Lecture 8:
Impedance Spectroscopy

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Solid State Ionics

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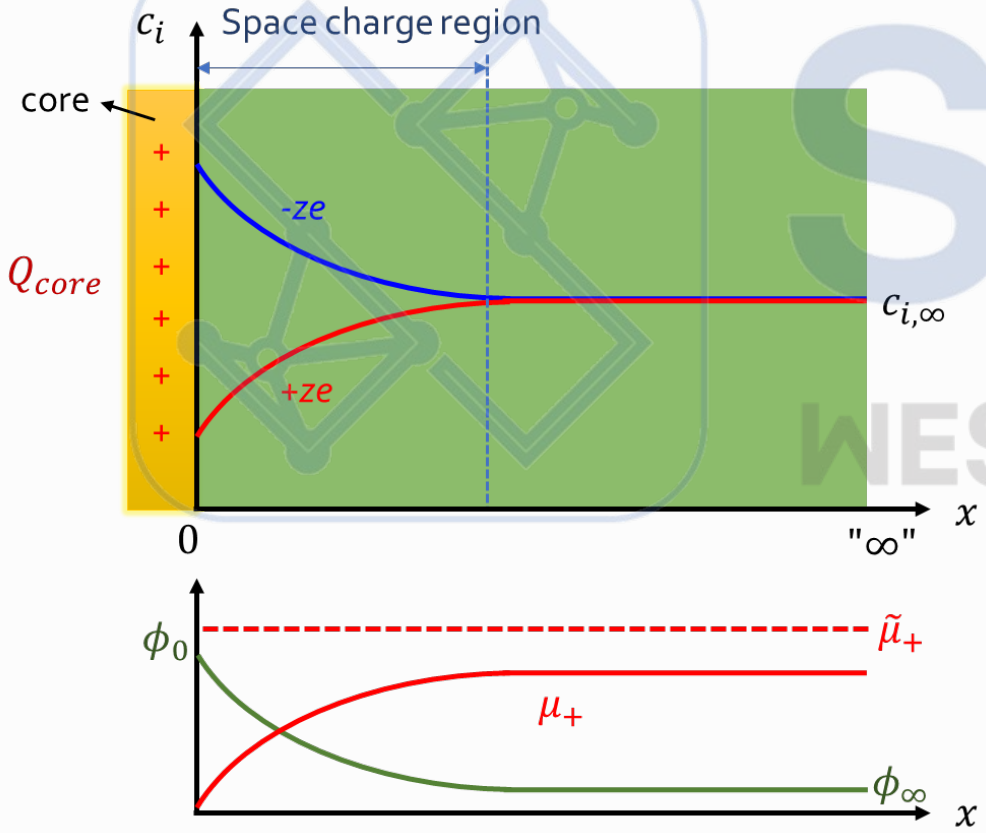
Space charge layers

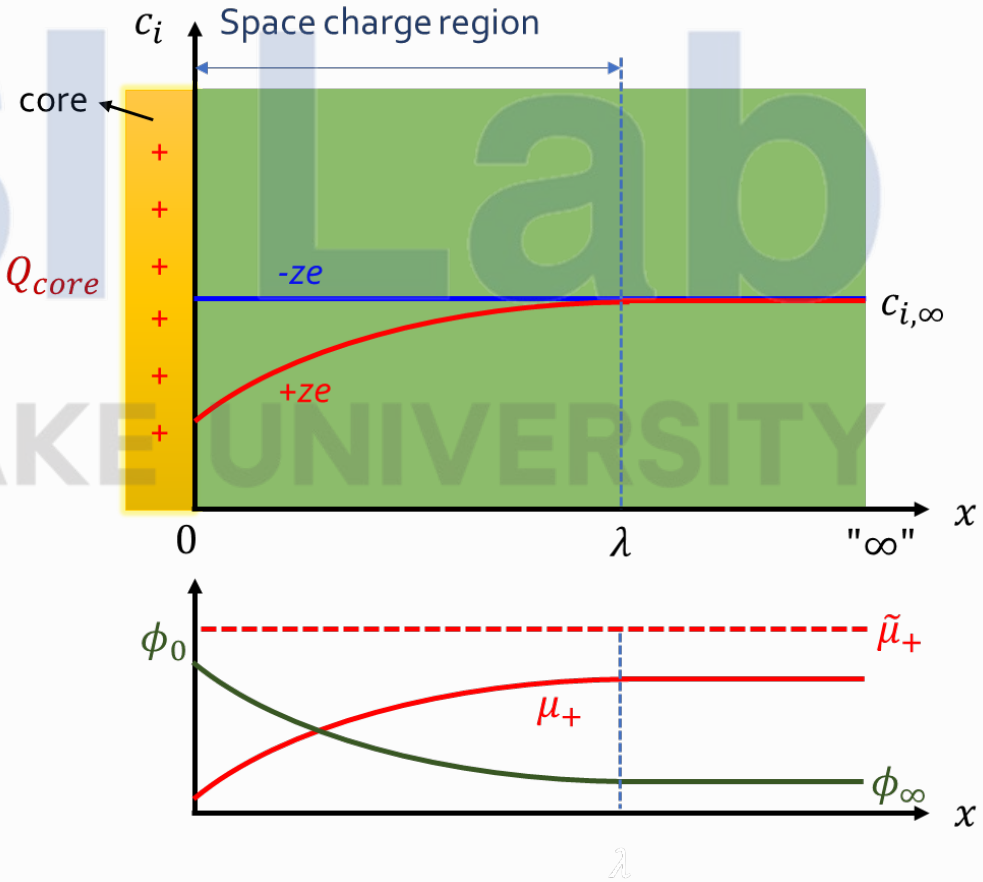
Electric double layers (EDLs)

Gouy-Chapman case

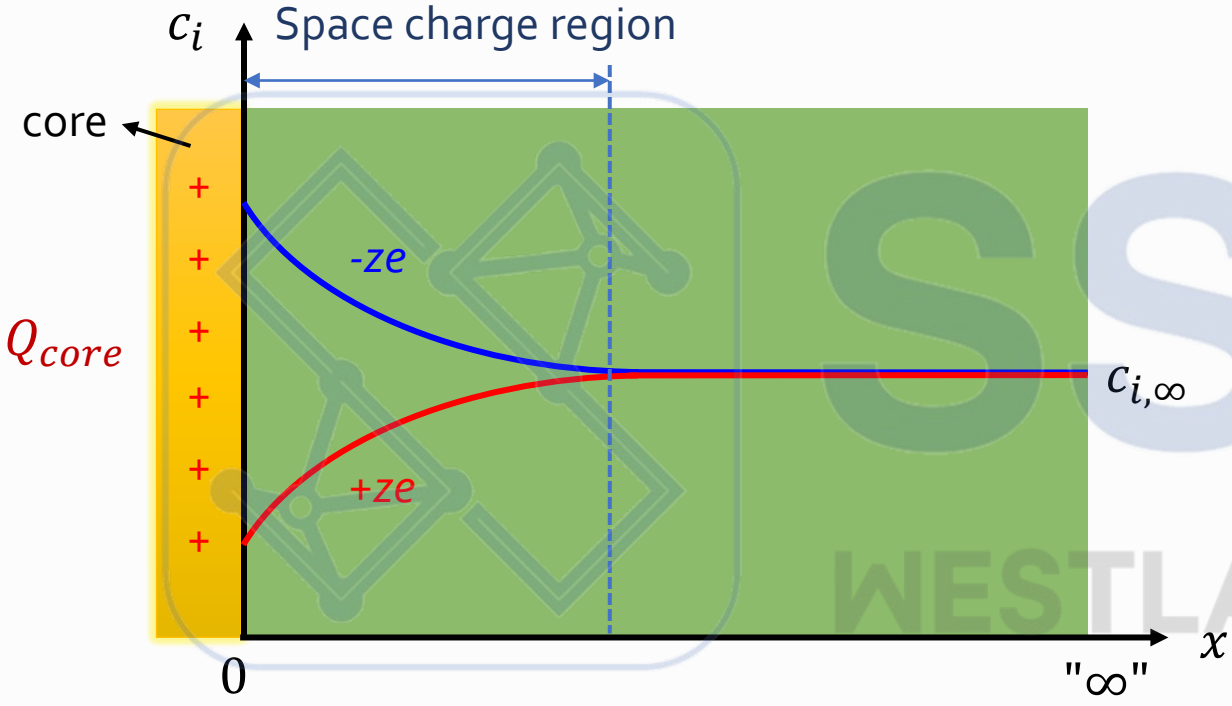


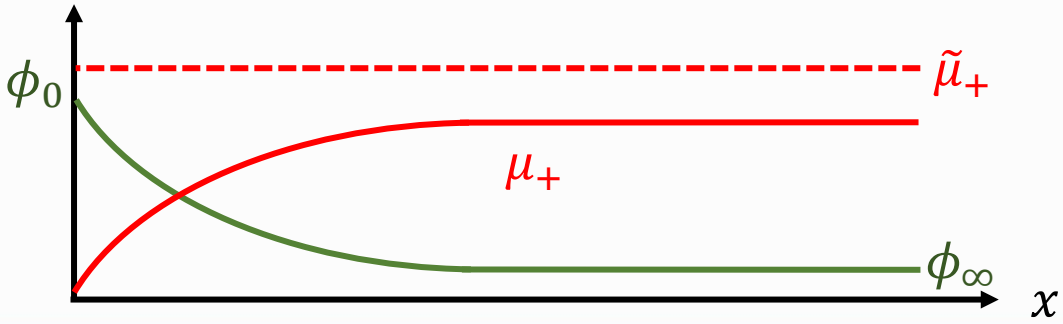
p-n junctions (diodes)

Mott-Schottky case



Gouy-Chapman case: concentration/potential profile





$$\rho(x) = -2zec_{i,\infty}\frac{ze\phi(x)}{k_BT}$$

Apply Poisson's equation:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{2z^2e^2c_{i,\infty}}{\varepsilon_0\varepsilon_r k_BT}\phi(x)$$

