A method for determining anode and cathode impedances of a DMFC running on a load

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Abstract

A new method for measuring separately anode and cathode impedances (Z_A and Z_C) of an electrochemical generator running on constant load is proposed. In these conditions, the measurement of Z_A and Z_C is not as simple as under galvanostatic conditions. Measurements are carried out first on a dummy cell and next on a commercial direct methanol fuel cell (DMFC) under galvanostatic conditions and using the new proposed method. The comparison of the results validate our method, showing that it is a powerful method for fuel cell EIS characterization under natural running conditions.

Keywords : Direct Methanol Fuel Cell (DMFC), Electrochemical Impedance Spectroscopy (EIS), Anode and Cathode Impedance Measurements, Transfer Functions.

1 Introduction

To the best of our knowledge, only three papers [1–3] have been published concerning impedance measurements on direct methanol fuel cells (DMFCs).

The first group of authors (Mueller *et al.* [1, 2]) have studied a fuel cell under conditions of practical interest : large area electrodes, high temperatures and large dc currents. By replacing the oxygen stream with a hydrogen one at the cathode, they were able to separate the anode impedance from the cathode impedance. Indeed, by replacing O_2 by H_2, the cathode reaction becomes : $2\,H^+ + 2\,e^- \leftrightarrow H_2$. In fuel cell research, this reaction is usually considered as a very fast electrode reaction. Hence, its impedance (Z_C) can be considered as negligible compared to the anode impedance ($|Z_C| \ll |Z_A|$). The total impedance of the generator, which is the sum of the cathode and anode impedances ($Z_G = Z_C + Z_A$), can then be taken approximately equal to the anode impedance ($Z_G \simeq Z_A$). Their results show an inductive loop which occurs at low frequencies (LF) in the impedance diagram of the anode working without diffusion control. They have attributed this inductive loop to the methanol electro-oxidation reaction.

The second group of authors (Peppley *et al.* [3]) have studied the influence of the morphology of anode plates and the influence of the temperature. They have also replaced the oxygen at the cathode by another gas in order to measure the anode impedance. They have used nitrogen instead of hydrogen, and their results differ from Mueller *et al.* : no inductive loop is observed at low frequencies. Thus, one can think that the inductive loop measured by Mueller *et al.* could be an artifact due to the use of hydrogen at the cathode, given that a LF inductive behaviour is sometimes predicted due

to the hydrogen evolution reaction (HER) following the Volmer-Heyrovsky mechanism [4, 5].

In previous works focused on Ni-Cd and lead-acid batteries [6,7], as well as H_2/O_2 fuel cells [8], we proposed a method for measuring the total impedance (anode + cathode) of a generator while it is running on a load. The main aim of this work is to answer the question : "Is the measurement of separated impedances (anode and cathode) of an electrochemical generator running on a load possible ?" Indeed, in these conditions, the measurement of Z_A (anode impedance) and Z_C (cathode impedance) is not as simple as in the pioneering study of Keddam *et al.* [9] on Pb/H_2SO_4 batteries, where a bias current was imposed (galvanostatic conditions). In addition, we show in this paper that the LF inductive loop in the impedance diagram of a DMFC anode is really due to the methanol electro-oxidation reaction, what was not achieved completely in Refs. [1–3].

In the first part of this paper, a new method is proposed for the measurement of separated electrode impedances of a generator running on constant load. In the second part, this method is tested and validated on a dummy cell. It is also, and above all, tested on a commercial DMFC (H-TEC, Luebeck, Germany [10]) running on a constant load. The total impedance (anode + cathode + membrane) of this DMFC is measured with a 0.5 M methanol anode solution and with an air stream at the cathode. Thanks to a platinum wire which plunges in the methanol solution and plays the role of a reference electrode, or more exactly a comparison electrode, the new method can be applied and it is shown that it is possible to separate the anode impedance from the cathode impedance without replacing

the air stream at the cathode by another gas nor imposing a constant current flowing through the cell. In this way, parasitic electrochemical reactions are eliminated. This method is transposable to any electrochemical generator provided that a reference electrode is present in the cell.

2 Theoretical

In this Section, we theoretically describe the method for the measurement of the electrode impedances of an electrochemical generator running on a load. Let us consider the electrical circuit shown in Fig. 1 simulating an electrochemical generator running on a constant load. The impedances of the cathode and of the anode are Z_{C} and Z_{A} respectively. The impedance of the load is Z_{l}.

The total impedance of the dummy generator Z_{G} is defined as :

$$Z_{\mathrm{G}}(s) = Z_{\mathrm{A}}(s) + Z_{\mathrm{C}}(s) \tag{1}$$

where s is the Laplace complex variable. First, using the connections presented in Fig. 1 A, the total impedance Z_{m} of the dummy electrochemical generator in parallel with the load can be measured [6–8]. It is given by :

$$\frac{1}{Z_{\mathrm{m}}(s)} = \frac{1}{Z_{\mathrm{l}}(s)} + \frac{1}{Z_{\mathrm{A}}(s) + Z_{\mathrm{C}}(s)} \tag{2}$$

Eqs. (1) and (2) can also be written as :

$$Z_{\mathrm{G}}(s) = \frac{Z_{\mathrm{l}}(s)\ Z_{\mathrm{m}}(s)}{Z_{\mathrm{l}}(s) - Z_{\mathrm{m}}(s)} \tag{3}$$

Hence the impedance of the dummy generator (Z_{G}) can be calculated from experimental measurements of Z_{l} and Z_{m}.

