Zurich Instruments

Hands-on Electrochemical Impedance Spectroscopy

Dr. Dino Klotz, Application Scientist

Dr. Magdalena Marszalek, Technical Sales

Your webinar will start at 5pm CEST / 11am EDT

Zurich Instruments

Hands-on Electrochemical Impedance Spectroscopy

Dr. Dino Klotz, Application Scientist

Dr. Magdalena Marszalek, Technical Sales

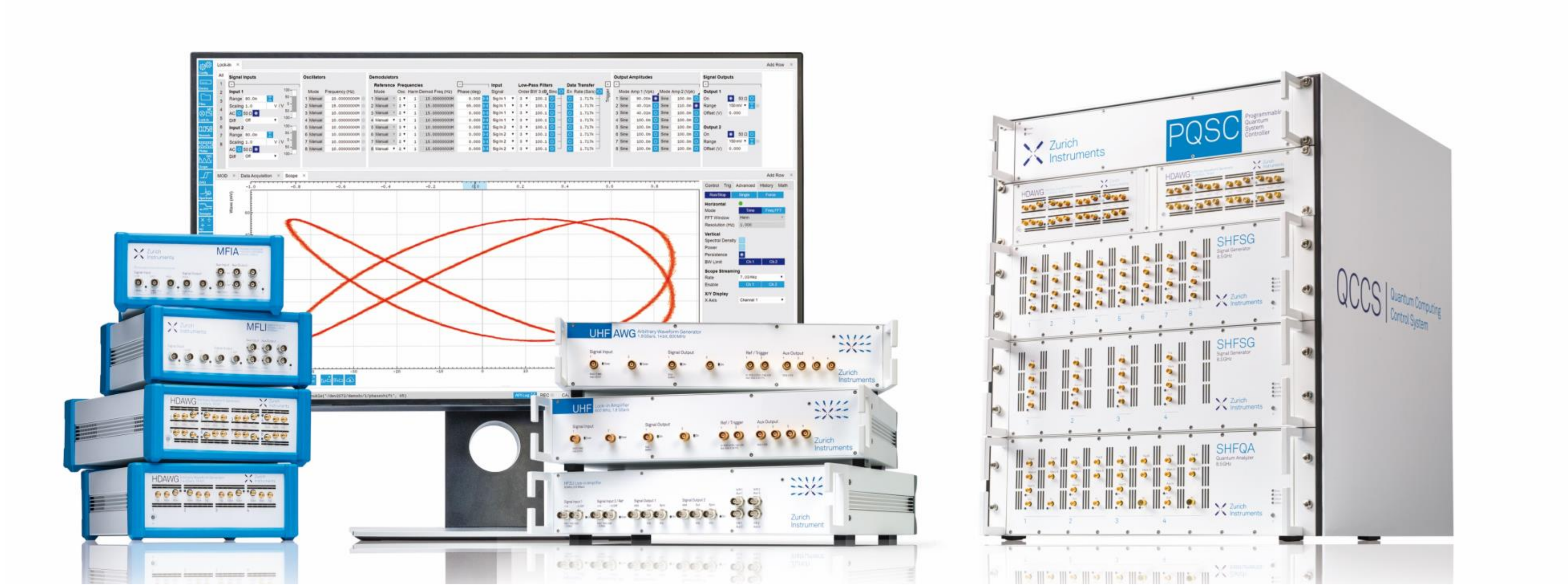
Zurich Instruments
Company profile

- Headquarters in Zurich, Switzerland
- Founded in 2008, 100+ people, 25+ nations
- Offices in USA, China, Italy, Korea, France, Japan
- Run by scientists for scientists
- As of July 1st, 2021, Zurich Instruments is a Rohde & Schwarz Company

Zurich Instruments

Zurich Instruments
Mission

Provide **best-in-class** dynamic-signal instruments for **advanced R&D labs.**



Zurich Instruments

What do we do?

experience LabOne

Hardware

- Adequate speed
- High sensitivity
- Low noise
- High resolution

+

Software

- Efficient workflows
- Functionality & features
- UI & APIs
- Value added over time

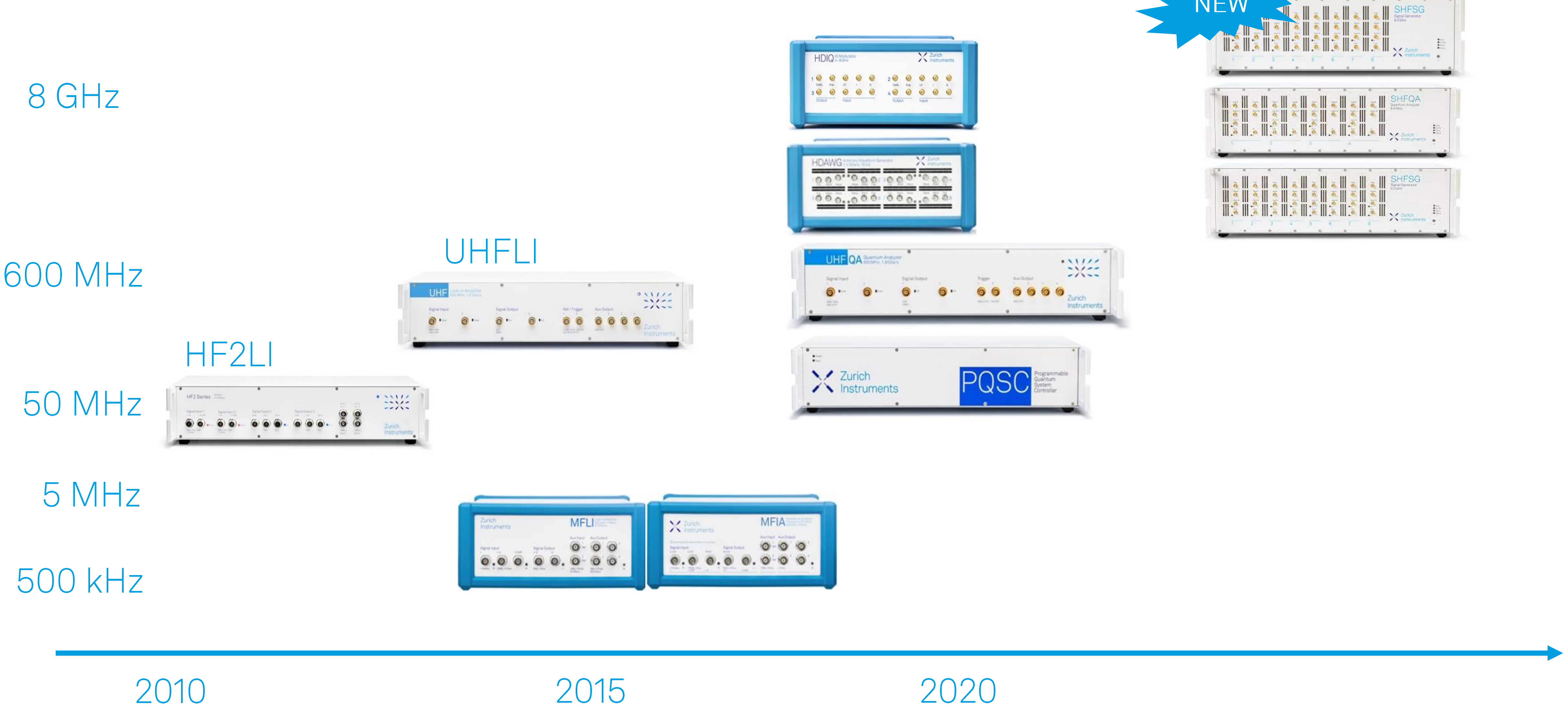
→

Instruments

- Lock-in amplifiers
- Impedance analyzers
- Boxcar averagers
- Quantum control systems

