A user’s guide to the distribution of relaxation times (DRT)

Concepts for robust application

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Colorado School of Mines

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ARL

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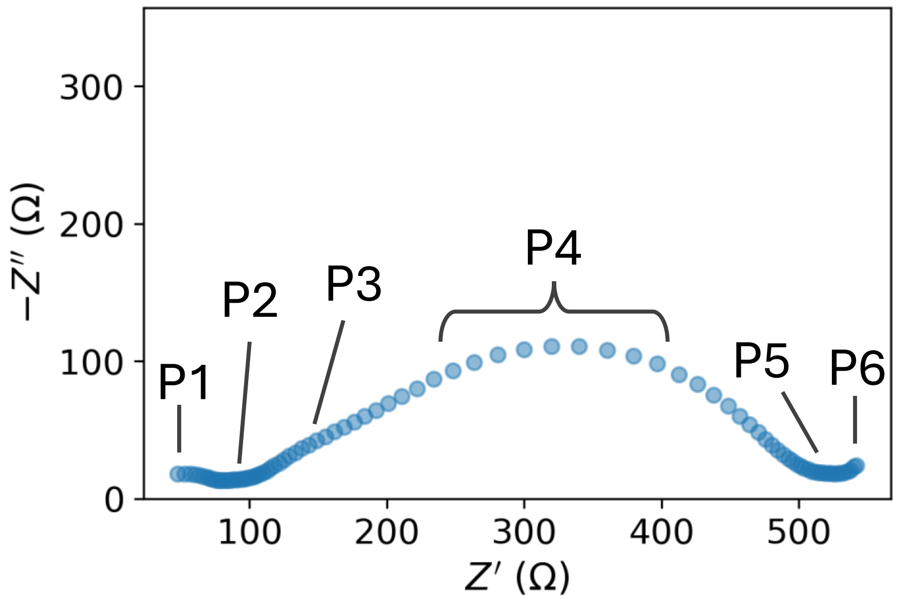
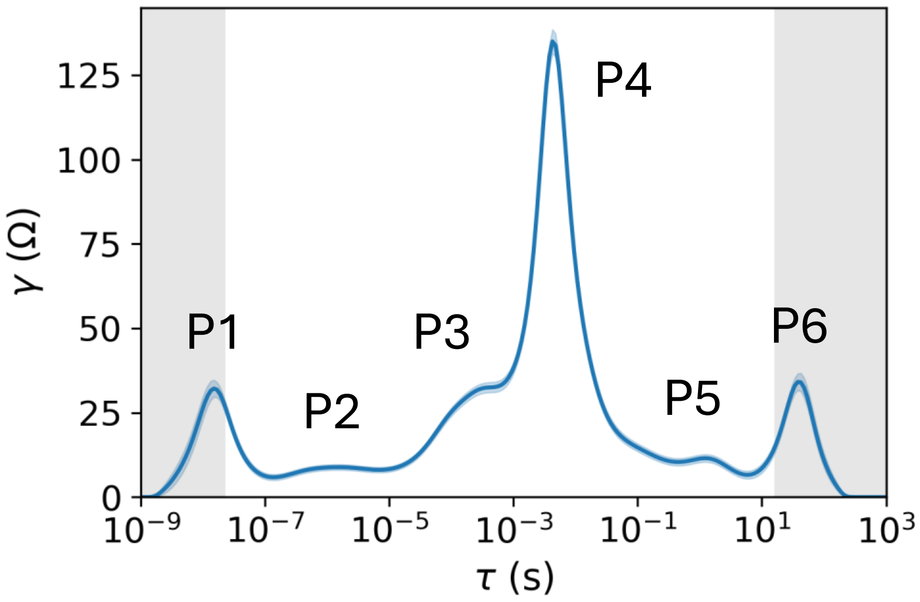
The DRT is a powerful tool for EIS analysis

Versatile: can adapt to virtually any system

Intuitive: clear visualization of time constants





…but there's a lot to understand

What does the DRT really represent?

How does the DRT relate to equivalent circuit models?

Which algorithm should I use?

How should I tune the DRT?

How can I distinguish "real" peaks from "false" peaks?

How can I extract quantitative parameters?

Preview

1. Understanding the DRT concept

2. A light introduction to DRT estimation algorithms

3. Using the DRT

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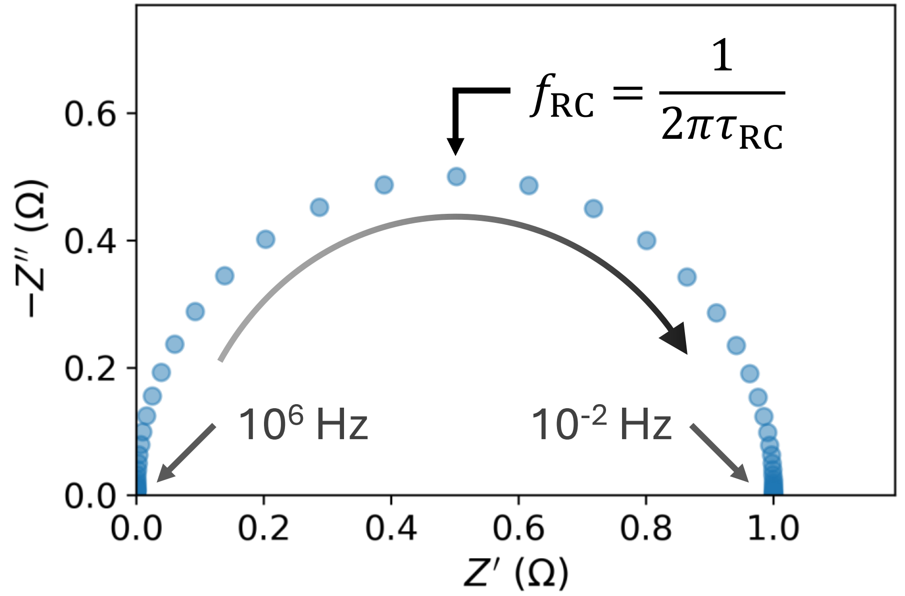
A quick note on terminology

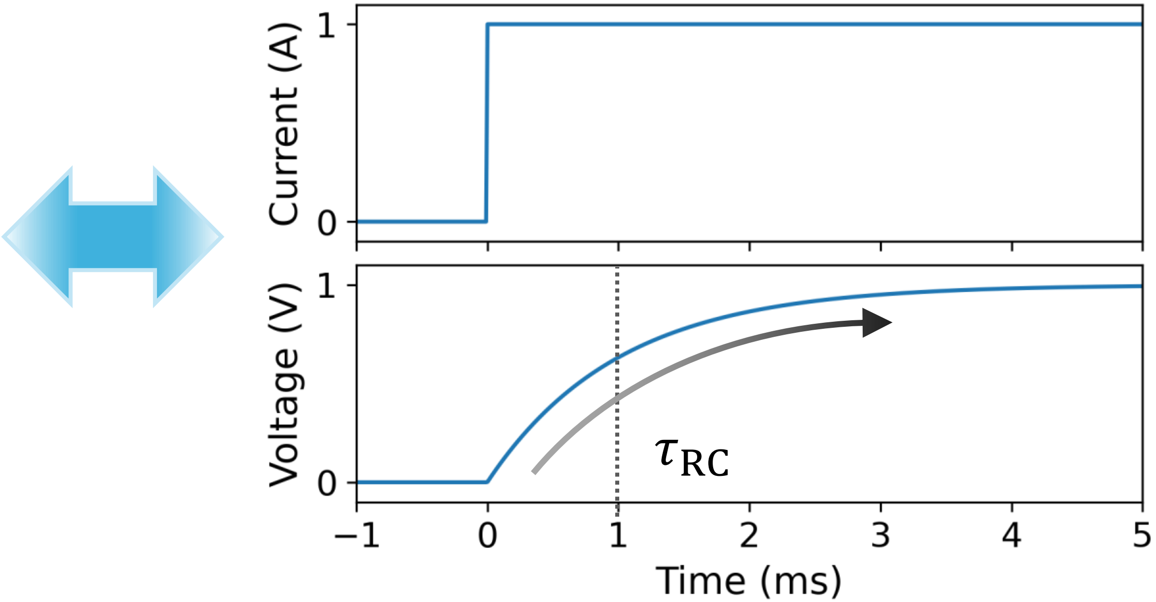
Relaxation: measured electrical signal arising from a *process* in the sample

Process: a physicochemical process, e.g. ion transport, surface reaction

Relaxation: frequency domain



Relaxation: time domain



The DRT concept: what *is* the DRT?

DRT = Distribution of relaxation times

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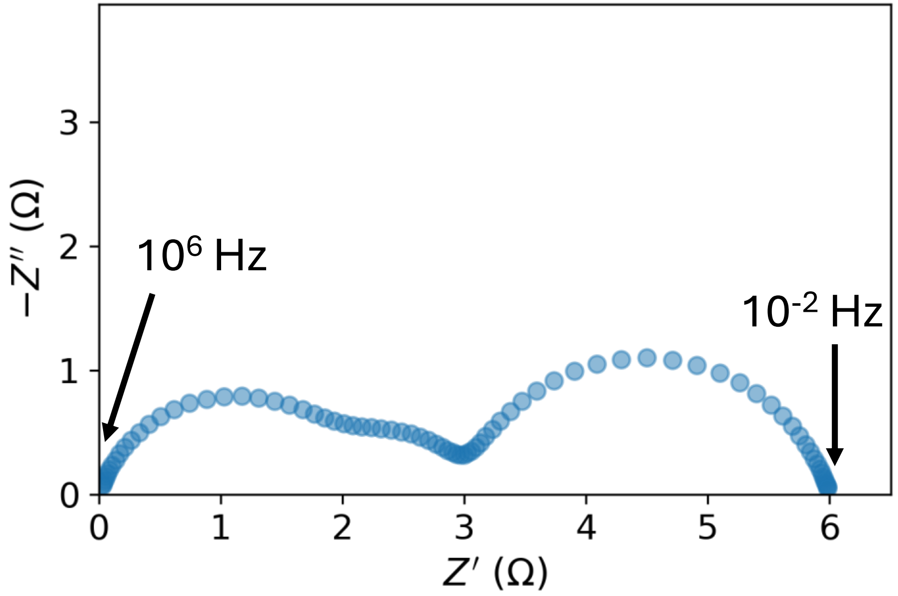
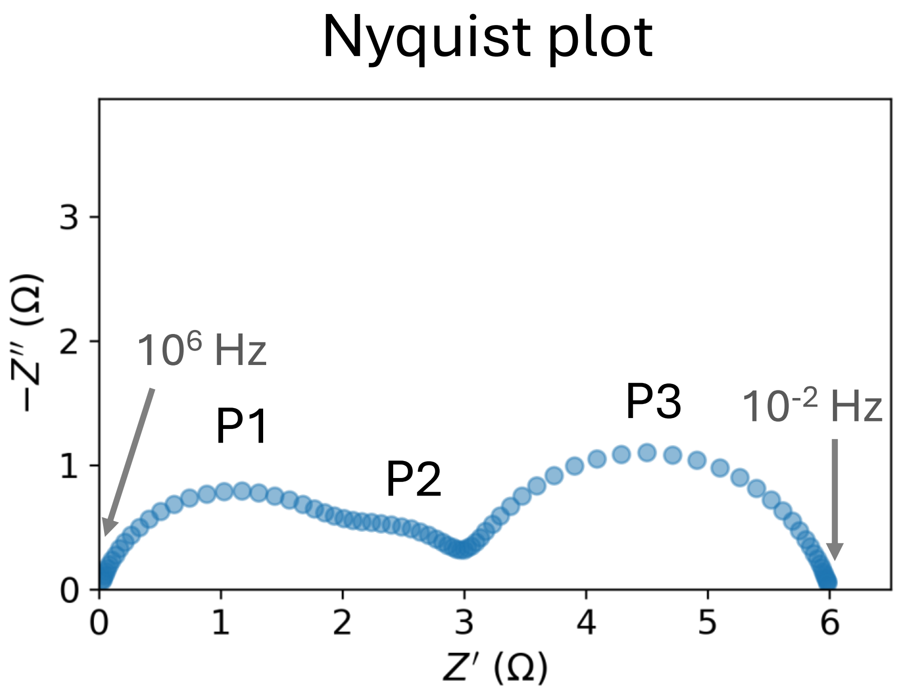
DRT = Distribution of *resistance over relaxation times*

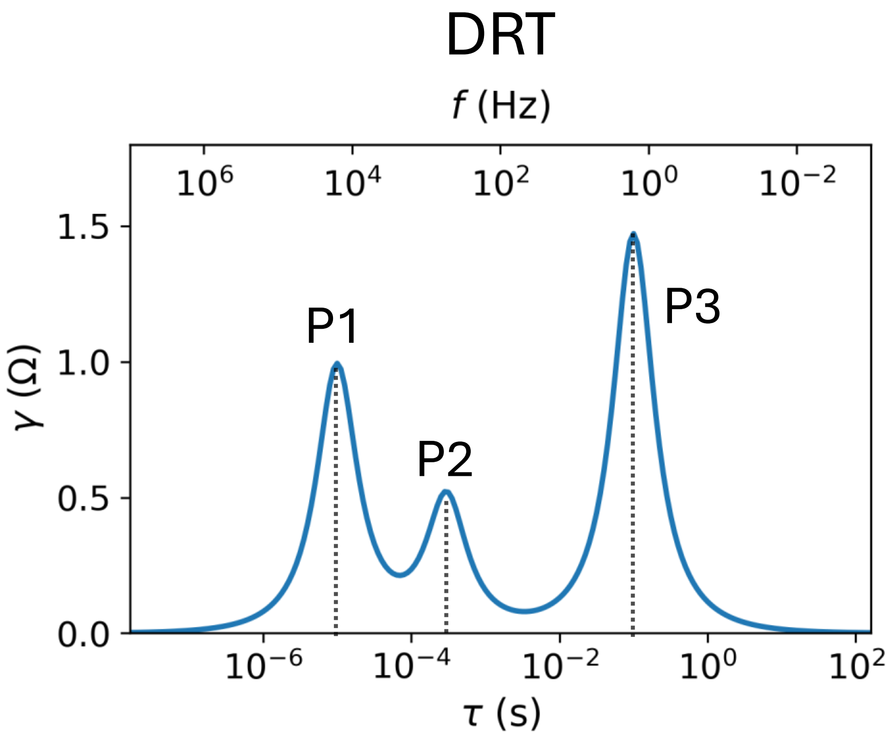
Nyquist plot



The DRT concept: what *is* the DRT?

