# Electrochemistry for Materials Technology

# Chapter Z: Electrochemical Impedance Spectroscopy (EIS)

# Part I: Fundamentals of Dielectric Spectroscopy

1 – Electrochemical interfacial processes

2 – Principle of impedance spectroscopy

3 – Ideal Circuit elements

4 – Case study 1: the RC element

5 – Representing EIS data: Bode and Nyquist plots

6 – Treatment of a ZARC element

7 – Faradaic reaction: the Randles circuit

8 – Non ideal elements

# Part II: Practical aspects and data treatment

1 – Impedance measurements

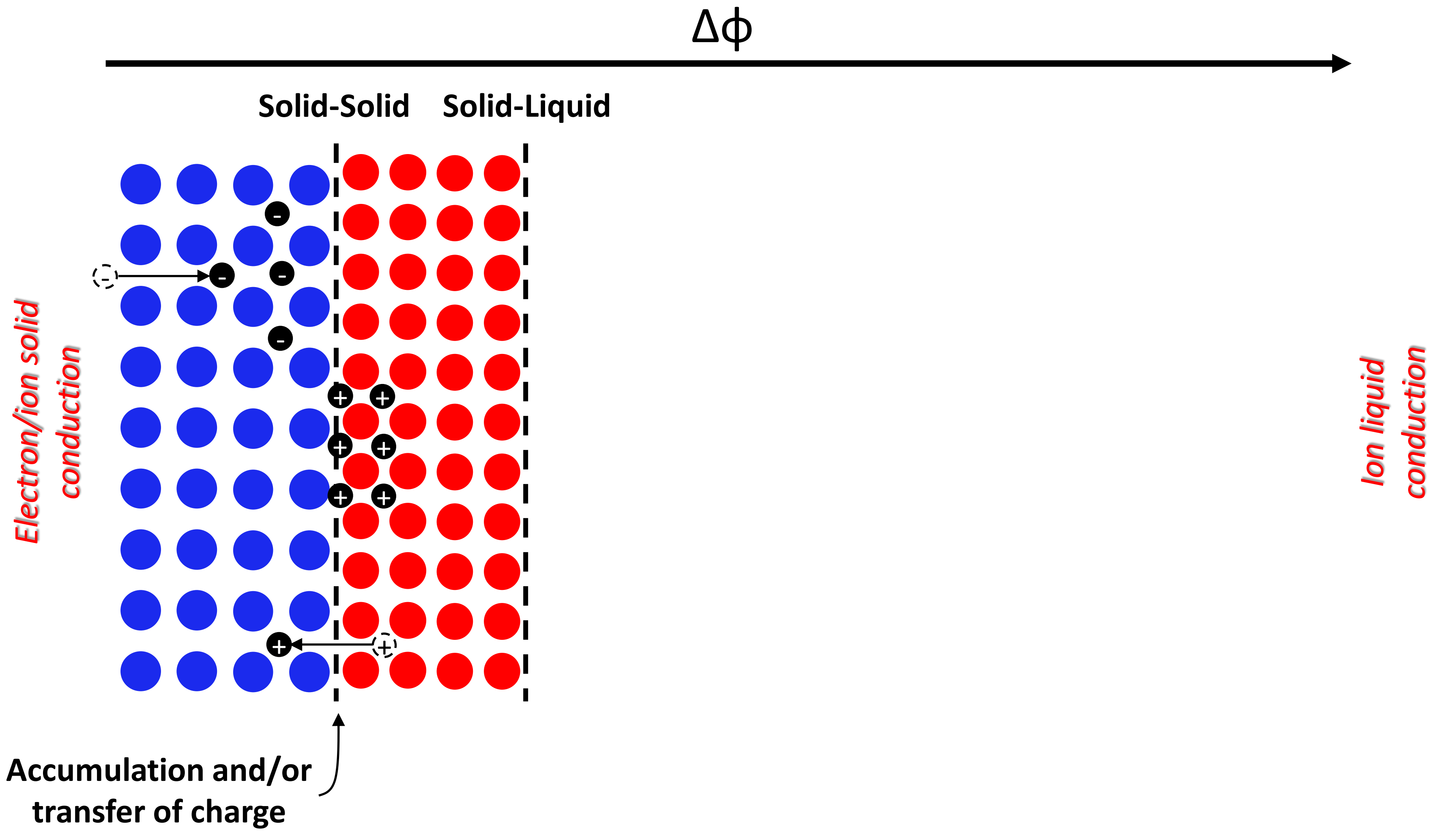
2 – Data treatment

3 – Derived impedance techniques

4 – Some applications

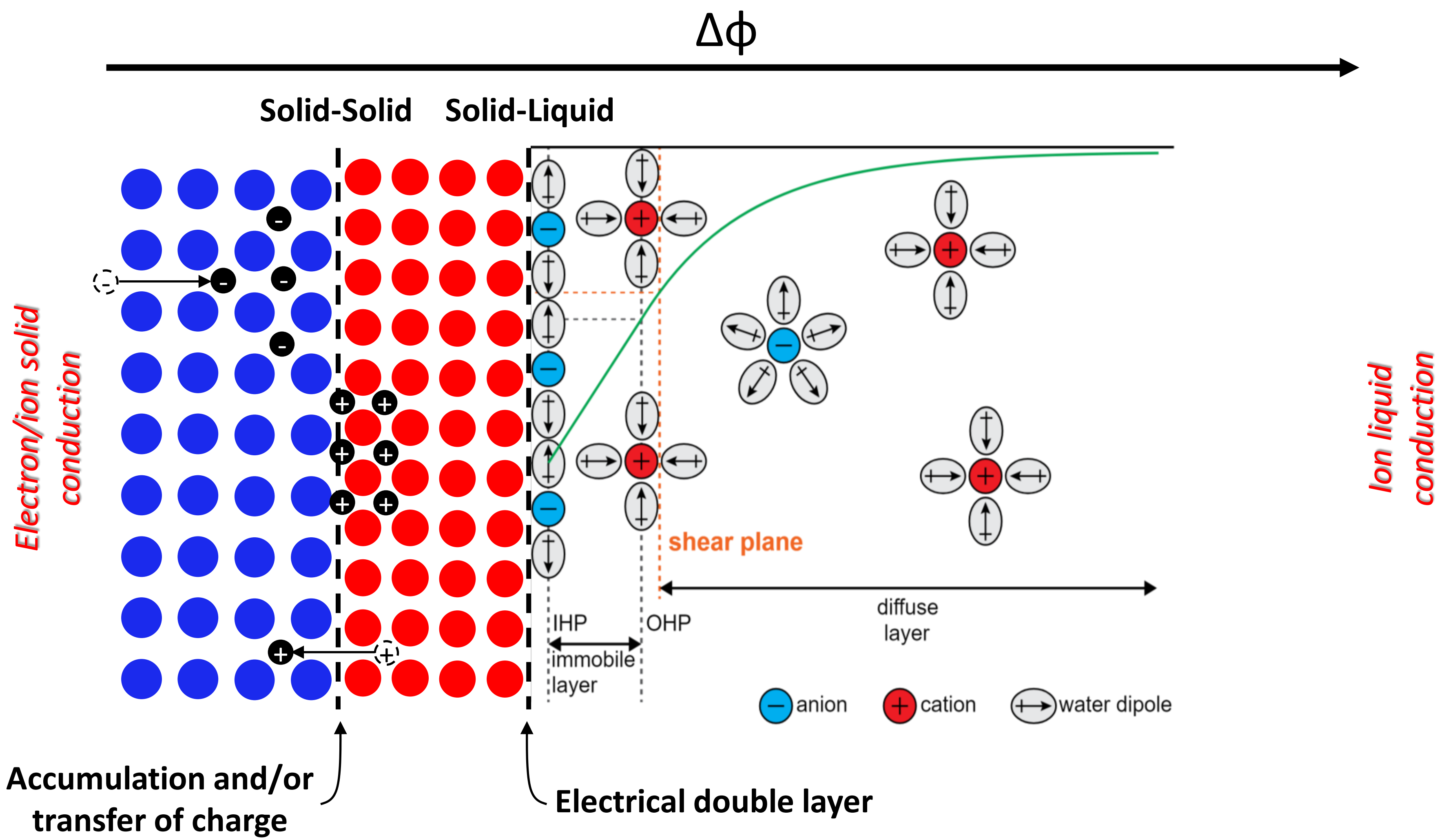
# I) Fundamentals of EIS

## 1) Electrochemical interfacial processes



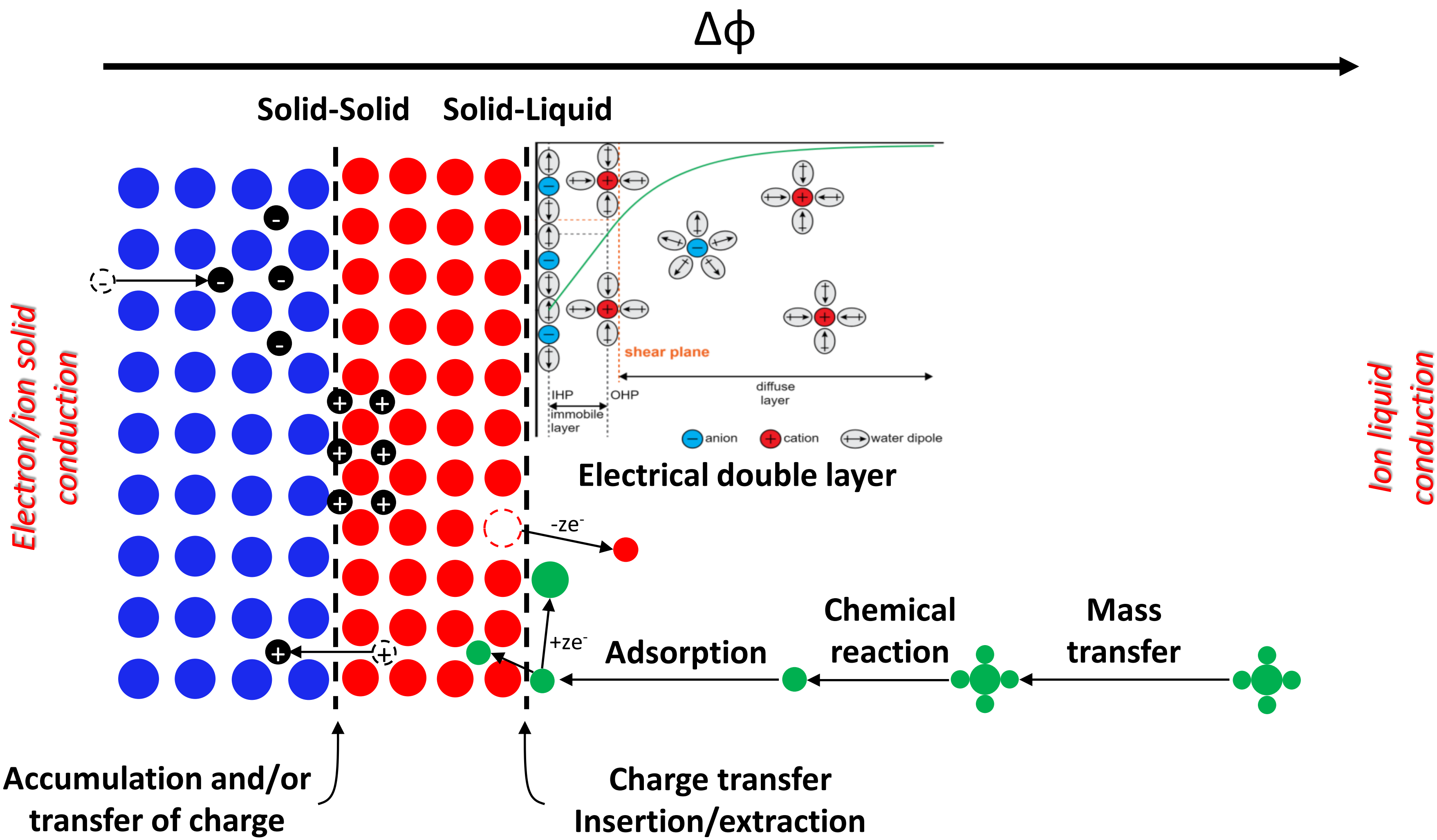