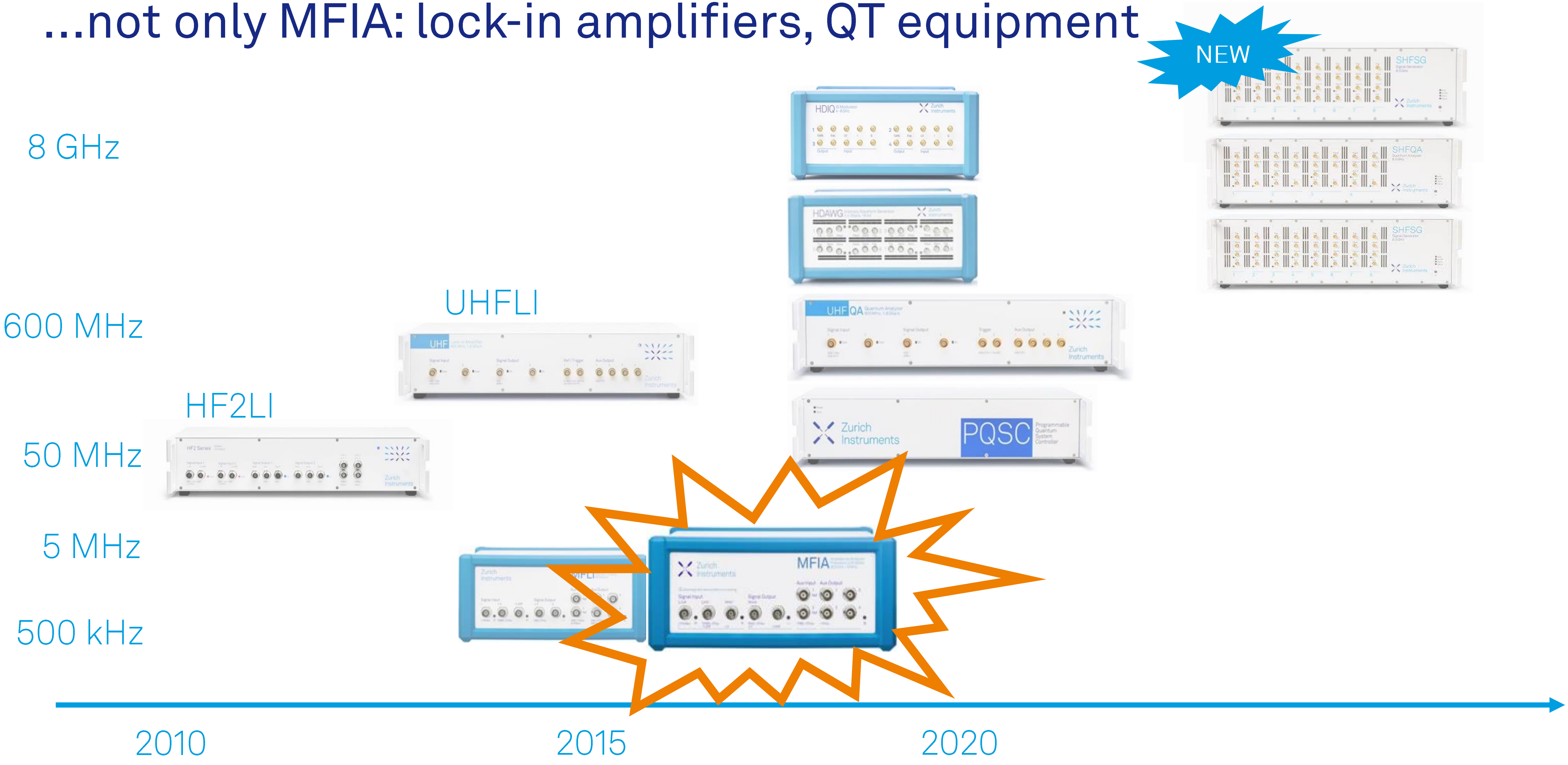
Zurich Instruments’ Innovations

...not only MFIA: lock-in amplifiers, QT equipment



Zurich Instruments' Innovations

...not only MFIA: lock-in amplifiers, QT equipment



Zurich Instruments

Hands-on Electrochemical Impedance Spectroscopy

Dr. Dino Klotz, Application Scientist

Introduction

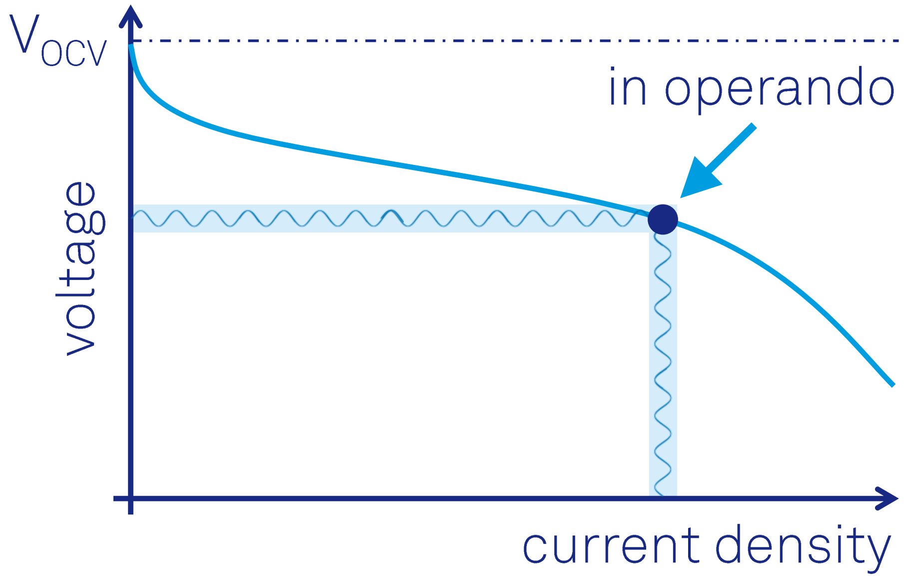
Why do we measure?

1. Characterize your system/sample
   - Measure performance
   - Measure distinct physical parameters
   - Identify loss processes
   - Determine device physics
2. Compare different samples
3. Check with literature
   - Does my sample show the right signature as reference work in the literature?
4. Specify degradation
5. Quality check

Why Electrochemical Impedance Spectroscopy (EIS)?

1. EIS is a non-destructive method with only a small-signal perturbation
2. EIS can be measured in situ / in operando, in an operating point or in equilibrium
3. EIS can be performed during degradation studies or as state-of-health monitoring
4. EIS provides the most detailed information of the sample by purely electrical means
5. EIS is inexpensive (no extra cost for each measurement and very little maintenance)

Current-voltage curve



Comment on open circuit voltage (OCV):

- Common in electrochemistry
- Sources: concentration gradient, selective contacts, for example

Introduction

How does it work?

1. Sinusoidal excitation plus optional bias (voltage or current)
2. Sinusoidal response signal of the DUT (current or voltage)
3. Calculation of the impedance Z for every measured frequency

- Time domain:

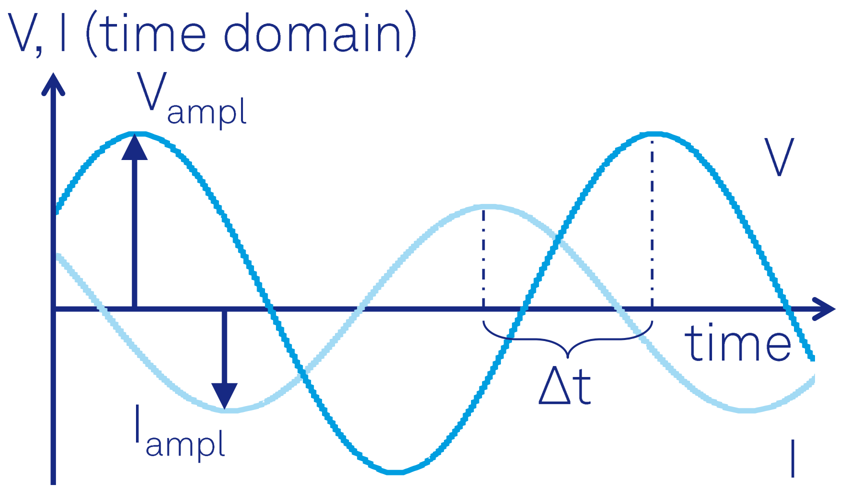
→ $|Z| = V_{ampl} / I_{ampl}$; $\theta = 2\pi f \cdot \Delta t$; $\underline{Z} = |Z| \cdot e^{j\theta}$

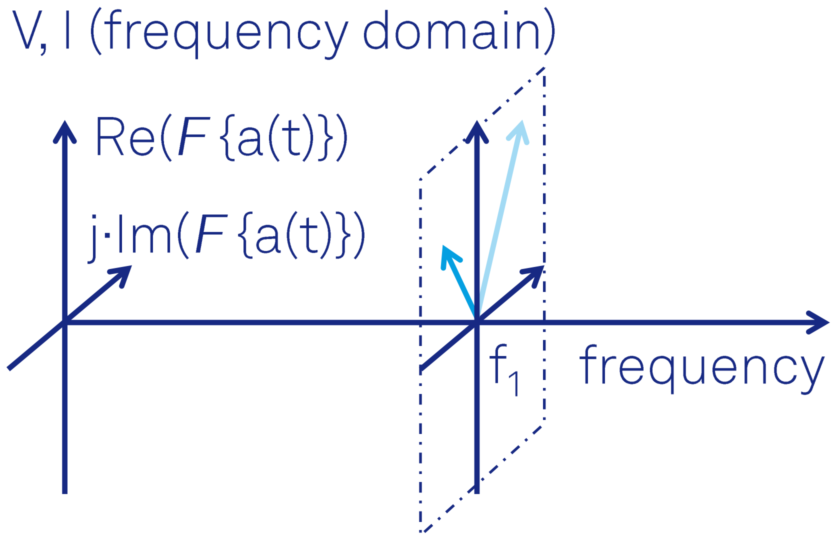
- Frequency domain:

→ $Z(f) = F_f\{V(t)\} / F_f\{I(t)\}$

In practice, realized by different techniques

- Digitally, but applying concepts like auto-balanced bridge (ABB) or digital Lock-in





Complementary Instrument to the MFIA Impedance Analyzer

LCX Advanced LCR Meter

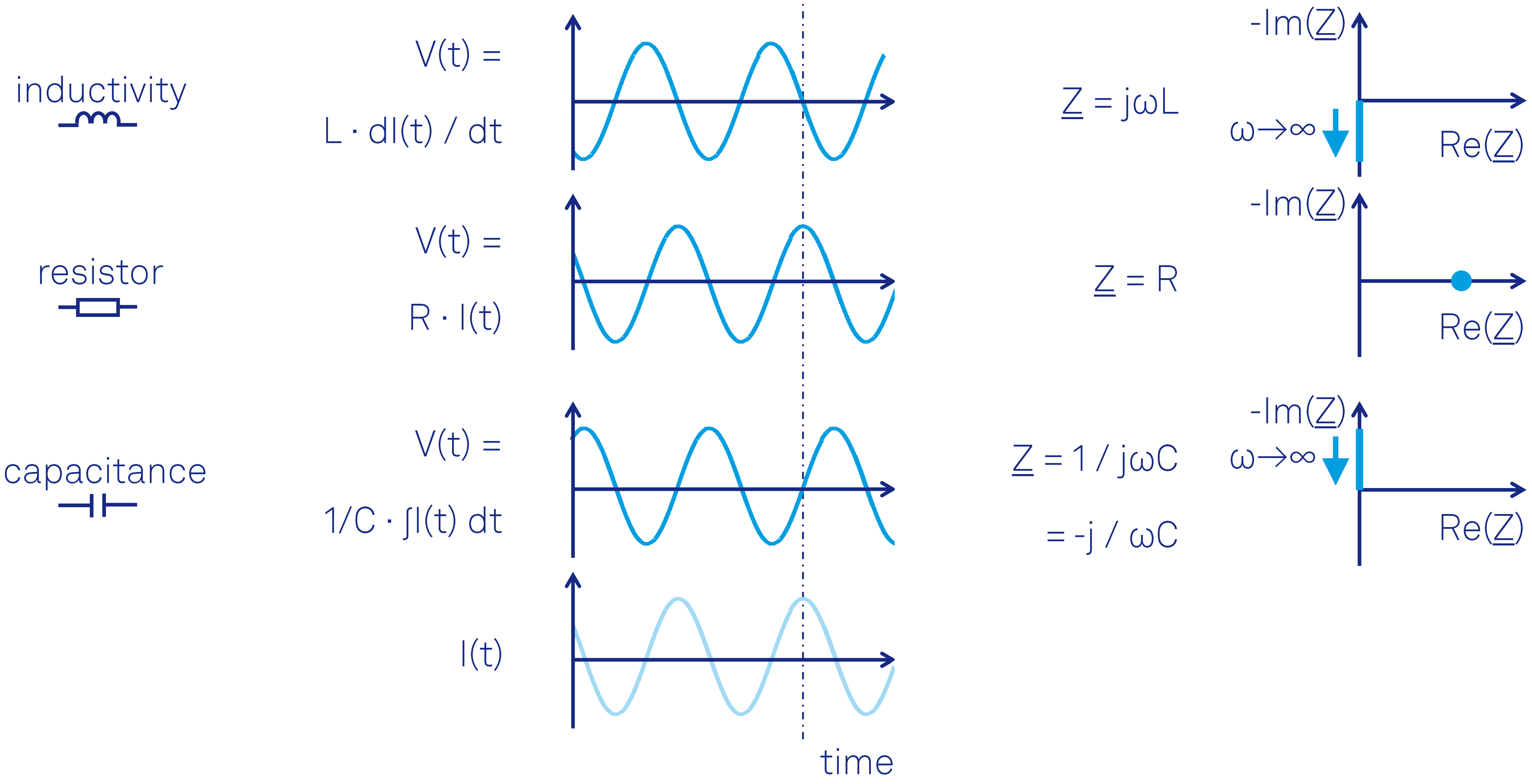
- MFIA suits materials and device characterization

