Lecture 5:

Types of Diffusion Coefficients Chemical Diffusivity

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Solid State Ionics

SSI Lab WESTLAKE UNIVERSITY

Things we will discuss in this lecture

Type of diffusivities:

- What are the different types of diffusivities?
- What physical mechanism and concept does each diffusivity describe?

Chemical diffusivity:

- What physical process does the chemical diffusion describe?
- What are the key factors that govern the chemical diffusivity?

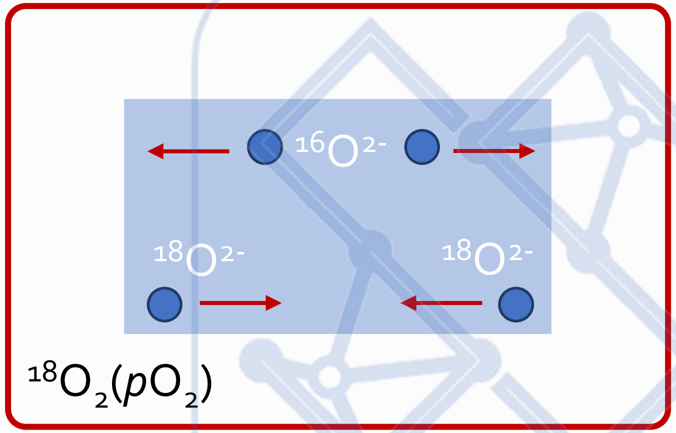
Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

A test on your intuition: *Is the diffusion coefficient dependent on the concentration of ionic defects?*

Types of diffusivities (or diffusion coefficients)

We can measure *phenomenological* diffusivity by using the three different experiments:

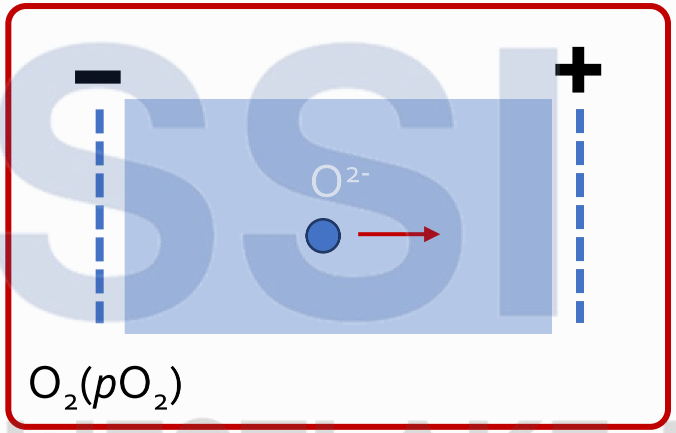
Tracer experiment



Tracer diffusivity

$\boxed{D^{*}_{O^{2-}}}$

Stationary conductivity experiment

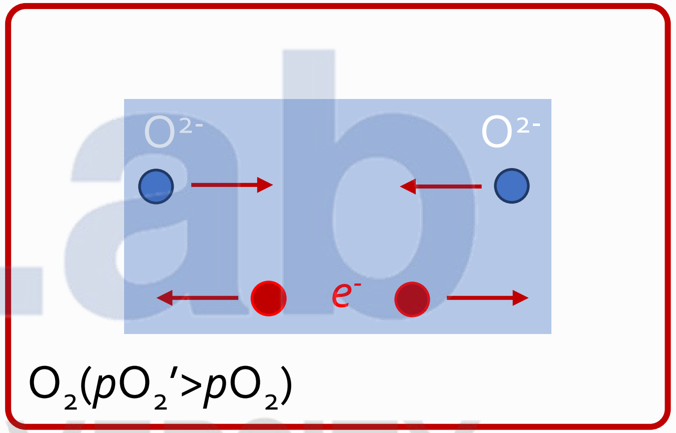


Self-diffusivity

$\boxed{D^{q}_{O^{2-}}}$

No compositional (stoichiometric) change

Chemical diffusion experiment



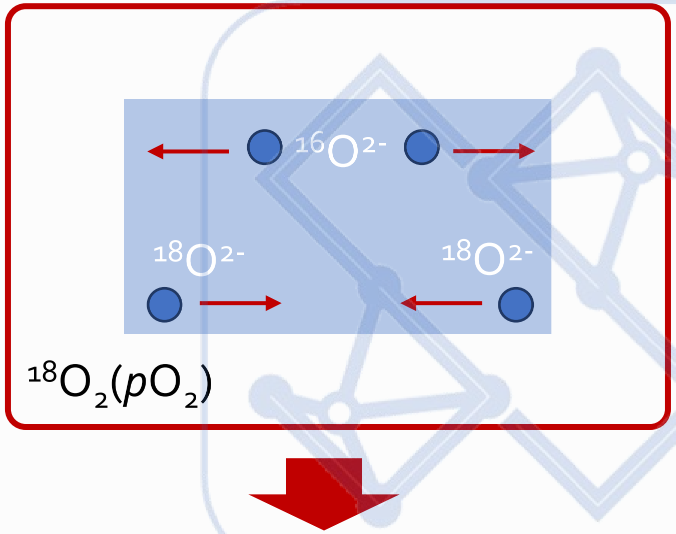
Chemical diffusivity

$\boxed{D^{\delta}_{O}}$

Composition (stoichiometry δ) changes

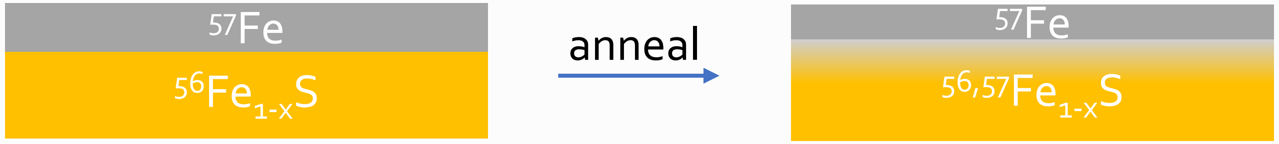
Tracer diffusivity: isotope exchange profile