# I) Fundamentals of EIS

## 1) Electrochemical interfacial processes



# I) Fundamentals of EIS

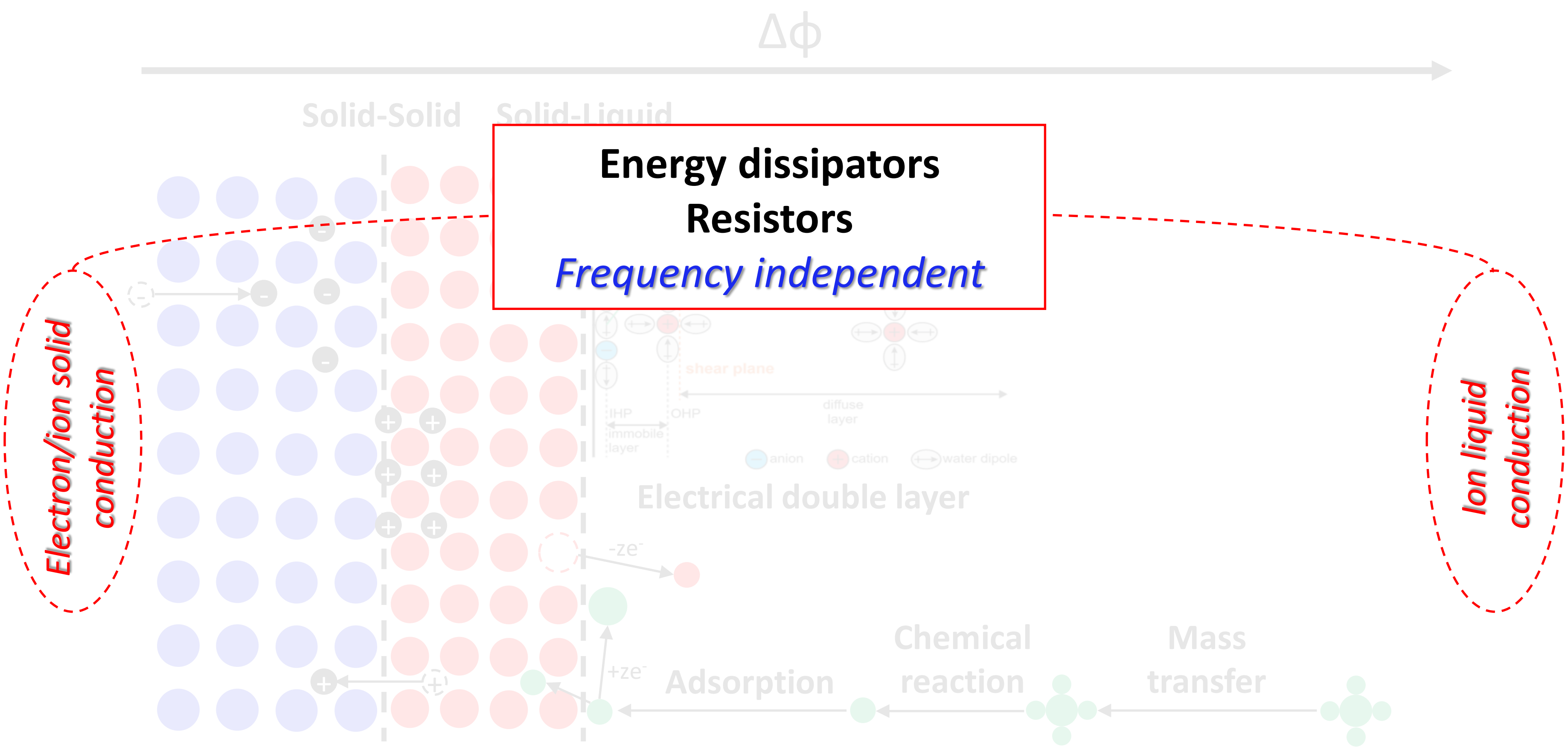
## 1) Electrochemical interfacial processes




**Process rates** ≈1 MHz — 100 kHz — 1 kHz — 10 Hz — 100 mHz

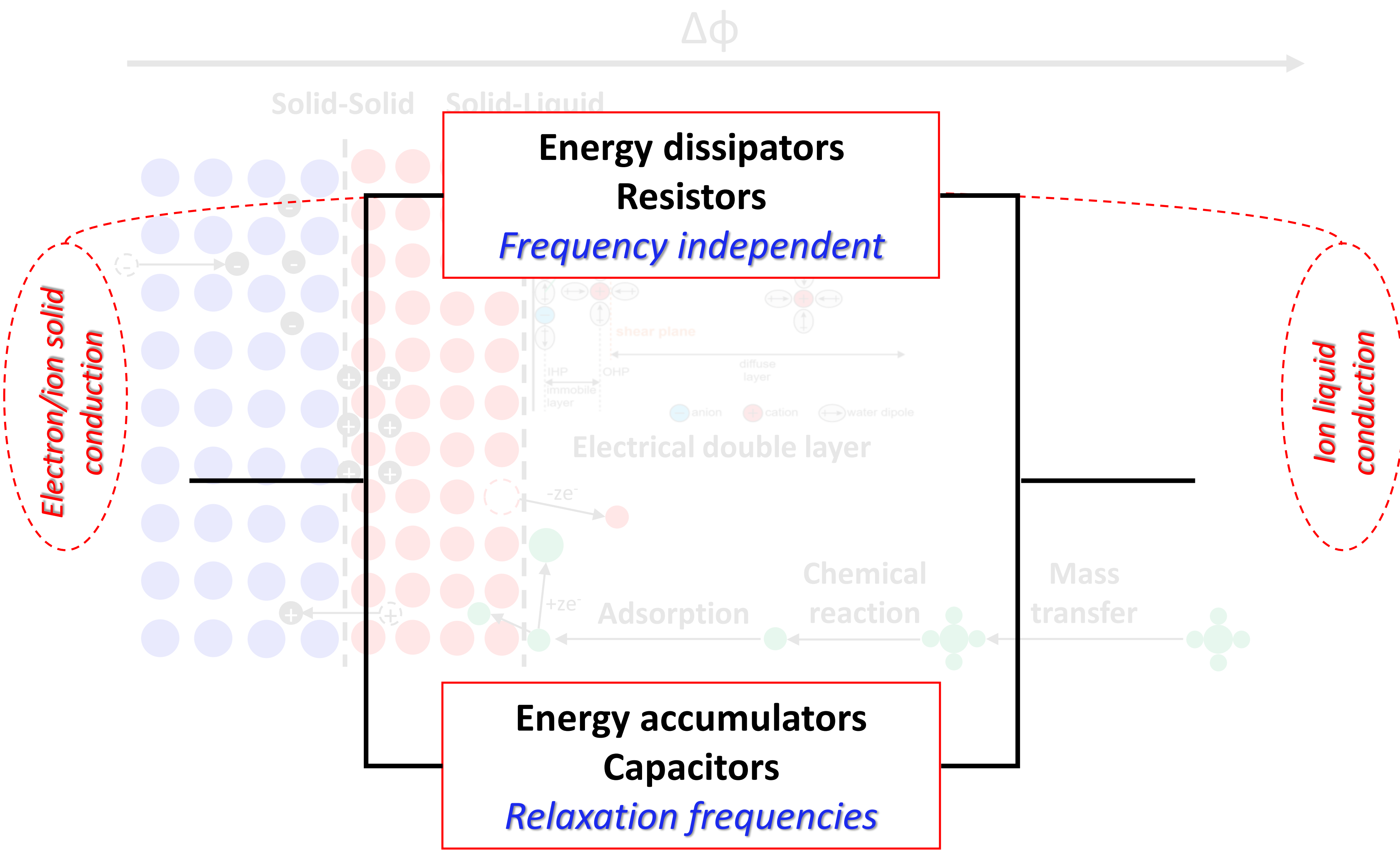
# I) Fundamentals of EIS

## 1) Electrochemical interfacial processes



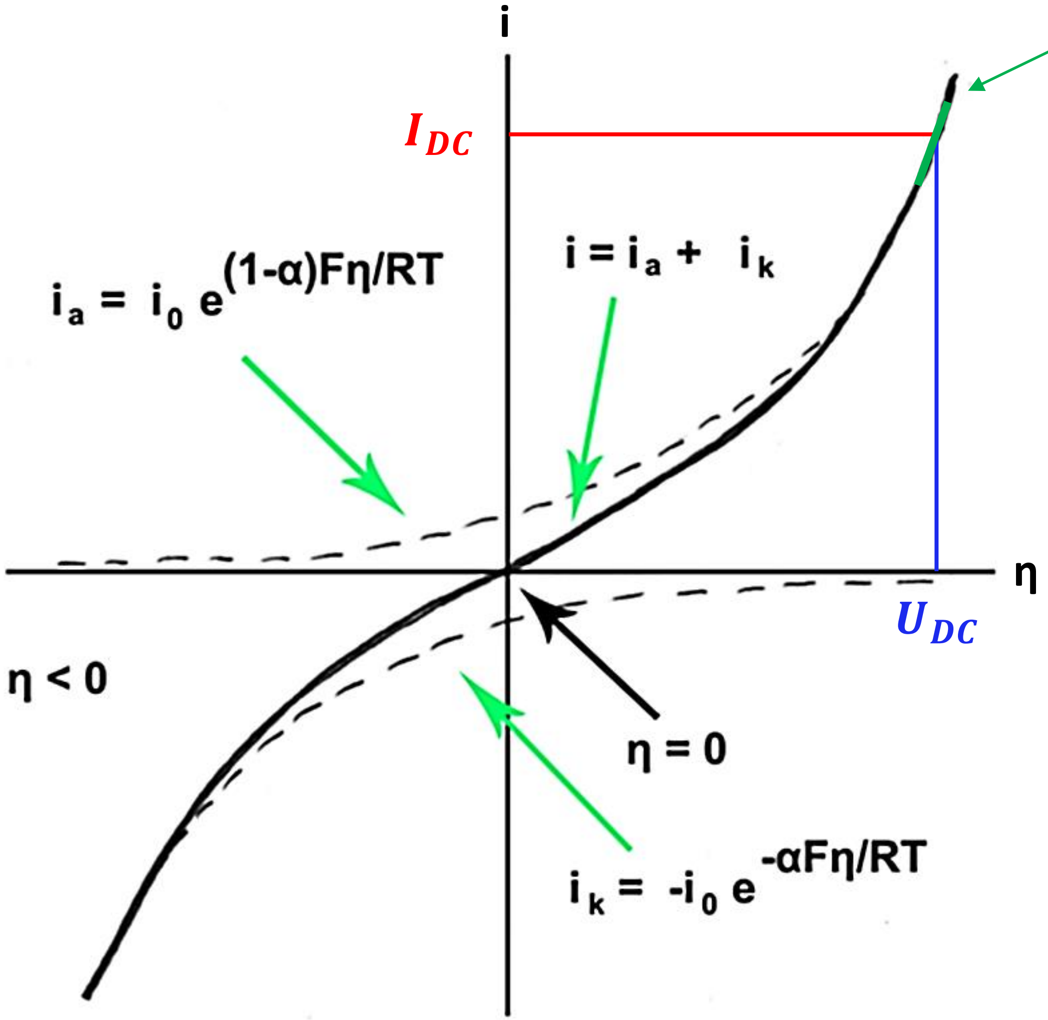
# I) Fundamentals of EIS

## 1) Electrochemical interfacial processes



# I) Fundamentals of EIS

## 2) Principle of impedance spectroscopy



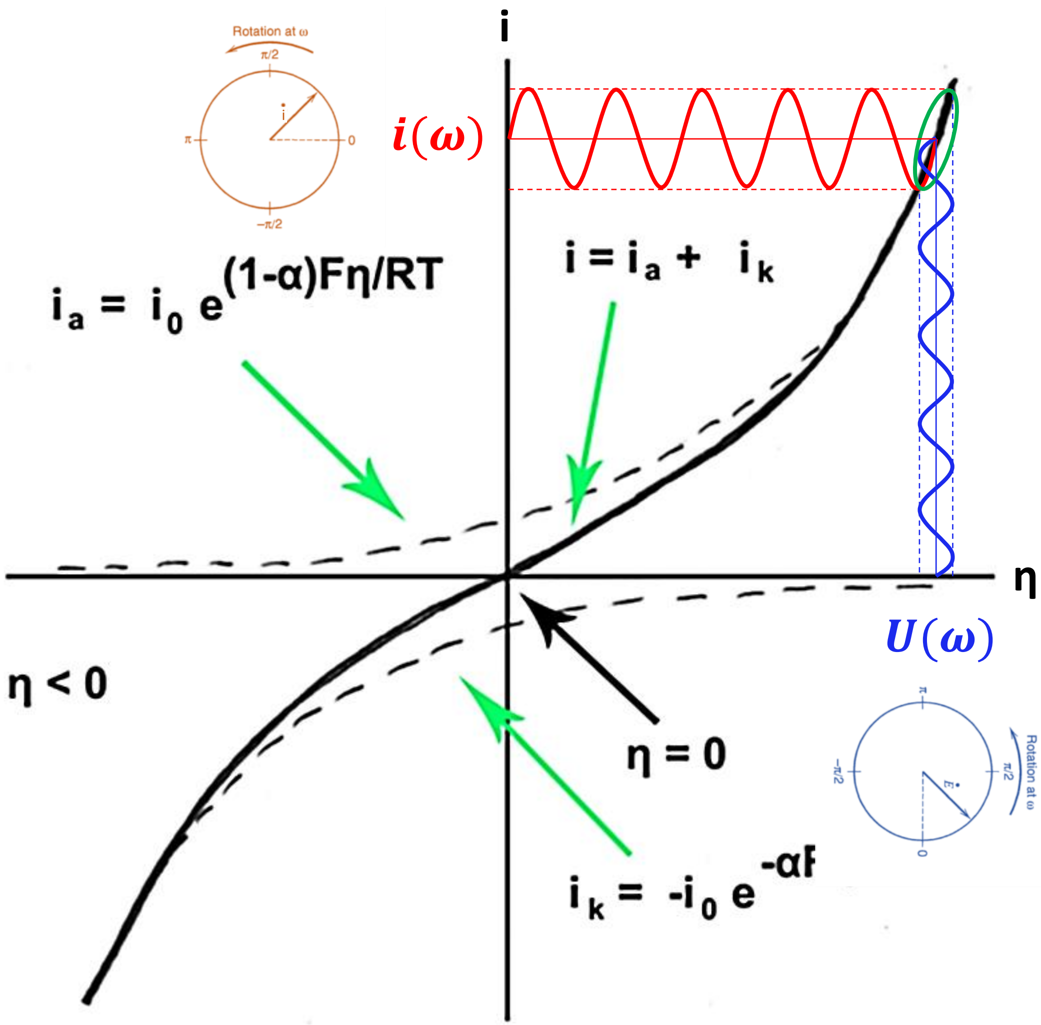

Local ASR (Area Specific Resistance)

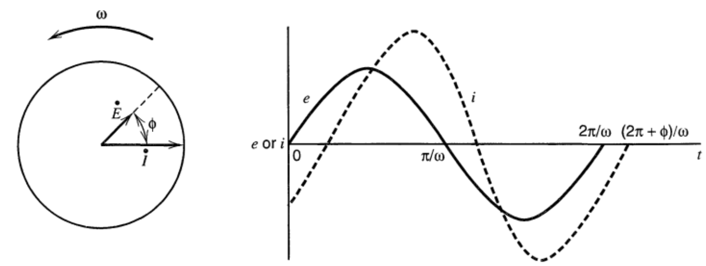
$$ASR = \lim_{\Delta U \to 0} \left( \frac{\Delta U}{\Delta i} \right)$$

Only measures dissipators !

