Electrochemistry in Solids
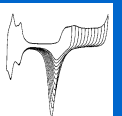## *Thermodynamics and Kinetics*
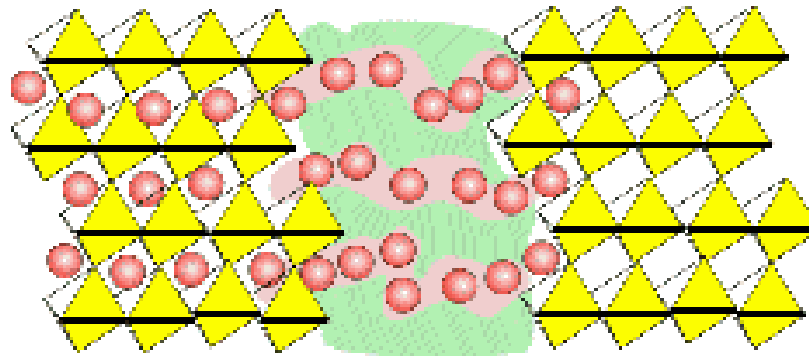
Electrochemistry at the other side of the interface
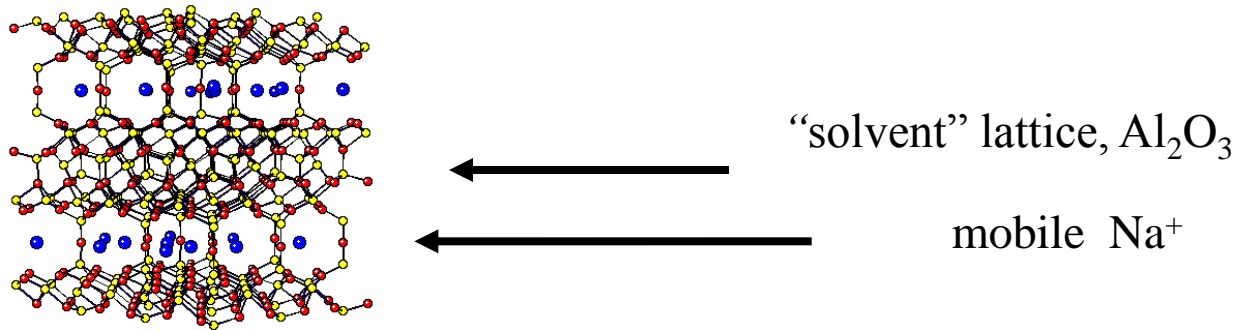
ICMAB
EXCELENCIA SEVERO OCHOA
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA

SEPTEMBER 17-20, 2018
SALA D'ACTES CARLES MIRAVITLLES
ICMAB-CSIC, Bellaterra, Spain

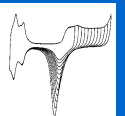**Southampton Electrochemistry Group**

Ions can be mobile in a solid lattice - as in Solid Electrolytes

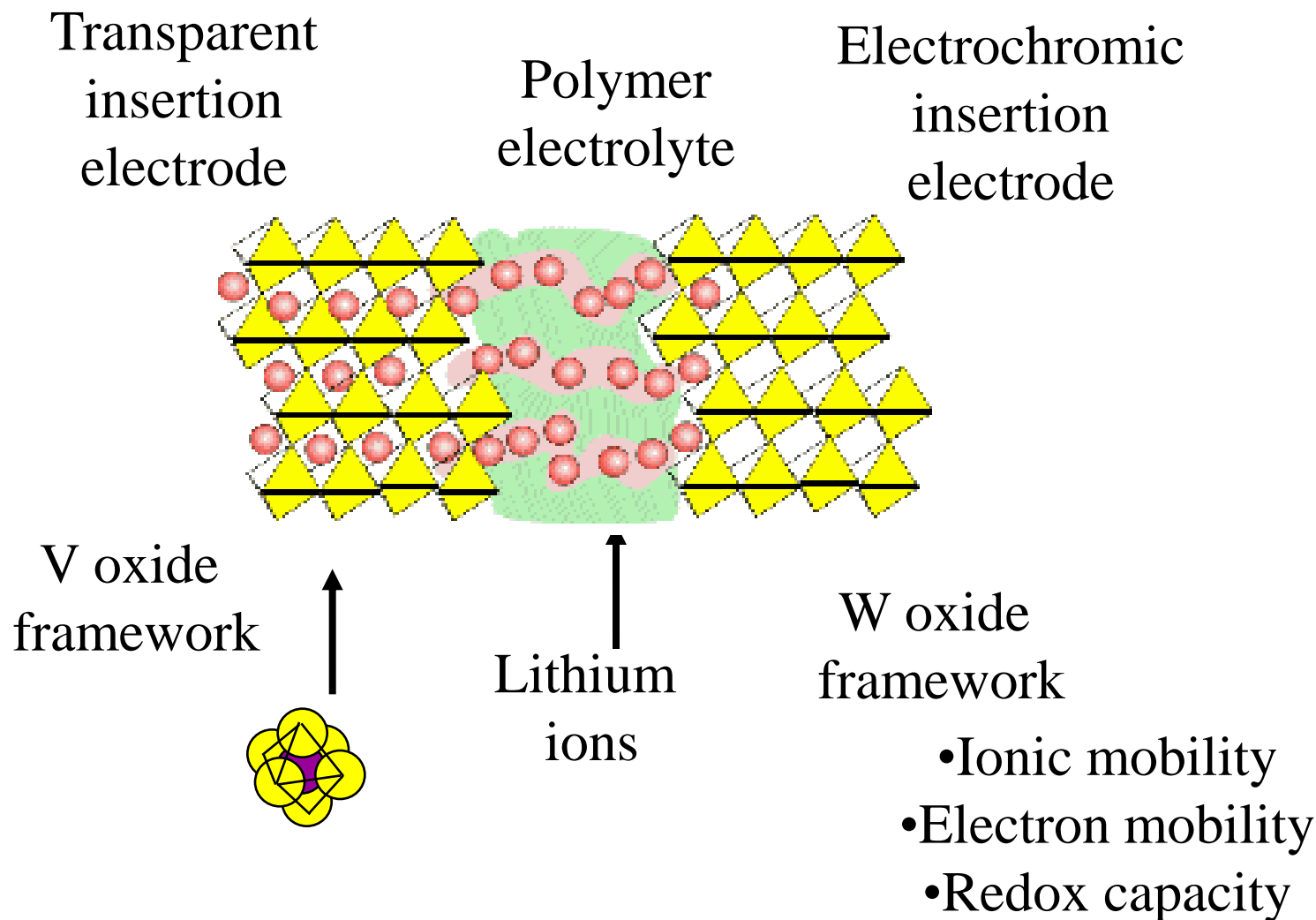*e.g. Interstitial type, β-Alumina*

"solvent" lattice, Al_2O_3

mobile Na^+

e.g. Vacancy type, Yttria stabilized zirconia (YSZ)

