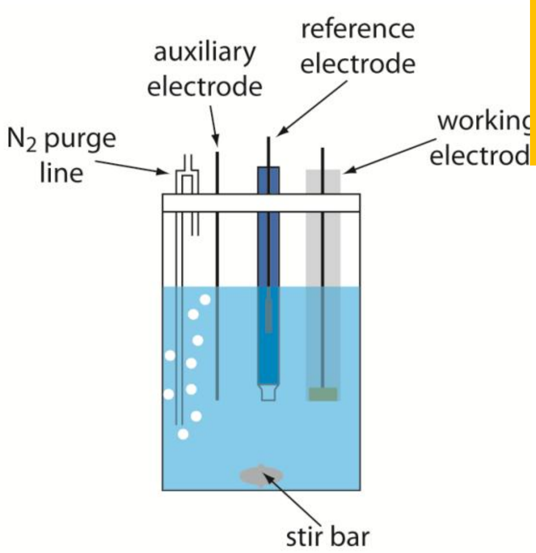
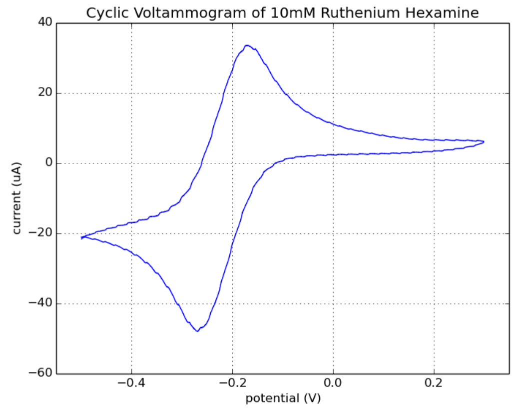
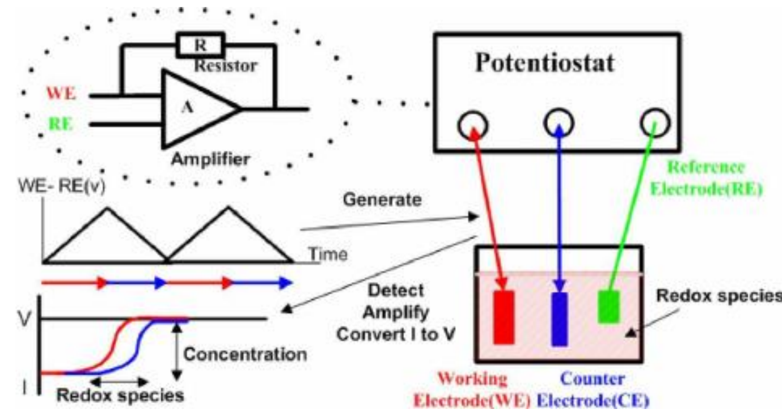
VOLTAMMETRY OF MOST COMMON SURFACE REDOX MECHANISMS

