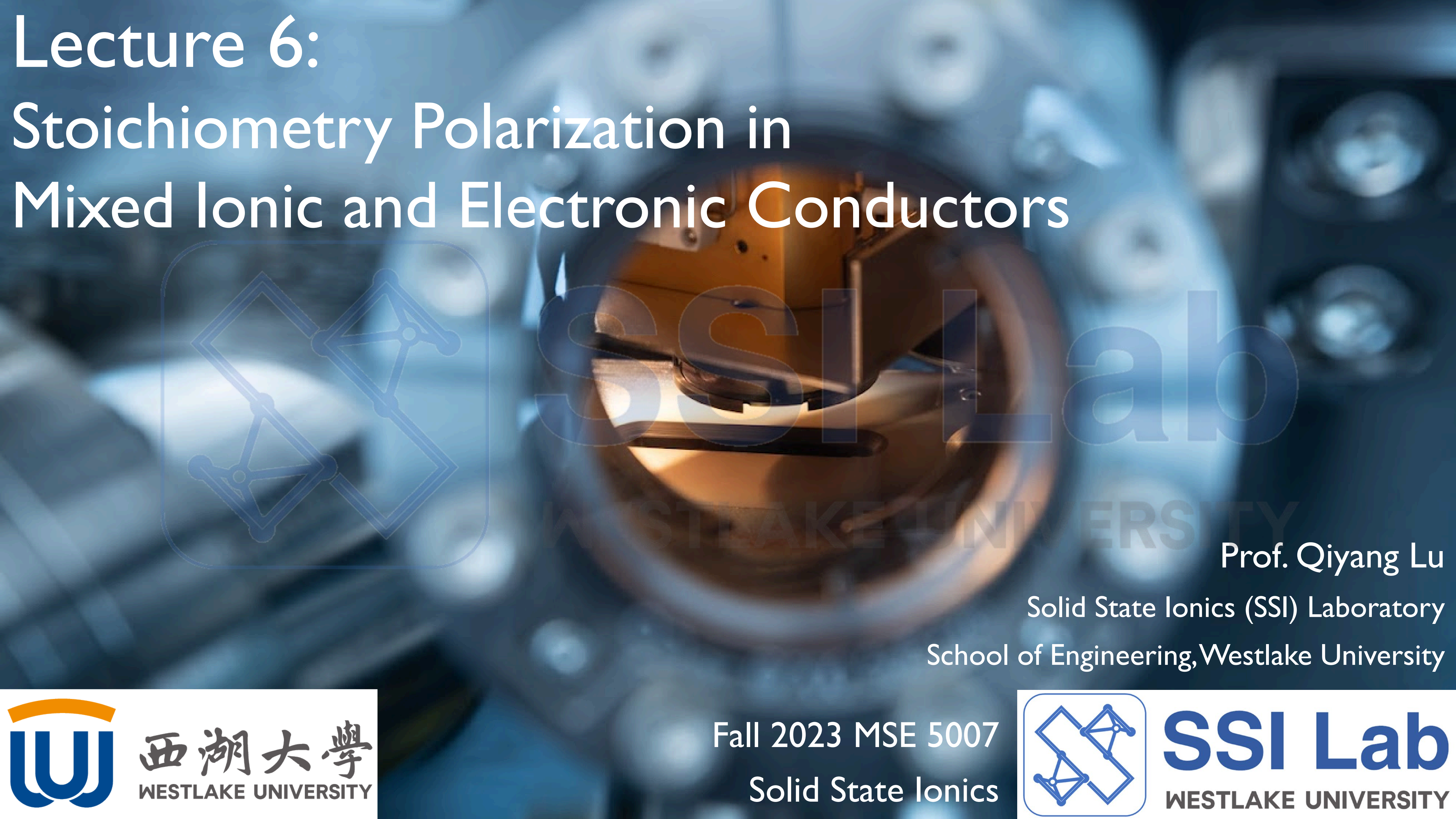

Lecture 6:
Stoichiometry Polarization in Mixed Ionic and Electronic Conductors

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Solid State Ionics (SSI) Laboratory
School of Engineering, Westlake University

Fall 2023 MSE 5007
Solid State Ionics

Things we will discuss in this lecture

Type of electrodes and Stoichiometry polarization:

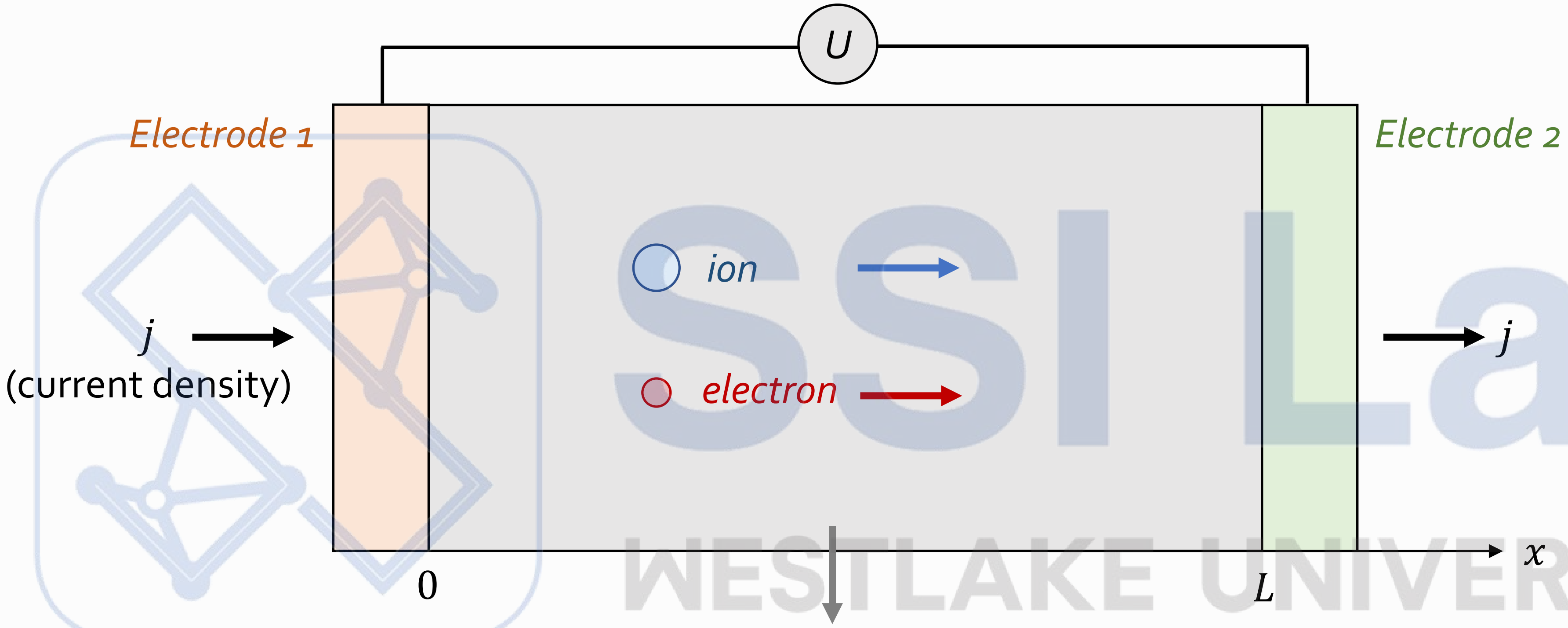
- What are the different types of electrodes used for measuring conductivity?
- How to understand the stoichiometry polarization with ion-blocking electrodes?

Electron-blocking electrodes and the Hebb-Wagner method:

- How to understand the intercalation process of ions & electrons?
- What is the Hebb-Wagner method for measuring conductivity?

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

Problem set-up: MIEC + partially blocking electrodes



Mixed ionic and electronic conductor (*e.g.*, Ag_2Te, $SrTiO_3$, $LiCoO_2$, $\mathbf{H_xNdNiO_3}$, $\mathbf{MAPbI_3}$...)

Electrodes can be:

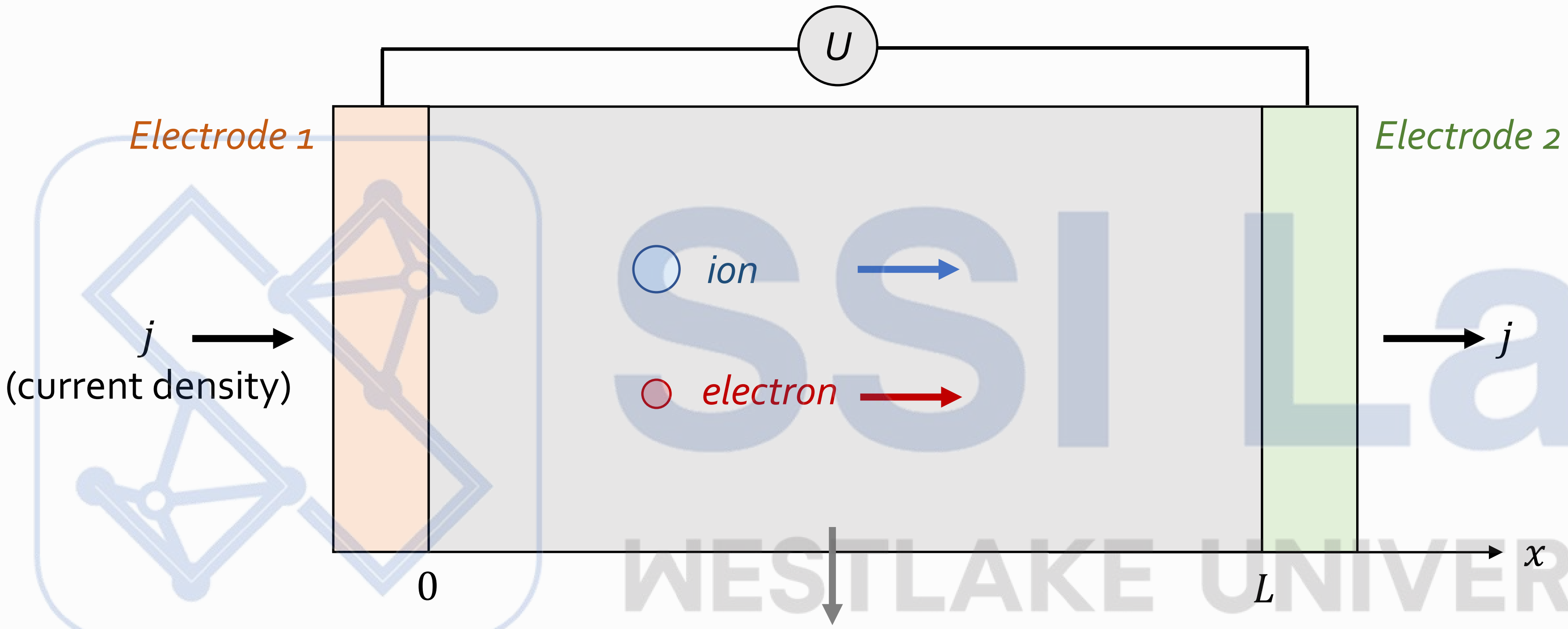
- reversible (*ion*+*eon*)
- *ion* blocking
- *eon* blocking

We want to know:

- Concentration of charge neutral species (chemical composition) as a function of lateral position (x) and time (t);
- Chemical potential of charge-neutral species and the potential between two electrodes as a function of x and t.

