Theory and Application of Porous Electrodes in Fuel Cell Characterization

Dr. Norbert Wagner
DLR, Institut für Technische Thermodynamik, Stuttgart

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Presentation outline

- Introduction
  - Examples of porous (technical) electrodes

- Theory and models of porous electrodes
  - Impedance models

- Application of Göhr's porous electrode model
  - EIS measured at PEFC
  - EIS measured during oxygen reduction on silver in alkaline solution

- Outlook
  - Experimental set up for EIS applied for stack measurements
Why porous electrodes?

- Enlargement of active electrode surface
- Lowering of overvoltage at same current input (electrolyzer) or output (fuel cell)
- Increasing of power density (galvanic cells)
- Increasing of storage capacity (supercaps)
- Lowering catalyst loading by increasing active surface

**Butler-Volmer equation** for hydrogen oxidation (HOR) and hydrogen evolution reaction (HER)
Fuel cell overvoltage and current density / voltage characteristic

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

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

Ohmic loss
\[ \eta_\Omega = iR \]

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

Fuel cell voltage
\[ U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega \]
Field of application of porous electrodes

Batteries and supercaps

Water purification and treatment
(Bio)-Organic synthesis

Fuel Cells

Electrolysis (Water, NaCl, etc.)
Electrochemical Impedance Spectroscopy: Application to Fuel Cells

Potential excitation signal - $E(t)$

Current response signal - $I(t)$

U/I - Characteristic of a Fuel Cell
Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance Measurements

Cell voltage

\[ \Delta U = i R_M \]

Anodic Overvoltage

Cathodic Overvoltage

\[ R_{An}^{\text{ac}} = \frac{\Delta U(\text{Anode})}{\Delta i} \]

\[ R_{Cath}^{\text{ac}} = \frac{\Delta U(\text{Cathode})}{\Delta i} \]

\[ R_{\text{Cell}}^{dc} = \frac{\Delta U(\text{Cell})}{\Delta i} \]

Current density

\[ i_n \]

Cell voltage

\[ U_n \]
PEFC: Schematic Diagram (cross section)
SEM picture of PTFE/C powder
Multi-layer Gas Diffusion Electrodes with different porous layers

Carbon-PTFE Layer (Dry sprayed)

Ag-PTFE Layer (Rolled Layer)
### Brief Overview of Porous electrode models and Applications

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Simple pore model of interface charging
RC-transmission line of a flooded pore

\[ R = \text{electrolyte resistance inside the pore per unit length} \]
\[ C = \text{interface capacitance per unit length} \]

\[ Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC} \]
Nyquist representation of Impedance of RC-transmission line, model of a flooded pore

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

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

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

\( R = 3 \ \Omega \)
\( C = 0.5 \ \text{F} \)

C = 500 mF
Pore

100 mHz

real part / Ω

imaginary part / Ω

C = 500 mF
Pore

R = 3 Ω
C = 0.5 F

Nyquist representation of Impedance of RC-transmission line, model of a flooded pore

Nyquist representation of Impedance of RC-transmission line, model of a flooded pore
Simple pore model with faradaic processes in pores
RC-transmission line of a flooded pore

\[ r = \text{electrolyte resistance inside the pore per unit length} \]
\[ c = \text{interface capacitance per unit length} \]
\[ r_{ct} = \text{interface charge transfer resistance per unit length (Faraday impedance } y_2) \]
Nyquist representation of porous electrode impedance with faradaic impedance element

\begin{align*}
\text{real part / } \Omega & \\
\text{imaginary part / } \Omega & \\
\end{align*}

- C = 500 mF
- C + R_{por}(3 \, \Omega)
- C/R_{ct}(1.5 \, \Omega)

\begin{align*}
r &= 3 \, \Omega \\
c &= 500 \, \text{mF} \\
r_{ct} &= 1.5 \, \Omega
\end{align*}
Generalization of RC-transmission line of a flooded pore

\[
Z = \frac{(z_1 L) \frac{1}{Z_t} + \sqrt{\frac{(z_1 L)}{(y_2 L)}} \text{coth} \sqrt{(z_1 L) \cdot (y_2 L)}}{1 + \sqrt{\frac{(z_1 L)}{(y_2 L)}} \frac{1}{Z_t} \text{coth} \sqrt{(z_1 L) \cdot (y_2 L)}}
\]
Thin-film model of a porous electrode
Thin-film model and agglomerate plus thin-film model of a porous electrode

Theory of Agglomerated Electrodes

Hierarchical model
(Cantor-block model)

\[ Z_n^k(\omega) = R_{\mu} + \frac{R_{\mu}}{j\frac{\omega}{\omega_{\mu}}} + \frac{R_{\mu}}{\left(1 + j\frac{\omega}{\omega_{\mu}}\right)^{1+N^2a_z/a^2} + \frac{1}{1 + j\frac{\omega}{\omega_{\mu}^{(2)}} + \frac{N^2a_z/a^2}{1 + j\frac{\omega}{\omega_{\mu}^{(3)}} + \ldots}}} \]

