# Reliability of electrochemical impedance spectroscopy measurements : results of round-robin testing

François Huet, Kieu Ngo

# Reliability of electrochemical impedance spectroscopy measurements: Results of round-robin testing

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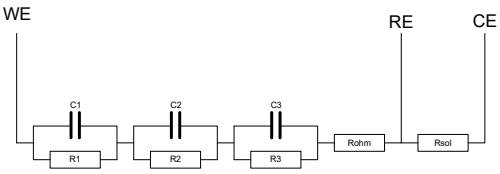
## Round-Robin tests on EIS measurements

- 19 laboratories participated in the RR tests
- 23 measurement systems (mainly general-purpose potentiostats and frequency response analyzers):
  - Bio-Logic: 1 SP-200
  - Gamry: 8 Ref600, 1 PC3/750, 1 PCI4/750, 1 PCI4/300, 1 Interface 1000
  - Ivium Technologies: 1 ??
  - IPS: 1 PGU 10V-1A-IMP-S
  - Metrohm: 1 Autolab PGSTAT302N + FRA32M
  - Solartron: 1 FRA 1260 + 1287, 2 FRA 1255B + 1287a, 1 Modulab, 1 FRA 1250 + Macrostat MGS-03 (home made potentiostat)
  - Solartron 1 FRA 1255 + Autolab PGSTAT 302N
  - Zahner: 1 IM6e

## Results of RR1 (2010): dummy cell

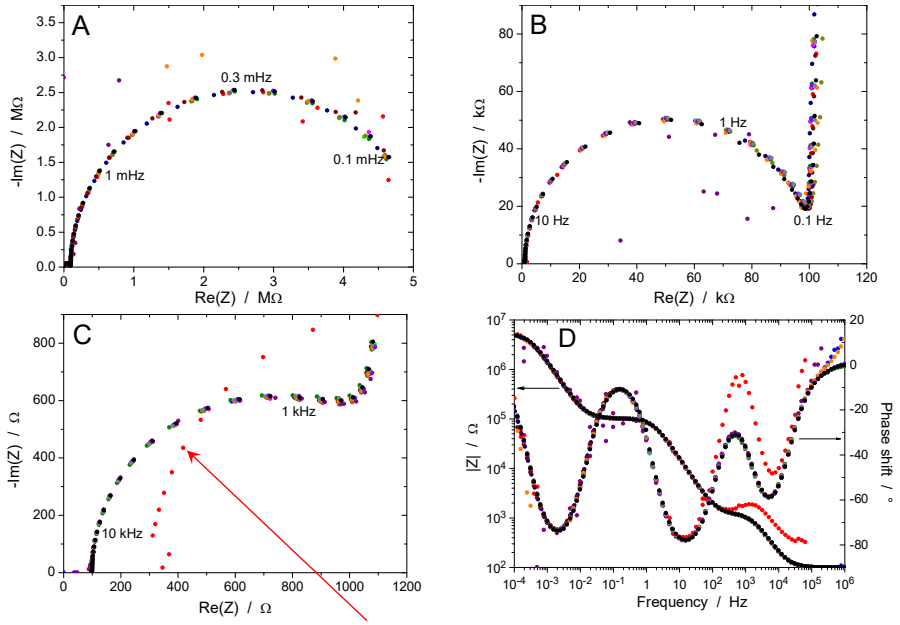



**5.1 MΩ // 100 µF + 100 kΩ // 1 µF + 1 kΩ // 100 nF + 100 Ω (Rsol = 1 kΩ)**

14 participants: AEKI, AREVA, Cadiz, CNRS, GAMRY, ICT-Prague, IPS, KTH, Magdeburg, PSI, SCK•CEN, SERCO, Studsvik, ZAG

