# Principles and practices of electrochemical impedance

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# Outline of the whole course

Lecture 1: mathematical and physical basis

Lecture 2: principles and practices

Lecture 3: electrochemical interfaces

Lecture 4: porous electrodes

Lecture 5: model implementation in Matlab – interfaces

Lecture 6: model implementation in Matlab – porous electrodes

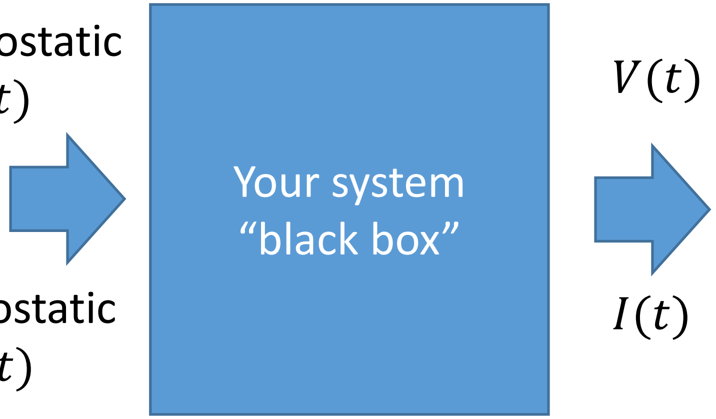
# Outline of today's lecture

- Principles
  - Definition
  - Advantages
  - Systematic view
- Practices
  - Devices
  - Cells
  - Cables
  - Parameters
  - Data handling

# What is EIS?

Galvanostatic
$I(t)$

Potentiostatic
$V(t)$



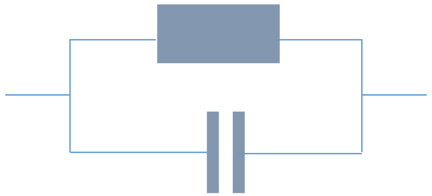

$V(t)$

$I(t)$

Definition

$$Z(\omega) = \frac{\mathcal{F}(V(t))}{\mathcal{F}(I(t))}$$

$\mathcal{F}$ represents Fourier transform



Time domain,

$$I(t) = \frac{V(t)}{R} + C\frac{dV(t)}{dt}$$

Applying Fourier transform

$$\mathcal{F}(I(t)) = \frac{\mathcal{F}(V(t))}{R} + C\mathcal{F}\left(\frac{dV(t)}{dt}\right)$$

$$\mathcal{F}(I(t)) = \frac{\mathcal{F}(V(t))}{R} + j\omega C\mathcal{F}(V(t))$$

$f^{(n)} \rightarrow (j\omega)^n F(f)$

Frequency domain

$$Z(\omega) = \frac{\mathcal{F}(V(t))}{\mathcal{F}(I(t))} = \frac{R}{1 + j\omega RC}$$

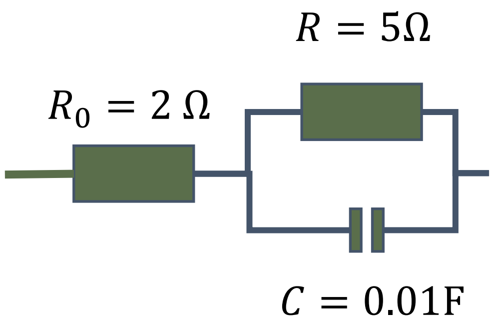
$\tau = RC$, the time constant of this circuit

**Differential eq.**

**↓ Fourier transform**

**Algebra eq.**

# Representation of EIS




$$Z(\omega) = R_0 + \frac{R}{1 + j\omega RC}$$

$$Z(\omega) = R_0 + \frac{R}{1 + \omega R^2 C^2} - j\frac{\omega R^2 C}{1 + \omega R^2 C^2}$$

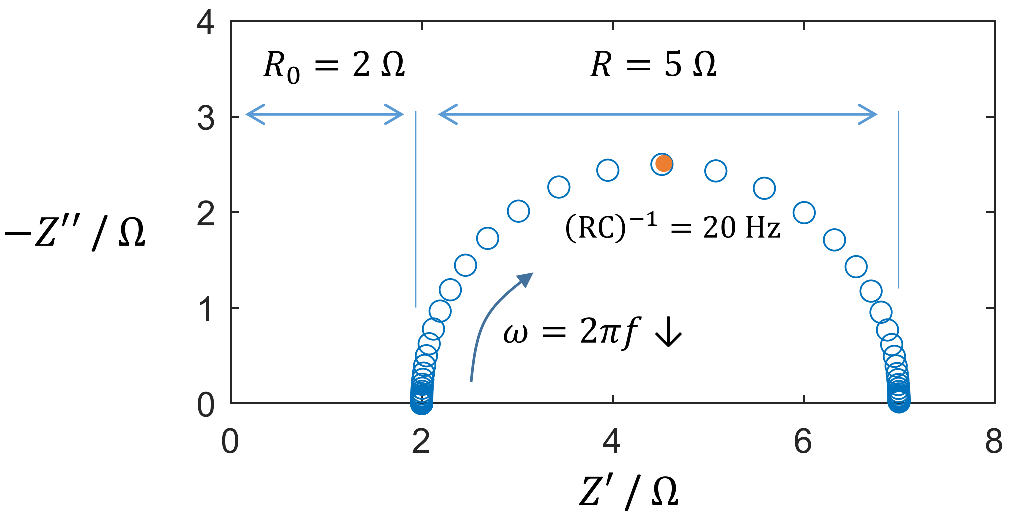
The real part of impedance

$$Z'(\omega) = R_0 + R\frac{1}{1 + (\omega\tau)^2}$$

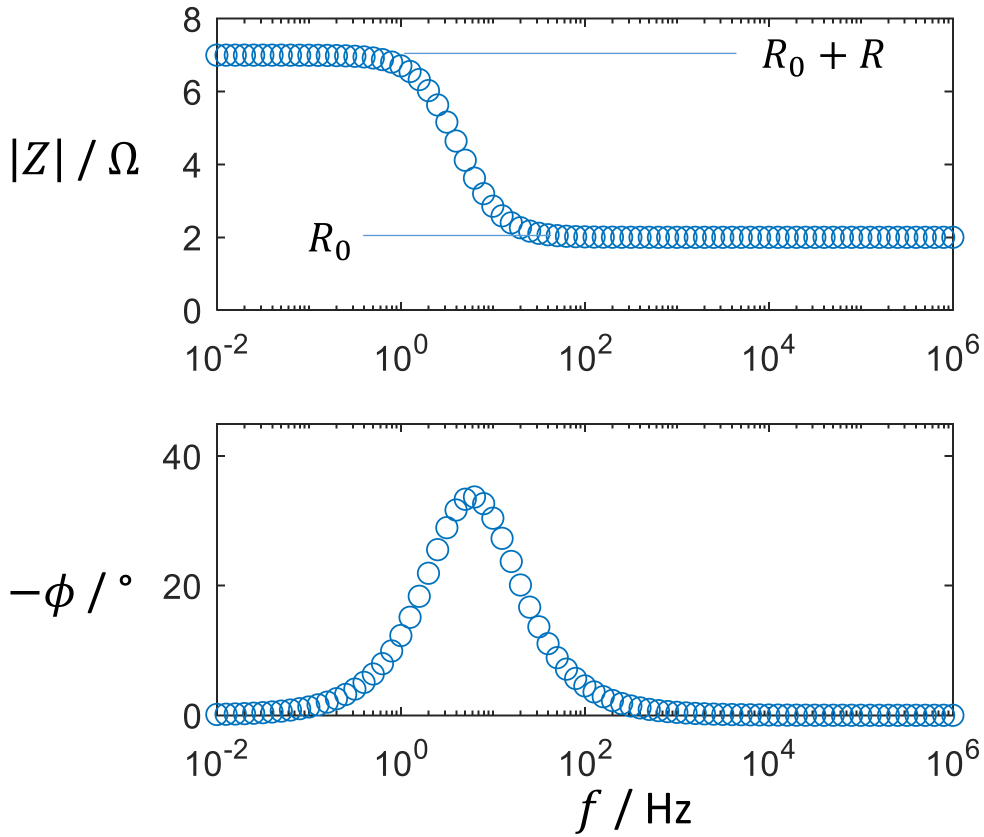
The imaginary part of impedance

$$Z''(\omega) = -R\frac{\omega\tau}{1 + (\omega\tau)^2}$$

$\tau = RC$ is the time constant




Nyquist plot




Bode plots

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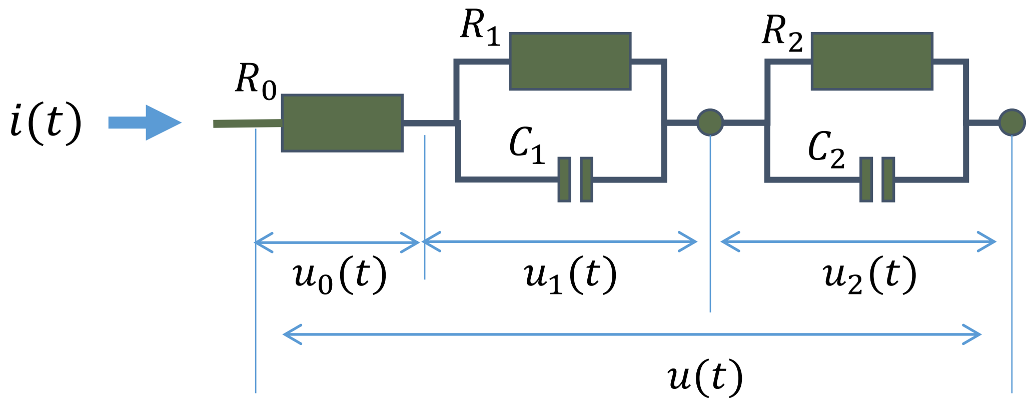
# Why do we need EIS? A new look at this question using a simple electric circuit model.




