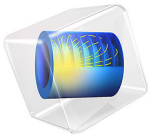

Model created in COMSOL Multiphysics 6.4

Electrochemical Impedance Spectroscopy in a Fuel Cell

Introduction

The electrochemical (AC) impedance technique is based on the analysis of current response to small sinusoidal perturbation in potential. This perturbation is applied for a given frequency range, from hundreds of kHz down to the mHz scale. The variation in frequency response makes it possible to separate processes and mechanisms in the electrochemical phenomena that is occurring at electrode surfaces. In particular, AC impedance or impedance spectroscopy is utilized to separate slow processes from fast, by analyzing the phase shift, while the impedance absolute value can also give a lot of information about electrochemical systems.

Electrochemical impedance spectroscopy (EIS) is used in all areas of electrochemistry such as fuel cells, batteries, electrolytic processes, and corrosion. Information gathered from such studies helps in extracting values for important design parameters in electrochemical processes, such as effective transport properties, reaction kinetics and mechanisms, and Ohmic losses (Ref. 1 and Ref. 2).

This example looks specifically at the AC impedance of a porous cathode of a generic fuel cell in 1D.

At open circuit and for high electrode conductivities, the model has been validated against the analytical solution presented in Ref. 3.

Model Definition

The geometry is set up as a 1D model, according to Figure 1. The geometry represents a fuel cell half cell and consists of two domains: a membrane and a gas diffusion electrode (GDE) domain.

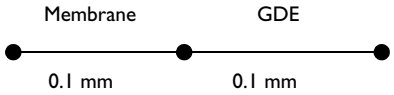

Figure 1: Half cell 1D geometry.

The Hydrogen Fuel Cell interface is used to model a secondary current distribution along with a Butler-Volmer expression to describe the fuel cell cathode kinetics in the GDE.

The electrolyte potential at the outer membrane boundary is set to zero. At the outer GDE boundary the electrode current density is set to -0.1 A/cm^2. A harmonic perturbation of 5 mA/cm^2 is also applied to this boundary.

The model is solved in two steps. The first step solves for the stationary solution, in a second step solves for the frequency domain, for a range of frequencies from 1 to 10^5 Hz. Additionally, a parametric sweep is set up for the electrical conductivity of the GDE.

Results and Discussion

Figure 2 shows the Nyquist plot of the impedance for the two different values for the electrical conductivity in the GDE.

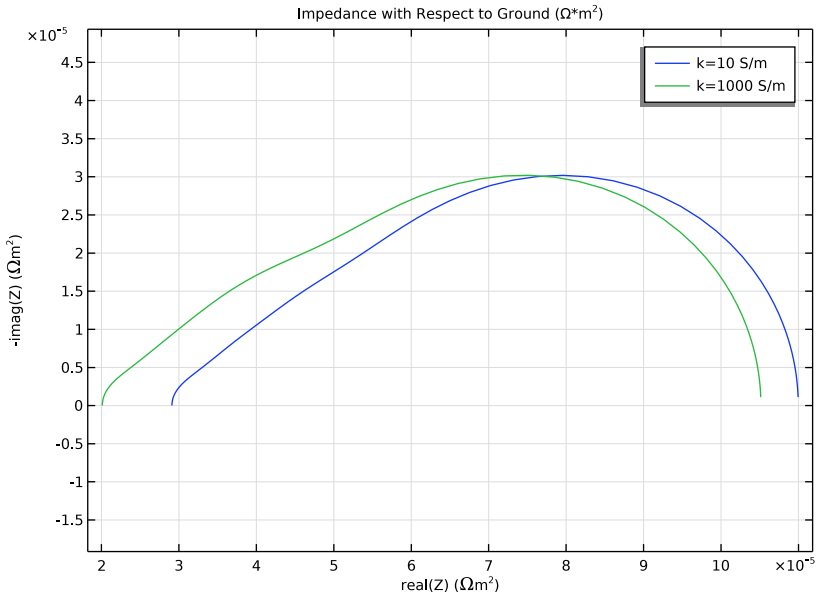

Figure 2: Nyquist plot.