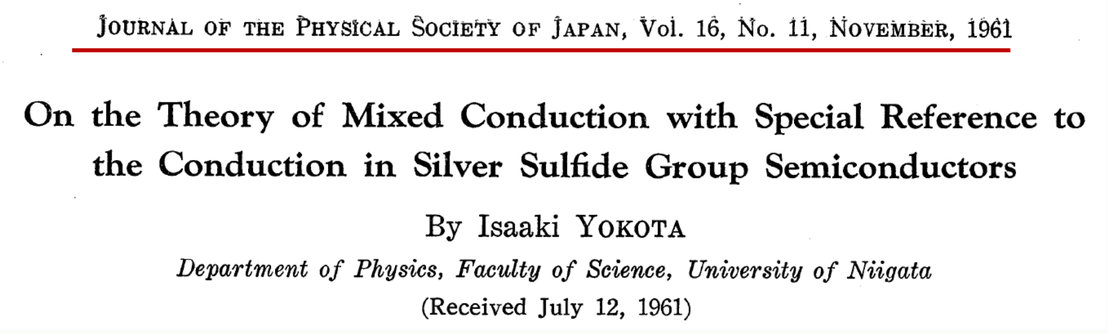
Yokota, ***J. Phys. Soc. Jpn.***, 1961

Problem set-up: MIEC + partially blocking electrodes



Electrodes can be:
- reversible (*ion*+*eon*)
- *ion* blocking
- *eon* blocking

Mixed ionic and electronic conductor (*e.g.*, Ag_2Te, $SrTiO_3$, $LiCoO_2$, $\mathbf{H_xNdNiO_3}$, $\mathbf{MAPbI_3}$...)


JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 16, No. 11, NOVEMBER, 1961

On the Theory of Mixed Conduction with Special Reference to the Conduction in Silver Sulfide Group Semiconductors

By Isaaki YOKOTA
Department of Physics, Faculty of Science, University of Niigata

(Received July 12, 1961)

This is a solved problem (横田伊佐秋, 新潟大学, 1961)

However, this does not mean that the solution is easy to understand.

Yokota, ***J. Phys. Soc. Jpn.***, 1961

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 $c = 6.02\times 10^{19}cm^{-3})$

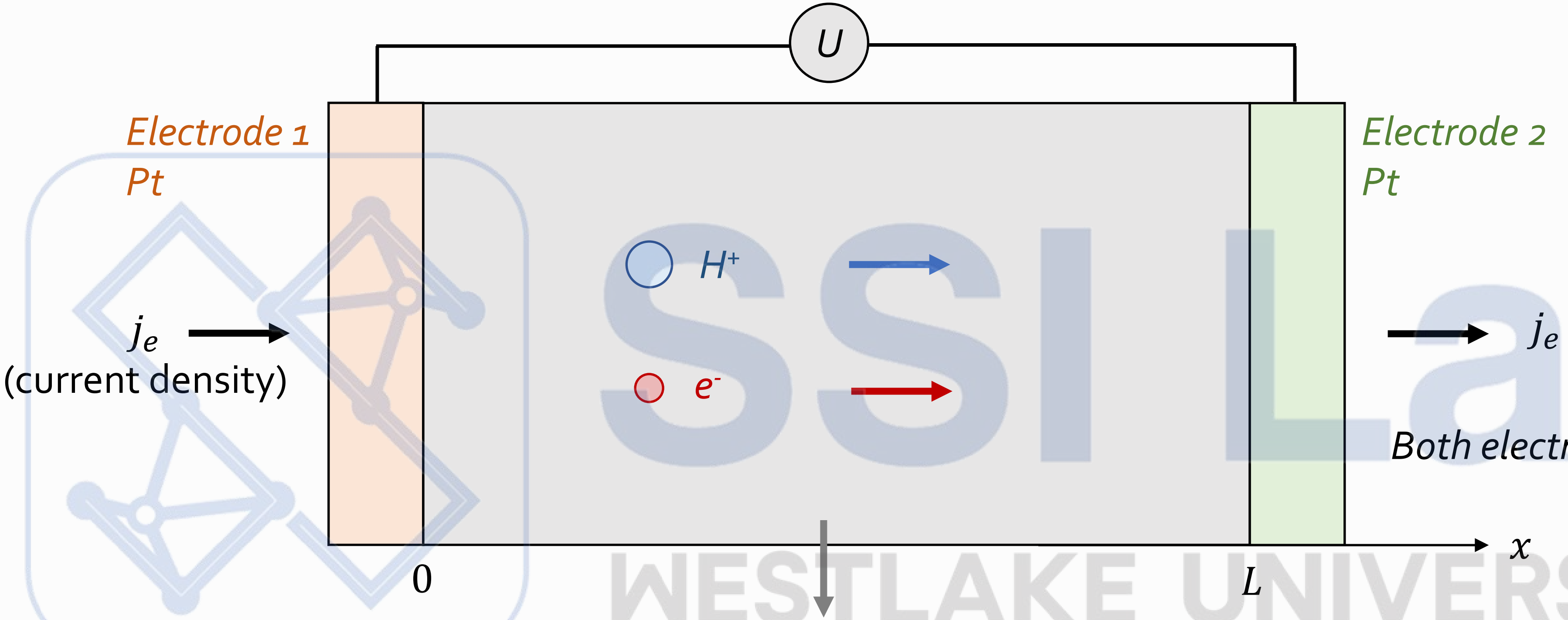
$$\Delta E = \frac{\Delta V}{\Delta x} = 1\times 10^{18}\ V/m^2\Delta x$$

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
$U_E = \rho\ \Delta V$

Master equations: potentials, transport equations



Both electrodes are ***ion-blocking***

H_xNdNiO_3 (as an example)

Transport equations:

$$j_e = j_{e^-} = -FJ_e = \frac{\sigma_e}{F}\frac{\partial \tilde{\mu}_e}{\partial x}$$

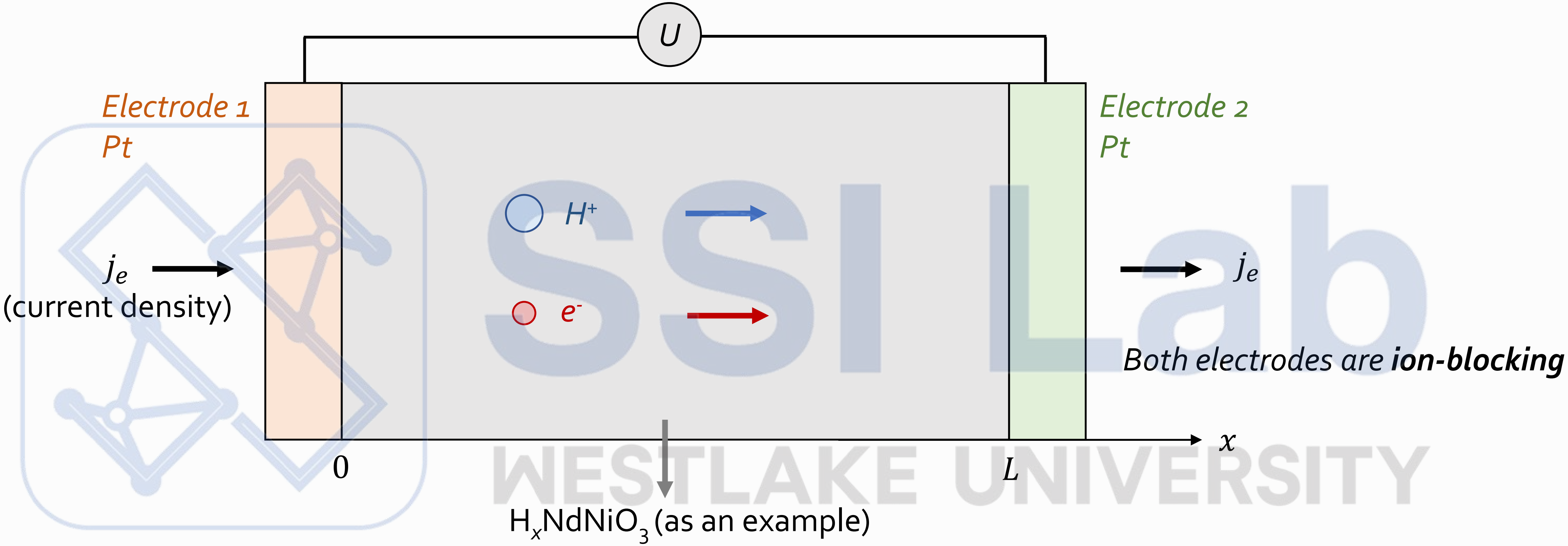
$$j_i = j_{H^+} = FJ_i = -\frac{\sigma_i}{F}\frac{\partial \tilde{\mu}_i}{\partial x}$$

$$\mu = \mu_H = \tilde{\mu}_e + \tilde{\mu}_i$$

⟶ Potential difference between electrode 1&2

$$U = (\tilde{\mu}_e(x = L) - \tilde{\mu}_e(x = 0))/F$$

Master equations: potentials, transport equations

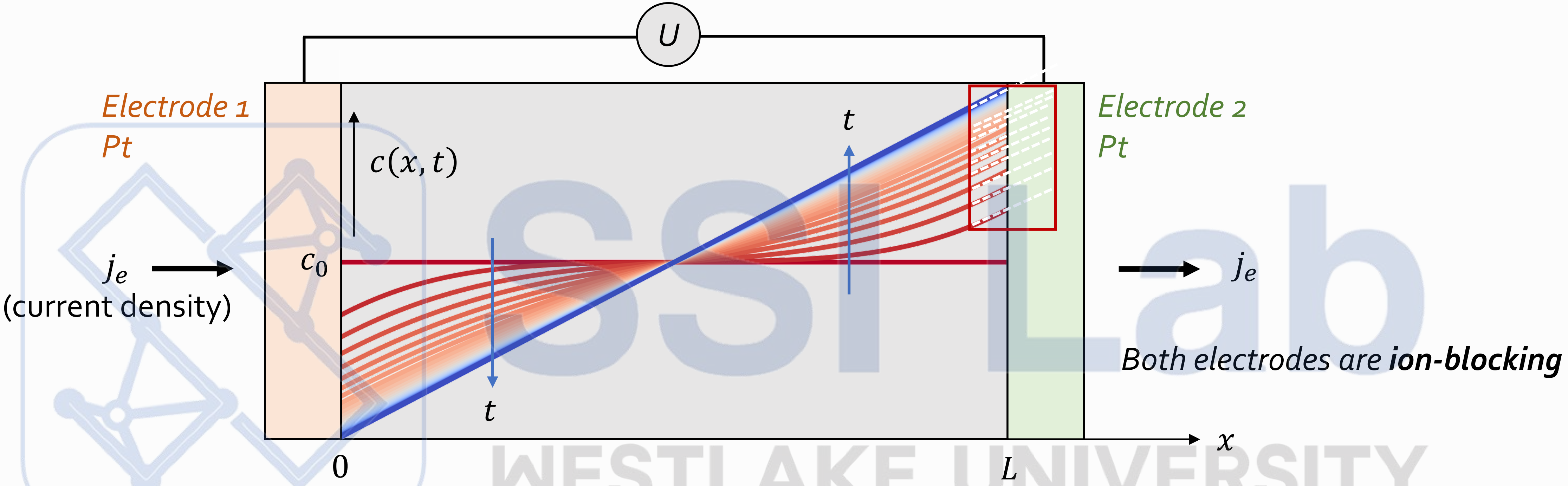


What happens at steady state? $\boxed{j_i = -\frac{\sigma_i}{F}\frac{\partial \tilde{\mu}_i}{\partial x} = 0}$ → $\frac{\partial \tilde{\mu}_i}{\partial x} = 0$

$\boxed{U = (\tilde{\mu}_e(x = L) - \tilde{\mu}_e(x = 0))/F}$ → $\boxed{U = (\mu(x = L) - \mu(x = 0))/F}$

i.e., the measured voltage is ***Nernstian*** (*stoichiometry polarization*).