Next, using the connections presented in Fig. 1 B and C, two "pseudo-impedances" can be measured :

$$H_{\mathrm{C}}(s) = \frac{Z_{\mathrm{C}}(s)\ \Delta I_1(s)}{\Delta I(s)} \tag{4}$$

and :

$$H_{\mathrm{A}}(s) = \frac{Z_{\mathrm{A}}(s)\ \Delta I_1(s)}{\Delta I(s)} \tag{5}$$

where $\Delta I(s)$ is the Laplace transform of the sinusoidal current modulation and $\Delta I(s) = \Delta I_1(s) + \Delta I_2(s)$ (cf. Fig. 1). The term "pseudo-impedance" is used in this paper because, under the above conditions, the two signals ΔI and $\Delta E = Z_{\mathrm{A}}\,\Delta I_1$ (or $\Delta E = Z_{\mathrm{C}}\,\Delta I_1$) are not measured in a standard way. The unit of H_{A} and H_{C} is Ω but the measured voltage does not result directly from the current flowing through the electrode.

The ratio :

$$\frac{H_{\mathrm{A}}(s)}{H_{\mathrm{C}}(s)} = \frac{Z_{\mathrm{A}}(s)}{Z_{\mathrm{C}}(s)} \tag{6}$$

can be calculated in order to eliminate the variable ΔI_1. Thanks to Eqs. (3) and (6), the sum $Z_{\mathrm{A}} + Z_{\mathrm{C}}$ and the ratio $Z_{\mathrm{A}}/Z_{\mathrm{C}}$ are known. Hence, Z_{A} and Z_{C} are easily calculable separately at each frequency.

The main advantage of this method is to study the electrodes of an electrochemical generator during its discharge through a constant load. This situation is, in this case, a situation of natural running. The electrochemical reactions that are studied are the reactions really occuring during the discharge.

It is possible to follow another way for determining Z_C and Z_A. Indeed, Eqs. (4) and (5) can also be written as :

$$H_C(s) = \frac{Z_C(s)\ Z_l(s)}{Z_l(s) + Z_A(s) + Z_C(s)} \tag{7}$$

and :

$$H_A(s) = \frac{Z_A(s)\ Z_l(s)}{Z_l(s) + Z_A(s) + Z_C(s)} \tag{8}$$

Strictly speaking, knowing (or measuring) Z_l, and measuring H_A and H_C is enough to derive Z_A and Z_C, and it is not necessary to measure Z_G. Nevertheless, it is more reasonable to measure $Z_G = Z_A + Z_C$ afterwards in order to verify the calculation.

It is interesting to note that if the magnitude of the load impedance is much higher than the magnitude of the generator impedance :

$$|Z_l| \gg |Z_G| \tag{9}$$

then the current flowing through the load becomes very low ($\Delta I_2 \approx 0$). So the current flowing through the generator roughly equals the total current ($\Delta I_1 \approx \Delta I$), and the pseudo-impedances defined above and the impedances of the electrodes become equal :

$$H_A \approx Z_A\ ,\ H_C \approx Z_C \tag{10}$$

That also means :

$$Z_G \approx Z_m \tag{11}$$

However, it should be noticed that in most cases the condition of a high load impedance is not fulfilled because the new impedance measurement technique has no interest when the discharging current is low. For high

discharging currents, the value of Z_l is of the same order of magnitude as the impedance of the electrochemical generator, so Eqs. (9) to (11) do not apply, and the general Eqs. (1) to (8) should be used to determine the electrode impedances.

3 Experimental

The DMFC used for the present study is made by H-TEC (Luebek, Germany [10]). The membrane electrode assembly (MEA) has a surface area of 16 cm^2 (4×4 cm) and is sandwiched between two metallic grids. These grids play the role of current collectors. The cathode (positive electrode) operates on air. A 0.5 M aqueous methanol solution circulates at the anode (negative electrode) with the aid of a centrifugal pump (Heidolph, Germany). The flow rate is constant and equal to 1 L min^{-1}. For confidentiality reasons, the DMFC manufacturer does not reveal the composition of the electrodes and of the membrane. Nevertheless, one can suppose that the electrodes contain two different electrocatalysts : Pt/Ru particles at the anode and Pt particles at the cathode. The membrane is probably made with Nafion®. The power given by the manufacturer is 50 mW.

An Autolab PGSTAT30 (Eco Chemie, The Netherlands) is used to perform impedance measurements. This apparatus is controlled by FRA 4.8 software. DMFC impedance is measured in the 100 kHz–10 mHz frequency range, from high to low frequency, with 10 steps per logarithmic decade. The results were processed using Mathematica 4.1 software [11]. The connections between the DMFC and the Autolab device are presented in Fig. 2 A for DMFC total impedance measurements under galvanostatic conditions and in

Fig. 2 B for the study of the DMFC running on constant load. Fig. 3 shows the connections for anode (A) and cathode (B) impedance measurements under galvanostatic conditions, and for anode (C) and cathode (D) impedance measurements for the DMFC running on constant load. Whatever the connections used in Figs. 2 and 3, the perturbation signal is a sinusoidal current with amplitude $\delta I = 1$ mA. A platinum wire, which plunges in the methanol solution, plays the role of a reference electrode, more exactly a comparison electrode [12]. It must be pointed out that, with these connections, the cathode impedance includes the membrane impedance.