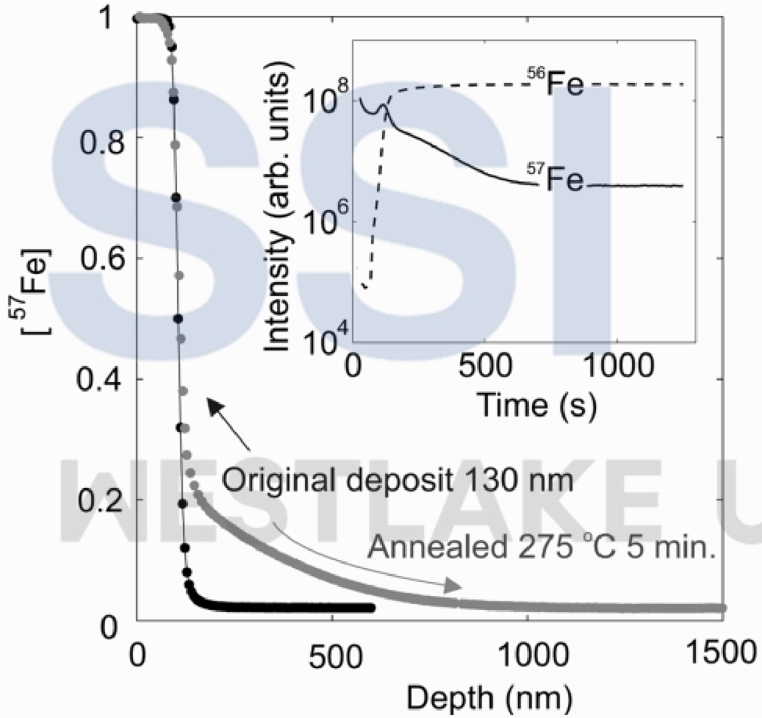
Tracer experiment

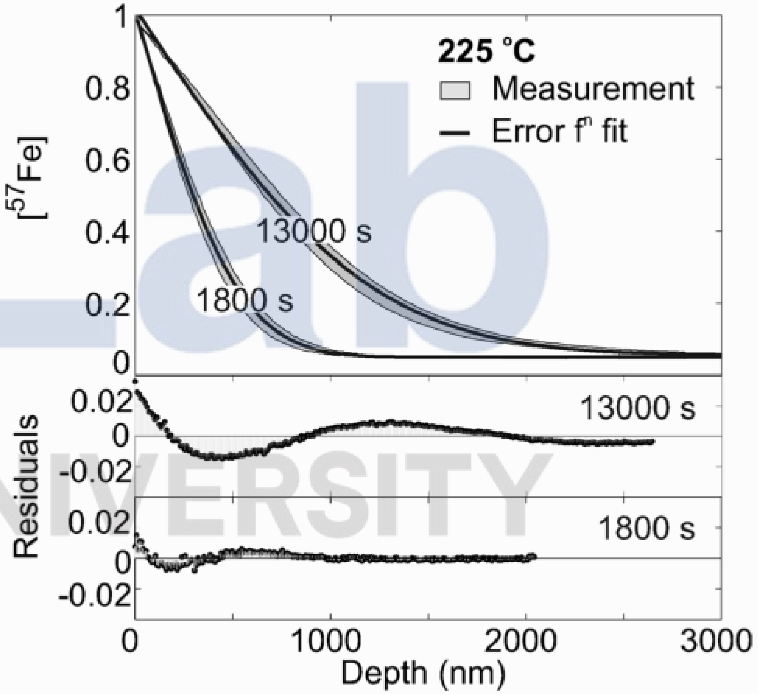


Tracer diffusivity

$\boxed{D^*_{O^{2-}}}$





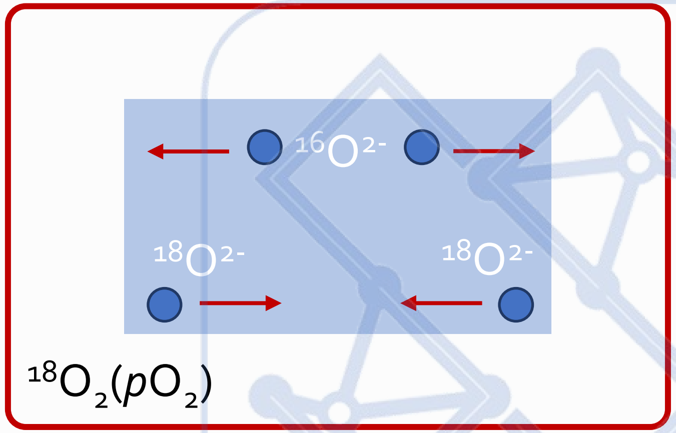


- ^{57}Fe isotope profile measured by using secondary-ion mass spectrometry (SIMS)
- Concentration profile modeled by solving semi-infinite diffusion equation

$$\boxed{c(x,t) = c_0\left(1 - \mathrm{erf}\left(\frac{x}{4D^*t}\right)\right)}$$

Tracer diffusivity: isotope exchange profile

Tracer experiment

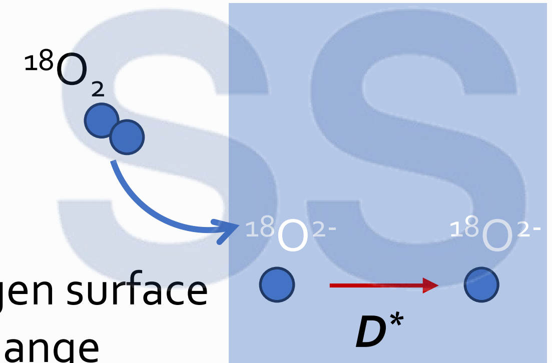


Tracer diffusivity

$$\boxed{D^*_{O^{2-}}}$$

Fick's 2nd Law:

$$\boxed{\frac{\partial c(x,t)}{\partial t} = D^* \frac{\partial^2 c(x,t)}{\partial x^2}}$$



oxygen surface exchange

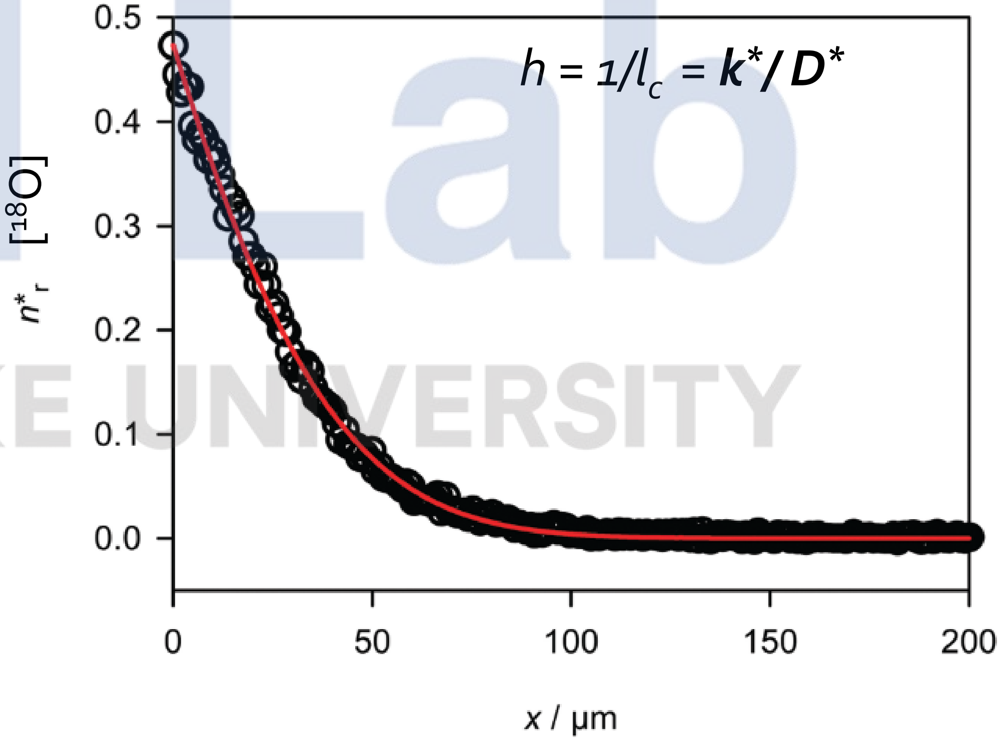
rate constant $\boldsymbol{k^*}$

$\boldsymbol{k^*}$: unit cm/s

$\boldsymbol{D^*}$: unit cm²/s

$$\boxed{\text{Critical length } l_c = \boldsymbol{D^*/k^*}}$$

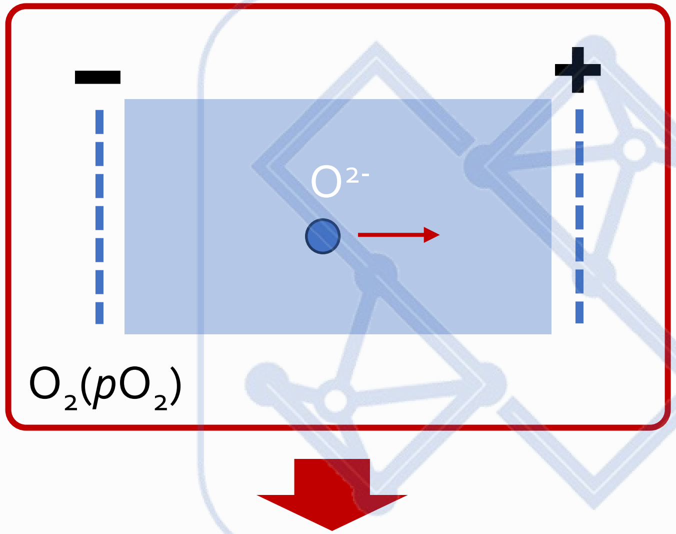
$$\frac{n^*(x) - n_{bg}^*}{n_g^* - n_{bg}^*} = \operatorname{erfc}\left(\frac{x}{2\sqrt{D^* t_{ex}}}\right) - \exp\left(hx + h^2 D^* t_{ex}\right) \times \operatorname{erfc}\left(\frac{x}{2\sqrt{D^* t_{ex}}} + h\sqrt{D^* t_{ex}}\right)$$



Metlenko, de Souza *et al.*, ***PCCP***, 2016

Self-diffusivity: steady-state conductivity measurement

Stationary conductivity experiment



Self-diffusivity

$\boxed{D^q_{O^{2-}}}$

Consider **Nernst-Einstein** relation $\boxed{\frac{D}{M} = \frac{RT}{zF}}$

$$\sigma = c\,zF\,M = c\,zF\,D\,\frac{zF}{RT} = c\,\frac{z^2F^2}{RT}D$$

Therefore, we can get diffusivity by measuring ionic conductivity.

We have: $\boxed{D = \frac{RT}{z^2F^2}\frac{\sigma}{c}}$

Confusing question: *which concentration should we plug in here?*

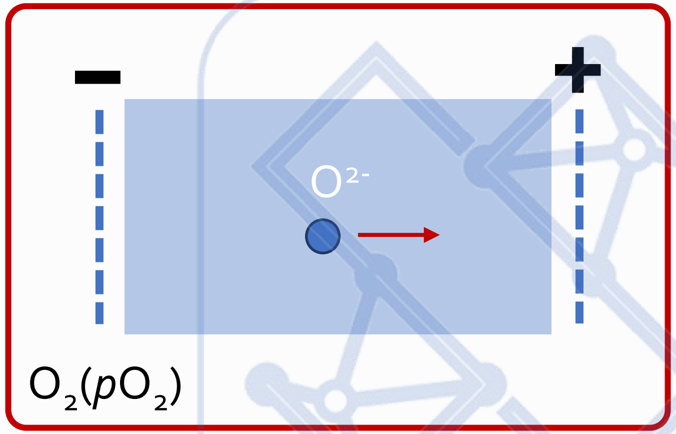
$$\boxed{D^q_{O^{2-}} = \frac{RT}{4F^2}\frac{\sigma_{O^{2-}}}{c_{O^{2-}}}}$$

q: charge transport

Oxide ion (O^{2-}) concentration
(**NOT** defect concentration)

Self-diffusivity: steady-state conductivity measurement

Stationary conductivity experiment



Self-diffusivity

$$\boxed{D^q_{O^{2-}}}$$

$$\boxed{D^q_{O^{2-}} = \frac{RT}{4F^2}\frac{\sigma_{O^{2-}}}{c_{O^{2-}}}}$$

q: charge transport

Oxide ion (O^{2-}) concentration (**NOT** defect concentration)

In reality, the O^{2-} conductivity is contributed by defects (either oxygen vacancies $V_O^{\cdot\cdot}$ or oxygen interstitials O_i'').

