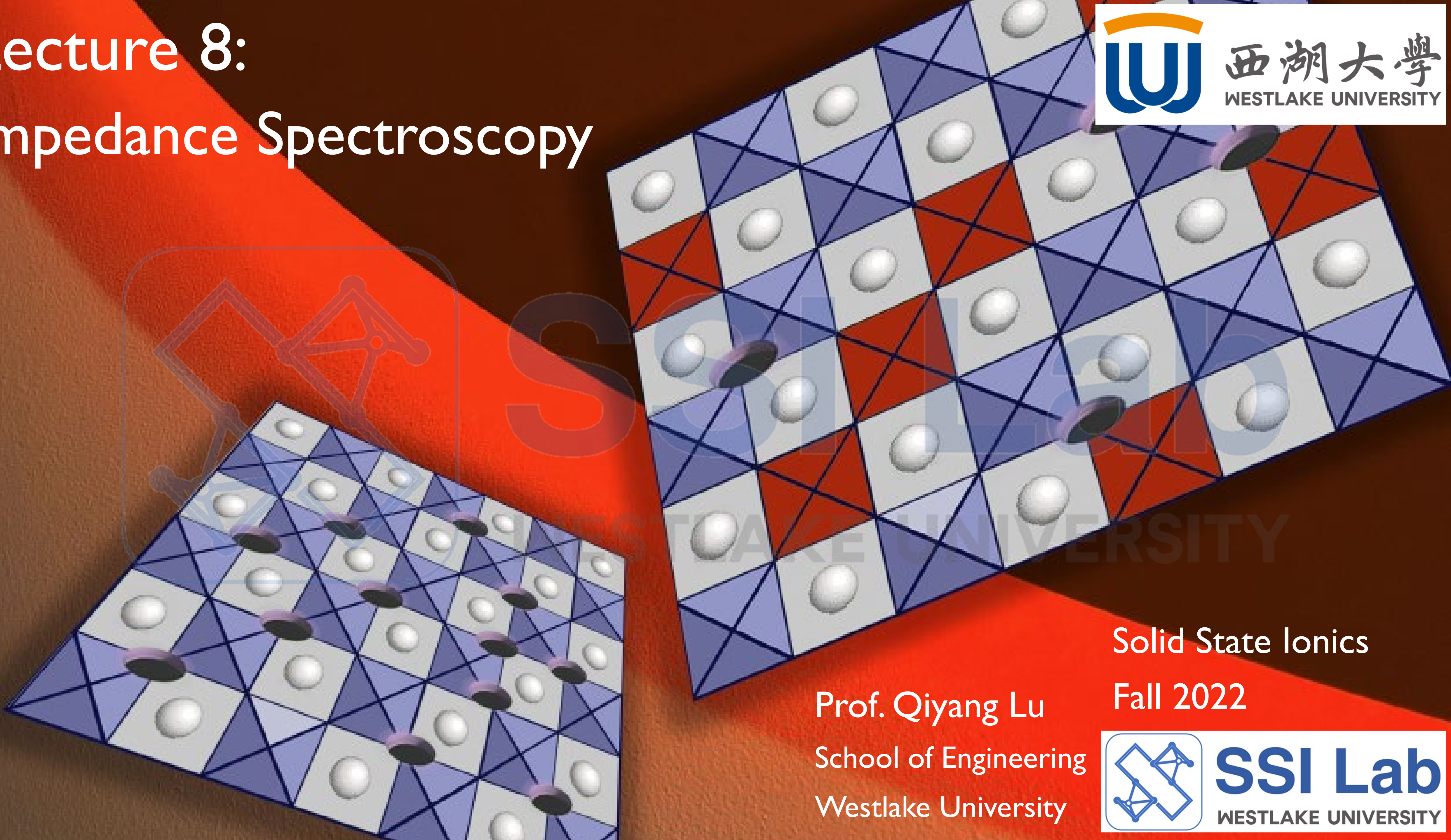
Lecture 8:
Impedance Spectroscopy



Solid State Ionics

Fall 2022

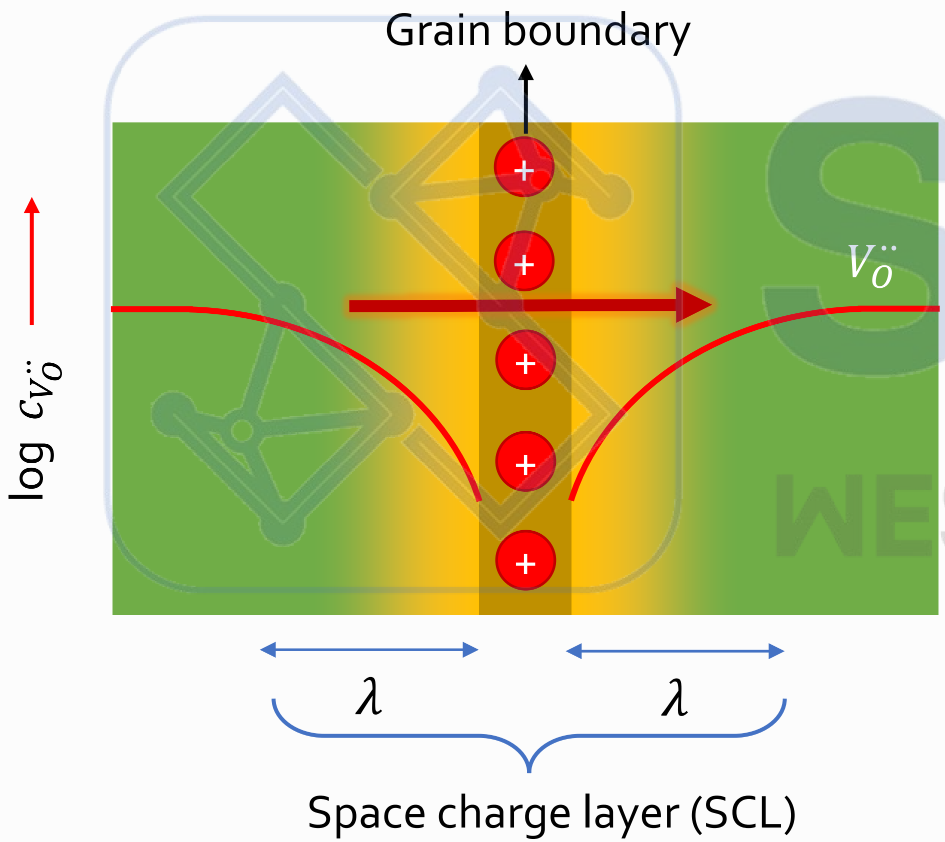
Prof. Qiyang Lu

School of Engineering

Westlake University

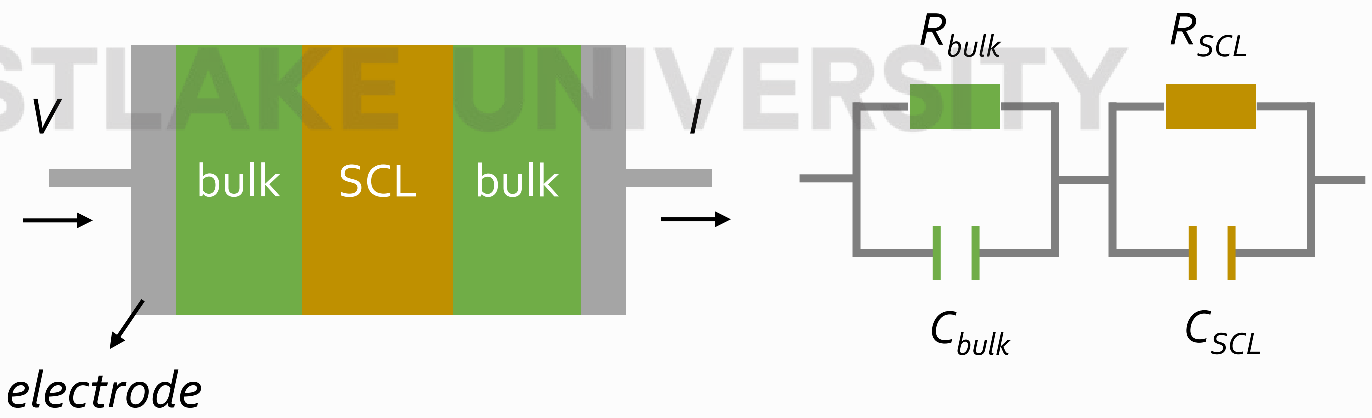
Implications on the conductivity: series layer model