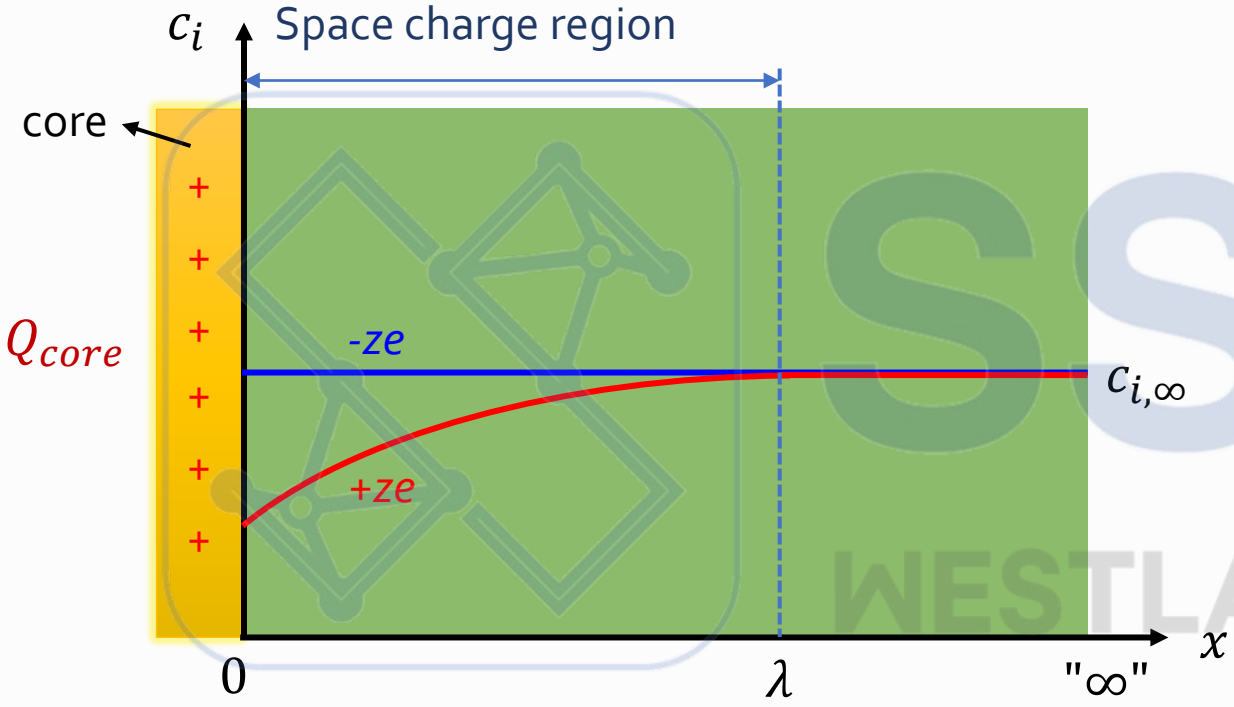
We define ***Debye length*** λ_D as: $\lambda_D = \sqrt{\frac{\varepsilon_0\varepsilon_r k_BT}{2z_i^2 c_{i,\infty} e^2}}$

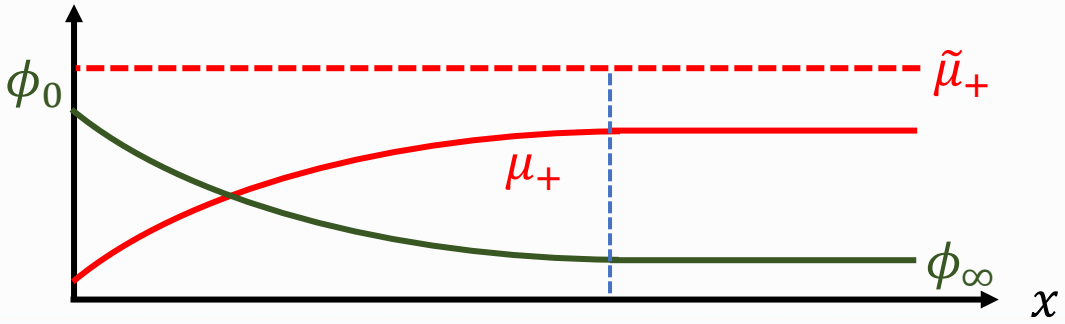
Then we have:

$$\frac{d^2\phi}{dx^2} = \frac{\phi(x)}{{\lambda_D}^2} \rightarrow \phi(x) = \phi_0\exp(-x/\lambda_D)$$

(We set $\phi_\infty = 0$)

Mott-Schottky case: concentration/potential profile





Poisson's *eqn.*

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r} = \frac{zec_{i,\infty}}{\varepsilon_0\varepsilon_r}$$

We need to integrate ***twice*** to get the potential profile.

Boundary conditions are:

$$\phi(0) = \phi_0 \;\&\; \phi(\lambda) = \phi_\infty = 0$$

$$\phi'(\lambda) = 0$$

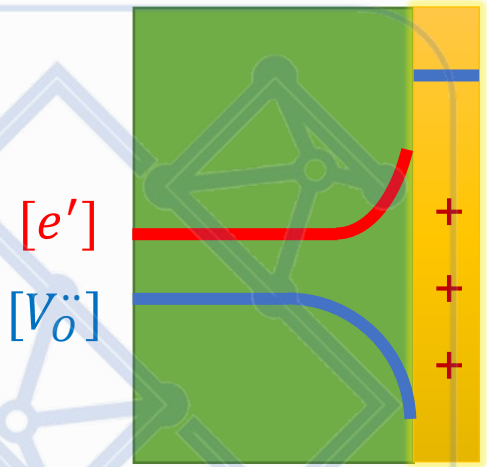
$$\phi'(x) = \frac{zec_{i,\infty}}{\varepsilon_0\varepsilon_r}(x-\lambda)$$

$$\phi(x) = \frac{zec_{i,\infty}}{2\varepsilon_0\varepsilon_r}(x-\lambda)^2$$

$$\lambda = \sqrt{\frac{2\varepsilon_0\varepsilon_r\phi_0}{zec_{i,\infty}}}$$

Compare Gouy-Chapman and Mott Schottky cases

Gouy-Chapman case
(All defects are mobile)

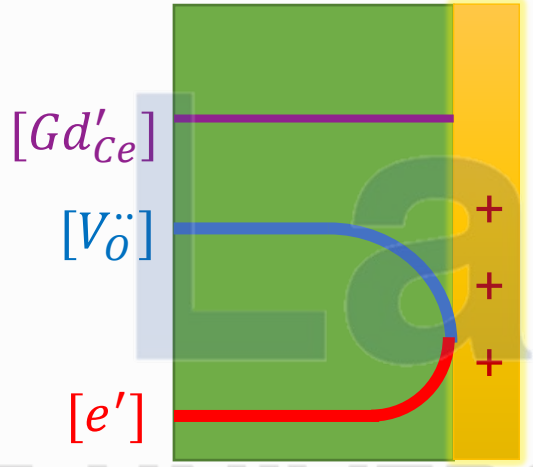


Space charge layer (SCL) width

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2 z_i^2 c_{i,\infty} e^2}}$$

Independent on the core charge Q_{core}

Mott-Schottky case
(Majority dopants are frozen (*immobile*))



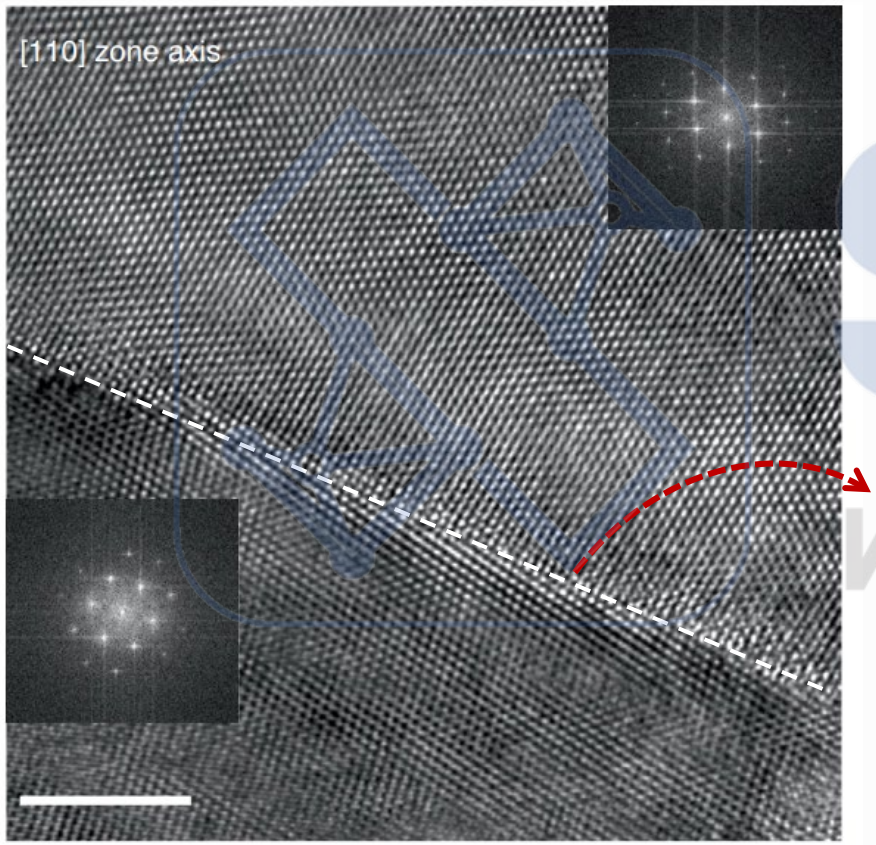
$$\lambda = \sqrt{\frac{2\varepsilon_0 \varepsilon_r \phi_0}{zec_{i,\infty}}} \quad \text{or} \quad \lambda = \frac{Q_{core}}{zec_{i,\infty}}$$

Dependent on the core charge Q_{core}

In both cases, a higher bulk concentration $c_{i,\infty}$ → shorter SCL width (*faster screening*)

Can we see the potential profile in the real space?

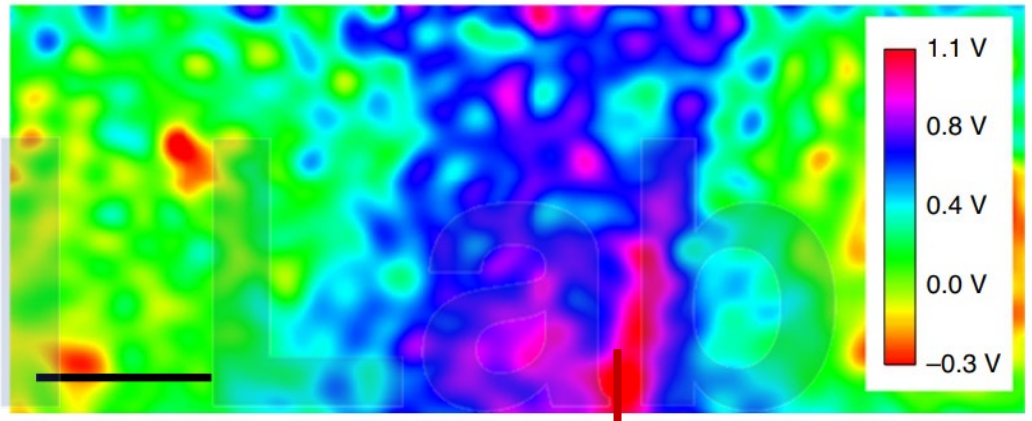
0.2% at. Sm-doped $CeO_{2-\delta}$

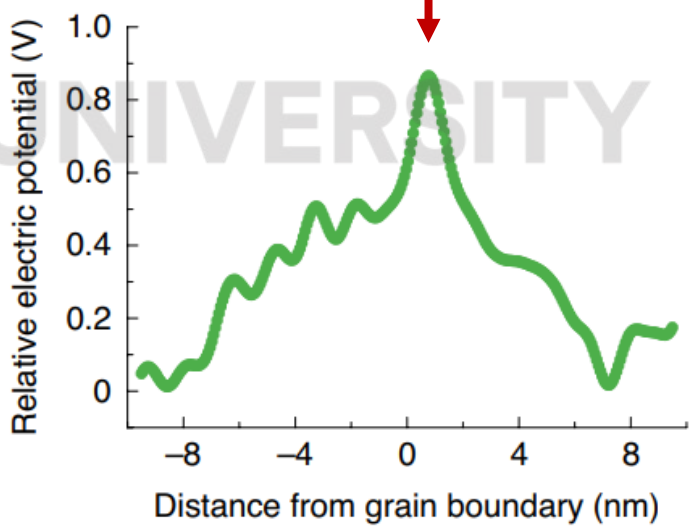


Grain boundary (GB) "core"

