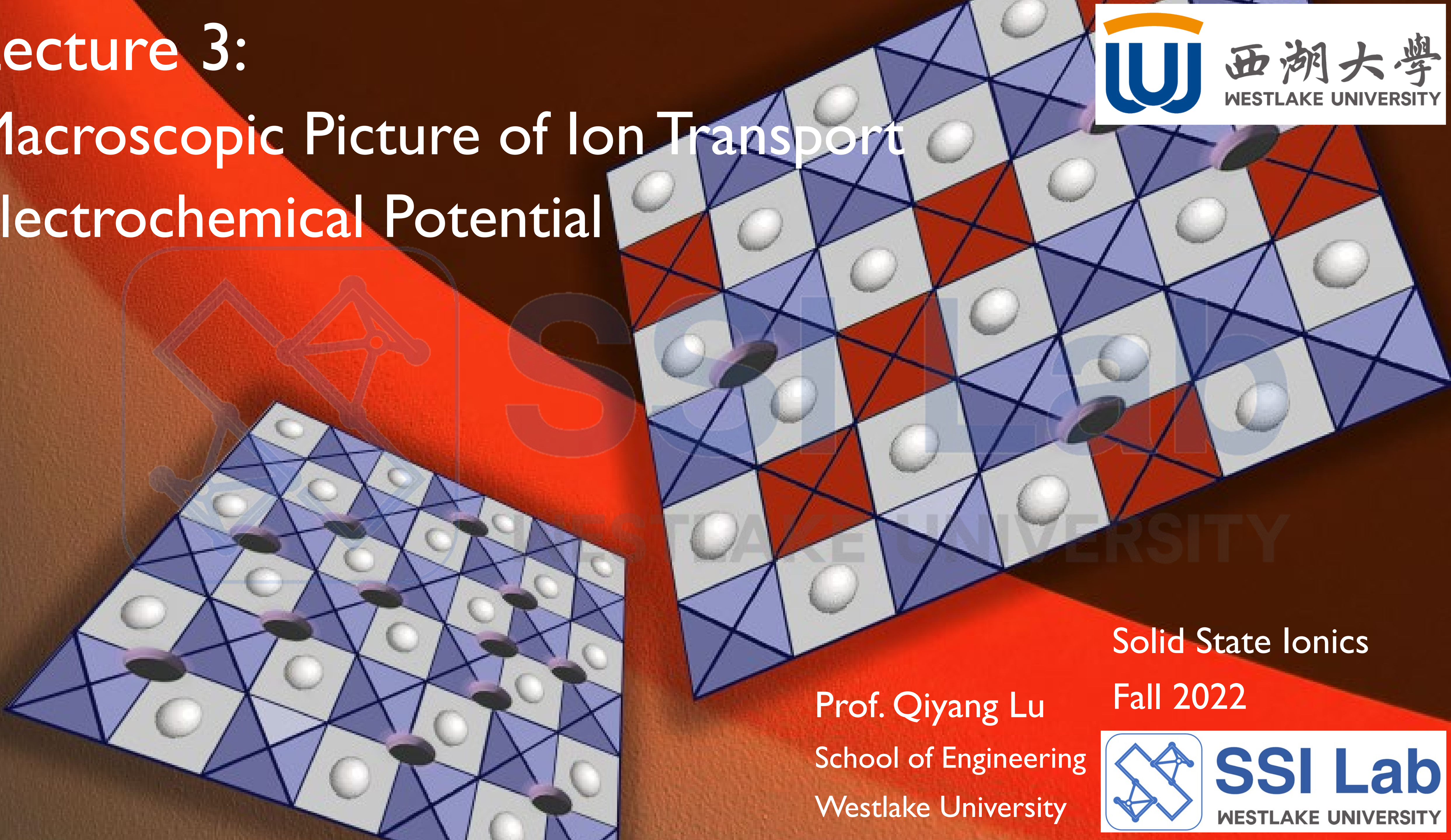
Lecture 3:
Macroscopic Picture of Ion Transport
Electrochemical Potential

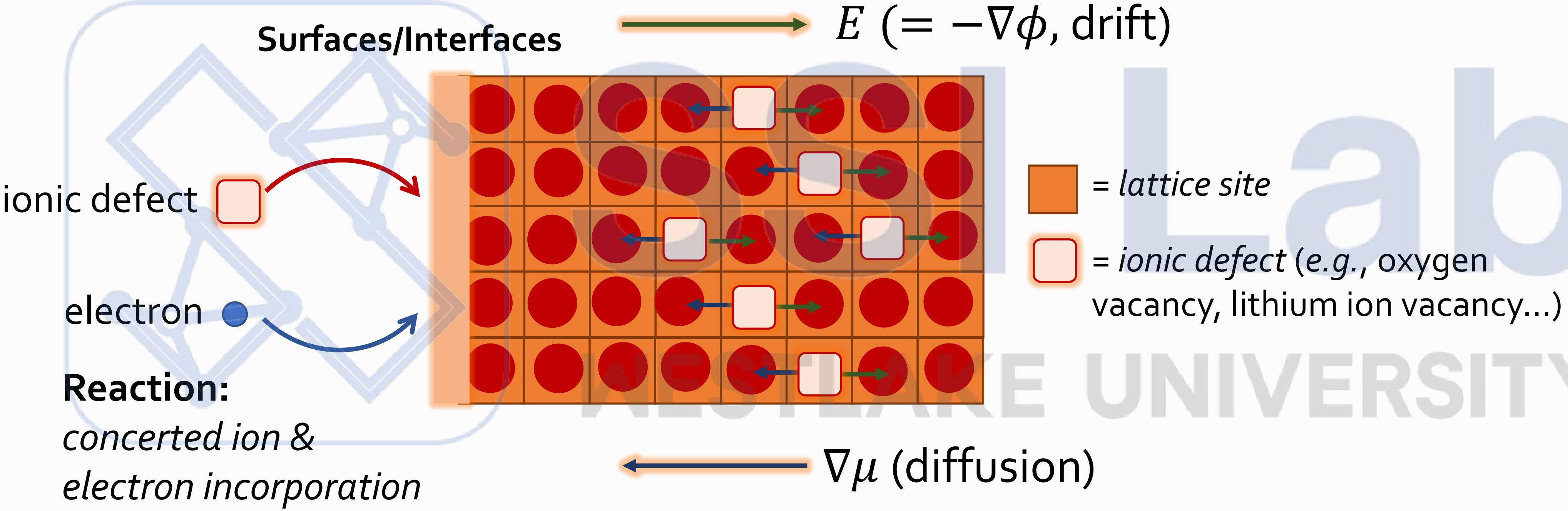


Solid State Ionics

Fall 2022

Prof. Qiyang Lu
School of Engineering
Westlake University

Diffusion and reactions in solid states w/ the picture of ionic defects



Surfaces/Interfaces

$E\ (= -\nabla\phi$, drift)

ionic defect ▢

electron ●

Reaction:
concerted ion &
electron incorporation

🟧 = *lattice site*

▢ = *ionic defect* (*e.g.*, oxygen vacancy, lithium ion vacancy…)

$\nabla\mu$ (diffusion)

Ion motion: *drift + diffusion*
(similar to electrons/holes in semiconductor physics)

Things we will discuss in this lecture

Macroscopic picture of ion transport:

- What are the governing equation of diffusion and drift of ionic/electronic defects?
- How to solve the case of ion transport when both diffusion and drift occur simultaneously?

Electrochemical potential:

- What is the difference and relationship between chemical potential, electrostatic potential and electrochemical potential?
- How to express the open-circuit-potential of an electrochemical system by using electrochemical potential of electrons?

Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

A review (hopefully?) on thermodynamics

Gibbs free energy

$$G = U + PV - TS$$

$$G = H - TS$$

H: enthalpy

the *maximum reversible work* that may be performed by a thermodynamic system at a ***constant temperature*** **(*T*)** ***and pressure*** **(*P*)**

The differential Gibbs free energy

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

Chemical potential μ_i is the ***partial molar*** Gibbs free energy of species *i* at constant *T* and *P*

At constant T and P, we define chemical potential of species *i* (μ_i)as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = h_i - Ts_i$$

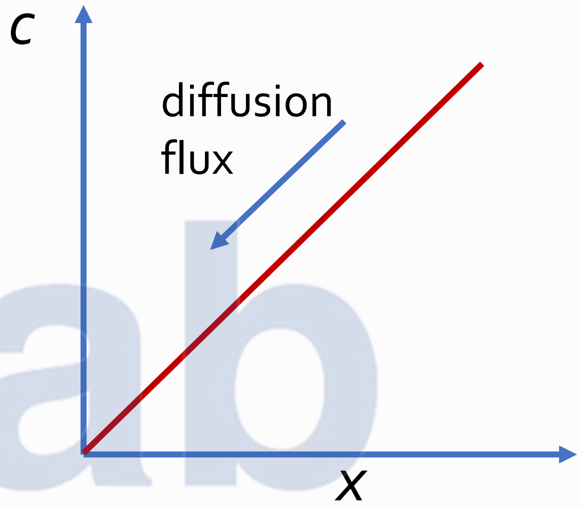
Chemical potential difference → driving force for diffusion

How to link chemical potential of species *i* (μ_i) with its concentration c_i?

$$\mu_i = \mu_i^0 + RTlna_i = \mu_i^0 + RTln(\gamma_i c_i)$$

μ_i^0: chemical potential at ***standard*** condition

At dilute limit, γ_i → 1, therefore $\mu_i = \mu_i^0 + RTlnc_i$



Diffusion: Fick's first law

$$J_{diff} = -D\frac{\partial c}{\partial x}$$

J_{diff} Net flux
(unit: mol/L·cm/s = mol/(cm²· s))
substance *per area per second*

