Characterization of direct methanol fuel cells by ac impedance spectroscopy

Jens T. Mueller [*], Peter M. Urban

Daimler-Benz AG, Forschungszentrum— FT1 / EG, Wilhelm-Runge-Strasse, 89013 Ulm, Germany

Abstract

The processes taking place in direct methanol fuel cells (DMFC) are characterized by ac impedance spectroscopy under realistic operating conditions. This method allows the separate examination of anode kinetics, anode mass transport, cathode kinetics, cathode mass transport, and membrane conductivity, making it a valuable diagnostic tool for DMFC development. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Recently, direct methanol fuel cells (DMFC) have been receiving increasing attention. Among their greatest advantages are ease of transportation and storage of the fuel, reduced system weight, size and complexity, high energy efficiency and low emissions. Conventional DMFC consist of a solid polymer electrolyte such as Nafion® membrane with catalysed electrodes bonded to both sides. Recent advances in power densities have been attributed to improvements in the electrode structure rather than to progress in electrocatalysis [1,2]: PtRu alloys are still considered to be the best catalysts for methanol electrooxidation [3], and Pt is still frequently used as the oxygen reduction catalyst. As far as we know, the method of ac impedance spectroscopy has not yet been applied to detailed studies of DMFC characteristics under conditions of practical interest. In this communication, we report on our results of DMFC impedance measurements carried out on large electrodes, at high temperatures, and in the presence of large dc currents.

2. Experimental

2.1. Cell hardware

Impedance measurements were conducted on a cell consisting of a Pt/Ru anode, a Nafion® membrane, and a Pt (4 mg/cm^2) cathode sandwiched between two conventional graphite flow field plates. The active area of each electrode was 49 cm^2, and the cell was thermostated. The anode was supplied with a 1 M aqueous solution of methanol at controlled flow rates. The cathode was operated either on air, oxygen, or hydrogen (see below); the flow rate and the pressure were controlled.

2.2. Electrochemical measurements

Fig. 1 illustrates the experimental setup employed in this work. The frequency generator/analyser was a Schlumberger Solartron FRA 1250 controlled by a personal computer. The generator was coupled to an electronic load (Zentro Elektrik, Germany) that allows modulation of large dc currents by ac signals up to 70 kHz. Impedance spectra were usually obtained at frequencies between 65 kHz and 3 mHz with 10–15 steps per decade. At frequencies higher than 10 Hz, an integration time of 3 s was chosen; at lower frequencies, smooth spectra were obtained with an integration time of 200 s. Impedances were measured under galvanostatic or potentiostatic control of the cell. The amplitude of the sinusoidal current

* Corresponding author. Tel.: +49-731-505-2995; Fax: +49-731-505-4220; E-mail: jens.mueller@dbag.ulm.daimlerbenz.com
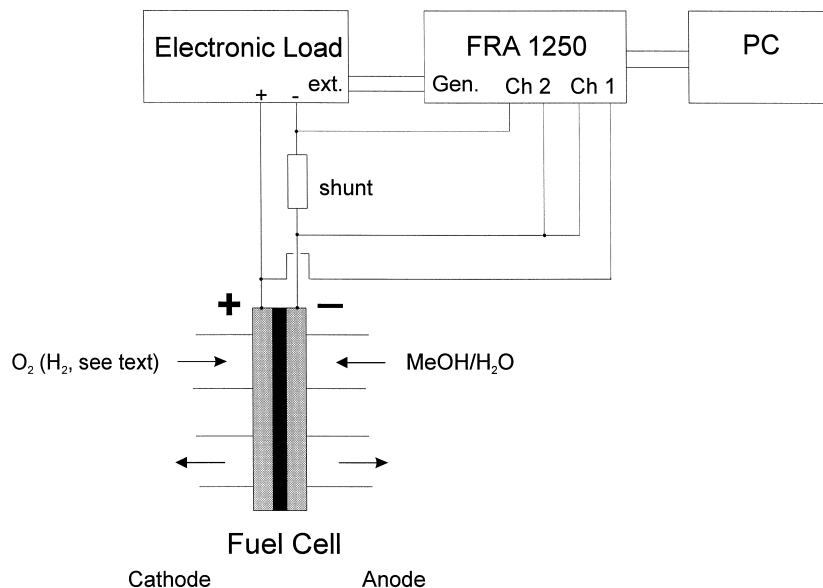
Fig. 1. Experimental setup for measuring impedance spectra of a direct methanol fuel cell (or of its anode vs. DHE).

