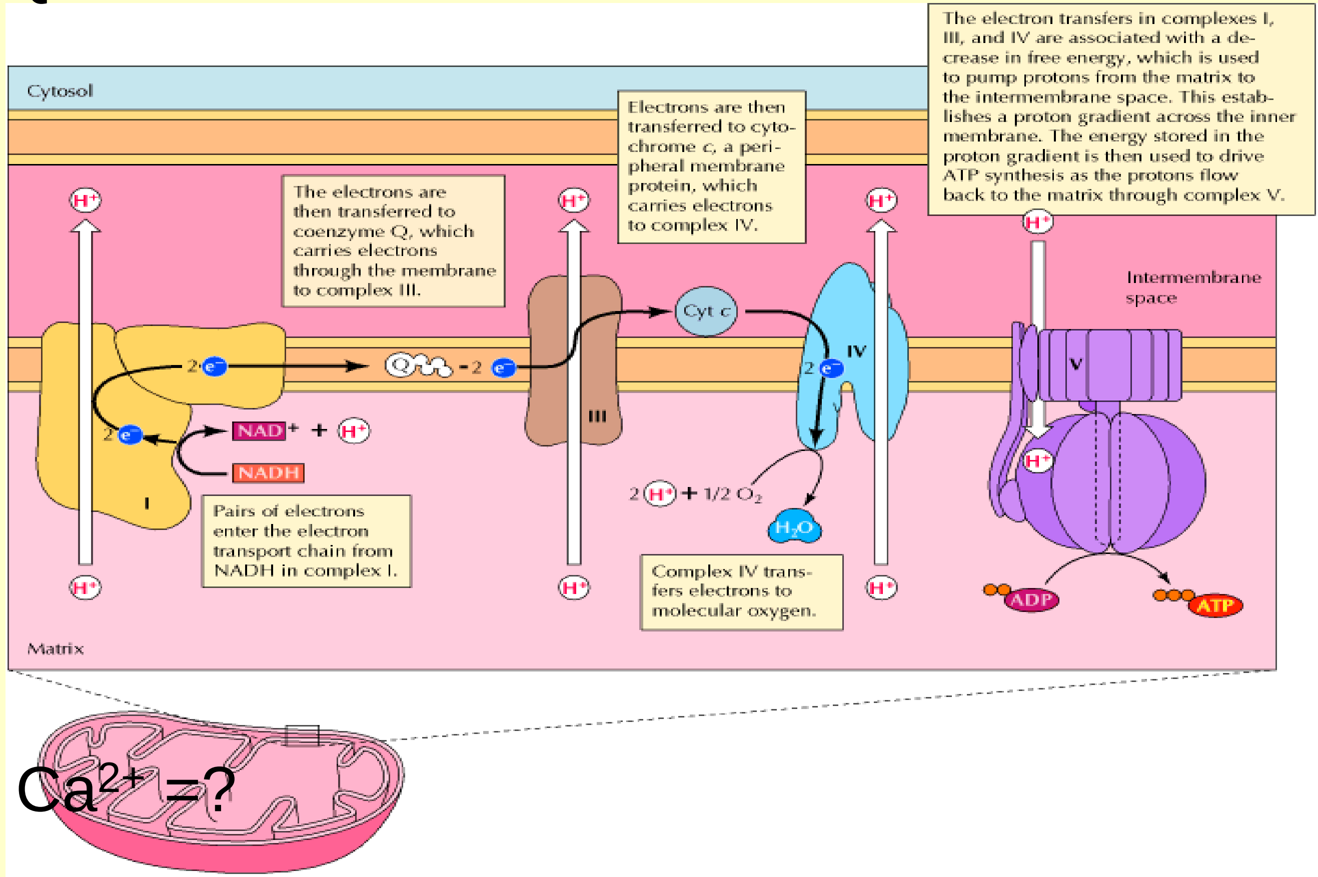


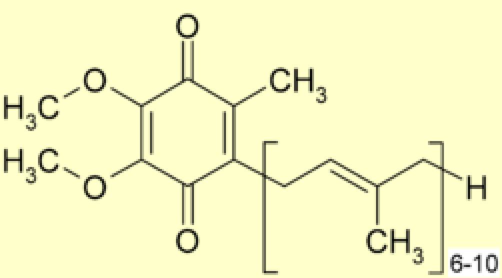
Transfer of Ionized Drugs-
heroin, cocaine and codeine
across biomimetic membranes



Current work:

Role of Coenzyme Q in Ca^{2+} transfer across membranes?