4 Results and discussion

4.1 Dummy cell measurements

What is theoretically described in Section 2 is now applied to a dummy electrochemical grenerator running on a constant load (Fig. 4). The load (l) is a resistor $R = 50\ \Omega$ in parallel with a capacitor $C = 9.4\ \mu$F, in order to show that the method is valid whatever the kind of the load (not only for a pure resistance). The cathode impedance (Z_{C}) is modelled, for example, by a resistor $R_2 = 10\ \Omega$ in series with a resistor $R_1 = 20\ \Omega$ and a capacitor $C_1 = 5.7\ \mu$F connected in parallel. The anode impedance (Z_{A}) is modelled by a resistor $R_3 = 51\ \Omega$ in parallel with a capacitor $C_3 = 47\ \mu$F. All these components have a tolerance range of $\pm$ 5 %.

First, setting $s = \mathrm{i}\,\omega$, where ω is the angular frequency ($\omega = 2\,\pi\,f$), f the frequency (Hz) and $\mathrm{i} = \sqrt{-1}$, the impedance of the load Z_{l} is measured (Fig. 5 A). Using the connections presented in Fig. 4 A, the total impedance Z_{m} of the dummy electrochemical generator in parallel with the load is also

measured (Fig. 5 B). Thanks to Eq. (3), the impedance of the dummy generator (Z_G) is calculated from the experimental measurements of Z_l and Z_m. The impedance Z_G, which is the sum $Z_A + Z_C$, is shown in Fig. 5 C using the Nyquist representation.

Next, using the connections presented in Fig. 4 B and C, the two pseudo-impedances H_C and H_A are measured (Fig. 6). Thanks to Eqs. (3) and (6), the sum $Z_A + Z_C$ and the ratio Z_A/Z_C are known. Hence, Z_A and Z_C are easily calculable separately at each frequency. Fig. 7 shows the impedance diagrams for Z_A and Z_C calculated from the data of Figs. 5 C and 6 using Mathematica 4.1 software [11].

These results validate the method proposed above. The impedance diagrams obtained with this method (Fig. 5 C and 7) are identical to those that one can obtain under galvanostatic or potentiostatic conditions (not shown here for lightening reasons).

4.2 DMFC measurements

4.2.1 Polarisation curve

Fig. 8 shows the steady-state voltage (U) vs. current (I) curve of the H –TEC DMFC, which is characteristic of DMFCs in general (see for example Ref. [13]). This curve is plotted for the DMFC running on several resistors (from $R = 10$ kΩ to $R = 4.6$ Ω). The value of the current is determined thanks to the measurement of the voltage and to Ohm's law, $I = U/R$.

4.2.2 Total impedance measurements

All the impedance measurements were carried out at the steady-state current corresponding to the circled dot in Fig. 8 ($I = 31$ mA and $U = 0.315$ V). All the measurements were made at least twice, and no difference can be seen between them, i. e. no temporal drift is observed. A complete EIS study of the DMFC all along the steady-state U vs. I curve will be the subject for another paper [14].

In Fig. 9 C, a typical Nyquist plot of the total impedance $Z_A + Z_C$ of the DMFC is shown. This diagram is obtained using the connections presented in Fig. 2 B, the experimental data of Figs. 9 A and B and Eq. (3), as explained in Section 2. At the highest frequencies, an inductive behaviour characteristic of the apparatus and connections can be seen. The impedance diagram in the Nyquist representation is made up of three capacitive arcs : in the 10 kHz–1 Hz frequency range, two arcs are coalescent, and in the 1 Hz–10 mHz frequency range, a third arc can be observed. Note that in the 10 kHz–1 Hz frequency range, the shape of the diagram can also be interpreted as a single depressed semi-circle or a skewed arc.

4.2.3 Anode and cathode impedance measurements

In order to separately determine the anode and cathode impedances, the procedure described in Section 2 is applied to our system. First, the two "pseudo-impedances" H_A and H_C are measured (Fig. 10) using the connections presented in Fig. 3 C and D. Then, knowing the sum $Z_A + Z_C$ and the ratio Z_A/Z_C, Z_A and Z_C can be calculated separately at each frequency (Fig. 11). Only the low frequency parts of the diagrams are shown (below 100 Hz) because a parasitic high-frequency (HF) arc appears in the second

quadrant of the complex plane (Re $Z < 0$ and $-\text{Im}\ Z > 0$) when the Pt wire is used as a reference electrode. This parasitic arc depends on the position of the Pt wire in the methanol solution. The reason for this observed arc has to be clarified in order to avoid this parasitic noise [14]. Note that HF artefacts due to the reference electrode were already observed for electrochemical systems in low conductivity media [15].