◆ Zr^{4+}

◻ O^{2-}

◇ Y^{3+}

◻ V_O

"solvent" lattice, ZrO_2

immobile solute Y^{3+}

mobile O^{2-} vacancies

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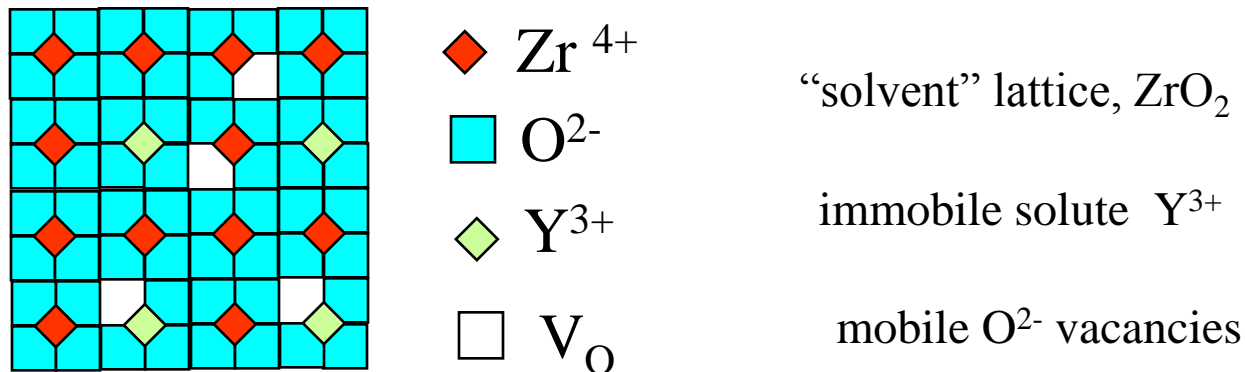
Insertion Electrodes in Cells

Transparent insertion electrode

Polymer electrolyte

Electrochromic insertion electrode

V oxide framework

Lithium ions

W oxide framework

- Ionic mobility
- Electron mobility
- Redox capacity
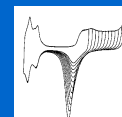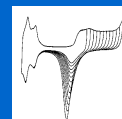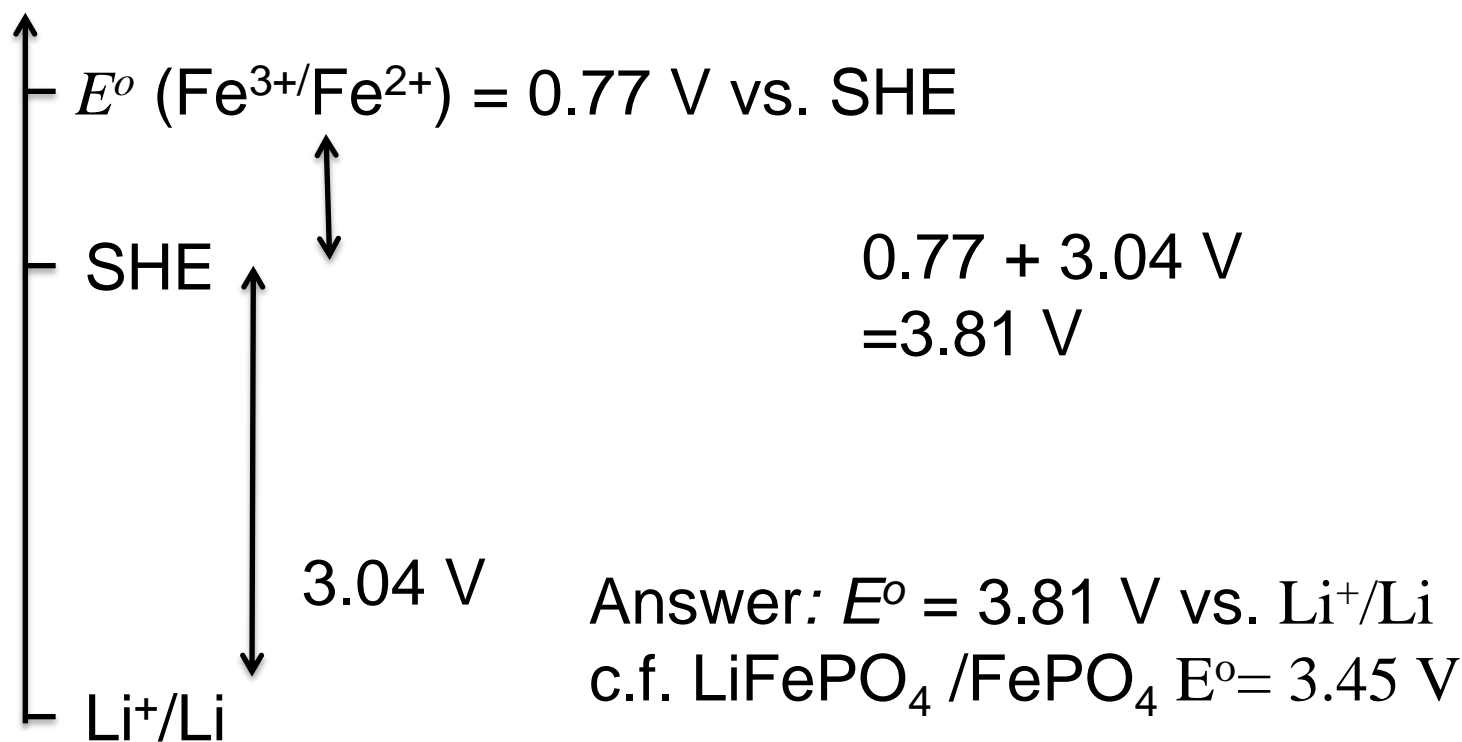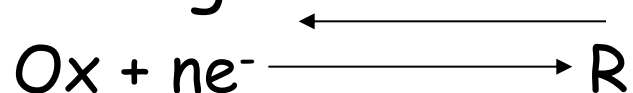
Conversion of potentials

