EIS in Fuel Cell Science

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Electrochemical Impedance Spectroscopy
Fundamentals and Applications
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Presentation outline

• Introduction
  • Motivation
  • Types of Fuel Cells
  • Experimental set-up for different types of FCs

• Microstructure of fuel cells and modeling of fuel cells with equivalent circuits

• Impedance models of porous electrodes

• Different applications of EIS in FC research
  • Contributions to performance loss of PEFC
  • Degradation mechanism of PEFC
  • Time dependent EIS
    • CO poisoning of PEFC-anodes
    • Flooding of PEFC cathodes
  • EIS measured on Ag-Gas Diffusion Electrodes (GDE) during Oxygen Reduction in alkaline electrolyte (AFC)
  • EIS measured at fuel cell stack (SOFC)

• Conclusion
Motivation

Characterization of Fuel Cells by Electrochemical Impedance Spectroscopy:

- Determination of electrode structure and reactivity, separation of electrode structure from electrocatalytically activity
- Determination of reaction mechanism (kinetic) and separation of different overvoltage contributions to the fuel cell performance loss
- Determination of degradation mechanism of electrodes, electrolyte and other fuel cell components (bipolar plates, end plates, sealings, etc.)
- Determination of optimum operation condition (e.g. gas composition, temperature, partial pressure), cell design (flow field) and stack design

Schematic representation of main types of fuel cells
Experimental set up and cells used for EIS
Segmented and single PEFC cell (polymer electrolyte)

Fuel "half" cell with liquid electrolyte

Test cell for SOFC (short stack)
(Solid Oxide Electrolyte)

Fuel cell overvoltage and current density / voltage characteristic

Hydrogen Oxidation Reaction (HOR):
\[ \eta_{H_2} = \frac{RT}{2F} \ln \left( \frac{i}{i^*} \right) \]

Oxygen Reduction Reaction (ORR):
\[ \eta_{O_2/air} = \frac{RT}{(1-\alpha)2F} \ln \left( \frac{i}{i^*} \right) \]

Ohmic loss
\[ \eta_O = iR \]

Transport limitation (diffusion)
\[ \eta_d = -\frac{RT}{2F} \ln \left( \frac{1}{i/i_{lim}} \right) \]

Fuel cell voltage
\[ U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_O \]
Electrochemical Impedance Spectroscopy: Application to Fuel Cells

Potential excitation signal - E(t)

U/I - Characteristic of a Fuel Cell

Cell voltage U

Current I

Ruhespannung (ohne Stromfluß)

Anode

ΔU = iRM

Cathode

EIS in Fuel Cell Science, Norbert Wagner, 06.11.2015

www.DLR.de  •  Chart 7

Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance

ΔU = iRM

Anodic Overvoltage

Cathodic Overvoltage

Cell voltage

ΔU(Cell)

Current density

Δi

U-i measured
Overview of the wide range of dynamic processes in FC

- Electric double layer charging
- Membrane humidification
- Charge transfer fuel cell reactions
- Liquid water transport
- Gas diffusion processes
- Degradation and ageing effects
- Changes in catalytic properties / poisoning
- Temperature effects

Time / s

- microseconds
- milliseconds
- seconds
- minutes
- hours
- days
- months

Bode representation of EIS measured at different current densities, PEFC operated at 80°C with H₂ and O₂ at 2 bar

Field of application of porous electrodes

Water purification and treatment
(Bio)-Organic synthesis

Fuel Cells

Electrolysis (Water, NaCl, etc.)

Batteries and supercaps
PEFC: Schematic Diagram (cross section)

Common Equivalent Circuit for Fuel Cells
SEM micrograph of PEFC electrode (Pt/C+PTFE)

TEM micrograph of Carbon Supported Platinum Catalyst
SEM picture of PTFE/C powder

Field of application of porous electrodes

- Water purification and treatment
- (Bio)-Organic synthesis
- Batteries and supercaps
- Fuel Cells
- Electrolysis (Water, NaCl, HCl, etc.)
Nyquist representation of Impedance of RC-transmission line, model of a flooded pore

\[ Z(i\omega) = \frac{R}{i\omega C} \coth(\sqrt{i\omega RC}) \]

\[ R_0 = \frac{R}{3} = \frac{\delta L}{3\pi r^2} \]

