

Application Area: Fuel Cell

Impedance Measurements on Fuel Cells and Fuel Cell Stacks at High Currents: Autolab in Combination with an Electronic Load – Part I

Keywords

Fuel cells; High current measurements; Electronic load; Electrochemical impedance spectroscopy

Summary

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study different fuel cell elements and their influence on the overall performance of fuel cell. EIS also gives valuable information on degradation mechanism of a fuel cell over its life time. Most of the fuel cells operate at high currents, while the maximum current of most of PGSTATs are limited to few amps. The maximum current of the Autolab PGSTAT302N can be extended to 20 A by using an Autolab Booster20A. However, even 20 A might not be enough to study a Polymer Fuel Cell of reasonable size (50 cm² for example) as they might deliver currents higher than 20 A. Therefore, to perform EIS on fuel cells, a combination of PGSTAT and electronic load (e-load), is desirable. The electronic load is then capable of drawing the high currents from the fuel cell, and the Autolab PGSTAT performs the impedance measurements.

Choice of electronic load

For the experiments, an Agilent 6060B electronic load has been used. The experiments described below also can be performed in combination with many other commercially available loads as well.

There are however some important requirements for the e-load:

1. The e-load needs to have the possibility for an external input. This is needed to take the frequency signal from the FRA module into the electronic load.
2. Output of the current as well as the potential needs to be present. These are connected to the external inputs of the FRA32M module.
3. The bandwidth of the electronic load is the limiting factor in the frequency range that can be used. The Agilent 6060B has a bandwidth of 10 kHz, limiting the frequency

range that can be used to 2 kHz. Other electronic loads are available with higher bandwidths.

4. The voltage range of the electronic load should preferably start at 0 Volt, especially if the measurements are done at single cells. Although the Agilent 6060B is capable of measuring voltages below 3 Volt, the maximum current in that case is no longer 60 A and decreases rapidly with the voltage (see Figure 1).

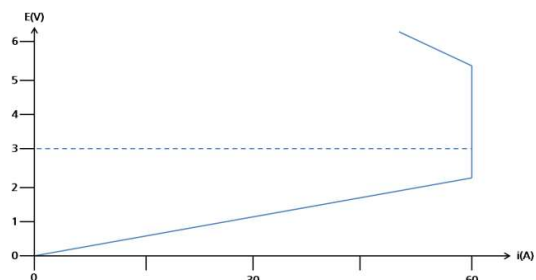


Figure 1 – Contour plot of the Agilent 6060B, in constant current mode.

Connections between Autolab and the electronic load

The connections described in this section are specific for the Agilent 6060B load. For most other loads, however, the connections are very similar.

1. The FRA32M $\leftarrow V$ output of the digital signal generator (DSG) is connected to the pin “Ext Prg” on the back of the load as shown in Figure 2.
2. The pin IM (Current monitor) on the back of the load is connected to the $\rightarrow Y$ input of the FRA32M module.
3. The E_{out} (monitor cable of the PGSTAT302N) is connected to the $\rightarrow X$ input of the FRA32M module.

By using the connections described above, the current of the fuel cell is modulated by the DSG signal from the FRA32M module, and the impedance is calculated based on that current and the measured potential response from the differential amplifier.

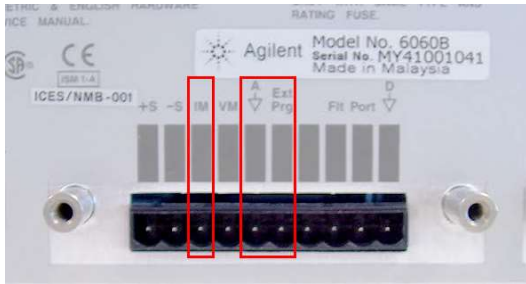


Figure 2 – Connections to the Agilent 6060B load (back panel).

Experimental conditions

The load used in these experiments has a maximum current of 60 A in constant current mode, and a voltage range between 3 V and 60 V, in constant voltage mode.