Rubin Gulaboski



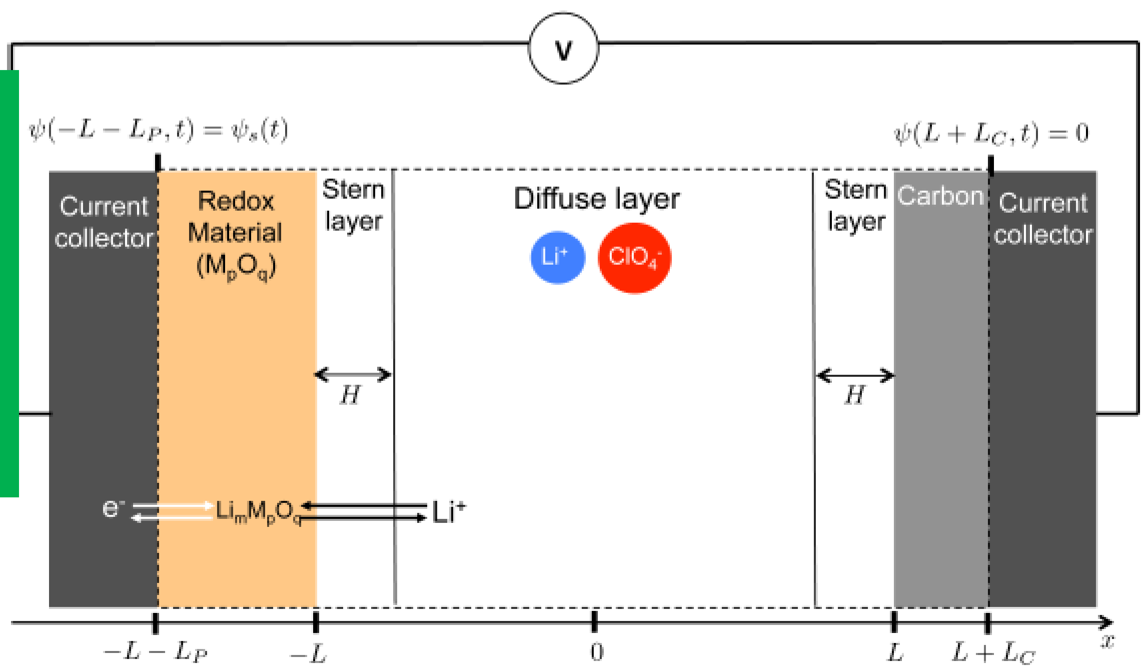




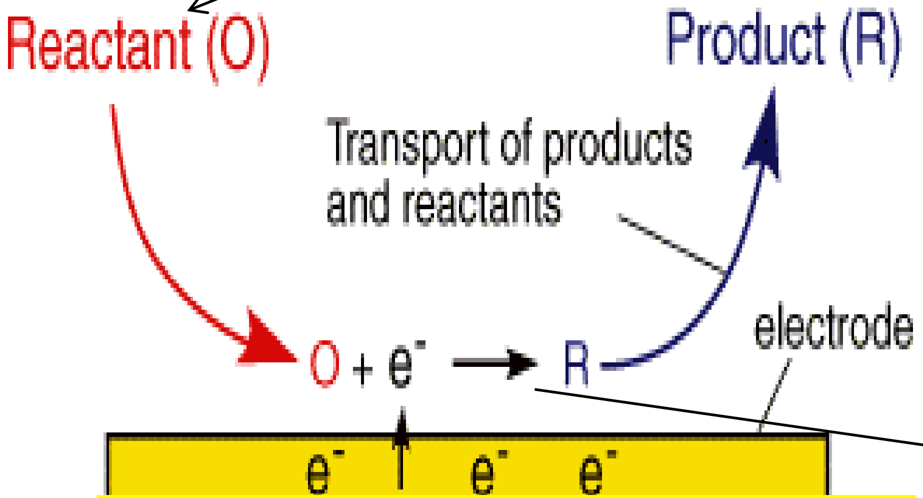
Volt-Am-Metry

Volt-Amper-Metry

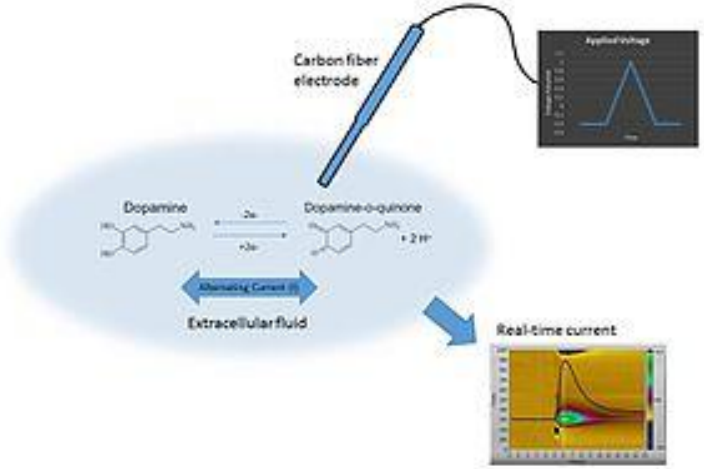
Apply Potential And Measure Current



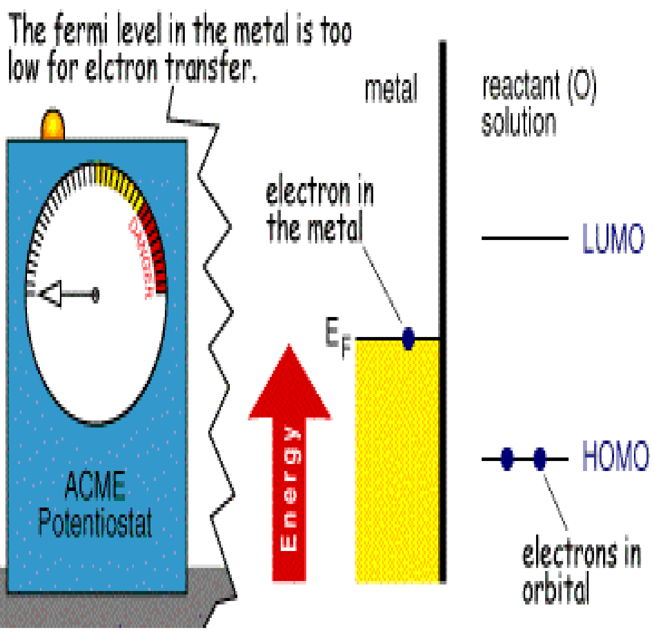
„O“-e reaktant prisuten vo rastvor

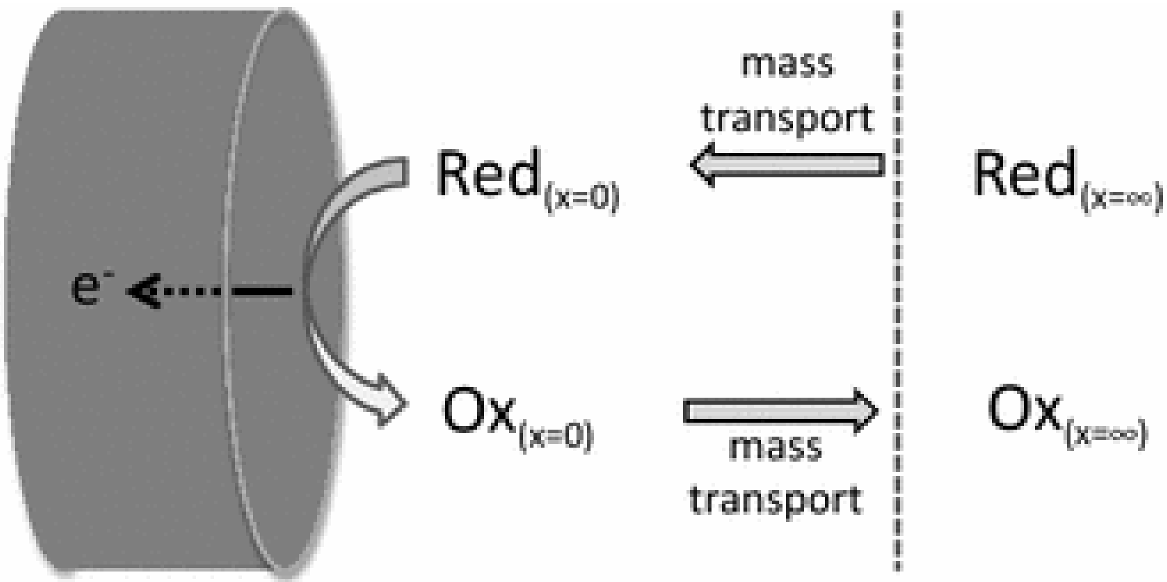


Working electrode
e- →travel from electrode towards „O“



Electron transfer between electrode and “O” analyte

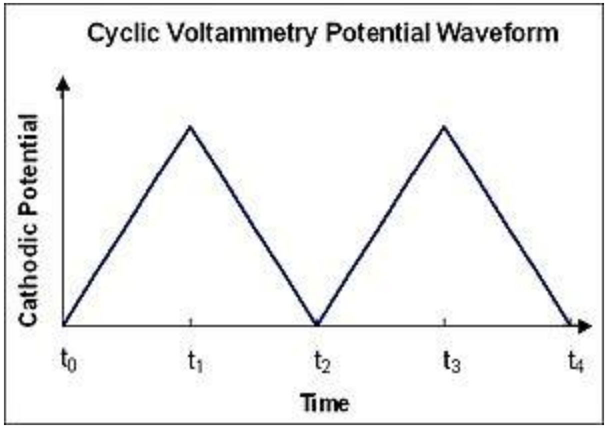


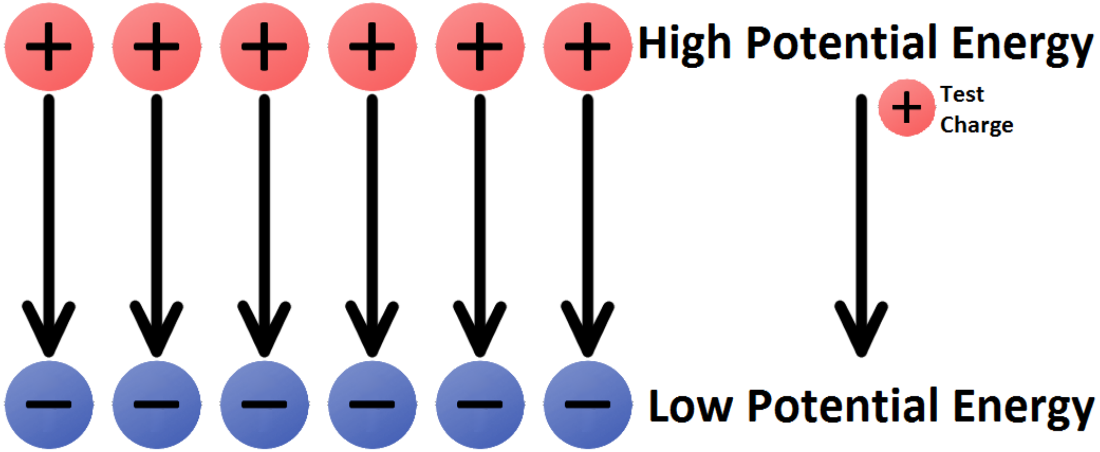


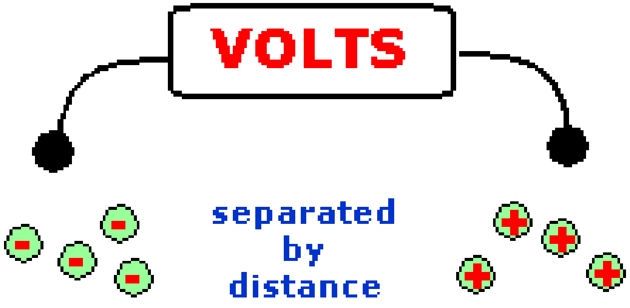
What is THE ELECTRICAL POTENTIAL?

Electrical potential (or electrical potential difference) is simply the MEASURE OF the ENERGY of ELECTRONS flowing between two systems that are close to eachother

By changing the electrode potential, we actually affect the energy (velocity)of ELECTRONS from the outher surface of a given electrode vs their environment







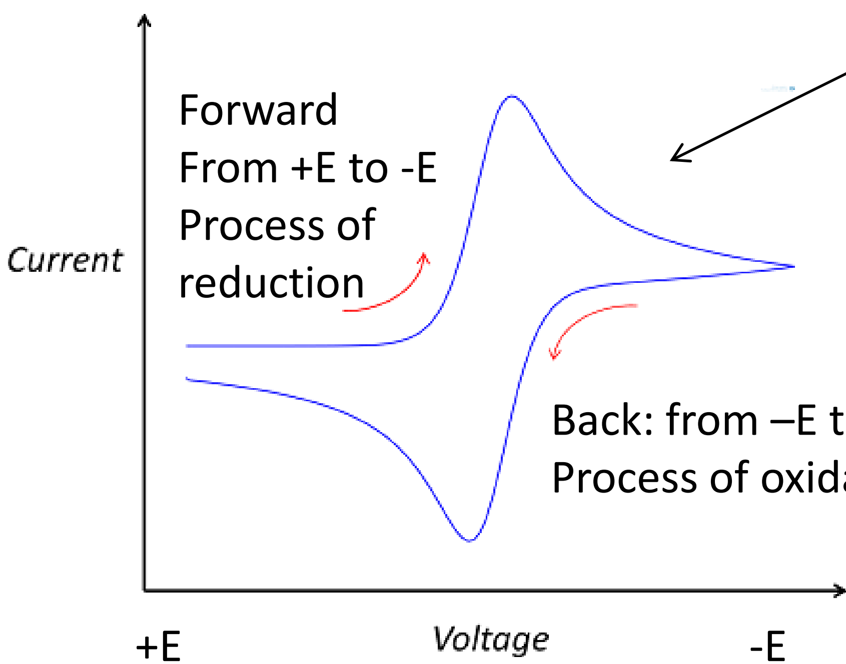
Cyclic Voltammetry

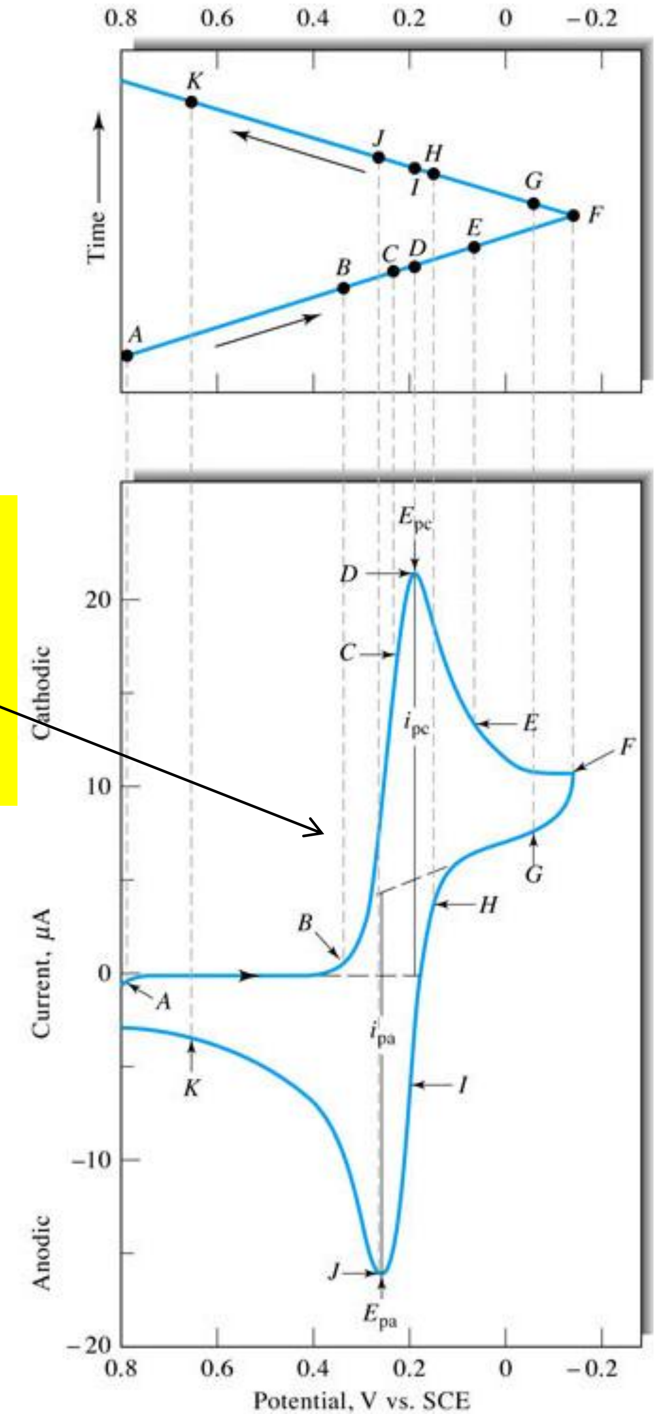
1) is a voltammetric Method used to look at mechanisms of redox reactions in solution.