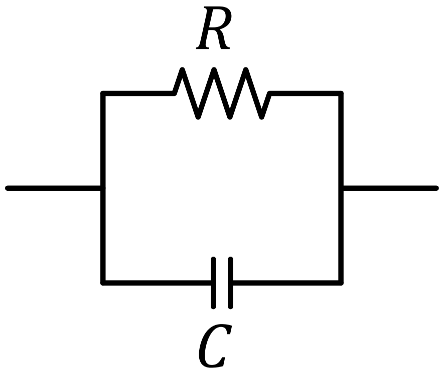
DRT = Distribution of *resistance over relaxation times*





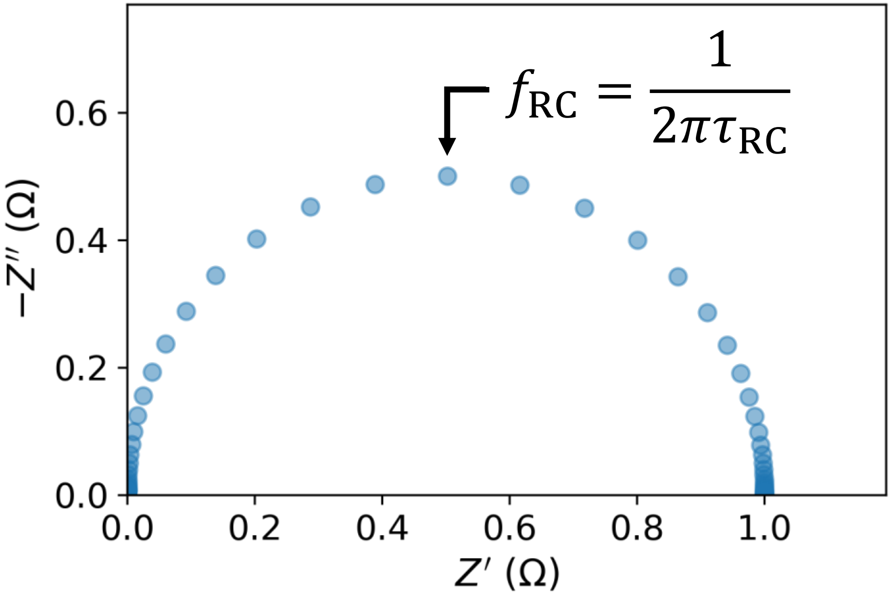
DRT peaks indicate processes with different relaxation times

The RC element is a single peak in the DRT

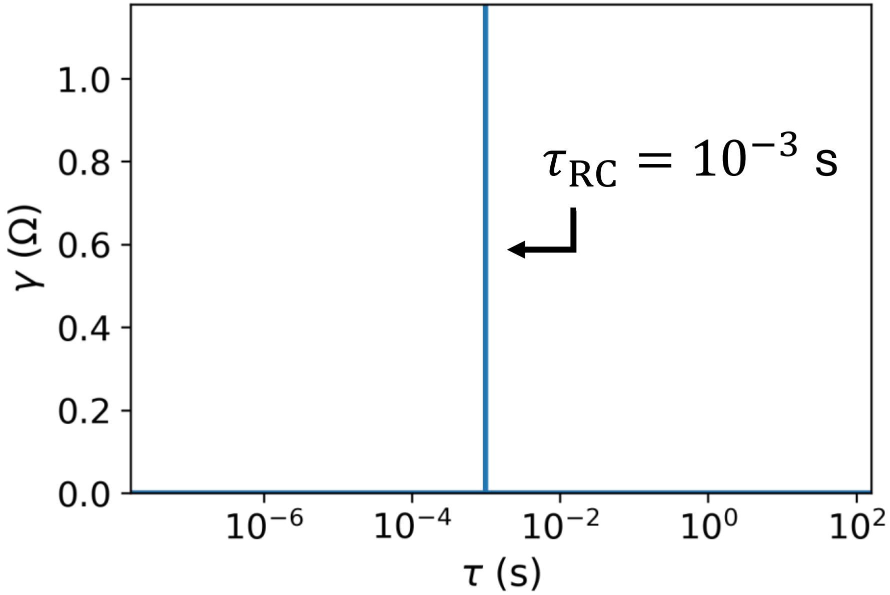


$$\tau_{\mathrm{RC}} = R \cdot C$$

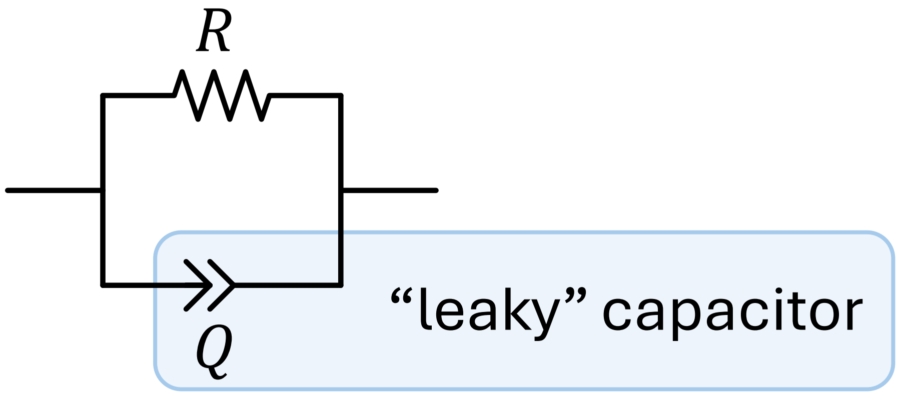
Nyquist



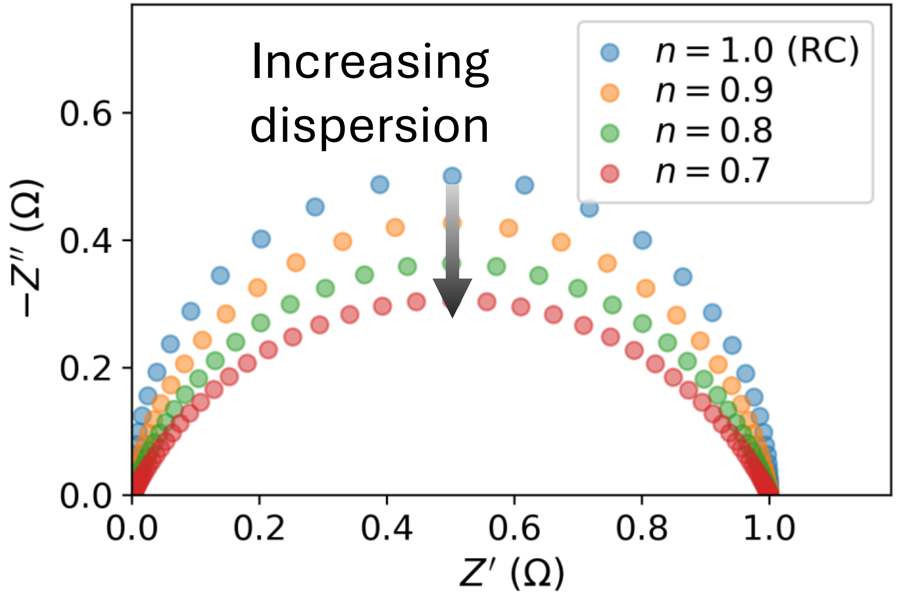
DRT



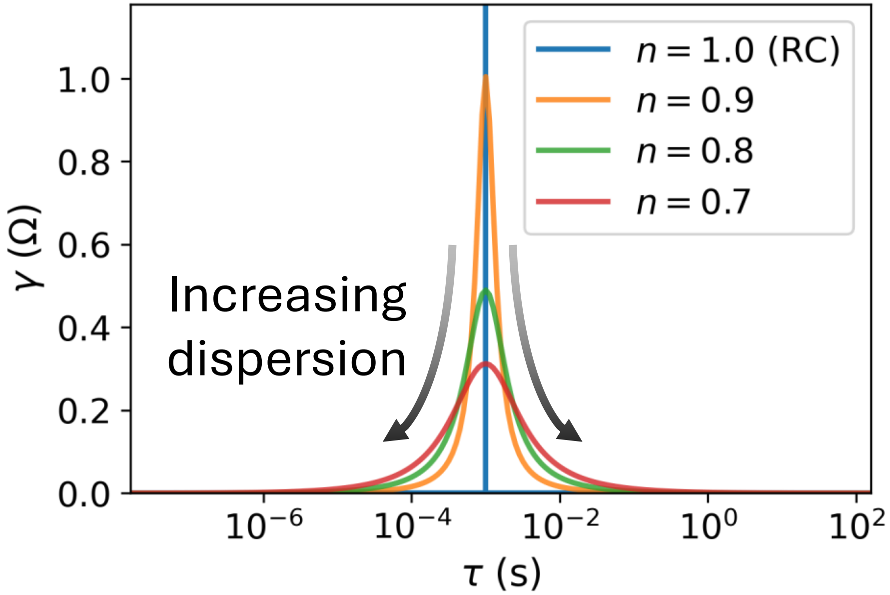
Broad DRT peaks correspond to “depressed” semicircles