signal was adjusted so that the potential amplitude did not exceed 10 mV.

Regarding the low resistance of our large cell and the high frequency of the measurements, special care had to be taken in order to avoid lead inductance. (It is essential to keep the current conducting cables short, twisted, and as far away as possible from the sense wires which should also be twisted.) By short-circuiting of the cell, it was checked that lead inductance is negligible. Instead, a little capacitive behaviour was observed for the short-circuited cell at high frequencies. This was attributed to the large graphite plates whose area significantly exceeded the active electrode area, and to a small contribution of the input capacity of the electronic load. Compared to the high capacity of our electrodes which contain high surface area catalysts, these spurious capacities are low and practically do not affect the shape of impedance spectra.

2.3. Procedure to measure anode and cathode impedances

A standard practice in hydrogen-air fuel cell research consists in measuring cell impedances and considering them as cathode impedances [4]. Contributions of the anode are usually negligible due to fast kinetics and mass transport of the H_2 oxidation reaction. Consequently, it is possible to eliminate contributions of the cathode in a DMFC by operating it without oxygen, so that protons are reduced and hydrogen is evolved. In order to control the potential and to remove permeating water, the cathode is supplied with a continuous stream of hydrogen. This cathode will be denoted as a dynamic hydrogen electrode (DHE). All anode impedance spectra reported here were measured between anode and DHE in the complete fuel cell. No significant difference was recorded when anode

impedances were measured against a reversible hydrogen electrode contacted to the membrane. Thus, the DHE is suitable as a reference electrode and counter electrode for DMFC anode measurements.

DMFC cathode impedance spectra were obtained as follows. The impedance spectrum of a complete DMFC, the cathode being operated as usual on air or oxygen, is recorded. Then the anode spectrum is recorded as described above. The anode impedances are subsequently subtracted from complete cell impedances, resulting in a cathode impedance spectrum.

The quality of the spectra can be checked by comparing the overall polarization resistance obtained from the Nyquist plot to the slope of the $i–E$-curve obtained at the same current density:

$$\text{Re}_{max}(Z) = \frac{\delta E}{\delta i}.$$

In all the experiments that we conducted, the consistency result was good. This suggests that the processes in the fuel cell are correctly described by the resistances observed in the spectra.

3. Results and discussion

3.1. Anode impedance spectra

Fig. 2 shows a typical Nyquist plot of the impedance of a DMFC anode. It consists of three separate arcs which are examined and discussed separately below. The three corresponding resistances are denoted as R_1, R_2, R_3, respectively.
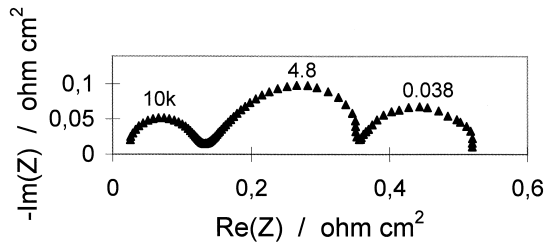
Fig. 2. Nyquist plot of a typical DMFC anode impedance spectrum (frequencies of the maxima in hertz).

Fig. 4. Effect of anode potential (measured against DHE) on the medium-frequency arc of DMFC anode impedance plots. ■, 200 mV; ▲, 250 mV; ●, 300 mV.

