Diagnosing the Porous Structure of Fuel Cell Electrodes

Jasmin Kaur and Thomas Kadyk

IEK- 13, Forschungszentrum Jülich

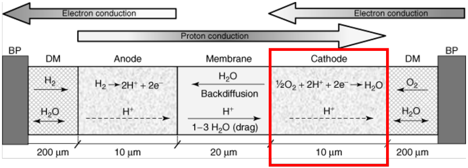
RWTH Aachen University

Steinfeld, September 2020

Diagnosing the Porous Structure of Fuel Cell Electrodes

Polymer Electrolyte Membrane Fuel Cell (PEMFC)

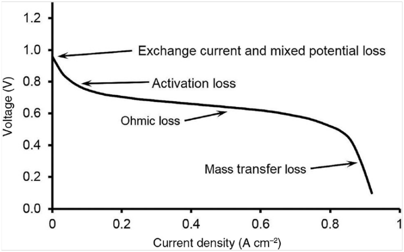
The Challenges



Performance limitations

Material degradation

Diagnosis of state of health



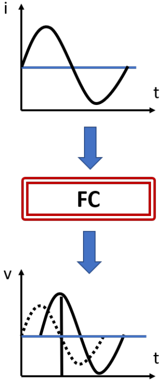
Voltage drop caused by charger transfer, membrane and mass transfer resistances at different current densities at 80 °C.

R. Gloukhovski et al. Reviews in Chem. Eng. (2017) 34, 455-479

Tang et al. J Electrochem. Soc. (2006) 153, A2036–43.

Diagnosing the Porous Structure of Fuel Cell Electrodes

Frequency response analysis

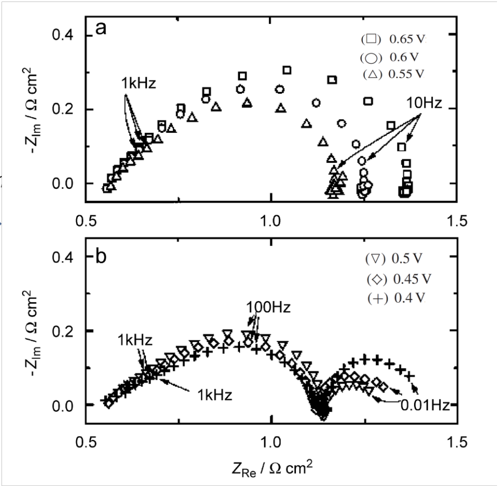


IV scan over range of frequency

$Z = Zre + i\, Zir$

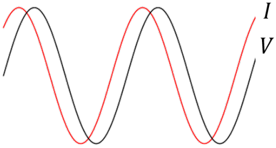
Nyquist plot

Electrochemical Impedance Spectra



Paganin et al., Electrochim. Acta (1998) 43, 3761.

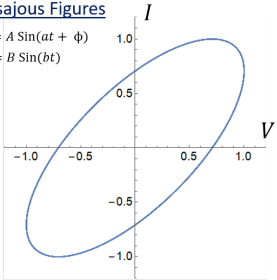
Diagnosing the Porous Structure of Fuel Cell Electrodes



Lissajous Figures

$x = A\,\mathrm{Sin}(at + \phi)$

$y = B\,\mathrm{Sin}(bt)$

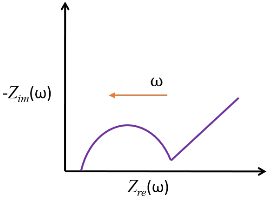


IV scan over range of frequency

Impedance Spectroscopy

$Z = Zre + i\,Zim$

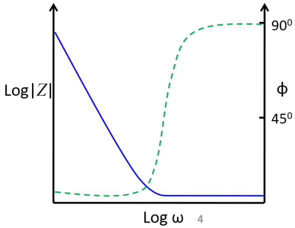
Nyquist plot



$|Z| = \sqrt{Z_{re} + Zi_m}$

$\phi = \mathrm{Arctan}\left[\frac{-Z_{im}}{Z_{re}}\right]$

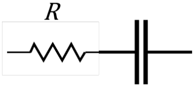
Bode plot

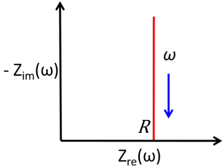


4

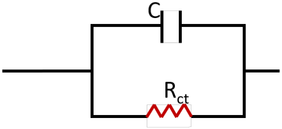
Diagnosing the Porous Structure of Fuel Cell Electrodes

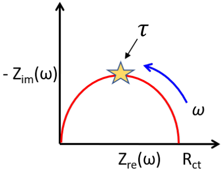
Nyquist Plot





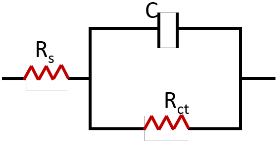
$$Z = R + \frac{1}{i\omega C}$$

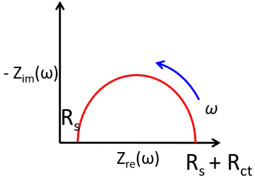




$$Z = \left(\frac{1}{R_{ct}} + i\omega C\right)^{-1}$$

$$R_{ct} = \frac{R\,T}{nF\,i_0}$$

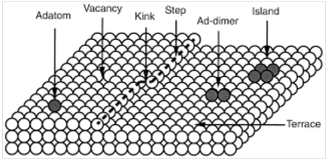


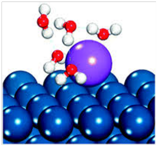


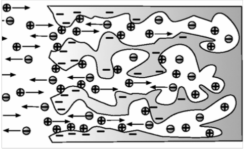
$$Z = R_s + \left(\frac{1}{R_{ct}} + i\omega C\right)^{-1}$$