$u(t) = u_0 + u_1 + u_2$ and

$$i(t) = \frac{u_0}{R_0} = \frac{u_1}{R_1} + C_1 \frac{du_1}{dt} = \frac{u_2}{R_2} + C_2 \frac{du_2}{dt} \rightarrow$$

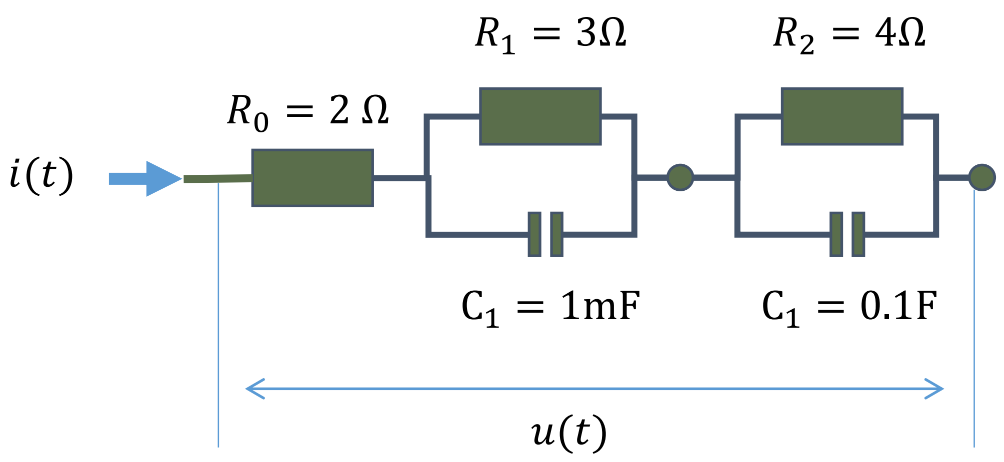
$$u_2 = u - R_0 \left( \frac{u_1}{R_1} + C_1 \frac{du_1}{dt} \right) - u_1 = u - \frac{R_0 + R_1}{R_1} u_1 - R_0 C_1 \frac{du_1}{dt} \rightarrow$$

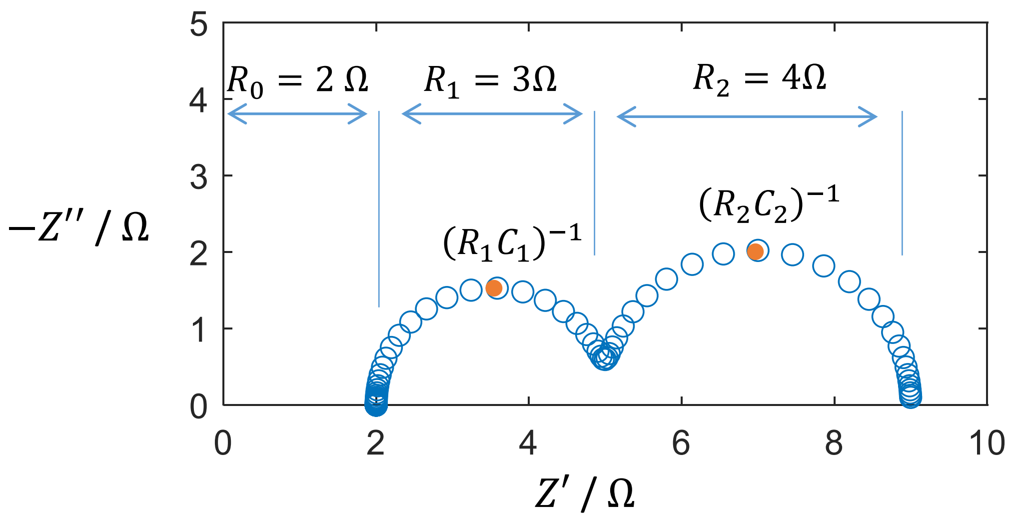
$$\left( \frac{R_0 + R_1 + R_2}{R_1 R_2} \right) u_1 + \left( C_1 + C_2 \frac{R_0 + R_1}{R_1} \right) \frac{du_1}{dt} + R_0 C_1 C_2 \frac{d^2 u_1}{dt^2} = \frac{u}{R_2} + C_2 \frac{du}{dt},$$

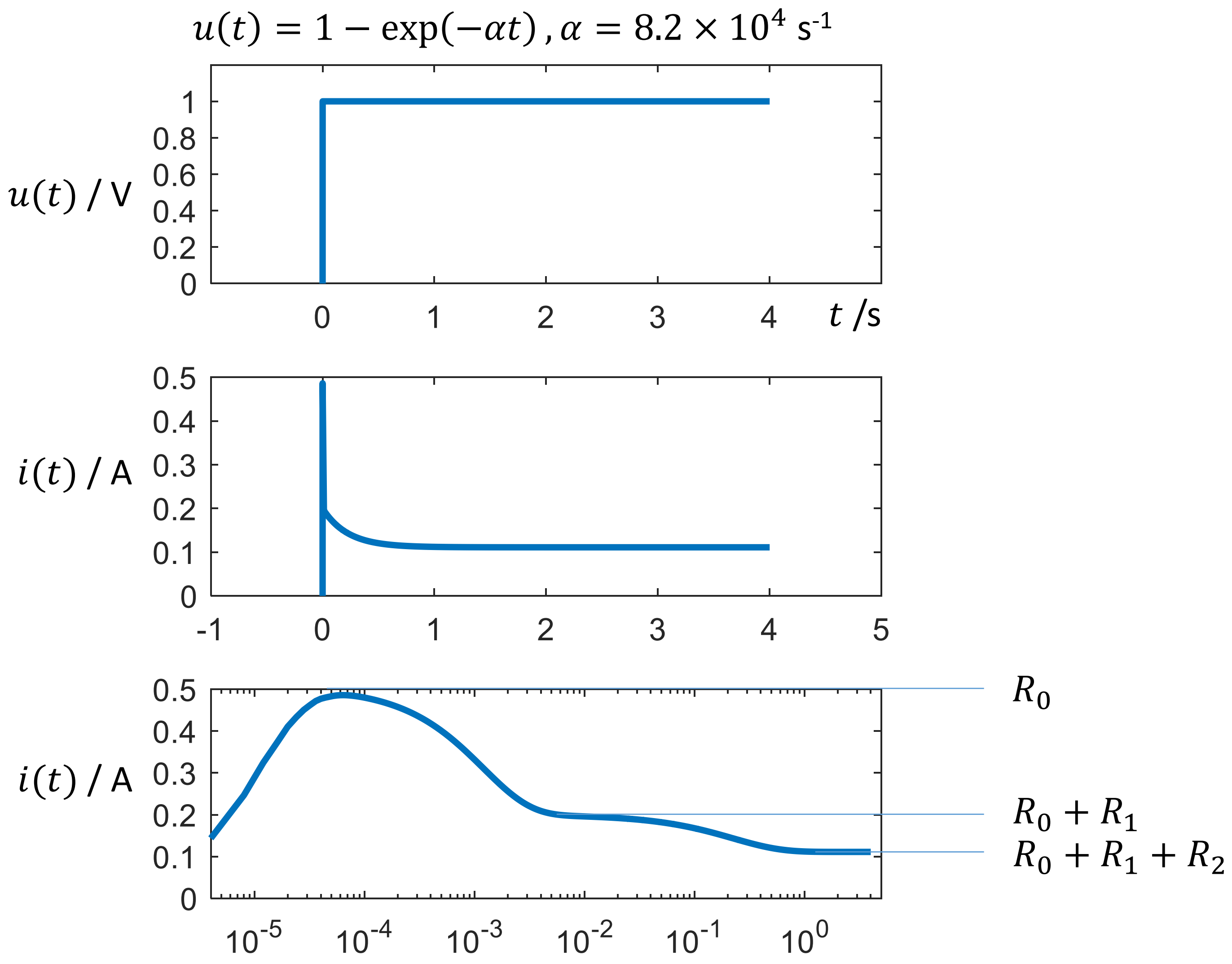
which is a 2nd order ODE.

Boundary conditions ($u_1 = 0, \frac{du_1}{dt} = 0$) @ t=0.

# Why do we need EIS?



# Advantages of EIS: Increased sensitivity and reliability

- High S/N ratio
  - Improves information content and frequency range by repeated sampling
- Wide frequency range
  - Better decoupling of physical phenomena
- Self-consistency check
  - Takes advantage of relationship between real and imaginary impedance to check consistency
- Easy to implement and process
  - Modern hardware and software

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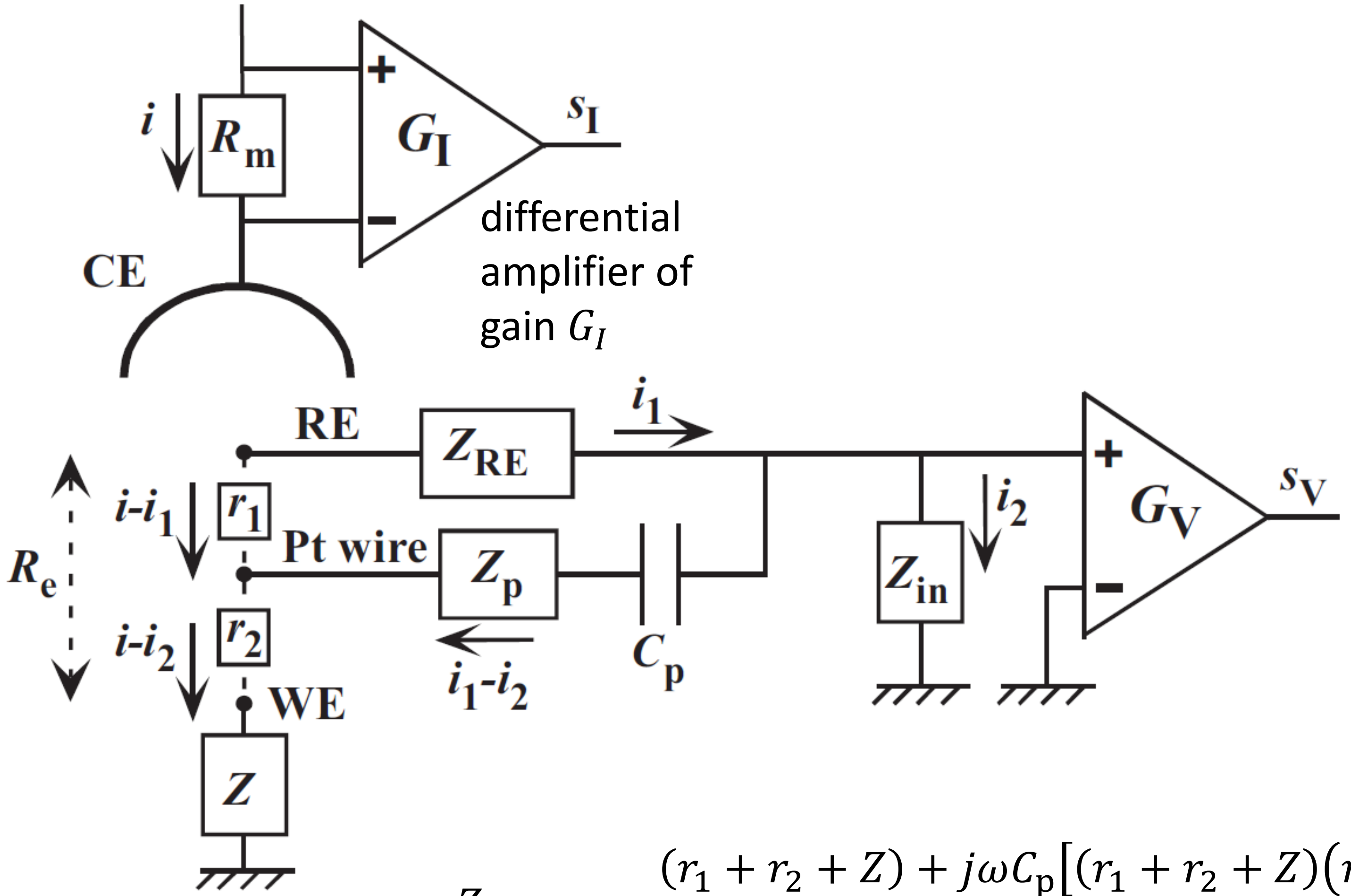
# A holistic model of the measurement setup




$Z_{in}$: input impedance of the amplifier and the impedance of the cable connected to the RE.