+ Ca^{2+} =?

"All truth passes through three stages:
First, it is ridiculed; Second, it is violently opposed; and
Third, it is accepted as self-evident."

Final Conclusions:

Voltammetry is a SIMPLE, CHEAP and powerful tool for:

-Quantitative determination (sensing) of various biologically active compounds

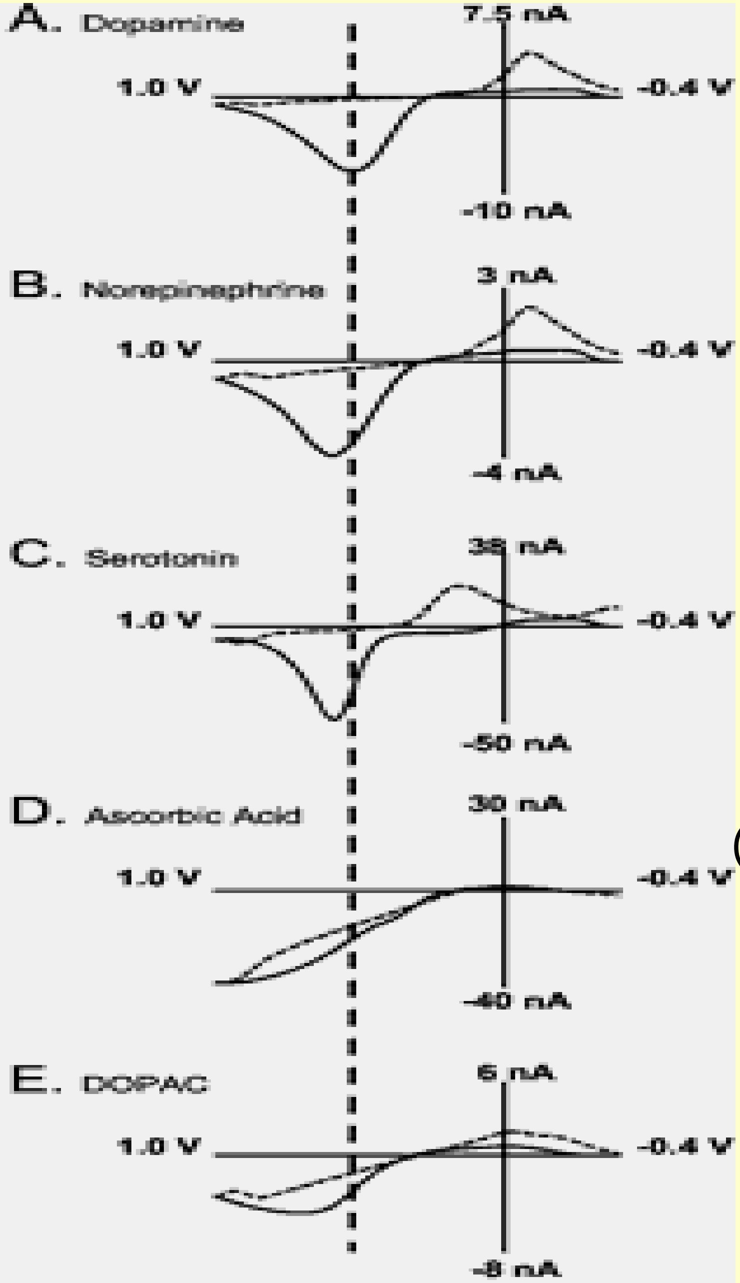
-simple technique for revealing the mechanistic pathways

