zeo direct

Institute for Microelectronics and Microsensors

IMPEDANCE SPECTROSCOPY FOR INVESTIGATION OF CRYSTALLIZATION PROCESSES

NDT4Industry

Doppelhammer Nikolaus

NDT4Industry, 22.06.2022

JOHANNES KEPLER UNIVERSITY LINZ

KU LEUVEN

FWF Der Wissenschaftsfonds.

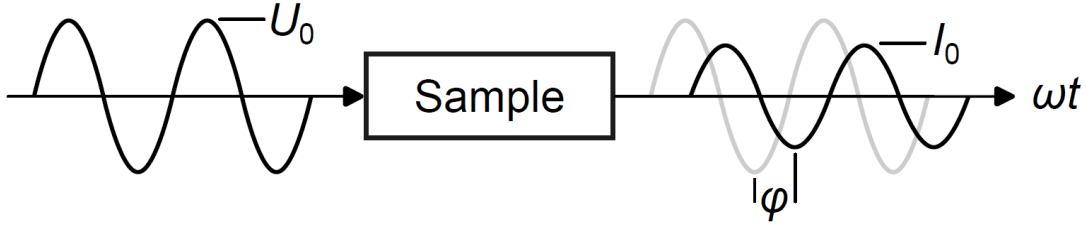
fwo

OUTLINE

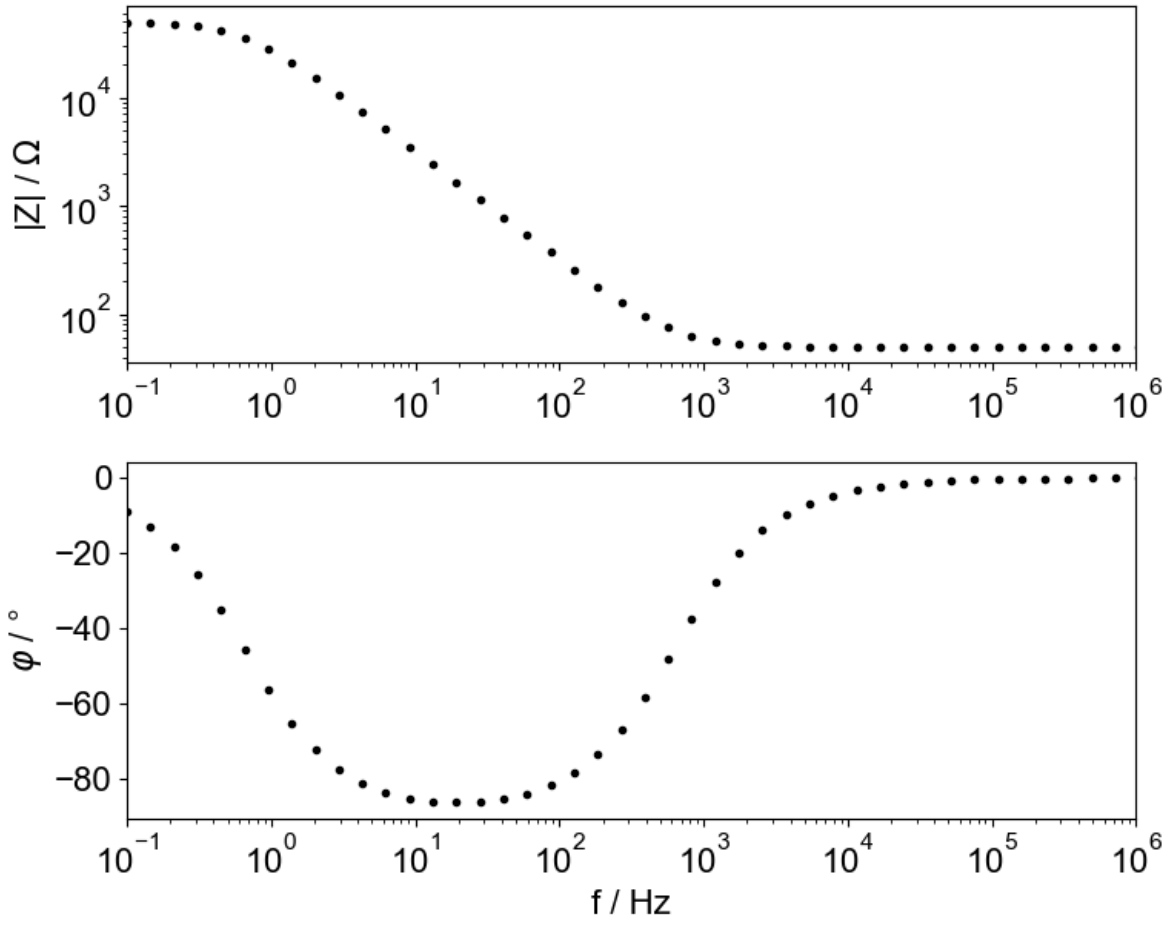
- Short introduction to **E**lectrochemical **I**mpedance **S**pectroscopy (EIS)
- Problems with classical EIS
- The concept of **M**oving **E**lectrode **EIS** (MEEIS)
  - Basic principle
  - Cell design
  - Advantages over classical EIS
- Selected application: In-situ investigation of crystal formation
  - Zeolite formation in highly alkaline media
- Summary

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- "Electrochemical" → **ionically** conducting sample
- "Impedance" → $Z = \frac{\underline{U}}{\underline{I}} = \frac{U_0}{I_0} e^{j\varphi} = |Z| e^{j\varphi}$