At high frequencies, the double layer contributes with very low impedance, which means that the alternating current is transferred between the electrode and the electrolyte at a position close to the free electrolyte-electrode interface. The real part of the impedance, given by the Ohmic losses in the free electrolyte, therefore dominates the total impedance at high frequencies. For electrodes of high electronic conductivity, compared to the electrolyte, the Nyquist plot can be used to extract the pure Ohmic resistance in the

electrolyte during measurements. Extrapolating the impedance from the frequency of 50 kHz to the intersection with the x-axis in Figure 2, gives a value for the real impedance of around 0.2 Ωcm^2.

The diameter of the semicircle in the Nyquist plot gives a measure of the kinetic resistance in the electrode. If the performance of the electrode is limited by the electrode kinetics, and the current distribution is fairly uniform along the thickness of the electrode, the diameter gives the Tafel slope divided by the current density (Ref. 1). The expected value of the diameter, at a steady state current of 0.1 A/cm^2 in a unit square, is according to the following:

$$\frac{RT}{0.5FI} = \frac{8.314 \cdot 353}{0.5 \cdot 96485 \cdot 1000} \approx 0.61\ \Omega\text{cm}^2$$

The value obtained from the simulation is 0.64 Ωcm^2. The deviation from the value in the above calculation is due to the fact that the current distribution is not perfectly uniform in our simulation.

Figure 2 also shows that the real part of the impedance at high frequency increases from around 0.2 Ωcm^2 to 0.3 Ωcm^2 when lowering the electrode conductivity. At very low frequencies the difference in the real part impedance is lower than for high frequencies, indicating that the current distribution in the electrode is more uniform.

In a detailed study of the electrode, the current density is varied from small to large values and the EIS simulations are compared at each single current density. The model should be able to describe the qualitative and quantitative changes in both impedance spectra and steady-state performance along the whole polarization of the electrode.

When including spatial dependencies in more dimensions, the effects of nonuniform current densities, and their influence on the impedance spectra, become even more intricate.

References

1. C. Lagergren, *Electrochemical Performance of Porous MCFC Cathodes*, Doctoral Thesis, Department of Chemical Engineering and Technology, Applied Electrochemistry, Kungliga Tekniska Högskolan, Stockholm, Sweden, 1997.

2. F. Jaouen, *Electrochemical Characterization of Porous Cathodes in the Polymer Electrolyte Fuel Cell*, Doctoral Thesis, Department of Chemical Engineering and Technology, Applied Electrochemistry, Kungliga Tekniska Högskolan, Stockholm, Sweden, 2003.

3. G. Lindbergh, "Experimental determination of the effective electrolyte conductivity in porous lead electrodes in the lead-acid battery," *Electrochimica Acta*, vol. 42, no. 8, pp. 1239–1246, 1997.

Application Library path: `Fuel_Cell_and_Electrolyzer_Module/Fuel_Cells/ac_fuel_cell`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **1D**.

2 In the **Select Physics** tree, select **Electrochemistry** > **Hydrogen Fuel Cells** > **Generic (fc)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces** > **AC Impedance, Stationary**.

6 Click **Done**.

GLOBAL DEFINITIONS

Load model parameters from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `ac_fuel_cell_parameters.txt`.

GEOMETRY 1

Create the geometry consisting of two intervals, the membrane and the oxygen gas diffusion electrode (O2 GDE).

Interval 1 (i1)

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

2 In the **Settings** window for **Interval**, locate the **Interval** section.

3 From the **Specify** list, choose **Interval lengths**.

4 In the table, enter the following settings:

Lengths (m)
L
L

5 Click **Build All Objects**.

HYDROGEN FUEL CELL (FC)

Set up the electrochemical model. Start with adding the relevant domain nodes.

Membrane 1

1 In the **Physics** toolbar, click **Domains** and choose **Membrane**.

2 Select Domain 1 only.

O2 Gas Diffusion Electrode 1

1 In the **Physics** toolbar, click **Domains** and choose **O2 Gas Diffusion Electrode**.

2 Select Domain 2 only.

Electrolyte Phase 1

Set up the electrolyte conductivity in the **Electrolyte Phase** node.

