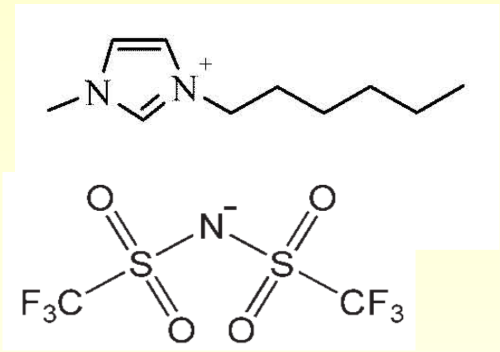
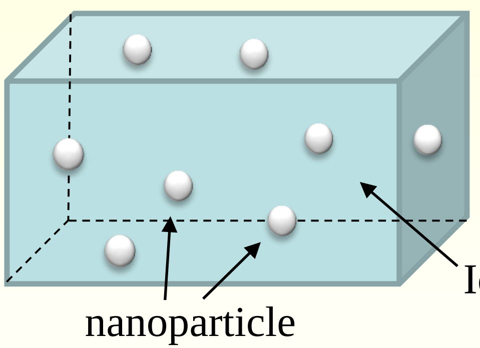
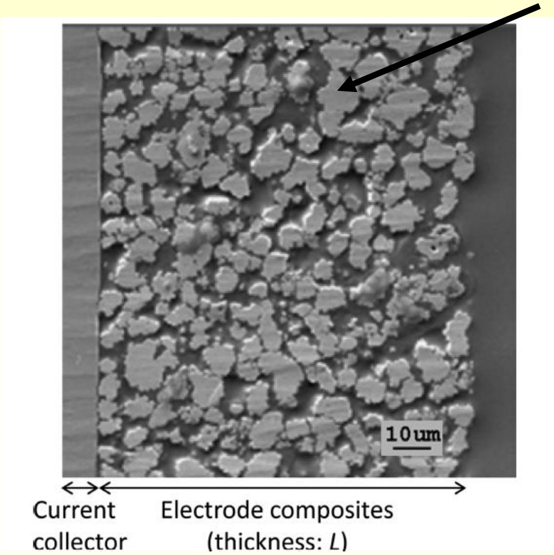
Ionic Materials:

Information from Impedance and Capacitance Spectra

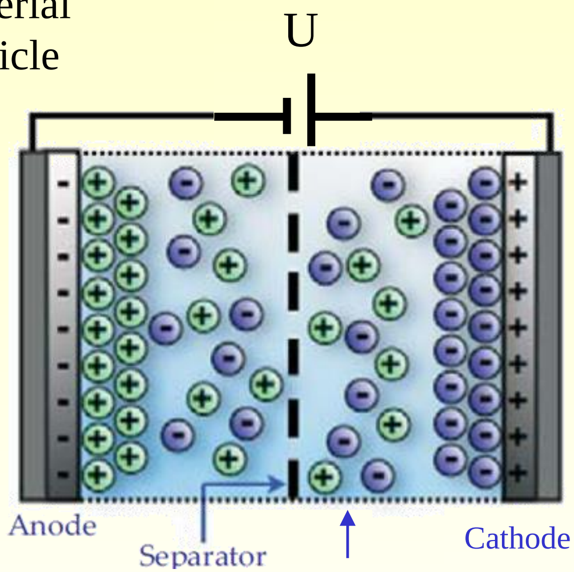




Active material particle



Liquid electrolyte floods pore space



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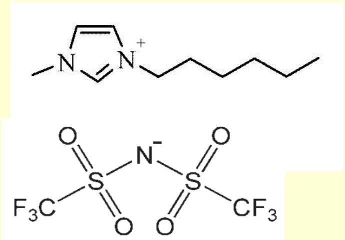
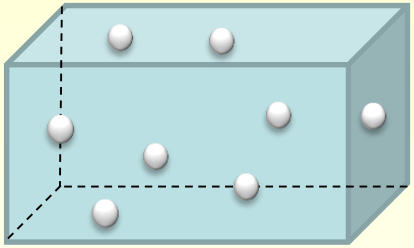
Outline

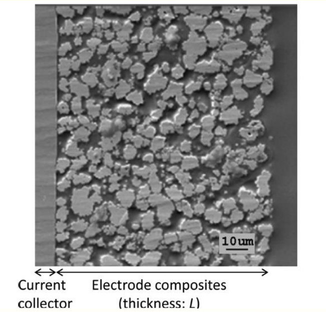
1. Ion Transport in Homogeneous Materials



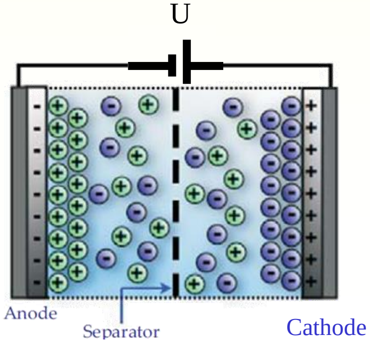
2. Ion Transport in Heterogeneous Materials



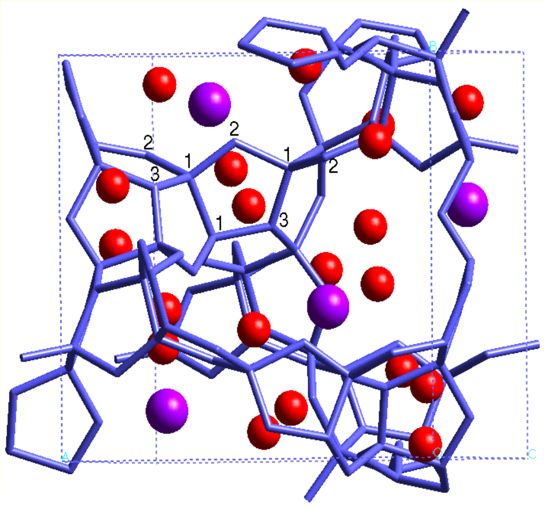
3. Ion Transport in Porous Battery Electrodes



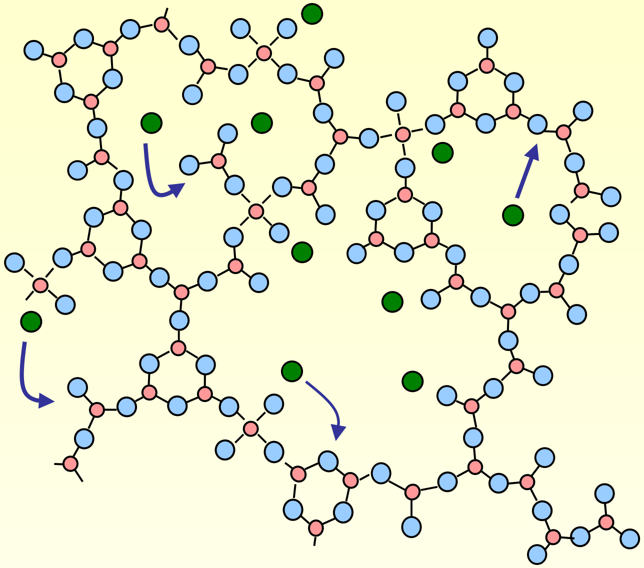
4. Double Layer Formation at Electrode Surfaces



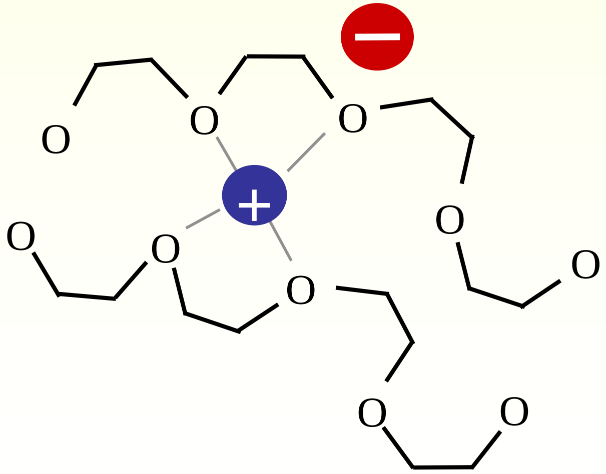
1. Ion Transport in Homogeneous Materials



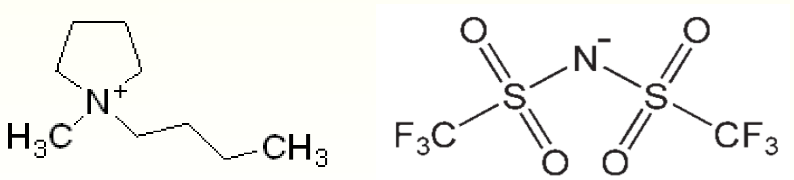
Single crystals ($RbAg_4I_5$)



Inorganic glasses

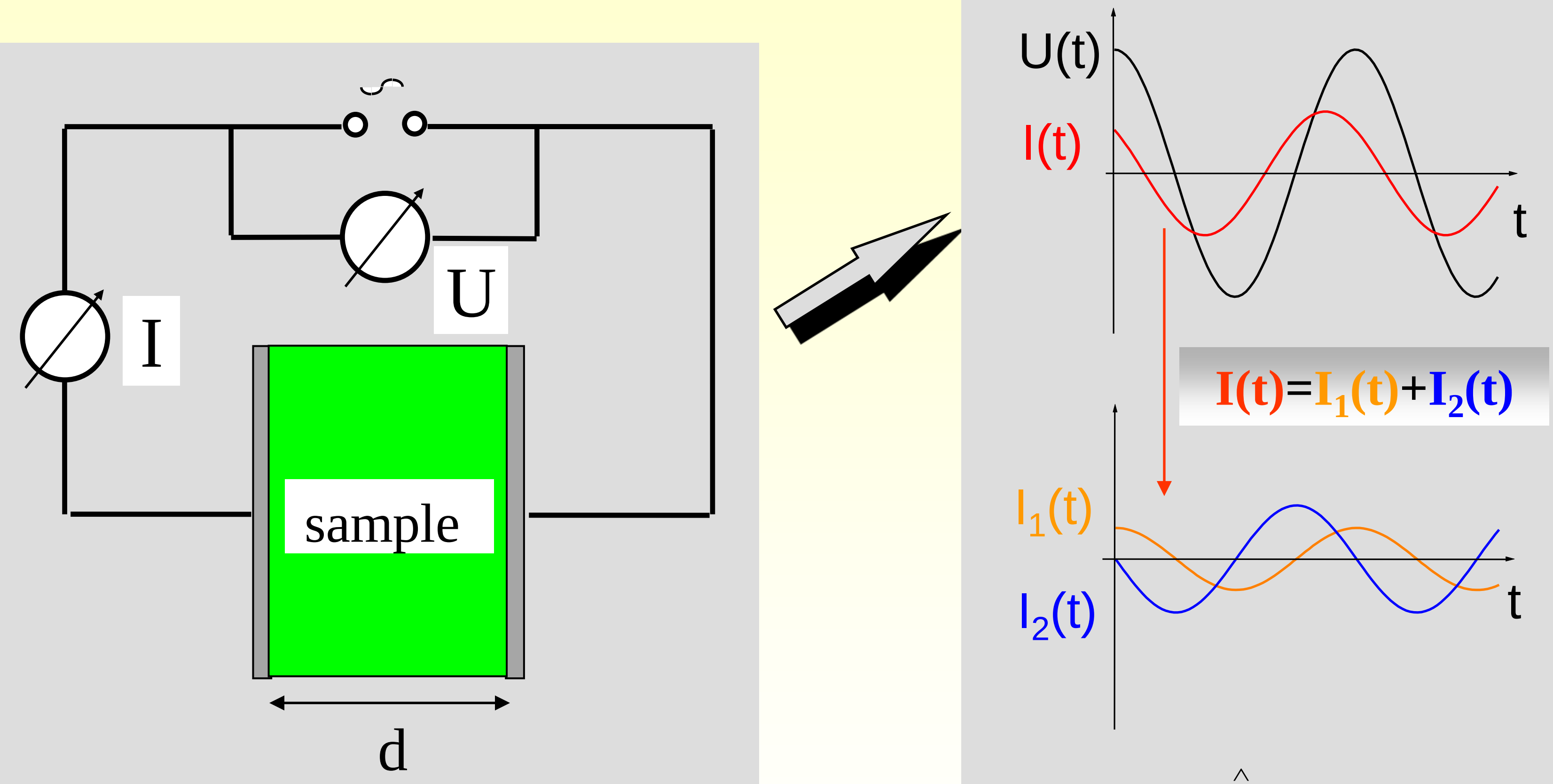


Amorphous polymers (PEO + Salt)