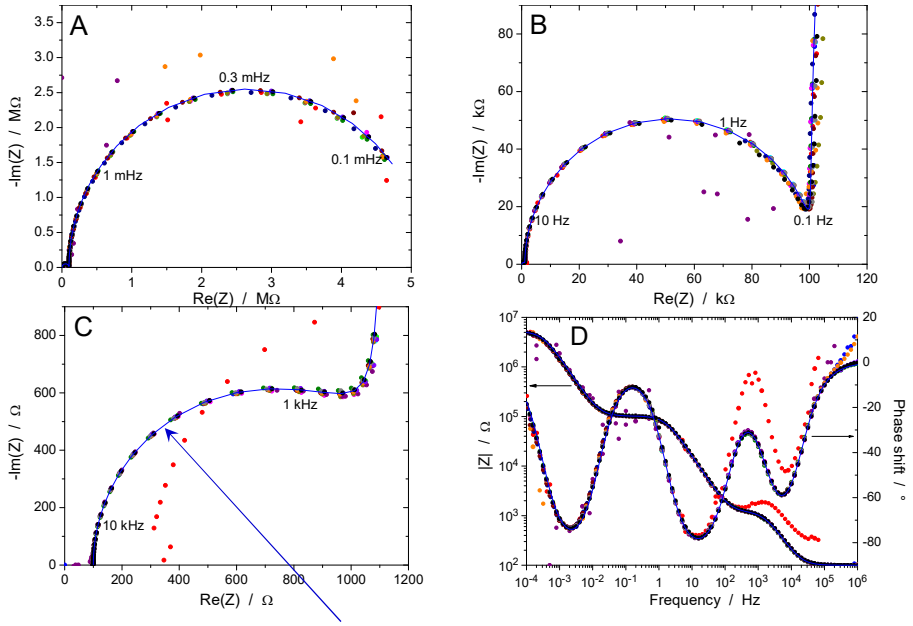
Equipment used: 10 Gamry (7 Ref600, 2 PC4/750, PC3-750), 2 Solartron 1255 + 1287, 1 Autolab PGSTAT 30, 1 PGU 10V-1A-IMP-S

## Results of RR1: dummy cell



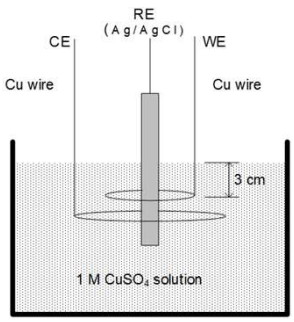

AEKI (Autolab PGSTAT 30)

## Results of RR1: dummy cell




impedance simulated with the fitted values of the components

## Results of RR2 (2012): Cu in 1 M $CuSO_4$




Question

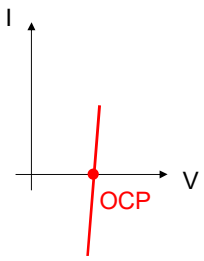
The position of the CE was not specified in the test procedure. In the figure, the RE is not between the WE and CE. In practice, where did you place the CE?

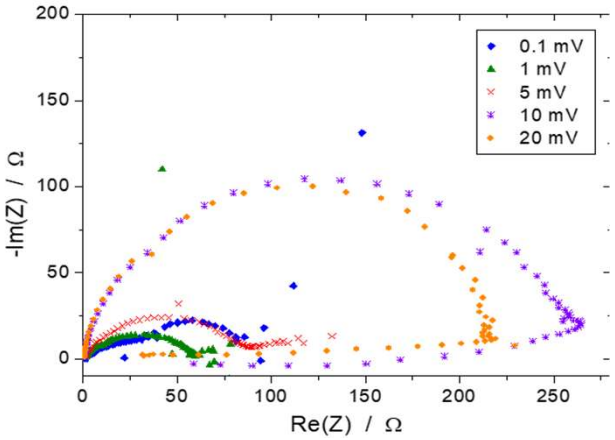
13 participants: AREVA, AEKI, BAM, GAMRY, PSI, SCK-CEN, SERCO, SIKA, STUDSVIK, TITANIA, UMIST, Univ. Czech, VTT

Equipment used: 8 Gamry (6 Ref600, 1 PC3/750, 1 PC4/750), 3 Solartron 1287 + 1255 or 1260, 1 Autolab PGSTAT 30, 1 Zahner IM6e

## Results of RR2 (2012): Cu in 1 M $CuSO_4$

used as reference electrode




$\Delta V_{rms} \approx 1$ mV

A: galvanonostatic, 1 hour after immersion, I = 0, $\Delta I_{rms}$ = 10 μA, 100 kHz to 1 mHz