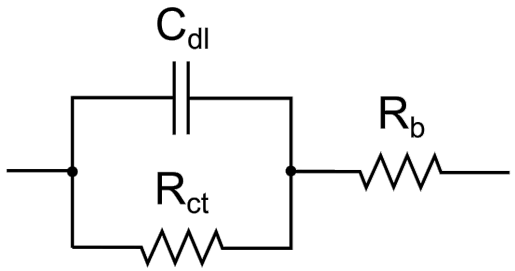
- "Spectroscopy" → $Z(\omega)$



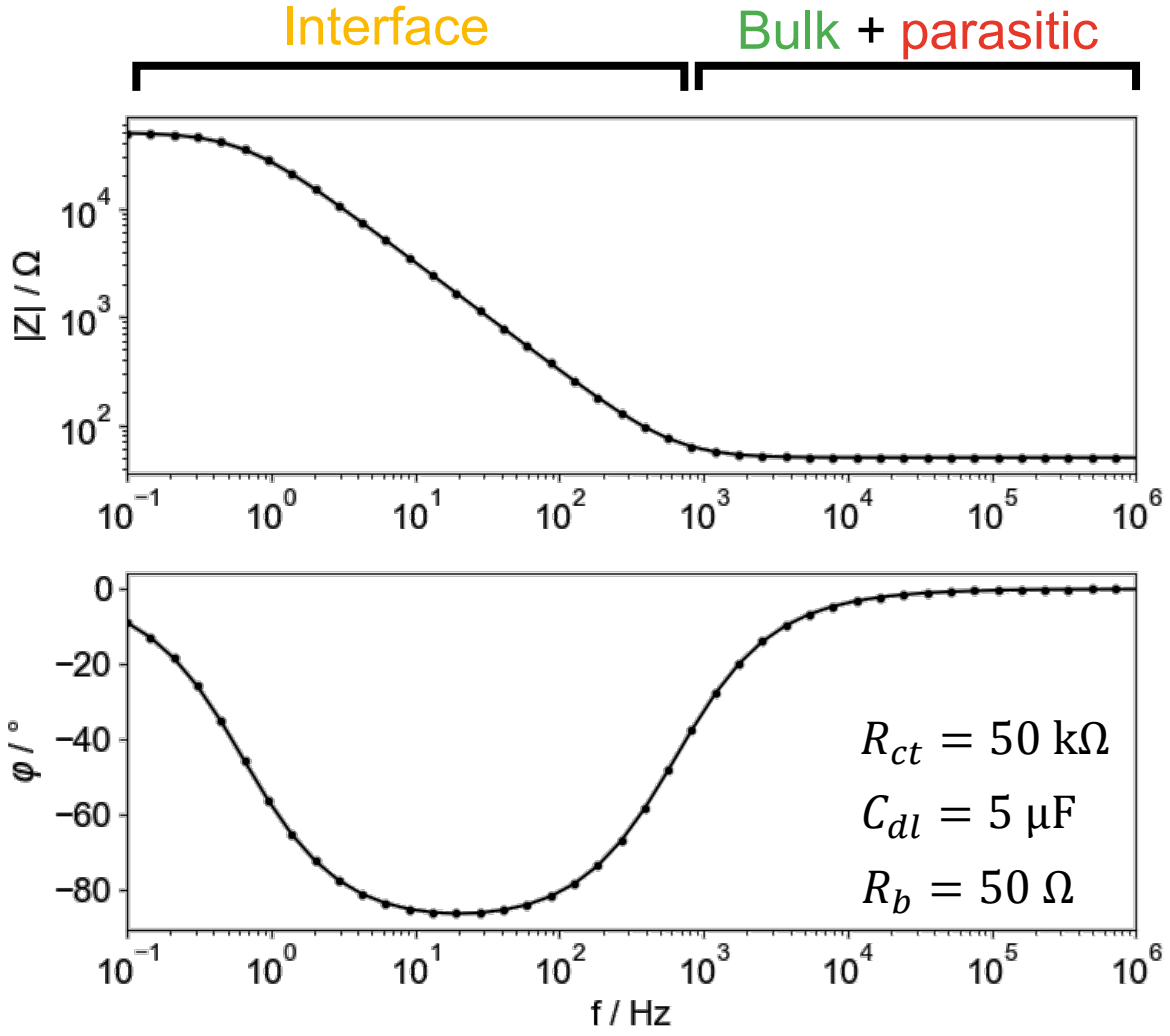
DATA ANALYSIS

- Impedance spectra analysed with **equivalent circuit models**, e.g.

Simplified Randles circuit



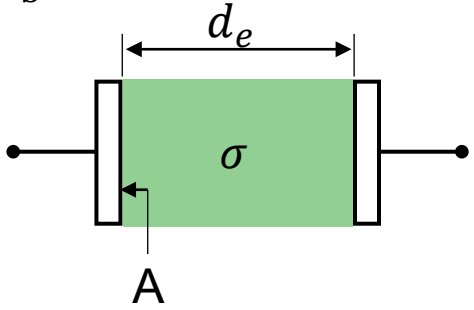
- Enables determination of interface- and bulk parameters
  - Double layer capacitance C_{dl}
  - Charge transfer resistance R_{ct}
  - Solution resistance R_{b}
- Can also contains parasitic contributions
  - E.g. wire resistance or inductance



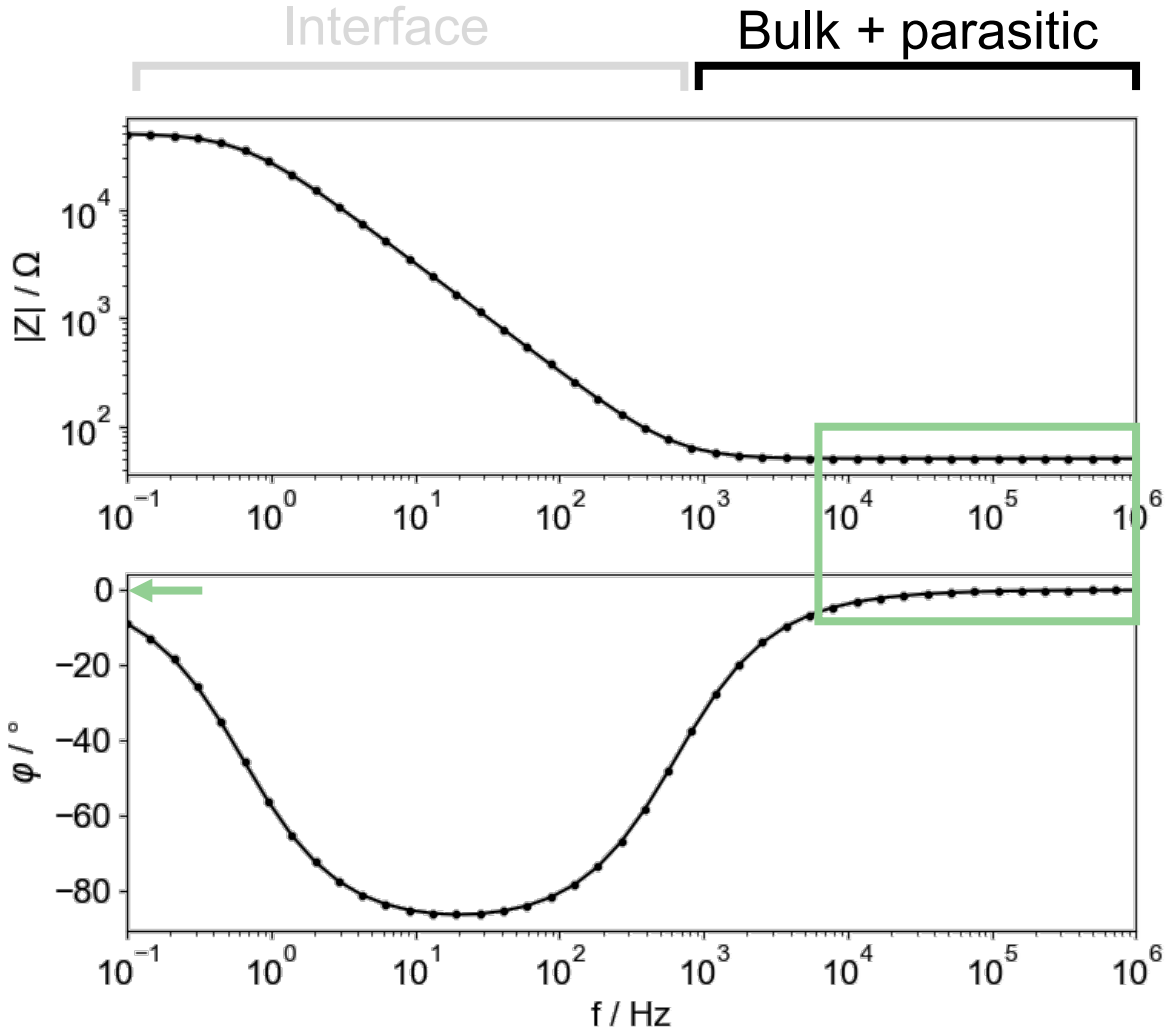
DATA ANALYSIS (CONT'D)

- Bulk resistance R_b

  $\sigma = \frac{d_\mathrm{e}}{R_\mathrm{b}\, A}$ … "DC" conductivity

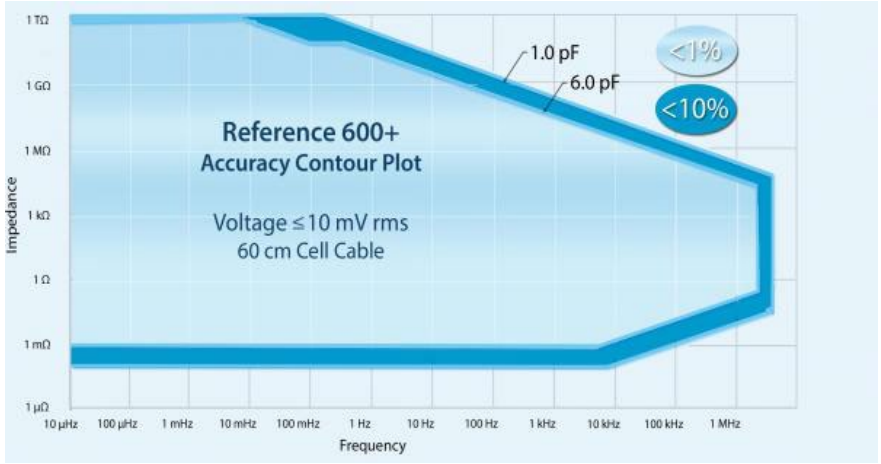


- Requirements
  - ☐ Homogeneous sample
  - ☐ $R_\mathrm{b} \gg R_\mathrm{parasitic}$
- R_b can also be determined by hand, if a clear "Ohmic" plateau in the DC conductivity range exists