1. Measure at low frequency, to 1 mHz
2. Measure high impedances, to 1 TΩ
3. Measure impedance fast (10 us at 1 MHz)
4. LabOne: Time & frequency domain toolset; Sweeper, Plotter, DAQ, Scope
5. API (C, MATLAB®, LabVIEW®, Python, .NET)

- LCX suits component test, production test, QA, education

1. Measure up to 10 MHz
2. Voltage bias up to 40 V
3. Current bias up to 200 mA
4. Industry standard handler interface
5. Intuitive and familiar panel interface
6. GPIB control

Introduction
Basic Circuit Elements

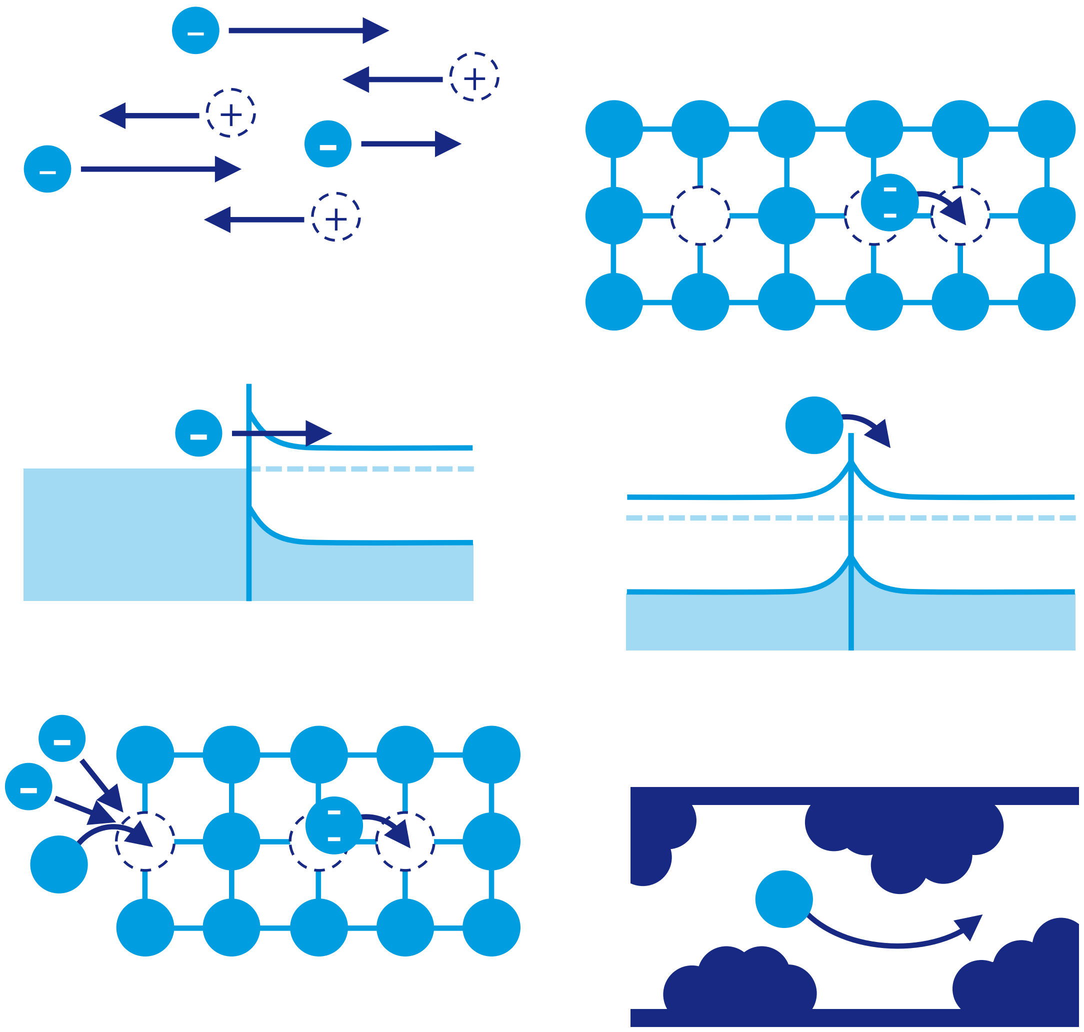


Resistance – Losses

Where are they originating from?

1. Electronic conductivity
   - Electrons or holes
   - Positive/negative temperature activation
   - “Fast” (short time constant)
2. Ionic conductivity
   - Protons or ions
   - Arrhenius behavior
3. Schottky barrier
   - Potential barrier
   - Grain boundary resistance
4. Charge transfer resistance
5. Diffusion resistance