$\phi(x)$

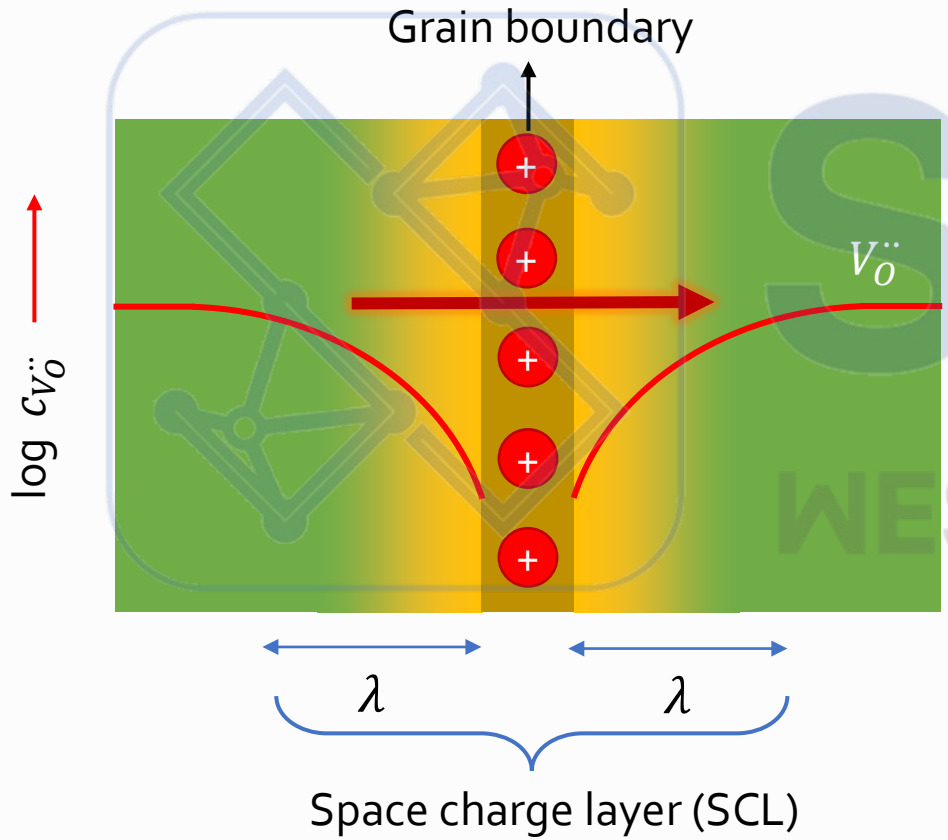
Electron holography in TEM





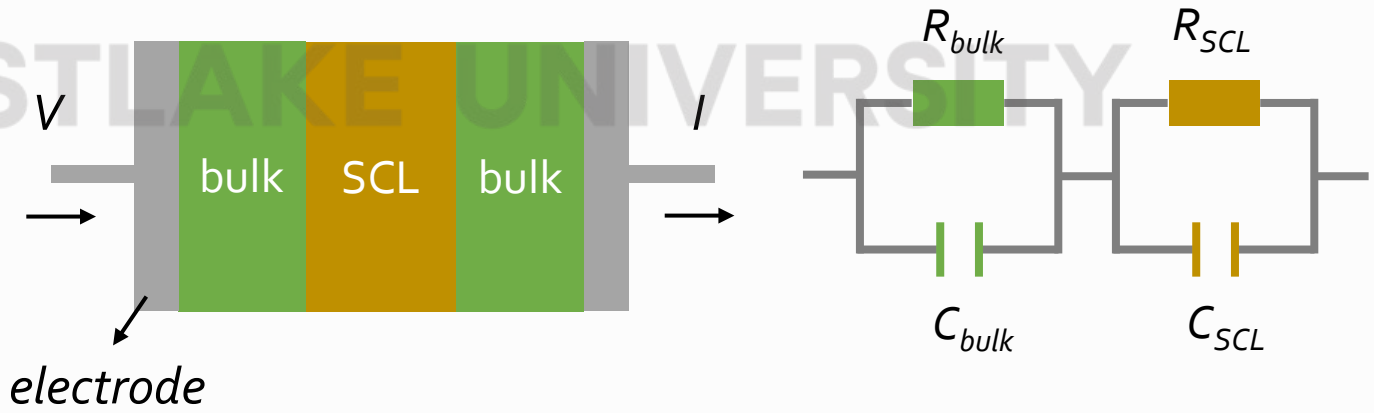
Recap: Implications on the conductivity: series layer model

$$\sigma_{ion} = c_{V_O^{\cdot\cdot}} z_{V_O^{\cdot\cdot}} F M_{V_O^{\cdot\cdot}}$$



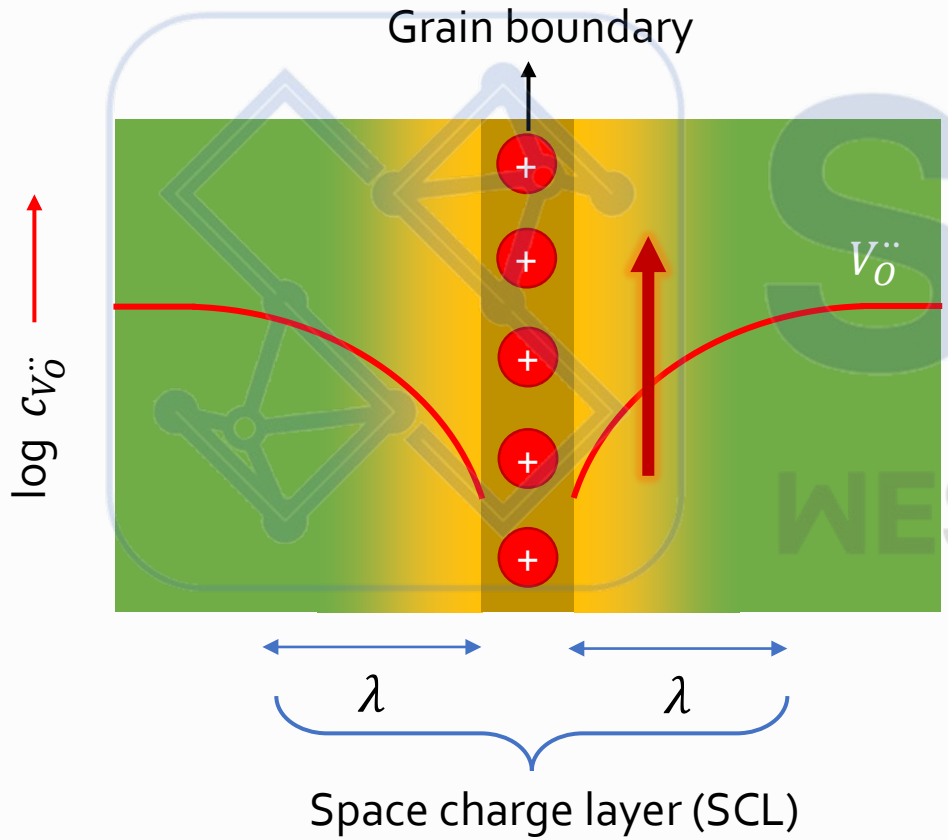
If we assume the mobility of $V_O^{\cdot\cdot}$ is the same in the bulk and grain boundary, then the ionic conductivity is mainly affected by the depletion of oxygen vacancies.

Consider the series layer model:

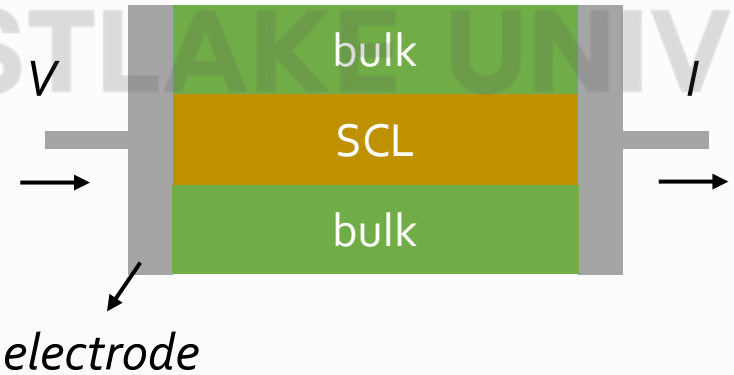


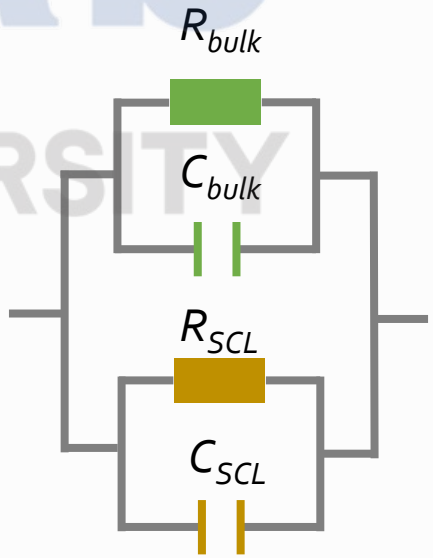
Recap: Implications on the conductivity: parallel layer model

$$\sigma_{ion} = c_{V_O^{\cdot\cdot}} z_{V_O^{\cdot\cdot}} F M_{V_O^{\cdot\cdot}}$$



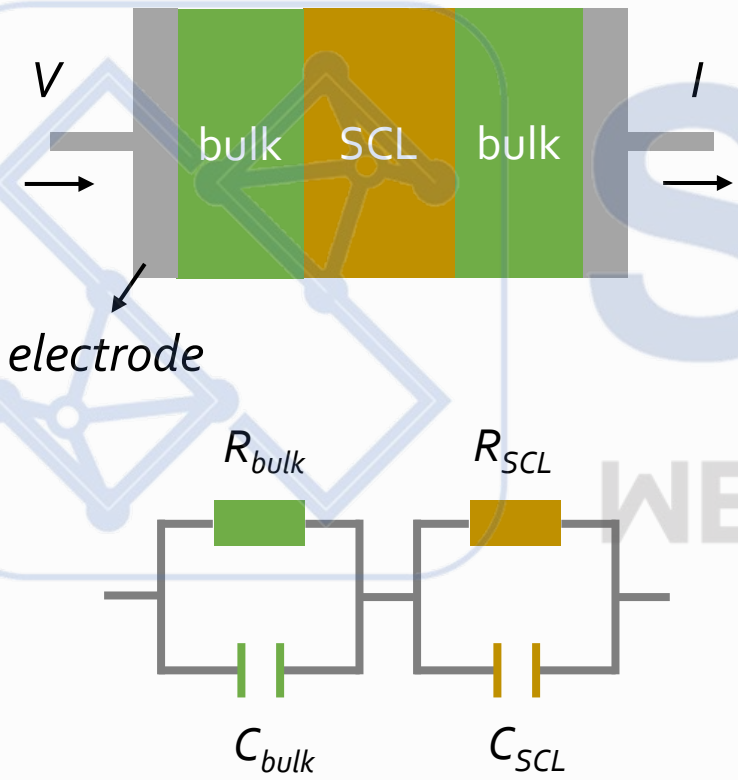
We can also construct the parallel layer model:



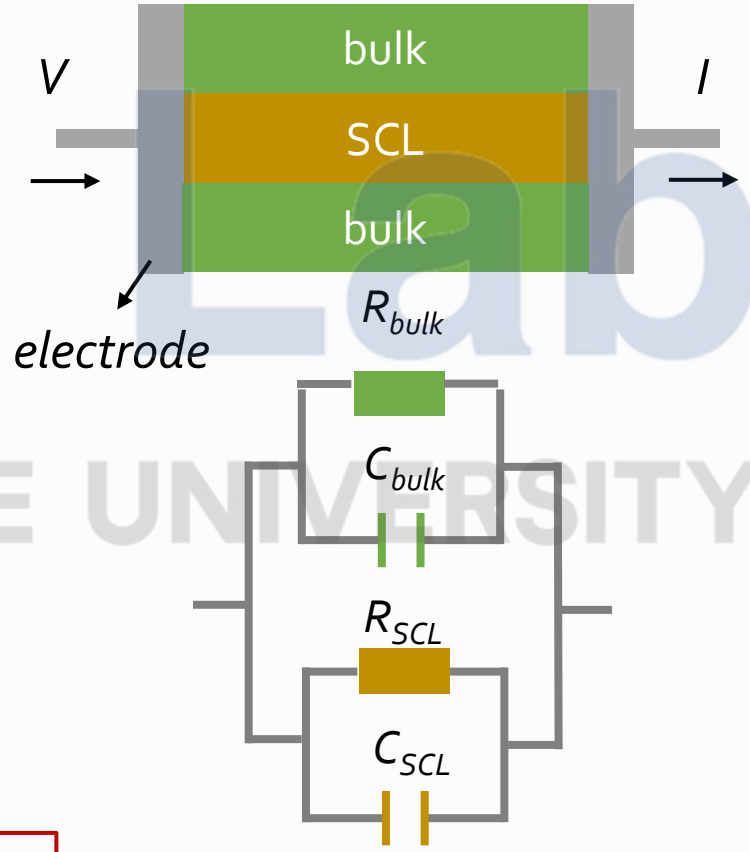


How to evaluate resistance and capacitance?

Series layer model



Parallel layer model



How to theoretically model and experimentally measure R_{SCL} & C_{SCL} ?

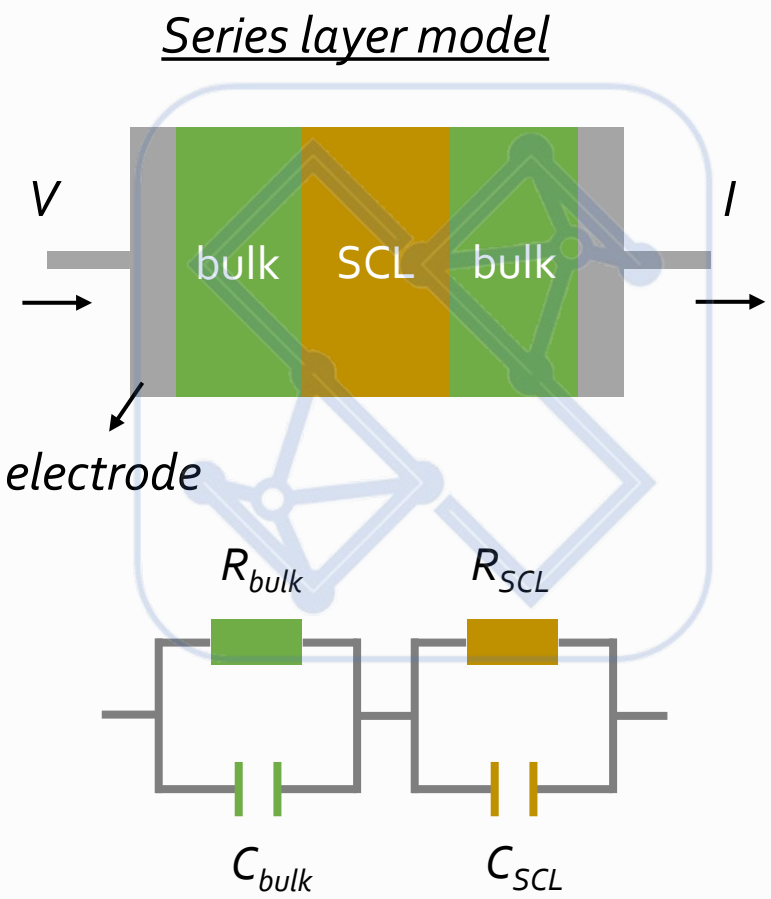
Things we will discuss in this lecture

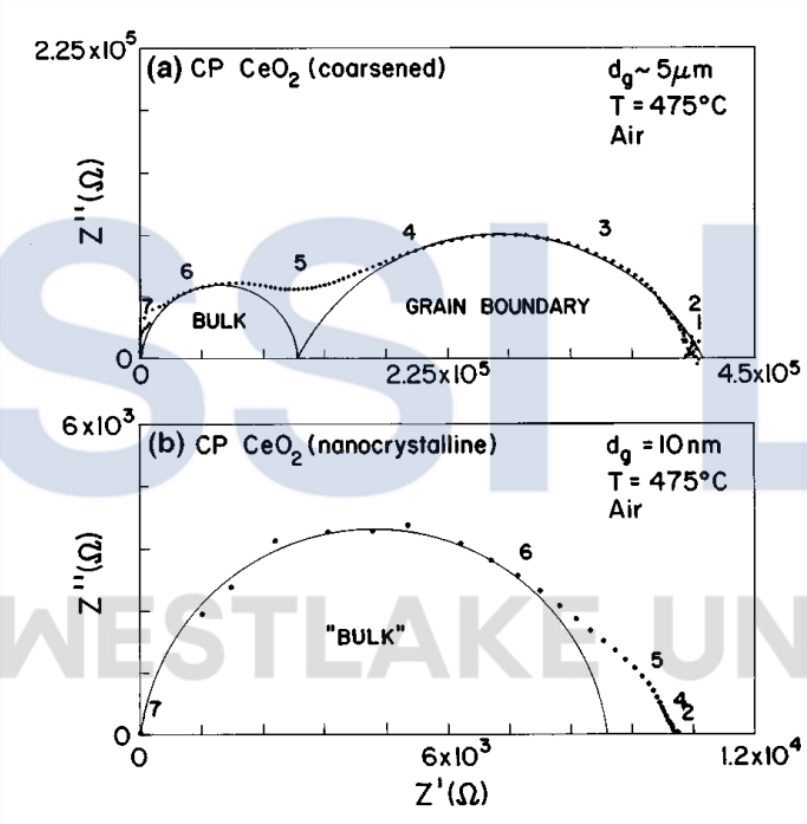
Electrochemical Impedance Spectroscopy (EIS):

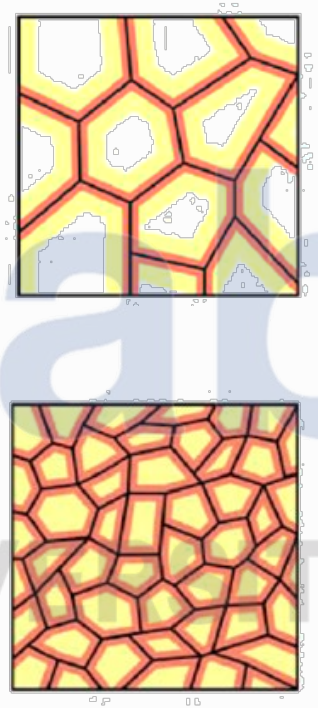
- Why do we need electrochemical impedance spectroscopy? What problem are we trying to solve with this technique?
- How to understand the equivalent circuit model? How does the equivalent circuit model for a polycrystalline sample with grain boundaries look like?

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

Why do we need Electrochemical Impedance Spectroscopy?







Coarse-grained

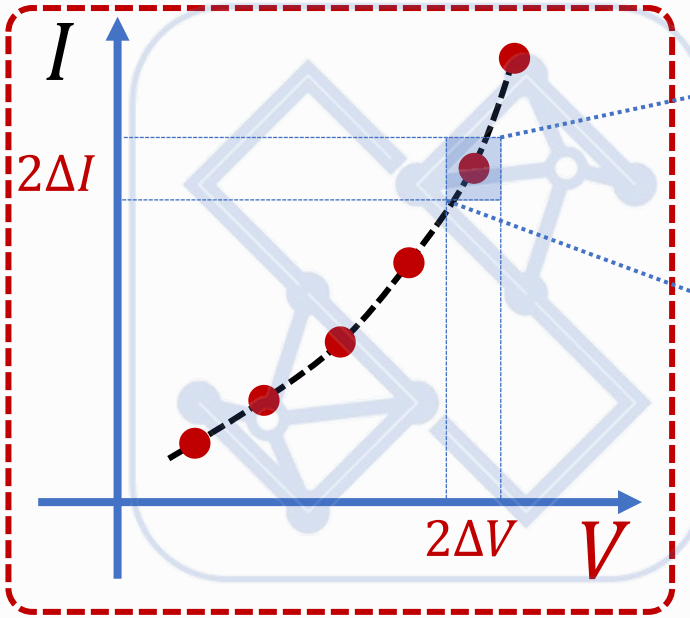
Nanocrystalline

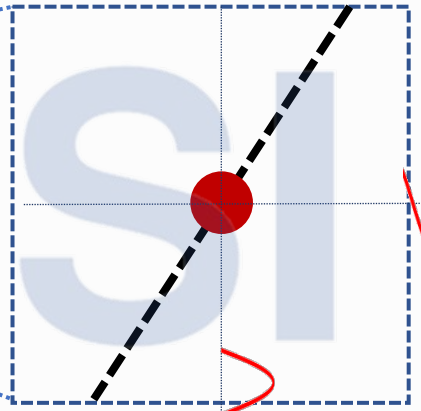
Time constant $\tau = RC$ → separate the contribution of bulk and SCL in the ***frequency domain*** ($f = 1/\tau$).