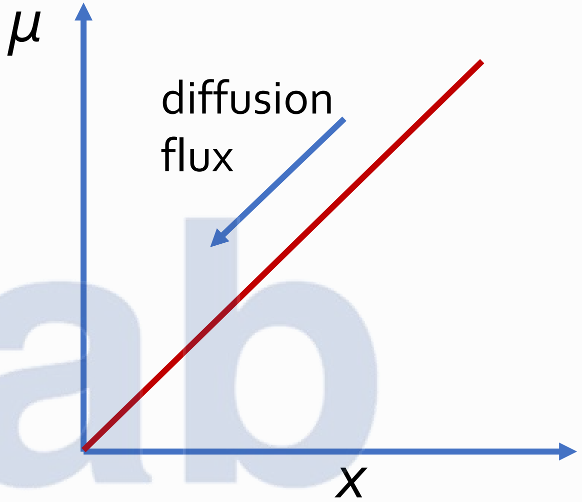
D for diffusivity
(unit: cm²/s)

$\frac{\partial c}{\partial x}$ Concentration gradient
(unit: M/cm, M = mol/L)

Chemical potential difference → driving force for diffusion

At dilute limit, $\gamma_i \rightarrow 1$, therefore $\mu_i = \mu_i^0 + RTlnc_i$

$$\frac{\partial \mu}{\partial x} = RT\frac{1}{c}\frac{\partial c}{\partial x} \longrightarrow J_{diff} = -D\frac{\partial c}{\partial x} = -D\frac{c}{RT}\frac{\partial \mu}{\partial x}$$



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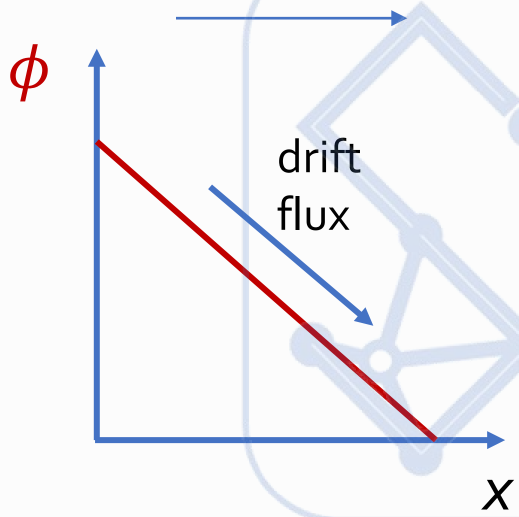
$\frac{\partial c}{\partial x}$ Concentration gradient
(unit: M/cm, M = mol/L)

Charged species, electrostatic potential and Ohm’s Law

$$E = -\frac{\partial \phi}{\partial x}$$



Drift: Ohm’s law

$$j_{drift} = \sigma E = -\sigma \frac{\partial \phi}{\partial x}$$

j_{drift} Net flux of *charge*
(unit: $C/(cm^2 \cdot s)$)
charge *per area per second*

σ Conductivity
(unit: S/cm, *i.e.* (A/V)/cm)

$E = -\frac{\partial \phi}{\partial x}$ Electric field
(unit: V/cm)

ϕ: ***Electrostatic*** potential
E: Electric field, *i.e.* ***gradient*** of electrostatic potential

If the charge carriers are ions (or electrons) with ze charge, then:

$$J_{drift} = j_{drift} / zF$$

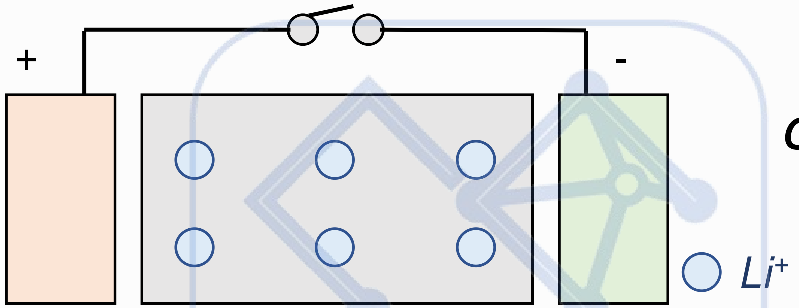
Net flux of *matter*
(unit: $mol/(cm^2 \cdot s)$)

Net flux of *charge*
(unit: $C/(cm^2 \cdot s)$)

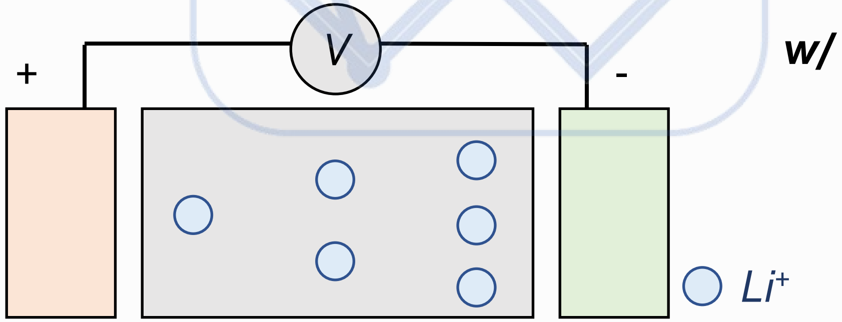
F: Faraday constant, ~96500 C/mol
the charge of 1 mol e^- $F = eN_A$

The concept of electrochemical potential and equilibrium condition of charged species

Thought experiment: what happens when a voltage is applied between two parallel electrodes?



Open-circuit condition: no concentration gradient



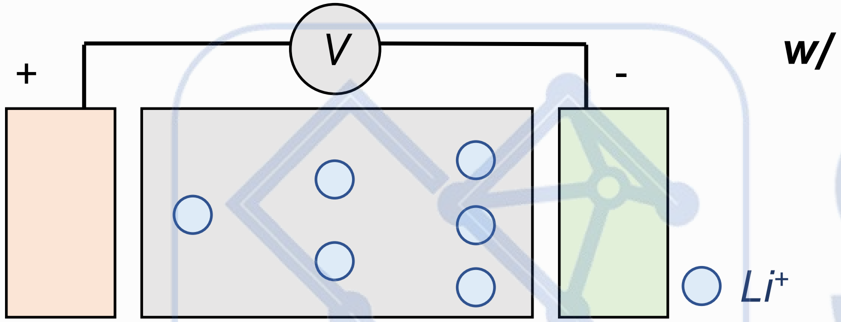
w/ an applied voltage: concentration gradient forms

$$J_{drift} = \frac{j_{drift}}{zF} = \frac{\sigma E}{zF} = -\frac{\sigma}{zF}\frac{\partial \phi}{\partial x}$$

$$J_{diff} = -D\frac{\partial c}{\partial x} = -D\frac{c}{RT}\frac{\partial \mu}{\partial x} \qquad (\mu = \mu^0 + RT\ln c)$$

The concept of electrochemical potential and equilibrium condition of charged species (cont'd)

Thought experiment: what happens when a voltage is applied between two parallel electrodes?



w/ an applied voltage: concentration gradient forms

$$J_{drift} = \frac{j_{drift}}{zF} = \frac{\sigma E}{zF} = -\frac{\sigma}{zF}\frac{\partial \phi}{\partial x}$$

$$J_{diff} = -D\frac{\partial c}{\partial x} = -D\frac{c}{RT}\frac{\partial \mu}{\partial x} \qquad (\mu = \mu^0 + RTln\, c)$$

At equilibrium condition, we have:

$$\boxed{J_{tot} = J_{drift} + J_{diff} = 0}$$

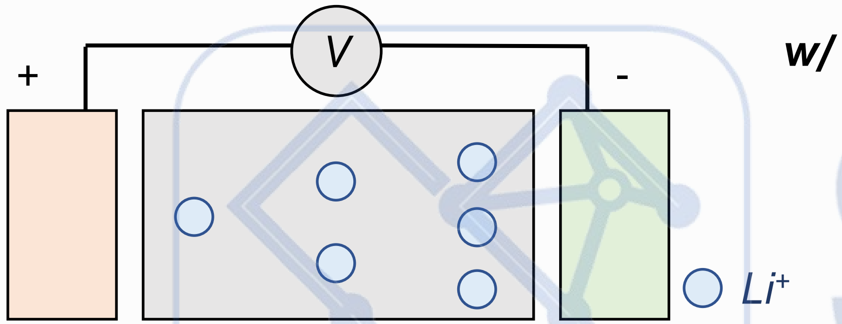
Expression of conductivity:

$$\sigma = n \cdot ze \cdot \mathrm{M} = cN_A \cdot ze \cdot \mathrm{M} = czFM$$

σ : Conductivity
c : Charge carrier concentration; N_A: Avogadro constant
ze : Electric charge, for Li⁺, $z = 1$
M: Mobility (usually denoted as μ, but not to be confused with chem. potential)

The concept of electrochemical potential and equilibrium condition of charged species (cont'd)

Thought experiment: what happens when a voltage is applied between to parallel electrodes?



w/ an applied voltage: concentration gradient forms

$$J_{drift} = \frac{j_{drift}}{zF} = \frac{\sigma E}{zF} = -\frac{\sigma}{zF}\frac{\partial\phi}{\partial x} = -\frac{c\, zF\, \mathrm{M}}{zF}\frac{\partial\phi}{\partial x}$$

$$J_{diff} = -D\frac{\partial c}{\partial x} = -D\frac{c}{RT}\frac{\partial\mu}{\partial x} \qquad (\mu = \mu^0 + RT\ln c)$$

We need to have a way to connect diffusivity D and mobility M

$$\boxed{D = \mathrm{M}\frac{RT}{zF}}$$

Nernst-Einstein equation

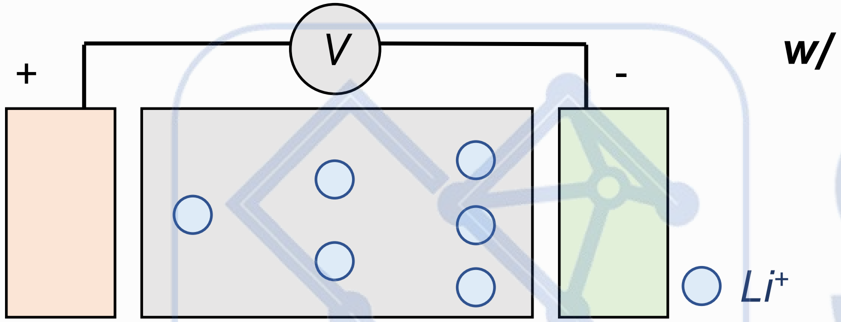
(We will discuss how to derive Nernst-Einstein equation in the next lecture.)

