

CYCLIC VOLTAMMETRY-FUNDAMENTALS

RUBIN GULABOSKI

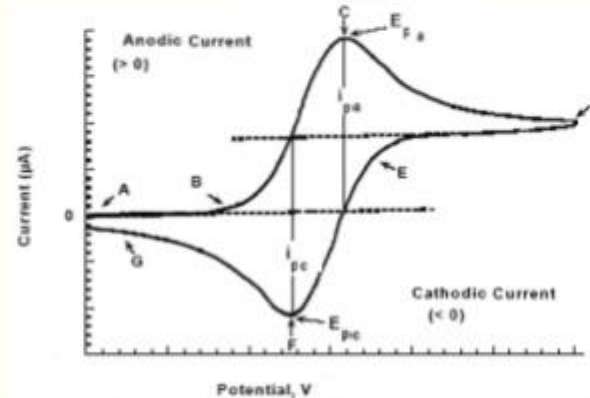
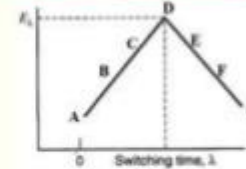
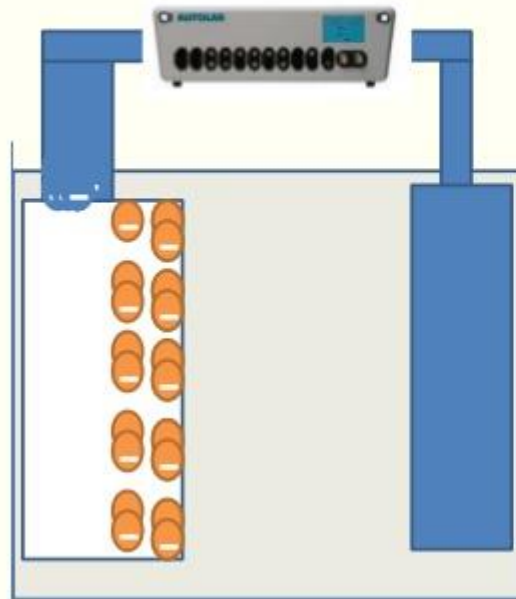
Macedonia



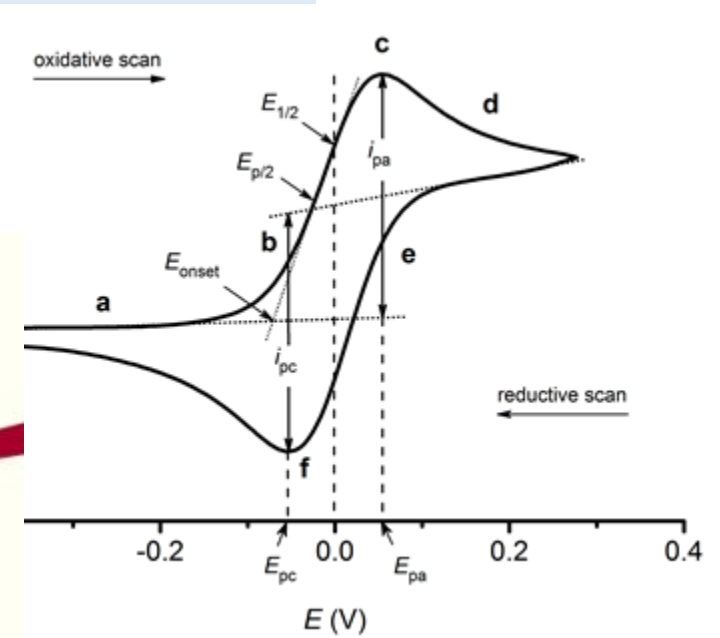
Double Layer Charging



From A to B



The expected response of a reversible redox couple



IMPORTANT DEFINITIONS IN VOLTAMMETRY

-VOLTAMMETRY (abbreviation of VOLT-AMPER METRY) is a potentiodynamic electrochemical technique that involves application of a potential that varies with time, and measures the corresponding current that flows between the working and reference electrodes.

-VOLTAMMETRY Relays ON EXCHANGE OF CHARGE BETWEEN TWO PHASES THAT ARE BROUGHT IN CONTACT.

-CHARGE CAN BE EITHER ELECTRONS OR IONS. ONE OF THE PHASES IS ELECTRONIC CONDUCTOR-WORKING ELECTRODE, IN WHICH WE CONTROL THE ENERGY OF THE ELECTRONS PRESENT IN OUTER SHELL OF THE ELECTRODE.

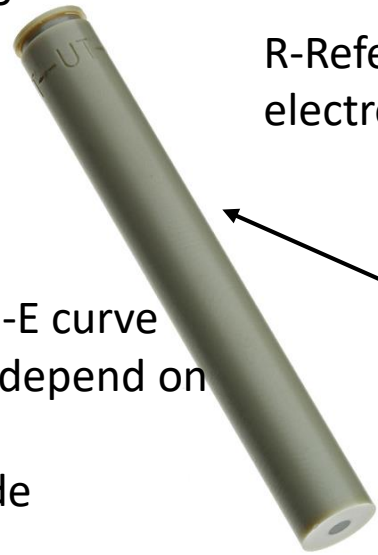
-ELECTRODE POTENTIAL IS CONSIDERED AS A PARAMETER THAT CONTROLS THE ENERGY OF ELECTRONS

-One can think of the potential as the intensive variable (energy in V or J/C) applied to the working electrode, and one can think of the current as the extensive variable (current in A or C/s) corresponding to the rate of an electrode reaction in response to the potential perturbation. Thus, the resulting voltammogram of current versus potential may be either transient or steady-state, in which a potential ramp serves as the potential perturbation.

-ELECTRIC CURRENT is INTENSIVE VARIABLE (measures the flow of charge) THAT IS PROPORTIONAL TO THE NATURE AND THE DIMENSION OF THE WORKING ELECTRODE. AND THE CONCENTRATION OF THE ANALYTE

EXPERIMENT in Cyclic Voltammetry-electrochemical cell

W-working electrode



R-Reference electrode

V

A

C-Counter electrode

W

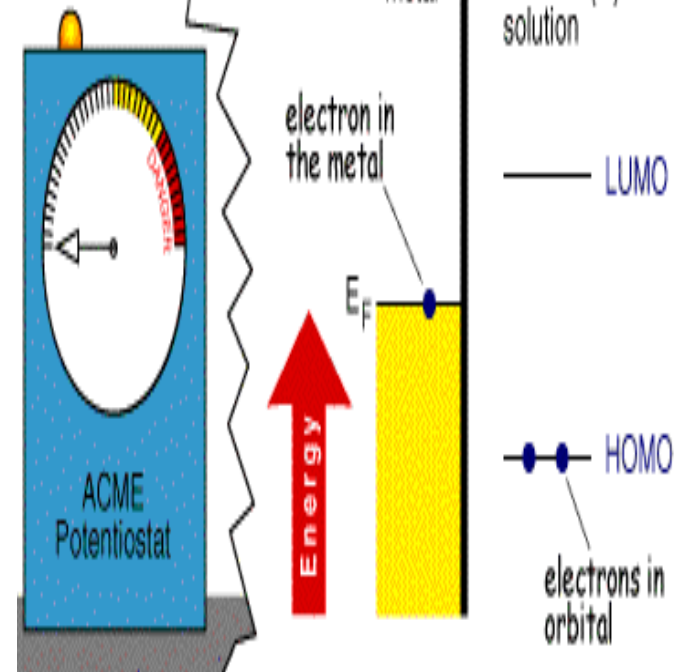
C

purging gas

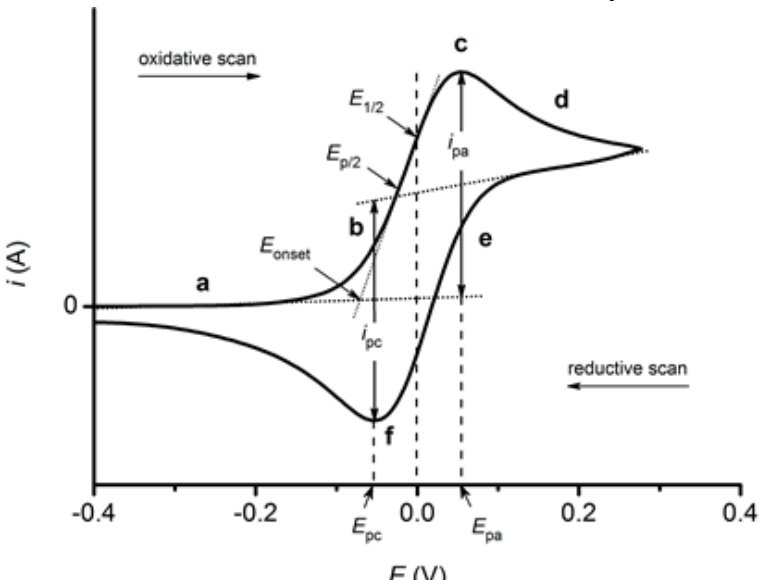
Electrolyte-Ions in water solution

Analyte present in electrochemical cell

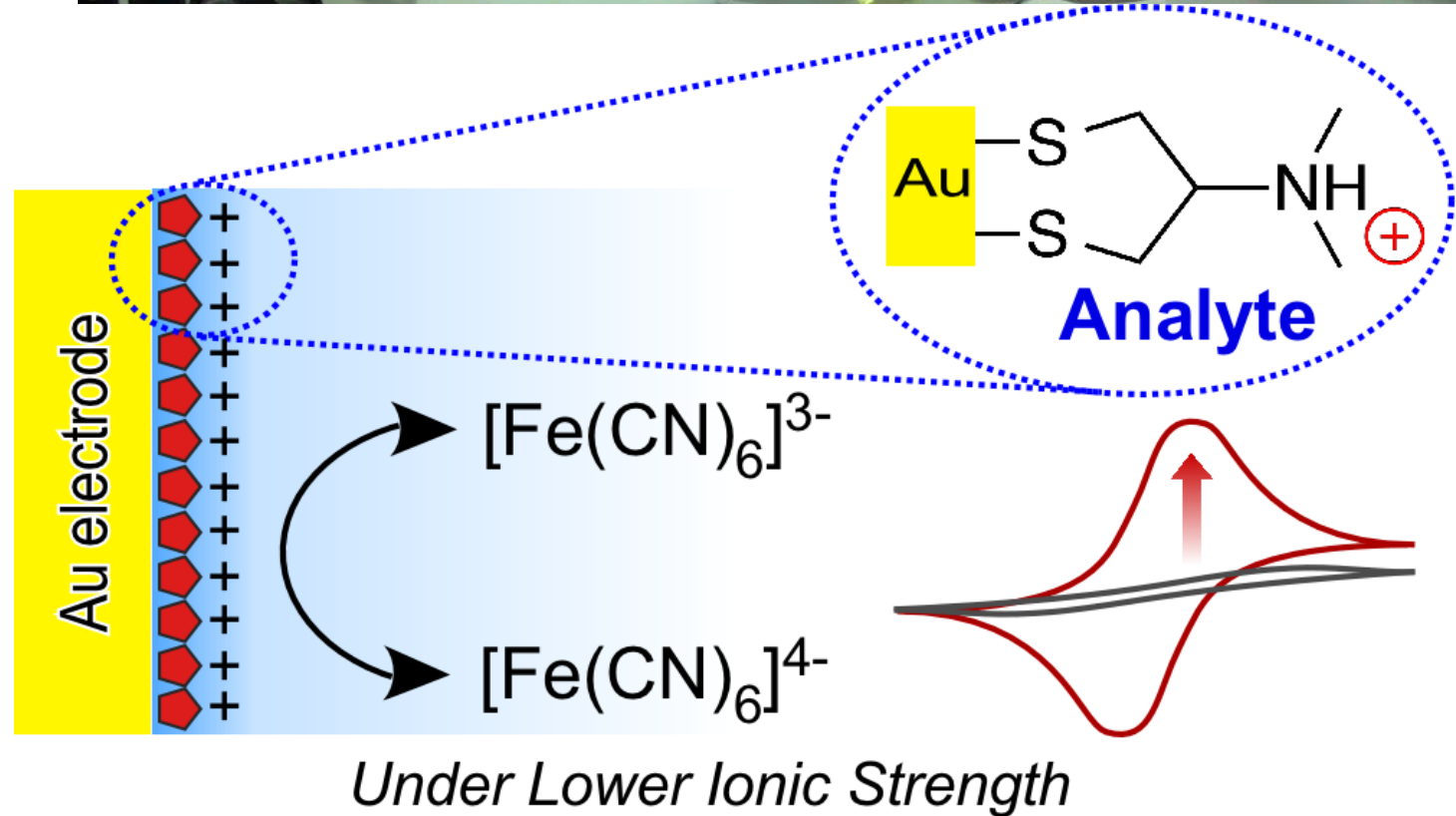
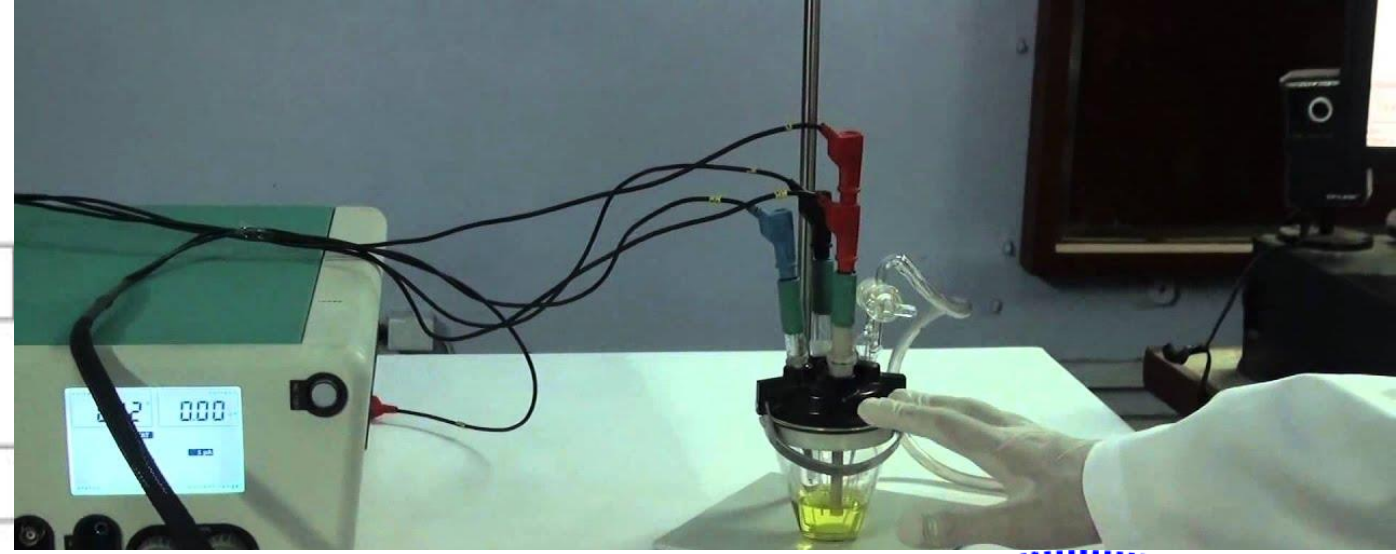
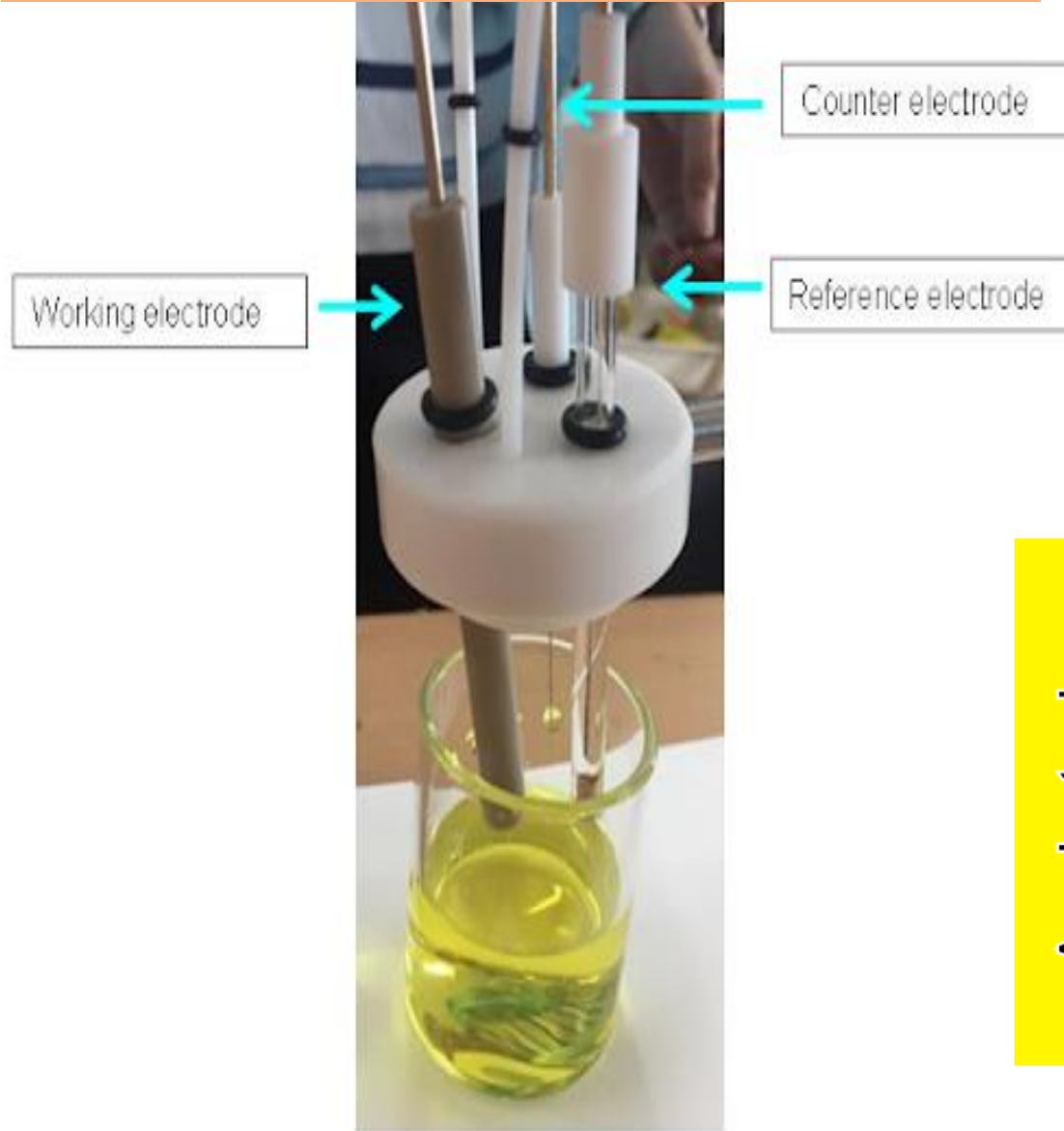
The fermi level in the metal is too low for electron transfer.