For a potential value equal to 0.77 V vs SHE, convert it to the Li scale taking into account that Li equals -3.04 V vs. SHE

E^o (Fe^{3+}/Fe^{2+}) = 0.77 V vs. SHE

SHE

0.77 + 3.04 V
=3.81 V

3.04 V

Answer: E^o = 3.81 V vs. Li$^+$/Li
c.f. LiFePO$_4$ /FePO$_4$ E^o= 3.45 V

Li$^+$/Li

THERMODYNAMICS The Classical Nernst equation for single reactant and product

$$Ox + ne^- \longrightarrow R$$

$$E_e = E^0 - \frac{RT}{nF} \ln \frac{a_R}{a_{Ox}} = E^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_R}$$
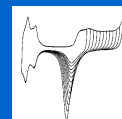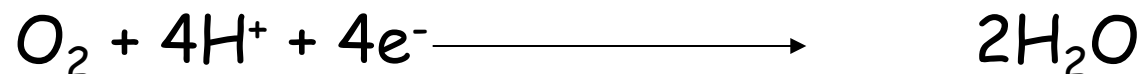
E_e: equilibrium potential

E^0 : standard potential

a_{Ox}, a_R : activities of oxidized and reduced species

For *ideal* solutions $a = c/c^0$, *e.g.* where $c^0 = 1M$

The standard potential, E^0, equals the equilibrium potential under conditions of unity activity of all reactants and products
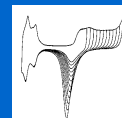
The General Nernst equation

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

$$E_e = E^0 + \frac{RT}{nF} \ln \frac{\prod a_{Ox}}{\prod a_R} = E^0 + \frac{RT}{4F} \ln \frac{a_{O_2} a_{H^+}^4}{a_{H_2O}^2}$$

E_e : equilibrium potential

E^0 : standard potential

What is the activity?

- For *ideal* solutions $a = c/c^0$, where c^0 could be 1M

- *activity* expresses the *effective* concentration, pressure, or any other deviation from the standard state.

- For real solutions the activity is obtained from the concentration through the activity coefficient γ which describes a surprised or enhanced reactivity for values less than or greater than 1.

$$a = \gamma(c/c^o)$$

- *If the concentration of a component is constant, e.g. due to a 2-phase equilibrium, we can set the standard state ΔG^o so that a= 1.*

- In solid state electrochemistry we often use the thermodynamic factor (d ln a/ d ln c) to express non ideality c.f. ideal solutions in which (d ln a/ d ln c) = 1 (see later)
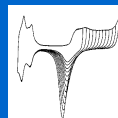
The potential-composition relation
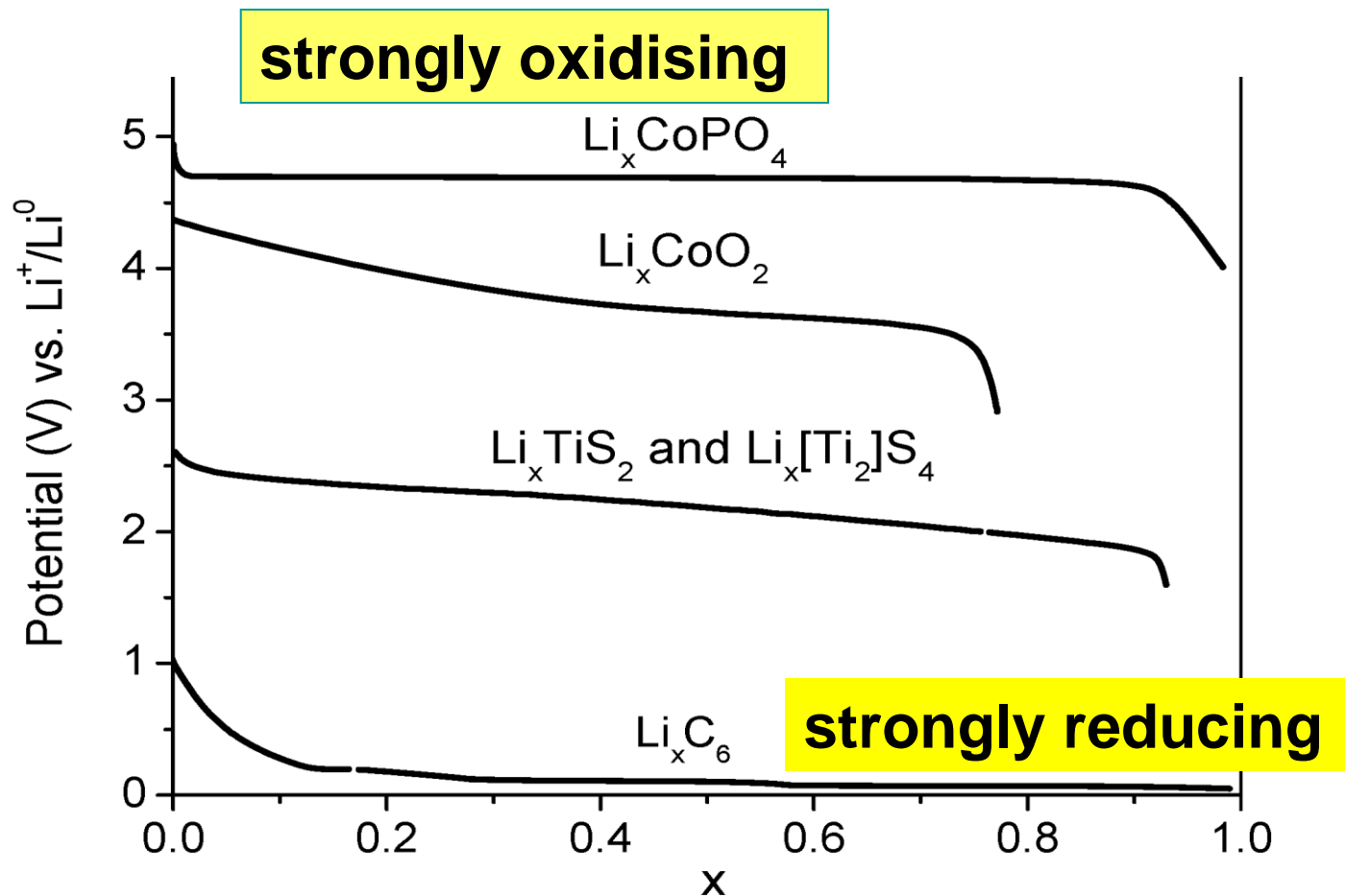
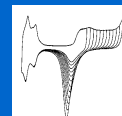# The potential-composition relation

