Basic electrochemical techniques in energy research

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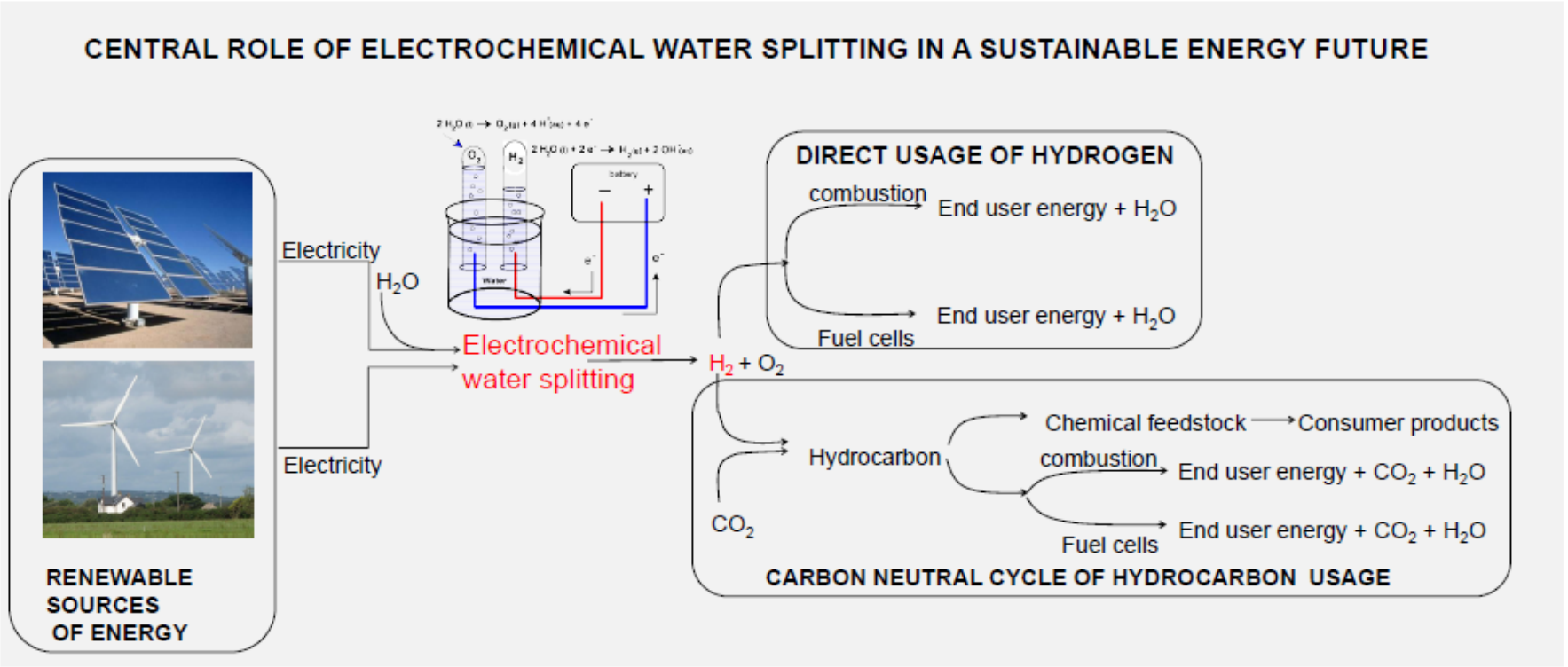
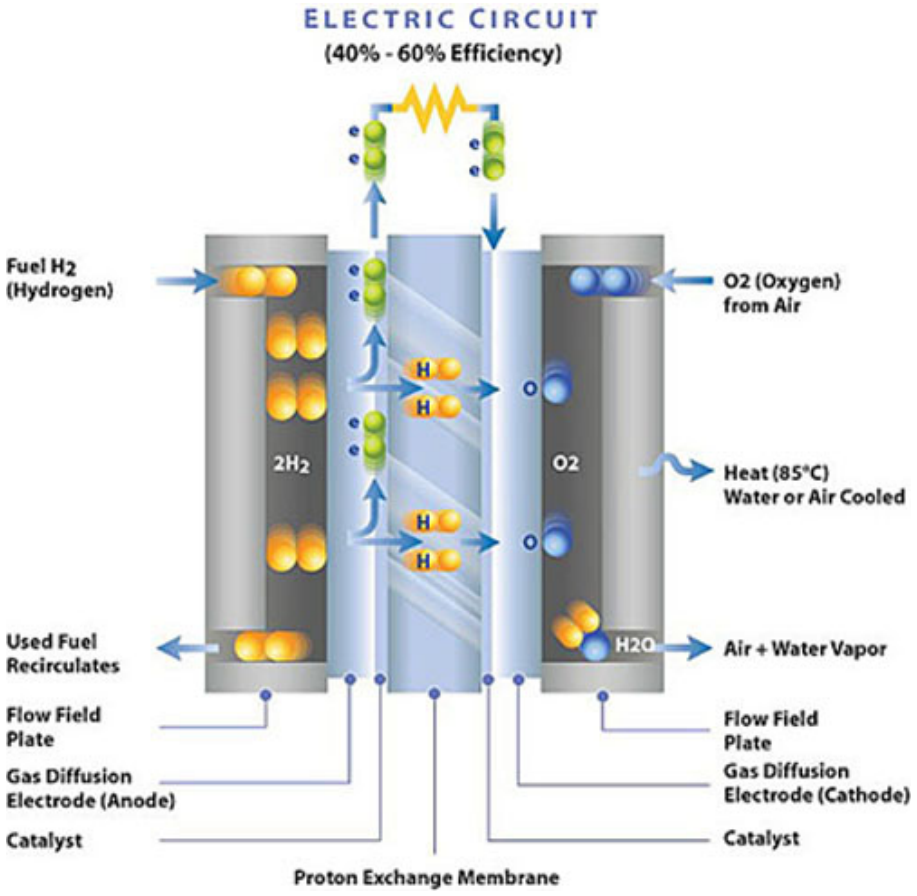
Electrochemistry

- Biological electron transfer reactions: Life sustaining processes: Respiration, photosynthesis.
- Energy storage and conversion: Water splitting, Batteries, fuel cells.

Central Role of Electrochemistry



Fuel Cell


ELECTRIC CIRCUIT
(40% - 60% Efficiency)
Fuel H2
(Hydrogen)
O2 (Oxygen)
from Air
2H2
O2
H
H
H
H
Heat (85°C)
Water or Air Cooled
Used Fuel
Recirculates
H2O
Air + Water Vapor
Flow Field
Plate
Gas Diffusion
Electrode (Anode)
Catalyst
Flow Field
Plate
Gas Diffusion
Electrode (Cathode)
Catalyst
Proton Exchange Membrane

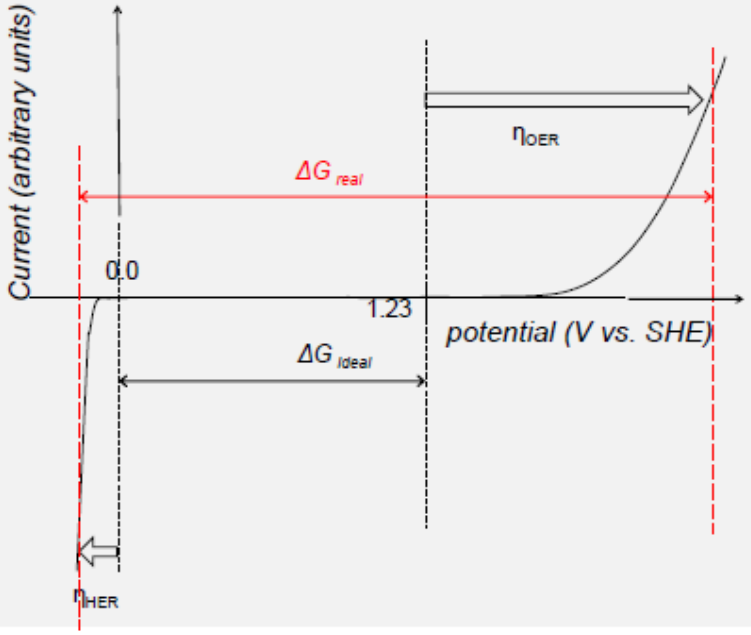
Water Splitting

ELECTROCHEMCAL HALF REACTIONS

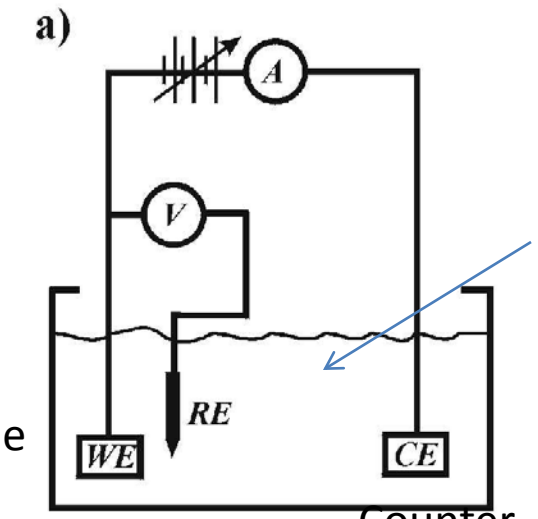
$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ *E (anodic) = 1.23V vs. SHE*

$4H^+ + 4e^- \longrightarrow 2H_2$ *E (cathodic)= 0V vs. SHE*

CURRENT VOLTAGE CHARACTERISTICS OF A ELECTROLYZER



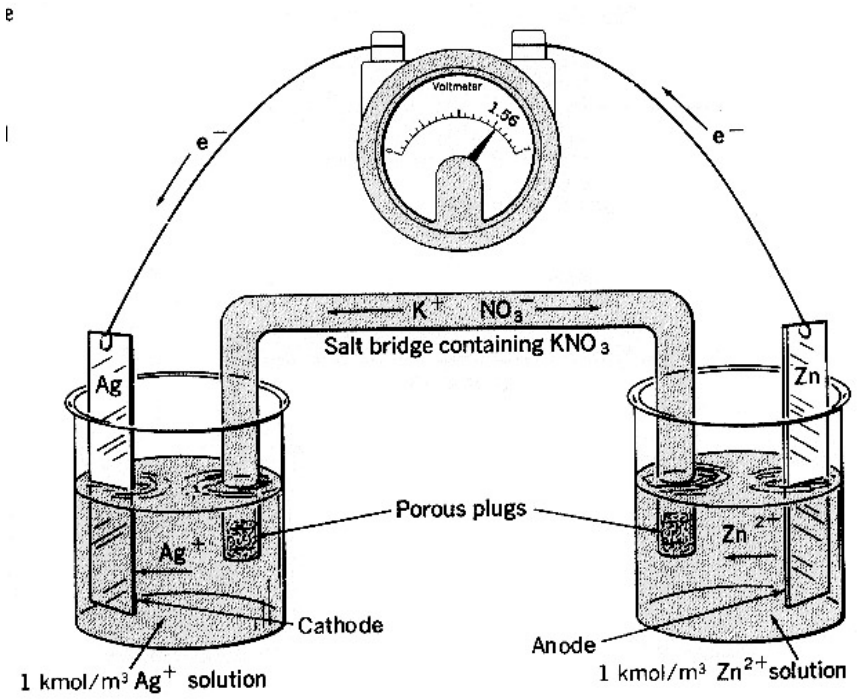
Electrode assembly



Factors affecting a electrode reaction

- Mass transfer
- Electron transfer at electrode surface
- Chemical Reactions preceding or following electron transfer
- Other reactions such as adsorption, desorption etc.

emf of a cell reaction



$\Delta G = -nfE_{rxn}$

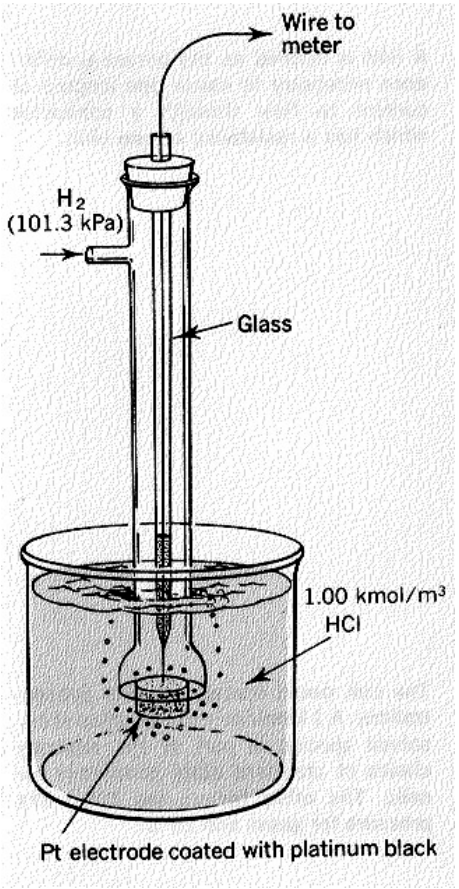
emf is positive when reaction is spontaneous by definition

$Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^-$

Zn/Zn^{2+} (a =1), $Cl^-/AgCl/Ag$

Cell emf = E_{rxn}= Electrostatic potential of the RHS – electrostatic potential of LHS

Primary reference

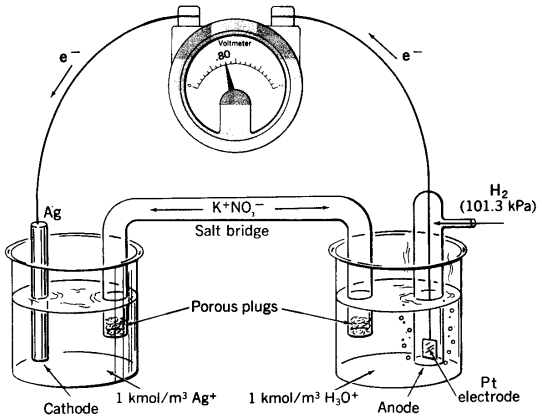


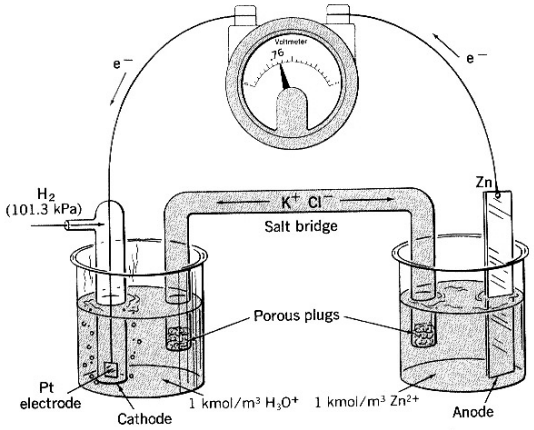
The standard half-cell assumed to be zero (0), is the H_2 half-cell. It is a half cell with H_2 gas bubbled in at SATP over an inert platinum electrode

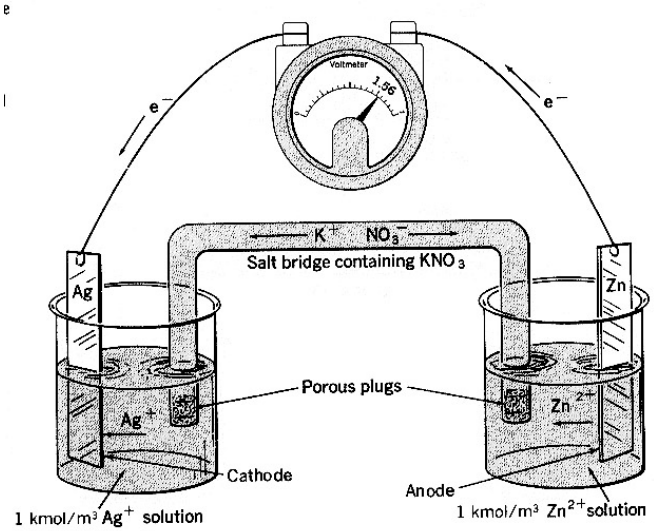
Normal/Standard Hydrogen Electrode
Its emf taken as 0 at all temperatures

$H_2 (g) = 2H^+ + 2e^-$

Half Cells







E^o = +0.80 V $Ag^{+1}_{(aq)} + e^{-1}$ ---> $Ag_{(s)}$ reduction

E^o = -0.76 V $Zn^{+2}_{(aq)} + 2e^{-1}$ ---> $Zn_{(s)}$ oxidation

E^o = +0.80 V $Ag^{+1}_{(aq)} + e^{-1}$ ---> $Ag_{(s)}$ reduction

E^o = +0.76 V $Zn_{(s)}$ ---> $Zn^{+2}_{(aq)} + 2e^{-1}$ oxidation

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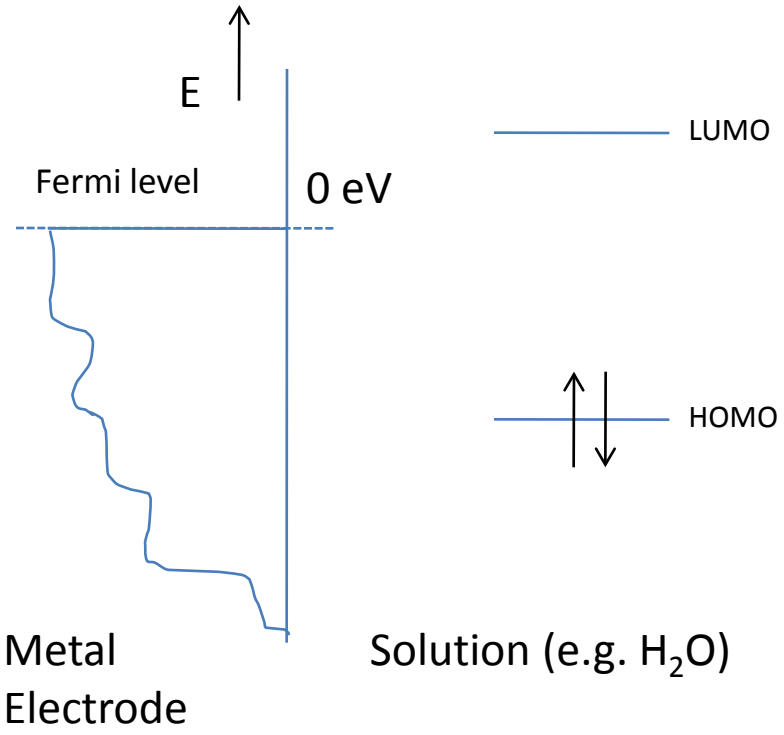
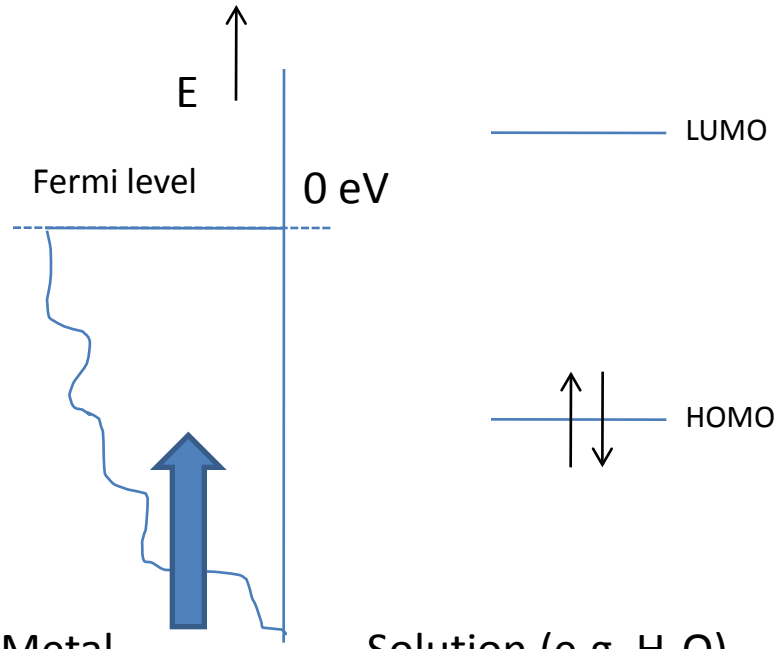
E_{cell} = +1.56 V $2\,Ag^{+1}_{(aq)} + Zn_{(s)}$ ---- > $2Ag_{(s)} + Zn^{+2}_{(aq)}$

Electron transfer event; Oxidation/Reduction

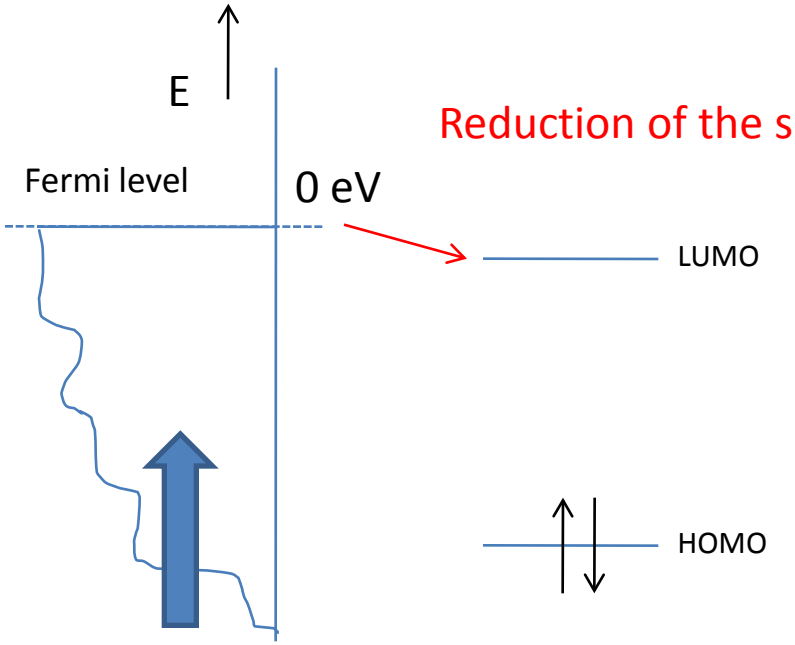


Electron transfer event; Oxidation/Reduction



-ve potential

Electron transfer event; Oxidation/Reduction



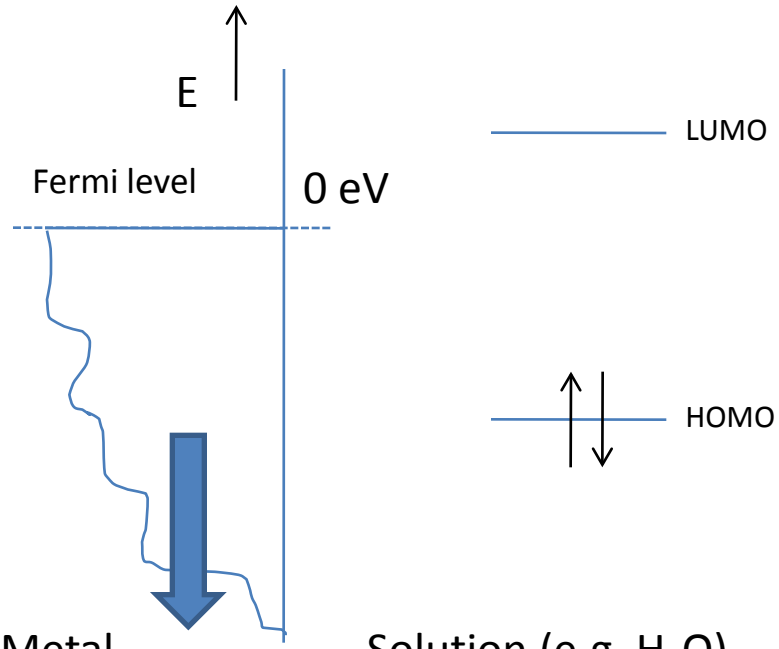
Reduction of the solution/ oxidation of electrode

Metal Electrode

Solution (e.g. H_2O)