Cyclic voltammogram is a I-E curve
 With specific features that depend on
 -nature of the analyte
 -nature of working electrode
 -pH
 -presence/absence of chemical reaction,
 Phase transformation, adsorption...



ELECTROCHEMICAL CELL AND POTENTIOSTAT USED IN VOLTAMMETRY



Segment of the
DRIVING FORCE

i.e. the ELECTRODE POTENTIAL
DIFFERENCE

That is applied between working
And the reference electrode

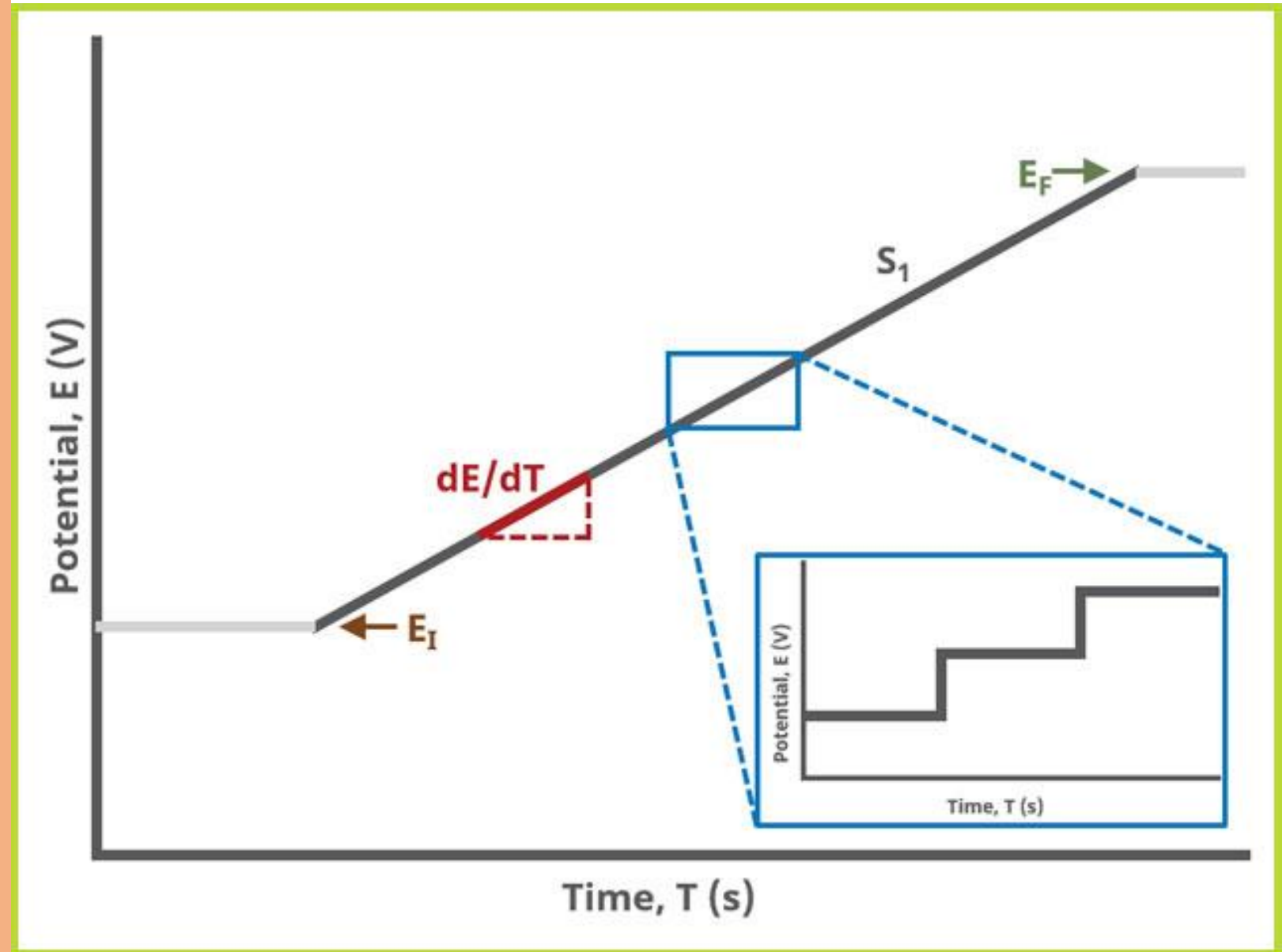
NEGATIVE ELECTRODE POTENTIAL

Means HIGH ENERGY of the
ELECTRONS at the outer shell
Of working electrode and this
Is precondition for

REDUCTION REACTION, i.e.

Electrons have huge kinetic energy
To be transferred from the
Working electrode to the
Molecular/atomic orbitals of the
Analyte that is studied (drug,
Metal ion, enzyme...)

**-Opposite holds true for
POSITIVE ELECTRODE POTENTIALS**



SCAN RATE or how fast we change the potential in a given time period

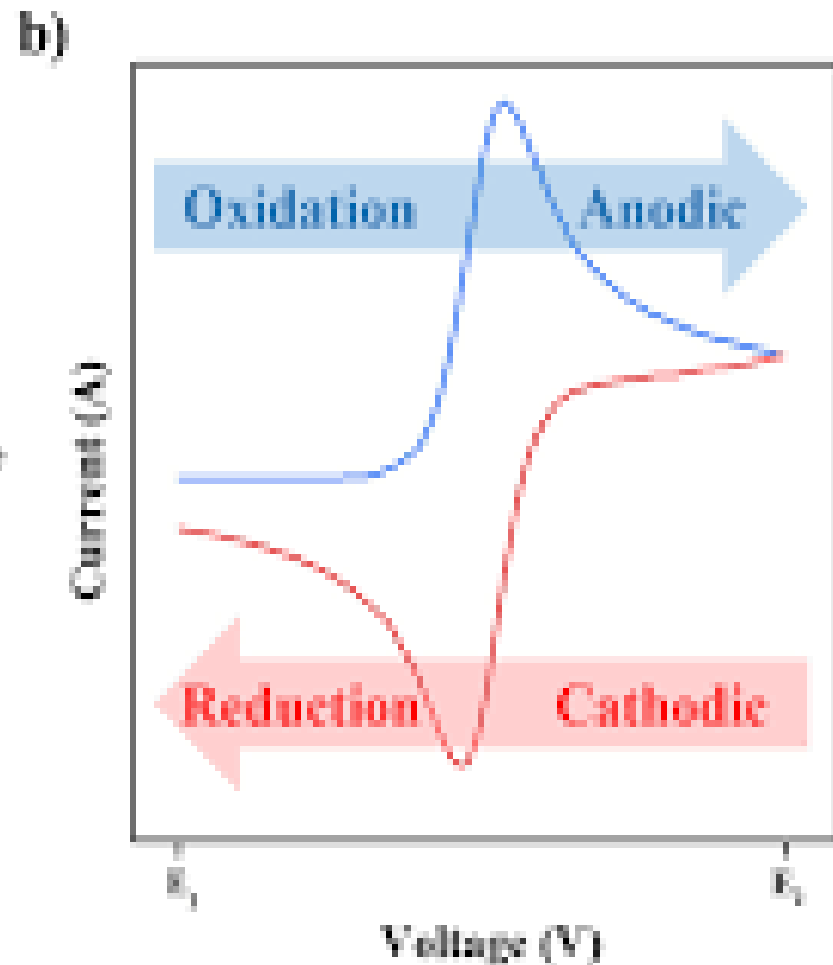
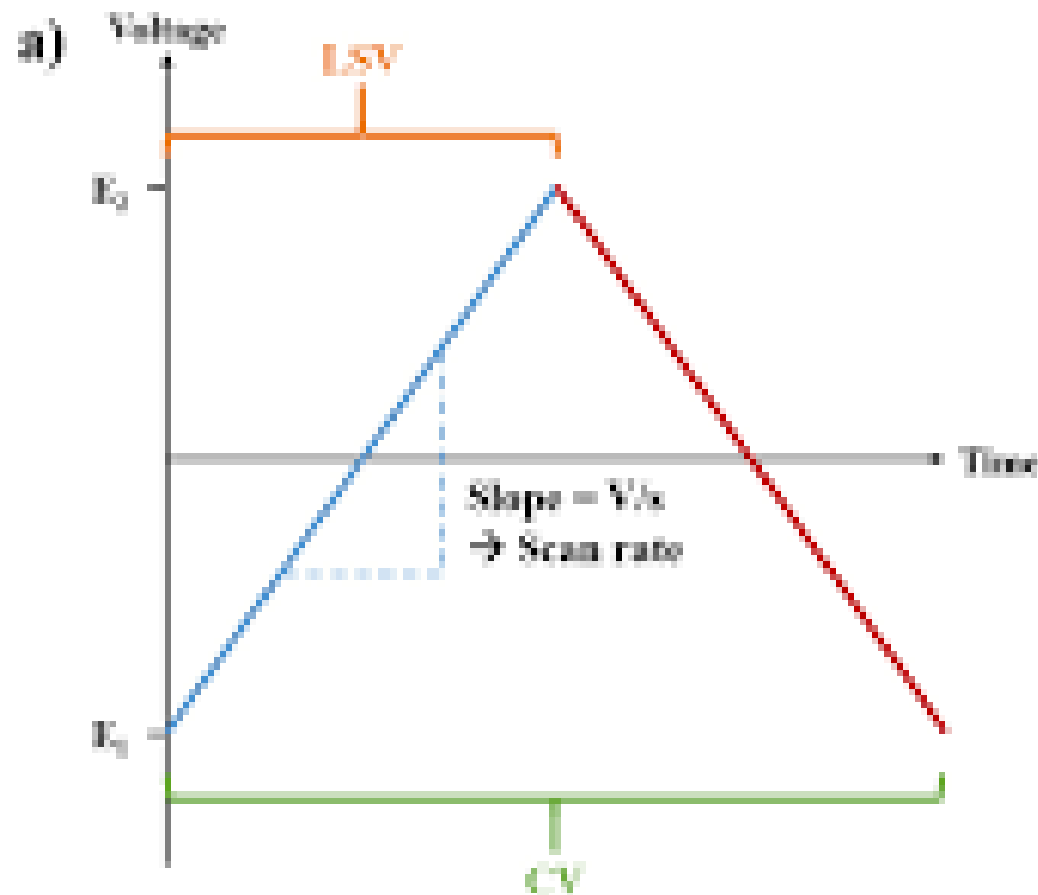
IS MAIN INSTRUMENTAL PARAMETER

