Echem Rnx. Engg. CL 611

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Lecture **x**
Transport in Ionic Solutions

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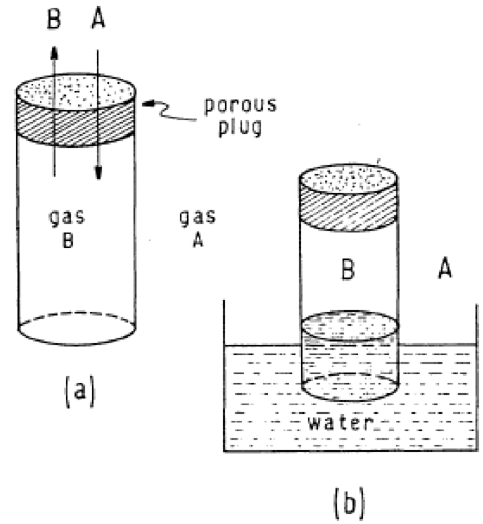
Outline

- Transport in the ionic solutions
  - Parameters:
    - Diffusivity
    - Conductivity
    - Transference number
  - Dilute solution theory
    - Concentration gradient with 0 net current
      - To demonstrate we need to use combined flux equation
      - Nernst-plank equation
    - Application of current on a symmetric cell
      - Reaction not possible
      - Reaction is present

Diffusion Process:

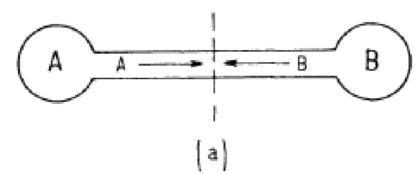
Example of coupled transport

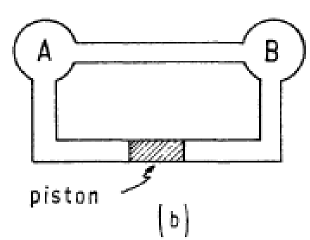
1. Systems used by Graham. Gas B in the tube diffuses through a porous plug into gas A (usually air) and A diffuses into the tube. In (b), the water level rises or drops depending on whether the molecular weight of B is less than or greater than that of A. (For more details see Section 6.1.1.1.)



2. (a) A system used by Graham and Loschmidt. Gases A and B are initially kept separate in two bulbs and then (by, for example, turning a stopcock) are allowed to interdiffuse. A porous plug may be used in the joining tube.

   (b) The gas chambers are joined by a second tube with a movable piston; then any change in pressure in the chambers resulting from the diffusion will be dissipated by movement of the piston. (For more details see Section 5.3.1.)





Diffusion in Gases and Porous Media: Cunningham and Williams

Fick's Law:

Introduction

The transport of material by diffusion is due to the random thermal movement of molecules and is described by Fick's law:

$$\mathbf{J}_i = -D_i \nabla c_i, \tag{4.1}$$

$$J_{i,x} = -D_i \frac{dc_i}{dx}.$$

The flux defined here, **J**, is the flux relative to the molar average velocity.

A more generalized form:

$$J_i = -Bc_i \frac{d\mu_i}{dx}$$

$$\mu_i = \mu_i^0 + RT \ln c_i f_i$$

f_i activity coefficient

$$J_i = -\underbrace{BRT\left(1 + \frac{d\ln f_i}{d\ln c_i}\right)}_{D?}\frac{dc_i}{dx}$$

Fuller and Bockris and Reddy

Diffusion vs Migration

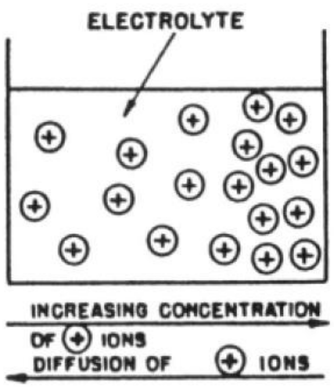


Fig. 4.1. The diffusion of positive ions resulting from a concentration gradient of these ions in an electrolytic solution. The directions of increasing ionic concentration and of ionic diffusion are shown below the diagram.

$$J_{i,x} = -D_i \frac{dc_i}{dx}.$$

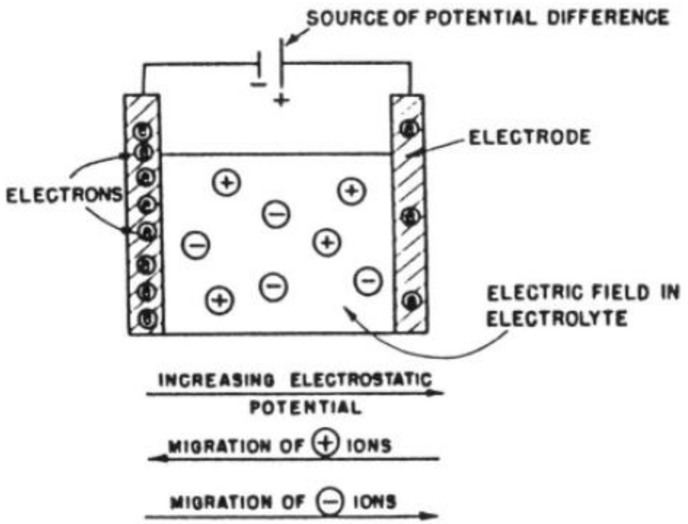


Fig. 4.2. The migration of ions resulting from a gradient of electrostatic potential (i.e., an electric field) in an electrolyte. The electric field is produced by the application of a potential difference between two electrodes immersed in the electrolyte. The directions of increasing electrostatic potentials and of ionic migration are shown below the diagram.

migration or conduction

Image: Bockris and Reddy:Vol 1: Modern Electrochemistry-Ionics

Typical Diffusion Coefficients

TABLE 4.2

Diffusion Coefficient *D* of Ions in Aqueous Solutions

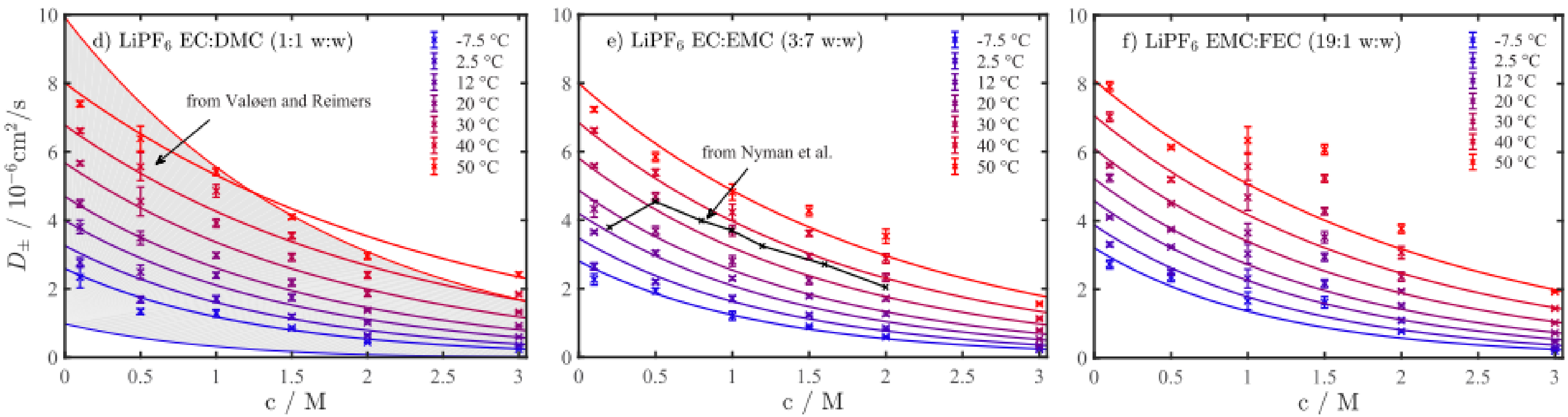
Ion	Diffusion Coefficient, ($cm^2\ s^{-1}$)
Li^+	1.028×10^{-5}
Na^+	1.334×10^{-5}
K^+	1.569×10^{-5}
Cl^-	2.032×10^{-5}
Br^-	2.080×10^{-5}

- Food for thought: What experiments can I perform to extract the diffusion coefficient of various ions?
- Since +ve and –ve ions are connected through electroneutrality, can I measure the *D* of individual ionic species?

Image: Bockris and Reddy:Vol 1: Modern Electrochemistry-Ionics

Diffusivity Measured for Li-ion Battery Elyt

function of T and c



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Migration

- In solid metal conductor:
- Ohm's law

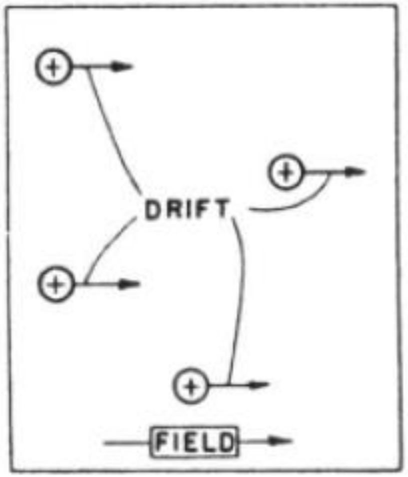
$$I = -\sigma \nabla \phi$$

$$I = \frac{\Delta V}{R}$$

- In ionic solutions:
- Migration:
- Force due to electric field $\vec{F} = \underbrace{(z_i F)}_{q\left[\frac{\mathrm{C}}{\mathrm{mol}}\right]} \underbrace{(-\nabla \phi)}_{\vec{E}}$
- Molar flux $(N_i) \propto c_i$
- Using proportionality constant u_i

$$N_i = \underbrace{u_i}_{\text{Prop. Const.}} \times c_i \times (z_i F)(-\nabla \phi)$$

$\vec{F} = q\vec{E}$



(b) MACROSCOPIC VIEW

ϕ is the potential in the solution, not the potential in the solid/electrodes

Consider binary electrolyte

- Molar fluxes of both ions (w/o conc. gradient):
  - $N_+ = u_+ \times c_+ \times (-z_+ F \nabla\phi)$
  - $N_- = u_- \times c_- \times (-z_- F \nabla\phi)$

- Net current is due to both fluxes: (ignoring concentration gradient)
  - $i = \sum_i z_i F N_i$
  - $i = -(u_+ c_+ z_+^2 F^2 \nabla\phi + u_- c_- z_-^2 F^2 \nabla\phi)$
  - $i = -\underbrace{F^2(u_+ c_+ z_+^2 + u_- c_- z_-^2)}_{\kappa} \nabla\phi$
    - Ionic conductivity
      - $\kappa = F^2(u_+ c_+ z_+^2 + u_- c_- z_-^2)$
      - Units S/cm, battery electrolyte: ~10 mS/cm
  - $i = -\kappa \nabla\phi$

Typical Conductivity Values

TABLE 4.7

Representative Values of Specific Conductivity

Substance	Type of Conductor	Specific Conductivity ($S\ cm^{-1}$)	T (K)
Copper	Metallic	5.8×10^5	293
Lead	Metallic	4.9×10^5	273
Iron	Metallic	1.1×10^5	273
4 M H_2SO_4	Electrolytic	7.5×10^{-1}	291
0.1 M KCl	Electrolytic	1.3×10^{-2}	298
Xylene	Nonelectrolyte	1×10^{-19}	298
Water	Nonelectrolyte	4×10^{-8}	291

How do I measure the conductivity of solutions?

Bockris and Reddy:Vol 1: Modern Electrochemistry-Ionics

Molar conductivity

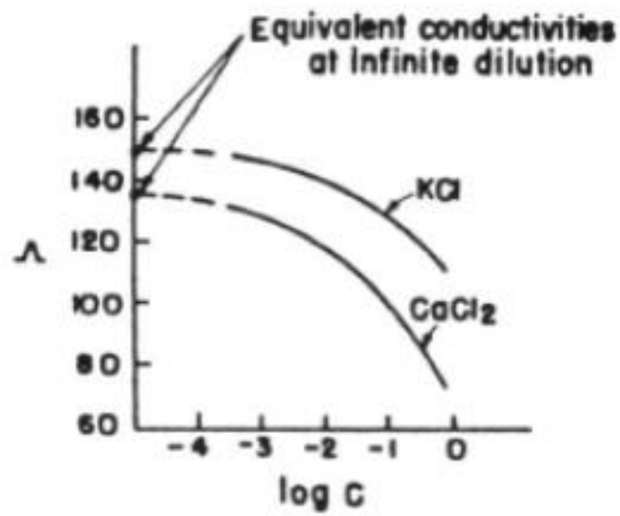
- Ionic conductivity

  $\kappa = F^2(u_+c_+z_+^2 + u_-c_-z_-^2)$ Eq[1]

  Units S/cm, battery electrolyte: ~10 mS/cm

  - Example:
    - Take KCl solution of concentration c.
    - $z_+ = z_- = 1, \&\ c_+ = c_- = c$, simplifies eqn 1 as follows:
      - $\kappa = F^2(u_+ + u_-)c$ Eq [2]
    - Conductivity is proportional to concentration, hence κ/c is supposed to be constant.
      - $\kappa/c = F^2(u_+ + u_-)$ Eq [3]
    - κ/c is also known as molar conductivity ($\Lambda_{m,}$)
      - Only at concentration below 0.1 mM, one see Λ_m to be constant.

Sym	Name	Units
G	Conductance	$\mathrm{S\ or\ 1/\Omega}$
ρ	Resistivity	$\mathrm{cm/S}$
σ, κ	Specific conductivity	$\mathrm{S/cm}$
Λ_m	Molar conductivity	$\mathrm{S\ cm^2/mol}$
Λ	Equivalent conductivity	$\mathrm{S\ cm^2/(mol\ eq)}$



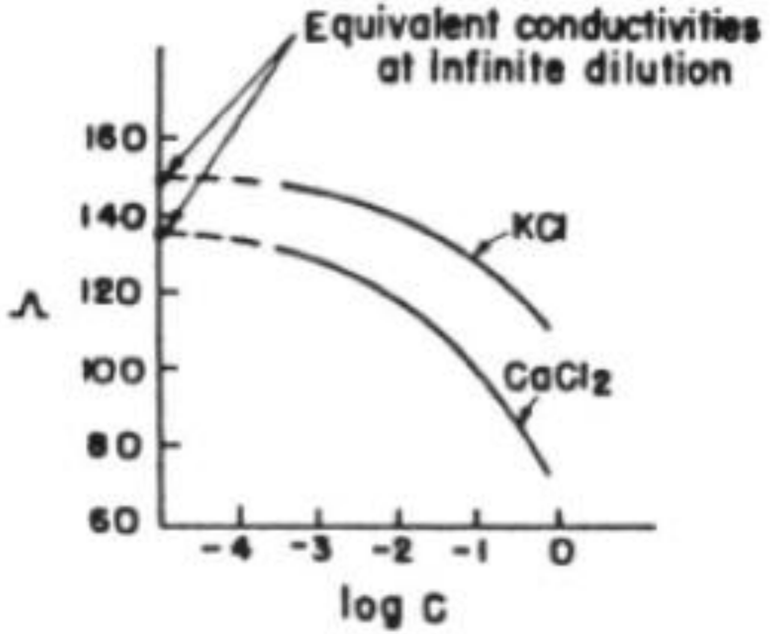
Equivalent conductivity

- Ionic conductivity

  $\kappa = F^2(u_+c_+z_+^2 + u_-c_-z_-^2)$ Eq[1]

  Units S/cm, battery electrolyte: ~10 mS/cm

  - Example:
    - Take $CaCl_2$ solution of concentration c.
    - $z_+ = 2, z_- = 1, \&\ c_+ = c_-/2 = c$, simplifies eqn 1 as follows:
      - $\kappa = F^2(4u_+ + 2u_-)c$ Eq [2]
      - $\kappa = F^2(2u_+ + u_-)2c$ Eq [2]
      - Equivalent= 2c
    - **Equivalent conductivity is defined as** $\boldsymbol{\kappa/zc}$ (Λ)
      - Only at concentration below 0.1 mM, one see Λ to be constant.

