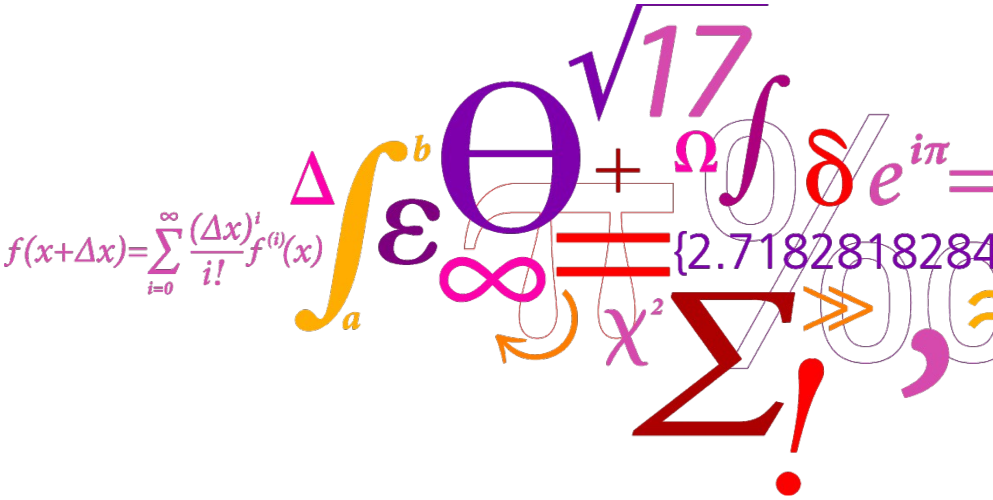
Hands-on electrochemical impedance spectroscopy
Discussion session

Literature:

ELECTROCHEMISTRY – 26240
Sven Atlung
Torben Jacobsen
2009



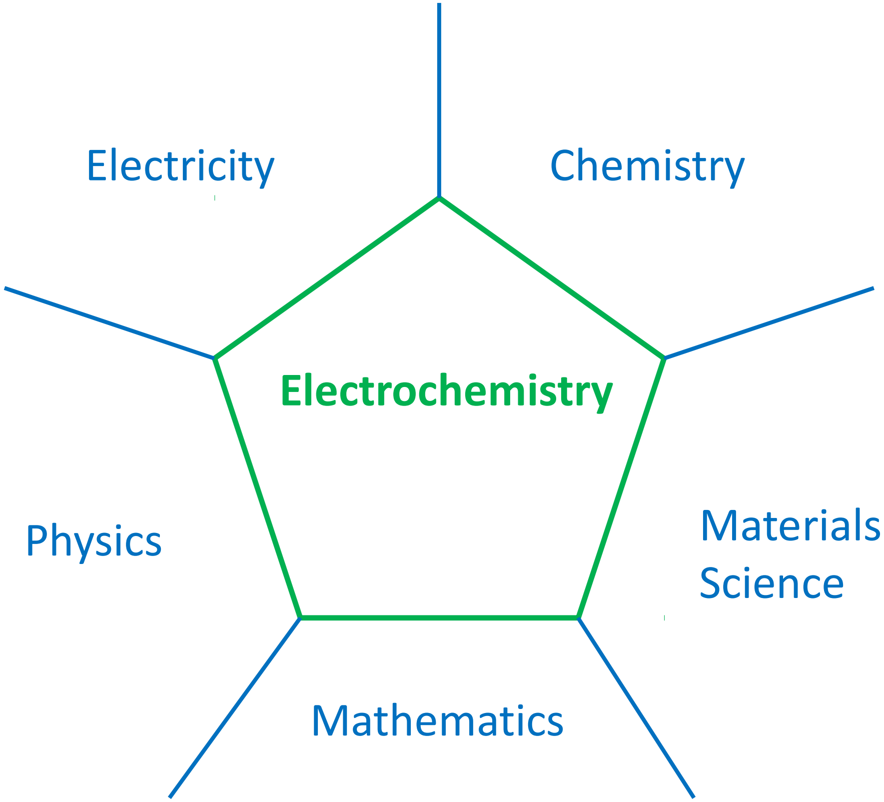
Program for the day

- 10.00-10.30 General electrochemistry (shjj)
- 11.10-11.20 Relationship between EIS and electrochemical processes (shjj)
- 11.20-11.40 EIS techniques, (multi-sine, Laplace, etc) (shjj)
- Pause
- 11.50-12.30 Interpretation of EIS signals (Effect of double layer capacitance, Angle of tail, Temperature dependencies, Blocking electrode / non-blocking) (johh)
- Frokost
- 13.30-14.00 Equivalent circuits for EIS measurements, most used and why. (johh)
- 14.00-14.30 Data integrity and verification methods (Kramers-Krönig, etc) (johh)
- Pause
- 14.40-15.10 Battery characterization based on EIS parameters. (johh/shjj)
- 15.10-15-30 Examples, questions from students
- 15.30-16.00 Topic for next DBS meeting (Martin Søndergaard)
- 16.00-17.00 Laboratorie tur.

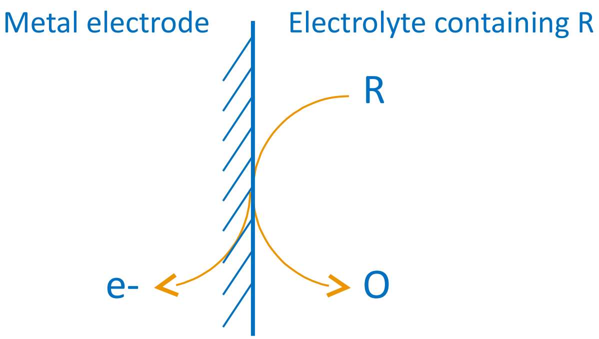
Contents

- Introduction
- Electrode-Electrolyte Interface - The Double Layer
- Nernst equation and Volmer-Butler equation
- Electrolyte Conductivity – Thermal activation

Electrochemistry is an Interdisciplinary Science



A simple electrochemical reaction:

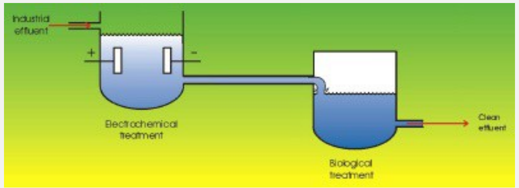


$$R \rightleftarrows O + e^-$$

Electrochemical reactions largely takes places at interfaces – chemistry and physics of surfaces & interfaces important!

Electrochemistry – Some Applications

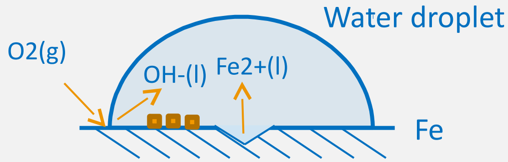
Environmental



Direct oxidation of organics

Electrokinetic remediation

Corrosion



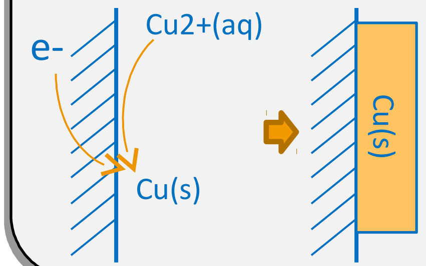
O2(g) + 2H2O(l) + 4e- -> 4OH-(aq)

Fe(s) -> + Fe2+(aq) + 2e-

Fe2+(aq) + 2OH-(aq) -> Fe(OH)2(s)

4Fe(OH)2(s) + O2(g) -> 2Fe2O3·H2O(s) + 2H2O(l)

Electroplating



Sensors / Analytical

Clark Electrode:

O2 + 4 e− + 2 H2O → 4 OH−

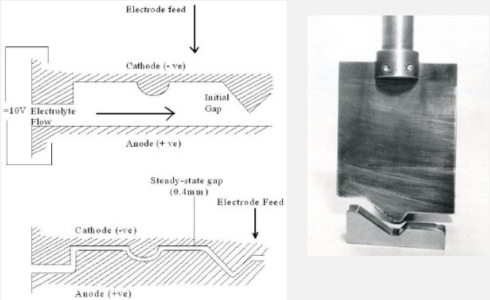
(amperometric sensor)

Lambda Probe / Zirconia Sensor:

Pt / O2(g) / stab. ZrO2 / O2(g) / Pt

(potentiometric sensor)

Electrochemical Machining



Batteries

Energy Storage

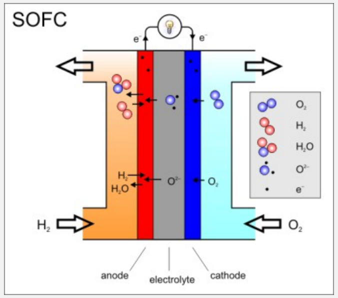
Anode:

x Li+(l) + x e- + C6(s) -> LixC6 (s)

Cathode:

LixCoO2 -> Li(1-x)CoO2 + x Li+ + x e-

Fuel Cells



Electrolysers

Chemicals Production by Electrolysis

2H2O(g) + 4e- -> 2O2-(s) + H2 (g)