Master equations: Fick's second law



*Both electrodes are **ion-blocking***

Since charge neutral is met, then the process can be described as ***chemical diffusion***

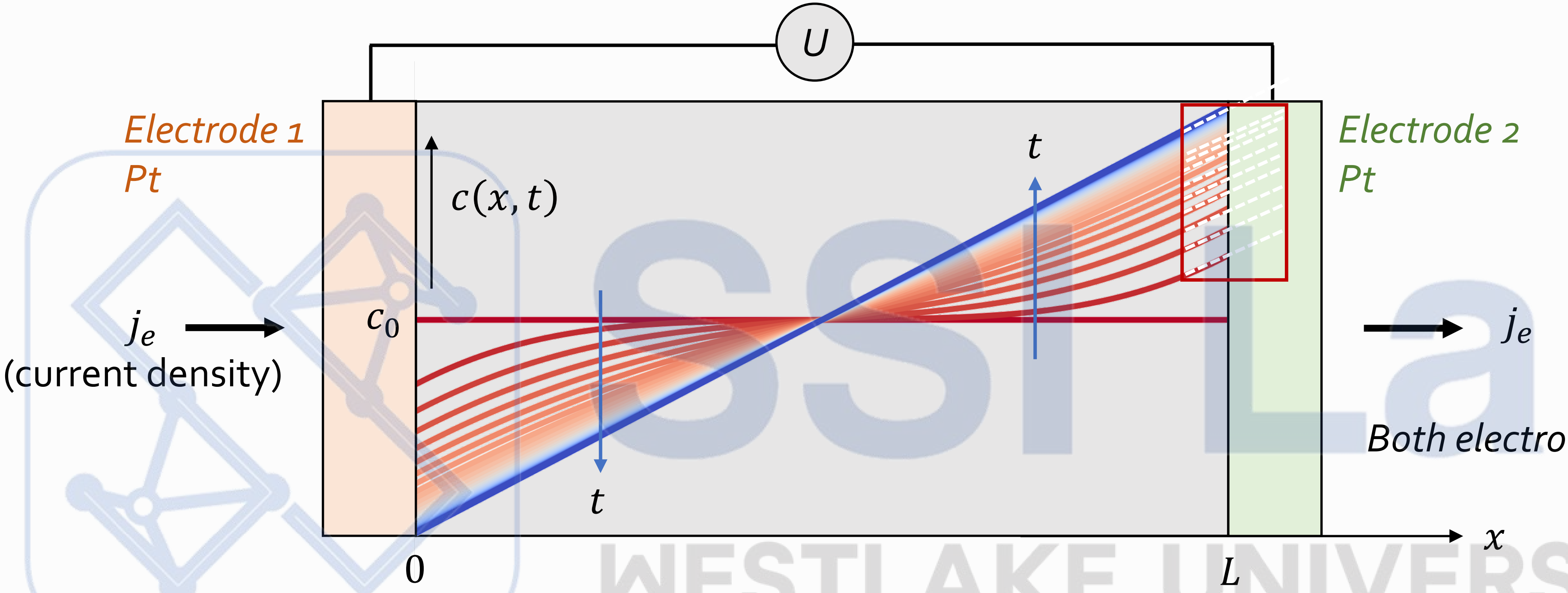
Fick's 2nd law: $$\boxed{\frac{\partial c(x,t)}{\partial t} = \underset{\downarrow}{D^{\delta}} \frac{\partial^2 c(x,t)}{\partial x^2}}$$

chemical diffusivity

Boundary condition: $$\boxed{\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0,L} = \frac{Fj}{\sigma_e}\left(\frac{\partial \mu}{\partial c}\right)^{-1}} \longrightarrow = \frac{Fj}{\sigma_e}\frac{c_0}{RT}$$

Dilute limit
Small current

Solution to the partial differential equation



Both electrodes are ***ion-blocking***

Solution to the PDE:

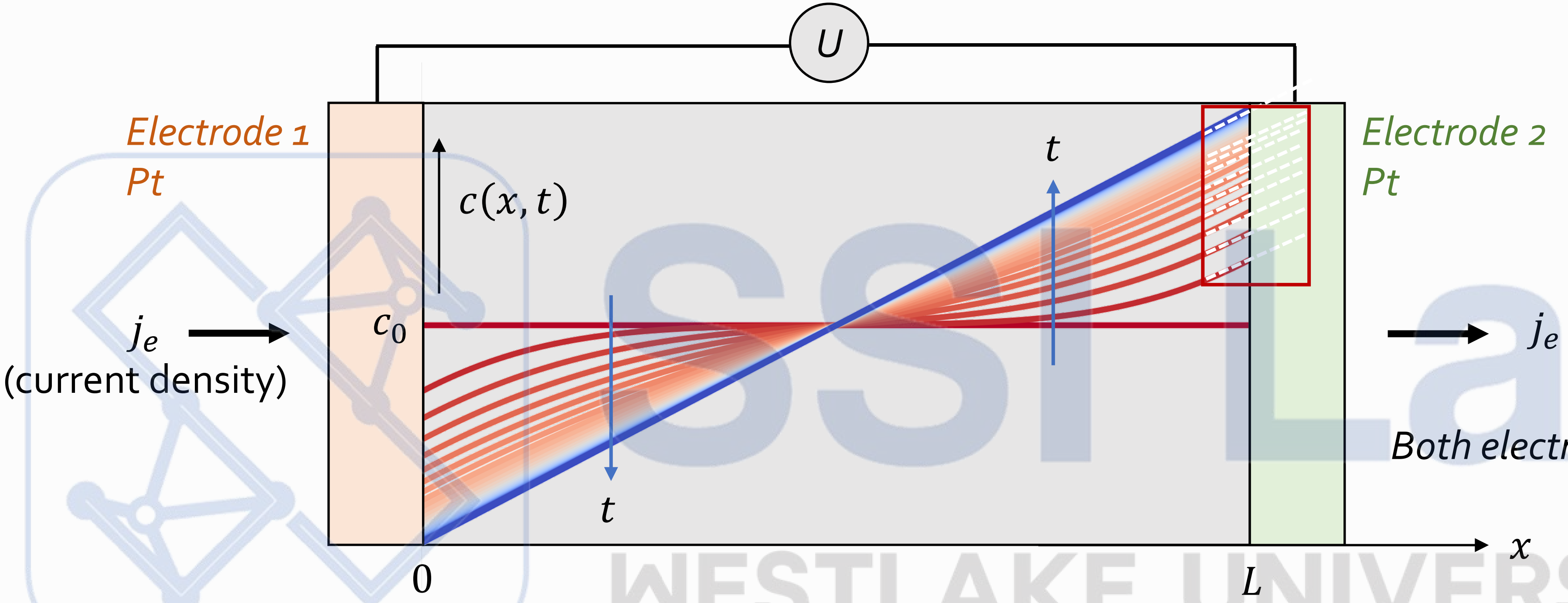
$$c({\color{red}x},{\color{blue}t}) = c_0 + \frac{Fj}{\sigma_e}\frac{c_0}{RT}L\left[\frac{{\color{red}x}}{L} - \frac{1}{2} + \Phi\left(\frac{{\color{red}x}}{L},\frac{{\color{blue}t}}{\tau^\delta}\right)\right]$$

$$\tau^\delta = \frac{1}{\pi^2}\frac{L^2}{D^\delta}$$

$$\Phi({\color{red}\xi},{\color{blue}s}) = \frac{4}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp[-(2m+1)^2{\color{blue}s}]\cos[(2m+1)\pi{\color{red}\xi}]$$

Yokota, ***J. Phys. Soc. Jpn.***, 1961

Solution to the partial differential equation



*Both electrodes are **ion-blocking***

The voltage measured between two electrodes:

$$U = \frac{RT}{F}\ln\left(\frac{c(L,t)}{c(0,t)}\right) \approx \frac{RT}{F}\frac{\Delta c}{c_0} = \frac{RT}{F}\frac{c(L,t)-c(0,t)}{c_0}$$

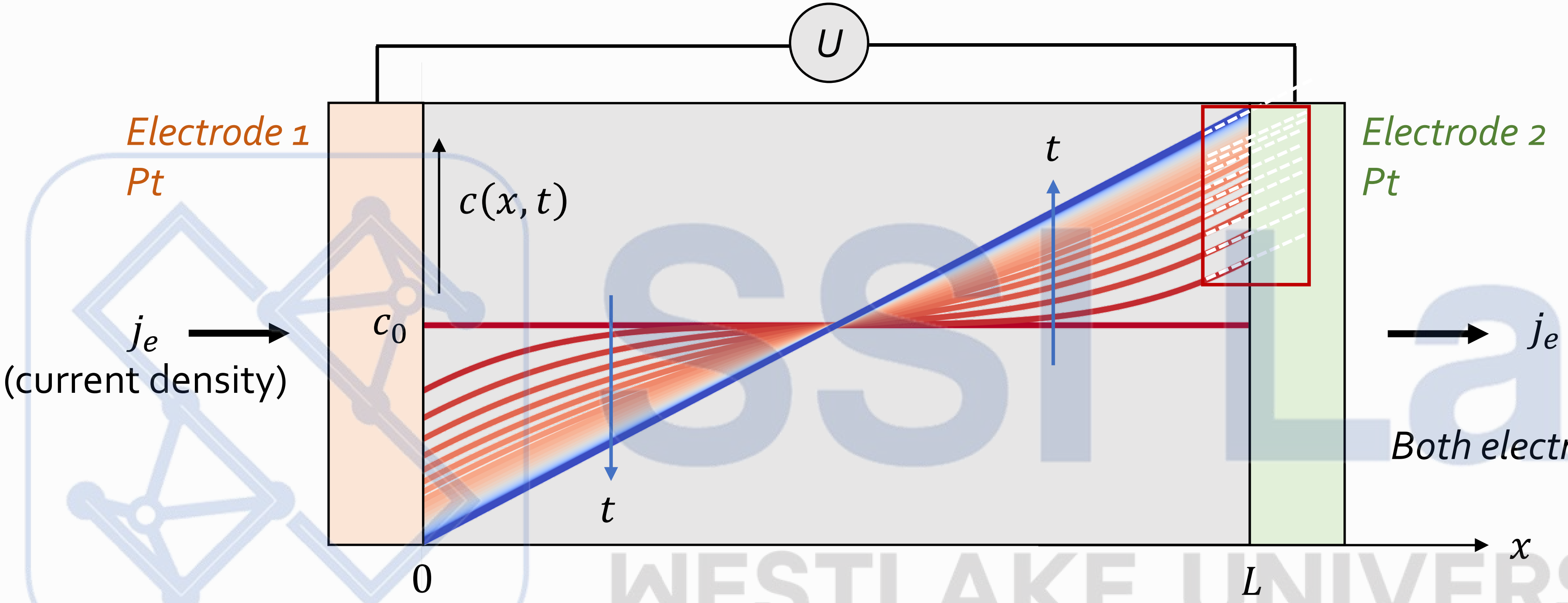
$$U(t) = \frac{jL}{\sigma_e}\left(1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-(2m+1)^2\frac{t}{\tau^\delta}\right]\right)$$

$$U(t)\Big|_{t\to\infty} = \frac{jL}{\sigma_e}$$

If we wait infinitely long time...
Ohm's law (!)

