Short Course of Electrochemistry
L2: Polarization and Kinetics

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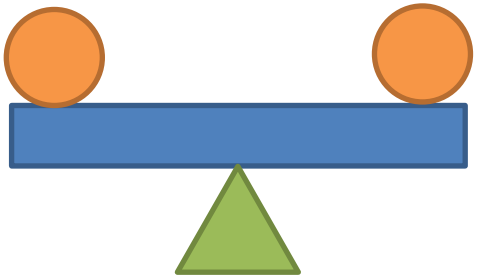
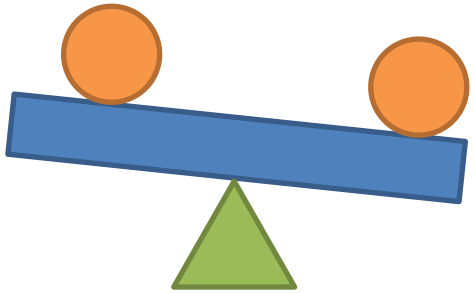
Polarization of Electrochemistry

Equilibrium or Not

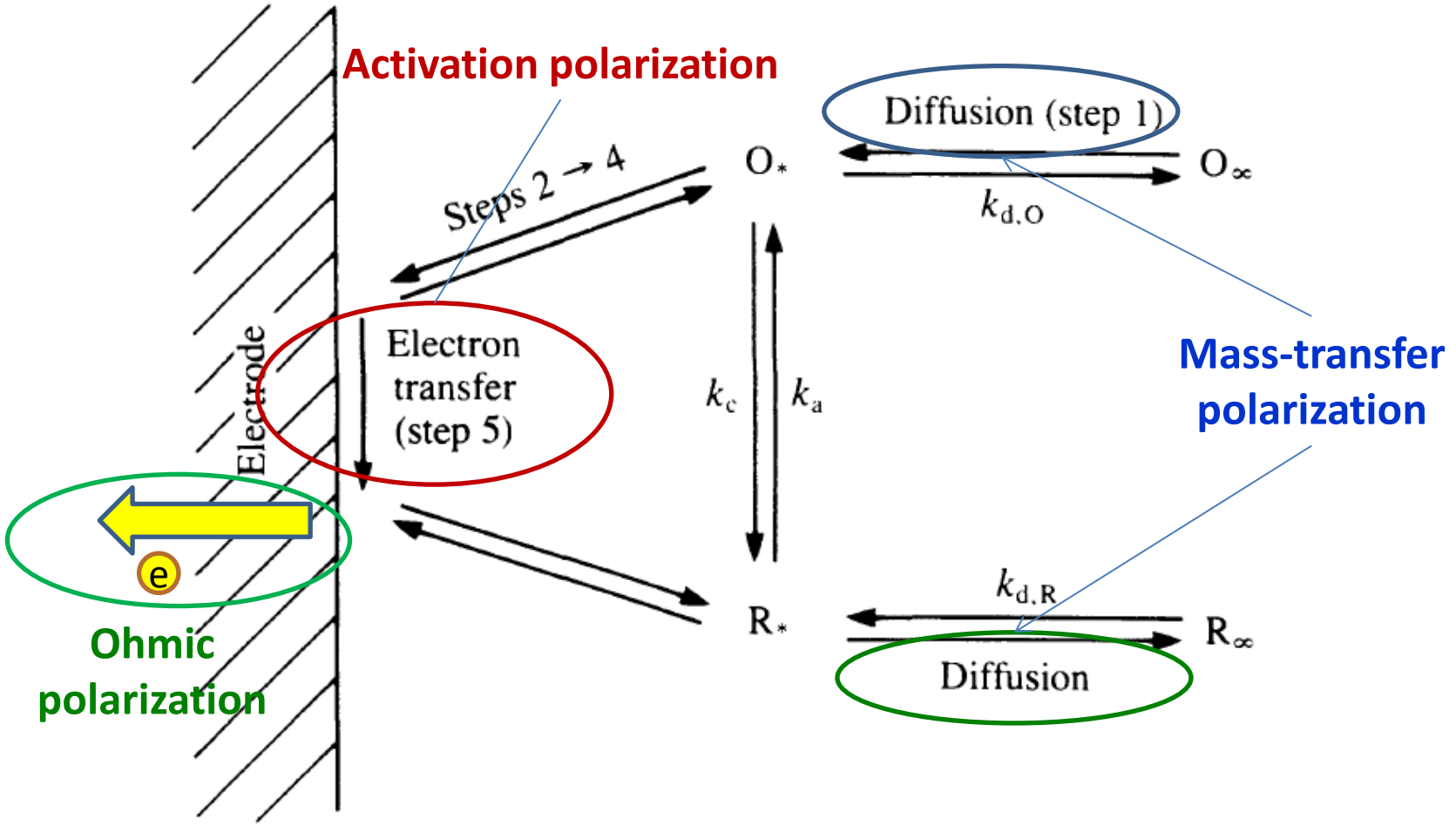
Equilibrium



Far from equilibrium



Polarization of Electrode



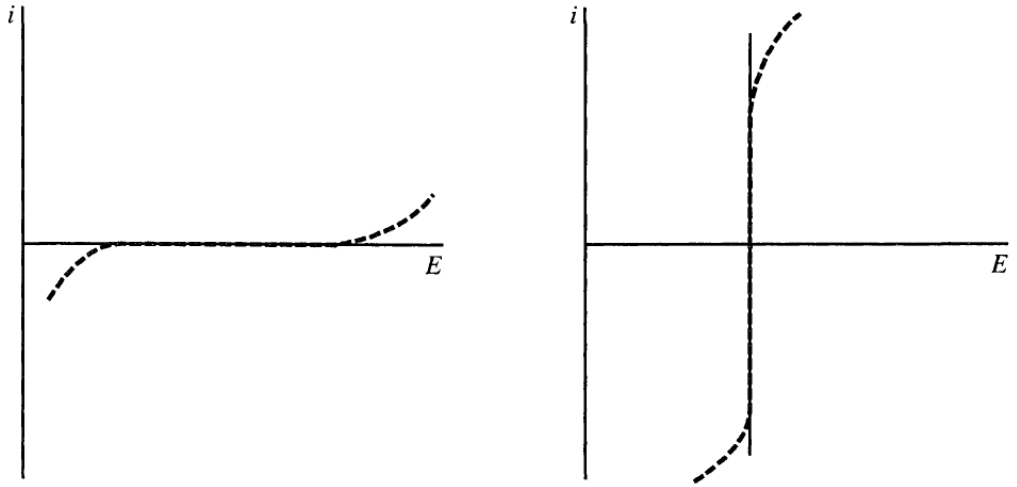
Electrochemistry, Principles, Methods, and Applications, Christopher M. A. Brett and Ana Maria Oliveira Brett, Oxford University Press, 1993.

極化產生之三主要因素

- **活化極化→活化過電位**
  - 氧化還原反應克服「活化能」障礙所導致，稱為「活化極化」(activation polarization)。此時所導致的電位損失，稱為「活化過電位」(activation overpotential)。
- **歐姆極化→歐姆過電位**
  - 電子移動必須消耗能量於電極和導線之阻抗，而離子移動必須消耗能量於溶液之阻抗。此整體之「內阻消耗」被稱為「歐姆極化」(ohmic polarization)。此時所導致的電位損失，稱為「歐姆過電位」(ohmic overpotential)。
- **質傳極化→質傳過電位**
  - 離子移動之擴散速率遠慢於電流之移動速率。由於離子擴散導致之極化，被稱為「質傳極化」(Mass-transfer polarization)。此時所導致的電位損失，稱為「質傳過電位」(Mass-transfer overpotential)。

Polarized and Non-polarizable Electrode

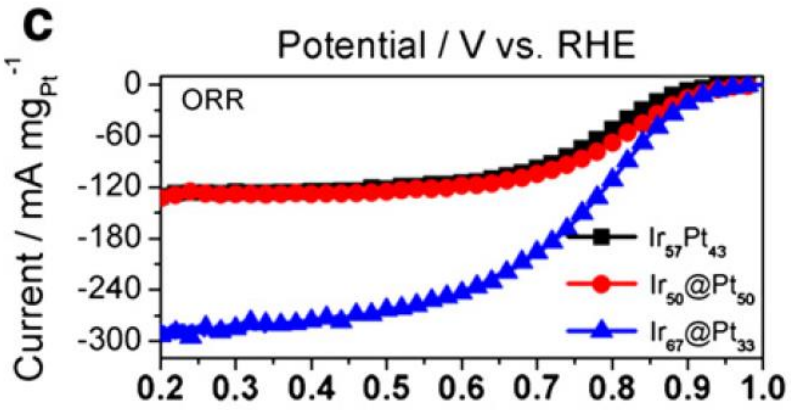
- **Ideal polarized electrode**
  - It shows a very large change in potential upon the passage of an infinitesimal current.
- **Ideal non-polarizable electrode (or ideal depolarized electrode)**
  - It is thus an electrode whose potential does not change upon passage of current.



(*a*) Ideal polarizable electrode (*b*) Ideal nonpolarizable electrode

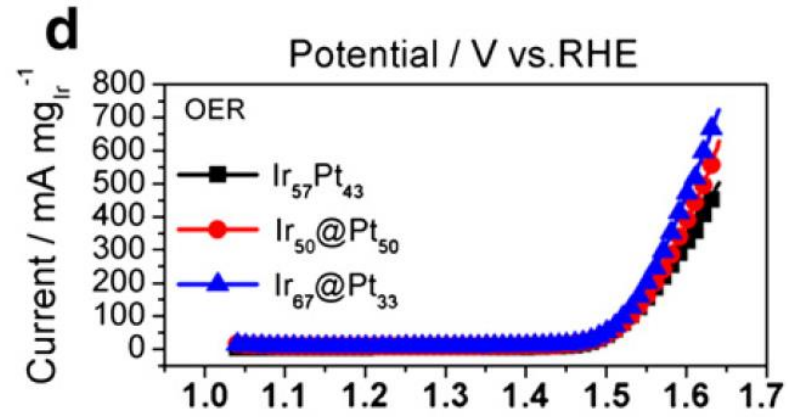
Dashed lines show behavior of actual electrodes that approach the ideal behavior over limited ranges of current or potential

Overpotential and Polarization



$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \ldots E^0 = 1.23\ V$$

The standard potential of oxygen reduction reaction is 1.23 V; However, it happens below 1.0 V.