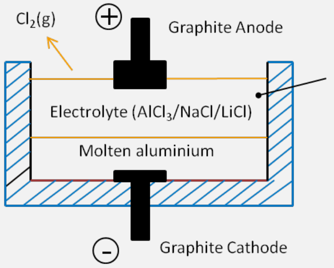
2O2-(s) -> O2(g) + 4e-

2H2O(g) -> O2(g) + H2 (g)

Gas Production is a big industry

Chlor-Alkali, Hydrogen

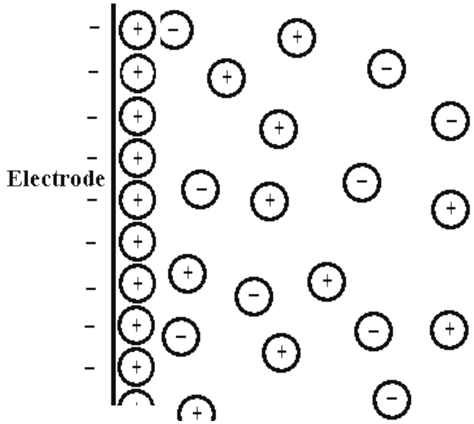
Electrowinning/refinement

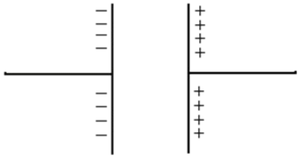


Double layer – Definition

Electrode

Electrolyte





Electrode potentials– Definition

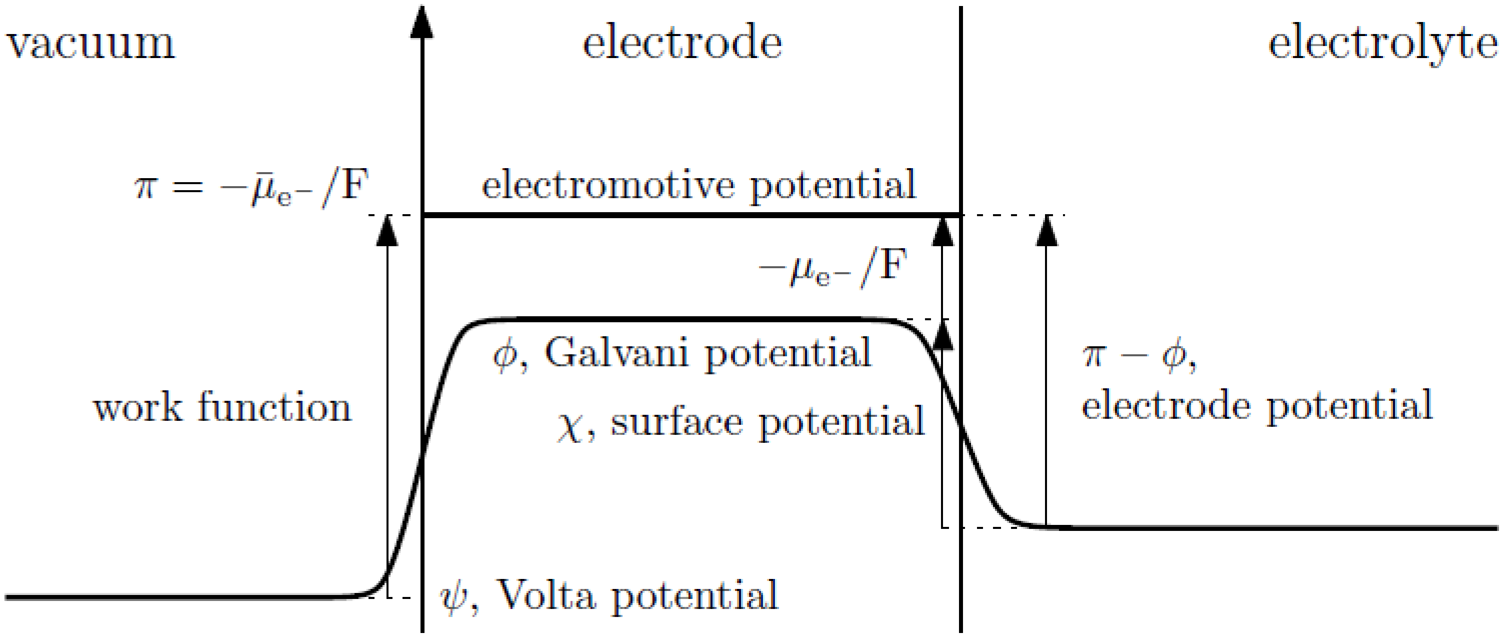
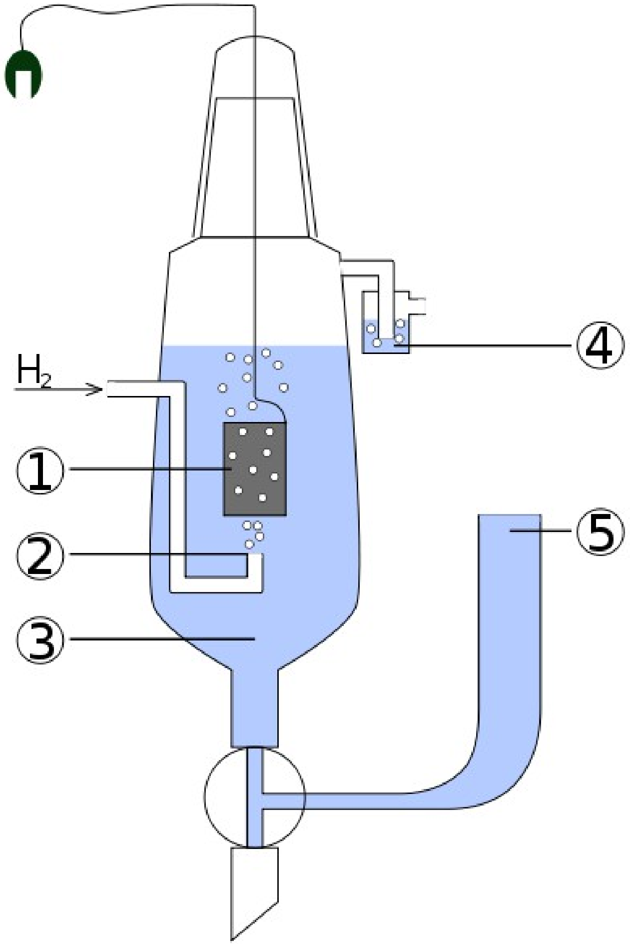


Figure 1.2: *Potentials at the electrode – electrolyte interface.*

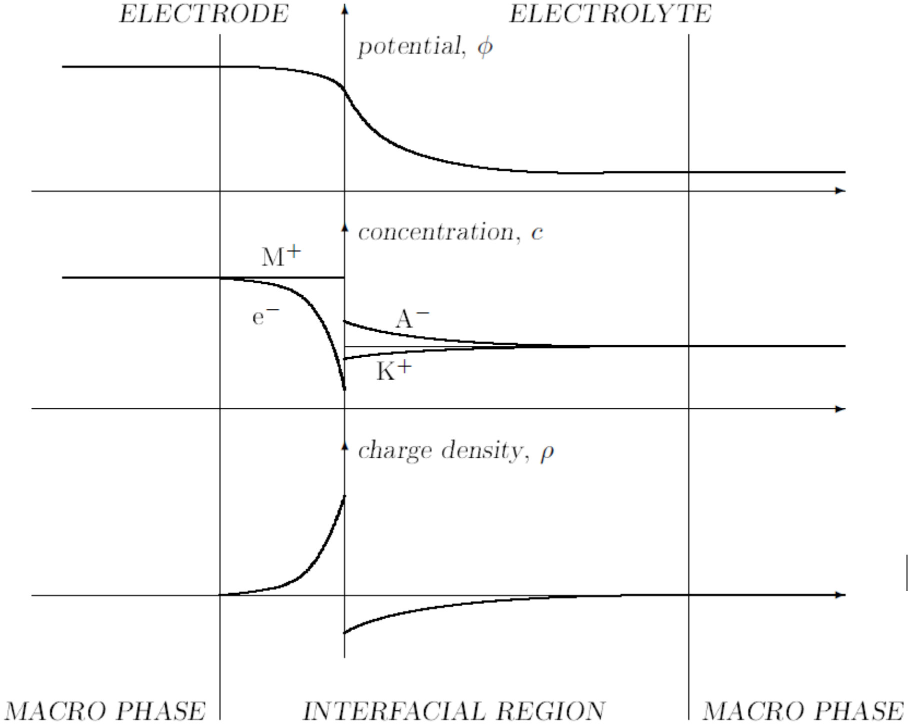
$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad , \quad (\pi - \phi)^{\ominus}_{\mathrm{SHE}} = 0, \qquad (1.27)$$

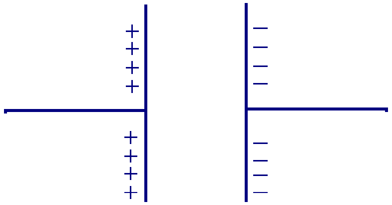
Standard Hydrogen Electrode (wikipedia)

1. platinized platinum electrode
2. hydrogen blow
3. solution of the acid with activity of H+ = 1 mol dm−3
4. hydroseal for prevention of the oxygen interference
5. reservoir through which the second half-element of the galvanic cell should be attached. The connection can be direct, through a narrow tube to reduce mixing, or through a salt bridge, depending on the other electrode and solution. This creates an ionically conductive path to the working electrode of interest.