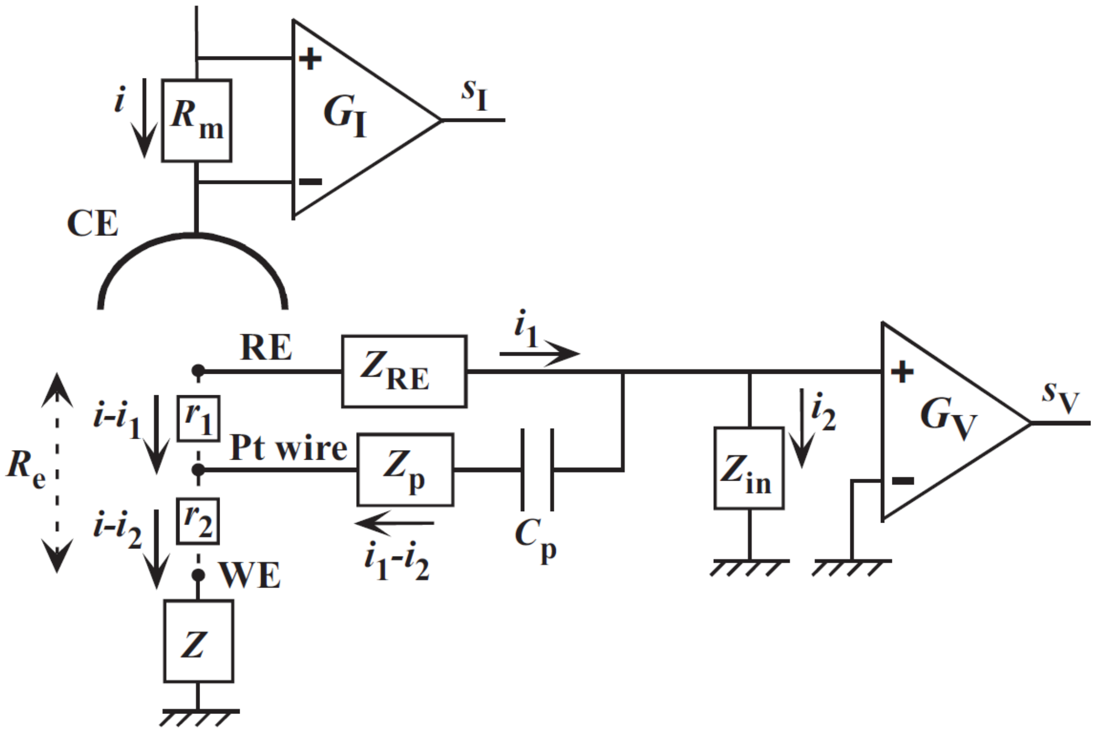
$$Z_{in} = \frac{1}{\frac{1}{R_{in}} + j\omega C_{in}} \approx \frac{1}{j\omega C_{in}}, R_{in} \gg 10^{12}\ \Omega$$

$C_{in}$ is the sum of the input capacitance of the amplifier and of the RE cable capacitance, which has to be taken into account especially when a grounded coaxial cable is used to minimize interference of the mains.

$$Z_{\mathrm{meas}} = \frac{(r_1 + r_2 + Z) + j\omega C_{\mathrm{p}}\left[(r_1 + r_2 + Z)\left(r_1 + Z_{\mathrm{RE}} + Z_p\right) - r_1(r_1 + Z_{\mathrm{RE}})\right]}{\left(1 + \frac{(r_2 + Z)}{Z_{\mathrm{in}}}\right)\left(1 + j\omega C_{\mathrm{p}}\left(r_1 + Z_{\mathrm{RE}} + Z_{\mathrm{p}}\right)\right) + \frac{(r_1 + Z_{\mathrm{RE}})}{Z_{\mathrm{in}}}\left(1 + j\omega C_{\mathrm{p}} Z_{\mathrm{p}}\right)}$$

Tran, A-T., et al. *Electrochimica Acta* 56.23 (2011): 8034-8039.

# A holistic model of the measurement setup




Single reference electrode ($C_p = 0, r_1 = 0$)

$$Z_{meas} = \frac{(r_2 + Z)Z_{in}}{r_2 + Z + Z_{RE} + Z_{in}}$$

If $Z_{in} = \frac{1}{j\omega C_{in}}$, we have

$$Z_{meas} = \frac{r_2 + Z}{1 + j\omega C_{in}(r_2 + Z + Z_{RE})}$$

If we assume, $Z_{RE} \gg r_2 + Z$, we have

$$Z_{meas} = \frac{r_2 + Z}{1 + j\omega C_{in} Z_{RE}}$$

This means that the RE resistance and the stray capacitance results in an extra semicircle, usually in the high frequency range.

At very low frequency, $Z_{meas} = r_2 + Z$, as we expect.

The full model

$$Z_{meas} = \frac{(r_1 + r_2 + Z) + j\omega C_p\left[(r_1 + r_2 + Z)\left(r_1 + Z_{RE} + Z_p\right) - r_1(r_1 + Z_{RE})\right]}{\left(1 + \frac{(r_2 + Z)}{Z_{in}}\right)\left(1 + j\omega C_p\left(r_1 + Z_{RE} + Z_p\right)\right) + \frac{(r_1 + Z_{RE})}{Z_{in}}\left(1 + j\omega C_p Z_p\right)}$$

Tran, A-T., et al. *Electrochimica Acta* 56.23 (2011): 8034-8039.

# The influence of a dual RE

$$Z_{\text{meas}} = \frac{(r_1 + r_2 + Z) + j\omega C_{\text{p}}[(r_1 + r_2 + Z)(r_1 + Z_{\text{RE}} + Z_p) - r_1(r_1 + Z_{\text{RE}})]}{\left(1 + \frac{(r_2 + Z)}{Z_{\text{in}}}\right)\left(1 + j\omega C_{\text{p}}(r_1 + Z_{\text{RE}} + Z_{\text{p}})\right) + \frac{(r_1 + Z_{\text{RE}})}{Z_{\text{in}}}(1 + j\omega C_{\text{p}} Z_{\text{p}})}$$

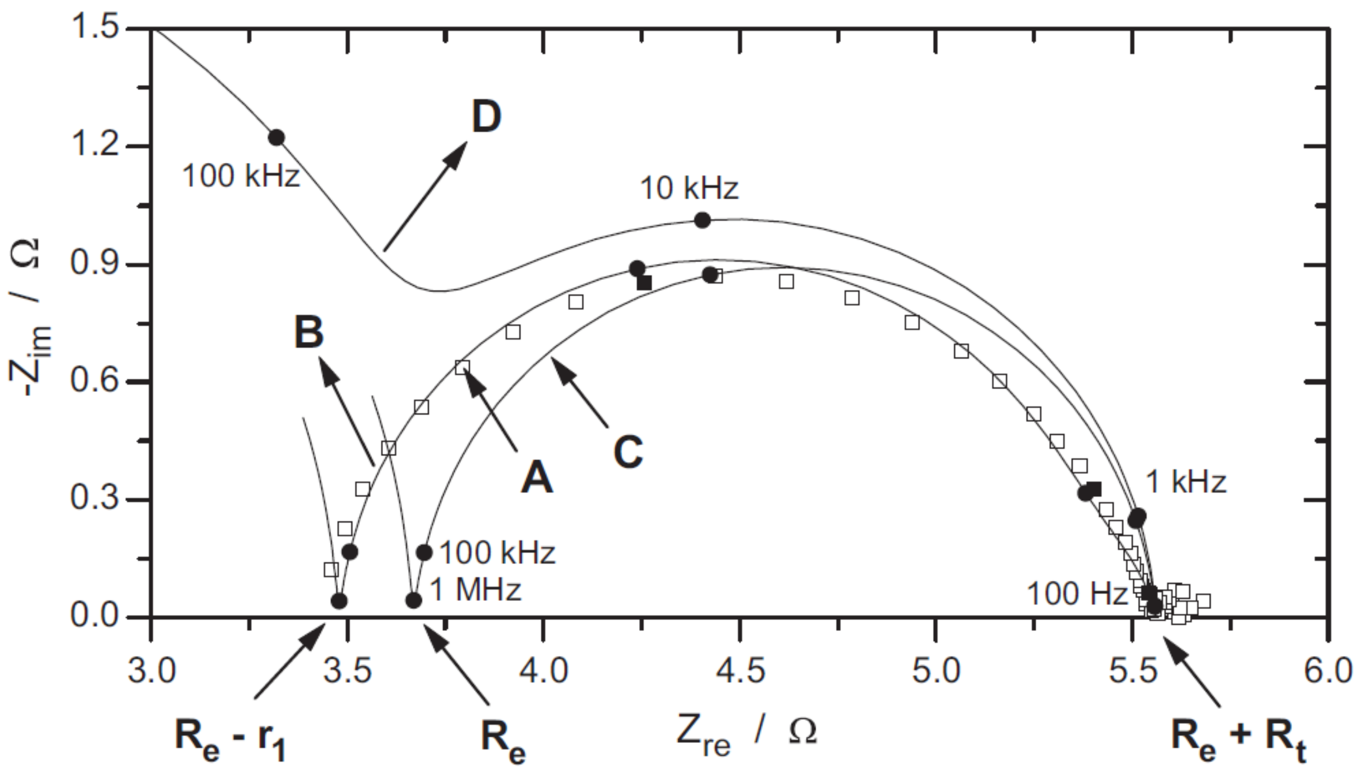



**Fig. 5.** EIS Nyquist diagrams of $H_2$ evolution on a Pt disk electrode in 1 M $H_2SO_4$ under current control (−100 mA/cm$^2$): (A) measured with a dual RE ($C_p$ = 0.47 µF), (B) fitted from Eq. (11) and $R_e$ = 3.69 Ω, $R_{t1}$ = 1.87 Ω, $\alpha_1$ = 0.969, $Q_1$ = 14.8 µF s$^{\alpha_1 - 1}$, $r_1$ = 0.19 Ω, (C) simulated with Eq. (11) with the same parameters except $r_1$ = 0, and (D) simulated with Eq. (11) with the same parameters and no Pt wire ($C_p$ = 0, $r_1$ = 0).