Cylindrical homogeneous porous electrode model (H. Göhr) I

H. Göhr in *Electrochemical Applications/97*, www.zahner.de
Cylindrical homogeneous porous electrode model (H. Göhr) II

\[ Z^* = \sqrt{(Z_p + Z_s) \cdot Z_q} \]

\[ Z^\# = \frac{Z_p \cdot Z_s}{(Z_p + Z_s)} \]

\[ C = \cosh \left( \frac{Z_p + Z_s}{Z^*} \right) \]

\[ S = \sinh \left( \frac{Z_p + Z_s}{Z^*} \right) \]

\[ P = \frac{Z_p}{Z_p + Z_s} \]

\[ q_0 = \frac{Z^*}{Z_o} \]

\[ v = \frac{Z_p + Z_s}{Z^*} \]

\[ q_n = \frac{Z^*}{Z_n} \]

\[ s = \frac{Z_s}{Z_p + Z_s} = 1 - p \]

\[ Z = Z^\# + Z^* \cdot \frac{C + (1 - C) \cdot 2 \cdot p \cdot s + S \cdot (p^2 \cdot q_n + s^2 \cdot q_o)}{S \cdot (1 + q_n \cdot q_o) + C \cdot (q_n + q_o)} \]
Porous electrode model with faradaic impedance
Simulation of Impedance Spectra using Porous Electrode Model

\[ (R_{ct}||C_{dl} + R_{el,por}) + R_M + L \]

- \( R_{ct} = 50 \, \text{m}\Omega \)
- \( C_{dl} = 50 \, \text{mF} \)
- \( R_M = 3 \, \text{m}\Omega \)
- \( L = 20 \, \text{nH} \)
- \( R_{el,por} = 0 \, \text{m}\Omega \)
- \( R_{el,por} = \{10, 20, 30\} \, \text{m}\Omega \)
Electrochemical Impedance Spectroscopy: Experimental Set-up
Bode diagram of measured EIS at different cell voltages (current densities)
Bode diagram of measured EIS at different cell voltages (current densities) II

Phase \( \phi \)

Impedance / m\(\Omega\)

Frequency / Hz

0

20

40

60

80

10

20

30

40

50

0

10

20

30

40

50

10m 100m 1 10 100 1K 10K 100K

\( E=597 \text{ mV}; i=400 \text{ mA cm}^{-2} \)

\( E=497 \text{ mV}; i=530 \text{ mA cm}^{-2} \)

\( E=397 \text{ mV}; i=660 \text{ mA cm}^{-2} \)

\( E=317 \text{ mV}; i=760 \text{ mA cm}^{-2} \)
Bode diagram of measured EIS at different cell voltages (current densities) III

- $E=1024\, \text{mV}; \, I=0\, \text{mA}$
- $E=841\, \text{mV}; \, I=1025\, \text{mA}$
- $E=597\, \text{mV}; \, I=9023\, \text{mA}$
- $E=317\, \text{mV}; \, I=17510\, \text{mA}$
Common Equivalent Circuit for Fuel Cells

- $Z_{\text{diff}}$
- $R_{\text{ct,e}}$
- $R_{\text{ct,a}}$
- $C_{\text{dl,e}}$
- $C_{\text{dl,a}}$

Diffusion of $\text{O}_2$
Common Equivalent Circuit for Fuel Cells

\[ Z_{\text{diff}} \quad R_{\text{ct,c}} \quad R_{\text{m}} \quad R_{\text{ct,a}} \quad Z_{\text{diff}} \]

Diffusion of H\textsubscript{2}
EIS at Polymer Fuel Cells (PEFC):
Common equivalent circuit and boundary case

Equivalent circuit of the PEFC: anode and cathode simulated without pores, without diffusion (valid for example at lower current densities)
Bode diagramm of the EIS, measured at the PEFC at 80°C, symmetrical gas supply of the cell
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: \( U_n = a_n i_n + b_n \)

\[
R_n = \frac{\partial U}{\partial I} \bigg|_n
\]

**Integration method I:**

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

**Integration method II:**

\[
U_n = a_n I_n^2 + b_n I_n + c_n \quad \text{with:}
\]

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

\[
b_n = R_{n+1} - 2 a_n I_{n+1}
\]

\[
c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1}
\]
EIS at Polymer Fuel Cells (PEFC):
Contributions to the overall U-i characteristic determined by EIS
Evaluation of EIS with the porous electrode model

Porous electrode resistance ($R_{p,a}$), charge transfer resistance ($R_{ct,a}$) and electrolyte resistance ($R_{por,a}$) in the pore of the anode at different current densities.
Evaluation of EIS with the porous electrode model
i-V characteristic and current dependency of pore electrolyte resistance
of the anode and cathode
Impedance Measurements during Oxygen Reduction Reaction (ORR) in 10 N NaOH, on Silver Electrodes at Different Current Densities
Outlook

- Further improvement of porous electrode models
- Combination and extension of existent and new models
- Application of EiS to segmented cells
- Experimental validation of models using
  - PEFC and DMFC electrodes with different porous structure
  - Gas Diffusion Electrodes (GDE) for Oxygen Consumption Reaction (OCR) in alkaline solution using different gas compositions