Simulation of Electrochemical Impedance Spectroscopy

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, through investigating phase shift, while the absolute value of impedance 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 [1, 2].

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

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; an electrolyte and a porous electrode domain.

Electrolyte   Porous Electrode

0.1 mm   0.1 mm
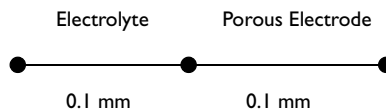
Figure 1: Half cell 1D geometry.

A secondary current distribution is assumed and a Butler-Volmer expression is used to describe the fuel cell cathode kinetics in the porous electrode,.

The settings used in the model are shown in Table 1.

TABLE 1: MODEL PARAMETERS

PARAMETER	VALUE	UNIT	DESCRIPTION
Cdl	0.5	F/m2	Double layer capacitance
Av	1e6	m2/m3	Specific surface area
i0	1	A/m2	Exchange current density
alpha_a	3.5	1	Anodic transfer coefficient
alpha_c	0.5	1	Cathodic transfer coefficient
Eeq	1.0	V	Equilibrium potential
T	353	K	Temperature
Kl	5	S/m	Electrolyte conductivity
Kl_p	1	S/m	Electrolyte conductivity, porous electrode
Ks	1000	S/m	Electrode conductivity

The potential at the outer electrolyte boundary is set to zero. At the outer porous electrode boundary the electrode current density is set to $0.1\ A/cm^2$. A harmonic pertubation 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.

In a second study, the electrode conductivity is lowered to 10 S/m.

Results and Discussion

Figure 2 shows the Nyquist plot of the impedance for the two different values for the electric conductivity in the porous electrode.
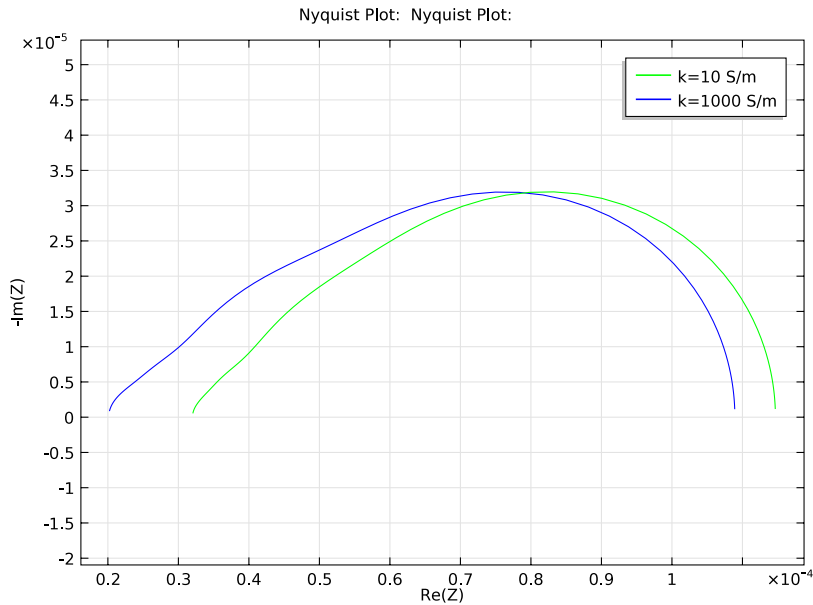
Figure 2: Nyquist plot.

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 dominate 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. If we extrapolate the impedance from the frequency of 50 kHz to the intersection with the x-axis in Figure 2, we get a value for the real impedance of around 0.2 $\Omega.\text{cm}^2$.

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 [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:

$$\frac{RT}{0{,}5FI} = \frac{8{,}314 \cdot 353}{0{,}5 \cdot 96485 \cdot 1000} \approx 0{,}61 \ \Omega\text{cm}^2 \tag{1}$$

The value obtained from the simulation is $0.64\ \Omega.\text{cm}^2$. 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 also shows that the real part of the impedance at high frequency increases from around $0.2\ \Omega.\text{cm}^2$ to $0.3\ \Omega.\text{cm}^2$ 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.