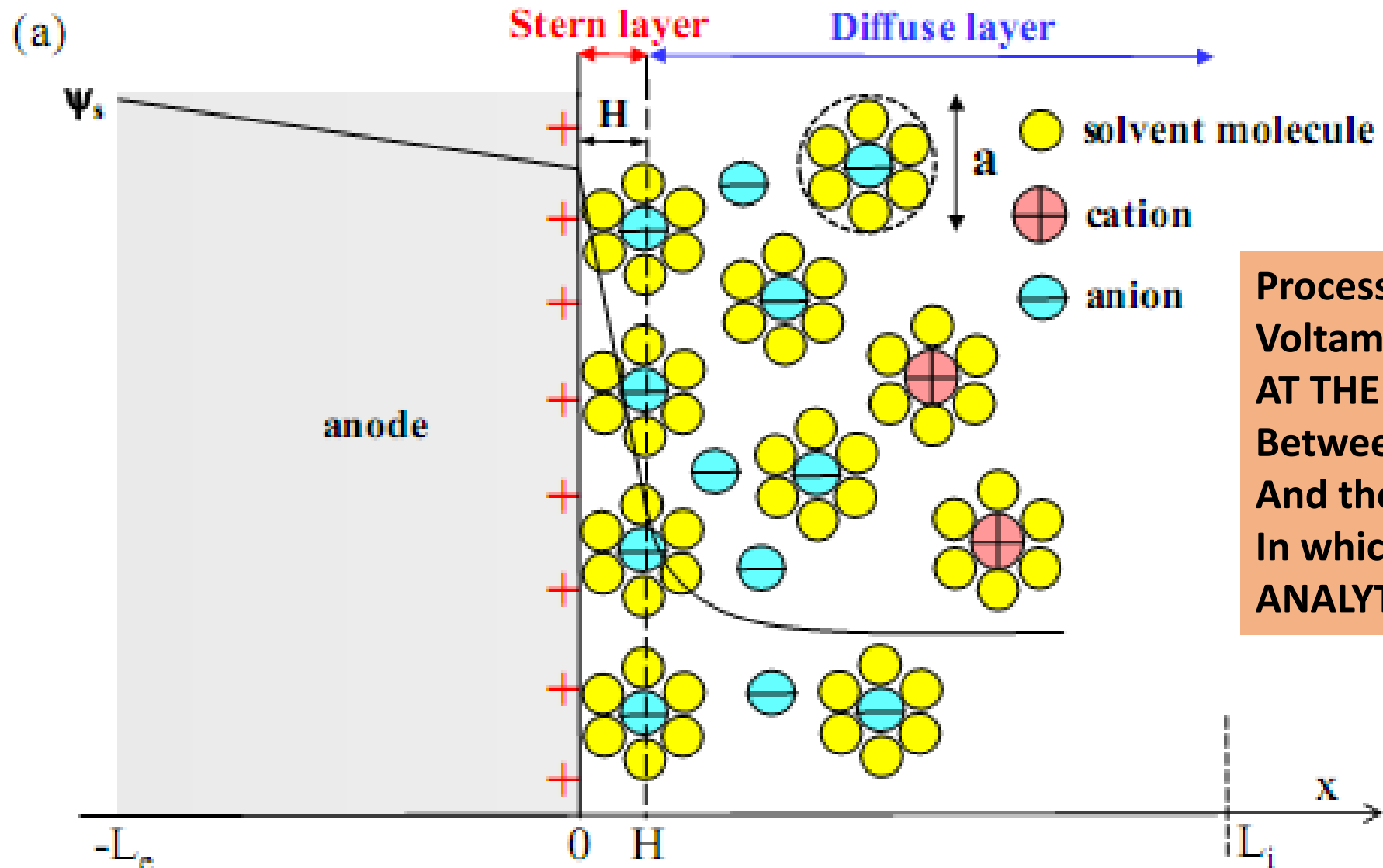
That IS ADJUSTABLE IN CYCLIC VOLTAMMETRY

Ex. 100 mV/s means that we run 100 millivolts in one second etc.

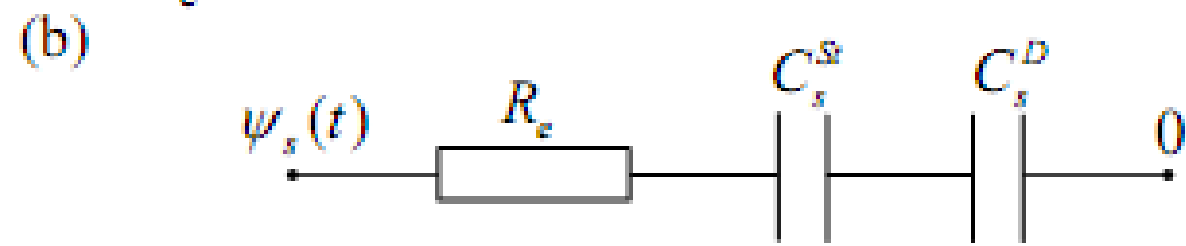
1 mV/s is slow scan rate...we run 1 millivolt in 1 second

.....by changing the scan rate we can investigate the KINETICS of electron exchange



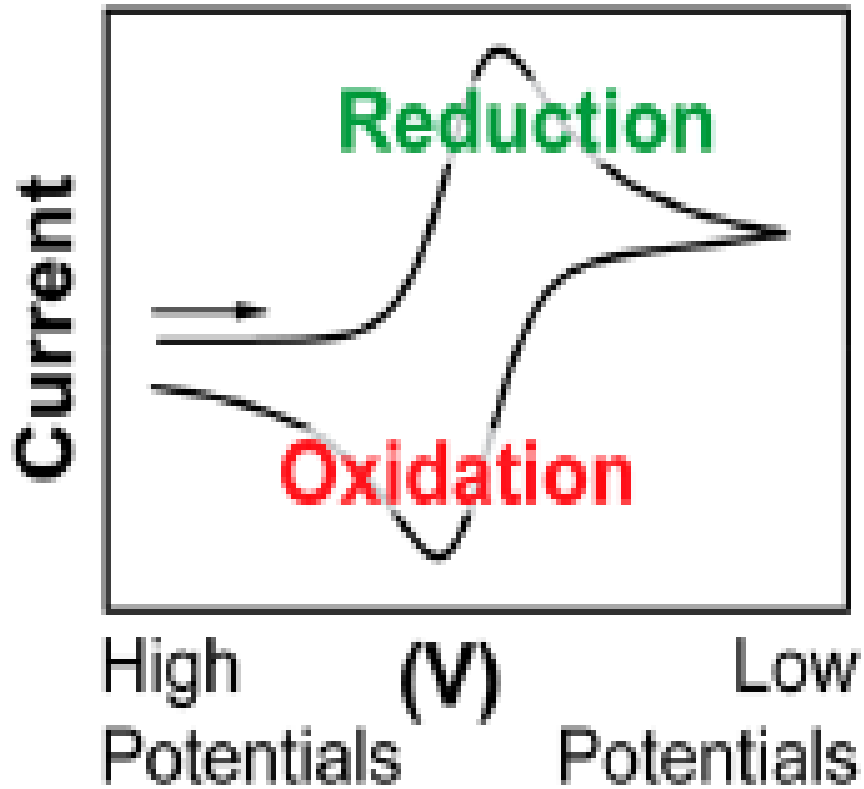


Processes of interest in Voltammetry take place AT THE INTERFACE Between the WORKING ELECTRODE And the electrolyte In which our ANALYTE IS DISSOLVED

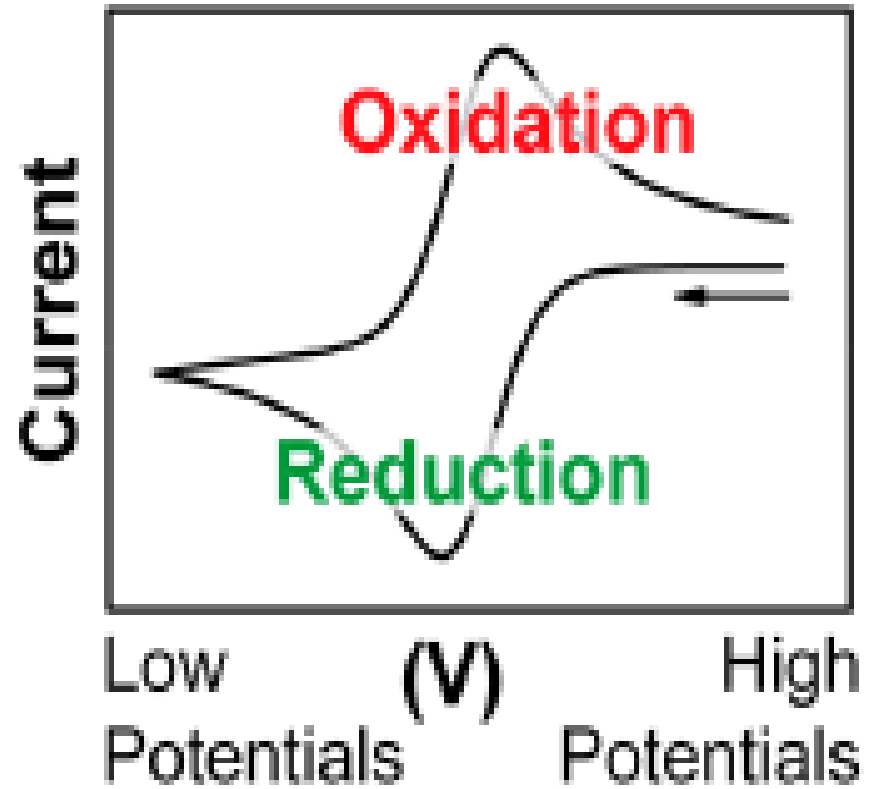


CYCLIC VOLTAMMOGRAM is resulting current-potential (I-E) output of the applied potential difference Between working and the reference electrode, and it reflects the oxidation/reduction Process of the analyte studied, i.e. its exchange of electrons with the working electrode