Tran, A-T., et al. *Electrochimica Acta* 56.23 (2011): 8034-8039.

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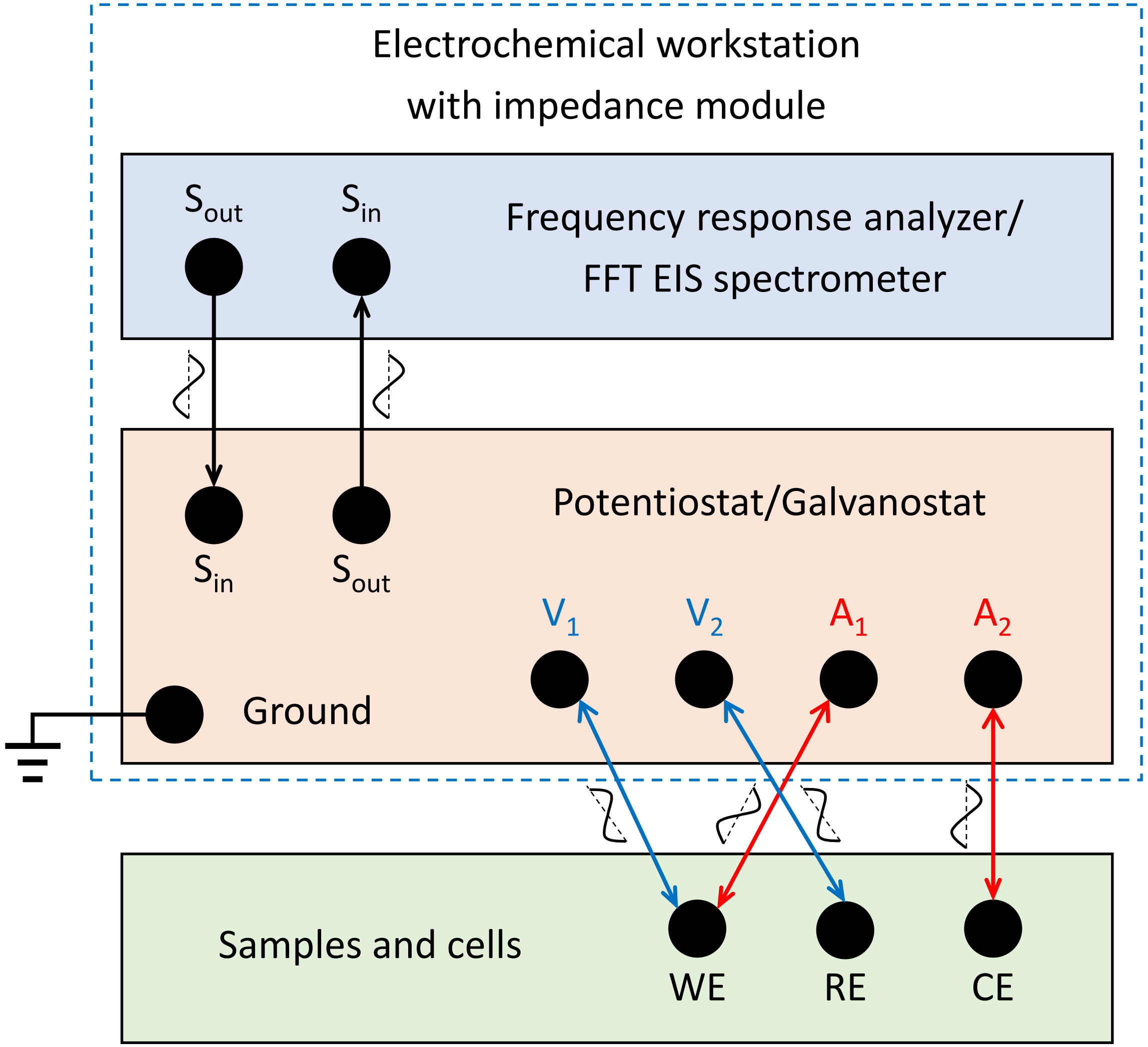
# Setup of EIS measurement: overview

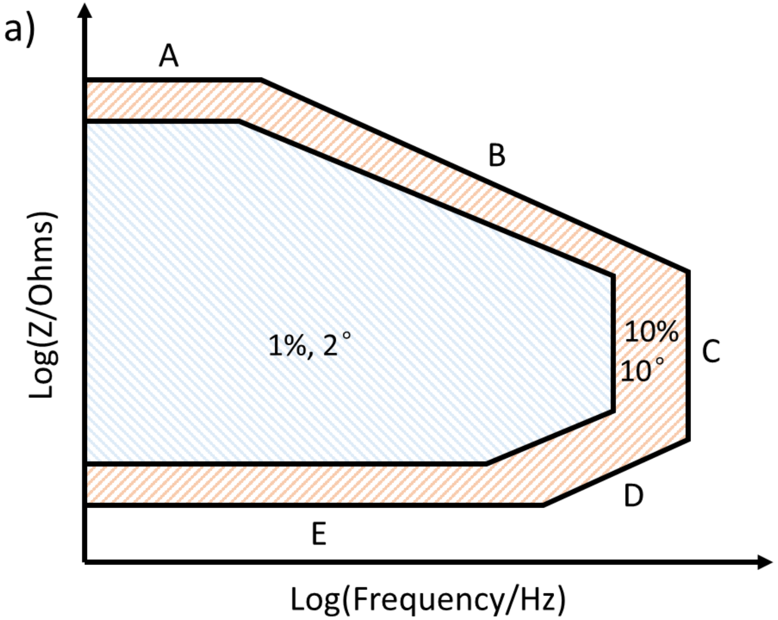



**A recent tutorial on EIS measurement and data analysis**
Wang, S., Zhang, J., Gharbi, O. et al. Nat Rev Methods Primers 1, 41 (2021)

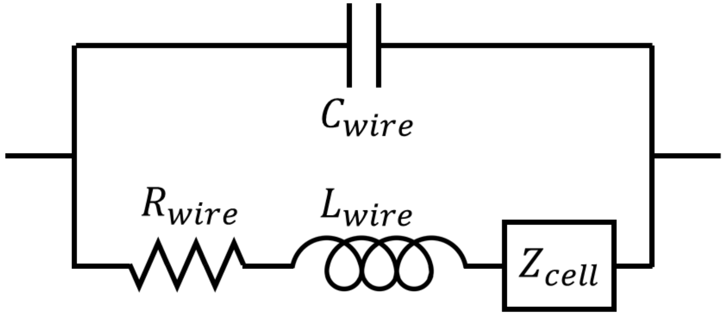
**Lift the lid on potentiostat**
Phys. Chem. Chem. Phys., Alex W. Colburn, Katherine J. Levey, Danny O'Hare and Julie V. Macpherson 2021,23, 8100-8117

# Instrumentation: accuracy contour map

a)




b)




$$Z_{meas} = \frac{\left(R_{wire} + Z_{L,wire} + Z_{cell}\right) \times Z_{C,wire}}{R_{wire} + Z_{L,wire} + Z_{cell} + Z_{C,wire}}$$

- Limit A: the maximum measurable impedance, limited by current accuracy
- Limit C: the maximum measurable frequency, related to the bandwidth of the instrument.
- Limit E: the lowest measurable impedance, limited by current range
- Limit B: the capacitive limit, related to the stray capacitor
- Limit D: the inductive limit, related to the stray inductor

Wang, S., Zhang, J., Gharbi, O. et al. Nat Rev Methods Primers 1, 41 (2021)

# An example of accuracy contour map

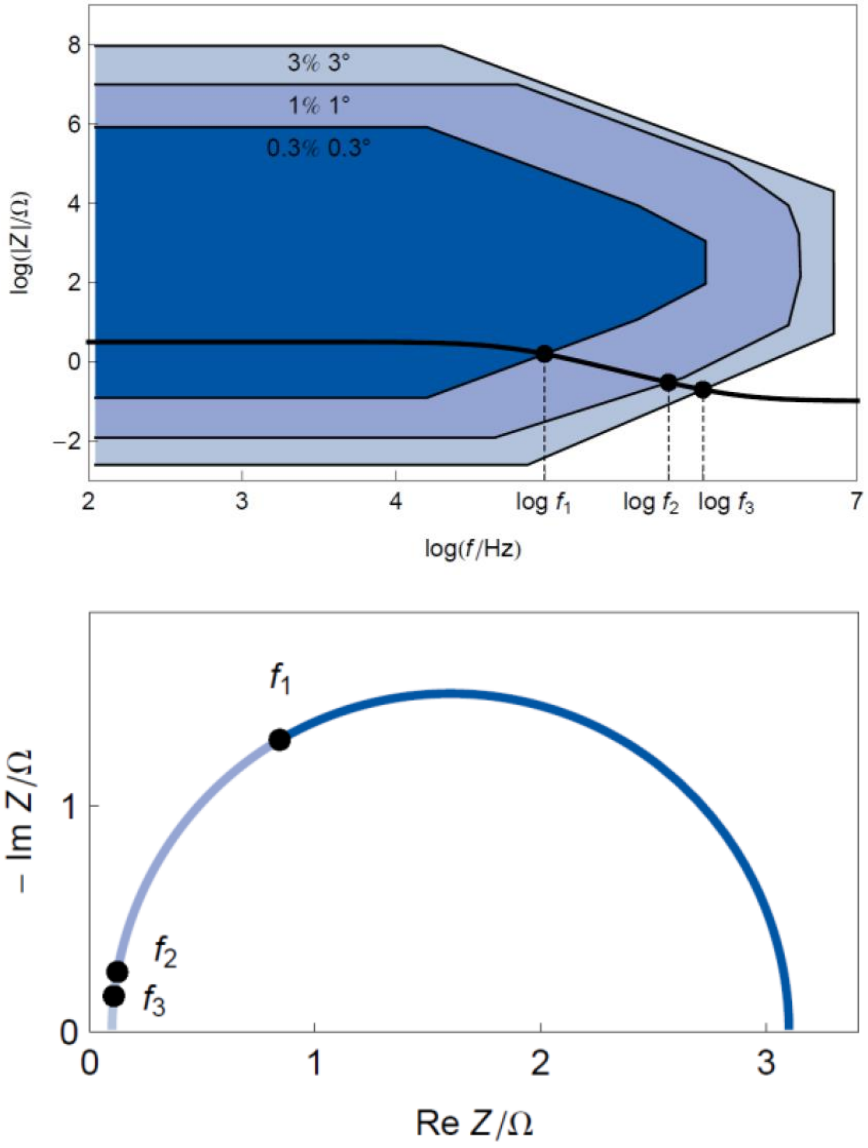



**Table I: Impedance measurement accuracy as a function of the frequency. $R_1$ = 0.1 Ω, $R_2$ = 3 Ω and $C_2$ = $10^{-6}$ F.**

| Frequency | Impedance modulus | Impedance phase |
|---|---|---|
| $f < f_1$ | $\Delta\|Z\|/\|Z\| < 0.3\ \%$ | $\phi_Z < 0.3°$ |
| $f_1 < f < f_2$ | $0.3\ \% < \Delta\|Z\|/\|Z\| < 1\ \%$ | $0.3° < \Delta\phi_Z < 1°$ |
| $f_2 < f < f_3$ | $1\ \% < \Delta\|Z\|/\|Z\| < 3\ \%$ | $1° < \Delta\phi_Z/° < 3°$ |
| $f > f_4$ | $\Delta\|Z\|/\|Z\| > 3\ \%$ | $\phi_Z > 3°$ |

https://www.biologic.net/documents/eis-contour-plot-electrochemistry-application-note-54/