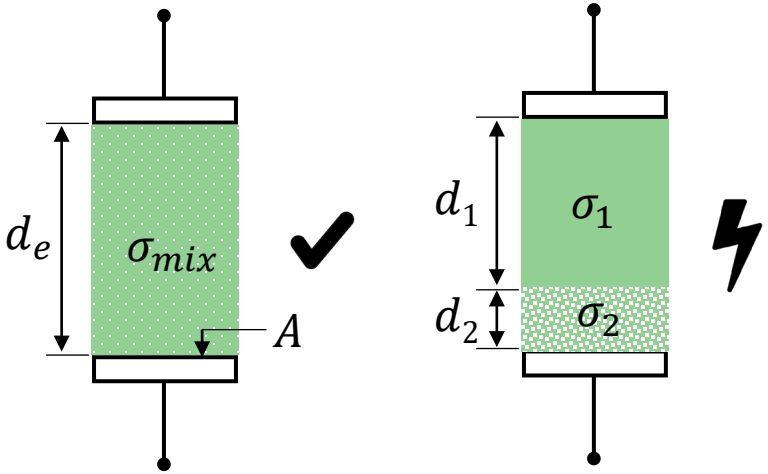


PROBLEMS OF CLASSICAL EIS

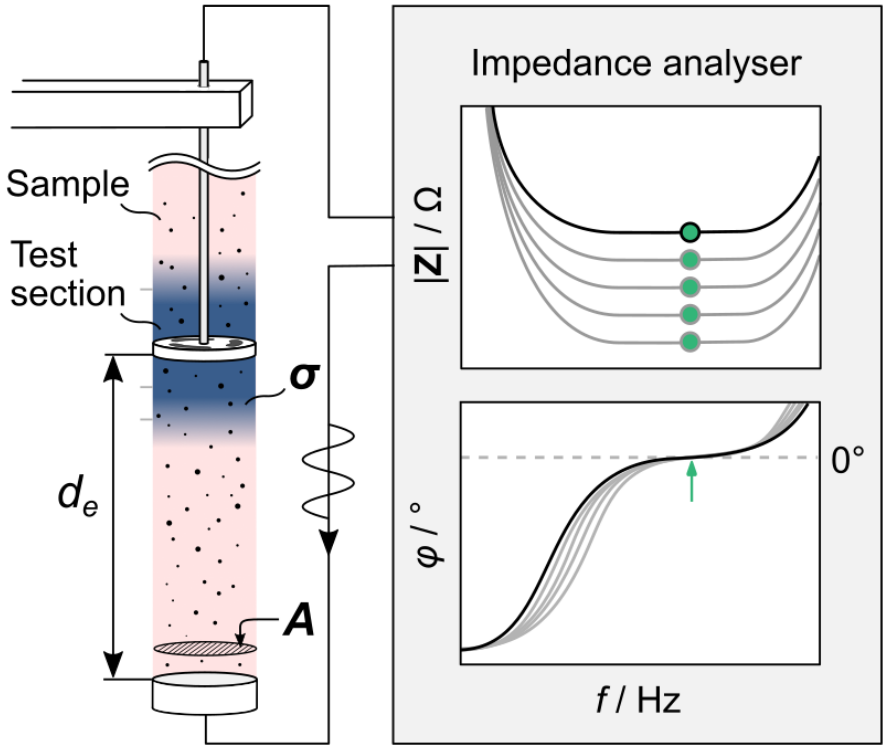
- Highly conductive samples → Hardware limitation
- Corrosive or passivating samples → (Long-term) accuracy
- (Macroscopically) heterogeneous samples cannot be characterised

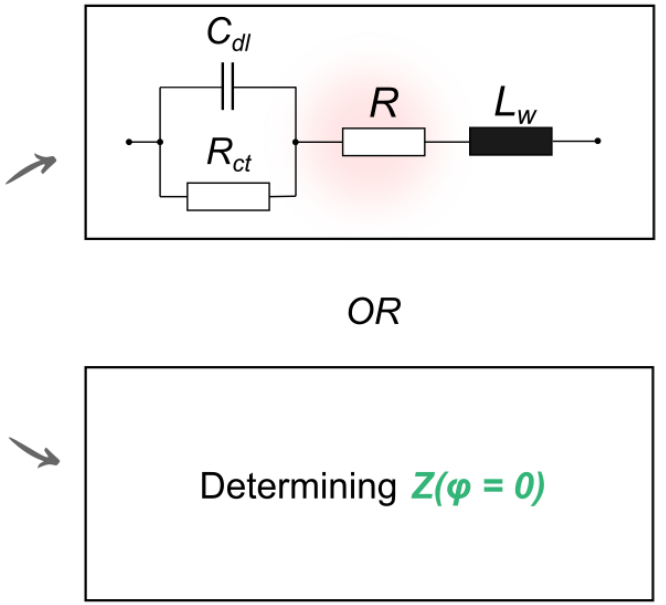


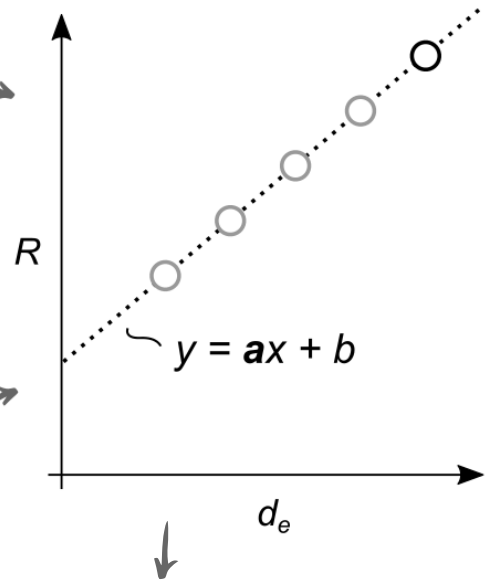
https://www.gamry.com/potentiostats/reference-600-plus/



BASIC PRINCIPLE OF MOVING ELECTRODE EIS (MEEIS)