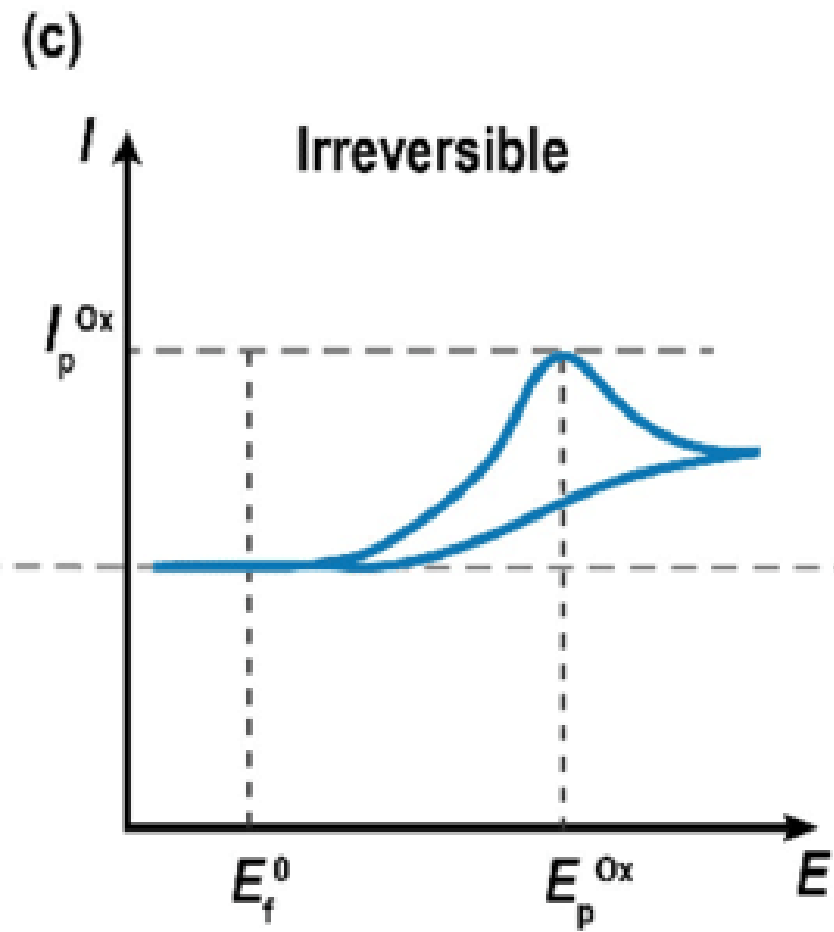
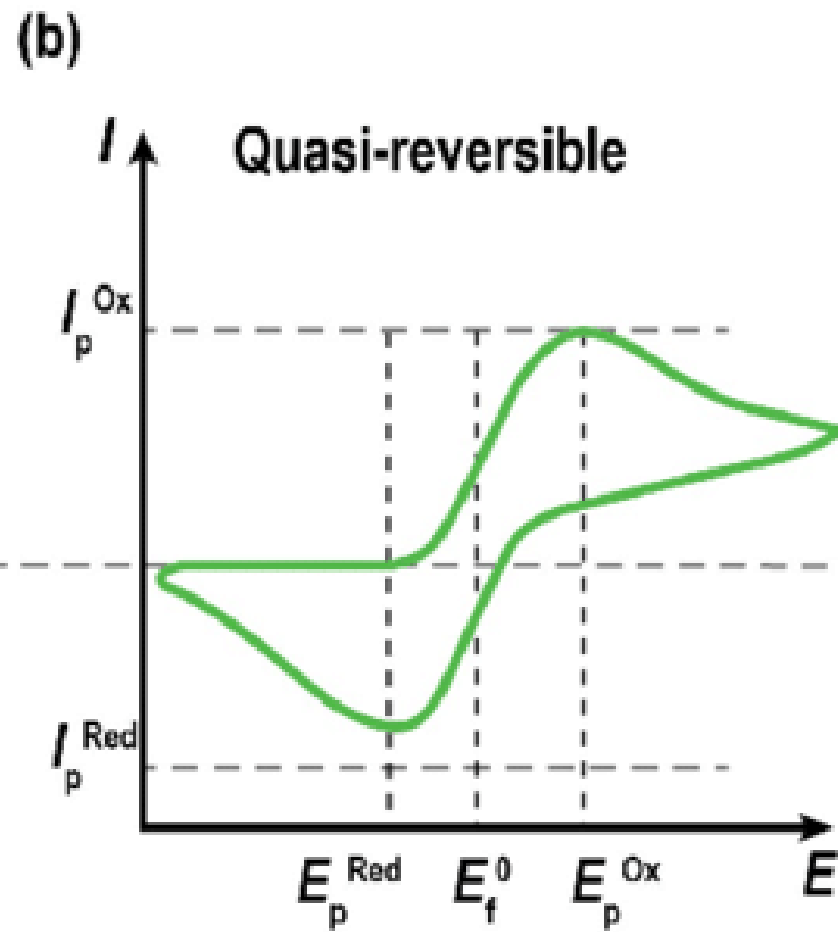
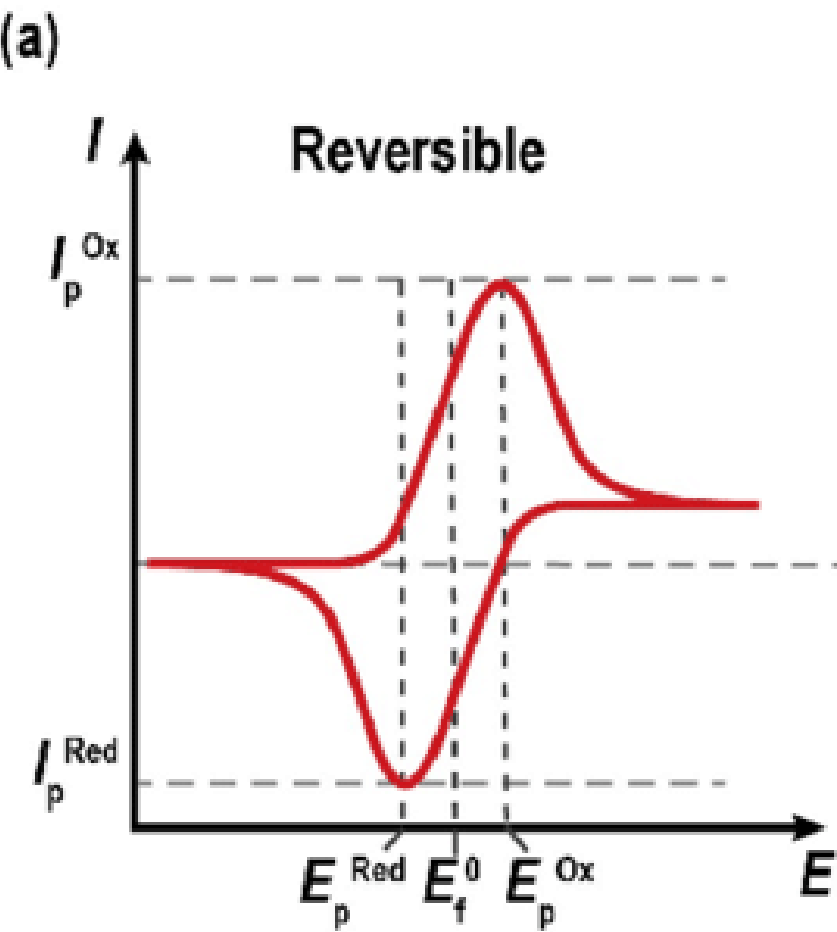
US Convention



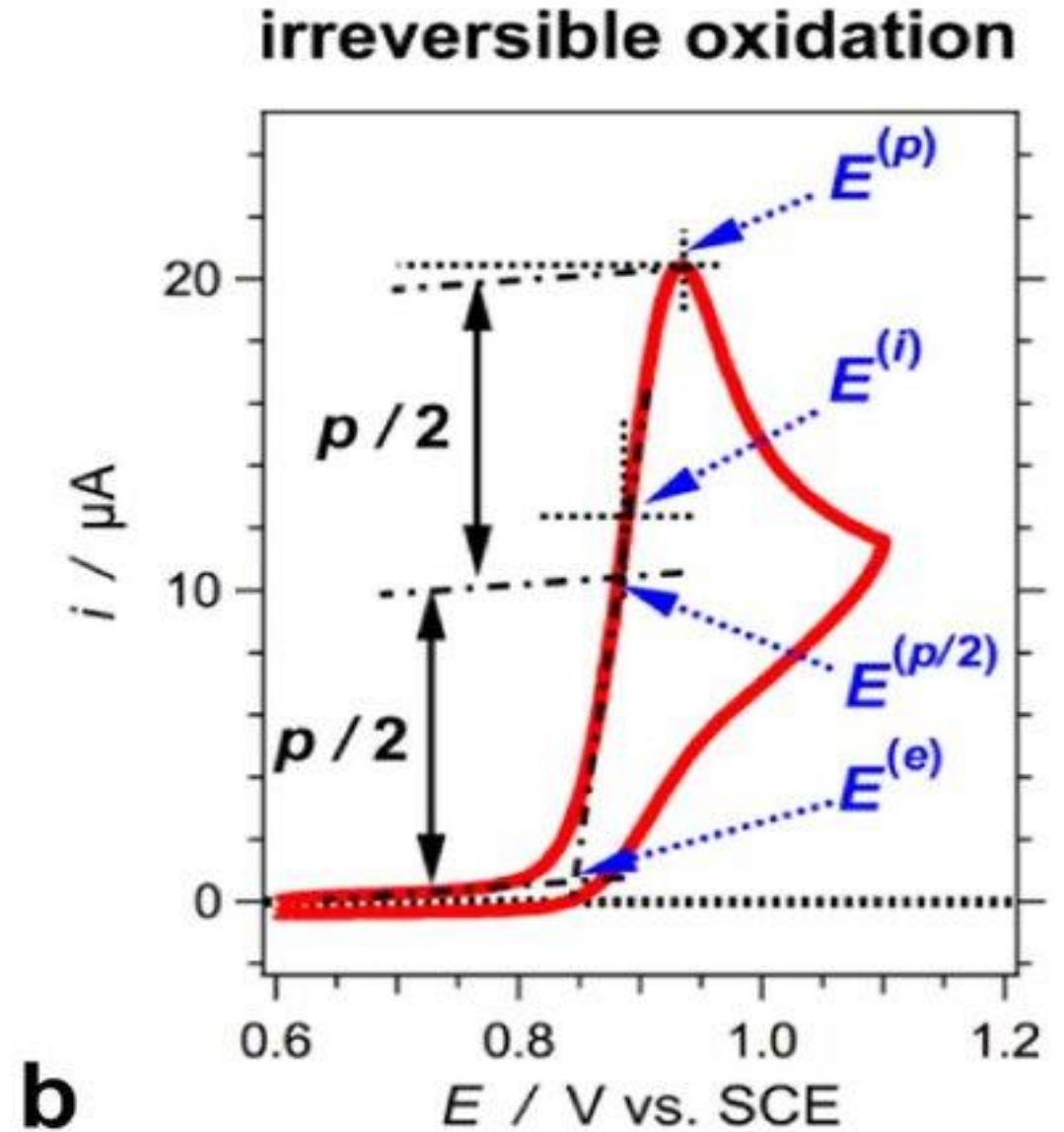
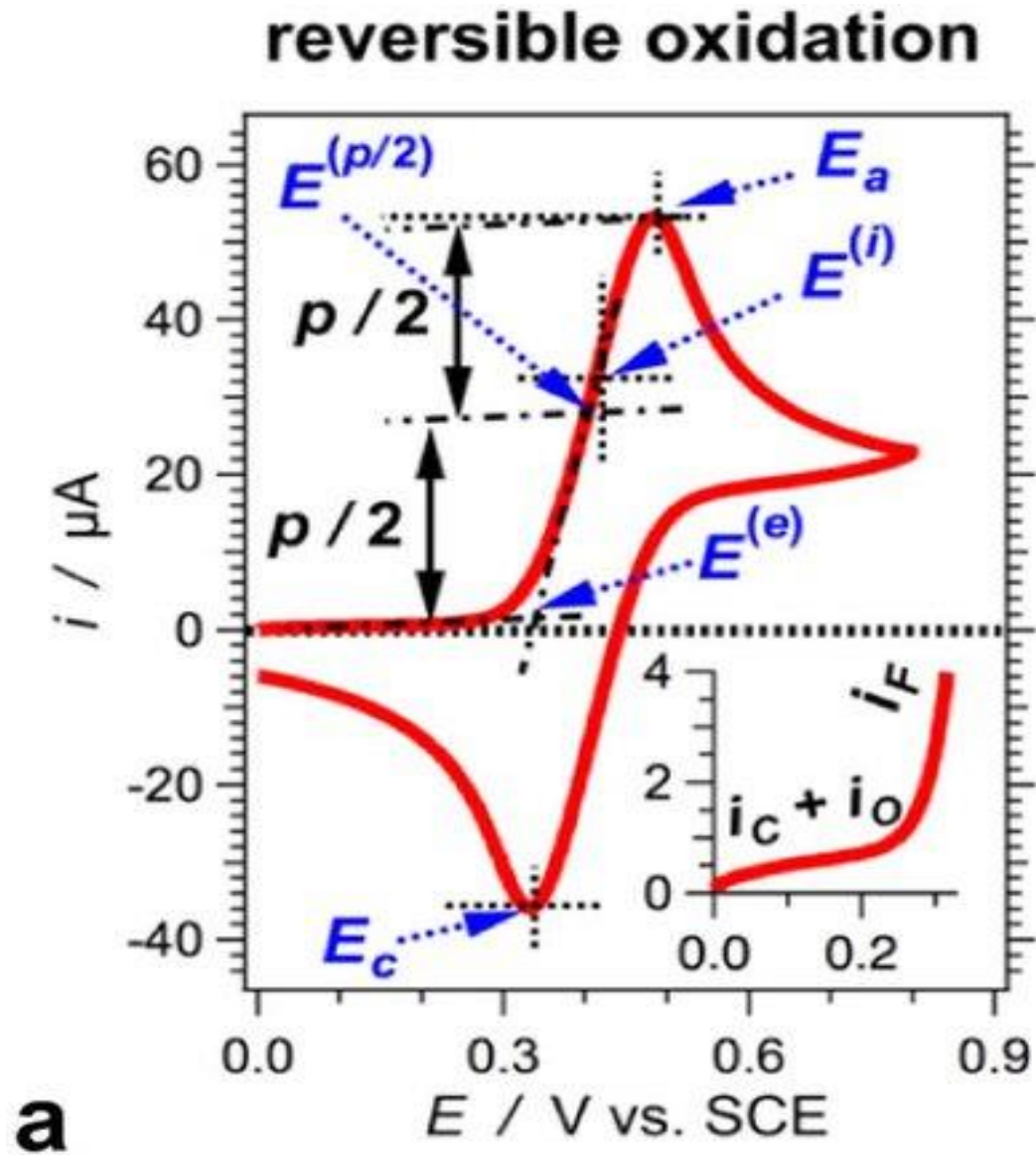
IUPAC Convention



Cyclic voltammograms that feature FAST electron exchange between working electrode and the analyte are often Names with therm REVERSIBLE Voltammograms (a), while those with very slow electron exchange are known as IRREVERSIBLE processes. In between (moderate rate of electron exchange) are depicted as QUASIREVERSIBLE processes



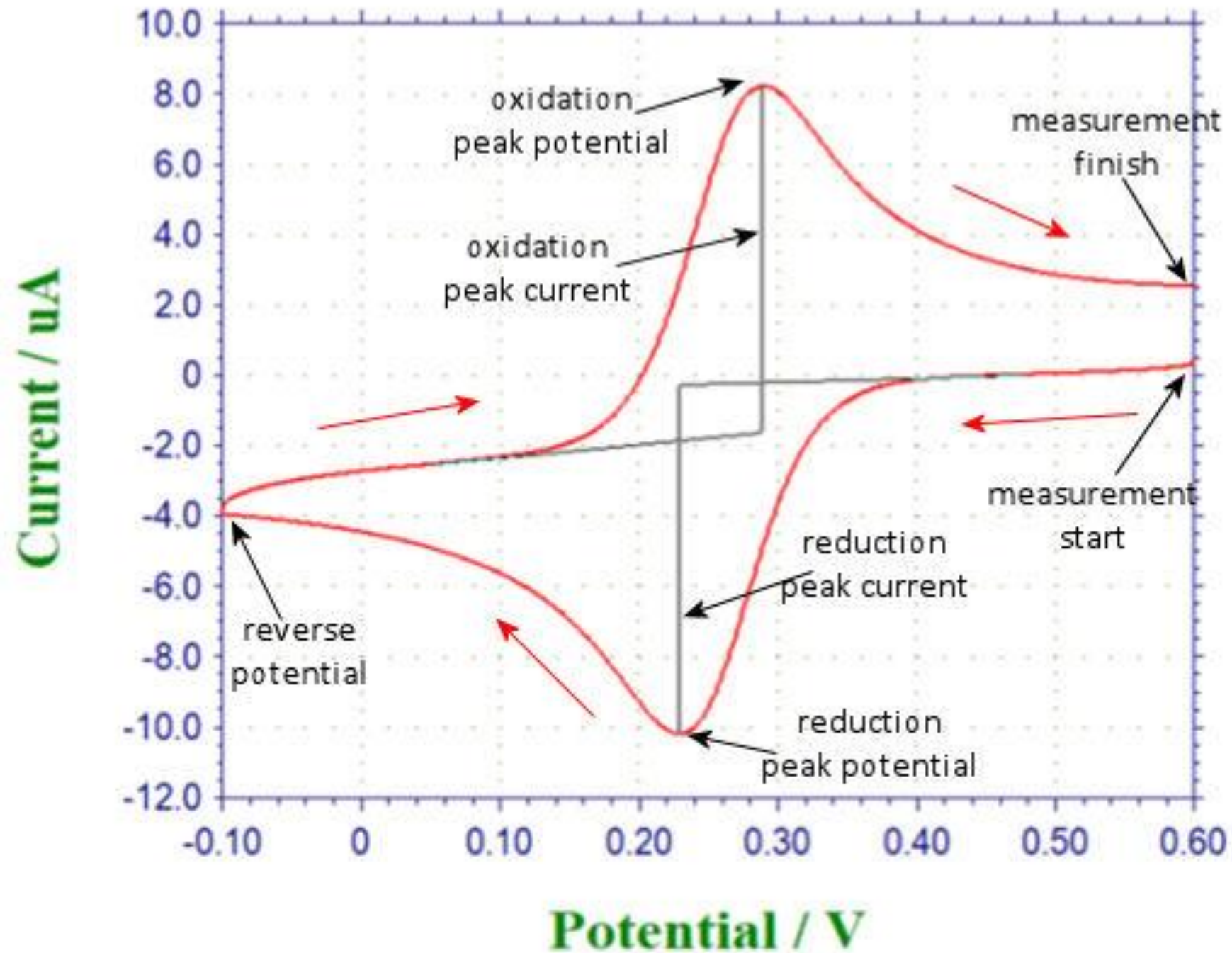
Relevant Parameters at the cyclic voltammograms of Reversible and Irreversible processes