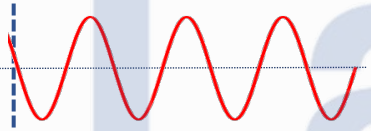
The working principle of EIS

I-V characteristics of an electrochemical system

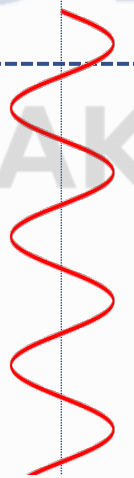
Assumption: if the perturbation is small, then the ***I-V*** curve can be *linearized.*







$$I(t) = \Delta I \cos(\omega t - \varphi)$$

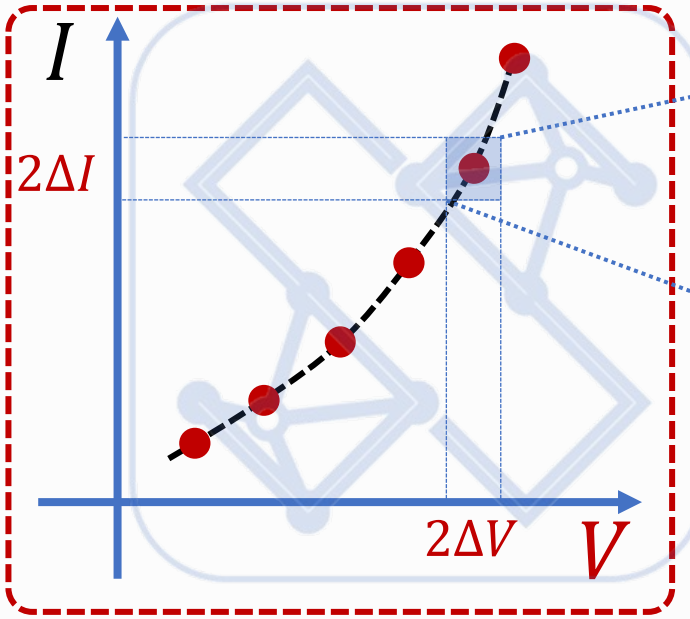


$$V(t) = \Delta V \cos(\omega t)$$

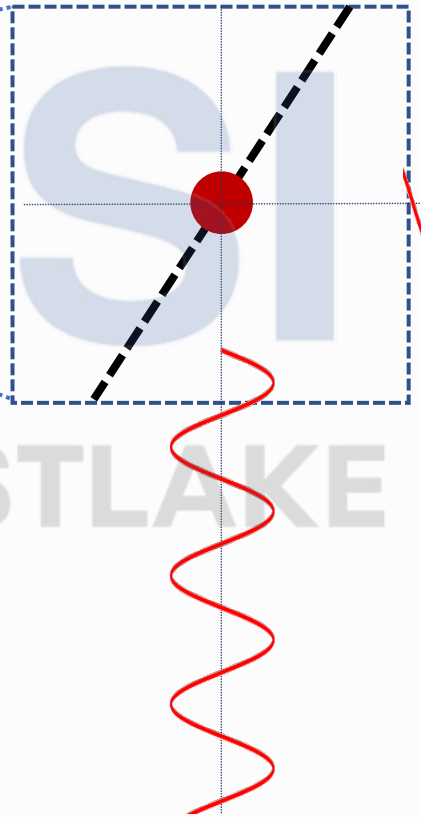
$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{\Delta V}{\Delta I} \frac{\cos(\omega t)}{\cos(\omega t - \varphi)}$$

The working principle of EIS

I-V characteristics of an electrochemical system



Assumption: if the perturbation is small, then the ***I-V*** curve can be *linearized.*



$$I(t) = \Delta I e^{i(\omega t - \varphi)}$$

Note: $i = \sqrt{-1}$

$$V(t) = \Delta V e^{i\omega t}$$

It is easier to use the complex form of waves, we have:

$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{\Delta V}{\Delta I} \frac{e^{i\omega t}}{e^{i(\omega t - \varphi)}}$$

$$Z(\omega) = |Z|\cos\varphi + i|Z|\sin\varphi$$

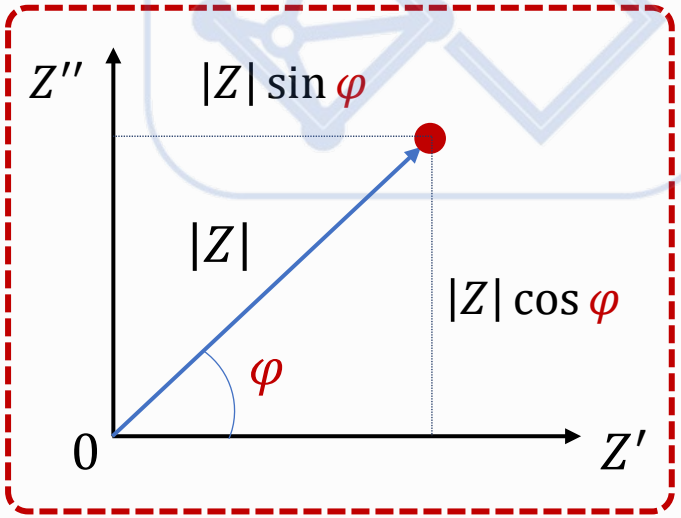
Z' or $Re(Z)$ $\quad$ Z'' or $Im(Z)$

The working principle of EIS: Nyquist plot

$$Z(\omega) = |Z|\cos\varphi + i|Z|\sin\varphi$$

Z' or $Re(Z)$ $\quad$ Z'' or $Im(Z)$

$$Z(\omega) = Z' + iZ''$$



Nyquist plot
(Z'~Z'' plot)

Note: more commonly we plot Z'~ $-Z''$

For a resistor, since ***I*** and ***V*** should always be ***in phase***, we have:

Note: only has the real part; invariant w/ frequency ω

For a capacitor, ***I*** and ***V*** should always be completely ***out of phase***

$$I(t) = \Delta I e^{i(\omega t - \varphi)}$$

$$I(t) = \frac{dQ(t)}{dt}$$

$$Q(t) = \frac{\Delta I}{i\omega} e^{i(\omega t - \varphi)}$$

The working principle of EIS: Nyquist plot

For a capacitor, ***I*** and ***V*** should always be completely ***out of phase***

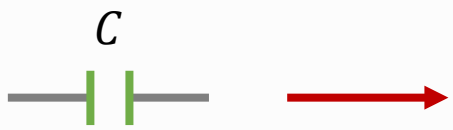
$$I(t) = \Delta I e^{i(\omega t - \varphi)}$$

$$I(t) = \frac{dQ(t)}{dt}$$

$$Q(t) = \frac{\Delta I}{i\omega} e^{i(\omega t - \varphi)}$$

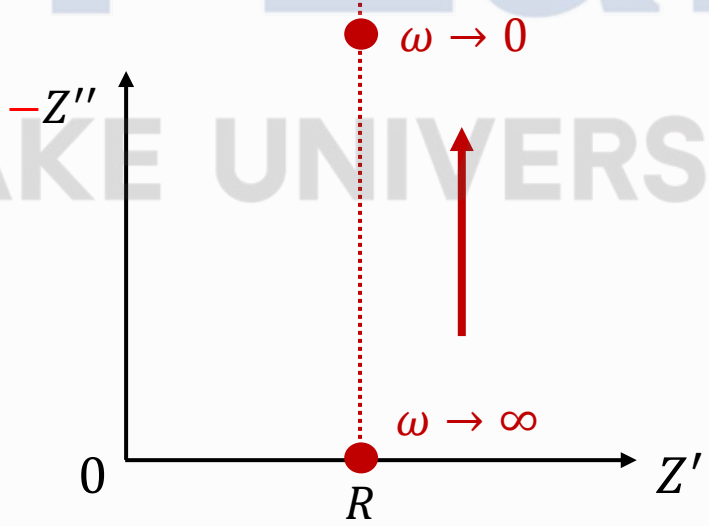
$$V(t) = \frac{Q(t)}{C} = \frac{\Delta I}{i\omega C} e^{i(\omega t - \varphi)} = \frac{I(t)}{i\omega C}$$

$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{1}{i\omega C}$$



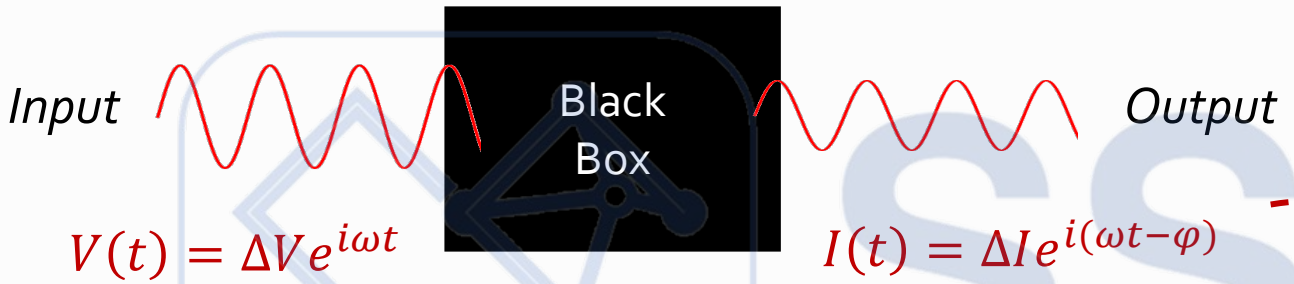
$$Z(\omega) = \frac{1}{i\omega C} = -i\frac{1}{\omega C}$$

$$Z(\omega) = R + \frac{1}{i\omega C} = R - i\frac{1}{\omega C}$$



Nyquist plot
($Z' \sim -Z''$ plot)

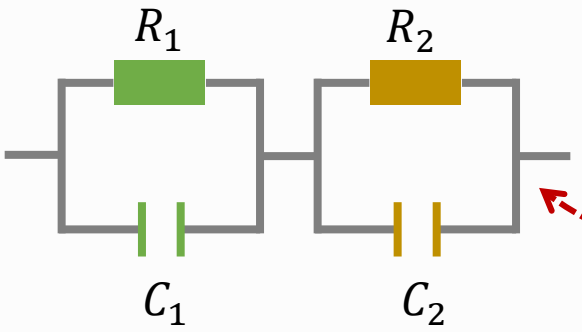
Which equivalent circuit should be chosen?

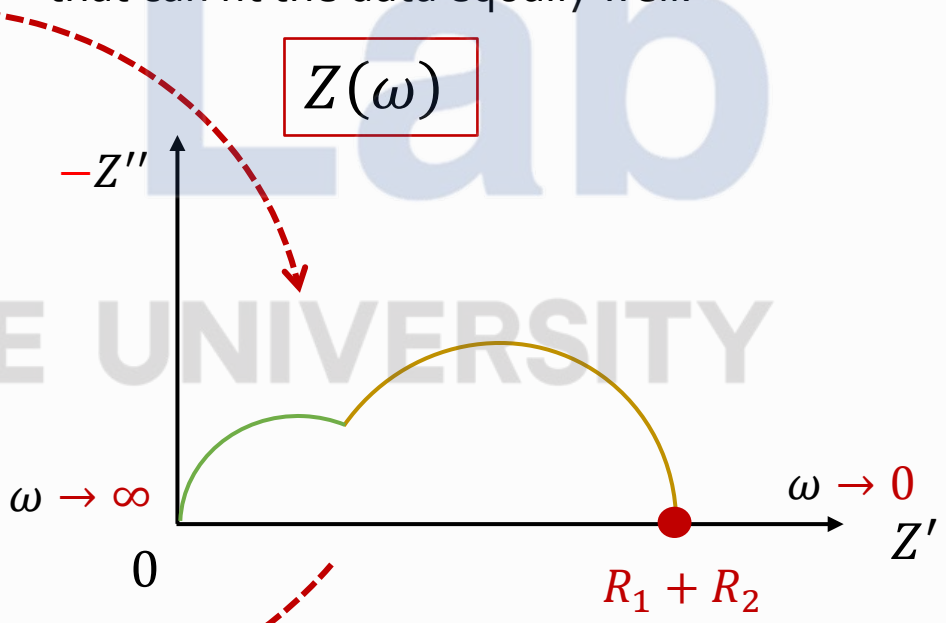


Note:

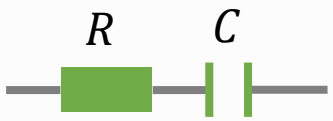
- The electrochemical system is a black box, *i.e.*, there is no prior knowledge on which circuit model should be used;
- There might be more than one equivalent circuit that can fit the data equally well.