-effective tool for thermodynamic and kinetic measurements

-Inevitable technique in almost ALL research laboratories

In GENERAL: FOR EVERY SYSTEM (Compound) ONE CAN GET ELECTROCHEMICAL INFORMATION REGARDLESS OF ITS STRUCTURE

Cyclic Voltammograms of some NUEORTRANSMITTERS



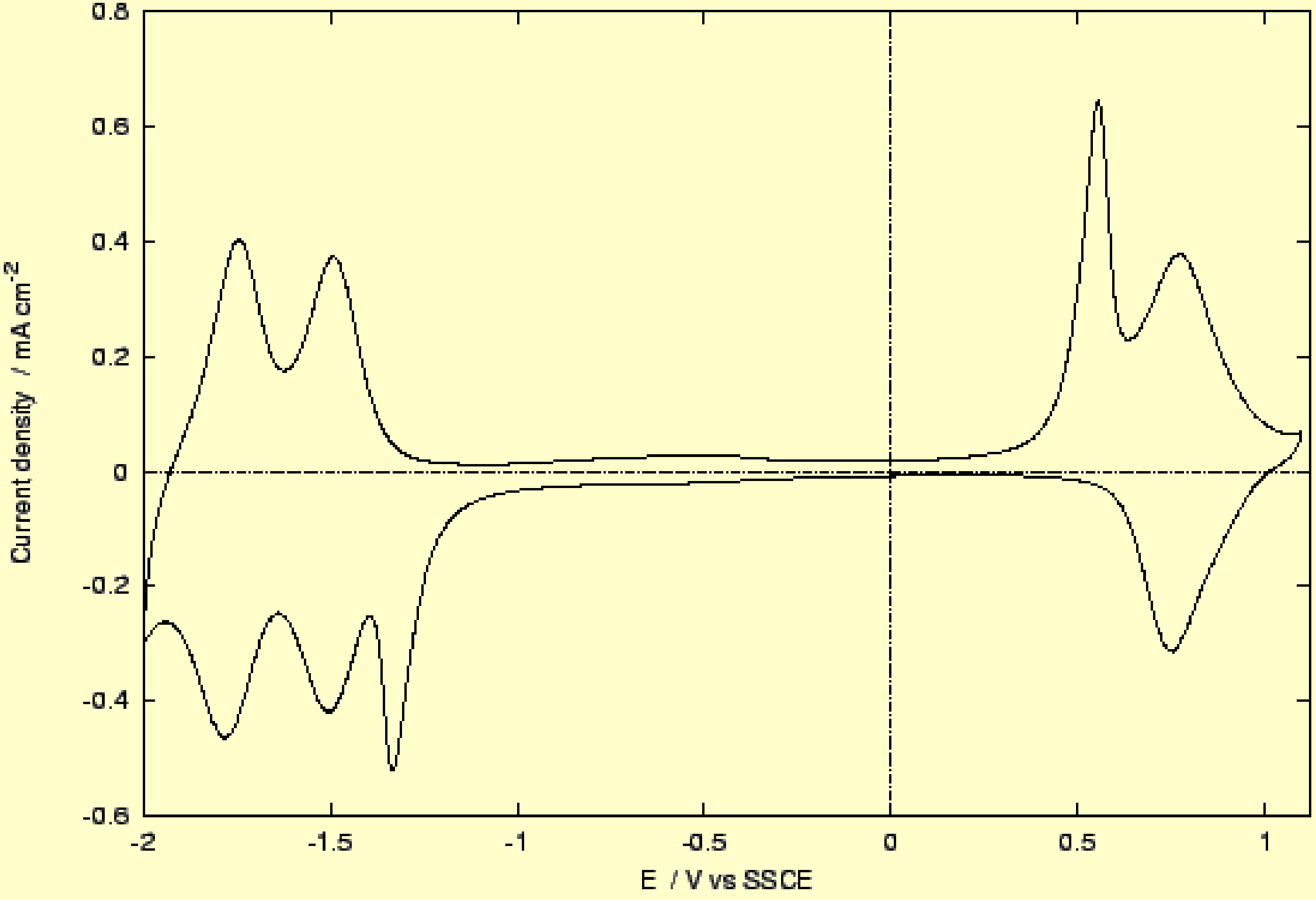
A), cyclic voltammogram for 2 µmol/L **dopamine**.