Yokota, ***J. Phys. Soc. Jpn.***, 1961

Solution to the partial differential equation



Both electrodes are ***ion-blocking***

The voltage measured between two electrodes:

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$$\boxed{U(t)=\frac{jL}{\sigma_e}\left(1-\frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-(2m+1)^2\frac{t}{\tau^\delta}\right]\right)}$$

$$\boxed{U(t)=\frac{jL}{\sigma_e}\left[1-\frac{8}{\pi^2}\exp\left(-\frac{t}{\tau^\delta}\right)\right]}\quad(t\gg\tau^\delta)\quad\boxed{\ln\big(U(t)-U(\infty)\big)\sim-\frac{t}{\tau^\delta}}$$

Yokota, ***J. Phys. Soc. Jpn.***, 1961

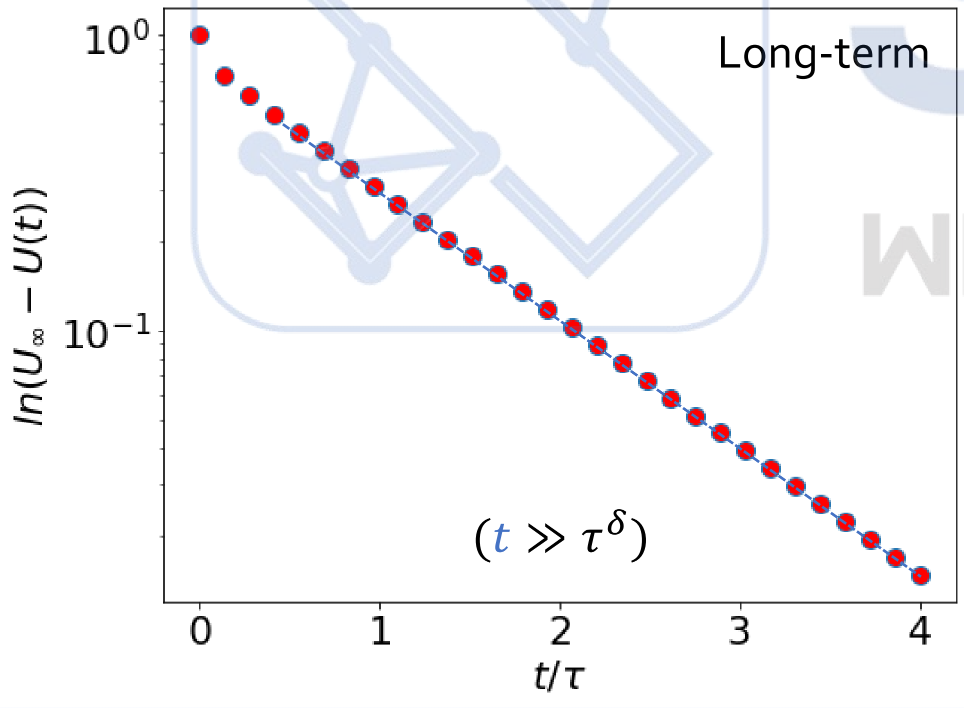
Potential measured across the sample as a function of time

$$U(t) = \frac{jL}{\sigma_e}(1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp[-(2m+1)^2\frac{t}{\tau^{\delta}}])$$

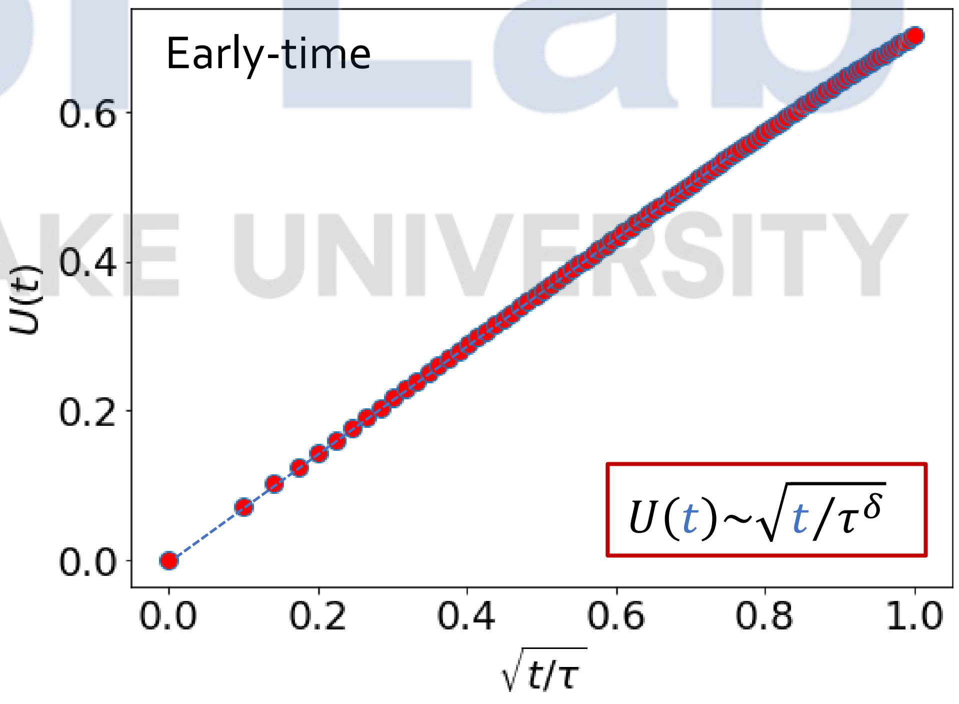
$$U(t) = \frac{jL}{\sigma_e}[1 - \frac{8}{\pi^2}\exp\left(-\frac{t}{\tau^{\delta}}\right)]$$

$(t \gg \tau^{\delta})$

$$\ln\left(U(t) - U(\infty)\right) \sim -\frac{t}{\tau^{\delta}}$$

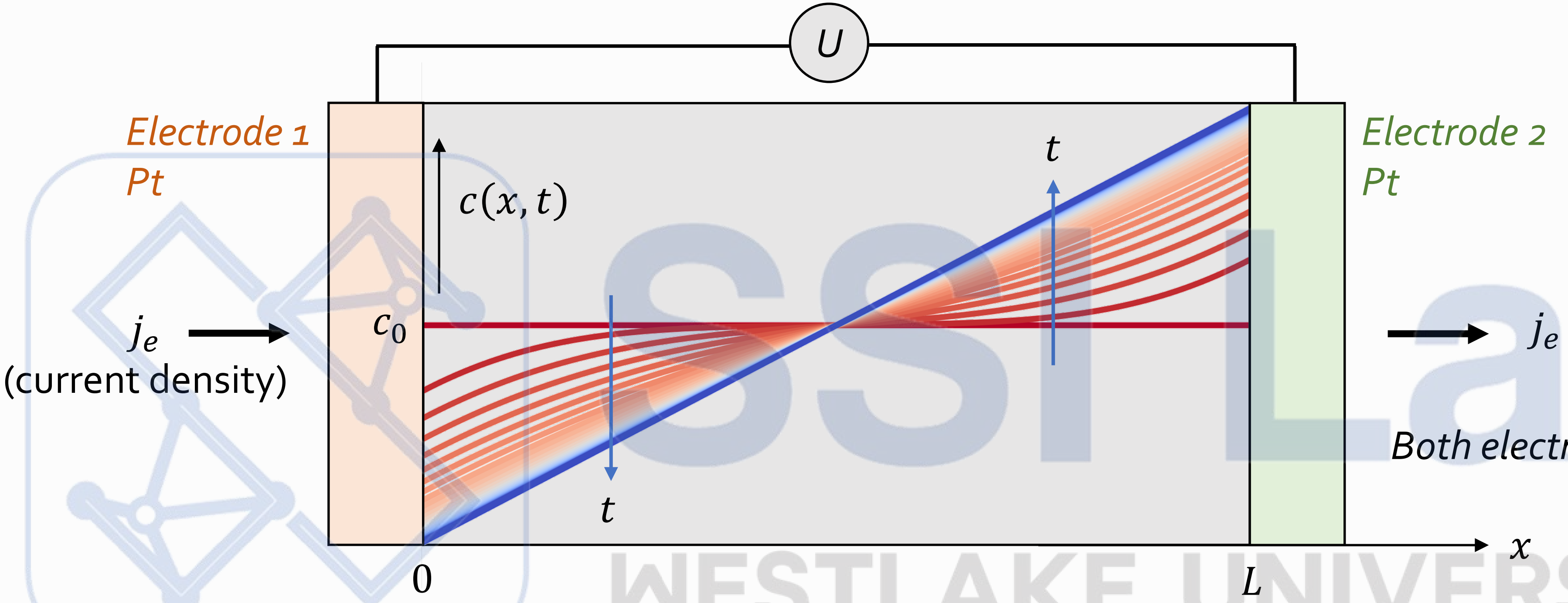


$(t \gg \tau^{\delta})$



$U(t) \sim \sqrt{t/\tau^{\delta}}$

Master equations: Fick's second law



Both electrodes are ***ion-blocking***

Since charge neutral is met, then the process can be described as ***chemical diffusion***

Fick's 2nd law:

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

chemical diffusivity

Steady state $\longrightarrow$ $\boxed{\left.\frac{\partial c(x,t)}{\partial t}\right|_{t\to\infty} = 0}$ $\longrightarrow$ $c(x,\infty)$ must be *linear*

Assumption: D^{δ} is constant (which means small $\Delta\mu$)

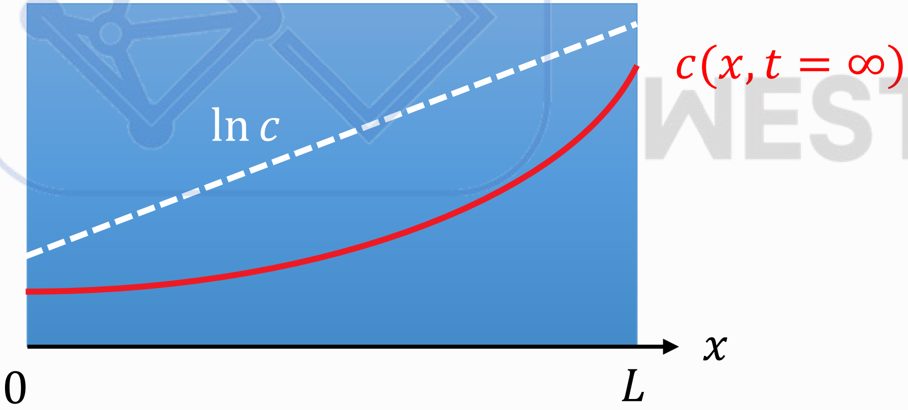
Mystery: steady-state diffusion and Fick's law

Approach 1:

At steady state, we have: $\frac{\partial J}{\partial x} = 0$

$J = -\frac{\sigma}{z^2F^2}\frac{\partial \mu}{\partial x} \longrightarrow$ μ should be linear