…but also for thermodynamic and kinetic measurements

2) triangular potential waveform for excitation

Cyclic voltammogram of a reversible redox reaction of simple diffusional Redox reaction

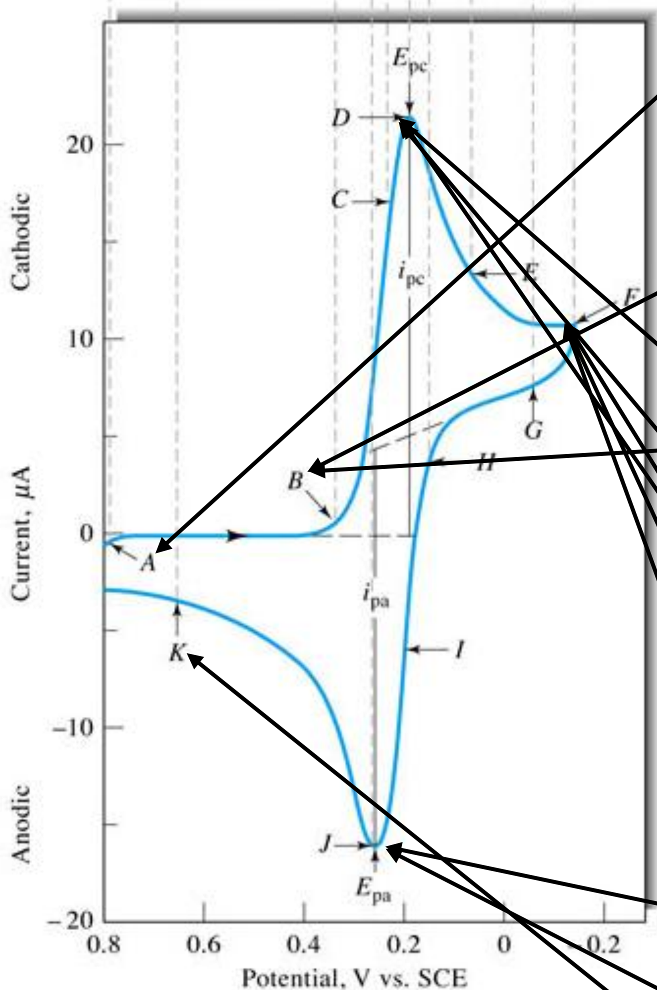




Practical Example: reduction of K3[Fe(CN)6]; explanation on what happens at every potential

Working Electrode is Pt & Reference electrode is SCE

6 mM $K_3Fe(CN)_6$ & 1 M KNO_3



A. Initial negative current due to oxidation of H_2O to give O_2

No current between A & B (+0.7 to +0.4V) no reducible or oxidizable species present in this potential range

B. At 0.4V, current begins because of the following reduction at the cathode:

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

B.-D. Rapid increase in current as the surface concentration of $Fe(CN)_6^{3-}$ decreases

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

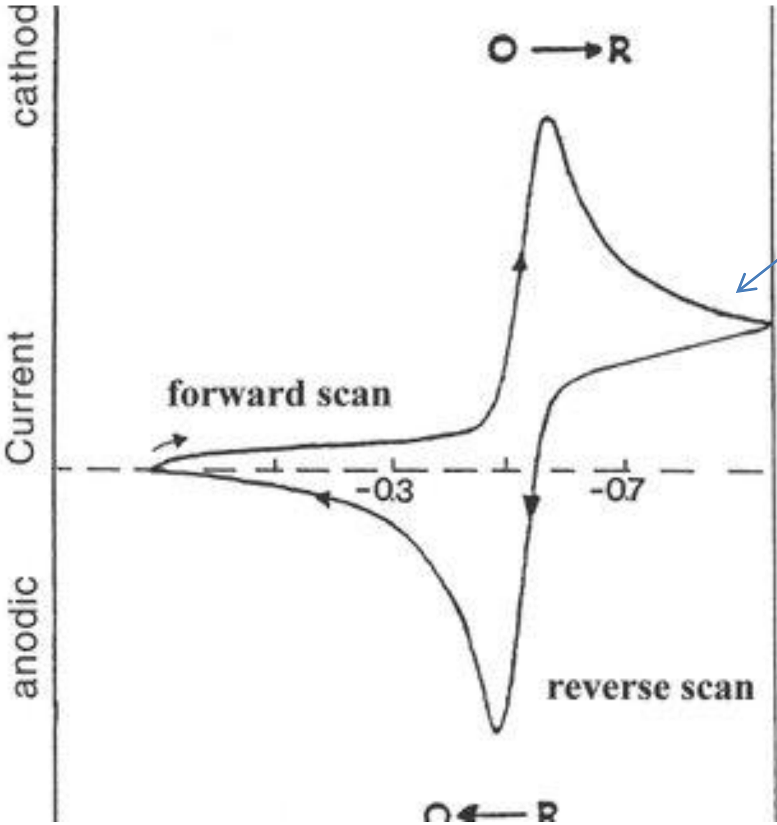
D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface

F. Scan direction switched (-0.15V), potential still negative enough to cause reduction of $Fe(CN)_6^{3-}$

F.-J. Eventually reduction of $Fe(CN)_6^{3-}$ no longer occurs and anodic current results from the reoxidation of $Fe(CN)_6^{4-}$

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

K. Anodic current decreases as the accumulated $Fe(CN)_6^{4-}$ is used up at the anodic reaction



Redox reakcii so DIFUZIJA kako forma na transfer na masa

ZABELEZI GI RAZLIKITE POMEGJU OVIE DVA VIDA NA VOLTAMOGRAMI!!!

POVRSINSKi (SURFACE) redox reakcii-NEMA DIFUZIJA!!