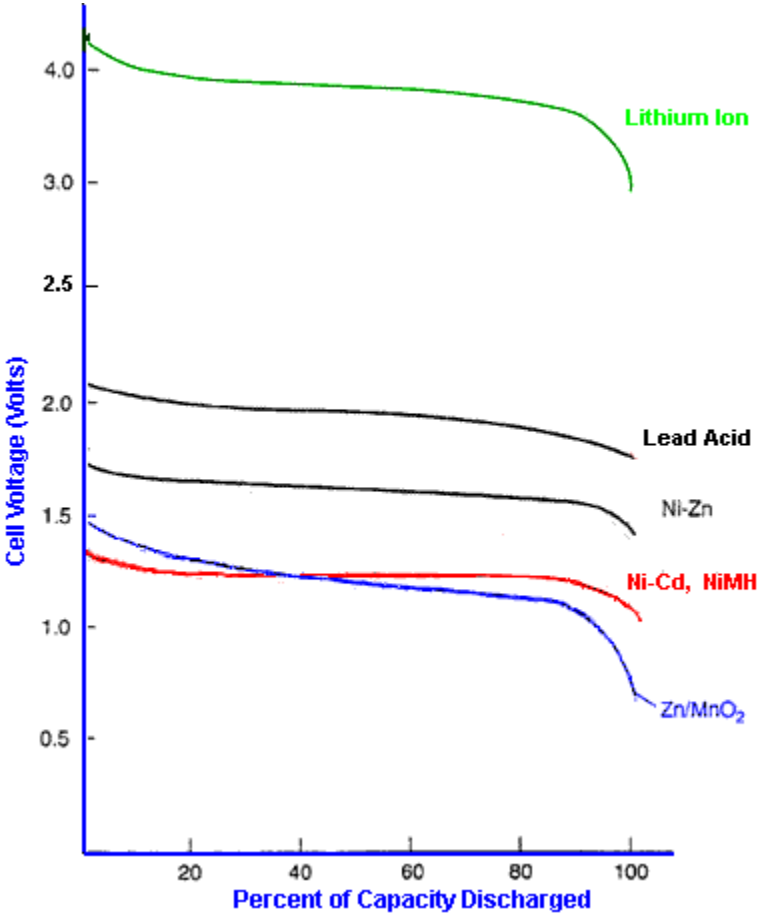
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \ldots E^0 = -1.23\ V$$

The standard potential of oxygen evolution reaction is 1.23 V; However, it needs at least 1.48 V.

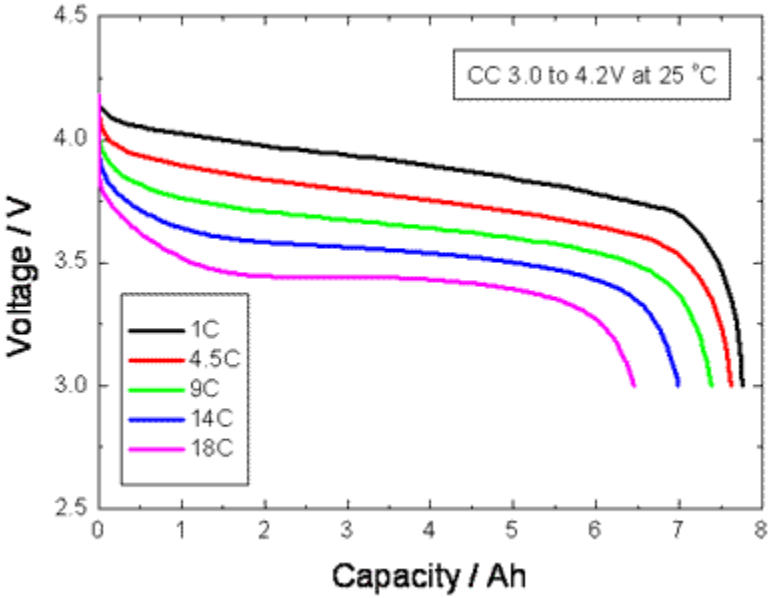
G. Zhang, Z.-G. Shao, W. Lu, G. Li, F. Liu, B. Yi, Electrochemistry Communications, 22 (2012) 145-148.

Polarization Curve of Battery

Various current-voltage curves of batteries

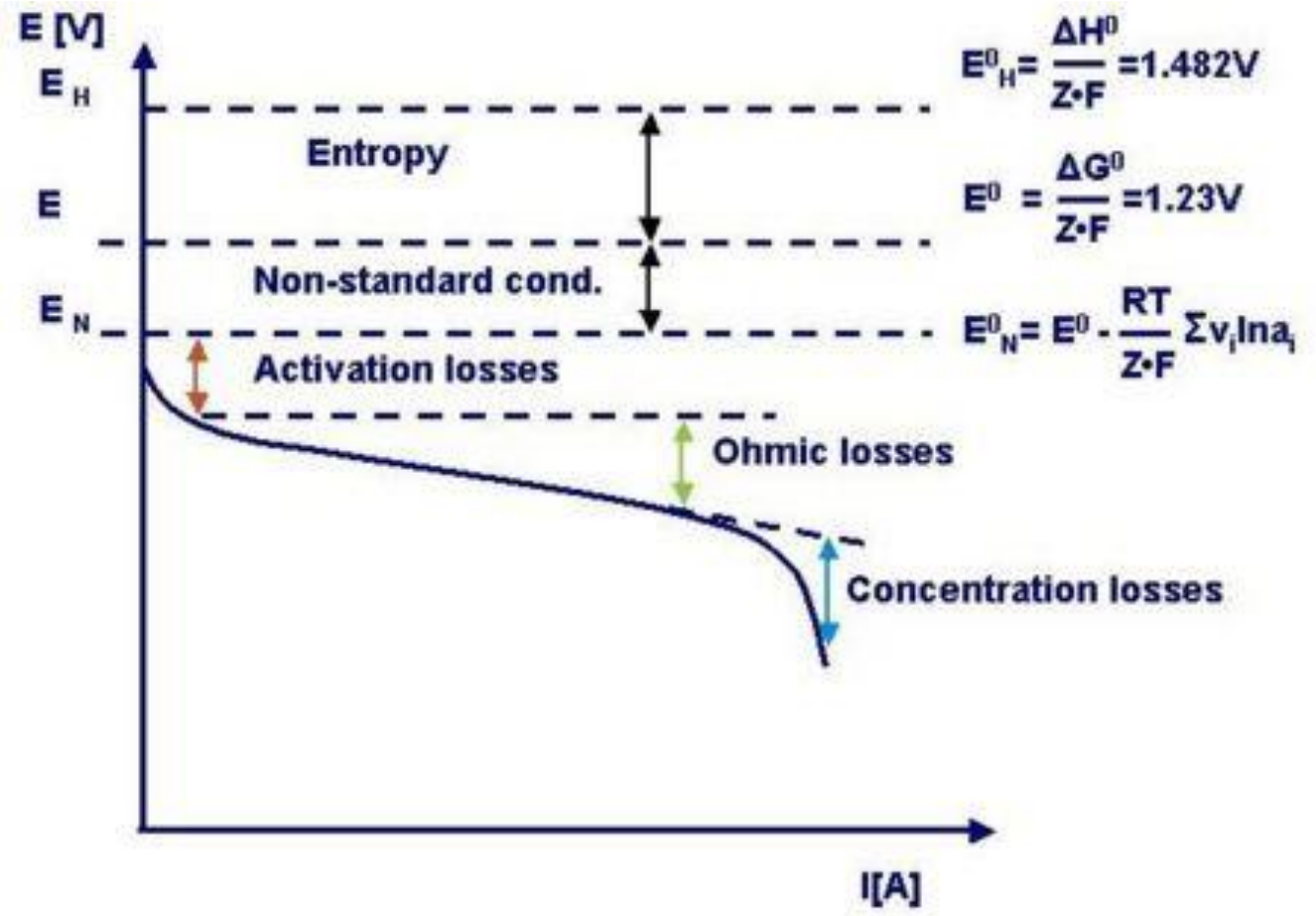


Lithium-ion battery discharged by various C-rate



Ref.: http://www.mpoweruk.com/performance.htm

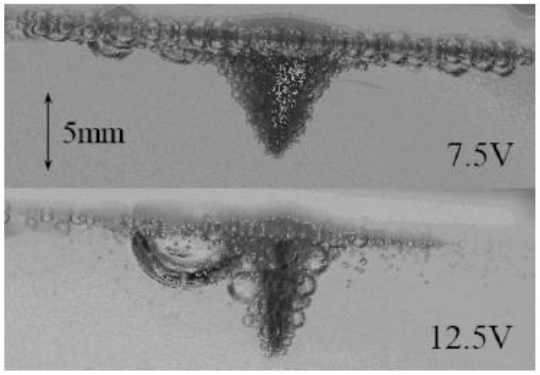
Heat, Polarization and Loss

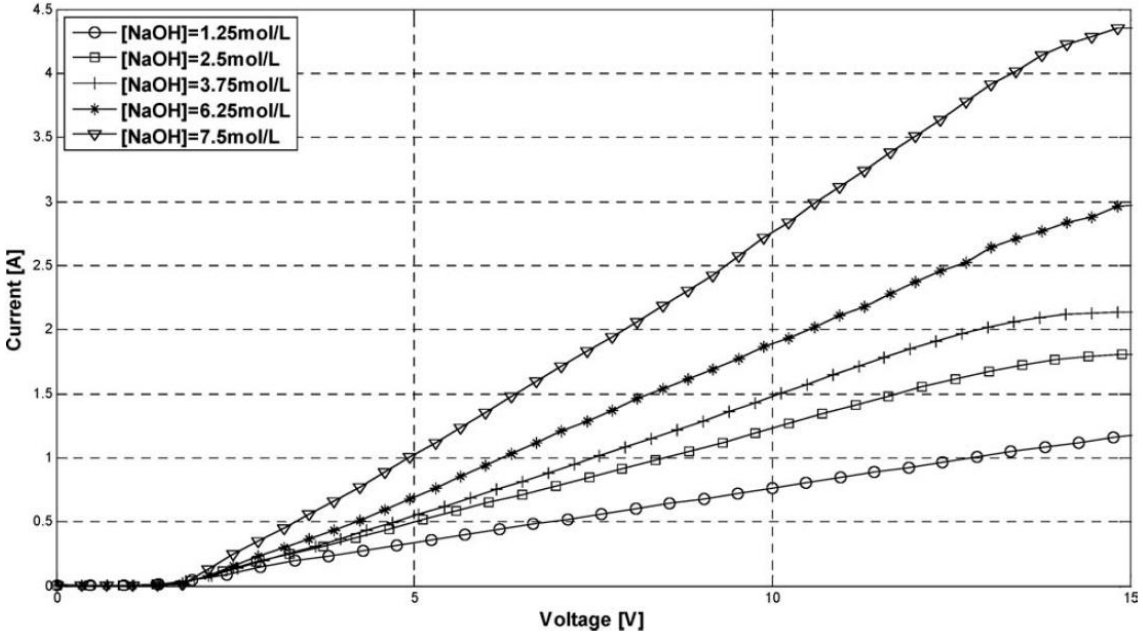


http://www.ika.rwth-aachen.de/r2h/index.php/Introduction_to_PEFC_Operation.html

Polarization of Water Electrolysis

Evolution of the I-V characteristic with NaOH electrolyte by stainless steel working electrode (SS304L)

