Warsaw University of Technology

Transport properties of electrolytes

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Introduction

„Although the role of electrolyte is often considered trivial, its choice is actually crucial…”

J.-M. Tarascon & M. Armand, NATURE, 414, 2001

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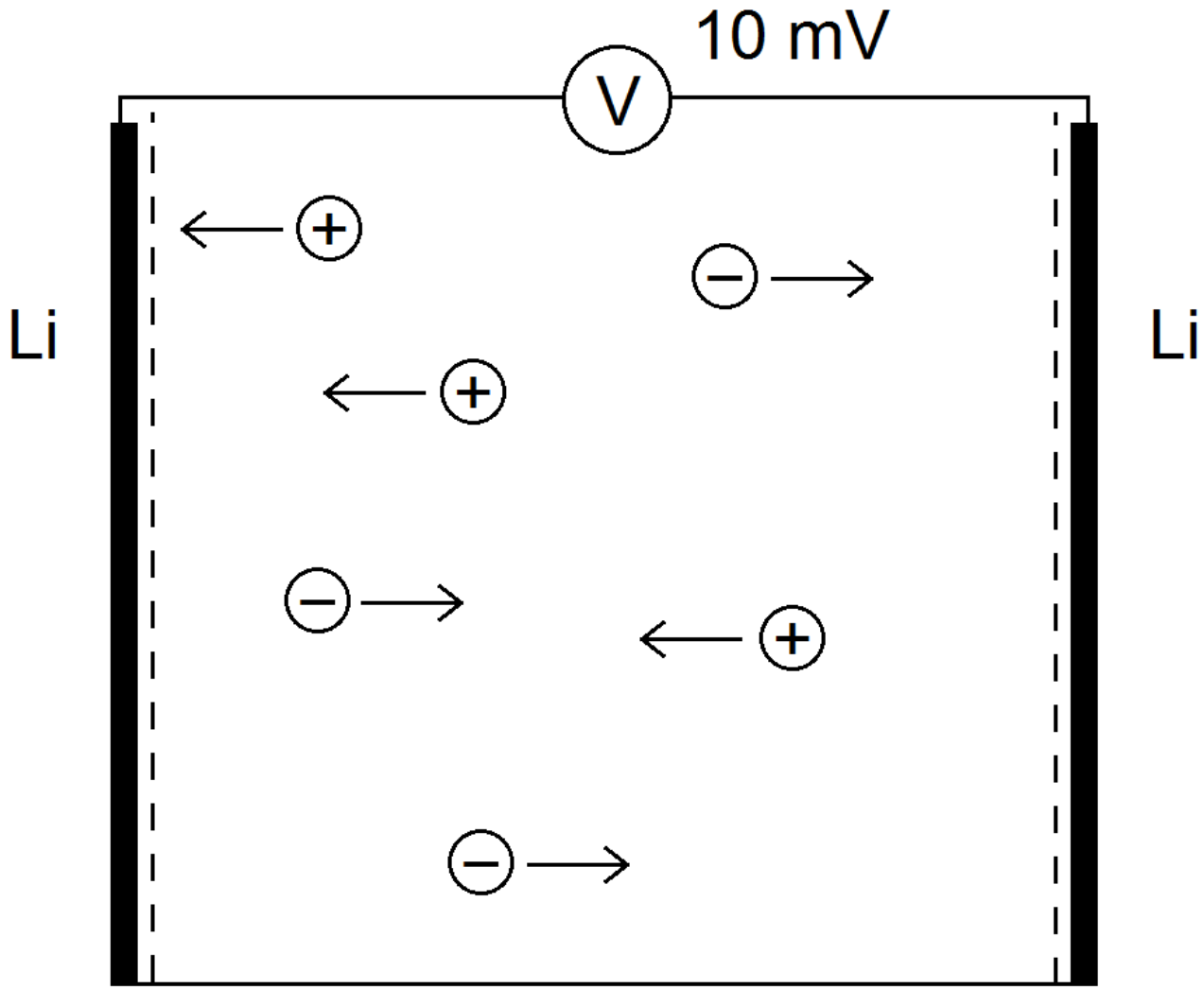
The ion transport properties are one of the most important aspects taking to account during development of new electrolytes