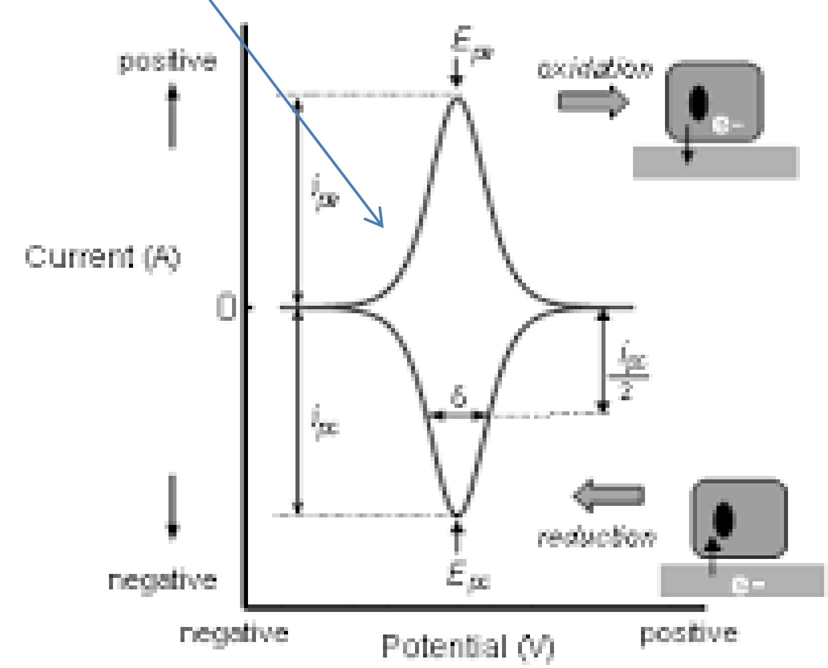
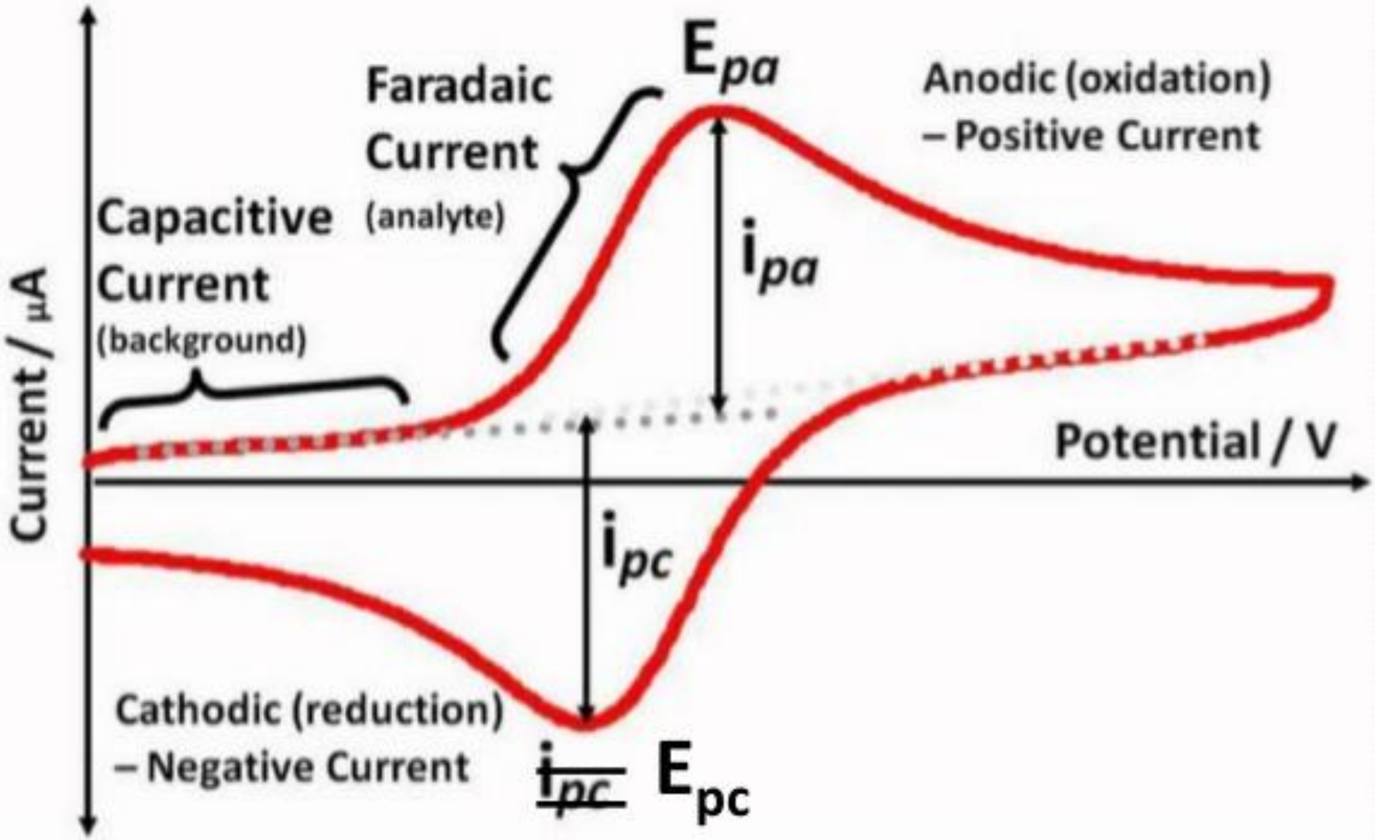
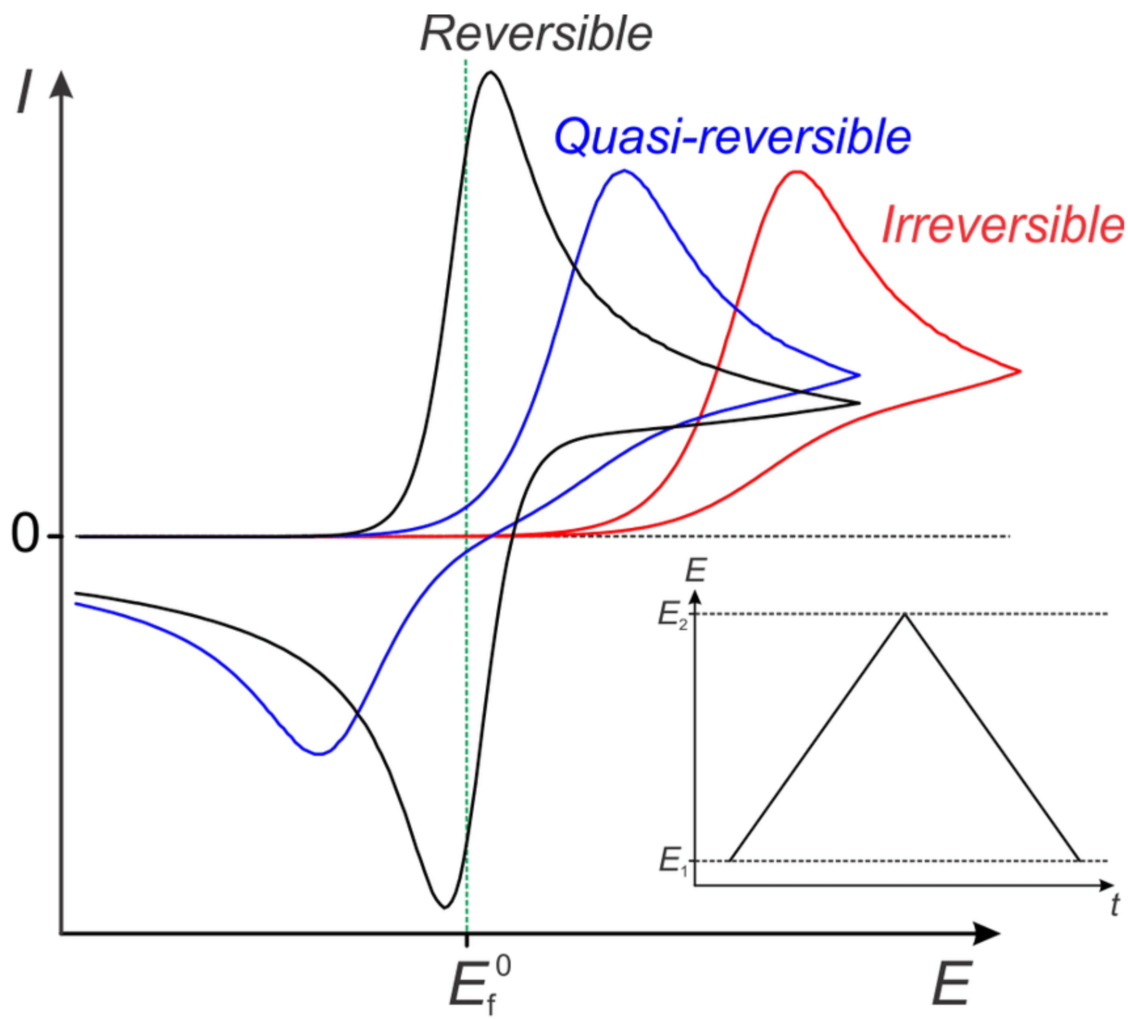


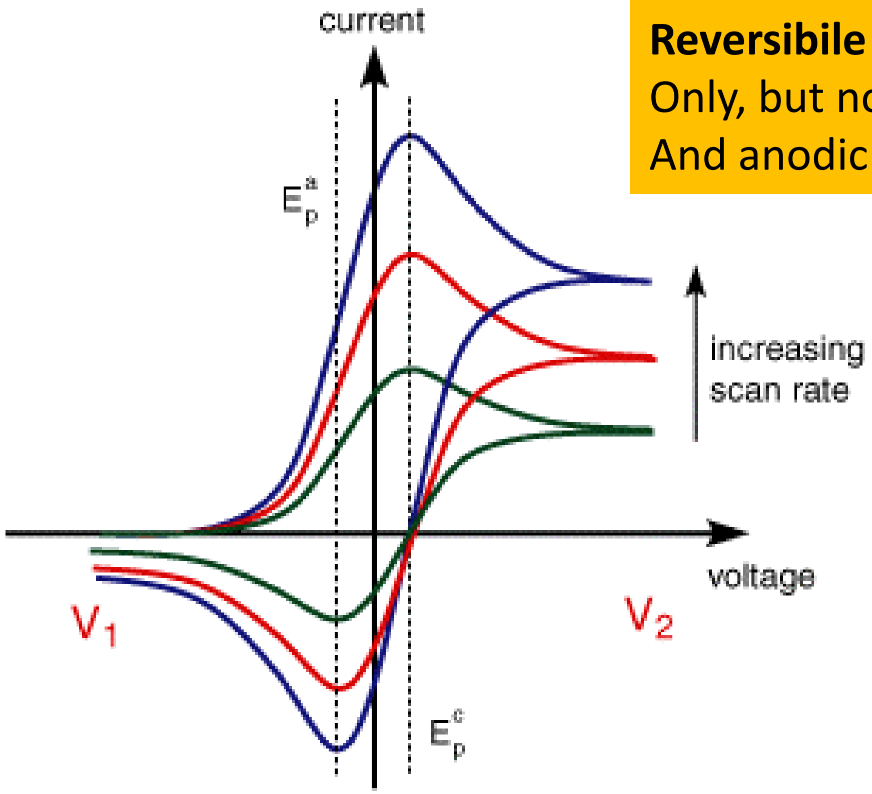
Figure 2. Cyclic voltammetric response from a film of adsorbed protein containing a single redox active centre undergoing reversible electron transfer.