Double layer – Definition





Equilibrium potential :

$$\pi - \phi)^{eq}$$

Over voltage :

$$\eta = (\pi - \phi) - (\pi - \phi)^{eq}$$

Capacitance :

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Second level

Capacitive current :

$$i_C = C\frac{d(\pi - \phi)}{dt} = C\frac{d\eta}{dt}$$

Electrode current

$$i = \underbrace{i_C}_{\text{Transient}} + \underbrace{\boxed{i_F}}_{\text{Steady state}}$$

Electrode reaction:

- Example: H2 evolution on a pt-electrode

$$\begin{aligned} \mathrm{H}^+ + \mathrm{e}^- &\rightleftharpoons \mathrm{H}_{ads} \\ \mathrm{H}_{ads} + \mathrm{H}^+ + \mathrm{e}^- &\rightleftharpoons \mathrm{H}_2 \end{aligned}$$

Adsorption rate depends of the number of free sites

$$Red \underset{v_-}{\overset{v_+}{\rightleftharpoons}} Ox + ne^-$$

Electrode reaction in equilibrium

-Exhange current

$$\boxed{i_o = i_+ = -i_- = nFv_o = nFv_{+,eq} = nFv_{-,eq}}$$

$$\begin{aligned} v_+ &= [Red]k_+, \\ v_- &= [Ox]k_-, \end{aligned}$$

$$\frac{k_+}{k_-} = \frac{[Ox]}{[Red]}$$

Electrode reaction in equilibrium

-Nernst equation

$$\bar{\mu}_{Red} = \bar{\mu}_{Ox} + n\bar{\mu}_{e^-}$$

Assuming all charged species except e- are present in the solution

$$\mu_{Red} + z_{Red}F\phi = \mu_{Ox} + z_{Ox}F\phi + n\bar{\mu}_{e^-}$$

$$z_{Ox} - z_{Red} \quad e^{-} = -F\pi$$

$$\pi - \phi = \frac{\mu_{Ox} - \mu_{Red}}{nF} \quad \frac{\mu_{Ox} - \mu_{Red}}{nF} + \frac{RT}{nF}\ln\frac{a_{Ox}}{a_{Red}}$$

$$= (\pi - \phi)^{\circ} + \frac{RT}{nF}\ln\frac{a_{Ox}}{a_{Red}}$$

Electrode reaction
-reaction rate constant relation

$$\frac{k_+}{k_-} = \exp\left[\left\{(\pi - \phi) - (\pi - \phi)^{\ominus}\right\}\frac{n\mathrm{F}}{\mathrm{R}T}\right]$$

$$\begin{aligned} k_+ &= k_+^{\ominus}\exp\left[(1-\alpha)\left\{(\pi - \phi) - (\pi - \phi)^{\ominus}\right\}\frac{n\mathrm{F}}{\mathrm{R}T}\right] \\ k_- &= k_-^{\ominus}\exp\left[-\alpha\left\{(\pi - \phi) - (\pi - \phi)^{\ominus}\right\}\frac{n\mathrm{F}}{\mathrm{R}T}\right] \end{aligned}$$

$$\boxed{\begin{aligned} k_+ &= k_+^{ref}\exp\left[(1-\alpha)n\left\{(\pi - \phi) - (\pi - \phi)^{ref}\right\}\frac{\mathrm{F}}{\mathrm{R}T}\right] \\ k_- &= k_-^{ref}\exp\left[-\alpha n\left\{(\pi - \phi) - (\pi - \phi)^{ref}\right\}\frac{\mathrm{F}}{\mathrm{R}T}\right] \qquad (4.24) \end{aligned}}$$

Electrode reaction

-Volmer-Butler equation

$$i = i_+ + i_- = n\mathrm{F}(v_+ - v_-)$$

$$\boxed{\eta = (\pi - \phi) - (\pi - \phi)^{eq}}$$

$$v_+ = [Red]k_+^{eq} \exp\left[(1-\alpha)n\eta\frac{\mathrm{F}}{RT}\right]$$

$$v_- = \underbrace{[Ox]k_-^{eq}}_{=} \exp\left[-\alpha n\eta\frac{\mathrm{F}}{RT}\right]$$

At the equilibrium potential, i.e. $\eta = 0$, we have $v_+ = v_- = v_o = \frac{i_o}{n\mathrm{F}}$

$$\boxed{i = i_o\left(\exp\left[(1-\alpha)n\eta\frac{\mathrm{F}}{RT}\right] - \exp\left[-\alpha n\eta\frac{\mathrm{F}}{RT}\right]\right)}$$

Electrode reaction

-small overvoltage

$$\epsilon \simeq 0 \quad \Rightarrow \quad \exp[\epsilon] \simeq 1 + \epsilon + \frac{\epsilon^2}{2} + \dots$$

$$i_F = i_o \left(1 + (1-\alpha)\eta \frac{nF}{RT} - \left(1 - \alpha\eta \frac{nF}{RT} \right) \right) = i_o \eta \frac{nF}{RT} = \frac{\eta}{R_r}$$

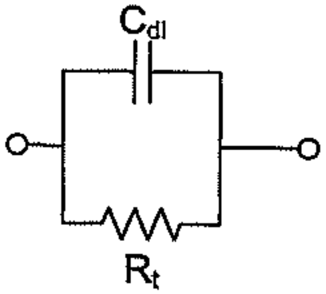
$$\boxed{R_r = \frac{RT}{i_o nF}}$$

Equivalent circuit

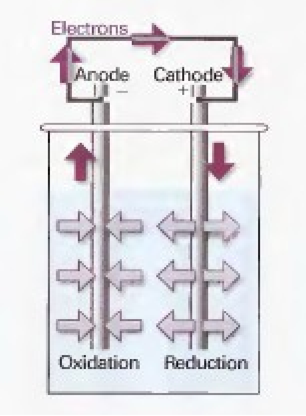
- The total current is the sum of two currents

$$i = i_C + i_F$$

- Therefore, the equivalent circuit for the electrode/electrolyte interface is a parallel connection between a capacitor and a resistor:



Electromotive force



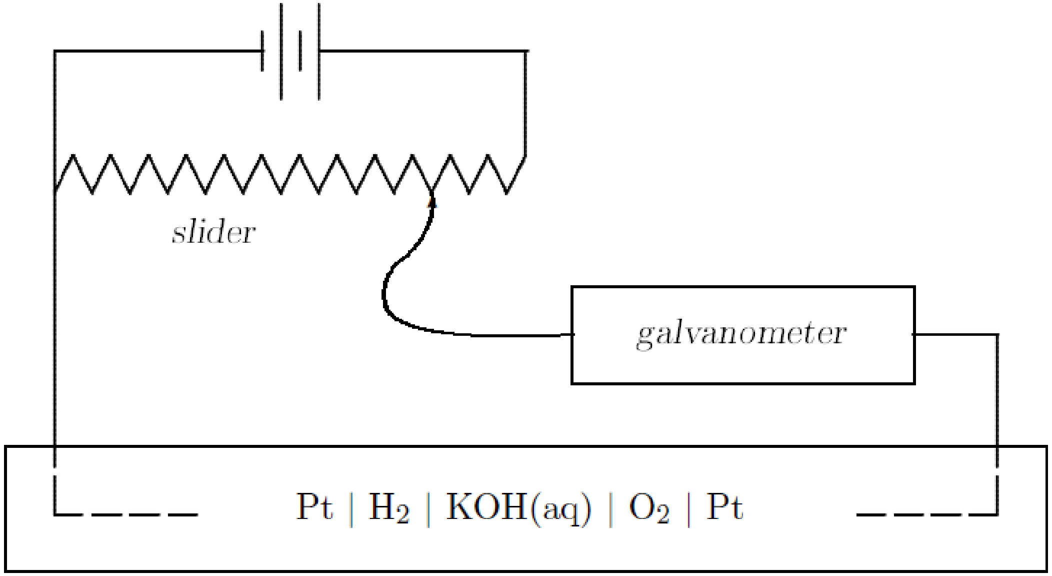


Figure 1.1: *Determination of electromotive force by a compensation bridge.*

positive charge from the left to the right inside the element are positive.

$$\begin{array}{lrcl} \text{Left electrode:} & H_2 & \rightarrow & 2H^+ + 2e^- \\ \text{Right electrode:} & 1/2O_2 + 2H^+ + 2e^- & \rightarrow & H_2O \\ \hline \text{Total reaction} & H_2 + 1/2O_2 & \rightarrow & H_2O \end{array}$$

$$\boxed{\epsilon = \pi_{right} - \pi_{left}}$$

$$\epsilon = -\frac{\Delta G}{nF}$$

$$\epsilon = -\frac{\Delta G^{\ominus}}{nF} + \frac{RT}{nF} \ln \left[\frac{a_{Ox_r} a_{Red_l}}{a_{Red_r} a_{Ox_l}} \right]$$