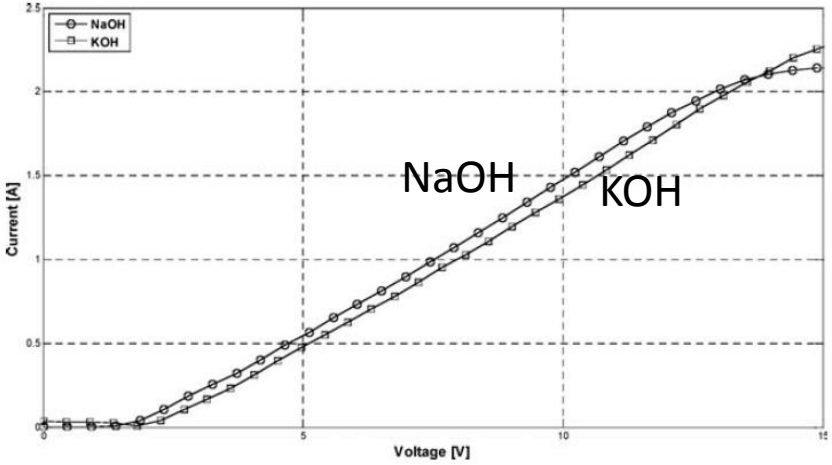




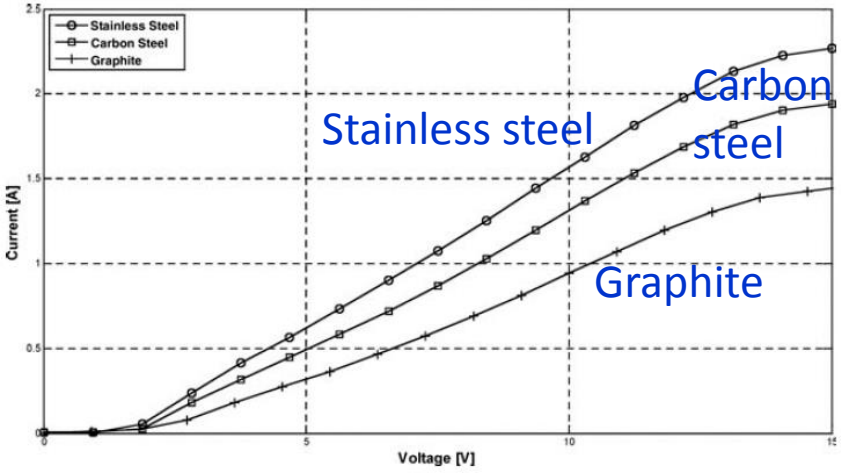
P. Mandin, R. Wuthrich and H. Roustan (2010). "Polarization curves for an alkaline water electrolysis at a small pin vertical electrode to produce hydrogen." AIChE Journal **56(Compendex): 2446-2454.**

Cont'd

Electrolyte: KOH vs. NaOH



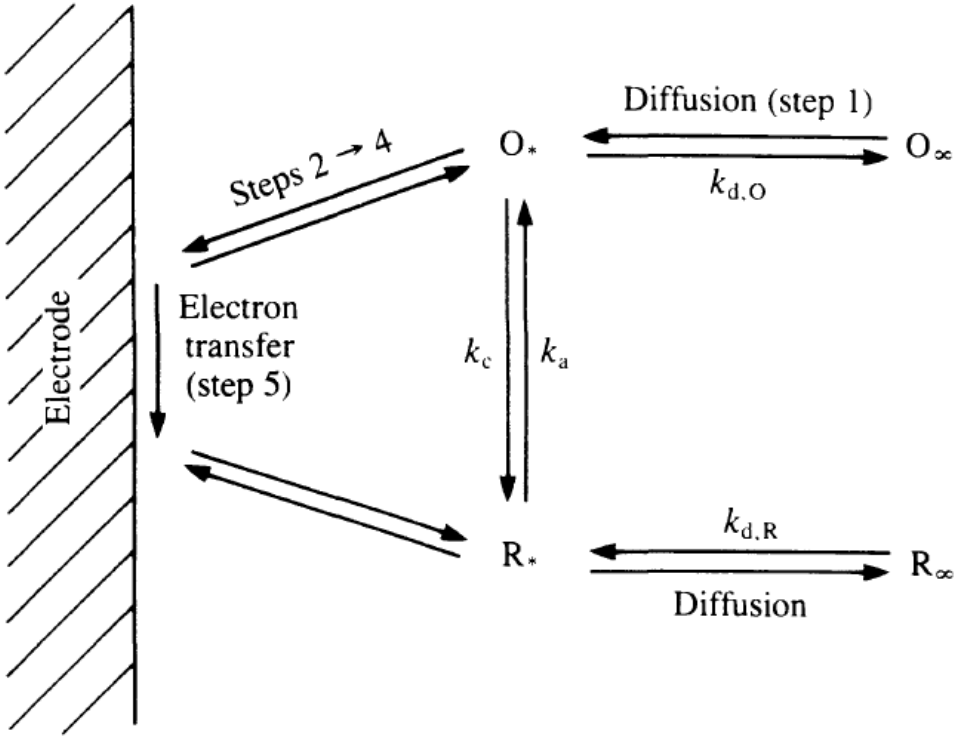
Electrode: Stainless steel vs. Carbon steel vs. Graphite



P. Mandin, R. Wuthrich and H. Roustan (2010). "Polarization curves for an alkaline water electrolysis at a small pin vertical electrode to produce hydrogen." AIChE Journal **56(Compendex): 2446-2454.**

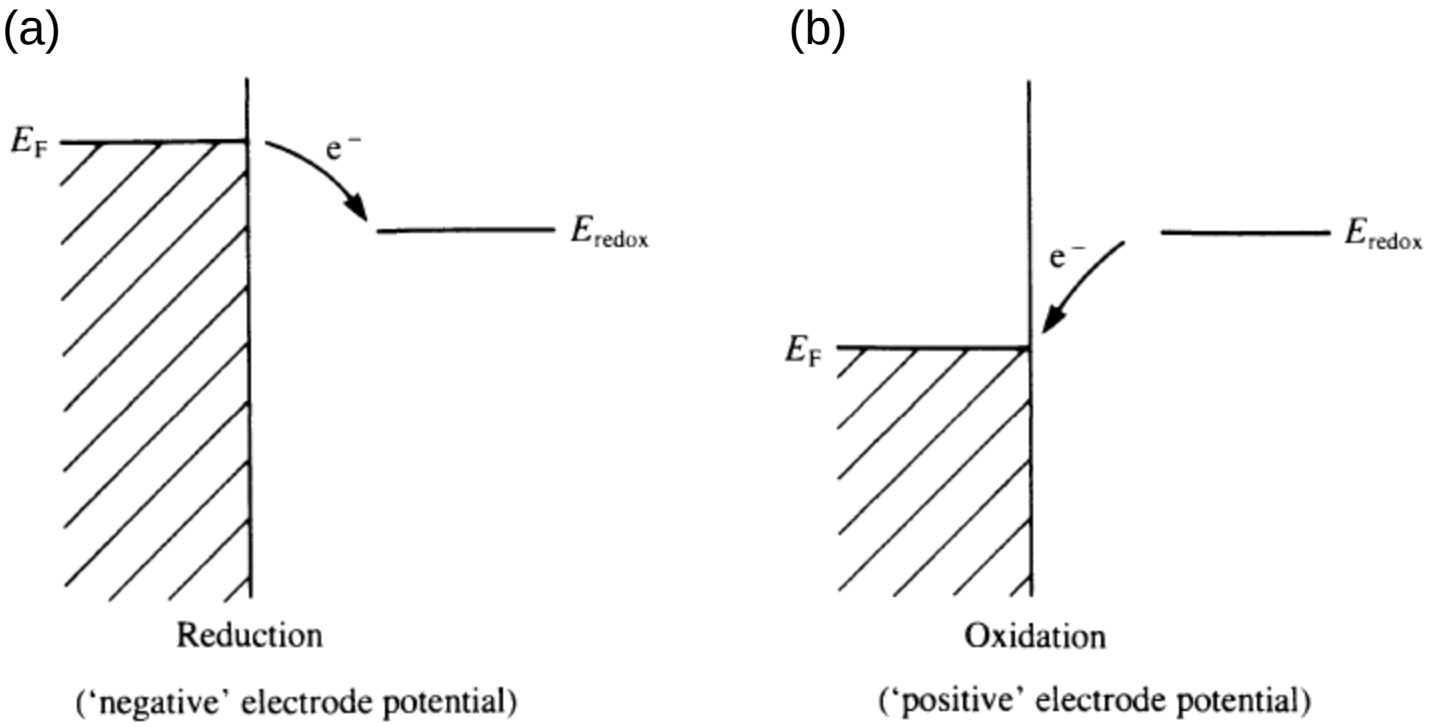
Kinetics of Electrochemistry

Electrochemical Process



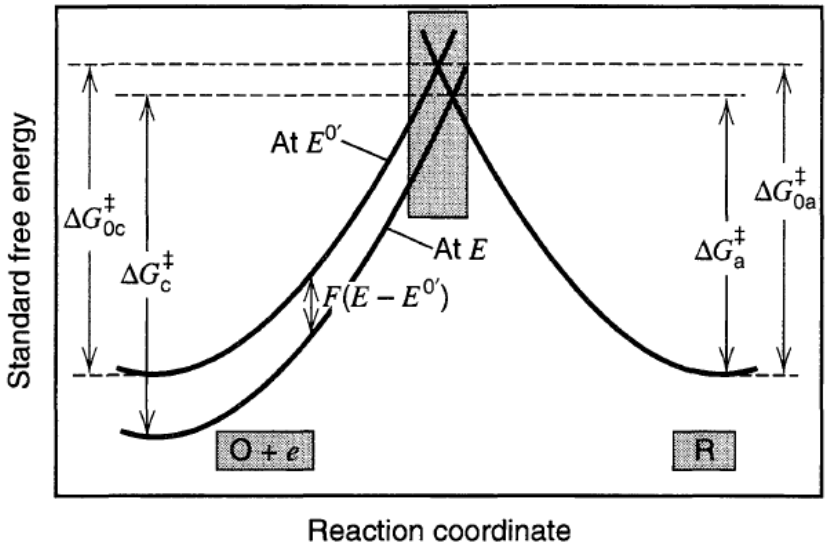
1. **Diffusion of the species to where the reaction occurs by a mass transfer coefficient.**
2. **Rearrangement of the ionic atmosphere (10^{-8} s).**
3. **Reorientation of the solvent dipoles (10^{-11} s).**
4. **Alterations in the distances between the central ion and the ligands (10^{-14} s).**
5. **Electron transfer (10^{-16} s).**
6. **Relaxation in the inverse sense.**