B: potentiostatic, 5 hours after immersion, OCP, $\Delta V_{rms}$ = 0.1 mV, 100 kHz to 1 mHz

C: potentiostatic, 9 hours after immersion, OCP, $\Delta V_{rms}$ = 1 mV, 100 kHz to 1 mHz

## Results of RR2 (2012): Cu in 1 M $CuSO_4$

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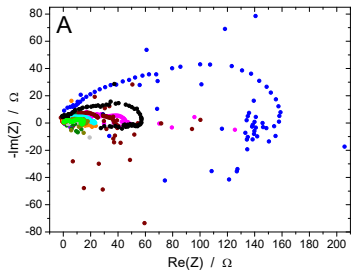
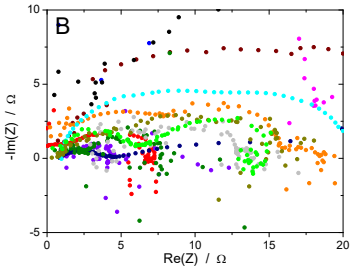
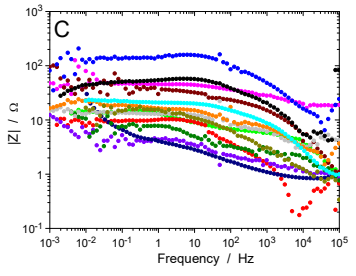
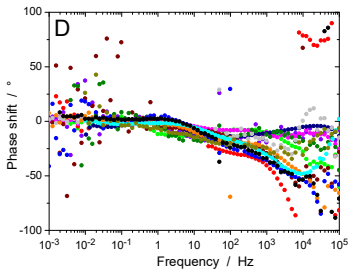


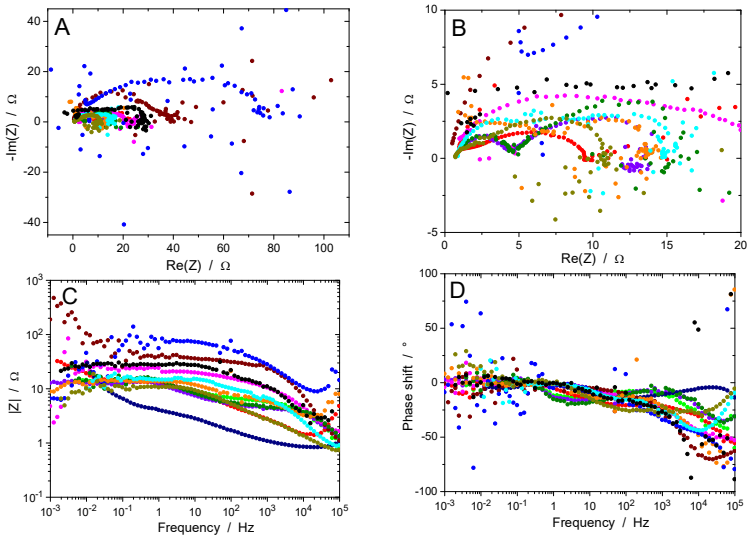




large scatter due to the EC system

## Results of RR2 (2012): Cu in 1 M $CuSO_4$

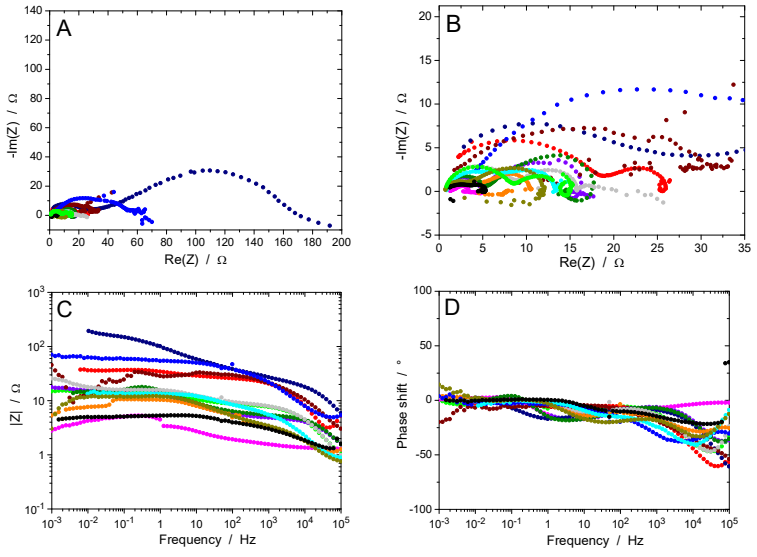
B: potentiostatic, 5 hours after immersion, OCP, $\Delta V_{rms}$ = 0.1 mV, 100 kHz to 1 mHz