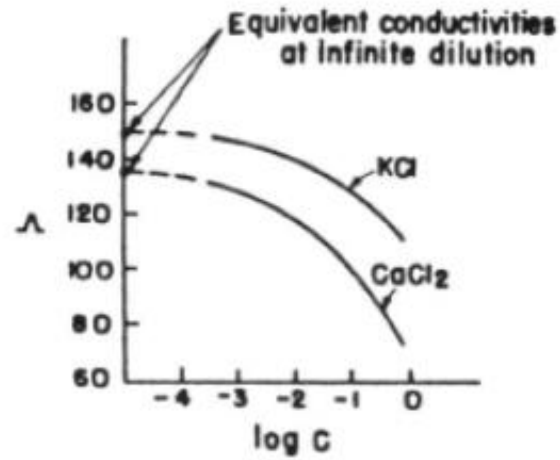


Kohlrausch's Law at low concentrations

- Kohlrausch's Law at low concentrations:

$$\Lambda = \Lambda^{\circ} - K\sqrt{c}$$

  - Particularly for strong electrolytes.
  - For weak elyt, where dissociation is not full, it is not fully applicable.

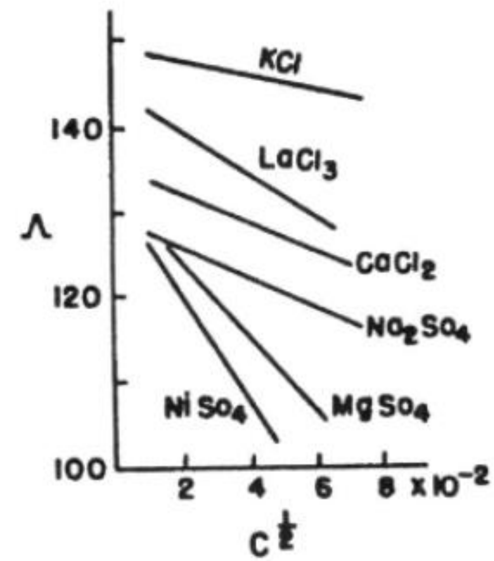


Example:

The figure shows the max concentration value of

$$\sqrt{c} = 8 \times 10^{-2}$$

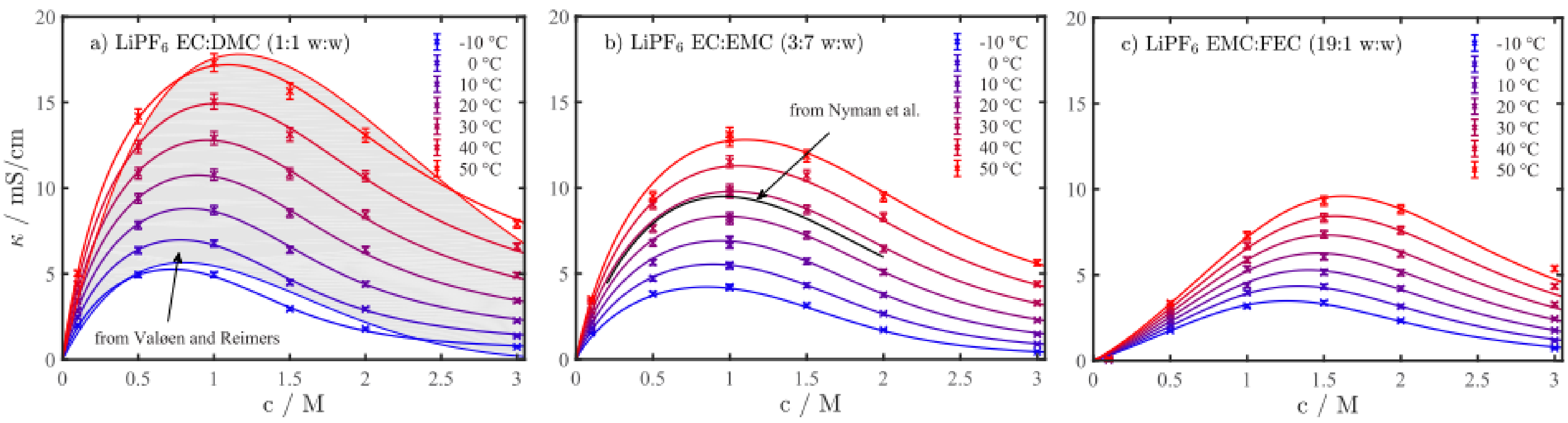
$$c = 6.4\ \mathrm{mM}$$



Bockris and Reddy:Vol 1: Modern Electrochemistry-Ionics

Conductivity for Li-ion Battery Elyt

function of T and c



The measured conductivity at c > 10 mM deviates significantly from the kohlrausce law.

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Transference Number:

Binary electrolyte (no conc. gradient)

- $i = -\underbrace{F^2(u_+c_+z_+^2 + u_-c_-z_-^2)}_{\kappa}\nabla\phi$
  - Ionic conductivity κ
    - $\kappa = F^2(u_+c_+z_+^2 + u_-c_-z_-^2)$
    - Units S/cm, battery electrolyte: ~10 mS/cm
- Current is being carried by two species:
  - How much is due to single specie:
    - $t_+ = \frac{u_+c_+z_+^2}{u_+c_+z_+^2+u_-c_-z_-^2}$
    - $t_- = \frac{u_-c_-z_-^2}{u_+c_+z_+^2+u_-c_-z_-^2}$
    - $t_+ + t_- = 1$
  - Generally:
    - $\Sigma t_i = 1$

Transference Number:

TABLE 4.16

Transport Numbers of Cations in Aqueous Solutions at 298 K in 0.1 *N* Solutions

Electrolyte	HCl	LiCl	NaCl	KCl	KNO_3	$AgNO_3$	$BaCl_2$
Transport number of cation, t_+	0.83	0.32	0.39	0.49	0.51	0.47	0.43

For Nafion the transference number $t_+ = 1$

For solid state electrolyte for Li-ion battery, $t_+ = 1$

For anionic exchange membrane, $t_- = 1$

Bockris and Reddy:Vol 1: Modern Electrochemistry-Ionics

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  - Dilute solution theory contd.
    - **Concentration gradient with 0 net current**
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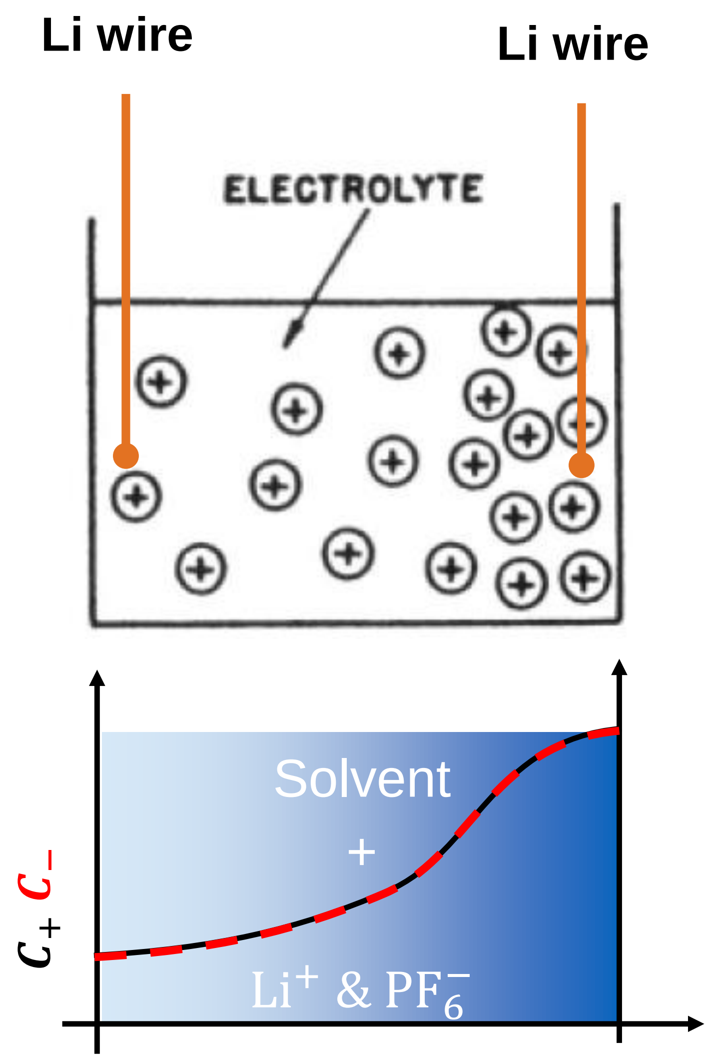
Example: Concentration Gradient System

Case: Concentration gradient exists in the following system. No applied electric field.

- Is molar flux nonzero?
- Is current nonzero?
- What types of transport processes are taking place in this system?
- Will there be a potential gradient as well?
- Say its LiPF6 system:
- If I dip a lithium wire at two different location, will I measure potential difference?
- If there is a potential gradient, will there be migration?



NERNST–PLANCK EQUATION

$$\mathbf{N}_i = \underset{migration}{-z_i u_i F c_i \nabla \phi} \quad \underset{diffusion}{-D_i \nabla c_i} \quad + \quad \underset{convection}{c_i \mathbf{v}}$$

N-P eqn is also referred to as dilute solution theory.

$$i = \sum_i z_i F N_i$$

$$\mathbf{i} = -F^2 \nabla \phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i + F \mathbf{v} \cancelto{0}{\sum_i z_i c_i}$$

$$\mathbf{i} = -F^2 \nabla \phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i$$

Charge balance: (assuming electroneutrality)

$$\nabla . i = 0$$

Special case:

When no current is flowing in the system:

$$i = 0$$

Example revisited

When no current is flowing in the system:

$$i = 0$$

N-P relation:

$$i = -F^2 \nabla\phi \Sigma z_i^2 u_i c_i - F \Sigma z_i D_i \nabla c_i$$

$$0 = -F^2 \nabla\phi \Sigma z_i^2 u_i c_i - F \Sigma z_i D_i \nabla c_i$$

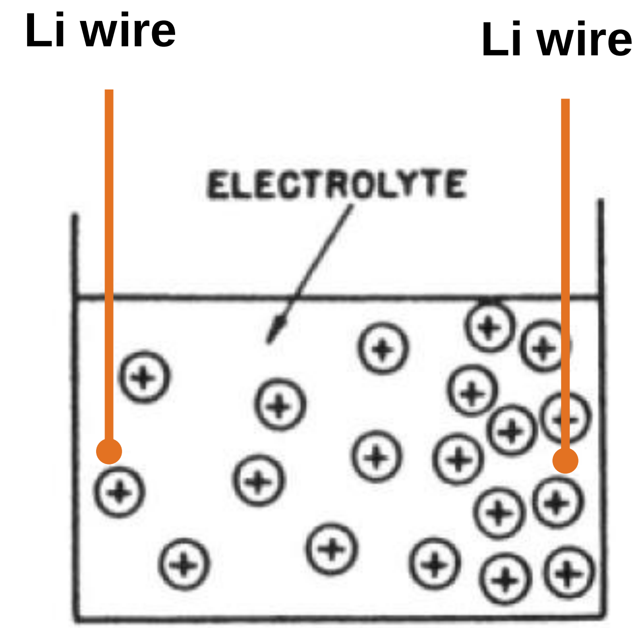
$$\nabla\phi = -\frac{\Sigma z_i D_i \nabla c_i}{F\ \Sigma z_i^2 u_i c_i}$$

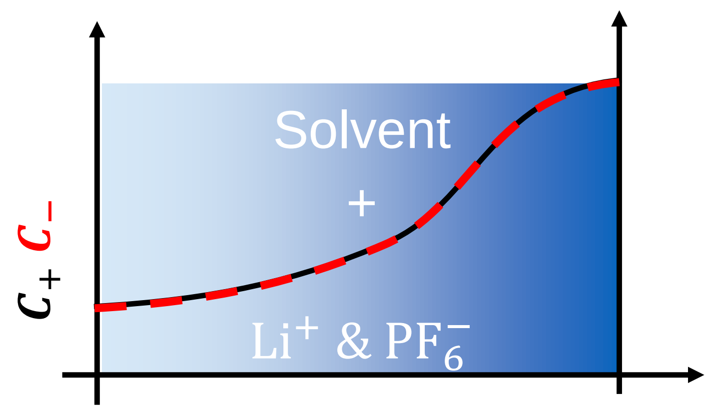
Easy case: $\mathrm{Li}^+\ \mathrm{PF}_6^-$ with $\nu_+ = \nu_- = 1$

$$c = c_+ = c_-$$

$$\nabla\phi = -\frac{\Sigma z_i D_i}{F\ \Sigma z_i^2 u_i} \nabla \ln c$$

This is also termed as diffusion potential





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N-P Equation: Dilute Solution Theory

Molar Flux:

$$\mathbf{N}_{\boldsymbol{i}} = -z_i u_i F c_i \nabla\Phi - D_i \nabla c_i + c_i \mathbf{v}$$

flux migration diffusion convection

Electroneutrality

$$\mathbf{i} = F \sum_i z_i \mathbf{N}_{\boldsymbol{i}}$$

$$\mathbf{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i + F\mathbf{v} \sum_i z_i c_i$$

Current in the solution:

$$\mathbf{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i$$

Expression in terms of κ and D_i: $\kappa = F^2 \sum_i z_i^2 u_i c_i$

Transference number: t_+

Thermodynamic factor: $1 + \frac{d \ln f_+}{d \ln c_+}$

Too many parameters:

How many parameters do I need to know the potential drop in the solution?

For the following binary soln

$$AB = \nu_+ A^{Z_+} + \nu_- B^{Z_-}$$

Example:

$$LiPF_6 = 1\ Li^{+1} + 1 PF_6^{-1}$$
$$MgCl_2 = 1\ Mg^{+2} + 2\ Cl^{-1}$$

What are the fundamentally essential parameters to describe transport?