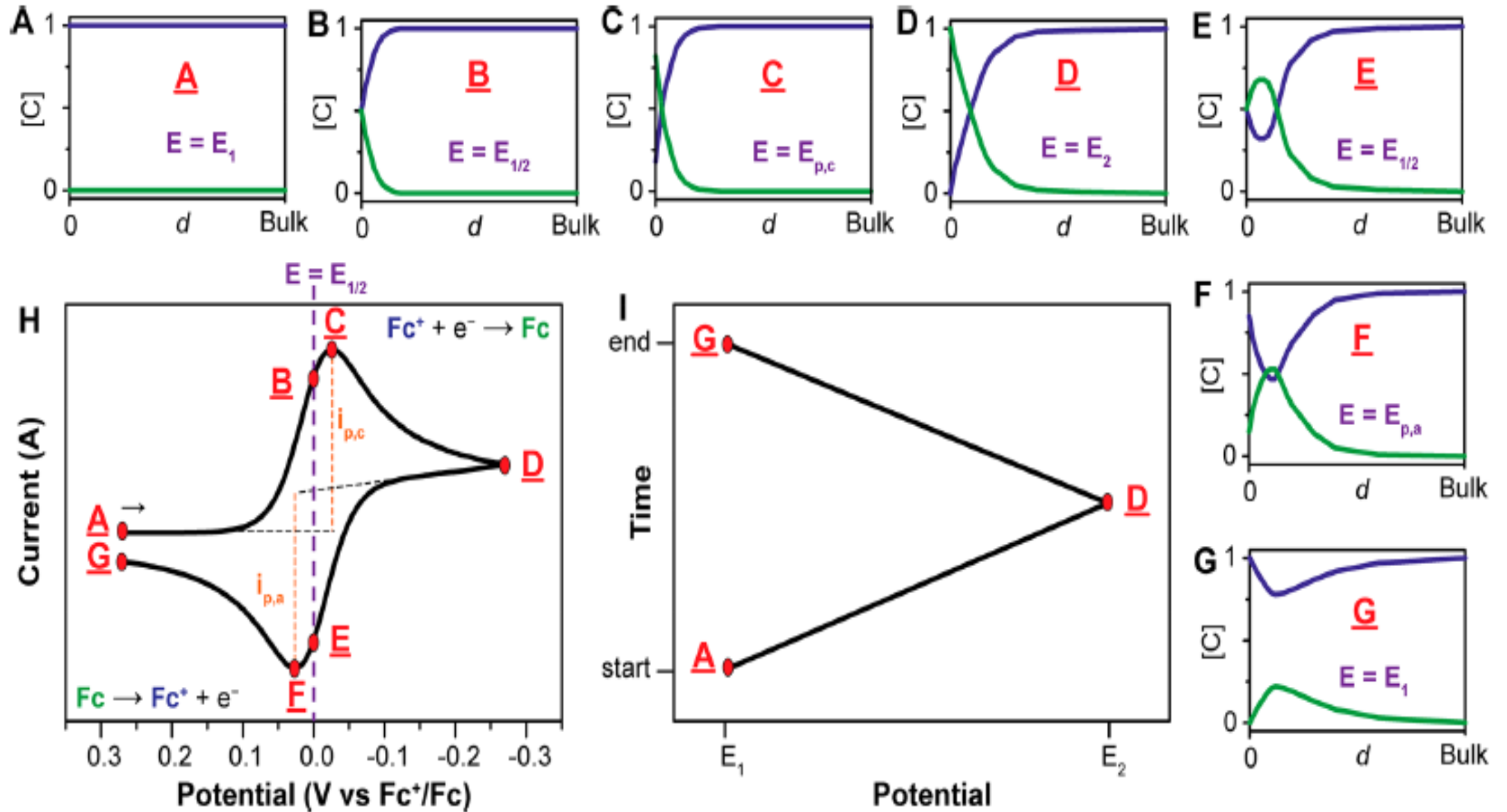
Description of the
Relevant parameters
at cyclic voltammograms

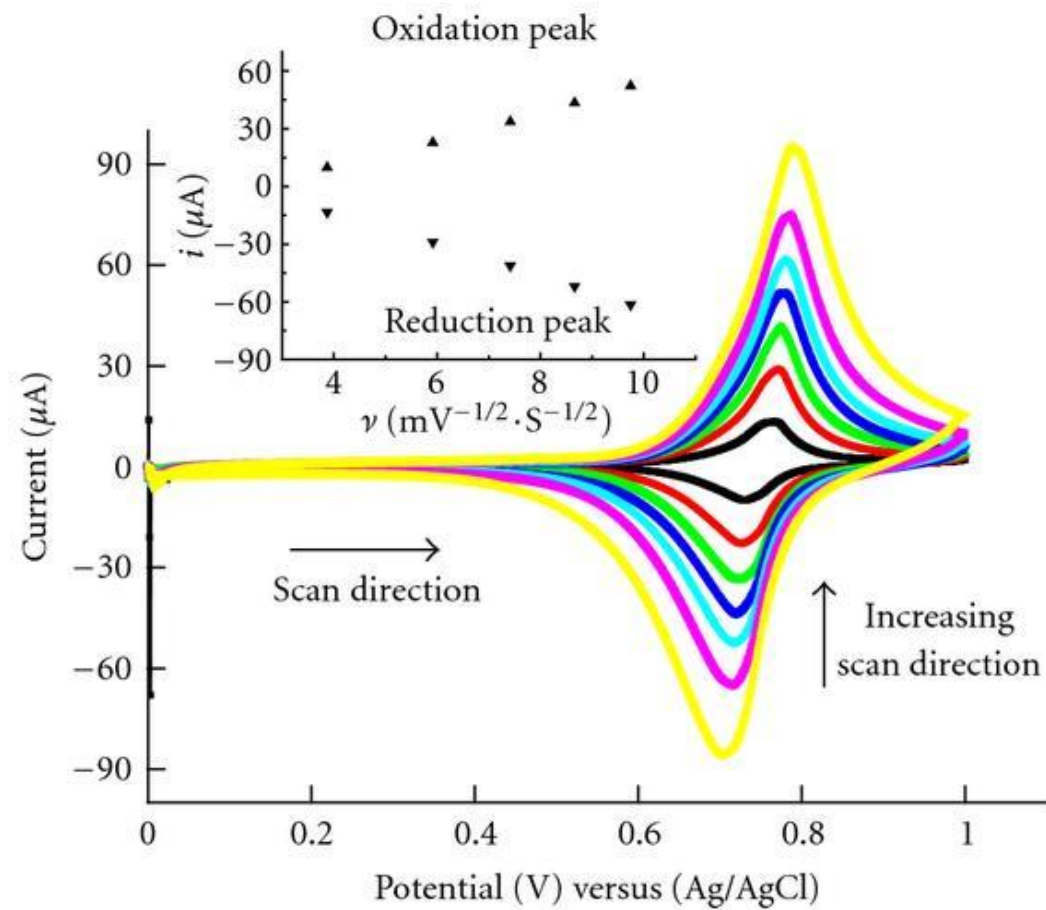
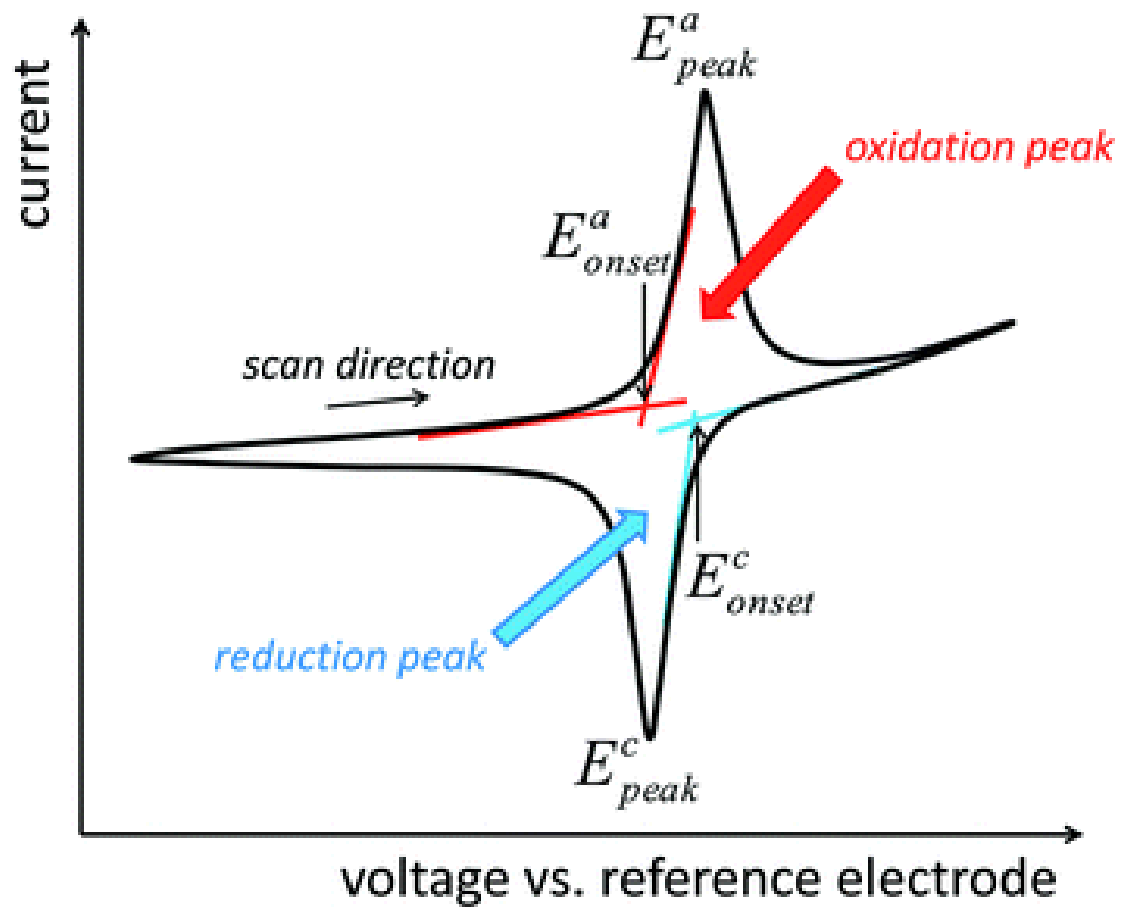
MOST IMPORTANT
THERMODYNAMIC
PARAMETER IS THE
MEDIAN between
Oxidation and the
Reduction potential-
Which is named
MID-PEAK Potential

Current magnitude is
Measure of the
Analyte concentration
And the KINETICS of
Electron exchange

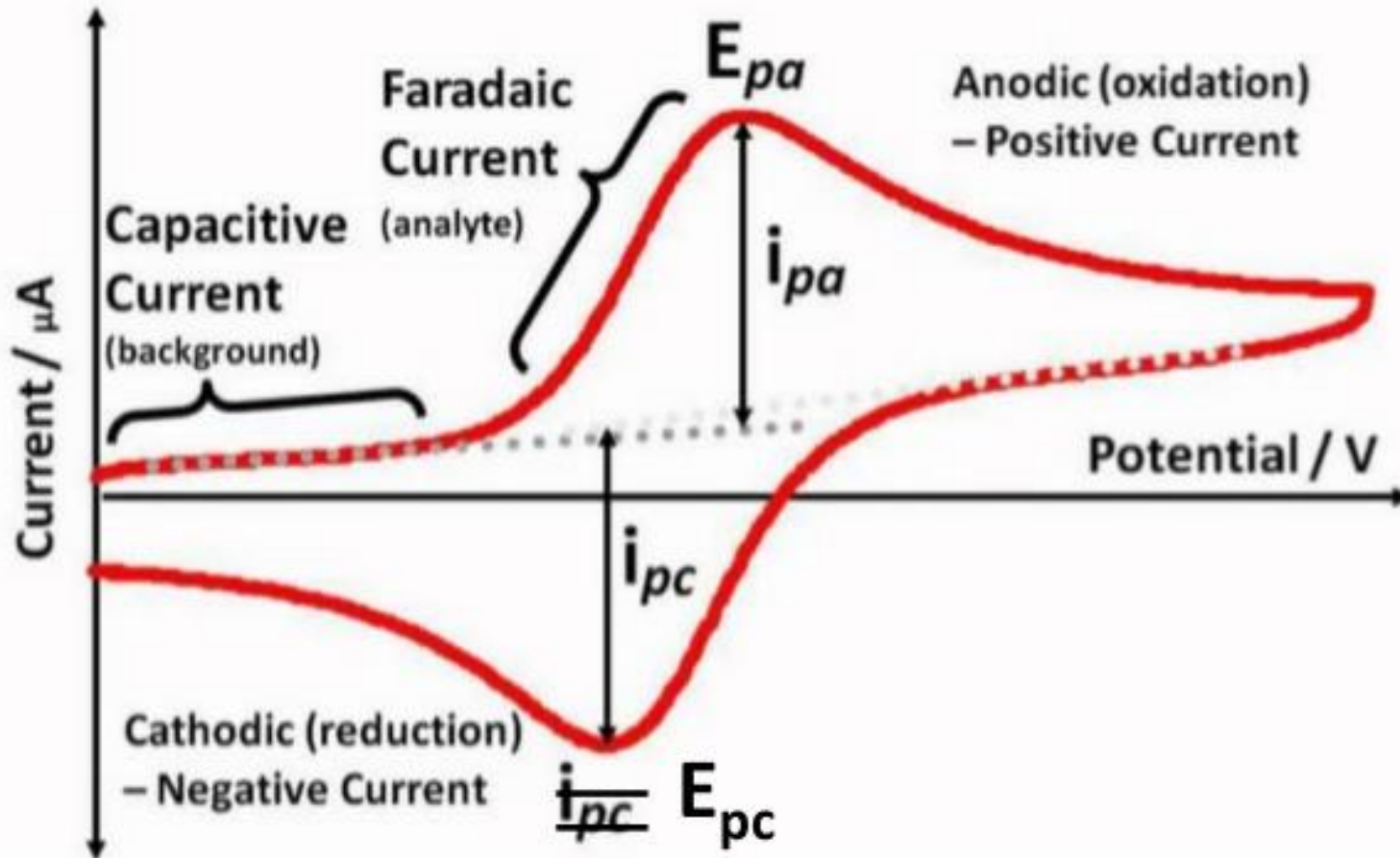


Description of the all relevant segments of the cyclic voltammogram at every important potential