Cyclic Voltammogram

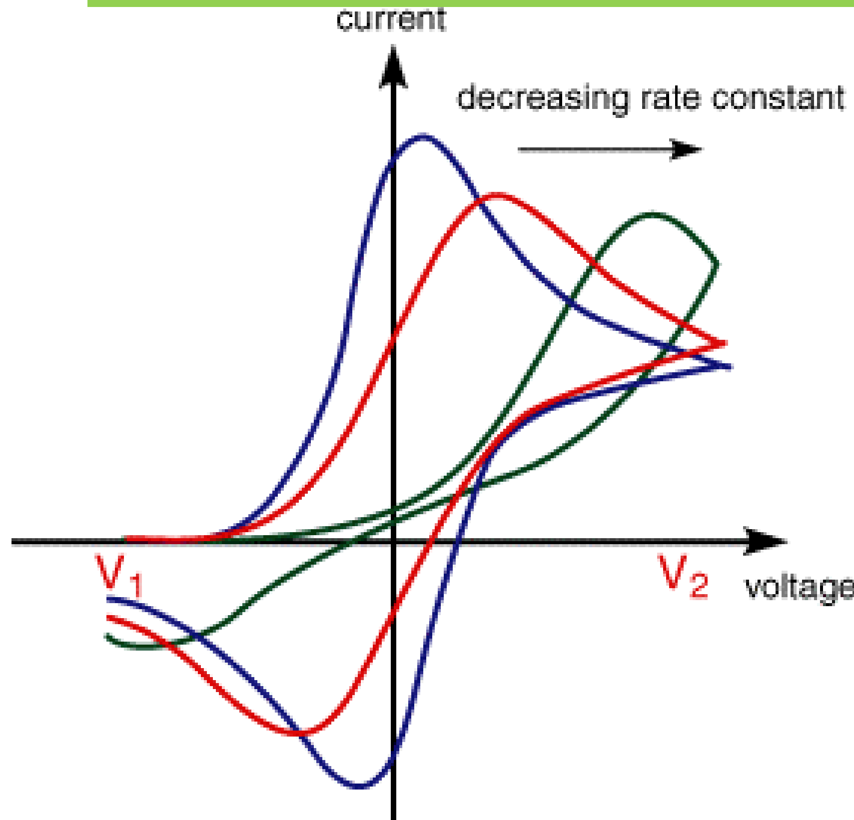



Reversible
Quasi-reversible
Irreversible
I
0
E_f^0
E
E
E_2
E_1
t

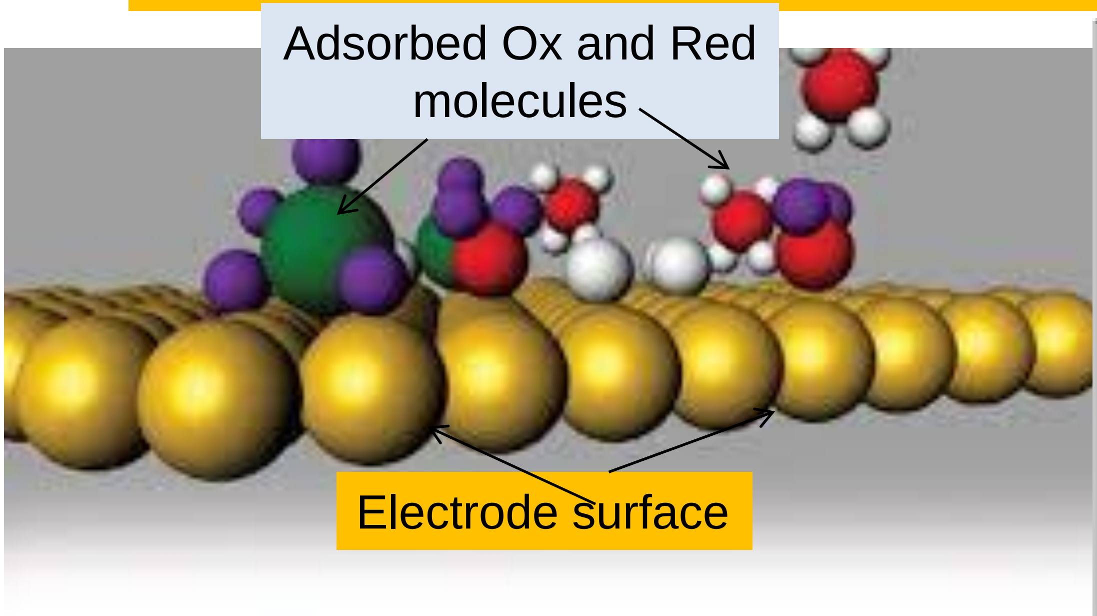
Reversibile reaction-scan rate inlfuences the peak currents
Only, but not the peak-to-peak separation of cathodic
And anodic peak



<u>QUASI-REVERSIBLE</u> reactions-scan rate
Produces changes in the
Peak-to-peak separation



SURFACE REDOX REACTIONS-Diagnostic critera, Features and Specific behaviour



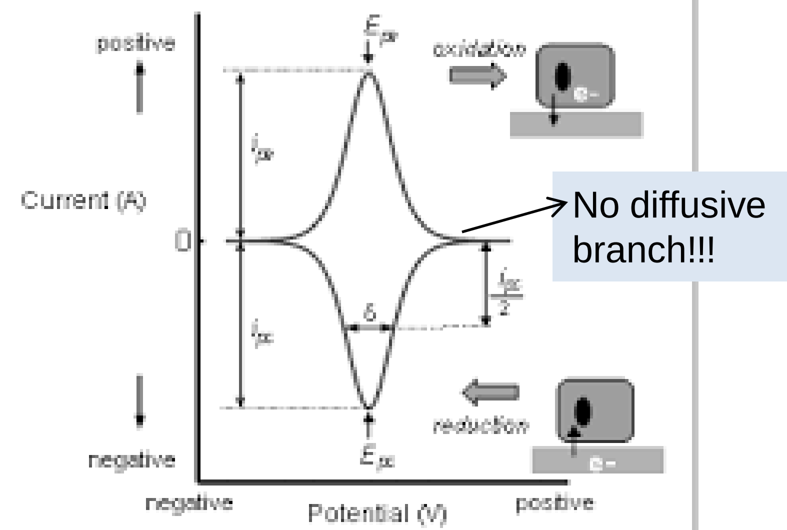
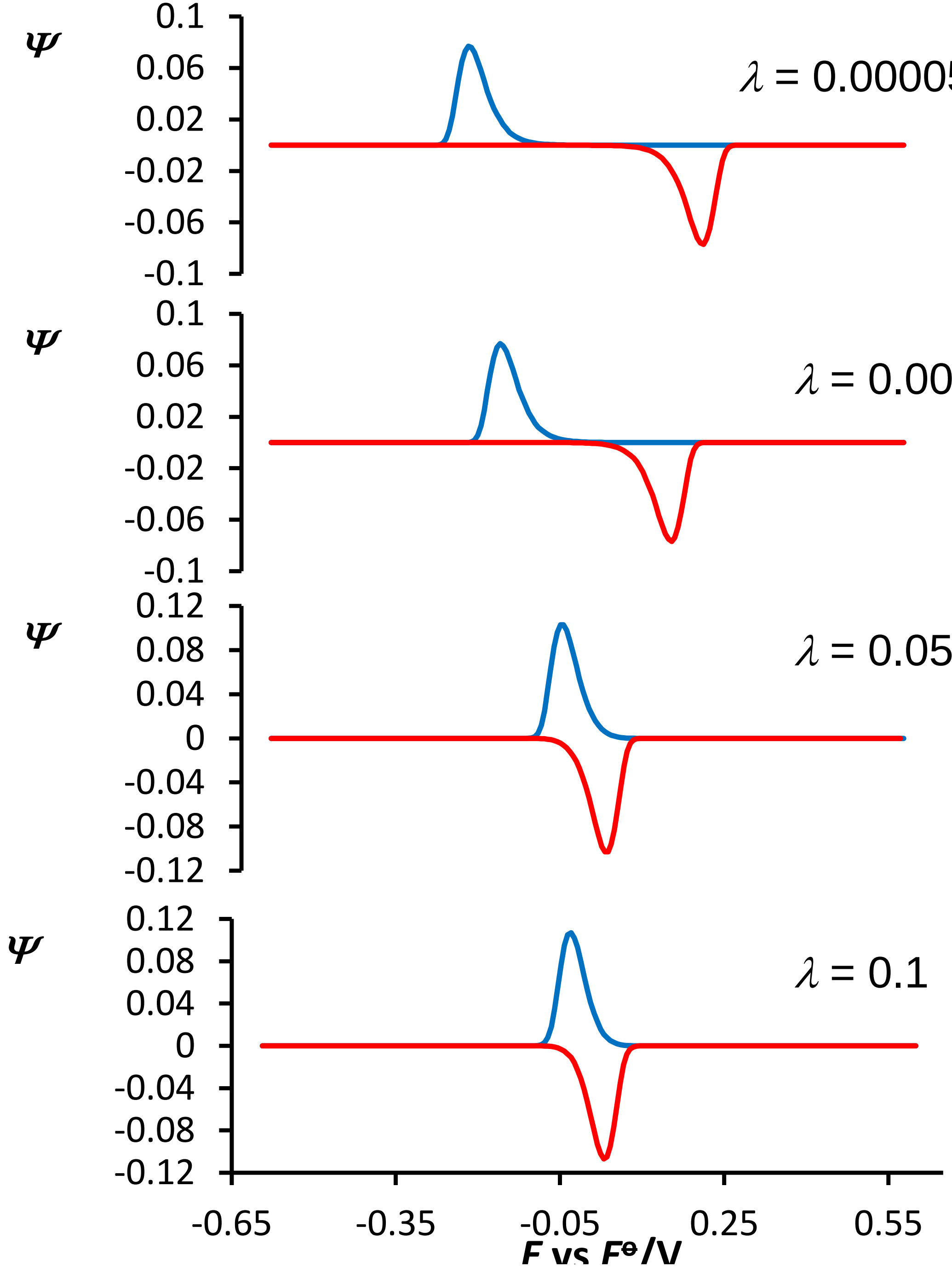


Figure 2. Cyclic voltammetric response from a film of adsorbed protein containing a single redox active centre undergoing reversible electron transfer.

Ox(adsorbed) + ne- = Red(adsorbed)

NO DIFFUSION!!!

Both, Ox and Red stay firmly adsorbed on electrode surface at all potentials



Simple surface
Redox reactions

-sharp peaks
-zero“ background current

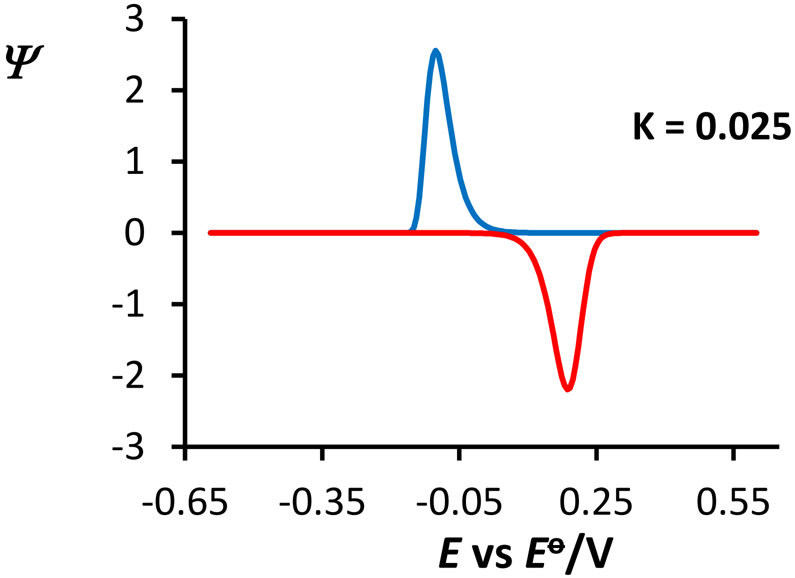
- λ is dimensionless kinetic Parameter of electrode Reaction