What are the essential macro parameters to describe transport?

u_+	Mobility of + ions
u_-	Mobility of - ions
D_+	Diffusivity of + ions (N-E)
D_-	Diffusivity of – ions (N-E)
t_+	Transference number of + ions
t_-	Transference number of - ions
κ	Conductivity of electrolyte
$1 + \frac{d \ln f_+}{d \ln c_+}$	Thermodynamic factor for + ions
$1 + \frac{d \ln f_-}{d \ln c_-}$	

Electrochemical Potential:

$$\mathbf{N}_i = -u_i z_i F \times c_i(\nabla\Phi) - D_i \nabla c_i$$

$$\mathbf{N}_i = -u_i z_i F \times c_i(\nabla\Phi) - D_i c_i \nabla \ln c_i$$

$$\nabla c_i = c_i \nabla \ln c_i$$

Rearrangement: (take ∇ out)

$$\mathbf{N}_i = -c_i \times \nabla[u_i z_i F \cdot \Phi + D_i \ln c_i]$$

$$\mathbf{N}_i = -c_i \times \nabla\left[u_i z_i F \cdot \Phi + \frac{D_i}{RT} RT \ln c_i\right]$$

$$\mathbf{N}_i = -c_i \times \frac{D_i}{RT} \nabla\left[\underbrace{\frac{u_i RT}{D_i}}_{\text{N−E Relation}} z_i F \cdot \Phi + RT \ln c_i\right]$$

$$\mathbf{N}_i = -c_i \times \frac{D_i}{RT} \nabla\left[\underbrace{z_i F \cdot \Phi + RT \ln c_i}_{\bar{\mu}_i \text{ Echem Pot.}}\right]$$

Flux can be expressed using one driving force $\nabla\bar{\mu}_i$!

$$\mathbf{N}_i = -c_i \times \frac{D_i}{RT} \nabla\bar{\mu}_i$$

$$\bar{\mu}_i = z_i F \cdot \Phi + \underbrace{\mu_i^0 + RT \ln c_i}_{\text{Chemical Pot.}}$$

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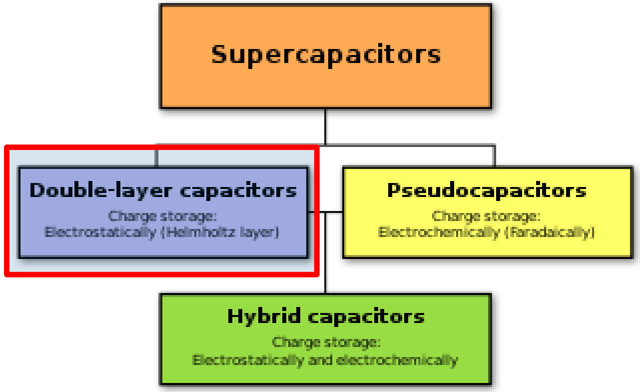
Symmetric Cell: No Faradaic Rxn @ Interface

- Example:
  - Conductivity Cell
  - Supercapacitor



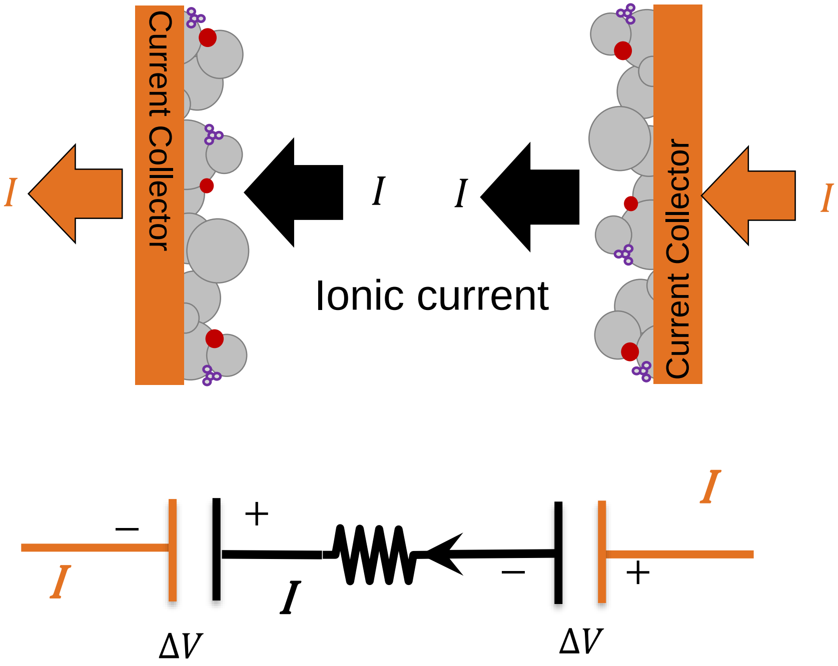


Image: Wiki

Symmetric Cell: No Faradaic Rxn @ Interface

Molar Flux:

$$\underset{\text{flux}}{\mathbf{N}_i} = \underset{\text{migration}}{-z_i u_i F c_i \nabla\Phi} \underset{\text{diffusion}}{- D_i \nabla c_i} \underset{\text{convection}}{+ c_i \mathbf{v}}$$

Current Eqn.

$$\mathbf{i} = F \sum_i z_i \mathbf{N}_i$$

Electroneutrality

$$\mathbf{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i + F\mathbf{v} \sum_i z_i c_i$$

Current in the solution:

$$\mathbf{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i$$

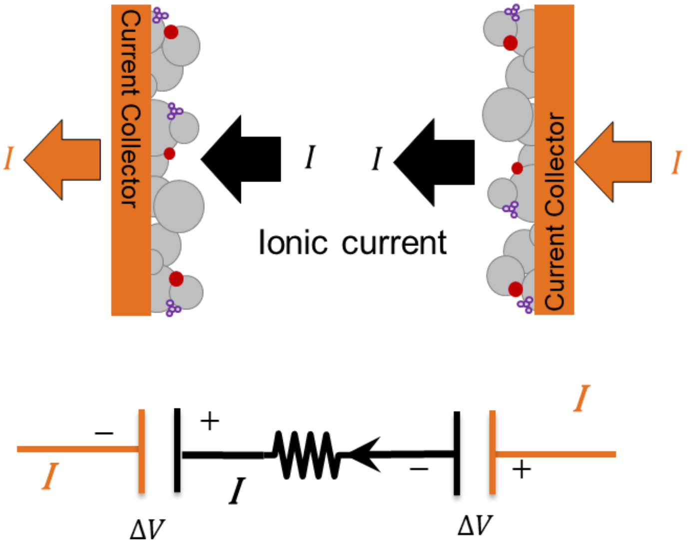
Expression in terms of κ and D_i: $\kappa = F^2 \sum_i z_i^2 u_i c_i$

Modified Ohm's law (McInnis Equation)

$$\nabla\Phi = -\frac{\mathbf{i}}{\kappa} - \frac{F}{\kappa} \sum_i z_i D_i \nabla c_i$$

In the absence of conc. gradient (Ohm's law):

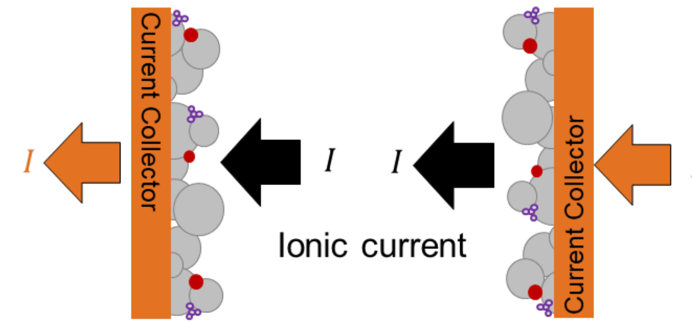
$$\nabla\Phi = -\frac{\mathbf{i}}{\kappa}$$



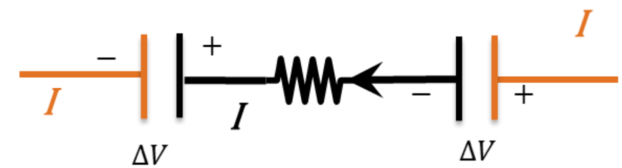
Symmetric Cell: No Faradaic Rxn @ Interface

Conservation of charge:

$$\nabla \cdot \mathbf{i} = 0$$



Where i is given as: $\nabla\Phi = -\frac{\mathbf{i}}{\kappa} - \frac{F}{\kappa}\sum_i z_i D_i \nabla c_i$



Gives the following expression:

$$\nabla \cdot (\kappa \nabla \Phi) + F \sum_i z_i \nabla \cdot (D_i \nabla c_i) = 0$$

When no concentration gradient exits:

$$\nabla^2 \Phi = 0$$

$$\text{Ohm's Law}$$

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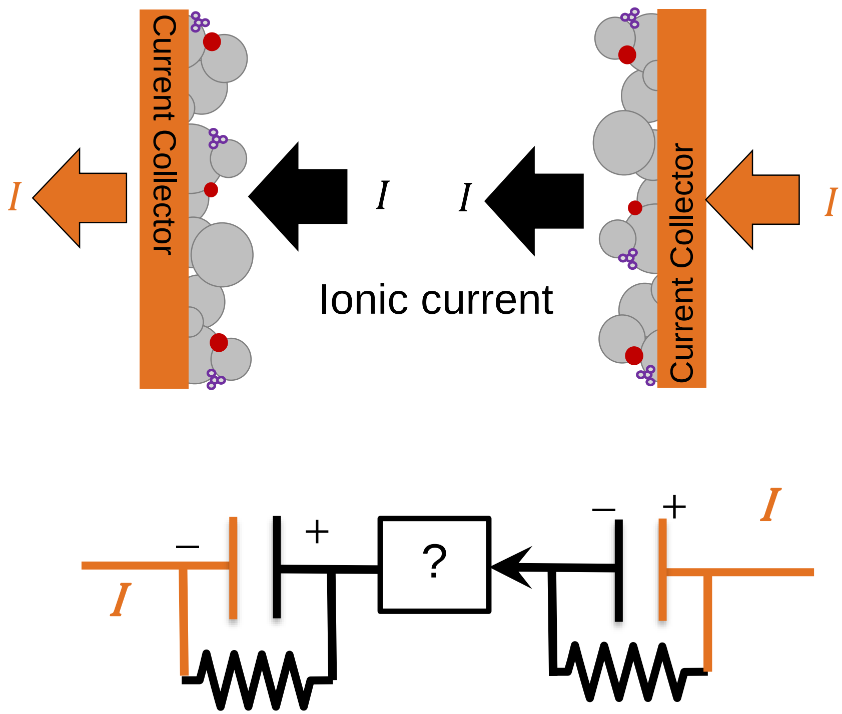
Faradaic Rxn @ Interface

Simple cases of symmetric cell

Case of Battery



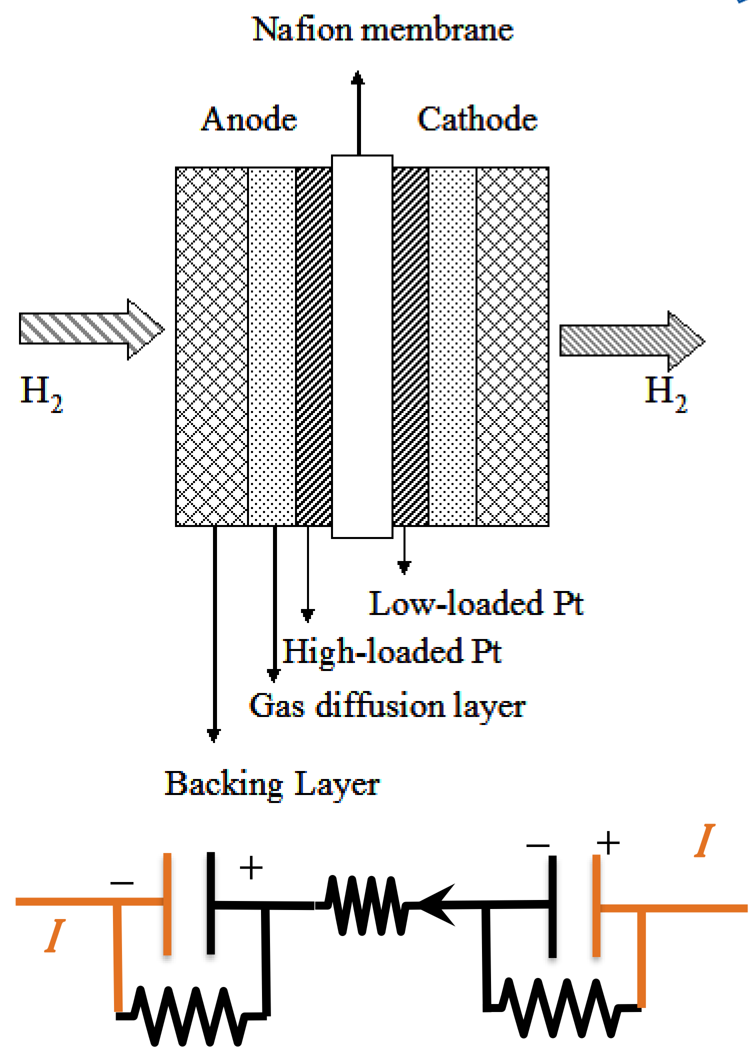


Image: Simple cases of symmetric cell Hydrogen pump experiment**Anodic oxidation of hydrogen in PEFCs at varying platinum loadings**
G. Selvarania, Bincy Johnb, P. Sridhara, S. Pitchumania and A. K. Shukla

Example: Li-Li symmetric cell

$$\underbrace{\frac{\partial c_i}{\partial t}}_{\text{Accumulation}} = \underbrace{-\nabla.\mathbf{N}_i}_{\text{Net Input}} + \text{Bulk Rnx}$$

$$\frac{\partial c_i}{\partial t} = -\nabla.(-z_i u_i F c_i \nabla\Phi - D_i \nabla c_i)$$

$$\frac{\partial c_i}{\partial t} = z_i u_i F \nabla.(c_i \nabla\Phi) + D_i \nabla^2 c_i$$

Individual governing eqn.

$$\frac{\partial c_+}{\partial t} = z_+ u_+ F \nabla.(c_+ \nabla\Phi) + D_+ \nabla^2 c_+$$

$$\frac{\partial c_-}{\partial t} = z_- u_- F \nabla.(c_- \nabla\Phi) + D_- \nabla^2 c_-$$

$$\mathbf{i} = F \sum_i z_i \mathbf{N}_i$$

$$\mathbf{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i$$

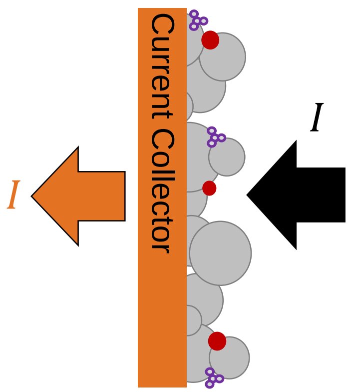
$$\mathbf{i} = -\kappa \nabla\Phi - F \sum_i z_i D_i \nabla c_i$$

Current equation:

$$\mathbf{i} = -\kappa \nabla\Phi - F(z_+ D_+ \nabla c_+ + z_- D_- \nabla c_-)$$

Complete System of Eqn.