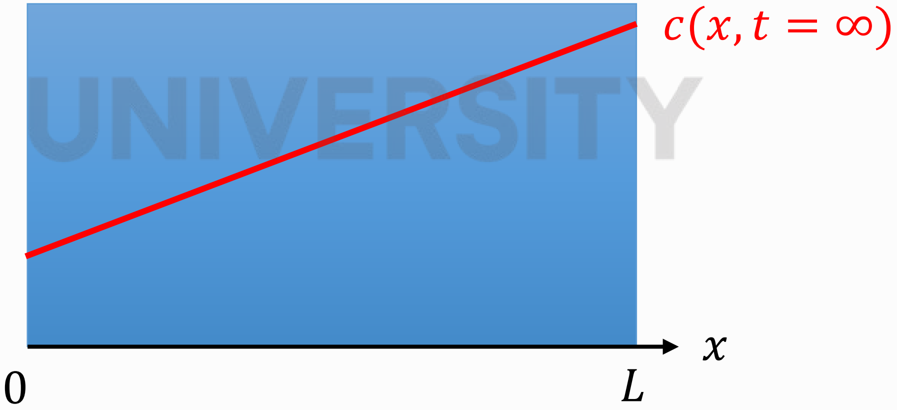
If we assume dilute limit $\boxed{\frac{\partial \mu}{\partial x} = \frac{\partial \ln c}{\partial x} = const}$



Approach 2:

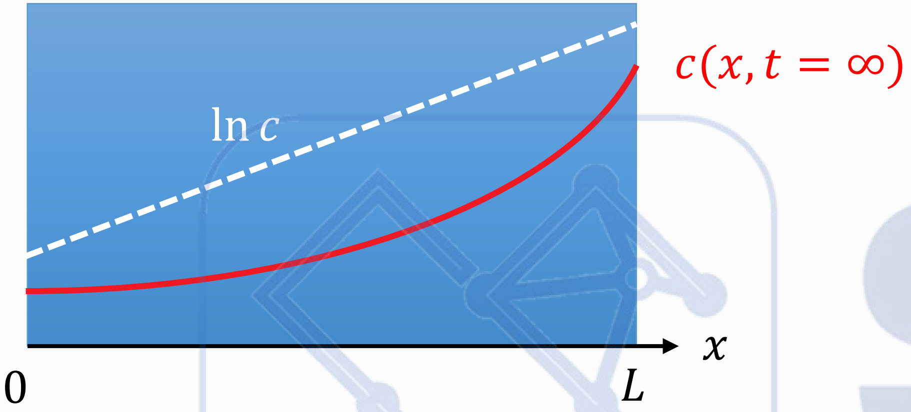
At steady state, we have: $\frac{\partial c}{\partial t} = D^{\delta}\frac{\partial^2 c}{\partial x^2} = 0$

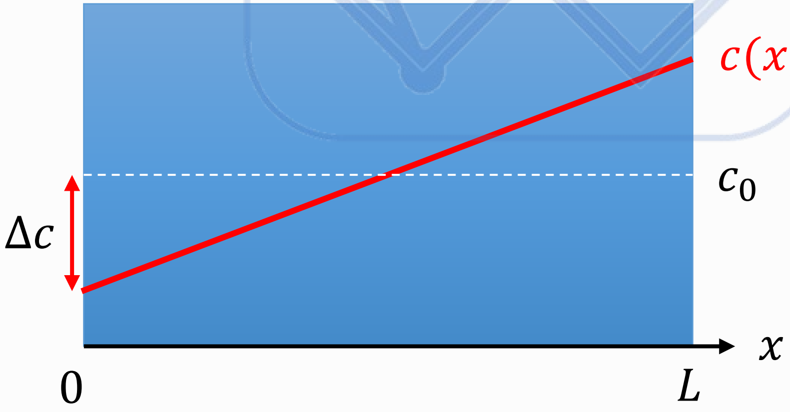
$\boxed{\frac{\partial^2 c}{\partial x^2} = 0} \longrightarrow$ c should be linear



Which approach is correct?

Mystery: steady-state diffusion and Fick's law





$$\boxed{J = -\frac{\sigma}{z^2F^2}\frac{\partial \mu}{\partial x} = -D\frac{c}{RT}\frac{\partial \mu}{\partial x}}$$

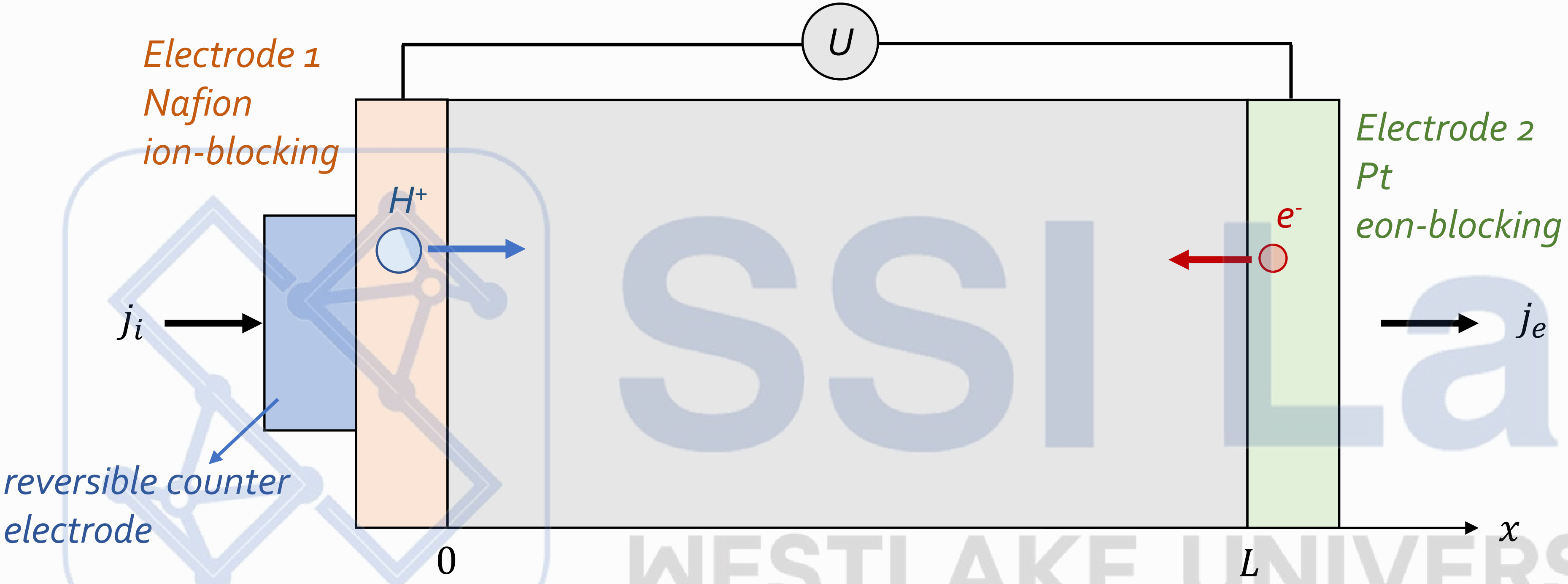
- In principle, D should be a function of chemical potential (or concentration), *i.e.*, $D(\mu)$ or $D(c)$
- In both approaches, we have assumed a *constant* diffusivity D, which means small variation in driving forces;
- In reality, D is probably more strongly affected by a varying in μ ($\ln c$) rather than c.

Small flux: $$\boxed{\Delta\mu = RT\ln\left(\frac{c_0 \pm \Delta c}{c_0}\right) \underset{\uparrow}{\approx} RT\frac{\Delta c}{c_0}}$$

$\Delta c \ll c_0$

"first-order approximation"

Asymmetric blocking electrodes



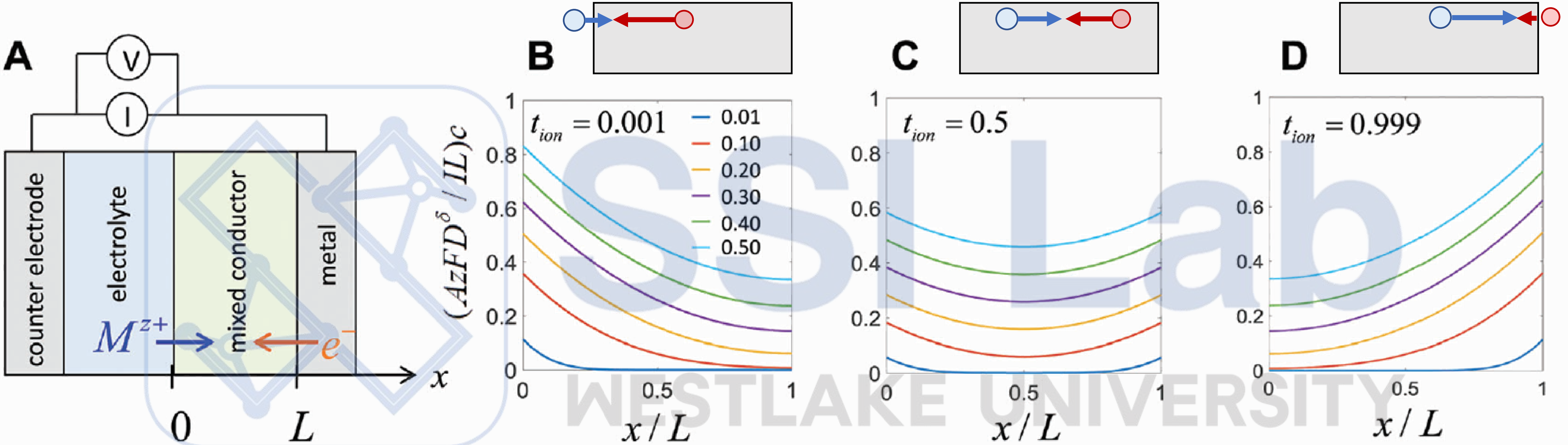
Fick's 2nd law: $$\boxed{\frac{\partial c(x,t)}{\partial t} = \underbrace{D^{\delta}}_{\text{chemical diffusivity}} \frac{\partial^2 c(x,t)}{\partial x^2}}$$

Boundary conditions: $$\boxed{\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} = -\frac{t_e j}{F D^{\delta}}} \qquad (z = 1)$$

$$\boxed{\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=L} = \frac{t_i j}{F D^{\delta}}} \qquad t_{e,i} = \frac{\sigma_{e,i}}{\sigma_e + \sigma_i}$$