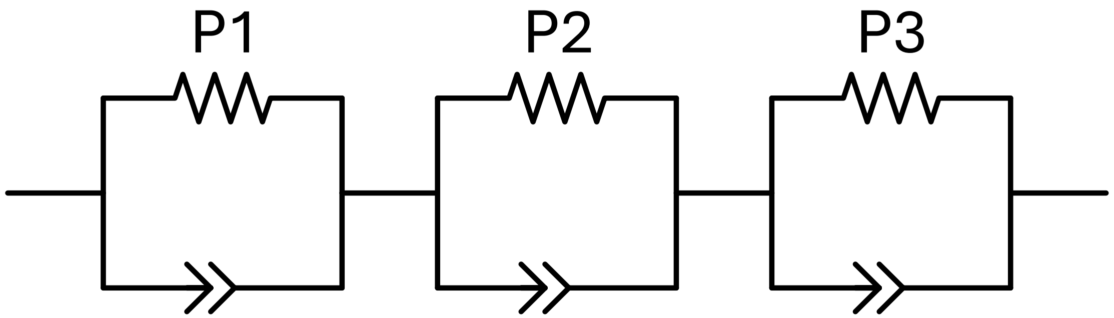
Nyquist



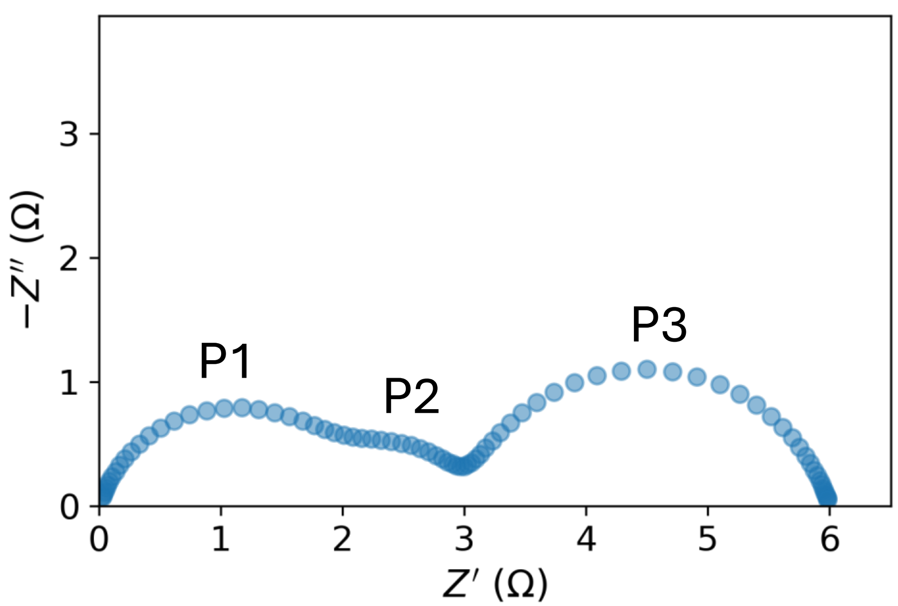
DRT



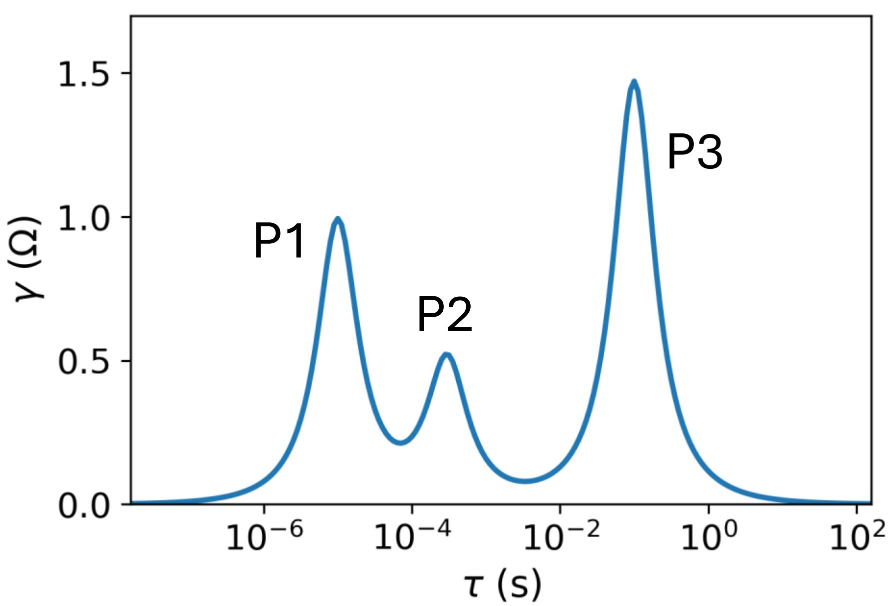
DRT peak area quantifies process resistance



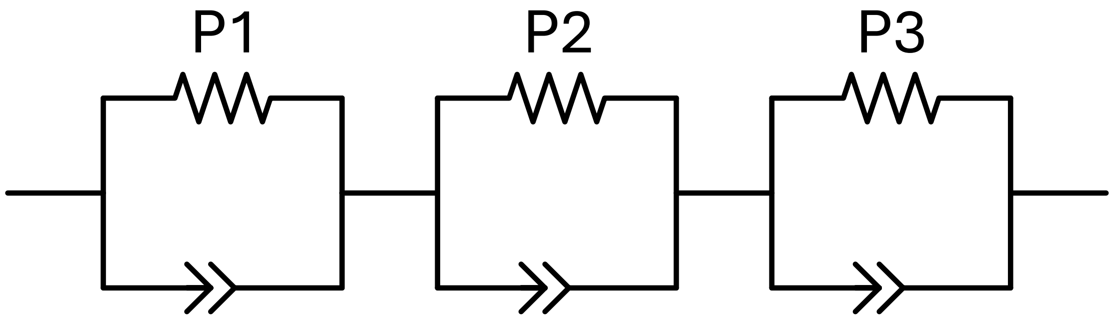
Nyquist



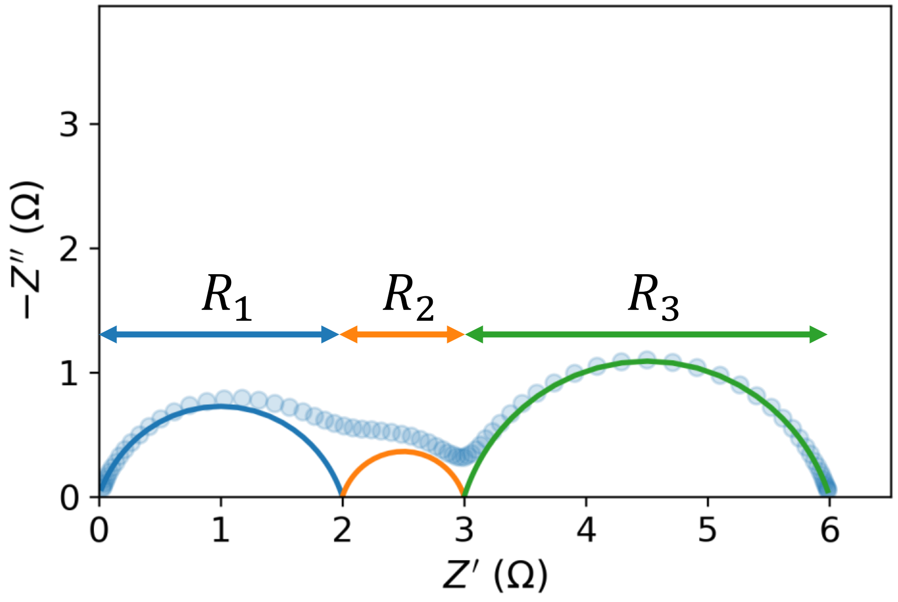
DRT



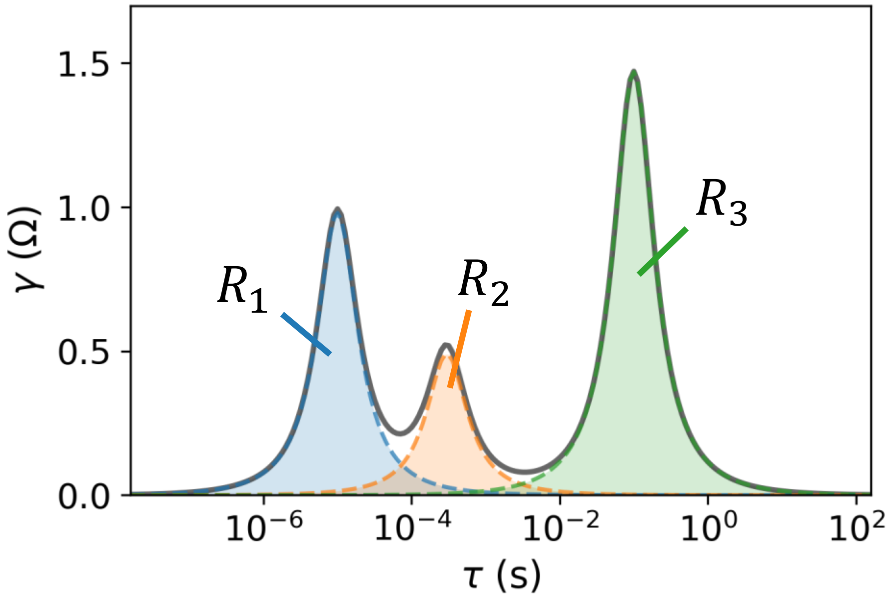
DRT peak area quantifies process resistance