Fit the impedance data with equivalent circuit





Nyquist plot: *R*-*C* in series

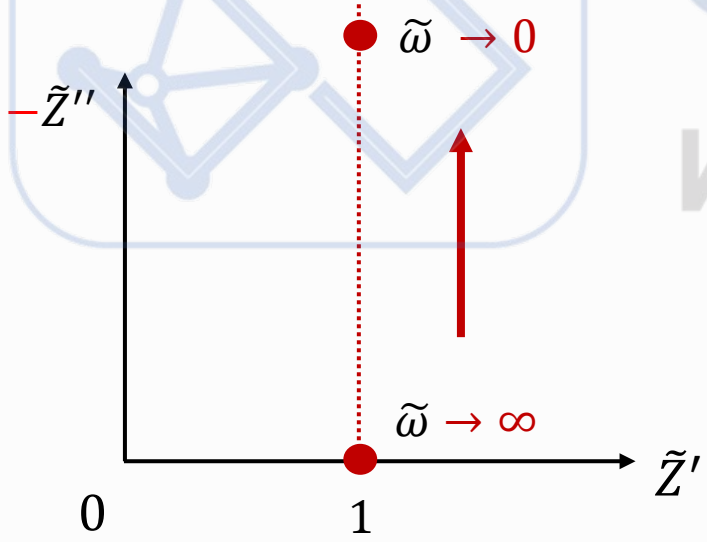


$$Z(\omega) = R + \frac{1}{i\omega C}$$

$$Z(\omega) = R(1 + \frac{1}{i\omega CR})$$

We can define dimensionless impedance $\tilde{Z} = Z/R$
dimensionless frequency $\tilde{\omega} = \omega RC$

$$\tilde{Z}(\omega) = 1 + \frac{1}{i\tilde{\omega}}$$

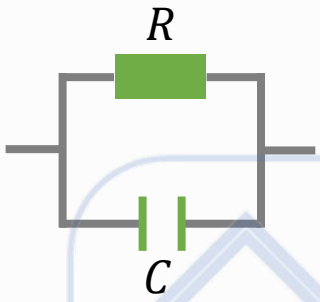


Nyquist plot for dimensionless $\tilde{Z}$ ($\tilde{Z}' \sim -\tilde{Z}''$ plot)

Note: the advantages of using normalized dimensionless quantities are:

- The equations are much easier to write :)
- We can see how each physical quantity scales, *e.g.*
  - $\tilde{Z} = Z/R \rightarrow Z$ scales with resistance R;
  - $\tilde{\omega} = \omega RC \rightarrow \omega$ scales inversely with RC. Keep in mind that time constant $\tau = RC$

Nyquist plot: *R*-*C* in parallel



$$\tilde{Z}(\omega) = \frac{1}{1 + i\tilde{\omega}}$$

$$\tilde{Z}(\omega) = \frac{1}{1 + i\tilde{\omega}} = \frac{1}{1 + \tilde{\omega}^2} - \frac{i\tilde{\omega}}{1 + \tilde{\omega}^2}$$

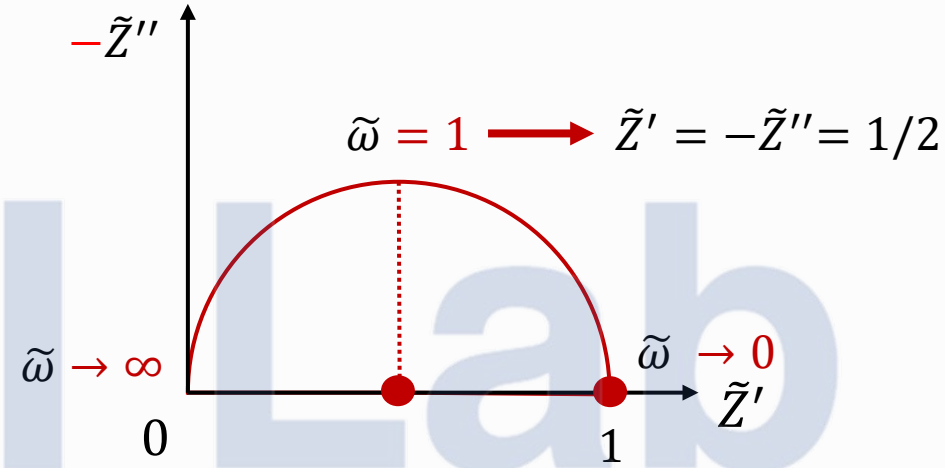
$$\tilde{Z}' = \frac{1}{1 + \tilde{\omega}^2}$$

$$-\tilde{Z}'' = \frac{\tilde{\omega}}{1 + \tilde{\omega}^2}$$

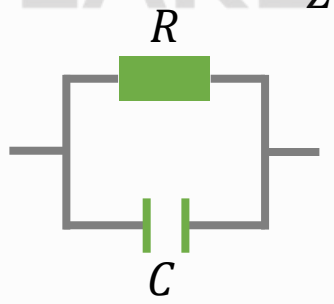
$$(\tilde{Z}' - \frac{1}{2})^2 + (-\tilde{Z}'')^2 = (\frac{1}{2})^2$$

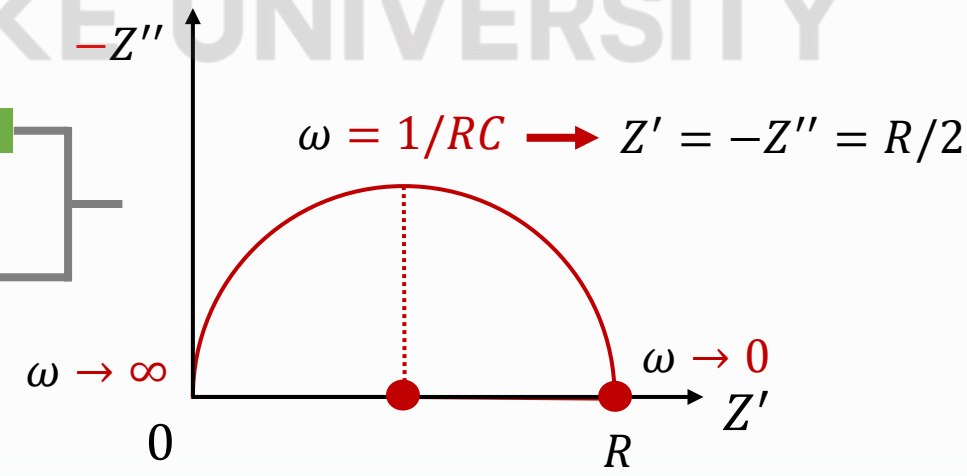
It is a semi-circle ($\tilde{\omega} > 0$):

- Radius = 1/2
- Center = (1/2, 0)