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



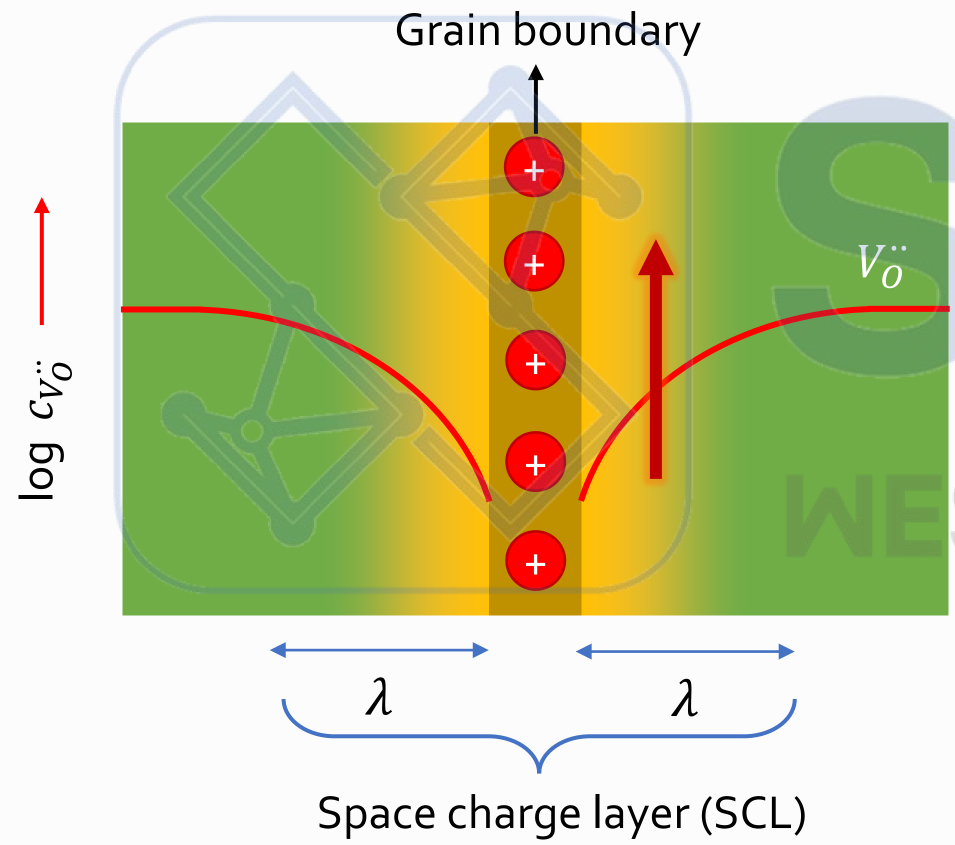
If we assume the mobility of $V_O^{\cdot\cdot}$ is the same in the bulk and grain boundary, then the ionic conductivity is mainly affected by the depletion of oxygen vacancies.

Consider the series layer model:

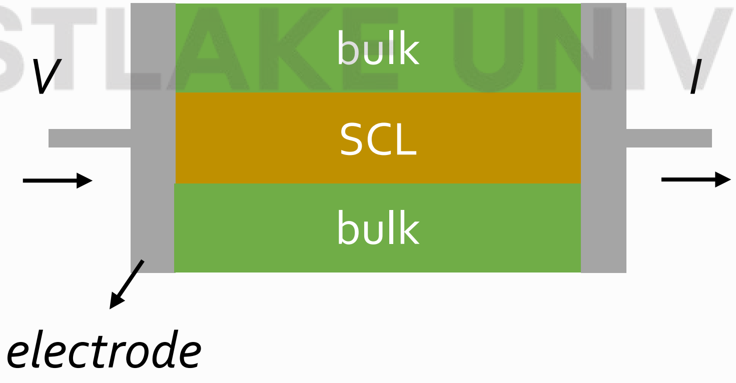


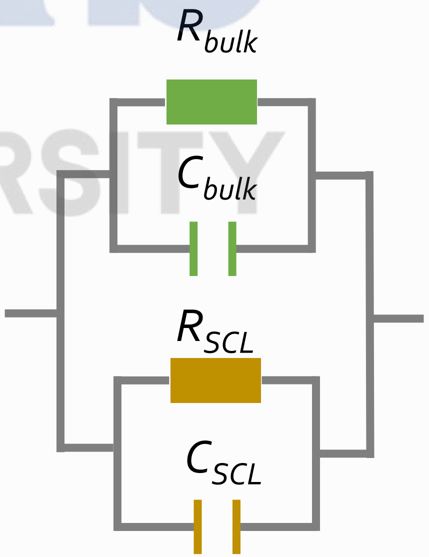
Implications on the conductivity: parallel layer model

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



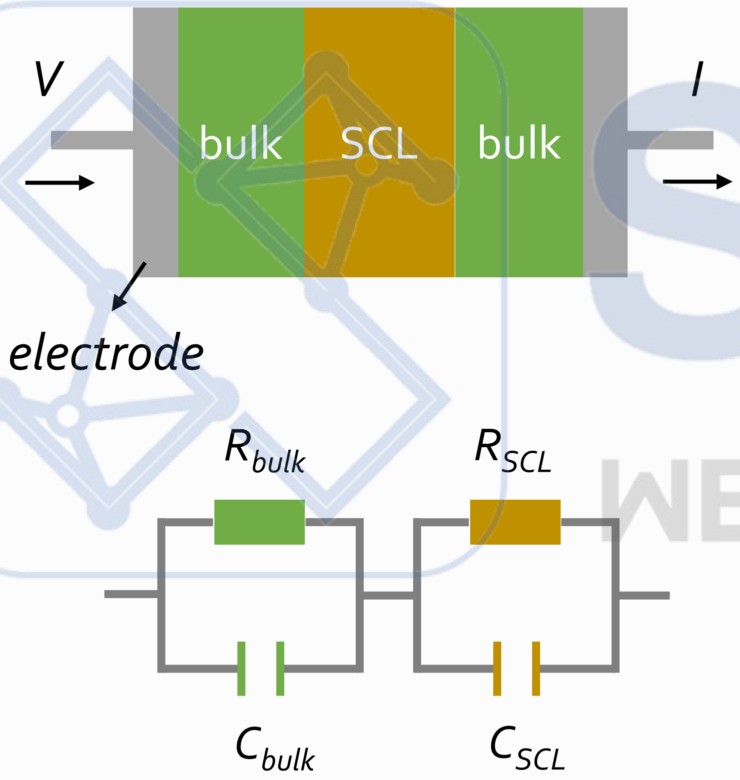
We can also construct the parallel layer model:



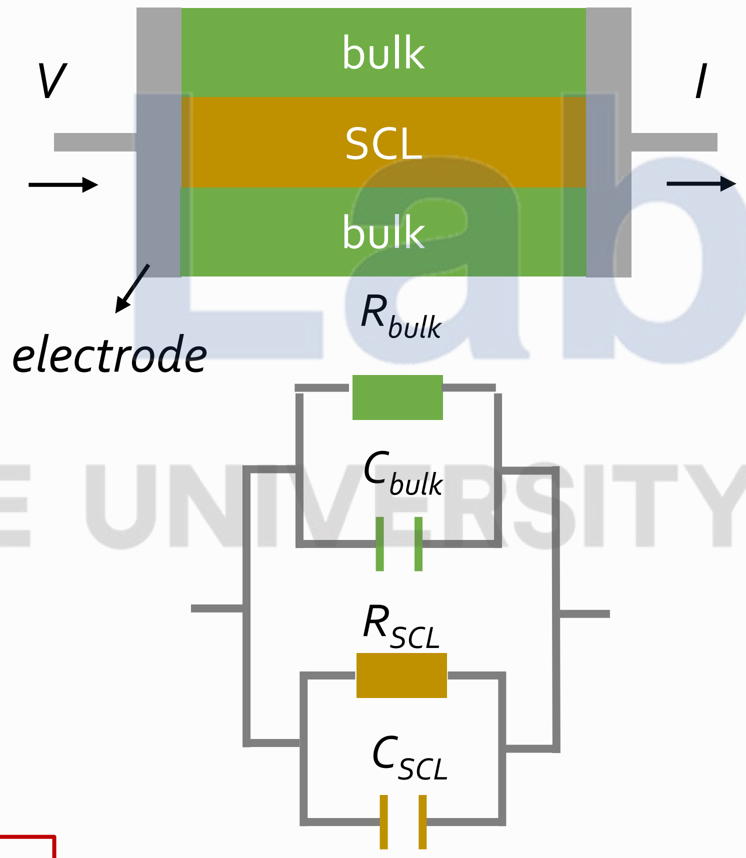


How to evaluate resistance and capacitance?