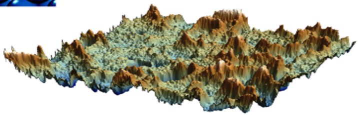
Diagnosing the Porous Structure of Fuel Cell Electrodes

Sensitivity of EIS response and physics based modeling approaches

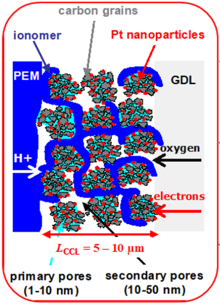








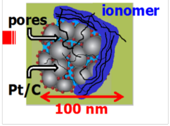
Porous Cathode Catalyst Layer
In PEMFC



Interface model

Macrohomogeneous model

Agglomerate model



M. Eikerling and A. Kulikovsky. Polymer Electrolyte Fuel Cells –Physical Principles of Materials and Operation. CRC Press, 2017. ISBN 9781138077447

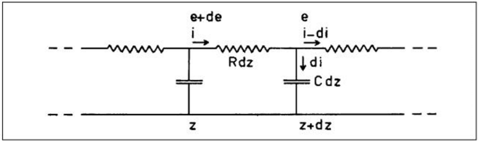
Diagnosing the Porous Structure of Fuel Cell Electrodes

Transport in porous electrodes

Electrochimica Acta, 1963, Vol. 8, pp. 751 to 780.

ON POROUS ELECTRODES IN ELECTROLYTE SOLUTIONS*

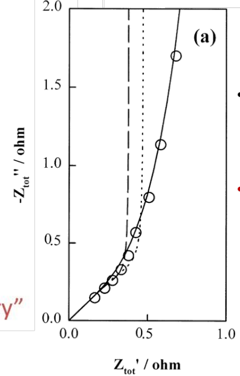
R. DE LEVIE§
Electrochemistry Laboratory, University of Amsterdam, Holland



"RC Transmission Line Theory", or "De Levie Theory"

Distributed circuit elements

$$Z(\omega) = \sqrt{\frac{R_{sol}}{i\omega C_{dl}}} \coth \sqrt{R_{sol}\, i\omega C_{dl}}$$



- Not any random distribution would work.
- Distributed time constant, pore size distribution.

Song et al. Electrochimica Acta 44 (1999) 3513-3519

M. E. Orazem and Bernard Tribollet. Electrochemical Impedance Spectroscopy. John Wiley \& Sons, 2018. DOI:10.1002/9780470381588

Diagnosing the Porous Structure of Fuel Cell Electrodes

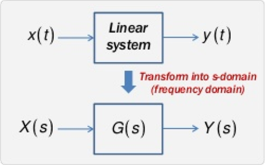
Frequency Response Analysis

Transfer Functions

Assume an initially relaxed linear system excited at t=0 by an input $x(t)$, and assume that $y(t)$ is the corresponding output. Let

$$X(s) = \mathcal{L}[x(t)]$$

$$Y(s) = \mathcal{L}[y(t)]$$



For a linear system

$$Y(s) = G(s)\, X(s)$$

where $G(s) = \dfrac{Y(s)}{X(s)}$ is called the transfer function of the circuit or system, and it provides a direct mathematical relationship between the input and the output for any arbitrary input.

Transient response function
response of a system to a change from an equilibrium or a steady state

Impedance response probe
Small harmonic perturbation
Linear response

M. E. Orazem and Bernard Tribollet. Electrochemical Impedance Spectroscopy. John Wiley \& Sons, 2018. DOI:10.1002/9780470381588

M. Eikerling and A. Kulikovsky. Polymer Electrolyte Fuel Cells –Physical Principles of Materials and Operation. CRC Press, 2017. ISBN 9781138077447

A. A.Kulikovsky. Analytical Modeling of Fuel Cells. Second Edition, Elsevier, 2017. ISBN 978-0-444-64222-6

Diagnosing the Porous Structure of Fuel Cell Electrodes

MODELING METHODOLOGY

Conservation equations:
Mass, charge, momentum, energy

$$\frac{\partial c_{H^+}}{\partial t} - D_{H^+}\nabla.\left(\nabla c_{H^+} + \frac{F c_{H^+}}{RT}\nabla\varphi\right) = 0$$

$$\frac{\partial c_{O_2}}{\partial t} - D_{O_2}(\nabla c_{O_2}) = 0$$

For concentration and potential

$$x = \bar{x} + \delta x\, e^{i\omega t}$$

Linearization in Fourier space

Boundary conditions:

- reaction kinetics,
- metal charging,
- surface charge density

For concentration and potential

$\delta\varphi, \delta c$

Electrochemical Impedance response of a pore

$$Z(\omega) = \frac{1}{2\pi R} \cdot \frac{\delta\phi^M(\omega)}{\int_0^L \delta j(\omega, z)\,dz}$$

Pore size distribution

Particle size distribution

M. Eikerling, A.A. Kornyshev, J. Electroanal. Chem. 475 (1999) 107–123
K. Chan, M. Eikerling, J. Electrochem. Soc. 159 (2012) B155-B164
A. Kulikovsky, J. Electrochem. Soc. 164 (2017) F374-F386