If we assume that oxygen interstitials O_i'' are the major oxygen ionic defects,

we have: $\boxed{\sigma_{O^{2-}} = \sigma_{O_i''} = 2Fc_{O_i''}M_{O_i''}}$

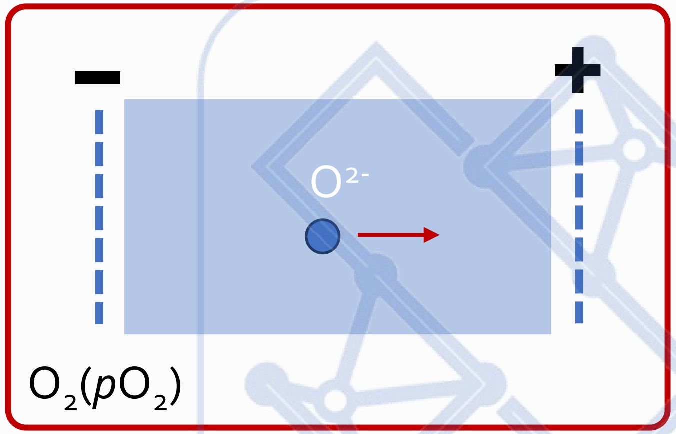
$$D^q_{O^{2-}} = \frac{RT}{4F^2}\frac{\sigma_{O^{2-}}}{c_{O^{2-}}} = \frac{RT}{4F^2}\frac{\sigma_{O_i''}}{c_{O_i''}}\frac{c_{O_i''}}{c_{O^{2-}}} = D_{O_i''}\frac{c_{O_i''}}{c_{O^{2-}}}$$

$$\boxed{D^q_{O^{2-}} = D_{O_i''}\frac{c_{O_i''}}{c_{O^{2-}}} = x_{O_i''}D_{O_i''}}$$

Fraction of oxygen interstitials O_i''

Self-diffusivity: steady-state conductivity measurement

Stationary conductivity experiment



Self-diffusivity

$\boxed{D^q_{O^{2-}}}$

$$\boxed{D^q_{O^{2-}} = D_{O_i''}\frac{c_{O_i''}}{c_{O^{2-}}} = x_{O_i''} D_{O_i''}}$$

Fraction of oxygen interstitials O_i''

Since $x_{O_i''} = c_{O_i''}/c_{O^{2-}}$ is far less than 1 → $\boxed{D_{O_i''} \gg D^q_{O^{2-}}}$

The self-diffusivity of defect species is *much higher* than that of ionic species.

Contain information on both ion migration and defect formation ← $\boxed{D^q_{O^{2-}} = x_{O_i''} D_{O_i''}}$

Related to defect formation

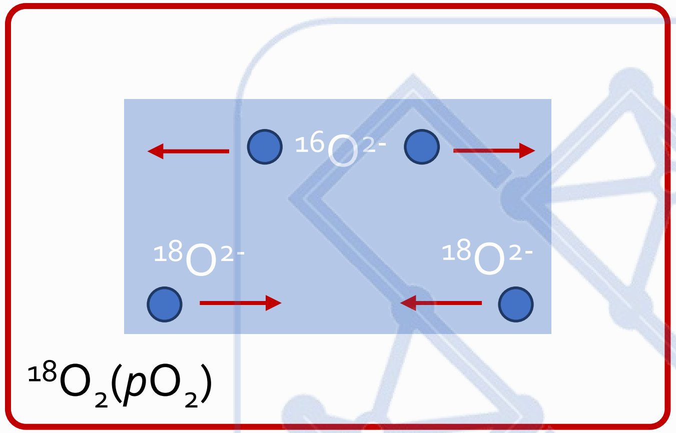
$\propto \exp\left(-\frac{\Delta H_f}{k_B T}\right)$

Reflect the "true" mechanism of ion migration

$\propto \exp\left(-\frac{\Delta H_{mig}}{k_B T}\right)$

Relationship between tracer diffusivity and self-diffusivity

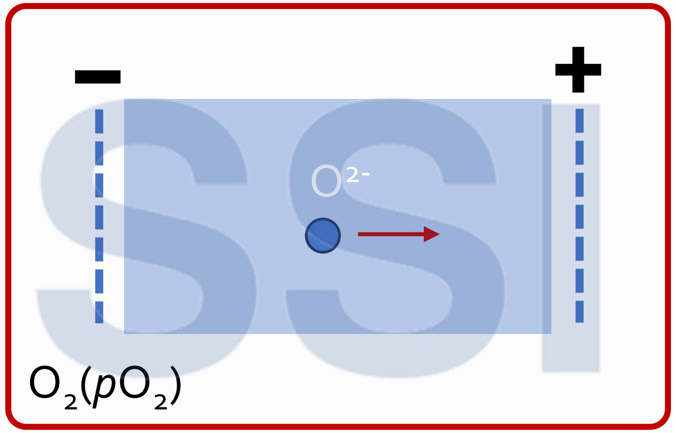
Tracer experiment



Tracer diffusivity

$\boxed{D^*_{O^{2-}}}$

Stationary conductivity experiment



Self-diffusivity

$\boxed{D^q_{O^{2-}}}$

No compositional (stoichiometric) change

Tracer diffusivity and self-diffusivity are usually on the same order of magnitude, since they both describe the process ***without*** compositional changes.

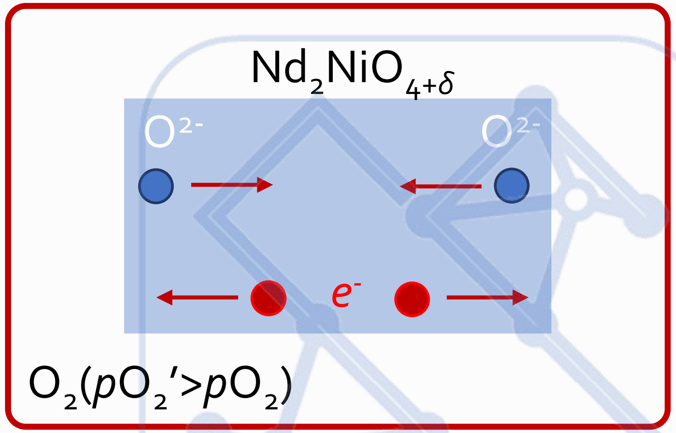
$$\boxed{D^*_{O^{2-}} = H_{O^{2-}} D^q_{O^{2-}}}$$

Haven ratio

- *Haven ratio* mainly describes the correlations between each hops.
- $H_{O^{2-}}$ is usually of the order of 1

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$$\boxed{D_O^{\delta}}$$

Composition (stoichiometry δ) changes

Very different from tracer diffusivity and self-diffusivity, chemical diffusion describe the process that involves ***compositional or stoichiometric changes***.

$$e.g., \; Nd_2NiO_{4+\delta} + \Delta\delta/2\, O_2 \rightarrow Nd_2NiO_{4+\delta+\Delta\delta}$$

In order to change oxygen stoichiometry ($\Delta\delta$), oxide ions O^{2-} and electrons e^- must diffuse to opposite directions, to maintain ***charge neutrality***.

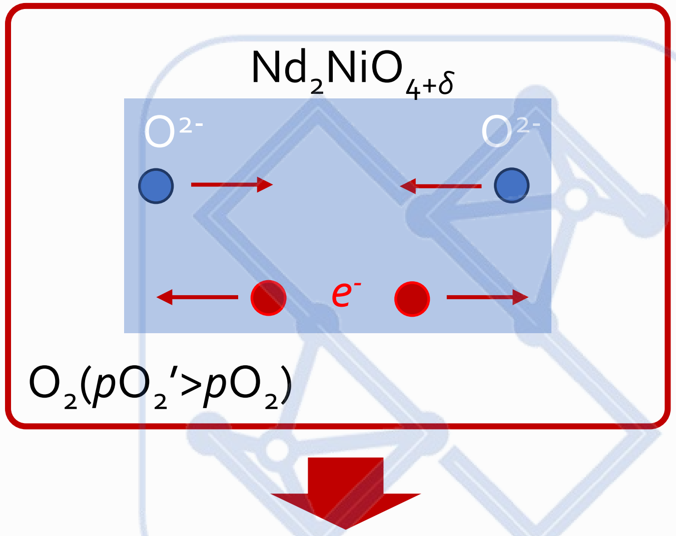
Therefore, chemical diffusivity is called ***ambipolar diffusivity***, meaning that chemical diffusion involves the motion of ***two charged species***.