→ Characteristic temperature dependence



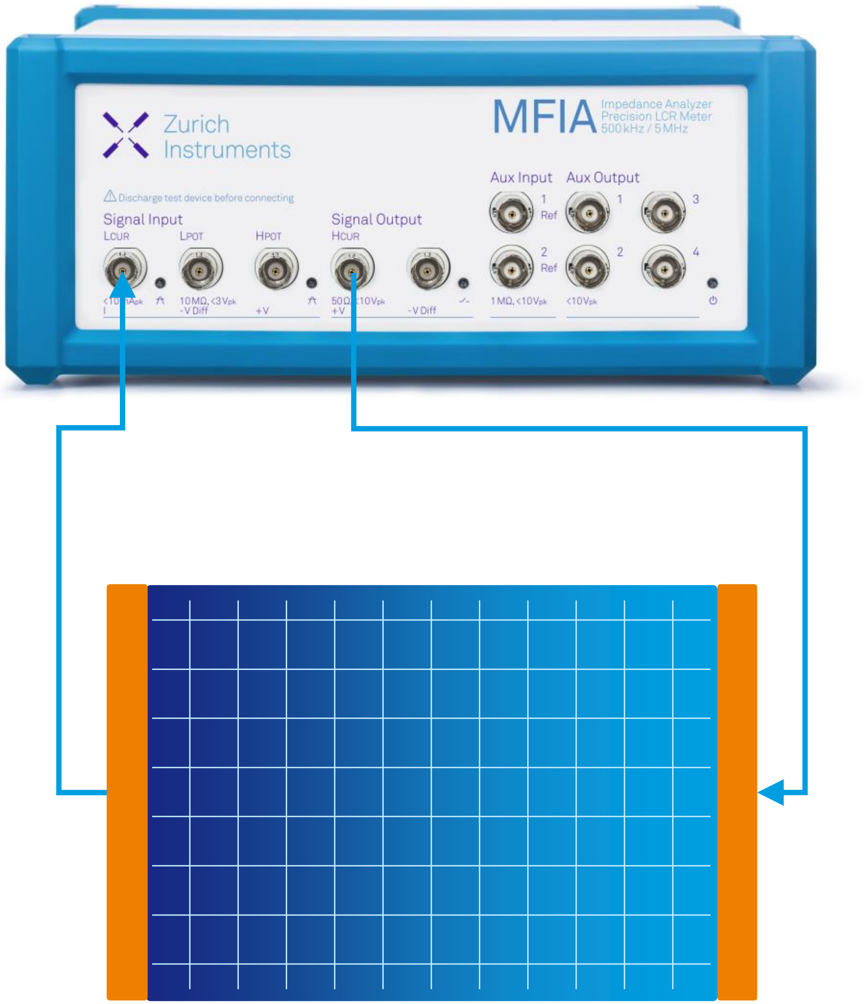
Capacitances

Capacitances in Materials Science

List adapted from P. Holtappels / B. A. Boukamp

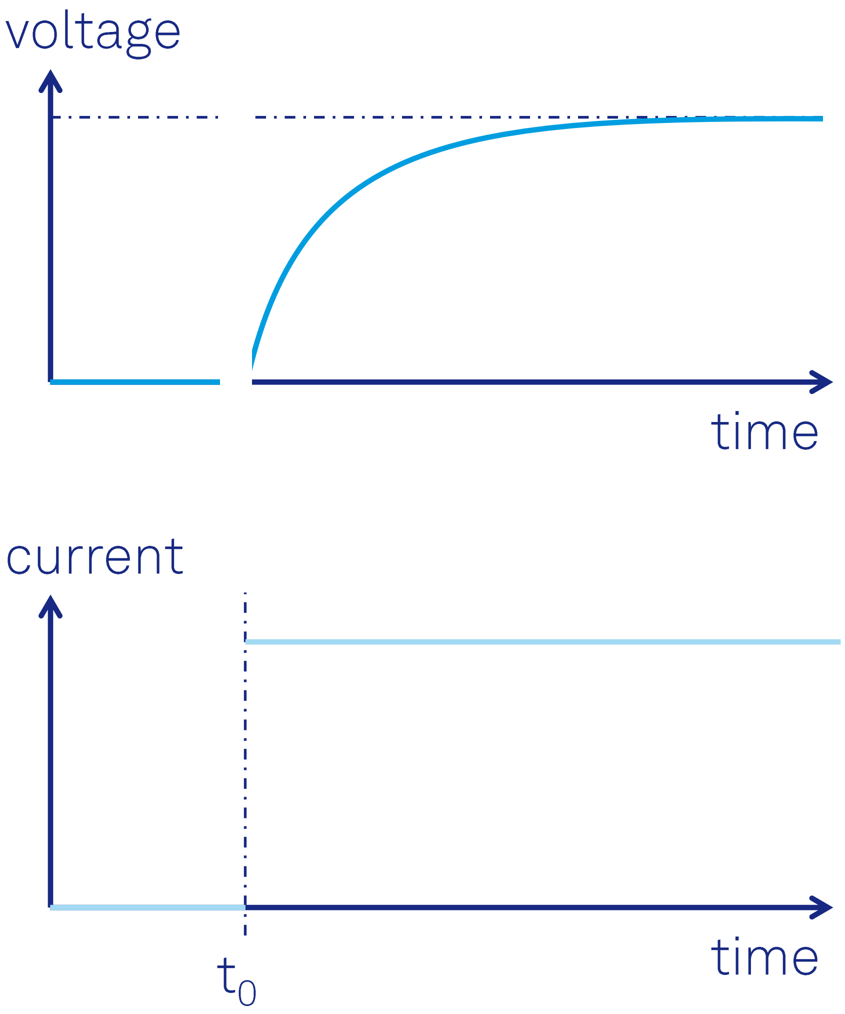
1. Measurement “input” (< 5 fF)
2. Setup (1-5 pF)
3. Geometric/stray capacitances (2-20 pF/cm)
4. Grain boundary capacitance (1-10 nF/cm)
5. Double layer / space charge capacitance (0.1- 10 μF/cm^2)
6. Surface charge / “adsorbed species” (0.2 mF/cm^2)
7. (Closed) pores (1-100 F/cm^3)
8. Chemical capacitances or stoichiometric changes (large ~1000 F/cm^3)

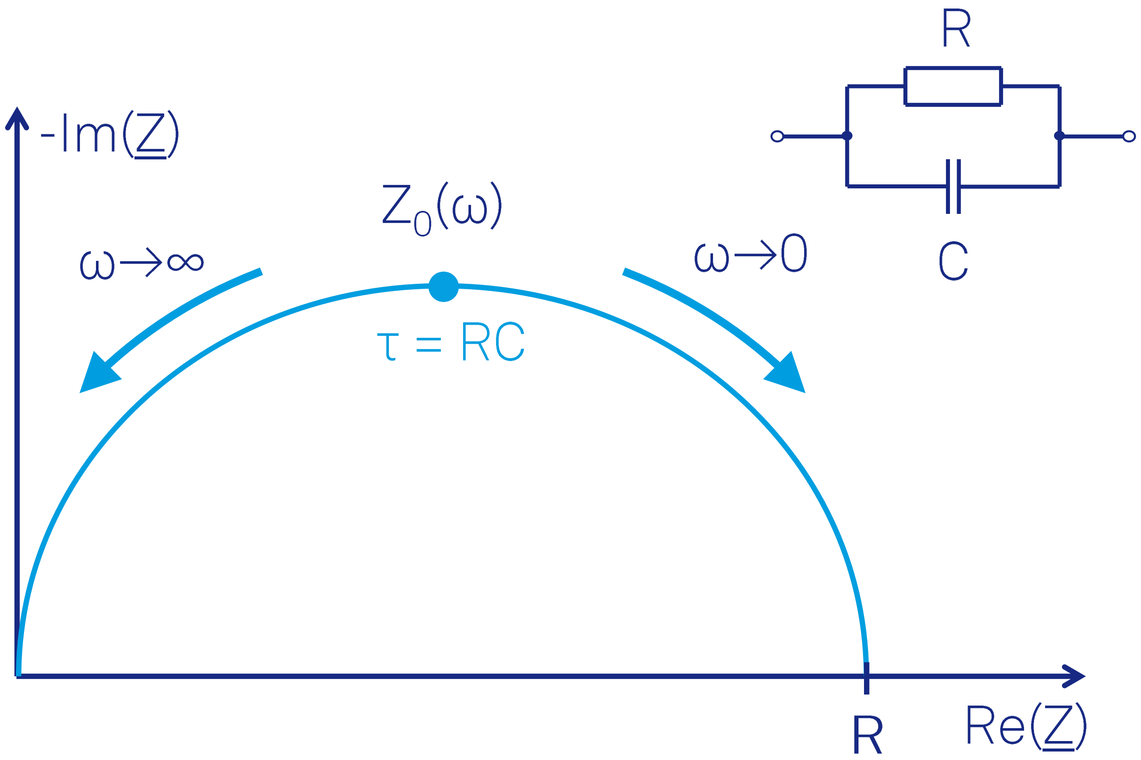
→ Little temperature dependence



Model Development

RC Circuit as Fundamental Impedance Response





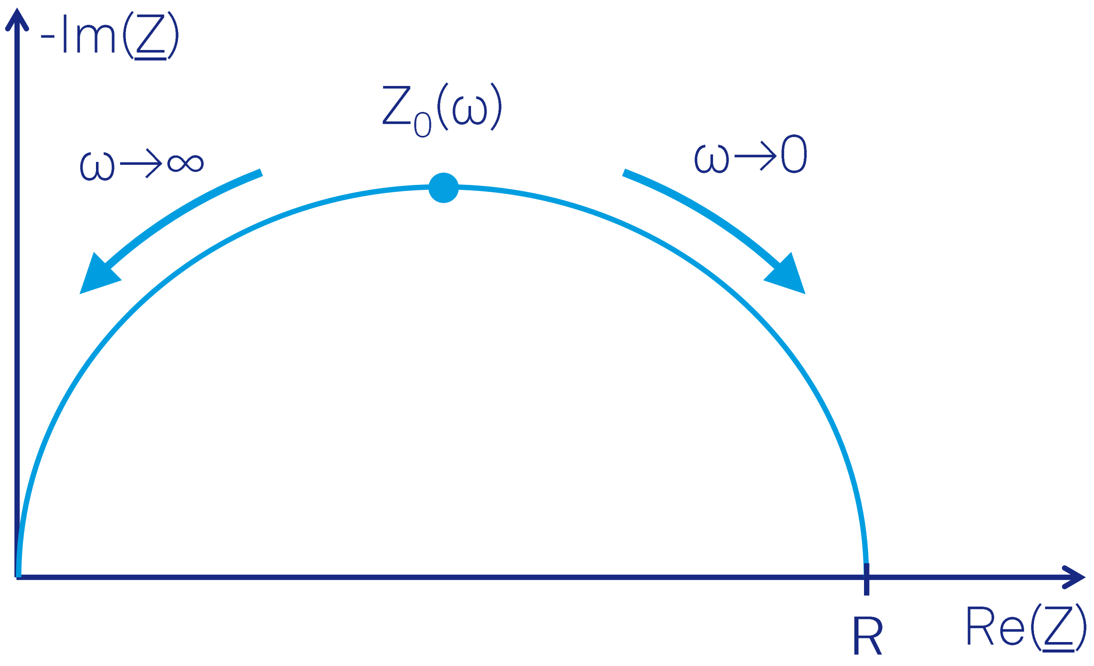
$$\underline{Z} = \frac{V}{I} = \frac{R}{1 + j\omega RC} \leftrightarrow \frac{\text{output}}{\text{input}} = \frac{k}{1 + j\omega\tau}$$

Applies to many technical processes (electro-chemical interface, spring, furnace, car,...)

Visualizing

Nyquist Plot

1. In electrochemistry, the Nyquist plot is the most common form of displaying impedance.
2. Alternative: imaginary part of impedance over logarithmic frequency.
3. Phase angle not helpful (for a change in series resistance, for example)
4. Features (semicircles) can be distinguished.
5. Equally scaled axis – degree of ideality can be assessed visually.