Measurements were performed on a PEMFC fuel cell (7 cm²) with Pt catalyst on both anode and cathode side. The fuel cell was operated on humidified H₂/O₂ at 65 °C. For the impedance measurements an Autolab PGSTAT302N equipped with a FRA32M module was used, in combination with the NOVA software.

The load was only used to draw the current. The voltage of the cell was measured by the differential amplifier of the PGSTAT302N.

The load was operated in constant current mode, whereas the PGSTAT302N was operated in potentiostatic mode.

Experimental Results

The initial part of a full i-V curve of the fuel cell is shown in Figure 3.

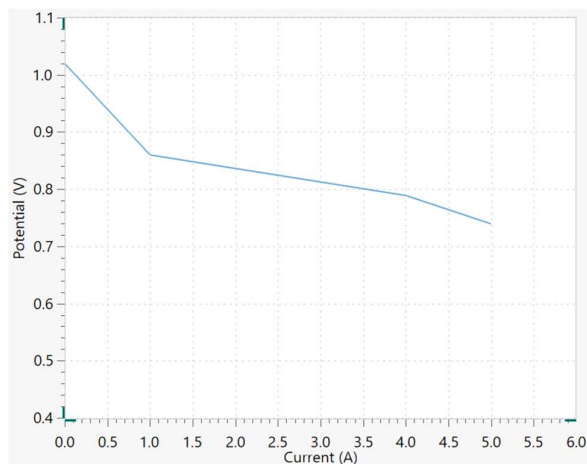


Figure 3 – i-V curve of the fuel cell.

The impedance measurements were done on several points along the i-V curve presented in Figure 3. EIS was performed at a frequency range of 1 kHz to 100 mHz, with an amplitude of 400 mA, which resulted in a response voltage amplitude of maximum 10 mV.

Figure 4 shows the Nyquist plot associated with EIS measurement results at a DC current of 4.6 A, and a fuel cell voltage of 0.76 Volt.

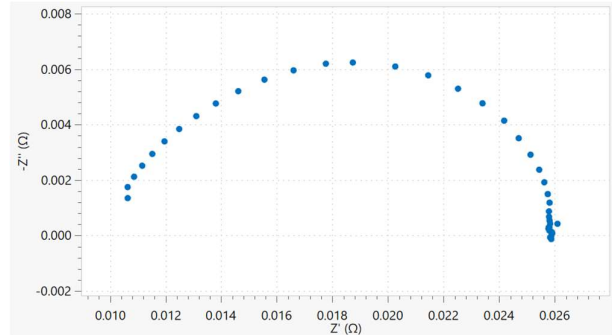


Figure 4 – Nyquist plot obtained at a DC current of 4.6 A.

Figure 5 shows a comparison of impedance measurements at different fuel cell currents: 1 A (black triangles); 2 A (green dots), 4 A (red squares); 4.6 A (blue dots). As the DC current increases, the total resistance of the cell decreases, as expected.

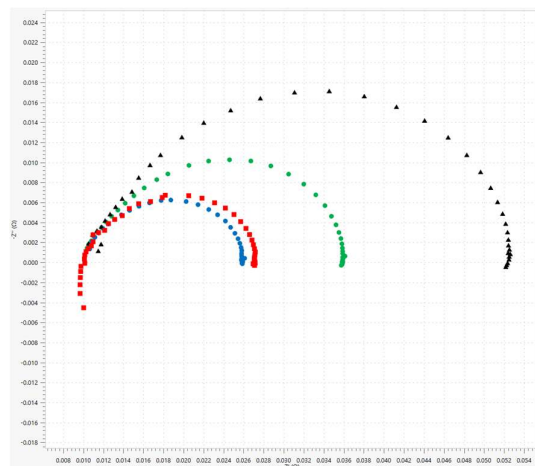


Figure 5 – Comparison of Nyquist plots obtained at different DC currents: 1 A (black triangles); 2 A (green dots), 4 A (red squares); 4.6 A (blue dots).

Data Analysis

Choice of equivalent circuit

All data were analyzed using the fit and simulation command in the NOVA software. The equivalent circuit shown in Figure 6 was used to fit the experimental data.