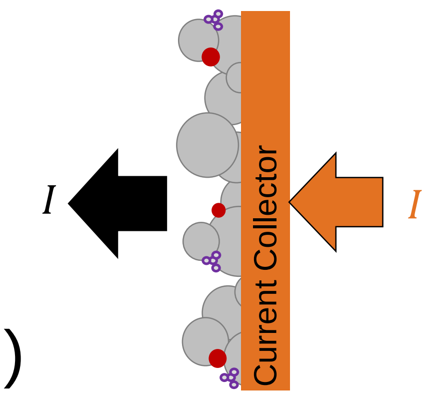
Along with Boundary Conditions:



$$\frac{\partial c_+}{\partial t} = z_+ u_+ F \nabla.(c_+ \nabla \Phi) + D_+ \nabla^2 c_+$$

$$\frac{\partial c_-}{\partial t} = z_- u_- F \nabla.(c_- \nabla \Phi) + D_- \nabla^2 c_-$$

$$\mathbf{i} = -\kappa \nabla \Phi - F(z_+ D_+ \nabla c_+ + z_- D_- \nabla c_-)$$



Only + reacts

$$\mathbf{i} = F z_+ \mathbf{N}_+$$

$$\mathbf{N}_- = \mathbf{0}$$

$$F z_+ \mathbf{N}_+ = F z_+(-z_i u_i F c_i \nabla \Phi - D_i \nabla c_i) = i$$

$$\mathbf{N}_- = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i = 0$$

Only + reacts

$$\mathbf{i} = F z_+ \mathbf{N}_+$$

$$\mathbf{N}_- = \mathbf{0}$$

$$F z_+ \mathbf{N}_+ = F z_+(-z_i u_i F c_i \nabla \Phi - D_i \nabla c_i) = i$$

$$\mathbf{N}_- = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i = 0$$

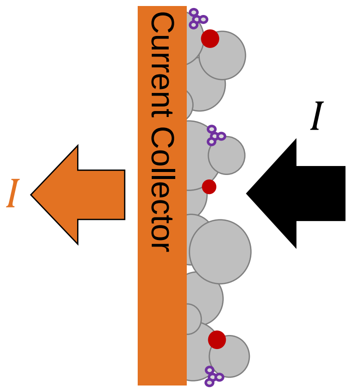
Complete System of Eqn.

Along with Boundary Conditions:

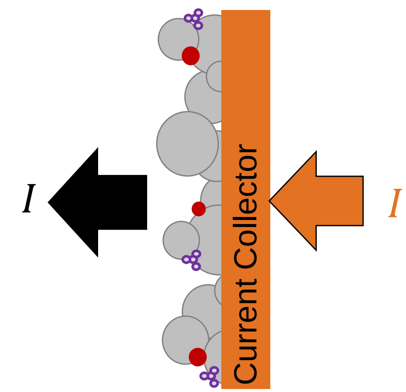
Using Electroneutrality $c_+ = c_-$

Elimination of potential from the governing equation.

Parameters used: $t_+ = \dfrac{u_+ z_+}{u_+ z_+ - u_- z_-}$ & $D = \dfrac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-}$ and κ



$$\frac{\partial c}{\partial t} = D \nabla^2 c$$



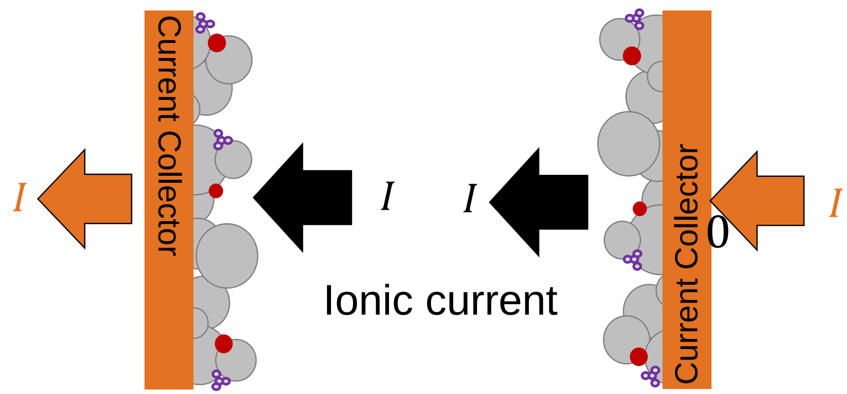
$$\frac{\mathbf{i}}{z_+ F} = \frac{D}{1 - t_+} \nabla c$$

$$\frac{\mathbf{i}}{z_+ F} = \frac{D}{1 - t_+} \nabla c$$

Solve for $c(x, t)$ first, then integrate the following equation to get ϕ

$$\mathbf{i} = -\kappa \nabla \Phi - F(z_+ D_+ + z_- D_-)\, \nabla c_+$$

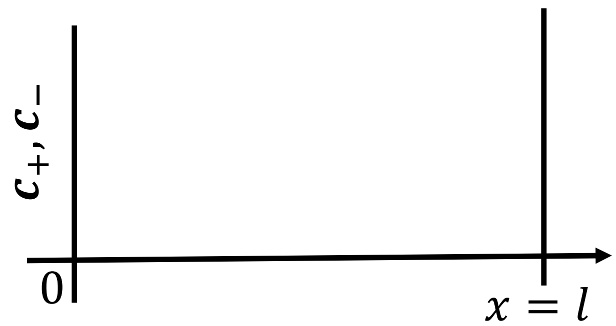
Pictorial Description: Board work

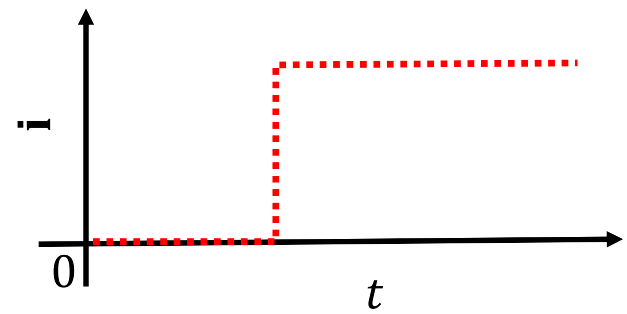


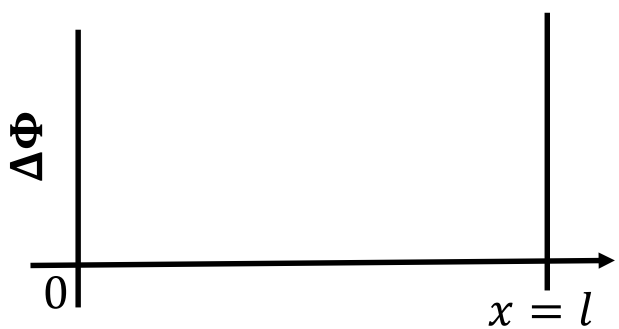
c_+ with x and t

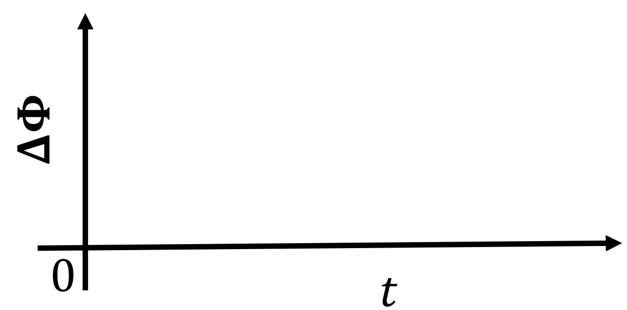
c_- with x and t

$\mathbf{i}, \boldsymbol{\Phi}$ with x and t



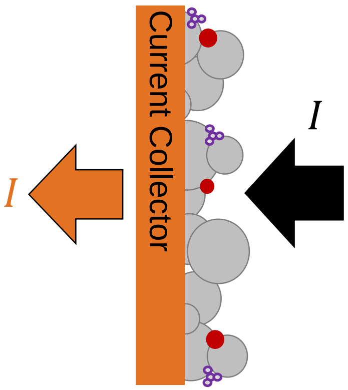




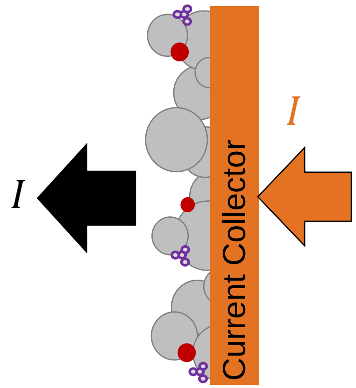


Complete System of Eqn.

Along with Boundary Conditions:



$$\frac{\partial c}{\partial t} = D\nabla^2 c$$



$$\frac{\mathbf{i}}{z_+F} = -\frac{D}{1-t_+}\nabla c \qquad \frac{\mathbf{i}}{z_+F} = -\frac{D}{1-t_+}\nabla c$$

Solve for $c(x,t)$ first, then integrate the following equation to get ϕ

$$\mathbf{i} = -\kappa\nabla\Phi - F(z_+D_+ + z_-D_-)\,\nabla c_+$$

$$F\left(z_+\frac{D}{2(1-t_+)} + z_-\frac{D}{2t_+}\right)$$

For case when $-z_- = z_+$

$$= \frac{FzD}{2}\left(\frac{1}{(1-t_+)} + \frac{-1}{t_+}\right)$$

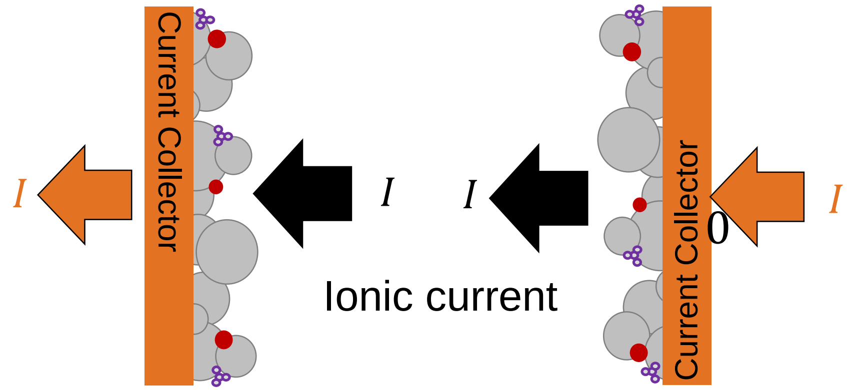
$$= -\frac{Fz_+D}{2}\left(\frac{1-2t_+}{(1-t_+)t_+}\right)$$

$$\kappa = F^2\sum_i z_i^2 u_i c_i = F^2\left(\frac{z_-^2 D c_0}{2RTt_+} - \frac{z_+^2 D c_0}{2RT(1-t_+)}\right)$$

For case when $-z_- = z_+ = z$

$$\kappa = \frac{F^2z^2Dc_0}{2RT}\left(\frac{1}{t_+} + \frac{1}{(1-t_+)}\right) = \frac{F^2z^2c_0}{2RT}\frac{D}{t_+(1-t_+)}$$

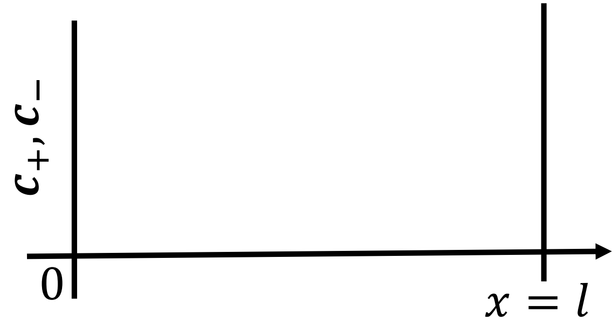
Pictorial Description: Board work

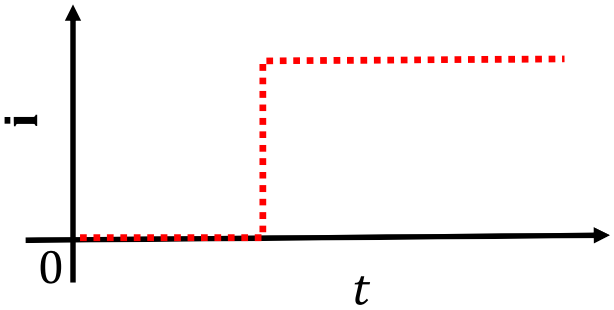


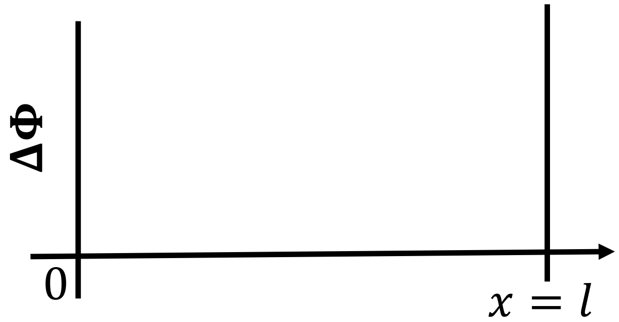
c_+ with x and t

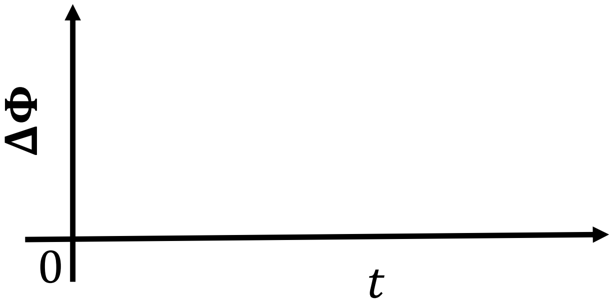
c_- with x and t

$\mathbf{i}, \mathbf{\Phi}$ with x and t









Parameters in Dilute Solution Theory

D Given
t_+ Given

$$u_+ = \frac{D}{2RT(1-t_+)}$$
$$u_- = \frac{D}{2RT t_+}$$
$$D_+ = u_+ RT = \frac{D}{2(1-t_+)}$$
$$D_- = u_- RT = \frac{D}{2t_+}$$
$$t_- = 1 - t_+$$

$$\mathbf{i} = -\kappa \nabla \Phi - F(z_+ D_+ + z_- D_-)\, \nabla c_+$$

$$\kappa = F^2 \sum_i z_i^2 u_i c_i$$
$$\kappa = F^2 \left(z_-^2 \frac{D}{2RT t_+} c_0 + z_+^2 \frac{D}{2RT(1-t_+)} c_0 \right)$$

For case when $-z_- = z_+$

$$= \frac{F^2 z^2 D c_0}{2RT} \left(\frac{1}{t_+} + \frac{1}{(1-t_+)} \right)$$
$$= \frac{F^2 z^2 c_0}{2RT} \frac{D}{t_+(1-t_+)}$$

$$F(z_+ D_+ + z_- D_-)$$
$$= F\left(z_+ \frac{D}{2(1-t_+)} + z_- \frac{D}{2t_+} \right)$$