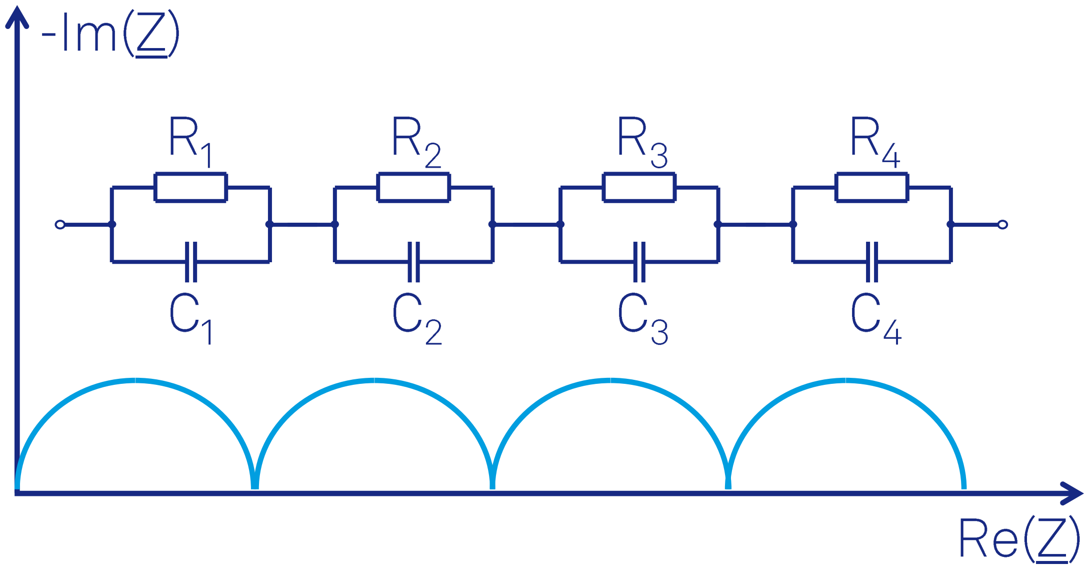
Equivalent Circuit Model

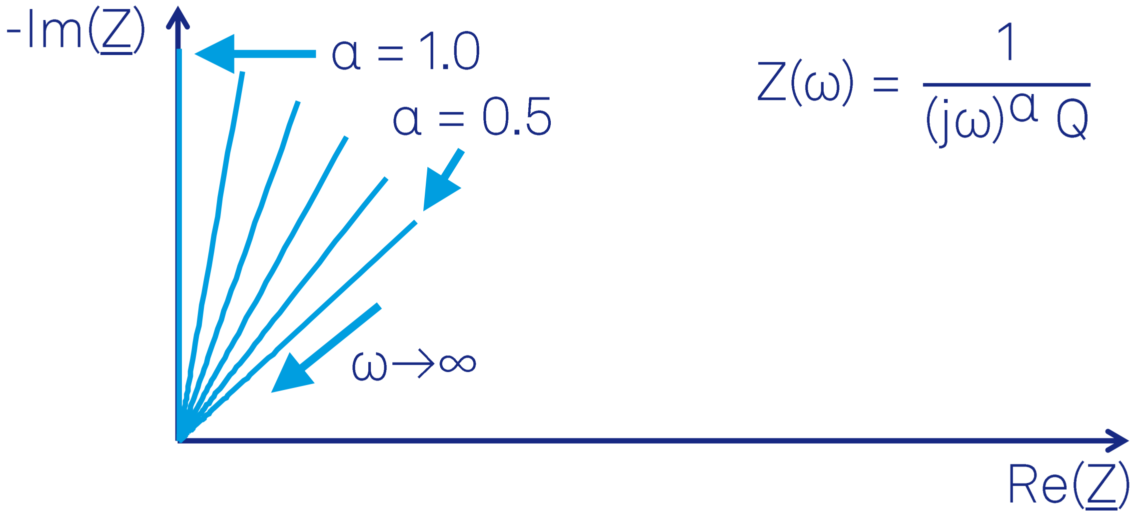
RC/RQ Circuits and Series Connections of Those

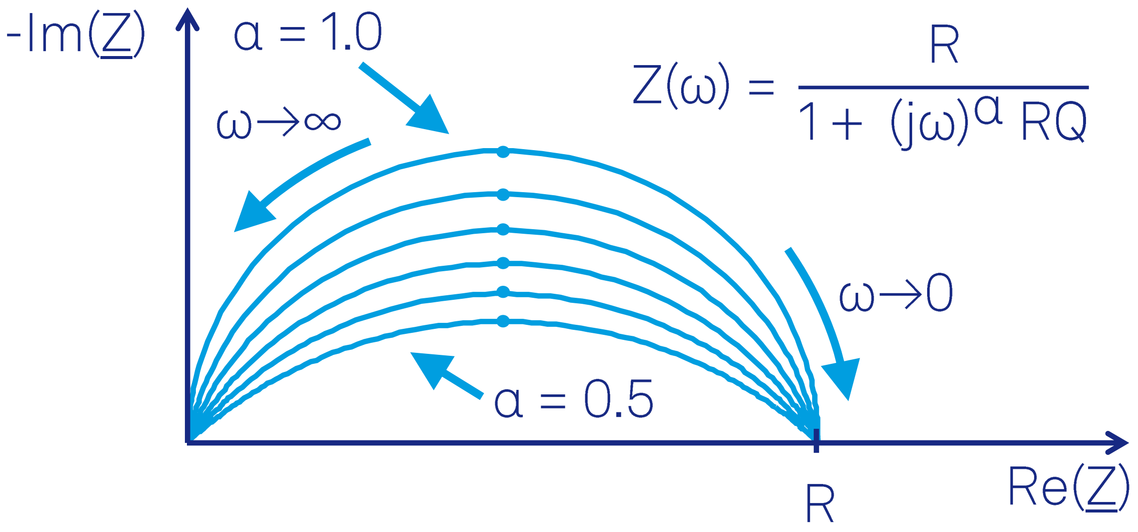
- Ideal electrochemical process: R||C
- Non-ideal processes: RQ (a.k.a. R||CPE, cole-cole, ZARC)

Case of more than one process?

- Mostly possible as series connection (truly in series, or simplified)





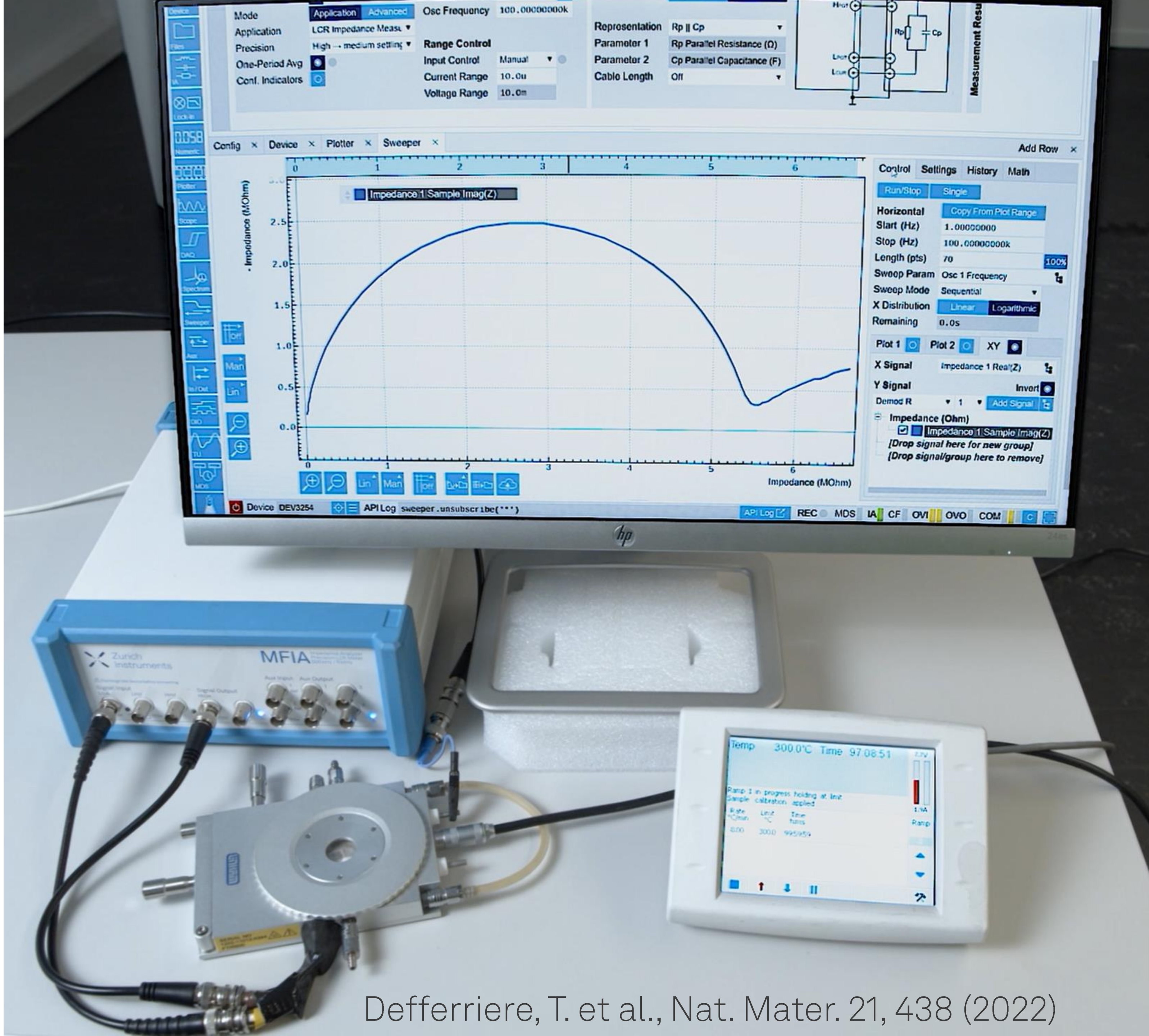


van Hauff, E., Klotz, D., J. Mater. Chem. C 10, 742 (2022)

Example Measurement

Thin Film

1. Gd-doped CeO_2 thin film
2. Ionic conductor
3. Polycrystalline
4. Interdigitated electrodes

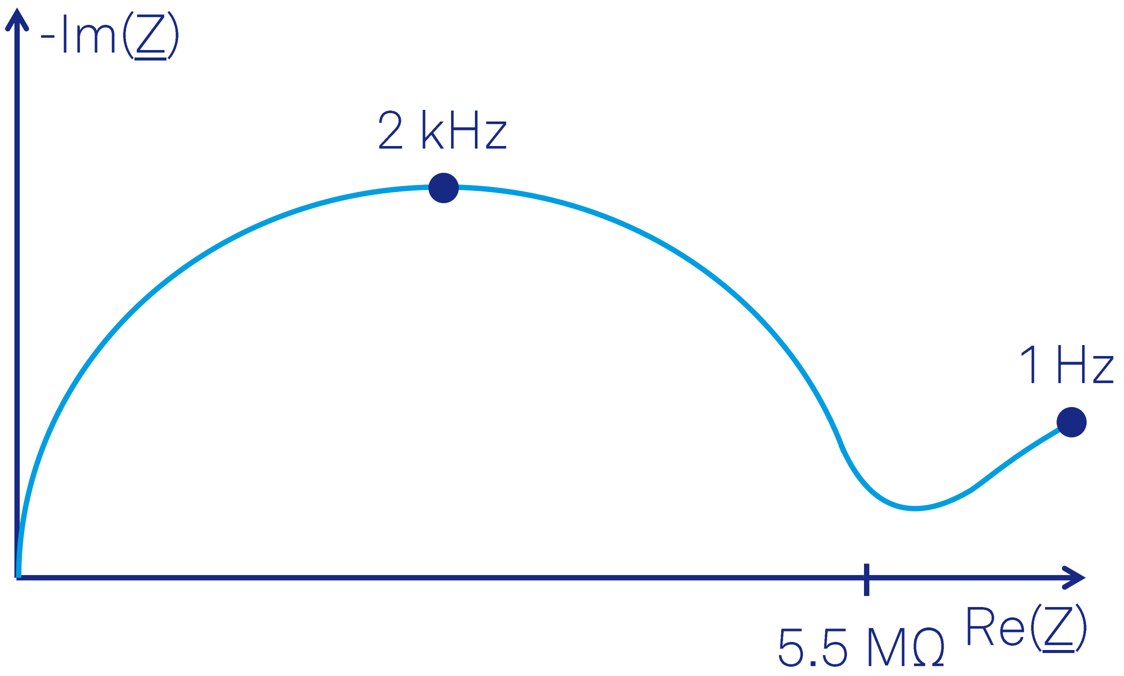


Defferriere, T. et al., Nat. Mater. 21, 438 (2022)

Quick Analysis of this Measurement

Thin Film Ion Conductor

1. Main semicircle:
   - $f = 2$ kHz → $\tau = 1 / (2\pi f) = 80$ µs
   - $R = 5.5$ MΩ
   - $C = \tau / R = 14$ pF
   - → Setup/stray capacitance
2. Mechanism? → Temperature variation
   - Arrhenius behavior reveals grain boundary resistance
3. Leftovers?
   - Electrochemical double-layer?
   - Adsorbed species (electrode)?