Preis and Sitte, ***J. Chem. Soc., Faraday Trans.***, 1996

Asymmetric blocking electrodes: the effect of transference number



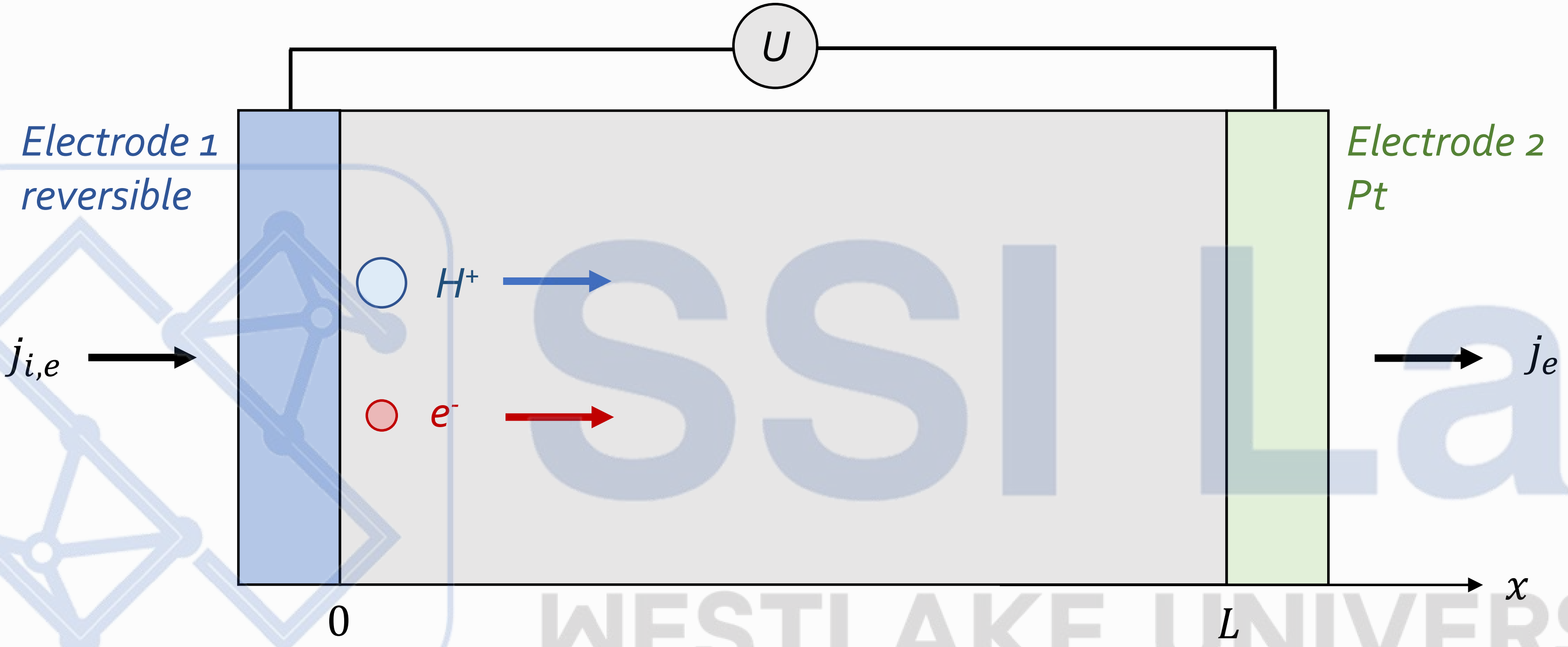
Boundary conditions:

$$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} = -\frac{(1-t_{ion})j}{zFD^{\delta}}$$

$$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=L} = \frac{t_{ion}j}{zFD^{\delta}}$$

Usiskin and Maier, *PCCP*, 2018

Reversible electrode: Hebb-Wagner measurement



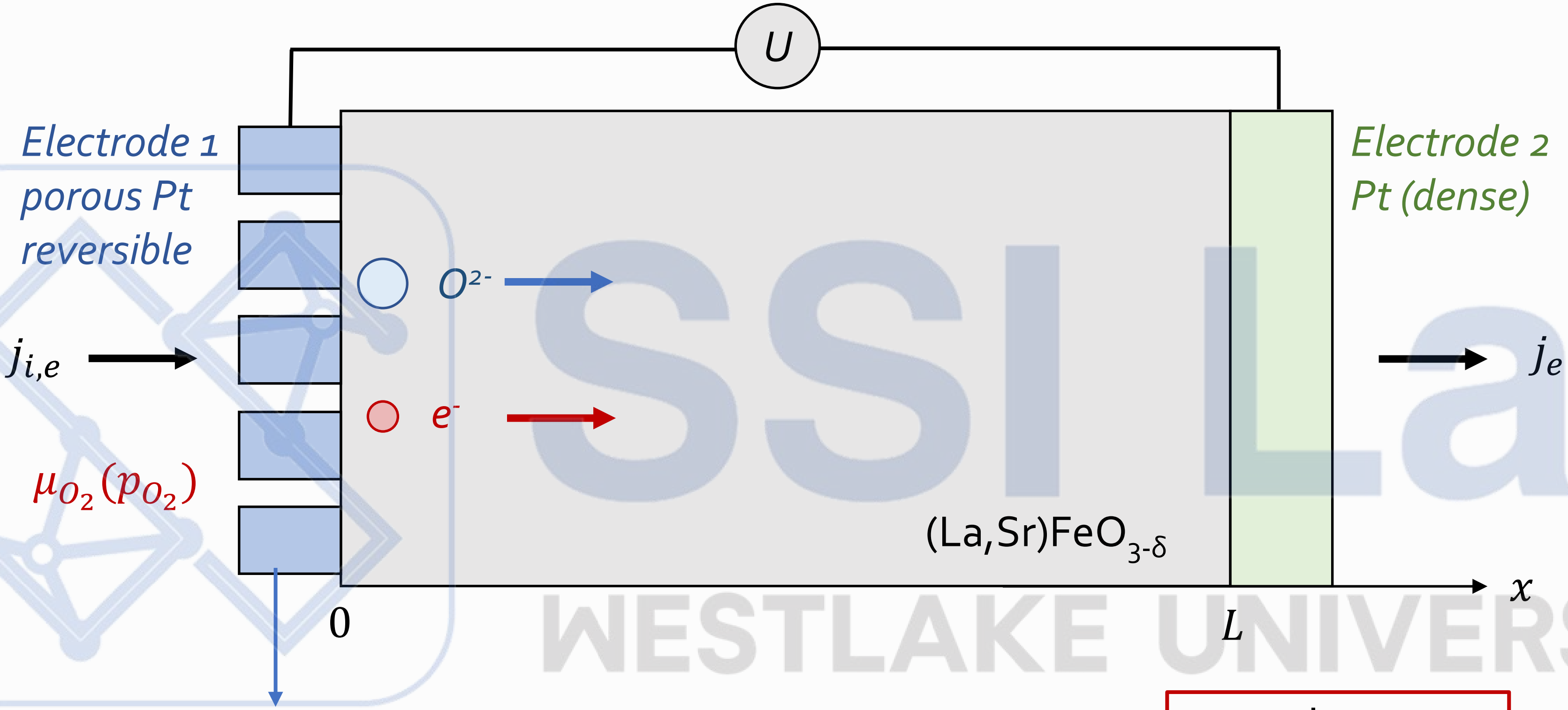
Fick's 2nd law: $$\boxed{\frac{\partial c(x,t)}{\partial t} = D^{\delta}\,\frac{\partial^2 c(x,t)}{\partial x^2}}$$

chemical diffusivity

Boundary conditions: $$\boxed{c(x,t)\Big|_{x=0} = c_0}$$ *(Why?)*

$$\boxed{\frac{\partial c(x,t)}{\partial x}\Bigg|_{x=L} = \frac{Fj}{\sigma_e}\,\frac{c_0}{RT}}$$

Reversible electrode: Hebb-Wagner measurement

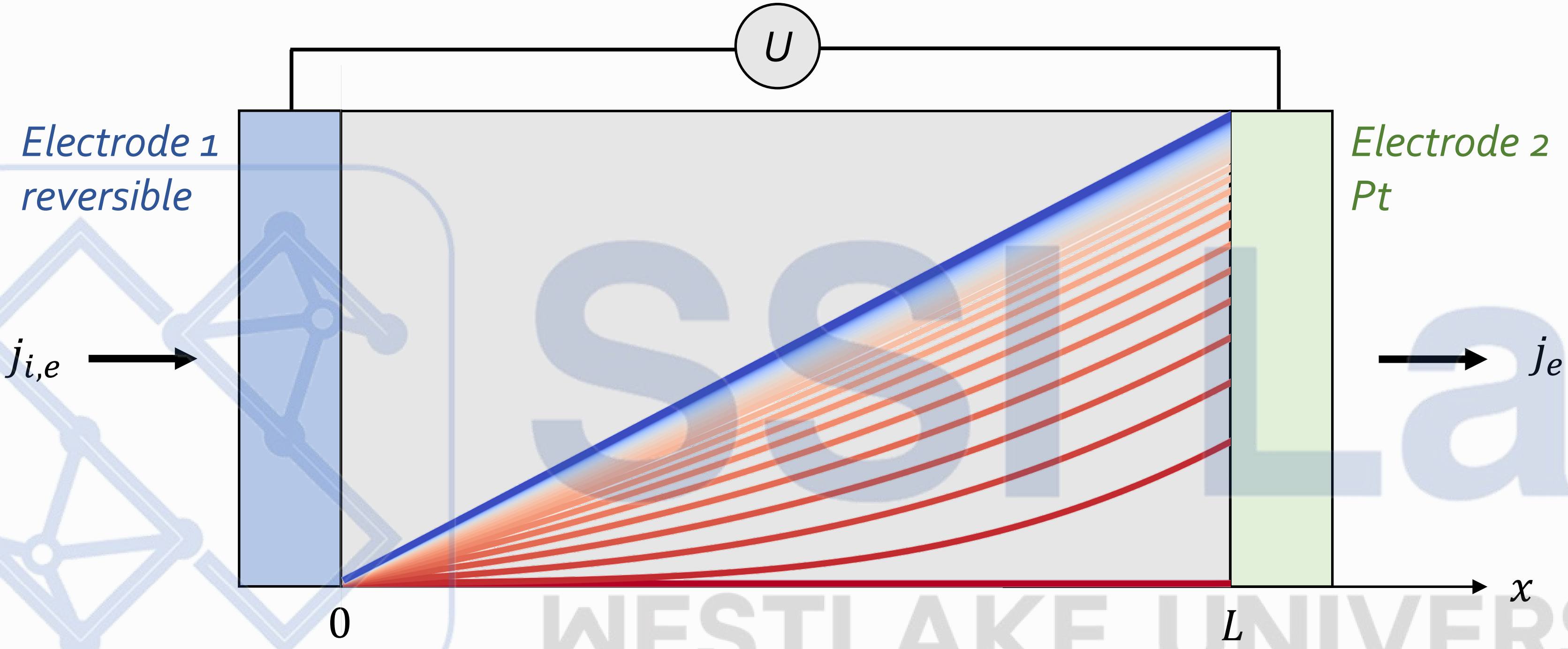


Reversible means the *chemical potential* must be equal at $x = 0$
(similar to the use of a reference electrode)

Boundary conditions: $\boxed{c(x,t)\Big|_{x=0} = c_0}$ at $\mu_{O_2}(x=0)$

$$\boxed{\frac{\partial c(x,t)}{\partial x}\Bigg|_{x=L} = \frac{Fj}{\sigma_e}\frac{c_0}{RT}}$$

Reversible electrode: Hebb-Wagner measurement



Fick's 2nd law: $$\boxed{\frac{\partial c(x,t)}{\partial t} = D^{\delta}\frac{\partial^2 c(x,t)}{\partial x^2}}$$