- \( \delta \) = specific electrolyte resistance
- \( r \) = pore radius
- \( L \) = pore length

Simple pore model with faradaic processes in pores
RC-transmission line of a flooded pore

- \( r \) = electrolyte resistance inside the pore per unit length
- \( c \) = interface capacitance per unit length
- \( r_{ct} \) = interface charge transfer resistance per unit length
Nyquist representation of porous electrode impedance with faradaic impedance element

\[
\begin{align*}
\ imag. \ part / \Omega & \quad \ real \ part / \Omega \\
-3 & \quad -2 \quad -1 \quad -0.5 \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5 \\
\end{align*}
\]

-3 \quad -2 \quad -1 \quad -0.5 \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5

-3 \quad -2 \quad -1 \quad -0.5 \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5

\[
\begin{align*}
C = 500 \text{ mF} \\
C + R_{\text{por}} (3 \text{ Ohm}) \\
C \parallel R (1.5 \text{ Ohm}) \\
\end{align*}
\]

-3 \quad -2 \quad -1 \quad -0.5 \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5

\[
\begin{align*}
l = 3 \text{ } \Omega \\
c = 500 \text{ mF} \\
r_{\text{ct}} = 1.5 \text{ } \Omega \\
\end{align*}
\]

Thin-film model and agglomerate plus thin-film model of a porous electrode

Agglomerated Electrodes

Hierarchical model
(Cantor-block model)

M. Eikerling, A.A. Kornyshev, E. Lust


Cylindrical homogeneous porous electrode model (H. Göhr)

H. Göhr in Electrochemical Applications/97, www.zahner.de
Bode diagram of EIS at different cell voltages measured at PEFC (H₂/O₂) at 80°C,

EIS at Polymer Fuel Cells (PEFC):
Contributions to the cell impedance at different current densities
Evaluation of the U-i characteristics from EIS

- measured curve: $U_n = f(i_n)$
- calculated curve: $U_n = i_n R_n$ (without integration)
- calculated curve using method II: $U_n = a_n i_n^2 + b_n i_n + c_n$
- calculated curve using method I: $U_n = a_n i_n + b_n$

Integration method I:

$$ R_n = \left. \frac{\partial U}{\partial I} \right|_n $$

$$ U_n = U_{n-1} - \frac{1}{2} \left( \left. \frac{\partial U}{\partial I} \right|_{n-1} + \left. \frac{\partial U}{\partial I} \right|_n \right) \ast (I_n - I_{n-1}) $$

Integration method II:

$$ U_n = a_n I_n^2 + b_n I_n + c_n $$

with:

$$ a_n = \frac{R_{n-1} - R_n}{2 (I_{n-1} - I_n)} $$

$$ b_n = \frac{R_{n-1} - 2 a_n I_{n-1}}{I_{n-1}} $$

$$ c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1} $$

EIS at Polymer Fuel Cells (PEFC):
Contributions to the overall U-i characteristic determined by EIS

$$ E_0 $$
$$ \Delta E_C $$
$$ \Delta E_A $$
$$ \Delta E_M $$
$$ \Delta E_{Diff.} $$

Current density / mAcm$^2$

Cell voltage / mV
Evaluation of EIS with the porous electrode model
Summary of current density dependency of pore resistance elements

Improved Evaluation Techniques for Time Resolved Electrochemical Impedance Spectroscopy (TREIS)

- Real time drift compensation
- Time course interpolation
- Z-HIT compensation
**Improved evaluation technique:**
Time course interpolation

Requirements
- Series measurement
- Time for each measured frequency AND for each spectrum

**Reforming of Methane**

\[ 	ext{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2 (\text{CO}) \]

- **Methane**
  - Compress.
  - a) Reformer-heating
  - b) Cat-Burner

- **Reformer**
  - Shift-reactor HT
  - 9% CO
  - 3% CO

- **Shift-reactor LT**
  - CO-cleaning
  - 0.5% CO

- **Residual Gas**
- **PEM-Fuel Cell**
  - H\textsubscript{2}, CO\textsubscript{2} < 0.005% CO

- **E-Energy**
- **Heat**

Air (O\textsubscript{2})
Appearance of voltage oscillations during galvanostatic operation of PEFC with H₂ + 100ppm CO