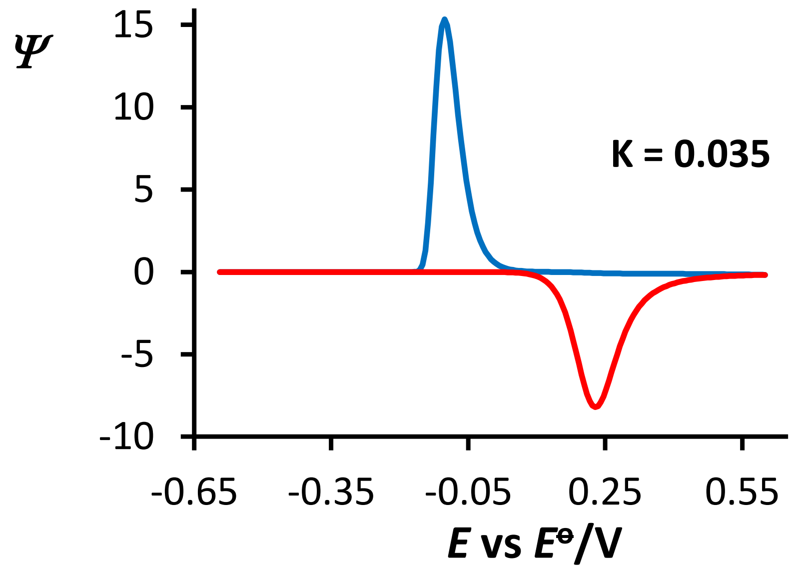
-by increasing of the Kinetics parameter λ, the peak to peak λseparation becomes smaller

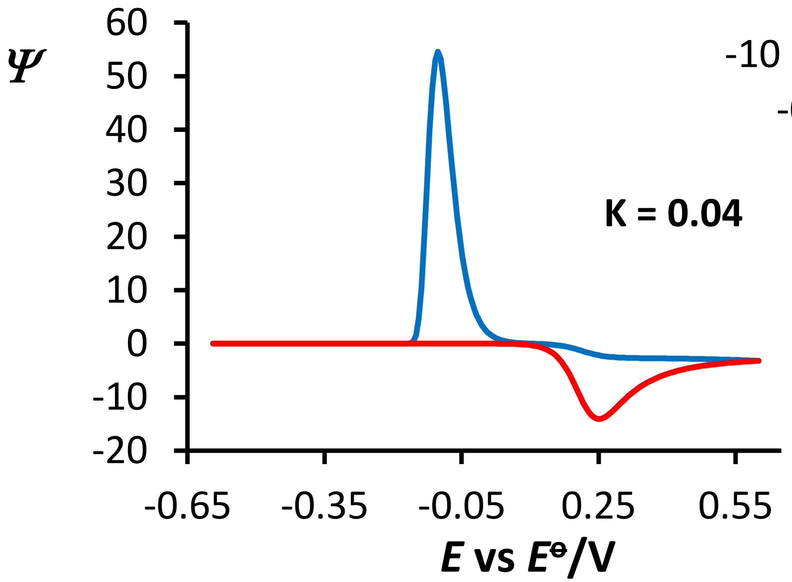
SURFACE ECirreversible reaction

K-is chemical kinetics parameter

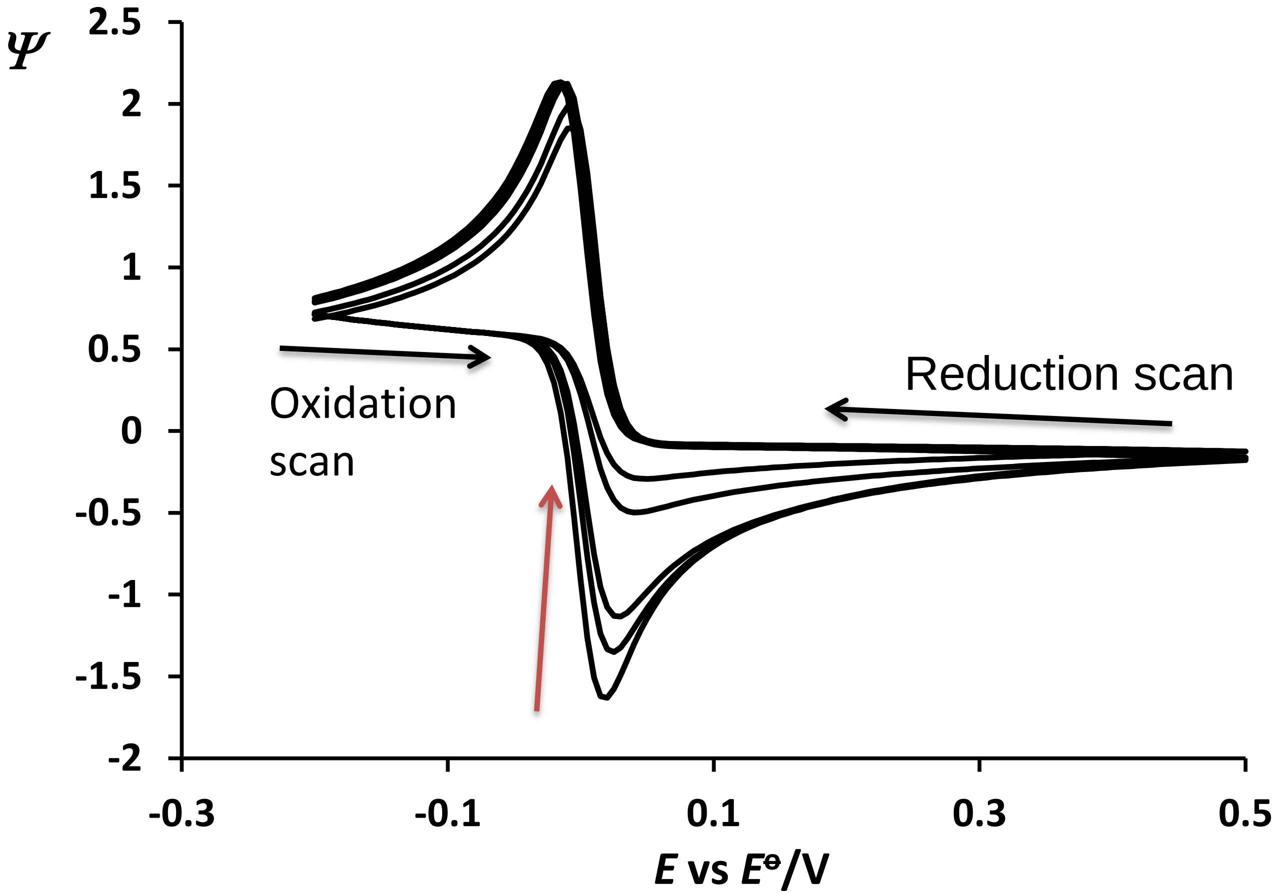
-increasing „K“ chemical kinetics Produces effects on backward currents mainly





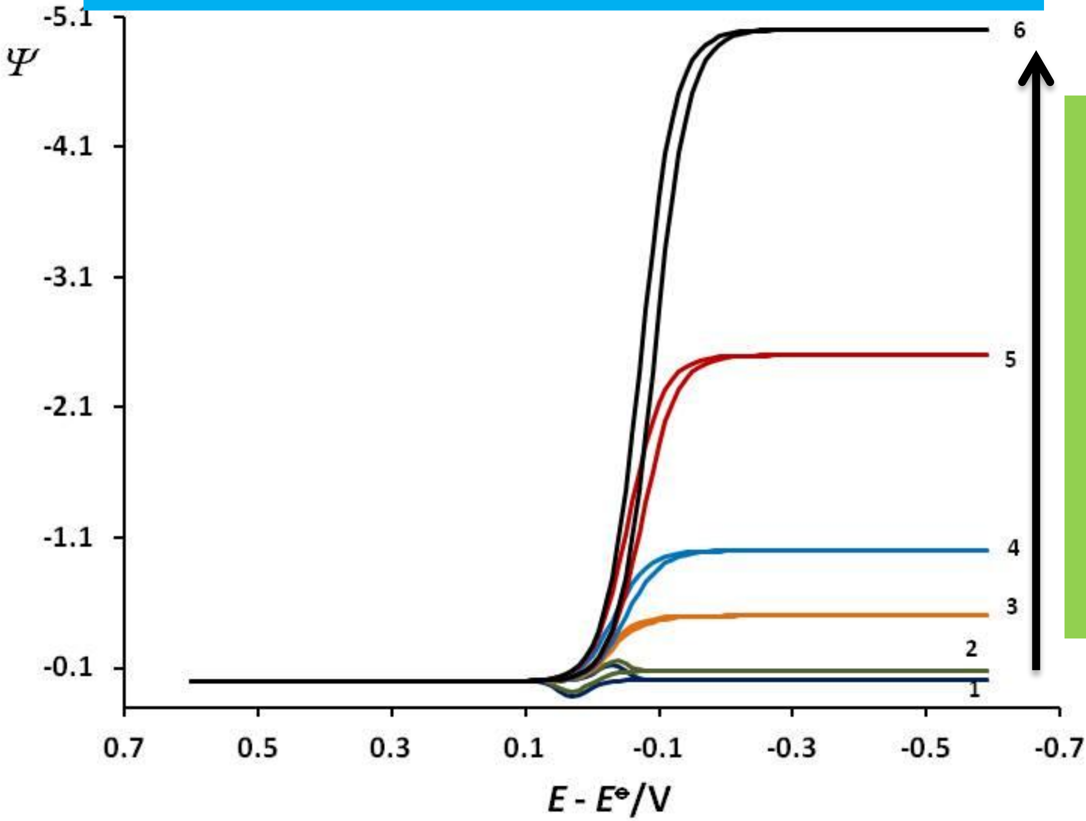


ECirr from diffusion state-Compare with ürevios slides of Surface ECirreversible reaction!!!