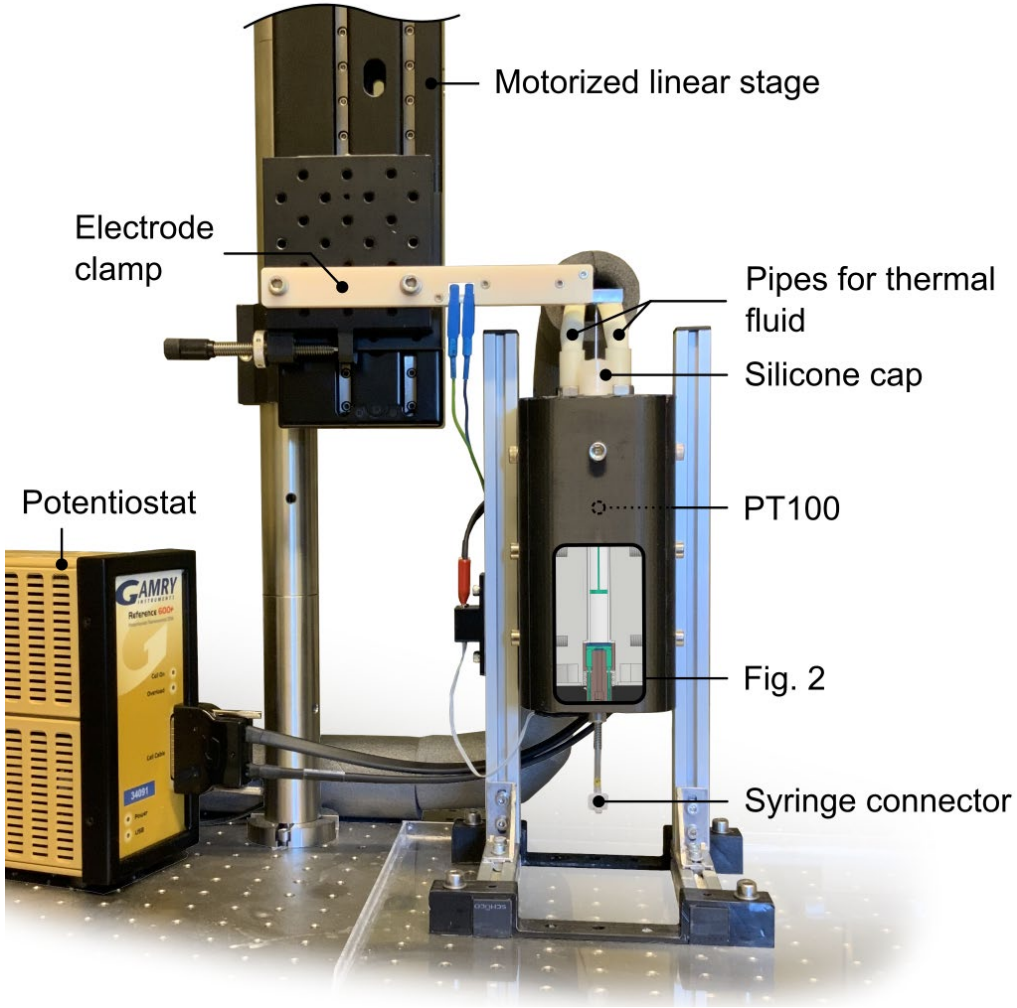


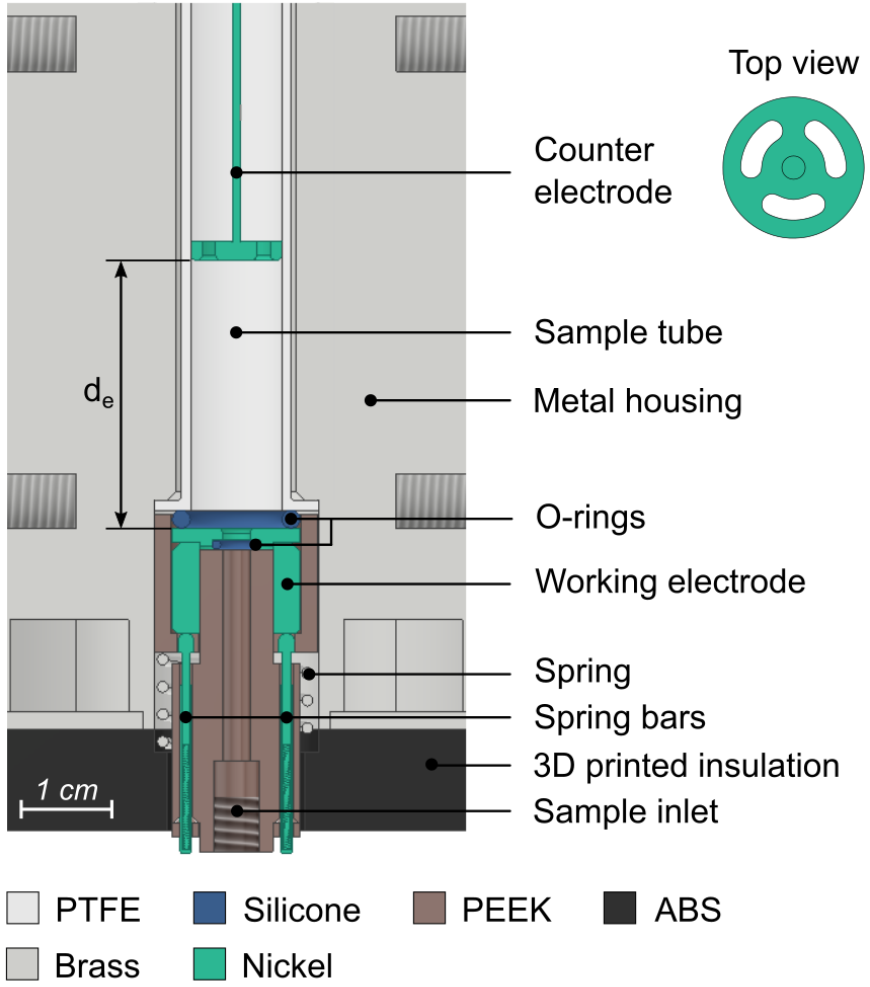




$$\sigma_{MEEIS} = \frac{1}{aA}$$

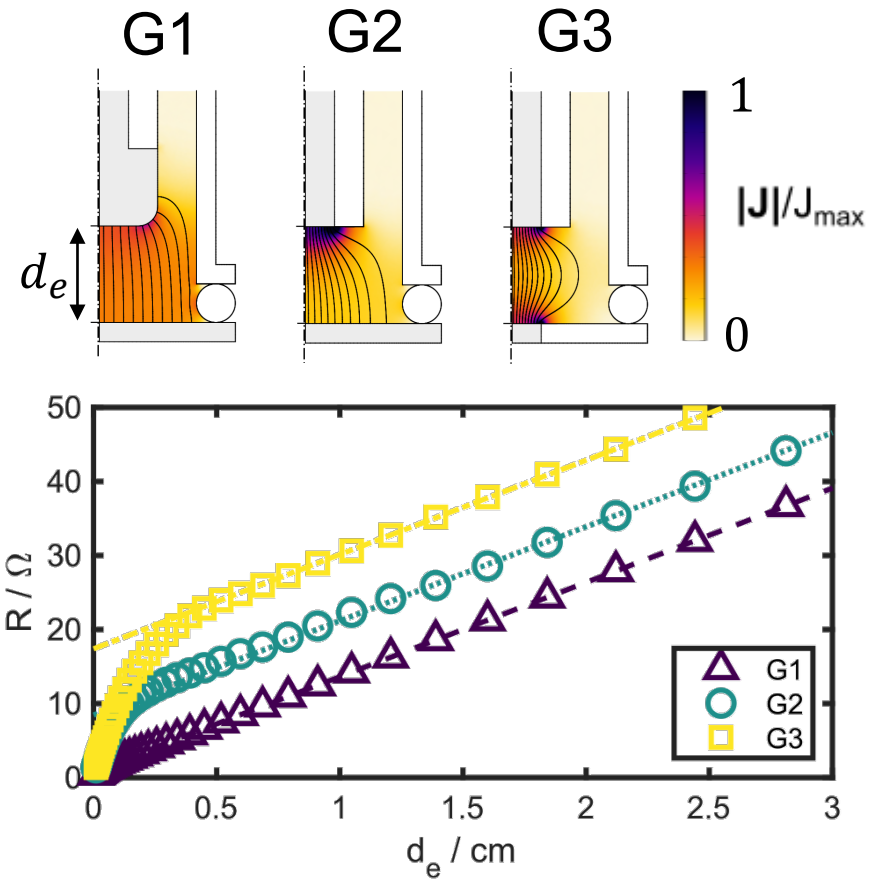
CELL DESIGN


Motorized linear stage
Electrode clamp
Pipes for thermal fluid
Silicone cap
Potentiostat
PT100
Fig. 2
Syringe connector
GAMRY

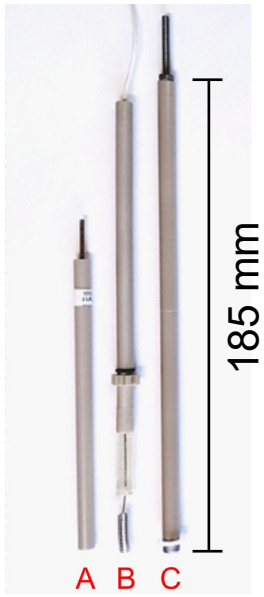

Top view
Counter electrode
Sample tube
Metal housing
d_e
O-rings
Working electrode
Spring
Spring bars
3D printed insulation
Sample inlet
1 cm
PTFE
Silicone
PEEK
ABS
Brass
Nickel