1 In the **Model Builder** window, click **Electrolyte Phase 1**.

2 In the **Settings** window for **Electrolyte Phase**, locate the **Electrolyte Charge Transport** section.

3 From the σ_l list, choose **User defined**. In the associated text field, type `sigmal`.

O2 Gas Diffusion Electrode 1

Set up the electric conductivity and the effective electrolyte conductivity correction in the **O2 Gas Diffusion Electrode** node. The details of electrode kinetics and double layer are set in the child nodes.

1 In the **Model Builder** window, click **O2 Gas Diffusion Electrode 1**.

2 In the **Settings** window for **O2 Gas Diffusion Electrode**, locate the **Electrode Charge Transport** section.

3 In the σ_s text field, type `k`.

The electric conductivity of the O2 GDE will be used later when setting up a parametric sweep.

4 Locate the **Effective Electrolyte Charge Transport** section. From the **Effective conductivity correction** list, choose **User defined**. In the f_l text field, type `fl`.

O2 Gas Diffusion Electrode Reaction 1

1 In the **Model Builder** window, click **O2 Gas Diffusion Electrode Reaction 1**.

2 In the **Settings** window for **O2 Gas Diffusion Electrode Reaction**, locate the **Equilibrium Potential** section.

3 From the E_{eq} list, choose **User defined**. In the associated text field, type `Eeq`.

4 Locate the **Electrode Kinetics** section. In the i_0 text field, type `i0`.

5 Locate the **Active Specific Surface Area** section. In the a_v text field, type `av`.

O2 Gas Diffusion Electrode 1

In the **Model Builder** window, click **O2 Gas Diffusion Electrode 1**.

Porous Matrix Double Layer Capacitance 1

1 In the **Physics** toolbar, click **Attributes** and choose **Porous Matrix Double Layer Capacitance**.

2 In the **Settings** window for **Porous Matrix Double Layer Capacitance**, locate the **Porous Matrix Double Layer Capacitance** section.

3 In the C_{dl} text field, type `Cdl`.

4 In the $a_{v,dl}$ text field, type `avdl`.

Electrolyte Phase 1

Finally, set up the boundary conditions.

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Hydrogen Fuel Cell (fc)** click **Electrolyte Phase 1**.

Electrolyte Potential 1

1 In the **Physics** toolbar, click **Attributes** and choose **Electrolyte Potential**.

2 Select Boundary 1 only.

Electronic Conducting Phase 1

In the **Model Builder** window, under **Component 1 (comp1)** > **Hydrogen Fuel Cell (fc)** click **Electronic Conducting Phase 1**.

Electrode Current 1

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Current**.

2 Select Boundary 3 only.

3 In the **Settings** window for **Electrode Current**, locate the **Electrode Current** section.

4 From the list, choose **Average current density**.

5 In the $i_{\mathrm{s,average}}$ text field, type `iavg`.

6 Click to expand the **Harmonic Perturbation** section. Add a harmonic perturbation to be used in the frequency domain study.

7 Select the **Include harmonic perturbation** checkbox.

8 In the $\Delta i_{\mathrm{s,average}}$ text field, type `delta_iavg`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General** > **Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T`.

STUDY 1

Add a parametric sweep to solve for two different electric conductivities of the O2 GDE.

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
k (Electric conductivity in porous electrode)	10 1000	S/m

Step 2: Frequency-Domain Perturbation

Set up the frequency range of the solver.

1. In the **Model Builder** window, click **Step 2: Frequency-Domain Perturbation**.
2. In the **Settings** window for **Frequency-Domain Perturbation**, locate the **Study Settings** section.
3. In the **Frequencies** text field, type `10^range(0,0.05,4.95) 10^range(5,0.5,7)`.

Step 1: Stationary

The problem is now ready for solving. Lower the relative tolerance of the first solver step in the default solver sequence. This will improve the accuracy of the static solution for which the frequency perturbation study step is run. Then solve the problem.

1. In the **Model Builder** window, click **Step 1: Stationary**.
2. In the **Settings** window for **Stationary**, locate the **Study Settings** section.
3. From the **Tolerance** list, choose **User controlled**.
4. In the **Relative tolerance** text field, type `1e-5`.
5. In the **Study** toolbar, click **Compute**.

RESULTS

Impedance with Respect to Ground, Nyquist (fc)

In the **Settings** window for **1D Plot Group**, click **Plot**.