For case when $-z_- = z_+$

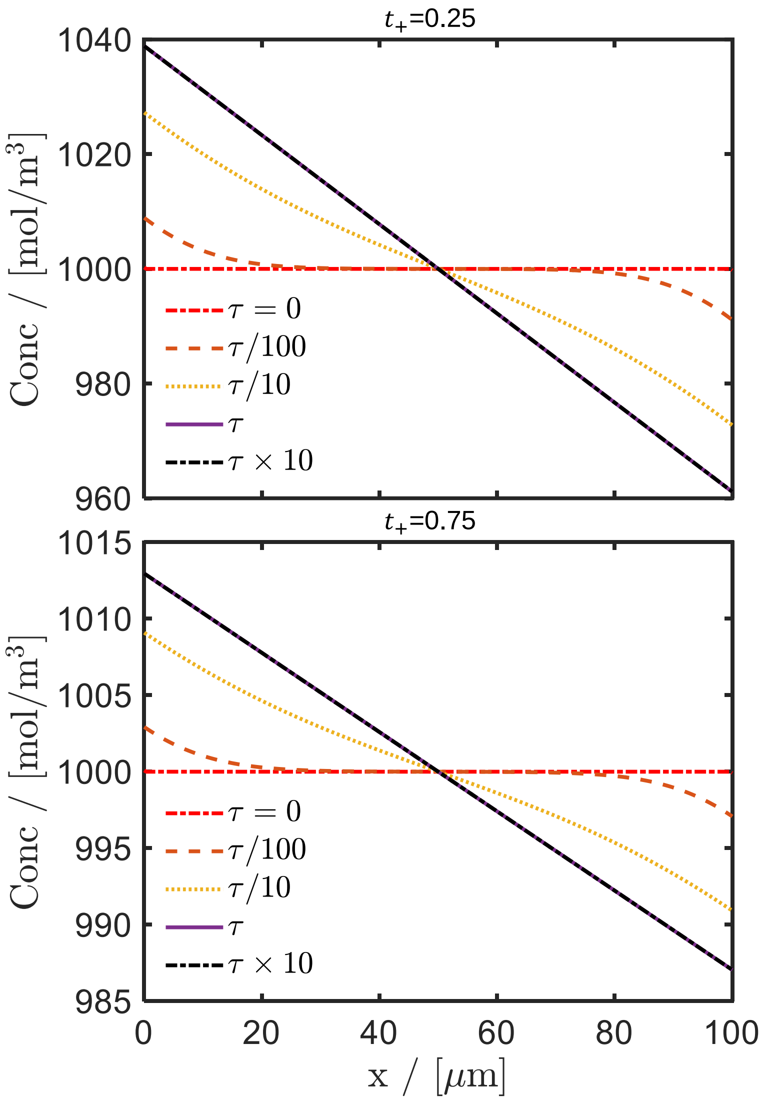
$$= \frac{Fz\, D}{2} \left(\frac{1}{(1-t_+)} + \frac{-1}{t_+} \right)$$
$$= -\frac{F z_+ D}{2} \left(\frac{1-2t_+}{(1-t_+)t_+} \right)$$

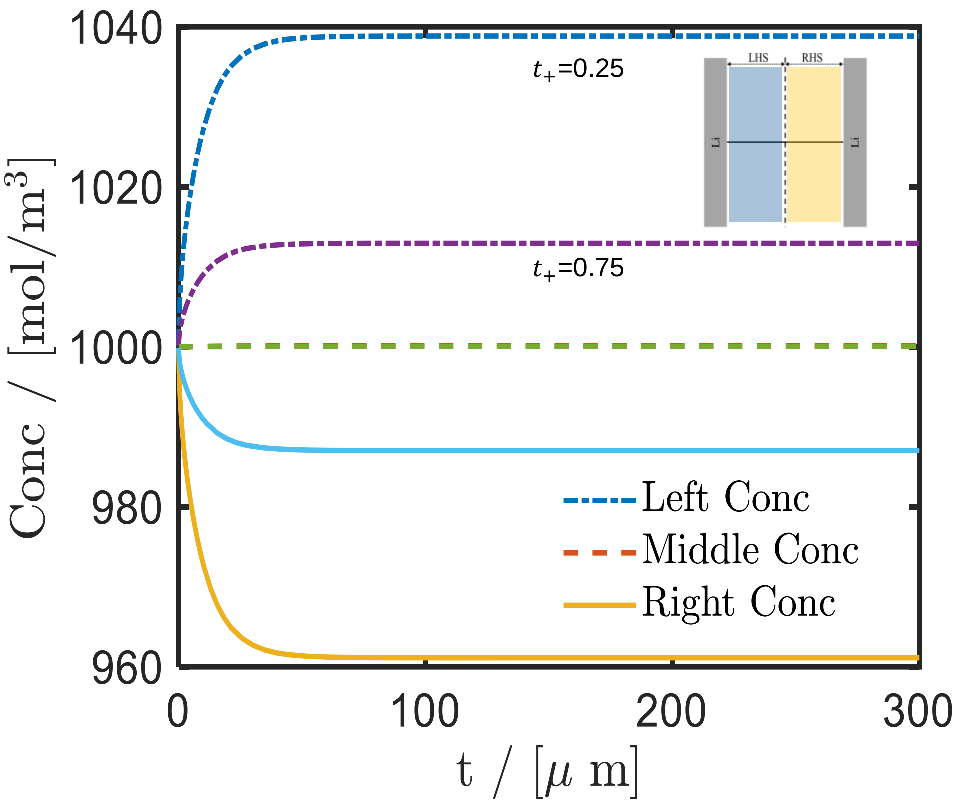
Typical Numbers!

z_+	1 (e.g Li^+)				
z_-	-1 (e.g PF_6^-)				
D	1.00E-10 [m^2/s]				
t_+	$\rightarrow 0$	¼	½	¾	$\rightarrow 1$
t_-	$\rightarrow 1$	¾	½	¼	$\rightarrow 0$
$\boldsymbol{u_+}$	2.02E-14	2.69E-14	4.04E-14	8.07E-14	2.02E-10
u_-	2.02E-10	8.07E-14	4.04E-14	2.69E-14	2.02E-14
D_+	5.00E-11	6.67E-11	1.00E-10	2.00E-10	5.00E-07
D_-	5.00E-07	2.00E-10	1.00E-10	6.67E-11	5.00E-11
$\boldsymbol{\kappa}$	$\rightarrow \infty$	1	0.75	1	$\rightarrow \infty$
C_0	1 molar				
$F(\boldsymbol{z_+ D_+} + \boldsymbol{z_-} D_-)$	-4.82E-02	-1.29E-05	0	1.29E-05	4.82E-02

Transference No. 0.25 and 0.75

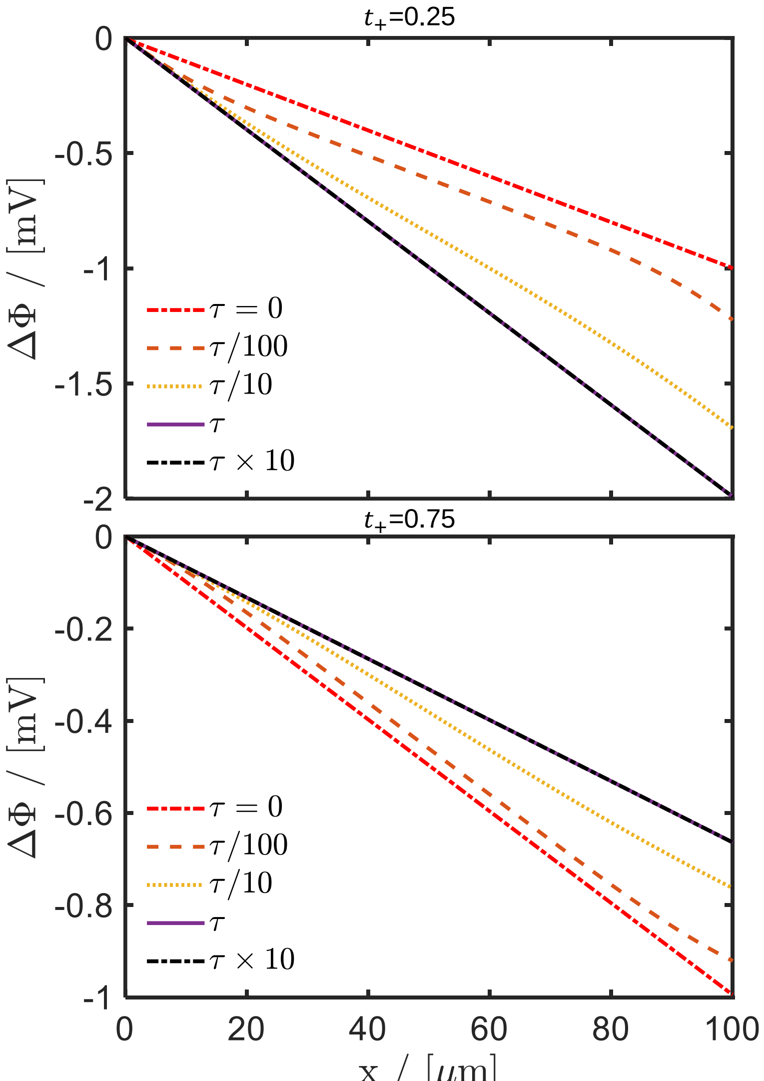
Development of concentration gradient with time:

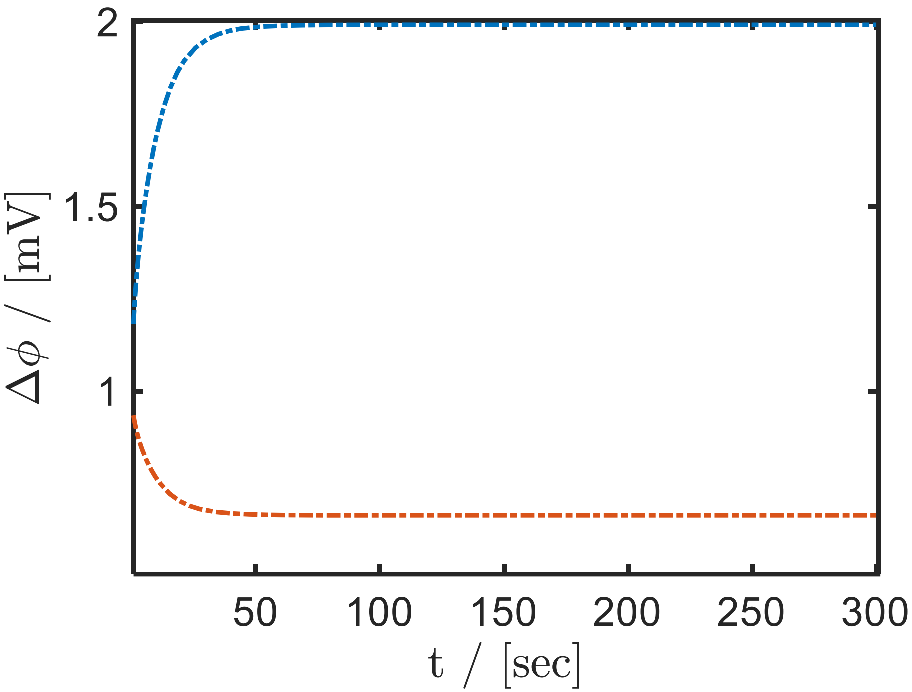




Transference No. 0.25 and 0.75

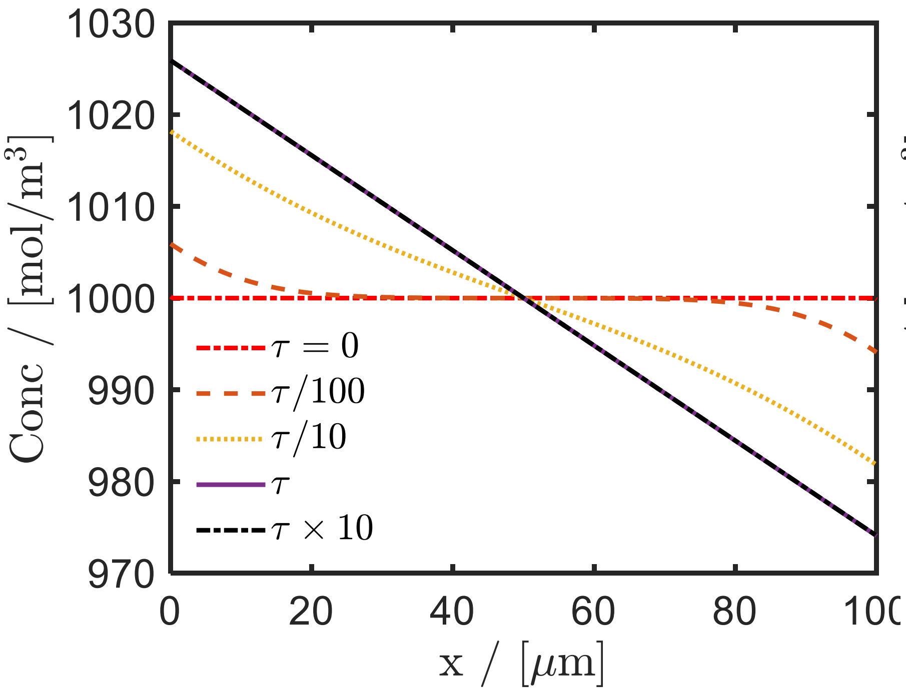
Potential drop across the separator with time:

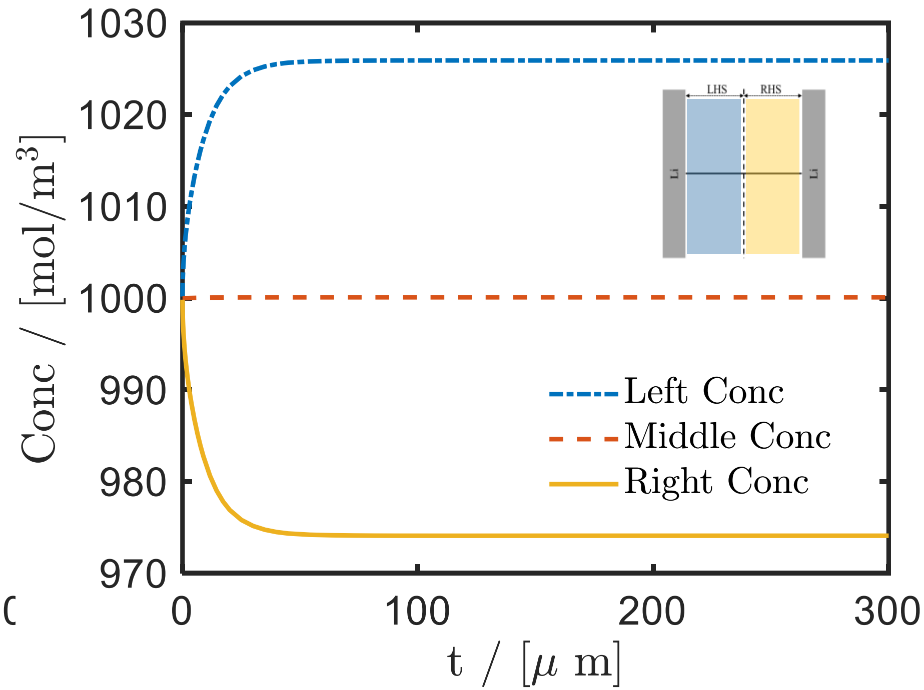




Transference No. 0.5

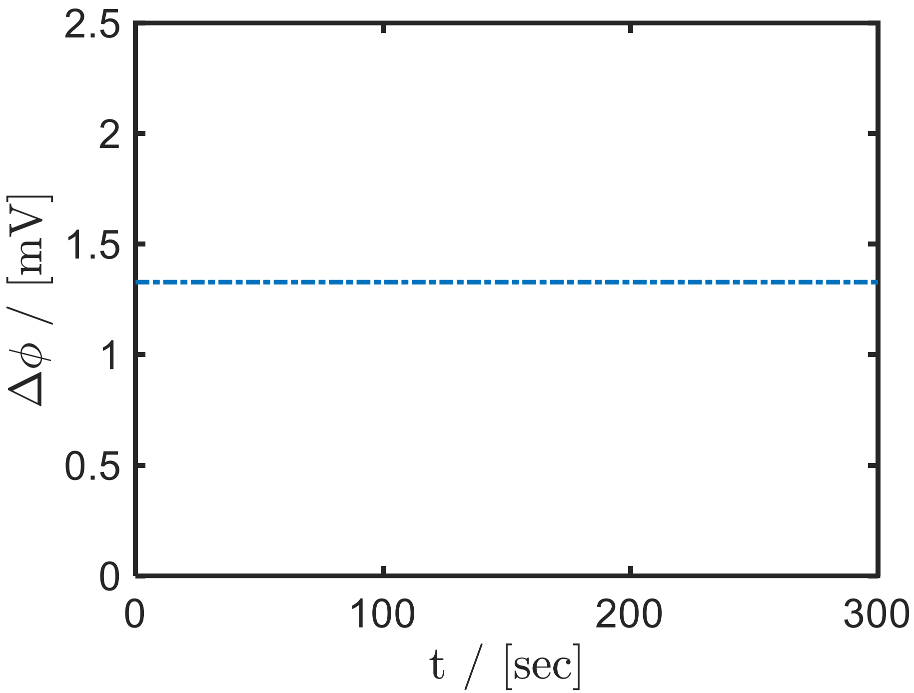
Development of concentration gradient with time:

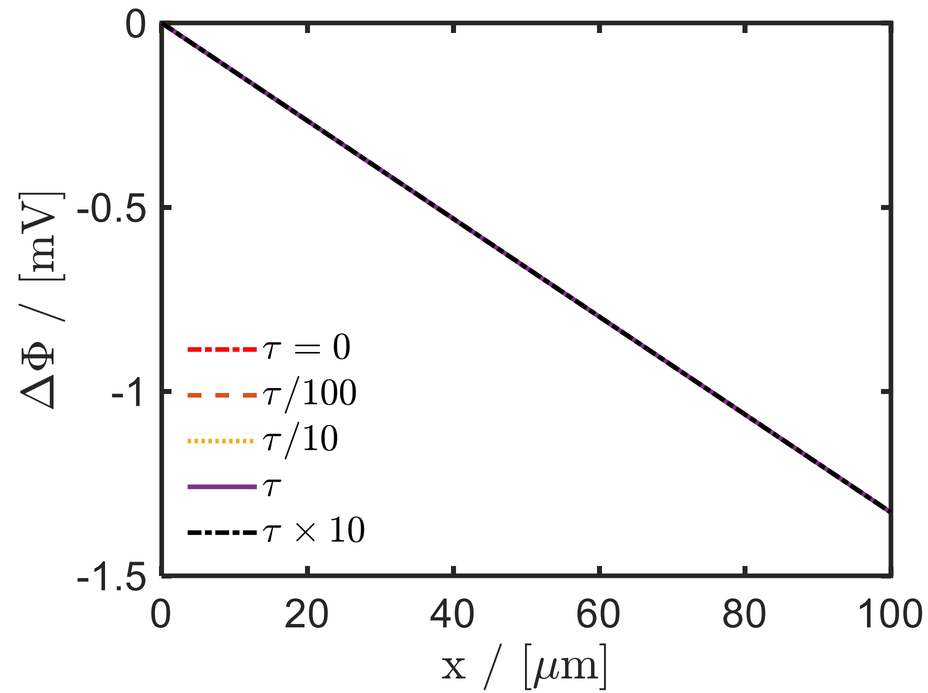




Transference No. 0.5

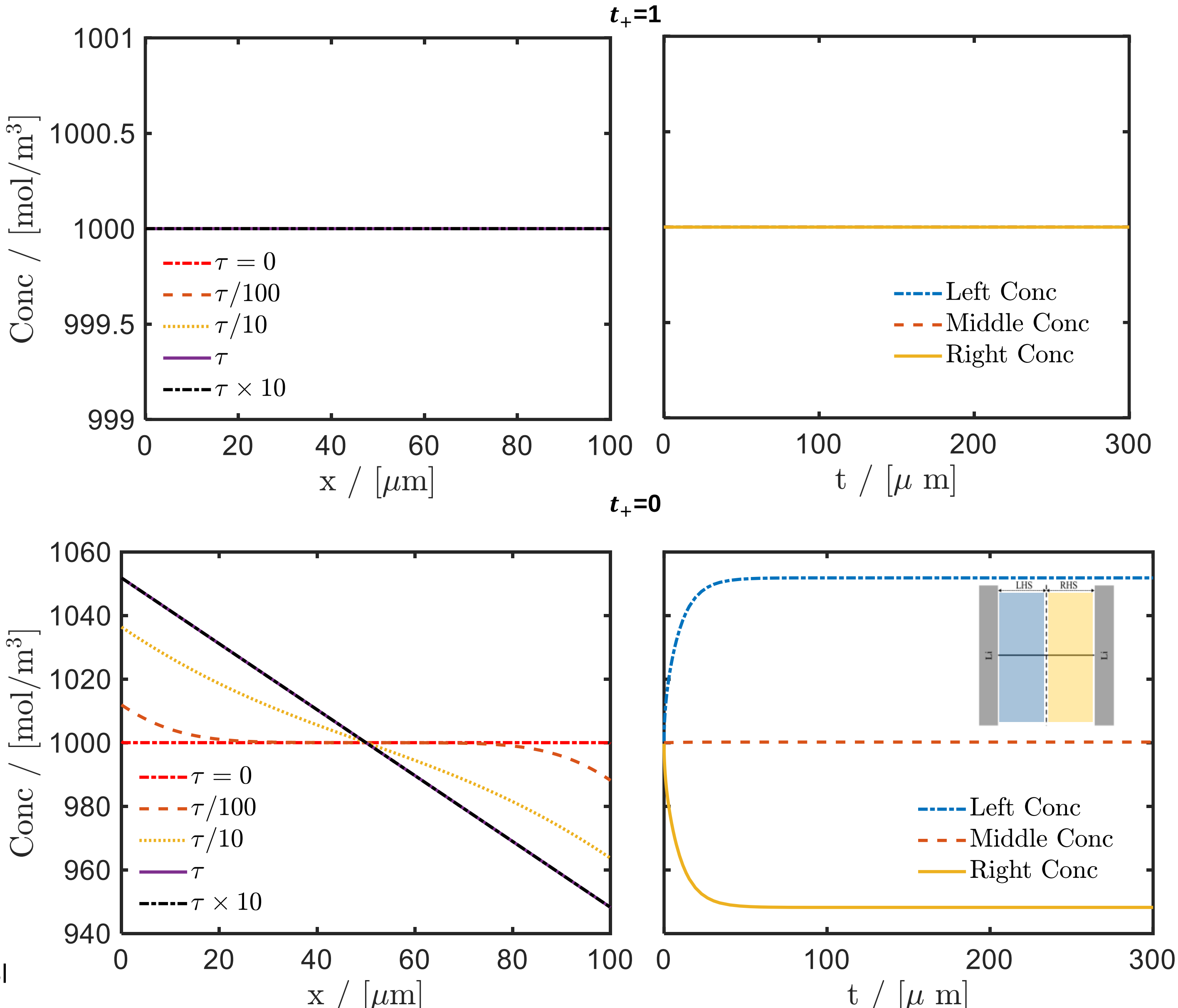
Potential drop across the separator with time:





Transference No. 0 and 1

Development of concentration gradient with time:



Excess Supporting Electrolyte

- Excess salt which is not involve in Rxn.
- What type of influence it will have?
  - There are more than 2 ionic species. E.g. $CuSO_4$ and H_2SO_4 in water

$$\mathbf{N}_i = \underbrace{-z_i u_i F c_i \nabla \phi}_{migration} \quad \underbrace{-D_i \nabla c_i}_{diffusion} \quad + \quad \underbrace{c_i \mathbf{v}}_{convection} \quad .$$

- What can we say about N_i of nonreacting species.
  - What is ∇c_i of these species?
- $\nabla \phi$ drops down in the solution

$$\mathbf{N}_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i \mathbf{v}$$

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i = D_i \nabla^2 c_i .$$

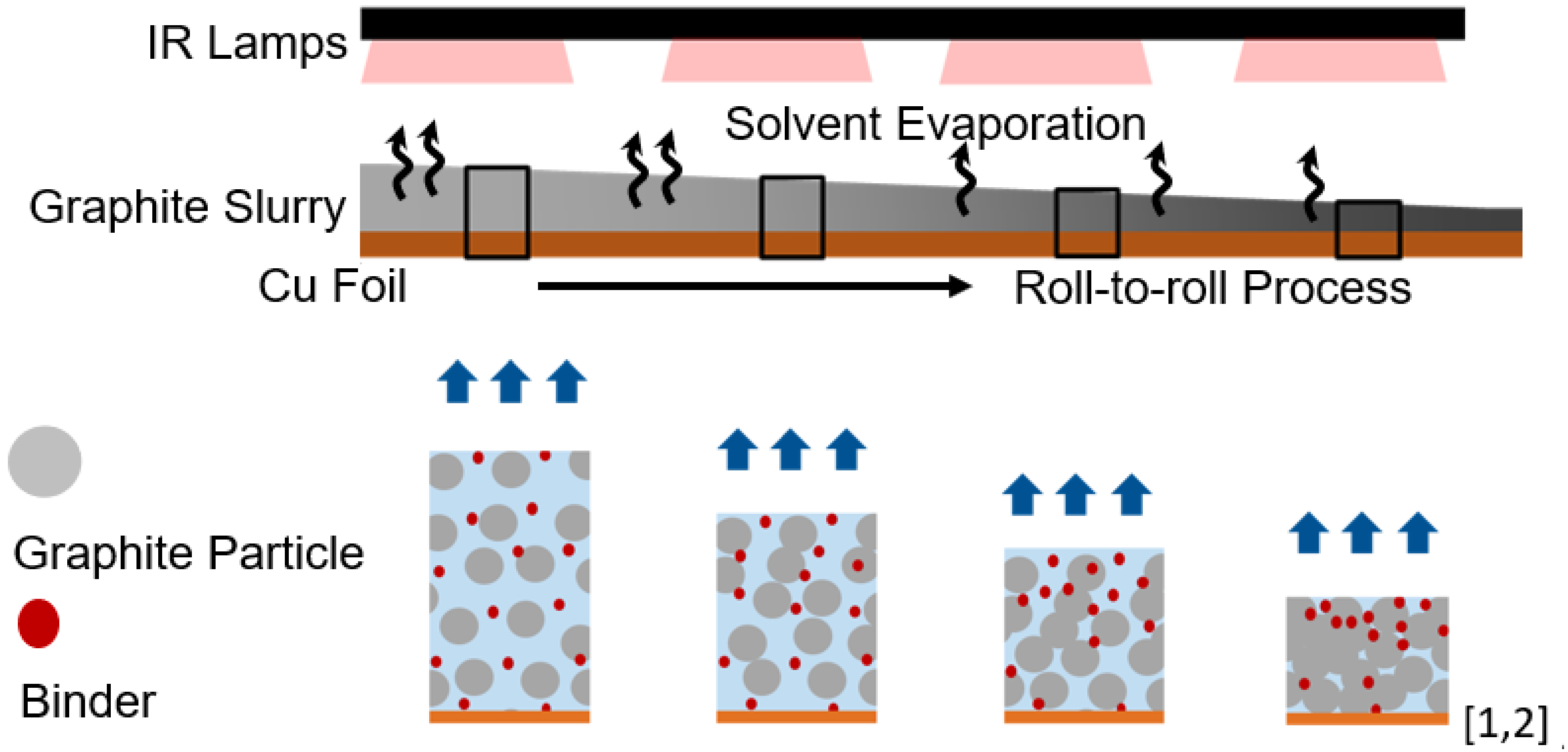
$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i .$$

Porous Media:

Highly porous

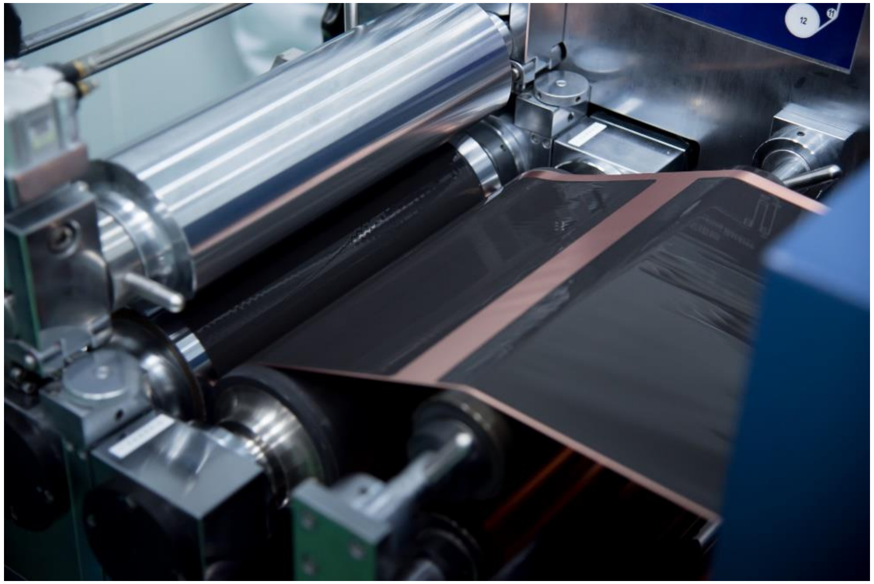
Not porous

How porous electrodes are made?