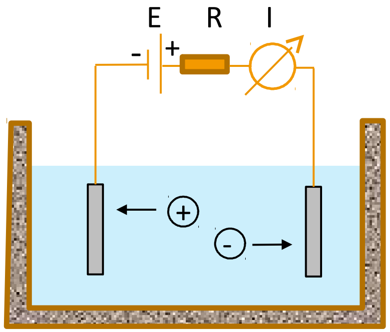
Emf and thermodynamic functions from the total reaction

$$\epsilon = -\frac{\Delta G}{n\mathrm{F}}$$

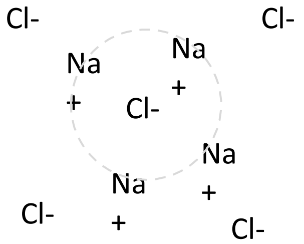
$$\boxed{\begin{aligned} \left(\frac{\partial \epsilon}{\partial T}\right)_p &= -\frac{1}{n\mathrm{F}}\left(\frac{\partial \Delta G}{\partial T}\right)_p = \frac{\Delta S}{n\mathrm{F}} && (1.16) \\ \Delta H &= \Delta G + T\Delta S = -n\mathrm{F}\left(\epsilon - T\left(\frac{\partial \epsilon}{\partial T}\right)_p\right) && (1.17) \end{aligned}}$$

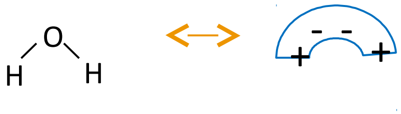
Conductivity in Electrolytes

Transition from electronic to ionic conductivity in an electrochemical cell



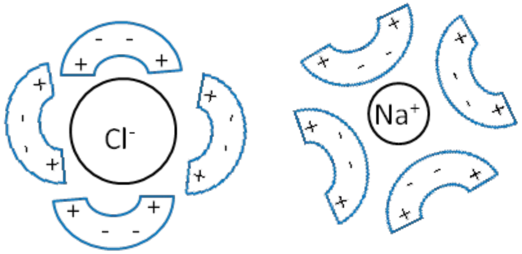
Liquid Electrolytes





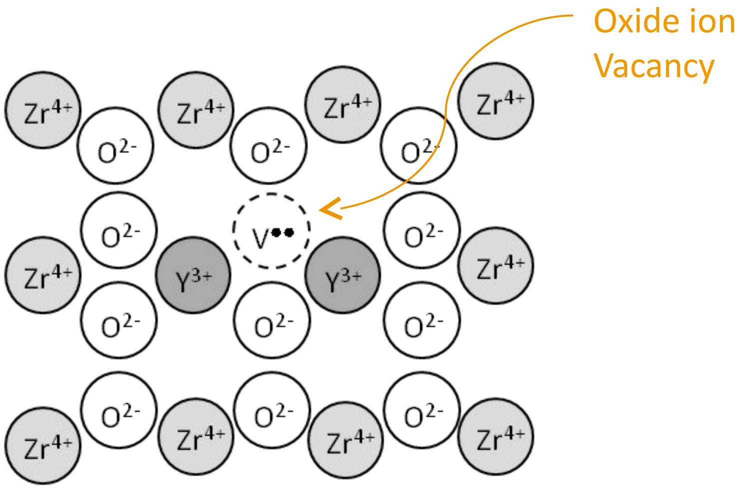
Liquid Electrolytes

Ionic solvation of NaCl



Solid Electrolytes

View down the 110 plane in YSZ



Defects and Kröger Vink notation

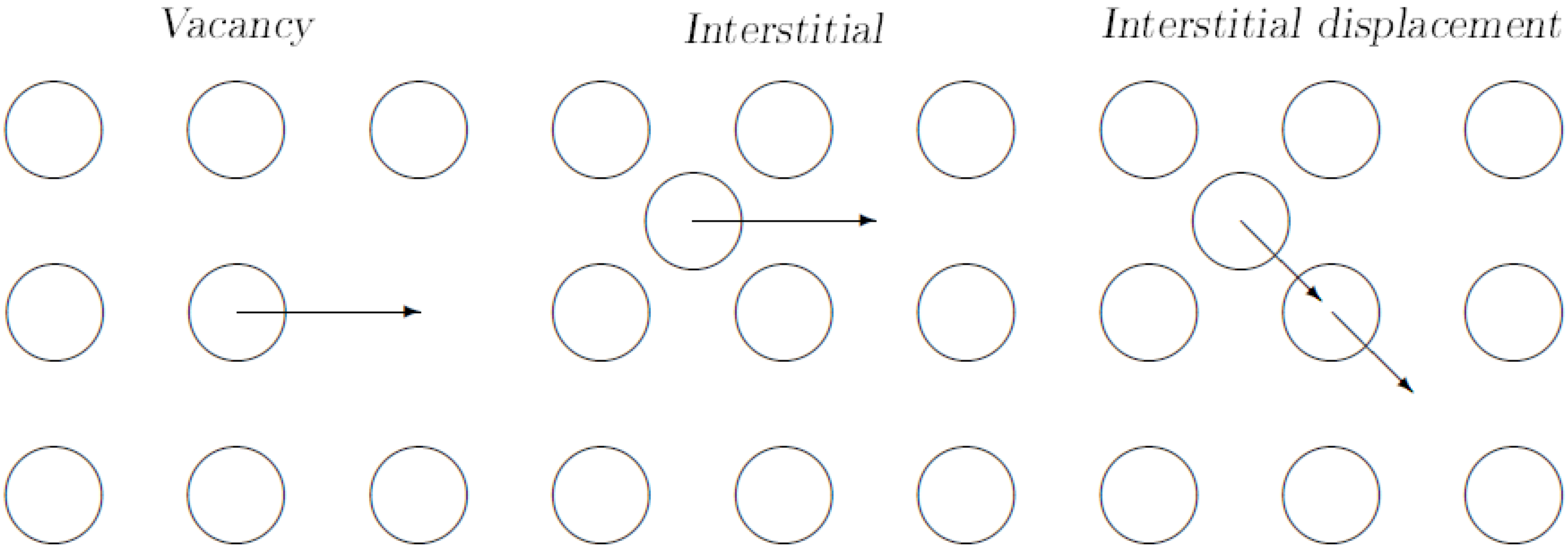


Figure 2.2: *Transport mechanisms in a lattice*

An Ion in an Electric Field

Probability of an ion having the energy u (Bolzmann distribution):

$$\exp\left[-u/\mathrm{k}T\right]$$

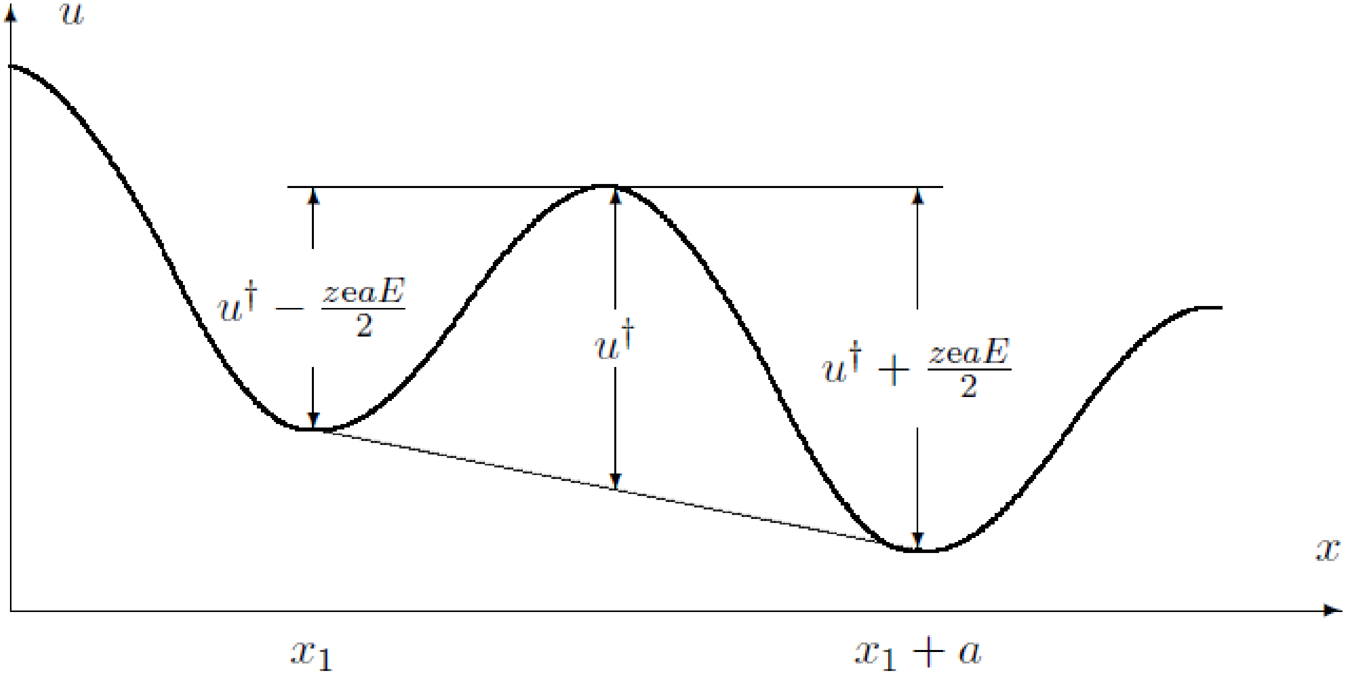


Figure 2.3: *Potential energy, u, for an interstitial ion in an electric field with field strength, E., as function of the position, x,. a is the lattice constant.*