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):

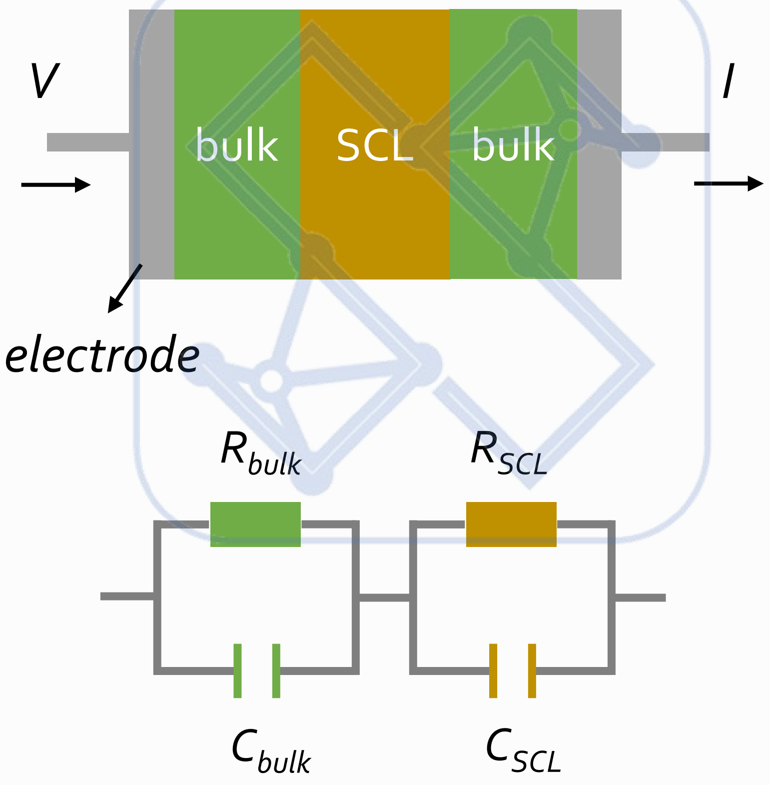
- Why do we need electrochemical impedance spectroscopy? What problem are we trying to solve with this technique?

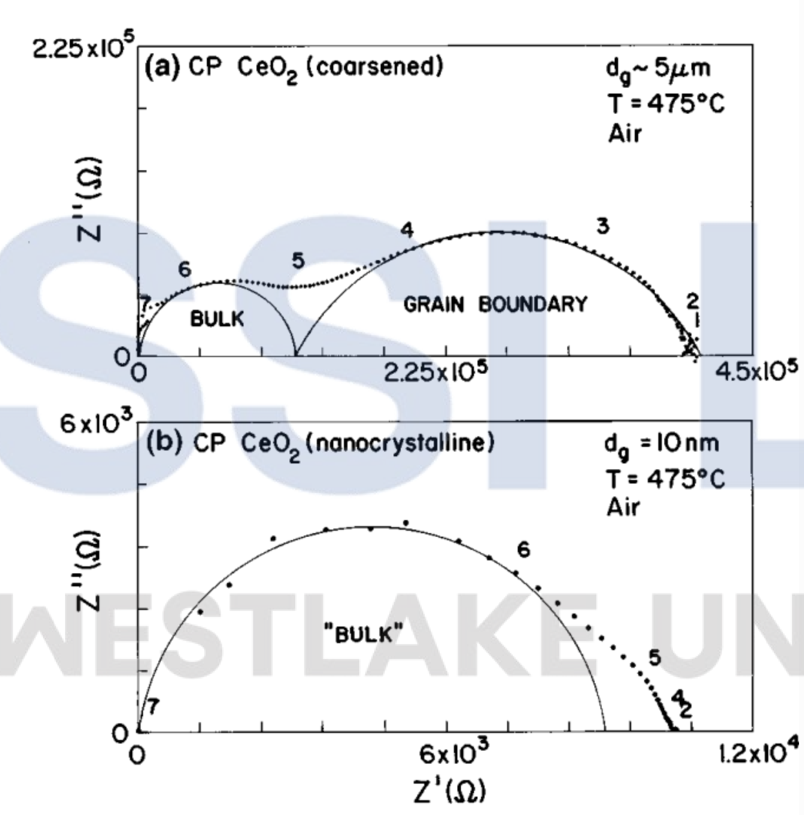
- How to understand the equivalent circuit model? How does the equivalent circuit model for a polycrystalline sample with grain boundaries look like?

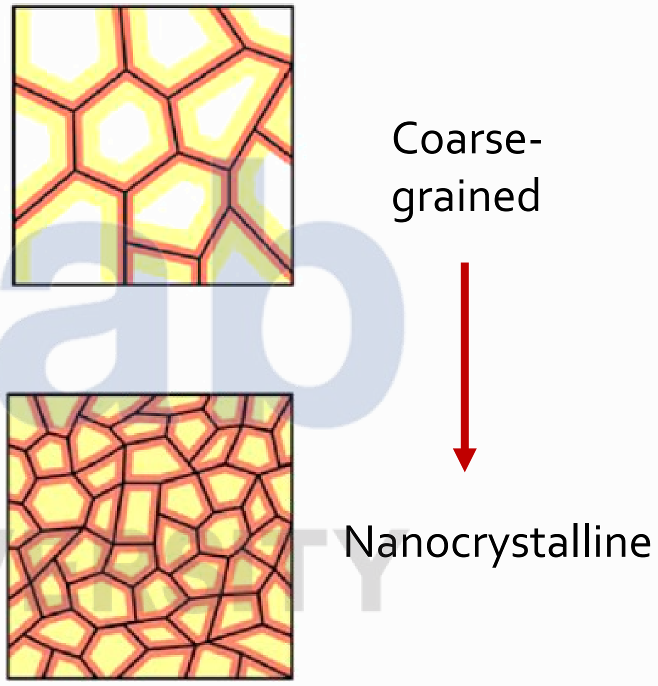
Goal of this lecture: you should be able to answer the questions above by the end of this lecture :)

Why do we need Electrochemical Impedance Spectroscopy?