Introduction

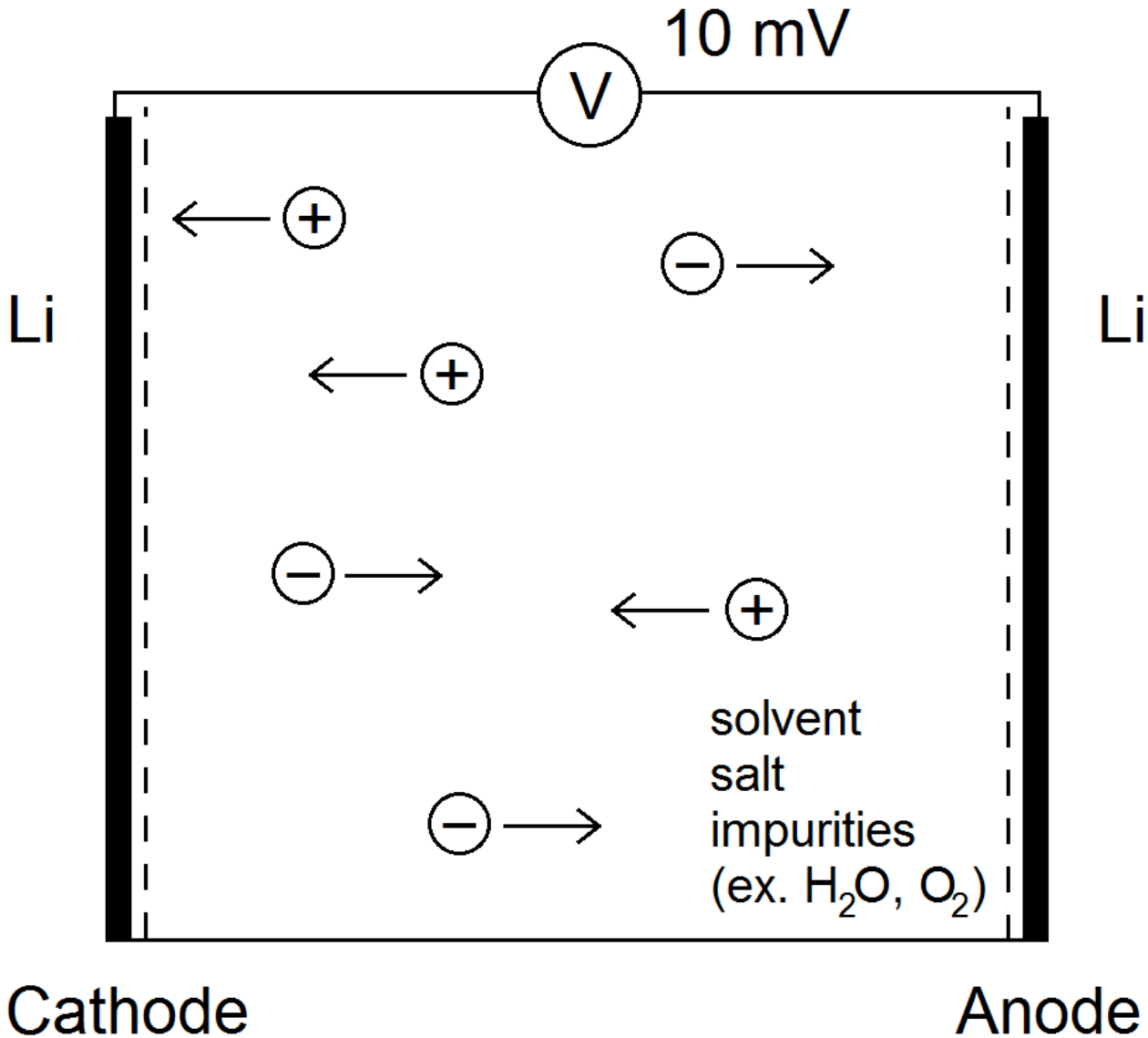
- The ability to conduct ions is the basic function of electrolytes

- In liquid electrolytes, the transport of ions is realized via a two-step process:
  - (1) the solvation and dissociation of ionic compounds (usually crystalline salts) by polar solvent molecules and
  - (2) the migration of these solvated ions through the solvent media.