For the reaction:

$$\text{Host} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x(\text{Host})$$
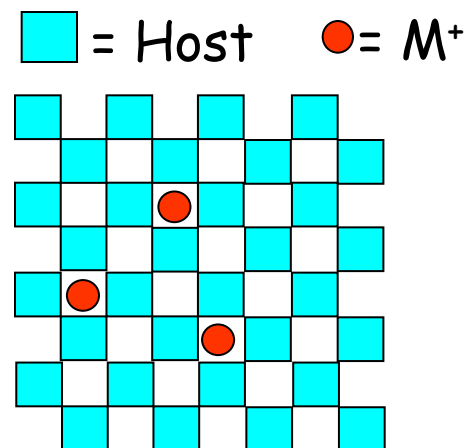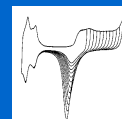
The lattice gas model results in a Nernst-like expression:

$$E_e = E^0 - \frac{RT}{F} ln\left(\frac{x}{1-x}\right)$$

Host   Li$_x$(Host)

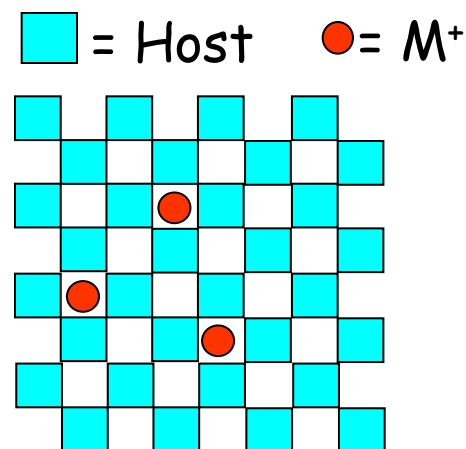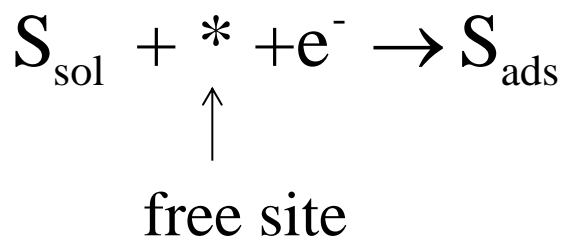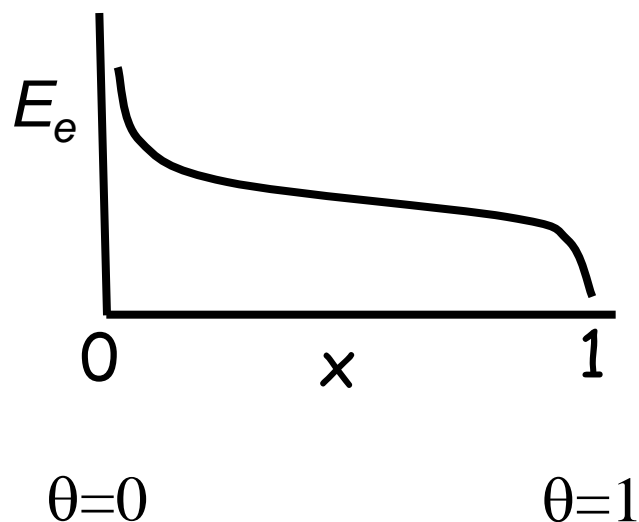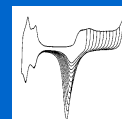$\square$ = Host $\bullet$ = M$^+$

(The Lattice Gas Model)

The potential-composition relation

Also the Langmuir Isotherm has

$$E_e = E^0 - \frac{RT}{F} ln\left(\frac{x}{1-x}\right)$$

$\theta=0$ $\theta=1$

$$S_{sol} + * + e^- \rightarrow S_{ads}$$

$\uparrow$
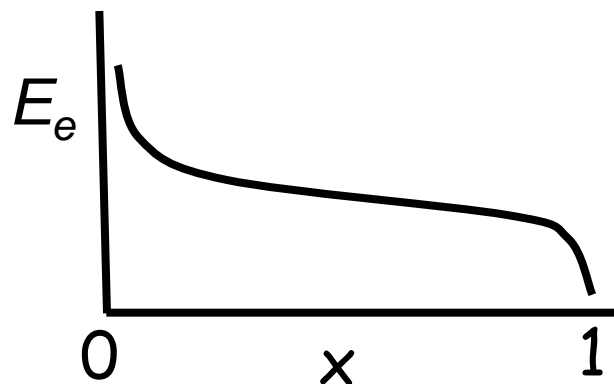
free site

= Host   ● = M$^+$

(The Lattice Gas Model)