$$J_{tot} = J_{drift} + J_{diff} = -\frac{c\, zF\, \mathrm{M}}{zF}\frac{\partial\phi}{\partial x} - D\frac{c}{RT}\frac{\partial\mu}{\partial x}$$

$$J_{tot} = -\frac{c\, zF\, \mathrm{M}}{zF}\frac{\partial\phi}{\partial x} - \mathrm{M}\frac{\cancel{RT}}{zF}\frac{c}{\cancel{RT}}\frac{\partial\mu}{\partial x} = -\frac{c\mathrm{M}}{zF}\frac{\partial(\boldsymbol{\mu} + \boldsymbol{zF\phi})}{\partial x}$$

The concept of electrochemical potential and equilibrium condition of charged species (cont'd)

Thought experiment: what happens when a voltage is applied between to parallel electrodes?



w/ an applied voltage: concentration gradient forms

$$J_{tot} = -\frac{c\mathrm{M}}{zF}\frac{\partial(\boldsymbol{\mu}+\boldsymbol{zF\phi})}{\partial x} = -\frac{\sigma}{z^2F^2}\frac{\partial(\boldsymbol{\mu}+\boldsymbol{zF\phi})}{\partial x} = -\frac{\sigma}{z^2F^2}\frac{\partial(\tilde{\boldsymbol{\mu}})}{\partial x}$$

$$(\sigma = czFM)$$

$$\boxed{\tilde{\mu} = \mu + zF\phi}$$

Electrochemical potential

Unit: J/mol (or eV/mol)

Chemical potential

Unit: J/mol (or eV/mol)

Electrostatic potential

Unit: V

F: ~96500 C/mol

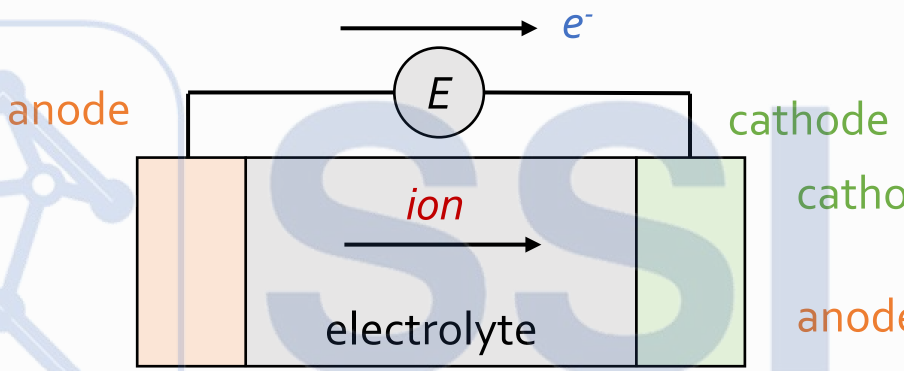
At equilibrium: $J_{tot} = 0 \rightarrow \frac{\partial(\tilde{\boldsymbol{\mu}})}{\partial x} = 0$

For charged species, the equilibrium condition is that *the gradient* of ***electrochemical potential*** $\tilde{\boldsymbol{\mu}}$ is 0

For charge neutral species (such as Li or O_2), $\tilde{\boldsymbol{\mu}}$ is reduced to $\boldsymbol{\mu}$

Applications to Electrochemical Energy Systems

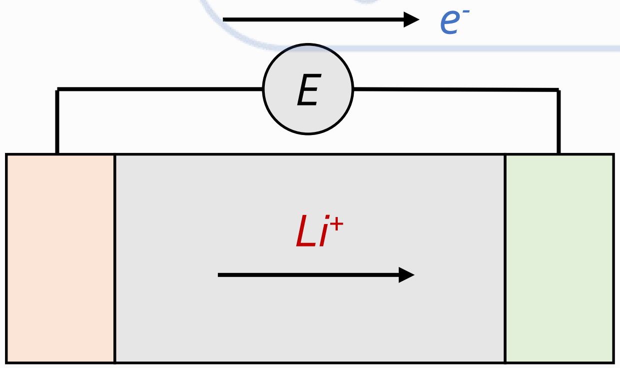
Electrochemical energy systems are based on **concerted motion (transport) of ions + electrons**



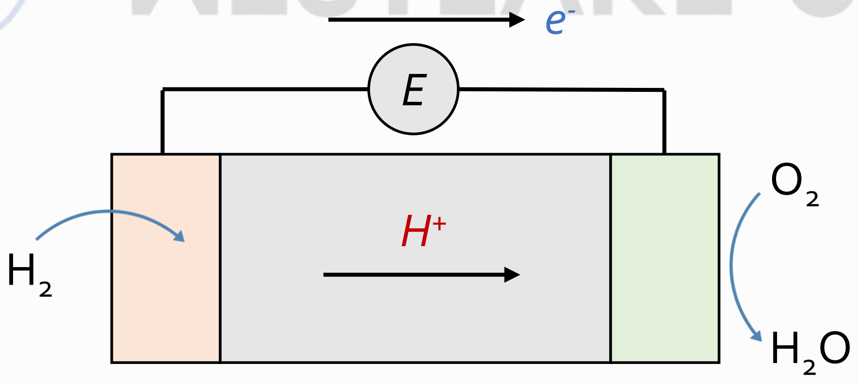
cathode: where ***conventional*** current leaves
reduction reaction

anode: where ***conventional*** current enters
oxidation reaction

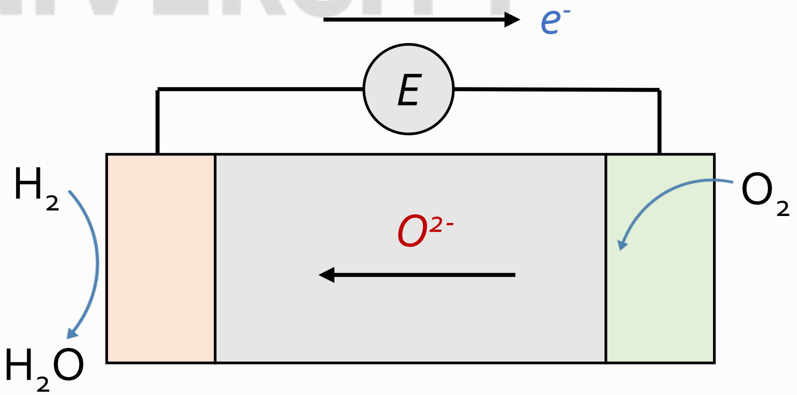
Lithium-ion battery



Proton-**E**xchange **M**embrane **F**uel **C**ell (**PEMFC**)

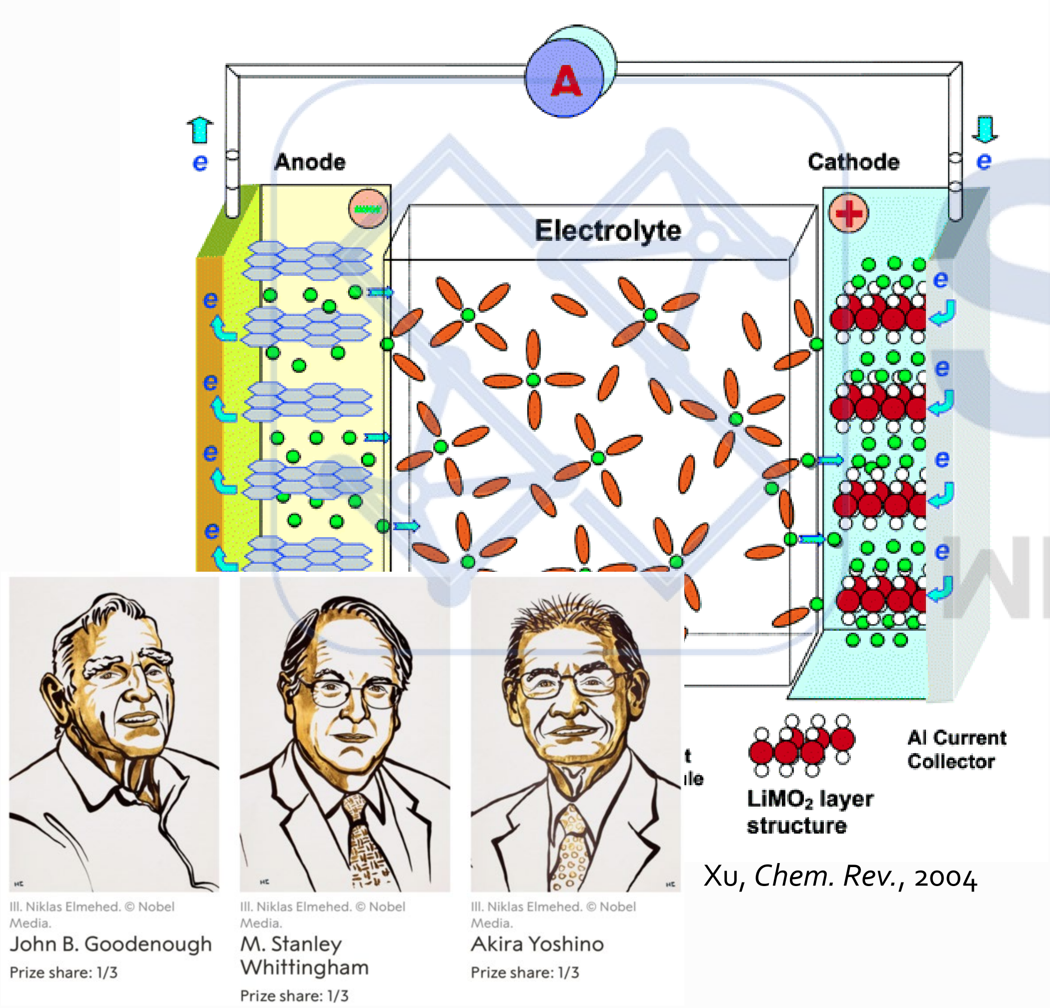


Solid **O**xide **F**uel **C**ell(**SOFC**)