In $Nd_2NiO_{4+\delta}$ the change of oxygen stoichiometry can be expressed by the defect chemical reaction below:

$$\frac{1}{2}O_2 \rightleftharpoons O_O^{\times} \rightleftharpoons O_i'' + 2h^{\cdot}$$

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment

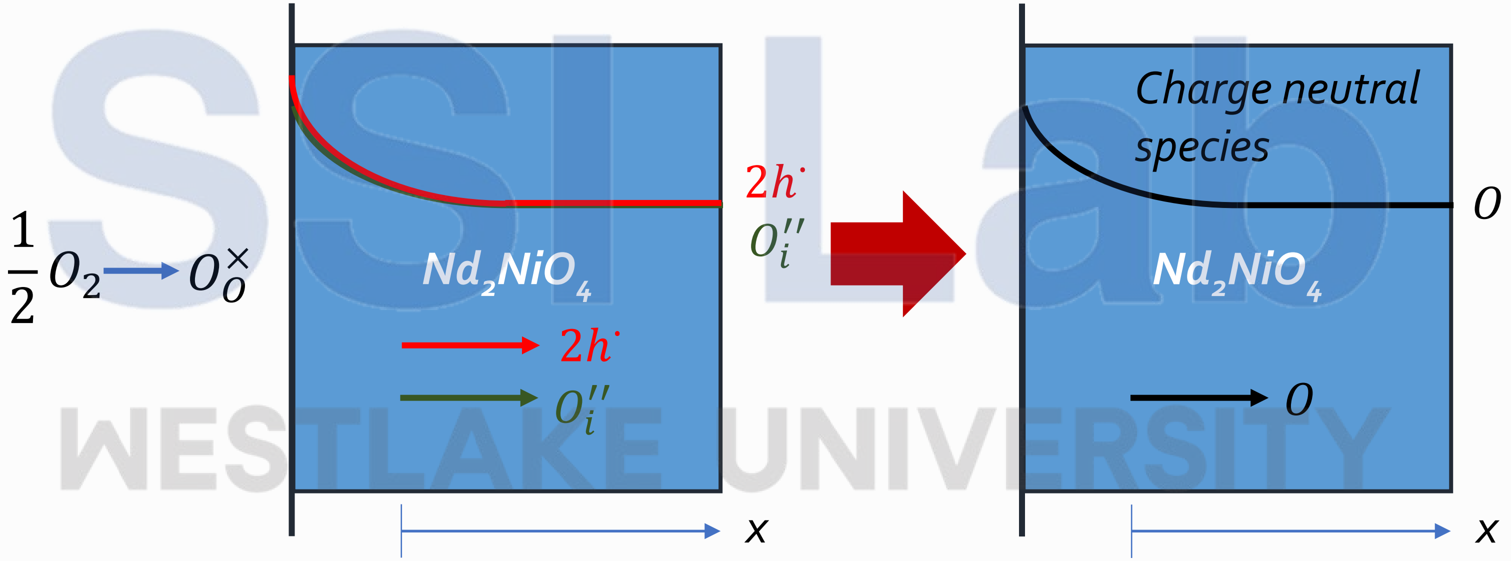


Chemical diffusivity

$\boxed{D_O^\delta}$

Composition (stoichiometry δ) changes

$$\boxed{\frac{1}{2}O_2 \rightleftharpoons O_O^\times \rightleftharpoons O_i'' + 2h^\cdot}$$



Our goal: find the expression of chemical diffusivity based on properties of defects (O_i'' & $h^\cdot$) so that we can use Fick's law to predict the concentration profile, *i.e.*:

$$\boxed{J_O = -D_O^\delta \nabla c_O \text{ or } J_O = -D_O^\delta \frac{\partial c_O}{\partial x} \text{ (1D)}}$$

MIECs should be charge neutral except at interfaces

Poisson's equation: connecting (net) charge with potential

$$\boxed{\frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r}}$$

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

Electrostatic potential

Electric field

1 TNT equivalent:
4.184 X 10^9 J

Let's say if an MIEC contains 0.1 mol/L of net charge, then:

$$\boxed{\frac{\Delta E}{\Delta x} = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{Fc}{\varepsilon_0 \varepsilon_r} = -\frac{\frac{96500C}{mol} \times \frac{0.1mol}{L}}{8.8 \times \frac{10^{-12}F}{m} \times 10} = 0.1 \times 10^{18} V/m^2}$$

($c = 1\ mol/L$ or $c = 6.02 \times 10^{19} cm^{-3}$)

$$\Delta E = \frac{\Delta V}{\Delta x} = 1 \times 10^{18}\ V/m^2 \Delta x$$

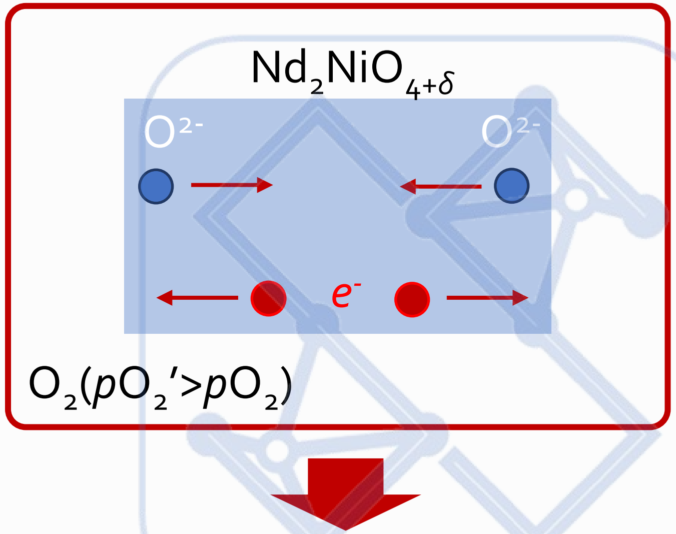
For a sample with area of 1 cm²

Δx	ΔV	U_E
1 nm	1 V	~10^{-6} J
1 μm	10^6 V	~10^3 J
1 mm	10^{12} V	~10^{12} J

Electric potential energy
$U_E = \rho\ \Delta V$

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$$\boxed{D_O^{\delta}}$$

Composition (stoichiometry δ) changes

$$\frac{1}{2}O_2 \rightleftharpoons O_O^{\times} \rightleftharpoons O_i'' + 2h^{\cdot}$$

Flux of oxygen interstitials: $J_{O_i''} = -\frac{\sigma_{O_i''}}{4F^2}\nabla\tilde{\mu}_{O_i''} = -\frac{\sigma_{O_i''}}{4F^2}(\nabla\mu_{O_i''} - 2F\nabla\phi)$

Flux of holes: $J_{h^{\cdot}} = -\frac{\sigma_{h^{\cdot}}}{F^2}\nabla\tilde{\mu}_{h^{\cdot}} = -\frac{\sigma_{h^{\cdot}}}{F^2}(\nabla\mu_{h^{\cdot}} + F\nabla\phi)$

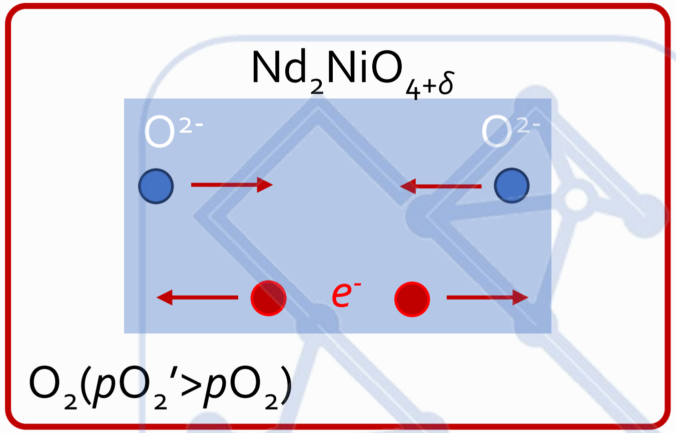
To satisfy the local electro-neutral condition (we will discuss why it holds):

$$J_{O_i''} = \frac{1}{2}J_{h^{\cdot}}$$

$$\frac{\sigma_{O_i''}}{4F^2}\left(\nabla\mu_{O_i''} - 2F\nabla\phi\right) = \frac{\sigma_{h^{\cdot}}}{2F^2}(\nabla\mu_{h^{\cdot}} + F\nabla\phi) \rightarrow \frac{\sigma_{O_i''}}{4F^2}\nabla\mu_{O_i''} - \frac{\sigma_{h^{\cdot}}}{2F^2}\nabla\mu_{h^{\cdot}} = \frac{\sigma_{O_i''} + \sigma_{h^{\cdot}}}{2F}\nabla\phi$$