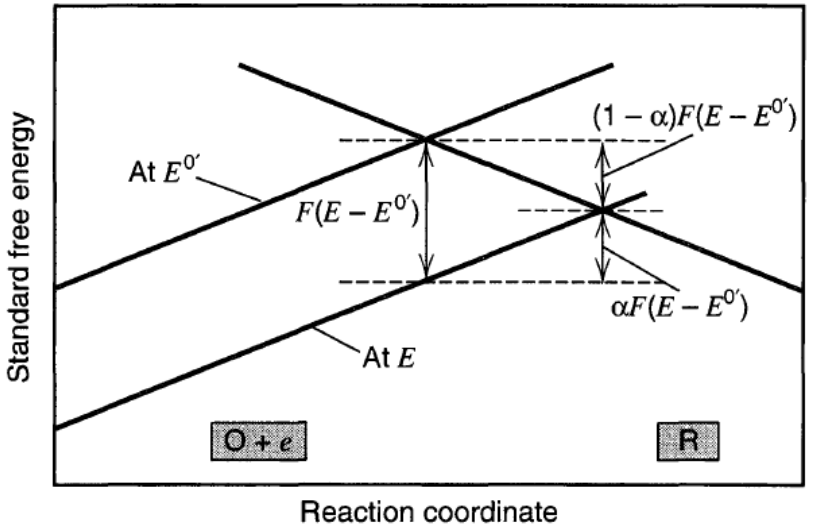
Electron Transfer at an Inert Metallic Electrode



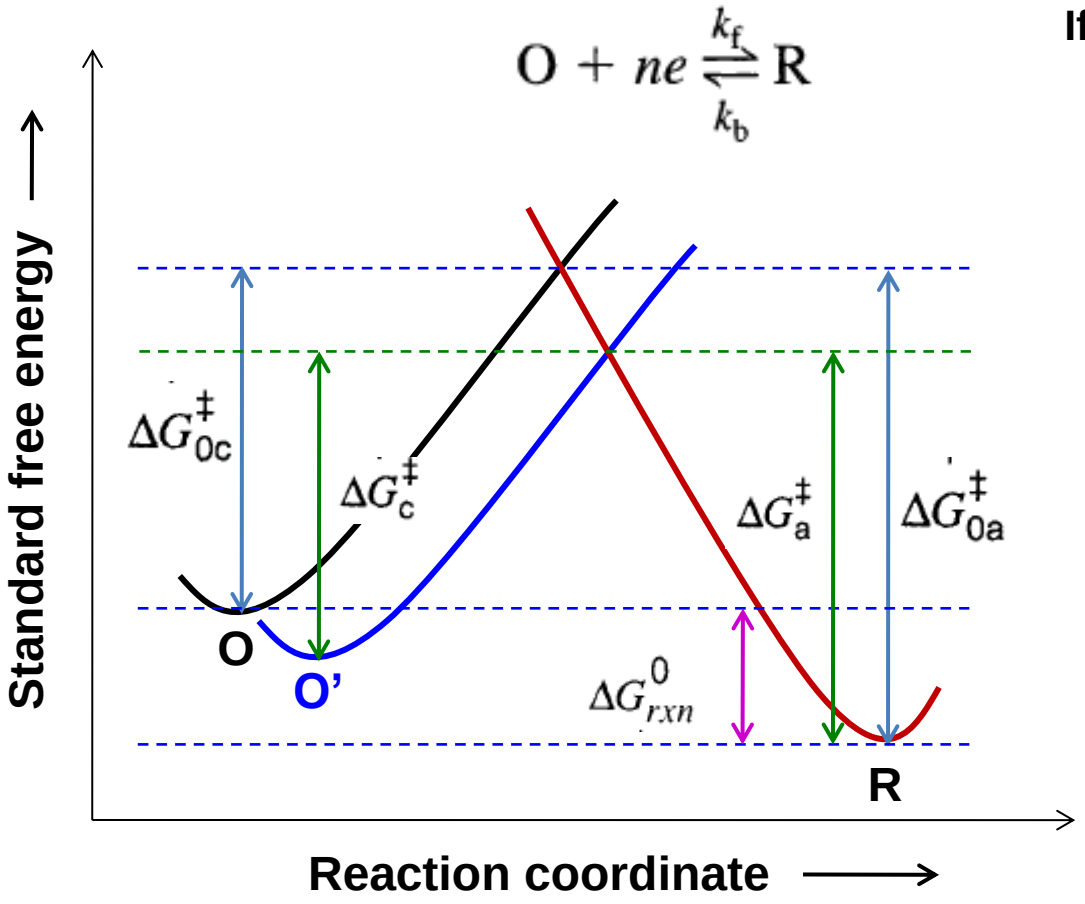
The potential applied to the electrode alters the highest occupied electronic energy level, E_F, facilitating (a) reduction or (b) oxidation.

ΔG Variation





ΔG and Reaction Coordinate



If the reaction is at standard situation,

$$\Delta G_{rxn}^{0} = \Delta G_{0a}^{\ddagger} - \Delta G_{0c}^{\ddagger} \quad \text{At } E^{0'}$$

$$\Delta G_{rxn}^{0} = -nFE^{0'}$$

Now, the reaction is subjected to a new potential of *E*,

$$\Delta G_{rxn} = \Delta G_{a}^{\ddagger} - \Delta G_{c}^{\ddagger}$$

$$\Delta G_{rxn} = -nFE = \Delta G_{rxn}^{0} - nF\,(E - E^{0'})$$

If n = 1, we can define:

$$\Delta G_{a}^{\ddagger} = \Delta G_{0a}^{\ddagger} - (1-\alpha)F(E - E^{0'})$$

$$\Delta G_{c}^{\ddagger} = \Delta G_{0c}^{\ddagger} + \alpha F(E - E^{0'})$$

α: Transfer coefficient

Rate constants are: $k = A'\, e^{-\Delta G^{\ddagger}/RT}$

$$k_f = A_f \exp\,(-\Delta G_{c}^{\ddagger}/RT)$$

$$k_b = A_b \exp\,(-\Delta G_{a}^{\ddagger}/RT)$$

$$k_f = A_f \exp\,(-\Delta G_{0c}^{\ddagger}/RT)\exp[-\alpha f(E - E^{0'})]$$

$$k_b = A_b \exp\,(-\Delta G_{0a}^{\ddagger}/RT)\exp[(1-\alpha) f(E - E^{0'})]$$

where $f = F/RT$

Butler-Volmer Equation

$$i = i_c - i_a = nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$

$$k_f = A_f \exp(-\Delta G^{\ddagger}_{0c}/RT) \exp[-\alpha f(E - E^{0'})]$$

$$k_b = A_b \exp(-\Delta G^{\ddagger}_{0a}/RT) \exp[(1 - \alpha) f(E - E^{0'})]$$

Standard situation

If we set ***k⁰*** is the standard rate constant, which is:

$$k^0 = A_f \exp(-\Delta G^{\ddagger}_{0c}/RT) = A_b \exp(-\Delta G^{\ddagger}_{0a}/RT)$$

$$k_f = k^0 \exp[-\alpha f(E - E^{0'})] \qquad k_b = k^0 \exp[(1 - \alpha) f(E - E^{0'})]$$

Butler-Volmer Equation (One-step, one-electron process)

$$i = FAk^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha) f(E - E^{0'})} \right]$$

This equation is for one-electron process; if *n* is not equal to 1, what does the equation express?

α: Transfer coefficient

$$i = FAk^0 \left[C_O(0, t) e^{-\alpha f (E - E^{0'})} - C_R(0, t) e^{(1-\alpha) f (E - E^{0'})} \right]$$

- **α should be between 0 – 1.**
  - In most systems α turns out to lie between 0.3 and 0.7
  - α can usually be approximated by 0.5 in the absence of actual measurements.
- **α should generally be a potential-dependent factor.**
  - However, in the great majority of experiments, a appears to be constant, if only because the potential range over which kinetic data can be collected is fairly narrow.

Equilibrium Conditions: Exchange Current

At equilibrium, the current is zero and the potential is E_{eq}.

$$i = FAk^0 \left[C_{\mathrm{O}}(0,t) e^{-\alpha f (E - E^{0'})} - C_{\mathrm{R}}(0,t) e^{(1-\alpha) f (E - E^{0'})} \right] = 0$$

$$FAk^0 C_{\mathrm{O}}(0,t) e^{-\alpha f (E_{\mathrm{eq}} - E^{0'})} = FAk^0 C_{\mathrm{R}}(0,t) e^{(1-\alpha) f (E_{\mathrm{eq}} - E^{0'})}$$

You can know bulk concentration at the equilibrium ($E = E_{eq}$, $i = 0$).

$$C_O(0,t) = C_O^*, C_R(0,t) = C_R^*$$

$$E_{eq} = E^{0'} + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*}$$

$$\frac{C_O^*}{C_R^*} = e^{\frac{nF(E_{eq} - E^{0'})}{RT}} = e^{nf(E_{eq} - E^{0'})}$$

At equilibrium $v_f = v_b = v_0$ ⟹ $i_f = i_b = i_0$ i_0: Exchange current

$$i_0 = FAk^0 C_{\mathrm{O}}^* e^{-\alpha f (E_{\mathrm{eq}} - E^{0'})} \Longrightarrow$$

Exchange current

$$i_0 = FAk^0 C_{\mathrm{O}}^{*(1-\alpha)} C_{\mathrm{R}}^{*\alpha}$$

Thinking: If the exchange current is higher, the reaction rate should be higher or lower?

Current-Overpotential Equation

$$i = FAk^0 \left[C_O(0, t) e^{-\alpha f (E - E^{0'})} - C_R(0, t) e^{(1-\alpha) f (E - E^{0'})} \right]$$

$$i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$$

$$\frac{i}{i_0} = \frac{C_O(0, t) e^{-\alpha f (E - E^{0'})}}{C_O^{*(1-\alpha)} C_R^{*\alpha}} - \frac{C_R(0, t) e^{(1-\alpha) f (E - E^{0'})}}{C_O^{*(1-\alpha)} C_R^{*\alpha}}$$

Current-Overpotential Equation

$$i = i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

$$\eta = E - E_{eq}$$

Exchange Current

$$i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$$

- **Exchange current is related to:**
  - Bulk concentration
    - $[C_O^{*(1-\alpha)} \times C_R^{*\alpha}]$ in the equation
  - Rate constant, k^0
    - The rate constant is theoretically dependent on the electrode type and the solution and independent on the concentration and the potential. (See right table.)