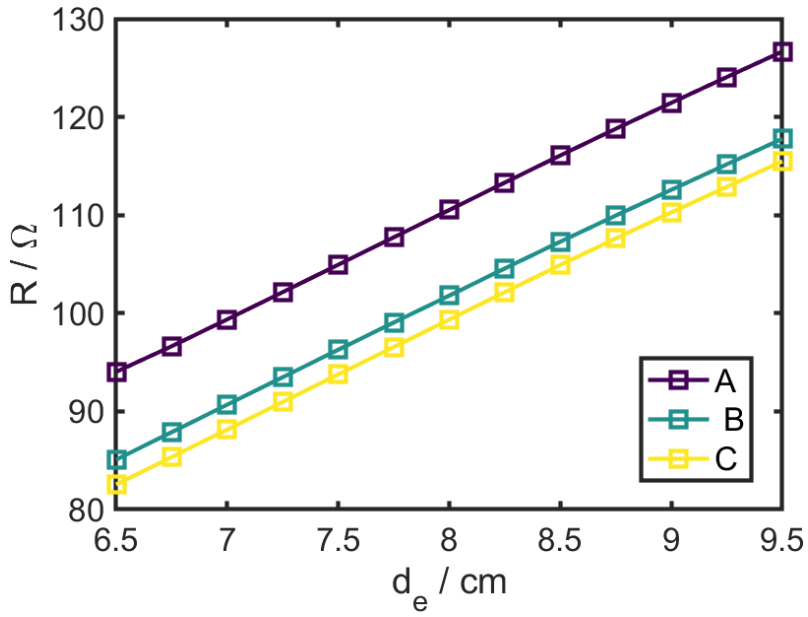
MEEIS VS EIS: INFLUENCE ELECTRODE GEOMETRY

Simulation (COMSOL)



Lab experiment





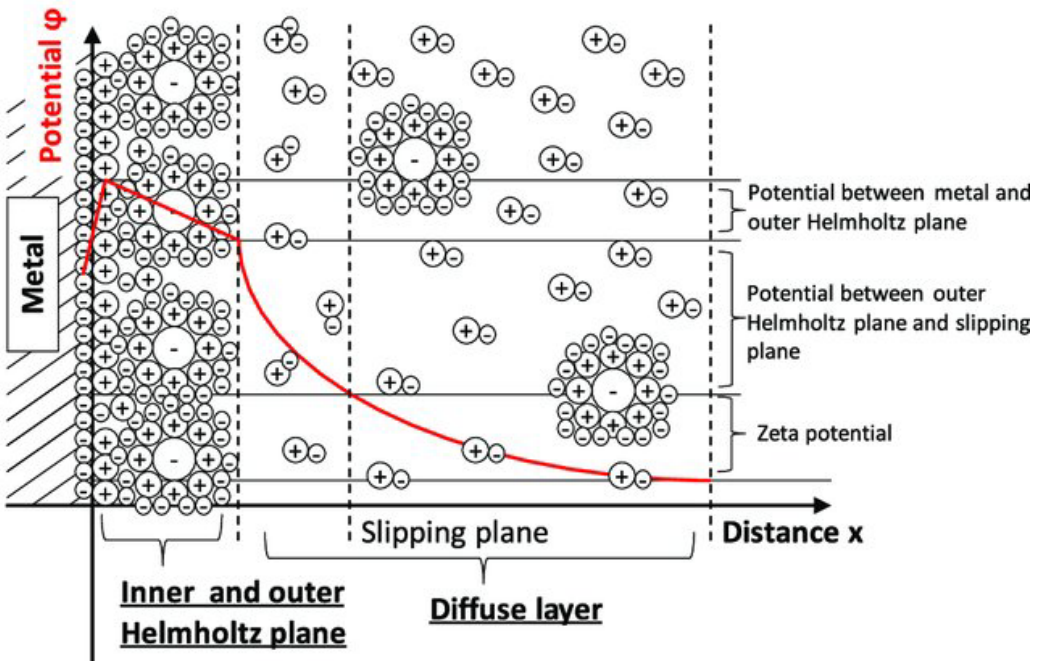
$$\sigma_{static} = \frac{l}{RA} \rightarrow \sigma_{G1} \neq \sigma_{G2} \neq \sigma_{G3}$$

$$\sigma_{MEEIS} = \frac{1}{aA} \rightarrow \sigma_{G1} = \sigma_{G2} = \sigma_{G3}$$

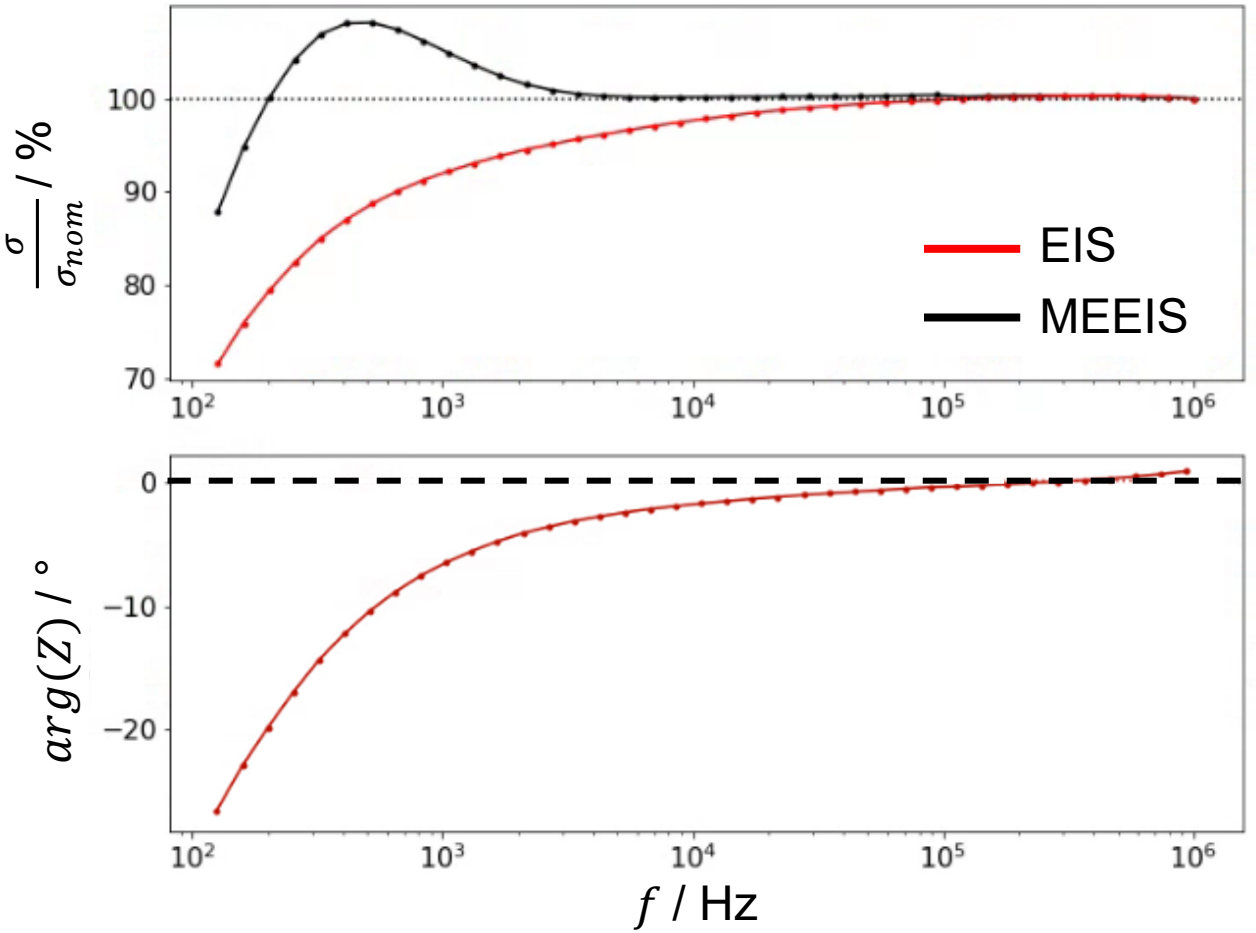
JKU ime

Doppelhammer, N., et. al., *ACS Sensors*, *5*(11), 3392-3397.