Model Library path: `Batteries_and_Fuel_Cells_Module/Tutorial_Models/ac_fuel_cell`

Modeling Instructions

MODEL WIZARD

1 Go to the **Model Wizard** window.

2 Click the **1D** button.

3 Click **Next**.

4 In the **Add physics** tree, select **Electrochemistry>Secondary Current Distribution (siec)**.

5 Click **Add Selected**.

6 Click **Next**.

7 In the **Studies** tree, select **Preset Studies>AC Impedance Stationary**.

8 Click **Finish**.

GEOMETRY 1

Create the geoemtry to consist of two intervals (the electrolyte and the porous electrode.

Interval 1

1 In the **Model Builder** window, right-click **Model 1>Geometry 1** and choose **Interval**.

2 Go to the **Settings** window for Interval.

3 Locate the **Interval** section. From the **Number of intervals** list, select **Many**.

4 In the **Points** edit field, type 0, 1e-4,2e-4.

SECONDARY CURRENT DISTRIBUTION

Set up the electrochemical model, start with the settings for the electrolyte.

Electrolyte 1

1 In the **Model Builder** window, expand the **Model 1>Secondary Current Distribution** node, then click **Electrolyte 1**.

2 Go to the **Settings** window for Electrolyte.

3 Locate the **Electrolyte** section. From the σ_l list, select **User defined**. In the associated edit field, type 5.

Porous Electrode 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Porous Electrode**.

2 Select Domain 2 only.

3 Go to the **Settings** window for Porous Electrode.

4 Locate the **Electrolyte Current Conduction** section. From the σ_l list, select **User defined**. From the **Effective conductivity correction** list, select **No correction**.

5 Locate the **Electrode Current Conduction** section. From the σ_s list, select **User defined**. In the associated edit field, type 1000.

6 From the **Effective conductivity correction** list, select **No correction**.

Porous Electrode Reaction 1

1 In the **Model Builder** window, expand the **Porous Electrode 1** node, then click **Porous Electrode Reaction 1**.

2 Go to the **Settings** window for Porous Electrode Reaction.

3 Locate the **Model Inputs** section. In the T edit field, type 353.

4 Locate the **Equilibrium Potential** section. In the $E_{0,ref}$ edit field, type 1.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, select **Butler-Volmer**.

6 In the i_0 edit field, type 1.

7 In the α_a edit field, type 3.5.

Porous Matrix Double Layer Capacitance 1

1 In the **Model Builder** window, right-click **Porous Electrode 1** and choose **Porous Matrix Double Layer Capacitance**.

2 Go to the **Settings** window for Porous Matrix Double Layer Capacitance.

3 Locate the **Porous Matrix Double Layer Capacitance** section. In the C_{dl} edit field, type 0.5.

Electrolyte Potential 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte Potential**.

2 Select Boundary 1 only.

Electrode Current Density 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrode>Electrode Current Density**.

2 Select Boundary 3 only.

3 Go to the **Settings** window for Electrode Current Density.

4 Locate the **Electrode Current Density** section. In the $\mathbf{i}_{n,s}$ edit field, type -0.1[A/cm^2].

Electrode Current Density 2

Add a harmonic pertubation current density to be used in the frequency domain study.

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrode>Electrode Current Density**.

2 Select Boundary 3 only.

3 Go to the **Settings** window for Electrode Current Density.

4 Locate the **Electrode Current Density** section. In the $\mathbf{i}_{n,s}$ edit field, type `5[mA/cm^2]`.

5 Right-click **Electrode Current Density 2** and choose **Harmonic Perturbation**.

DEFINITIONS

Add a probe for the impedance. (To be used for plotting.)