$H_2 \rightarrow 2H^+ + 2e$

Table 1. Exchange current densities of the hydrogen evolution/anodic oxidation reaction at different electrode materials in aqueous 1 N H_2SO_4 solution at ambient temperature

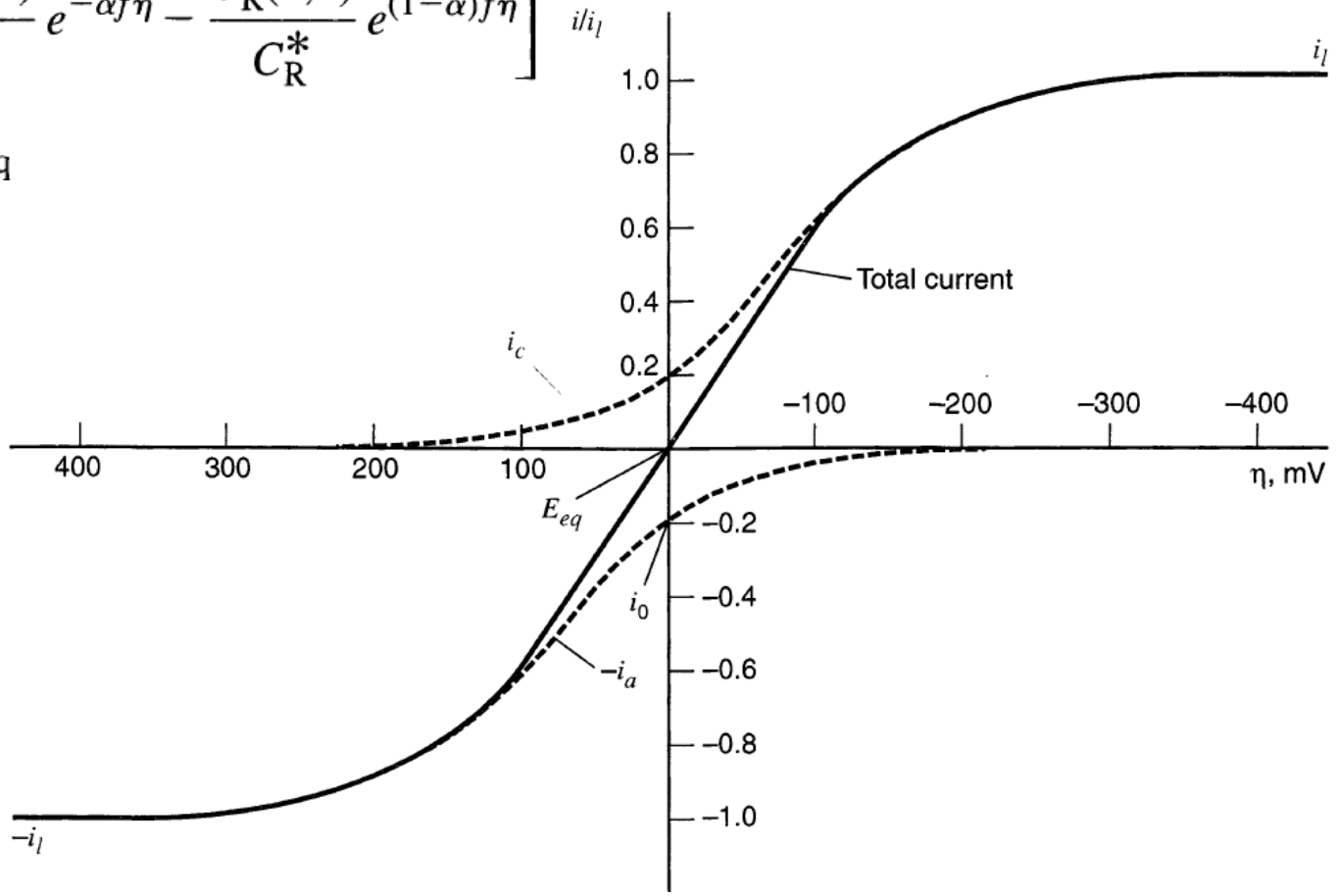
Metal	i_o/A cm^{-2}
Palladium, Pd	1.0×10^{-3}
Platinum, Pt	8.0×10^{-4}
Rhodium, Rh	2.5×10^{-4}
Iridium, Ir	2.0×10^{-4}
Nickel, Ni	7.0×10^{-6}
Gold, Au	4.0×10^{-6}
Tungsten, W	1.3×10^{-6}
Niobium, Nb	1.5×10^{-7}
Titanium, Ti	7.0×10^{-8}
Cadmium, Cd	1.5×10^{-11}
Manganese, Mn	1.3×10^{-11}
Thallium, Tl	1.0×10^{-11}
Lead, Pb	1.0×10^{-12}
Mercury, Hg	0.5×10^{-13}

Ref.: http://www.scielo.br/scielo.php?pid=S0100-40422005000600023&script=sci_arttext

Current-Overpotential Curve

$$i = i_0\left[\frac{C_O(0,t)}{C_O^*}\,e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}\,e^{(1-\alpha)f\eta}\right]$$

$$\eta = E - E_{eq}$$

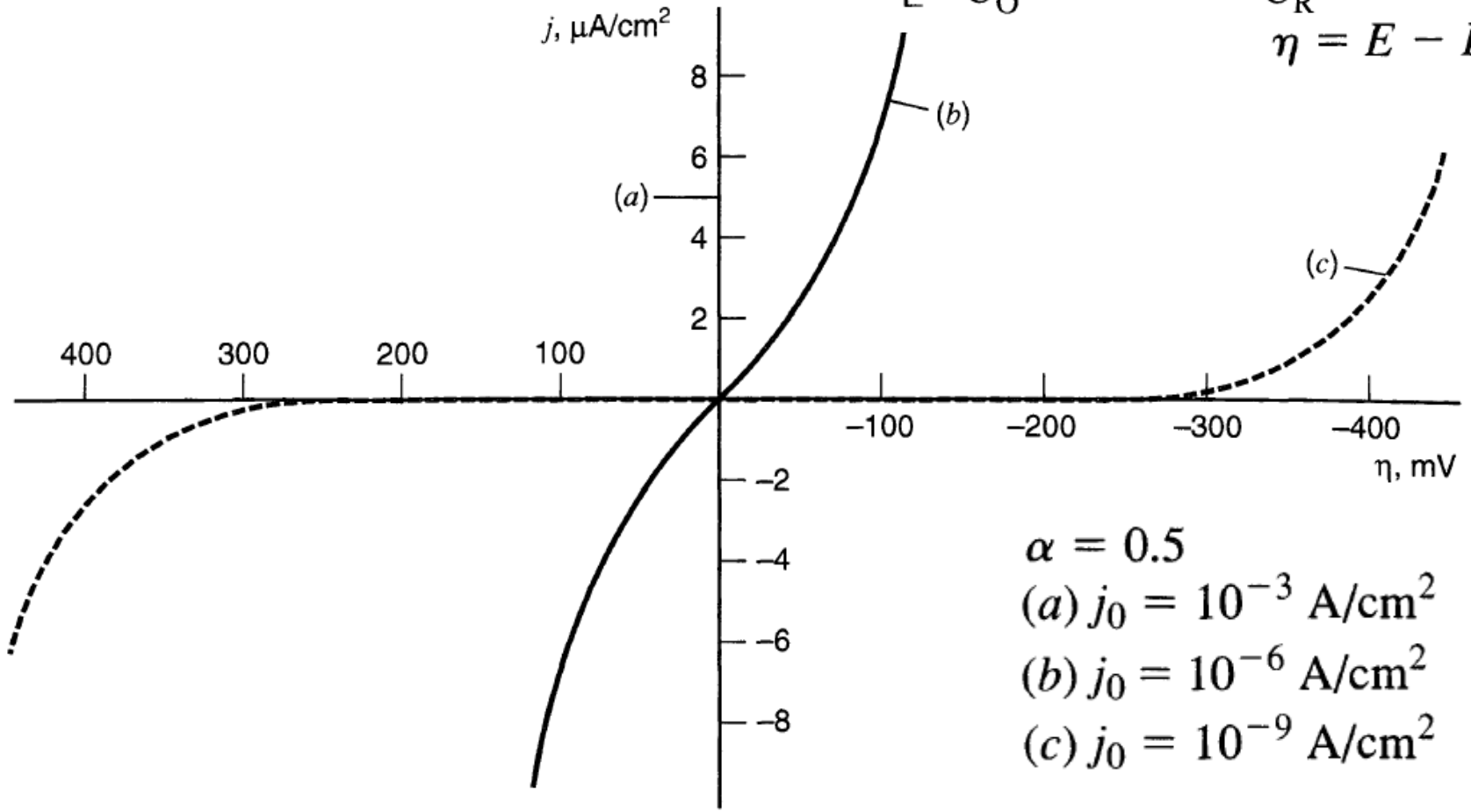


$\mathrm{O} + e \rightleftarrows \mathrm{R}$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$.