# I) Fundamentals of EIS

## 2) Principle of impedance spectroscopy




$$i(\omega) = i_{DC} + \Delta i \sin(\omega t)$$

$$U(\omega) = U_{DC} + \Delta U \sin(\omega t + \varphi(\omega))$$

Small excitation amplitude

↪ *Harmonic free linear response*

⇩

Measure of the complex impedance:

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

$\tilde{Z}(\omega)$ from 1 mHz to 1 MHz

# I) Fundamentals of EIS

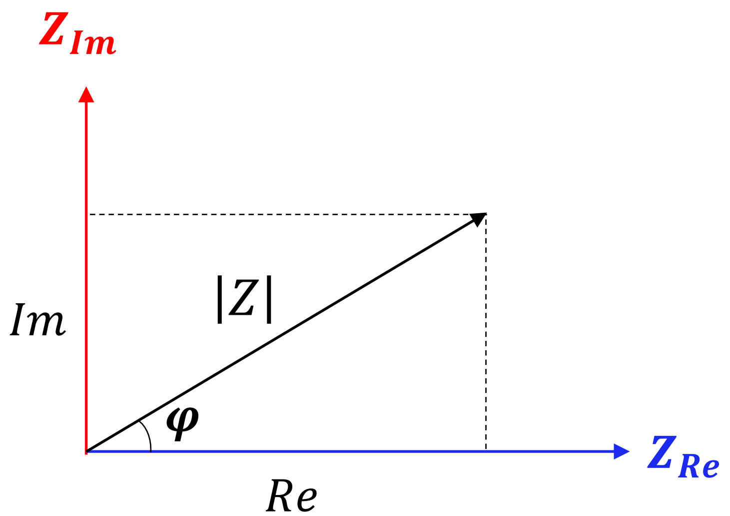
## 2) Principle of impedance spectroscopy

$$\widetilde{Z}(\omega) = \frac{U_0 \sin(\omega t + \varphi)}{i_0 \sin(wt)}$$

$$\widetilde{Z}(\omega) = \frac{U_0}{i_0} \cdot \frac{e^{j(\omega t+\varphi)} - e^{-j(\omega t+\varphi)}}{e^{j\omega t} - e^{-j\omega t}} = \frac{U_0}{i_0} \cdot e^{j\varphi}$$

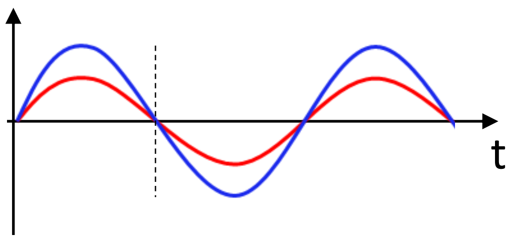
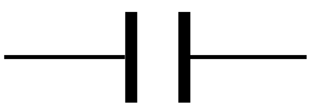
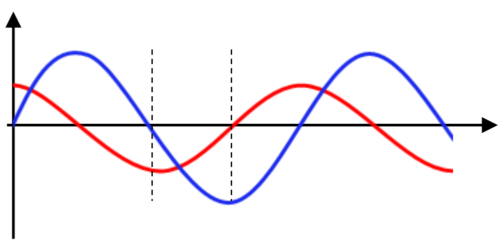
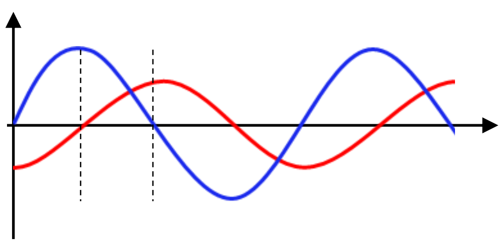
$$\widetilde{Z}(\omega) = \frac{U_0}{i_0} \cdot (\cos\varphi + j\sin\varphi) \qquad \widetilde{Z}(\omega) = Z_{Re} + jZ_{Im}$$

Vector representation:



# I) Fundamentals of EIS

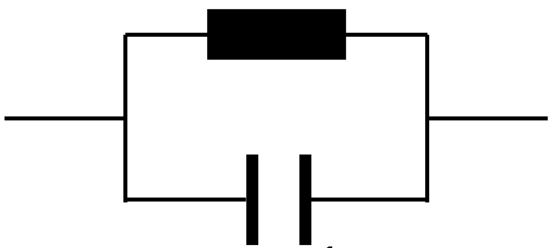
## 3) Ideal circuit elements

| **Element** | $U(\omega), i(\omega)$ | **Phase shift** $\varphi$ | $\tilde{Z}(\omega)$ |
|---|---|---|---|
| Resistor  |   | $\varphi = 0$ | $\tilde{Z}(\omega) = R$ |
| Capacitor  |  | $\varphi = -\frac{\pi}{2}$ | $\tilde{Z}(\omega) = -\frac{j}{C\omega}$ |
| Inductance  |  | $\varphi = +\frac{\pi}{2}$ | $\tilde{Z}(\omega) = jL\omega$ |

# I) Fundamentals of EIS

## 4) The RC element

$$\boldsymbol{Z = R}$$



$$\boldsymbol{Z = \frac{1}{jC\omega}}$$

$$\frac{1}{Z} = \frac{1}{R} + jC\omega = \frac{1 + jRC\omega}{R}$$

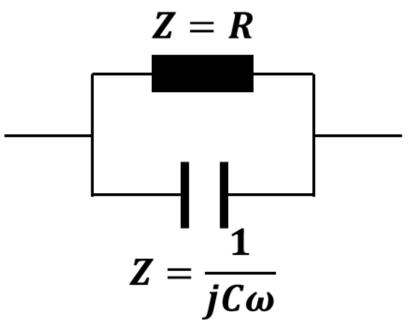
$$Z = \frac{R}{1 + jRC\omega} = \frac{R - jR^2C\omega}{1 + (RC\omega)^2}$$

$$\boxed{Z = \frac{R}{1 + (RC\omega)^2} - j\,\frac{R^2C\omega}{1 + (RC\omega)^2}}$$