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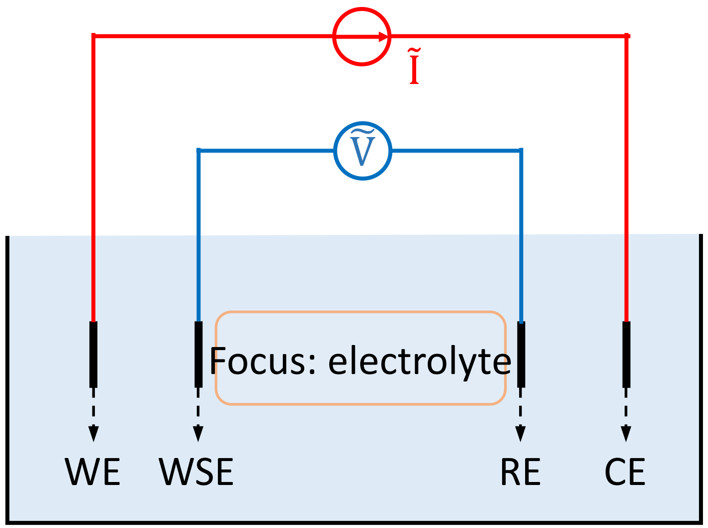
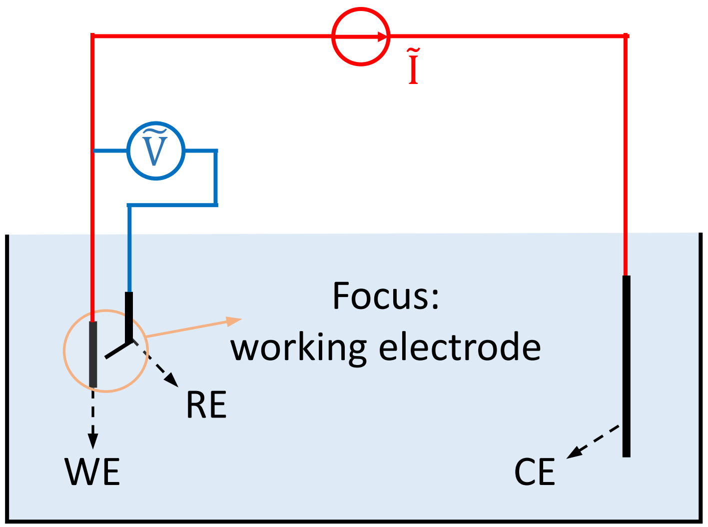
# Setup of EIS measurement: test samples and cells

a)



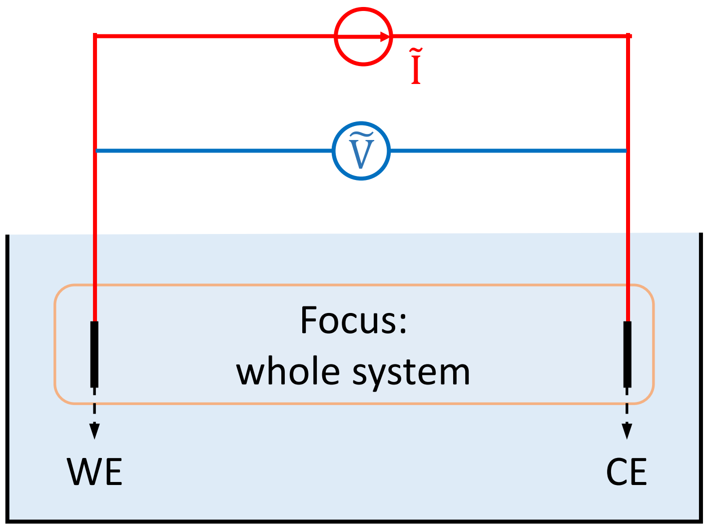

Four-electrode setup

b)




Three-electrode setup

c)




Two-electrode setup

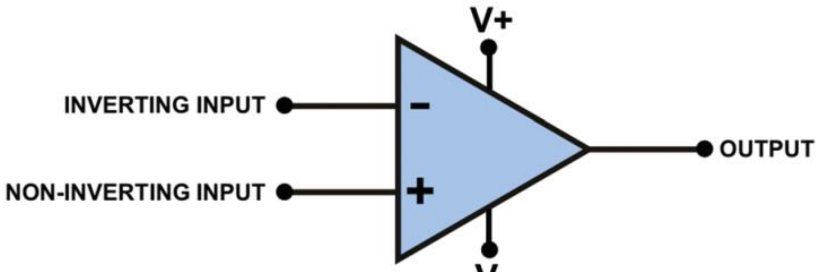
characterization of

- electrolyte conductivity
- a free-standing film
- embedded rebar in concrete
- the interface between two immiscible electrolyte solutions.

- enables study of the working electrode response independent of the processes taking place at the counter-electrode
- sometimes, dual REs are needed.

- when it is inconvenient to introduce a reference electrode (like LIB),
- when different electrodes have distinct signature,
- when the impedance of one electrode is negligibly small (like anode in PEFC fuel cell under pure $H_2$ supply, or an electrode with much larger size).

# Basics of a potentiostat




CHARACTERISITICS

- Two very high resistance voltage inputs > $10^{12}\ \Omega$
- One very low resistance voltage output < $100\ \Omega$
- Very high amplification gain – typically $10^6$

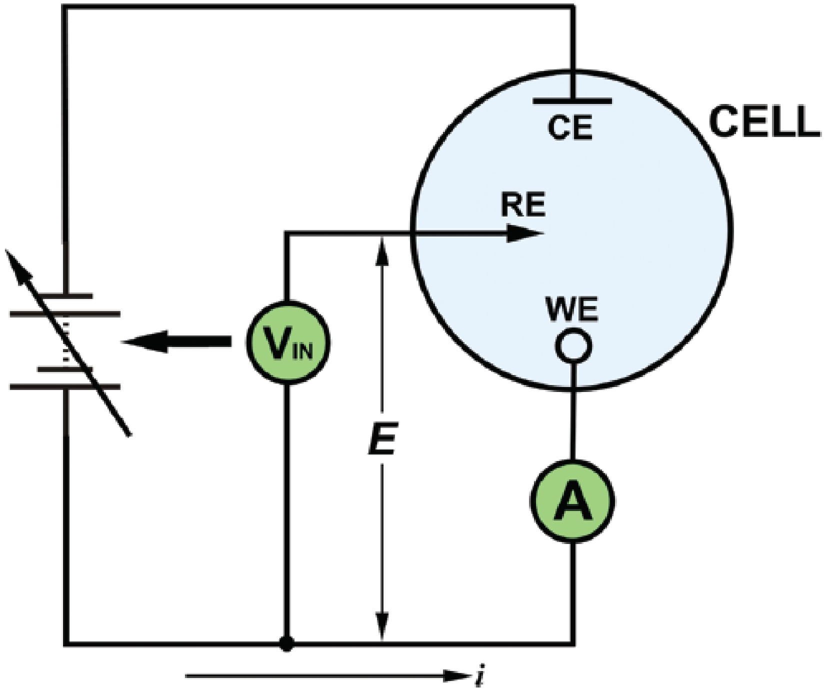
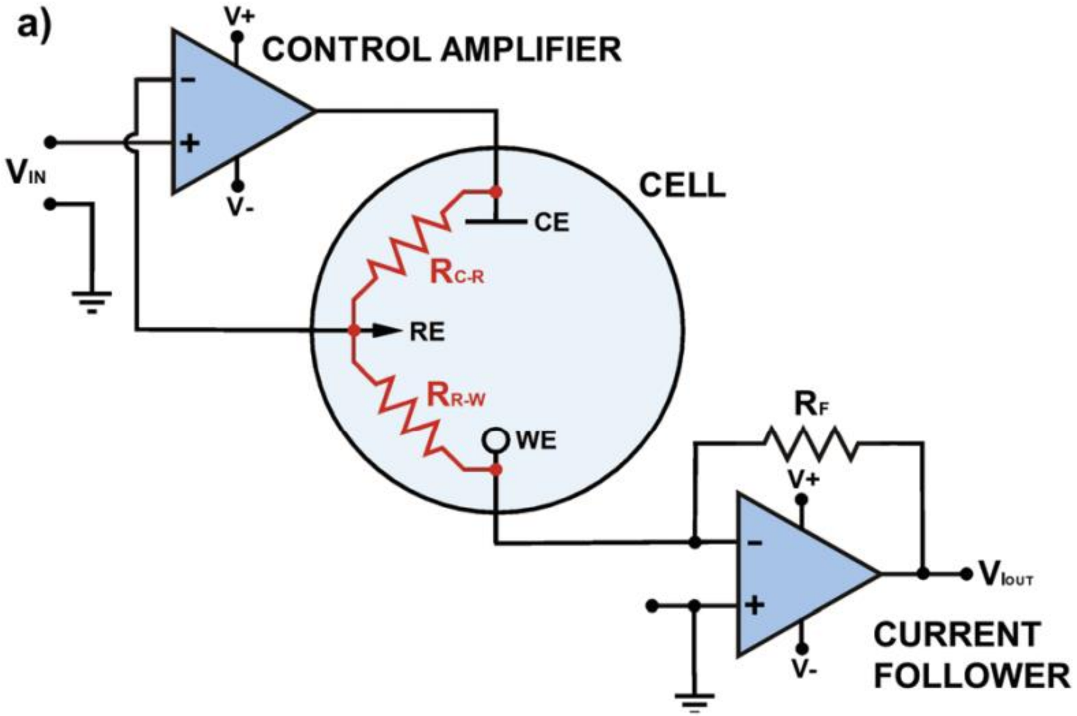



**Fig. 1** Schematic of a typical three electrode electrochemical set-up, with the appropriate symbols used for WE (O), RE (arrow) and CE (⊥). Current flows between CE and WE whilst *E* is controlled between WE and RE.