The potential-composition relation

Here comes non-ideality:

$$E_e = E^0 - \frac{RT}{F} ln\left(\frac{x}{1-x}\right) + kx$$

interactions

E_e

0   x   1

Host Li_x(Host)

$$Host + xLi^+ + xe^- \rightarrow Li_x(Host)$$

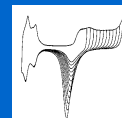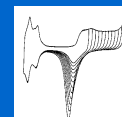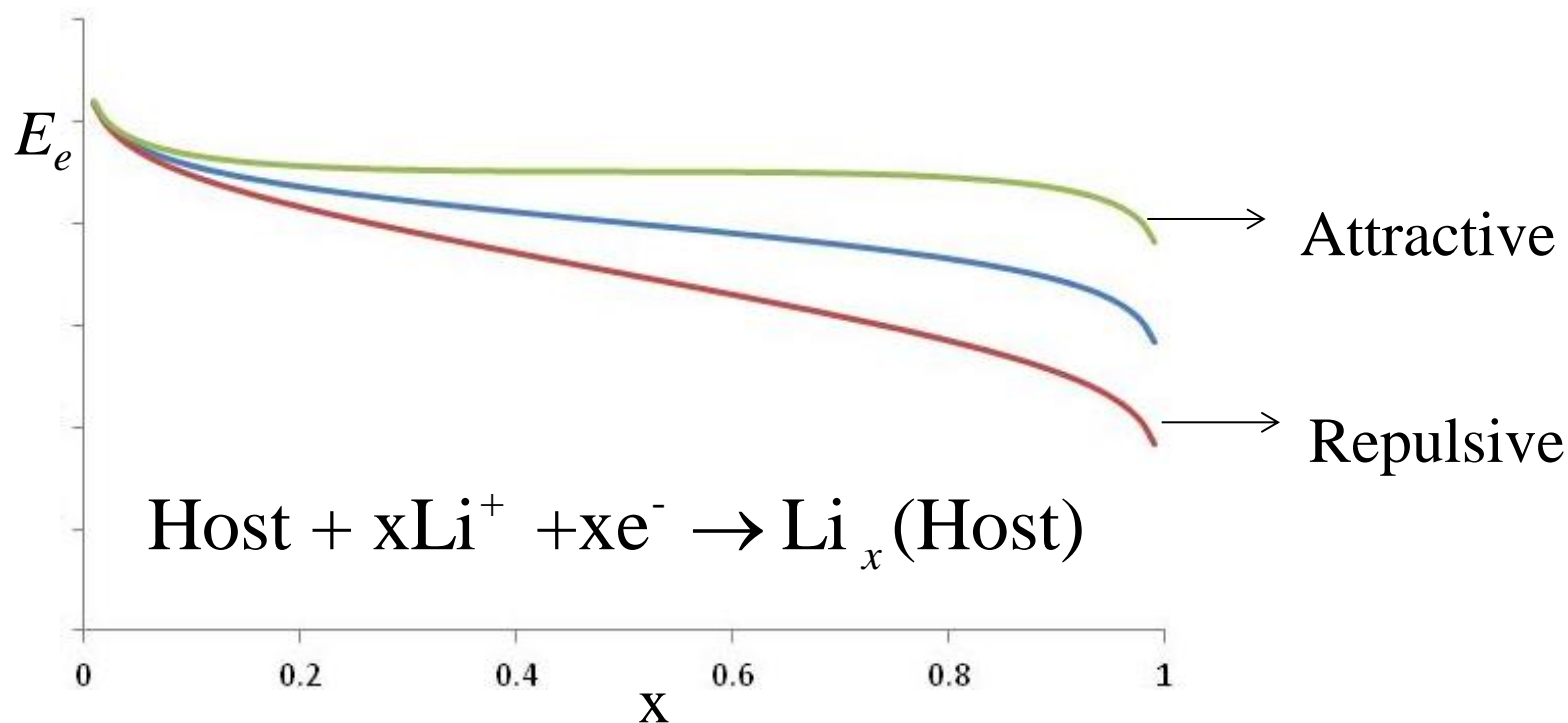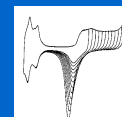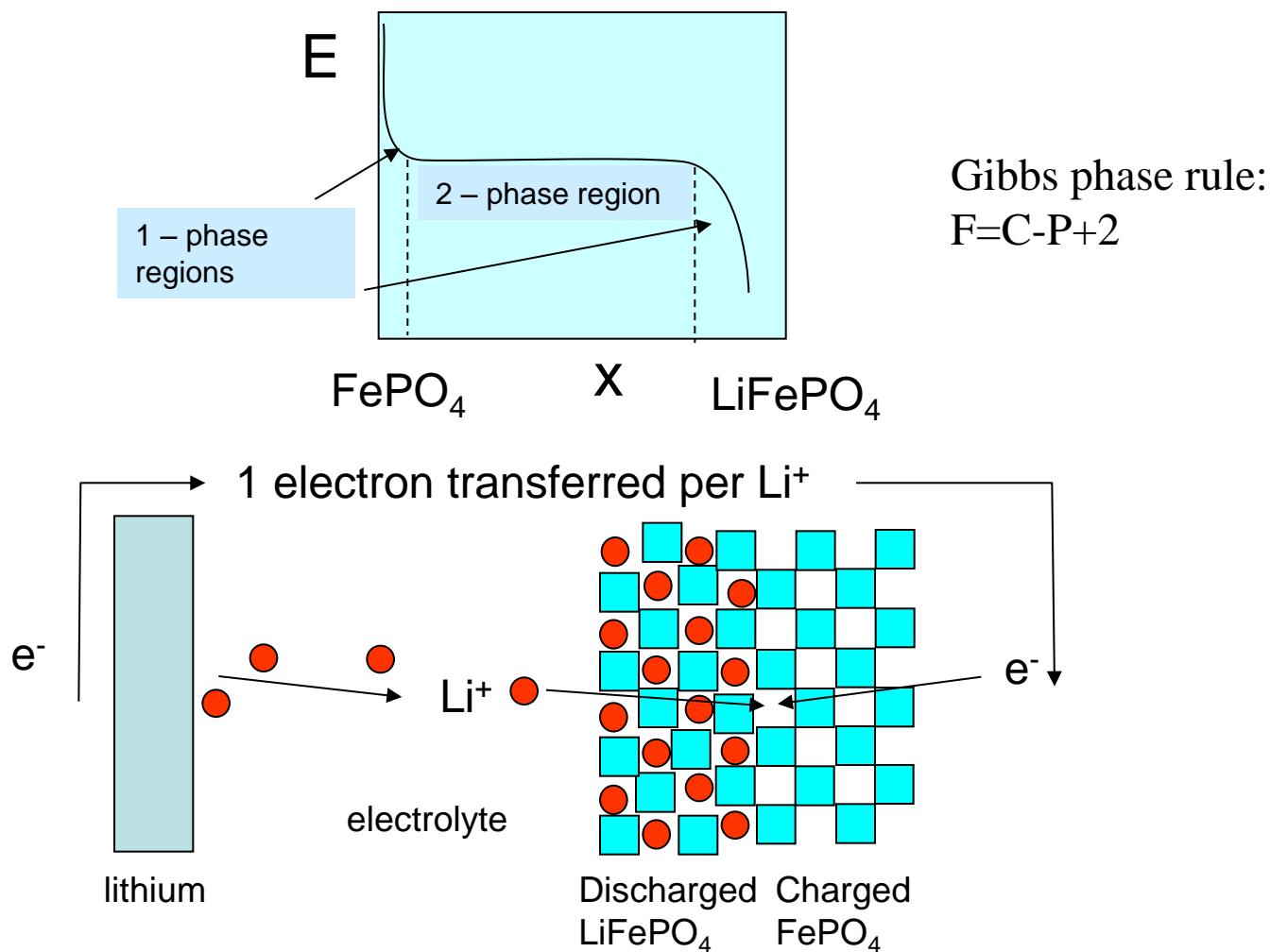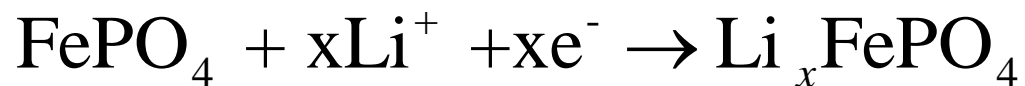☐ = Host   ● = M⁺
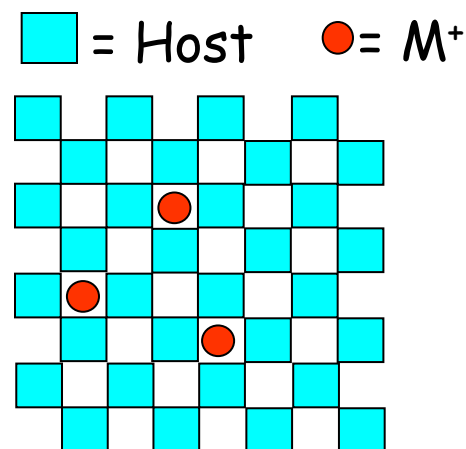
(The Lattice Gas Model)

