Impedance studies on direct methanol fuel cell anodes

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Abstract

The processes taking place in direct methanol fuel cell anodes are characterized by ac impedance spectroscopy. Under conditions of practical interest, i.e., low methanol stoichiometry factors, the kinetic and the mass-transport resistance give rise to two well-resolved semicircles in the Nyquist plot. When mass-transport limitations are excluded, inductive loops occur in the complex plane which are interpreted in terms of the most widely accepted reaction mechanism for methanol electrooxidation. A simple equivalent circuit is used to model this impedance behaviour. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Direct methanol fuel cells (DMFC) receive increasing attention. This is mainly due to their characteristics such as simple construction, reduced system weight, size and complexity, high energy efficiency and low emissions. Recently reported advances in DMFC power densities are very promising; however, they have been attributed to improvements in the electrode structure and optimization of operating conditions rather than to progress in electrocatalysis [1,2]. In a previous paper [3], we reported on our results of DMFC impedance measurements carried out under conditions of practical interest, i.e., low methanol stoichiometry factors were used in order to reduce the unwanted effect of fuel crossover. It was shown that anode kinetics, anode mass transport, cathode kinetics, cathode mass transport, and membrane resistance can be studied separately in situ. Here, we focus on the faradaic impedance of DMFC anodes operating without mass-transport limitations in order to investigate the kinetics and the mechanism of methanol electrooxidation.

2. Experimental

The experimental setup and the procedure to measure DMFC anode impedances have been earlier described in

detail [3]. In short, the cell consisted of a Pt/Ru anode, a Nafion® membrane, and a Pt cathode sandwiched between two thermostated graphite flow field plates. The anode was supplied with a 1 M aqueous solution of methanol at controlled flow rates. The cathode was operated on hydrogen; it served as a reference and counter electrode. For impedance measurements, the current was modulated by a small sinusoidal signal so that the potential amplitude did not exceed 15 mV. Impedance spectra were usually obtained at frequencies between 1 kHz and 3 mHz with 10–15 steps per decade.

3. Results and discussion

Depending on the mass-transport properties of the DMFC anode under investigation, its impedance plots can have different features. Fig. 1 shows a Nyquist plot of an anode working with significant mass-transport limitations due to a low methanol flow rate (twice the stoichiometric rate). A distorted kinetic semicircle occurs at higher frequencies, which is followed by a mass-transport related semicircle at the low-frequency end [3]. The impedance behaviour of the same anode under pure kinetic control at different current densities is shown in Fig. 2. In this case, mass-transport limitations have been eliminated by using very high fuel flow rates (10 times the stoichiometric rate). These plots consist of a loop reflecting an inductive behaviour. The fact that the loops shrink with increasing

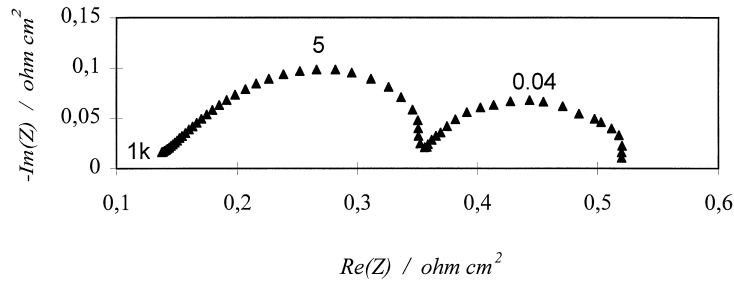* Corresponding author. Fax: +49-731-505-4220; E-mail: jens.mueller@Daimlerchrysler.com

Fig. 1. Nyquist plot of a typical DMFC anode impedance spectrum with significant mass-transport limitations (fuel stoichiometry: 2; frequencies given in Hertz).
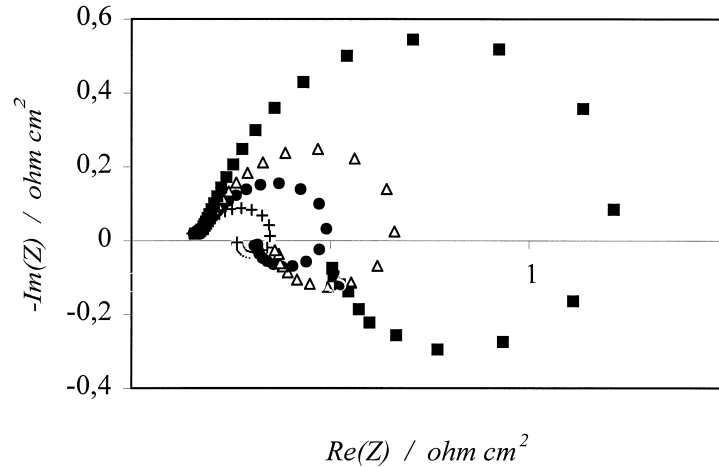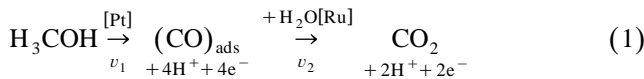

Fig. 2. DMFC anode impedance plots obtained under pure kinetic control (fuel stoichiometry: 10) at different current densities. $+$ 500 mA/cm², ● 300 mA/cm², △ 200 mA/cm², ■ 100 mA/cm².

current density, i.e., increasing anode potential clearly indicates that they are due to methanol electrooxidation kinetics.