Ionic liquids

Impedance Spectroscopy on Ion Conductor between Ion-Blocking Electrodes



A = contact area between sample and electrodes

Admittance $\hat{Y}(\omega) = Y'(\omega) + iY''(\omega)$

$Y'(\omega) = I_{0,1} / U_0$ (Energy dissipation)

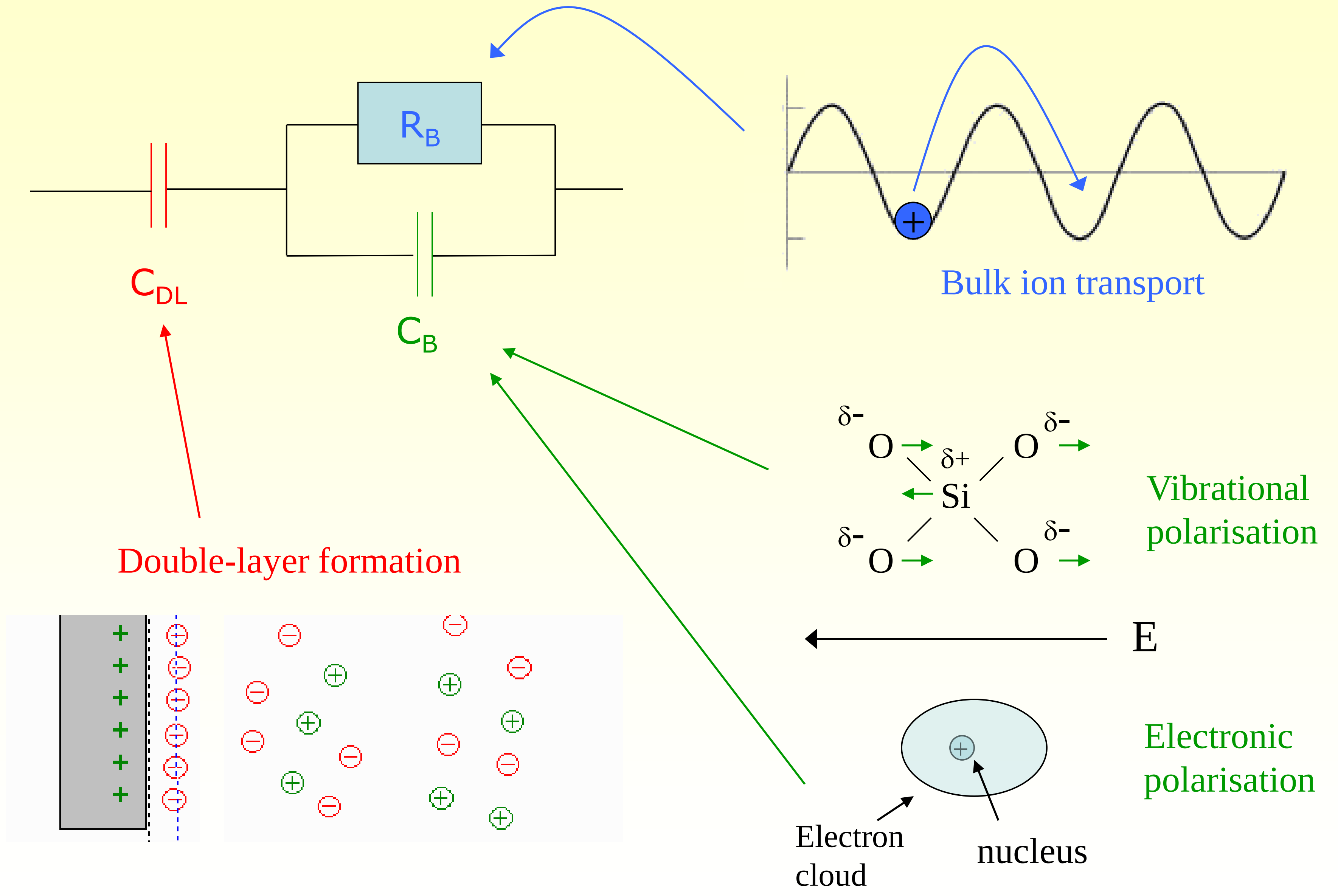
$Y''(\omega) = I_{0,2} / U_0$ (Energy storage)

Other quantities

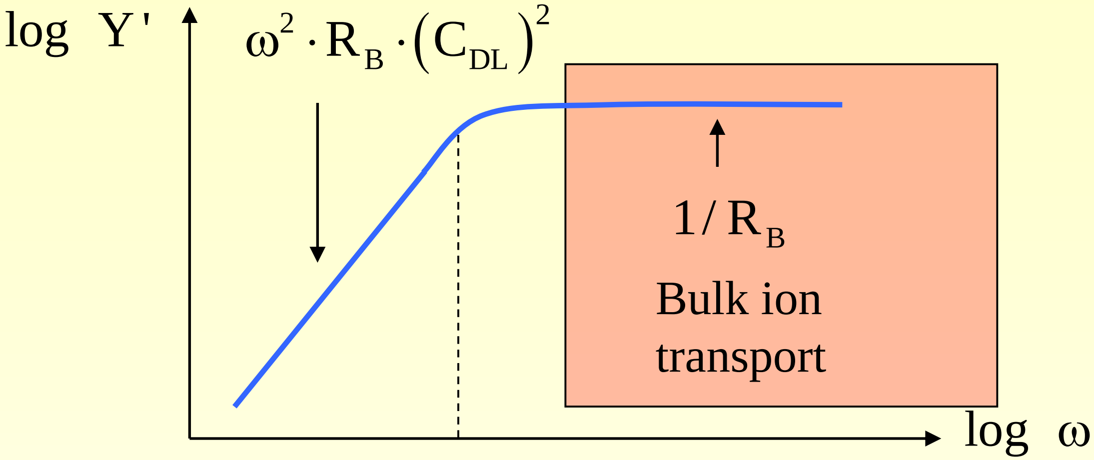
Impedance
$$\hat{Z}(\omega) = \frac{1}{\hat{Y}(\omega)} = Z'(\omega) + i\, Z''(\omega)$$

Capacitance
$$\hat{C}(\omega) = \frac{\hat{Y}(\omega)}{i\omega} = \frac{1}{i\omega \hat{Z}(\omega)} = C'(\omega) + i\, C''(\omega)$$

Simplest equivalent circuit for *homogeneous* ion conductor between ion-blocking electrodes



Real part of admittance



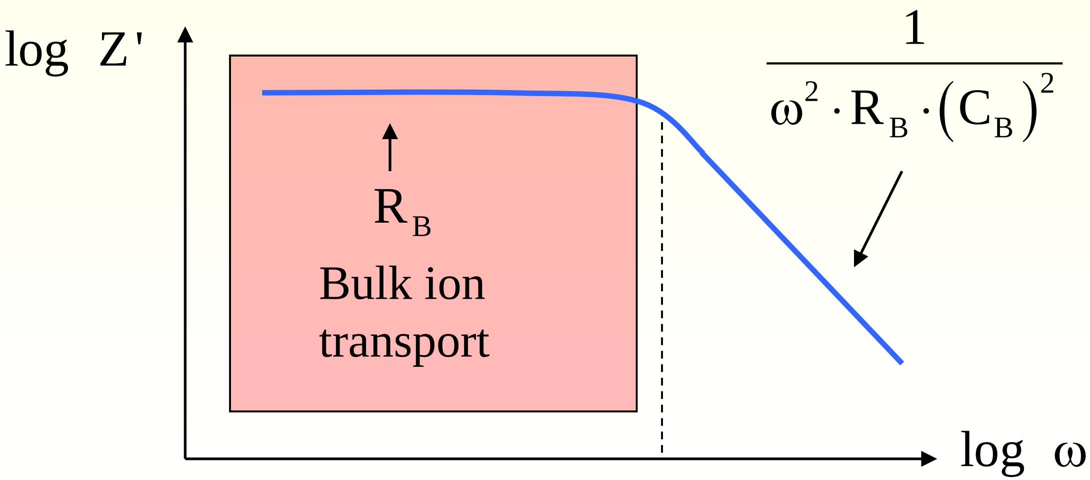
$$\omega_{DL} = \frac{1}{R_B \cdot C_{DL}} \propto \frac{1}{d}$$

- Bulk ionic dc conductivity

$$\sigma_{dc} = \frac{1}{R_B} \cdot \frac{d}{A}$$

- No information about C_B

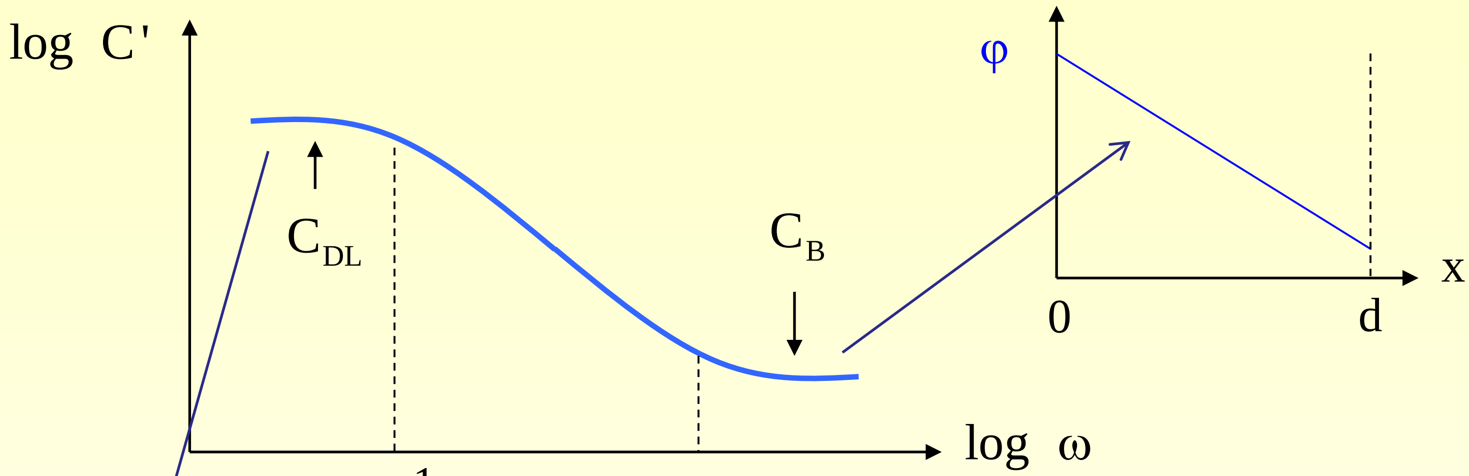
Real part of impedance



$$\omega_B = \frac{1}{R_B \cdot C_B}$$

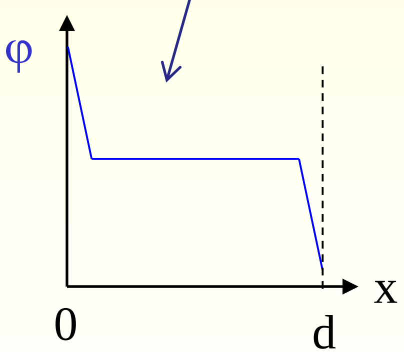
No information about C_{DL}

Real part of capacitance



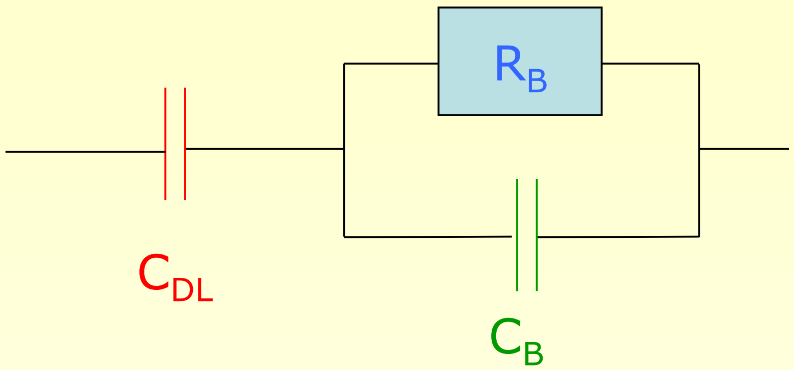
$$\omega_{DL} = \frac{1}{R_B \cdot C_{DL}} \propto \frac{1}{d}$$