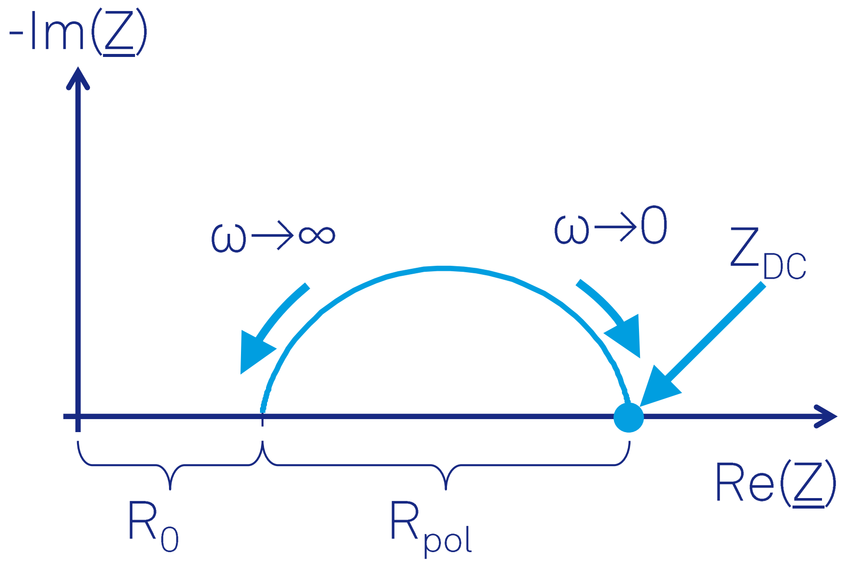


Impedance Spectroscopy

Fuel Cells versus Batteries

Fuel cell impedance

- Tertiary galvanic cells
- Reaction products are constantly supplied
- Capacitive features (negative imaginary half-plane) but DC impedance is "real"



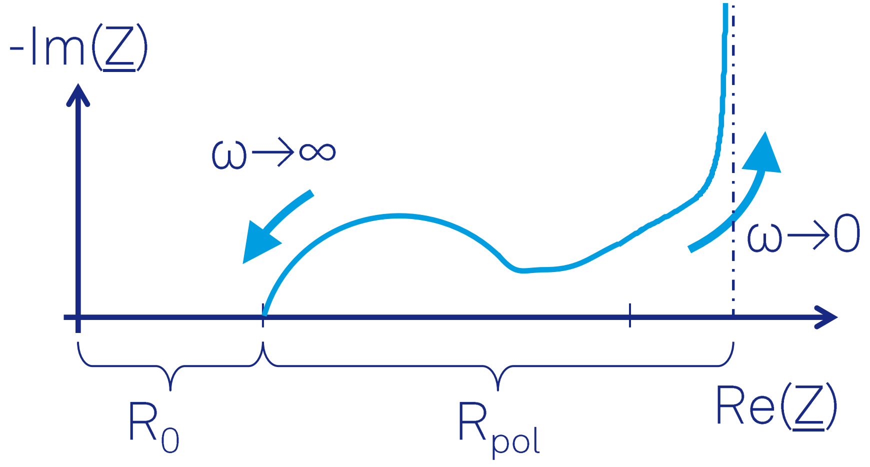
Battery impedance

- Secondary galvanic cell
- "Closed" system, reaction products are limited

→ Can be fully charged/discharged

- Capacitive features (negative imaginary half-plane) and no defined DC impedance

→ Capacitive branch



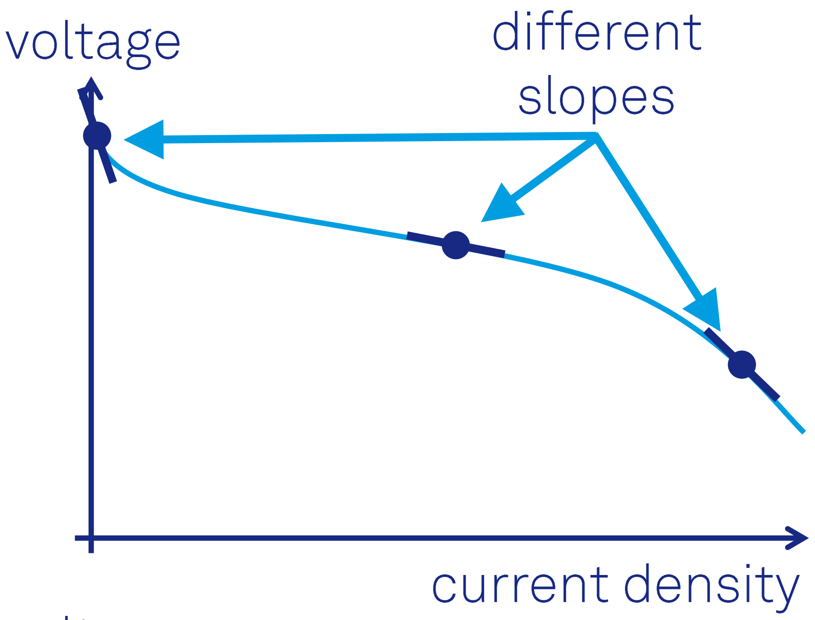
Impedance Spectroscopy

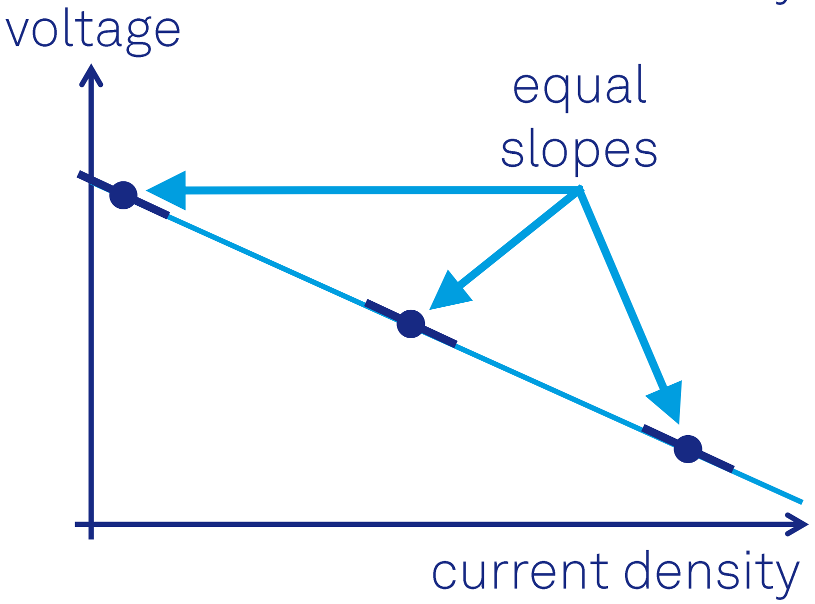
Linearity Considerations

Choosing the operating point

- In general, nonlinear behavior expected
- Amplitude trade-off between signal-to-noise and linearity
- Check: different amplitude should yield same result
- Linear curve means the impedance does not change with current density

→ In order to specify the losses at any current density, one impedance is not enough for a nonlinear curve (processes depend on current density)





Technical Aspects – Accuracy Chart

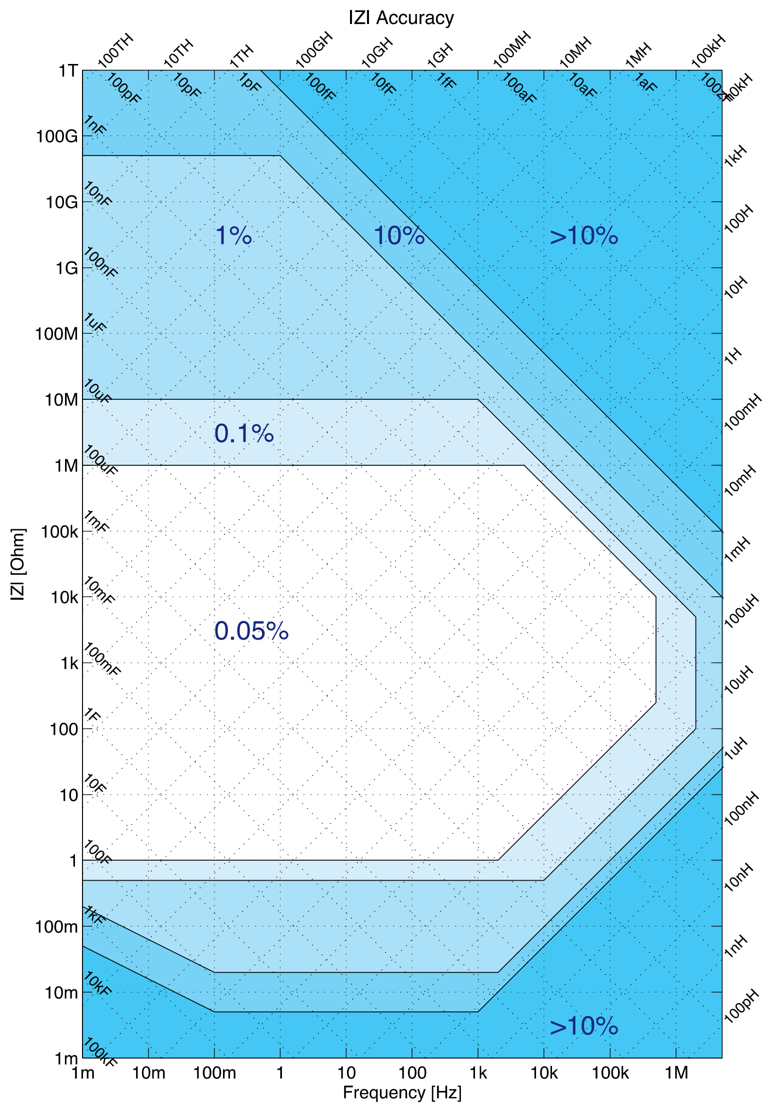
How to achieve the best accuracy?