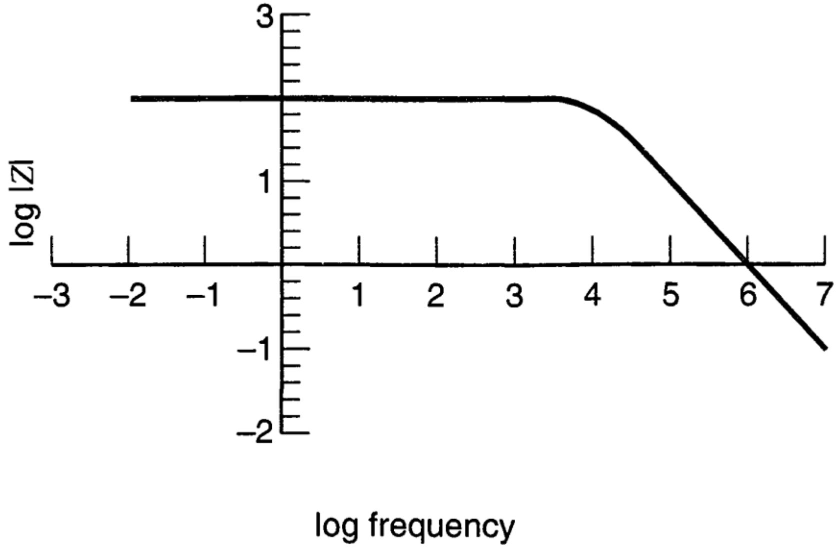
# I) Fundamentals of EIS

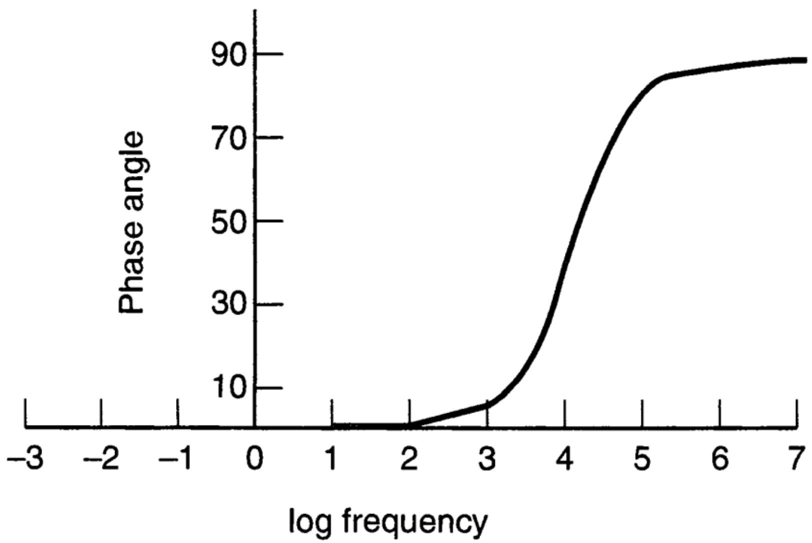
## 5) Representing EIS data

$$Z = \frac{R}{1 + (RC\omega)^2} - j\frac{R^2 C\omega}{1 + (RC\omega)^2}$$




### *Bode Plots*

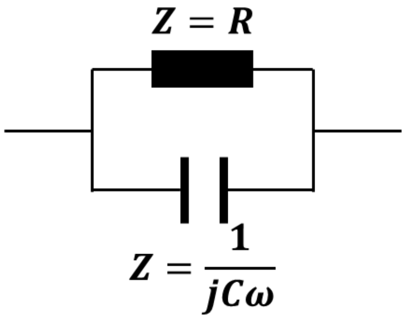


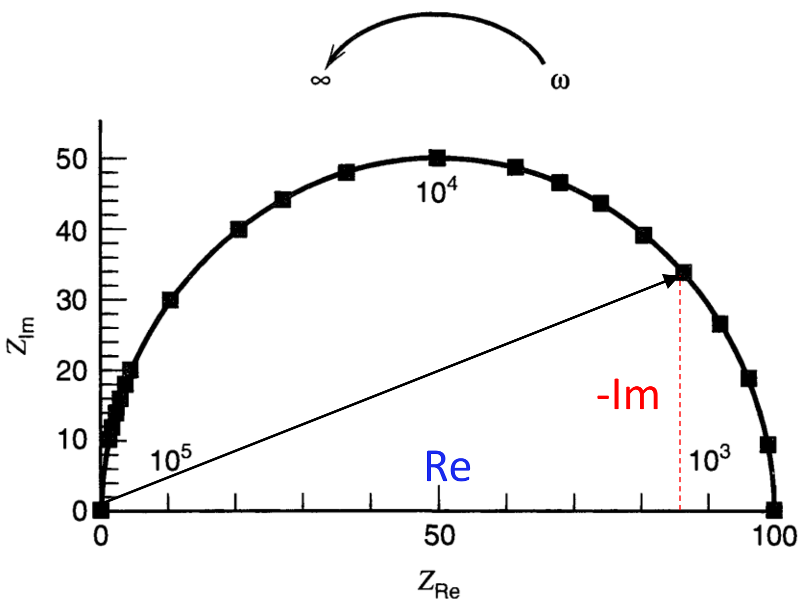
# I) Fundamentals of EIS

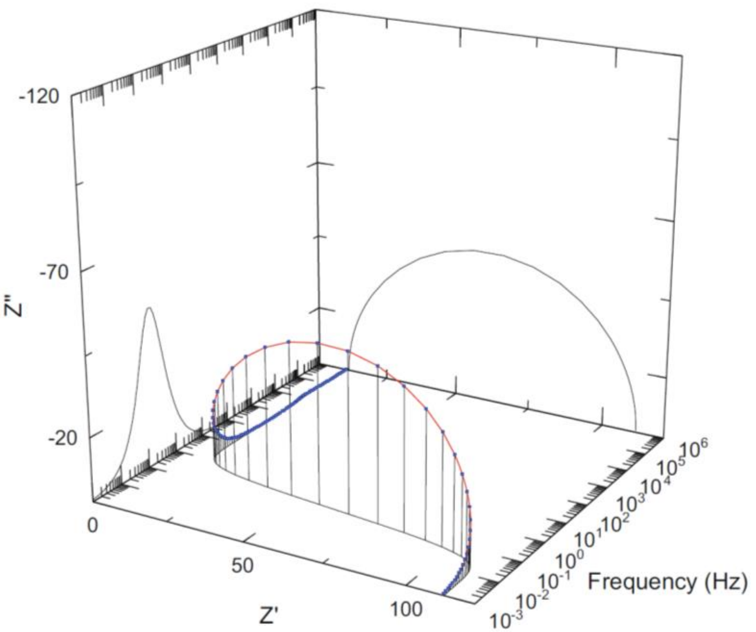
## 5) Representing EIS data

$$Z = \frac{R}{1+(RC\omega)^2} - j\frac{R^2C\omega}{1+(RC\omega)^2}$$




### *Nyquist Plots*

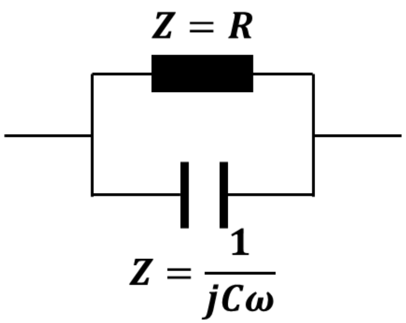


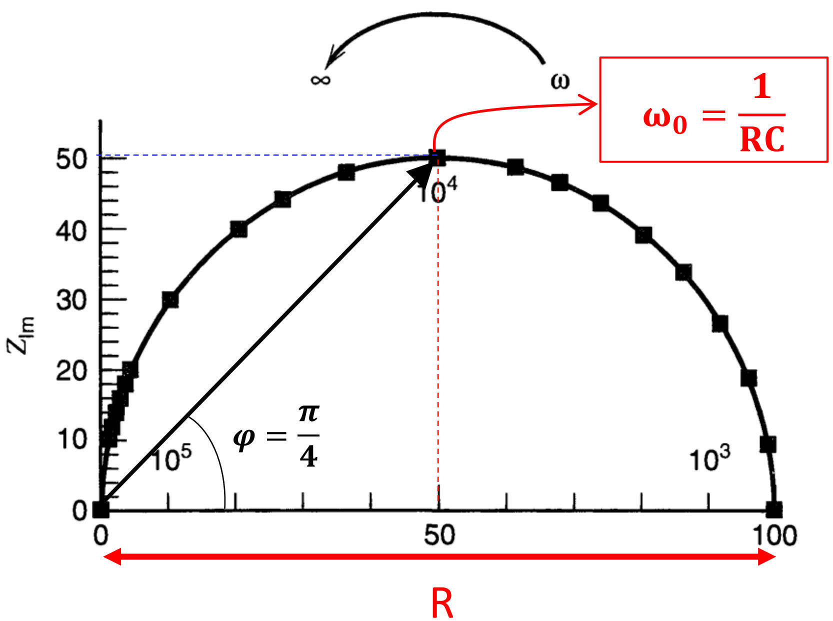
# I) Fundamentals of EIS

## 6) Treatment of a ZARC element

$$Z = \frac{R}{1 + (RC\omega)^2} - j\frac{R^2 C\omega}{1 + (RC\omega)^2}$$




*Nyquist Plots*




**Distinctive values:**

$$Z(\omega \mapsto \infty) = 0$$

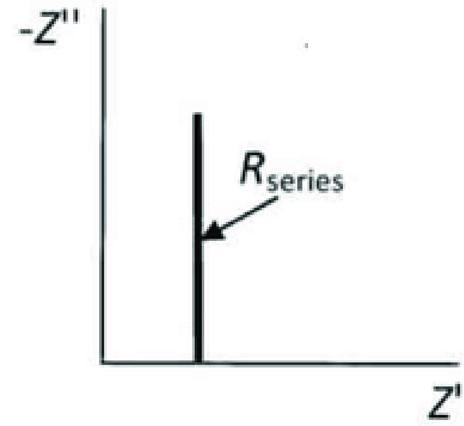
$$Z(\omega \mapsto 0) = Z_{Re} = R$$

$$Z_{Re}(\omega_0) = -Z_{Im}(\omega_0) \Longrightarrow \omega_0 = \frac{1}{RC}$$

# I) Fundamentals of EIS

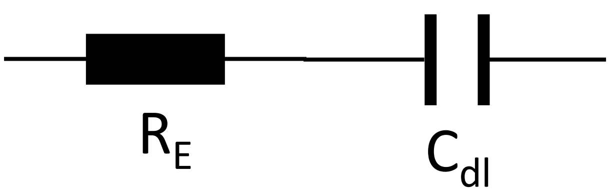
## 7) Faradaic reaction: the Randles circuit

### Ideally polarisable electrode


Electrolyte resistance $R_E$

Electrical double layer capacitance: $C_{dl}$

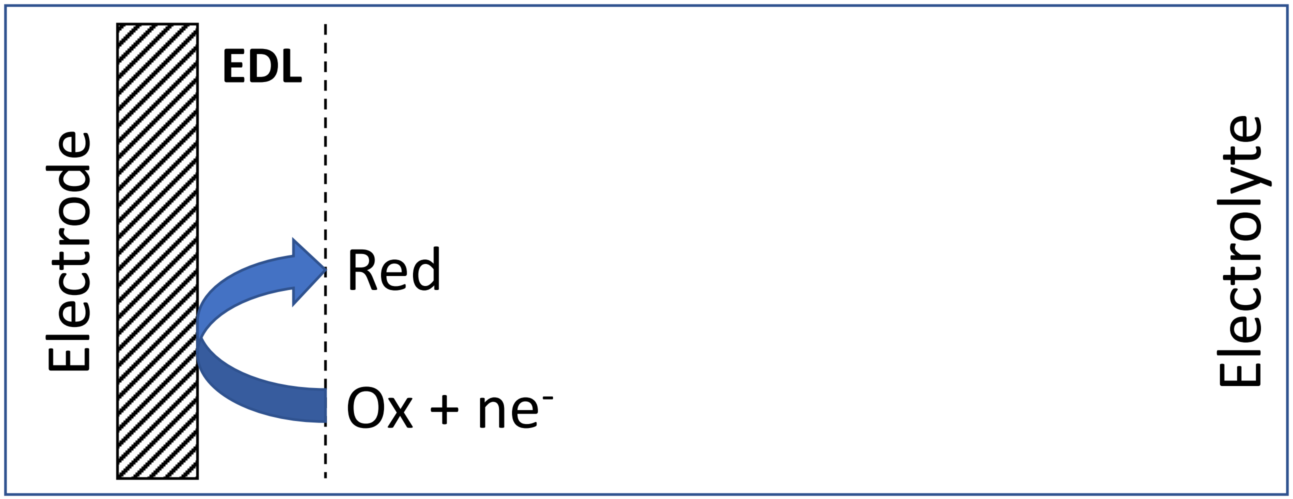



$$Z = R_E - j\frac{1}{C_{dl}\omega}$$

# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit

### Charge transfer reaction

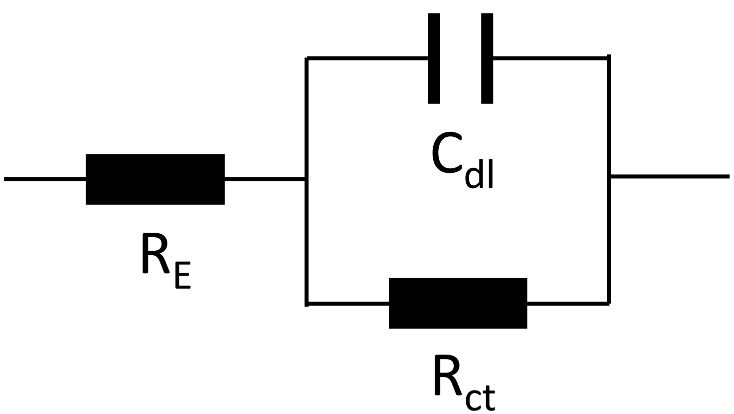



***Prerequisites:***

The system is linear

Ox and Red do not modify the electrode

High frequency ↔ no mass transfer limitation




Electrolyte resistance $R_E$

Electrical double layer capacitance: $C_{dl}$

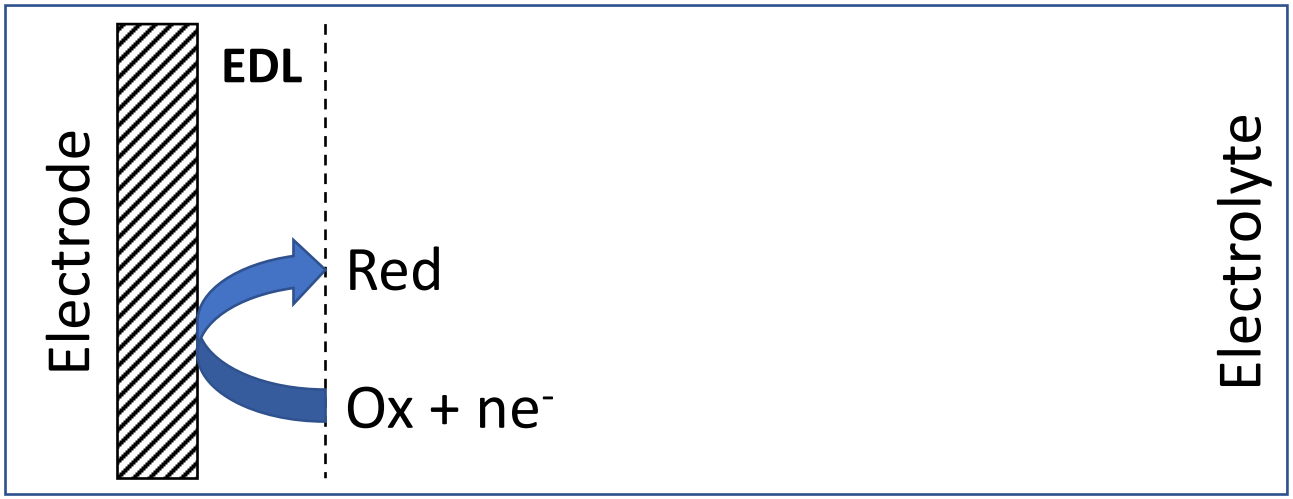
Charge transfer resistance $R_{ct}$

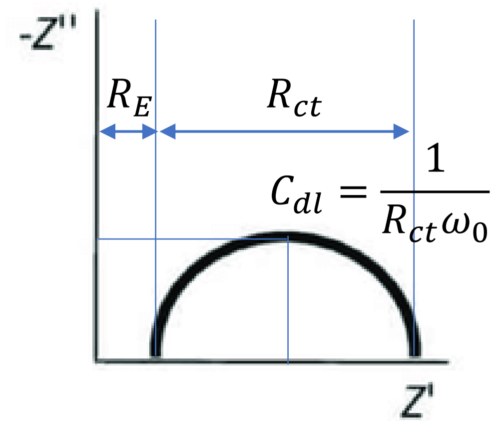
$$Z = R_E + \frac{R_{ct}}{1 + (R_{ct}C_{dl}\omega)^2} - j\frac{{R_{ct}}^2 C_{dl}\omega}{1 + (R_{ct}C_{dl}\omega)^2}$$

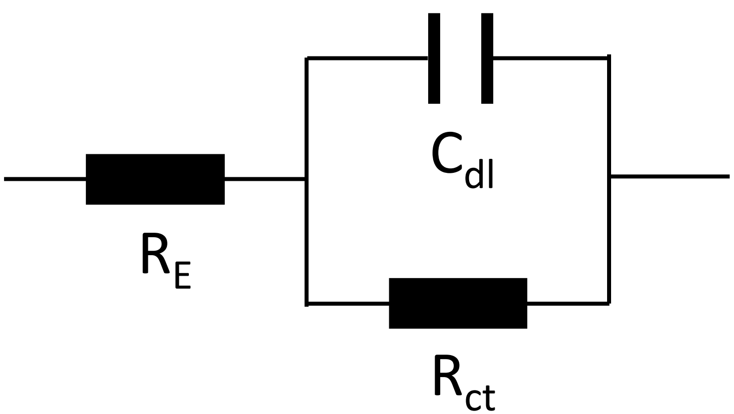
# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit

### Charge transfer reaction

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# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit

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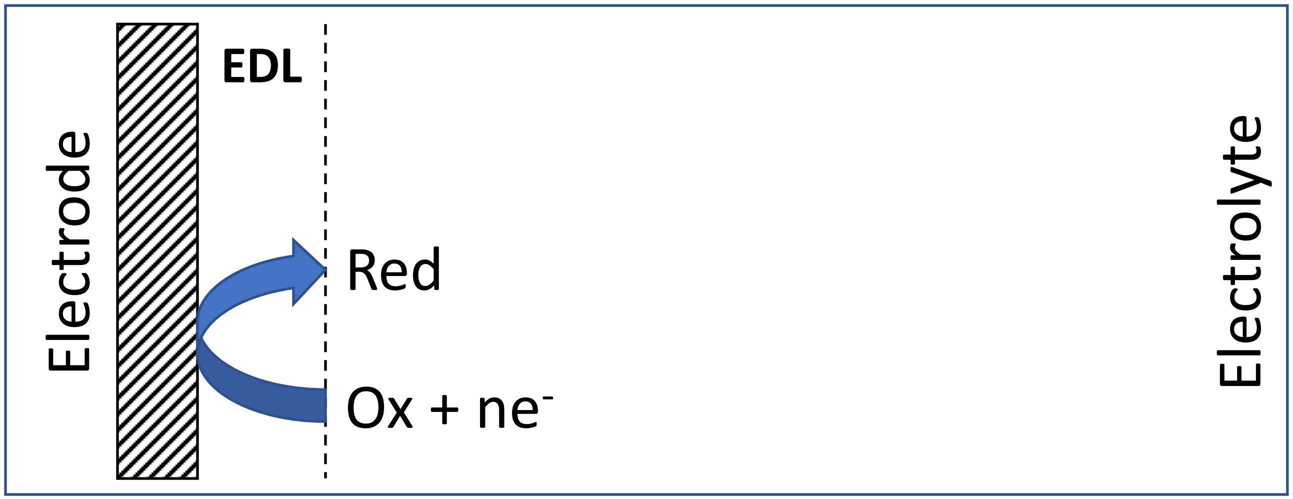
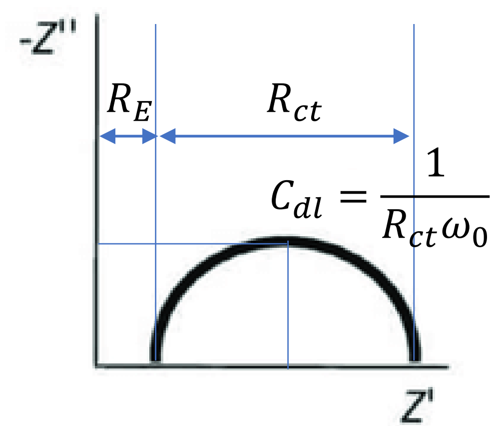
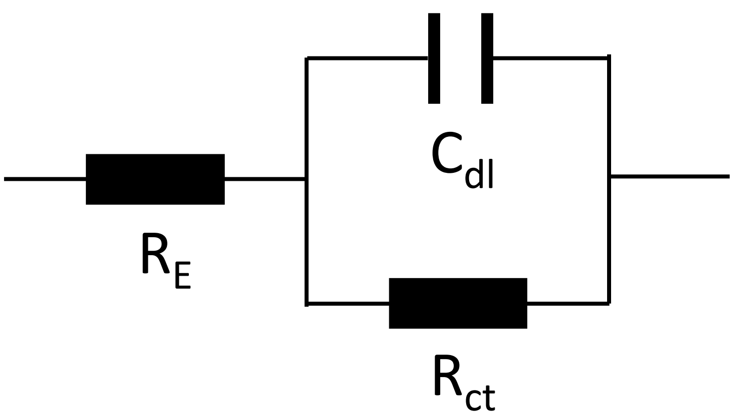