A test on your knowledge

Lithium-**i**on **b**attery (***LIB***, 2019 Nobel Chemistry Prize)



Ill. Niklas Elmehed. © Nobel Media.
John B. Goodenough
Prize share: 1/3

Ill. Niklas Elmehed. © Nobel Media.
M. Stanley Whittingham
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Ill. Niklas Elmehed. © Nobel Media.
Akira Yoshino
Prize share: 1/3

Xu, *Chem. Rev.*, 2004

Left is the typical structure of a ***LIB*** with graphite anode and $LiCoO_2$ cathode. A voltage of 4 V was measured by using a multimeter between the anode and the cathode. This 4 V voltage represents:

A. Difference of electrochemical potential of Li^+ ions ($\tilde{\mu}_{Li^+}$) between the anode and the cathode

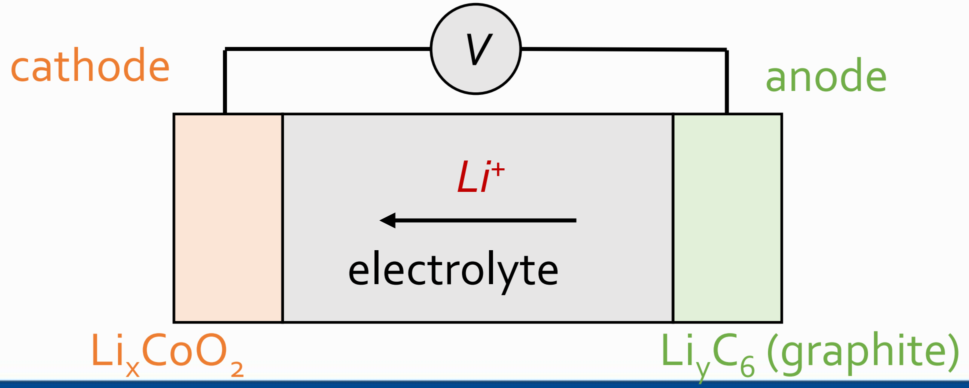
B. Difference of electrostatic potential (ϕ) between the anode and the cathode

C. Difference of chemical potential of Li (μ_{Li}) between the anode and the cathode

If you don't know the answer (or even do not understand the meaning of these terminologies), you should know better at the end of this lecture.

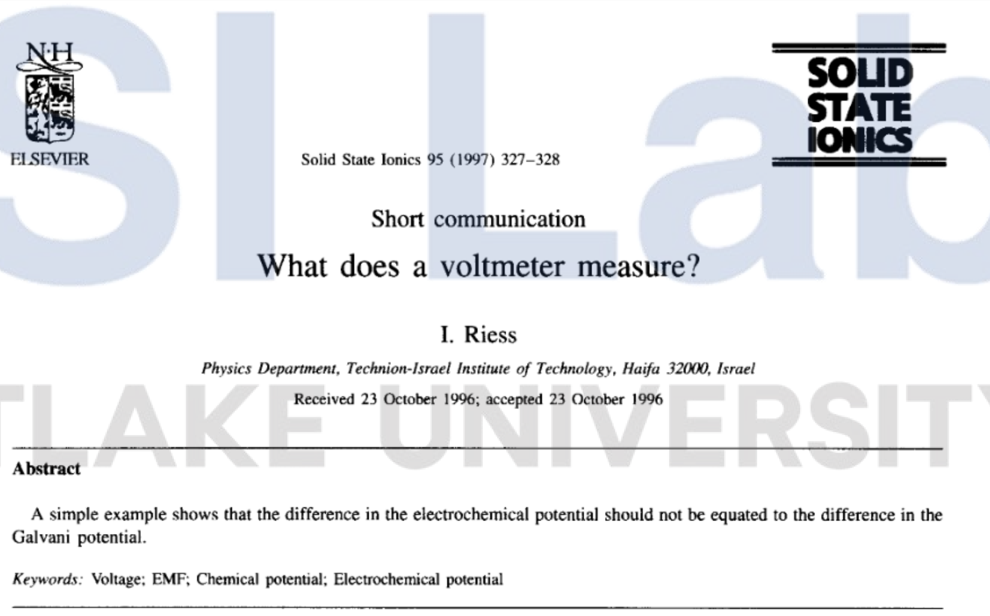
Question: what determines the open-circuit voltage of a battery?

Open-Circuit Voltage (**OCV**): voltage measured without any current loading



Question: What is the physical origin of measure OCV?

Related question: What does a voltameter measure?



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ELSEVIER
Solid State Ionics 95 (1997) 327–328
SOLID STATE IONICS

Short communication

What does a voltmeter measure?

I. Riess
Physics Department, Technion-Israel Institute of Technology, Haifa 32000, Israel

Received 23 October 1996; accepted 23 October 1996

Abstract

A simple example shows that the difference in the electrochemical potential should not be equated to the difference in the Galvani potential.

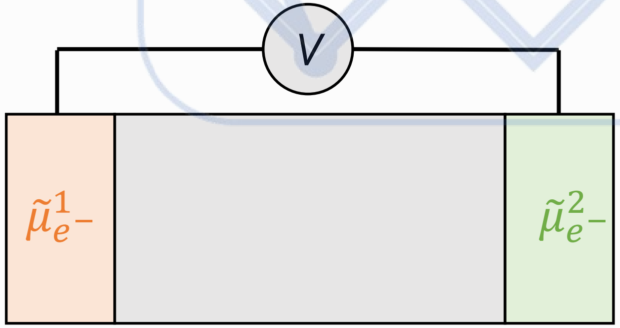
Keywords: Voltage; EMF; Chemical potential; Electrochemical potential

Short answers:

1. A voltameter measure the difference of ***electrochemical potential of electrons*** $(\tilde{\mu}_{e^-})$;
2. OCV = $(\tilde{\mu}_{e^-}(anode) - \tilde{\mu}_{e^-}(cathode))/F$

Why?

What does a voltameter measure?



A voltameter measure the difference of $-\tilde{\mu}_{e^-}/F$! (NOT ϕ!)

For electrons:

$$\boxed{\tilde{\mu}_{e^-} = \mu_{e^-} + z_{e^-}F\phi = \mu_{e^-} - F\phi}$$

$$(z_{e^-} = -1)$$

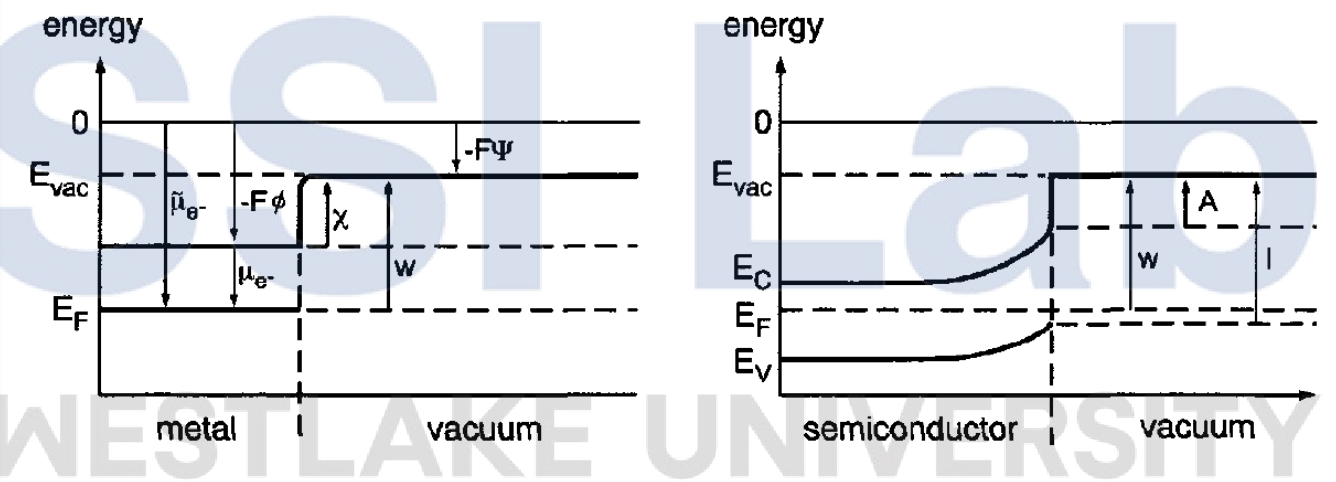
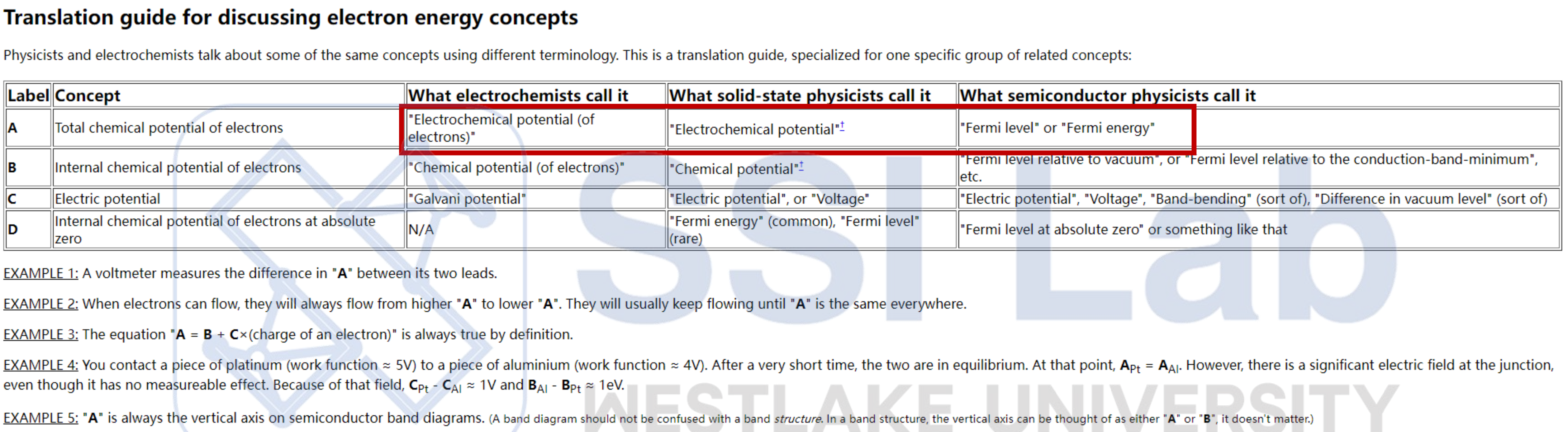