still large scatter due to the EC system

## Results of RR2 (2012): Cu in 1 M $CuSO_4$

C: potentiostatic, 9 hours after immersion, OCP, $\Delta V_{rms}$ = 1 mV, 100 kHz to 1 mHz

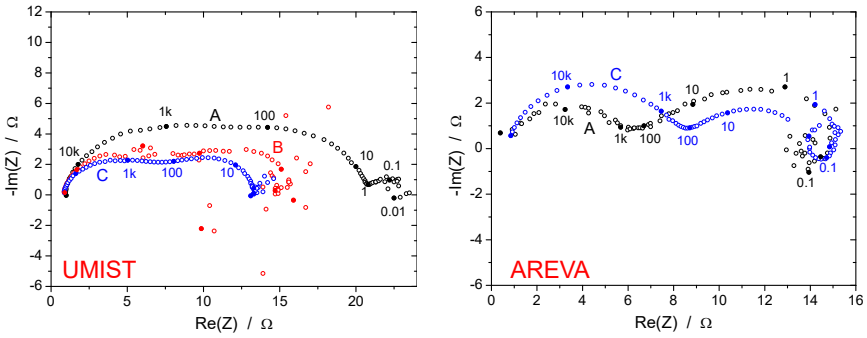



still large scatter due to the EC system

but more accurate impedances

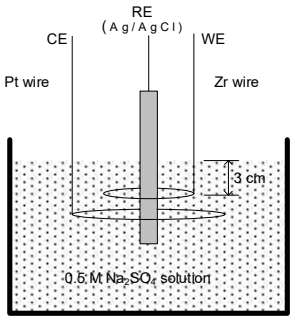
## Results of RR2 (2012): Cu in 1 M $CuSO_4$

- too-complex system for a RR test (RE, low $\Delta V_{rms}$, $\Delta I_{rms}$, RE position)
- AREVA and UMIST plots measured with a Gamry Ref600




- complex shape of the impedance diagram
- influence of the immersion time
- influence of the amplitude of the excitation signal

## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$




Question

The position of the CE was not specified in the test procedure. In the figure, the RE is not between the WE and CE. In practice, where did you place the CE?

10 participants: AMEC, AREVA, BAM, GAMRY, JRC Petten, SCK•CEN, TITANIA, UMIST, Univ. Czech, VTT

Equipment used: 6 Gamry (3 Ref600, 2 PCI4/300, Interface 1000), 1 Autolab PGSTAT302N + FRA32M, 1 Solartron Modulab, 1 Solartron 1287 + 1260, 1 Solartron 1255 FRA + Autolab PGSTAT 302N

## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

- 7 measurements in potentiostatic mode at OCP

  A: 6 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 5 mHz

  B: 24 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

  C: 120 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

  D: 168 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

  E: after measurement D, $\Delta V_{rms}$ = 2 mV, 100 kHz to 0.5 mHz

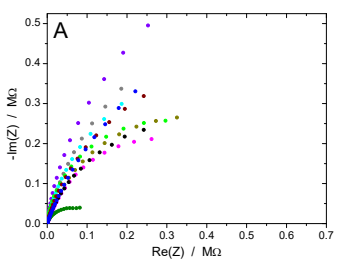
  F: after measurement E + 15 min at OCP, $\Delta V_{rms}$ = 5 mV, 100 kHz to 0.5 mHz