MEEIS VS EIS: INFLUENCE DOUBLE LAYER

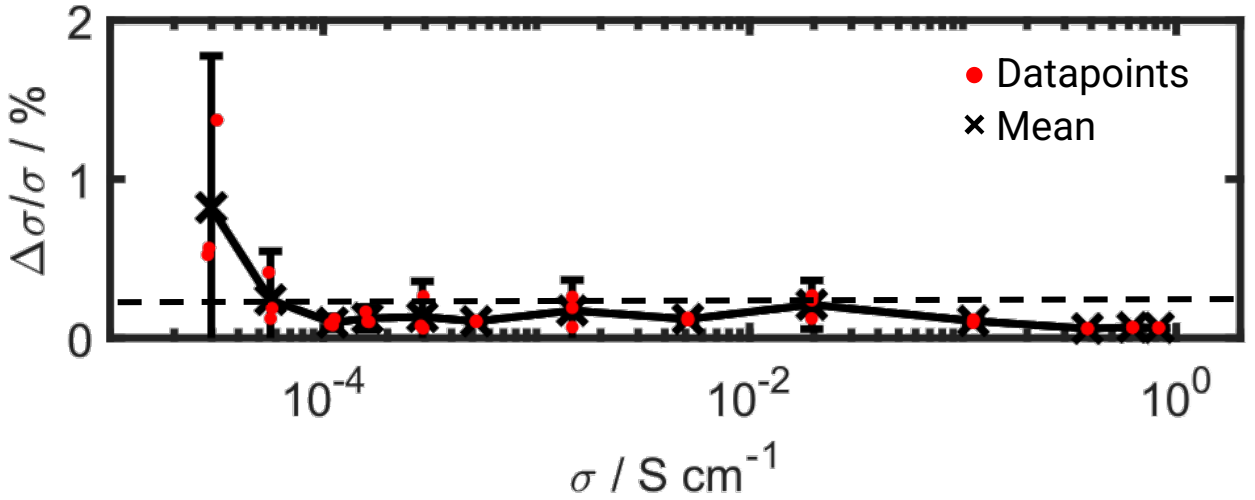


Hamann et.al., Electrochemistry



MEEIS VS EIS: ACCURACY (CONDUCTIVITY)

MEEIS cell



[1]

0.23%

Commercial systems

2-5: Datasheet specifications of Mettler Toledo InPro 7000-VP (2), Mettler Toledo InPro 7100-VP (3), Yokogawa ISC40 & Mettler Toledo InPro7250ST PEEK (4), Hanna Instruments HI7650-11xx (5)

Inductive sensors — $0.5\%^{4}$ … $2\%^{5}$

Static electrode sensors (2-pole) — $3\%^{2}$

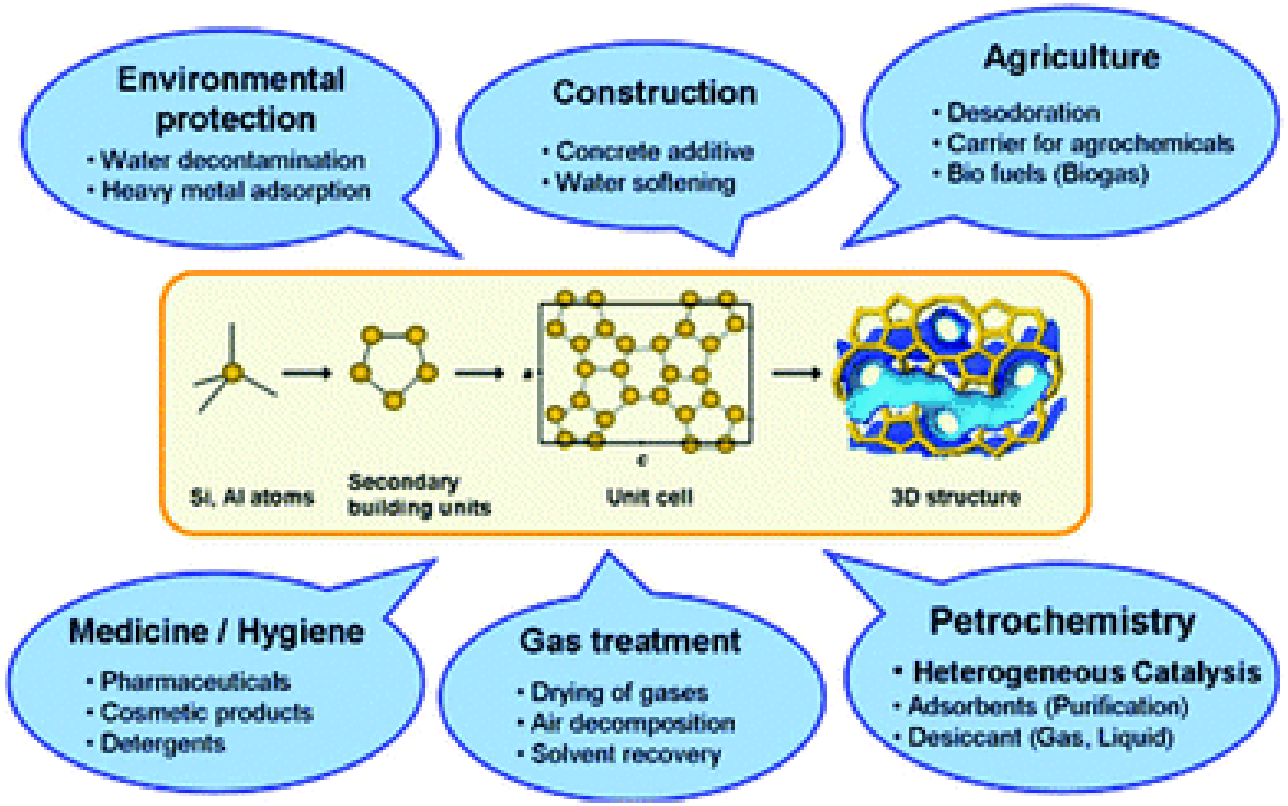
Static electrode sensors (4-pole) — $5\%^{3}$

[1] Doppelhammer et.al., *ACS Sensors*, *5*(11), 3392-3397

APPLICATION: IN-SITU INVESTIGATION OF CRYSTALLISATION PROCESSES

- Understanding crystallisation of complex materials
- Zeolites: Nanoporous, crystalline minerals with versatile application