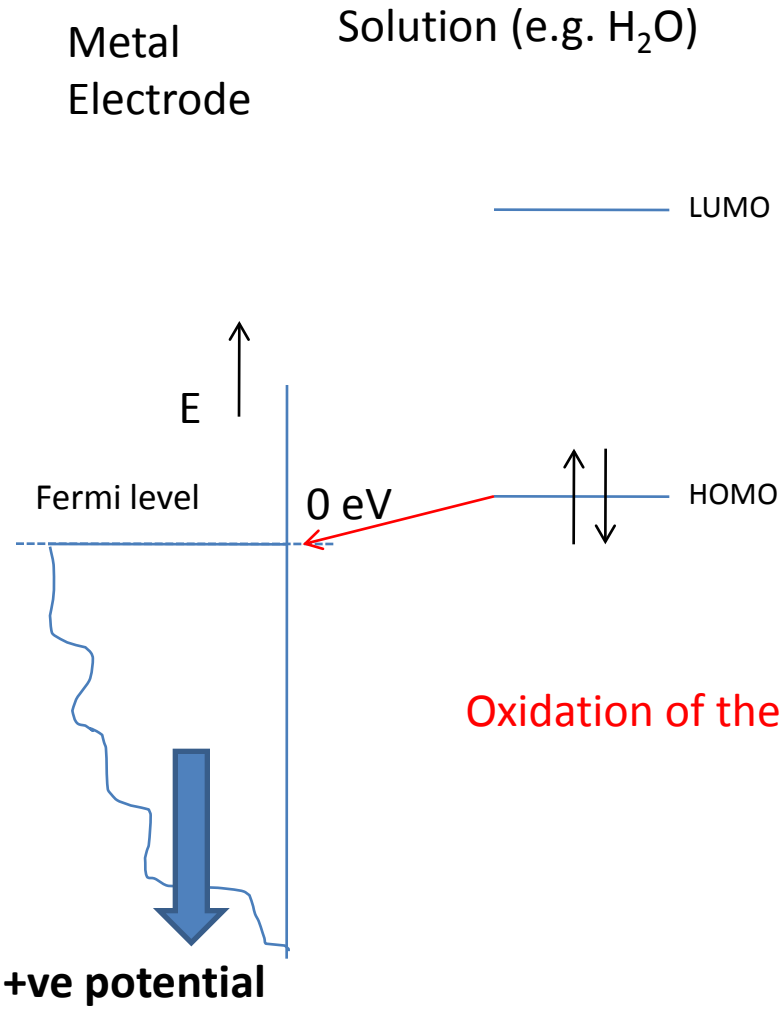
-ve potential

Electron transfer event; Oxidation/Reduction



+ve potential

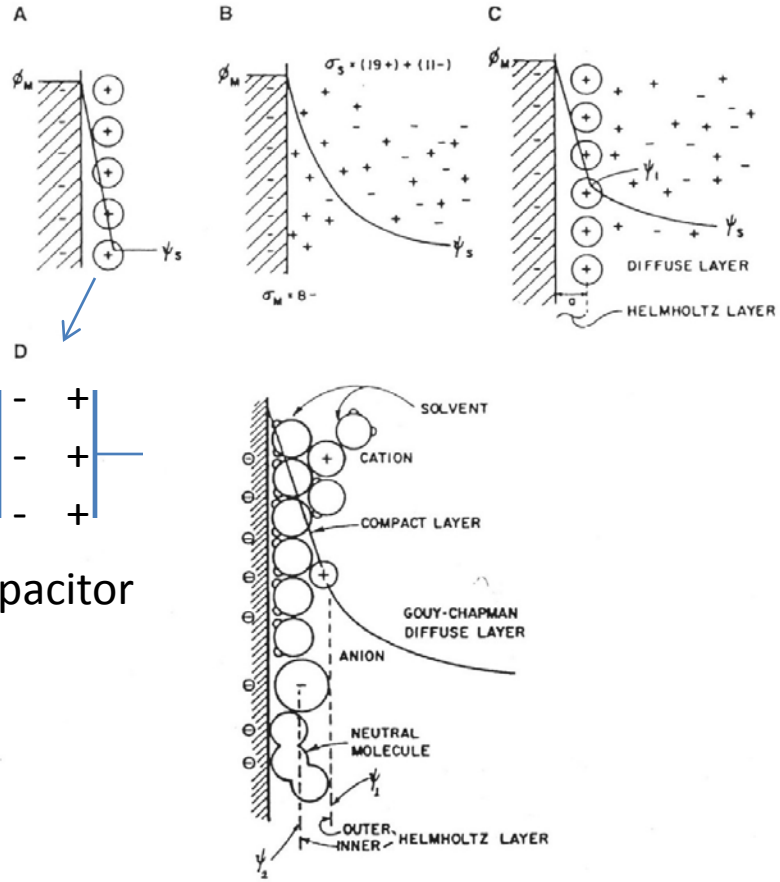
Electron transfer event; Oxidation/Reduction



Oxidation of the solution/ reduction of electrode

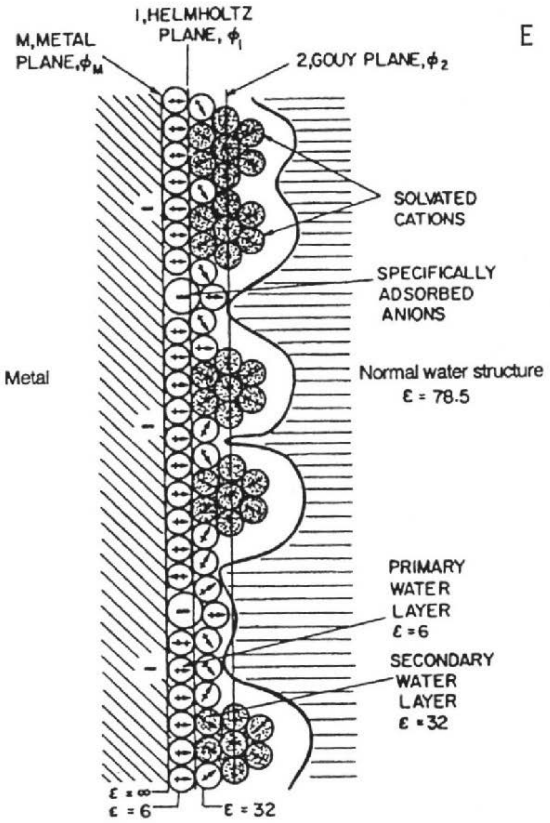
Electrochemical interface

Nature of ions in solution



capacitor

State of solvation



-Charge alignment

-Adsorption

Kinetics of Electrochemical Rxn

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$v_f = k_f C_A$$

$$v_b = k_b C_B$$

$$\Rightarrow \boxed{V_{net} = k_f C_A - k_b C_B}$$

At Equilibrium:

$$V_{net} = 0$$

$$\Rightarrow k_f C_A = k_b C_B \Rightarrow \frac{k_f}{k_b} = \frac{C_B}{C_A} = K_{eq}$$

At Equilibrium

$$V_o = k_f (C_A)_{eq} = k_b (C_B)_{eq} = \text{Exchange Velocity}$$

Phenomenological picture

$i = a' e^{\eta/b}$ where η = overpotential.

→ $\boxed{\eta = a + b \log i}$ ... Tafel Equation.

FOR Rxn: $O + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R$

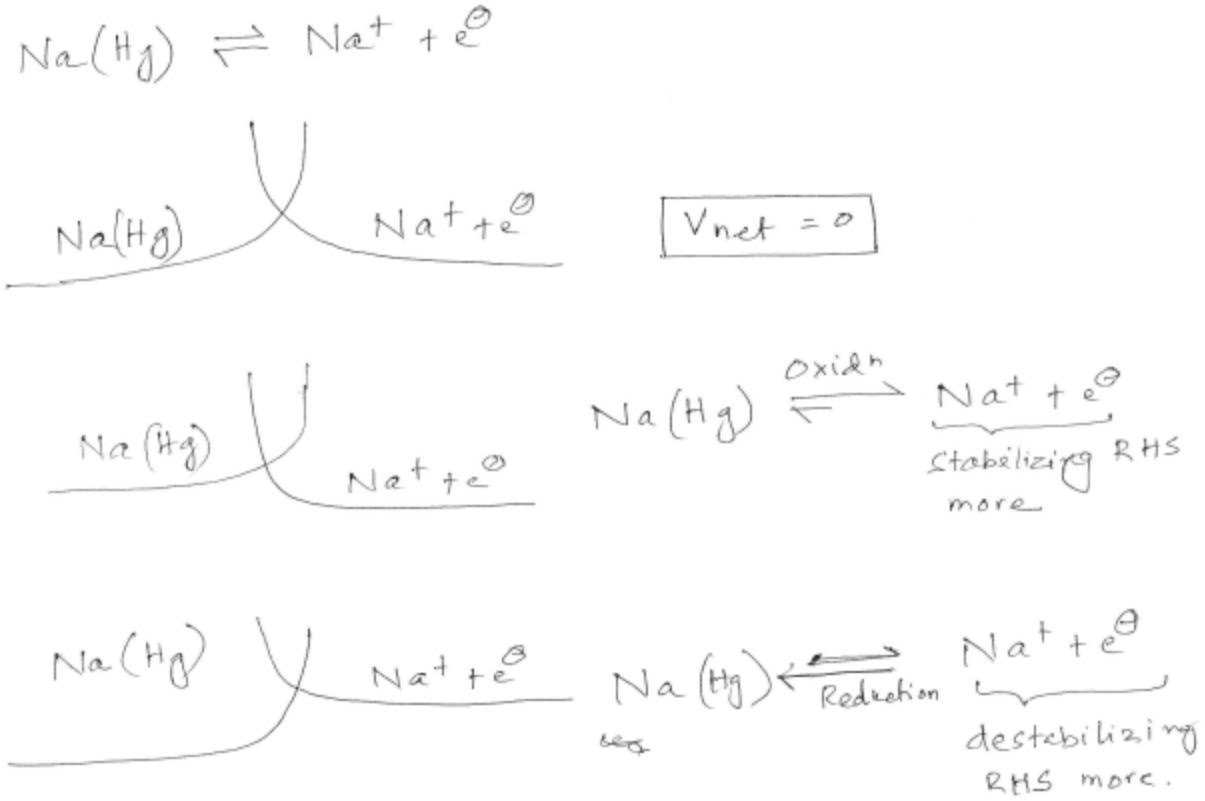
Work done (electrically)

$\Delta G = -nF\Delta E$ ... > charge moving across a potential drop.

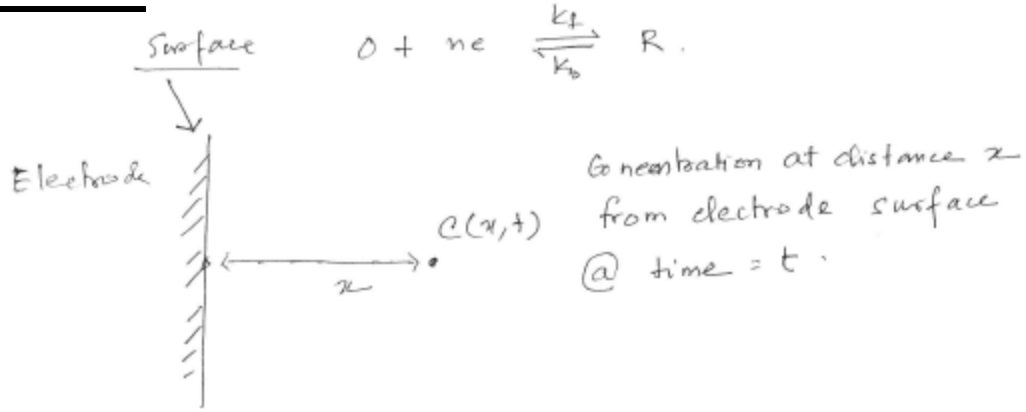
$\Delta G^\circ = -RT \ln K_{eq}$

$\boxed{E = E^\circ + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*}}$ .... Nernst Equation.

Interpreting potential



Overall Current



Surface Concentration $C(x=0,t) \equiv C(0,t)$

Rate of Fwd. Rxn. $V_f = k_f C_O(0,t) = i_c / nFA$

$V_b = k_b C_R(0,t) = i_a / nFA$.

Rate of Rxn. $V_{net} = V_f - V_b$

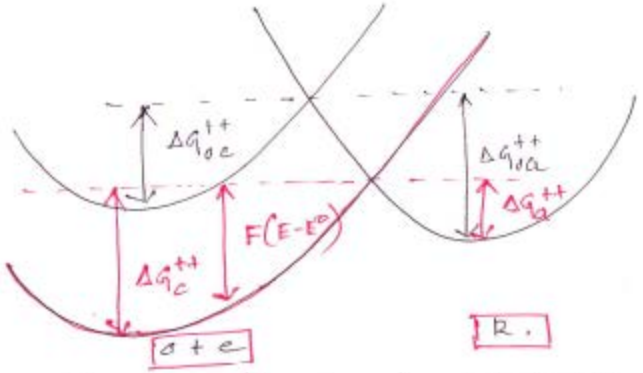
$= k_f C_O(0,t) - k_b C_R(0,t)$

$= \frac{i_c - i_a}{nFA}$.