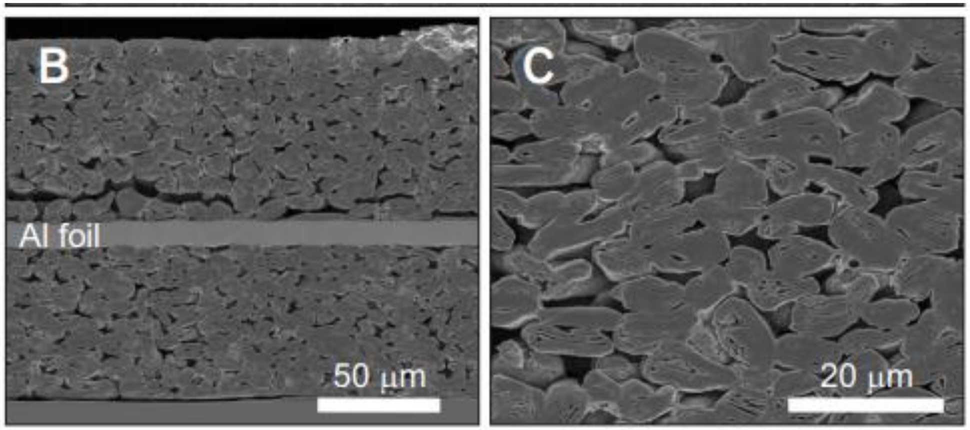


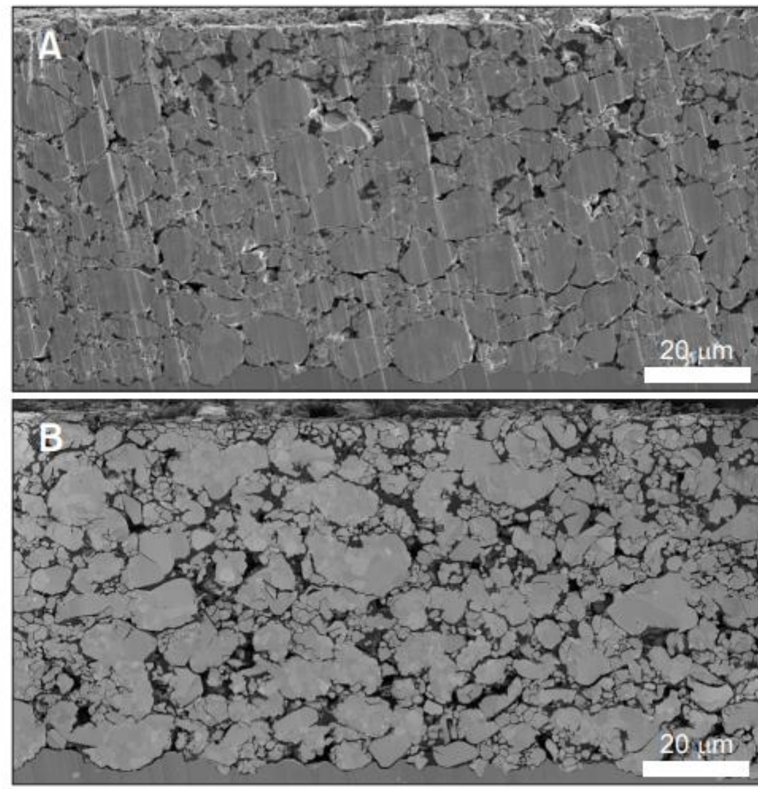
1. Muller et al., *J. Power Sources*, (2017)
2. Morasch et al., *J. Electrochem. Soc.*, (2018)

Porous Electrode:



Cross section of battery electrode





https://koreascience.kr/article/JAKO201720861274899.pdf

Porous Media: Separator vs Electrode

Dishwasher Plastic foam:
Porous separator equivalent

https://www.amazon.in/

Dishwasher metal mesh, or
metal foam
Porous electrode equivalent

https://www.recemat.nl/copper-foam/

1. Which porous media can support electronic current?
2. Which porous media can provide double layer capacitance?

Porous Electrode: Properties

- Volume Fractions: ε
- Characteristic pore size
  - Pore size distribution
- Specific surface area: a $\left[\frac{\mathrm{m}_{\mathrm{BET}}^2}{\mathrm{m}_{\mathrm{electrode}}^3}\right]$

- Effective resistance (R_{eff})
  - Tortuosity Factor (τ)
  - McMullin number ($\mathrm{N_m}$)

- Effective conductivity (κ_{eff})
- Effective diffusivity (D_{eff})

Porous Electrode:

Volume Fractions: $\boldsymbol{\varepsilon}$

1. Definition
2. Void volume fraction (Porosity)
    1. Electrolyte volume fraction ($\varepsilon_{\mathrm{elyt}}$)
3. Solid volume fractions
    1. Active material volume fraction ($\varepsilon_{\mathrm{AM}}$)
    2. Binder (polymer) volume fraction ($\varepsilon_{\mathrm{Binder}}$)
    3. Conductive carbon volume fraction ($\varepsilon_{\mathrm{CC}}$)
4. $\Sigma\varepsilon_i = 1$

5. For fuel cell void volume fraction and ionomer volume fractions both exists.
    1. Void volume fraction = mostly gas transport
    2. Ionomer volume fraction: mostly ion transport

Meaning of $\boldsymbol{\varepsilon = 0}$, examples?

Meaning of $\boldsymbol{\varepsilon = 1}$, examples?

Porous Electrode:

Specific Surface Area

1. Unit of $\left[\frac{\mathrm{m}^2_{\mathrm{BET}}}{\mathrm{m}^3_{\mathrm{superficial}}}\right]$
2. '*Electroactive*' surface area/volume element in the electrode.
    1. Should it be same for reaction and double layer capacitance?
    2. Conductive carbon based area, where should it be used?

$$a \equiv \frac{\text{interfacial area}}{\text{superficial volume}}.$$

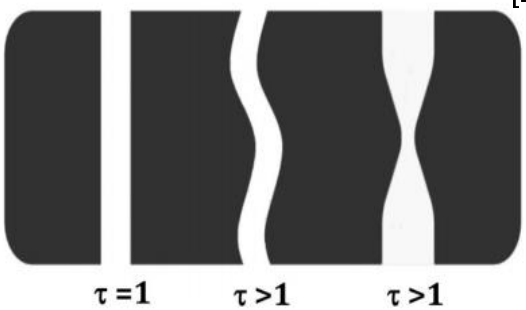
$$a = \frac{(\text{number of spheres})4\pi r^2}{\text{volume}} = \frac{\dfrac{V(1-\varepsilon)}{{}^4\!/_3\pi r^3}4\pi r^2}{V} = \frac{3(1-\varepsilon)}{r}.$$

1. Image Fuller and Harb

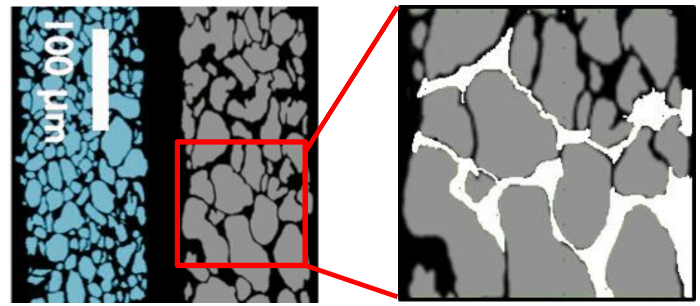
Porous Electrode:

Tortuosity

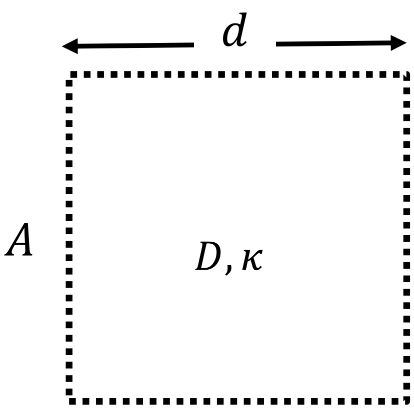
[1]



Tortuosity For Porous Media



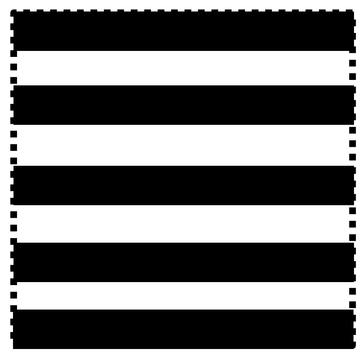
[2]



Pure Electrolyte

$$D_{\text{eff}} = D \quad \kappa_{\text{eff}} = \kappa$$

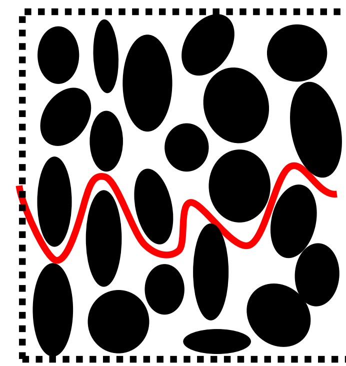
$$R_{\text{ion}} = d/(A\kappa_{\text{eff}})$$



Straight Pores

$$D_{\text{eff}} = D\varepsilon \quad \kappa_{\text{eff}} = \kappa\varepsilon$$

$$R_{\text{ion}} = d/(A\kappa_{\text{eff}})$$



Tortuous Pores

$$D_{\text{eff}} = D\frac{\varepsilon}{\tau} \quad \kappa_{\text{eff}} = \kappa\frac{\varepsilon}{\tau}$$

$$R_{\text{ion}} = d/(A\kappa_{\text{eff}})$$

1. Cooper et al., *J. Power Sources*, (2014)

2. Smith et al., *J. Electrochem. Soc.*, (2009).

Porous Electrode:

How to measure the porosity by using mass of the electrode only?

Does tortuosity depend on porosity?

Is tortuosity a geometric factor?

Porous Electrode:

McMullin Number

1. Ratio of tortuosity to porosity ($N_{\mathrm{m}} = \tau/\varepsilon_{\mathrm{elyt}}$ or $N_{\mathrm{m}} = \tau/\varepsilon_{\mathrm{ionomer}}$)
2. Used when the deconvolution of porosity and tortuosity is not straight forward
    1. E.g. fuel cell electrode where ionomer volume fraction may not be known exactly.

Ideal Porous Electrode

Tortuosity =1, straight pores with uniform cross section area

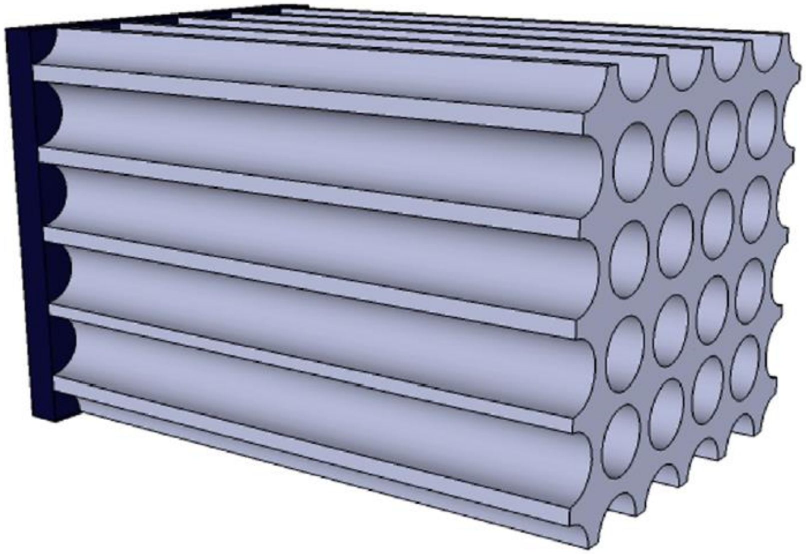
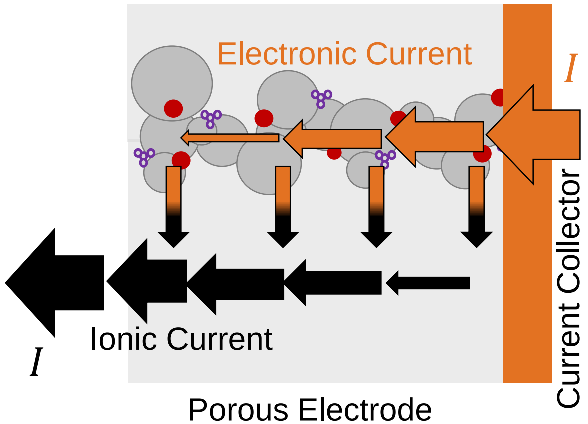
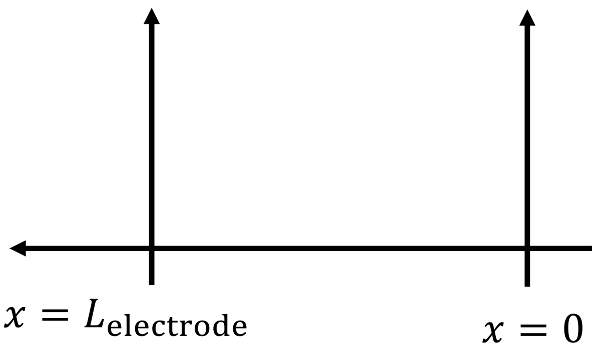


Figure 5.1 Straight pores of an idealized porous electrode.

1. Image Fuller and Harb

Transport in Porous Media





$$i_1(x=0) = \frac{I}{A}\left[\frac{\mathrm{A}}{\mathrm{m}^2_{\mathrm{x-sec}}}\right]$$

A cross section area (x-sec)

$$i_2(x=L) = \frac{I}{A}$$

$$i_1(x) + i_2(x) = \frac{I}{A}$$

Derivative wrt x.

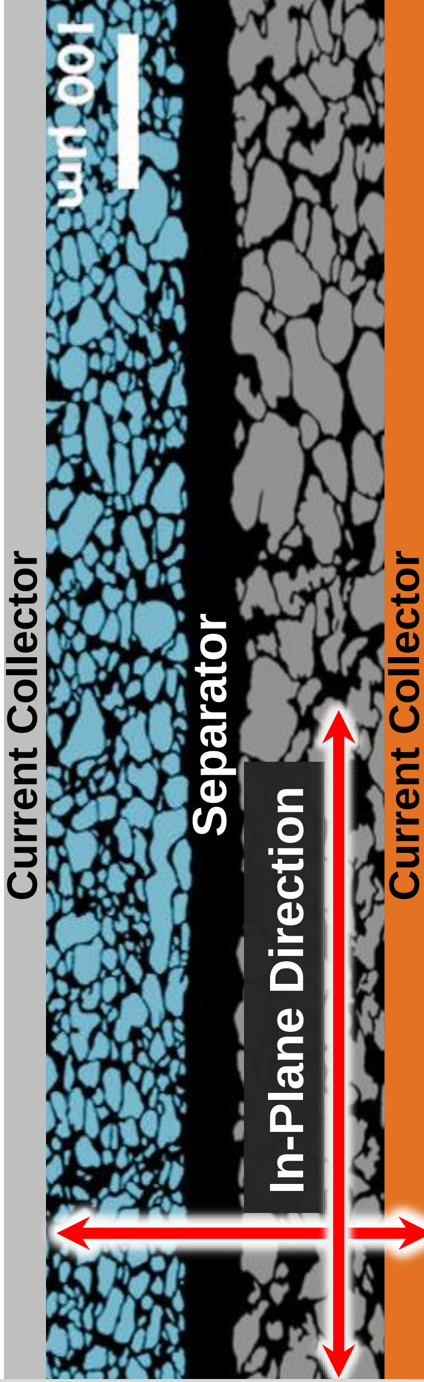
$$\nabla \cdot i_1(x) + \nabla \cdot \ i_2(x) = 0$$

What does $\nabla \cdot i_1(x)$ represent?

- Reaction and double layer current
- Source or sink terms

$$\nabla \cdot i_1(x) = -a i_n$$

$$\nabla \cdot \ i_2(x) = \underbrace{a i_n}_{\left[\frac{\mathrm{m}^2_{\mathrm{BET}}}{\mathrm{m}^3} \times \frac{\mathrm{A}}{\mathrm{m}^2_{\mathrm{BET}}} = \frac{\mathrm{A}}{\mathrm{m}^3}\right]}$$



1. Image: Smith et al., *J. Electrochem. Soc.*, (2009).

Transport in Porous Media

Analogy of flow in pipe.