1 Lithium Transference Number



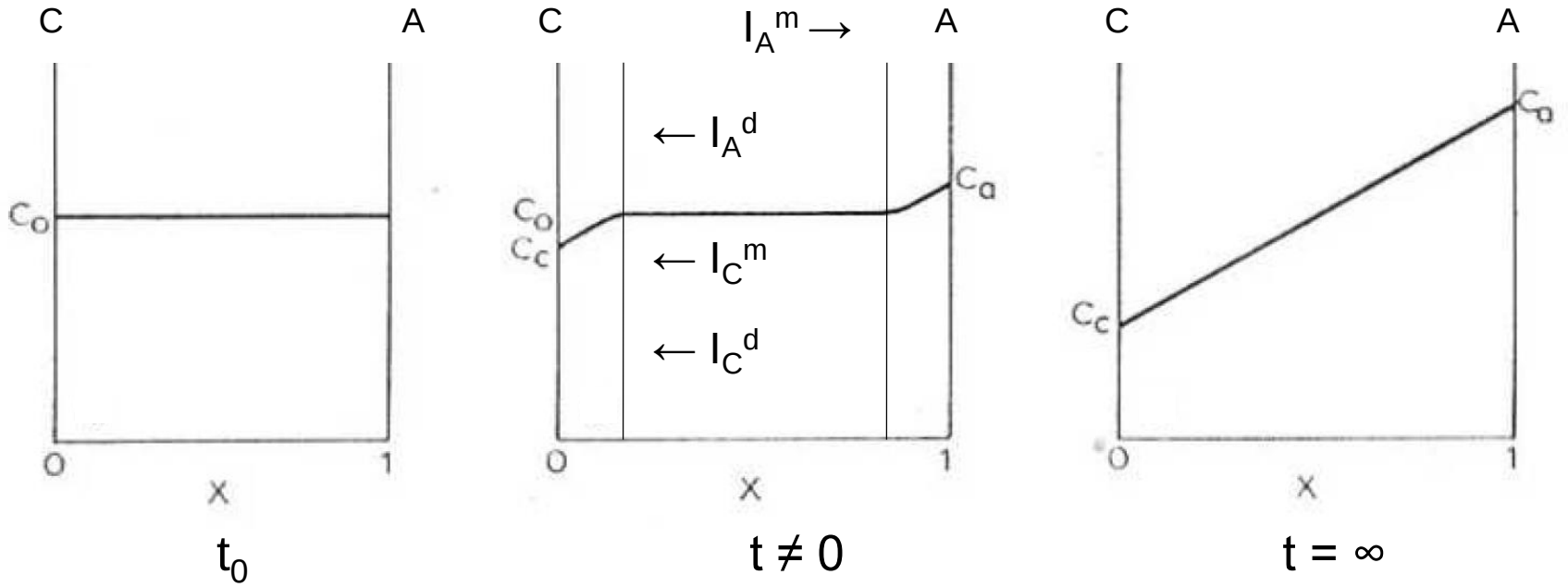
- diffusion
- migration
- convection


10 mV
V
Li
Li
solvent
salt
impurities
(ex. H_2O, O_2)
Cathode
Anode

Ideal electrolyte

- ion-ion interactions may be neglected
- $M \rightarrow M^+ + e^-$ and $M^+ + e^- \rightarrow M$ infinitely fast
- no convection
- c of M^+X^- remains high