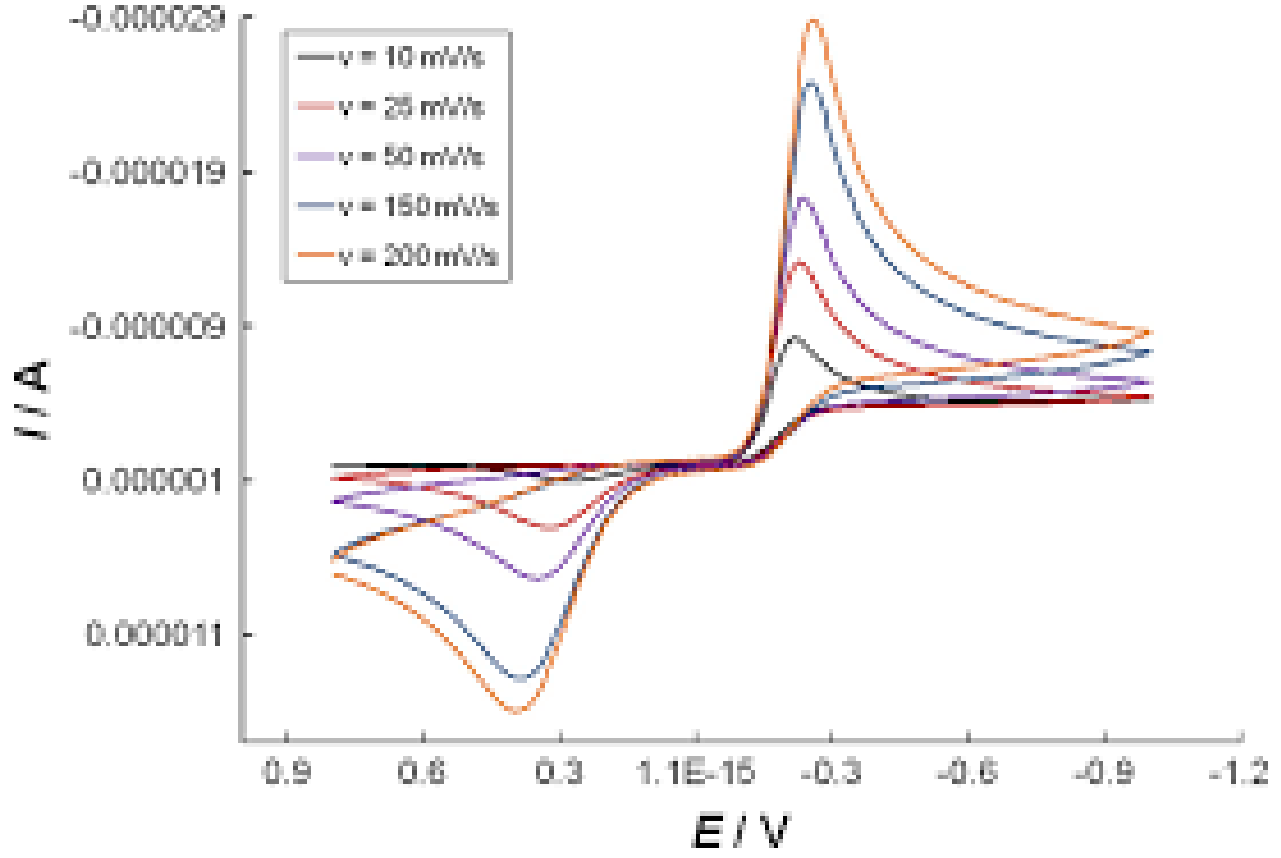
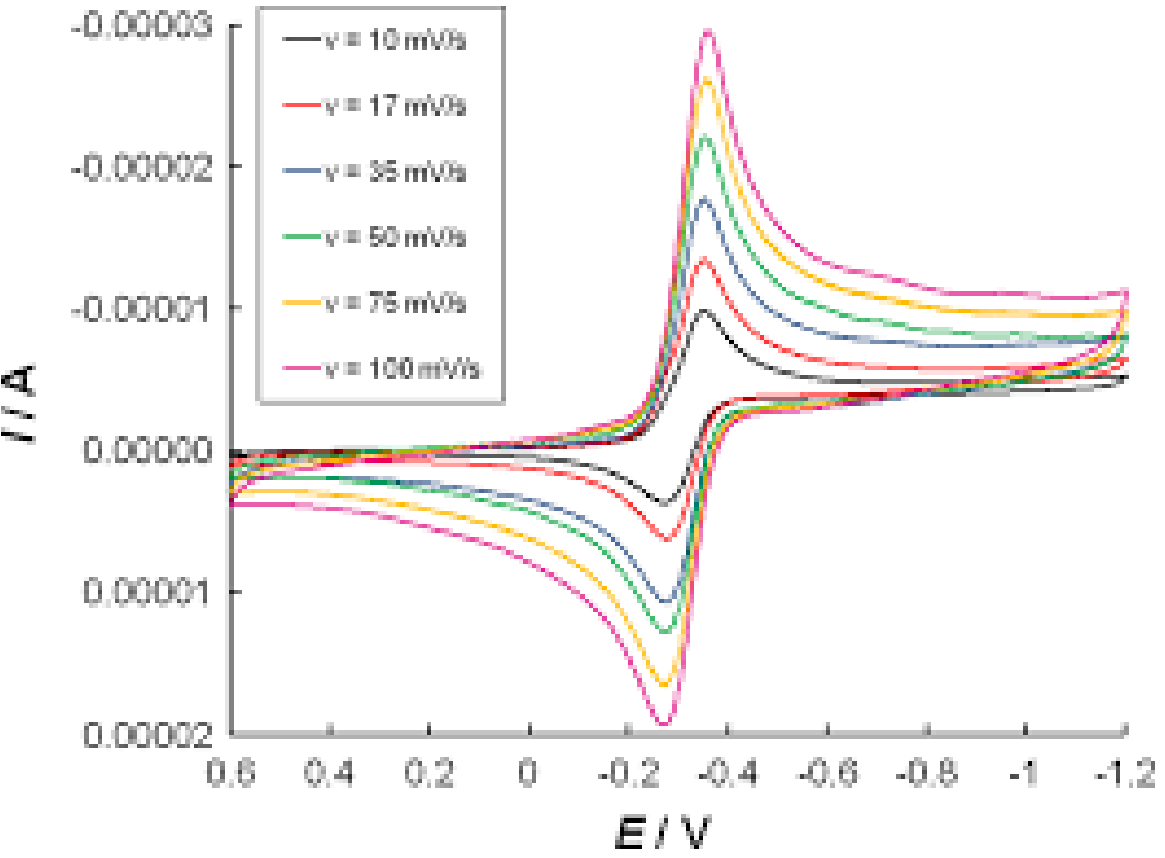




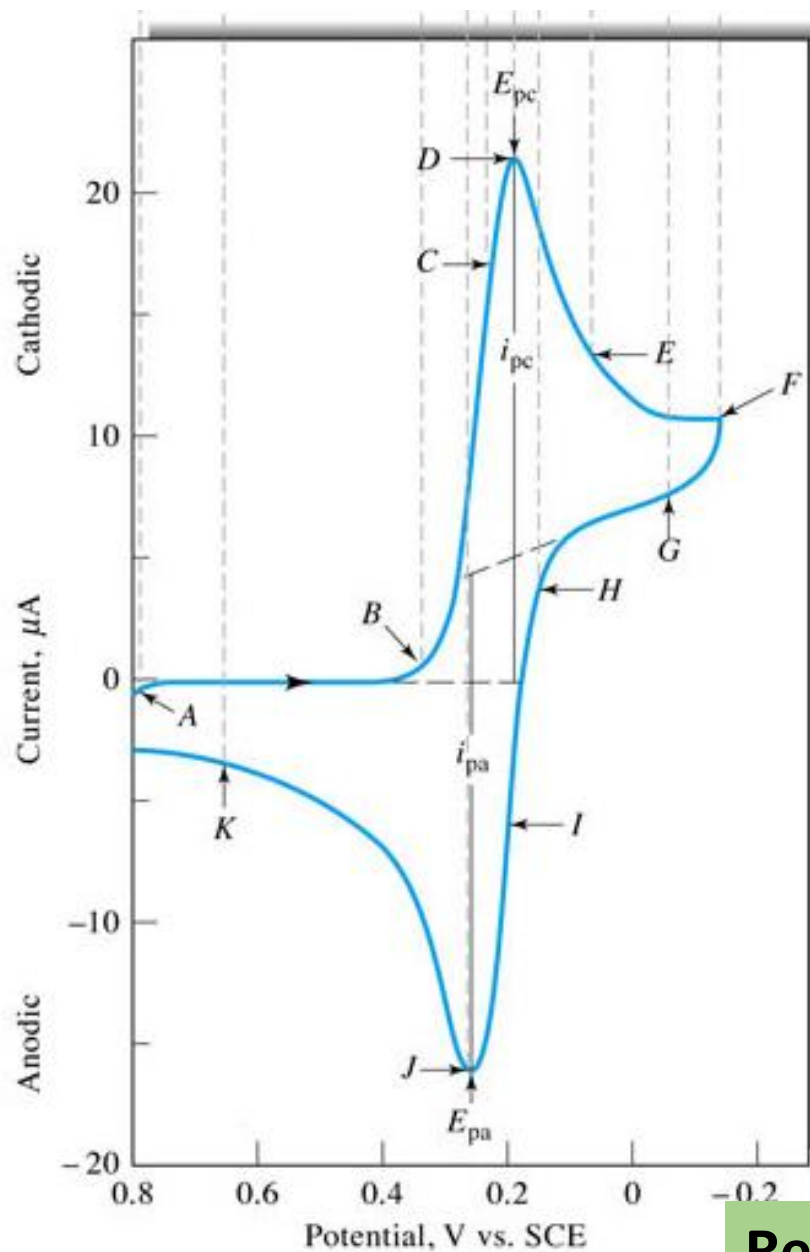
Cyclic Voltammogram



EXPERIMENTAL REVERSIBLE CYCLIC VOLTAMMOGRAMS



What do we get from cyclic voltammograms



< i_{pc} and i_{pa}

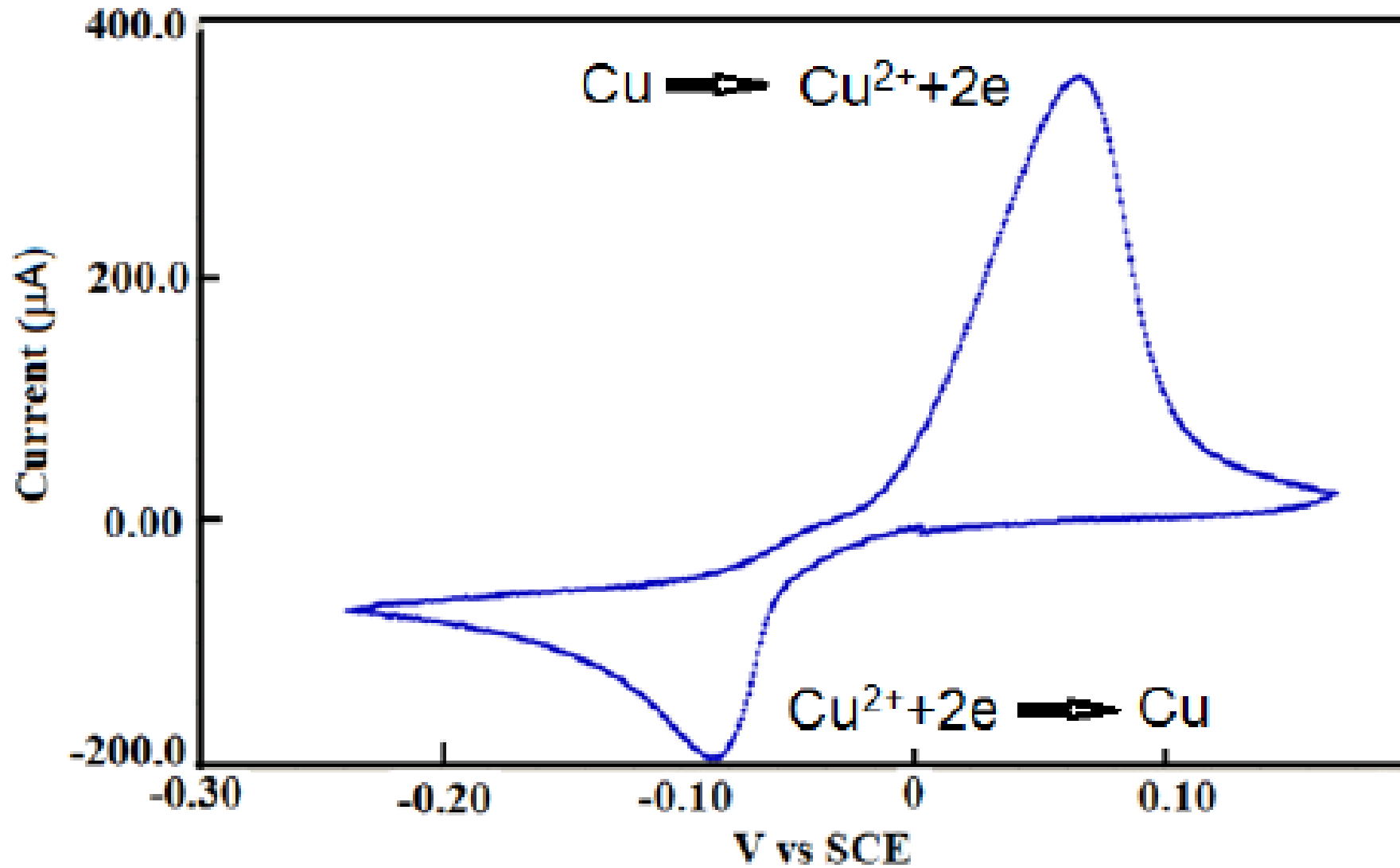
☐ $\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$,
n = number of electrons exchanged