Fig. 7.3: The relationship between the parameters work function (w), Galvani potential (ϕ), Volta potential (ψ) and surface potential (χ) and work function, electron affinity (A) and ionization energy (I) for metal (left) and semiconductor (right). E_{vac} is the energy of the electron in vacuum immediately in front of the

Maier, **Physical Chemistry of Ionic Materials**

Aka., $\tilde{\mu}_{e^-}$ is the same concept as the "Fermi level" or "Fermi Energy" (potentially with different units)

A translation guide for discussing electron energy concepts



Translation guide for discussing electron energy concepts

Physicists and electrochemists talk about some of the same concepts using different terminology. This is a translation guide, specialized for one specific group of related concepts:

Label	Concept	What electrochemists call it	What solid-state physicists call it	What semiconductor physicists call it
A	Total chemical potential of electrons	"Electrochemical potential (of electrons)"	"Electrochemical potential"[‡]	"Fermi level" or "Fermi energy"
B	Internal chemical potential of electrons	"Chemical potential (of electrons)"	"Chemical potential"[‡]	"Fermi level relative to vacuum", or "Fermi level relative to the conduction-band-minimum", etc.
C	Electric potential	"Galvani potential"	"Electric potential", or "Voltage"	"Electric potential", "Voltage", "Band-bending" (sort of), "Difference in vacuum level" (sort of)
D	Internal chemical potential of electrons at absolute zero	N/A	"Fermi energy" (common), "Fermi level" (rare)	"Fermi level at absolute zero" or something like that

EXAMPLE 1: A voltmeter measures the difference in "**A**" between its two leads.

EXAMPLE 2: When electrons can flow, they will always flow from higher "**A**" to lower "**A**". They will usually keep flowing until "**A**" is the same everywhere.

EXAMPLE 3: The equation "**A** = **B** + **C**×(charge of an electron)" is always true by definition.

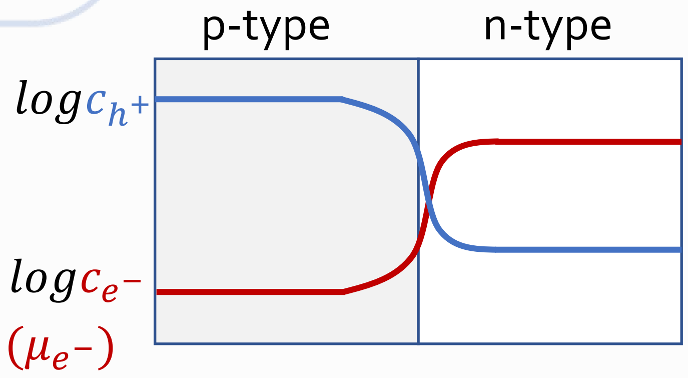
EXAMPLE 4: You contact a piece of platinum (work function ≈ 5V) to a piece of aluminium (work function ≈ 4V). After a very short time, the two are in equilibrium. At that point, $\mathbf{A}_{Pt} = \mathbf{A}_{Al}$. However, there is a significant electric field at the junction, even though it has no measureable effect. Because of that field, $\mathbf{C}_{Pt} - \mathbf{C}_{Al} \approx 1V$ and $\mathbf{B}_{Al} - \mathbf{B}_{Pt} \approx 1eV$.

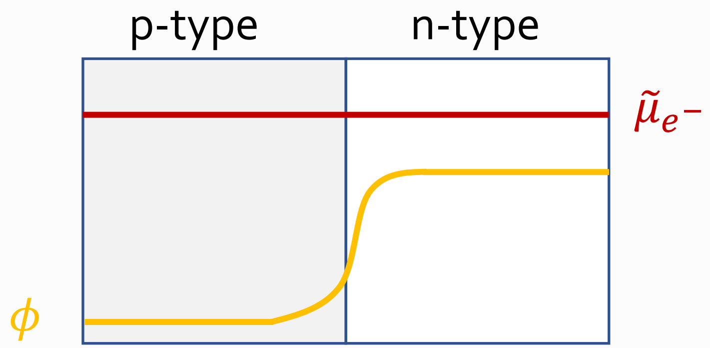
EXAMPLE 5: "**A**" is always the vertical axis on semiconductor band diagrams. (A band diagram should not be confused with a band *structure*. In a band structure, the vertical axis can be thought of as either "**A**" or "**B**", it doesn't matter.)

Ref: http://sjbyrnes.com/fermiterminology.html

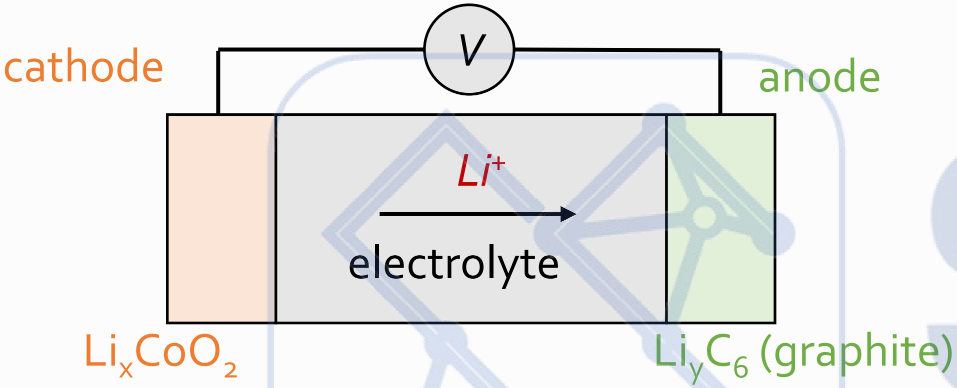
$$\boxed{\tilde{\mu}_{e^-} = \mu_{e^-} - F\phi}$$

$$\boxed{\tilde{\mu}_{e^-} = -\tilde{\mu}_{h^+}}$$





Question: how to understand the open circuit voltage (OCV)?

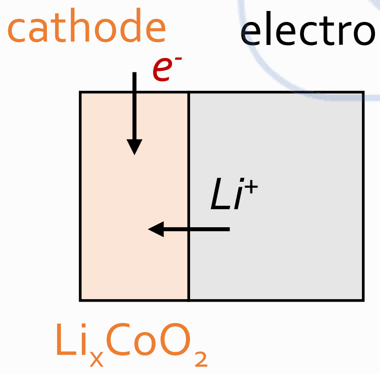


We already know:

1. A voltameter measure the difference of ***electrochemical potential of electrons*** ($\tilde{\mu}_{e^-}$) ;
2. OCV = $(\tilde{\mu}_{e^-}(anode) - \tilde{\mu}_{e^-}(cathode))/\mathrm{F}$

Following question:

What parameters are $\tilde{\mu}_{e^-}(anode)$ and $\tilde{\mu}_{e^-}(cathode)$ *related to?*

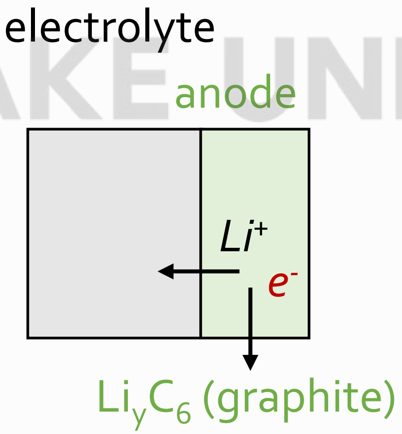


$Li^+ + e^- \rightarrow$ Li (in Li_xCoO_2)

$$\tilde{\mu}_{e^-}(c) + \tilde{\mu}_{Li^+}(lyte) = \mu_{Li}(c)$$

Overall: ("rocking-chair")

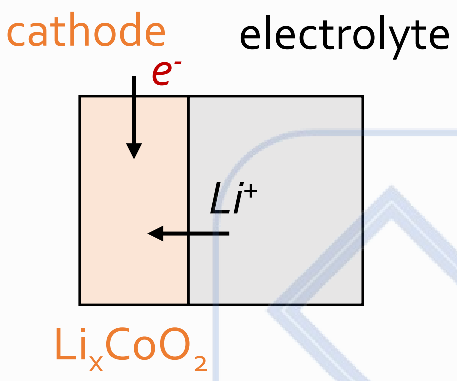
Li (in C_6) $\rightarrow$ Li (in Li_yCoO_2)



Li (in Li_yC_6) $\rightarrow Li^+ + e^-$

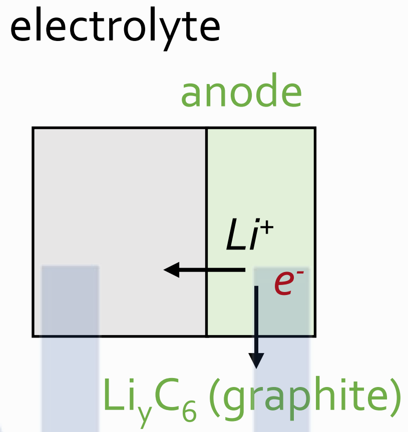
$$\mu_{Li}(a) = \tilde{\mu}_{e^-}(a) + \tilde{\mu}_{Li^+}(lyte)$$

Question: how to understand the open circuit voltage (OCV)?