Ideal electrolyte



$$|I_A^d| = |I_A^m| = 0$$

$$2I_C^d = 2I_C^m = I_\infty$$

1 $$I_0 = |I_C| + |I_A|$$

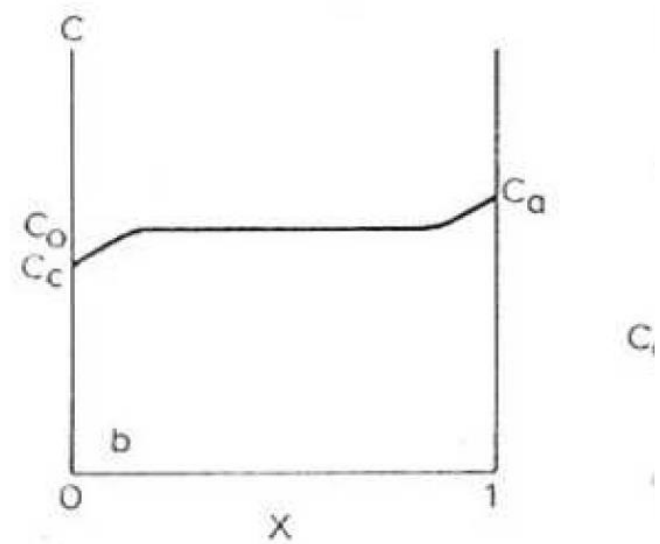
$$I_0 = \frac{U}{R}$$

$$t \neq t_0$$

2 $$E = \frac{RT}{F} \ln \frac{c_A}{c_C}$$

$$I = \frac{U - E}{R}$$

$$t_+ = \frac{I_\infty}{I_0}$$

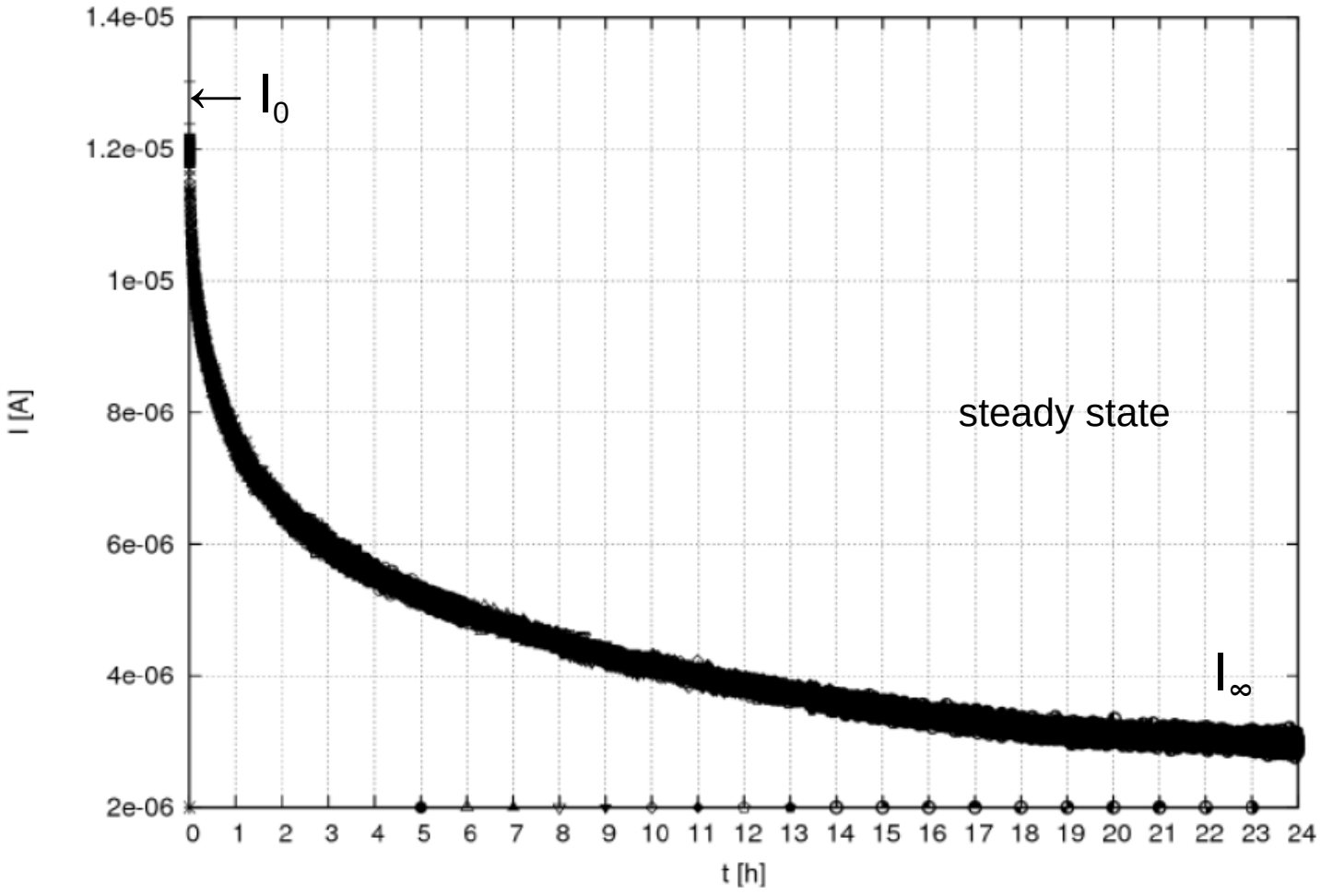


Non ideal electrolyte

$$I = \frac{U}{R}$$