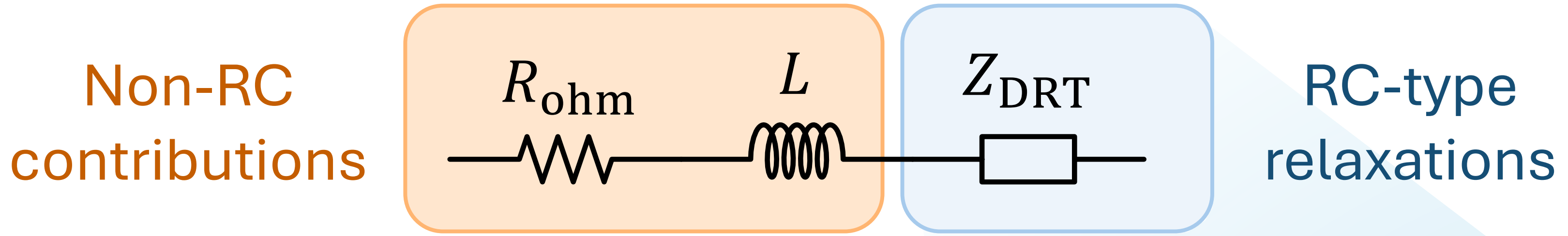
Nyquist

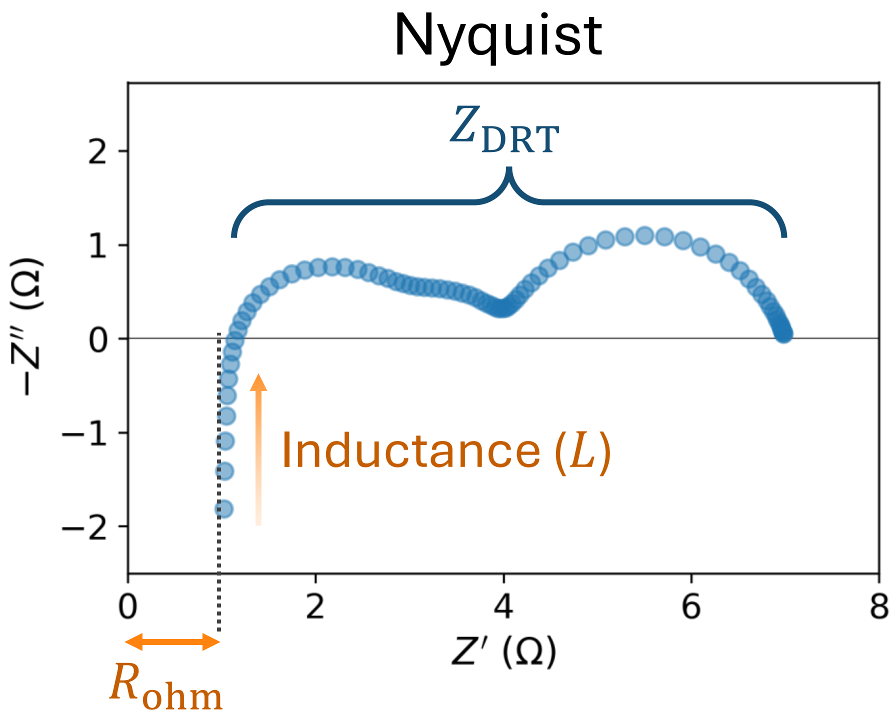


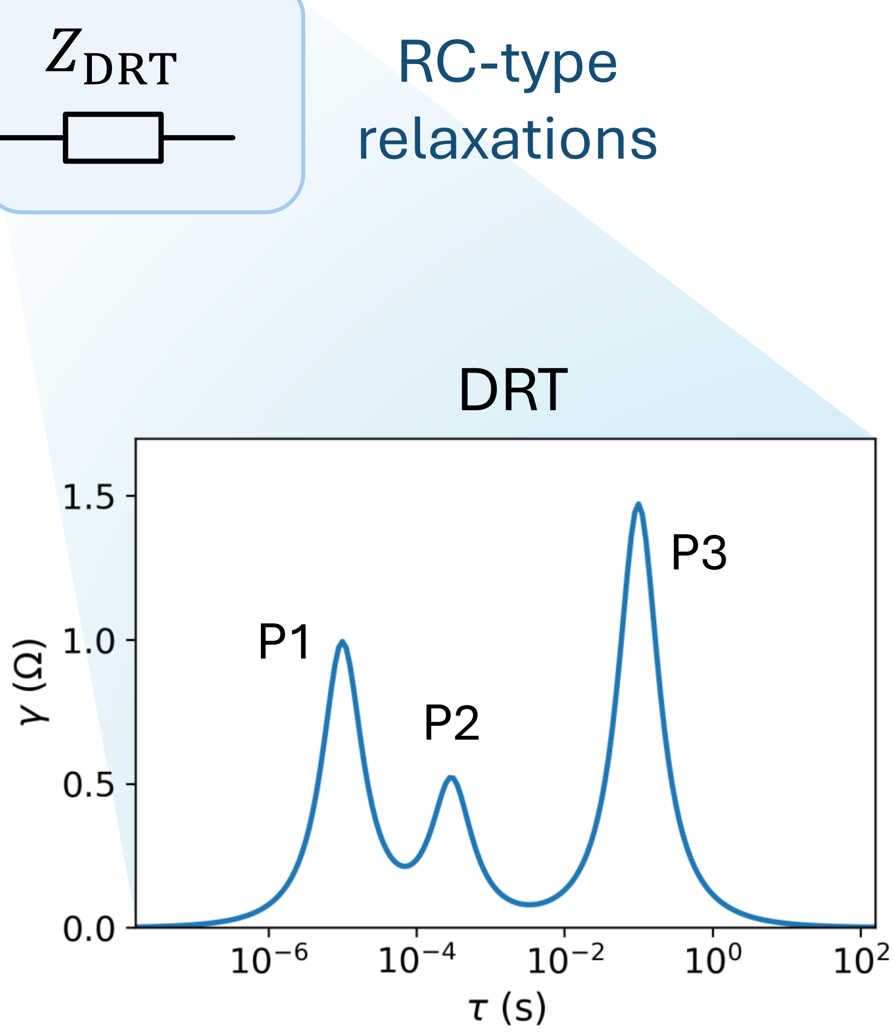
DRT



Series circuit additions account for non-RC phenomena

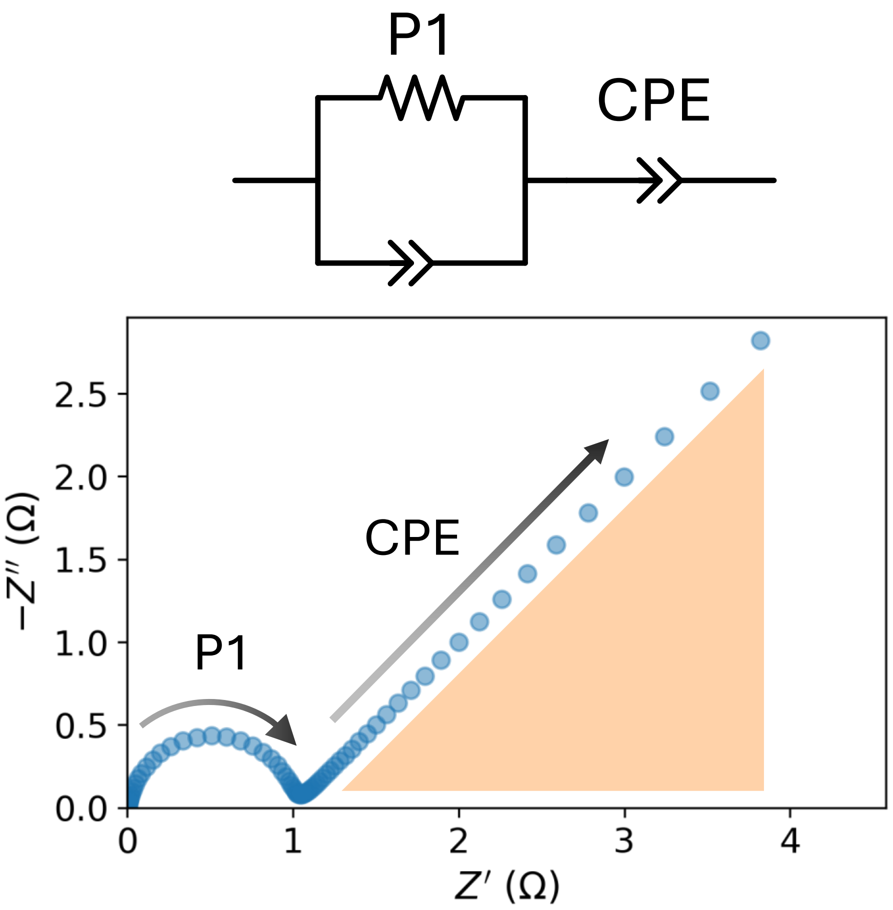




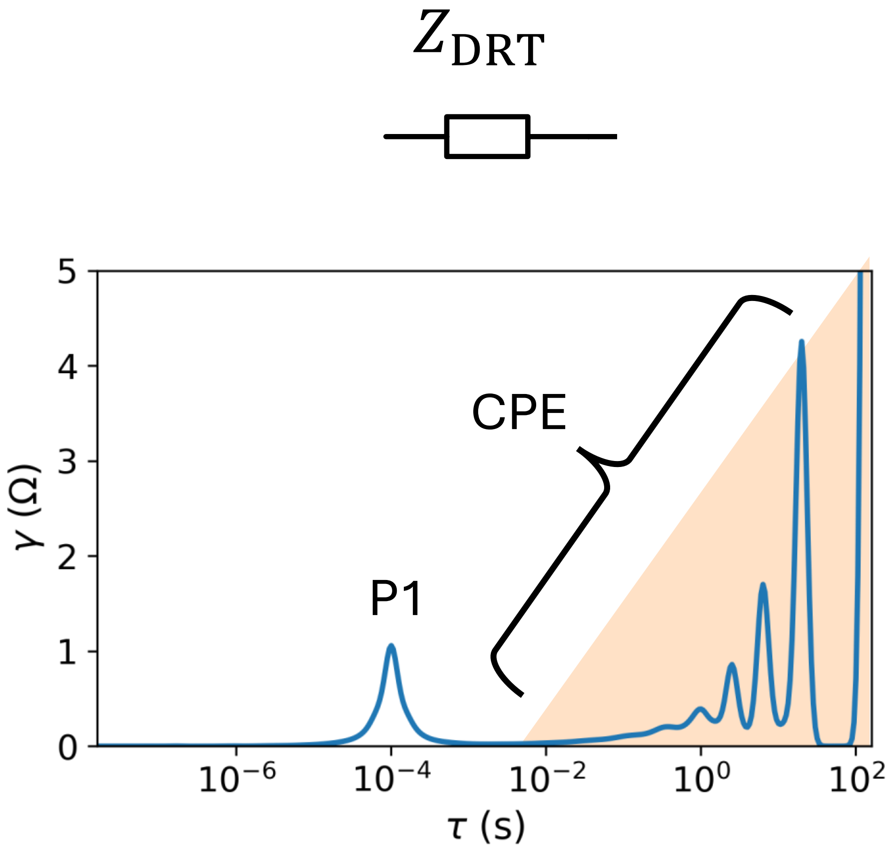


Series additions need to be adapted to the system under study

Model system (diffusion)



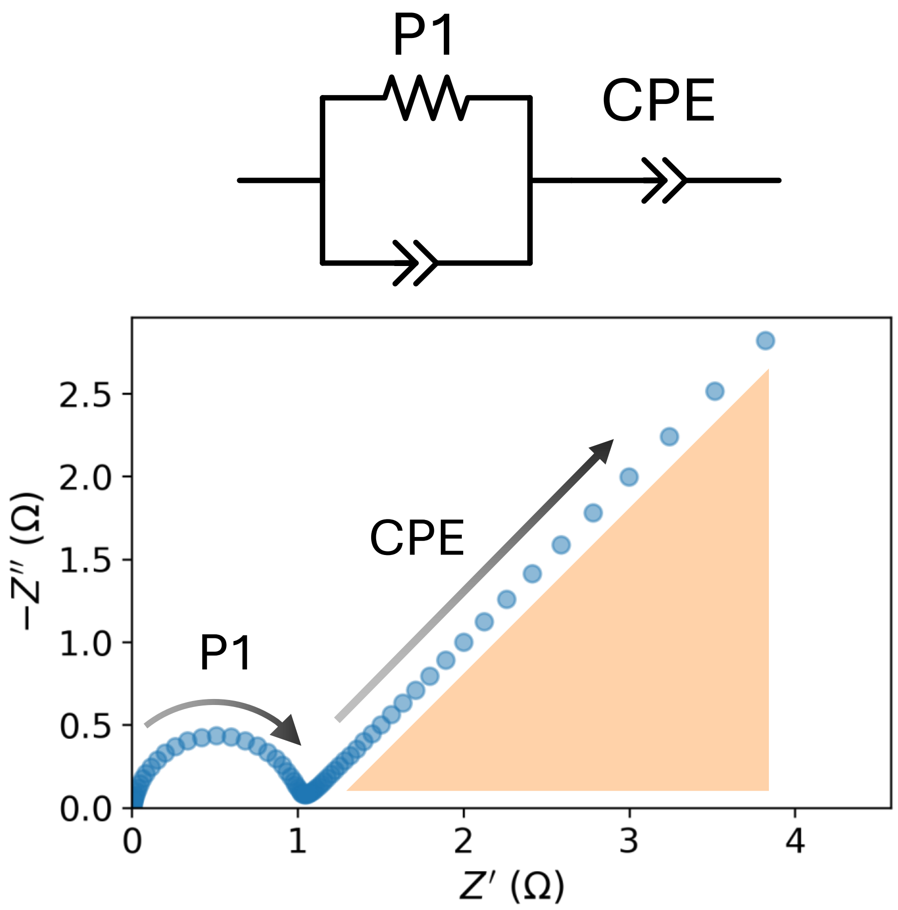
Naïve DRT fit



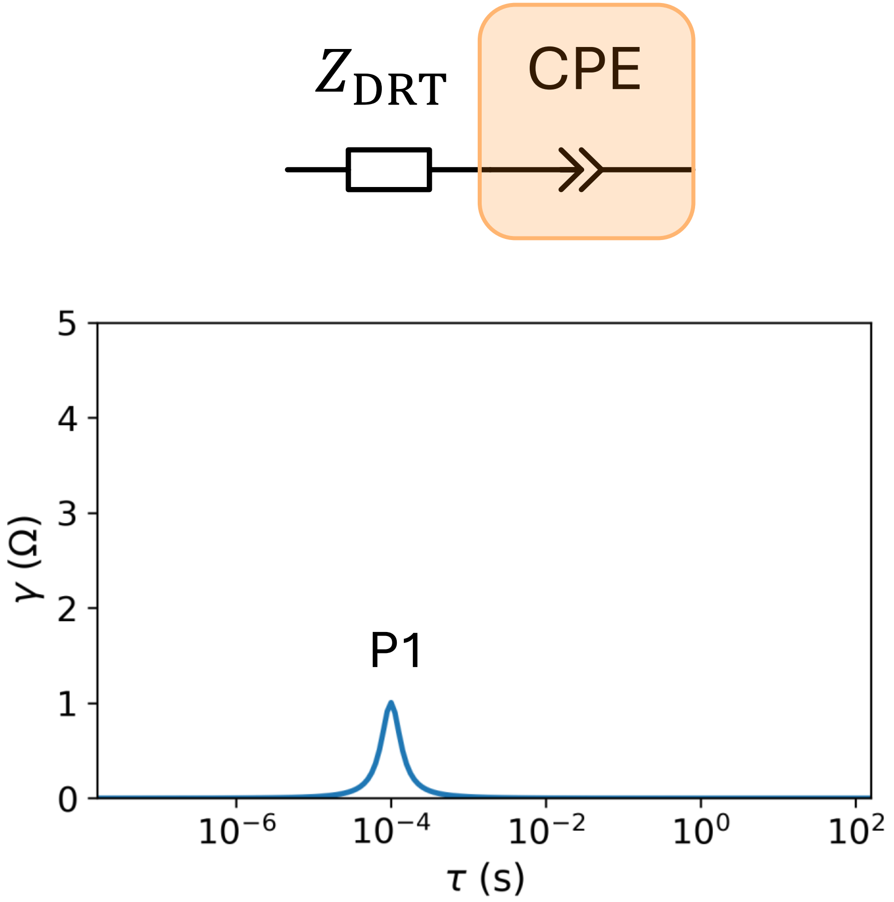
Directly fitting CPE/diffusion impedance perturbs the DRT

Series additions need to be adapted to the system under study

Model system (diffusion)

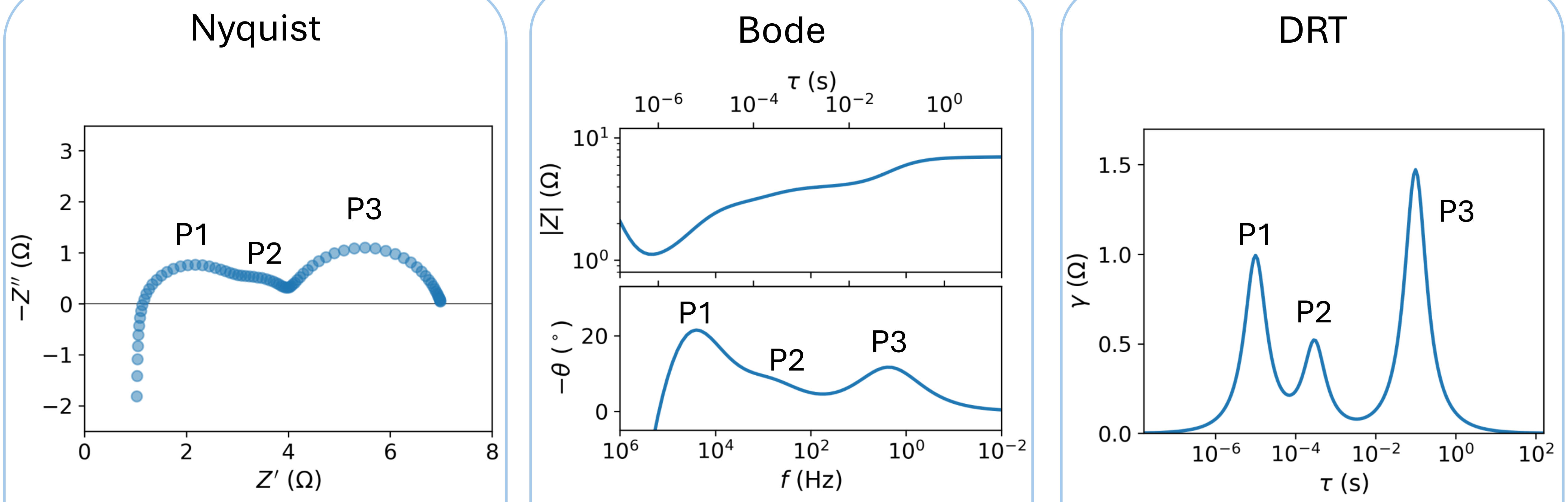


DRT fit with CPE



Incorporating a CPE into the DRT model prevents DRT perturbation

The DRT provides an intuitive visualization of impedance



Nyquist	Bode	DRT
Intuitive	Less intuitive	Intuitive
No frequency info	Frequency info	Frequency info
Relaxations overlap	Less overlap	Least overlap