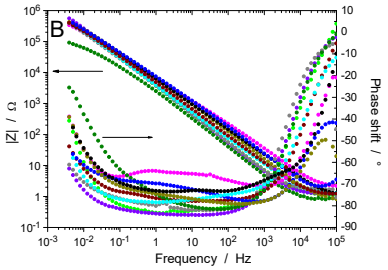
  G: after measurement F + 15 min at OCP, $\Delta V_{rms}$ = 50 mV, 100 kHz to 0.5 mHz

- influence of the immersion time: A, B, C, D
- influence of the amplitude of the excitation signal: D, E, F, G

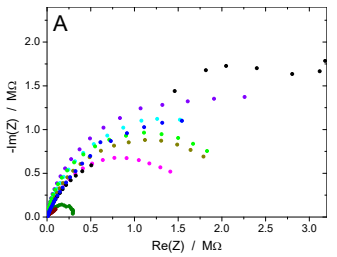
## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

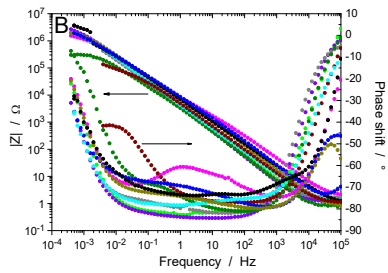
A: 6 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 5 mHz