Diffusional ECirr reaction: dE of 5 mV; scan rate of 100 mV;
Kincetic parameter log(l*)* of 2.80; D = 3 x 10-6 cm2 s-1
Chemicl parameter K = 0.05; 0.1; 0.5, 1, 15 (from bottom to top of backward)

SURFACE EC‘-Electrochemical „regenerative“ catalytic reaction



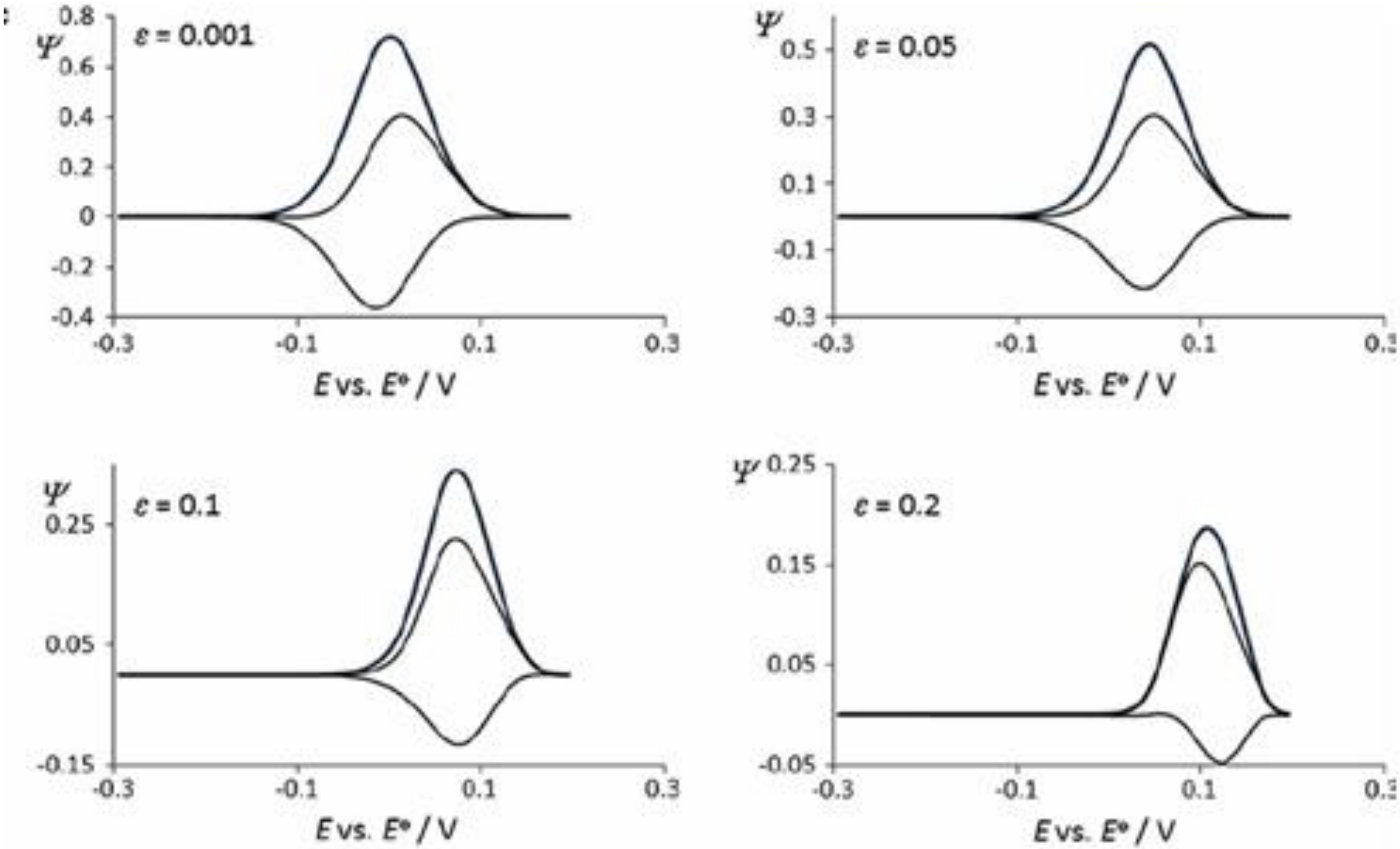
Current gets bigger as c(Y) increases i.e. As the catalytic effect gets bigger

Backward compnent becomes „forward“ as c(Y) increases

SURFACE EC‘-Electrochemical „regenerative“ catalytic reaction

Ox(ads) + ne- = Red(ads)
Red(ads) +Y → Ox (ads)
.....Y is substrate present in solutions
In this mechanisms, Ox(ads) regenerates via chemical reaction of product Red(ads) with a givensubrate „Y“

<u>SURFACE CE reaction</u>-----electroactive speciesOx(ads) get created via some preceeding chemical reaction

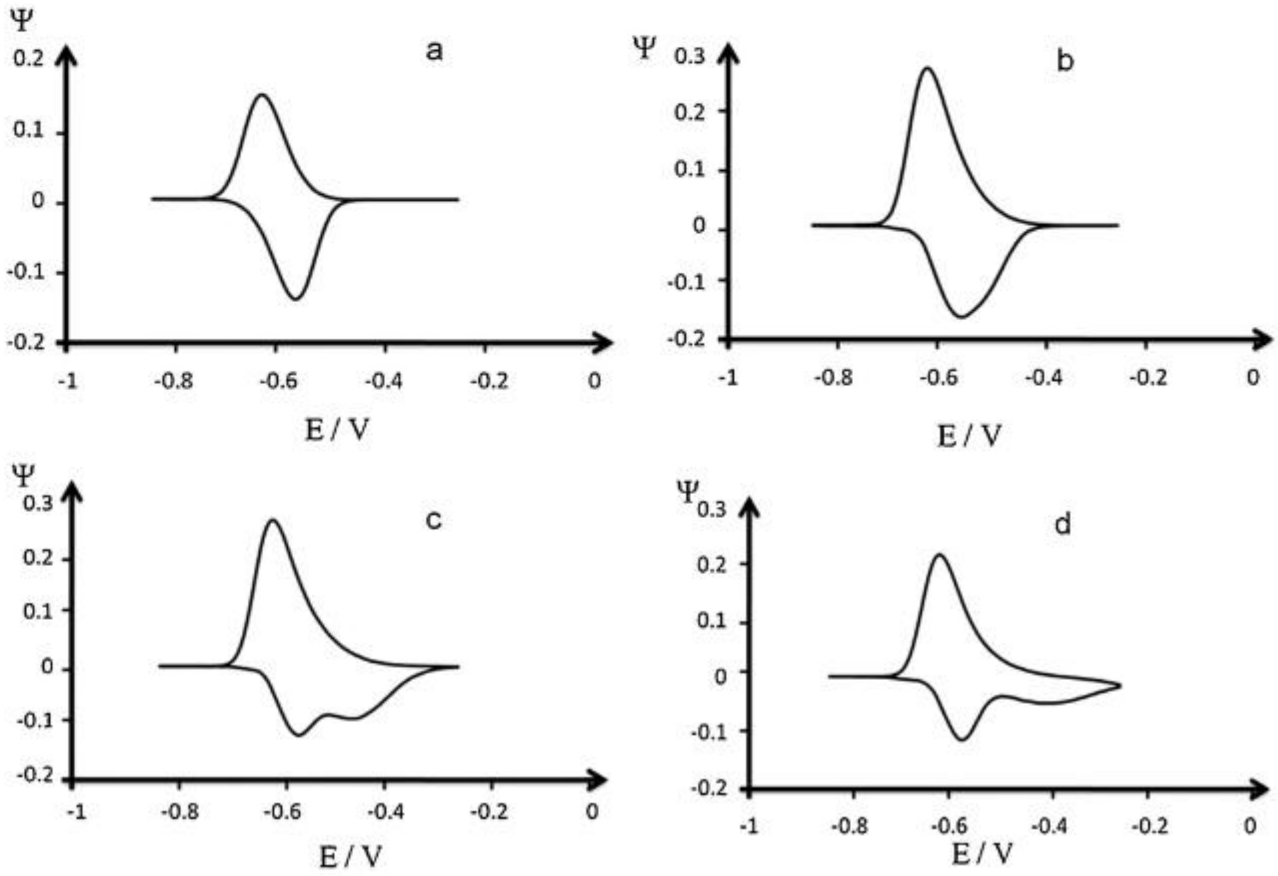


Y + B = Ox(ads) + ne- = B(ads)

Effect of chemical kinetic parameter ε to the features of square-Wave voltammograms