Summary of key concepts

1. DRT = distribution of RC-type resistance over timescales
2. Common circuit elements (RC, RQ) have exact DRT equivalents
2. Peaks correspond to RC-type processes (Nyquist semicircles)
3. Peak width corresponds to frequency dispersion
4. Peak area = process resistance
5. Non-RC features are fitted with series circuit additions

Advantages

No *a priori* model needed: great for initial analysis, complex systems

Intuitive visualization: clarifies time constants and guides model selection

System-agnostic: good for automated and high-throughput analysis

Misconceptions and limitations

Misconception: The DRT is a **deterministic transformation** of impedance

Reality: DRT transform is **strongly influenced by calculation method**

Misconception: The DRT **“improves resolution”** of spectra

Reality: Reduces visual overlap, but resolution is **determined by data**

Limitation: The DRT is an **empirical** representation of the data

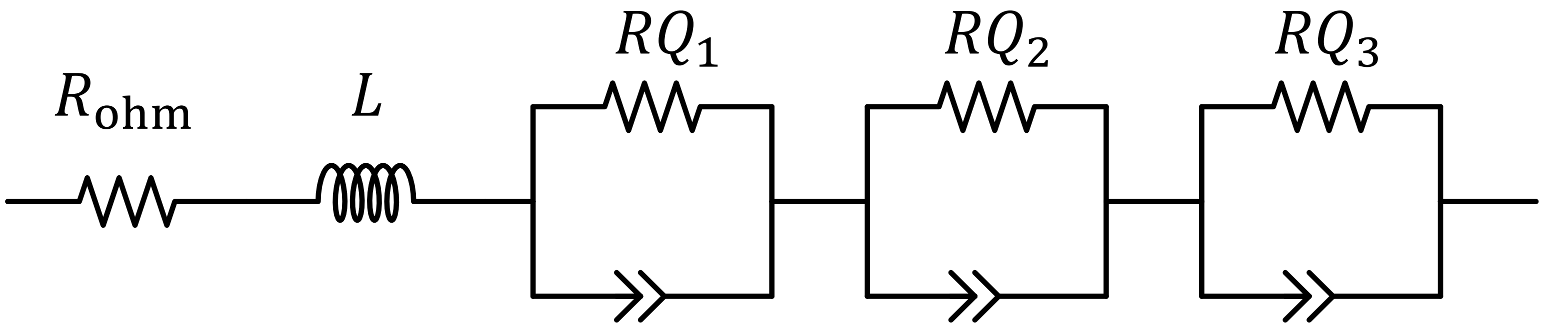
Best practice: **Use domain knowledge** to reasonably interpret the DRT

1. Understanding the DRT concept

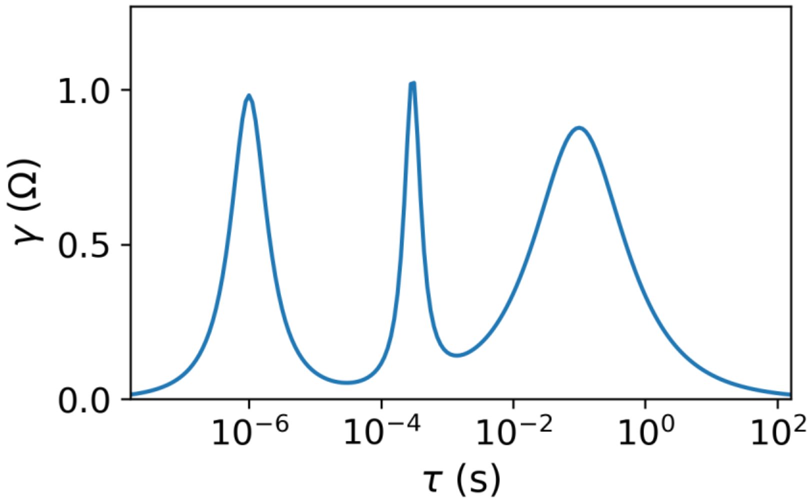
2. A light introduction to DRT estimation algorithms

3. Using the DRT

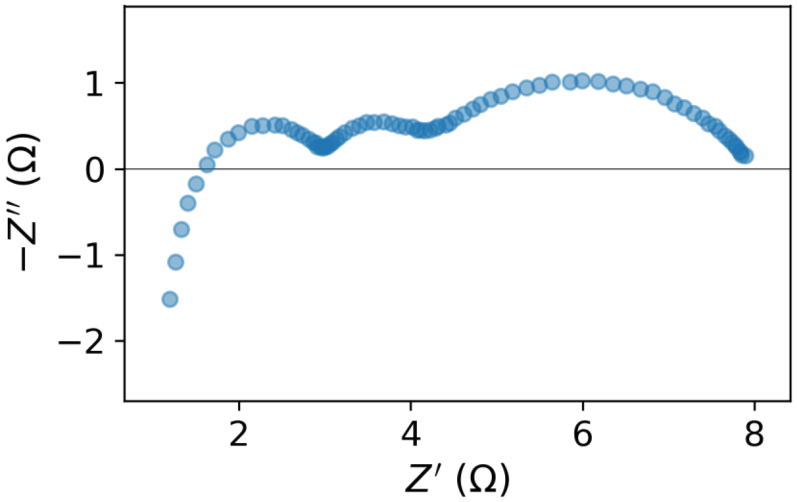
Circuit model for fitting illustration



Exact DRT



Noisy impedance



The DRT must be numerically estimated

$$\boxed{Z_{\mathrm{DRT}}(\omega)} = \int_{-\infty}^{\infty} \boxed{\gamma(\ln\tau)} \cdot \frac{1}{1 + j\omega\tau} \, \mathrm{d}\ln\tau$$

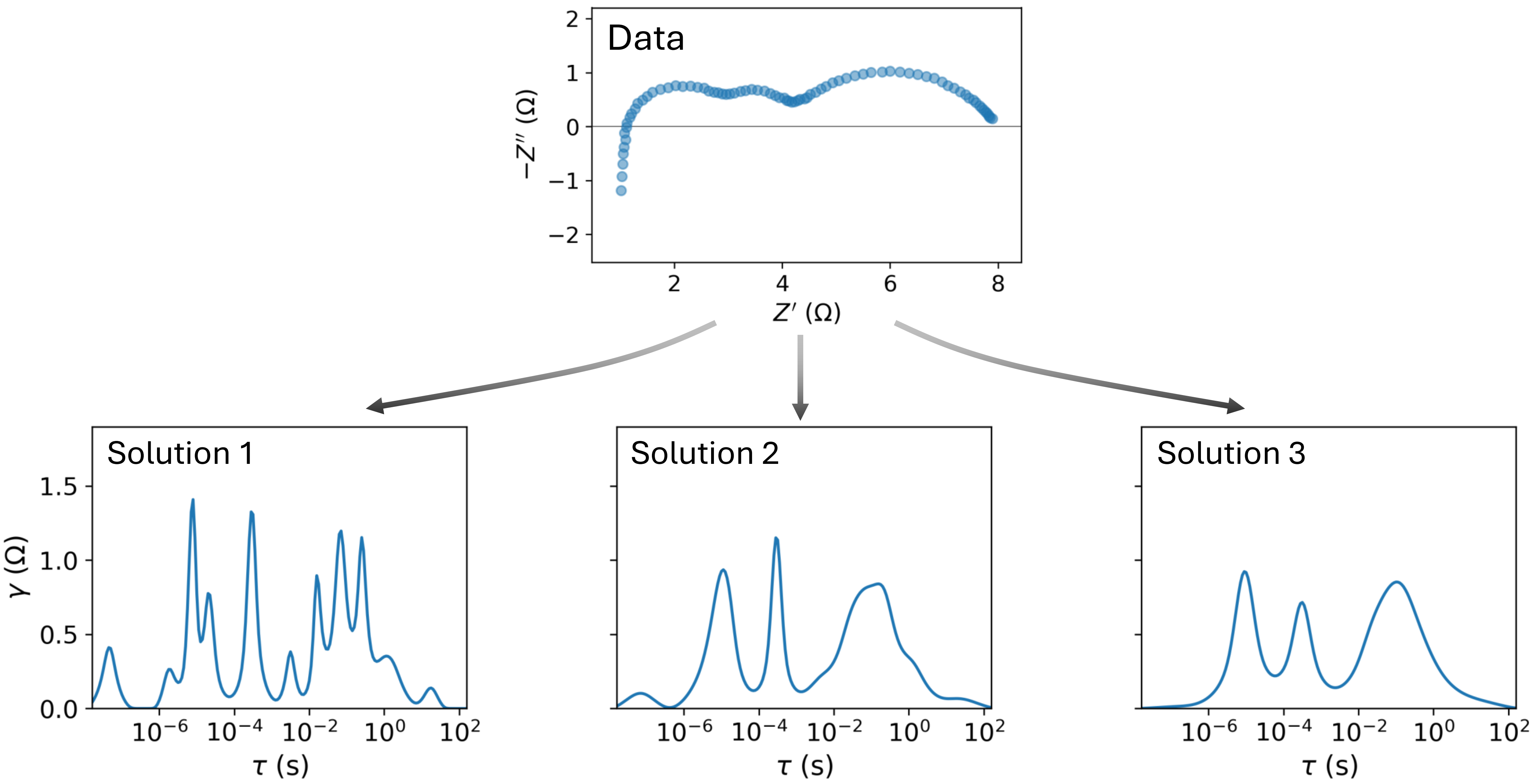
"Ill-posed inversion"

Measured spectrum $Z(\omega)$

$\gamma(\ln\tau)$ Unknown DRT

Deterministic (analytical)

Ill-posed inversion: many possible solutions



How do we find the “right” solution?

How do we find a reasonable solution?

- Fourier transform
- Penalized regression
- Discrete parametric
- Machine learning

Occam's razor: "simpler is better"

How do we find a reasonable solution?

Fourier transform

Penalized regression

Discrete parametric

Machine learning

Occam's razor: "simpler is better"

A general framework for DRT algorithms

1. **Representation**: how do we represent (approximate) the DRT?

2. **Complexity control**: how do we define a “reasonable” solution?

3. **Objective function**: how do we balance simplicity with goodness of fit?

4. **Optimization**: how do we find the optimum of the objective function?

Surya Effendy *et al.*, 2020. *J. Electrochem. Soc. 167*, 106508.