1 In the **Model Builder** window, right-click **Model 1>Definitions** and choose **Probes>Domain Point Probe**.

2 Go to the **Settings** window for Domain Point Probe.

3 Locate the **Point Selection** section. In row **Coordinate**, set **x** to `2e-4`.

4 Select the **Snap to closest point** check box.

5 In the **Model Builder** window, expand the **Domain Point Probe 1** node, then click **Point Probe Expression 1**.

6 Go to the **Settings** window for Point Probe Expression.

7 Locate the **Probe Settings** section. In the **Probe variable** edit field, type `Z`.

8 Locate the **Expression** section. In the **Expression** edit field, type `phis/siec.Isx`.

STUDY 1

Set up the frequency range of the solver.

Step 2: Frequency-Domain, Perturbation

1 In the **Model Builder** window, expand the **Study 1** node, then click **Step 2: Frequency-Domain, Perturbation**.

2 Go to the **Settings** window for Frequency-Domain, Perturbation.

3 Locate the **Study Settings** section. In the **Frequencies** edit field, type `10^range(0,0.05,5)`.

4 In the **Model Builder** window, right-click **Study 1** and choose **Compute**.

Solver 1

Make a copy of the solution for future comparison.

1 In the **Model Builder** window, expand the **Study 1>Solver Configurations** node.

2 Right-click **Study 1>Solver Configurations>Solver 1** and choose **Solution>Copy**.

RESULTS

Electrolyte Potential (siec)

The following steps creates the Nyquist plot. The conj() function is used to the shift the sign of the imaginary part.

1D Plot Group 3

1 In the **Model Builder** window, right-click **Results** and choose **1D Plot Group**.

2 Right-click **Results>1D Plot Group 3** and choose **Nyquist Plot**.

3 Go to the **Settings** window for Nyquist Plot.

4 Locate the **Data** section. From the **Data set** list, select **Solution 4**.

5 Locate the **Expressions** section. In the **Expressions** table, enter the following settings:

EXPRESSION	UNIT	DESCRIPTION
conj(-Z)		

6 Clear the **Compute differential** check box.

7 Click to expand the **Legends** section.

8 Select the **Show legends** check box.

9 From the **Legends** list, select **Manual**.

10 In the associated table, enter the following settings:

LEGENDS
k=1000 S/m

11 In the **Model Builder** window, click **1D Plot Group 3**.

12 Go to the **Settings** window for 1D Plot Group.

13 Locate the **Plot Settings** section. Select the **x-axis label** check box.

14 In the associated edit field, type Re(Z).

15 Select the **y-axis label** check box.

16 In the associated edit field, type -Im(Z).

17 Click to expand the **Axis** section.

18 Select the **Preserve aspect ratio** check box.

19 Click the **Plot** button.

SECONDARY CURRENT DISTRIBUTION

Modify the conductivity in the porous electrode and run the simulation again.

Porous Electrode 1

1 In the **Model Builder** window, click **Model 1>Secondary Current Distribution>Porous Electrode 1**.

2 Go to the **Settings** window for Porous Electrode.

3 Locate the **Electrode Current Conduction** section. In the associated edit field, type 10.

STUDY 1

In the **Model Builder** window, right-click **Study 1** and choose **Compute**.

RESULTS

1D Plot Group 3

1 In the **Model Builder** window, right-click **Results>1D Plot Group 3** and choose **Nyquist Plot**.

2 Go to the **Settings** window for Nyquist Plot.

3 Locate the **Data** section. From the **Data set** list, select **Solution 1**.

4 Locate the **Expressions** section. In the **Expressions** table, enter the following settings:

EXPRESSION	UNIT	DESCRIPTION
-conj(Z)		

5 Clear the **Compute differential** check box.

6 Locate the **Legends** section. From the **Legends** list, select **Manual**.

7 In the associated table, enter the following settings:

LEGENDS
k=10 S/m

8 Click the **Plot** button.