Nevertheless, numerous observations can be made from these measurements. First, the modulus of the anode impedance is about 20 times lower than the modulus of the cathode impedance, showing that the performance of the DMFC is mainly limited by the oxygen reduction reaction (ORR) at the cathode. This result is in good agreement with the conclusions of Peppley *et al.* [3]. The shape of the cathode impedance, which is quite similar to the shape of the total impedance, confirms also this observation.

Next, the impedance diagrams obtained using this new method are virtually identical to the impedance diagrams plotted under galvanostatic conditions (Fig. 12). It can be concluded here that this study validates the new method presented in this paper.

Finally, the impedance diagram of the anode at frequencies between 100 Hz to 1 mHz (Fig. 13) has roughly the same shape than the impedance diagram plotted by Mueller *et al.* [2]. It shows that the inductive behaviour at low frequencies is really due to the methanol electro-oxidation, and not to parasitic electrochemical reactions (i. e. proton reduction reaction if a dynamic hydrogen electrode (DHE) is used [1–3]). Nevertheless, the mechanism for methanol electro-oxidation is more complicated than the mechanism

proposed by Mueller *et al.* [2]. Indeed, the one-adsorbate mechanism proposed by Mueller *et al.* cannot explain the shape of the impedance diagrams they showed. The magnitude of the double layer capacitance (C_{dl}) they measured is in the order of 0.1–1 F cm^{-2}, whereas classical values for fuel cell electrodes are contained between 0.001 and 0.01 F cm^{-2}. Besides, they dealt with this point in their paper [2]. At frequencies lower than 100 Hz, it can be considered that only the faradaic impedance is measured. In other words, the semi-circle due to the charge transfer resistance (R_{ct}) in parallel with C_{dl} appears at frequencies higher than 100 Hz. Hence, the impedance diagram shown in Fig. 13, which is the faradaic impedance diagram, can only be modelled using a third-order impedance at least, because in the 100–0.1 Hz frequency range, the phase shift of $Z_{\mathrm{A}} - R_{\Omega}$ is less than $-\pi/2$, and because of the low frequency inductive loop. Consequently, the mechanism for methanol electro-oxidation should involve at least three adsorbates. Here, we remind the reader that a n-adsorbate mechanism leads to a n-order faradaic impedance, but not necessarily to a n-loop diagram [16, 17]. Note that Léger has recently proposed a three-adsorbate mechanism for methanol electro-oxidation on platinum-based electrocatalysts [18].

5 Conclusion

We have proposed and tested a new experimental method for anode and cathode impedance measurements of electrochemical generators running on constant load.

Impedance measurements were carried out first on a simple dummy cell. Then, a commercial DMFC running on a 10 Ω resistor was studied using the

new method. Anode and cathode impedances were obtained successfully. It has been determined that the performance of the DMFC is mainly limited by the oxygen reduction reaction (ORR) at the cathode. It has been also determined that the inductive loop which occurs at low frequencies in the impedance diagram of the anode can be definitively attributed to the mechanism for methanol electro-oxidation. Nevertheless, this mechanism is still unclear and has to be determined in the future.

The main advantage of this method is to study the electrodes of an electrochemical generator during its discharge through a constant load. This situation is, in this case, a situation of natural running. The electrochemical reactions that are studied are the reactions really occuring during the discharge. Moreover, by using this method, the current flowing through the generator can be greater than the maximum value that could be supplied by the regulation system (1 A for the Autolab PGSTAT 30).

Note that this article is focused on the new proposed method. This method is transposable to any electrochemical generator provided that a reference electrode is present in the cell and steady-state conditions are satisfied during EIS measurements. Explanation of the impedance diagrams in terms of reaction mechanisms is beyond the scope of this work.

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Figure captions

Figure 1 : Electrical circuit simulating an electrochemical generator running on a constant load, and connections used for the study of (A) the total impedance of a generator $Z_{\rm A} + Z_{\rm C}$, (B) the cathode impedance $Z_{\rm C}$ and (C) the anode impedance $Z_{\rm A}$. WE : working electrode, RE : reference electrode and CE : counter electrode.

Figure 2 : Connections used for the EIS study of a DMFC at constant current (A) or running on constant load (B).

Figure 3 : Connections used for the EIS study at constant current of the anode (A) and the cathode (B) of a DMFC, and of the anode (C) and the cathode (D) of a DMFC running on constant load. The platinum wire plunges into the methanol solution, very close to the anode (less than 1 mm).

Figure 4 : Electrical circuit used for the study of a dummy electrochemical generator running on a constant load. The connections are the same as in Fig. 1. $R = 50\ \Omega$, $C = 9.4\ \mu$F, $R_1 = 20\ \Omega$, $C_1 = 5.7\ \mu$F, $R_2 = 10\ \Omega$, $R_3 = 51\ \Omega$ and $C_3 = 47\ \mu$F.

Figure 5 : Impedance diagrams (Nyquist representation) measured (A) for the load and (B) for the dummy electrochemical generator in parallel with the load using the connections of Fig. 4 A. (C) Impedance diagram calculated from the data of Figs. A and B for the dummy generator, using Eq. (3). Sinusoidal perturbation amplitude $\delta I = 1$ mA. Decimal logarithm of the frequency (Hz) is given on the graphs.