Overall current: $i = i_c - i_a$

$= nFA \left[k_f C_O(0,t) - k_b C_R(0,t) \right]$

Kinetic Theory



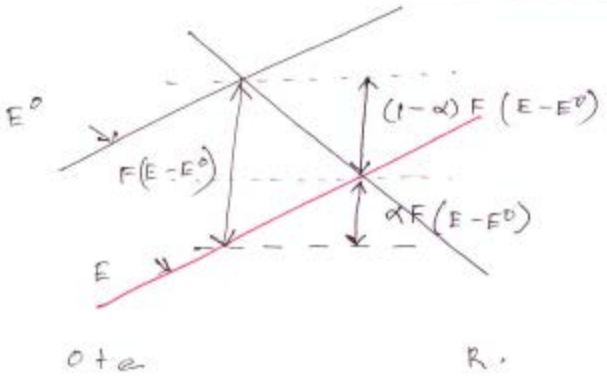
clearly barrier to oxidation has

Define α such that

$$\Delta G_a^{++} = \Delta G_{oa}^{++} - (1-\alpha)(E-E^0)$$

$$\Rightarrow \Delta G_c^{++} = \Delta G_{oc}^{++} + \alpha F (E-E^0)$$

α represents the symmetry of crossing



Butler Volmer Electrode Kinetics

$$k_f = A_f \exp\left(-\Delta G_c^{++}/RT\right)$$
$$k_b = A_b \exp\left(-\Delta G_a^{++}/RT\right)$$

Insert IC Activation Energy:

$$k_f = A_f \exp\left(-\Delta G_{oc}^{++}/RT\right) \exp\left[-\alpha(f(E-E^0))\right]$$
$$k_b = A_b \exp\left(-\Delta G_{oa}^{++}/RT\right) \exp\left[(1-\alpha) f(E-E^0)\right]$$

$f = F/RT$

at Equilibrium $k_f = k_b = k^0$

$$\Rightarrow k_f = k^0 \exp\left[-\alpha f(E-E^0)\right]$$
$$k_b = k^0 \exp\left[(1-\alpha) f(E-E^0)\right]$$
$$i = i_c - i_a = nFA\left[k_f C_O(0,t) - k_b C_R(0,t)\right]$$

$$\boxed{i = FAK^0\left[C_O(0,t)\, e^{-\alpha f(E-E^0)} - C_R(0,t)\, e^{(1-\alpha) f(E-E^0)}\right]}$$

Called Butler Volmer electrode kinetics.

Butler Volmer Electrode Kinetics

$$i = i_0 \left\{ \frac{C_o(0,t)}{C_o^*} \exp\left[\frac{\alpha_a n F \eta}{RT}\right] - \frac{C_r(0,t)}{C_r^*} \exp\left[-\frac{\alpha_c n F \eta}{RT}\right] \right\}$$

Exchange current Density.

k° → approach to equilibrium.

k° – large : approach Eqi fast. [1–10 cm/s]

k° – small : " " slow [$\sim 10^{-6} - 10^{-9}$ cm/s]

kinetic measurement over 10 orders of magnitude.

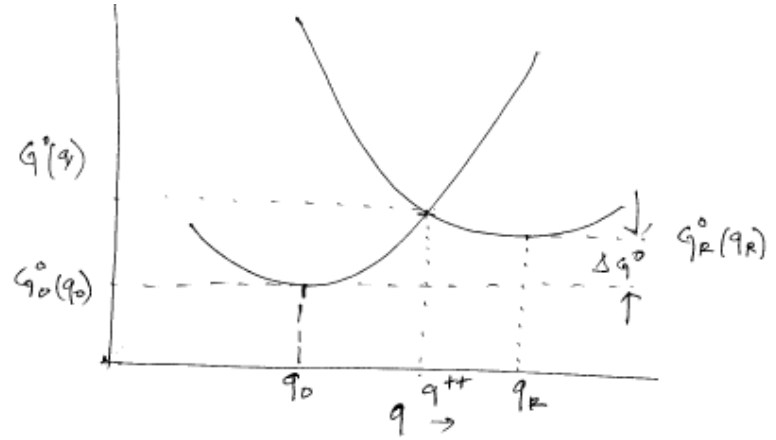
one drives an electrochemical Rxn by supplying activation energy electrochemically.

α = transfer coefficient :

$\alpha = 1/2$ ... typically assuming a symmetrical intersection. assuming energy profile is linear over relevant potential range.

α can vary between 0.3 – 0.7.

Marcus theory of electron transfer



$Ru(NH_3)_6^{3+} + e \rightarrow Ru(NH_3)_6^{2+}$

By Frank Condon principle $e^\ominus$ transfer happens at q^{++}.

$$G_O^\circ(q^{++}) = \frac{K}{2}(q^{++} - q_O)^2$$

$$G_R^\circ(q^{++}) = \frac{K}{2}(q^{++} - q_R)^2 + \Delta G^\circ$$

@ the point of $e^\ominus$ transfer.

$$G_O^\circ(q^{++}) = G_R^\circ(q^{++}) \Rightarrow \boxed{q^{++} = \frac{(q_R + q_O)}{2} + \frac{\Delta G^\circ}{K(q_R - q_O)}}$$

Marcus theory of electron transfer

$$\Delta G_f^{++} = K \frac{(q_R - q_0)^2}{8} \left[1 + \frac{2\Delta G^0}{K(q_R - q_0)^2} \right]^2$$

Define $\lambda := K_2 [q_R - q_0]^2$ ⟶ Reorganization Energy

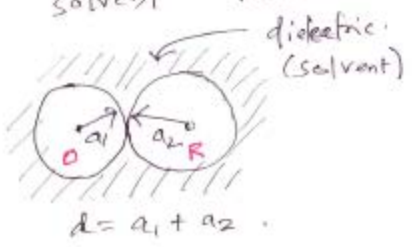
$$\Rightarrow \boxed{\Delta G_f^{++} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2}$$

Reorganization Energy: energy necessary to trasform the nuclear configuration in reactants + solvents ⟶ products + solvents.

$$\lambda = \underbrace{\lambda_o}_{\text{from solvent}} + \underbrace{\lambda_i}_{\text{from reactants}}$$

$$\lambda_i^o = \sum_j \tfrac{1}{2} k_j (q_{oj} - q_{Rj})^2$$

sum over all normal modes.

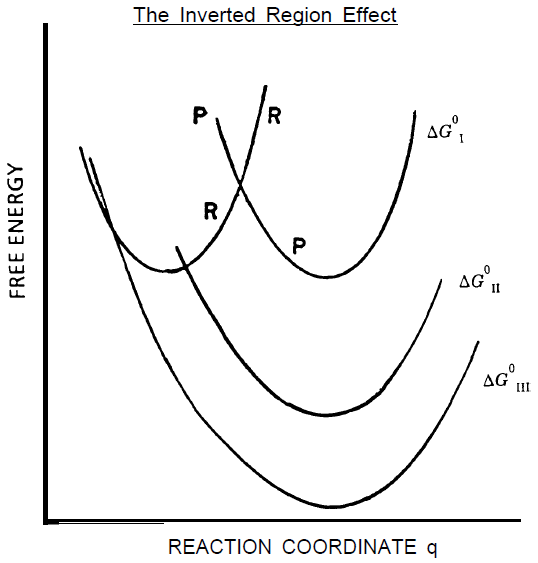


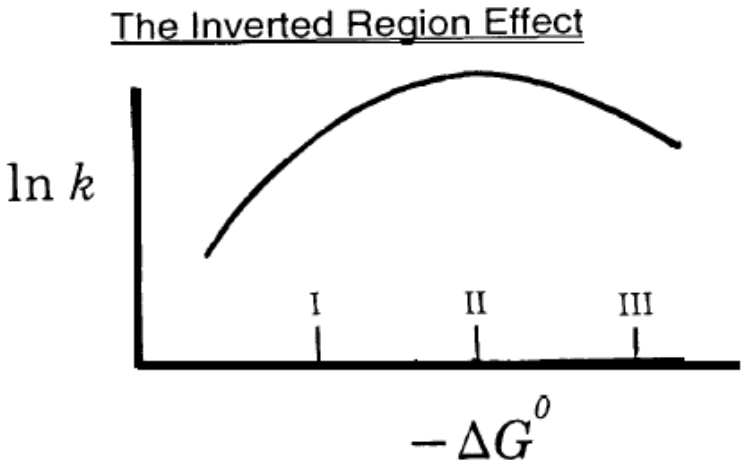
$$\boxed{\lambda_o = \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)}$$

Marcus theory of electron transfer

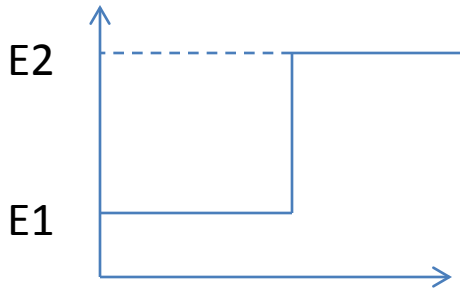
Value of alpha: ~ 0.5 are used in Butler Volmer theory but there is also some potential dependence

$$\alpha = \frac{1}{F}\frac{\partial G_f^{\ddagger}}{\partial E} = \frac{1}{2} + \frac{F(E - E^0)}{2\lambda}$$



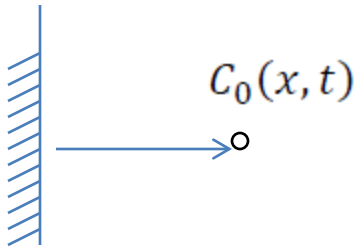


Potential step methods



E1: No electron transfer
E2: Fast electron transfer in MT regime

$$O + ne \overset{?}{\rightarrow} R$$



$$\frac{\partial C_0(x,t)}{\partial t} = D_0 \frac{\partial^2 C_0(x,t)}{\partial x^2}$$

Calculate the diffusion limited current

Boundary Conditions

$C_0(x,t) = C_0^* \ @t = 0$ Homogenous solution

$\lim_{x\to\infty} C_0(x,t) = C_0^*$ Semi-infinite condition

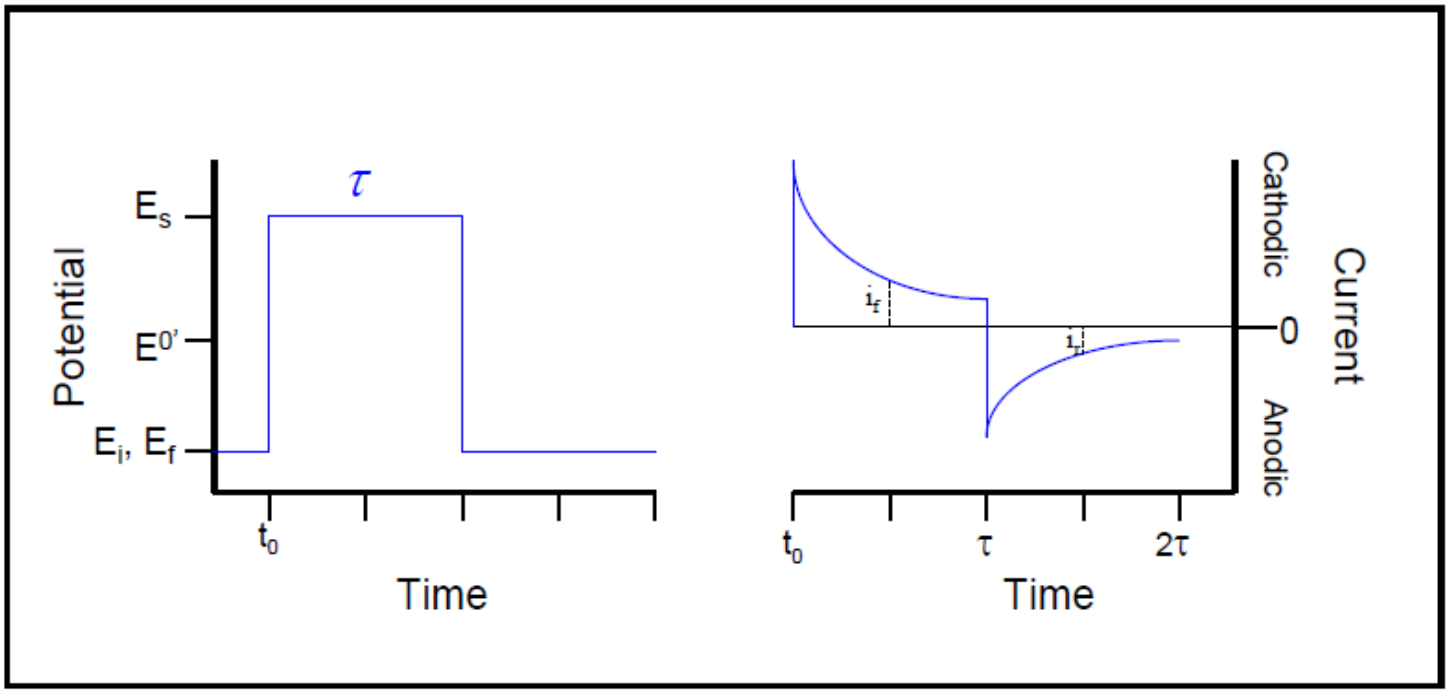
$C_0(0,t) = 0 \ @t > 0$ Special condition: by design

$$i_t = \frac{n F A C_0 D_0^{1/2}}{\pi^{1/2} t^{1/2}}$$

Cottrell Eqn.