- Basic accuracy is very good (0.05%).

What are typical limitations?

- High frequencies (long cables?, cables in furnace?)
- Small impedance (large currents, small voltage)
- Large impedance (low currents)
- Combinations of the above

→ User compensation can increase accuracy for extreme values



Technical Aspects – Wiring

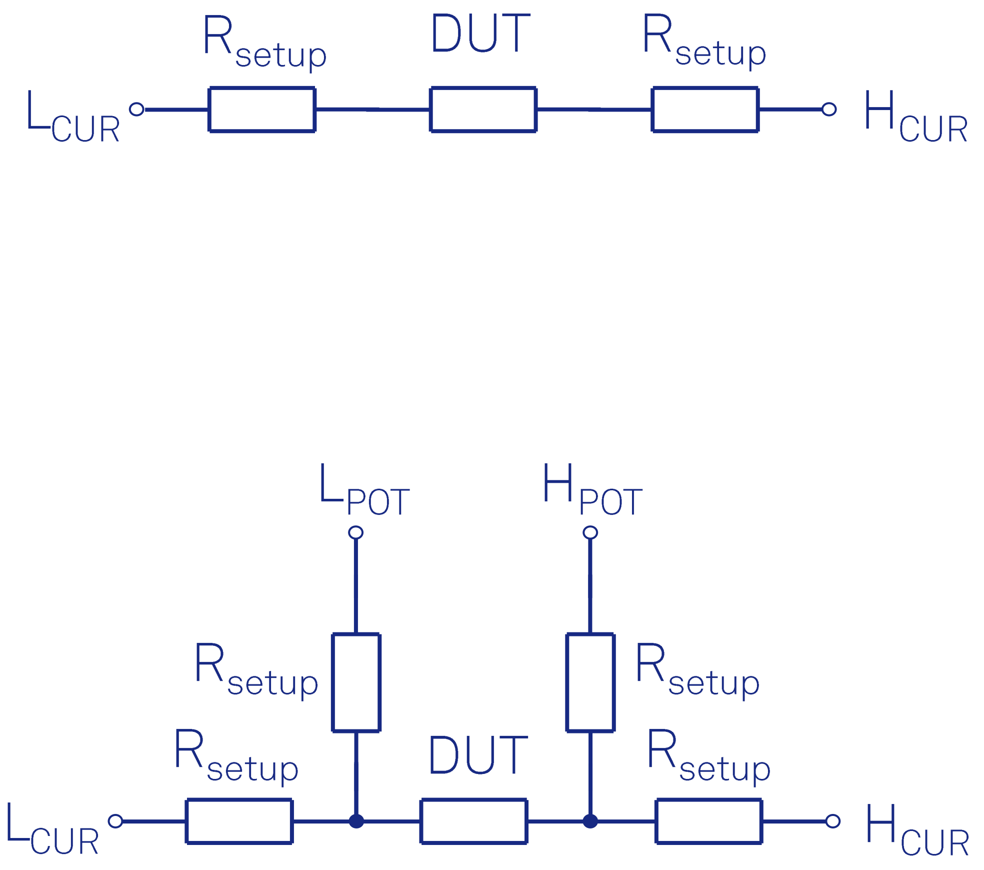
2 Terminal versus 4 Terminal

- R_{setup} (cables, input/output resistance)
- Systematic error for low-Z DUT
- No voltage drop in the 4 wire setup
- Check: 50 Ω MFIA output resistance; cable resistance 1 Ω (rule of thumb:)
- To avoid confusion:

→ 2/4 Terminal also called 2/4 wire

→ 2/3/4 electrode is different (reference electrode requires to have no current flowing)

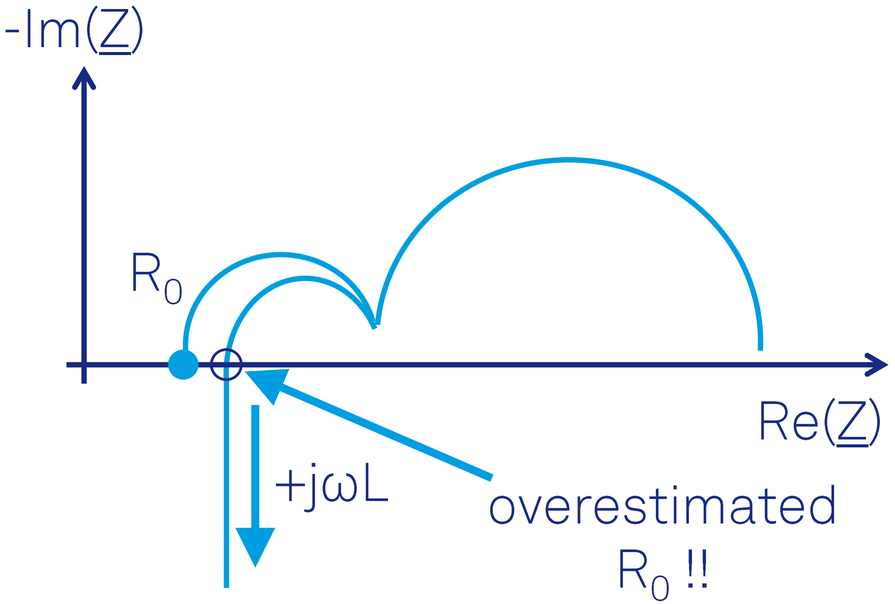
→ 4 Terminal also called “quasi”- 4 electrode

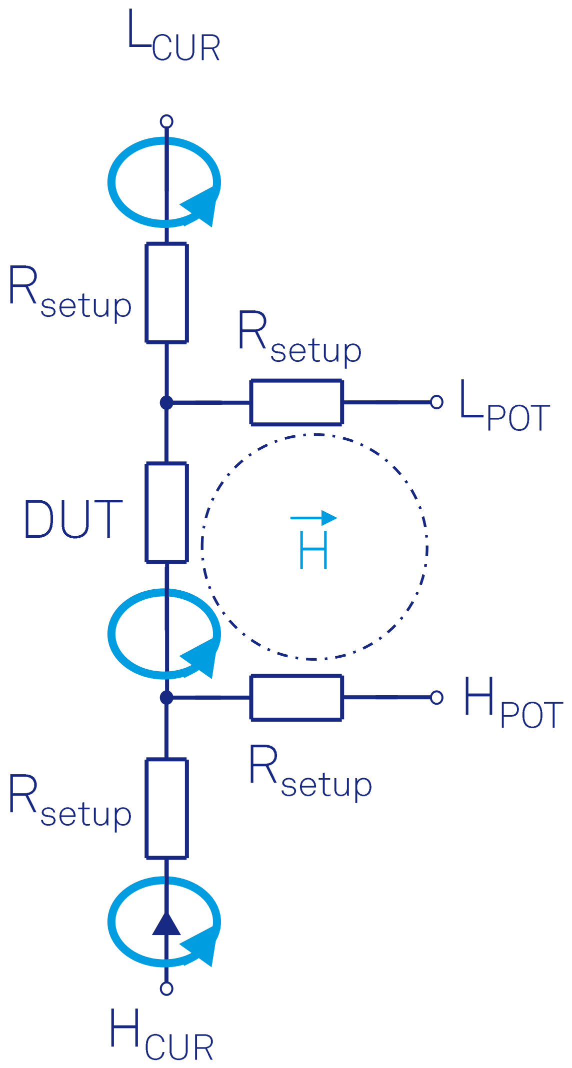


Technical Aspects – Inductive Coupling

Origin and Consequences

- Mutual inductance in voltage path
- Measured impedance shows errors at high frequencies
- Keep current small (difficult on low impedance objects)