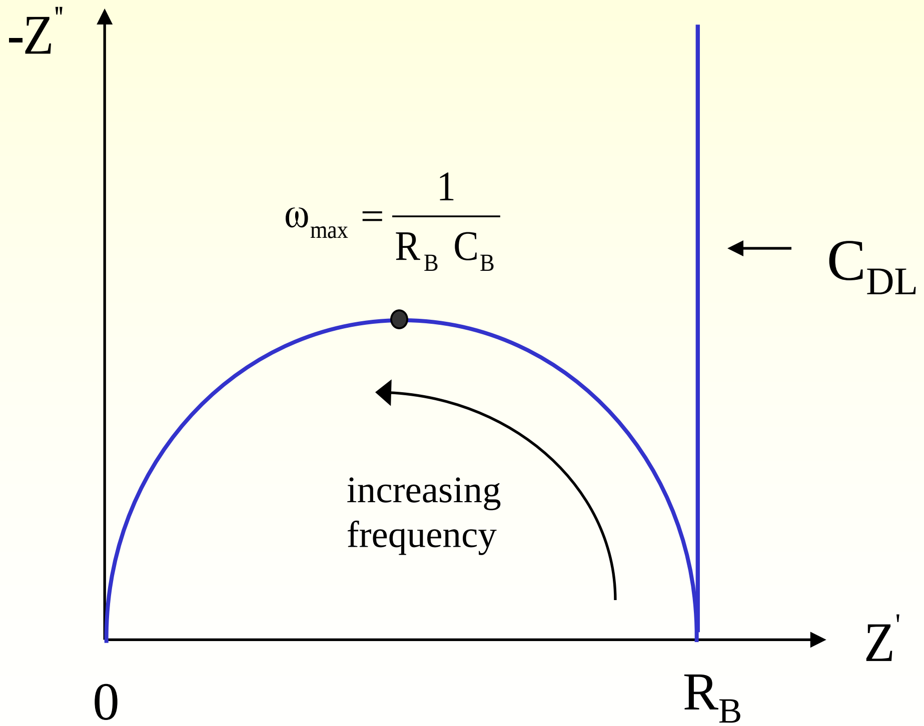
$$\sqrt{\omega_B \cdot \omega_{DL}} = \sqrt{\frac{1}{(R_B \cdot C_B)\cdot(R_B \cdot C_{DL})}} \propto \frac{1}{\sqrt{d}}$$



$$\frac{C_{DL}}{C_B} \approx \frac{\text{Thickness of sample}}{\text{Thickness of double layer}} \approx \frac{1\ \text{mm}}{1\ \text{nm}} = 10^6$$

Nyquist plot of impedance





Rather common mistake in the analysis of impedance spectra

Inductance of connecting cables

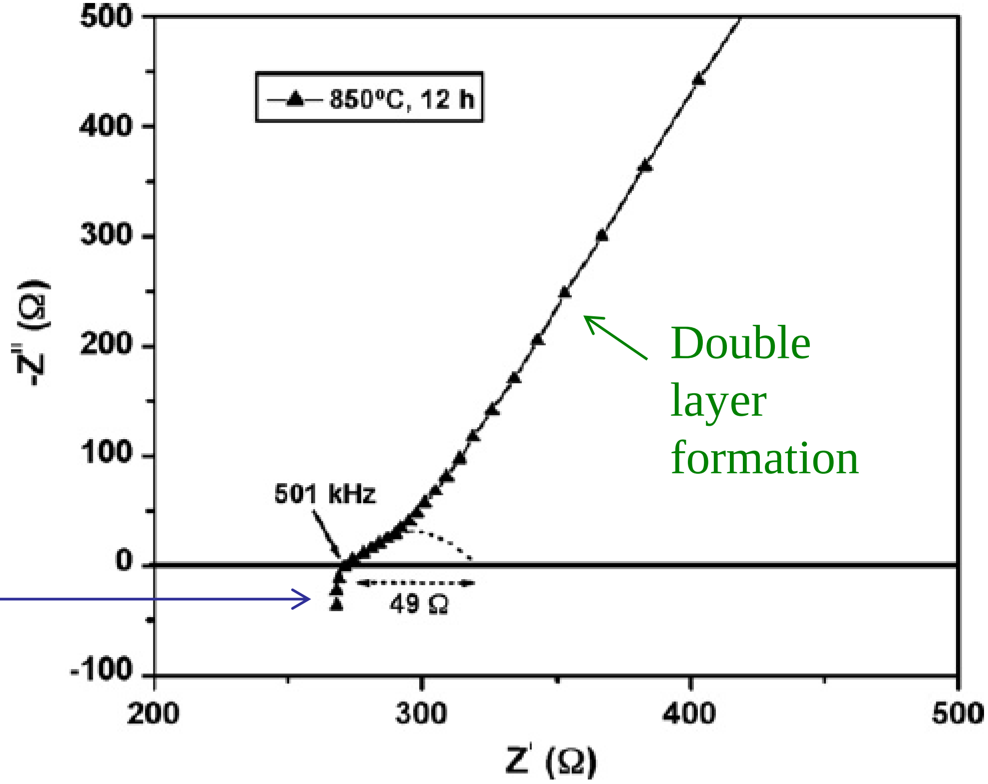
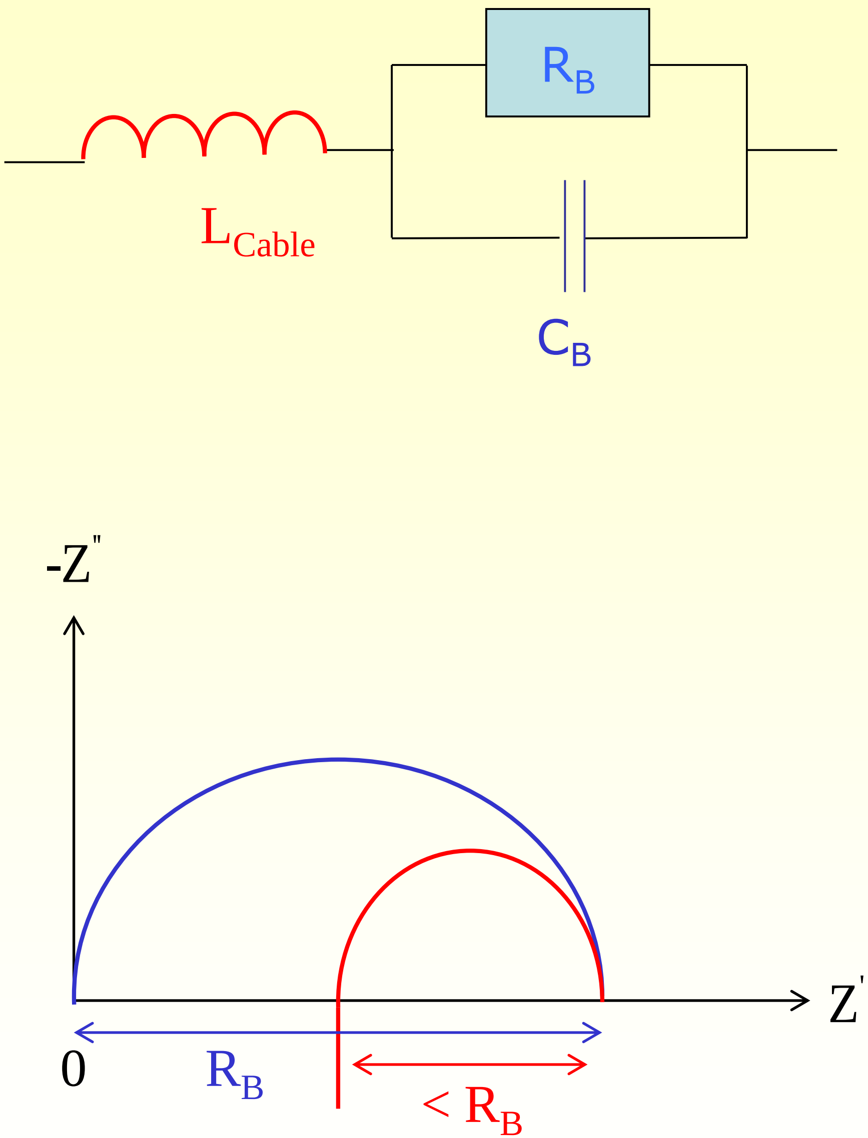


Fig. 4. Room temperature impedance spectra for LAGP glass sheet crystallized at 850 °C for 12 h.

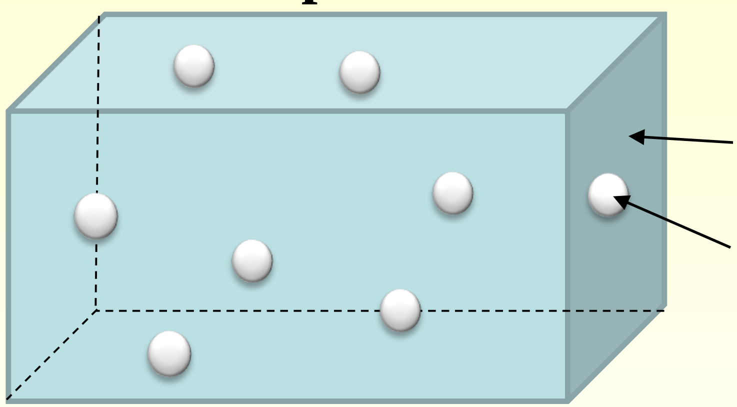
J. Thokchom, B. Kumar, J. Power Sources 185 (2008) 480.