SURFACE ECirrE mechanism

Ox(ads) + ne- = Red(ads) +Y = B(ads) + ne- = D(ads

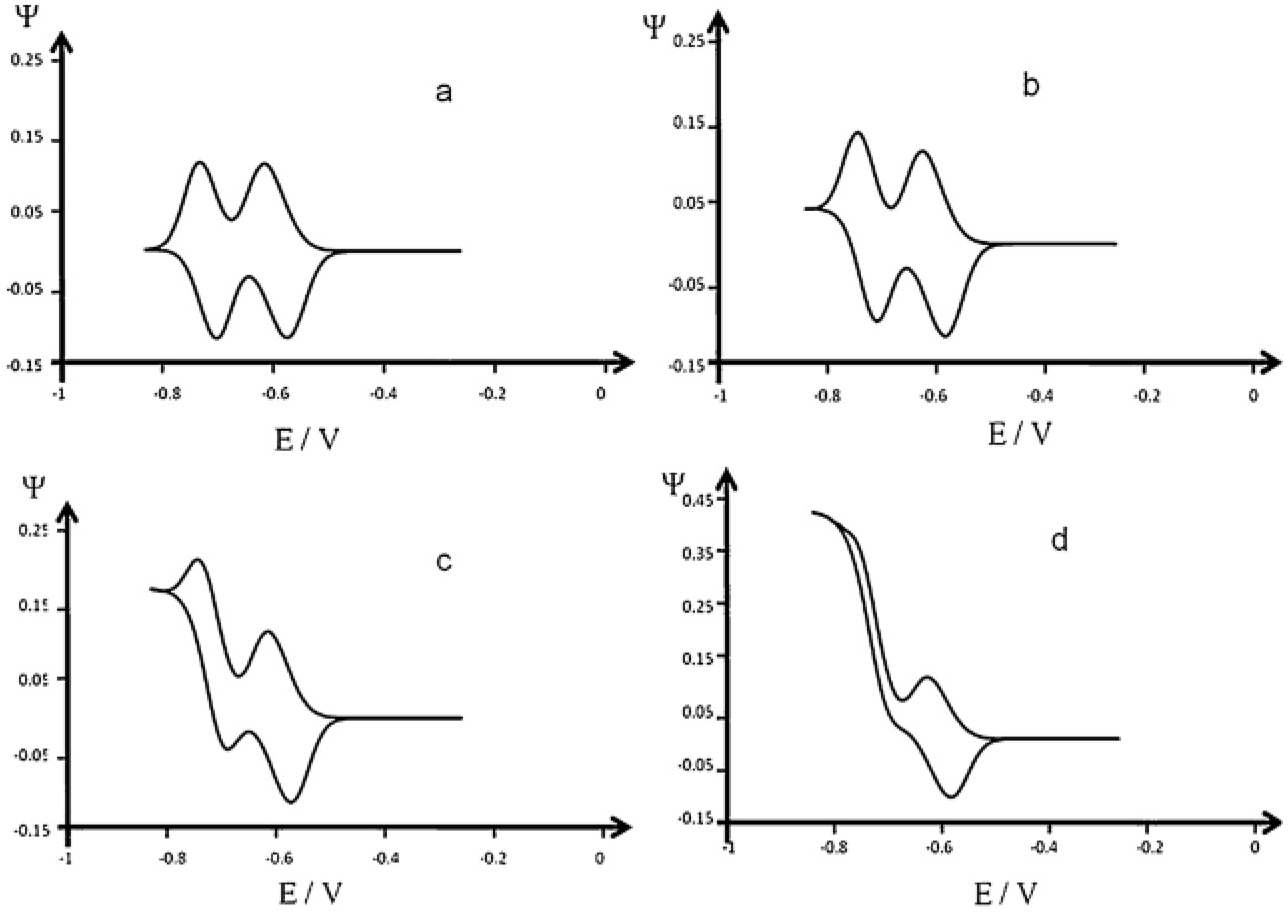


Effect of the chemical parameter „ε“ to the features of cyclic voltammograms when both redox processes are separated about 200 mV

Chemical parameter „ ε“ increases from „a“ to „d“ voltammograms

SURFACE EEC‘ mechanism-
Two step redox reaction coupled to Regenerative (catalytic) step

Ox(ads) + ne- = Red(ads) + ne = B(ads) + Y -→Red(ads)



Effect of the catalytic step to the features of the second electrode step. Chemical catalytic parameter increases from (a) to (d) voltammograms

REFERENCES

1.R Gulaboski, S Petkovska, A Time-Independent Approach to Evaluate the Kinetics of Enzyme-Substrate Reactions in Cyclic Staircase Voltammetry, ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY 10 (5), 566-575

2. S. Kostadinovic Velickovska, A. C. Mot, S. Mitrev, **R. Gulaboski**, L. Bruhl, H. Mirhosseini, R. Silaghi Dimitrescu, B. Matthaus, *Bioactive compounds and "in vitro" antioxidant activity 3 of some traditional and non-traditional cold-pressed edible oils from Macedonia*, ***J. Food Sci. Technol.*** (2018) doi: 10.1007/s13197-018-3050-0

3. R. Gulaboski, I. Bogeski, P. Kokoskarova, H. H. Haeri, S. Mitrev, M. Stefova, Marina, J. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, *New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study.* ***Bioelectrochem.*** 111 (2016) 100-108.

4. R. Gulaboski, V. Markovski, and Z. Jihe, *Redox chemistry of coenzyme Q—a short overview of the voltammetric features*, ***J. Solid State Electrochem.***,20 (2016) 3229-3238.

5. V. Mirceski, D. Guzijewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, Maced. J. Chem. Chem. Eng. 34 (2015) 1-12.

6. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.

7. **Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochim. Acta***, *167 (2015) 219-225.*

8. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.

9. V. Mirceski, **R. Gulaboski**, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, ***Electroanal.*** 25 (2013) 2411–2422.

10. R. Gulaboski, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers ***Sci. Reports***, 3 (2013) 1-8.

11. **R. Gulaboski**, V. Mirceski, I. Bogeski and M. Hoth, „Protein film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress„ ***J. Solid State Electrochem.*** 16 (2012) 2315-2328.

12. **R. Gulaboski,** P. Kokoskarova and S. Mitrev, "Theoretical aspects of several successive two-step redox mechanisms in

13. I. Bogeski, **R. Gulaboski***, R. Kappl, V. Mirceski, M. Stefova, J. Petreska and M. Hoth, „Calcium Binding and Transport by Coenzyme Q„ ***J. Am. Chem. Soc.*** 133 (2011) 9293-9303.

14. **R. Gulaboski** and L. Mihajlov, "Catalytic mechanism in successive two-step protein-film voltammetry—heoretical study in square-wave voltammetry", ***Biophys. Chem.***155 (2011) 1-9.

15. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, Protein-film voltammetry: a theoretical study of the temperature effect using square-wave voltammetry., ***Biophys. Chem***. 137 (2008) 49-55.

16. **R. Gulaboski**, Surface ECE mechanism in protein film voltammetry—a theoretical study under conditions of square-wave voltammetry, ***J. Solid State Electrochem***. 13 (2009) 1015-1024

17. **R. Gulaboski**, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garrau, V. Lippolis and A. F. Silva, Coupling of Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for Probing the Thermodynamics of Facilitated Ion Transfer Reactions Exhibiting Chemical Kinetic Hindrances, ***J. Phys. Chem. C*** 112 (2008) 153-161.

18. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, A new rapid and simple method to determine the kinetics of electrode reactions of biologically relevant compounds from the half-peak width of the square-wave voltammograms., ***Biophys. Chem***. 138 (2008) 130-137.

19. **R. Gulaboski**, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa and A. F. Silva, Probing of the Voltammetric Features of Graphite Electrodes Modified with Mercaptoundecanoic Acid Stabilized Gold Nanoparticles, ***J. Phys. Chem.*** *C* 112 (2008) 2428-2435.

20. R. **Gulaboski**, F. Borges, C. M. Pereira, M. N. D. S. Cordeiro, J. Garrido and A. F. Silva, Voltammetric insights in the transfer of ionizable drugs across biomimetic membranes: recent achievements., **Comb. Chem. High Throughput Screen.** 10 (2007) 514-526.

21. **R. Gulaboski**, V. Mirčeski, M. Lovrić and I. Bogeski, “Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry.” ***Electrochem. Commun***. 7 (2005) 515-522.

22. **R. Gulaboski**, V. Mirčeski, C. M. Pereira, M. N. D. S. Cordeiro, A F Silva, F. Quentel, M. L’Her and M. Lovrić, “A comparative study of the anion transfer kinetics across a water/nitrobenzene interface by means of electrochemical impedance spectroscopy and square-wave voltammetry at thin organic film-modified electrodes.” ***Langmuir*** 22 (2006) 3404-3412.

23. **R. Gulaboski**, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski, E. Fereira, D. Ribeiro, M. Chirea and A. F. Silva, “Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane.” ***J. Phys. Chem. B*** 109 (2005) 12549-12559.

24. F. Scholz and **R. Gulaboski** “Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes.” ***Chem. Phys. Chem***., 6 (2005) 1-13.

25. **R. Gulaboski**, V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, “Square-Wave Voltammetry of Cathodic Stipping Reactions. Diagnostic Criteria, Redox Kinetic Measurements, and Analytical Applications”, ***Electroanal.*** 16 (2004) 832-842.

26. V. Mirčeski and **R. Gulaboski**, “A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry” ***Croat. Chem. Acta*** 76 (2003) 37-48.

27. V. Mirčeski and **R. Gulaboski**, “The surface catalytic mechanism: a comparative study with square-wave and staircase cyclic voltammetry ”, ***J. Solid State Electrochem***. 7 (2003) 157-165.

28. R. Gulaboski, V. Mirčeski and Š. Komorsky-Lovrić, "Square-Wave Voltammetry of a Second Order Cathodic Stripping Process Coupled by Adsorption of the Reacting Ligand", ***Electroanal.*** 14 (2002) 345-354.

29. V. Mirčeski, M. Lovrić and **R. Gulaboski**, "Theoretical and experimental study of the surface redox reaction involving interactions between the adsorbed particles .under conditions of square-wave voltammetry.", ***J. Electroanal. Chem***., 515 (2001) 91-99.

30. V. Mirčeski and **R. Gulaboski**, "Surface Catalytic Mechanism in Square-Wave Voltammetry", ***Electroanal.*** 13 (2001) 1326-1334.

31. V. Mirčeski, **R. Gulaboski** and I. Kuzmanovski, "Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms", ***Bull. Chem. Technol. Macedonia*****,** 18 (1999) 57-64.

32. Scholz, F.; Schroeder U.; **Gulaboski R**. *Electrochemistry of Immobilized Particles and Droplets* Springer Verlag, New York, pp. 1-269, 2005.

33. **Gulaboski, R.** Pereira, C. M. In Electrochemical Methods and Instrumentation in Food Analysis, in Handbook of Food Analysis Instruments, Otles, S. (ed.) Taylor & Francis, 2015.

34. **Gulaboski R**. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2nd Edition in 2012.

35. I. Bogeski, R. Kappl, C. Kumerow, **R. Gulaboski**, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, ***Cell Calcium*** **50** (2011) 407-423.

36. R. Compton, Understanding Voltammetry, 2012.

37. V. Mirceski, S. Komorsky Lovric, M. Lovric, Square-wave voltammetry, Theory and Application, Springer 2008 (F. Scholz, Ed.)

38. Rubin Gulaboski, T**heoretical Contribution Towards Understanding Specific Behaviour of "Simple" Protein-film Reactions in Square-wave Voltammetry, Electroanalysis 2018,** https://doi.org/10.1002/elan.201800739

39.R. Gulaboski, P. Kokoskarova, S. Petkovska, Time-Independent Methodology to Access Michaelis-Menten Constant by Exploring Electrochemical-Catalytic Mechanism in Protein-Film Cyclic Staircase Voltammetry , Croatica Chemica Acta 91 (2018) https://doi.org/10.5562/cca3383