< $E^0 = \text{mid-peak potential } E_{pa} \rightarrow E_{pc}$

< $I_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$

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

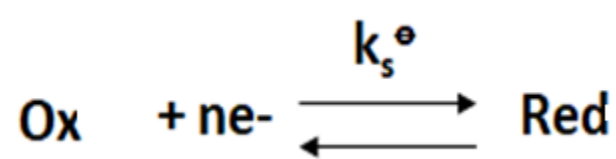
Reversible electrode reaction



Quasireversible electrode reaction

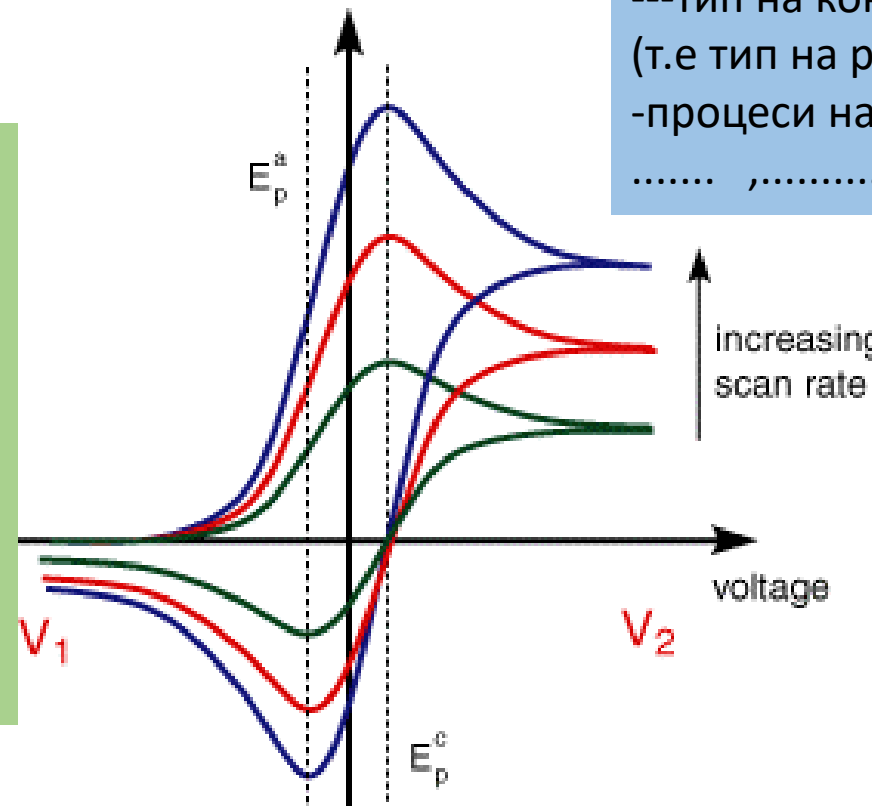
Electrode Mechanisms coupled with chemical Reactions-easily studied with Cyclic voltammetry

E-MECHANISM... E means Electrochemical „
EC-MECHANISM/..... „C„ ОЗНАЧУВА „ХЕМИСКИ„
CE-MECHANISM
EC' REGENERATIVE MECHANISM---
 where C' means regenerative or catalytic

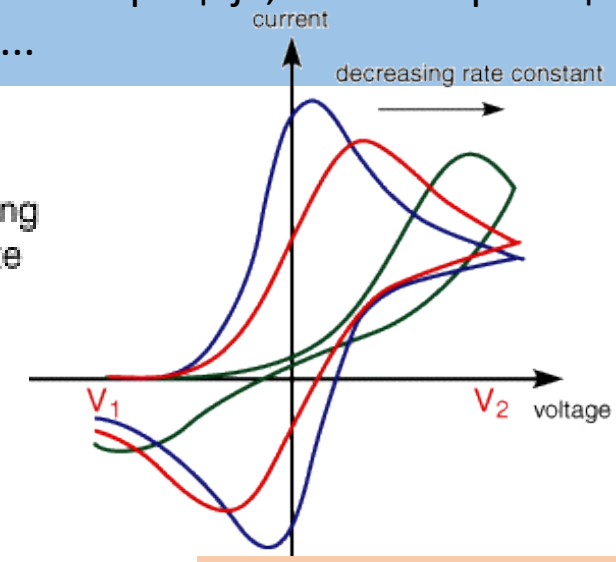


ТРЕБА ДА ЗНАЕМЕ
 ---кинетиката на сите хемиски реакции зависи од
 -концентрација на реактанти
 -температура
 -катализатори
 -pH (многу често)
 -природа на површина на кои се одвива реакција
 ---ВО ЕЛЕКТРОХЕМИЈА ЗАВИСИ кинетиката
 На ЕЛЕКТРОДНИТЕ РЕАКЦИИ ЗАВИСИ и од
ПОТЕНЦИЈАЛОТ!!!

Reversible electrode Reaction

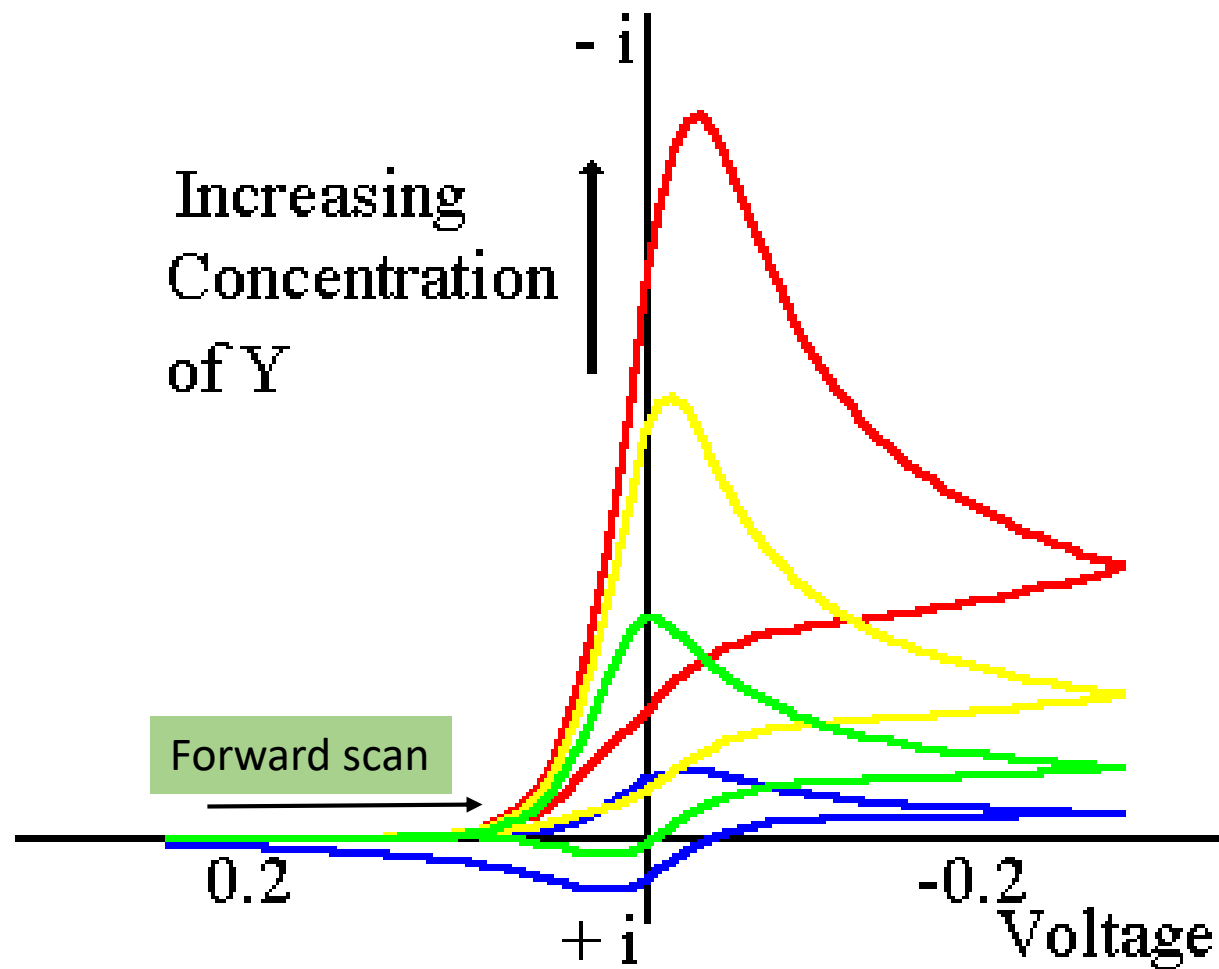
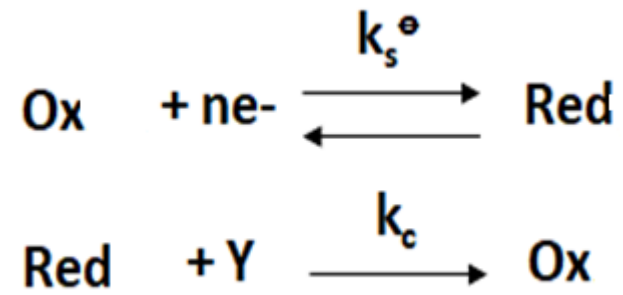


ЗА ДА ЗНАЕМЕ ДА ГО РАЗБЕРЕМЕ
 ФУНДАМЕНТОТ НА СЕКОЈА ЕДНА
 ФИЗИЧКА МЕТОДА ТРЕБА ДА ЗНАЕМЕ
 ДЕКА СИТЕ ФЕНОМЕНИ ШТО СЕ
 МАНИФЕСТИРААТ ВО
ЕЛЕКТРОХЕМИСКИТЕ МЕТОДИ се
ПОВРЗАНИ НА НЕКОЈ НАЧИН
 ---со ЕНЕРГИЈАТА НА ЕЛЕКТРОНИТЕ
 ---со транспортот на МАСА
 ...НО И СО
 ---тип на кондуктивен материјал
 (т.е тип на работна електрода)
 -процеси на адсорпција, хемиски реакции
 ,.....

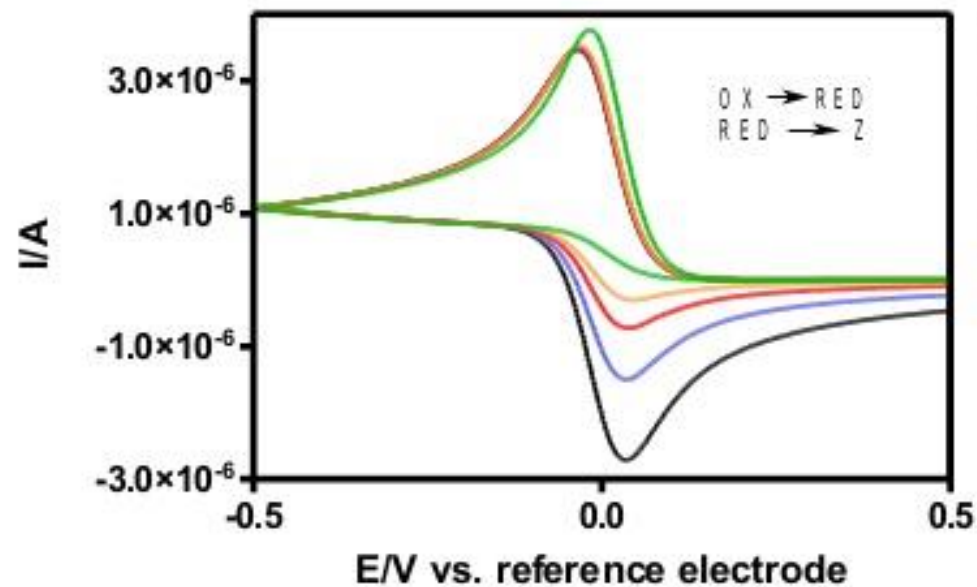


Irreversible electrode reaction

EC' MECHANISM



THE EC MECHANISM



Black: $k_f=0 \text{ cm.s}^{-1}$
 Blue: 0.2
 Red: 0.5
 Orange: 1
 Green: 10

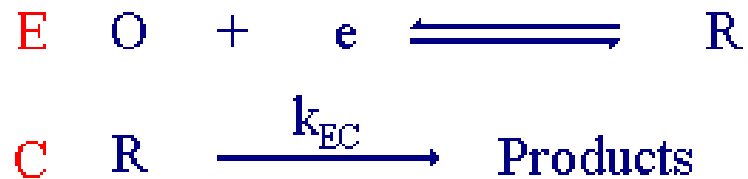
There are many variations of this mechanism:

Reaction with solvent

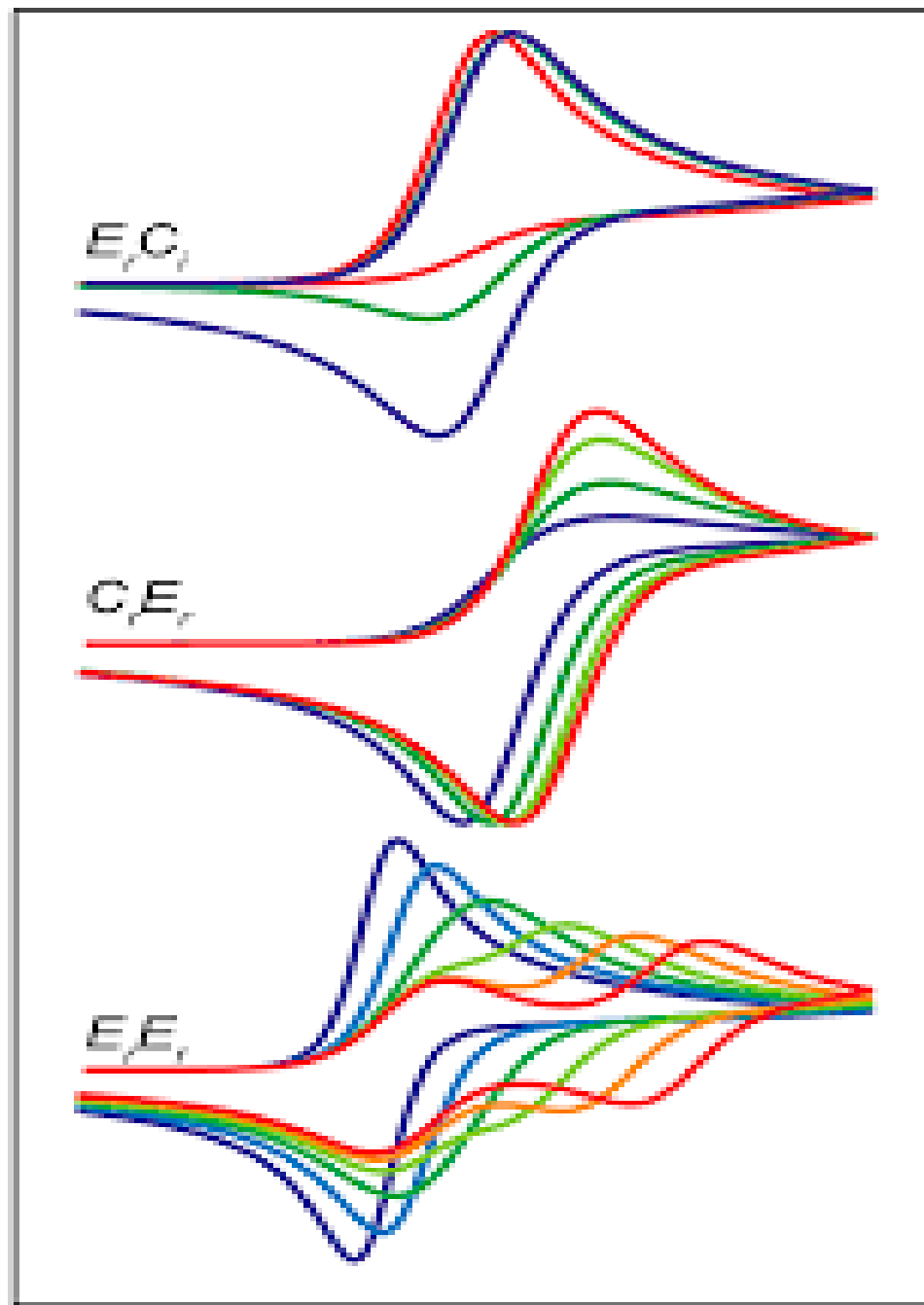
Dimerization

Radical substrate reaction

EC catalytic ... etc.

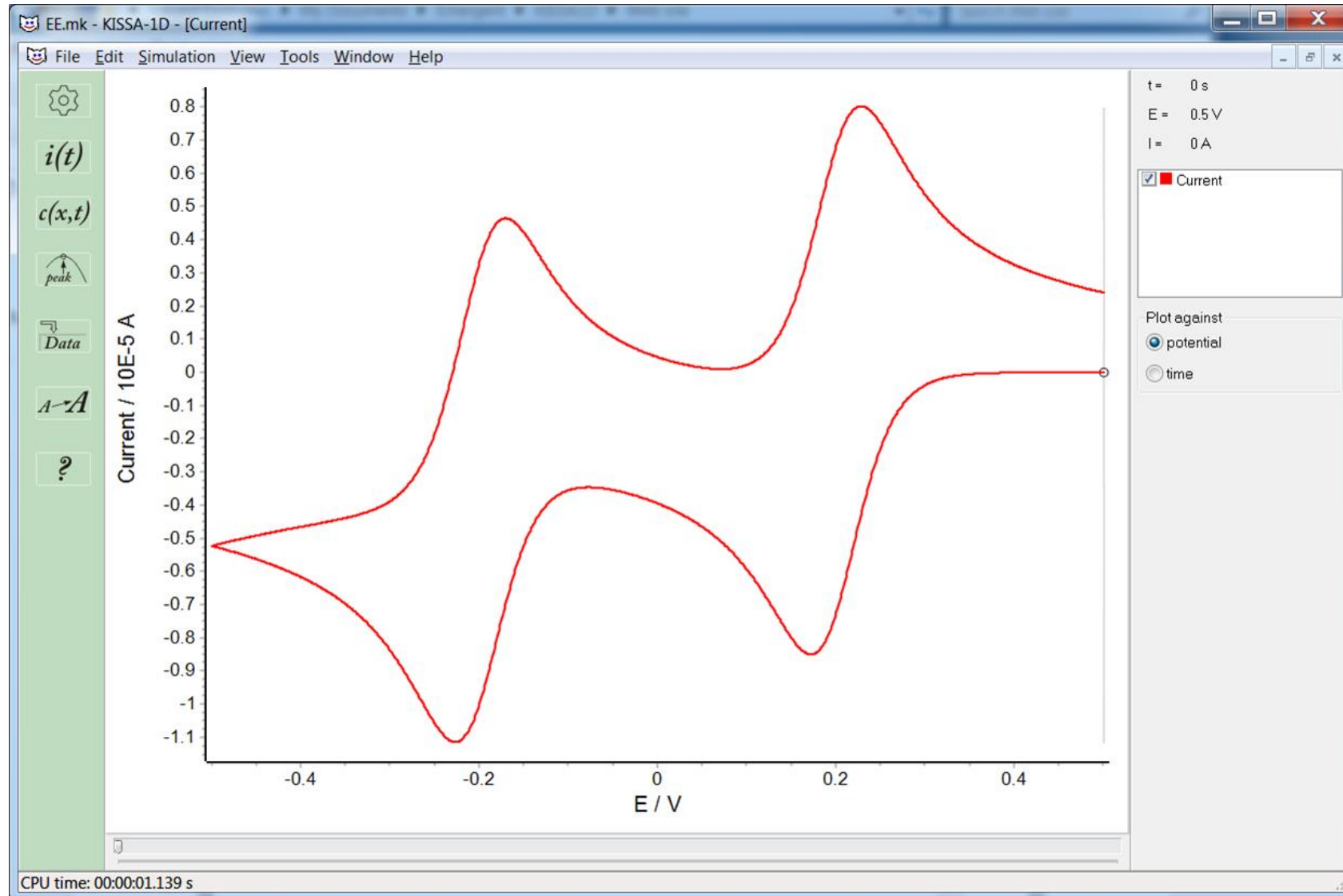


Current



Potential

ECE MECHANISM



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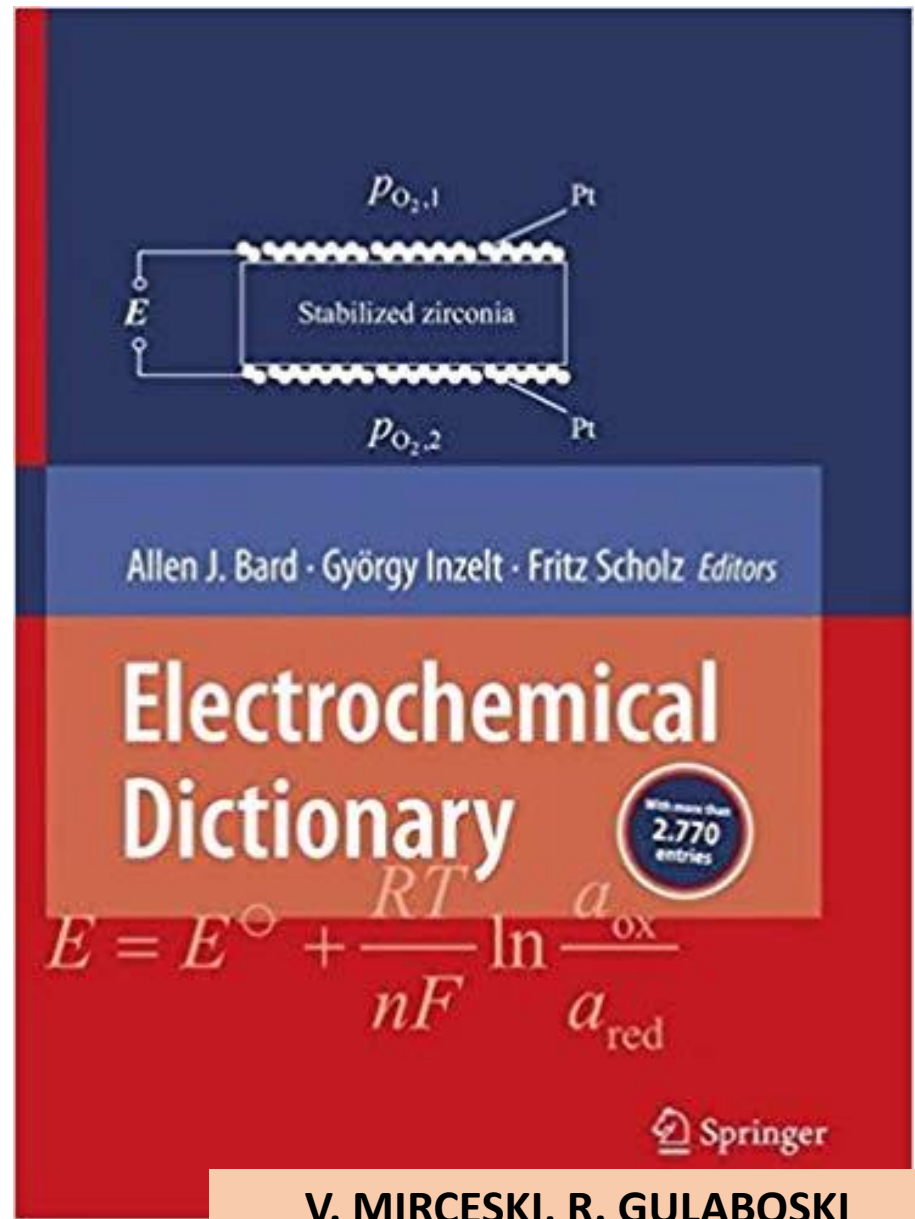
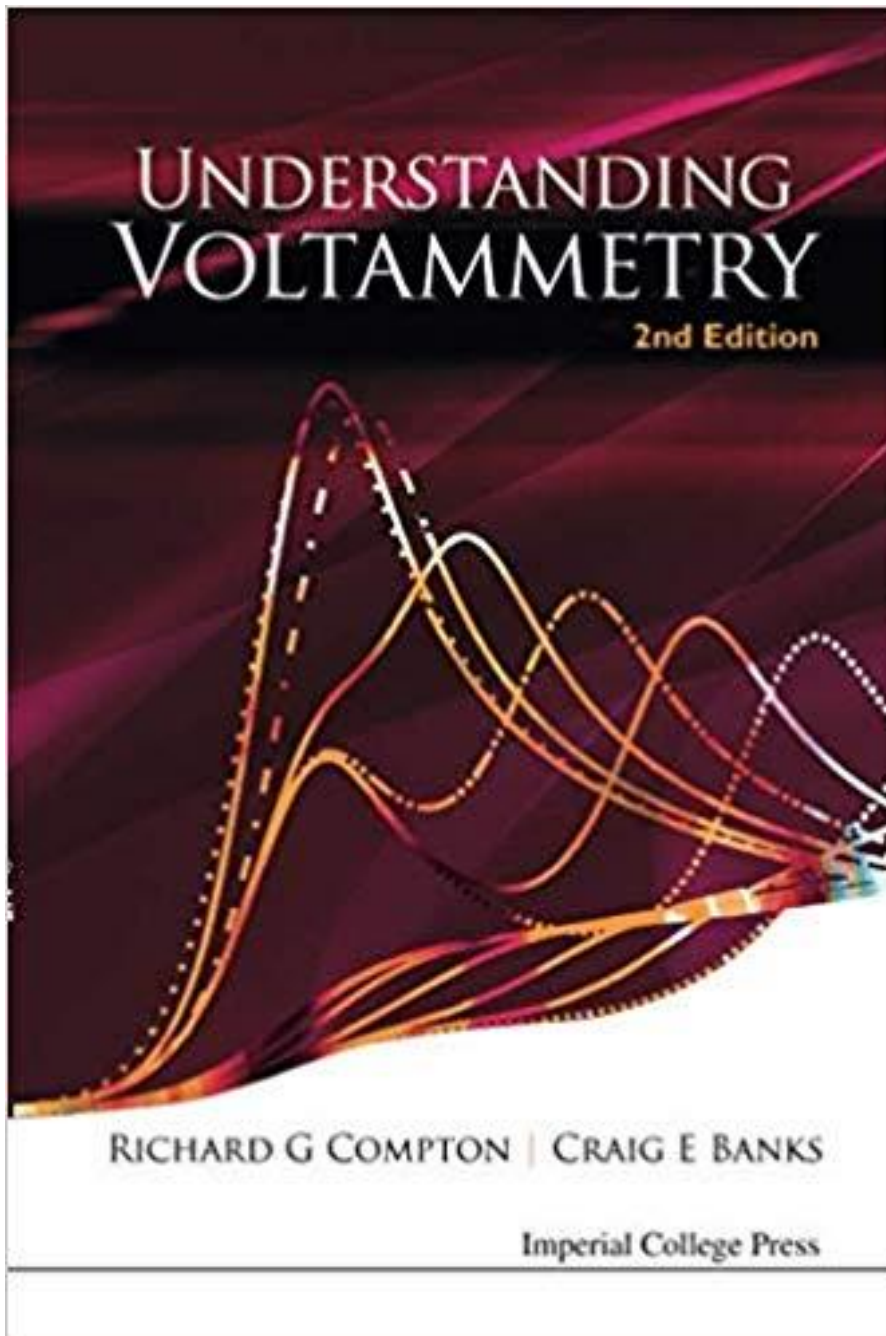
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V. MIRCESKI, R. GULABOSKI
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