Series layer model





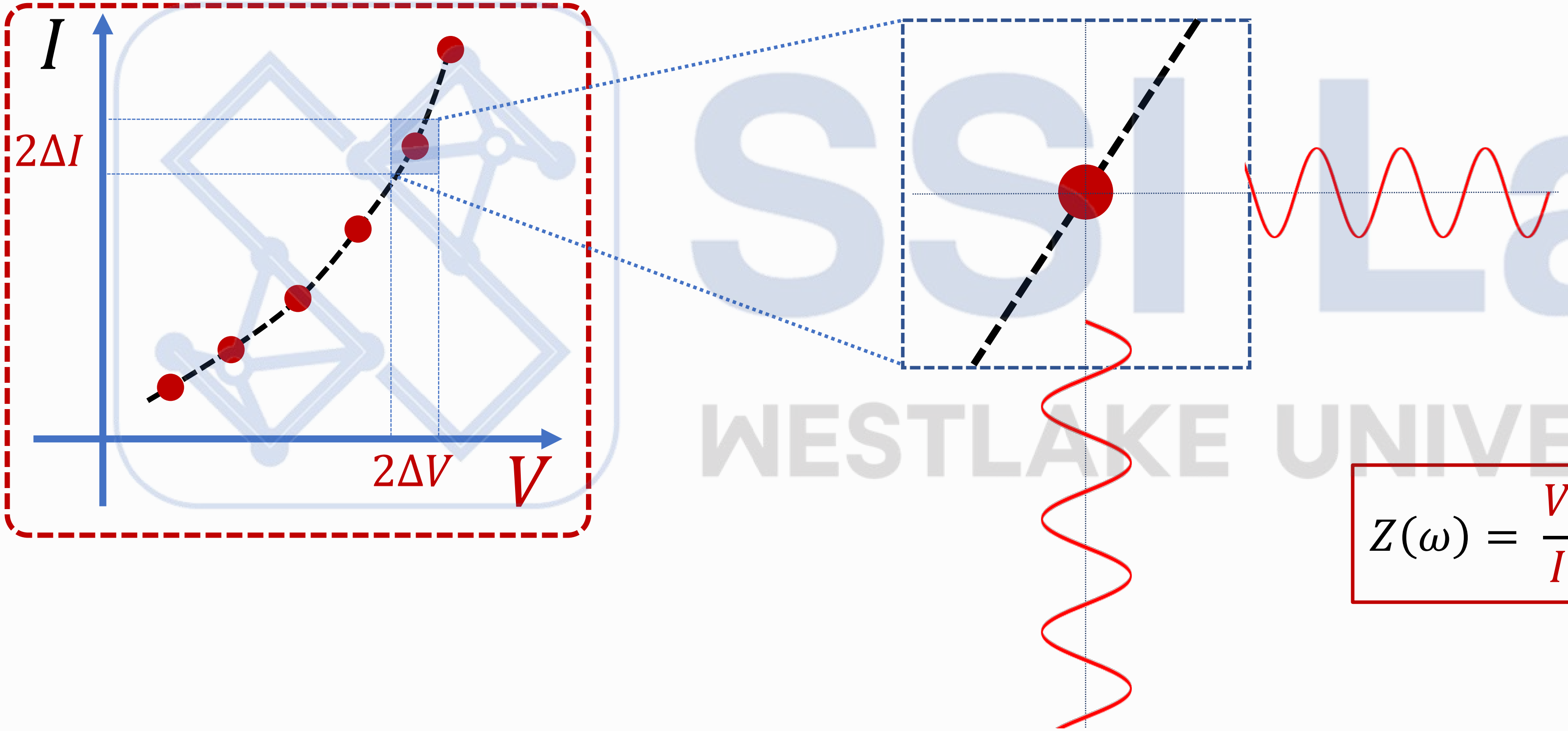


Time constant $\tau = RC$ → separate the contribution of bulk and SCL in the ***frequency domain*** ($f = 1/\tau$).

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.*



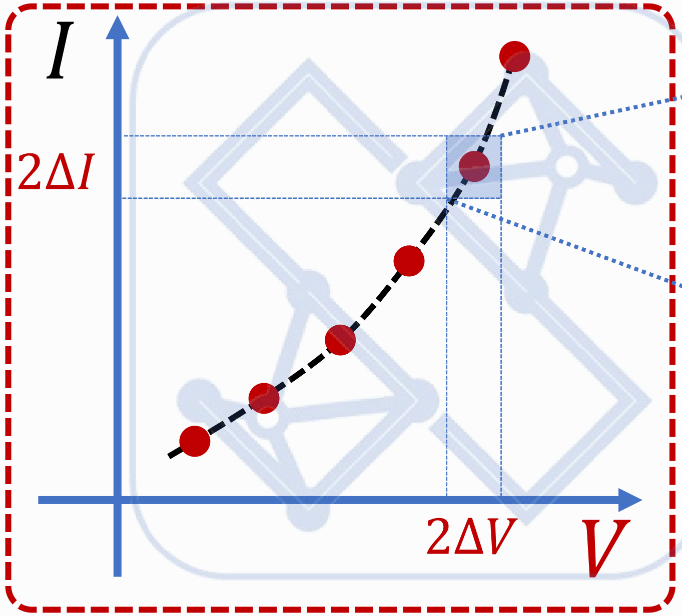
$$I(t) = \Delta I \cos(\omega t - \varphi)$$

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

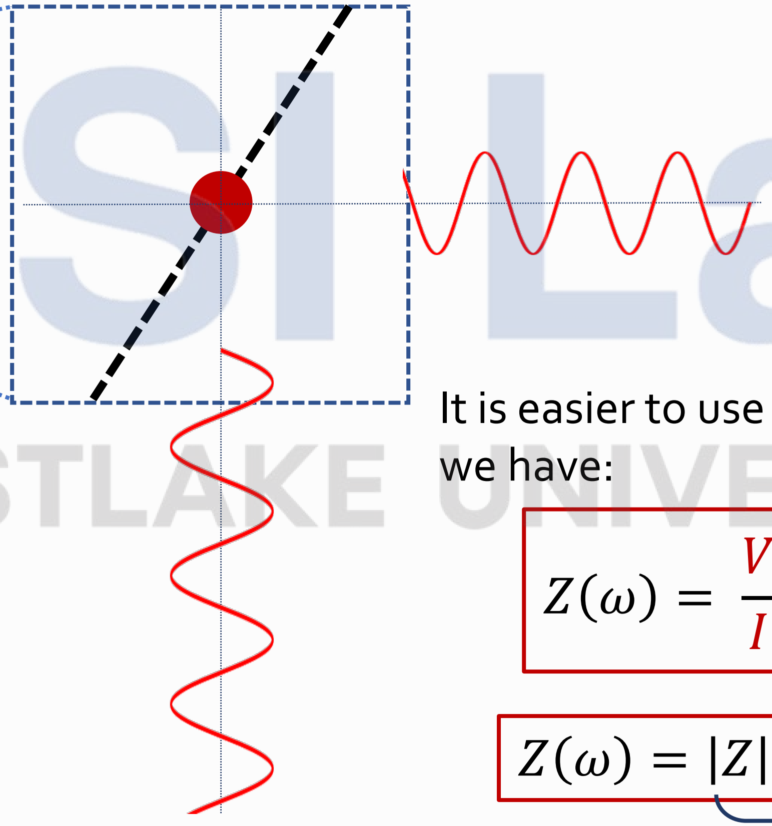
$$V(t) = \Delta V \cos(\omega t)$$

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:

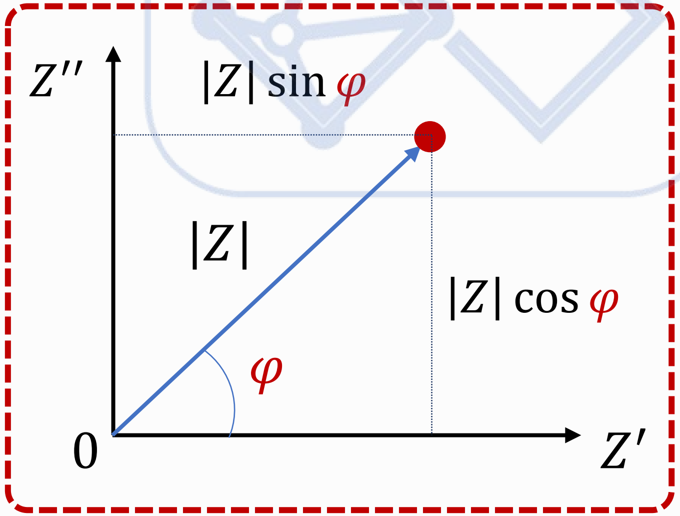
$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{\Delta V}{\Delta I}\frac{e^{i\omega t}}{e^{i(\omega t - \varphi)}}$$

$$Z(\omega) = \underbrace{|Z| \cos \varphi}_{Z' \text{ or } Re(Z)} + \underbrace{i|Z| \sin \varphi}_{Z'' \text{ or } Im(Z)}$$

The working principle of EIS: Nyquist plot

$$Z(\omega) = \underbrace{|Z|\cos\varphi}_{Z' \text{ or } Re(Z)} + \underbrace{i|Z|\sin\varphi}_{Z'' \text{ or } Im(Z)}$$