R_B
L_Cable
C_B
-Z"
Z'
0
R_B
< R_B

2. Ion Transport in Heterogeneous Materials

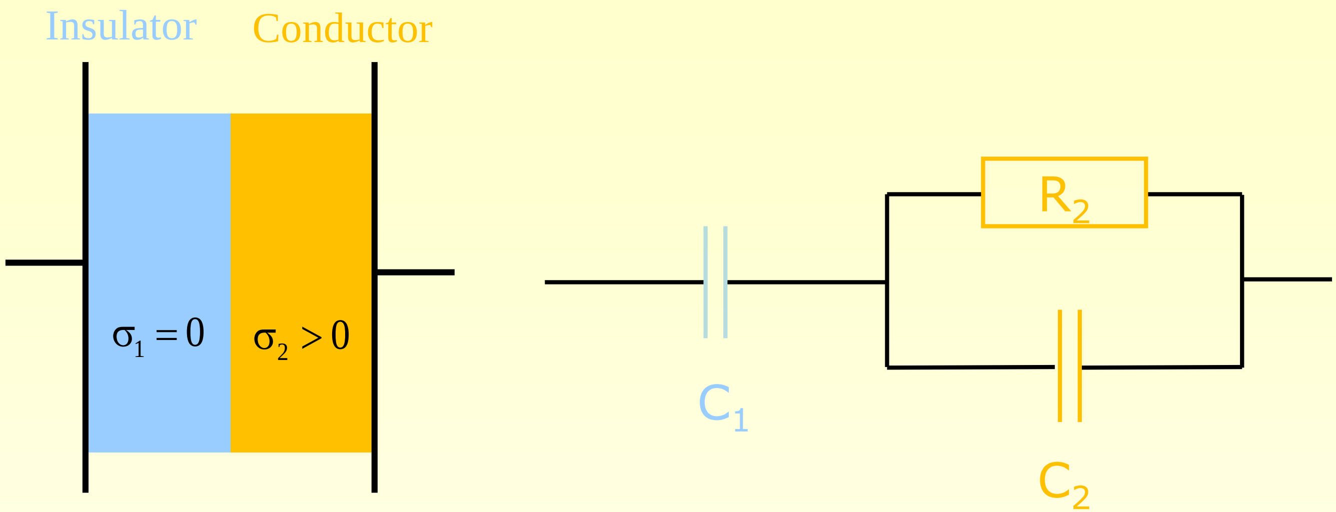
Dispersion



Examples:

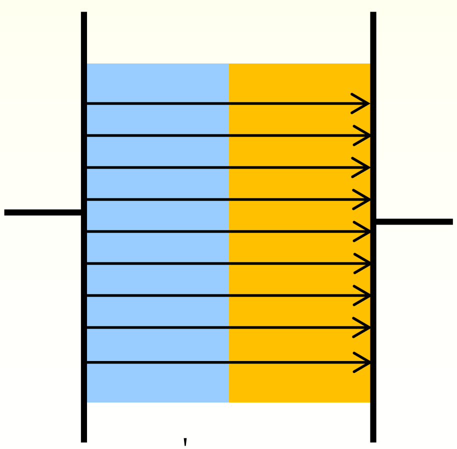
- Metallic particles in an insulating polymer matrix: $\sigma_2 \gg \sigma_1$
- Insulating particles in a gel electrolyte: $\sigma_1 \gg \sigma_2$

Two serial phases



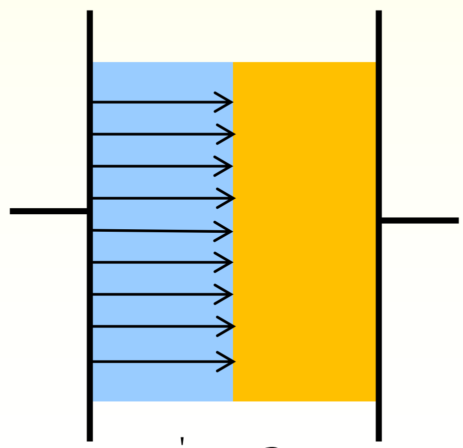
$$\varepsilon_1 = \varepsilon_2 = \varepsilon$$

High frequencies:

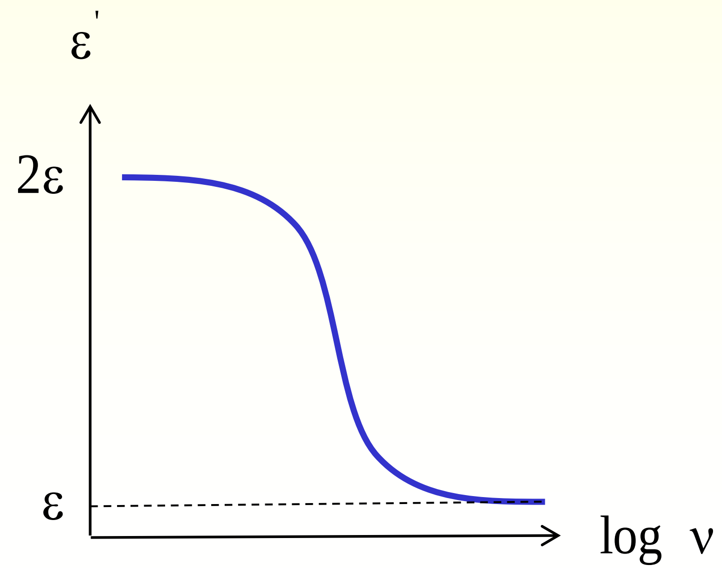


$$\varepsilon'_{hf} = \varepsilon$$

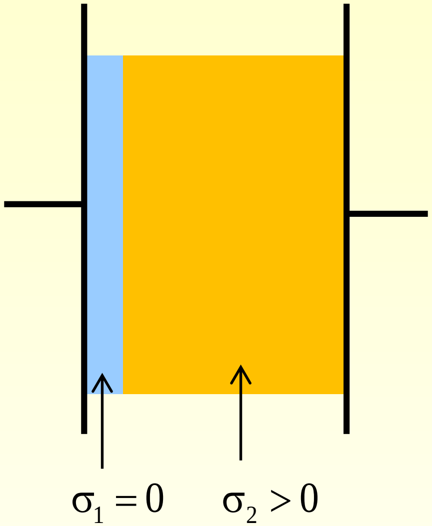
Low frequencies:

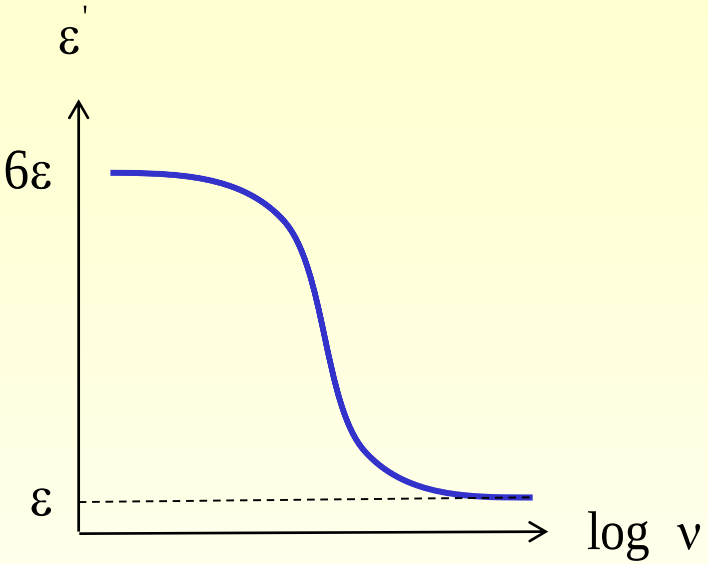


$$\varepsilon'_{lf} = 2\varepsilon$$



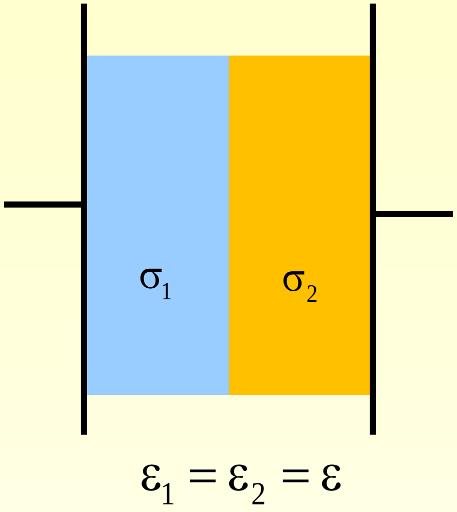
Two serial phases

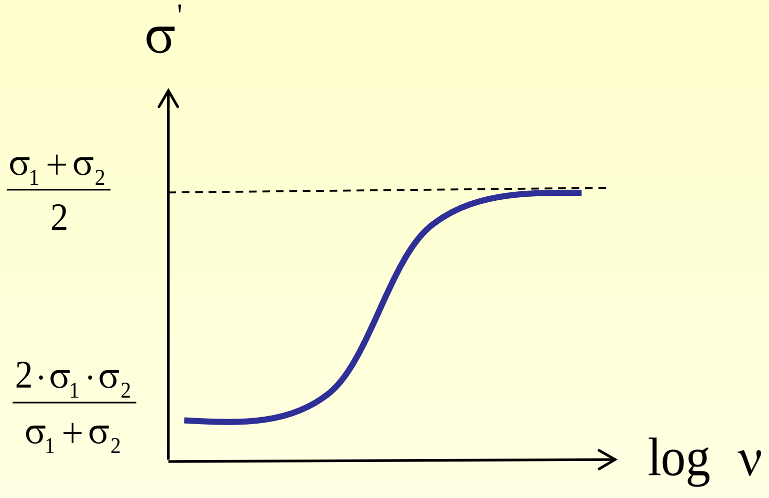




$$\frac{\varepsilon'_{lf}}{\varepsilon'_{hf}} = \frac{\text{Thickness of sample}}{\text{Thicknees of insulating phase}}$$

Two serial phases

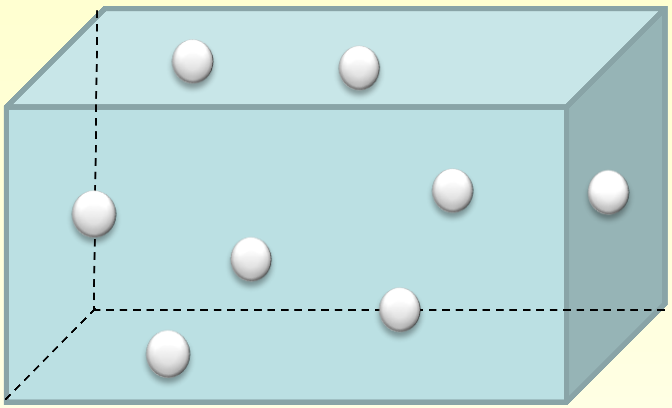




High frequencies: Averaging over the ***conductivity*** of different phases
(Charge carriers move only locally)

Low frequencies: Averaging over the ***resistivity*** of different phases
(Charge carriers move across the sample)

Dispersions



Continuous phase: σ_1, ε_1

Dispersed phase: σ_2, ε_2

Volume fraction of dispersed phase: ϕ

Basic assumptions for Maxwell-Wagner-Bruggemann approach:

- Dispersed particles are spheres.
- Small volume fraction ϕ (diluted system)
- Random spatial distribution of dispersed particles

  (no interactions between dispersed particles)

Maxwell-Wagner-Bruggemann equations

$$\hat{\sigma} = \sigma_{lf}^{'} + \frac{\left(\sigma_{hf}^{'} - \sigma_{lf}^{'}\right)\cdot i\omega\tau}{1+i\omega\tau} + i\omega\varepsilon_0\varepsilon_{hf}^{'}$$

with

$$\sigma_{lf}^{'} = \sigma_1 \frac{2\sigma_1 + \sigma_2 - 2\phi\left(\sigma_1 - \sigma_2\right)}{2\sigma_1 + \sigma_2 + \phi\left(\sigma_1 - \sigma_2\right)}$$

Low-frequency conductivity

$$\sigma_{hf}^{'} - \sigma_{lf}^{'} = \frac{9\left(\sigma_1\varepsilon_2 - \sigma_2\varepsilon_1\right)^2 \phi\left(1-\phi\right)}{\left(2\sigma_1 + \sigma_2 + \phi\left(\sigma_1 - \sigma_2\right)\right)\left(2\varepsilon_1 + \varepsilon_2 + \phi\left(\varepsilon_1 - \varepsilon_2\right)\right)^2}$$

Difference between high-frequency and low-frequency conductivity

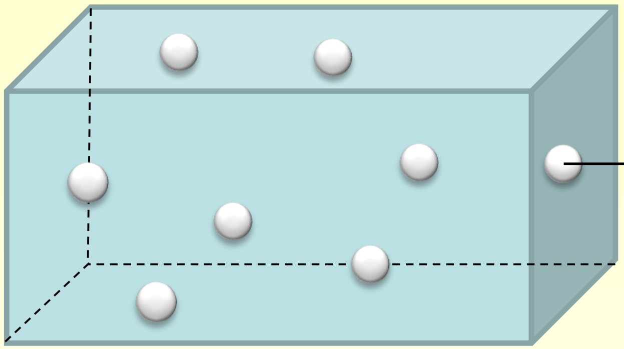
$$\varepsilon_{hf}^{'} = \varepsilon_1 \frac{2\varepsilon_1 + \varepsilon_2 - 2\phi\left(\varepsilon_1 - \varepsilon_2\right)}{2\varepsilon_1 + \varepsilon_2 + \phi\left(\varepsilon_1 - \varepsilon_2\right)}$$