Time resolved EIS - CO poisoning of Pt-anode

Time progression of cell voltage and overvoltage in galvanostatic mode of PEFC operation (217 mA cm⁻²) Pt-anode, H₂ + 100 ppm CO at 80°C

Nyquist plot of EIS measured at different times during poisoning of the Pt-anode with CO
Measured and simulated time resolved EIS - CO poisoning

Nyquist plot of EIS during CO poisoning of the Pt-anode at 217 mA cm\(^2\), H\(_2\)+100 ppm CO

Time resolved EIS - CO poisoning

Bode plot of EIS during CO poisoning of the Pt-anode at 217 mA cm\(^2\), H\(_2\)+100 ppm CO
Simulated EIS with Relaxation Impedance: Theory

\[ \tau = 1 \text{ s}; \quad R_k = 10 \text{ m}\Omega; \quad R_\eta = 100 \text{ m}\Omega \]
\[ R_M = 5 \text{ m}\Omega; \quad C_{dl} = 10 \text{ mF} \]
\[ Z_F(\omega \to 0) = R_F = 9.1 \text{ m}\Omega \]

**Faraday-impedance:**
\[ Z_F = R_\eta/(1 + R_\eta/Z_k) \]

**Relaxation imp.:**
\[ Z_k = (1 + i\omega \tau)/I_F \frac{d\ln k}{dE} \]

**Time constant:**
\[ \tau = R_k L_k \]

**Relaxation resistance:**
\[ R_k = 1/I_F \frac{d\ln k}{dE} \]

**Relaxation inductivity:**
\[ L_k = \tau R_k \]

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Time resolved EIS
Flooding the cathode at 2 A, dead end
Time resolved EIS, flooding the cathode at 2 A, 80°C; time dependency of the cell voltage and impedance elements

Change of cell voltage during constant load at 500 mA cm⁻²
Bode Plot of EIS measured during PEFC operation over 1000 h at 500 mA cm⁻²

Variation of RC during PEFC operation at 500 mA cm⁻²
Variation of $R_A$ during PEFC operation at 500 mA cm$^{-2}$

Evaluation and Analyse of Voltage Loss by EIS

AFC: Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, \( i < -50 \text{ mAcm}^{-2} \)

**Bode representation**

**Nyquist representation**

Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, \( i > -50 \text{ mAcm}^{-2} \)

**Bode representation**

**Nyquist representation**
Adsorptions- and heterogeous reaction impedance

Definition of $Z_{\text{ad/het}}$:

$$Z_{\text{ad/het}} = \frac{RT(k-\omega i)}{n^2F^2c_sA(k^2+\omega^2)}$$

With $A=$electrode surface, $k=$ first order reactions rate,
$F=$Faraday constant, $c_s=$surface concentration and angular frequency $\omega=2\pi f$.

The heterogenous reaction impedance can be converted into a parallel combination of $R_{\text{ad/het}}$ and $C_{\text{ad/het}}$:

$$R_{\text{ad/het}} = \frac{RT}{(n^2F^2c_sA)}$$

$$C_{\text{ad/het}} = \frac{n^2F^2c_sA}{(RT)}$$
Evaluation of EIS measured during ORR
Equivalent circuit and $R_{ad} = f(i)$

U-i characteristic and current density dependency of impedance elements $R_{ad}$ and $R_{ct}$
Current density dependency of $k_{ad}$, $R_{ad}$ and $R_{ct}$, determined from EIS evaluation

$k_{ad} = \frac{1}{C_{ad}R_{ad}}$

Impedance Spectroscopy at SOFC short stack

Voltage probes

Current probes

Potentiostat/Electronic Load
Comparison of the sequential measurement principle for impedance spectra data acquisition with the synchronous parallel approach

Nyquist impedance diagram of the five individual cells within the SOFC short stack at OCP (1.19 V), measured synchronously

Operation under dry fuel gas (50 % H₂ + 50 % N₂ and air at 750 °C. Symbols: measurement data, solid lines: model fit
Conclusion

• Determination of the individual potential losses during fuel cell operation
• Determination of degradation mechanism and performance loss
• Improvement of fuel cell performance and stability by understanding instead of trial and error
• Determination of critical operation conditions of fuel cells

Thank you for the attention!