The potential-composition relation

$$E_e = E^0 - \frac{RT}{F} ln\left(\frac{x}{1-x}\right) + kx$$

interactions

E_e

Attractive

Repulsive

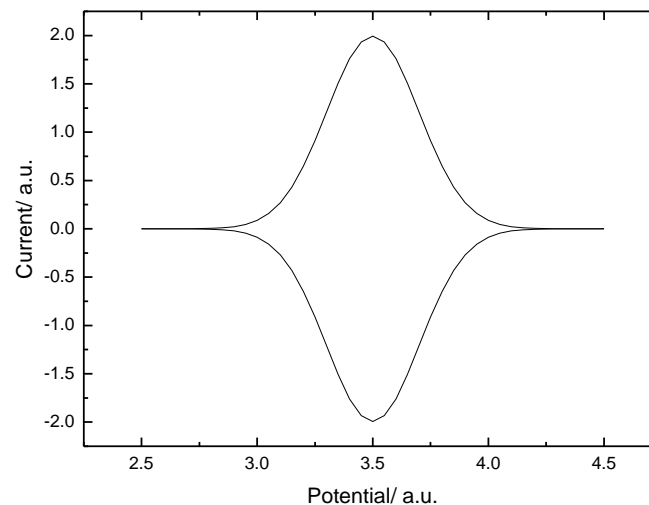$$\text{Host} + \text{xLi}^+ + \text{xe}^- \rightarrow \text{Li}_x(\text{Host})$$

x

Attractive interactions can lead to phase separation

$$FePO_4 + xLi^+ + xe^- \rightarrow Li_xFePO_4$$

E

2 – phase region

1 – phase regions

FePO$_4$ X   LiFePO$_4$

Gibbs phase rule:
F=C-P+2

1 electron transferred per Li⁺

e⁻

e⁻

Li⁺

electrolyte

lithium

Discharged LiFePO$_4$

Charged FePO$_4$

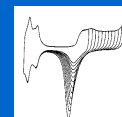# Slow cyclic voltammetry of **battery electrodes**

1 Phase

Li_xCoO_2

$$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + x\ Li^+ + x\ e^-$$

2 Phase

$FePO_4$

$LiFePO_4$

$$LiFePO_4 \rightleftharpoons FePO_4 + Li^+ + e^-$$

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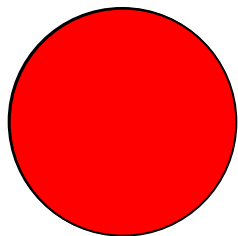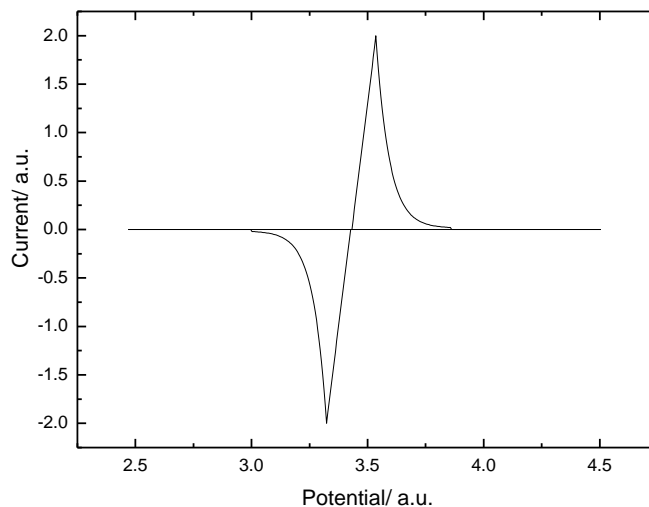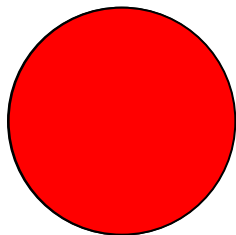
Solid redox reactions need solid diffusion