High-frequency permittivity

$$\tau = \frac{\varepsilon_0\left(2\varepsilon_1 + \varepsilon_2 + \phi\left(\varepsilon_1 - \varepsilon_2\right)\right)}{2\sigma_1 + \sigma_2 + \phi\left(\sigma_1 - \sigma_2\right)}$$

Relaxation time

Limiting case: Dispersed insulator



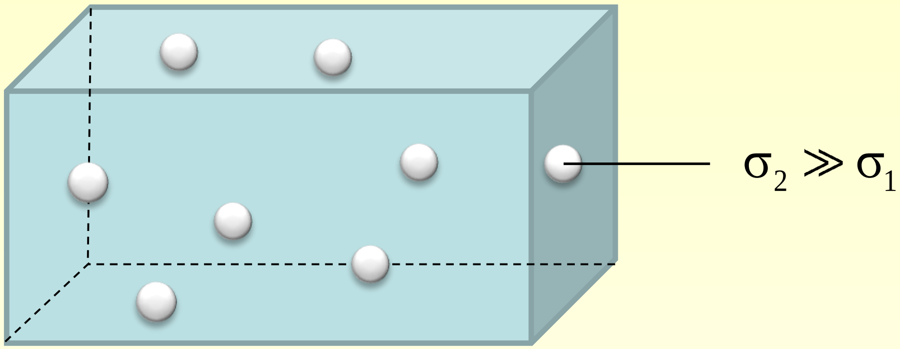
$\sigma_2 \ll \sigma_1$

Low-frequency conductivity

$$\sigma'_{lf} = \sigma_1 \frac{2\sigma_1 + \sigma_2 - 2\phi(\sigma_1 - \sigma_2)}{2\sigma_1 + \sigma_2 + \phi(\sigma_1 - \sigma_2)} \approx \sigma_1 \left(1 - \frac{3}{2}\phi\right)$$

The addition of 1% insulating particles results in a conductivity drop of about 1.5 %

Limiting case: Dispersed conductor



Low-frequency conductivity

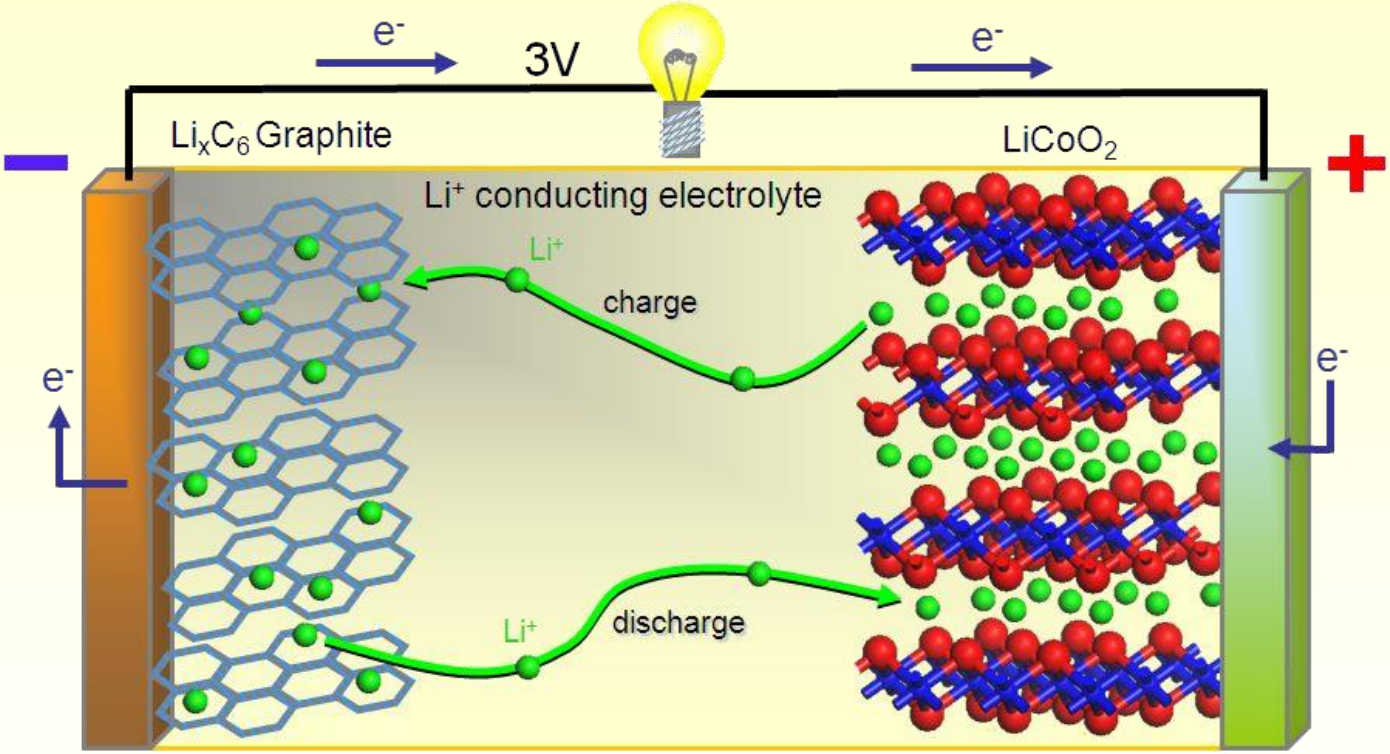
$$\sigma'_{\mathrm{lf}} = \sigma_1 \frac{2\sigma_1 + \sigma_2 - 2\phi(\sigma_1 - \sigma_2)}{2\sigma_1 + \sigma_2 + \phi(\sigma_1 - \sigma_2)} \approx \sigma_1(1 + 3\phi)$$

The addition of 1% conducting particles results in a conductivity rise of about 3%

Note: Since the conducting particles do not form percolating pathways, the composite conductivity is governed by the conductivity of the insulating phase, σ_1.

3. Ion Transport in Porous Battery Electrodes

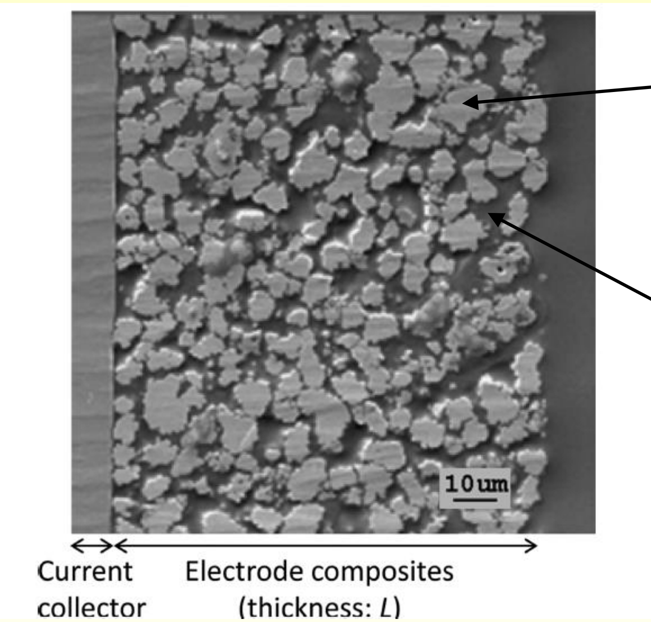
Example: Li-ion battery



Gravimetric energy density:

150-200 Wh / kg

Composite electrodes

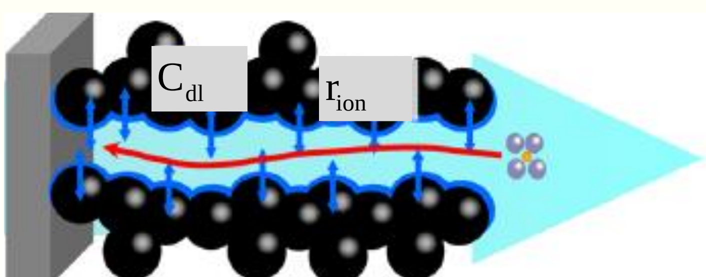


Active material particle (stores Li)

Pore space is flooded by the liquid electrolyte

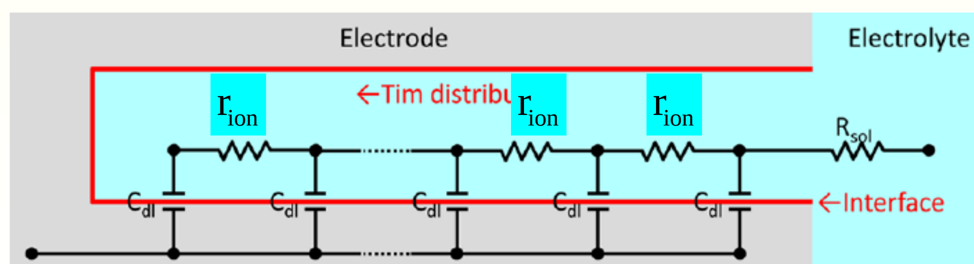
Ogihara et al,
J. Phys. Chem.
119 (2015) 4612

Idealized model approach with cylindrical pores:

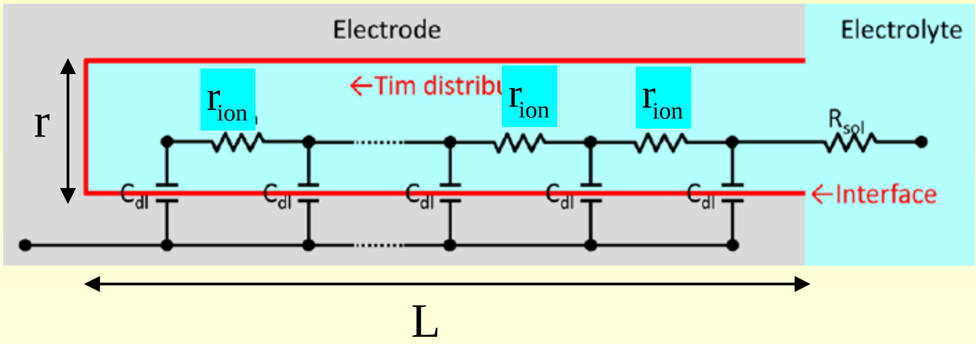


Active material particle

Transmission line circuit



Transmission line model



$$r_{ion} = \frac{1}{\sigma_{ion} \cdot 4\pi r^2}$$ Electrolyte resistance per unit length (Ω / m)

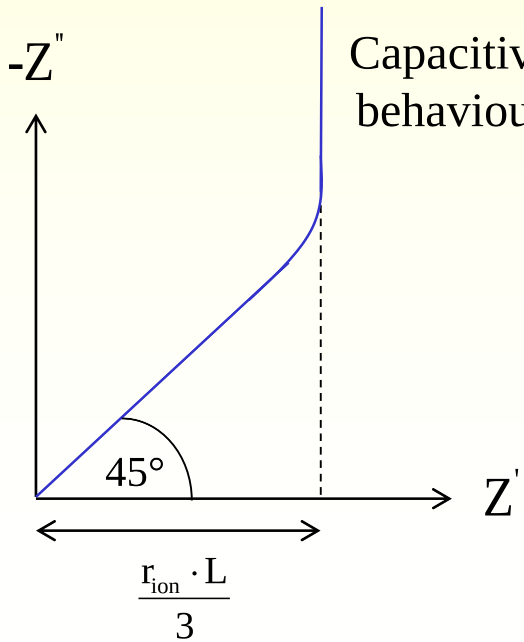
$$C_{dl} = \frac{C_{dl,pore}}{2\pi r L}$$ Double layer capacitance per unit area (F / m^2)

$$\hat{Z} = \sqrt{\frac{r_{ion}}{i\omega C_{dl} \cdot 2\pi r}} \cdot \coth\left(\sqrt{r_{ion} \cdot i\omega C_{dl} \cdot 2\pi r} \cdot L\right)$$

$$\hat{Z} = \sqrt{\frac{r_{ion}}{i\omega C_{dl} \cdot 2\pi r}} \cdot \coth\left(\sqrt{r_{ion} \cdot i\omega C_{dl} \cdot 2\pi r} \cdot L\right)$$