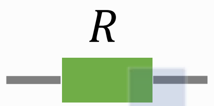
$$Z(\omega) = Z' + iZ''$$



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

Note: more commonly we plot $Z' \sim -Z''$

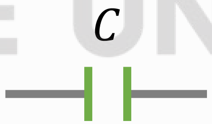
For a resistor, since ***I*** and ***V*** should always be ***in phase***, we have:



$$Z(\omega) = R$$

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

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



$$Z(\omega) = ?$$

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

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

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

The working principle of EIS: Nyquist plot

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

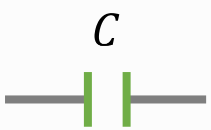
$$I(t) = \Delta I e^{i(\omega t - \varphi)}$$

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

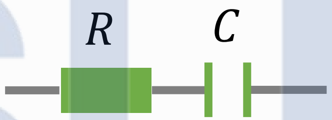
$$Q(t) = \frac{\Delta I}{i\omega} e^{i(\omega t - \varphi)}$$

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

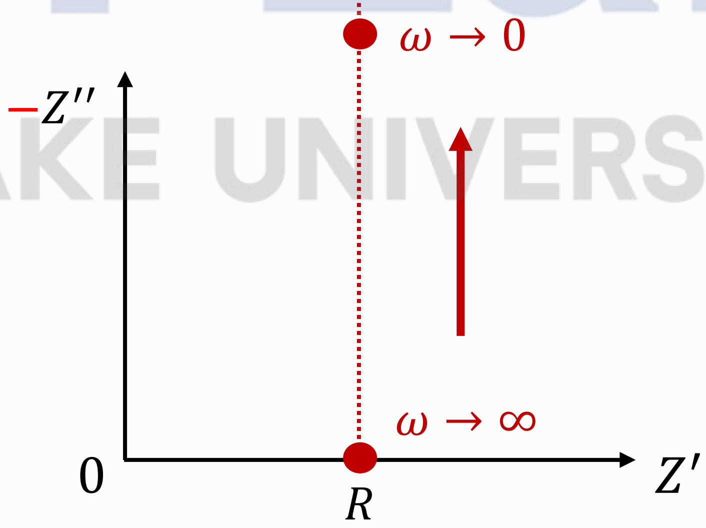
$$Z(\omega) = \frac{V(t)}{I(t)} = \frac{1}{i\omega C}$$



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

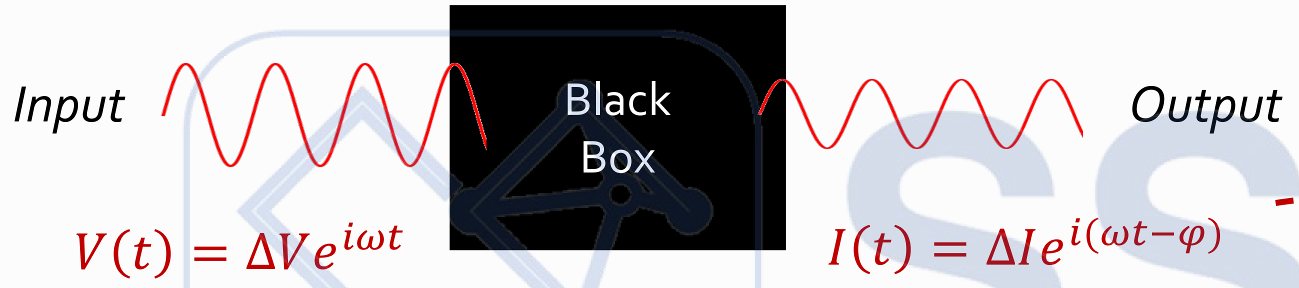


$$Z(\omega) = R + \frac{1}{i\omega C} = R - i\frac{1}{\omega C}$$



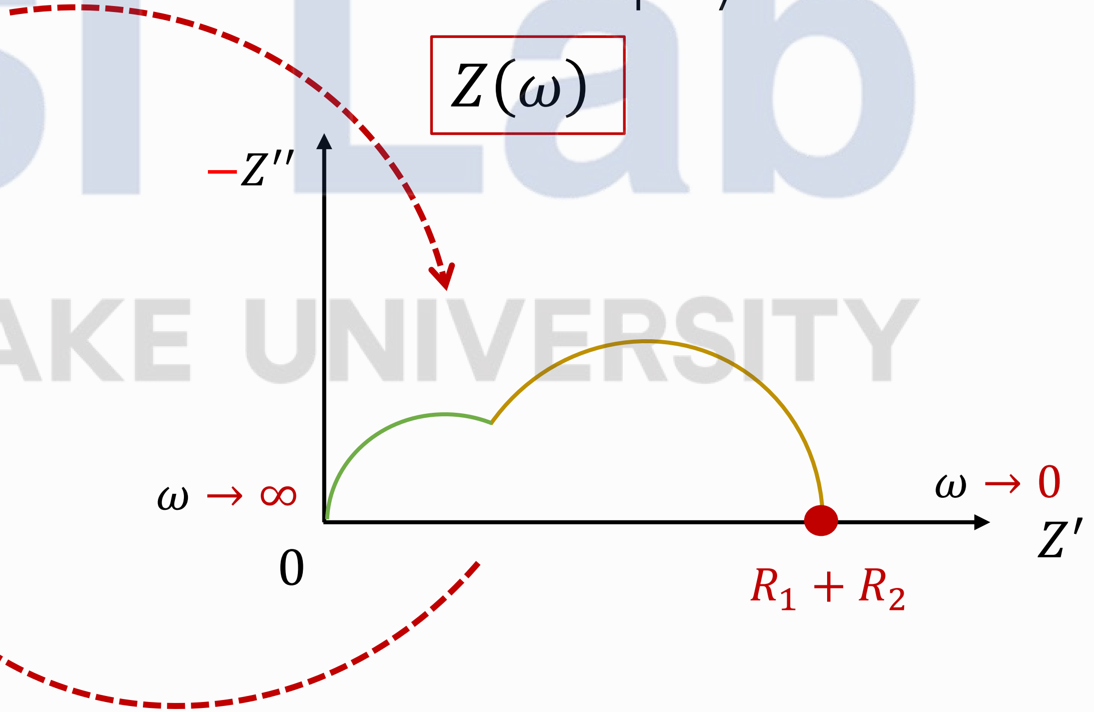
Nyquist plot ($Z' \sim -Z''$ plot)

Which equivalent circuit should be chosen?

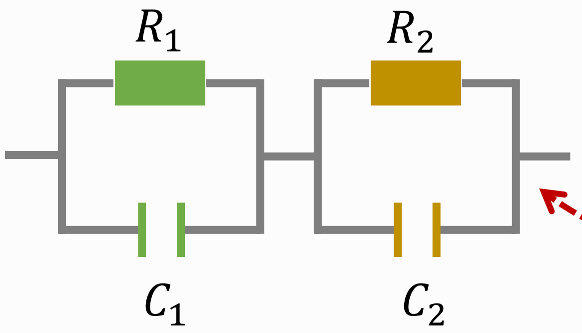


Note:

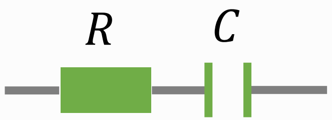
- The electrochemical system is a black box, *i.e.*, there is no prior knowledge on which circuit model should be used;
- There might be more than one equivalent circuit that can fit the data equally well.