$$i_t = \frac{n F A C_0 D_0^{1/2}}{\pi^{1/2} t^{1/2}}$$

The current is diffusion limited, no contribution from kinetic regime



Potential step methods

Stepping from E^0 where there is no electrochemical activity to region to some arbitrary potential within the region of reduction wave

$$E = E^0 + \frac{RT}{nF}\ln\frac{C_0(x,t)}{C_R(x,t)}$$

Assuming nernstian behavior

Fast kinetics

Diffusion Eqns.

$$\frac{\partial C_O(x,t)}{\partial t} = D_O\frac{\partial^2 C_O(x,t)}{\partial x^2}$$

$$C_0(x,t) = C_0^* \ @t = 0$$

$$\lim_{x\to\infty} C_0(x,t) = C_0^*$$

$$\frac{\partial C_R(x,t)}{\partial t} = D_R\frac{\partial^2 C_R(x,t)}{\partial x^2}$$

$$C_R(x,t) = C_R^* \ @t = 0$$

$$\lim_{x\to\infty} C_R(x,t) = C_R^*$$

Flux balance:

$$D_O\left(\frac{\partial C_O(x,t)}{\partial t}\right)_{x=0} + D_R\left(\frac{\partial C_R(x,t)}{\partial t}\right)_{x=0} = 0$$

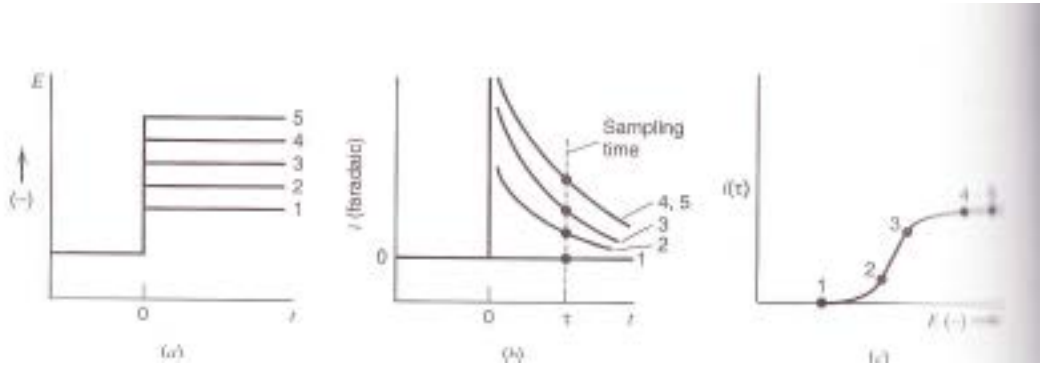
Potential step methods

$$i = \frac{nFAD_O^{\frac{1}{2}}C_O^*}{\pi^{\frac{1}{2}}t^{1/2}(1+\gamma\theta)}$$ … Solution

$$\frac{C_0(x,t)}{C_R(x,t)} = e^{\frac{nF}{RT}(E-E^{\mathbf{o}})} = \theta$$

From Nernst Eqn. Fast Kinetics

$$\gamma = \left(\frac{D_O}{D_R}\right)^{1/2}$$



Potential step methods

Shape of current potential curve

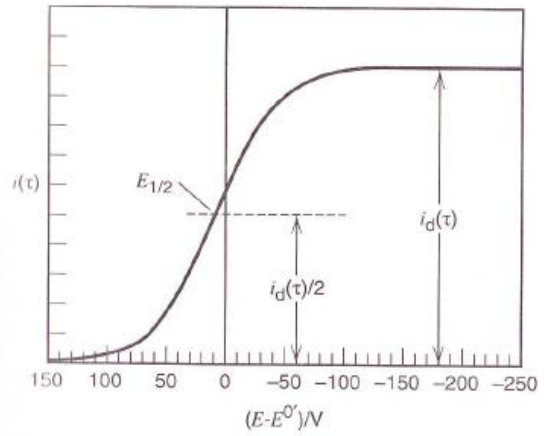


Figure 5.4.1 Characteristics of a reversible wave in sampled-current voltammetry. This curve is for $n = 1$, $T = 298$ K, and $D_O = D_R/2$. Because $D_O \neq D_R$, $E_{1/2}$ differs slightly from $E^{0'}$, in this case by about 9 mV. For $n > 1$, the wave rises more sharply to the plateau (see Figure 5.4.2).

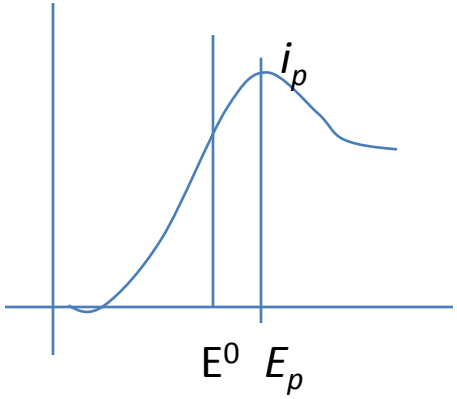
$$E = E^{0'} + \frac{RT}{nF} \ln \frac{D_R^{1/2}}{D_O^{1/2}} + \frac{RT}{nF} \ln \frac{i_d(\tau) - i(\tau)}{i(\tau)}$$

Cyclic Voltammetry

$$O + ne \rightleftarrows R \qquad E = E\,\text{-}vt$$

Assuming Nernstian Kinetics: FAST

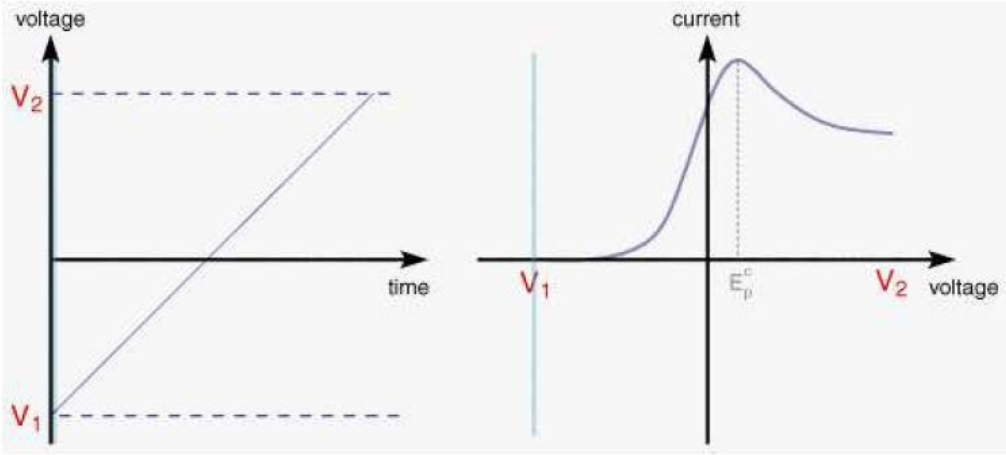
$$\frac{C_0(x,t)}{C_R(x,t)} = e^{\frac{nF}{RT}(E_i - vt - E^0)} = f(t)$$