Figure 6 : "Pseudo-impedance" diagrams (Nyquist representation) measured (A) for H_{A} (using the connections of Fig. 4 C) and (B) for H_{C} (using the connections of Fig. 4 B). $\delta I = 1$ mA.

Figure 7 : Impedance diagrams (Nyquist representation) for (A) the anode and (B) the cathode, calculated from the data of Figs. 5 C and 6, using Eqs. (3) and (6).

Figure 8 : Steady-state voltage (U) vs. current (I) curve of an air-feed H-TEC DMFC. Methanol concentration : 0.5 mol L^{-1}. Flow : 1 L min^{-1}. Circled dot A corresponds to the impedance diagrams in Figs. 9–13.

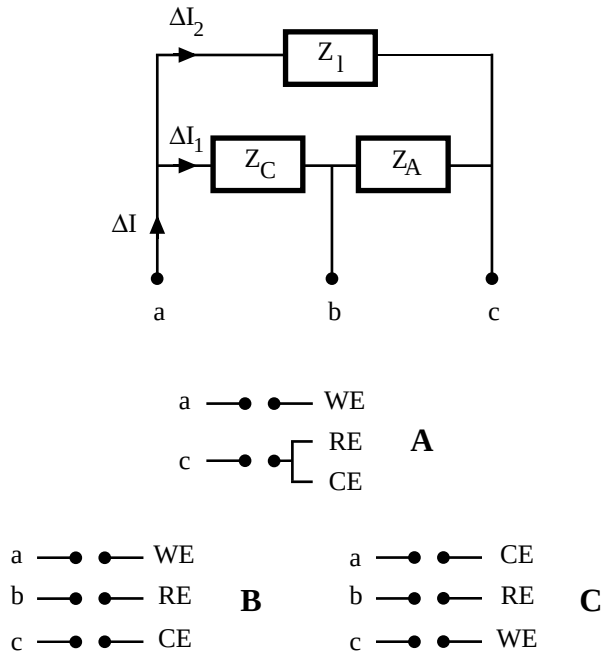
Figure 9 : Impedance diagrams (Nyquist representation) measured for the DMFC running on a constant load : (A) impedance of the load, with $R = 10.2\ \Omega$, (B) impedance of the DMFC in parallel with the load (using the connections of Fig. 2 B), and (C) impedance of the DMFC calculated using Eq. (3). $\delta I = 1$ mA.

Figure 10 : "Pseudo-impedance" diagrams (Nyquist representation) measured (A) for H_{A} (using the connections of Fig. 3 C) and (B) for H_{C} (using the connections of Fig. 3 D). $\delta I = 1$ mA.

Figure 11 : Impedance diagrams (Nyquist representation) for (A) the anode and (B) the cathode of the DMFC calculated from the data of Figs. 9 C and 10, using Eqs. (3) and (6).

Figure 12 : Impedance diagrams (Nyquist representation) measured for the DMFC under galvanostatic conditions : (A) anode impedance (using the connections of Fig. 3 A), (B) cathode impedance (cf. connections of Fig. 3 B), and (C) total impedance (using the connections of Fig. 2 A). Steady-state current $I = 31$ mA and perturbation amplitude $\delta I = 1$ mA.

Figure 13 : DMFC anode impedance (Nyquist representation). Conditions as in Fig. 12 A except for the low frequency limit : 1 mHz.



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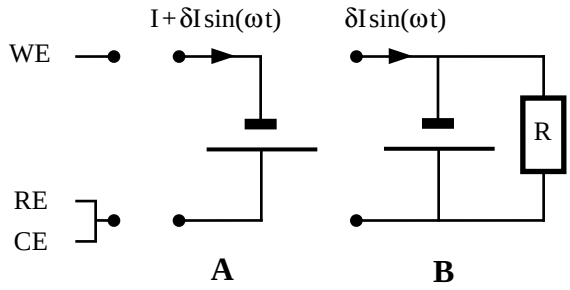

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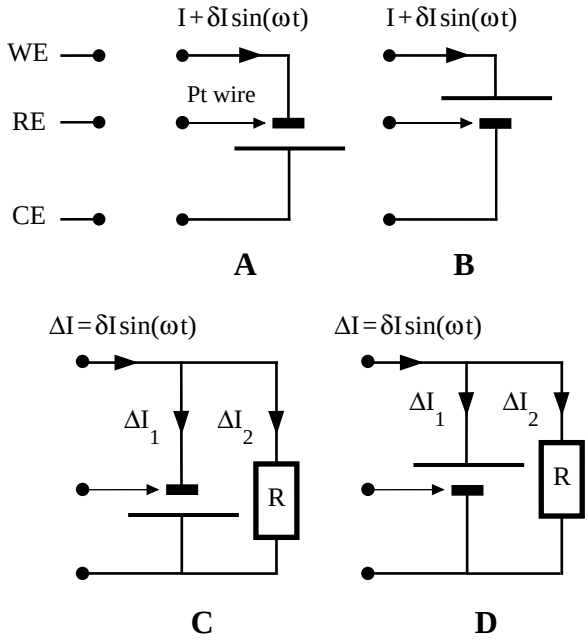