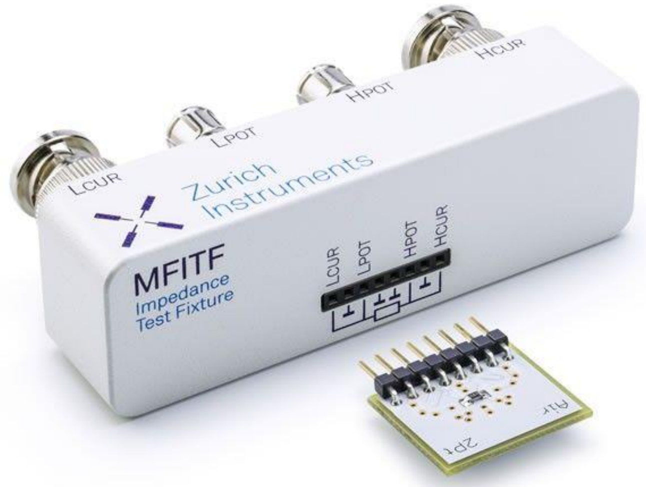


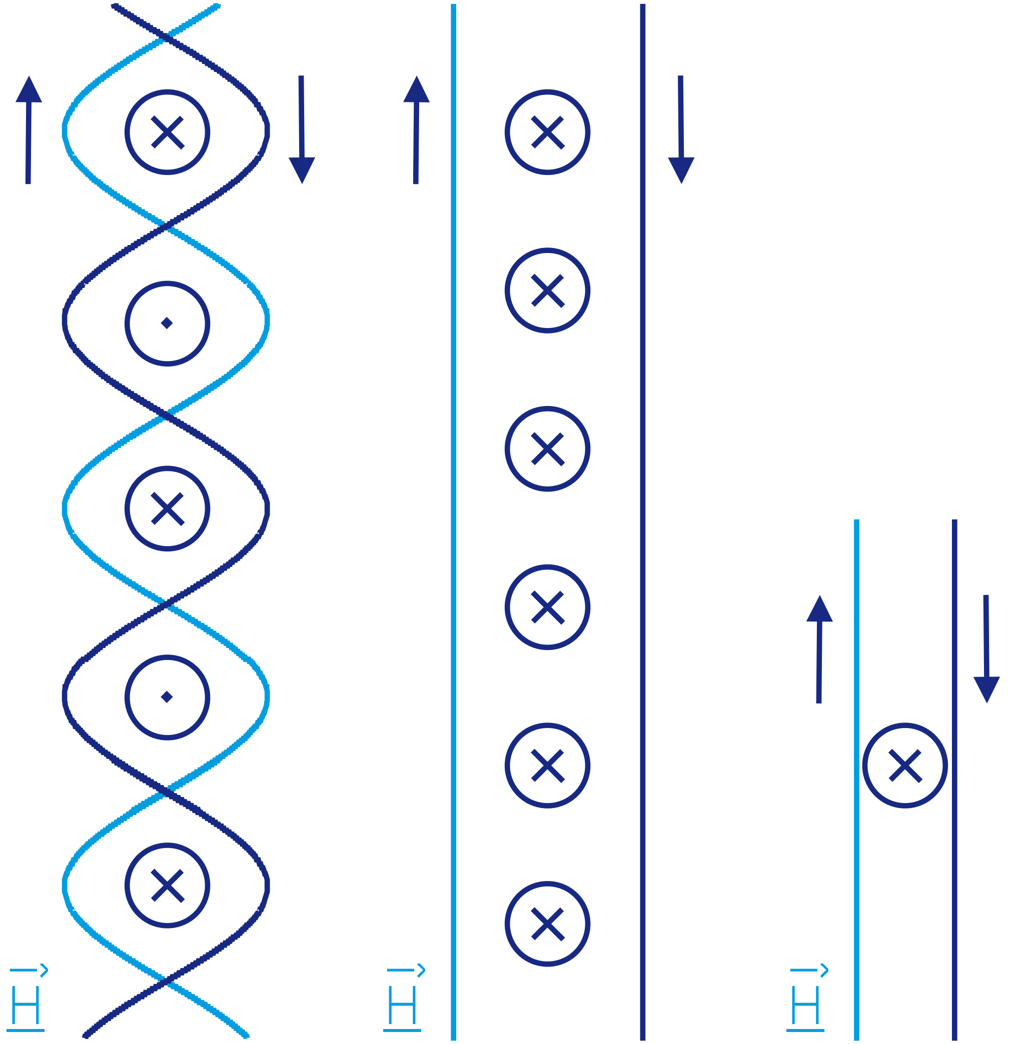


Technical Aspects – Inductive Coupling

How to minimize inductance artifacts?

1. Short cables/connections optimized
2. Voltage/current lines orthogonal
3. Twisting cables
   - Twisting cables inside furnaces
3. Minimize area between cables

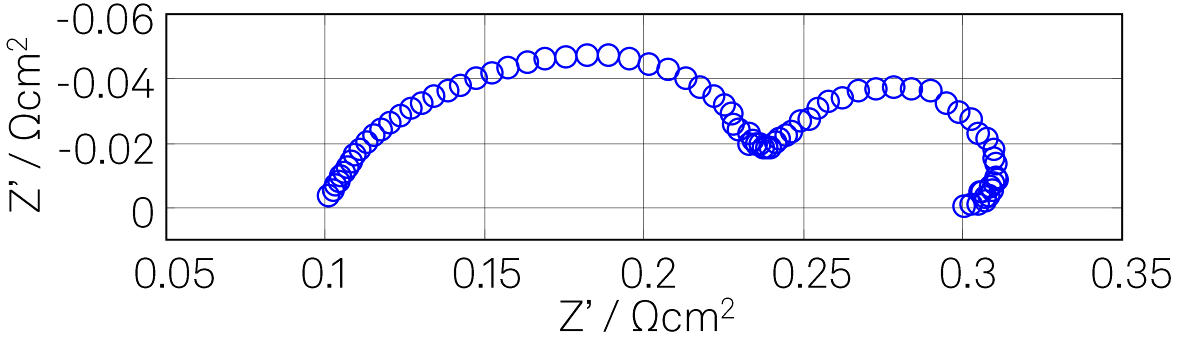


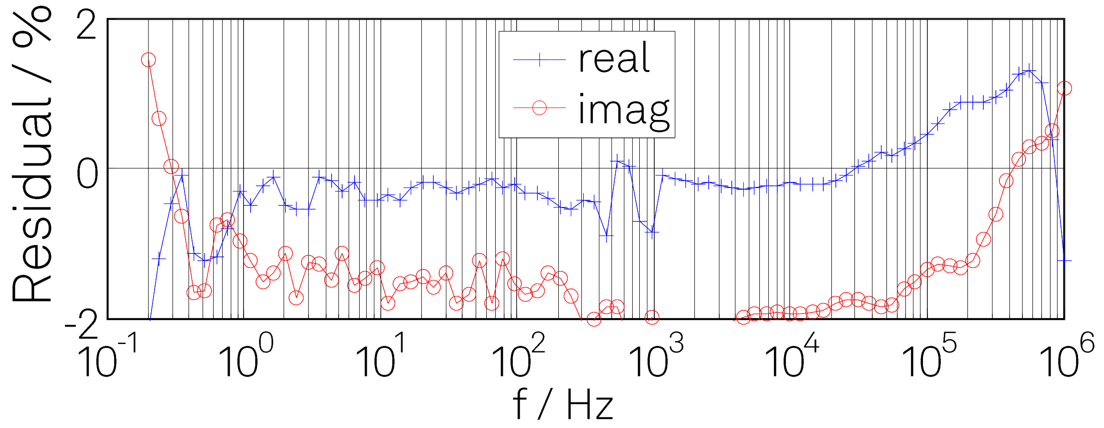


Methods for Impedance Validation

1. Measure the same DUT twice (consecutively) under same conditions – result must be the same!
2. Use Kramers-Kronig (KK) test

- For example, Lin-KK
- The Kramers-Kronig test is based on the fact that real and imaginary part can be related by the KK relations. If these are fulfilled, the criteria of linearity, causality, stability and finiteness are met.





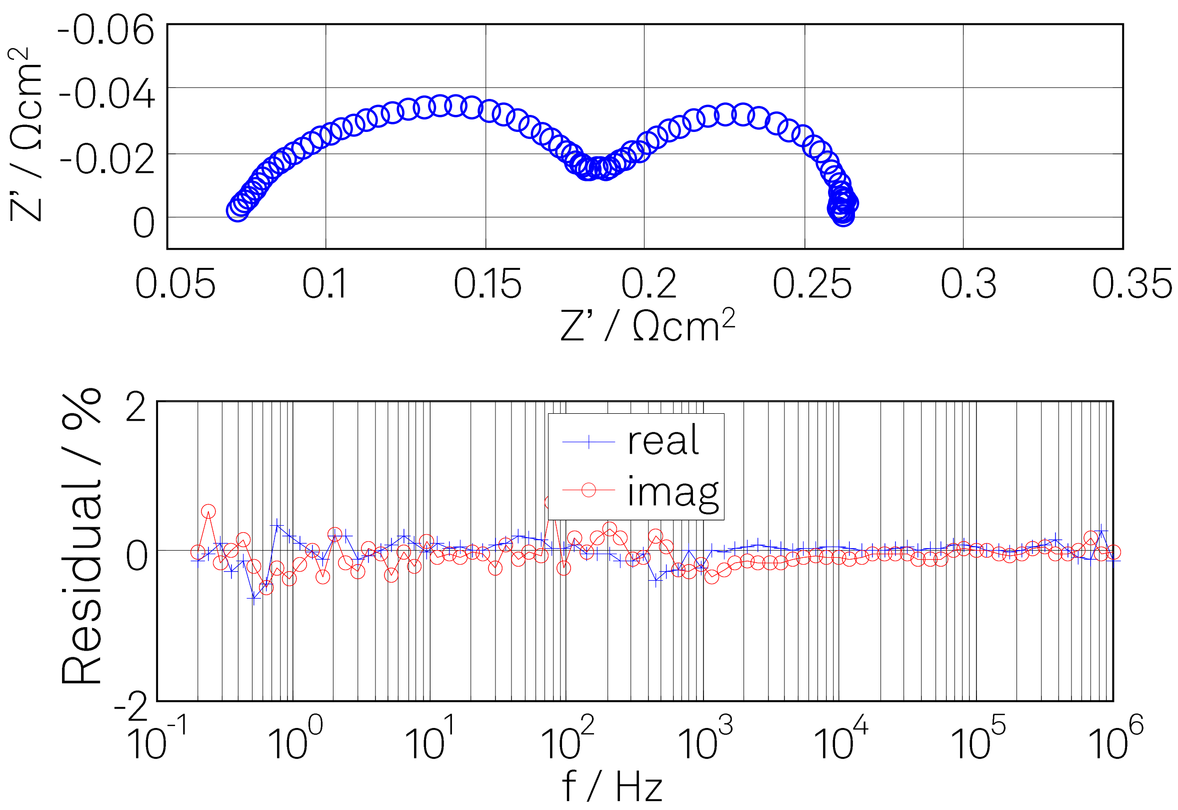
https://www.iam.kit.edu/et/english/Lin-KK.php
https://www.zhinst.com/ch/en/blogs/kramers-kronig-test-applied-impedance-measurements-electrical-circuits

Validating

Methods for Impedance Validation

1. Measure the same DUT twice (consecutively) under same conditions – result must be the same!
2. Use Kramers-Kronig (KK) test

- For example, Lin-KK
- The Kramers-Kronig test is based on the fact that real and imaginary part can be related by the KK relations. If these are fulfilled, the criteria of linearity, causality, stability and finiteness are met.
- Not a sufficient criterion to prove validity of the measurement, but most common problem (instability) is well recognized.



https://www.iam.kit.edu/et/english/Lin-KK.php
https://www.zhinst.com/ch/en/blogs/kramers-kronig-test-applied-impedance-measurements-electrical-circuits

Demos

How to...? Some useful tricks for your EIS measurement

The webinar featured four video demonstrations. To watch these, please visit:

Webinar (Demo section) on YouTube

You can also find the full recording of the webinar can be found here:

Recording of the full Webinar on YouTube

Zurich Instruments

Challenge us.

We help you measure impedance low and fast