SOLUTION

The redox reagent is initially in the solution. It diffuses to the interface, reacts, then returns to the solution,

Adsorption/desorption

e⁻

Mass transport

Electron transfer

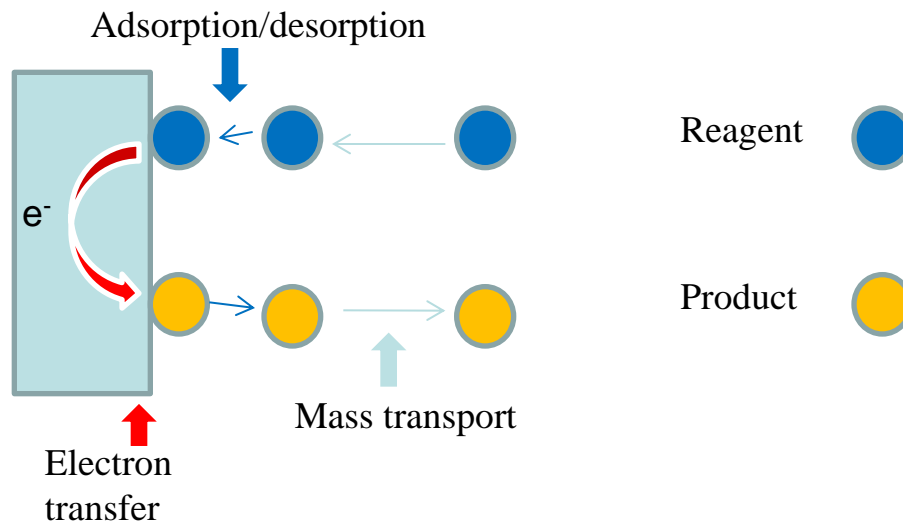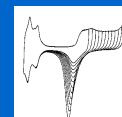Reagent

Product

SOLID

The reagent is a solid.

The guest ion enters the solid to compensate the charge.

Adsorption

e⁻   e⁻   e⁻   e⁻

Electron transfer

Ion transfer

Guest ion in solution, e.g. H^+, Li^+, Na^+ Ag^+, Cu^+

Ion in solid

ION INSERTION
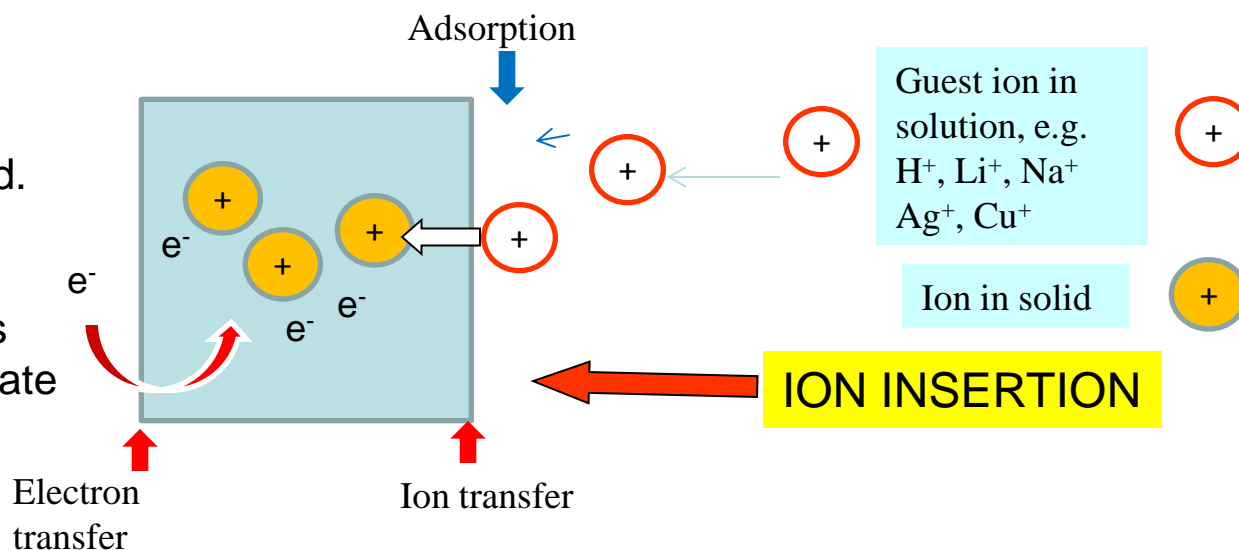
Kinetics in Solid State Electrochemistry