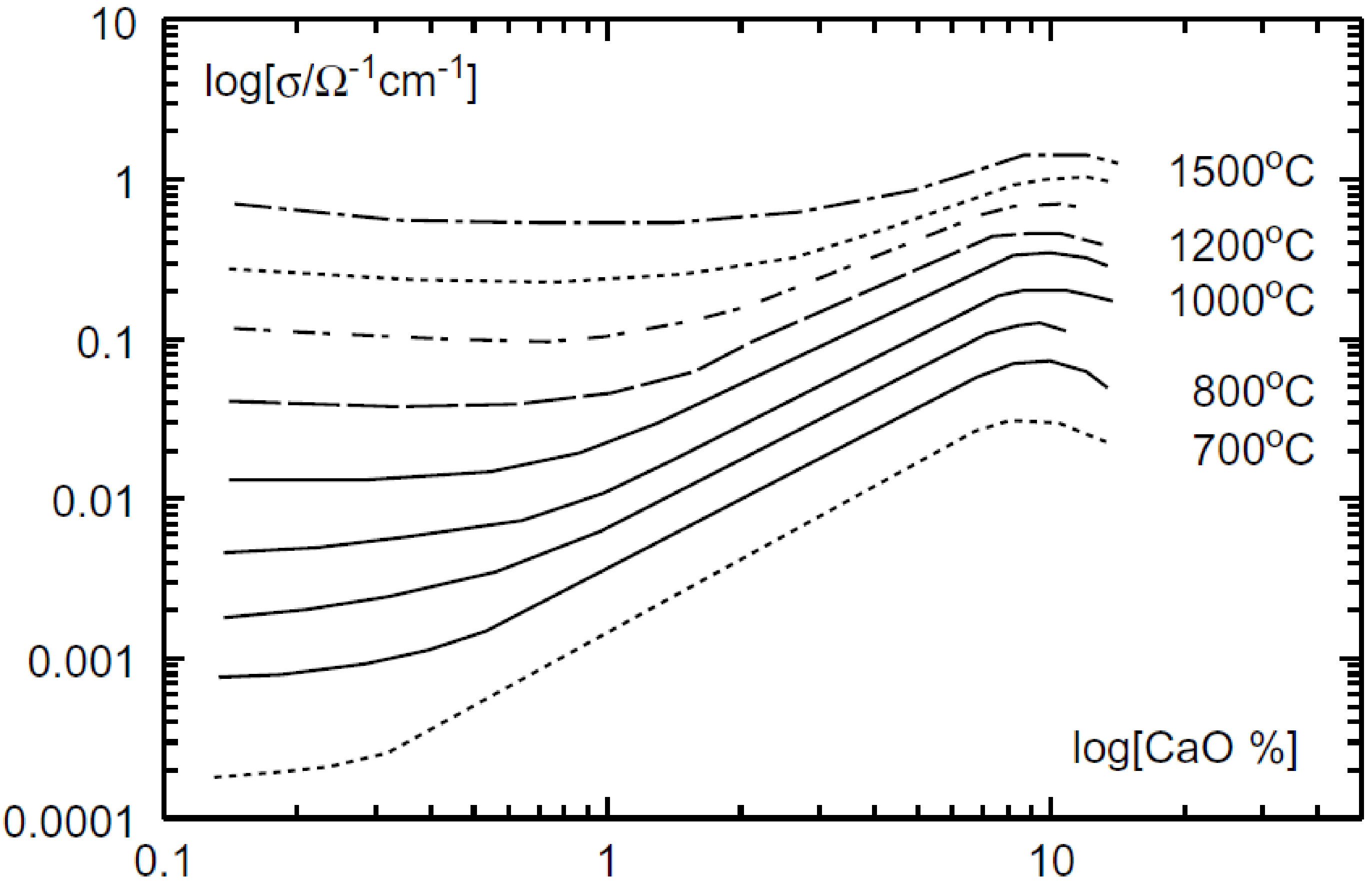
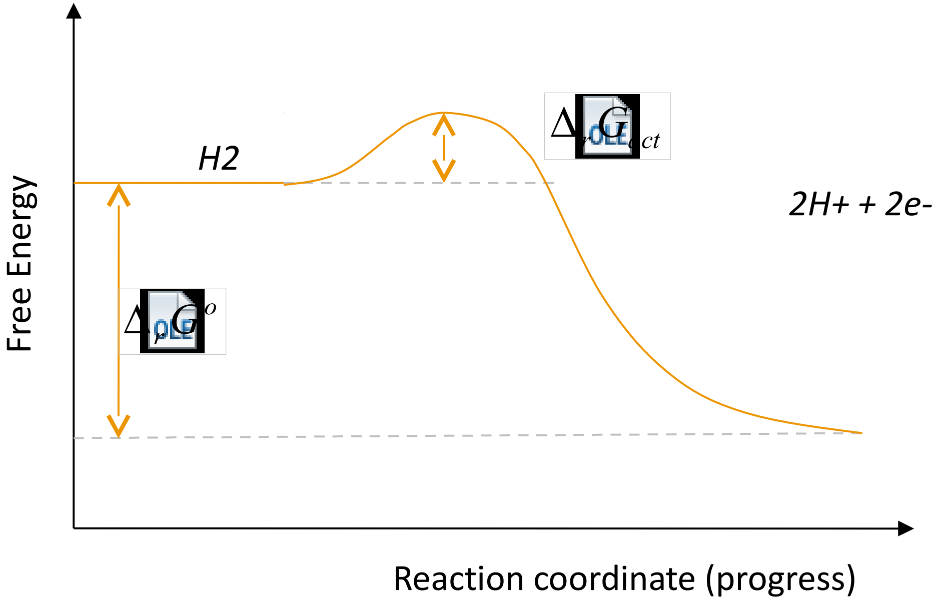


Figure 2.4: *Conductivity of Ca doped CeO_2. R.N. Blumenthal, F.S. Brugner and J.E. Garnier, J. Electrochem. Soc.*, **120**, *1230 (1973).*

Electrode Kinetics

Charge Transfer Reactions have an Activation Energy



Arrhenius Equation

$$k = Ae^{(-\Delta G_{act}/RT)}$$

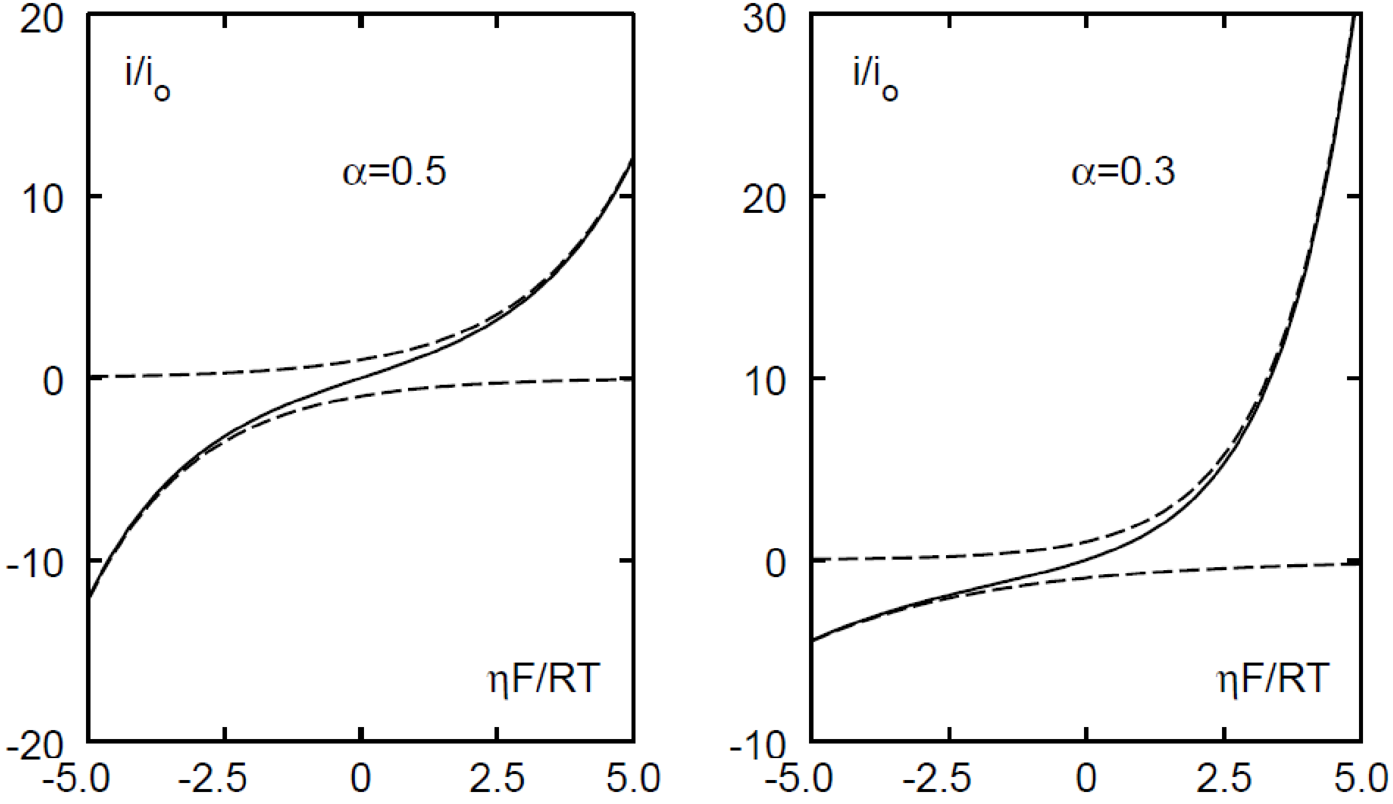


Figure 4.2: *Currents vs. overvoltage for an elementary reaction calculated as*

$$i = i_o \left(\exp\left[(1-\alpha) n \eta \frac{\mathrm{F}}{\mathrm{R}T} \right] - \exp\left[-\alpha n \eta \frac{\mathrm{F}}{\mathrm{R}T} \right] \right) \qquad (4.23)$$

for $n = 1$, $\alpha = 0.5$ *and* $\alpha = 0.3$.