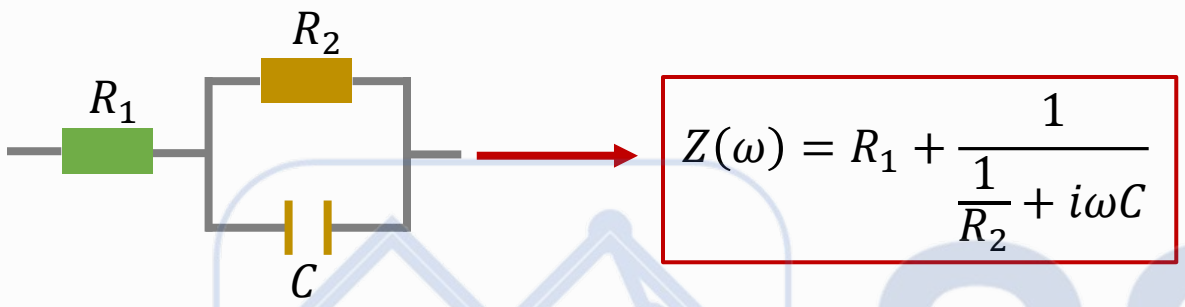


add dimensions

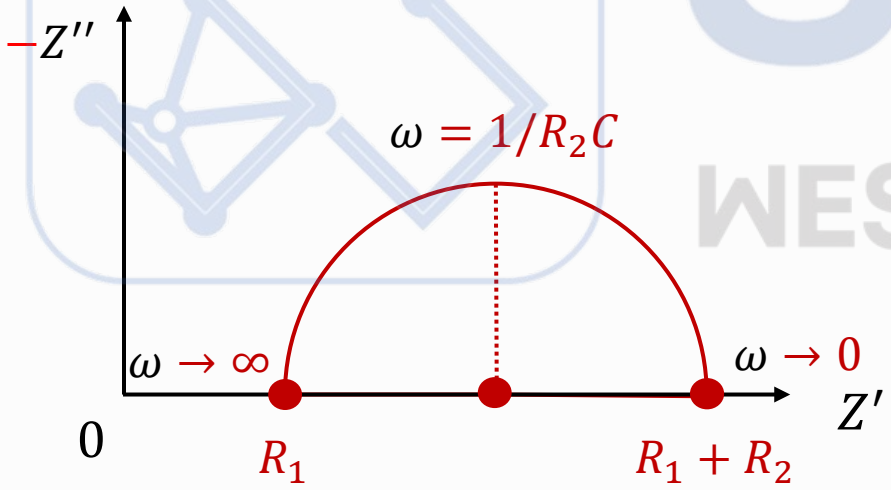


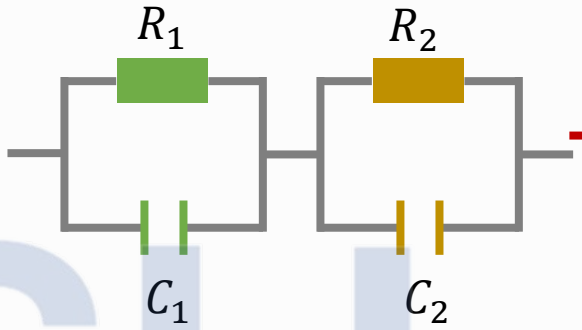


Nyquist plot: *more complicated circuits*

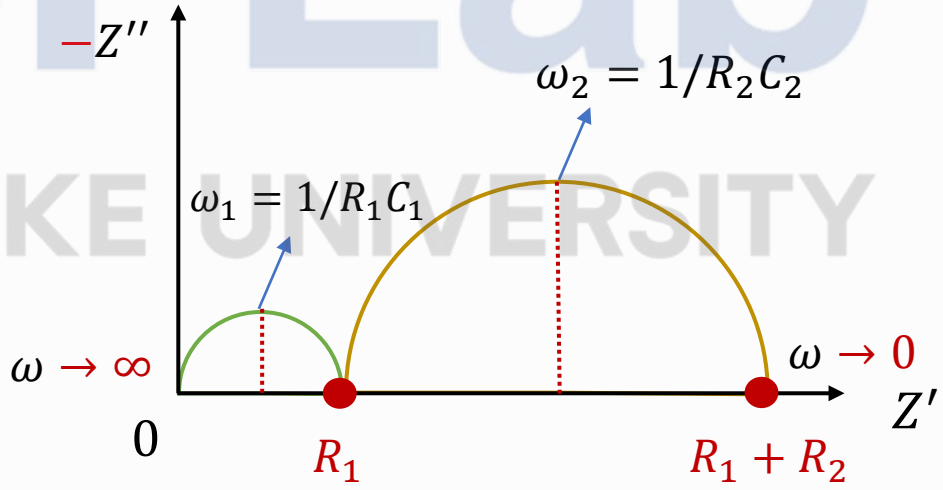


$$Z(\omega) = R_1 + \frac{1}{\frac{1}{R_2} + i\omega C}$$

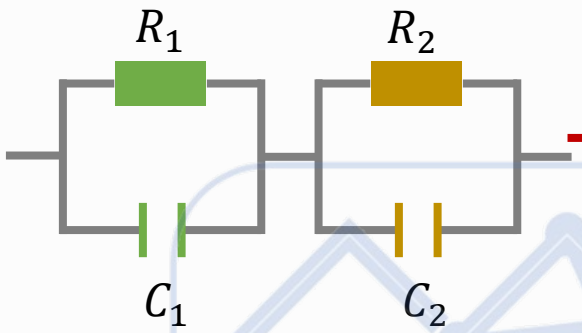




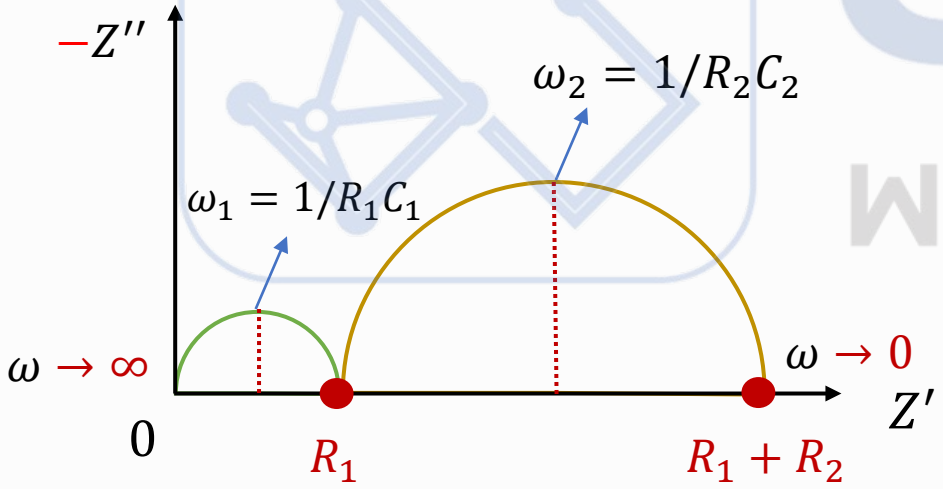
$$Z(\omega) = \frac{1}{\frac{1}{R_1} + i\omega C_1} + \frac{1}{\frac{1}{R_2} + i\omega C_2}$$



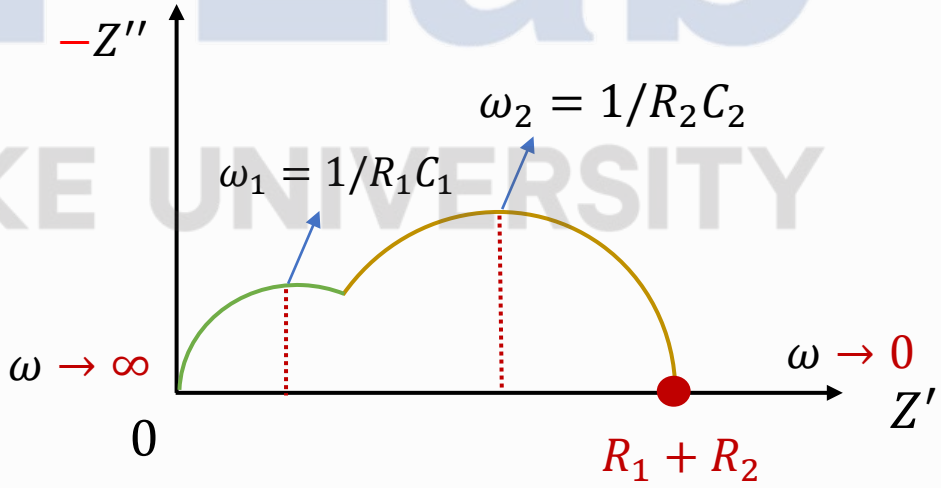
Nyquist plot: *more complicated circuits*



$$Z(\omega) = \frac{1}{\frac{1}{R_1} + i\omega C_1} + \frac{1}{\frac{1}{R_2} + i\omega C_2}$$

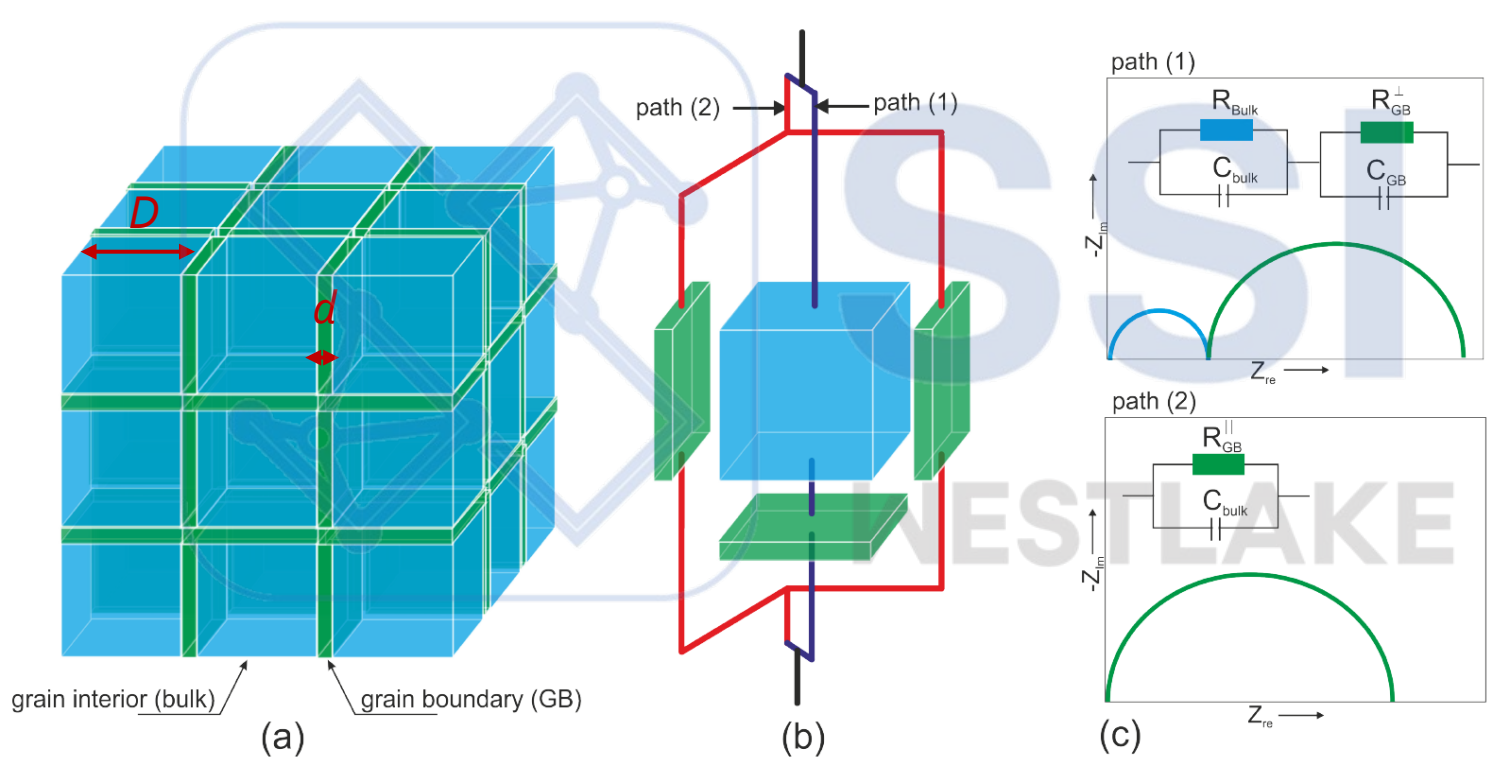


If ω_1 and ω_2 become closer



Brick layer model

Consider a polycrystalline material with much lower conductivity at the grain boundaries (GB) compared to the bulk



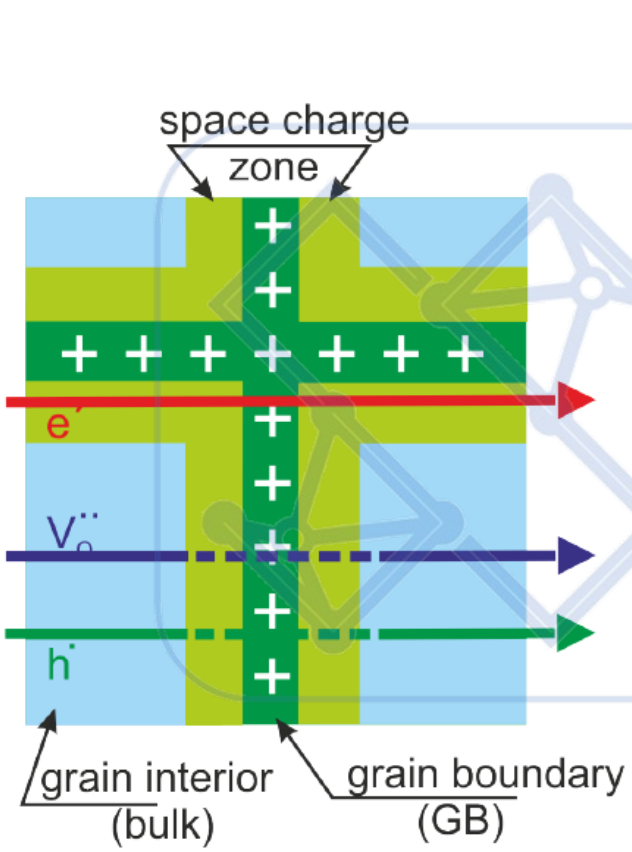
$$\frac{R_{bulk}}{R_{GB}} = \frac{\sigma_{GB}}{\sigma_{bulk}}\frac{D}{d} \qquad \frac{C_{bulk}}{C_{GB}} = \frac{\varepsilon_{bulk}}{\varepsilon_{GB}}\frac{d}{D}$$