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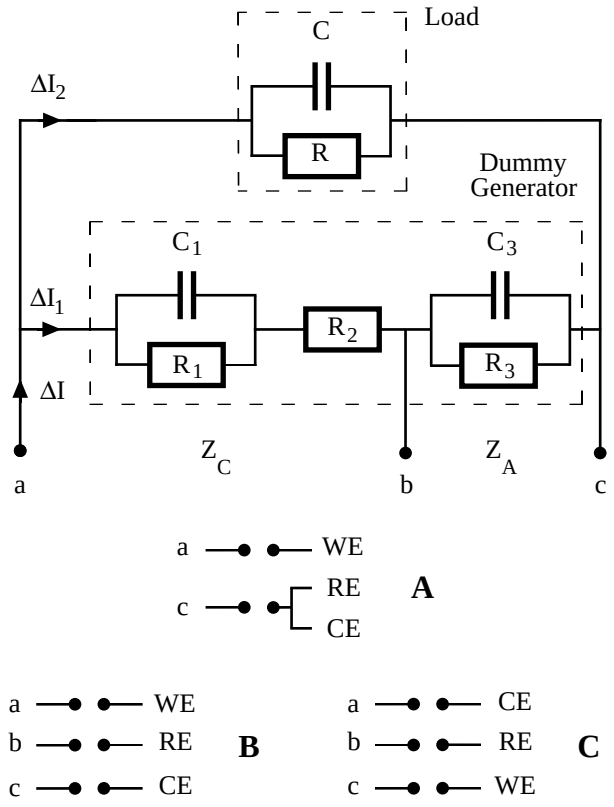

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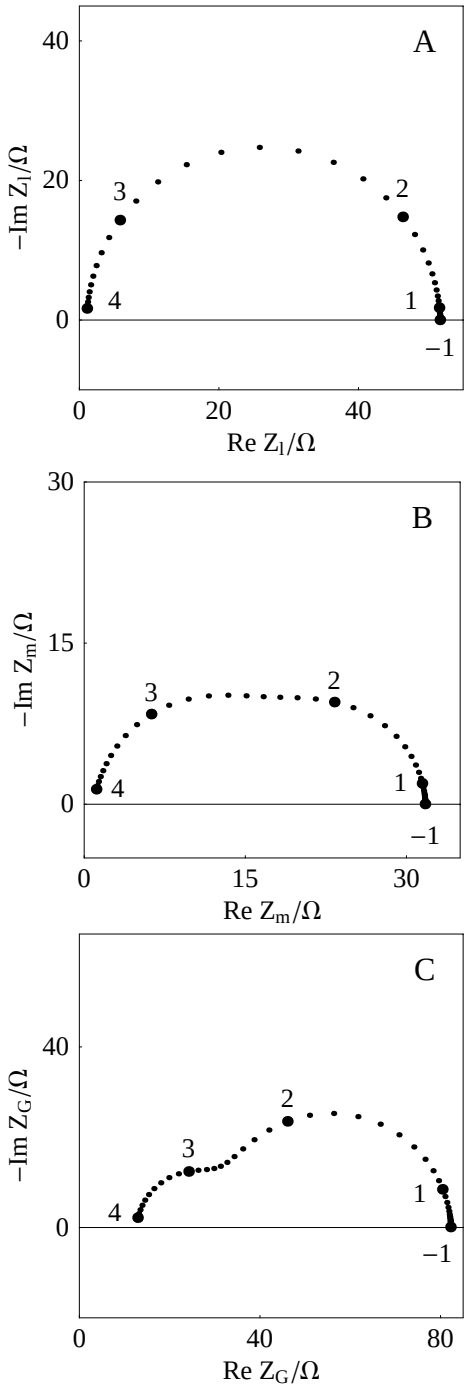

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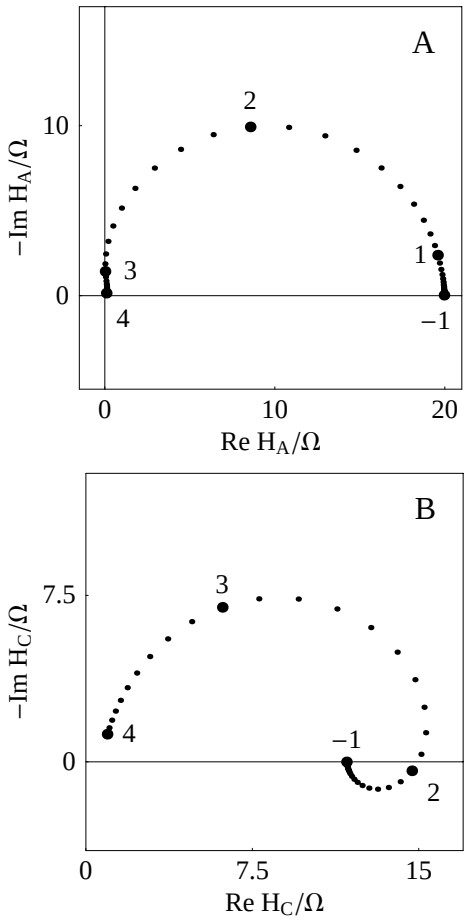