——— i, $- - -$ i_+ *and* i_-.

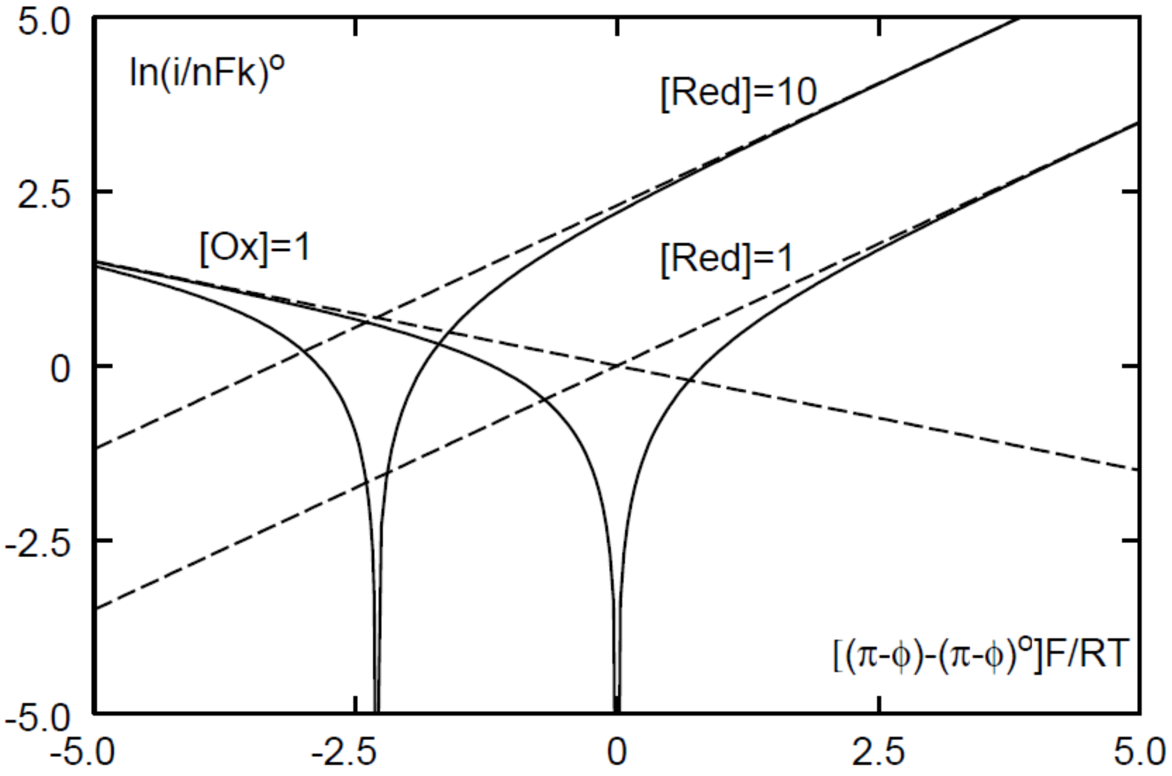


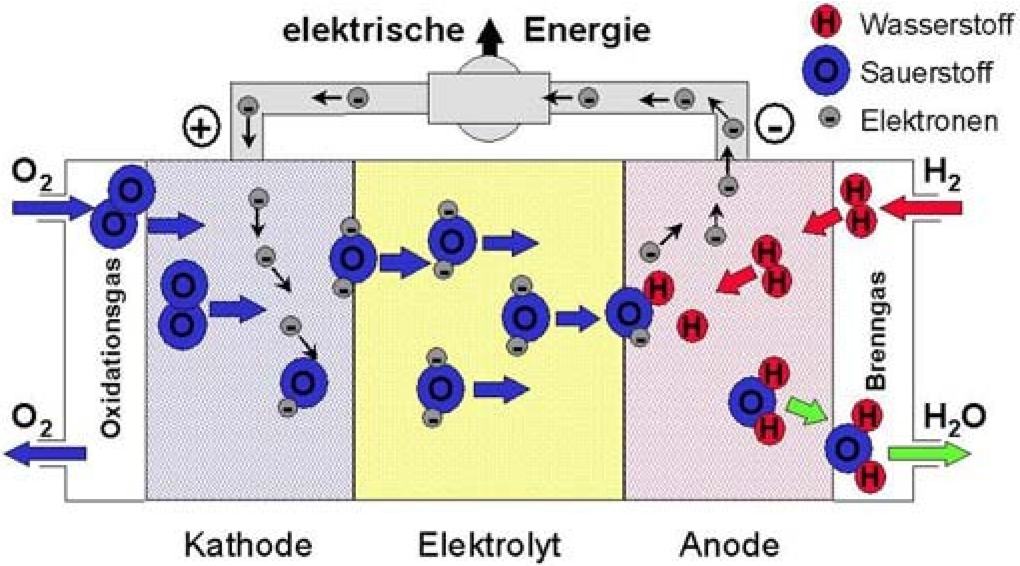
Figure 4.3: *Tafel plot*

——— $\ln\left[\frac{i}{n\mathrm{F}k^{\ominus}}\right]$ *calculated from eq. (4.18) for* $[Ox]=1,\ [Red]=1$ *and* $[Red]=10$.

– – – *partial currents from eqs. (4.24) and (4.25).*

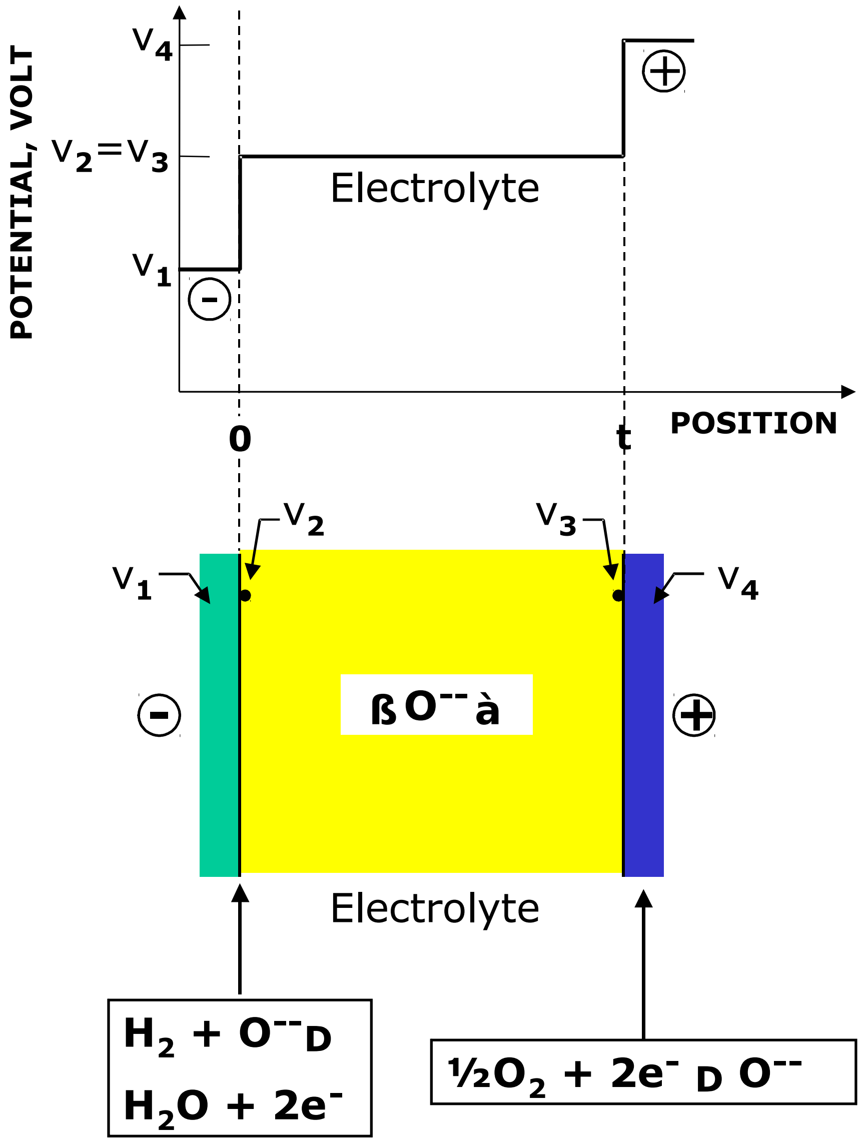
$$\frac{d\ln[i_+]}{d(\pi-\phi)} = \frac{(1-\alpha)n\mathrm{F}}{\mathrm{R}T}, \quad \frac{d\ln[|i_-|]}{d(\pi-\phi)} = \frac{-\alpha n\mathrm{F}}{\mathrm{R}T} \tag{4.26}$$