$Li^+ + e^- \rightarrow Li$ (in Li_xCoO_2)

$$\tilde{\mu}_{e^-}(c) + \tilde{\mu}_{Li^+}(lyte) = \mu_{Li}(c)$$



Li (in Li_yC_6) $\rightarrow Li^+ + e^-$

$$\mu_{Li}(a) = \tilde{\mu}_{e^-}(a) + \tilde{\mu}_{Li^+}(lyte)$$

Overall: ("rocking-chair")

Li (in Li_xC_6) → Li (in Li_yCoO_2)

Since the electrolyte can conduct Li^+ (but not e^-), at equilibrium ***electrochemical potential of Li⁺*** $\tilde{\mu}_{Li^+}(lyte)$ is ***uniform*** in the electrolyte, *i.e.*, $\frac{\partial \tilde{\mu}_{Li^+}(lyte)}{\partial x} = 0$

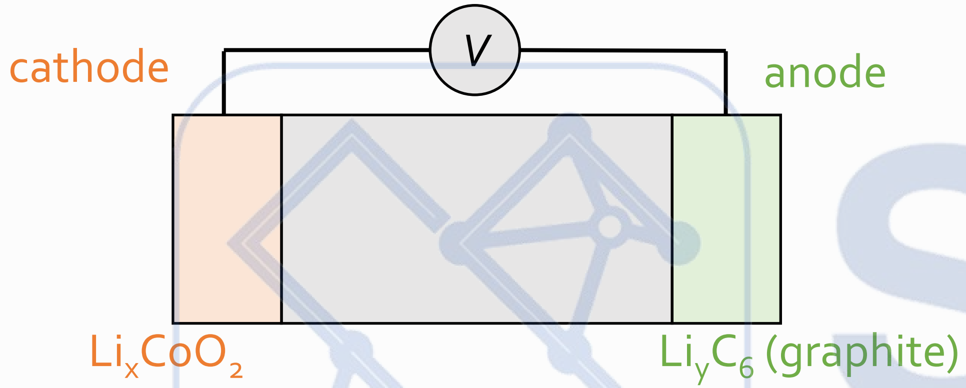
Then, we have:

$$\left.\begin{aligned} \mu_{Li}(a) &= \tilde{\mu}_{e^-}(a) + \cancel{\tilde{\mu}_{Li^+}(lyte)} \\ \tilde{\mu}_{e^-}(c) + \cancel{\tilde{\mu}_{Li^+}(lyte)} &= \mu_{Li}(c) \end{aligned}\right\}$$

$$\boxed{\begin{aligned} OCV &= -\frac{1}{F}\left(\tilde{\mu}_{e^-}(c) - \tilde{\mu}_{e^-}(a)\right) \\ &= -\frac{1}{F}\left(\mu_{Li}(c) - \mu_{Li}(a)\right) \end{aligned}}$$

Question: how to understand the open circuit voltage (OCV)?

Let's go back to the full cell:



Overall reaction: ("rocking-chair battery")

$\boxed{\text{Li (in } Li_xC_6) \rightarrow \text{Li (in } Li_yCoO_2)}$

Gibbs free energy (per mole) of the reaction:

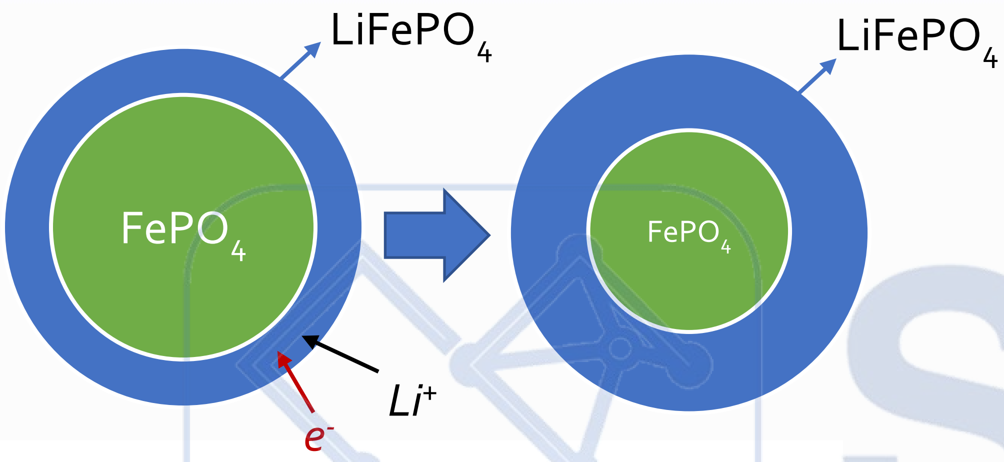
$$\Delta G_{rxn}(x,y) = \mu_{Li}(c, Li_xCoO_2) - \mu_{Li}(a, Li_yC_6)$$

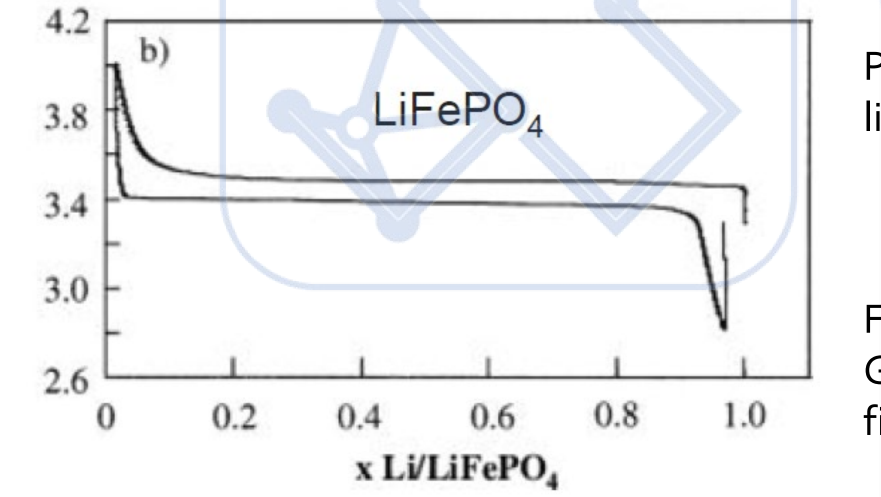
$$\boxed{OCV = -\frac{1}{F}\big(\mu_{Li}(c) - \mu_{Li}(a)\big) = -\frac{1}{F}\Delta G_{rxn}(x,y)}$$

"Gibbs free energy is the *maximum reversible work* that may be performed by a thermodynamic system at a ***constant temperature*** **(*T*)** ***and pressure*** **(*P*)"**

$\Delta G_{rxn}(x,y)$ has to be ***negative*** to make the OCV ***positive***;
In other words, the overall reaction must be ***spontaneous*** to be used in an electrochemical cell for energy extraction.

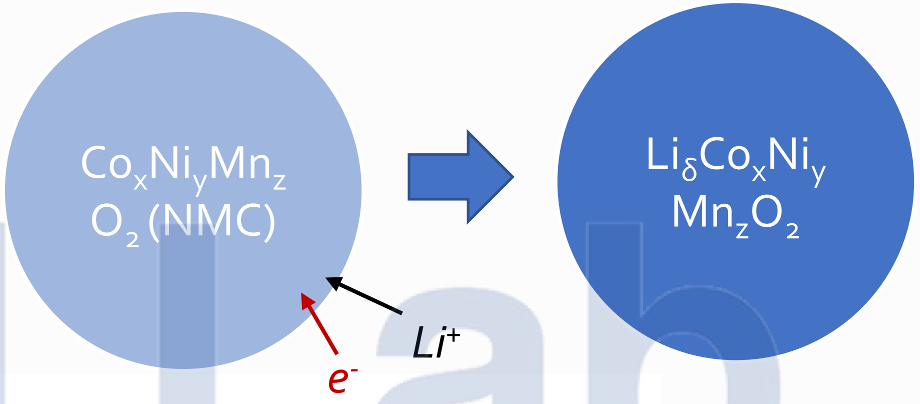
What factors influence the chemical potential of Li in electrodes?

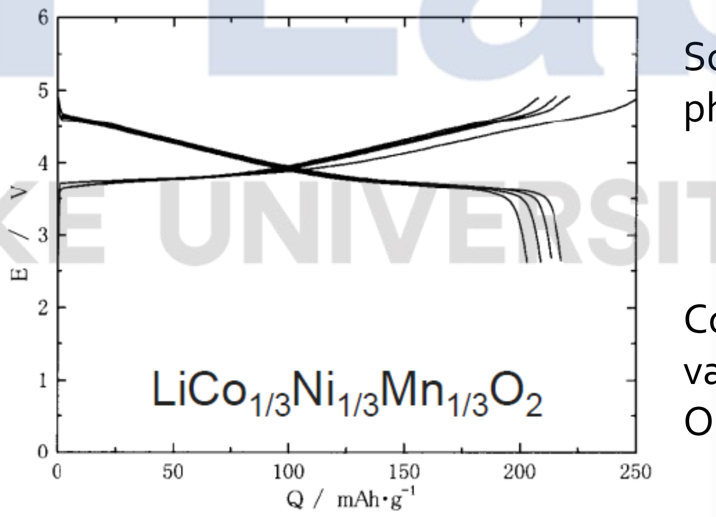




Phase transition induced by lithiation

Fixed μ_{Li} (governed by Gibbs phase rule) resulted in fixed OCV





Solid solution (no phase transition)

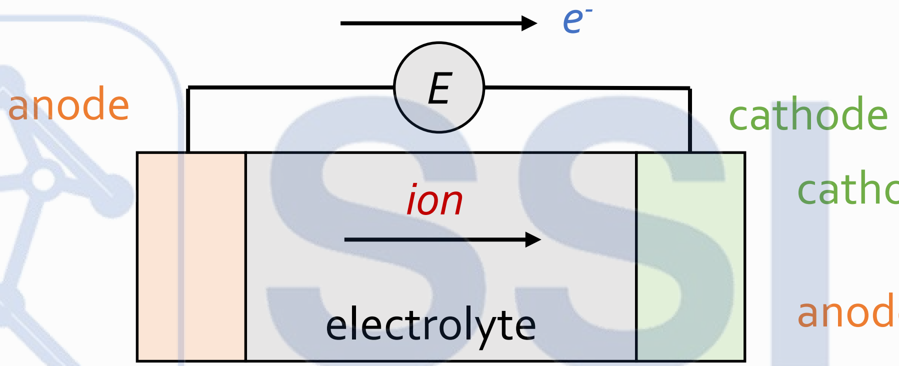
Continuously varying μ_{Li} and OCV

Huang, Nazar *et al.*, *Electrochem. and Solid-state Lett.*, 2001

Yabuuchi *et al.*, *Journal of Power Sources*, 2013

We are going to discuss this with more details in the future lectures on electrochemistry.