$$I_0 = \frac{U}{\frac{1}{\sigma_{\text{electrolyte}}} + R^0_{\text{interphase}}}$$

$$I_\infty = \frac{U}{\frac{1}{\sigma \cdot t_+} + R^\infty_{\text{interphase}}}$$



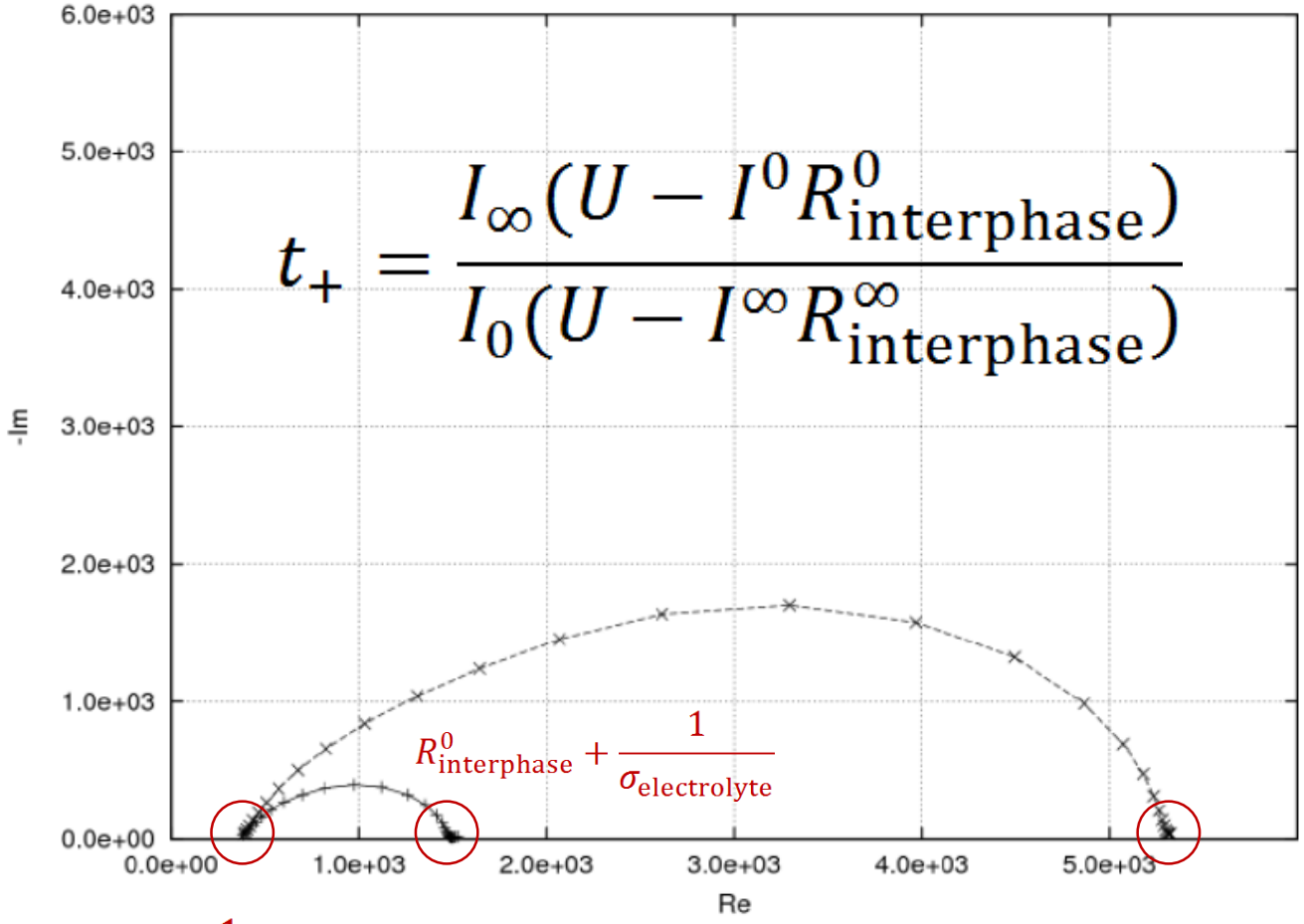
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$$t_+ = \frac{I_\infty (U - I^0 R^0_{\text{interphase}})}{I_0 (U - I^\infty R^\infty_{\text{interphase}})}$$