High frequencies: $\coth\left(\sqrt{R_{ion} \cdot i\omega C_{dl} \cdot 2\pi r} \cdot L\right) \to 1$

$\Rightarrow \quad \hat{Z} \propto (i\omega)^{-1/2}$



Low frequencies: $\coth(x) \approx \frac{1}{x} + \frac{x}{3}$

$$\Rightarrow \quad \hat{Z} = \frac{r_{ion} \cdot L}{3} - i\frac{1}{\omega C_{dl} \cdot 2\pi r L}$$

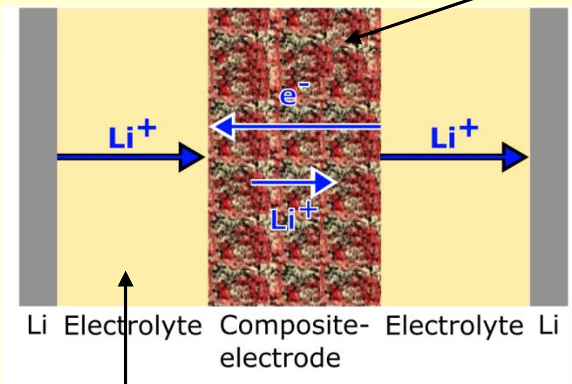
Ion transport resistance: $R_{ion} = r_{ion} \cdot L$ (Ω)

Stationary Ion Transport Measurements

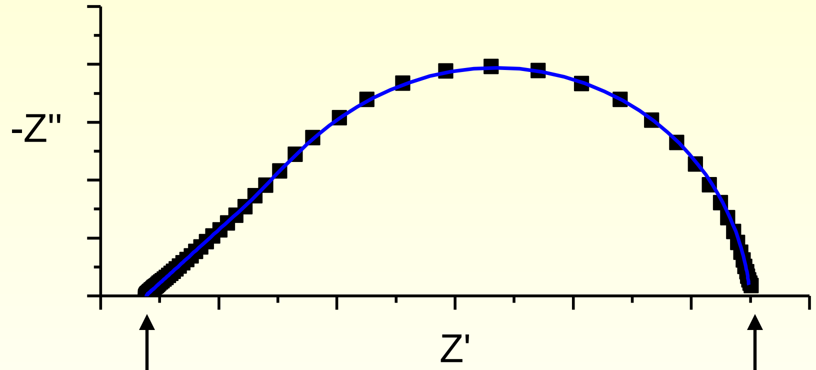
High frequencies:

$$R_{composite}(\omega \to \infty) = \frac{R_{ion} \cdot R_{electron}}{R_{ion} + R_{electron}} \approx R_{electron}$$

Ion and electrons move in parallel



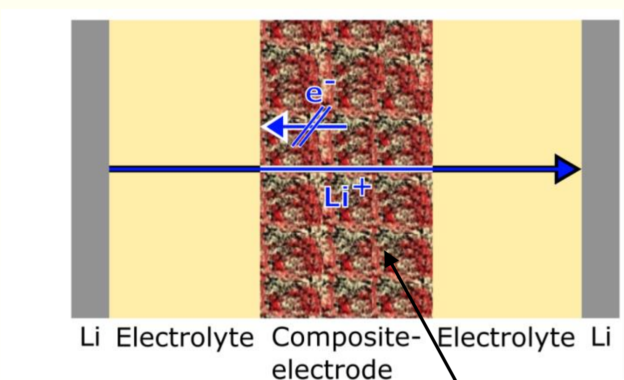
$R_{Electrolyte}$



$$Z'(\omega \to \infty) = 2 \cdot R_{Electrolyte} + R_{electron} \approx 2 \cdot R_{Electrolyte}$$

$$Z'(\omega \to 0) = 2 \cdot R_{Electrolyte} + R_{ion}$$

Low frequencies:

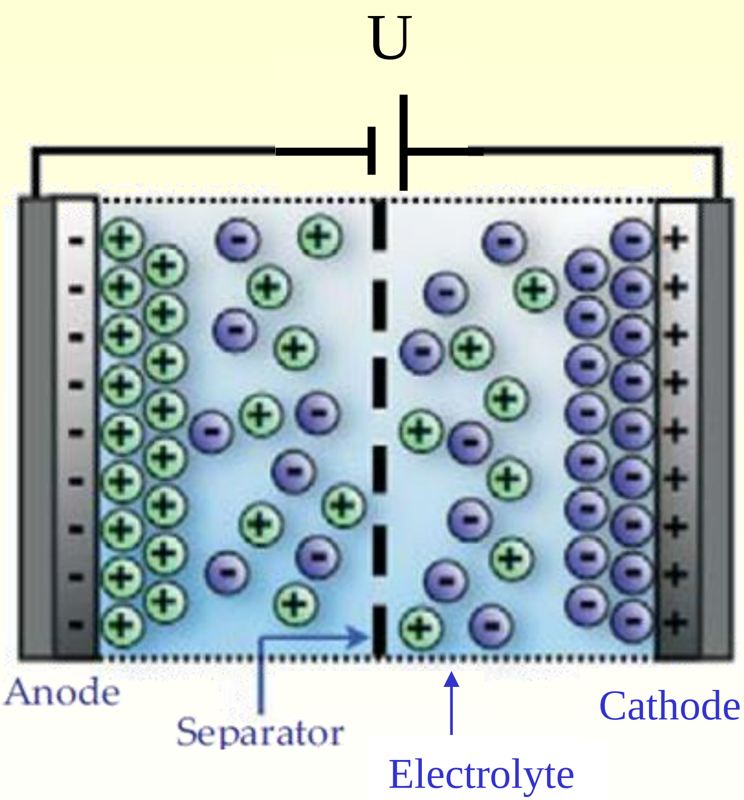


$$R_{composite}(\omega \to 0) = R_{ion}$$

$$R_{ion} = Z'(\omega \to \infty) - Z'(\omega \to 0)$$

4. Double Layer Formation at Electrode Surfaces

Energy storage in electrochemical supercapacitors



Stored energy

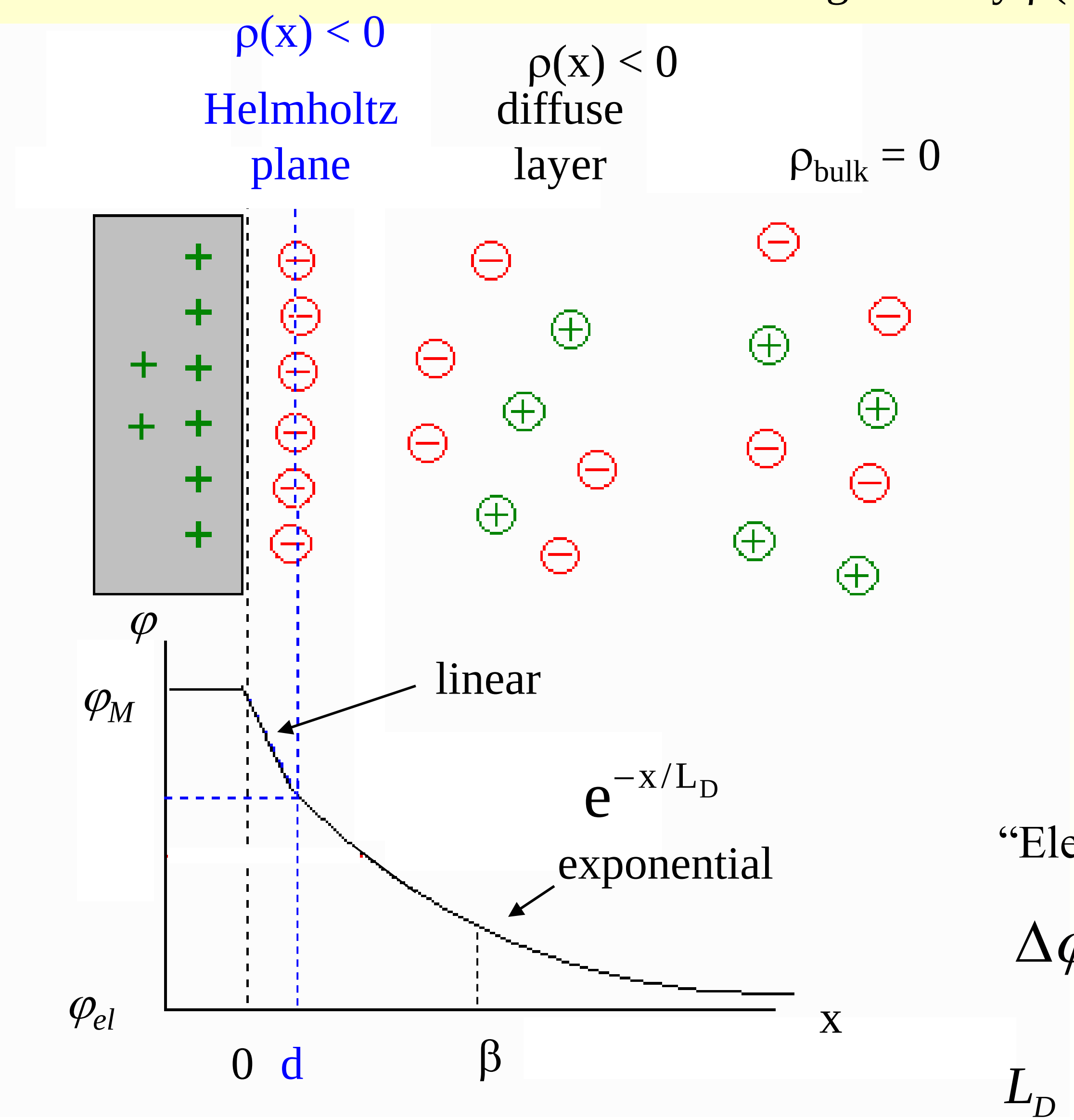
$$E = \frac{1}{2} \cdot C \cdot U^2$$

C = double layer capacitance

U = maximum voltage

Classical Stern model for **diluted** electrolytes

Charge density ρ(x)



“Electrode potential“

$$\Delta\varphi = \varphi_M - \varphi_{el}$$

L_D = Debye length

Differential capacitance of the double layer

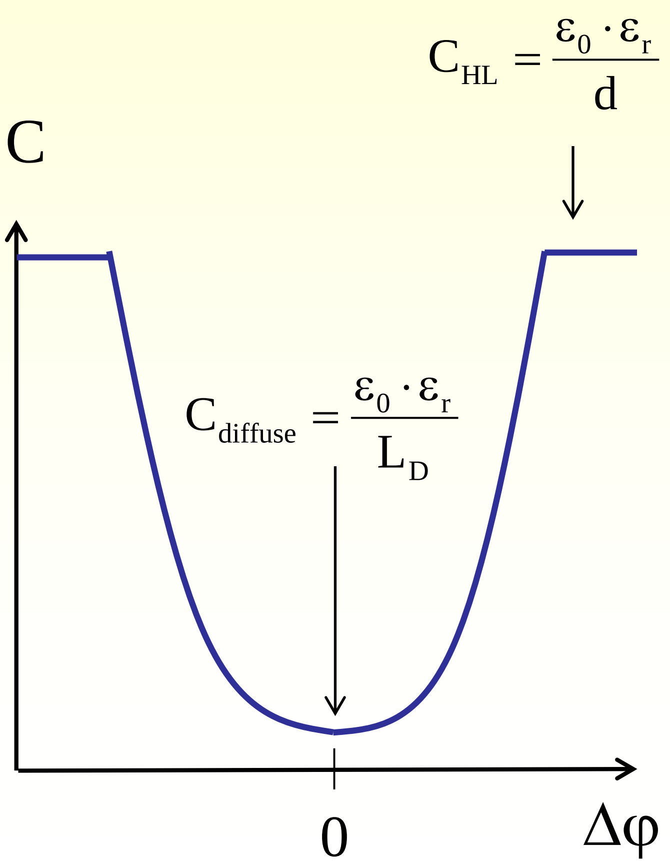
Differential capacitance per unit area $$C = \frac{d(Q_{electrode} / A)}{d(\Delta\varphi)}$$