Species Balance Equtions

For electrolyte only (no porous media)

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + \mathcal{R}_i.$$

$$\mathbf{N}_i = \underbrace{-z_i u_i F c_i \nabla \phi}_{migration} \underbrace{-D_i \nabla c_i}_{diffusion} + \underbrace{c_i \mathbf{v}}_{convection}.$$

For porous media:

$$\frac{\partial \varepsilon c_i}{\partial t} = -\nabla \cdot N_i + \mathcal{R}_i.$$

$$N_i = -\varepsilon D_i \nabla c_i - \varepsilon z_i u_i F c_i \nabla \phi + \varepsilon c_i \mathbf{v},$$

$$\mathcal{R}_i = a j_n, \qquad j_n = -\frac{s_i}{nF} i_n.$$

$$\frac{\partial \varepsilon c_i}{\partial t} = -\nabla \cdot \boldsymbol{N}_i - a \frac{s_i}{nF} i_n = -\nabla \cdot \boldsymbol{N}_i - \frac{s_i}{nF} \nabla \cdot \boldsymbol{i}_2.$$

EIS of a symmetric cell

Demo

Next

Current distribution (4.7 in Fuller Book)

Current Distribution

"*Current distribution refers to how the current density varies across the surface of an electrode.*"[1]

- Uniform current density
- Uniform deposition vs nonuniform deposition

- Relative weightage of ohmic and reaction resistance

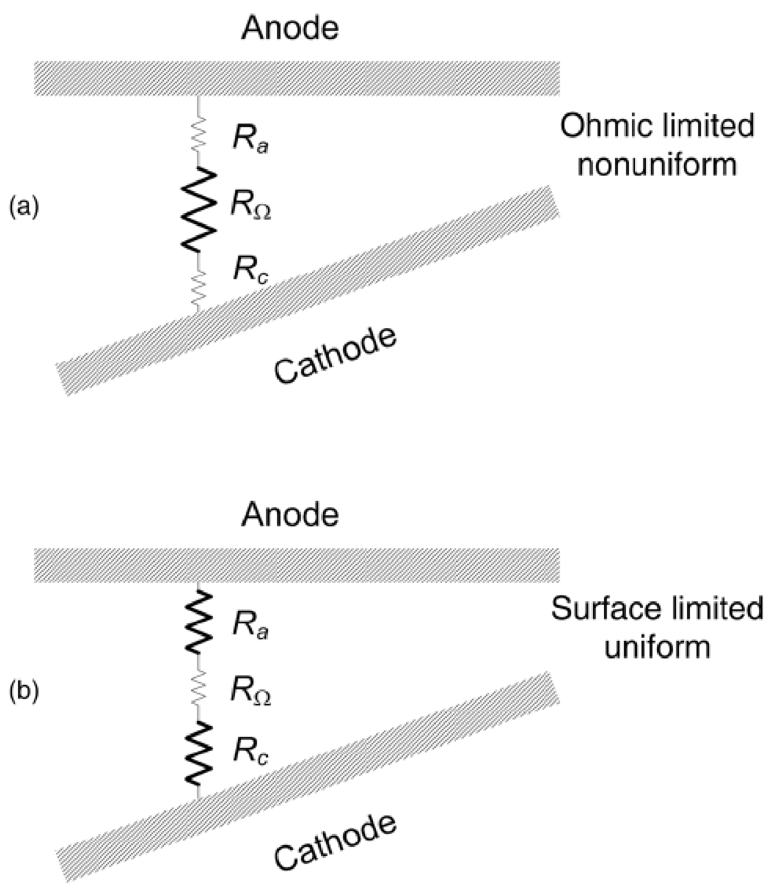


Figure 4.11 Ohmic and charge-transfer (surface) resistances.

1: Fuller and Harb

Current Distribution: No Conc Gradient

Ohmic resistance: $R_\Omega = \frac{L}{A\kappa}$

Charge transfer resistance: $R_{\text{ct}} = \frac{1}{A}\frac{d\eta_s}{di}$

Wagner Number = Wa $= \frac{R_{\text{ct}}}{R_\Omega} = \frac{\kappa}{L}\frac{d\eta_s}{di}$,

BV Kinerics

$$i = i_o\left[\exp^{\frac{\alpha_a F}{RT}\eta_s} - \exp^{\frac{-\alpha_c F}{RT}\eta_s}\right],$$

Wa

$$\text{Linear kinetics :} \quad \text{Wa} = \frac{\kappa}{L_c}\frac{RT}{F}\frac{1}{i_o(\alpha_a + \alpha_c)}.$$

$$\text{Tafel kinetics :} \quad \text{Wa} = \frac{RT\kappa}{FL_c}\frac{1}{|i_{avg}|\alpha_c}.$$

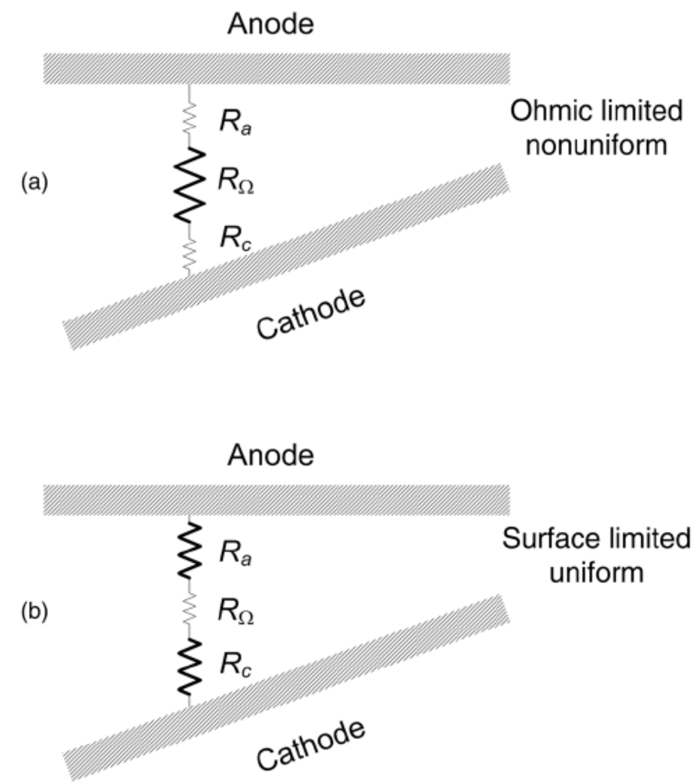


Figure 4.11 Ohmic and charge-transfer (surface) resistances.

- $Wa \gg 1$ Kinetics dominate Uniform current density
- $W \rightarrow 0$ Ohmic resistance dominate, Non-uniform current density

Influencing factors for Wa

How to change/influence the Wa?

Conductivity, Length scale, Exchange current density, Overall current?

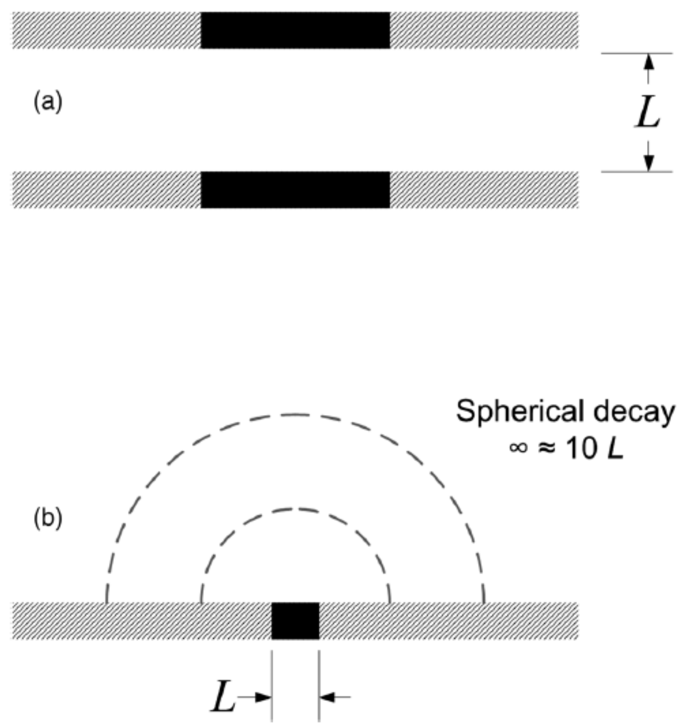
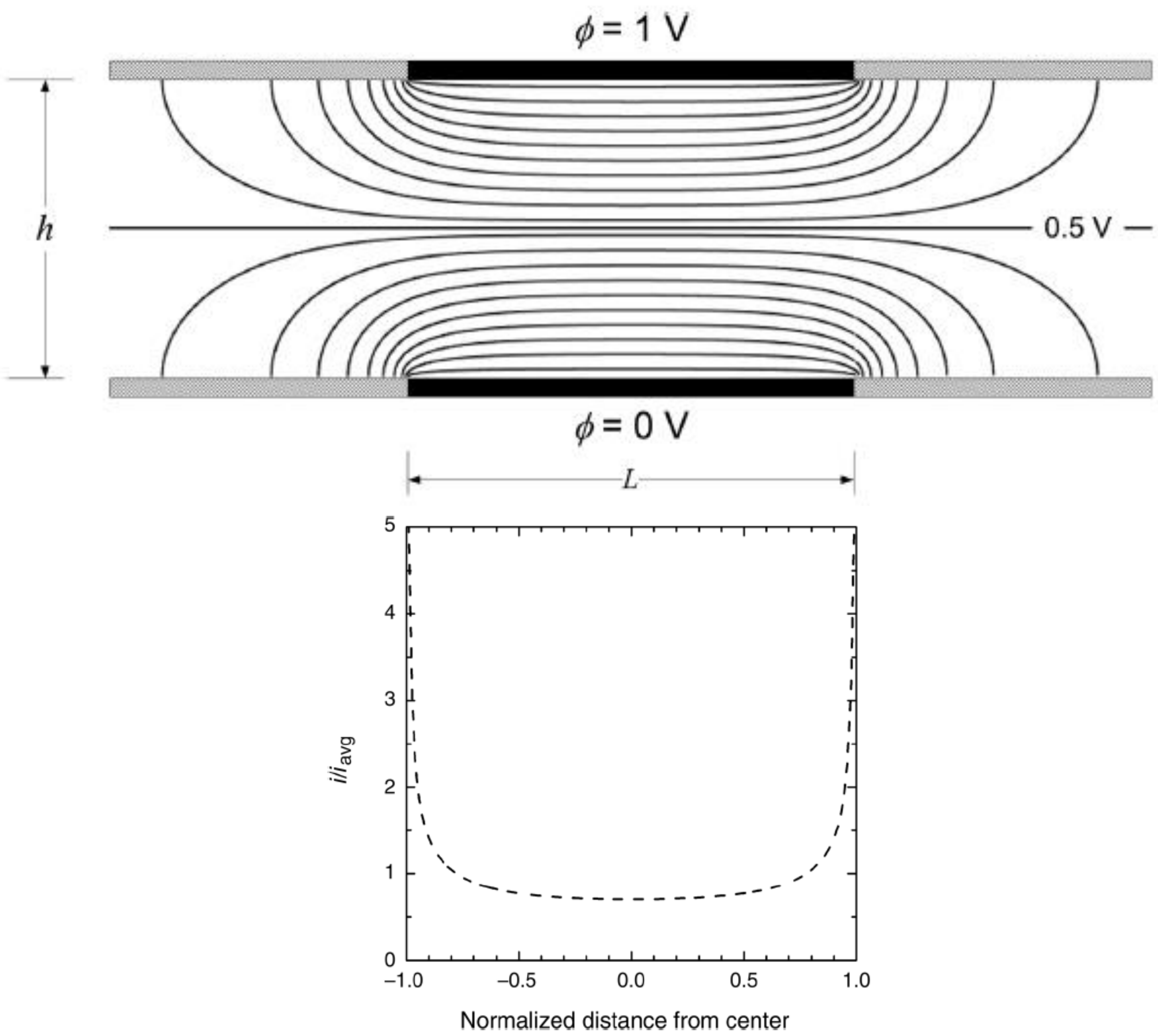
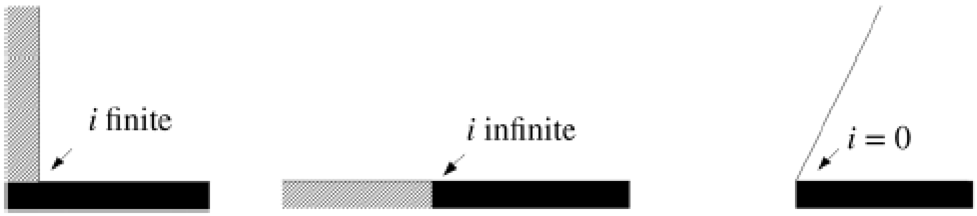


Figure 4.12 Characteristic length.

Primary Current Distirbution: Wa=0



Primary Current Distribution



Wa vs current density distribution

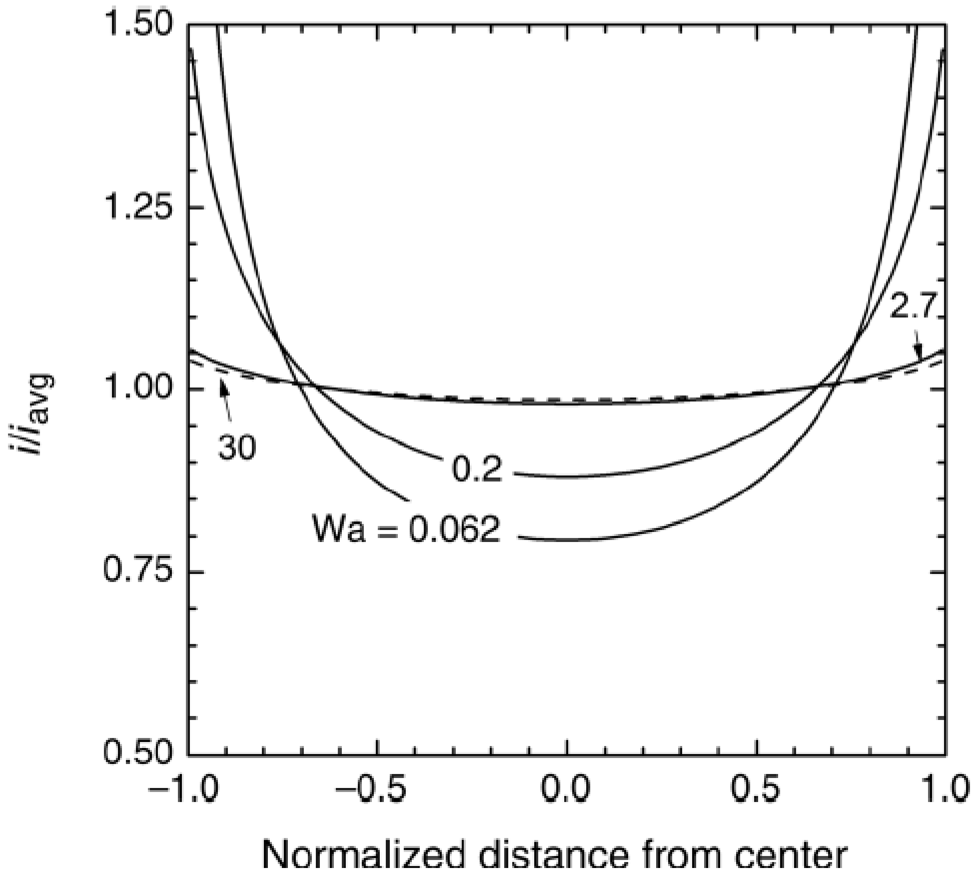


Figure 4.16 Primary current distribution between two parallel plate electrodes. The distance between the electrodes (h) is 1.25 times the electrode width (L). Geometry and conductivity.

Reference:

- Fuller and Harb
- Newman and xxx
- Bockris and Reddy