$$\frac{1}{\sigma_{\text{electrolyte}}}$$

2 Cation Diffusion Coefficient Determination

Diffiusion

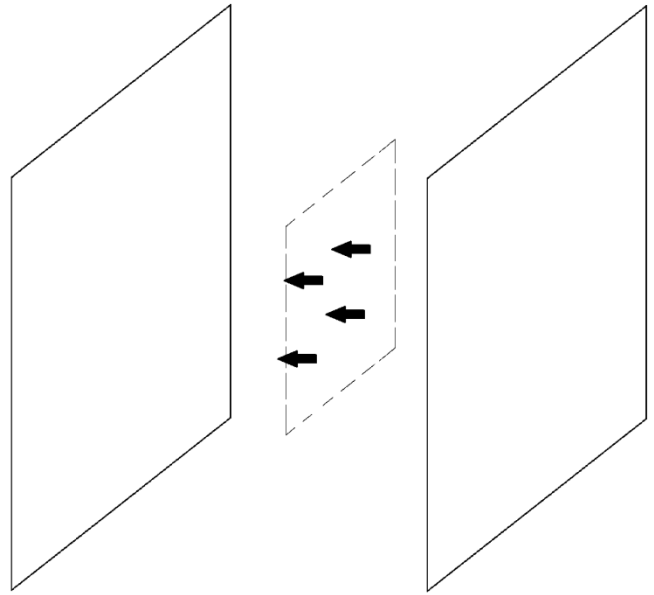
Diffusion is a parameter which informs about transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion.

Driving force of diffusion is concentration gradient.

Diffiusion

1) $$I = -D\frac{\partial c}{\partial x}$$

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



Boundary conditions:

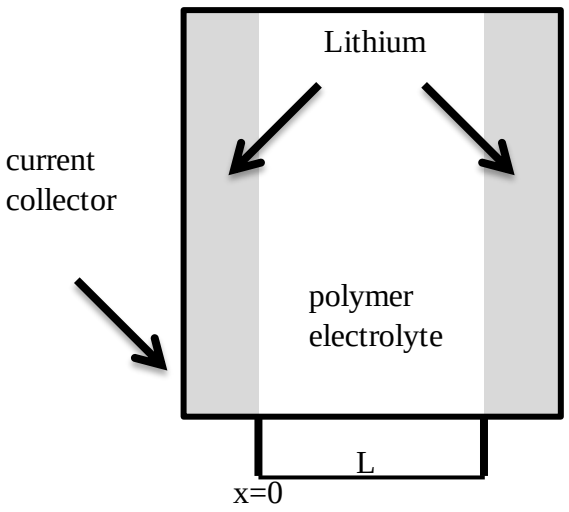
$$\frac{\partial c}{\partial x}(x=0) = -\frac{I(1-t_+)}{F \cdot D}$$