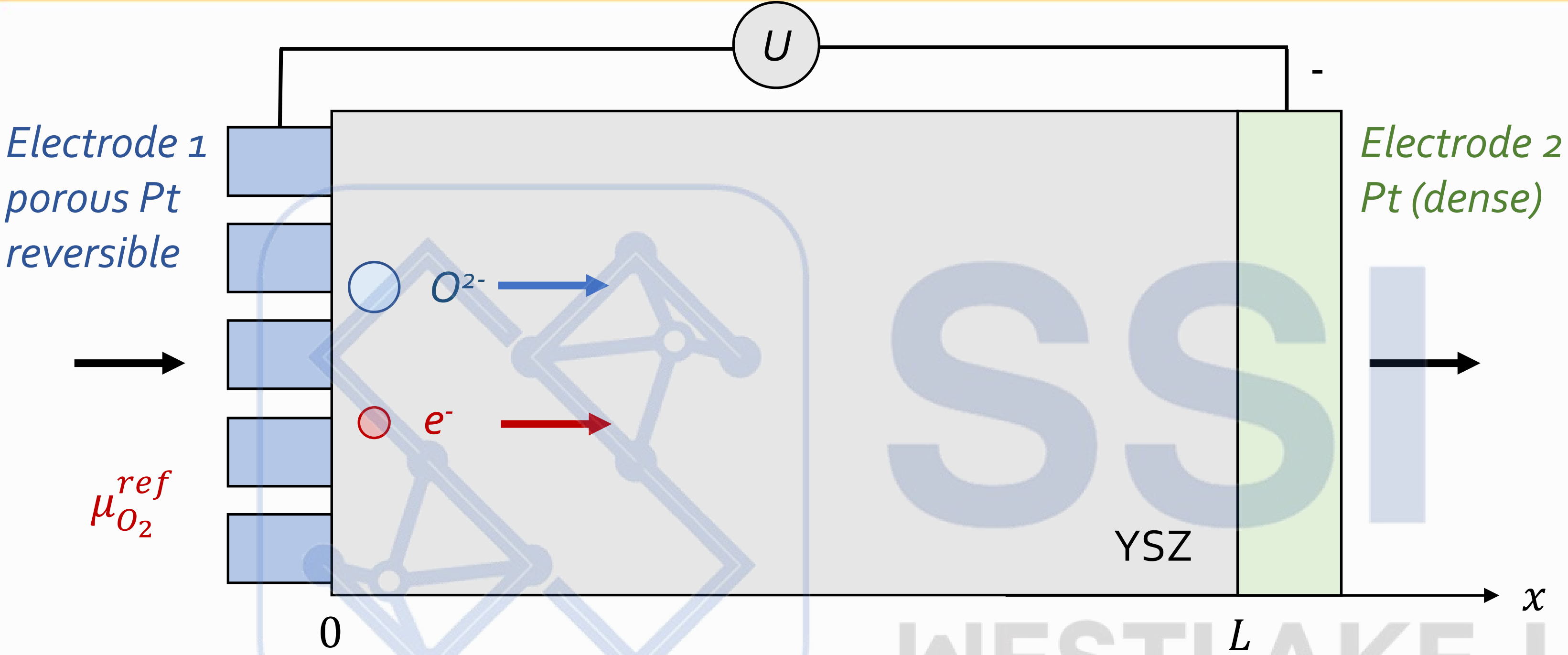
↓ *chemical diffusivity*

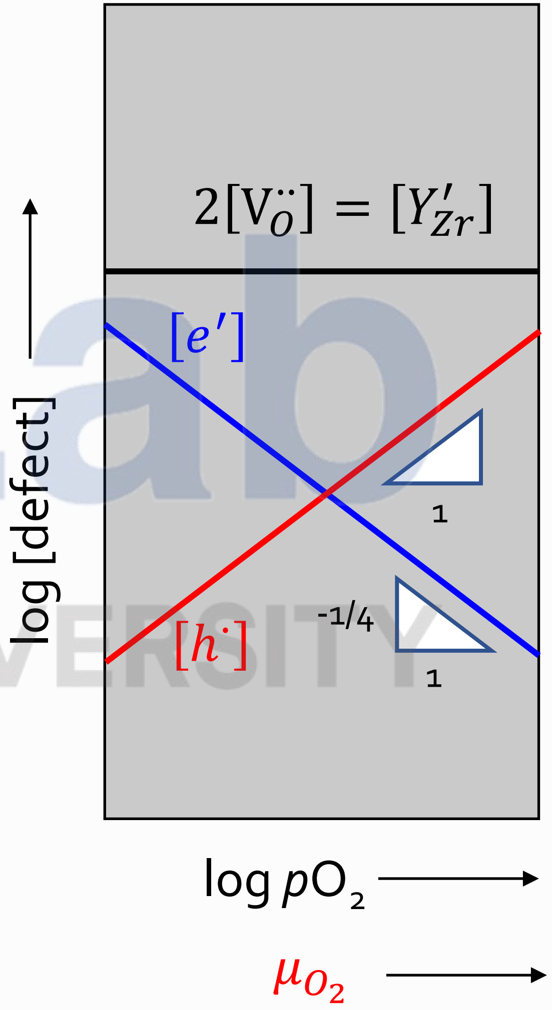
Boundary conditions: $$\boxed{c(x,t)\Big|_{x=0} = c_0}$$ (*Why?*)

$$\boxed{\frac{\partial c(x,t)}{\partial x}\bigg|_{x=L} = \frac{Fj}{\sigma_e}\frac{c_0}{RT}}$$

Notice that the concentration profile is the *right half* of the case with *two blocking electrodes*.

Reversible electrode: Hebb-Wagner measurement





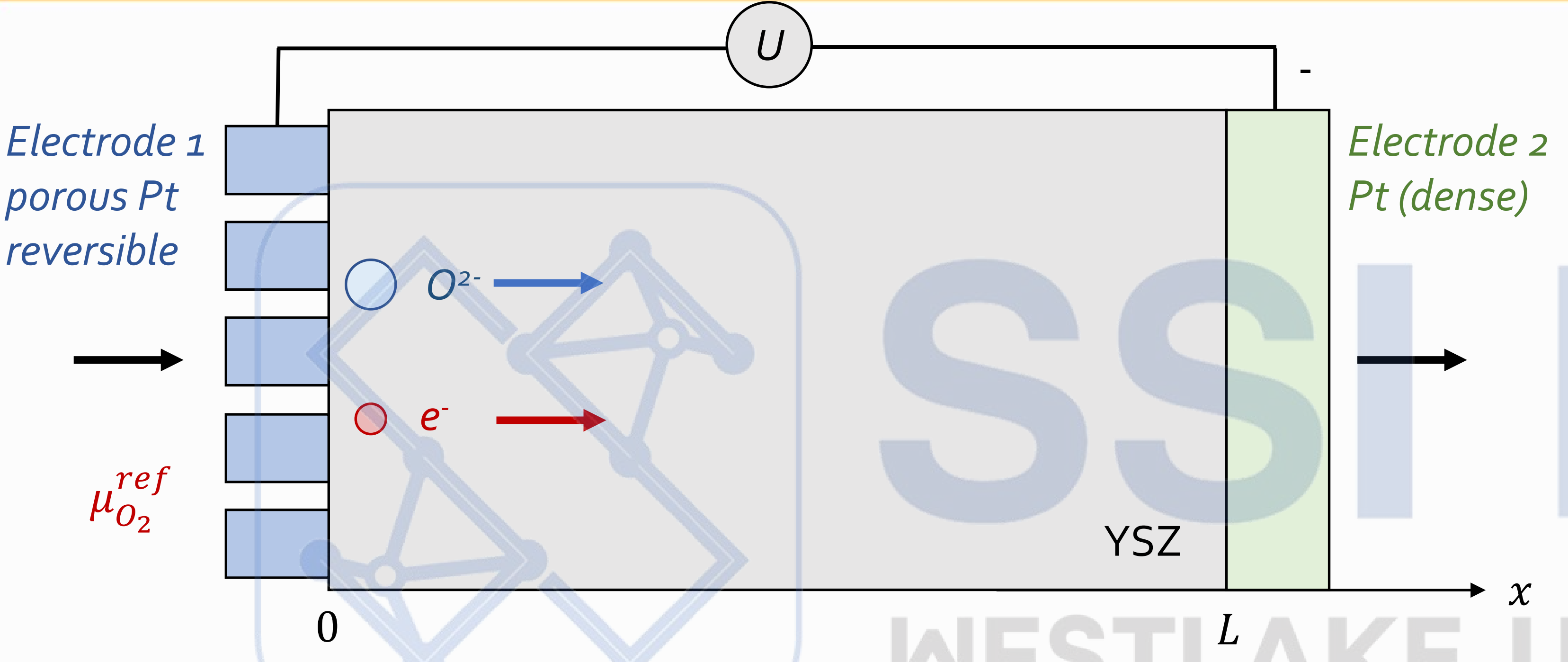
If we define $U = \Delta\tilde{\mu}_{e^-}/F$ $\boxed{\Delta\tilde{\mu}_{O^{2-}} = 0}$

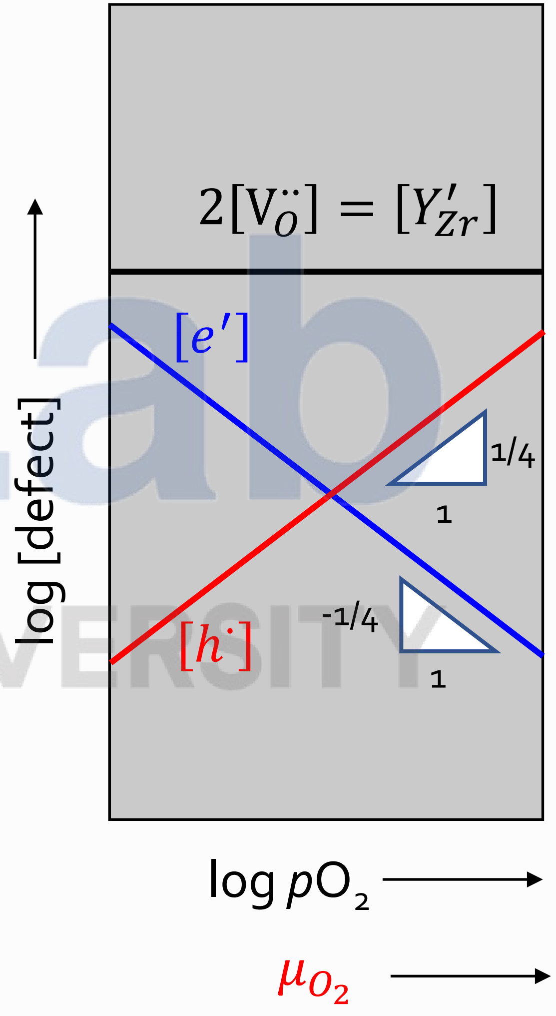
$$\boxed{2\Delta\tilde{\mu}_{O^{2-}} - 4\Delta\tilde{\mu}_{e^-} = \Delta\mu_{O_2} = \mu_{O_2} - \mu_{O_2}^{ref}} \rightarrow \boxed{U = \Delta\tilde{\mu}_{e^-}/F = -1/4\,(\mu_{O_2} - \mu_{O_2}^{ref})/F}$$

In this experiment, we control applied U, then measure current response $j_{eon} = j_e + j_h$

$$\boxed{\sigma_e = \sigma_e^{ref}\left(\frac{p_{O_2}}{p_{O_2}^{ref}}\right)^{-1/4} = \sigma_e^{ref}\exp\left(\frac{FU}{RT}\right)} \quad \boxed{\sigma_h = \sigma_h^{ref}\left(\frac{p_{O_2}}{p_{O_2}^{ref}}\right)^{1/4} = \sigma_h^{ref}\exp\left(-\frac{FU}{RT}\right)}$$