Variation of Exchange Current

$$i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]$$

$$\eta = E - E_{eq}$$



$\alpha = 0.5$

(a) $j_0 = 10^{-3}$ A/cm^2

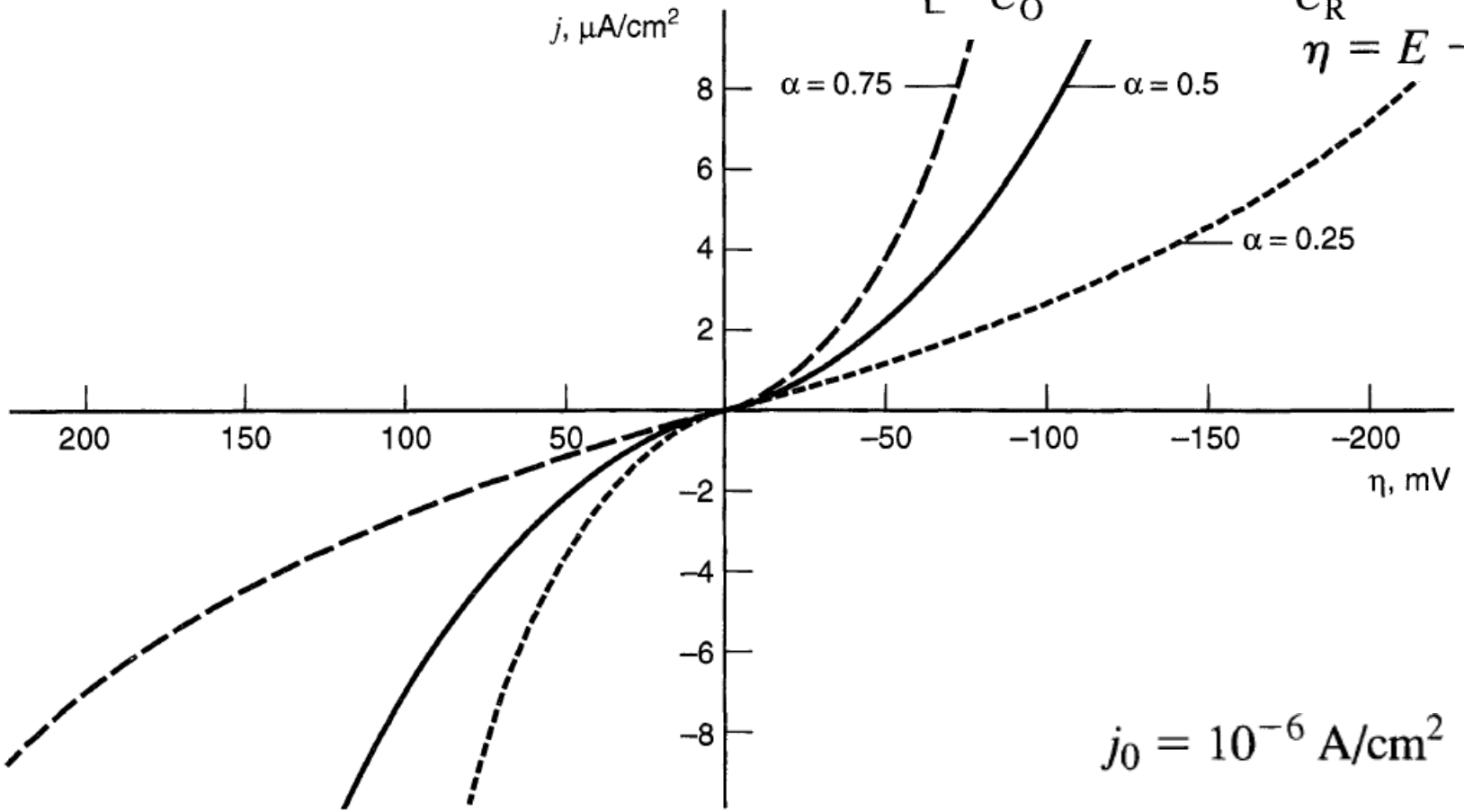
(b) $j_0 = 10^{-6}$ A/cm^2

(c) $j_0 = 10^{-9}$ A/cm^2

Variation of Transfer Coefficient

$$i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]$$

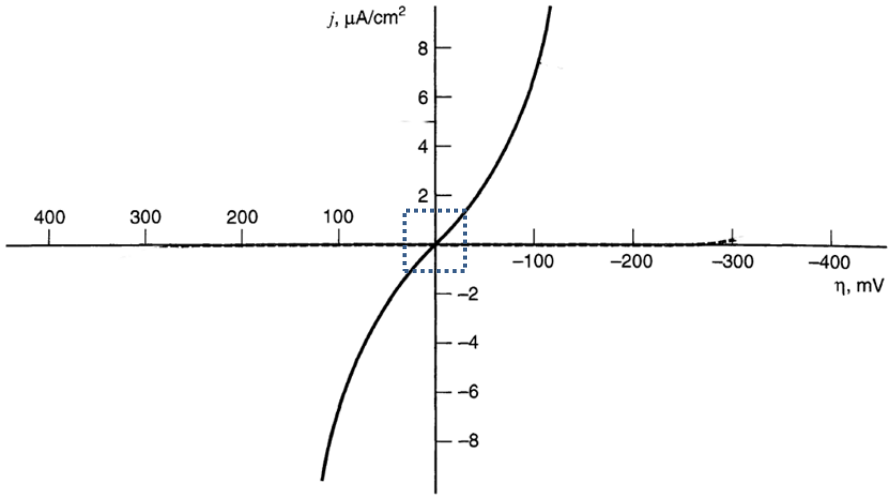
$$\eta = E - E_{eq}$$



$$j_0 = 10^{-6}\ \text{A/cm}^2$$

Linear Behavior, Small η

$$i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]$$



If the solution is well stirred (no mass-transfer effect), we can define

$$C_O(0,t) = C_O^*$$
$$C_R(0,t) = C_R^*$$

$$\Rightarrow \quad i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]$$

When the reaction is near equilibrium, $\eta = E - E_{eq} \rightarrow 0$

For small values of x, $e^x = 1 + x + \ldots$

$$i = -i_0 f\eta$$ **(Linear current-voltage curve)**

$-\eta/i$ is often called the **charge-transfer resistance**

$$R_{ct} = \frac{RT}{Fi_0}$$

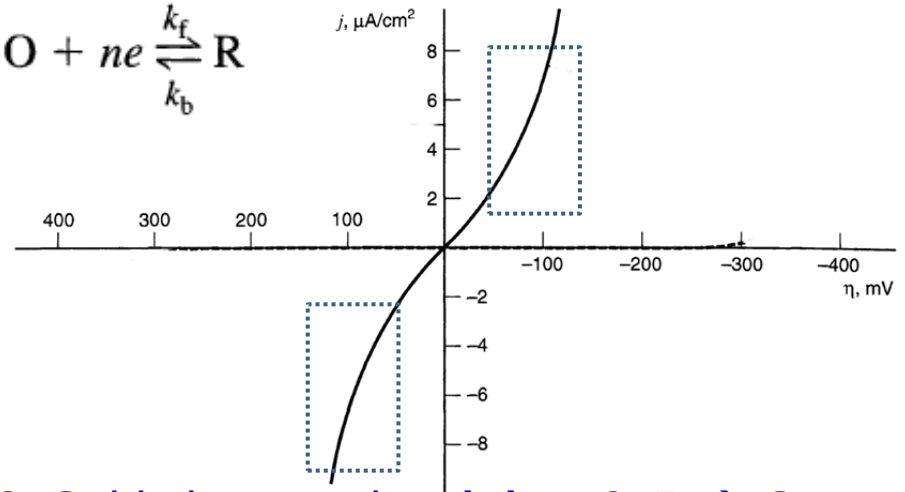
Tafel Behavior, Large η

$$i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]$$

$$C_O(0,t) = C_O^*$$
$$C_R(0,t) = C_R^*$$

$$i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]$$

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



1. Reduction reaction, **|η| >> 0**, O + ne → R

$$e^{-\alpha f\eta} >> e^{(1-\alpha)f\eta}$$

$$i = i_0 e^{-\alpha f\eta}$$ (Cathodic Tafel behavior)

$$\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i$$

$$= a + b\log i$$

2. Oxidation reaction, **|η| >> 0**, R → O + ne

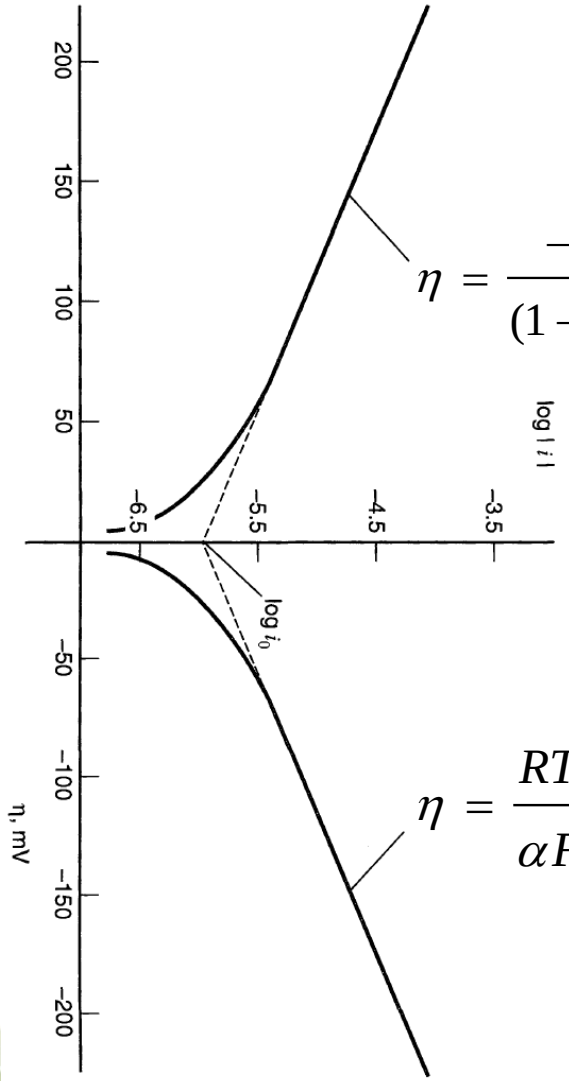
$$e^{-\alpha f\eta} << e^{(1-\alpha)f\eta}$$

$$|i| = i_0 e^{(1-\alpha)f\eta}$$ (Anodic Tafel behavior)

$$\eta = \frac{-RT}{(1-\alpha)F}\ln i_0 + \frac{RT}{(1-\alpha)F}\ln|i|$$

$$= a + b\log|i|$$

Tafel Plot (I)

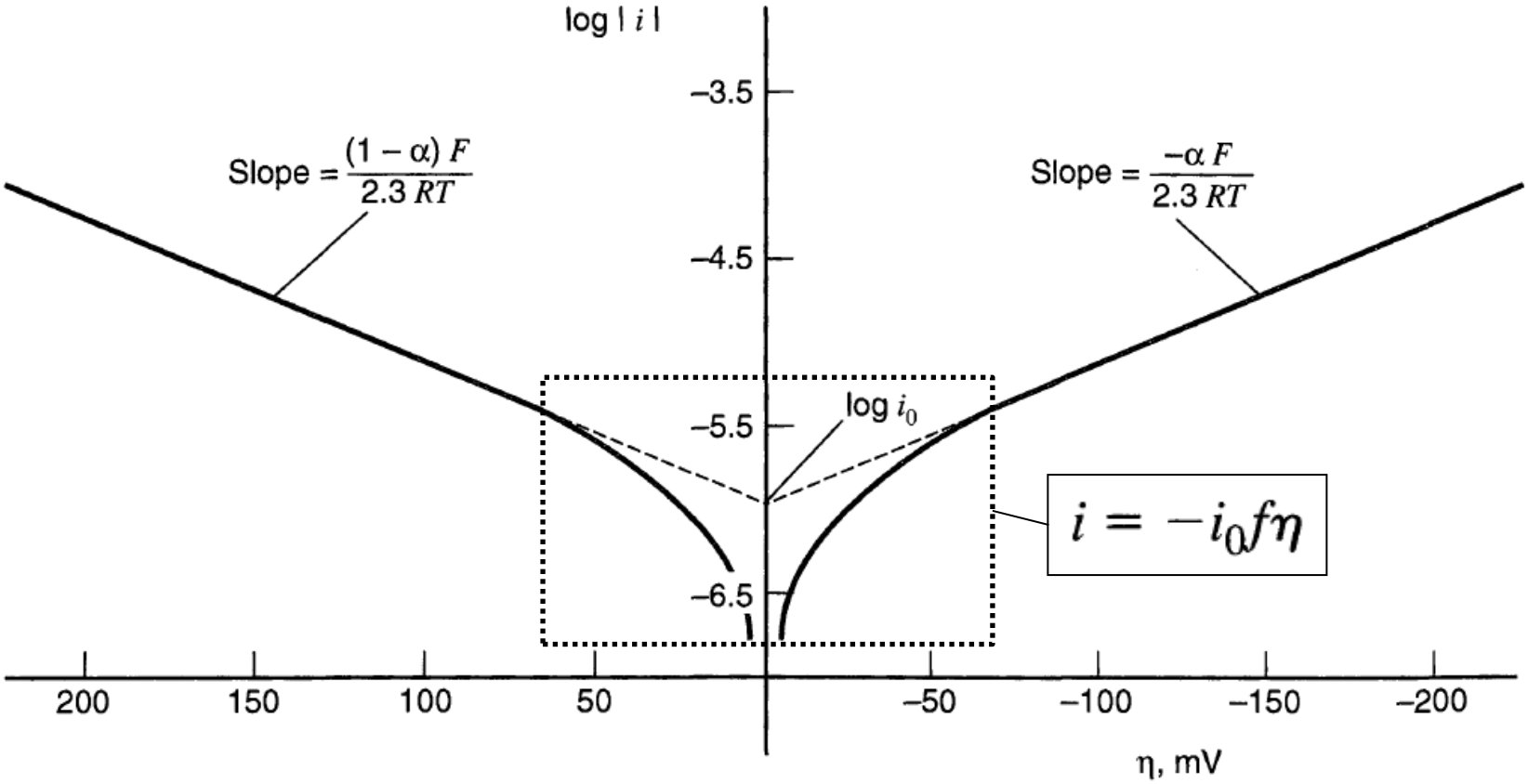


$$\eta = \frac{-RT}{(1-\alpha)F}\ln i_0 + \frac{RT}{(1-\alpha)F}\ln |i| = \frac{RT}{(1-\alpha)F}\ln \frac{|i|}{i_0}$$

$$\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i = \frac{RT}{\alpha F}\ln \frac{i_0}{i}$$