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$$\boxed{D_O^\delta}$$

Composition (stoichiometry δ) changes

$$\frac{1}{2}O_2 \rightleftharpoons O_O^\times \rightleftharpoons O_i'' + 2h^\cdot$$

$$\frac{\sigma_{O_i''}}{4F^2}\nabla\mu_{O_i''} - \frac{\sigma_{h^\cdot}}{2F^2}\nabla\mu_{h^\cdot} = \frac{\sigma_{O_i''}+\sigma_{h^\cdot}}{2F}\nabla\phi$$

$$J_O = J_{O_i''} = -\frac{\sigma_{O_i''}}{4F^2}\left(\nabla\mu_{O_i''} - 2F\nabla\phi\right) = -\frac{\sigma_{O_i''}}{4F^2}\nabla\mu_{O_i''} + \frac{\sigma_{O_i''}}{2F}\nabla\phi$$

$$= -\frac{\sigma_{O_i''}}{4F^2}\nabla\mu_{O_i''} + \frac{\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}\left(\frac{\sigma_{O_i''}}{4F^2}\nabla\mu_{O_i''} - \frac{\sigma_{h^\cdot}}{2F^2}\nabla\mu_{h^\cdot}\right)$$

$$J_O = -\frac{1}{4F^2}\frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}\left(\nabla\mu_{O_i''} + 2\nabla\mu_{h^\cdot}\right)$$

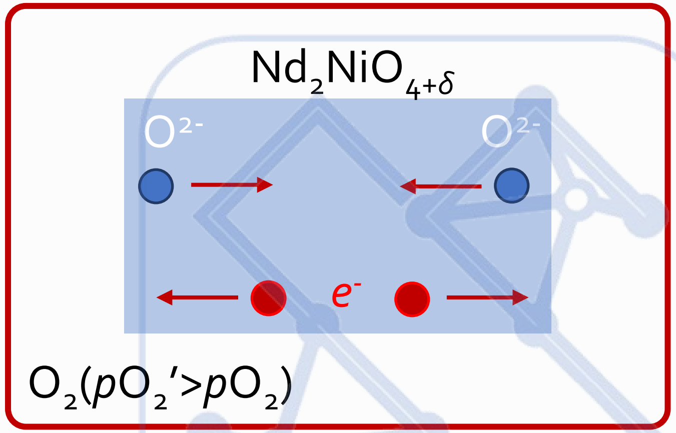
If we denote: $\mu_O = \mu_{O_i''} + 2\mu_{h^\cdot}$

$$J_O = -\frac{1}{4F^2}\frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}\nabla\mu_O = -\frac{1}{4F^2}\sigma_O^\delta\frac{\partial\mu_O}{\partial c_O}\nabla c_O$$

$$\sigma_O^\delta = \frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}$$

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$$\boxed{D_O^\delta}$$

$\downarrow$

Composition (stoichiometry δ) changes

$$J_O = -\underbrace{\frac{1}{4F^2}\sigma_O^\delta \frac{\partial \mu_O}{\partial c_O}}_{D_O^\delta}\nabla c_O$$

$$\sigma_O^\delta = \frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}$$

$$\mu_O = \mu_O^0 + RT\ln a_O \rightarrow \frac{\partial \mu_O}{\partial c_O} = \frac{\partial(\mu_{O_i''}+2\mu_{h^\cdot})}{\partial c_O}$$

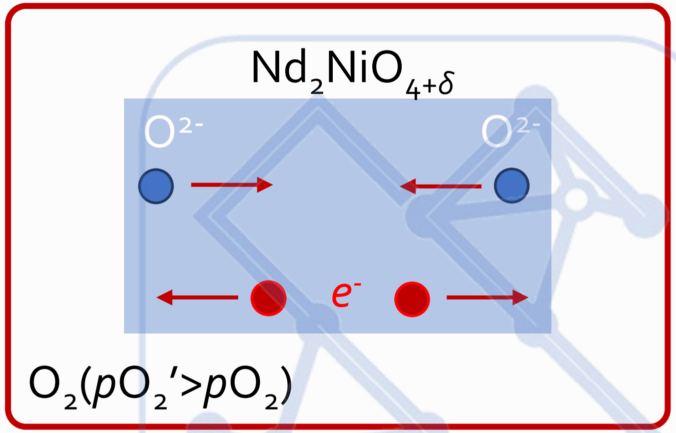
activity, dilute limit $\rightarrow c_O$

$$D_O^\delta = \frac{1}{4F^2}\sigma_O^\delta \frac{\partial \mu_O}{\partial c_O} = \frac{RT}{4F^2}\underbrace{\frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}}_{\text{“electrical”}}\underbrace{\left(\frac{1}{c_{O_i''}}+\frac{4}{c_{h^\cdot}}\right)}_{\text{“ionic”}}$$

$(\partial c_O = \partial c_{O_i''} = \frac{1}{2}\partial c_{h^\cdot})$

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$\boxed{D_O^\delta}$

Composition (stoichiometry δ) changes

$$D_O^\delta = \frac{1}{4F^2}\sigma_O^\delta\frac{\partial\mu_O}{\partial c_O} = \frac{1}{4F^2}\underbrace{\frac{\sigma_{h^\cdot}\sigma_{O_i''}}{\sigma_{O_i''}+\sigma_{h^\cdot}}}_{\text{“electrical”}}\underbrace{\left(\frac{1}{c_{O_i''}}+\frac{4}{c_{h^\cdot}}\right)}_{\text{“ionic”}}$$

(valid at dilute limit)

$$D_O^\delta = \frac{RT}{4F^2}\frac{\sigma_O^\delta}{c_O^\delta}$$

“electrical”: harmonic mean ***conductivity***

$$\frac{1}{\sigma_O^\delta} = \frac{1}{\sigma_{O_i''}} + \frac{1}{\sigma_{h^\cdot}}$$

“ionic”: harmonic mean ***concentration***

$$\frac{1}{c_O^\delta} = \frac{1}{C} + \frac{2^2}{c_{h^\cdot}}$$

$$\sigma_{O_i''} = 2c_{O_i''}FM_{O_i''} = \frac{RT}{4F^2}c_{O_i''}D_{O_i''}$$

$$\sigma_{h^\cdot} = c_{h^\cdot}FM_{h^\cdot} = \frac{RT}{F^2}c_{h^\cdot}D_{h^\cdot}$$

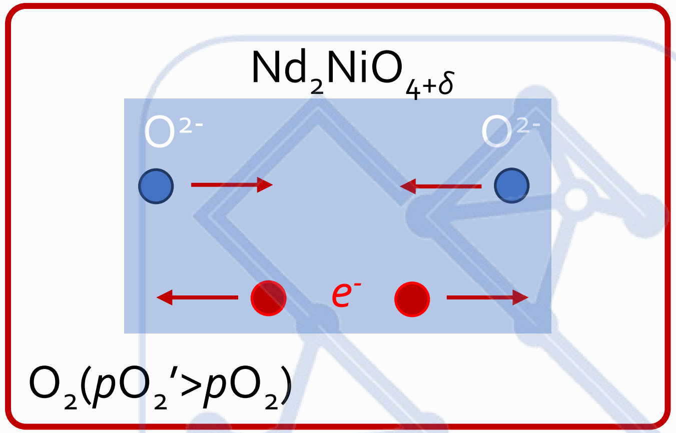
$$D_O^\delta = t_{h^\cdot}D_{O_i''} + t_{O_i''}D_{h^\cdot}$$

$$t_{h^\cdot} = \frac{\sigma_{h^\cdot}}{\sigma_{O_i''}+\sigma_{h^\cdot}}$$

Transference number

Chemical diffusivity: stoichiometric changes

Chemical diffusion experiment



Chemical diffusivity

$$\boxed{D_O^\delta}$$

Composition (stoichiometry δ) changes

$$\boxed{D_O^\delta = t_{h^\cdot} D_{O_i''} + t_{O_i''} D_{h^\cdot}}$$

$$\boxed{t_{h^\cdot} = \frac{\sigma_{h^\cdot}}{\sigma_{O_i''} + \sigma_{h^\cdot}}} \qquad \boxed{t_{O_i''} = \frac{\sigma_{O_i''}}{\sigma_{O_i''} + \sigma_{h^\cdot}}}$$

Transference number

If $\sigma_{h^\cdot} \gg \sigma_{O_i''}$, then $t_{h^\cdot} \rightarrow 1$ and if $D_{h^\cdot}$ is not too large $\longrightarrow$ $\boxed{D_O^\delta \approx D_{O_i''}}$

Note:

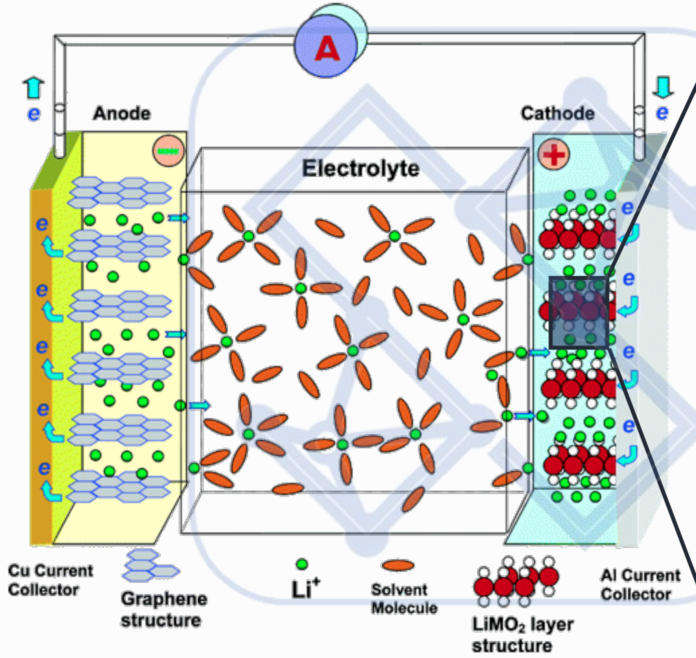
- In this scenario, $D_O^\delta \approx D_{O_i''} \gg D_{O^{2-}}^q$ (recall $D_{O^{2-}}^q = x_{O_i''} D_{O_i''}$, while usually $x_{O_i''} \ll 1$)
- If the system deviate from the dilute limit, then:

$$\boxed{D_O^\delta = \Gamma_{h^\cdot} t_{h^\cdot} D_{O_i''} + \Gamma_{O_i''} t_{O_i''} D_{h^\cdot}}$$

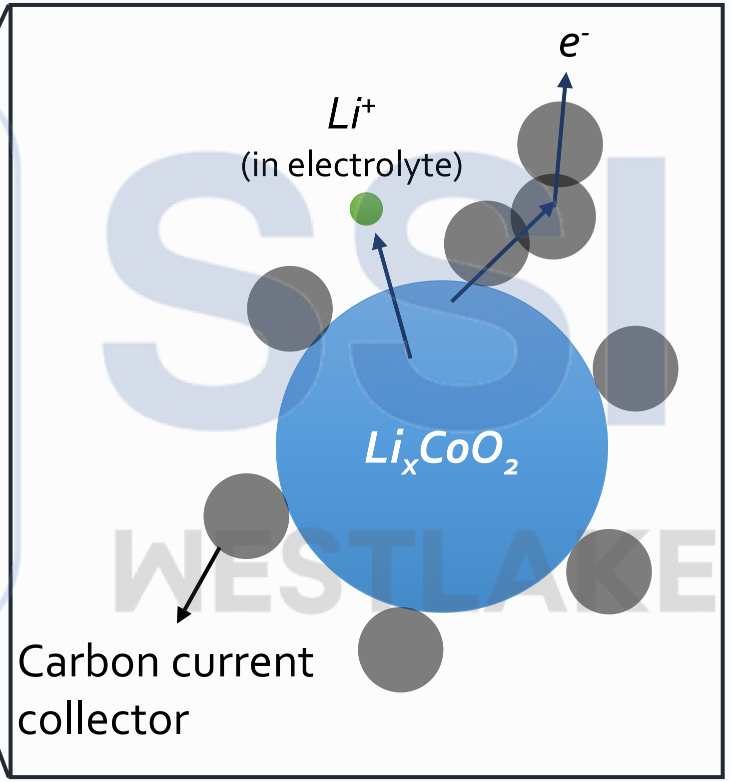
Γ: thermodynamic factor

Microscopic picture: how is Li intercalated into cathodes?

Question: how does *Li*-intercalation happen microscopically?

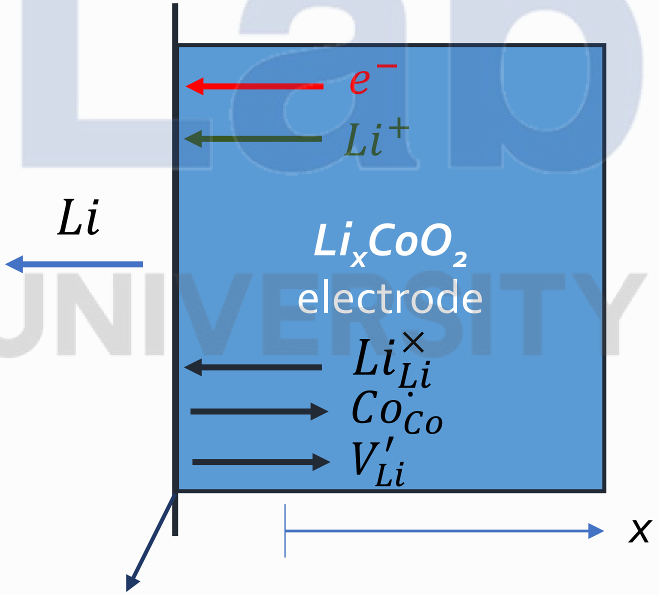


Xu, ***Chem. Rev.*** 2004



$$\boxed{Li \rightleftharpoons Li^{+} + e^{-}}$$

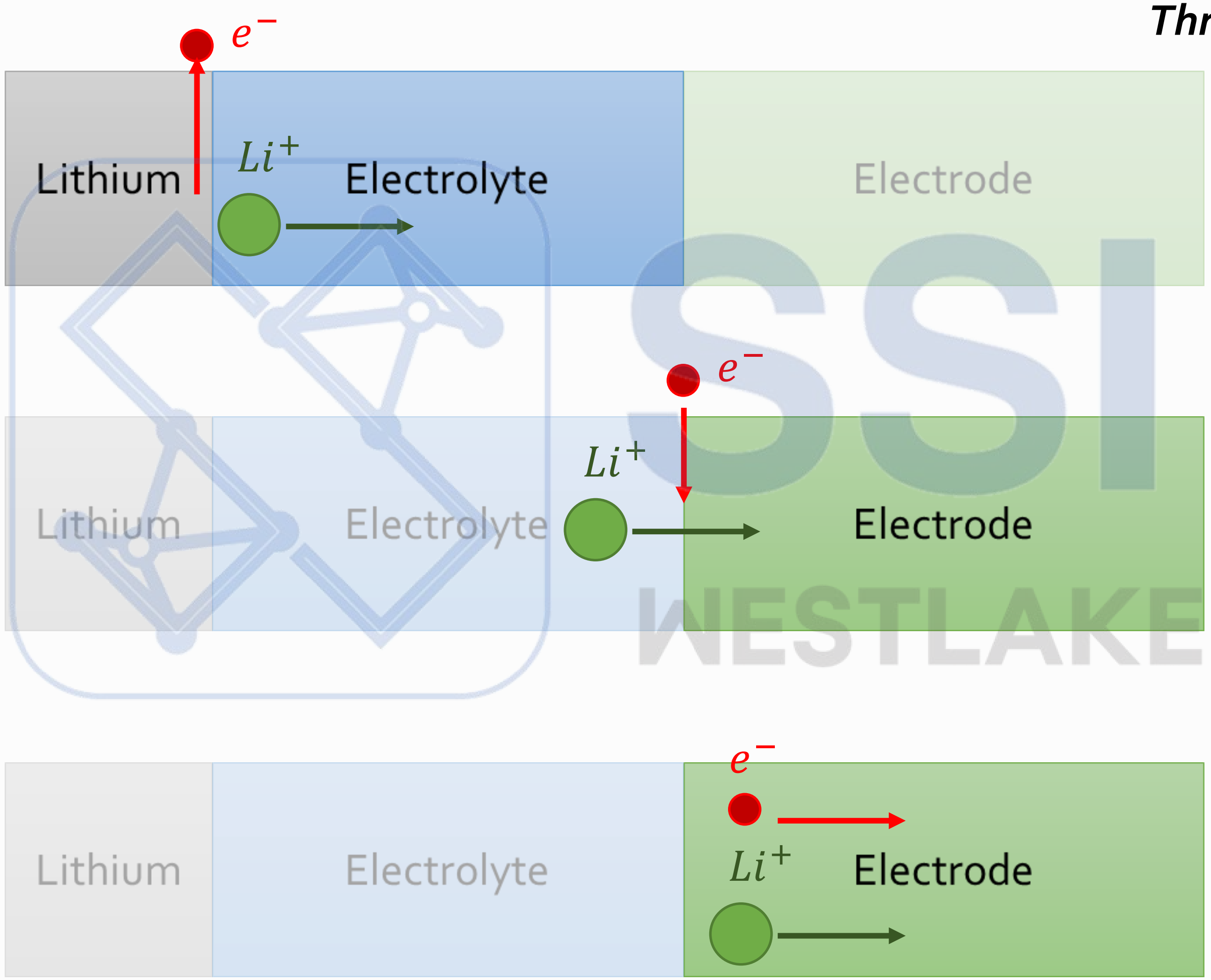
or $$\boxed{Li + V_{Li}' + Co_{Co}^{\cdot} \rightleftharpoons Li_{Li}^{\times}}$$



Li_xCoO_2/carbon/electrolyte interface

Kinetics and transport in Li-ion batteries

Three decisive mechanistic steps of a Li-ion battery



Ion transport
(through electrolyte)
$\tau \sim ns$

Ion transfer
(at electrolyte/electrode interface)
$\tau \sim \mu s$

Chemical diffusion
(in electrode bulk)
$\tau \sim \min, hr, yr$

Depend on the size of electrodes!