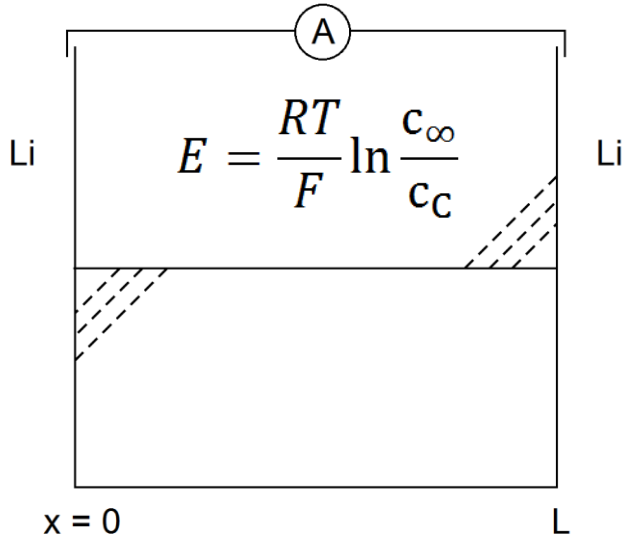
$$c_{(t=0 \text{ and } x=\infty)} = c_\infty$$

$$t \ll \frac{L^2}{D}$$

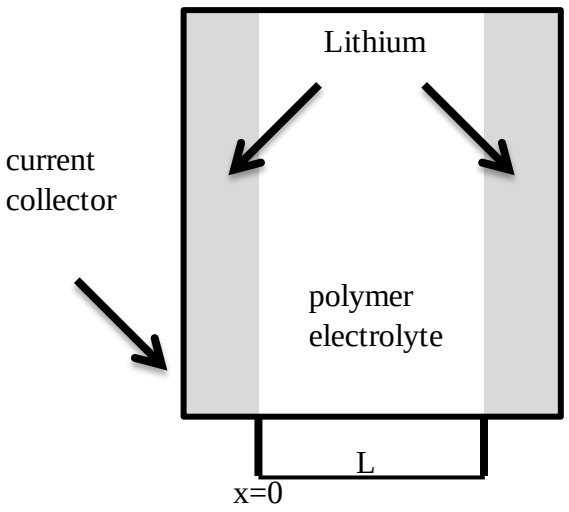
Li = $Li^+ + e^-$

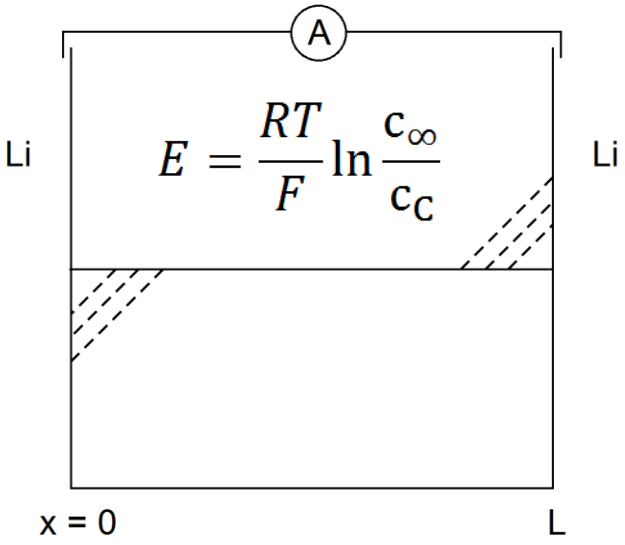
Diffiusion