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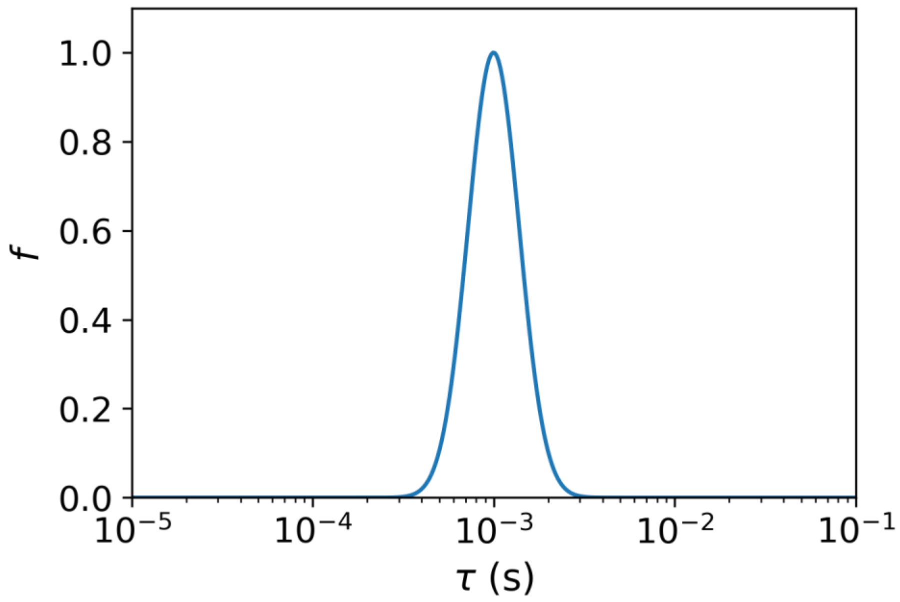
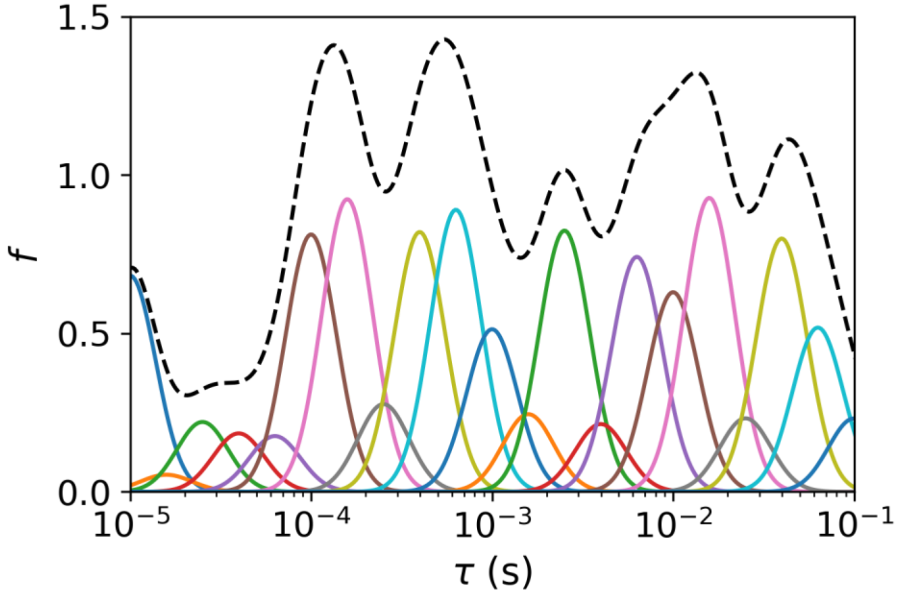
Surya Effendy *et al.*, 2020. *J. Electrochem. Soc.* **167,** 106508.

Representation: linear combination of basis functions

Radial basis function (RBF)



Linear combination of RBFs



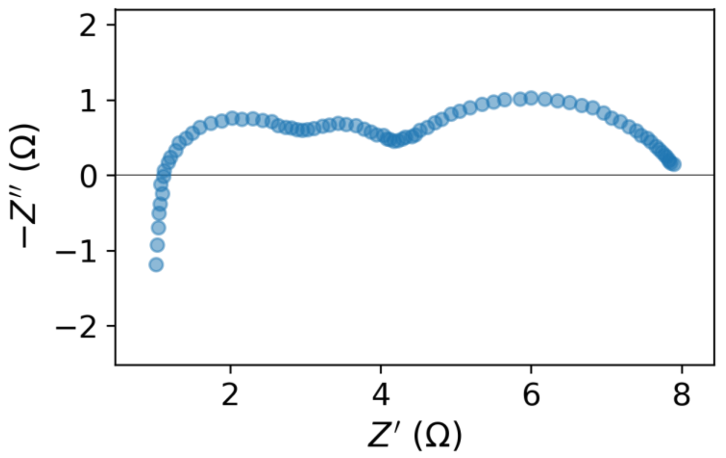
$$\gamma_{\mathrm{model}}(\ln \tau) = \sum_{i=1}^{M} \boxed{x_i} \cdot \boxed{\phi_i(\ln \tau)}$$

Magnitude

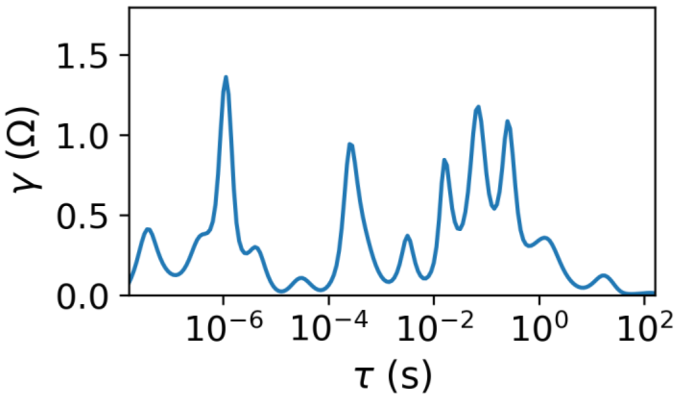
RBF at τ_i

Complexity control: quantifying simplicity/complexity

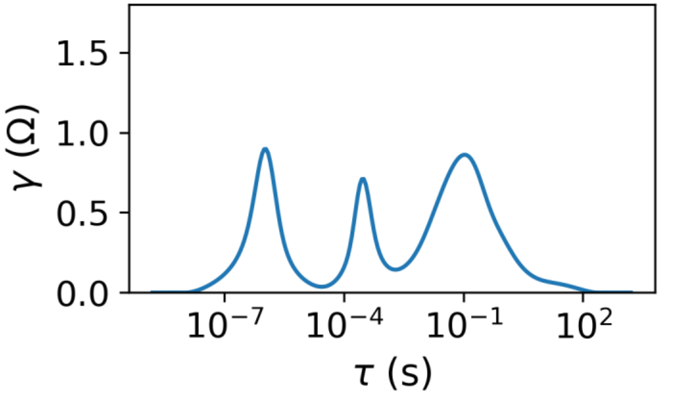
Data



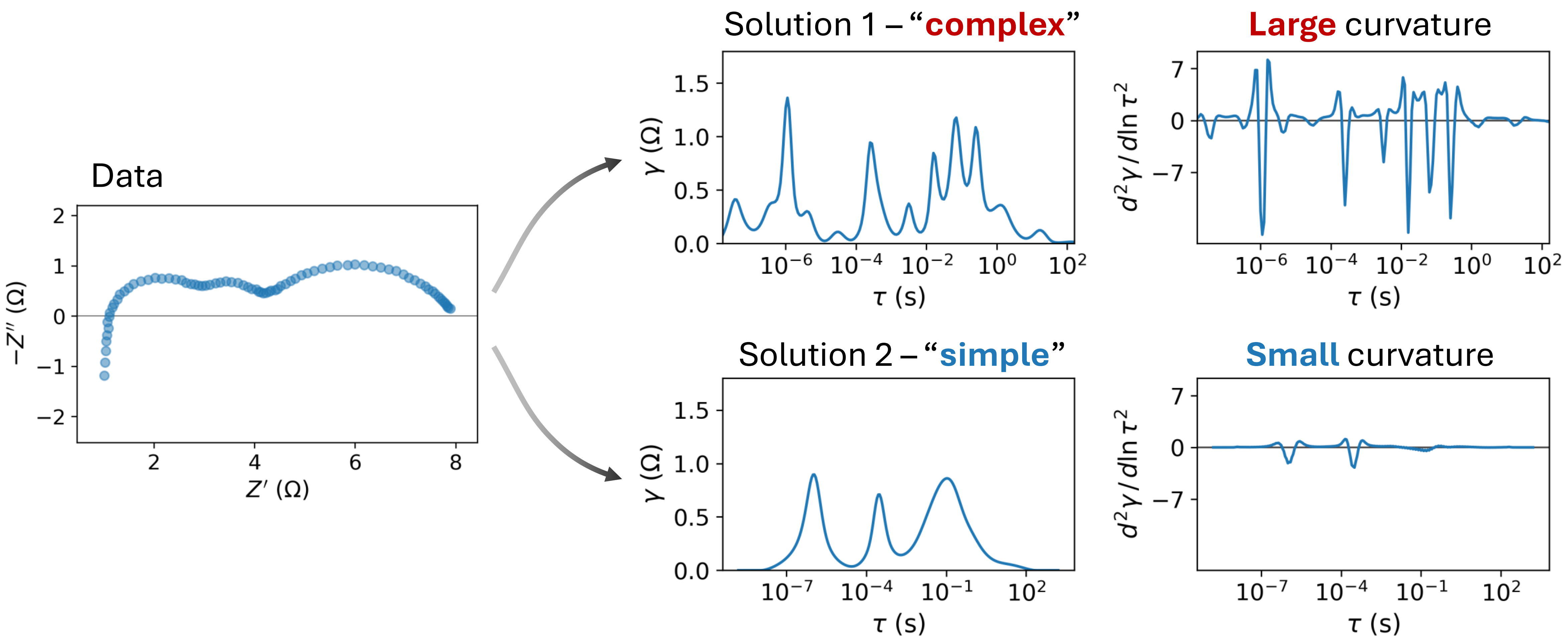
Solution 1 – "**complex**"



Solution 2 – "**simple**"



Complexity control: quantifying simplicity/complexity



Simpler solutions should have smaller curvature

Objective function: balancing simplicity with the data

Minimize $\mathbb{C}$ to find a balanced solution:

$$\mathbb{C} = \underbrace{\sum_{i=1}^{N} w_i \cdot \left|Z_{\mathrm{model},i} - Z_{\mathrm{meas},i}\right|^2}_{\text{Sum of squared errors}} + \underbrace{\lambda}_{\text{Penalty strength}} \cdot \underbrace{\int_{-\infty}^{\infty} \left(\frac{d^2\gamma}{d\ln\tau^2}\right)^2 d\ln\tau}_{\text{Curvature penalty}}$$

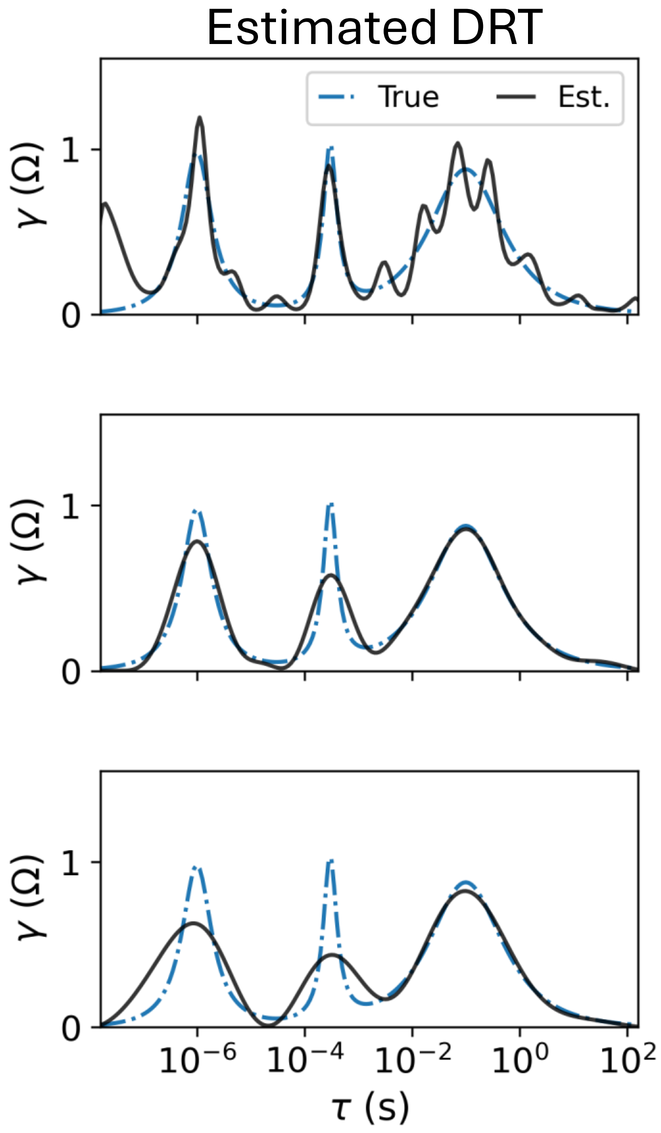
λ determines the tradeoff between fit error and simplicity