$$i_P = (2.69 \times 10^5) A D_O^{1/2} n^{3/2} C_O^* V^{1/2}$$

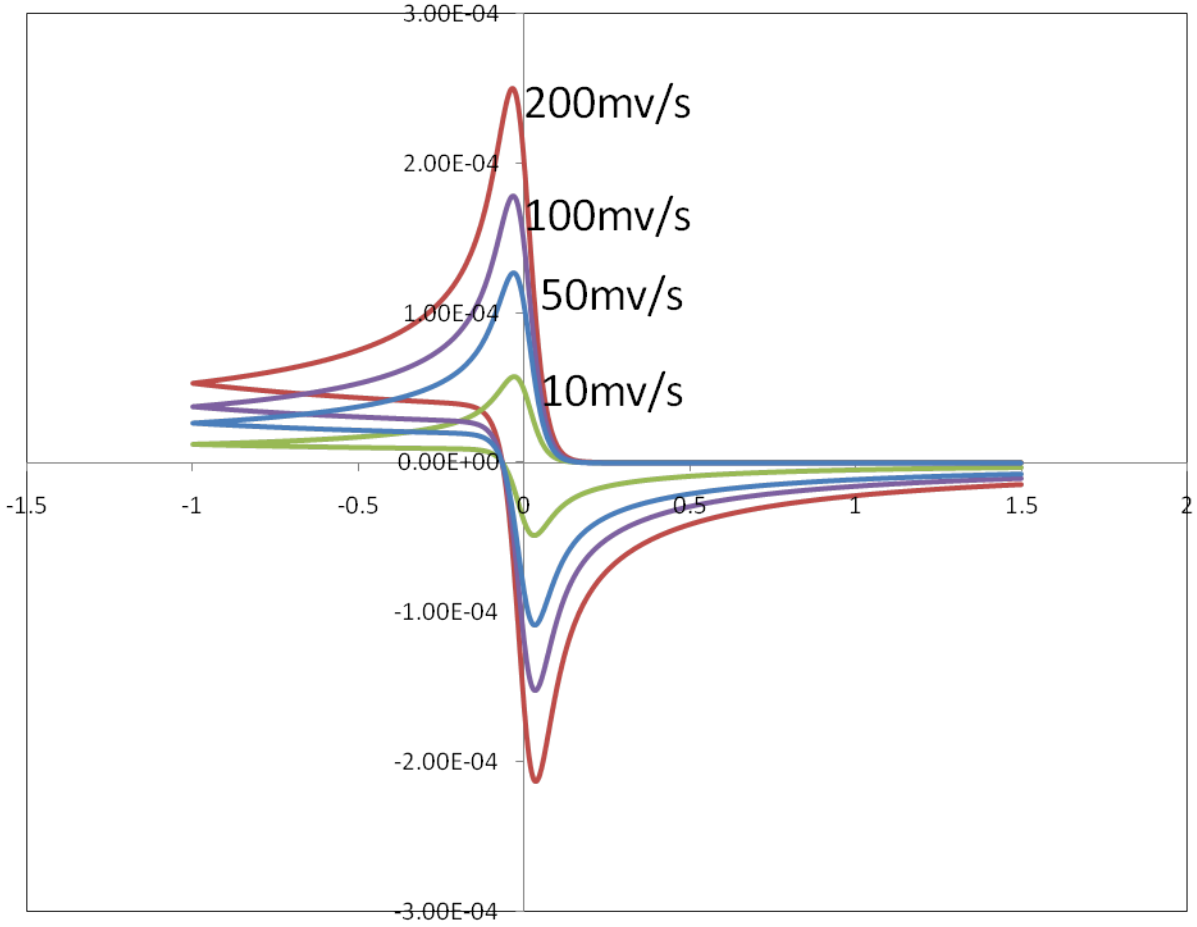
$$E_P = E_{1/2} - 1.109\frac{RT}{nF}$$

$$E_{1/2} = E^0 + \frac{RT}{nF}\ln\frac{D_0{}^{1/2}}{D_R{}^{1/2}}$$



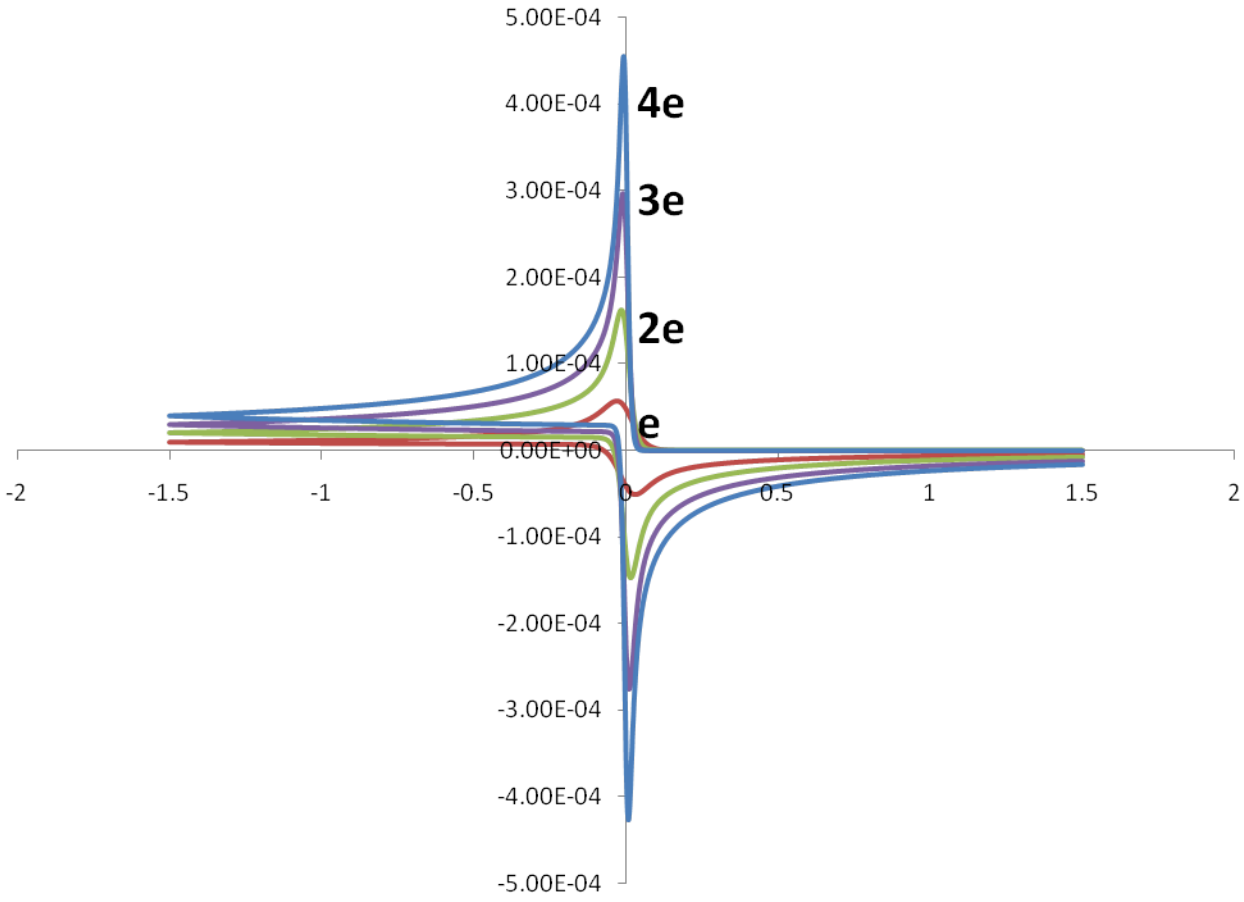
Scan rate-variation

Fast Kinetics



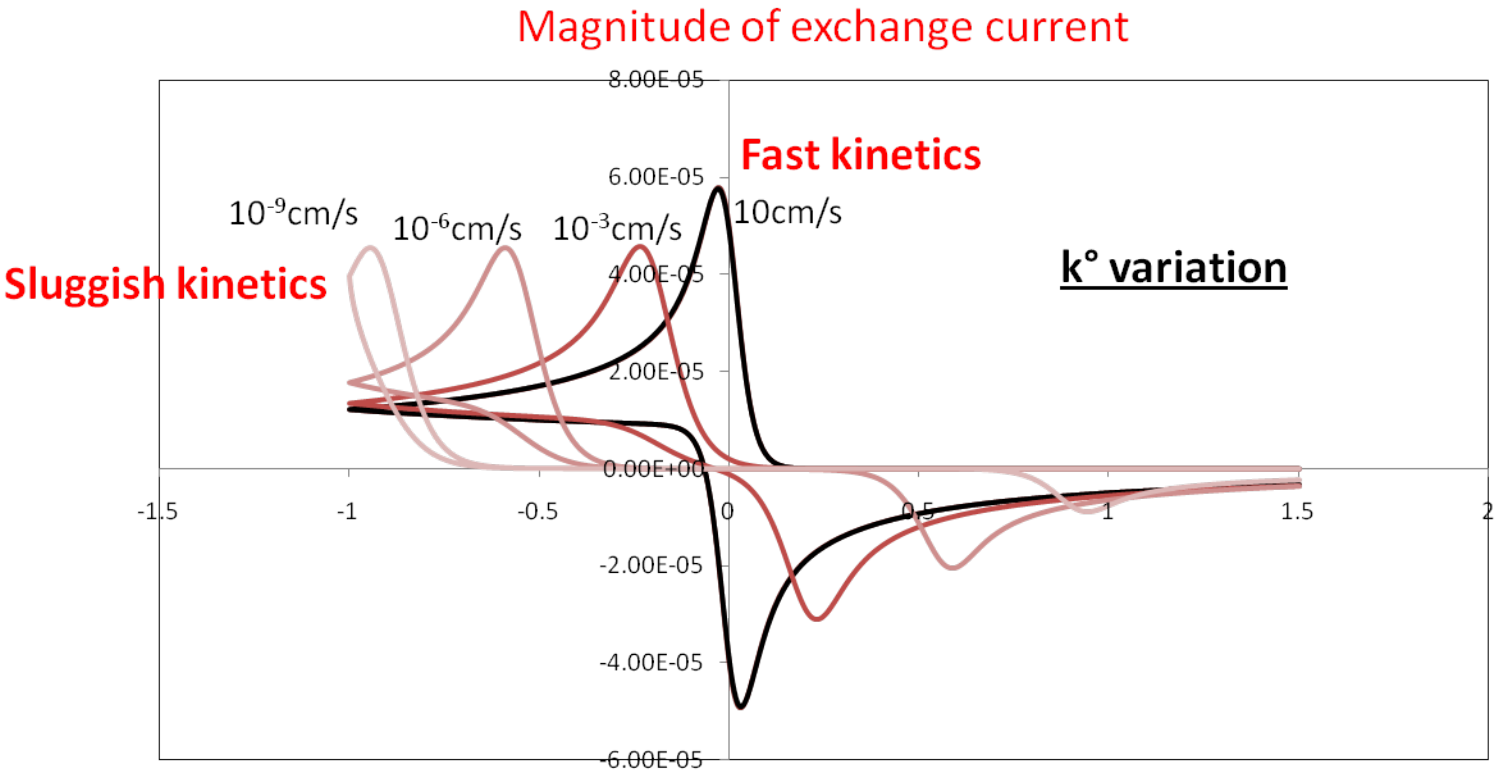
$$i_P = (2.69 \times 10^5) A D_O^{1/2} n^{3/2} C_O^* V^{1/2}$$