3.1.1. High-frequency arc

The arc occurring between 65 kHz and 900 Hz shrinks in diameter as the temperature is raised (cf. Fig. 3) but it does not vary with anode potential. It is obviously related to an ohmic process. The observed decrease of the resistance, designated R_1, with increasing temperature is typical of ionic conductors. Furthermore, R_1 resulted to be proportional to membrane thickness. Thus, the high-frequency arc can be ascribed to the ionic resistance of the membrane, which forms a parallel combination with a capacitance. This capacitance depends somewhat on membrane thickness, but not as strongly as expected for a geometric capacitance ($C \sim d^{-1}$); it is concluded that both double layer capacitances (cf. Ref. [5]) and the geometric capacitance of the electrode arrangement manifest themselves in this arc. Pure ohmic resistances of the electronically conducting cell components, as well as contact resistances, cause a shift of this arc to higher real parts. This feature of the spectra enables one to easily quantify the iR_1 loss arising from different membrane materials and varying operating conditions of the fuel cell. It should be emphasized that R_1 is not an anodic element; it appears in the anodic plots only because of the experimental procedure of measuring impedances of anode and membrane against the DHE as an internal reference and counter electrode.

3.1.2. Medium-frequency arc

As the frequency is lowered, a second arc occurs. Its size is a strong function of anode potential, as shown in Fig. 4. The corresponding resistance R_2 decreases with increasing overpotential, reflecting the increasing driving force for the related process and indicating that R_2 is due
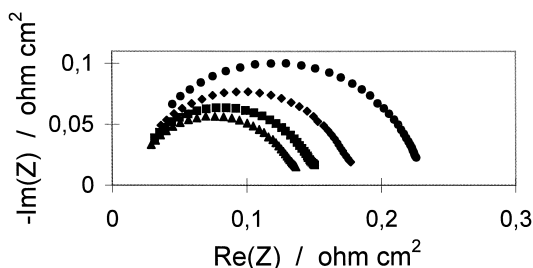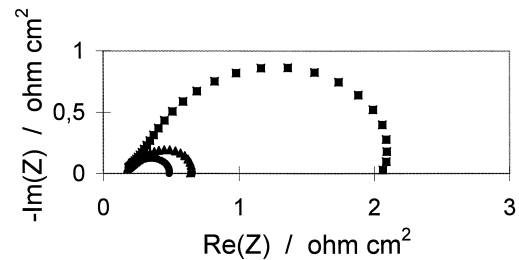
to methanol electrooxidation kinetics. Looking at this arc, different anode catalyst compositions and operating conditions of the fuel cell can be evaluated with respect to their effects on anode performance.

The arcs are not regular semicircles but contain straight lines at the high frequency end, and they are flattened. Such distorted semicircles have been attributed to the coupling of interfacial and diffusional impedances [6], and to the roughness of highly dispersed electrode surfaces [7]. The reason for this observed distortion still has to be clarified.

3.1.3. Low-frequency arc

At frequencies below 1 Hz, a third arc can be observed in the Nyquist plots. The magnitude of the corresponding resistance R_3 grows as either the methanol flow rate or the concentration is decreased. Fig. 5 illustrates the variation of the low-frequency arc with the methanol stoichiometry factor at constant current density. (The methanol stoichiometry factor is defined as the ratio of actual anode fuel flow rate to the stoichiometric anode fuel flow rate.) Also, the pressurizing of the anode chamber increases R_3; we ascribe this effect to hindered CO_2 removal. The low-frequency arc is obviously related to mass transfer of methanol in the anode.