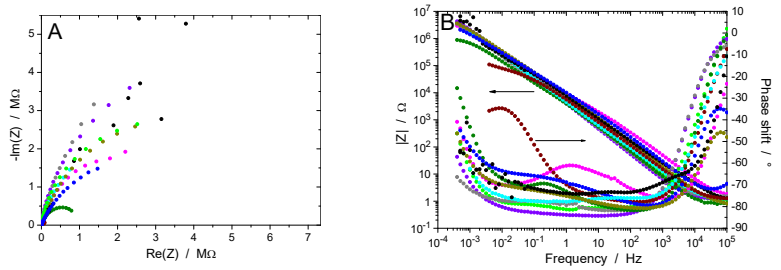

B: 24 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz



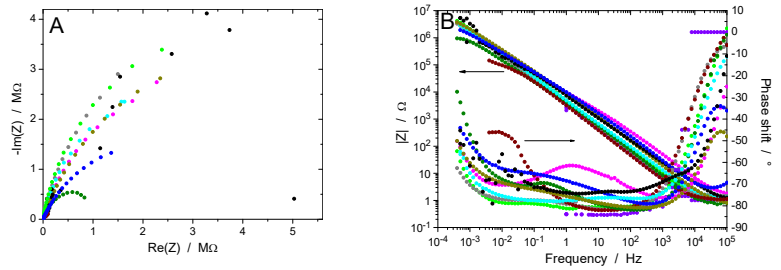



## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

C: 120 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

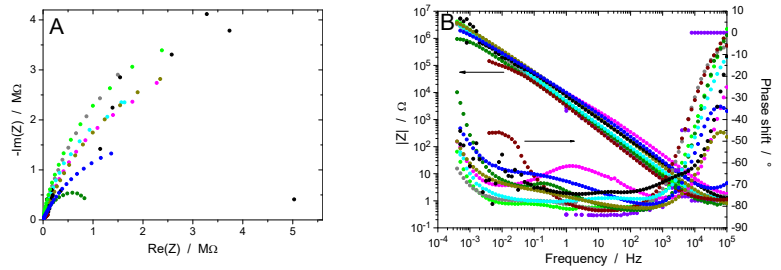



D: 168 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

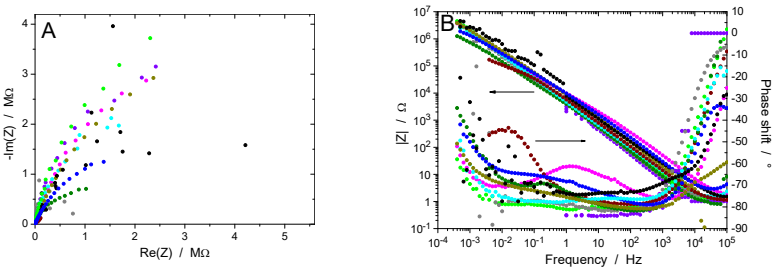



## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

D: 120 hours after immersion, $\Delta V_{rms}$ = 20 mV, 100 kHz to 0.5 mHz

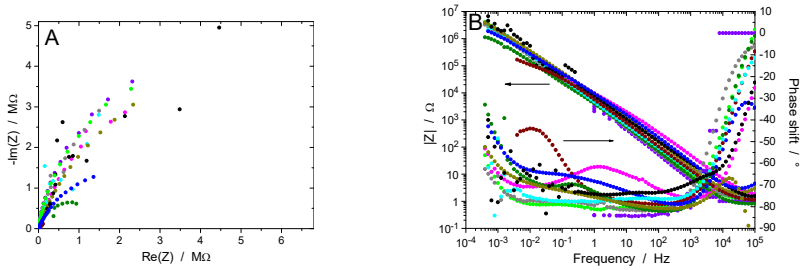



E: after measurement D, $\Delta V_{rms}$ = 2 mV, 100 kHz to 0.5 mHz

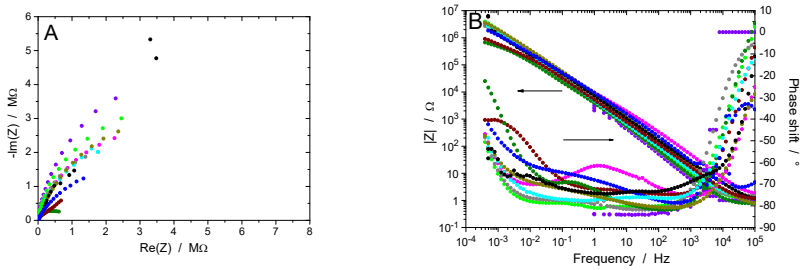


## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

F: after measurement E + 15 min at OCP, $\Delta V_{rms}$ = 5 mV, 100 kHz to 0.5 mHz

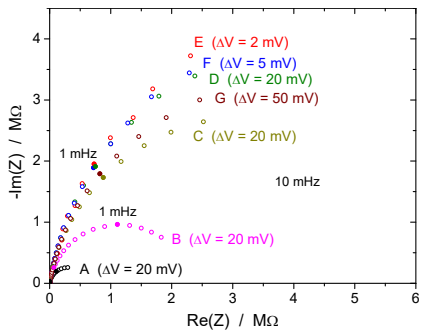



G: after measurement F + 15 min at OCP, $\Delta V_{rms}$ = 50 mV, 100 kHz to 0.5 mHz

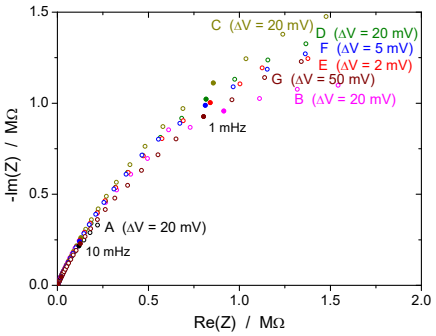



## Results of RR3 (2013): Zr in 0.5 M $Na_2SO_4$

- influence of the immersion time and amplitude of the excitation signal




AREVA using Gamry PCI4




TITANIA using Solartron 1255 FRA + Autolab PGSTAT 302N.

- results not quite similar in both cases

## Conclusions

- 3 RR tests: dummy cell, low-impedance system, high-impedance system
- dummy cell: all potentiostats performed well from 0.1 mHz to 1 MHz
- large scatter for Cu in $CuSO_4$: difficult system (RE, small excitation signal, position of the RE)
- much lower scatter for Zr in $Na_2SO_4$
- in both electrochemical systems: scatter not due to the potentiostat

Publication

- poster presented by Kieu at the 11th Int. Symposium on EIS, Lège-Cap-Ferret, France, 2-7 June 2019
  co-authors: R.-W. Bosch, R.A. Cottis, F. Huet, K. Ngo, S. Ritter
- publication: first version proposed by Rik, second version by François, submission to the special issue of Electrochimica Acta planned within 2-3 weeks
  co-authors: to be defined