Number of electrons transferred n

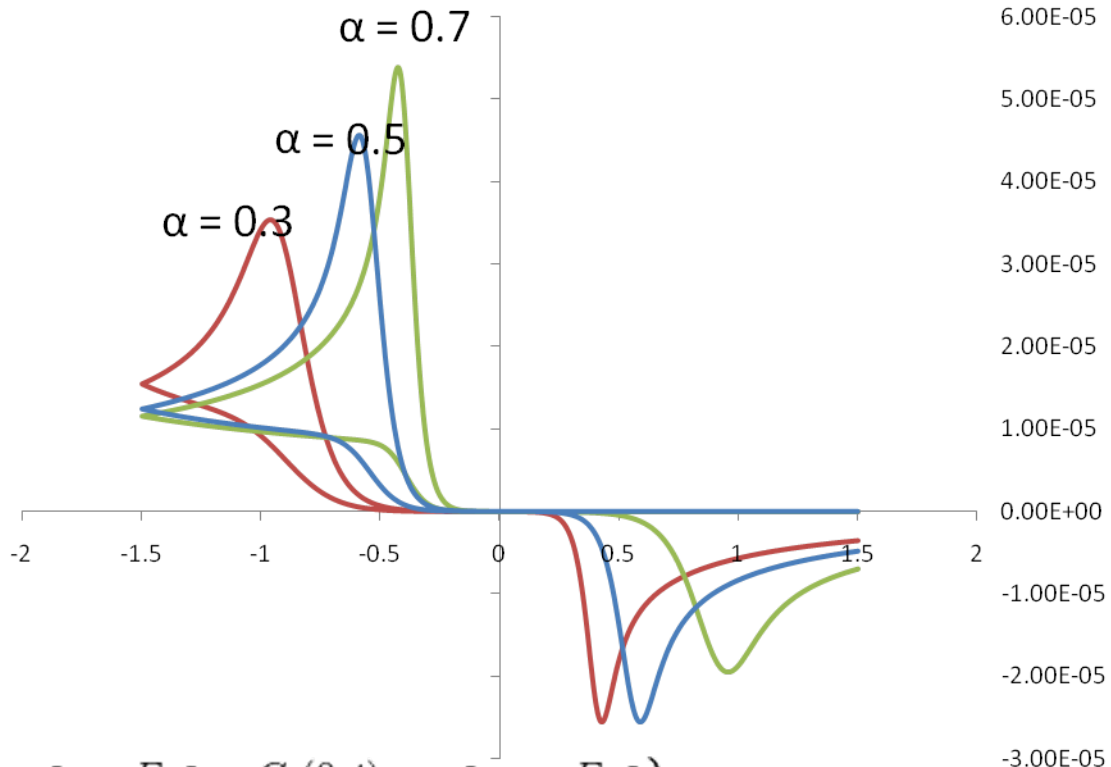


$$i_P = (2.69 \times 10^5) A D_O^{1/2} n^{3/2} C_O^* V^{1/2}$$

Non-nernstian kinetics

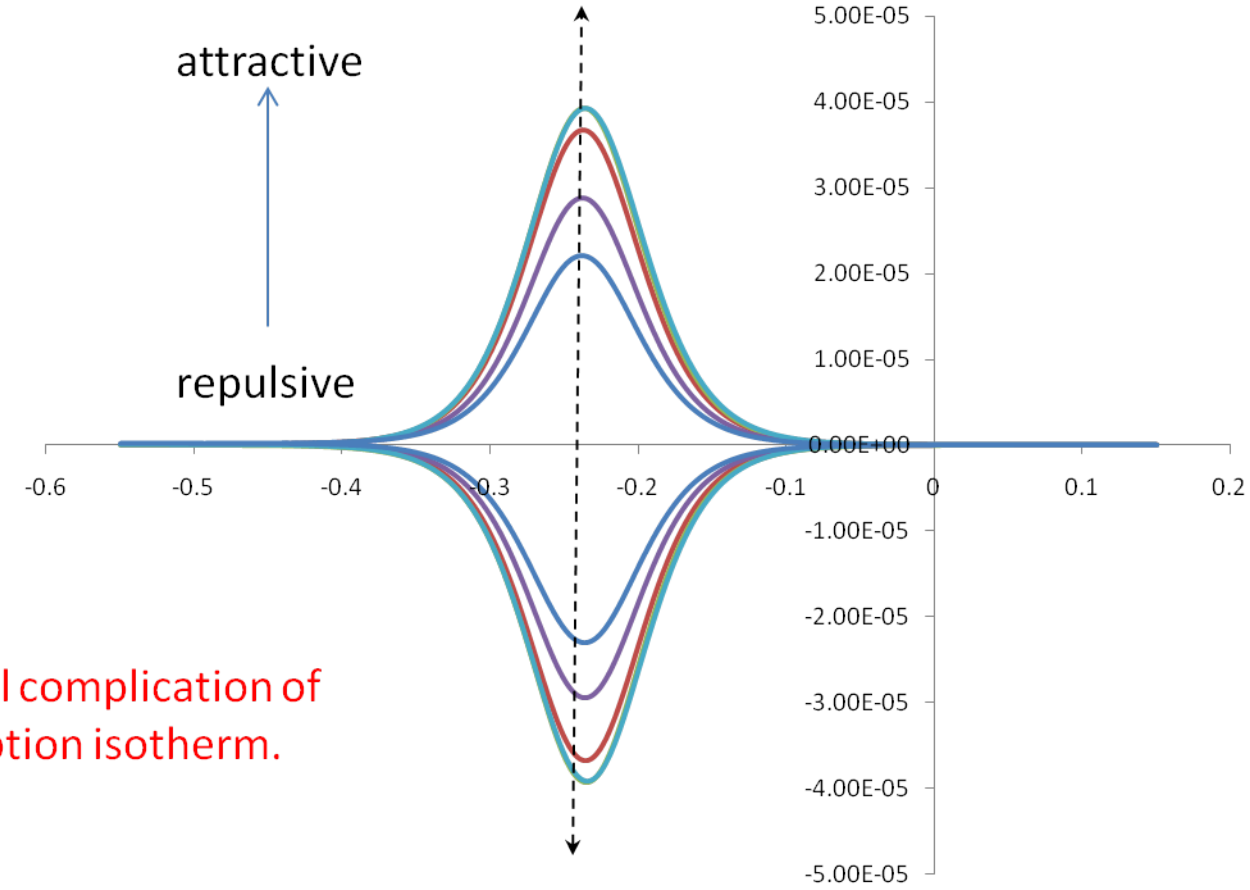


Transfer coefficient dependence
α variation



$$i = i_0 \left\{ \frac{C_o(0,t)}{C_o^*} \exp\left[\frac{\alpha_a n F \eta}{RT}\right] - \frac{C_r(0,t)}{C_r^*} \exp\left[-\frac{\alpha_c n F \eta}{RT}\right] \right\}$$

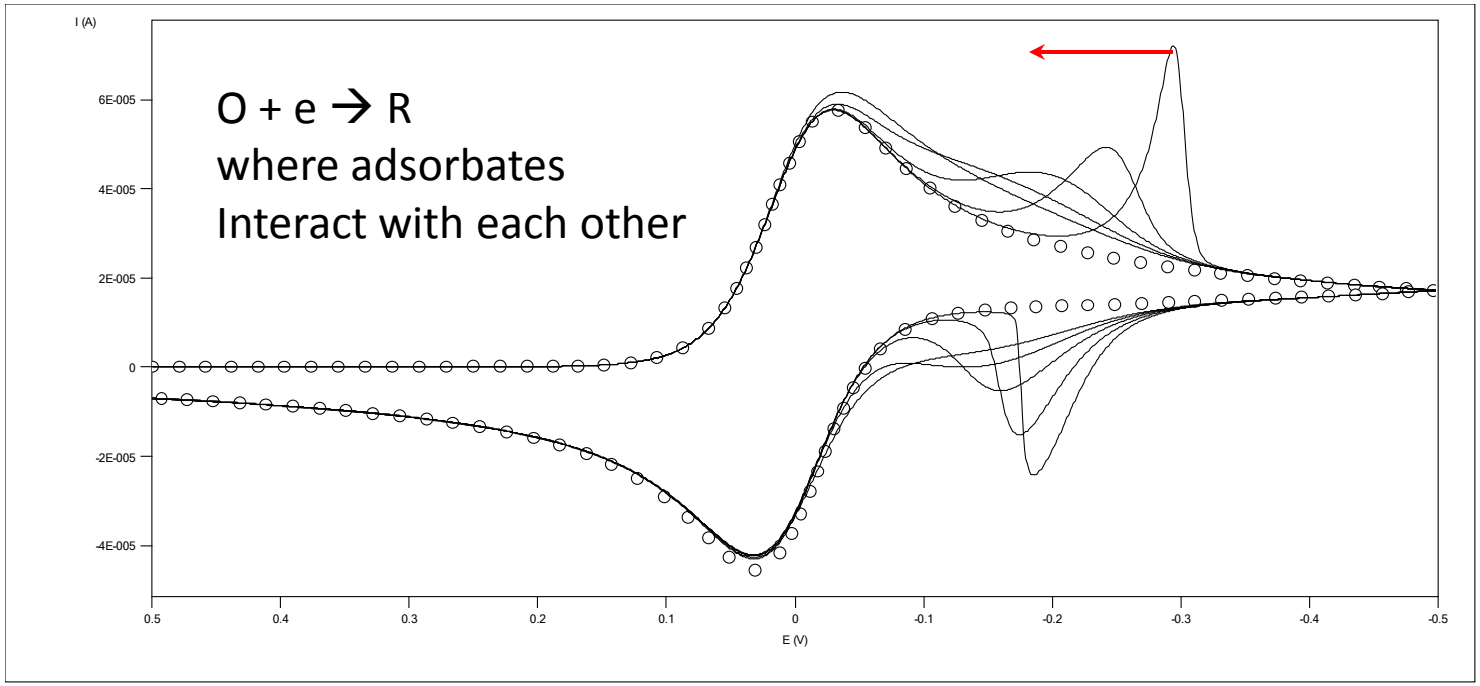
Adsorption/desorption

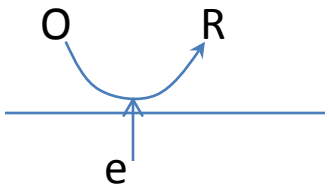


Additional complication of
An adsorption isotherm.

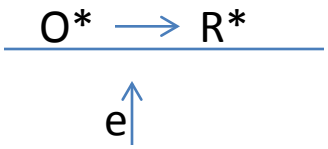
Adsorption + electron transfer

Attraction between
O* decreasing





Competes with



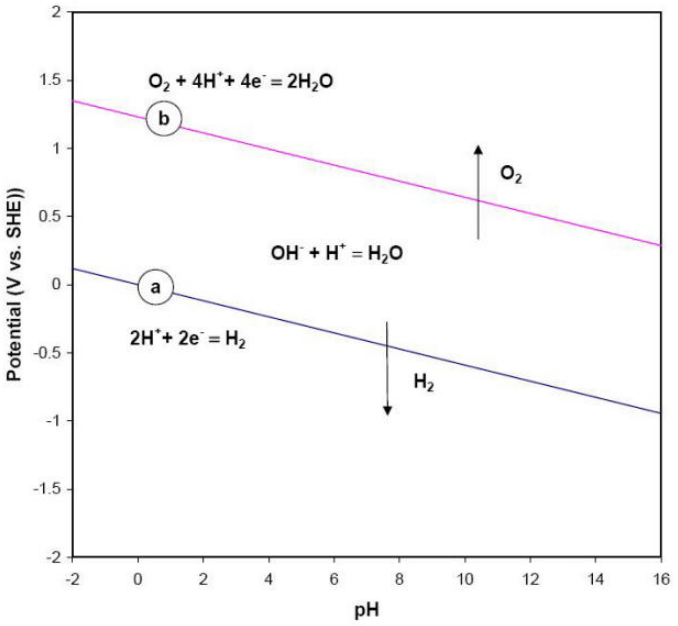
Pourbaix Diagram E-pH diagrams

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ 1.2V vs. SHE

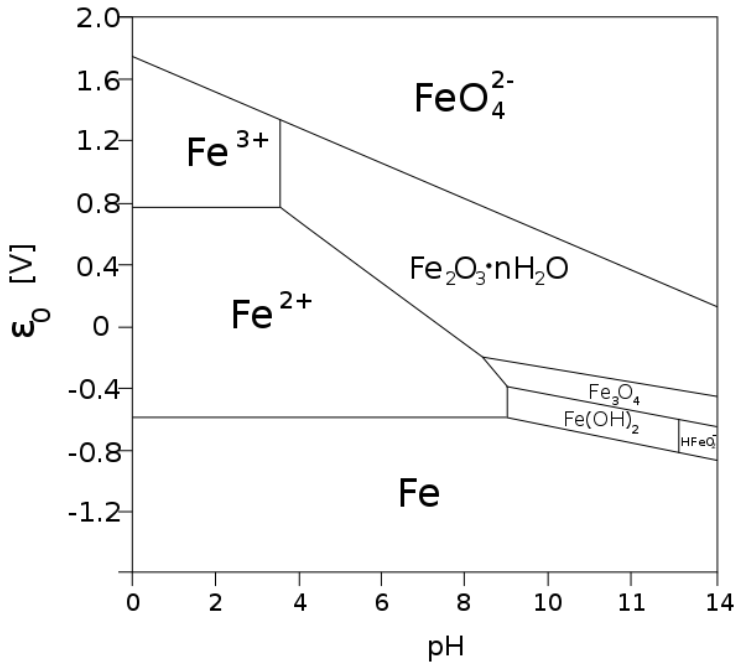
$2H^+ + 2e^- \rightarrow H_2$ 0V vs. SHE

Derive from Nernst Equation

Thermodynamic information only !

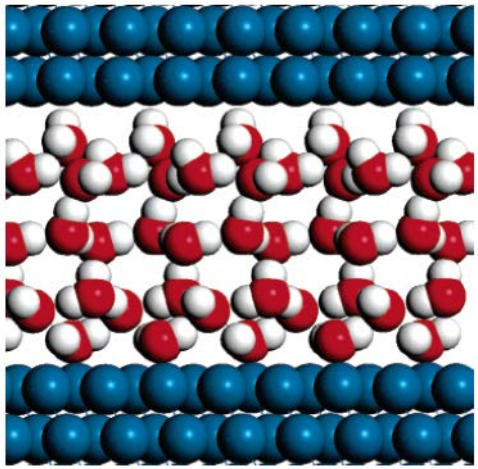


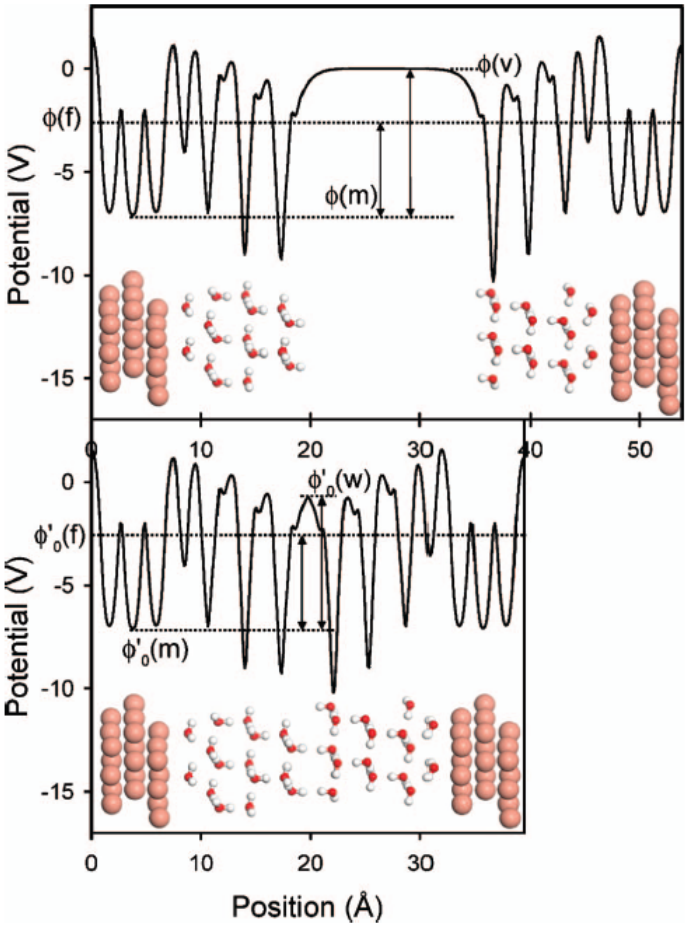
Pourbaix Diagram



Electrochemical stability of materials can be inferred instantly

Theory





Creation of internal standards in DFT have helped in referencing the electrode to potential