Low $\eta$: linearized Butler-Volmer $i = i_0 \cdot \frac{zF\eta}{RT}$

hence $\boxed{R_{ct} = \frac{RT}{zFi_0} \Leftrightarrow i_0 = \frac{RT}{zFR_{ct}}}$

$$i_0 = zF[Ox]\beta_{Red} \cdot exp^{\frac{-\Delta G^*_{\chi,Red}}{RT}} \cdot exp^{\frac{-\alpha zF\Delta\phi_{eq}}{RT}}$$

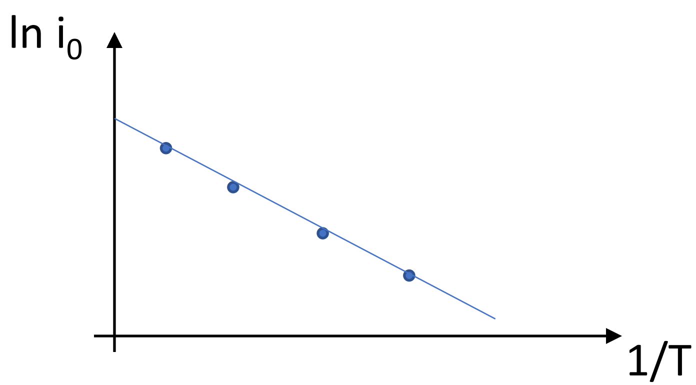
$$= zF[Red]\beta_{Ox} \cdot exp^{\frac{-\Delta G^*_{\chi,Ox}}{RT}} \cdot exp^{\frac{(1-\alpha)zF\Delta\phi_{eq}}{RT}}$$

# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit

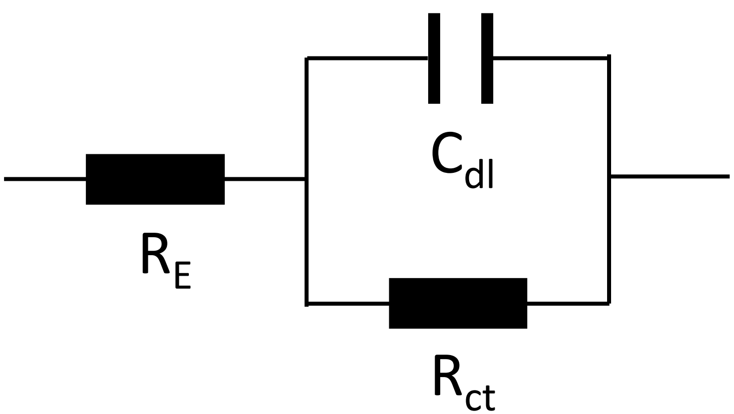
### Charge transfer reaction

Measure $R_{ct}$ at different temperatures: Arrhenius plot




$$\ln i_0 = -\frac{\Delta G^*_{\chi,\,Red} + \alpha z F \Delta\phi_{eq}}{RT} + \ln(zF[Ox]\beta_{Red})$$

$$\ln i_0 = -\frac{\Delta G^*_{\chi,\,Ox} + (1-\alpha) z F \Delta\phi_{eq}}{RT} + \ln(zF[Red]\beta_{Ox})$$

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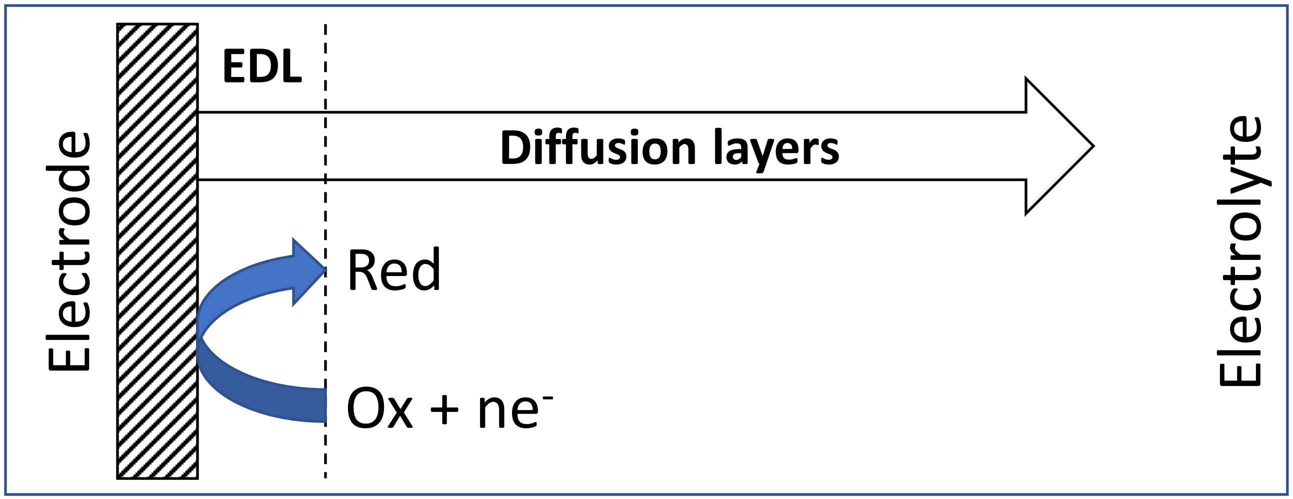
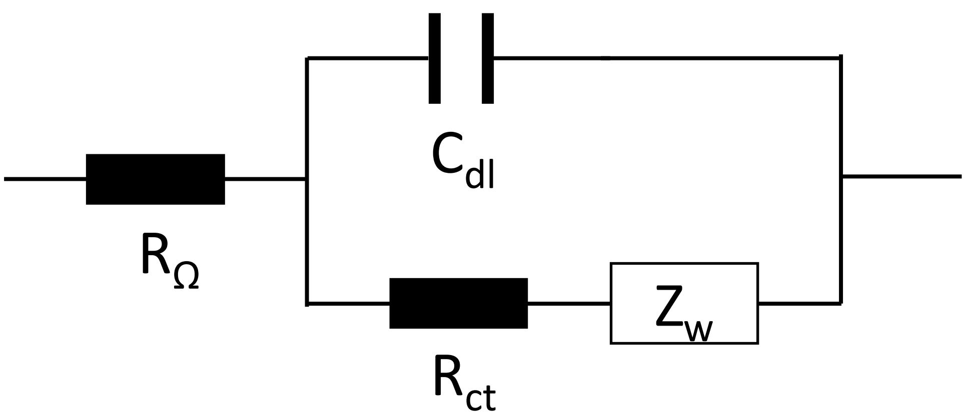
# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit

$[Ox]^{el}$ and $[Red]^{el}$ are time dependent




Ohmic resistance of the circuit $R_{\Omega}$

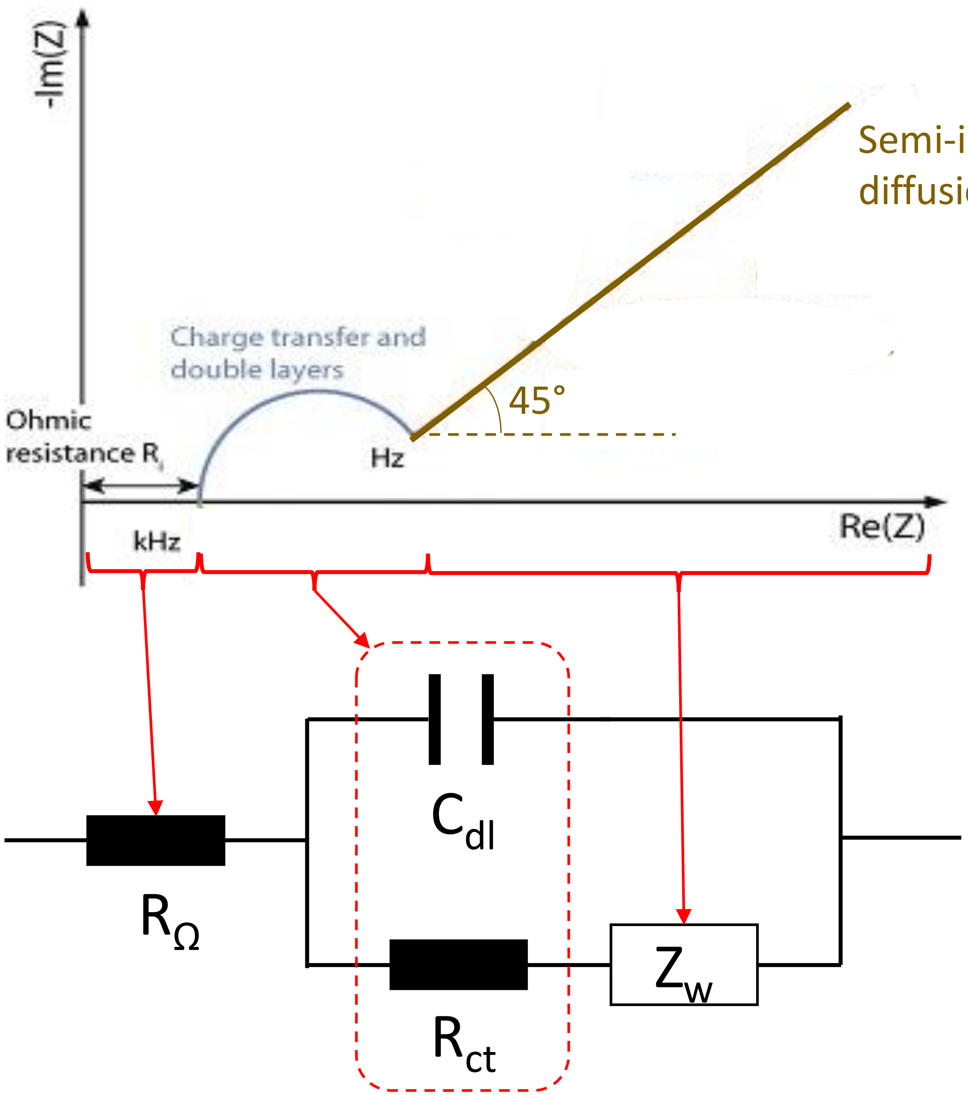
Electrical double layer capacitance: $C_{dl}$

Charge transfer resistance $R_{ct}$

Warburg Impedance $Z_w$ for diffusion

# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit




Ohmic resistance of the circuit $R_\Omega$

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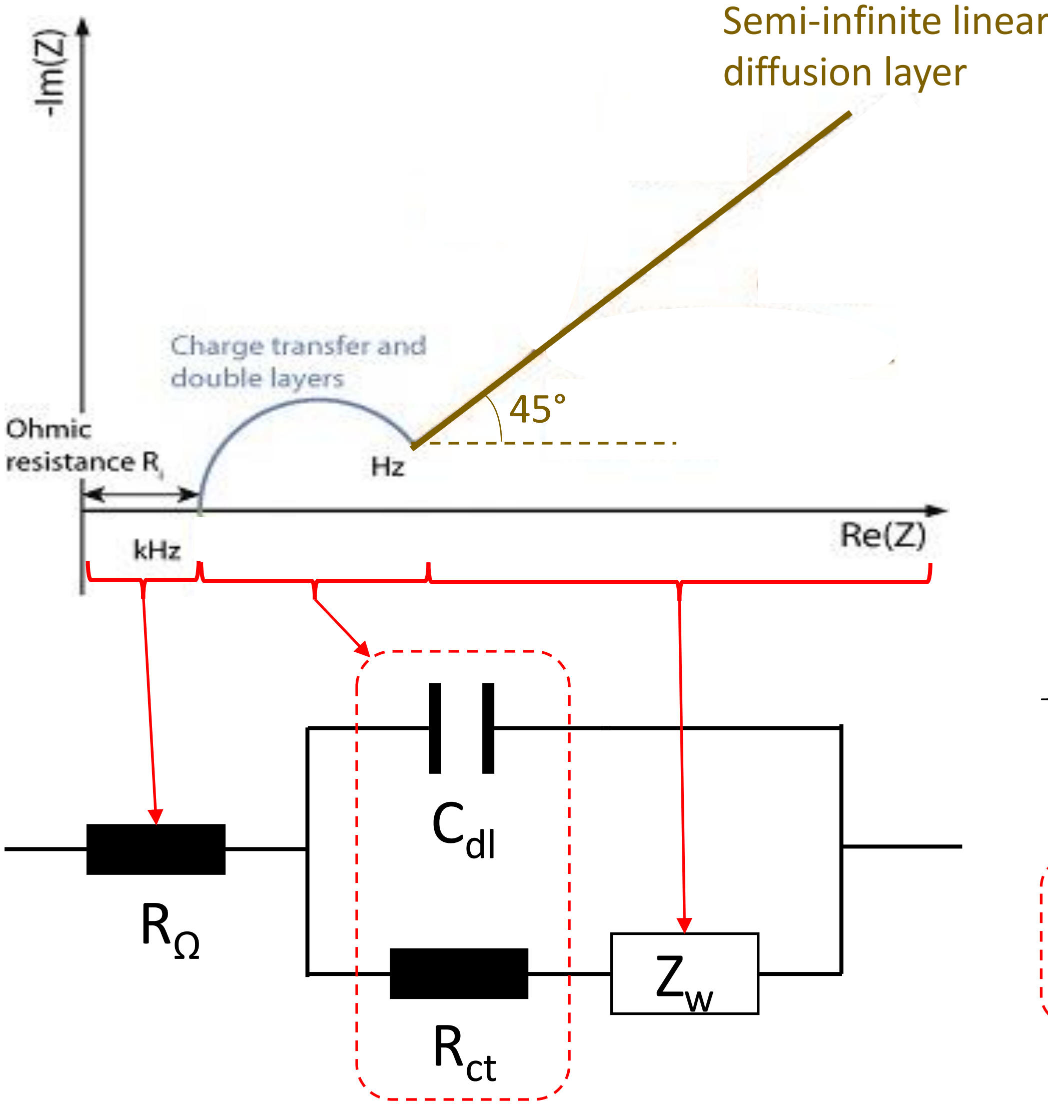
# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit




Butler-Volmer with mass limitation:

$$\tilde{i} = i_0\left(\frac{\widetilde{C_R}}{{C_R}^0}\exp^{\frac{(1-\alpha)zF\tilde{\eta}}{RT}} - \frac{\widetilde{C_O}}{{C_O}^0}\exp^{\frac{-\alpha zF\tilde{\eta}}{RT}}\right)$$

Fick's 2$^{nd}$ law of diffusion:

$$\frac{\partial C_i}{\partial t} = D_i\frac{\partial^2 C_i}{\partial x^2}$$

with $C_i(t) = {C_i}^{DC} + {C_i}^{AC}\exp^{j(\omega t+\varphi_i)}$

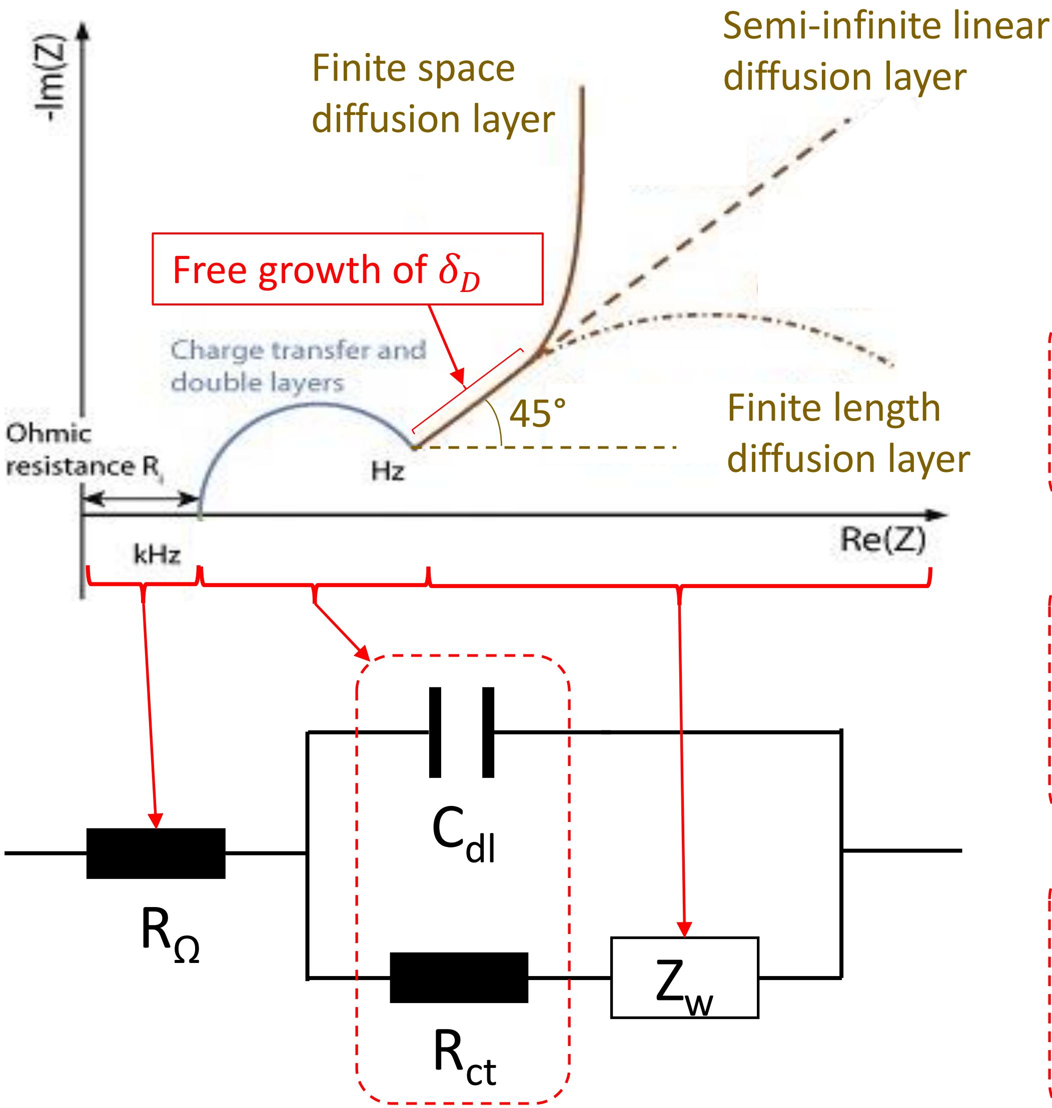
Boundary conditions:

$$\left\{\begin{array}{l} x \mapsto 0 \implies \tilde{i} = zFD_i\frac{d\widetilde{C_i}}{dx} \\ x \mapsto \infty \implies C_i = {C_i}^0 \\ D_R\frac{dC_R}{dx} = -D_O\frac{dC_O}{dx} \end{array}\right\} \quad \widetilde{C_i} = \frac{\tilde{i}}{zF\sqrt{j\omega D_i}}\exp^{-\sqrt{\frac{j\omega}{D_i}}x}$$

$$\boxed{{Z_W}^\infty = \frac{\tilde{E}}{\tilde{i}} = \frac{1-j}{\sqrt{\omega}}\cdot\frac{RT}{\sqrt{2}(zF)^2}\left\{\frac{1}{{C_O}^0\sqrt{D_O}} + \frac{1}{{C_R}^0\sqrt{D_R}}\right\}}$$

# I) Fundamentals of EIS

## 7) Faradaic reaction: the Randles circuit




Initial boundary conditions:

$$\begin{bmatrix} x \mapsto 0 \implies \tilde{\imath} = zFD_i \dfrac{d\widetilde{C}_i}{dx} \\ D_R \dfrac{dC_R}{dx} = -D_O \dfrac{dC_O}{dx} \end{bmatrix}$$

Semi-infinite $\delta_D$: $x \mapsto \infty \implies C_i = {C_i}^0$

$$Z_W{}^{\infty} = \frac{1-j}{\sqrt{\omega}} \cdot \frac{RT}{\sqrt{2}(zF)^2} \left\{ \frac{1}{C_O{}^0\sqrt{D_O}} + \frac{1}{C_R{}^0\sqrt{D_R}} \right\}$$

Finite space $\delta_D$: $x = l \implies \frac{dC_i}{dx} = 0$

$$Z_W{}^{FS} = \frac{1-j}{\sqrt{\omega}} \cdot \frac{RT}{\sqrt{2}(zF)^2} \left\{ \frac{coth\sqrt{\frac{j\omega l}{D_O}}}{C_O{}^0\sqrt{D_O}} + \frac{coth\sqrt{\frac{j\omega l}{D_R}}}{C_R{}^0\sqrt{D_R}} \right\}$$

Finite length $\delta_D$: $x = l \implies \delta_D = \delta_D{}^{max}$

$$Z_W{}^{FS} = \frac{1-j}{\sqrt{\omega}} \cdot \frac{RT}{\sqrt{2}(zF)^2} \left\{ \frac{tanh\sqrt{\frac{j\omega l}{D_O}}}{C_O{}^0\sqrt{D_O}} + \frac{tanh\sqrt{\frac{j\omega l}{D_R}}}{C_R{}^0\sqrt{D_R}} \right\}$$

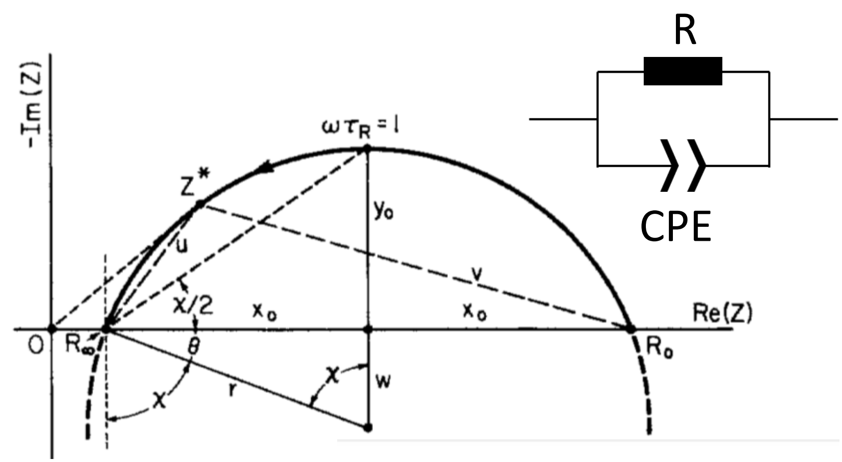
# I) Fundamentals of EIS

## 8) Constant phase element (CPE)

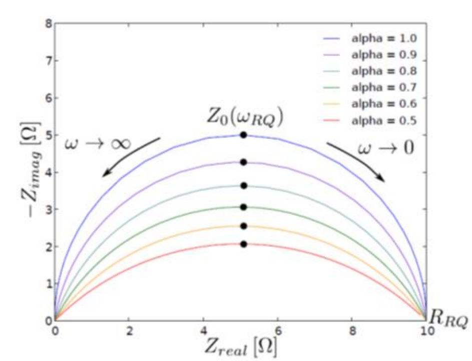
The Electrical Double Layer is not an ideal capacitor

There are distributed elements at the electrode/electrolyte interphase

$$\left.\begin{aligned} Z_Q &= \frac{1}{Q(j\omega)^{\alpha}} \quad with \quad 0 \leq \alpha \leq 1 \\[2em] Z_{ZARC} &= \frac{R}{(1+RQ(j\omega)^{\alpha})} \end{aligned}\right\} \quad \alpha = \frac{2\chi}{\Pi}$$



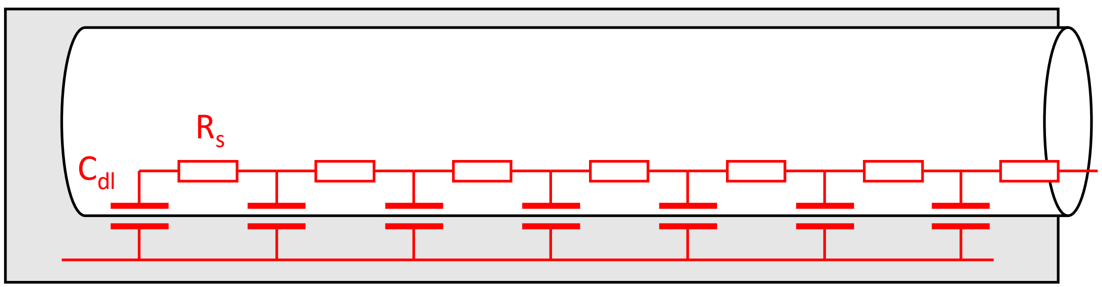

Dispersion of the relaxation frequency ↗ as α ↘



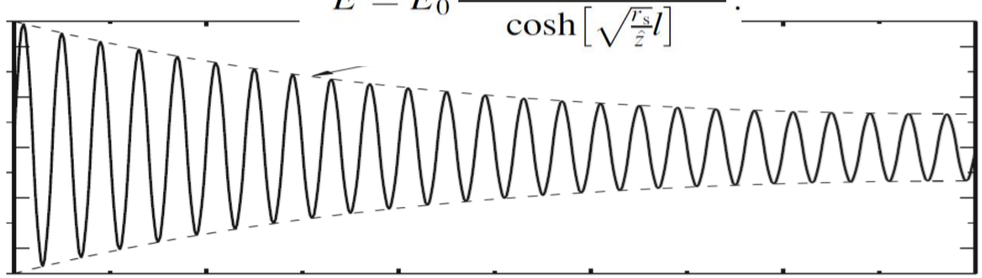
# I) Fundamentals of EIS

## 8) Transmission lines:
## De Levie model for porous media

A conductive pore in an ionic conductor




$$\widetilde{E} = \widetilde{E}_0 \frac{\cosh\left[\sqrt{\frac{r_s}{\hat{z}}}(l-x)\right]}{\cosh\left[\sqrt{\frac{r_s}{\hat{z}}}l\right]}.$$



$$\hat{Z}_{\text{pore}} = \frac{R_{\Omega,p}}{\Lambda^{1/2}} \coth\left(\Lambda^{1/2}\right)$$

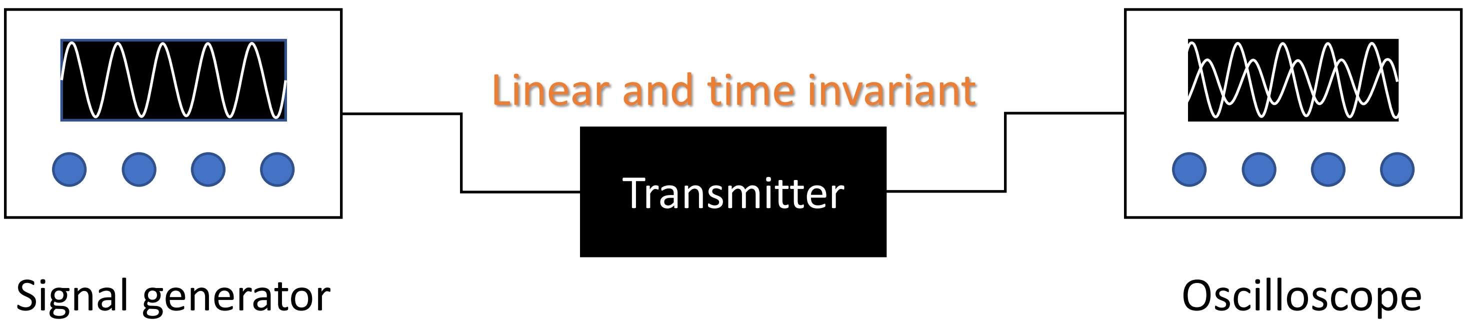
$$\Lambda = \frac{r_S l^2}{\hat{z}} = \frac{2\rho_s l^2}{r\hat{Z}_{\text{el}}} = \frac{2\rho_s l^2 j\omega C_{\text{dl}}}{r}$$