Alex W. Colburn, Katherine J. Levey, Danny O'Hare and Julie V. Macpherson
Phys. Chem. Chem. Phys., 2021,23, 8100-8117

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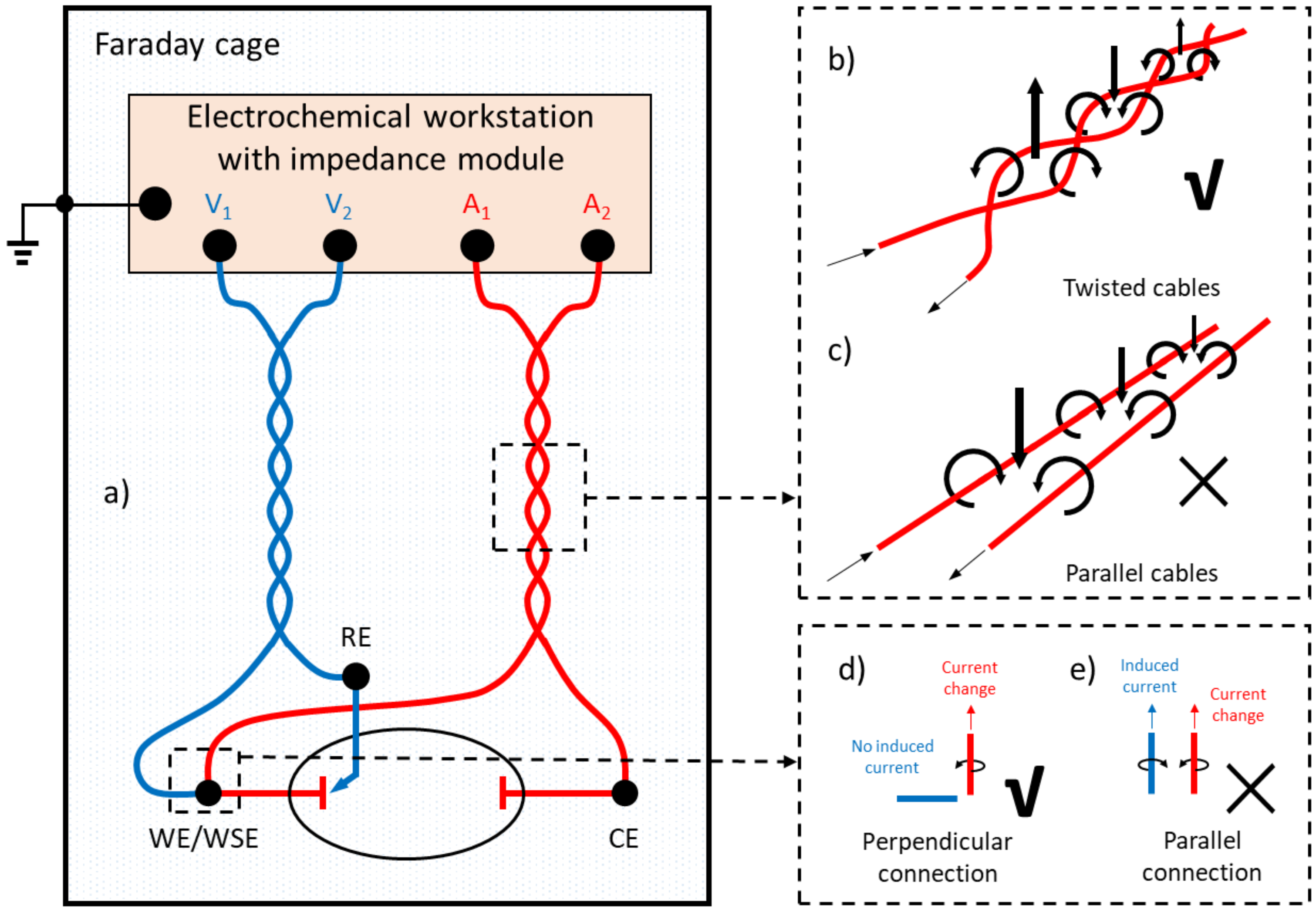
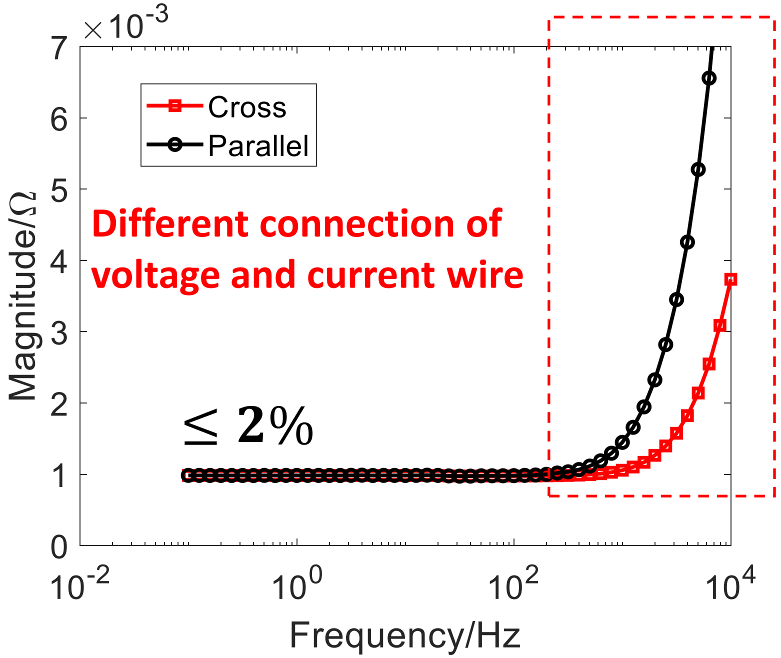
# Wire connection

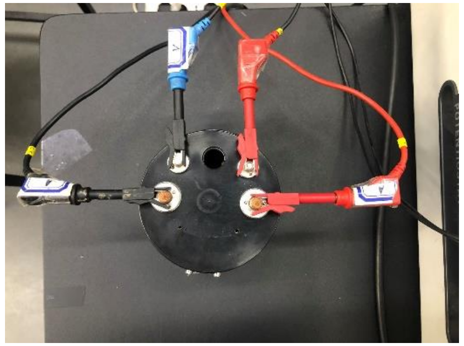


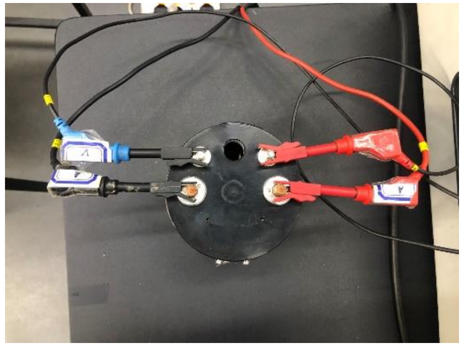

Wang, S., Zhang, J., Gharbi, O. et al. Nat Rev Methods Primers 1, 41 (2021)

# Wire connection: an example


1.Resistance: $1\mathrm{m}\Omega$
2.Current: ≤ 10A
3.Four-terminal measurement principle
4.Accuracy: 0.2%





Cross

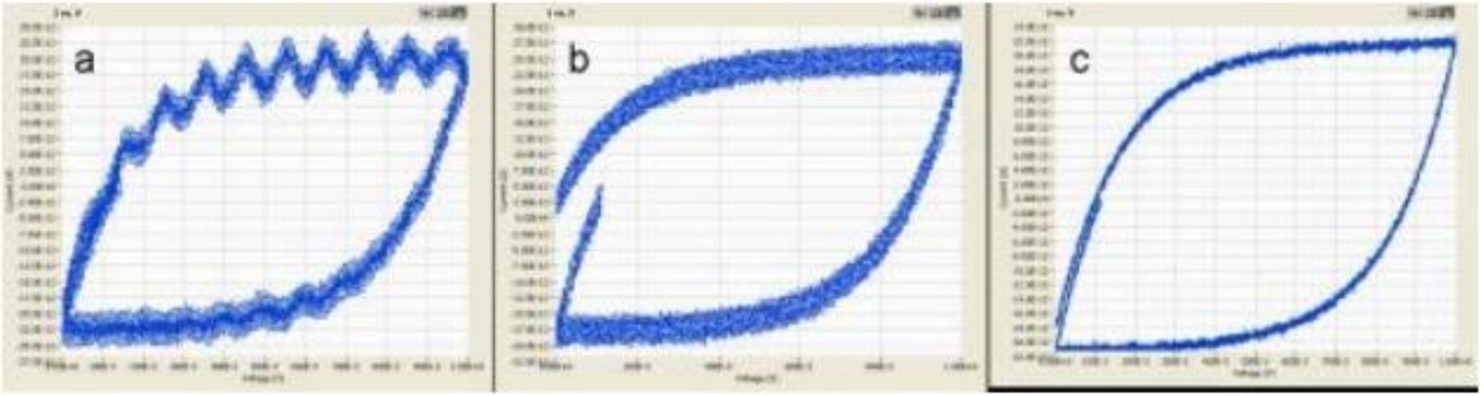

Parallel

- Room Temperature
- Current amplitude: 0.5A
- Freq. range： 10kHz-0.1Hz
- Instrument: Autolab
- Wiring and connection： Cross & Parallel

# Shielding with Faraday cage

Object: RC dummy cell
Test: Cyclic voltammograms

- 0–1 V
- 0.5 V/s
- 1 kHz acquisition frequency




No shielding

Shielded but not grounded with potential stat

Shielded and grounded with potential stat

https://www.gamry.com/application-notes/instrumentation/faraday-cage/

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# Three principles in EIS measurement

**Causality**

- Signal-to-noise ratio
- Instrument artifacts at high freq.

$$\chi(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{i\omega\tau} \mathrm{d}\tau$$

↓ Causality

$$\chi(\omega) = \int_{0}^{\infty} G(\tau) e^{i\omega\tau} \mathrm{d}\tau$$

- **Linearity**
  - Low amplitude perturbation
  - Depends on polarization curve for system under study
  - Determine experimentally

$$j = j_0 \left[ \exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \right]$$

$$\rightarrow j = j_0 \frac{F\eta}{RT} \rightarrow R_{ct} = \frac{RT}{F j_0}$$

- **Stationarity**
  - Non-stationary behavior at low freq.
  - Start from high f
    - Soon to see the result
    - Get more information while the system is stable

# How to improve Signal-to-Noise ratio

- Check current and voltage range
- Increase the integration time/cycles
- Adjust signal amplitude
- Introduce a delay time

  To avoid this undesired error caused by the transient, it is better to introduce a delay of one or two cycles between the change of frequency and impedance measurement.