Objective function: balancing simplicity with the data

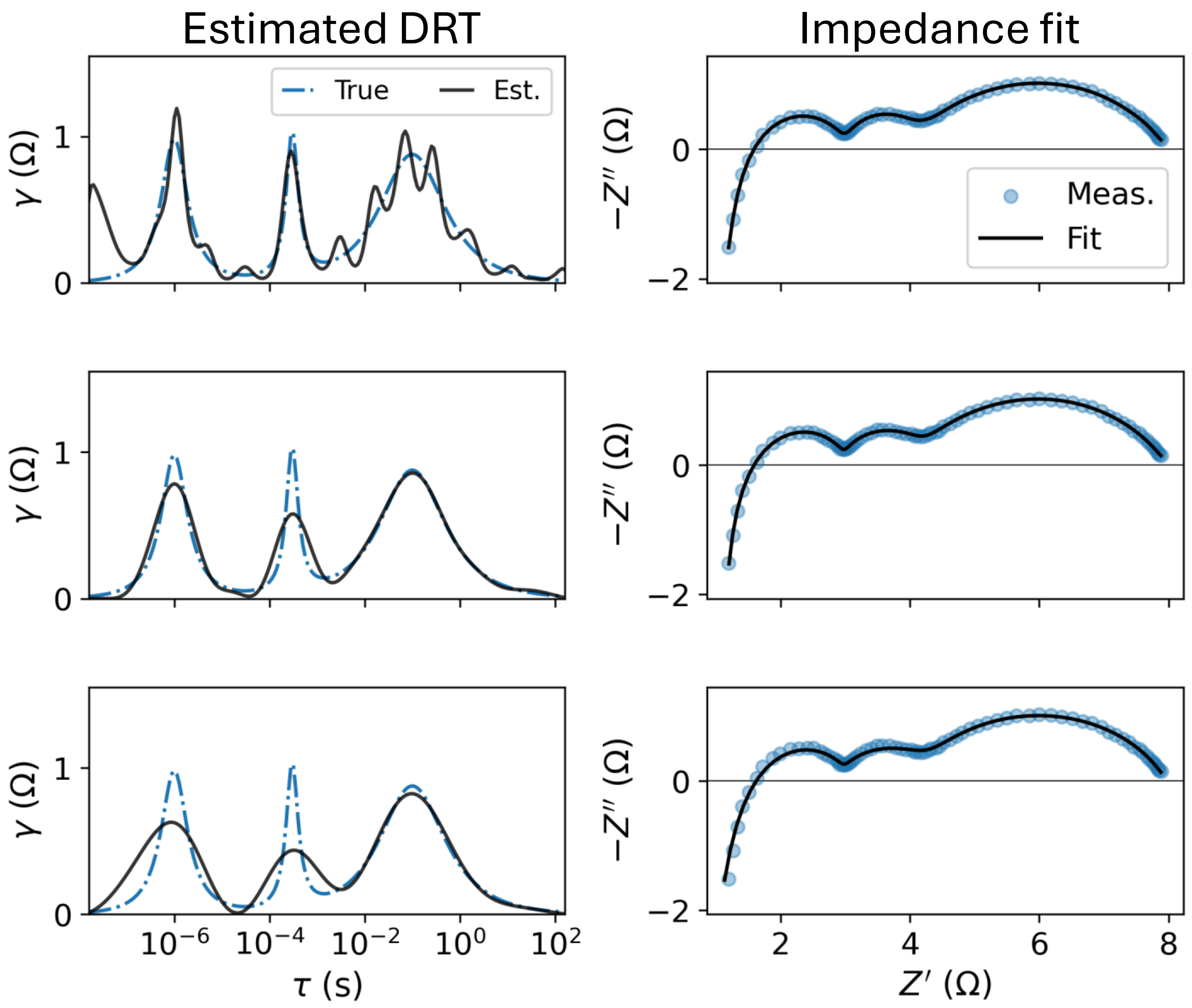
No penalty

Moderate penalty strength

High penalty strength



Objective function: balancing simplicity with the data



No penalty — Over-fitted

Moderate penalty strength — Well-fitted

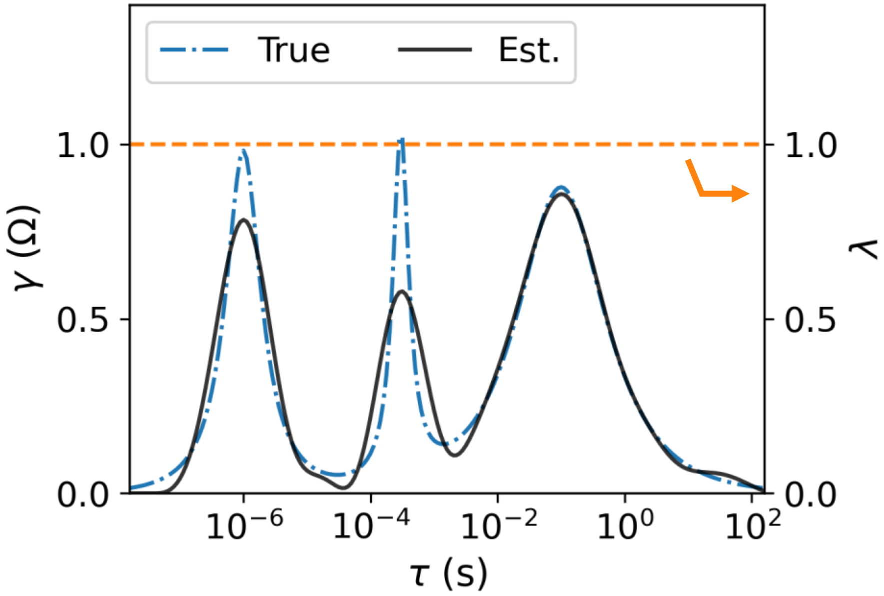
High penalty strength — Under-fitted

Hierarchical Bayesian models: more flexibility

Ridge regression

"The DRT should be *uniformly* smooth"

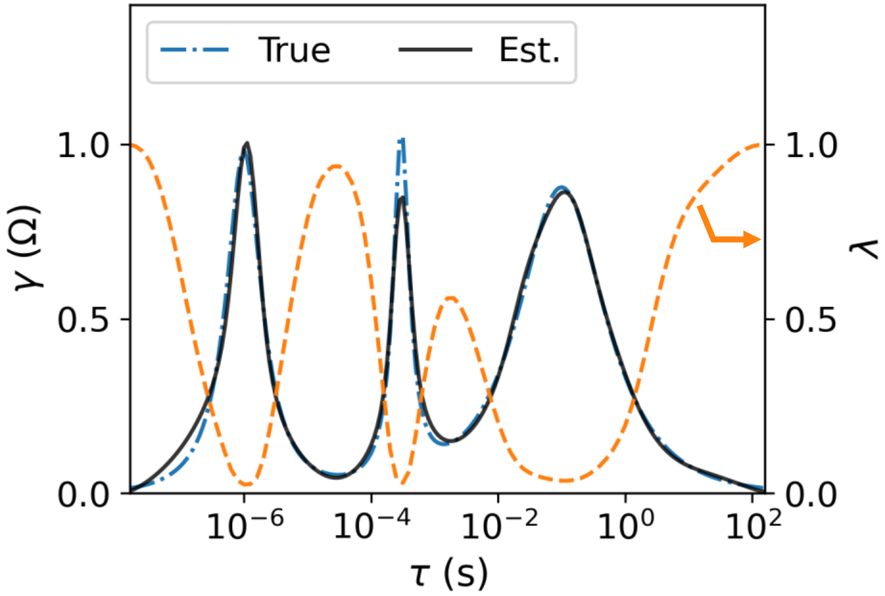
Uniform penalty: $\lambda = \text{constant}$



Hierarchical ridge regression

"The DRT should *generally* be smooth"

Variable penalty: $\lambda = \lambda(\ln \tau)$



Tuning: finding the right balance

How do we select a suitable penalty for experimental data?

- Manual tuning
- Cross-validation
- Automatic tuning (Bayesian)

Apply metrics to define the optimal balance

Summary of key concepts

1. Many DRT solutions are possible for a single spectrum
2. DRT algorithms use Occam's razor to find a reasonable solution
3. DRT complexity can be quantified by curvature
4. The objective function balances simplicity with goodness of fit
5. Tuning is necessary to find the right balance

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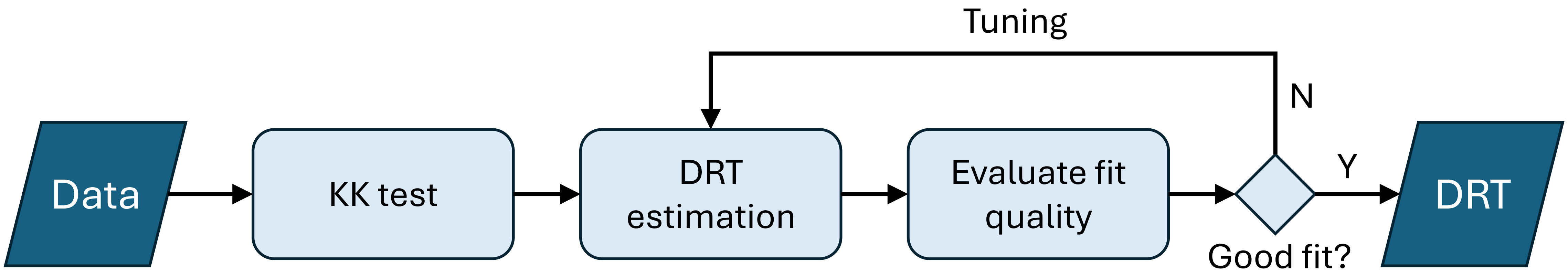
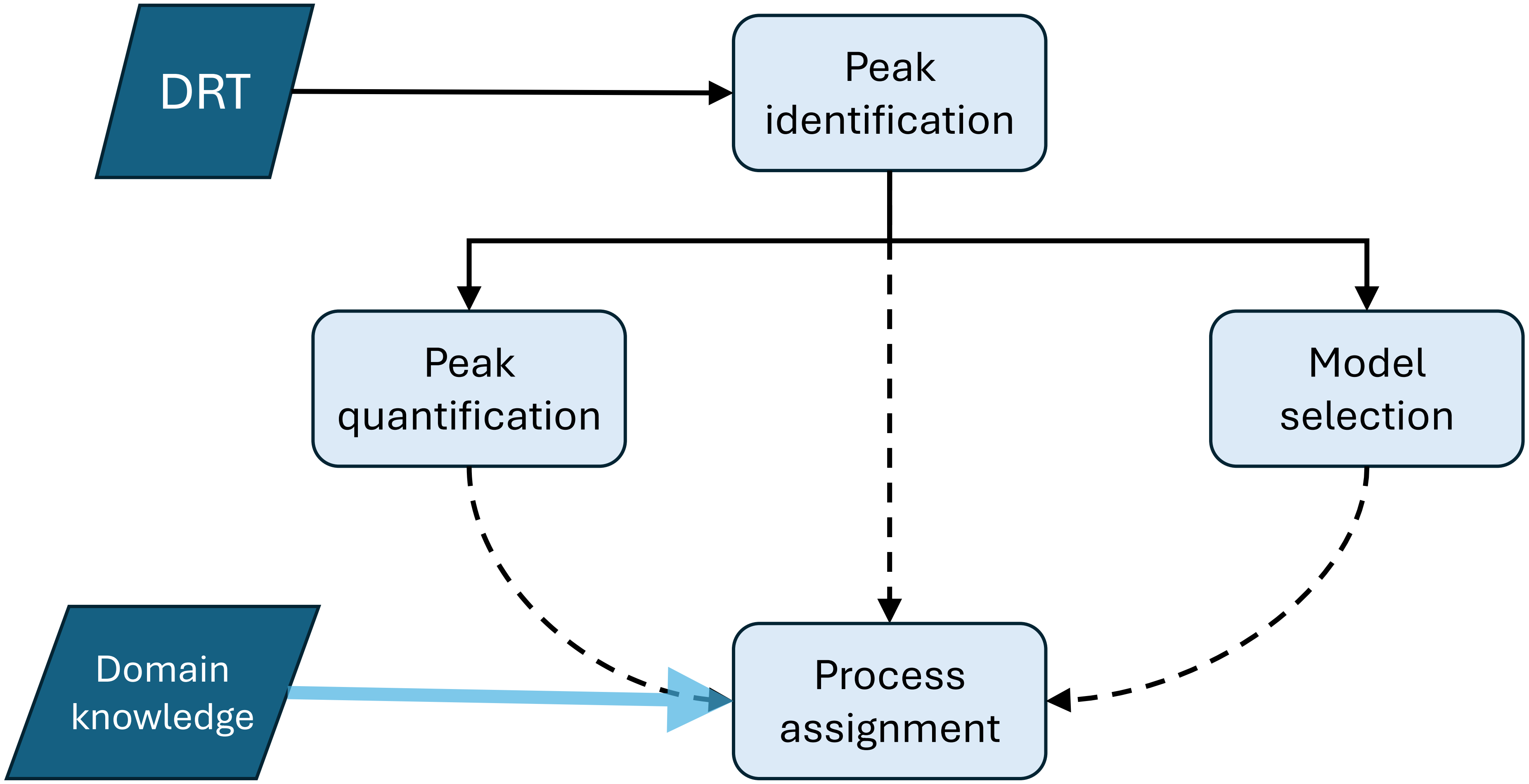
A DRT workflow: fitting



Software demo (I)

A DRT workflow: analysis



Software demo (II)