Reversible electrode: Hebb-Wagner measurement





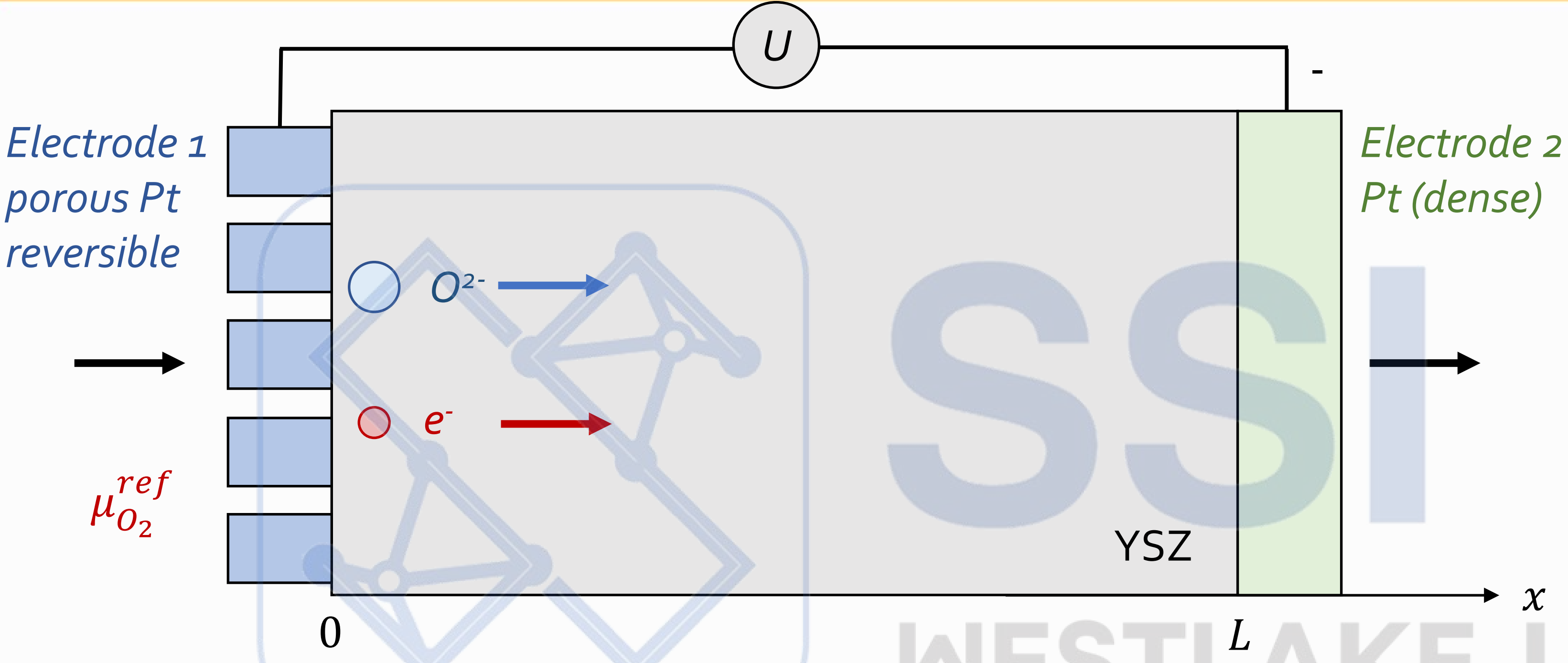
$$\sigma_e = \sigma_e^{ref}\left(\frac{p_{O_2}}{p_{O_2}^{ref}}\right)^{-1/4} = \sigma_e^{ref}\exp\left(\frac{FU}{RT}\right)$$

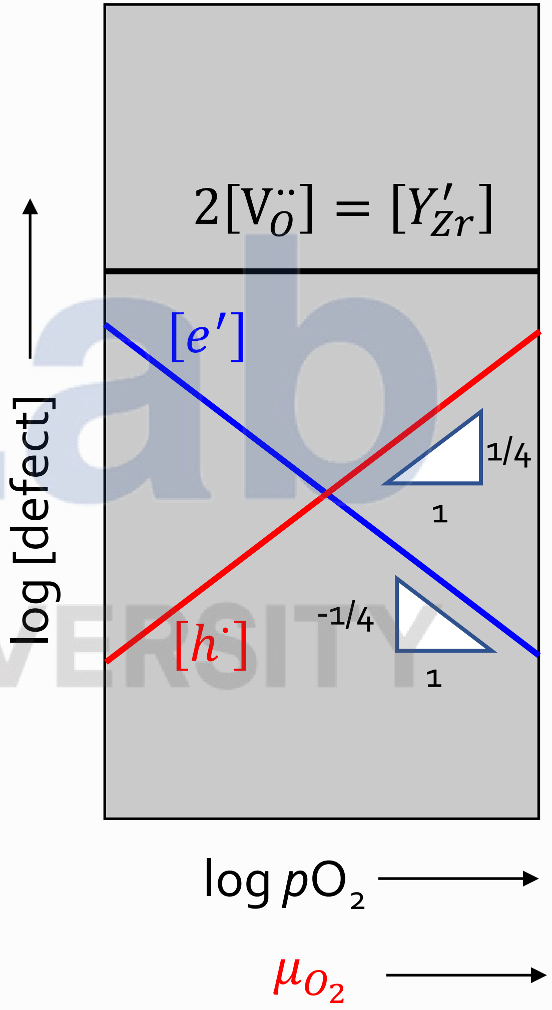
$$\sigma_h = \sigma_h^{ref}\left(\frac{p_{O_2}}{p_{O_2}^{ref}}\right)^{1/4} = \sigma_h^{ref}\exp\left(-\frac{FU}{RT}\right)$$

$$j_e = \frac{1}{L}\int_{\mu_{O_2}^{ref}}^{\mu_{O_2}(L)} -\frac{\sigma_e(x)}{4F}\,d\mu_{O_2} = \frac{1}{L}\int_{\mu_{O_2}^{ref}}^{\mu_{O_2}(L)} -\frac{1}{4F}\sigma_e^{ref}\exp\left(-\frac{\mu_{O_2}(x)-\mu_{O_2}^{ref}}{4RT}\right)d\mu_{O_2}$$

$$= \frac{RT}{FL}(\sigma_e^{ref}\left(\exp\left(\frac{FU}{RT}\right)-1\right)$$

Reversible electrode: Hebb-Wagner measurement





Hebb-Wagner relation:

$$\boxed{j_{eon} = j_e + j_h = \frac{RT}{FL}(\sigma_e^{ref}\left(\exp\left(\frac{FU}{RT}\right) - 1\right) + \sigma_h^{ref}\left(1 - \exp\left(-\frac{FU}{RT}\right)\right))}$$

Reversible electrode: Hebb-Wagner measurement

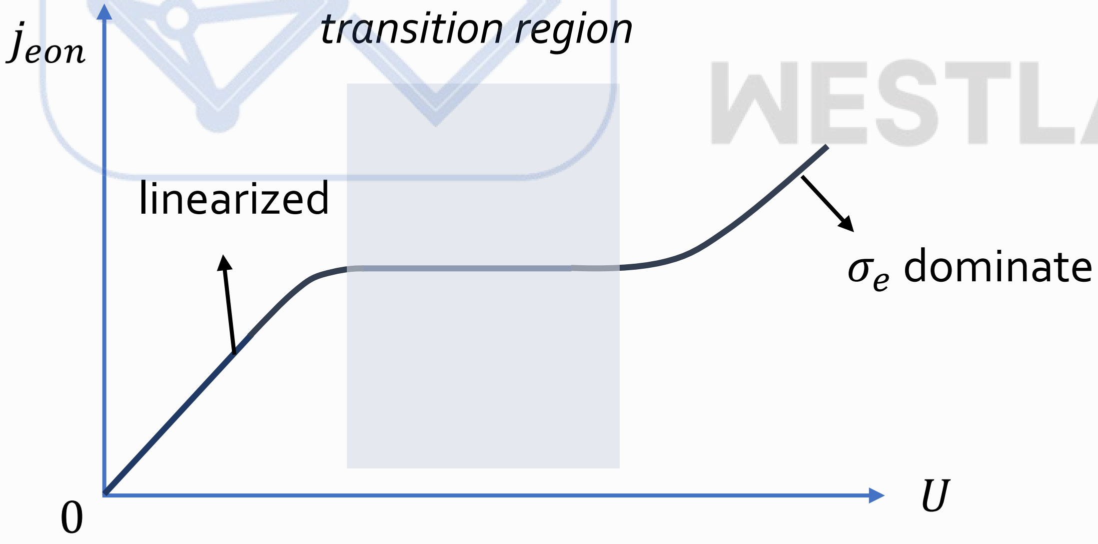
Hebb-Wagner relation:

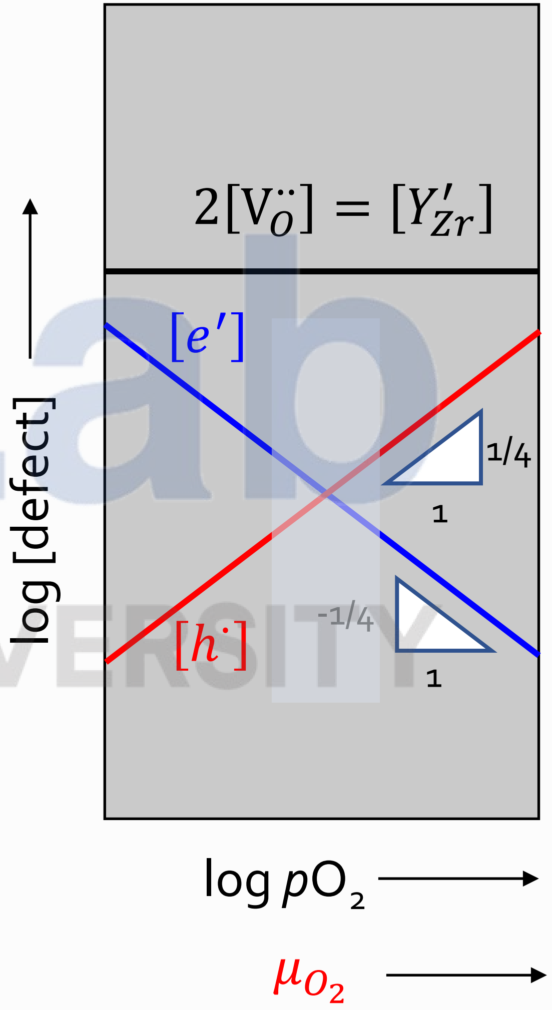
$$j_{eon} = j_e + j_h = \frac{RT}{FL}\left(\sigma_e^{ref}\left(\exp\left(\frac{FU}{RT}\right) - 1\right) + \sigma_h^{ref}\left(1 - \exp\left(-\frac{FU}{RT}\right)\right)\right)$$

For YSZ: (Remember, a large U means reducing potential)

Small U → linearized behavior

$$j_{eon} = j_e + j_h = \frac{U}{L}\left(\sigma_e^{ref} + \sigma_h^{ref}\right)$$





Things we will discuss in this lecture

Type of electrodes and Stoichiometry polarization:

- What are the different types of electrodes used for measuring conductivity?

- How to understand the stoichiometry polarization with ion-blocking electrodes?

Electron-blocking electrodes and the Hebb-Wagner method:

- How to understand the intercalation process of ions & electrons?

- What is the Hebb-Wagner method for measuring conductivity?

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

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End of Lecture 6
Solid State Ionics Fall 2023

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