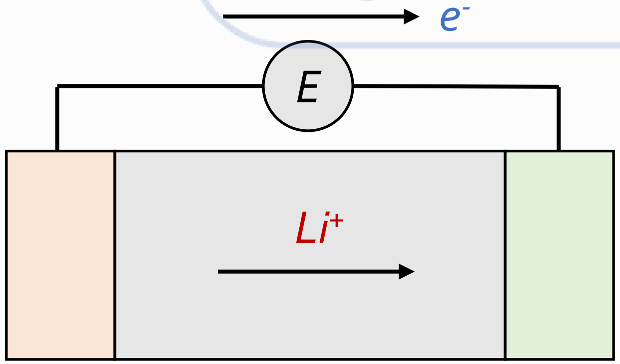
Electrochemical energy systems are based on **concerted motion (transport) of ions + electrons**



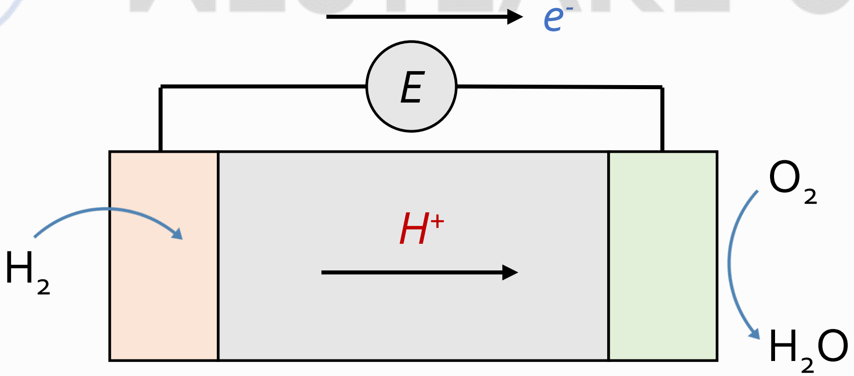
cathode: where ***conventional*** current leaves
reduction reaction

anode: where ***conventional*** current enters
oxidation reaction

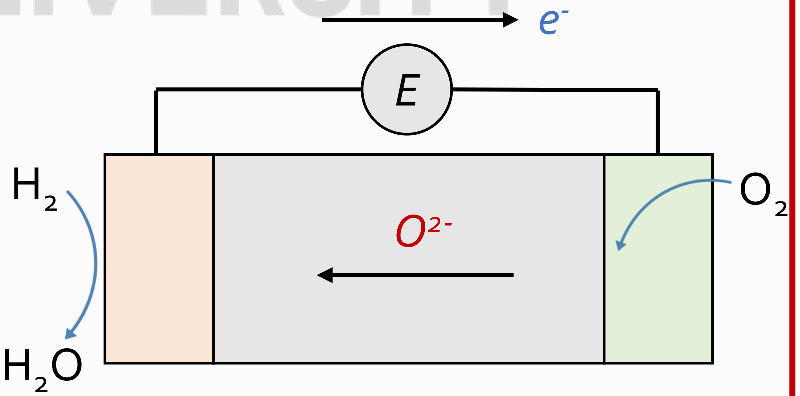
Lithium-ion battery



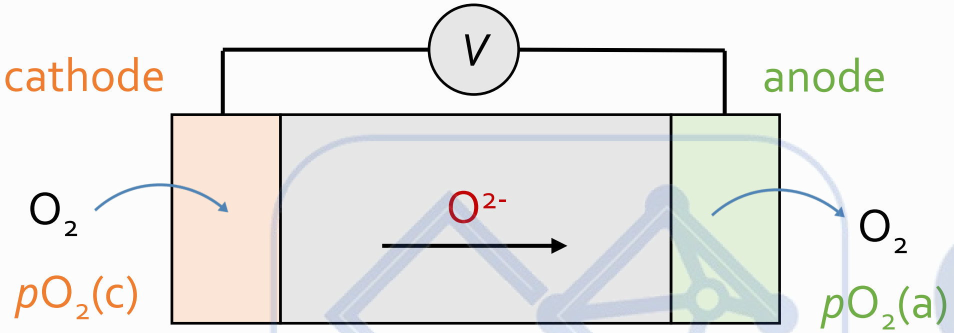
Proton-**E**xchange **M**embrane **F**uel **C**ell (**PEMFC**)



Solid **O**xide **F**uel **C**ell(**SOFC**)

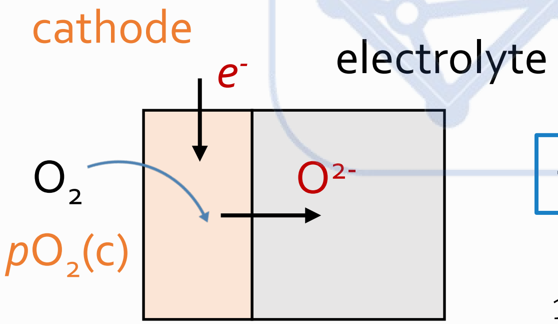


The OCV of solid oxide fuel cells: continuous supply of reactants



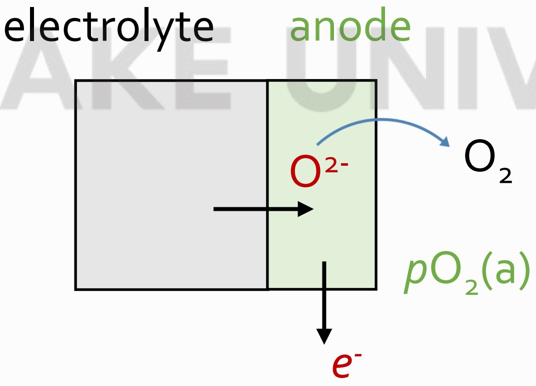
Different from a battery, in a fuel cell, the reactants at cathode and anode are ***continuously supplied*** ("an opened battery").
Let's first consider something very simple (so-called ***concentration cell***)

Total reaction: ½ O_2 (pO_2(c), cathode) → ½ O_2 (pO_2(a), anode)



$1/2O_2 + 2e^- \rightarrow O^{2-}$(electrolyte)

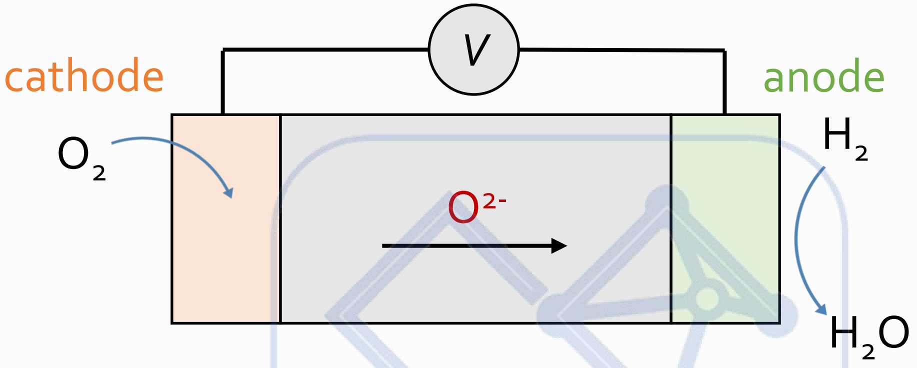
$$\tfrac{1}{2}\mu_{O_2}(c) + 2\tilde{\mu}_{e^-}(c) = \tilde{\mu}_{O^{2-}}(lyte)$$



O^{2-}(electrolyte) → $1/2O_2 + 2e^-$

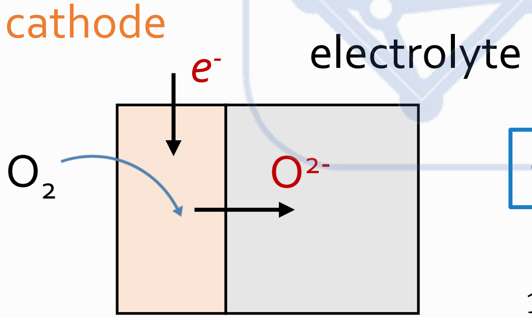
$$\tilde{\mu}_{O^{2-}}(lyte) = \tfrac{1}{2}\mu_{O_2}(a) + 2\tilde{\mu}_{e^-}(a)$$

The OCV of solid oxide fuel cells: continuous supply of reactants



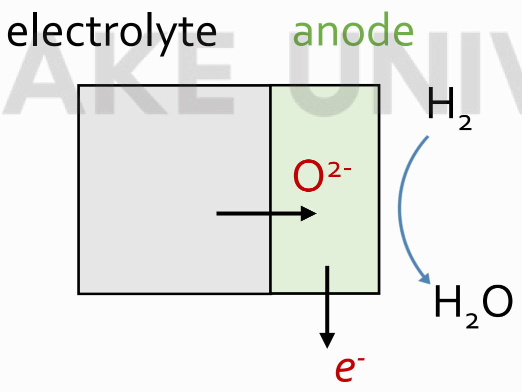
Different from a battery, in a fuel cell, the reactants at cathode and anode are ***continuously supplied*** (“an opened battery”).