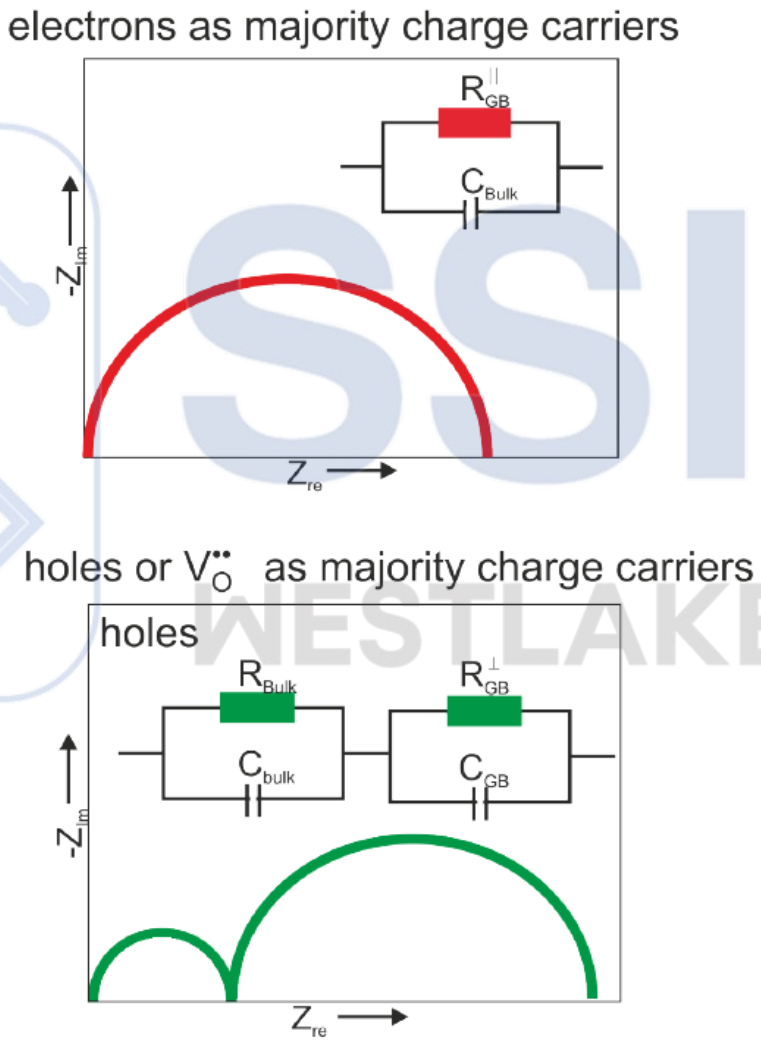
$(d \ll D)$

- If $\sigma_{GB} \ll \sigma_{bulk}$, then path (1) (*i.e.*, ***series layer model***) will be dominate;
- If $\sigma_{GB} \gg \sigma_{bulk}$, then path (2) (*i.e.*, ***conducting along GBs***) might be activated.

PhD Thesis, Kiran Adepalli, Max-Planck Institute for Solid State Research (2013)

Series layer model for different charge carriers



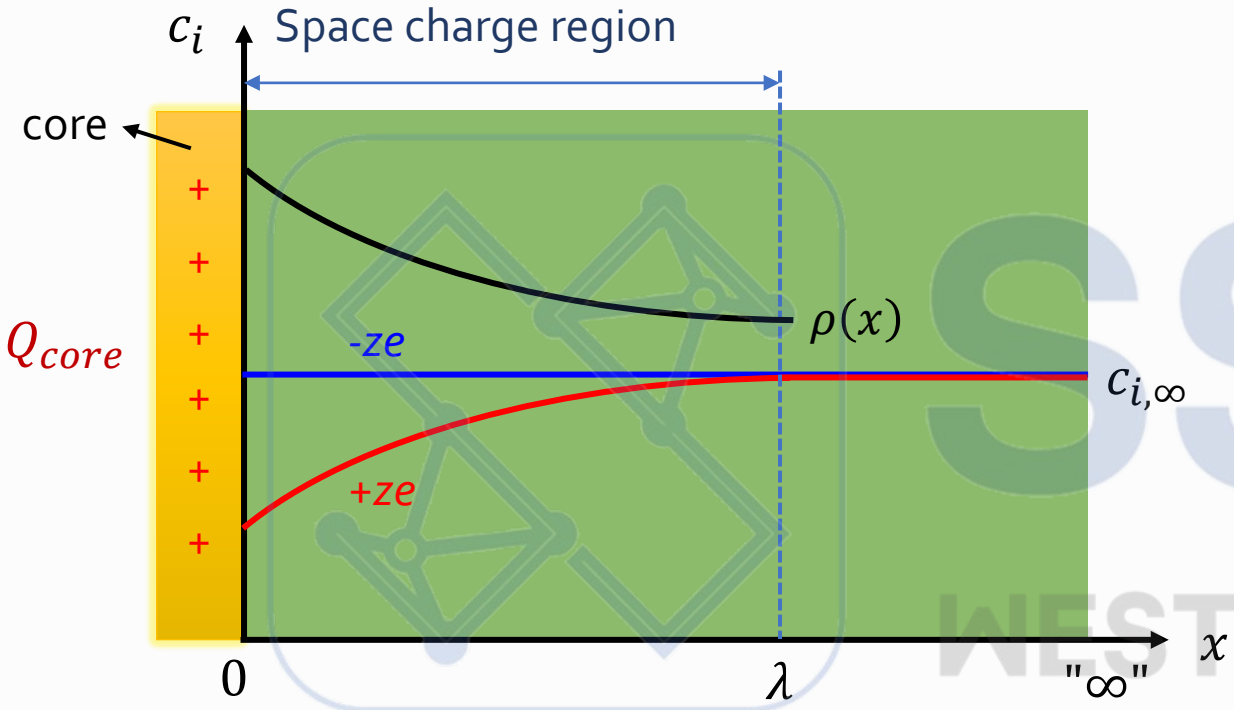


$$\frac{R_{bulk}}{R_{GB}} = \frac{\sigma_{GB}}{\sigma_{bulk}} \frac{D}{d}$$

$(d \ll D)$

- If $\sigma_{GB} \ll \sigma_{bulk}$, then path (1) (*i.e.*, ***series layer model***) will be dominate; → this is the case for $V_O^{\cdot\cdot}$ and $h^{\cdot}$
- If $\sigma_{GB} \gg \sigma_{bulk}$, then path (2) (*i.e.*, ***conducting along GBs***) might be activated. → this is the case for e'

How to calculate $\sigma_{GB}/\sigma_{bulk}$?



$$\phi(x) = \phi_0(\frac{x}{\lambda} - 1)^2 \rightarrow d\phi = \frac{2\phi_0}{\lambda}(\frac{x}{\lambda} - 1)dx$$

Assume **Mott-Schottky** case and **positive** core charge

If we are interested in the positive ion (defects) with charge +*ze*, *e.g.*, oxygen vacancies

We also need to assume that the ***mobility*** in the bulk and space charge layer is the same

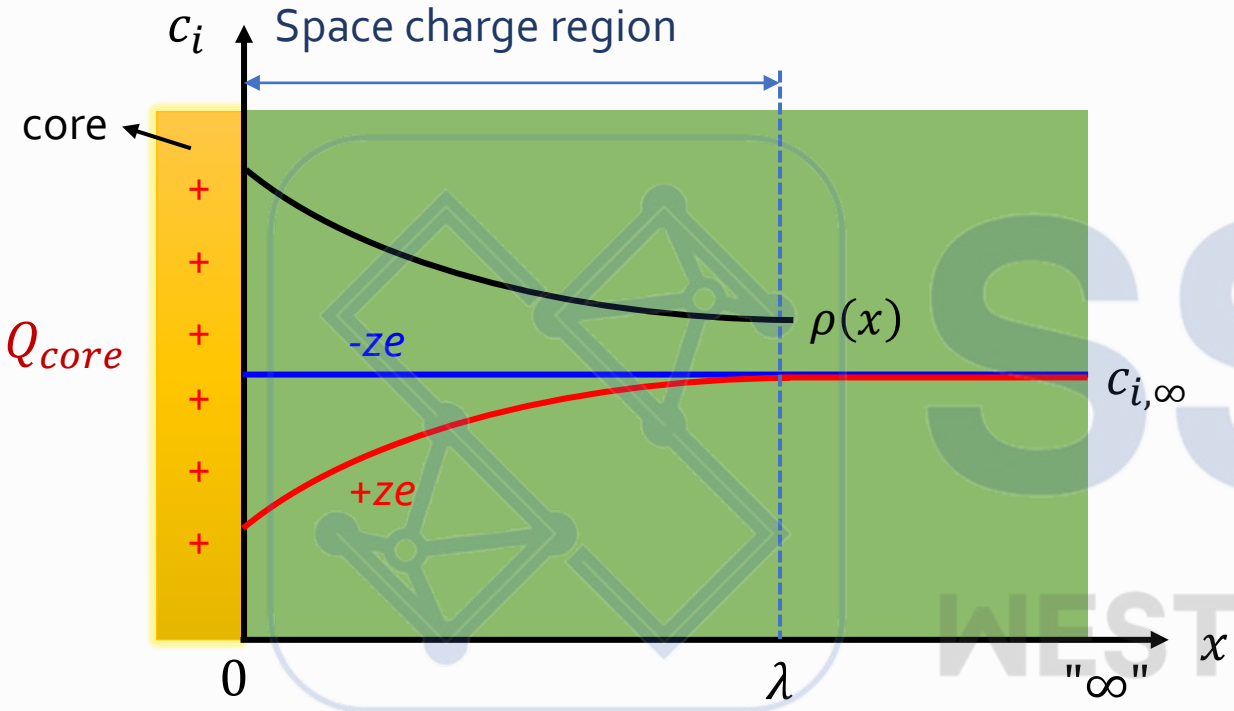
$$\rho(x) = \rho_{bulk}\exp(\frac{ze\phi(x)}{k_BT})$$

Integrate over space charge layer (λ)

$$\rho_{GB} = \frac{1}{\lambda}\int_0^{\lambda} \rho_{bulk}\exp\left(\frac{ze\phi(x)}{k_BT}\right)dx$$

$$\frac{\rho_{GB}}{\rho_{bulk}} = \frac{1}{2\phi_0}\int_{\phi_0}^{0} \exp\left(\frac{ze\phi(x)}{k_BT}\right)\frac{d\phi}{(\frac{x}{\lambda} - 1)} \rightarrow \approx -1$$

How to calculate $\sigma_{GB}/\sigma_{bulk}$?



$$\frac{\rho_{GB}}{\rho_{bulk}} = \frac{1}{2\phi_0}\int_0^{\phi_0} \exp\left(\frac{ze\phi(x)}{k_BT}\right) d\phi$$

$$\frac{\rho_{GB}}{\rho_{bulk}} = \frac{k_BT}{2ze\phi_0}\exp\left(\frac{ze\phi(x)}{k_BT}\right)\Big|_0^{\phi_0}$$

$$= \frac{\exp\left(\frac{ze\phi_0}{k_BT}\right) - 1}{2ze\phi_0/k_BT} \approx \frac{\exp(ze\phi_0/k_BT)}{2ze\phi_0/k_BT}$$

Therefore, we have:

$$\frac{\rho_{GB}}{\rho_{bulk}} \approx \frac{\exp(ze\phi_0/k_BT)}{2ze\phi_0/k_BT} \gg 1$$

Conclusion:

Higher ϕ_0 (more Q_{core}) → Higher grain boundary resistance

Things we have discussed in this lecture

Electrochemical Impedance Spectroscopy (EIS):

- Why do we need electrochemical impedance spectroscopy? What problem are we trying to solve with this technique?
- How to understand the equivalent circuit model? How does the equivalent circuit model for a polycrystalline sample with grain boundaries look like?

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

西湖大學
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End of Lecture 8
Solid State Ionics Fall 2023

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