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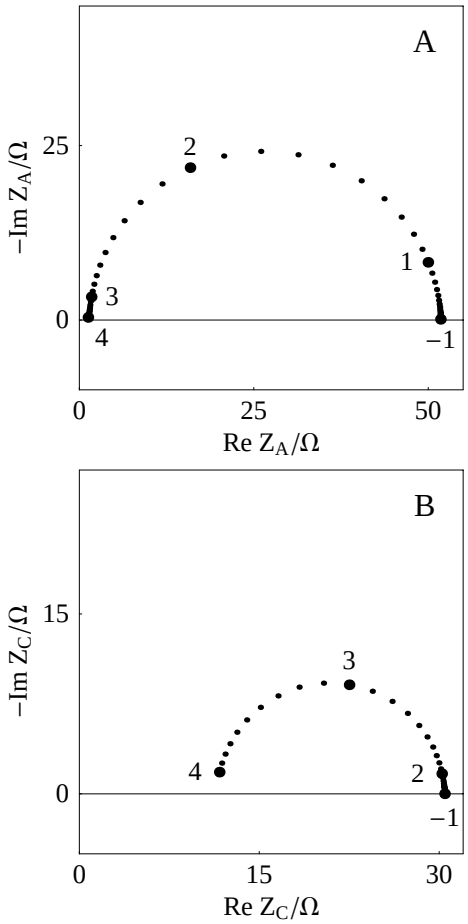

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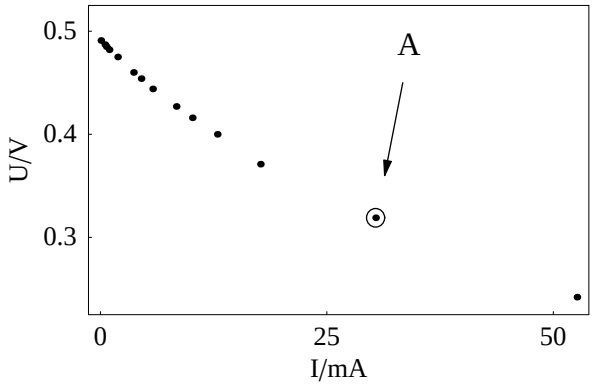

Figure 8 :

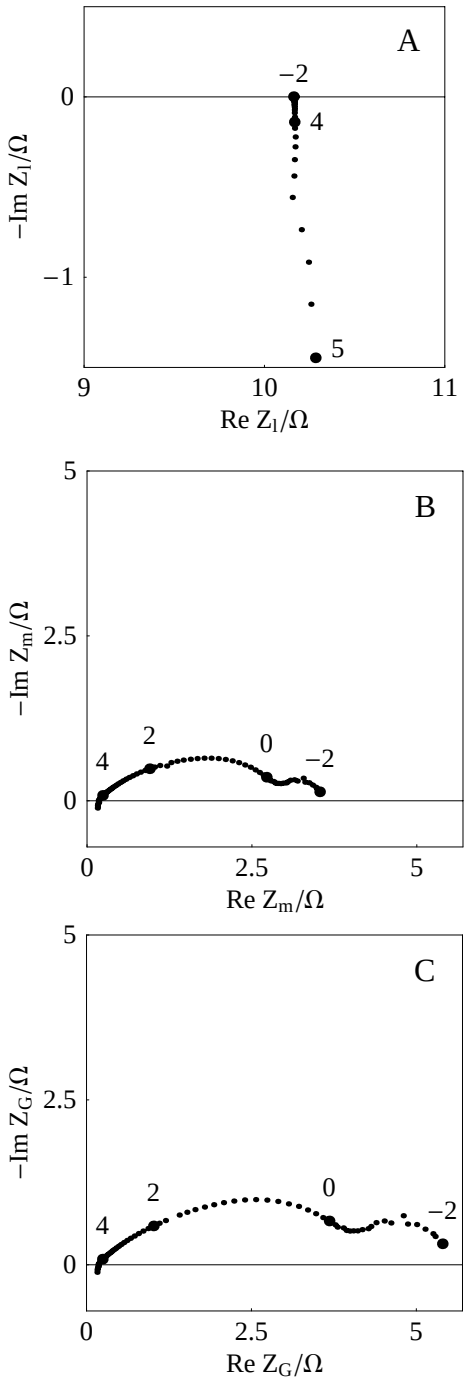

Figure 9 :