Several reasons can be given to explain why mass transfer can play a significant role in DMFC anodes even at relatively low current densities. Due to unwanted crossover effects, very low fuel concentrations are frequently used [8]; the reaction product, CO_2, partially blocks catalytically active sites against access of methanol, and

Fig. 3. Effect of temperature on high-frequency arc of DMFC anode impedance plots. ▲, 90°C; ■, 70°C; ◆, 50°C; ●, 30°C.
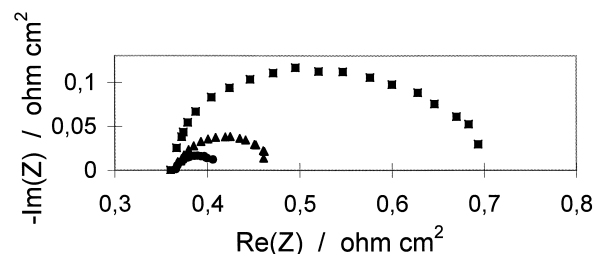

Fig. 5. Effect of anode fuel flow rate on the low-frequency arc of DMFC anode impedance plots. The numbers indicate methanol stoichiometry factors based on the current density: ■, 1.6; ▲, 2.0; ●, 5.0.
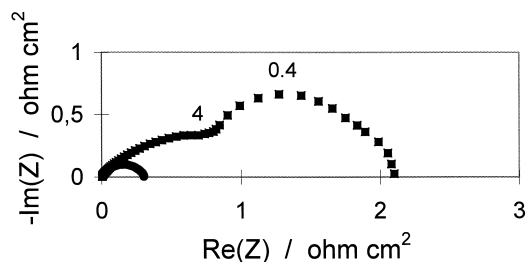
Fig. 6. Nyquist plots of typical DMFC cathode impedance spectra (frequencies in hertz). ■, Operation on air; ●, operation on oxygen.

Fig. 8. Impedance plots of a DMFC cathode operating on oxygen at low flow rates. The numbers indicate O_2 stoichiometry factors based on the current density. ■, 1.15; ▲, 1.3; ●, 1.5.

the CO_2 bubbles can be expected to be relatively big, since DMFC anodes work at potentials which are close to the potential of zero charge of the anode catalyst [9]. The low-frequency arc of anode spectra allows to determine the voltage loss arising from these mass transfer limitations.

3.2. Cathode impedance spectra

Fig. 6 shows typical Nyquist plots of the impedance of a DMFC cathode operating on air and pure oxygen. Two arcs can be observed in the case of operation on air; the low-frequency arc is absent from spectra of cathodes operating on pure oxygen. Again, the two arcs are discussed separately, and the corresponding resistances are denoted as R_4 and R_5. Note that R_1, the ionic resistance of the membrane that leads to the high-frequency arc in the anode spectra, is not observed here, since it appears in both anode spectra and complete cell spectra and is consequently eliminated when the spectra are subtracted.

3.2.1. Medium-frequency arc

Two sets of experiments were conducted to interpret this feature of the cathode spectra. Firstly, the variation of a cathode operating on pure oxygen at relatively high flow rates was studied with regard to current densities. Fig. 7 shows that with increasing current density, i.e., increasing overpotential, the diameter of this arc decreases, reflecting the increasing driving force of the related process. Thus, the medium-frequency arc, which occurs at frequencies between 3 kHz and 1 Hz, is due to the charge transfer

resistance of the oxygen reduction reaction (ORR), R_4. When very low flow rates of pure oxygen are employed (below 2.0 times the stoichiometric rate), the arc increases with a decreasing oxygen stoichiometry factor (cf. Fig. 8). Obviously, in this case oxygen transport limitations occur which lead to significant oxygen concentration gradients in the catalyst layer and manifest themselves in increasing effective charge transfer resistances. We conclude that both ORR kinetics and oxygen transport properties in the catalyst layer contribute to R_4. A similar behaviour was observed for H_2/air fuel cell cathodes [4]. The fact that even with pure oxygen significant mass transport limitations are observed in the DMFC cathode catalyst layer can be ascribed to the large amounts of water that permeate through the membrane as a consequence of the liquid anode feed concept.