Lithium
current
collector
polymer
electrolyte
L
x=0

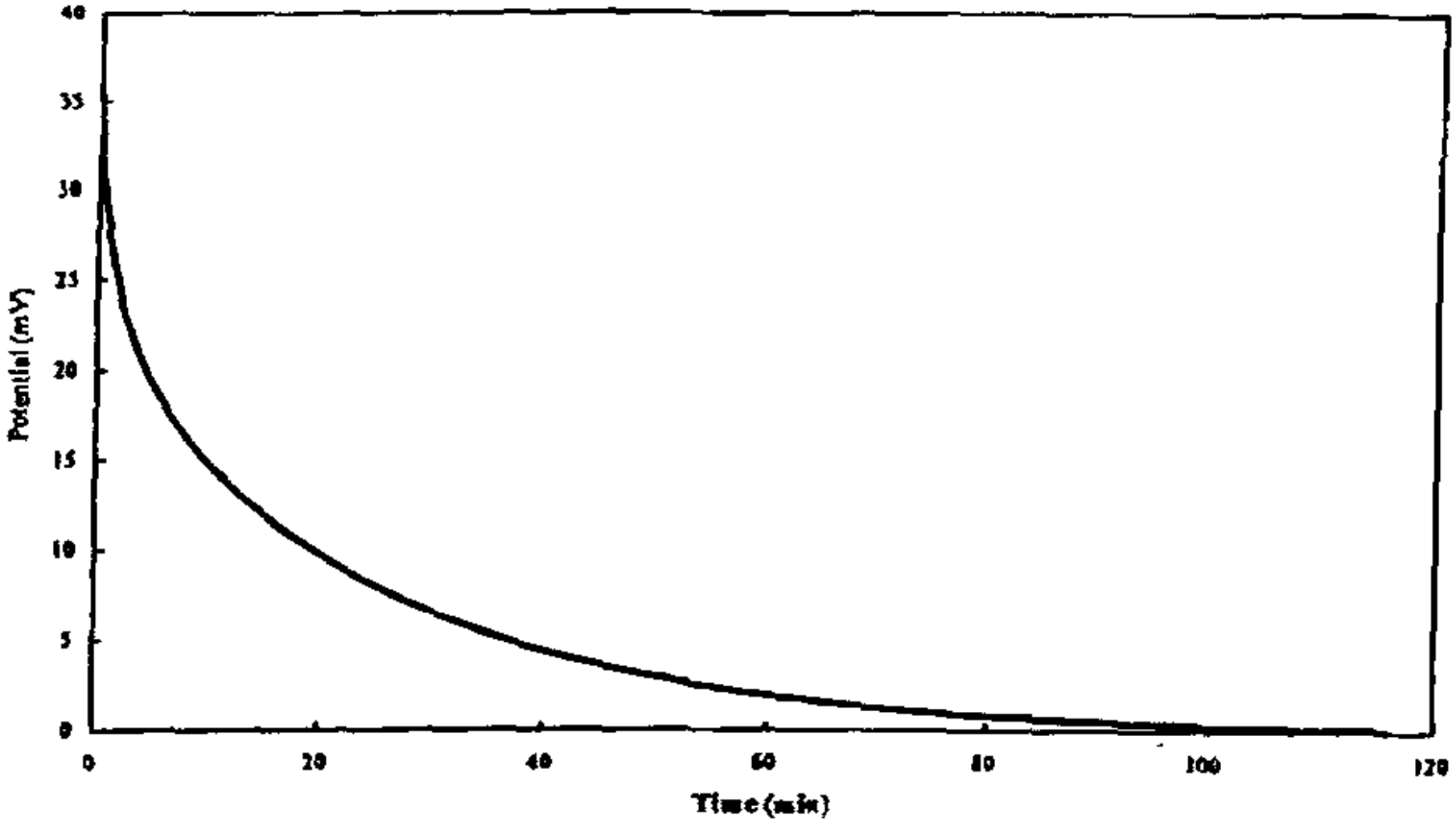

A
Li
$E = \frac{RT}{F} \ln \frac{c_\infty}{c_C}$
Li
x = 0
L

Diffiusion





OCV plot



Diffiusion

$$A = \frac{\pi^2 D}{L^2}$$