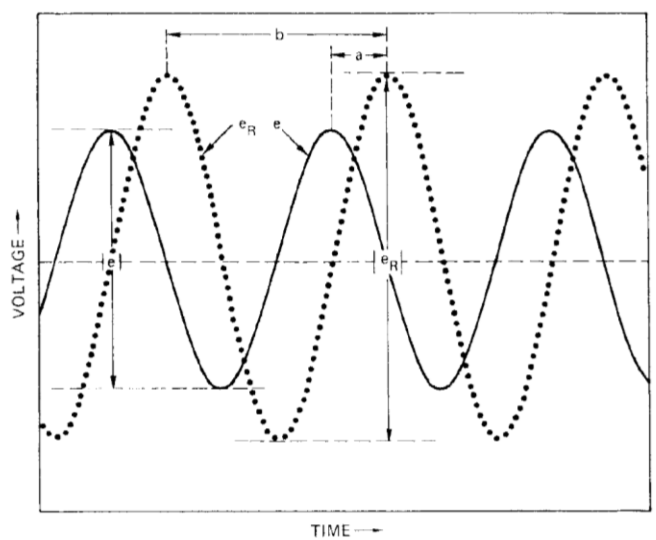
# I) Fundamentals of EIS

| element | impedance | process |
|---|---|---|
| (R) serial resistor | $R$ | contact and electrolyte resistance |
| (RQ) resistor and a constant phase element in parallel | $\frac{R}{1+RQ_0(j\omega)^n}$ | double layer capacitance and charge-transfer reactions in parallel |
| (G) Gerischer element | $\frac{R_{\text{chem}}}{\sqrt{1+j\omega t_{\text{chem}}}}$ | combination of electrochemical charge-transfer and diffusion |
| (W) Warburg element | $R_{\text{W}}\frac{\tanh[(j\omega T)^{\alpha}]}{(j\omega T)^{\alpha}}$ | diffusion processes |
| (TLM) transition line model | $\frac{R_{\text{el}}R_{\text{ion,L}}}{R_{\text{el}}+R_{\text{ion,L}}}\left(L+\frac{2\lambda}{\sinh(L/\lambda)}\right)+\lambda_{TLM}\frac{R_{\text{el}}^2+R_{\text{ion,L}}^2}{R_{\text{el}}+R_{\text{ion,L}}}\coth\left(\frac{L}{\lambda_{\text{TLM}}}\right)$ | porous electrode electrochemistry |

# II) Practical aspects, analyses, and applications

## 1) Impedance measurements




Measure f, $i_{DC}$, $E_{DC}$, $\Delta i$, and $\Delta E$

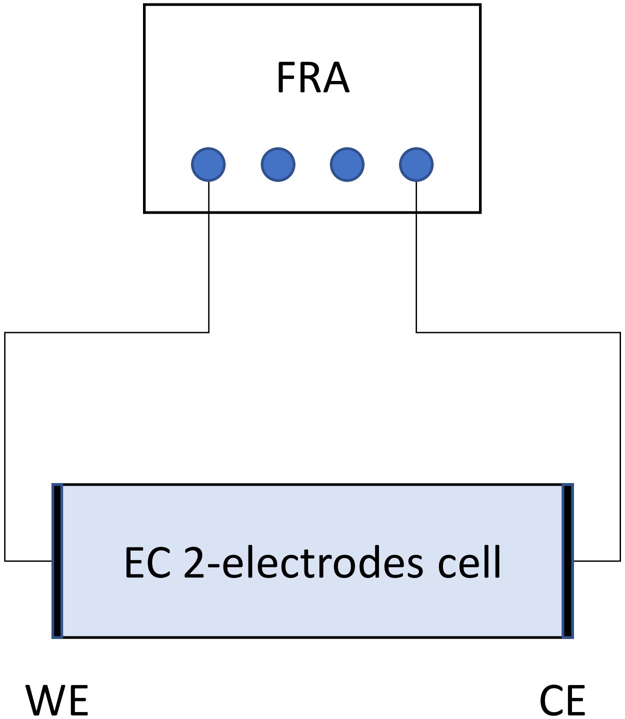
Visual control of harmonics

To ensure the system linearity, we typically target $\Delta E \approx 10$ mV

# II) Practical aspects, analyses, and applications

## 1) Impedance measurements

Potentiostat/galvanostat
+ Frequency Response Analyzer

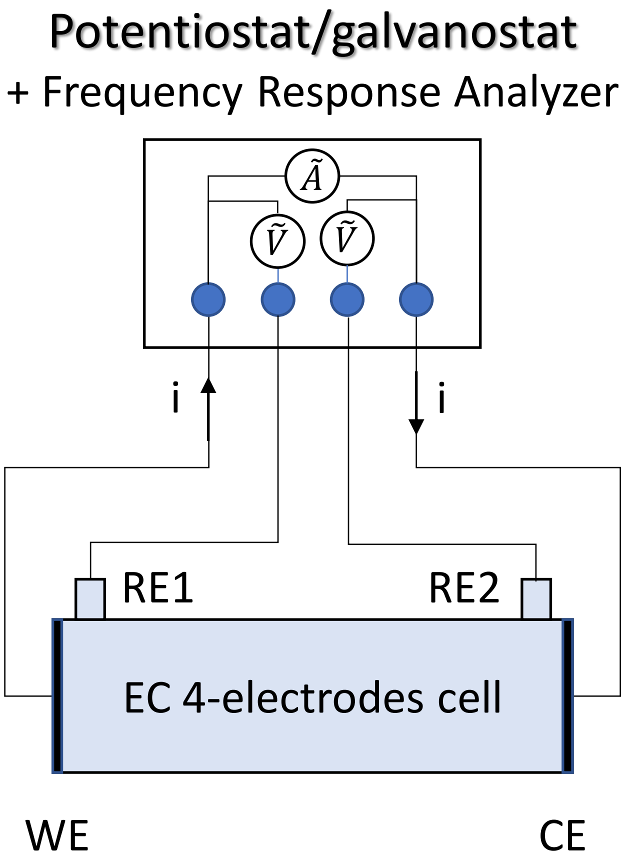



Possible to measure a 2-electrodes EC-cell

Complex equivalent circuit
- difficult to interpret
- deconvolute processes
- parametric study necessary