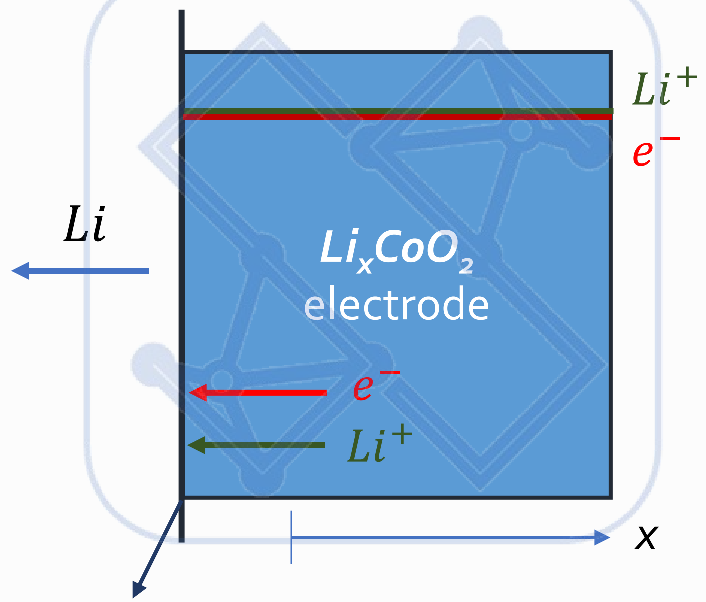
Maier, ***Journal of Power Sources*** 174 (2007) 569–574

Ambipolar diffusion: diffusion process involving both ions and electrons

$\boxed{Li \rightleftharpoons Li^{+} + e^{-}}$

Usually, the diffusivity (mobility) of ***electronic*** species (defects) is much faster than that of ***ionic*** species

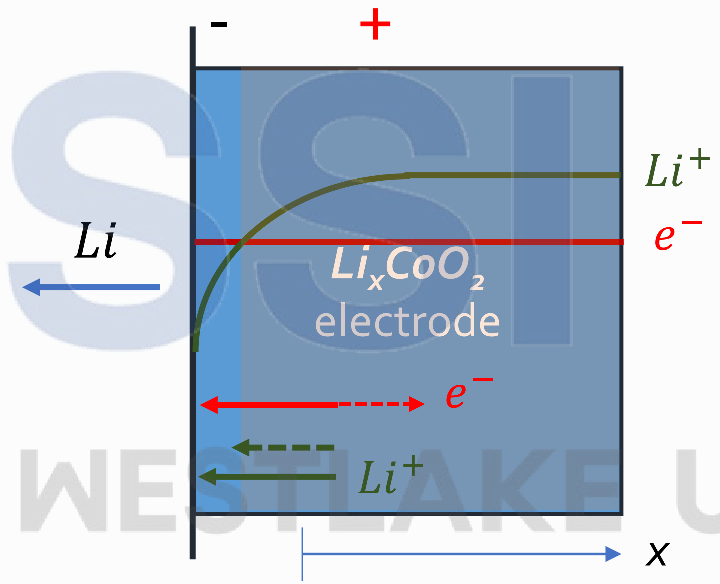
$\boxed{D_{Li^{+}} \ll D_{e^{-}}}$



Li_xCoO_2/carbon/electrolyte interface

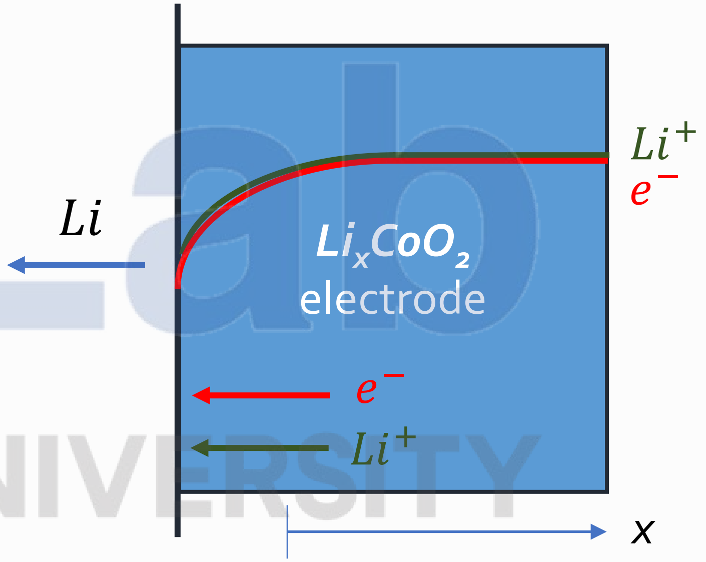
Initial state

Local charge neutral



Intermediate state (imaginary)

Local charge ≠ 0

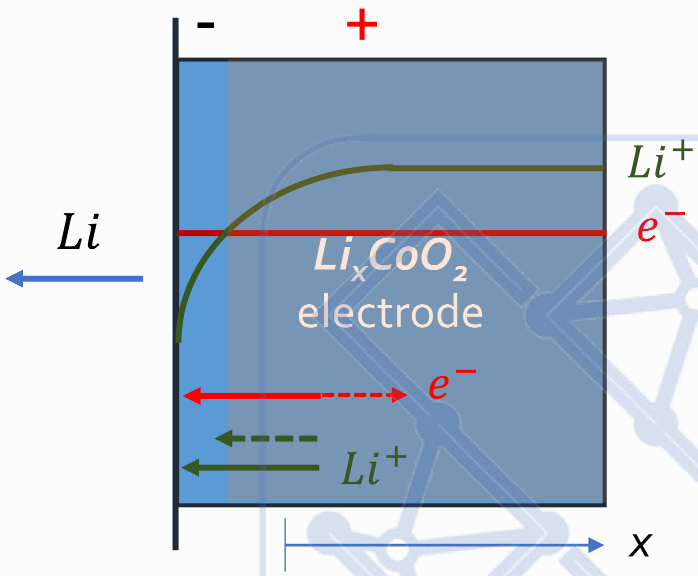


Final state

Local charge neutral

*The electric field **slows down** the fast-diffusing species and **speeds up** the slow diffusing species.*

Note: the bulk of the sample must be *charge neutral*



Intermediate state (imaginary)

Local charge ≠ 0

This picture on the left is an exaggeration to help you to understand the role of accelerating/decelerating electric field;

In a real world, the ***charge neutrality*** still holds (except for the interfaces)

We can do a simple back-on-envelope calculation:

$\boxed{E = -\frac{\partial \phi}{\partial x}}$ → Electrostatic potential

Electric field

$$\boxed{\frac{\partial E}{\partial x} = \frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r}}$$

Charge density $\rho = c \cdot F$

ε_0: vacuum permittivity

ε_r: relative permittivity

Poisson's equation: connecting charge with potential

$$\frac{\Delta E}{\Delta x} = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{Fc}{\varepsilon_0 \varepsilon_r} = -\frac{96500C/mol \times 1mol/L}{8.8 \times 10^{-12} F/m \times 10} = 1 \times 10^{18} V/m^2 \qquad (c = 1\ M)$$

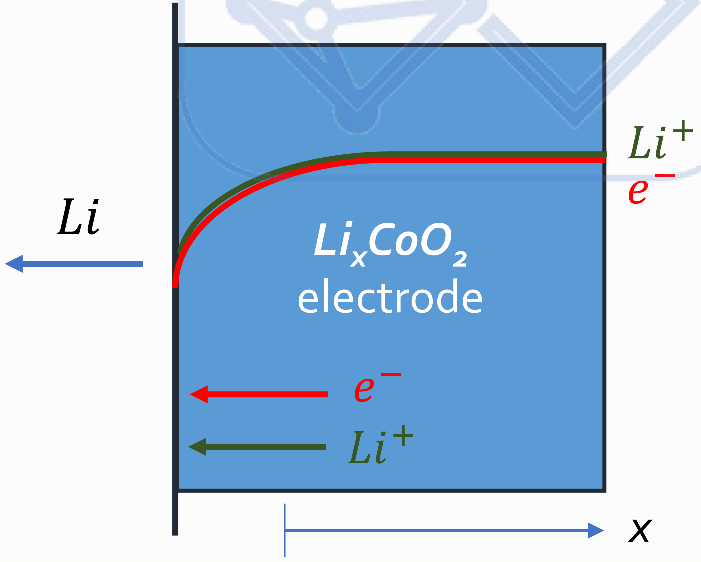
$\Delta E = \frac{\Delta V}{\Delta x} = 1 \times 10^{18}\ V/m^2 \Delta x$ If $\Delta x = 1$ nm → $\Delta V = 1\ V$ (!) → Unrealistic

How to solve for the diffusivity?