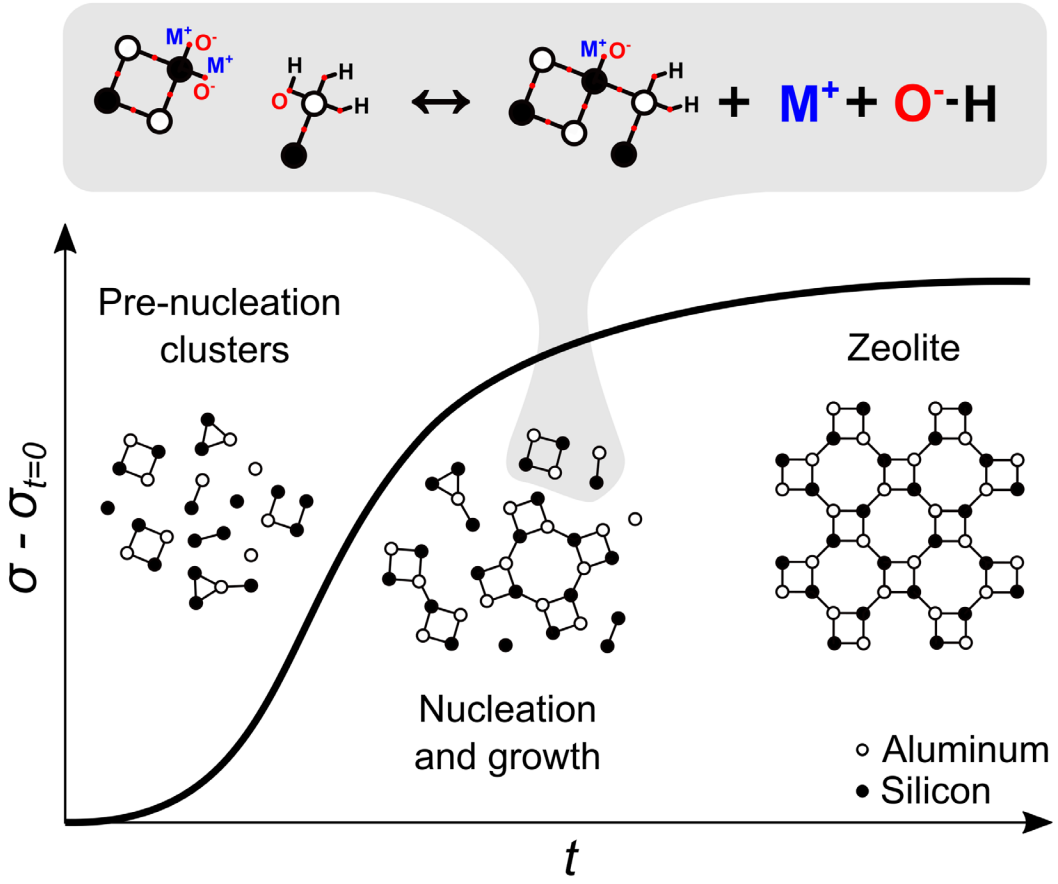
https://www.sercalia.com/en/zeolites/



Bacakova, Lucie, et al., *Biomaterials science* 6.5 (2018)

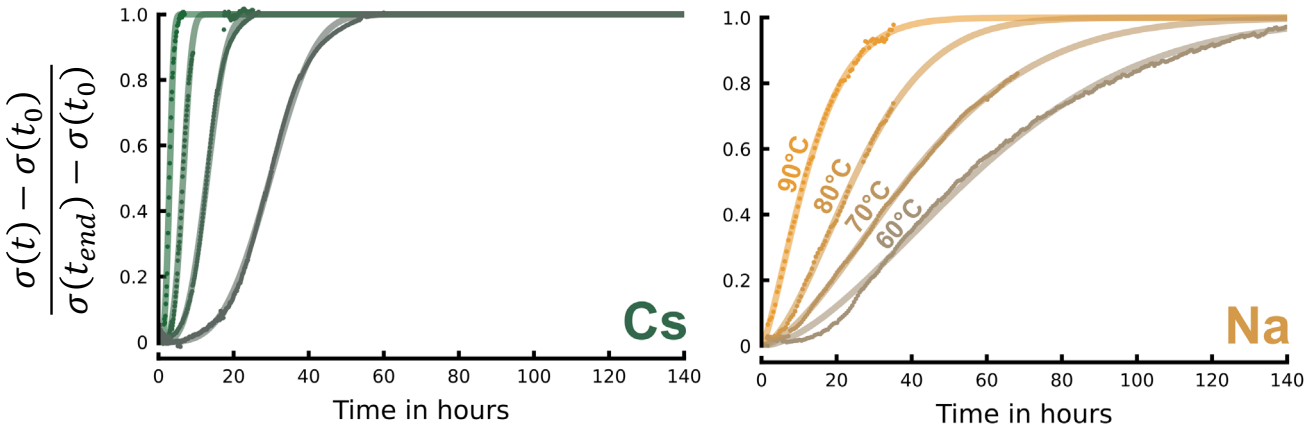
ZEOLITE FORMATION IN HYDRATED SILICA IONIC LIQUIDS (CONT'D)

- In highly alkaline conditions zeolites nucleate via ion-paired pre-nucleation clusters[1]
- Ion pairs act as dipols rather than free charges → weak contribution to σ
- Upon condensation, ion pair bond is broken and highly mobile ions are release back into the synthesis medium[2,3]
- $\sigma \sim$ **Number of (net) condensation events**



[1] Pellens, Nick, et al., *Chemistry of Materials* (2022).
[2] Doppelhammer, N., et. al., *2021 IEEE Sensors* (2021).
[3] Pellens, Nick, et al., *Faraday Discussions* (2021).

MEEIS IN-SITU CONDUCTIVITY MONITORING

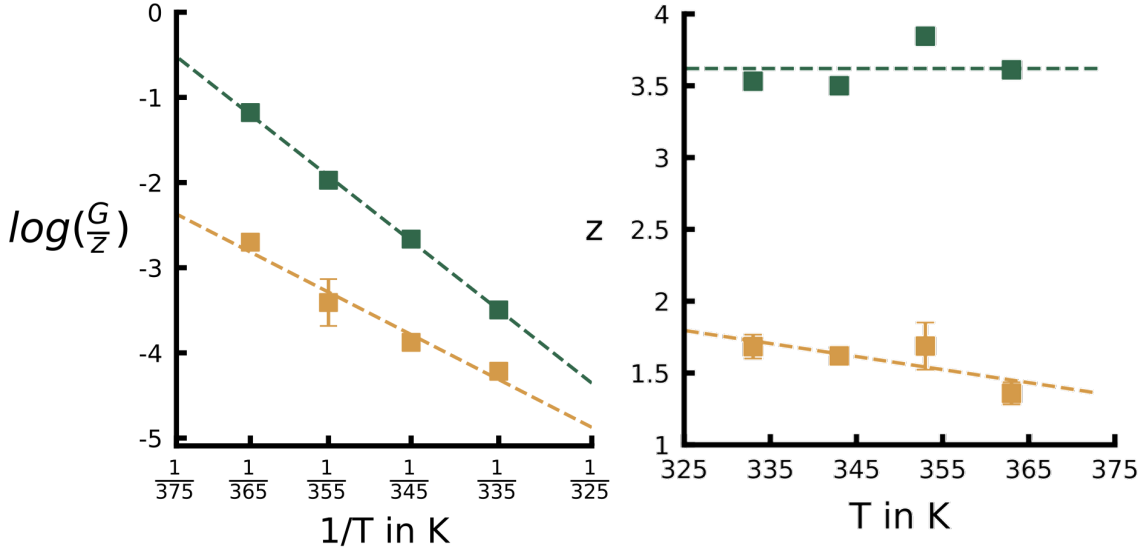


- MEEIS measurement data
- Model[1]

$$\frac{\sigma(t)-\sigma(t_0)}{\sigma(t_{end})-\sigma(t_0)} = 1 - \exp(-\boldsymbol{G}t^{\boldsymbol{z}})$$

- Fast crystallisation
- "Avrami"-type crystallisation ($z = 4$) → Spherical growth

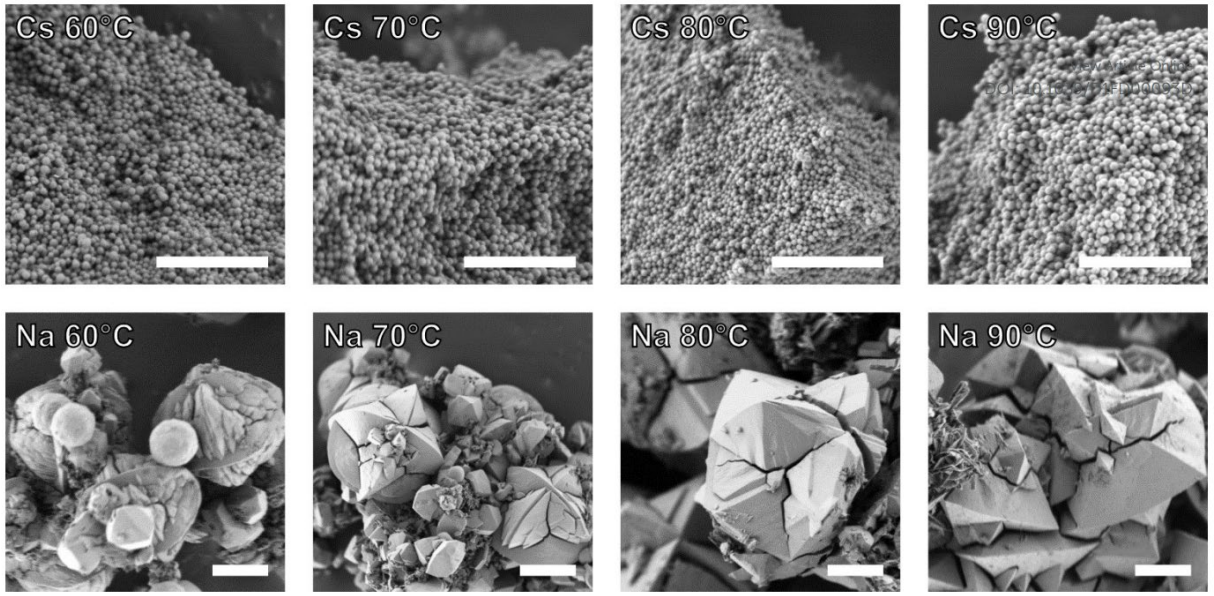
- Slow crystallisation
- Growth at preferred sites ($z \sim 1.5$) → Facetted growth



