Basics of electrochemical impedance spectroscopy, EIS (Třešť, June 13, 2024)

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1. Impedance of electric two-poles

Electrical two-poles can be characterized by I(t) vs U(t) transients in time domain or by periodic (e.g. sinewaves, multisines) voltages and their current responses.

Impedance: Operational definition: amplitude ratio and phase angle of two sine waves of U and I on a stable, linear system. Properties of impedance/immittance: complex function, frequency-dependent. Impedance of a network can be calculated analogously to that of network of resistances. Plotting: complex plane (Argand, Nyquist), Bode representations.

How do the spectra look like? Examples of functions and complex plane plots of simple RC circuits. Reciprocity, multiplicity of circuits. Empirical elements with impedance functions, which cannot be realized by RC circuits. Measurement of impedance of a two-pole.

2. What kind of impedances appear in electrochemical systems?

Impedance elements with physical-chemistry meanings: resistances related to process rates, double layer and adsorption capacitances, diffusional impedances, scrambled ones like those for porous electrodes, trivial elements. Important equivalent circuits: the Randles circuit and others

How to measure impedances of electrochemical systems: hardware, static EIS, single frequency scanned mode, dEIS.

3. Case studies

Determination of bulk resistances

Charge transfer reaction rate measurements (pure and applied electrochemistry, corrosion).

Characterization of the double layer by capacitance measurements (example: Mott-Schottky)

4. Experimental aspects of EIS

Spectrum evaluation: curve fitting and inspection of the fit results; how to select the fit model; how to plot/represent data; what if the system is not in steady state (simple visual inspection of the spectra, Kramers-Kronig tests, Stoynov's method for transforming to instantaneous state, multisine measurements)

Hardware and electronics: Measurement of various electrochemical cells; noise and its reduction; shielding, grounding; sampling rate and mode; testing and calibration

Cell construction principles: Clean cells vs cells with homogeneous current density; feedback ratio; reference electrode impedance reduction

5. Summary: Use EIS when you know what is the system – then you can get exact numbers for process rates, charge structures etc.

Suggested books:

- Andrzej Lasia: Electrochemical Impedance Spectroscopy and its Applications, Springer 2014, ISBN: 978-1-4614-8933-7
- Evgenij Barsoukov & J. Ross Macdonald: Impedance Spectroscopy: Theory, Experiment, and Applications, Wiley-Interscience; 3d ed. , 2018, ISBN: 978-1-119-07408-3
- Mark E. Orazem, Bernard Tribollet, Electrochemical Impedance Spectroscopy, 2nd Edition, Wiley-Interscience, 2017, ISBN: 978-1-118-52739-9

Application Notes are available at:

- https://www.ameteksi.com/library/application-notes/solartron-analytical
  in particular: Claude Gabrielli's Use and Applications of Electrochemical Impedance Techniques and Identification of electrochemical processes by frequency response analysis
- https://www.gamry.com/application-notes/EIS/complete-list
- https://www.zahner.de/service-support#applicationsNotes

See also T. Pajkossy: Impedance spectroscopy at interfaces of metals and aqueous solutions - surface roughness, CPE and related issues, Solid State Ionics 176 (25-28), 1997-2003 (2005), doi: 10.1016/j.ssi.2004.06.023