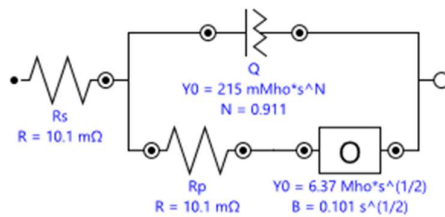


Figure 6 – The equivalent circuit used to fit the data.

Here, Q is the constant phase element, used to fit the double layer capacitance on a non-ideal surface; O is the cotangent hyperbolic diffusion element, used in cases where finite diffusion plays a role, like when diffusion takes place through a thin film or a coating. The concentration of the species involved is constant in the bulk, but is determined by diffusion in the thin film close to the electrode.

The impedance of O is defined by Equation 1

$$Z_O = \frac{1}{Y_0} \tanh(B\sqrt{j\omega}) \quad 1$$

Which upon fitting will result in two values for Y_0 and B, respectively. The value of B depends on the diffusion layer thickness and the diffusion coefficient.

Fitting of the Data

Figure 7 shows a comparison between the measured data obtained at 2 A DC and the fitted data, obtained using the equivalent in Figure 6.

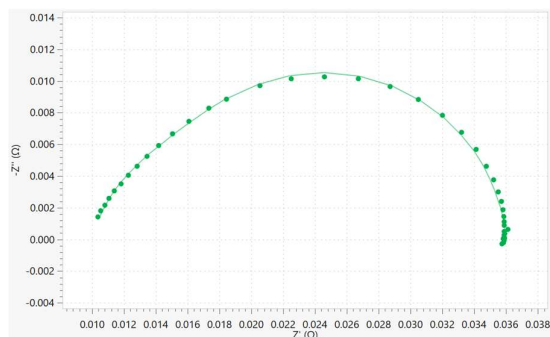
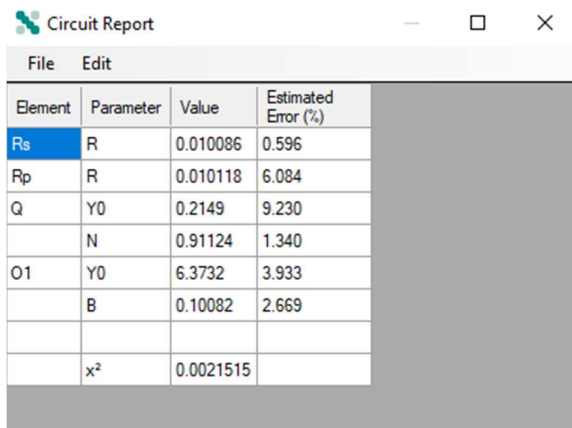


Figure 7 – Comparison of the measured and fitted data obtained at 2 A DC current.

The values for the different elements are shown in Figure 8 directly exported from NOVA software.



Element	Parameter	Value	Estimated Error (%)
Rs	R	0.010086	0.596
Rp	R	0.010118	6.084
Q	Y0	0.2149	9.230
	N	0.91124	1.340
O1	Y0	6.3732	3.933
	B	0.10082	2.669
	x ²	0.0021515	

Figure 8 – Results from the fitting of the data.

Table 1 provides a summary of the values obtained at different DC currents.

Table 1 – Overview of the fitting results at different DC currents.

	1 A	2 A	4 A	4.6 A
RS / mΩ	10.5	10.1	10.1	10.2
RP / mΩ	14.4	10.1	8.4	8.8
Q(Y0) / Mho · s ^N	0.247	0.215	0.113	0.156
Q(N)	0.890	0.911	1.000	0.943
O(Y0) / Mho · √s	4.33	6.373	11.39	11.86
O(B) / √s	0.12	0.10	0.097	0.082

It is clearly visible from the table that the values of modeled circuit are different at different DC currents. Specifically the diffusion behavior (O) and (RP) have dramatically changed at different DC currents.

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at www.metrohm.com/en/products/electrochemistry.