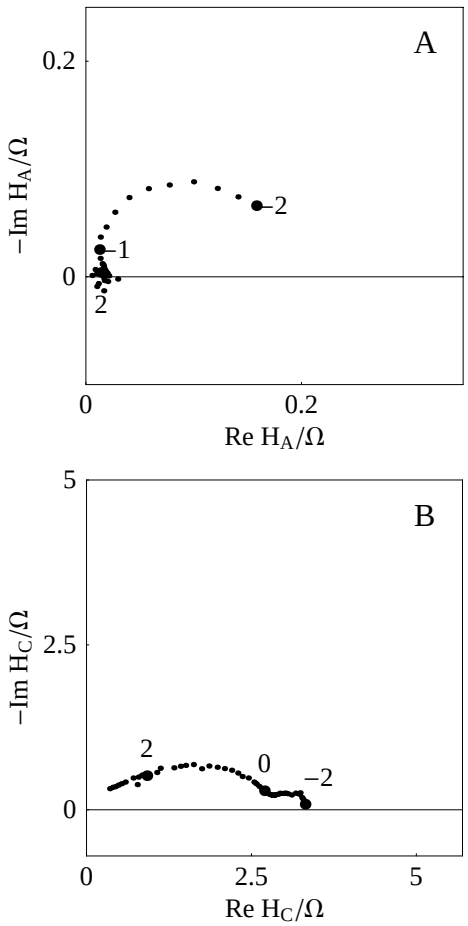

Figure 10 :

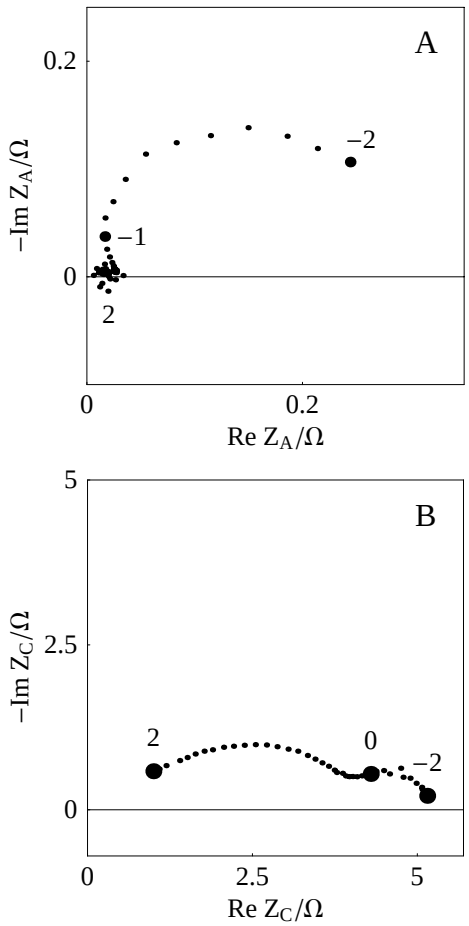

Figure 11 :

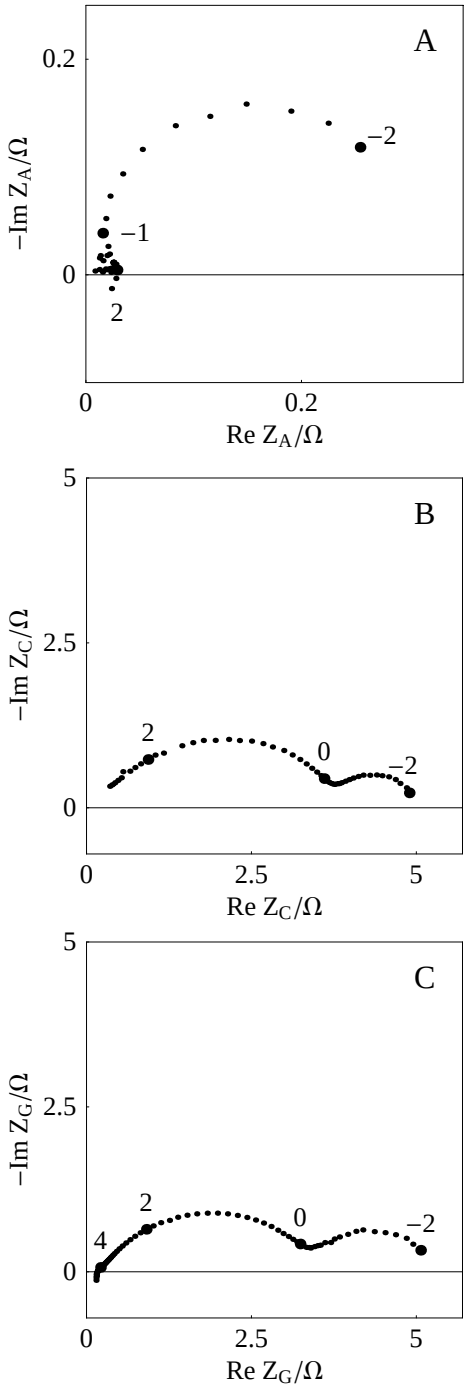

Figure 12 :

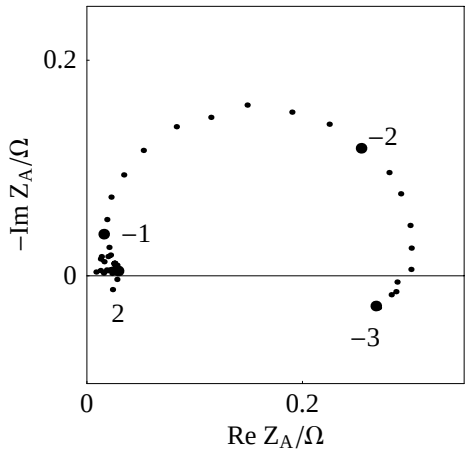

Figure 13 :