Solid Oxide Fuel Cell



- What is the potential ϕ across the cell in
  - A: OCV (0 A/cm2)
  - B: Fuel cell operation
  - C: Electrolysis

Potential Profiles in Solid Oxide Cells



$H_2 + O^{--}$ D

$H_2O + 2e^-$

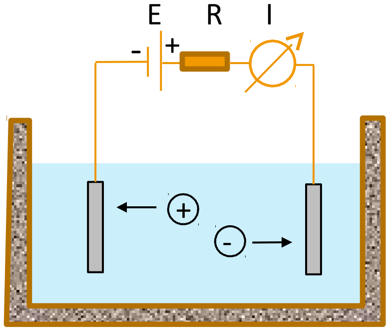
$\frac{1}{2}O_2 + 2e^-$ D O^{--}

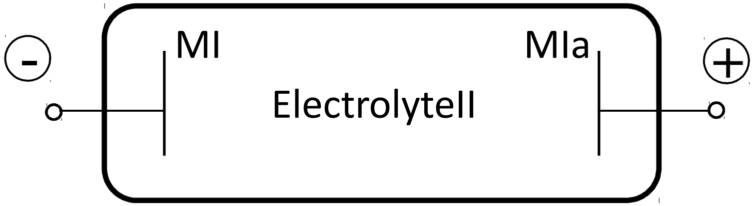
Potential through the electrode supported cell with <u>no</u> current

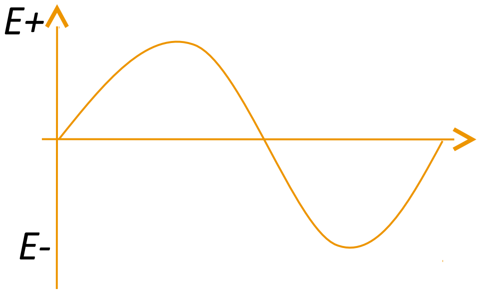
$V4 - V1 = Emf$

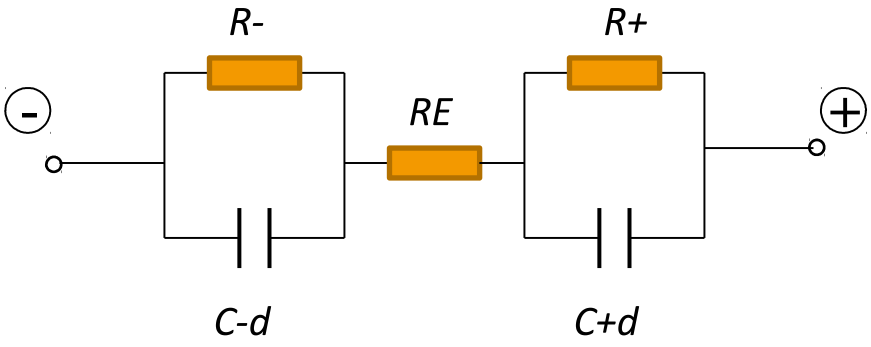
$Emf = -\Delta G/(n*F)$

Measurement of Electrolytic Conductivity & Equivalent Circuits for Electrochemical Cells









Equivalent Circuits for Batteries

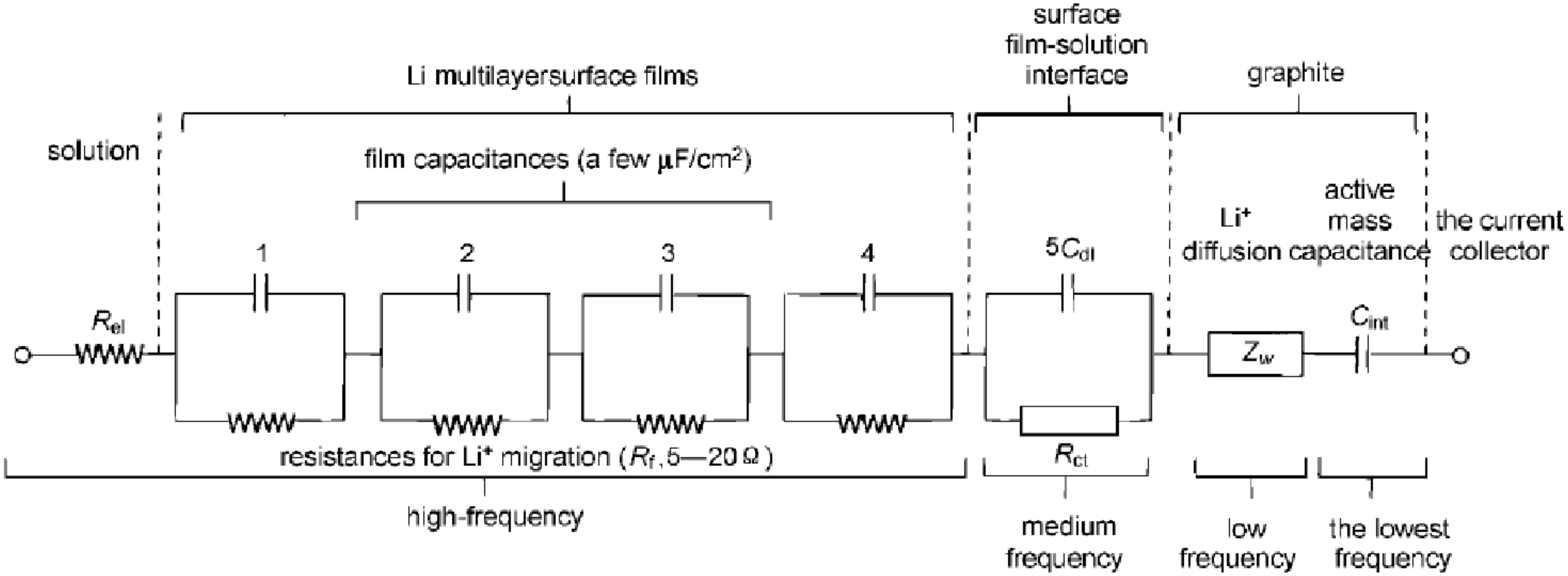


Fig. 2-2. EEC evolved by Aurbach used for analysis of impedance spectra of the lithium-ion insertion/desertion in the intercalation electrode[47].

LITHIUM ION BATTERIES – NEW DEVELOPMENTS, Edited by Ilias Belharouak

Equivalent Circuits for Batteries

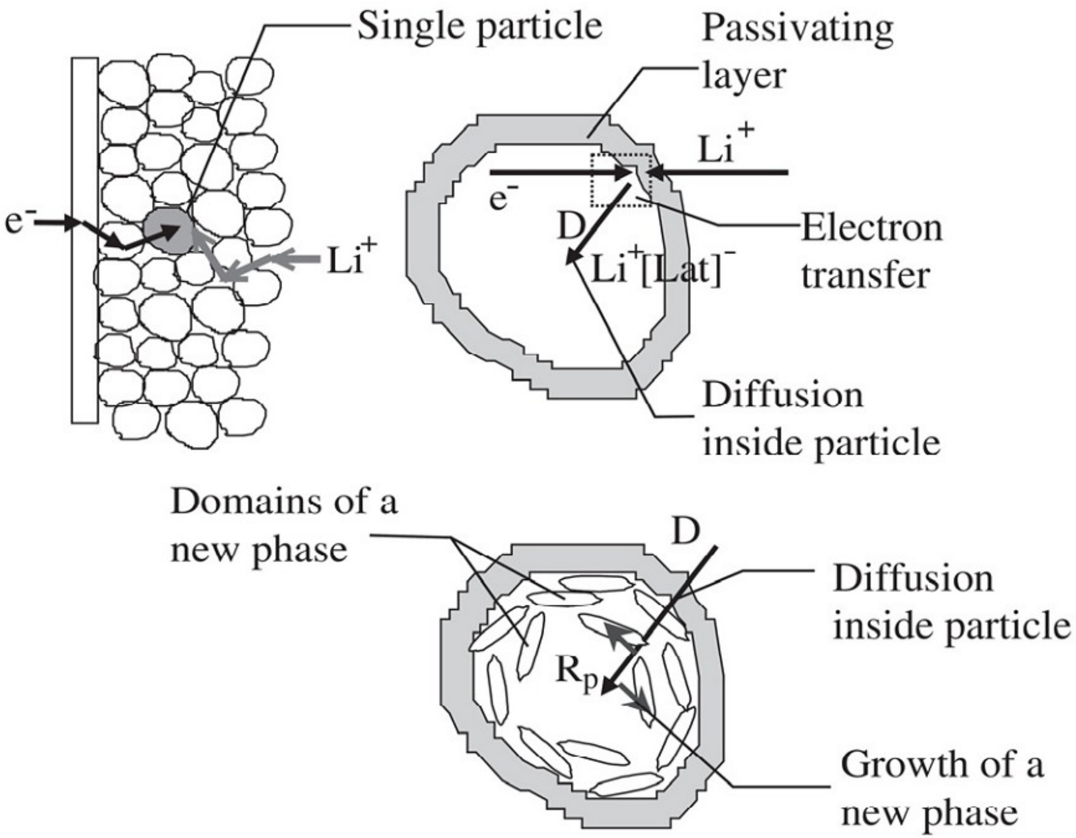


Fig. 2-3. Pictorial representation model for lithium-ion insertion/deinsertion into the intercalation electrode proposed by Barsoukov et al[12].