Helmholtz layer $$C_{HL} = \frac{\varepsilon_0 \cdot \varepsilon_r}{d}$$

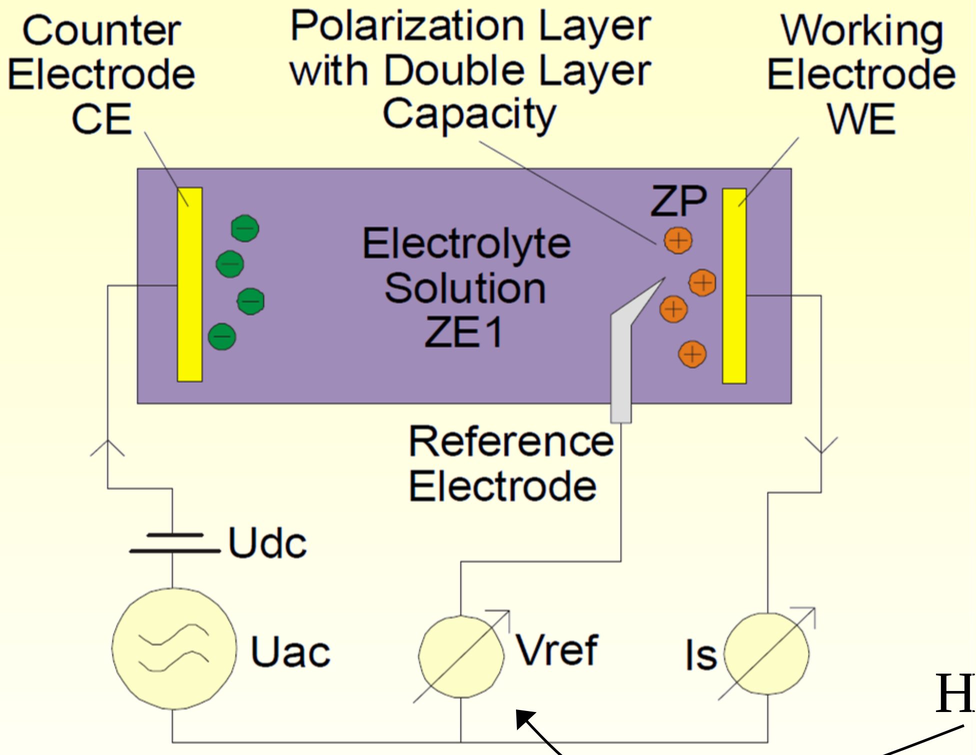
Diffuse layer $$C_{diffuse} = \frac{\varepsilon_0 \cdot \varepsilon_r}{L_D} \cdot \cosh\left(\frac{e \cdot \Delta\varphi}{2 \cdot kT}\right)$$

⬇

$$\frac{1}{C} = \frac{1}{C_{HL}} + \frac{1}{C_{diffuse}}$$



Experiment: Three-Electrode Configuration



High-resistance voltmeter

Impedance of working electrode: $\hat{Z}_{WE} = \dfrac{V_{WE} - V_{ref}}{I_S}$

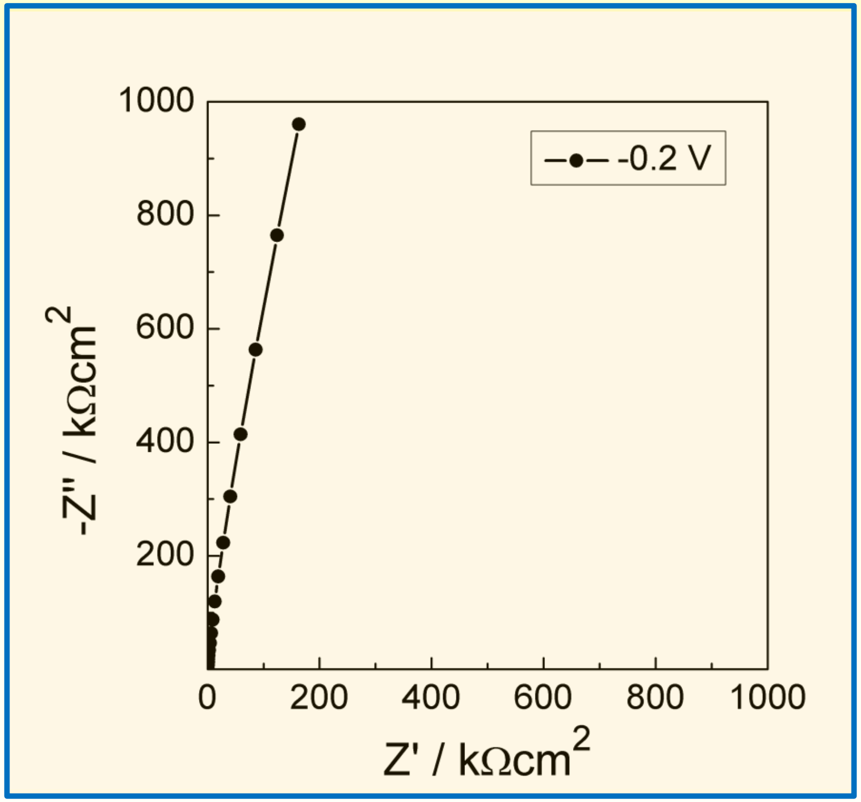
Nyquist plot of impedance

Frequency range:

ν = 10 mHz - 1 MHz

Ac potential

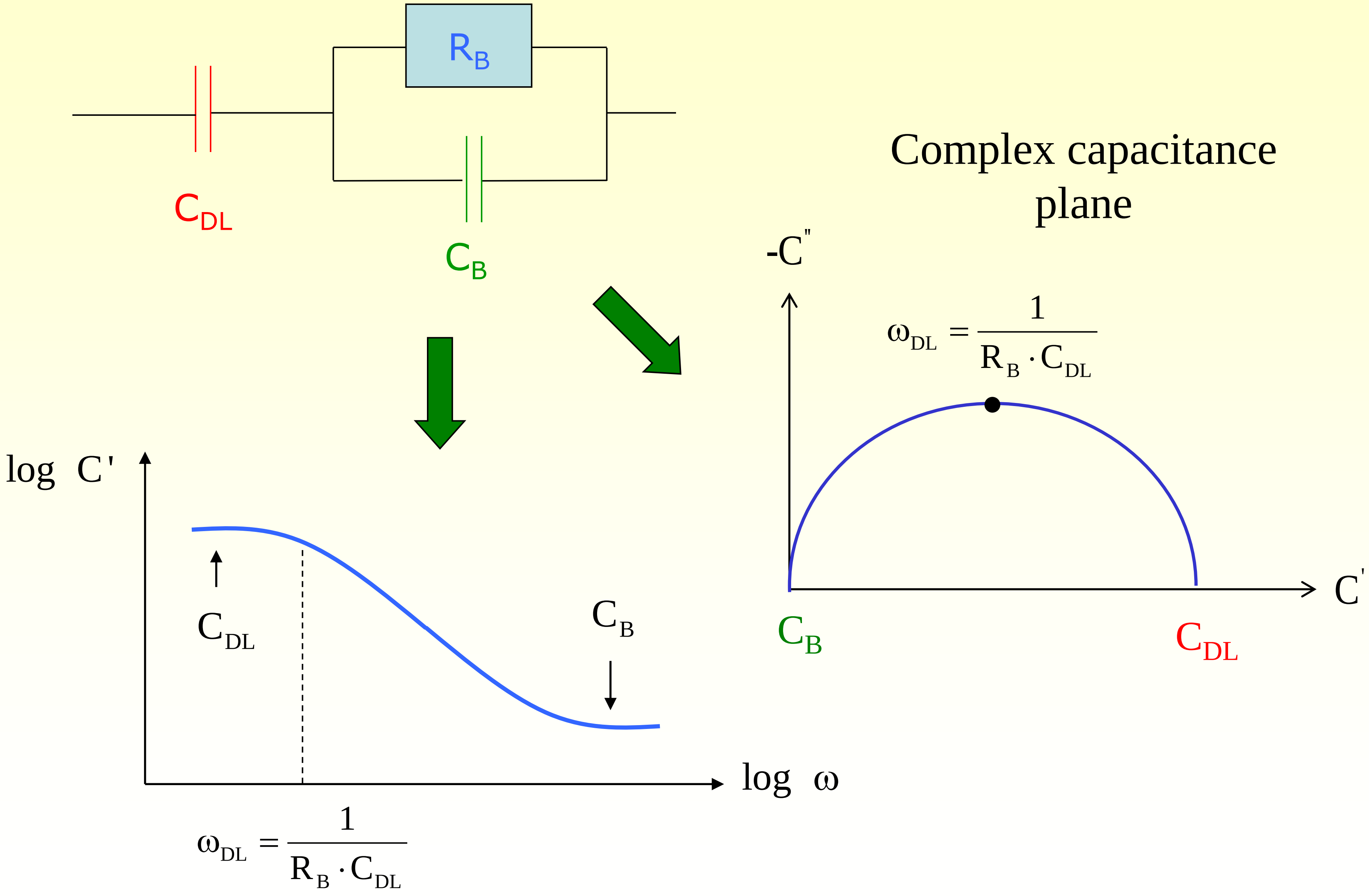
10 mV (rms)



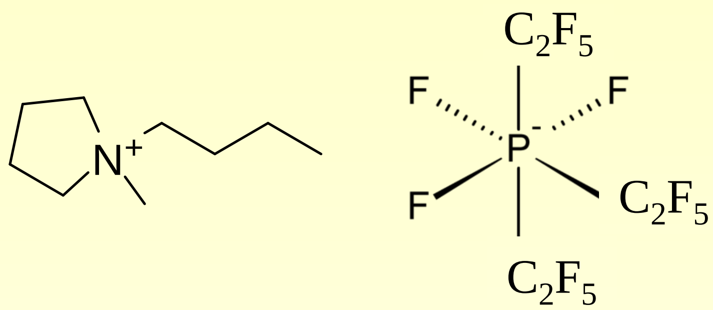
Non-ideal capacitance

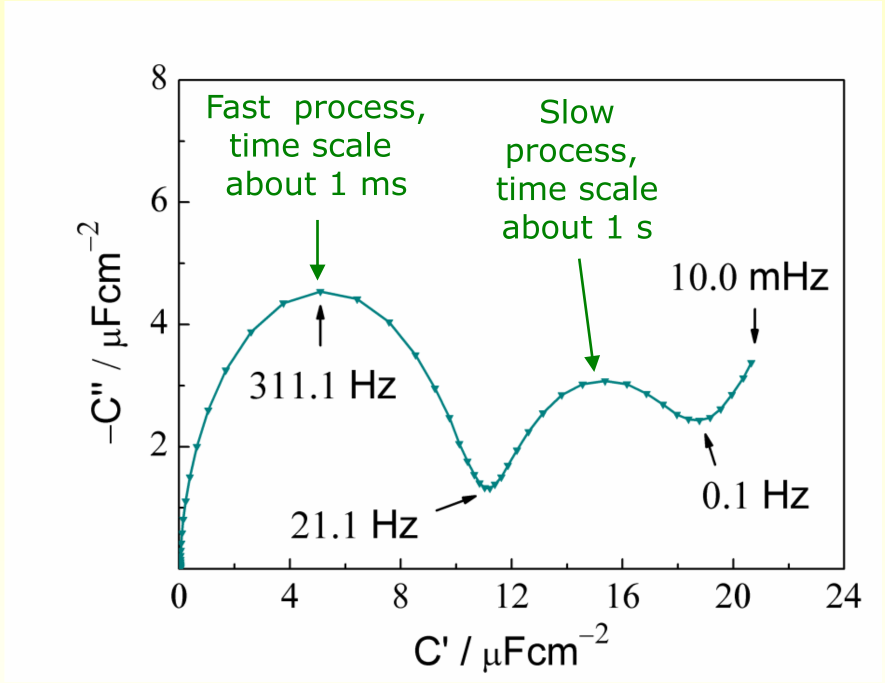
M. Drüschler, B. Roling
J. Phys. Chem. C
115 (2011) 6802.