Fit the impedance data with equivalent circuit



Nyquist plot: *R-C* in series

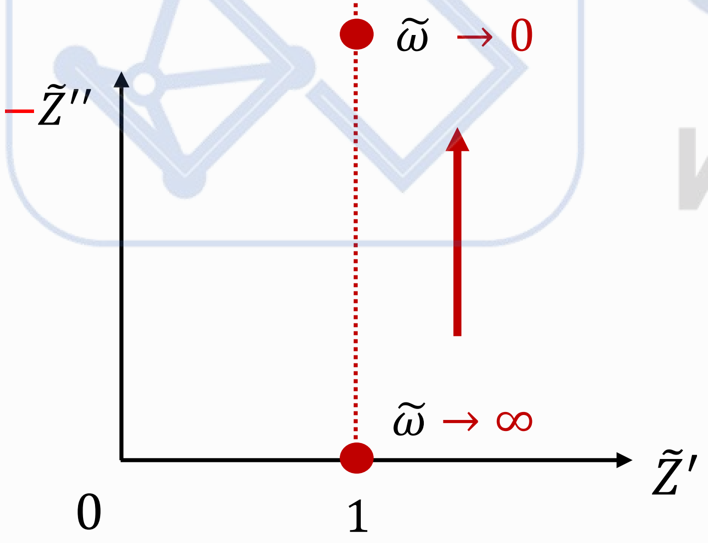


$$Z(\omega) = R + \frac{1}{i\omega C}$$

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

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

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

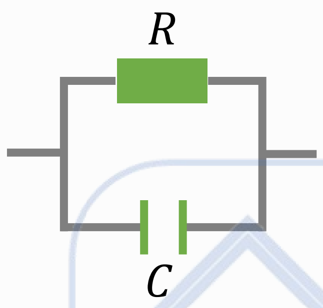


Nyquist plot for dimensionless $\tilde{Z}$ ($\tilde{Z}' \sim -\tilde{Z}''$ plot)

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.*
  - $\tilde{Z} = Z/R$ → Z scales with resistance R;
  - $\tilde{\omega} = \omega RC$ → ω scales inversely with RC. Keep in mind that time constant $\tau = RC$

Nyquist plot: *R-C* in parallel



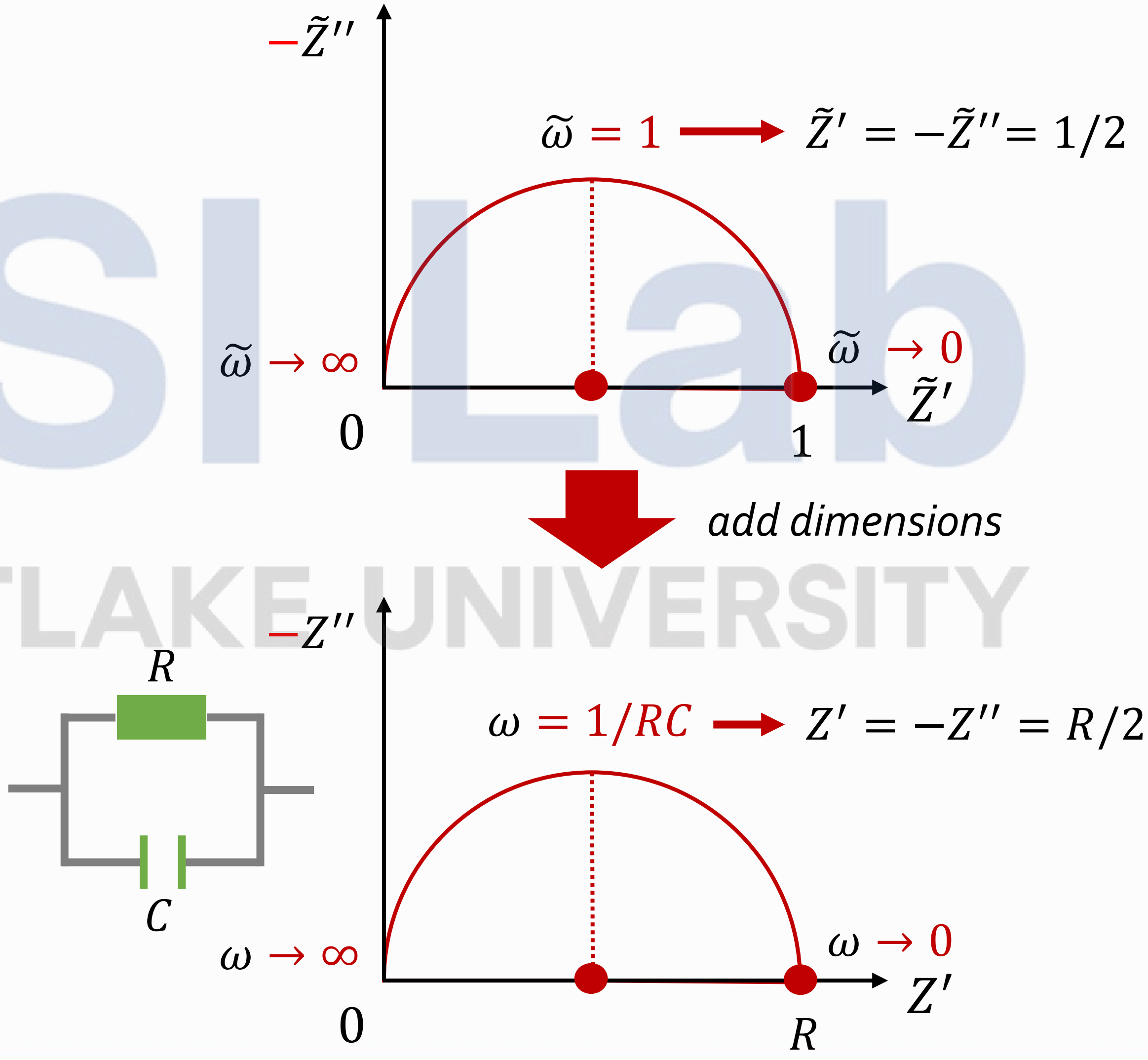
$$\tilde{Z}(\omega) = \frac{1}{1+i\tilde{\omega}}$$

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

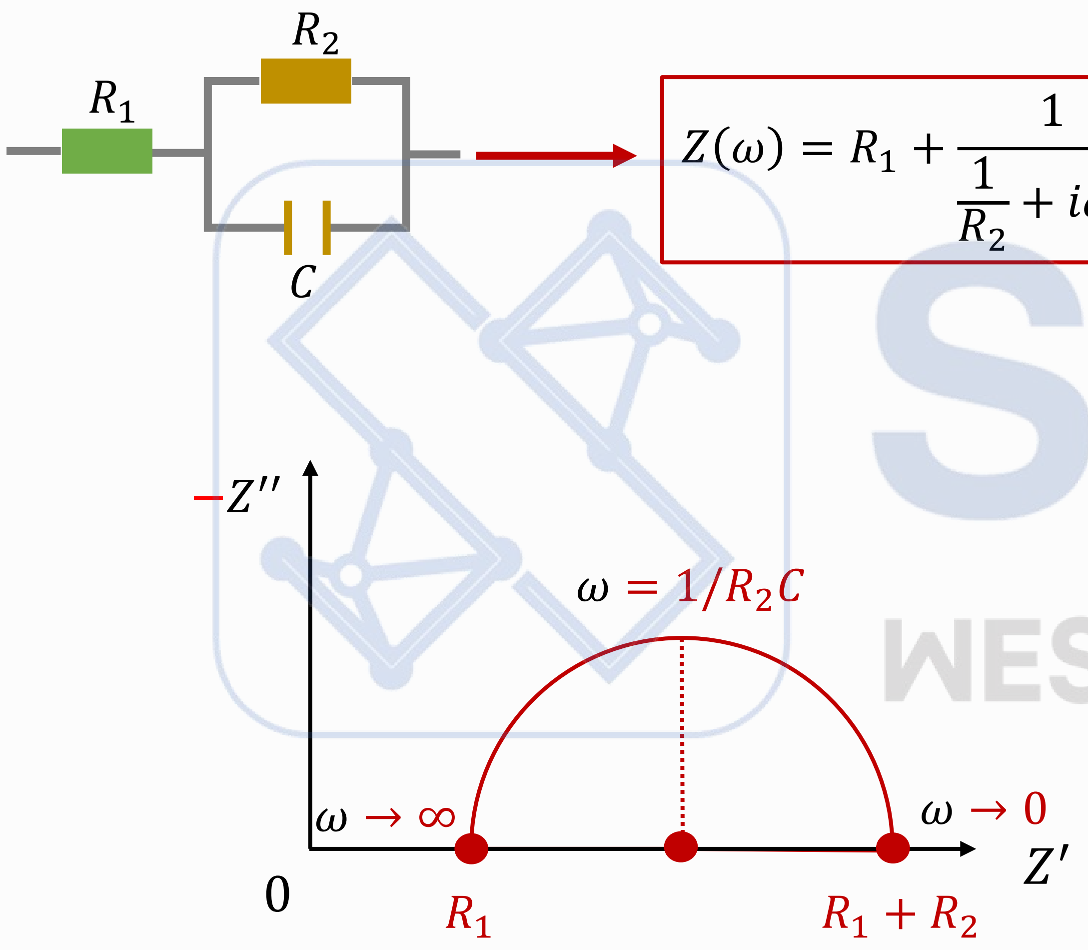
$$\tilde{Z}' = \frac{1}{1+\tilde{\omega}^2}, \quad -\tilde{Z}'' = \frac{\tilde{\omega}}{1+\tilde{\omega}^2} \quad \Rightarrow \quad (\tilde{Z}' - \frac{1}{2})^2 + (-\tilde{Z}'')^2 = (\frac{1}{2})^2$$