Potential Dependent Rate Constant
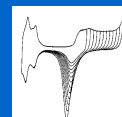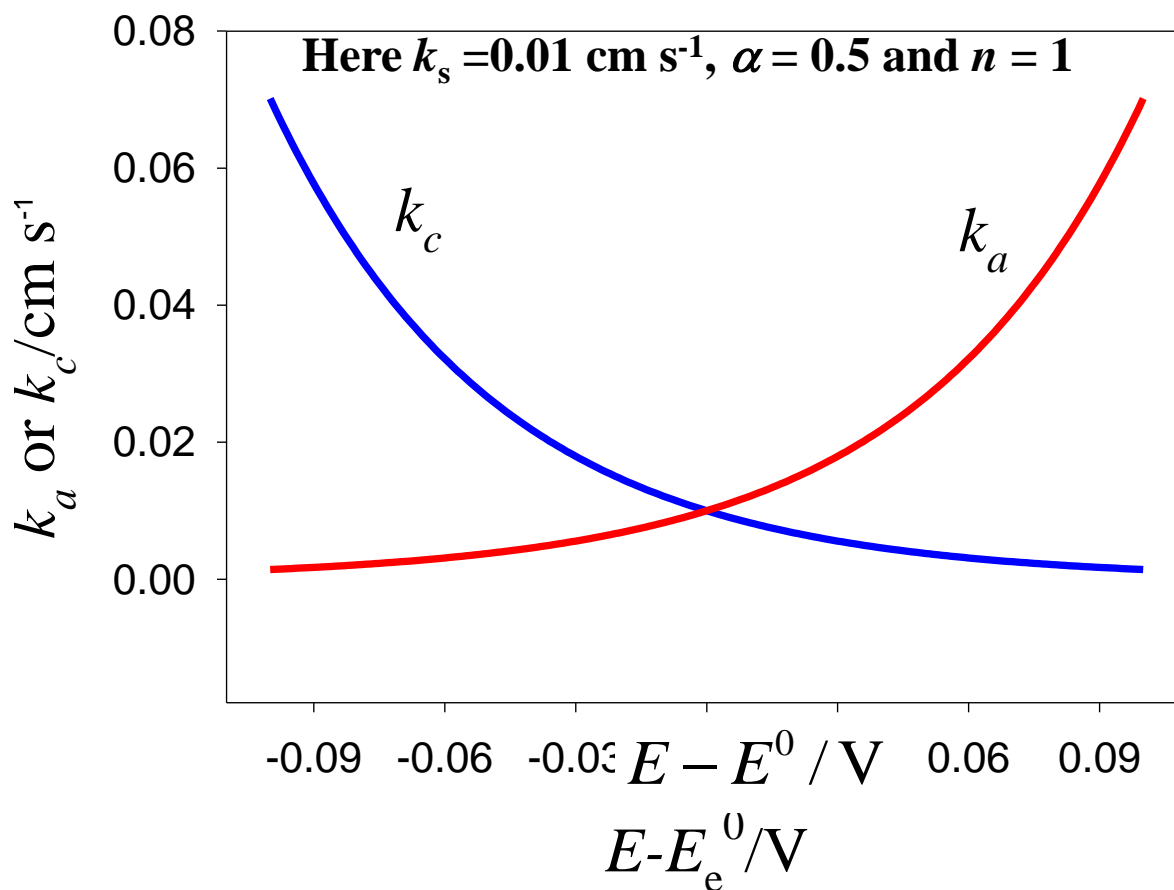
$$k_c = k_s e^{\frac{-\alpha_c nF(E-E^0)}{RT}}$$

$$\text{Rate} = kc$$

$$k_a = k_s e^{\frac{\alpha_a nF(E-E^0)}{RT}}$$

Here $k_s = 0.01$ cm s^{-1}, $\alpha = 0.5$ and $n = 1$

k_a or k_c/cm s^{-1}

k_c

k_a

$E - E^0$ / V

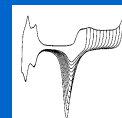E-E_e^0/V

Butler Volmer Kinetics

The kinetics of electron transfer shown above are expressed by the **Butler Volmer equation**

$$j = j_0 \left[\exp\left(\frac{\alpha_a nF}{RT} \eta \right) - \exp\left(\frac{-\alpha_c nF}{RT} \eta \right) \right]$$

where

Overpotential $\eta = E - E_e$

$j_o = exchange\ current\ at\ equilibrium$

Relevance of Butler -Volmer Kinetics for batteries

$$j = j_0 \left[\exp\left(\frac{\alpha_a nF}{RT}\eta\right) - \exp\left(\frac{-\alpha_c nF}{RT}\eta\right) \right]$$
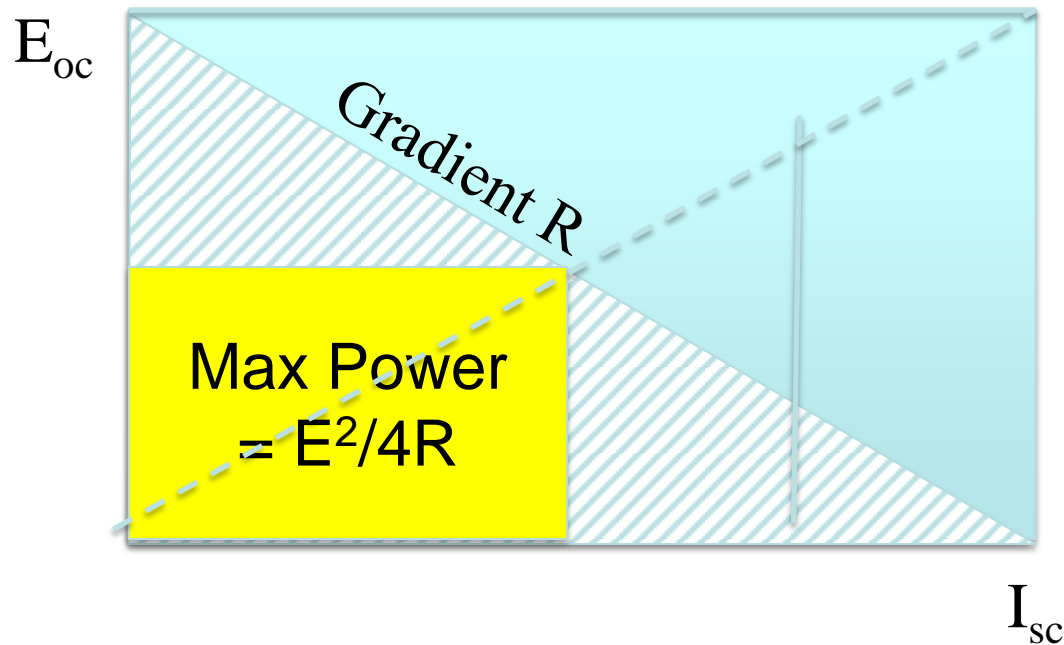
For a simple one-electron transfer reaction $\alpha_a + \alpha_c = 1$

- Typically the current should increase 10x for each 30 mV increase in overpotential – i.e. kinetics can be accelerated at low cost!

- j_o is proportional to c, *so the rate slows toward zero as reactant depletes at end of discharge –* an essential feature of a realistic model.
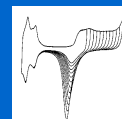
Also - Resistance limitations

- R= ionic resistance of the electrolyte + electronic resistance of the electrode

E_{oc}

Gradient R

Max Power
$= E^2/4R$

I_{sc}

- We need better electrolytes!