(*B*), cyclic voltammogram for 2 µmol/L **norepinephrine**

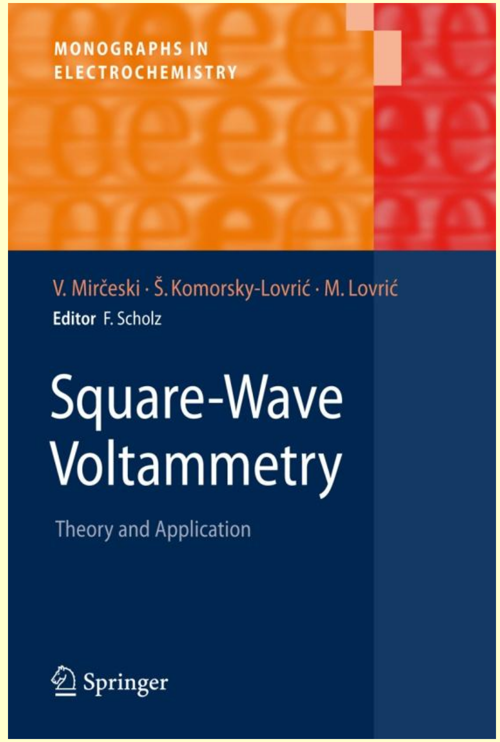
(*C*), cyclic voltammogram for 2 µmol/L **serotonin**

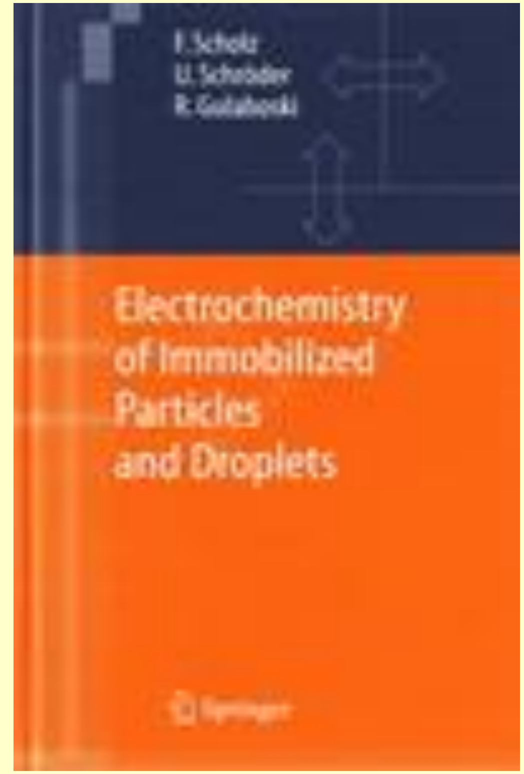
(*D*), cyclic voltammogram for 200 µmol/L **ascorbic acid**

(*E*), cyclic voltammogram for 20 µmol/L **DOPAC**



0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
Current density / mA cm-2
-2
-1.5
-1
-0.5
0
0.5
1
E / V vs SSCE





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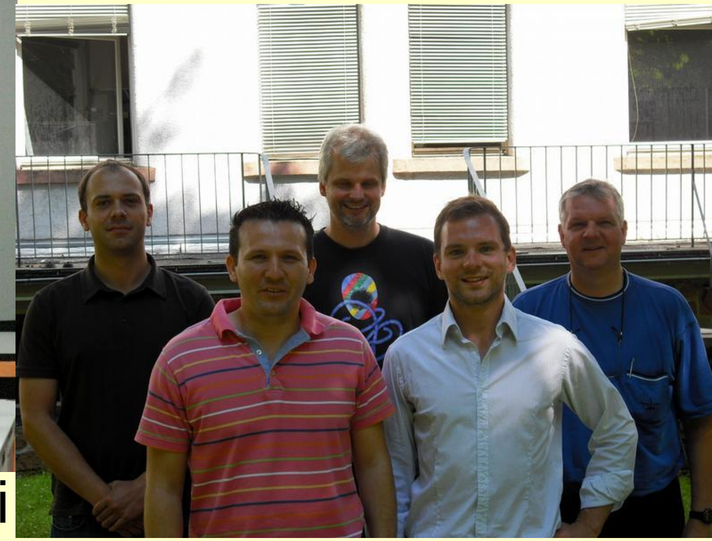

Valentin Mirceski

Prof. Fritz Scholz
Greifswald University

Prof. Natalia Cordeiro
prof Carlos Pereira

Prof. Milivoj and Sebojka Lovric
Croatia

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