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Equivalent Circuits for Batteries

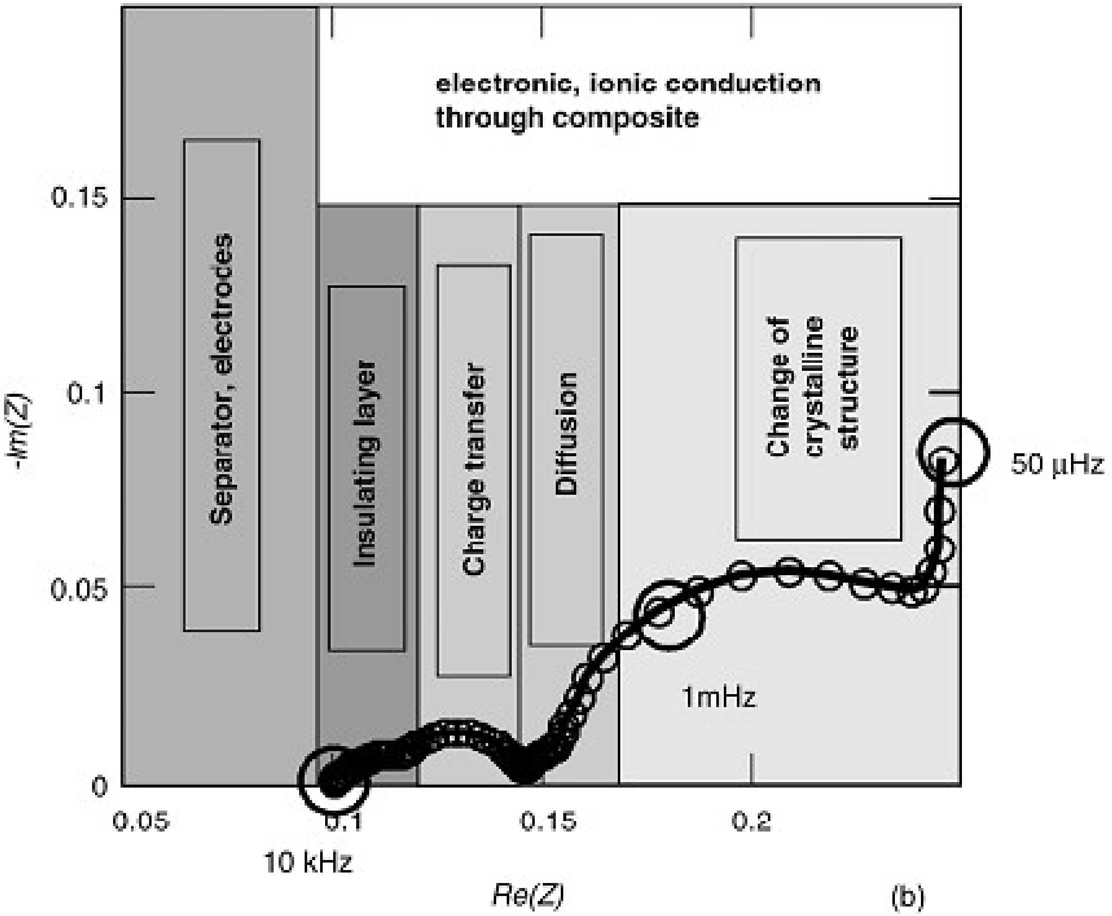

Fig. 2-4. Typical impedance spectra of intercalation electrode proposed by Barsoukov et al.[13].

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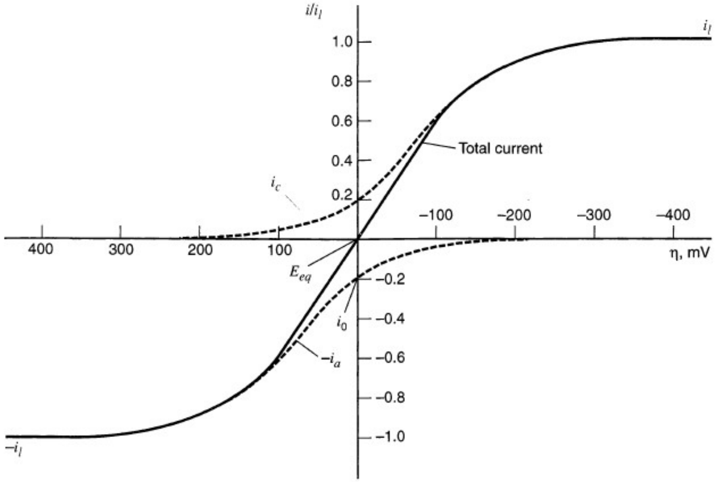
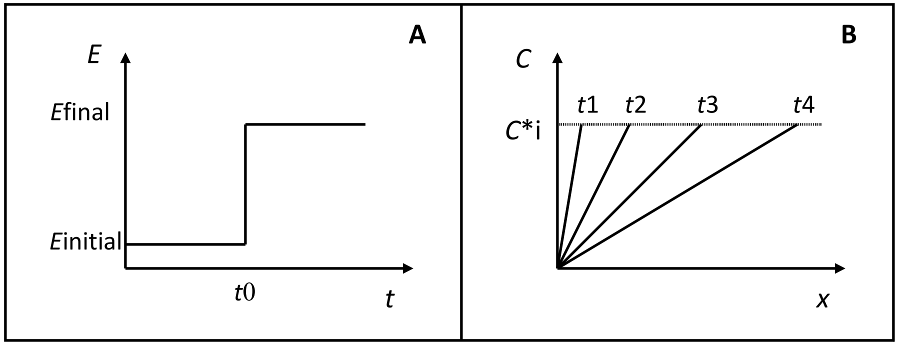
Mass Transport Effects





Mass Transport Effects in Electrochemical Cells

1. Migration (acts on ions, electric field driven)
2. Diffusion (acts on all dissolved – not solvent or balance gas - species, concentration gradient driven)
3. Convection (acts on all species, pressure gradient driven / depends on velocity of solution/gas)

Diffusion in a linear diffusion field (1-D concentration gradient):

$$J_i = -D\frac{\partial c}{\partial x}$$

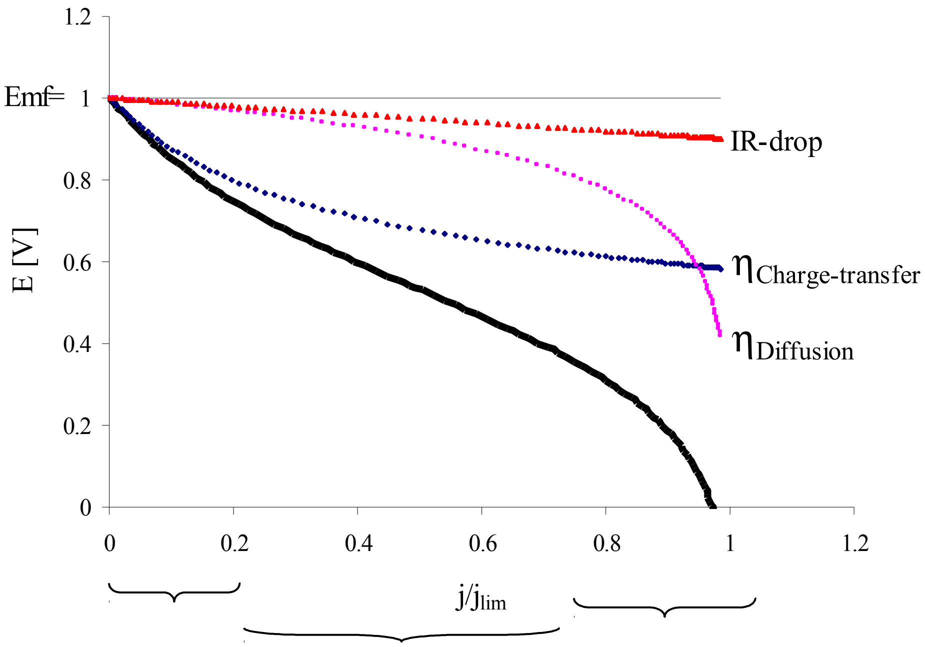
Nernst-Planck (Diffusion, Migration, Convection terms included)

$$J_i = -D_j \nabla c_j - \frac{z_j F}{RT} D_j c_j \nabla \phi + c_j v$$

Polarisation of a Fuel Cell

Secant Resistance:

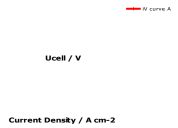
$$ASR = \frac{OCV - U_{cell}}{j_{cell}}$$



Activation region

Ohmic region

Mass transport region



Differential Resistance:

$$ASR = \frac{\Delta U_{cell}}{\Delta j_{cell}}\bigg|_{j_{cell}}$$

Concluding Remarks

You are welcome to contact me if you have questions, or want more information, reading tips etc

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Further Reading

Electrochemical Methods, A. J. Bard & L. R. Faulkner, 2nd ed., Wiley, 2001

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Fuel Cell Fundamentals, R. O'Hayre, S-W. Cha, W. Colella, F. B. Prinz, 2nd ed., Wiley, 2006