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

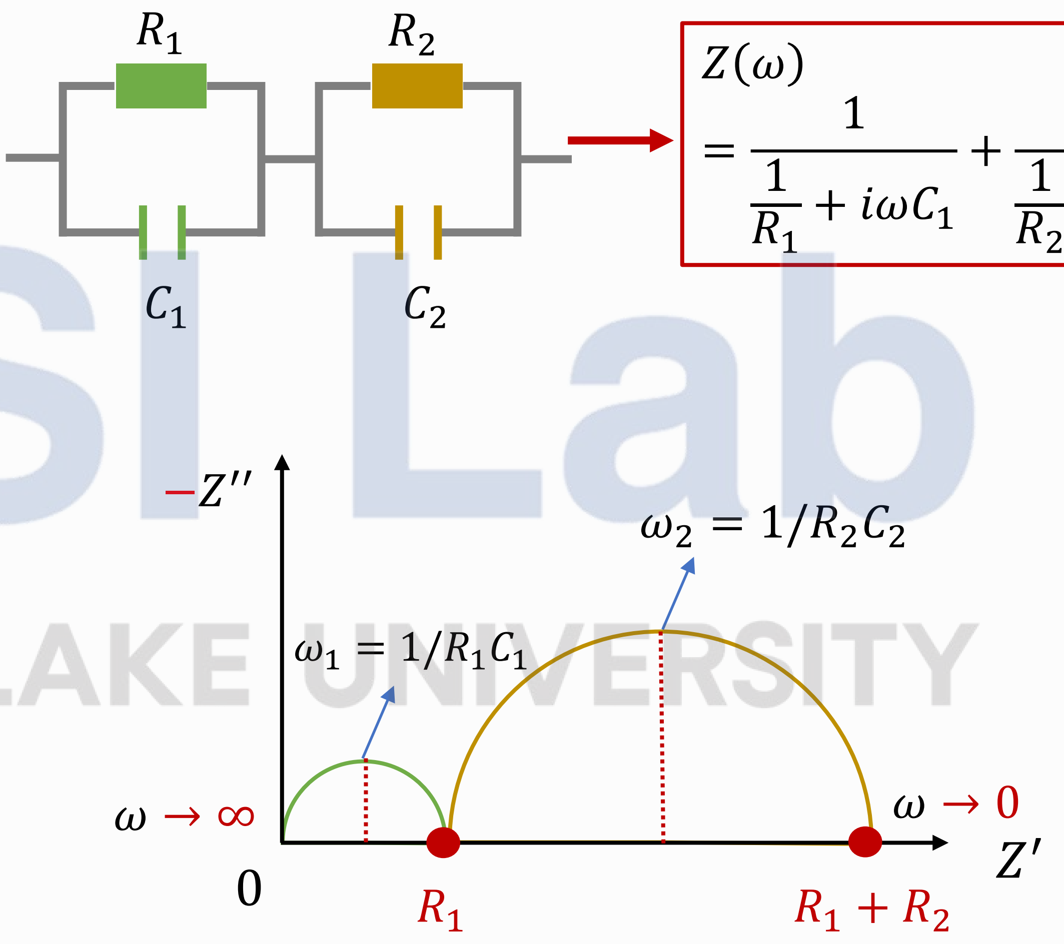
- Radius = 1/2
- Center = (1/2, 0)



Nyquist plot: *more complicated circuits*

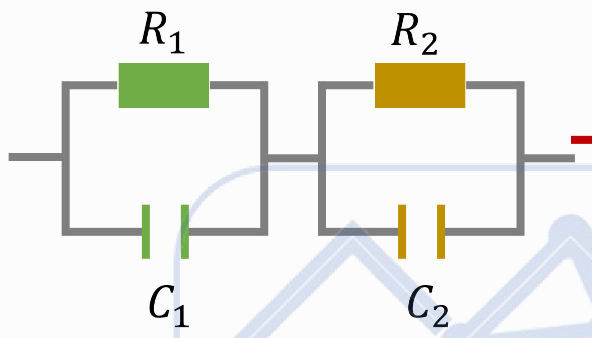


$$Z(\omega) = R_1 + \frac{1}{\frac{1}{R_2} + i\omega C}$$

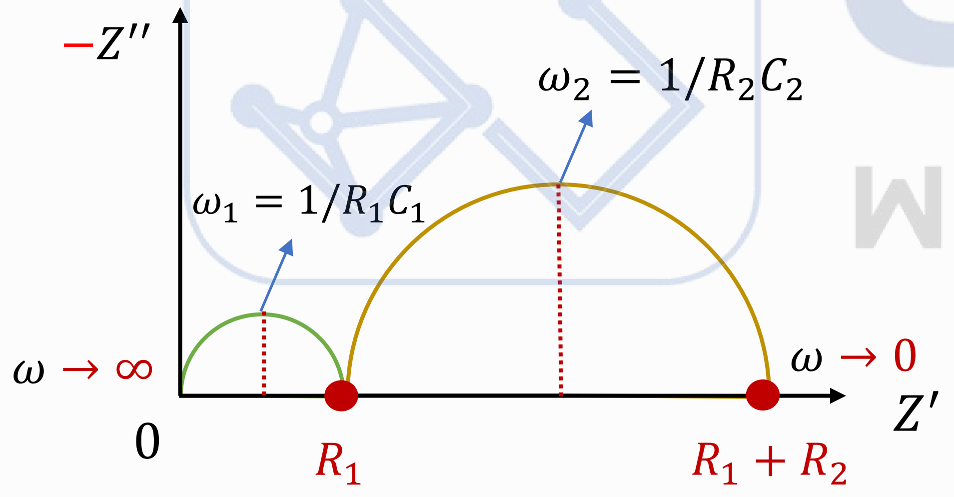


$$Z(\omega) = \frac{1}{\frac{1}{R_1} + i\omega C_1} + \frac{1}{\frac{1}{R_2} + i\omega C_2}$$

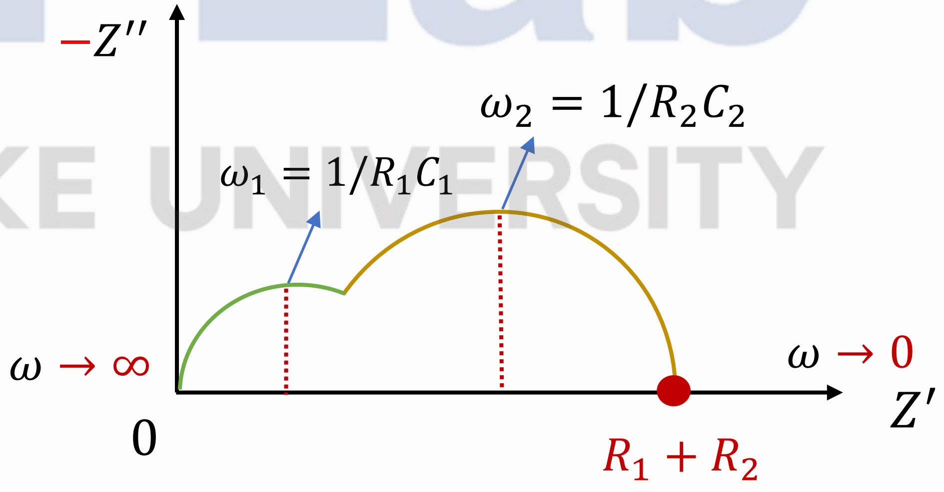
Nyquist plot: *more complicated circuits*