- Ignore the first frequency measured

  The impedance measured at the first frequency of measurement is often corrupted by a startup transient. The best option is to ignore the first measured frequency when regressing models to the data.

- Avoid external electric fields

  use of a Faraday cage

# Considerations in EIS measurement

- Modulation mode: GEIS vs PEIS
- Perturbation amplitude (balance between linearity and N/S ratio)
  - PEIS mode: 5~15 mV
  - GEIS mode: to be determined case by case
- Frequency range
  - 1 mHz~100 kHz
  - 7~10 points per decade
  - Starts from the high frequency limit, sweeping towards the low frequency limit
- Integration time/cycles
  - At least 3 times
- Environmental control
  - Temperature: thermal bath
  - Electric-magnetic noise: faraday cage
  - Mechanical vibration: anti-vibration table

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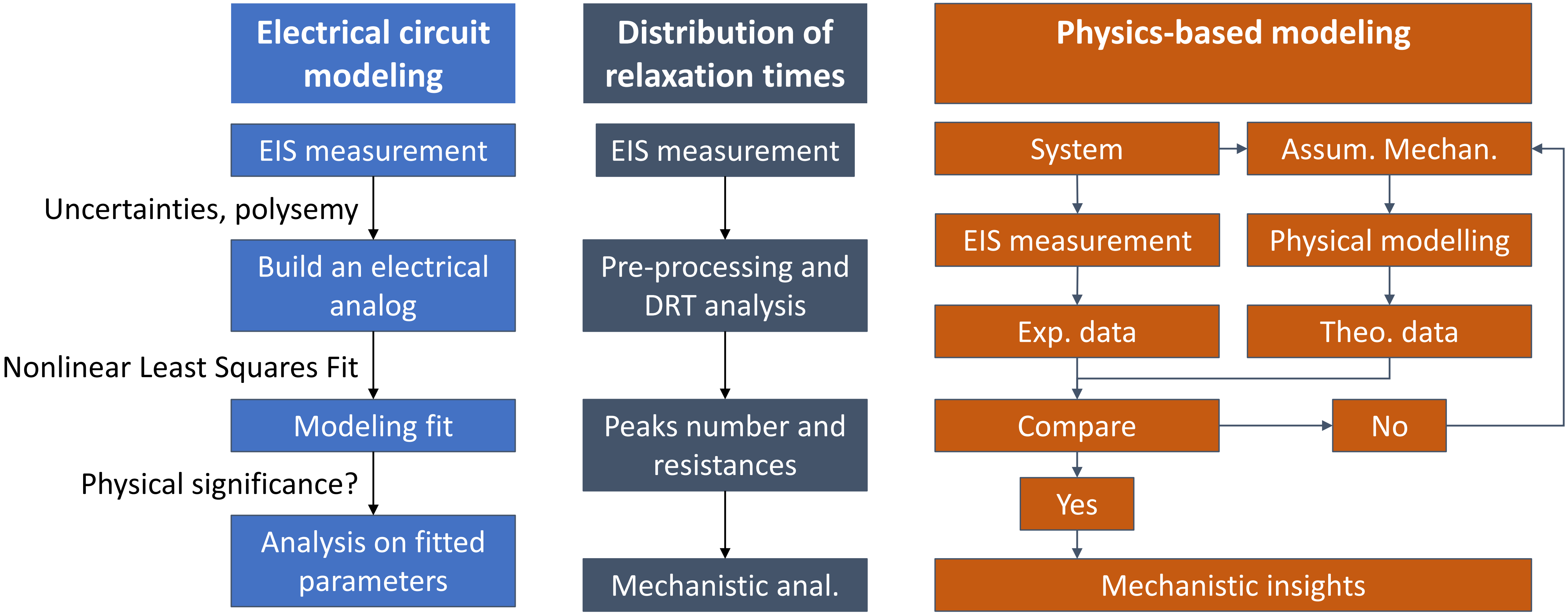
# Three methods for data analysis




"This is seldom, if ever, the case, and while the analog may produce plots that are impressive in their fit to the experimental data, they do little to advance the science." D.D. Macdonald

# Nonlinear least square fitting

Model fitting is usually conducted using the nonlinear least-squares solver, ‘lsqnonlin’, in Matlab. The algorithm is to minimize the following function,

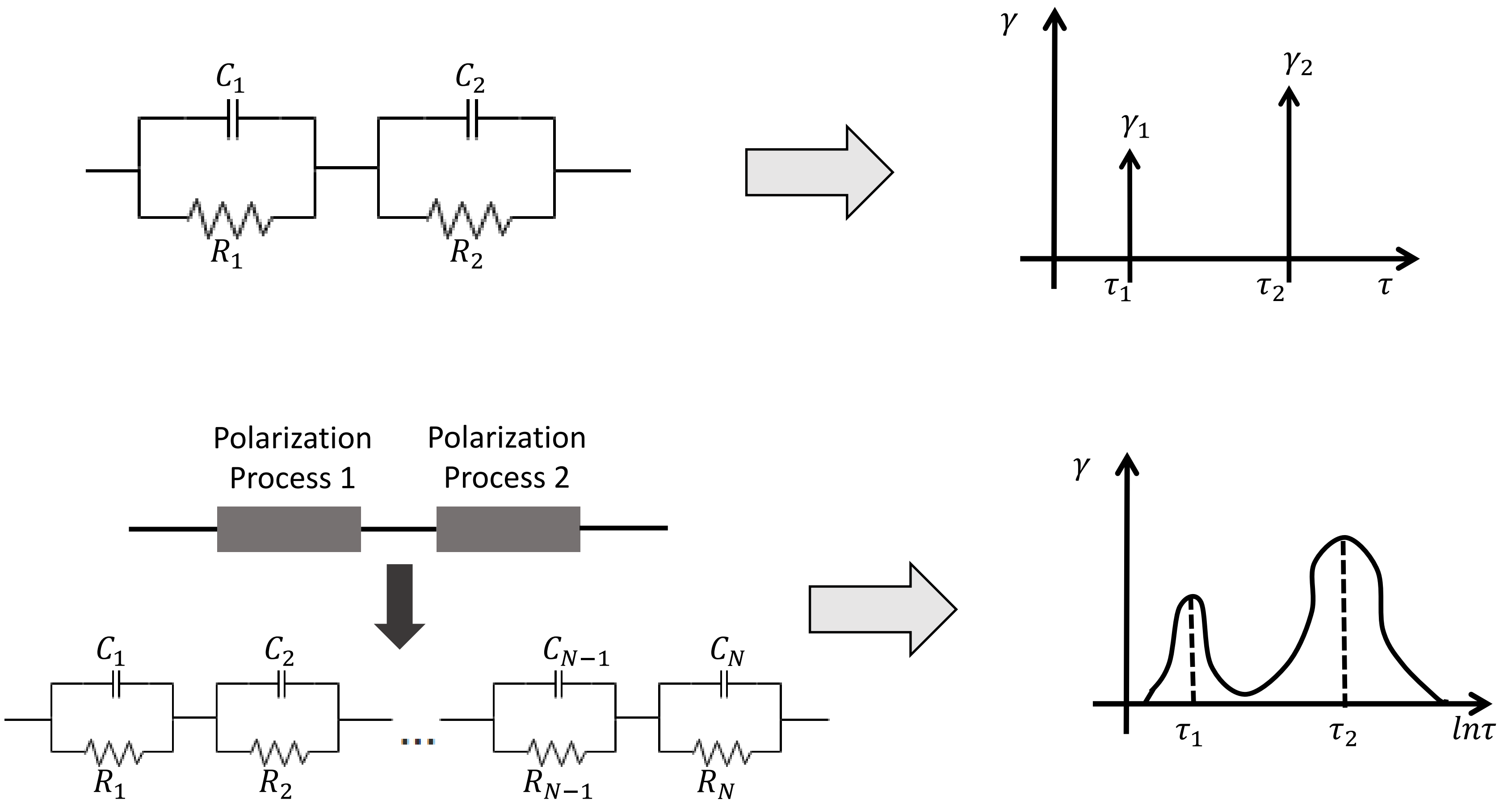
$$F(\mathbf{x}) = \sum_i \left( w_r \left( Re\left(Z(\omega_i, \mathbf{x})\right) - Re\left(Z_{mea}(\omega_i)\right)\right)^2 + w_i \left( Im\left(Z(\omega_i, \mathbf{x})\right) - Im\left(Z_{mea}(\omega_i)\right)\right)^2 \right)$$

by finding an optimal **x**, which is a vector consisting of model parameters, where $Z(\omega_i, \mathbf{x})$ is simulated impedance and $Z_{mea}(\omega_i)$ is the measured impedance, Re and Im denote the real and imaginary part of the impedance, respectively.

$w_r$ and $w_i$ are weighting coefficients

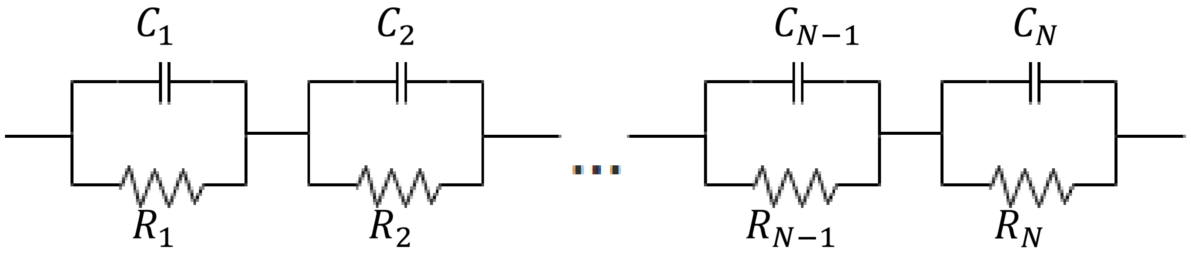
See more information on https://www.mathworks.com/help/optim/ug/lsqnonlin.html

# Distribution of relaxation times (DRT)




Illig, J., et al. Separation of Charge Transfer and Contact Resistance in LiFePO 4 -Cathodes by Impedance Modeling.