# II) Practical aspects, analyses, and applications

## 1) Impedance measurements



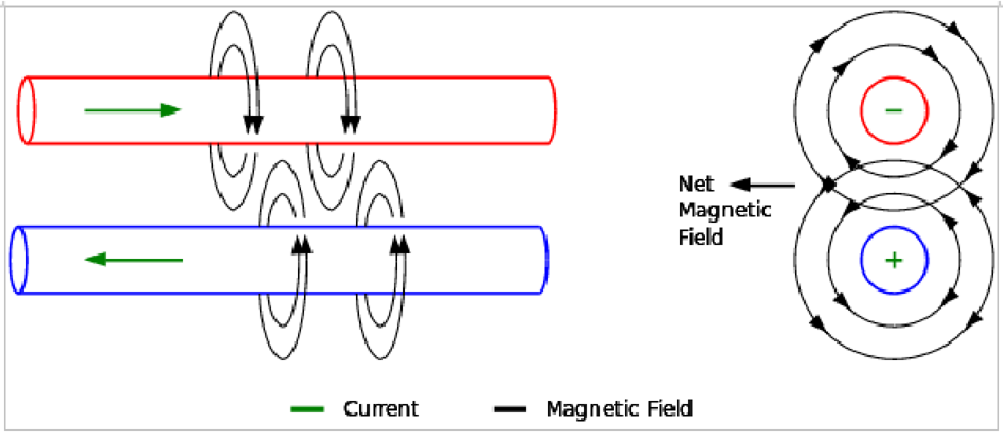

4-electrodes EC-cell easier to interpret

Separation of cathodic and anodic elements

# II) Practical aspects, analyses, and applications

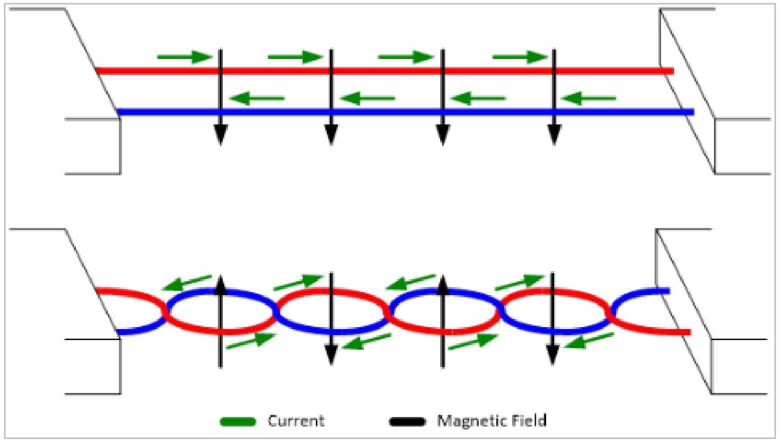
## 1) Impedance measurements

### Suppressing the wire inductance



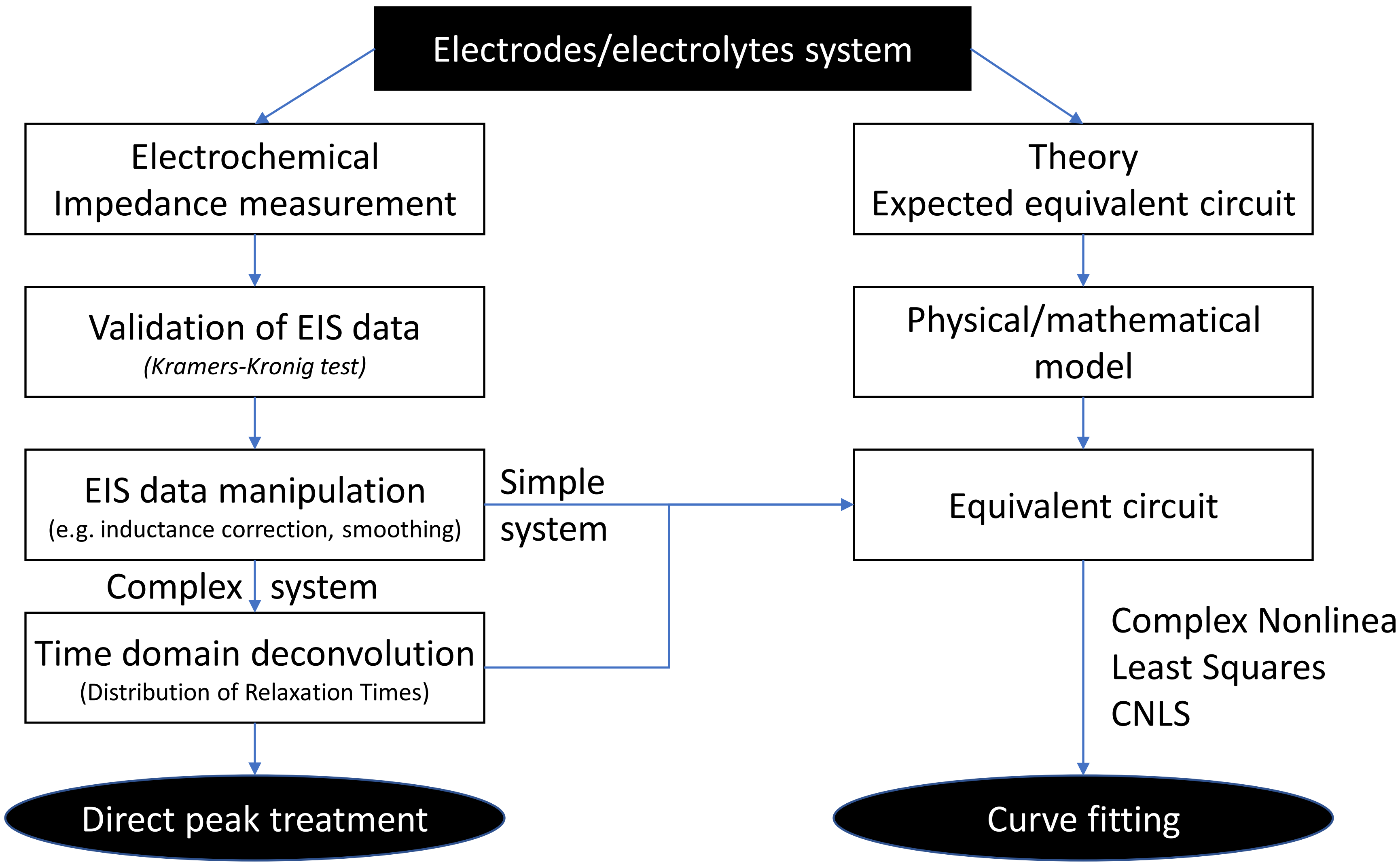

Wire inductance results from opposite currents flowing through parallel wires

Compensation of inductive currents by uniform twisting of the wires



# II) Practical aspects, analyses, and applications

## 2) Data treatment



# II) Practical aspects, analyses, and applications

## 2) Data treatment

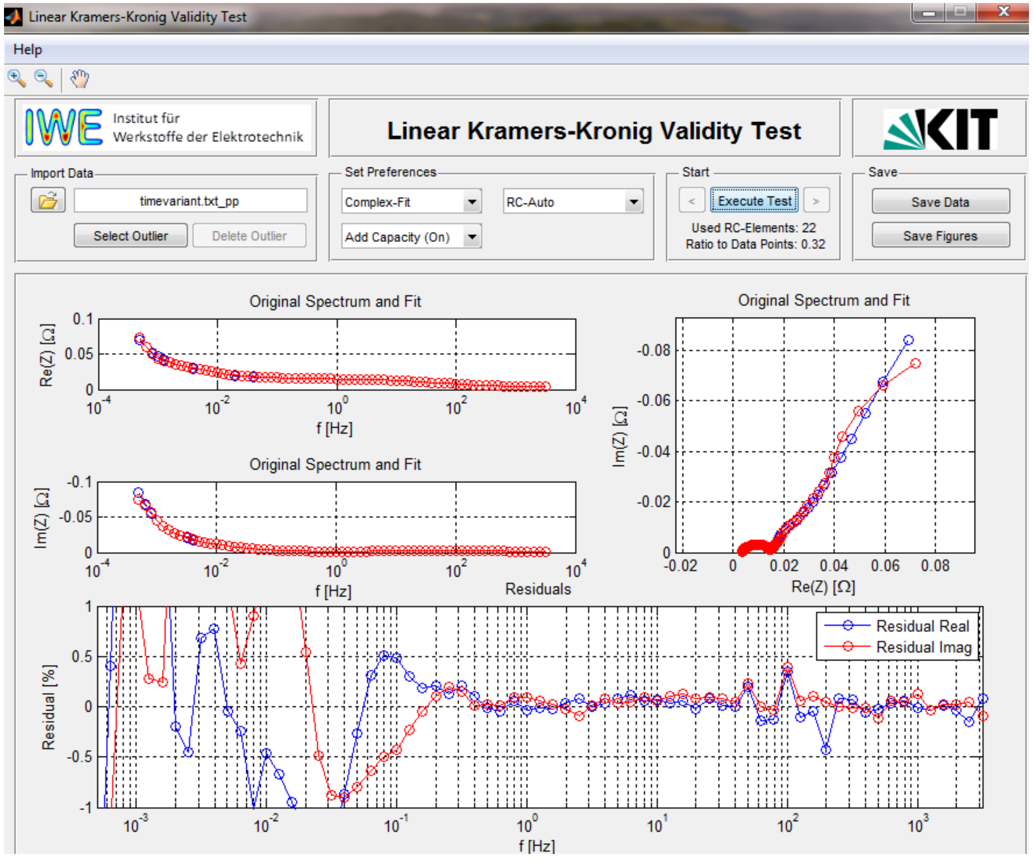
### Kramers-Kronig Transform: Linearity test

$$Z'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \, Z''(\omega^*)}{\omega^2 - (\omega^*)^2} d\omega^*$$

$$Z''(\omega) = \frac{-2}{\pi} \int_0^\infty \frac{\omega \, Z'(\omega^*)}{\omega^2 - (\omega^*)^2} d\omega^*$$

$$\Delta_{Re} = \frac{Z'(\omega) - \hat{Z}'(\omega)}{|Z(\omega)|}$$

$$\Delta_{Im} = \frac{Z''(\omega) - \hat{Z}''(\omega)}{|Z(\omega)|}$$




https://www.iam.kit.edu/et/Lin-KK.php

# II) Practical aspects, analyses, and applications

## 2) Data treatment

### Smoothing

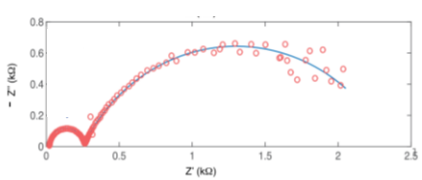
Several possibilities:

Polynomial

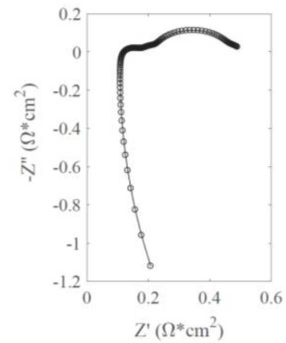
Spline

Fourier

Gauss



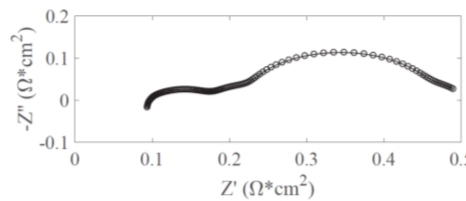

### Inductance correction




$$L = \frac{Z''(f_{\max})}{(2\pi f_{\max})}$$

$$Z_L(\omega) = 2\pi f L = \omega L$$

$$Z''_{corrected}(\omega) = Z''_{original}(\omega) - Z_L(\omega)$$




### Extrapolation

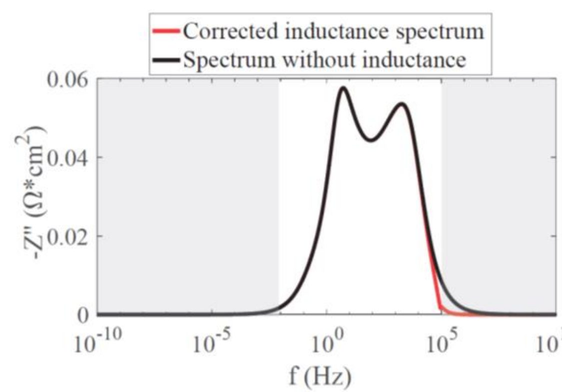
Extrapolation to $\omega \longmapsto 0$ and $\omega \longmapsto \infty$ :

Fit the first and last 5-10 points to ZARC elements

$$Z_{ZARC}(\omega) = \frac{1}{\left(\frac{1}{R} + Q(j\omega)^{\alpha}\right)} = \frac{R}{\left(1 + RQ\omega^{\alpha} e^{j\frac{\pi}{2}\alpha}\right)} = \frac{R}{1 + RQ\omega^{\alpha}\left(\cos\frac{\pi}{2}\alpha + j\sin\frac{\pi}{2}\alpha\right)}$$

$$Z'_{ZARC}(\omega) = \frac{R\left(1 + RQ\omega^{\alpha}\cos\left(\frac{\pi}{2}\alpha\right)\right)}{1 + 2RQ\omega^{\alpha}\cos\left(\frac{\pi}{2}\alpha\right) + R^2Q^2\omega^{2\alpha}}$$

$$Z''_{ZARC}(\omega) = -\frac{R^2Q\omega^{\alpha}\sin\left(\frac{\pi}{2}\alpha\right)}{1 + 2RQ\omega^{\alpha}\cos\left(\frac{\pi}{2}\alpha\right) + R^2Q^2\omega^{2\alpha}}$$



# II) Practical aspects, analyses, and applications

## 2) Data treatment

### Distribution of Relaxation Times (DRT)

$$Z(\omega) = \sum_{i=1}^{N} \frac{1}{\frac{1}{R_i} + j\omega C_i} = \sum_{i=1}^{N} \frac{R_i}{1 + j\omega\tau_i}$$

where $\tau_i = R_i C_i$ is the relaxation time of the i-th element

Let us introduce a probability density function $\Gamma(\tau) = \sum_{i=1}^{N} \Gamma(\tau_i) = 1$

$$\boxed{Z(\omega) = R_i \sum_{i=1}^{N} \frac{\Gamma(\tau_i)}{1 + j\omega\tau_i} = R_i \int_0^{\infty} \frac{\Gamma(\tau)}{1 + j\omega\tau} d\tau}$$

$\Gamma(\tau)$ has several possible solutions, $\Gamma(\tau)$ is affected by experimental conditions

Fourier Transform

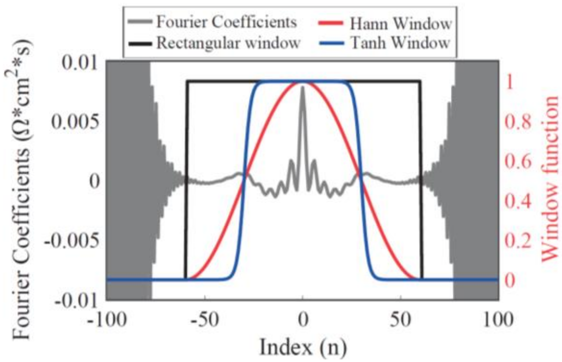
Tikhonov regularization

Solving strategies

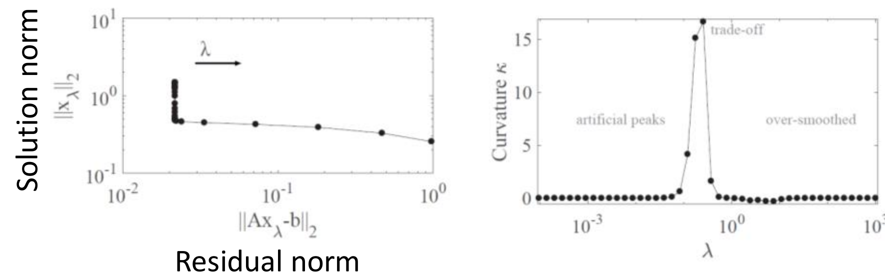
# II) Practical aspects, analyses, and applications

## 2) Data treatment

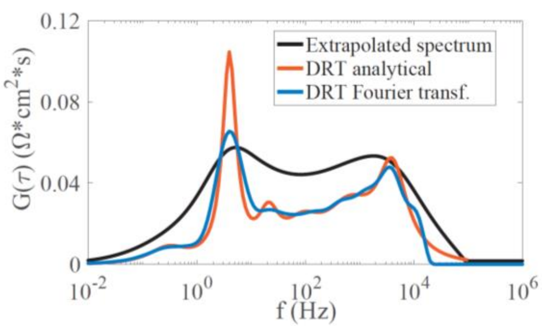
### Distribution of Relaxation Times (DRT)



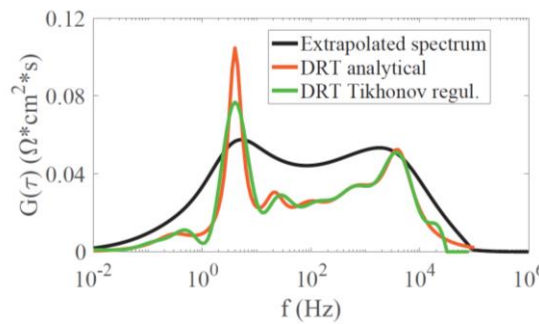

Fourier coefficients and filtering




Regularization parameter $\lambda = 0.08$




Fourier Transform



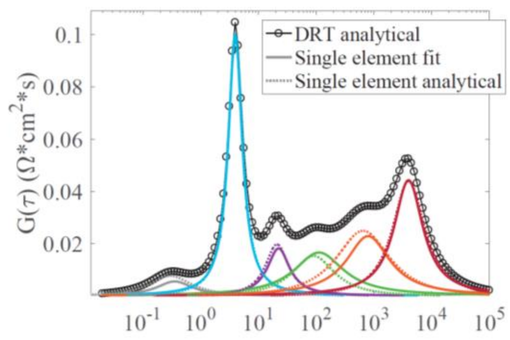

Tikhonov regularization

**Solving strategies**

# II) Practical aspects, analyses, and applications

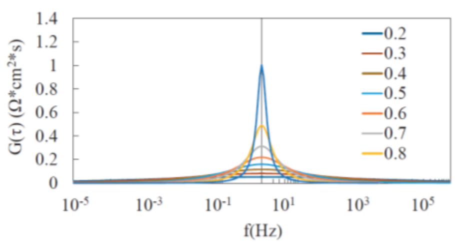
## 2) Data treatment

### Distribution of Relaxation Times (DRT)




| | |
|---|---|
| 1 $RQ^{\alpha} \equiv$ 1 DRT peak | Zw and ZG $\equiv$ 2 DRT peaks |

Direct treatment of DRT peaks




*Gaussian fit*
- $R_i$: peak surface area
- $\tau_i = R_i C_i$
- $\alpha = f(FWHM)$

Equivalent electrical circuit build-up

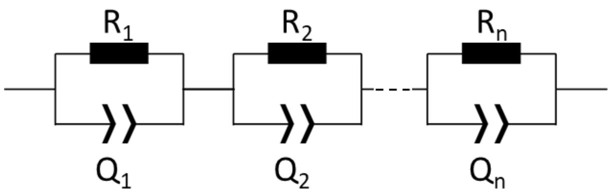
Fit EIS data

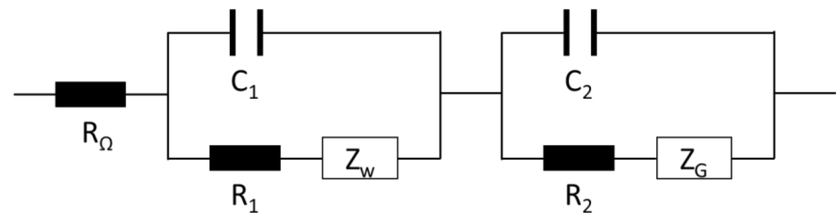
Complex Nonlinear Least Square fitting

# II) Practical aspects, analyses, and applications

## 2) Data treatment

### Complex Nonlinear Least Square fitting (CNLS)




Minimization of the sum of squares function:

$$S = \sum_{i=1}^{N} w_i \left( \left[ Z'_i(\omega_i) - Z'_{M,i}(\omega_i, x) \right]^2 + \left[ Z''_i(\omega_i) - Z''_{M,i}(\omega_i, x) \right]^2 \right)$$

where $Z_i(\omega)$ and $Z_{M,i}(\omega,x)$ are the measured and modeled impedance, respectively and $w_i$ is the weight factor $w_i = \left[ {Z_{Re,i}}^2 + {Z_{Im,i}}^2 \right]^{-1}$