Simplest equivalent circuit representation



Complex capacitance plane of Pyr14-FAP at Au(111)





Ionic liquids: $\tau_{DL} = R_{bulk} \cdot C_{DL} \approx 1$ **ms**

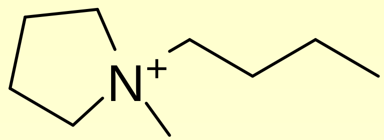
Fit with empirical Cole-Cole relation:

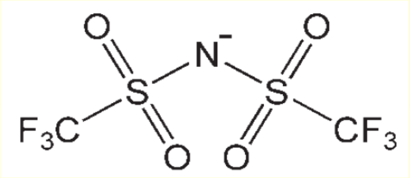
$$\left(\hat{C}(\nu) - C_\infty\right) = \sum_{i=1}^{n} \frac{\Delta C_i}{1 + \left(j2\pi\nu\tau_i\right)^{\alpha_i}}$$

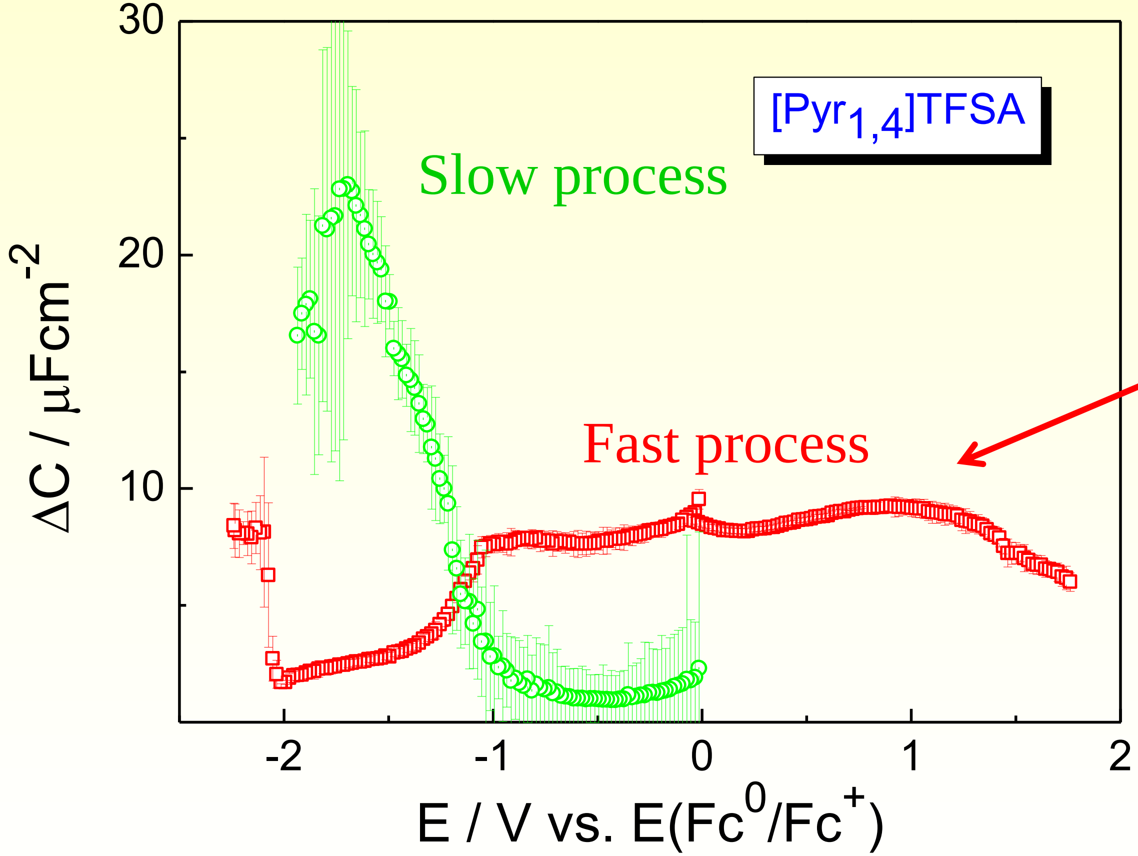
→ Differential capacitance of both processes ΔC_{fast} and ΔC_{slow}

R. Atkin, N. Borisenko, M. Drüschler, S.Z. El Abedin, F. Endres, R. Hayes, B. Huber, B. Roling, Phys. Chem. Chem. Phys. 13 (2011) 6849.

Fast and slow processes





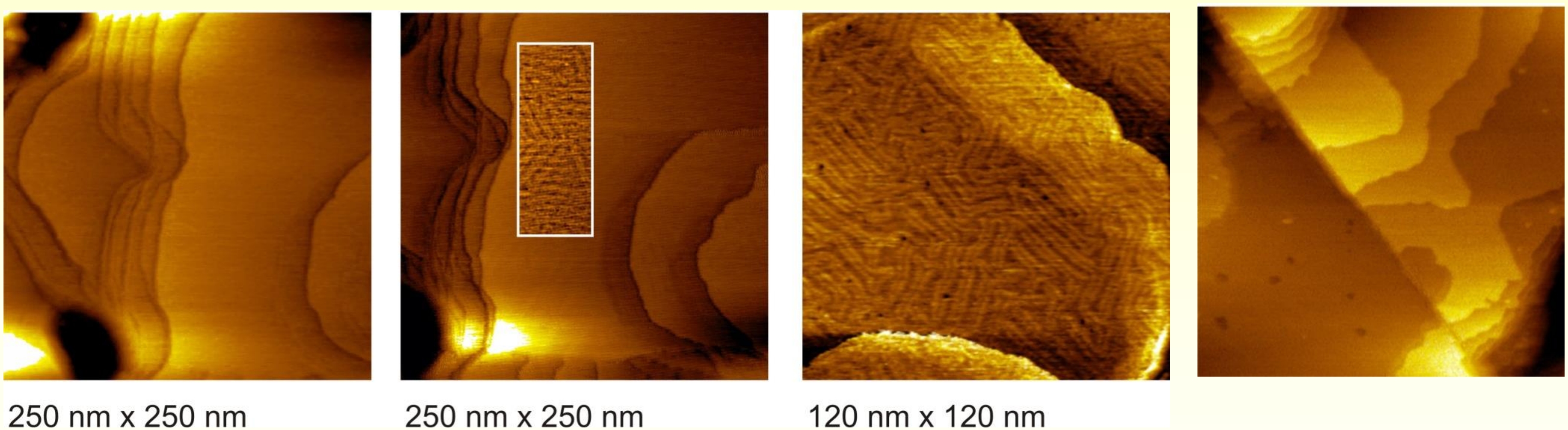


differs strongly from Stern model

J. Wallauer, M. Drüschler, B. Huber, B. Roling, Z. Naturforsch. 68b (2013) 1143.

Fast and slow processes

increasing negative potential / charge of the Au(111) electrode

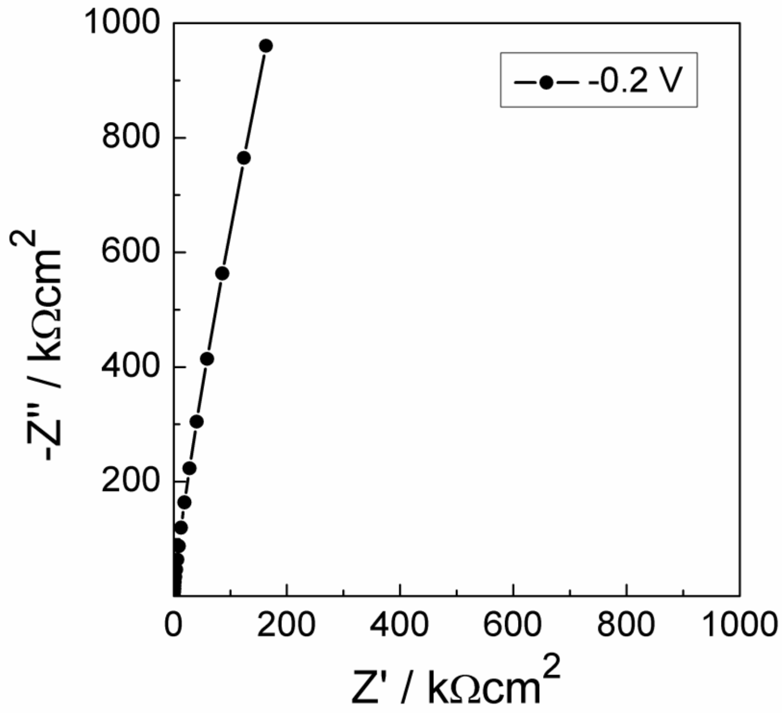


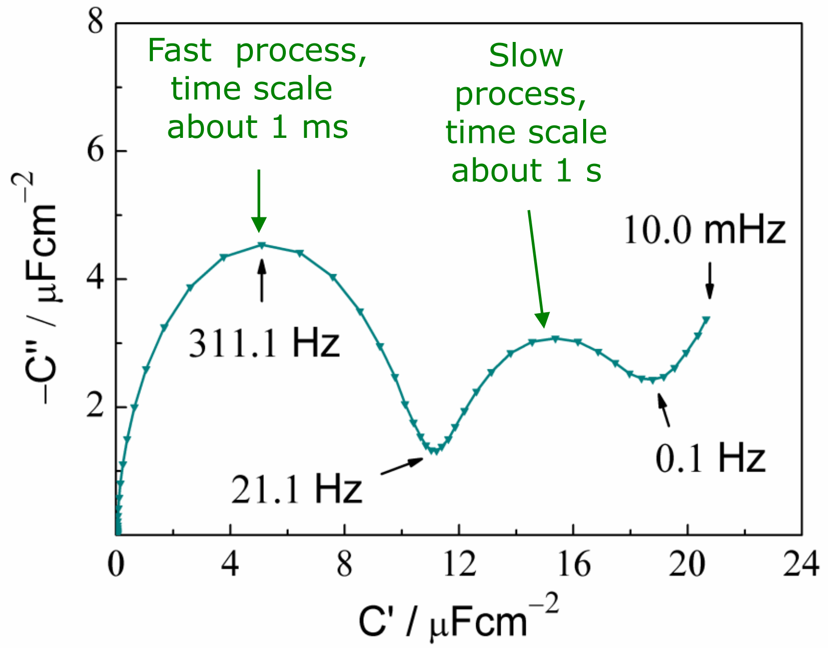
Herringbone-type
superstructure
of Au surface

Maximum of ΔC_{slow}

R. Atkin, N. Borisenko, M. Drüschler, S.Z. El Abedin, F. Endres, R. Hayes,
B. Huber, B. Roling, Phys. Chem. Chem. Phys. 13 (2011) 6849.

Impedance vs. capacitance spectra





Two capacitive processes clearly visible

Many thanks

for

your attention!