Images and [1]: Pellens, Nick, et al., *Faraday Discussions* (2021)

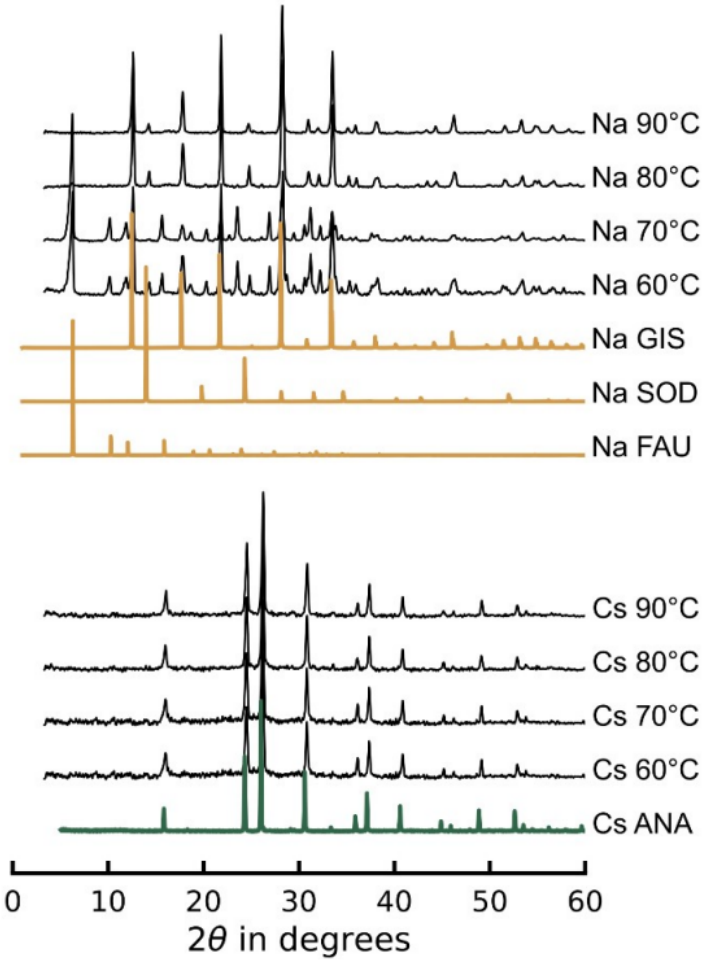
ZEOLITE FORMATION IN HYDRATED SILICA IONIC LIQUIDS (CONT'D)

SEM

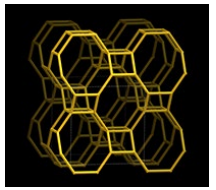


Marker length 2 μm

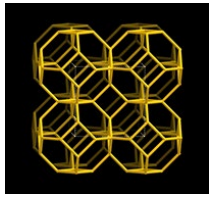
XRD



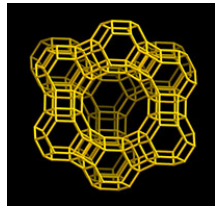
GIS



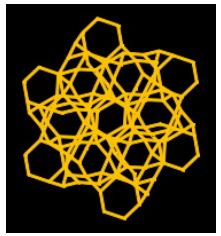
SOD



FAU



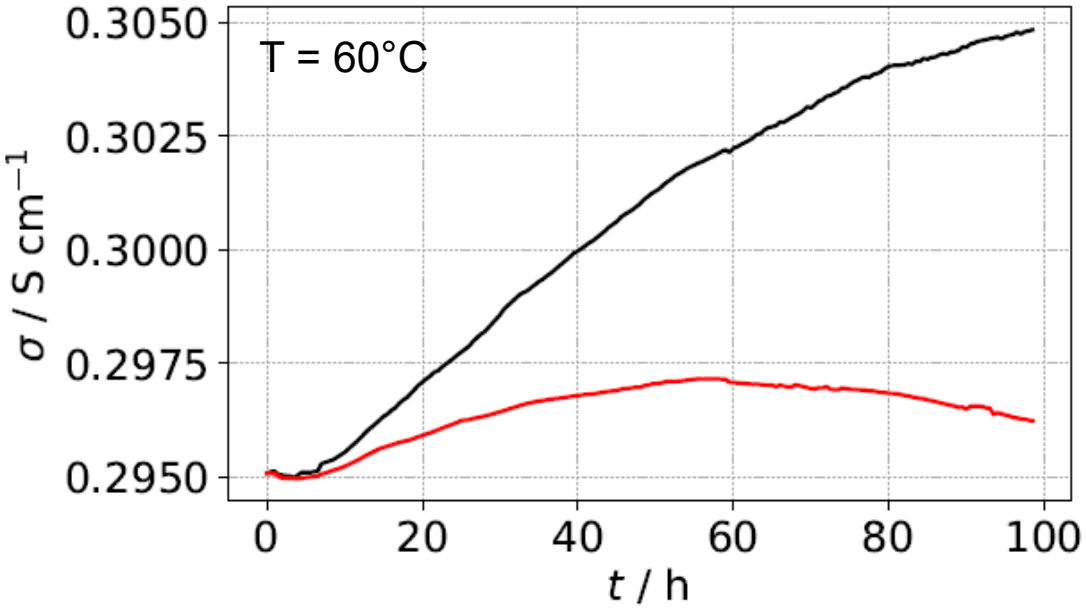
ANA



JKU ime

Images: Pellens, Nick, et al., *Faraday Discussions* (2021) & https://europe.iza-structure.org/

MONITORING ZEOLITE FORMATION: MEEIS VS EIS



Severely passivated electrode after zeolite synthesis experiment

SUMMARY

- **Heterogenous**, **highly conductive** and **corrosive** samples are problematic in EIS
- **MEEIS** → Variable electrode distance → Determination of sample properties from **impedance increments** instead of absolute impedance values
  - No influence of (quasi-)static contributions, e.g., electrode geometry, (slow) electrode passivation, wires, etc.
  - Extended frequency range (decreased influence of double layer)
  - Highly accurate and robust
- **In-situ monitoring** of alkaline **zeolite formation**
  - Conductivity reflects fraction of transformed volume
  - Harsh chemical conditions and small conductivity changes → MEEIS
  - Quantification of crystallisation process by kinetic chemical model[1]

[1] Pellens, Nick, et al., *Faraday Discussions* (2021)

ACKNOWLEDGEMENTS

... and my colleagues at IME!

- Special thanks to
  - Nick Pellens (COK-CAT, KUL)
  - Prof. Christine E.A. Kirschhock (COK-KAT, KUL)
  - Eric Breynaert (COK-CAT, KUL)
  - Prof. Bernhard Jakoby (IME, JKU)
  - Dr. DI Erwin Reichel (IME, JKU)
  - all **research partners** and **funders**!

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THANK YOU

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