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Theory

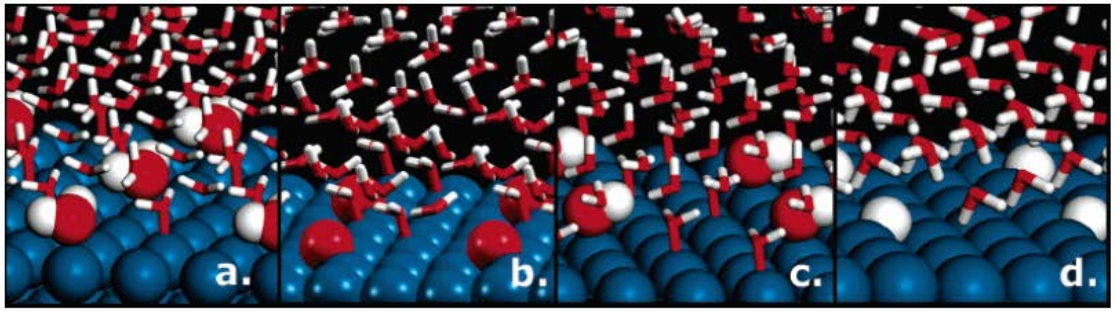
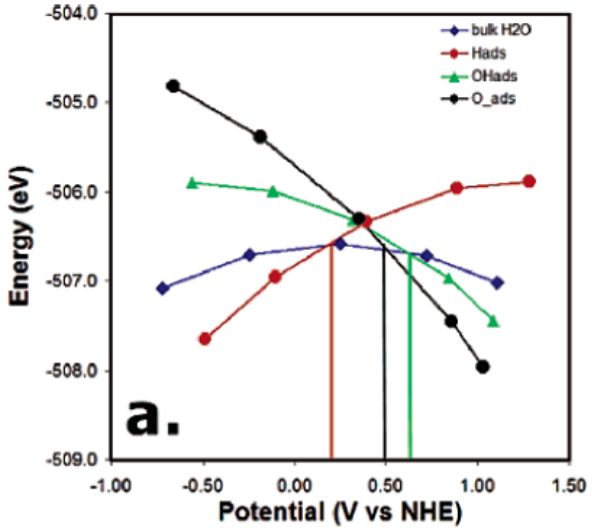
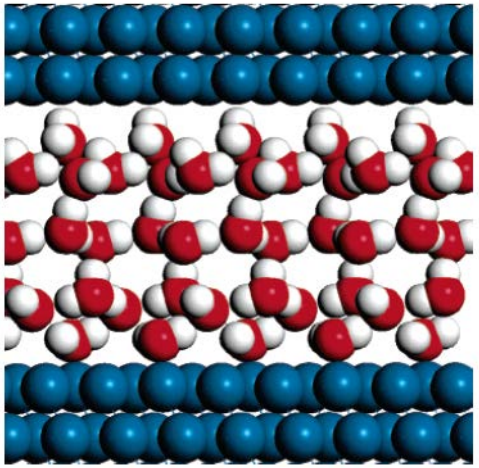


Figure 8. Snapshots indicating the adsorption geometry of (a) water, (b) oxygen, (c) hydroxyl, and (d) hydrogen for the neutral slabs utilized in Model 3.





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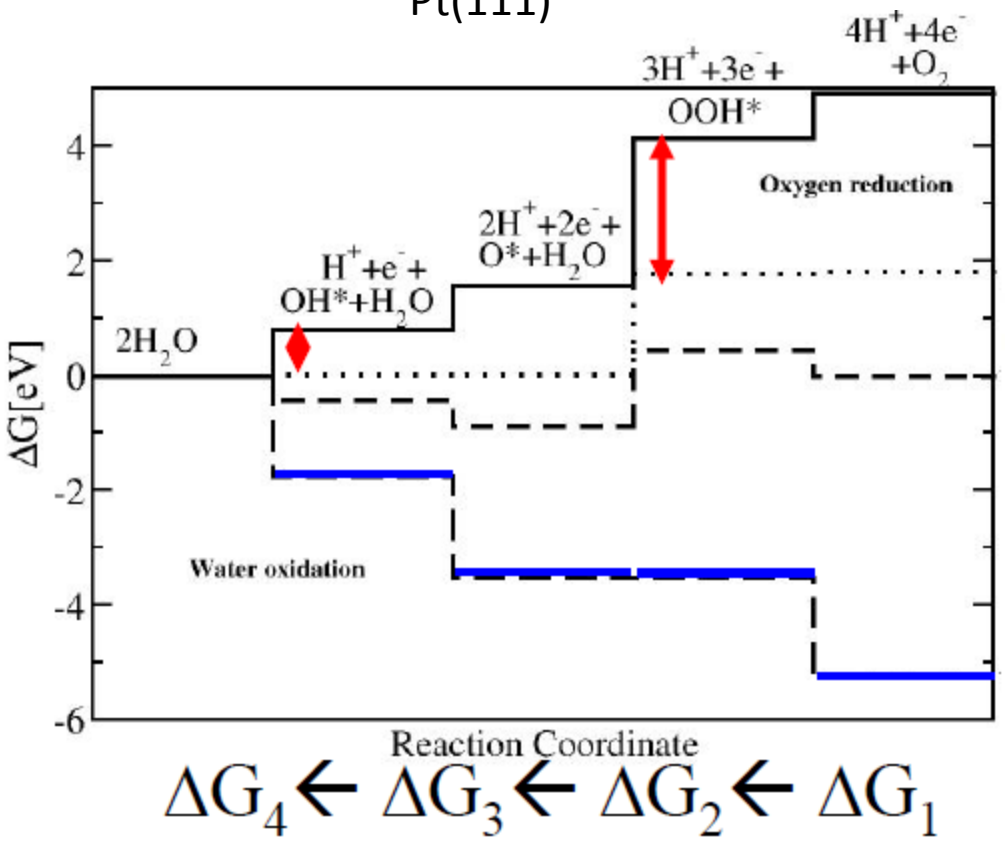
Idea of a limiting overpotential

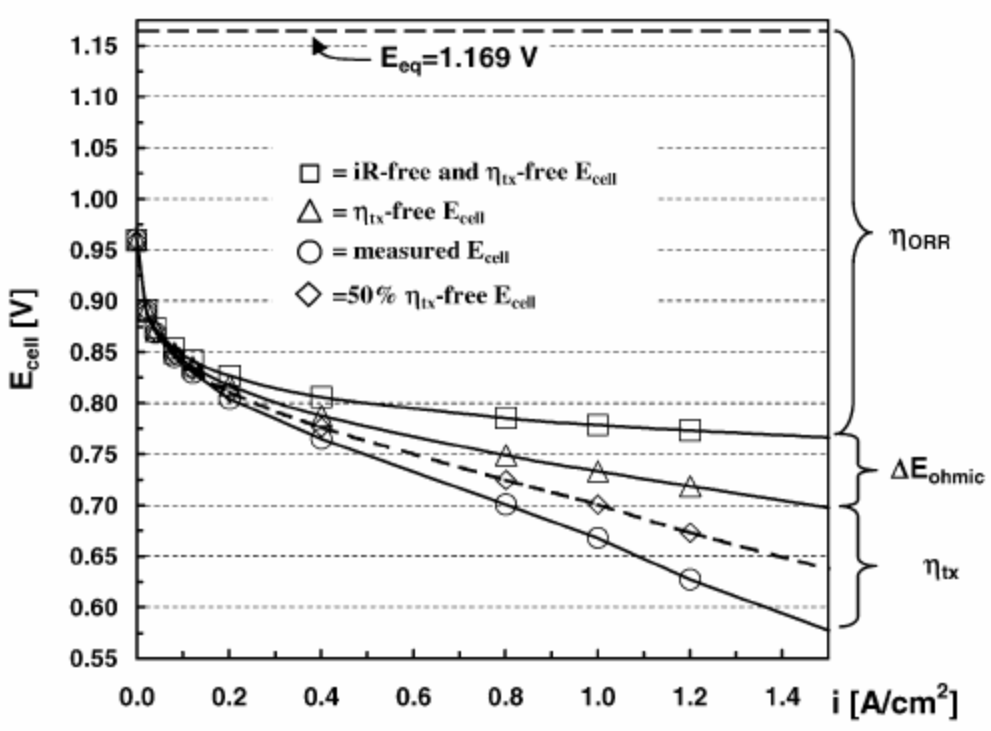
importance of intermediates

Pt(111)



Rossmeisl et. al.

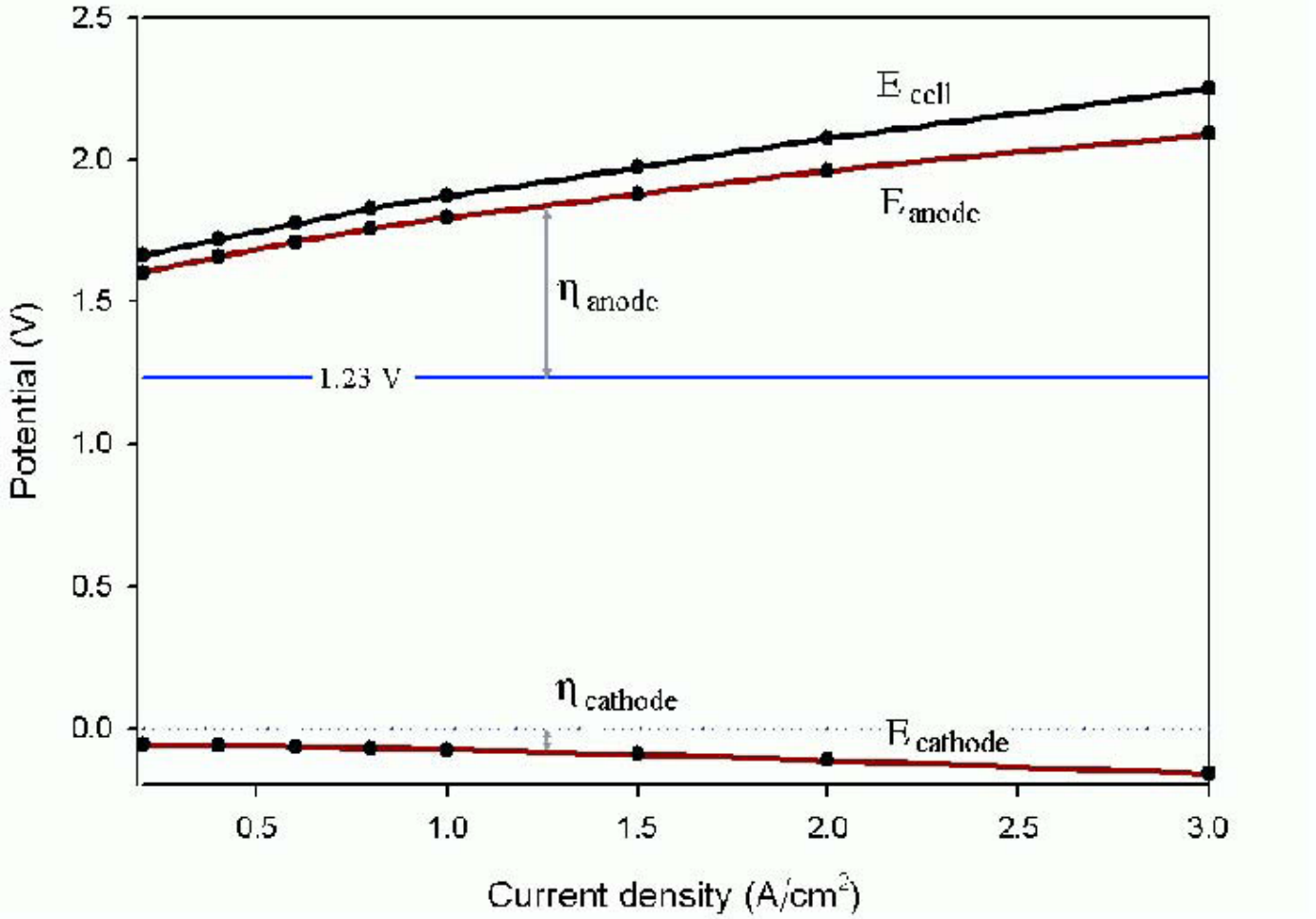
PEM Fuel cell Cathode (ORR)



Gasteiger, Kocha, Sompalli, Wagner, *Applied Catalysis B: Environmental,* ***56 (2005) 9-35.***

OER

$H_2O \rightarrow ½O_2+2H^+ +2e^-$



Marshall, Tsypkin, Børresen, Hagen, Tunold, Mater. *Chem. Phys.* ***94 (2005) 226–232.***

Summary

- Certain fundamental electrochemical challenges form the basis of sustainable energy scenario.
- Challenges coming from kinetics, stability, electron and mass transport need to be solved. Some can be solved by chemistry and some need to the solved through engineering design.