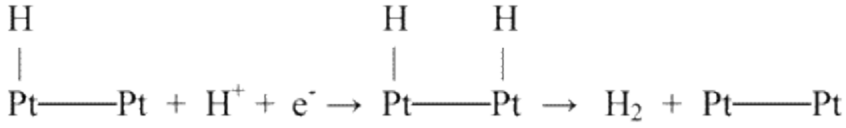
$O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

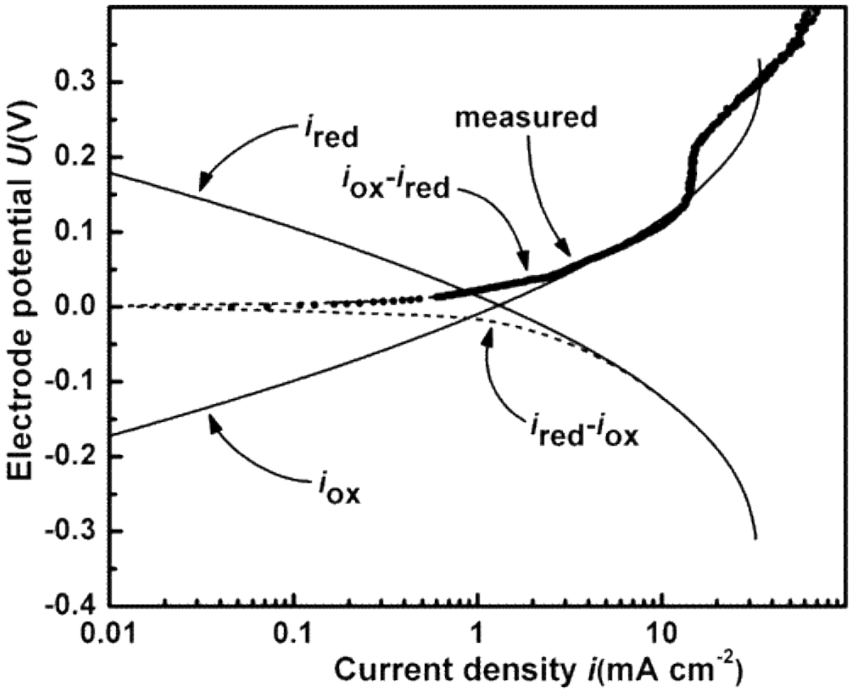
Tafel Plot (II)

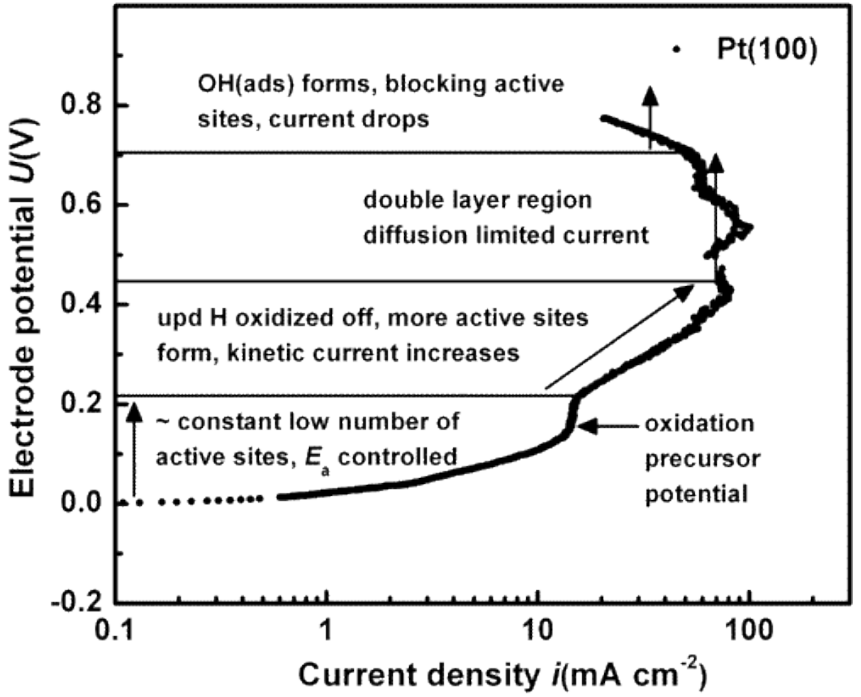


$O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2

Tafel Plot: Catalyst







$$i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]$$

A.B. Anderson, Y. Cai, Calculation of the Tafel plot for H2 oxidation on Pt(100) from potential-dependent activation energies. J. Phys. Chem. B, 108 (2004) 19917-19920.

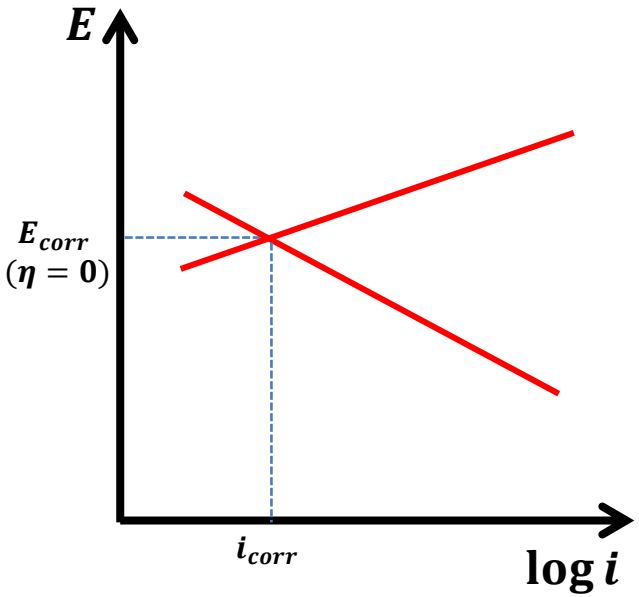
Tafel Plot of Corrosion

- **For the corrosion, the Tafel curve can be expressed by:**
  - Oxidation reaction (Anode)

$$\eta = b_A \log \frac{i}{i_0} = b_A \log \frac{i}{i_{corr}}$$

  - Reduction reaction (Cathode)

$$\eta = -b_C \log \frac{i}{i_0} = -b_C \log \frac{i}{i_{corr}}$$



Note:

$$\eta = E - E_{eq} = E - E_{corr}$$

Theory of Tafel Plot of Corrosion

- **Solution species**

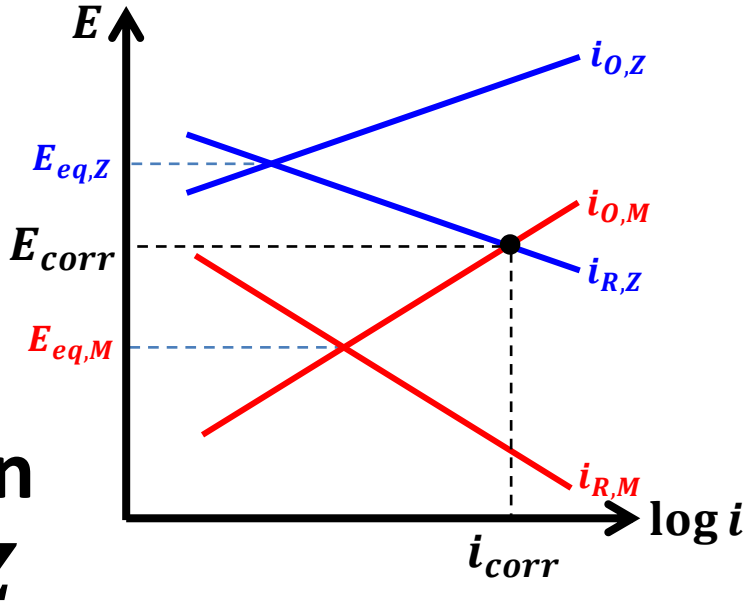
$$Z^+ + e^- \rightleftarrows Z$$

- **Metal species**

$$M^+ + e^- \rightleftarrows M$$

- **Metal corrosion in solution**

$$M + Z^+ \rightarrow M^+ + Z$$

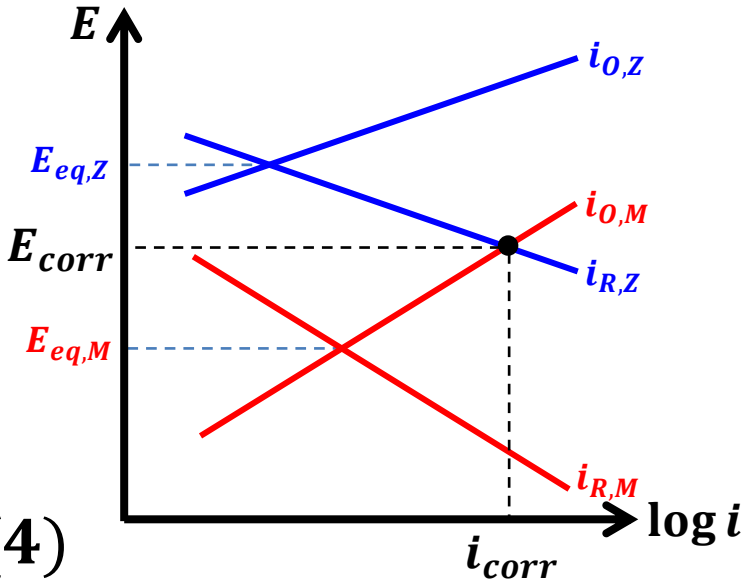


- **At the equilibrium of corrosion potential, E_{corr}**

$$i_{corr} = i_{R,Z} = i_{O,M}$$

Cont'd

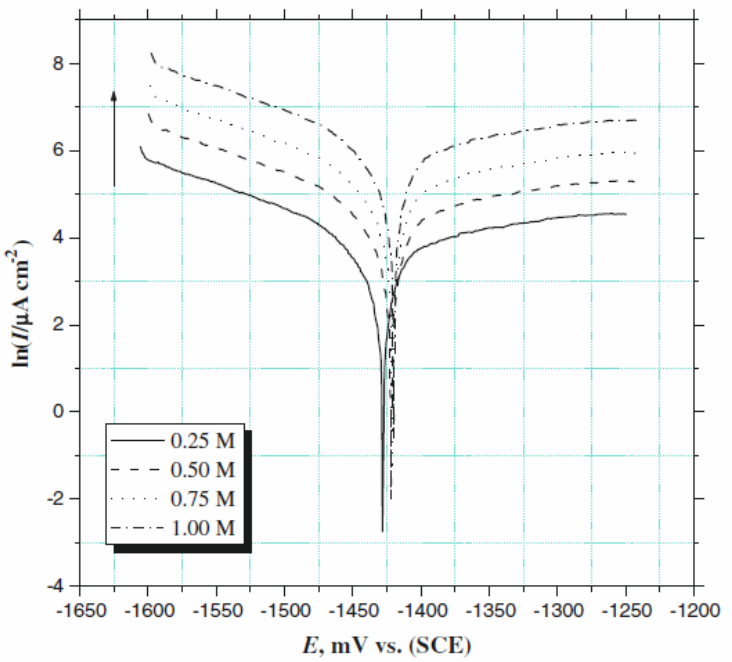
- $i_{MEAS} = i_{O,M} - i_{R,Z} \dots (1)$
- $\eta = b_A \log \frac{i_{O,M}}{i_{corr}} \dots (2)$
- $\eta = -b_C \log \frac{i_{R,Z}}{i_{corr}} \dots (3)$
- (2)&(3)⇒(1)
- $i_{MEAS} = i_{corr}\left(10^{\frac{\eta}{b_A}} - 10^{-\frac{\eta}{b_C}}\right) \dots (4)$
- $10^x = 1 + 2.303x + \frac{(2.303x)^2}{2!} + \cdots (5)$
- (5)⇒(4) & *x* is very small
- $i_{MEAS} = 2.303\eta \frac{b_A + b_C}{b_A b_C} \dots (6)$

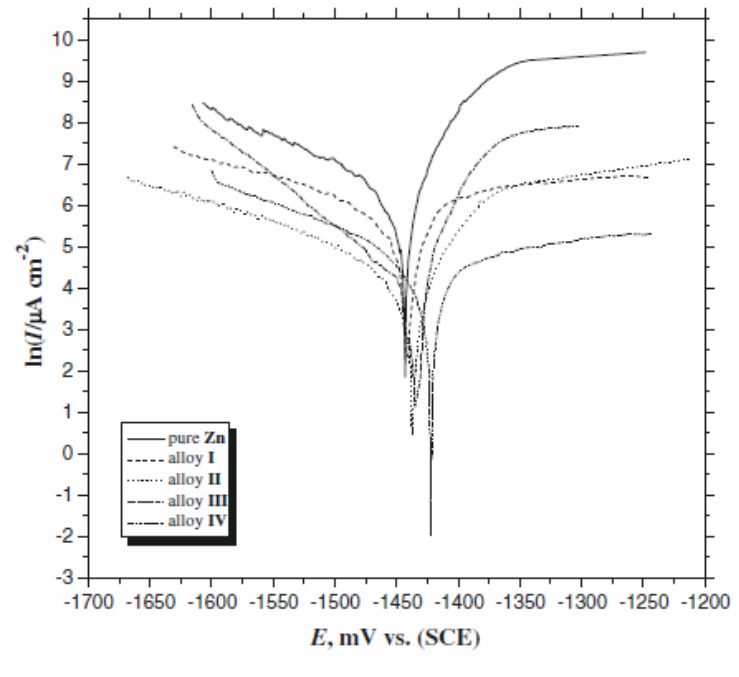


Corrosion of Zn-Ni Alloy

Materials: Zn-Ni alloy
Solution: KOH solution
Temperature: 298 K

System	Phase Designation	Crystal System	Crystal Size (nm)
$Zn_{99.5}Ni_{0.5}$	Zn	hexagonal	300
	γ-Zn_3Ni	body centered cubic	260
$Zn_{98}Ni_2$	Zn	hexagonal	264
	γ-Zn_3Ni	body centered cubic	335
$Zn_{95}Ni_5$	Zn	hexagonal	210
	γ-Zn_3Ni	body centered cubic	342
	γ-ZnNi		367
$Zn_{90}Ni_{10}$	Zn	hexagonal	149
	γ-Zn_3Ni	body centered cubic	210
	γ-ZnNi		140





A.-R. El-Sayed, H.S. Mohran, H.M. Abd El-Lateef, Corrosion study of zinc, nickel, and zinc-nickel alloys in alkaline solutions by Tafel plot and impedance techniques. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 43 (2012) 619-632

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Concentration (mol/L)	$-E_{corr}$ (mV *vs* SCE)	I_{corr} (μA/cm^2)	b_a (mV/decade)	$-b_c$ (mV/decade)	α
Pure Zn					
0.25 M	1446	140	48	120.2	0.49
0.50 M	1444	320	50	125.9	0.46
0.75 M	1441	712	54	127	0.46
1 M	1439	1635	57	130	0.45
Pure Ni					
0.25 M	273	0.55	70	175	0.330
0.50 M	270	1.21	71	175	0.330
0.75 M	269	1.47	72	176	0.335
1 M	260	3.32	72	176	0.335
Alloy I (0.5 pct Ni)					
0.25 M	1442	134	46	125	0.47
0.50 M	1440	253	47	126	0.46
0.75 M	1438	643	48	128	0.46
1 M	1437	953	50	128	0.46
Alloy II (2 pct Ni)					
0.25 M	1440	112	50	135	0.43
0.50 M	1438	210	50	140	0.42
0.75 M	1436	239	52	147	0.40
1 M	1435	445	52	149	0.39
Alloy III (5 pct Ni)					
0.25 M	1435	84	80	143	0.41
0.50 M	1433	150	80	146	0.40
0.75 M	1432	209	82	150	0.39
1 M	1430	343	83	152	0.38
Alloy IV (10 pct Ni)					
0.25 M	1427	45	94	166	0.35
0.50 M	1421	99	94	166	0.35
0.75 M	1419	164	95	167	0.35
1 M	1418	213	96	178	0.33

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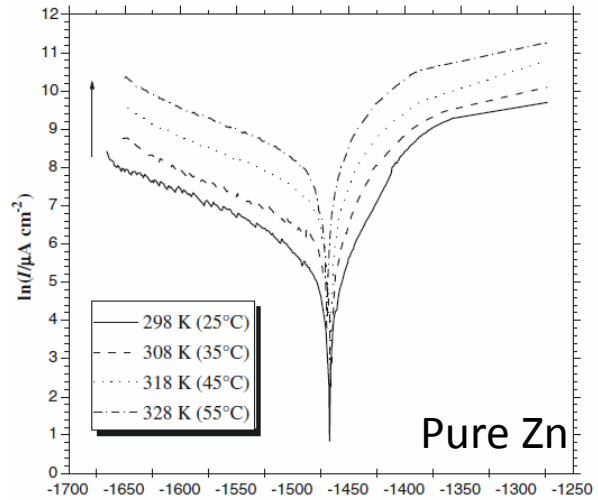

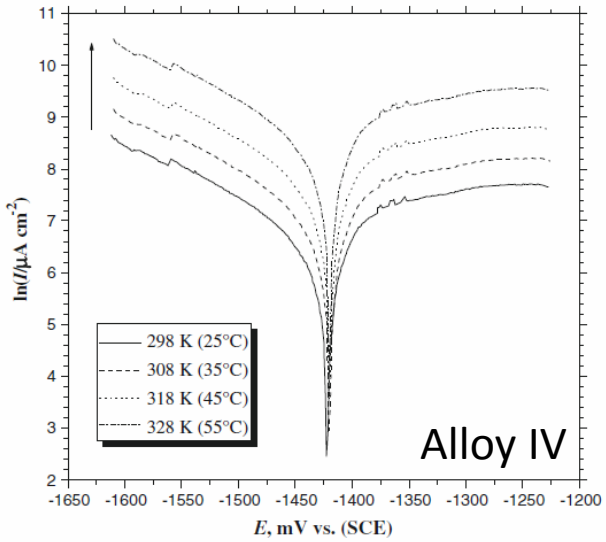

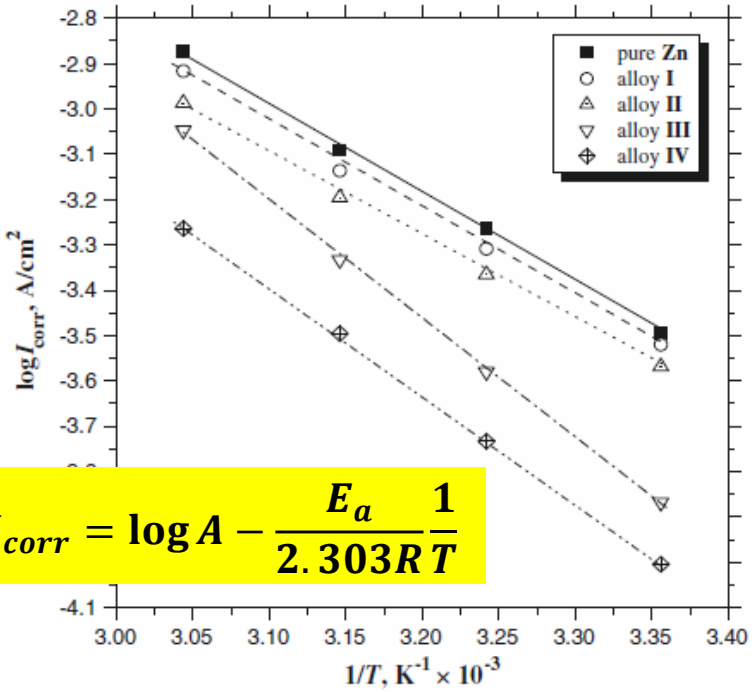

$$\log I_{corr} = \log A - \frac{E_a}{2.303RT}\frac{1}{T}$$

Metals and Alloys	E_a (kJ/mol)
Pure Zn	23.5
Alloy I (0.5 pct Ni)	26.62
Alloy II (2 pct Ni)	28.51
Alloy III (5 pct Ni)	36.75
Alloy IV (10 pct Ni)	42.62
Pure Ni	59.35

Higher corrosion resistance

Some Important Equations

- $O + ne^- \rightarrow R$
- Gibbs free energy: $\Delta G = -nFE$
- Nernst equation: $E = E^0 + \frac{RT}{nF} ln \frac{C_O}{C_R}$
- Current-overpotential equation:

$$i = i_0 \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

$$f = \frac{F}{RT}$$

- Overpotential: $\eta = E - E_{eq}$
- Small η: $i = -i_0 f \eta$
- Large η : $i = i_0 e^{-\alpha f \eta} \Rightarrow \eta = \frac{1}{\alpha f} ln i_0 - \frac{1}{\alpha f} ln i$ (Tafel equation)