3.2.2. Low-frequency arc

This arc is only observed when the cathode is operating on air. It is strongly dependent on the air flow rate, as shown in Fig. 9. This correlation and the absence of the arc in the case of cathodes operating on pure oxygen demonstrate that this feature of the spectra is related to a mass-transfer resistance (R_5) in the cathode backing. When air is used as oxidant, oxygen has to diffuse through nitrogen and water towards the catalytically active layer. Similar to the situation in H_2/air fuel cell cathodes described in Ref. [4], the backing traps water which repre-
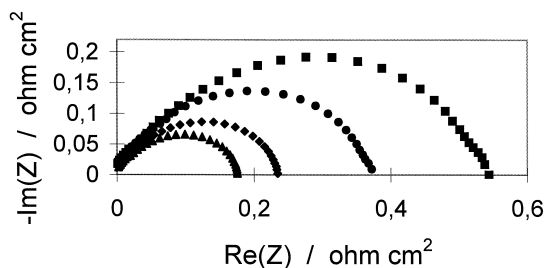

Fig. 7. Effect of current density on impedance plots of DMFC cathodes operating on oxygen at high flow rates. ▲, 0.3 A/cm²; ◆, 0.2 A/cm²; ●, 0.1 A/cm²; ■, 0.05 A/cm².
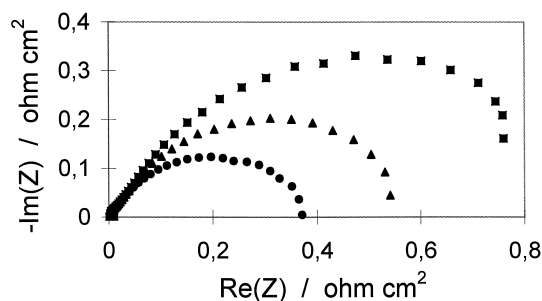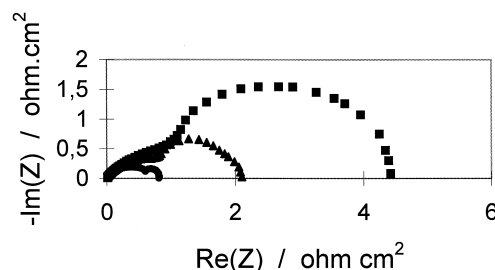

Fig. 9. Effect of air flow rate on DMFC cathode impedance plots. The numbers indicate oxygen stoichiometry factors based on the current density: ●, 6.0; ▲, 2.4; ■, 2.0.

sents a large diffusion resistance because of the low solubility of oxygen. From the large arc related to R_5 in the spectra and its strong dependence on the gas flow rate, it can be concluded that the DMFC cathode suffers from flooding under the conditions employed. If one compares the magnitude of the resistances R_1–R_5 in Figs. 2 and 6, it is evident that effective water removal from the backing is the most critical issue for DMFC performance improvement, as was suggested by Narayanan et al. [1].

4. Conclusion

We have presented impedance measurements as a diagnostic tool to investigate DMFC performance issues. This method enables researchers to gain insight into the effects of electrode morphology and operating parameters, to obtain detailed information about degradation phenomena, and will help to tailor-make DMFC electrodes with improved performance.

References

[1] S.R. Narayanan, G. Halpert, W. Chun, B. Jeffries-Nakamura, T.I. Valdez, H. Frank, S. Surampudi, Commercializing Fuel Cell Vehicles, conference abstracts, Chicago, IL, 17–19 September 1996, p. 96.
[2] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L12.
[3] C. He, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 144 (1997) 970.
[4] T.E. Springer, T.A. Zawodzinski, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) 587.
[5] S. Ahn, B.J. Tatarchuk, J. Electrochem. Soc. 142 (1995) 4169.
[6] H. Moreira, R. De Levie, J. Electroanal. Chem. 29 (1971) 353.
[7] A. Maritan, Electrochim. Acta 35 (1990) 141.
[8] X. Ren, T.A. Zawodzinski, F. Uribe, H. Dai, S. Gottesfeld, Electrochem. Soc. Proc. 95 23 (1996) 284.
[9] J.O'M. Bockris, S.U.M. Khan, Surface Electrochemistry, Chap. 2, Plenum, New York, 1993, and references therein.