# Basics of DRT




$$Z_p(\omega) = \sum_{k=1}^{N} \frac{R_k}{1 + j\omega\tau_k} = R_p \sum_{k=1}^{N} \frac{\gamma_k}{1 + j\omega\tau_k} \qquad \sum_{k=1}^{N} \gamma_k = 1$$

$$Z_p(\omega) = R_p \int_0^{\infty} \frac{\gamma(\tau)}{1 + jw\tau} d\tau \qquad \int_0^{\infty} \gamma(\tau) d\tau = 1$$

# Basics of DRT

DRT expression

$$Z(\omega) = R_{pol}\int_0^\infty \frac{\gamma(\tau)}{1+j\omega\tau}d\tau$$

$$\gamma(\tau) \geq 0, \quad \int_0^\infty \gamma(\tau)\,d\tau = 1$$

Transformed into
an optimization problem

$$min_{\bar{\gamma}}\{\|H\bar{\gamma} - \bar{Z}\|^2\}$$

Numerical integration

$$Z'(\omega) = R_{pol}\int_0^\infty \gamma(\tau)h'(\omega,\tau)d\tau$$

$$\approx R_{pol}\sum_{j=1}^{M} a_j\,\gamma(\tau_j)h'(\omega,\tau_j)$$

$$Z''(\omega) = R_{pol}\int_0^\infty \gamma(\tau)h''(\omega,\tau)d\tau$$

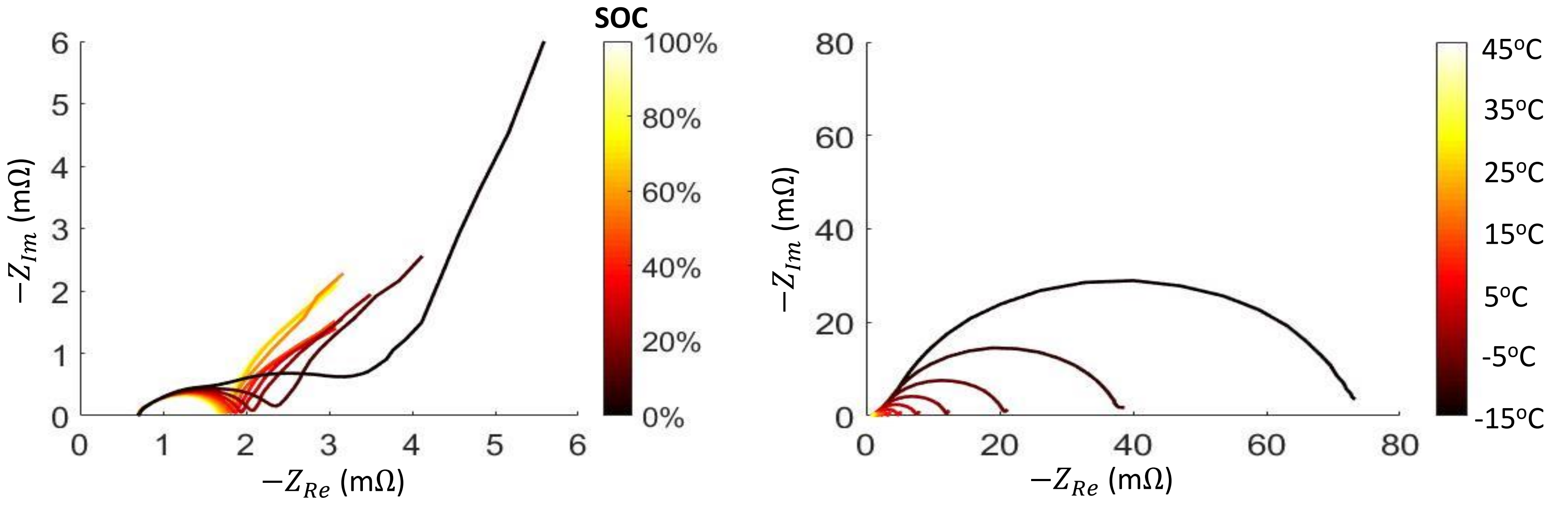
$$\approx R_{pol}\sum_{j=1}^{M} a_j\,\gamma(\tau_j)h''(\omega,\tau_j)$$

$$h'(\omega,\tau) = \frac{1}{1+\omega^2\tau^2}$$

$$h''(\omega,\tau) = \frac{-j\omega\tau}{1+\omega^2\tau^2}$$

A. L. Gavrilyuk, D. A. Osinkin and D. I. Broninc, The Use of Tikhonov Regularization Method for Calculating the Distribution Function of Relaxation Times in Impedance Spectroscopy

# An example of DRT application



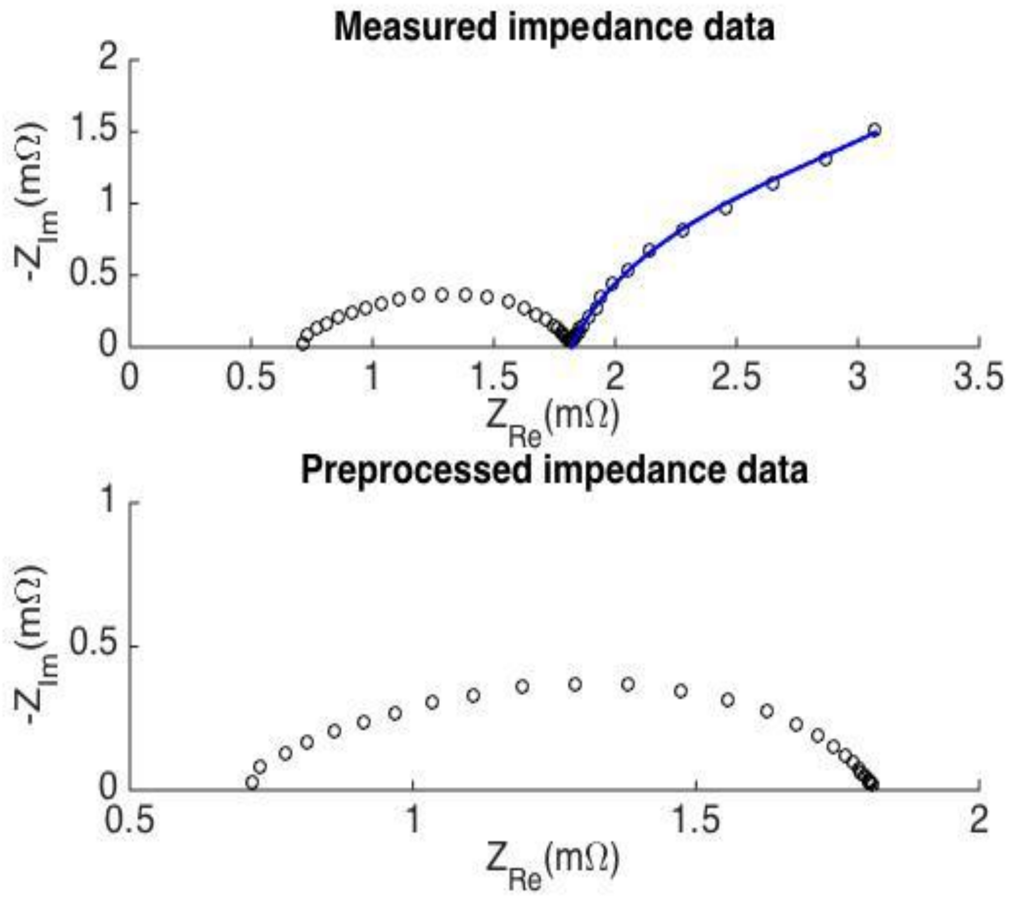

**The EIS data of NCM cells**

Zhou, X., Huang, J., Pan, Z., & Ouyang, M. (2019). Journal of Power Sources, 426, 216-222.

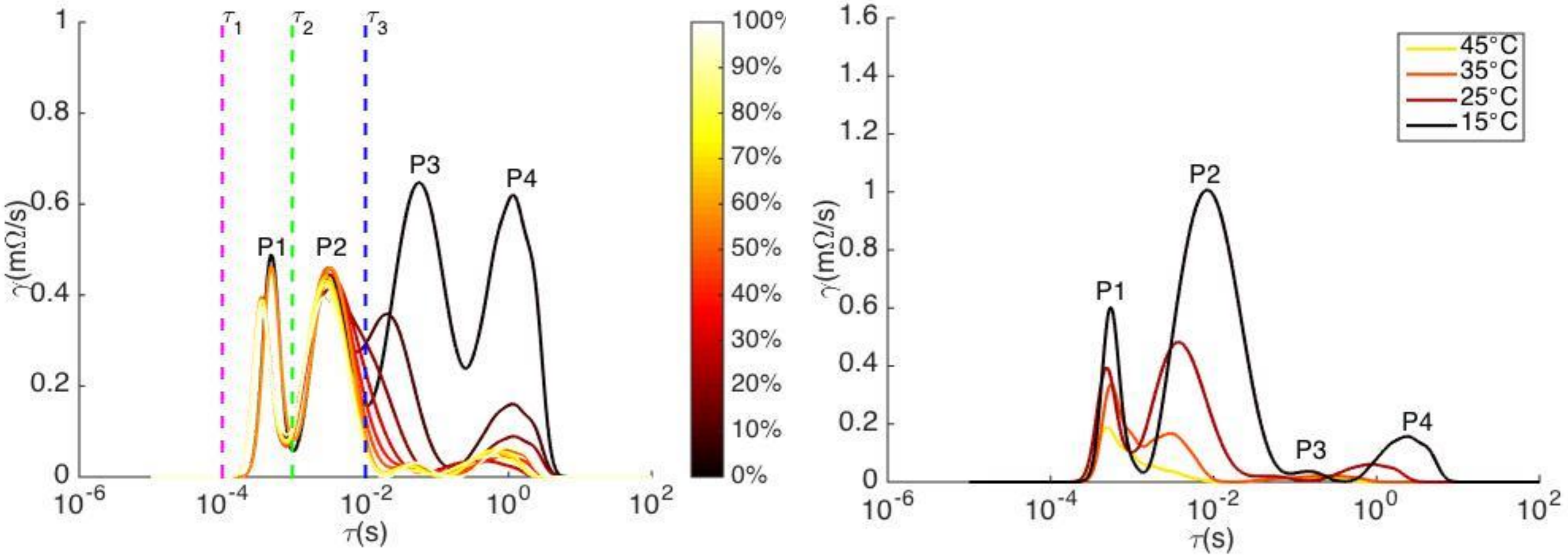
# An example of DRT application

**Preprocessing for the DRT analysis** Subtract the low-frequency diffusion impedance

$$Z(f) = R_O + \int_0^\infty \frac{\gamma(\tau)}{1 + j2\pi f\tau} d\tau + Z_{diff}(f)$$



# An example of DRT application

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# An example of DRT application