Fick's first law

$$J_{diff,Li} = -D_{Li}\nabla c_{Li}$$

How to express D_{Li} as a function of D_{Li^+} and D_{e^-}?



$$\boxed{Li \rightleftharpoons Li^+ + e^-}$$

Key equation: local equilibrium $\boxed{\mu_{Li} = \tilde{\mu}_{e^-} + \tilde{\mu}_{Li^+}}$

Flux: $J_i = -\frac{\sigma_i}{z_i^2 F^2}\nabla\tilde{\boldsymbol{\mu}}_i$

Ionic flow: $J_{Li^+} = -\frac{\sigma_{Li^+}}{F^2}\nabla\tilde{\mu}_{Li^+}$

Electronic flow: $J_{e^-} = -\frac{\sigma_{e^-}}{F^2}\nabla\tilde{\mu}_{e^-}$

Nernst-Einstein relation:
$$\frac{D_i c_i}{RT} = \frac{\sigma_i}{z_i^2 F^2}$$

At steady state: $J_{Li} = J_{Li^+} = J_{e^-}$

$$\mu_{Li} = \tilde{\mu}_{e^-} + \tilde{\mu}_{Li^+} \longrightarrow \nabla\mu_{Li} = \nabla\tilde{\mu}_{e^-} + \nabla\tilde{\mu}_{Li^+}$$

$$J_{Li^+} = J_{e^-} \longrightarrow \sigma_{Li^+}\nabla\tilde{\mu}_{Li^+} = \sigma_{e^-}\nabla\tilde{\mu}_{e^-}$$

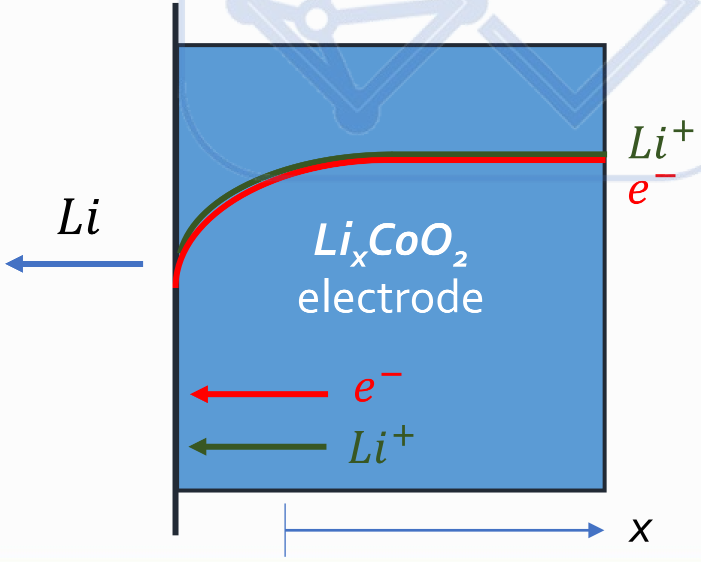
$$\boxed{\nabla\mu_{Li} = \left(1 + \frac{\sigma_{e^-}}{\sigma_{Li^+}}\right)\nabla\tilde{\mu}_{e^-}}$$

How to solve for the diffusivity?

Fick's first law

$$J_{diff,Li} = -D_{Li} \nabla c_{Li}$$

How to express D_{Li} as a function of D_{Li^+} and D_{e^-}?



$$\nabla \mu_{Li} = \left(1 + \frac{\sigma_{e^-}}{\sigma_{Li^+}}\right) \nabla \tilde{\mu}_{e^-}$$

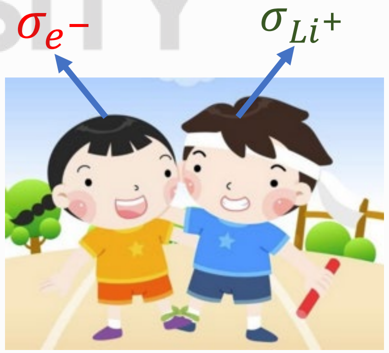
$$J_{Li} = J_{e^-} = -\frac{\sigma_{e^-}}{F^2} \nabla \tilde{\mu}_{e^-} = -\frac{1}{F^2} \frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-} + \sigma_{Li^+}} \nabla \mu_{Li}$$

$$J_{Li} = -\frac{1}{F^2} \frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-} + \sigma_{Li^+}} \nabla \mu_{Li}$$

Compare: $J_i = -\frac{\sigma_i}{z_i^2 F^2} \nabla \tilde{\boldsymbol{\mu}}_i$

We have reached a simple yet somewhat expected result:

$$"\sigma_{Li}" = \frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-} + \sigma_{Li^+}} = \frac{1}{1/\sigma_{e^-} + 1/\sigma_{Li^+}}$$



Chemical diffusivity is limited by the species that move ***more slowly***

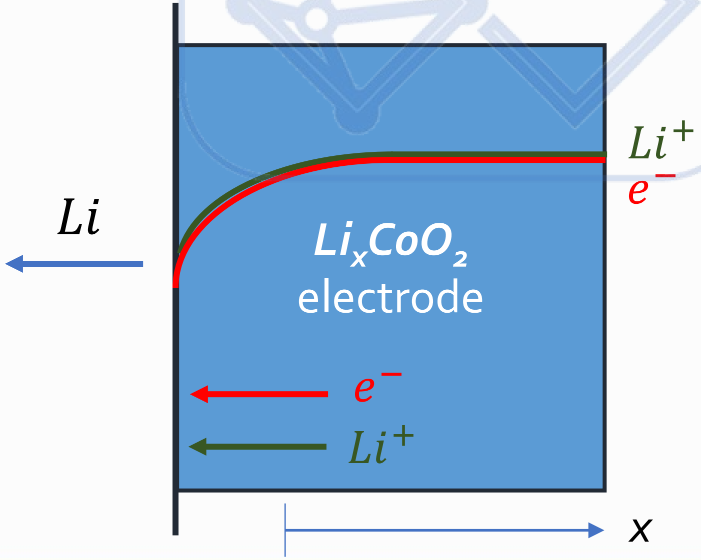
If $\sigma_{e^-} \gg \sigma_{Li^+}$, then $"\sigma_{Li}" \approx \sigma_{Li^+}$

How to solve for chemical diffusivity?

Fick's first law

$$J_{diff,Li} = -D_{Li}\nabla c_{Li}$$

How to express D_{Li} as a function of D_{Li^+} and D_{e^-}?



$$J_{Li} = -\frac{1}{F^2}\frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-}+\sigma_{Li^+}}(\nabla\tilde{\mu}_{e^-}+\nabla\tilde{\mu}_{Li^+})$$

$$\boxed{\nabla c_{e^-} = \nabla c_{Li^+} = \nabla c_{Li}}$$

$$= -\underbrace{\frac{RT}{F^2}\frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-}+\sigma_{Li^+}}\left(\frac{1}{c_{e^-}}+\frac{1}{c_{Li^+}}\right)}_{D_{Li}^{\delta}}\nabla c_{Li}$$ (Dilute limit)

δ means it describes the change of ***non-stoichiometry***

$$D_{Li}^{\delta} = \underbrace{\frac{RT}{F^2}\frac{\sigma_{e^-}\sigma_{Li^+}}{\sigma_{e^-}+\sigma_{Li^+}}}_{1/R^{\delta}}\underbrace{\left(\frac{1}{c_{e^-}}+\frac{1}{c_{Li^+}}\right)}_{1/C^{\delta}}$$

So-called "***chemical diffusivity***"

"Chemical Resistance" ***"Chemical Capacitance"***

Relaxation time $\tau^{\delta} = R^{\delta}C^{\delta} \propto \frac{L^2}{D_{Li}^{\delta}}$

For $\boldsymbol{D^{\delta}}$ = 10^{-10} cm^2/s

L	$\boldsymbol{\tau}$
10 mm	300 years
10 μm	2 hours
10 nm	0.01 s

Things we have discussed in this lecture

Type of diffusivities:

- What are the different types of diffusivities?
- What physical mechanism and concept does each diffusivity describe?

Chemical diffusivity:

- What physical process does the chemical diffusion describe?
- What are the key factors that govern the chemical diffusivity?

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

西湖大學
WESTLAKE UNIVERSITY

End of Lecture 5
Solid State Ionics Fall 2023

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