Total reaction: $H_2 + ½ O_2 \rightarrow H_2O$



$\boxed{1/2O_2 + 2e^- \rightarrow O^{2-}(electrolyte)}$

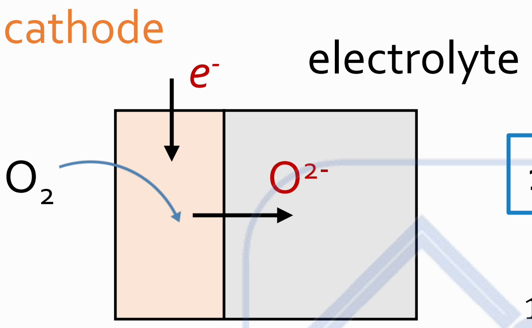
$$\frac{1}{2}\mu_{O_2}(c) + 2\tilde{\mu}_{e^-}(c) = \tilde{\mu}_{O^{2-}}(lyte)$$



$\boxed{H_2 + O^{2-}(electrolyte) \rightarrow 2e^- + H_2O}$

$$\tilde{\mu}_{O^{2-}}(lyte) + \mu_{H_2}(a) = 2\tilde{\mu}_{e^-}(a) + \mu_{H_2O}(a)$$

The OCV of solid oxide fuel cells: continuous supply of reactants



cathode

electrolyte

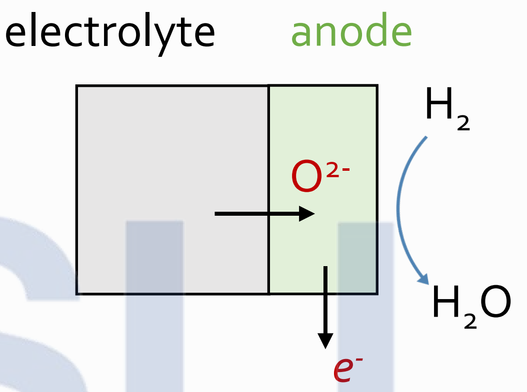
e^-

O_2

O^{2-}

$1/2O_2 + 2e^- \rightarrow O^{2-}$(electrolyte)

$$\frac{1}{2}\mu_{O_2}(c) + 2\tilde{\mu}_{e^-}(c) = \tilde{\mu}_{O^{2-}}(lyte)$$



electrolyte

anode

H_2

O^{2-}

H_2O

e^-

$H_2 + O^{2-}$(electrolyte) $\rightarrow 2e^- + H_2O$

$$\tilde{\mu}_{O^{2-}}(lyte) + \mu_{H_2}(a) = 2\tilde{\mu}_{e^-}(a) + \mu_{H_2O}(a)$$

Overall rxn: $H_2(a) + ½O_2(c) \rightarrow H_2O(a)$

$$\mu_{rxn} = \mu_{H_2O}(a) - \mu_{H_2}(a) - \frac{1}{2}\mu_{O_2}(c)$$

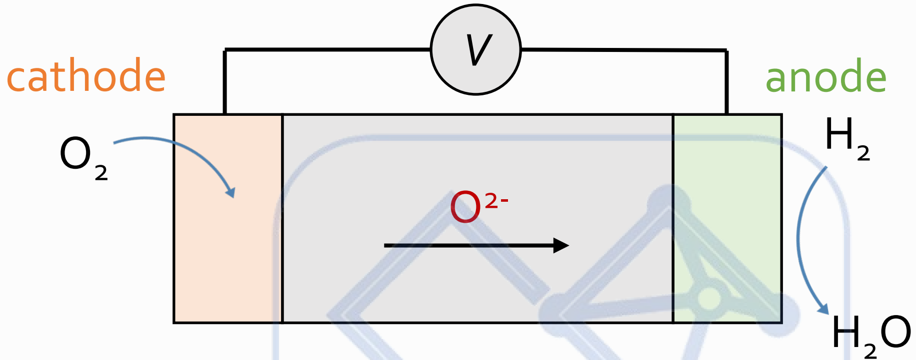
$$\left.\begin{aligned}&\frac{1}{2}\mu_{O_2}(c) + 2\tilde{\mu}_{e^-}(c) = \tilde{\mu}_{O^{2-}}(lyte)\\ &\tilde{\mu}_{O^{2-}}(lyte) + \mu_{H_2}(a) = 2\tilde{\mu}_{e^-}(a) + \mu_{H_2O}(a)\end{aligned}\right\}\quad \boxed{\begin{aligned}OCV &= -1/F\left(\tilde{\mu}_{e^-}(c) - \tilde{\mu}_{e^-}(a)\right)\\ &= -1/2F\left(\mu_{H_2O}(a) - \mu_{H_2}(a) - \frac{1}{2}\mu_{O_2}(c)\right)\\ &= -1/2F\ \mu_{rxn}\end{aligned}}$$

We have: $\mu_{H_2O}(a) = \mu^0_{H_2O} + RT\ln p_{H_2O}$

"Standard condition"

$$\Rightarrow\quad \boxed{OCV = -1/2F\left(\mu^0_{rxn} + RT\ln\frac{p_{H_2O}}{p_{H_2}p_{O_2}^{\frac{1}{2}}}\right) = E^0 + \frac{RT}{2F}\ln\frac{p_{H_2}p_{O_2}^{\frac{1}{2}}}{p_{H_2O}}}$$

The OCV of solid oxide fuel cells: continuous supply of reactants



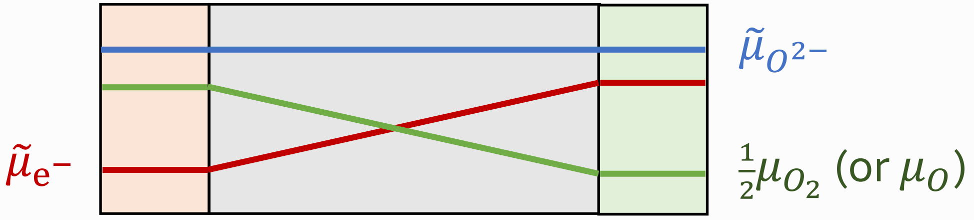
Overall rxn:

$$\boxed{H_2\,(a) + \tfrac{1}{2}\,O_2\,(c) \rightarrow H_2O(a)}$$

$$\mu_{rxn} = \mu_{rxn}^0 + RT\ln\frac{p_{H_2O}}{p_{H_2}p_{O_2}^{\frac{1}{2}}}$$

$$\boxed{OCV = -1/2\mathrm{F}\left(\mu_{rxn}^0 + RT\ln\frac{p_{H_2O}}{p_{H_2}p_{O_2}^{\frac{1}{2}}}\right) = E^0 + \frac{RT}{2F}\ln\frac{p_{H_2}p_{O_2}^{\frac{1}{2}}}{p_{H_2O}}}$$

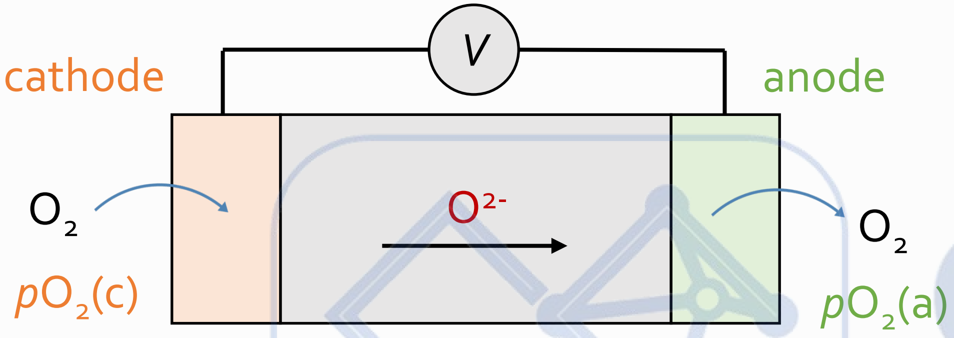
What about chemical & electrochemical potential distribution?



Local equilibrium: $1/2O_2 + 2e^- \rightarrow O^{2-}$

$$\frac{1}{2}\mu_{O_2} + 2\tilde{\mu}_{e^-} = \tilde{\mu}_{O^{2-}}$$

The OCV of solid oxide fuel cells: continuous supply of reactants



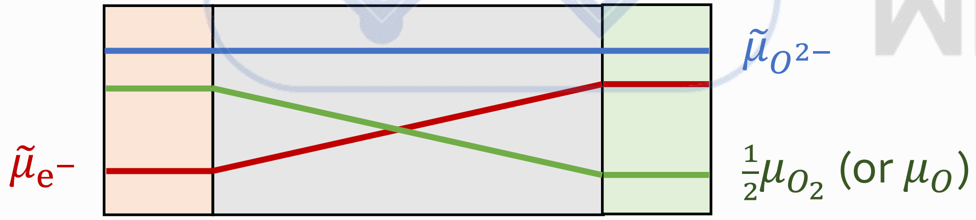
Overall rxn: $\boxed{O_2\,(pO_2(c),\ \text{cathode}) \rightarrow O_2\,(pO_2(a),\ \text{anode})}$

$$\boxed{OCV = E^0 + \frac{RT}{4F} ln \frac{p_{O_2}(a)}{p_{O_2}(c)}}$$

What is this useful for?
If we fix $p_{O_2}(a)$, we can determine $p_{O_2}(c)$ by measuring OCV. → *Oxygen sensor*

Lambda sensor

Local equilibrium: $1/2O_2 + 2e^- \rightarrow O^{2-}$



$$\frac{1}{2}\mu_{O_2} + 2\tilde{\mu}_{e^-} = \tilde{\mu}_{O^{2-}}$$

$\boxed{H_2\,(a) + ½\,O_2\,(a) \leftrightarrow H_2O(a)}$

If we change anode to H_2/H_2O, the same set of equations still apply by recognizing the chemical equilibrium between H_2, O_2 and H_2O

$$K(T) = \frac{p_{H_2O}(a)}{p_{H_2}(a)p_{O_2}(a)^{\frac{1}{2}}}$$

Things we have discussed in this lecture

Macroscopic picture of ion transport:

- What are the governing equation of diffusion and drift of ionic/electronic defects?
- How to solve the case of ion transport when both diffusion and drift occur simultaneously?

Electrochemical potential:

- What is the difference and relationship between chemical potential, electrostatic potential and electrochemical potential?
- How to express the open-circuit-potential of an electrochemical system by using electrochemical potential of electrons?

Goal of this lecture: you should be able to answer the questions above now (hopefully) :)

End of Lecture 3
Solid State Ionics Fall 2022

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