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

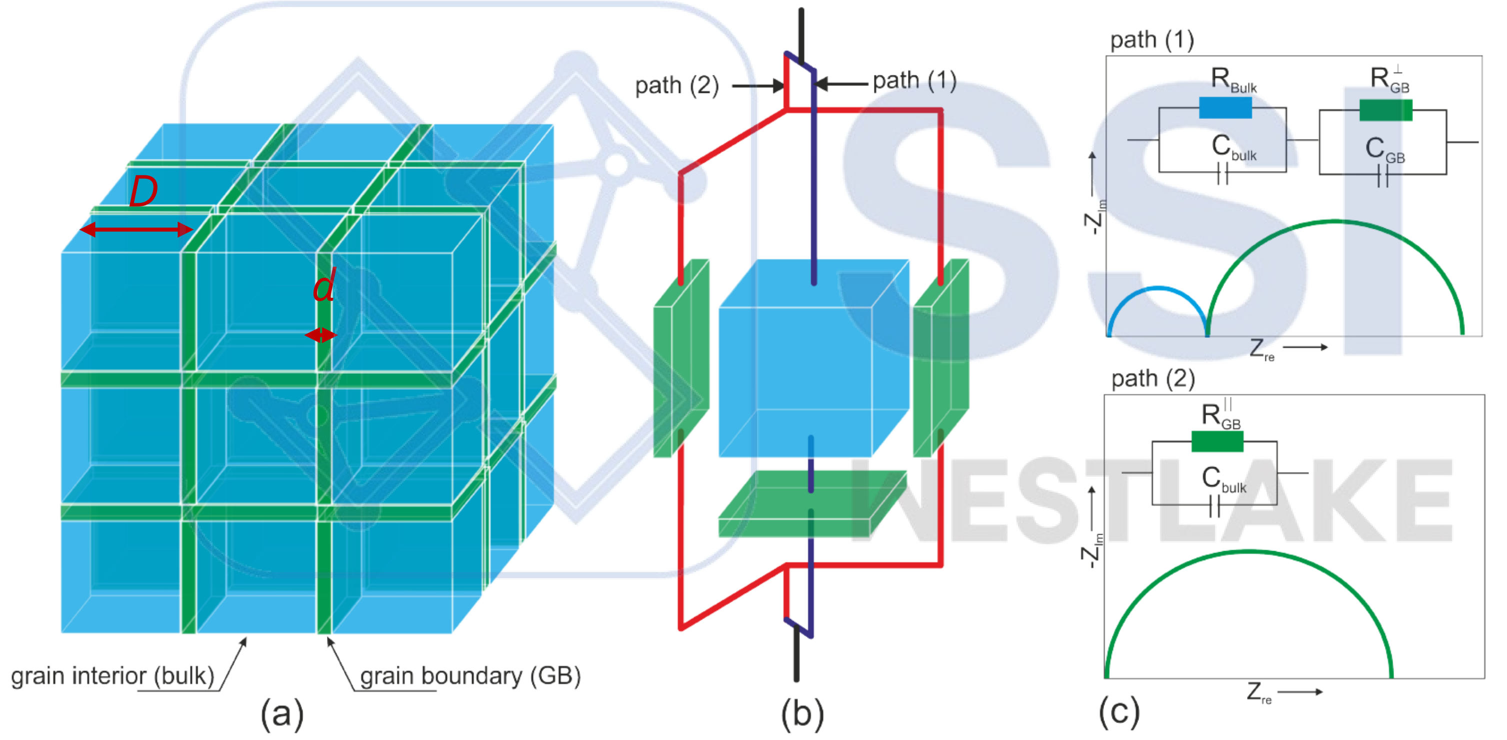


If ω_1 and ω_2 become closer



Brick layer model

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



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

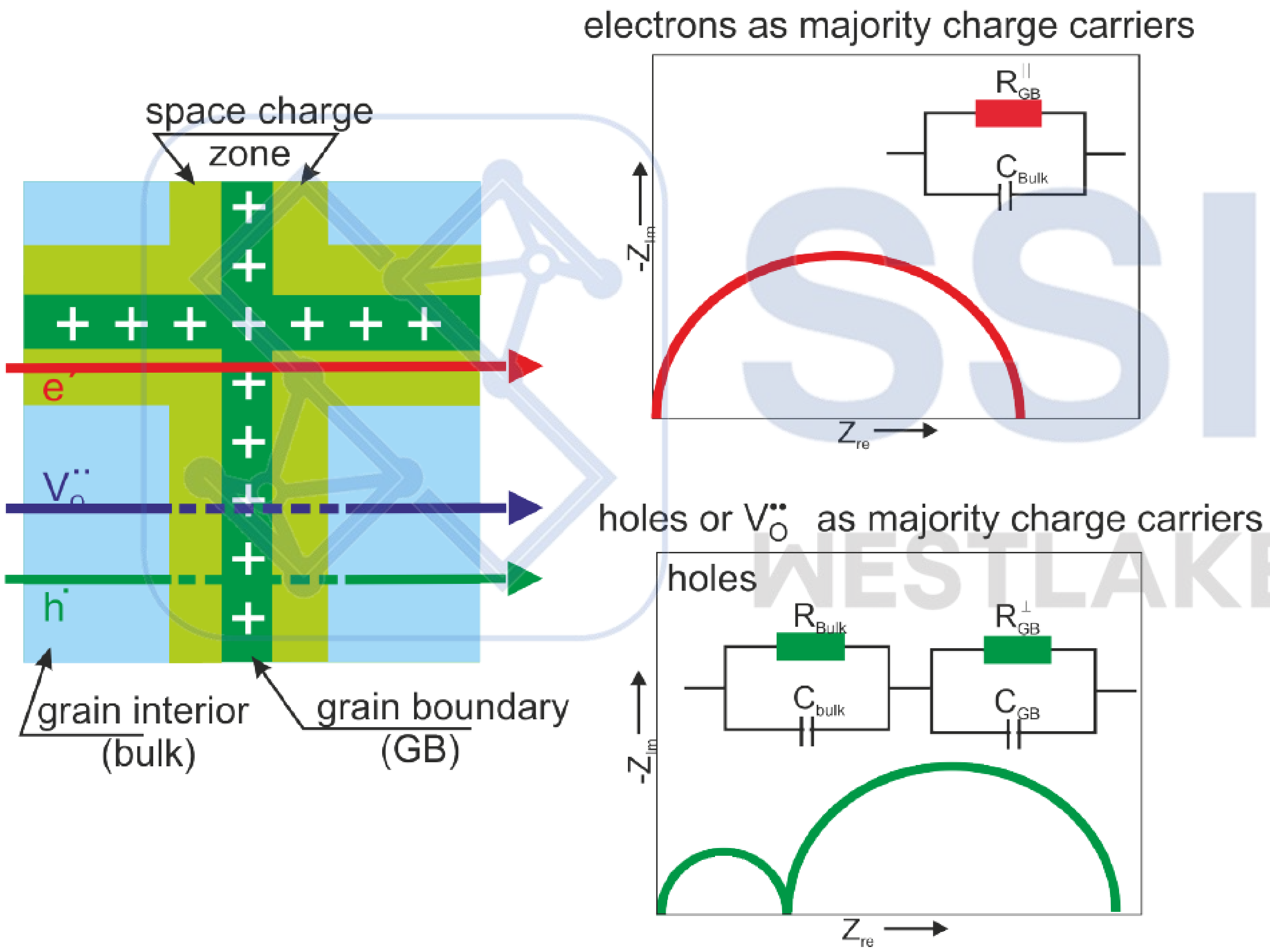
$$\frac{R_{bulk}}{R_{GB}} = \frac{\sigma_{GB}}{\sigma_{bulk}}\frac{D}{d}$$

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

$$(d \ll D)$$

- 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.

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'

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

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) :)

End of Lecture 8

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