Summary of key concepts

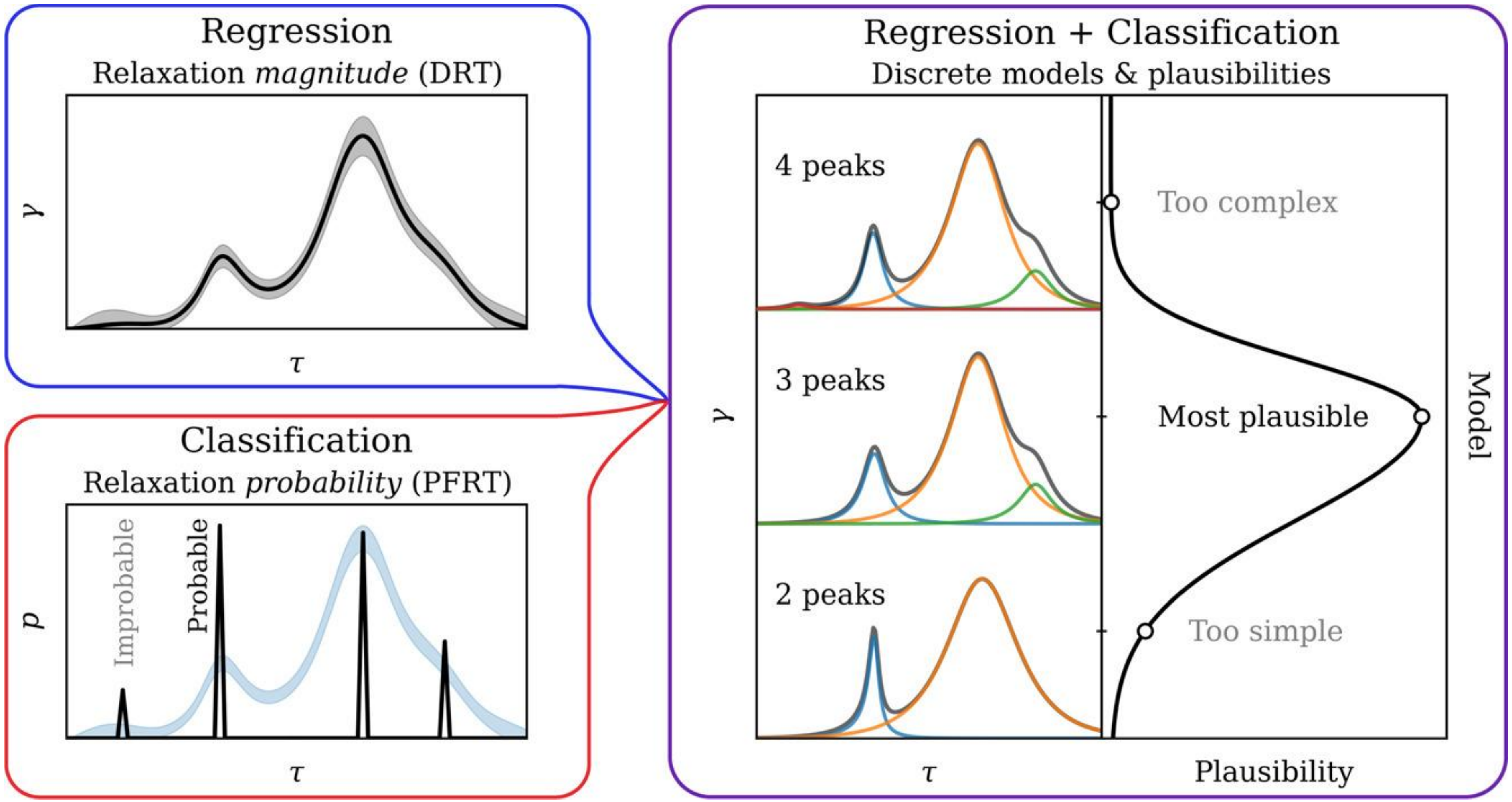
1. Start by checking data validity (KK test)
2. Tune the DRT using a reproducible procedure
3. Always check the impedance reconstruction (and residuals)
4. Beware of false peaks
5. Be aware of frequency bounds and series additions (e.g. ohmic resistance)

Setting up for success: experimental best practices

1. Ensure that valid, high-fidelity spectra are collected
    1. Linear, stable, KK-compliant
    2. Maximize signal-to-noise ratio
    3. Measure relevant frequency range
2. Measure spectra under multiple conditions to aid interpretation
    1. E.g.: vs. temperature, partial pressure, DC voltage/current
    2. Observe DRT variations with respect to conditions

Closing thoughts

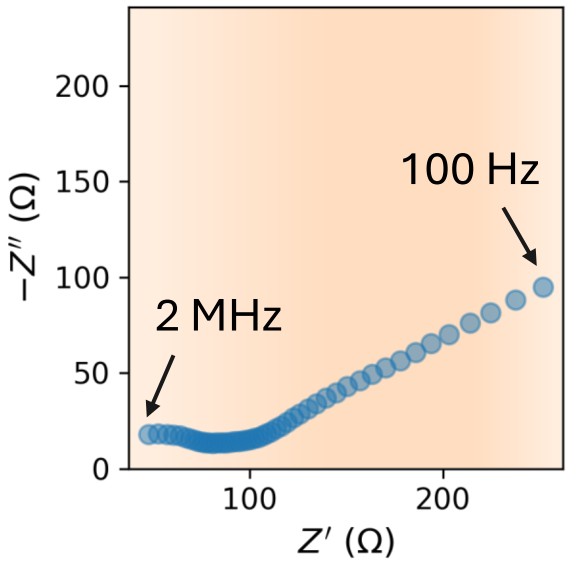
Extensions: probabilistic analysis



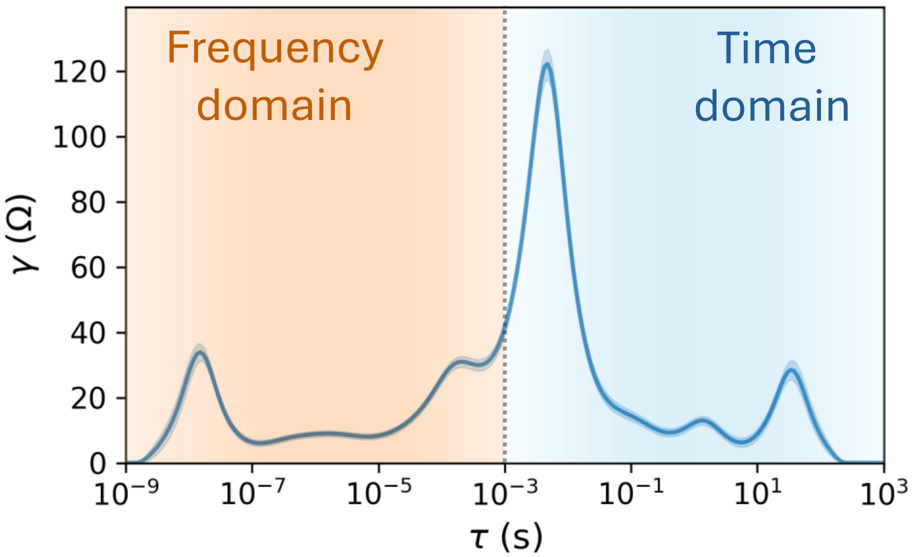
J. Huang *et al.*, 2023, *Electrochim. Acta 443*, 141879.

Extensions: faster impedance via domain joining

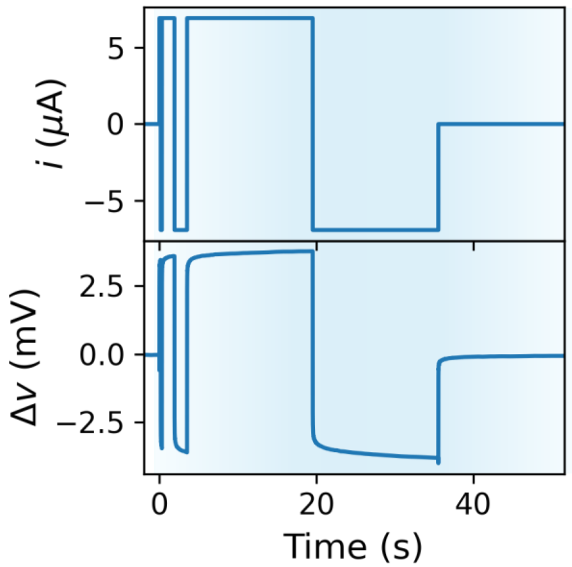
High-frequency EIS
$f > 100$ Hz



Joint-domain DRT
2 MHz – 10 mHz



Time-domain measurement
$f < 100$ Hz



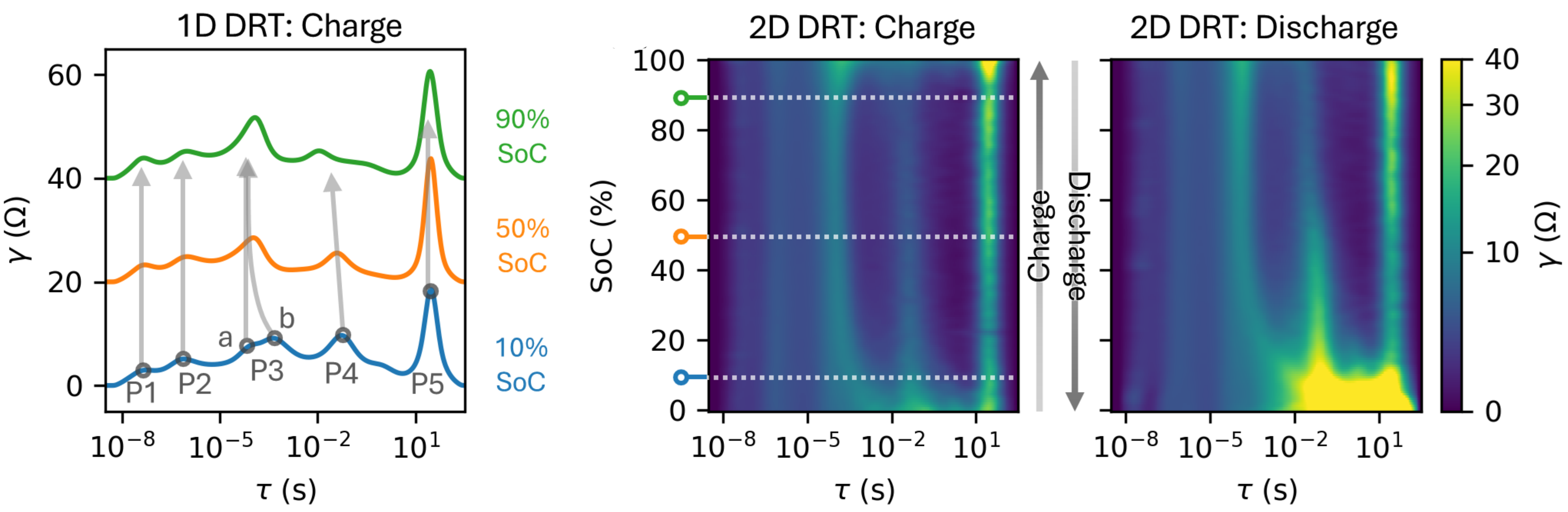
Conventional duration: **20 minutes**
Joint-domain duration: **1 minute**

Accelerate measurement ≥10x via DRT transformation of time-domain data

J. Huang *et al.*, 2024, *Joule 8(7)*, 2049-2072.

Extensions: 2D(+) spectroscopy

Solid-state battery: *operando* DRT



Visualizing the DRT vs. state of charge (SoC) provides detailed insight

J. Huang & W. Zeier, 2025, *ACS EL* (submitted).

Are you ready to use the DRT?

The DRT is a great tool to incorporate into your EIS workflow

The DRT can complement other modeling approaches

Just remember: it's not magic!

Contact:
jdhuang@mines.edu

jdhuang-csm / **hybrid-drt**

jdhuang-csm / **bayes-drt2**

Additional resources: publications

- M. Saccoccio *et al.*, 2014, *Electrochim. Acta* 147, 470–48:
  An introduction to penalized regression and tuning via cross-validation
- F. Ciucci & C. Chen, 2015, *Electrochim. Acta 167*, 439–454:
  An introduction to hierarchical ridge regression
- J. Huang *et al.*, 2021, *Electrochim. Acta 367*, 137493:
  Development of a self-tuning algorithm using a hierarchical Bayesian model
- J. Huang *et al.*, 2023, *Electrochim. Acta 443*, 141879:
  How to understand, evaluate, and improve DRT accuracy
- J. Huang *et al.*, 2024, *Joule 8* (7), 2049–2072:
  A method to obtain the DRT from time-domain data, accelerating EIS measurement ≥10x

Additional resources: software

Package	Description	GUI	Tuning	Automated/ batch fits
DRTtools	User-friendly graphical interface for DRT estimation via ordinary ridge regression	✓	Manual	✗
bayes-drt	Python package for self-tuning DRT estimation	✗	Auto	✓
★ hybrid-drt	Python package for faster self-tuning DRT estimation, DRT conversion to equivalent circuits, and various tools for DRT analysis	✗	Auto	✓

★ Package used for software demo