The inductive behaviour can be explained using the kinetic theory derived by Harrington and Conway [4] for reactions involving intermediate adsorbates. We assume the following mechanism for methanol electrooxidation:

$$H_3COH \underset{v_1}{\overset{[Pt]}{\rightarrow}} (CO)_{ads} \underset{v_2}{\overset{+H_2O[Ru]}{\rightarrow}} CO_2 \quad (1)$$
$$+4H^+ +4e^- \qquad +2H^+ +2e^-$$

Methanol is adsorbed, mainly on Pt sites, with a rate v_1 to give $(CO)_{ads}$ as the dominating intermediate species. Oxidative removal of the adsorbate with a rate v_2 is
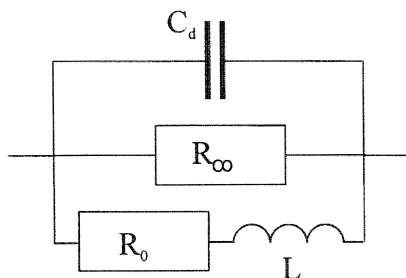
rate-limiting under conditions relevant to fuel cell operation, i.e., low anode potentials ($E < 400$ mV [RHE]) and high temperatures (ca. 100°C). Numerous authors have recently presented strong evidence for this mechanism [5–7].

It is furthermore assumed that mass transport limitations do not occur. Two rates can be defined as follows. r_e is the net rate of production of electrons:

$$r_e = 4v_1 + 2v_2 = i/F \quad (2)$$

r_{CO} is the net rate of production of $(CO)_{ads}$:

$$r_{CO} = v_2 - v_1 = \frac{q_{CO}}{F} \frac{d\theta}{dt} \quad (3)$$

where θ is the fractional surface coverage of CO, and q_{CO} is the charge required for adsorption of CO to complete coverage.

The full derivation is given in Ref. [4]. With the help of the auxiliary parameters,

$$A = F\left(\frac{\partial r_e}{\partial E}\right)_\theta, \quad B = \frac{F^2}{q_{CO}}\left(\frac{\partial r_e}{\partial \theta}\right)_E\left(\frac{\partial r_{CO}}{\partial E}\right)_\theta,$$

$$C = \frac{-F}{q_{CO}}\left(\frac{\partial r_{CO}}{\partial \theta}\right)_E,$$

Fig. 3. Equivalent circuit for modelling the Faradaic impedance of DMFC anodes.
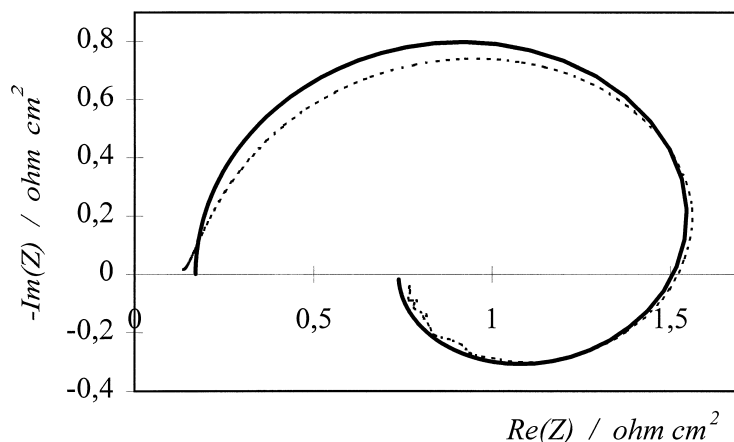
Fig. 4. Modelling of the Faradaic impedance of a DMFC anode. - - - measured spectrum, — simulated spectrum using equivalent circuit of Fig. 3 and fitting of parameters. $C_d = 0.135$ F cm^{-2}; $R_{00} = 1.705$ Ω cm^2; $R_0 = 0.863$ Ω cm^2; $L = 0.716$ H cm^{-2}.

the faradaic impedance can be expressed as:

$$Z_{\text{Faraday}} = \frac{j\omega + C}{A + B} = \left(\frac{1}{R_\infty} + \frac{1}{R_0 + j\omega L} \right)^{-1} \qquad (4)$$

where

$$R_\infty = \frac{1}{A}; \quad R_0 = \frac{C}{B}; \quad L = \frac{1}{B}.$$

This expression for the faradaic impedance leads to the equivalent circuit shown in Fig. 3, assuming additivity of the faradaic current and the charging current in the capacitor C_d (cf. Ref. [4]). When it is used to model the impedance behaviour of the DMFC anode, the resulting shape of the Nyquist plots agrees well with the experimentally observed plots, cf. Fig. 4. It should be noted that flattening of the measured spectrum is frequently observed on technical electrodes. The reason for this distortion is believed to be the roughness of the catalytic layer [8], or a current constriction effect [9]. These effects are not considered here; they are subject of further investigation.

The inductance L is characteristic of this equivalent circuit and thus deserves an explanation with respect to its mechanistic significance. Inductive behaviour means that the current signal follows a voltage perturbation with a phase delay ($\varphi = 90°$ for a pure inductor). In the DMFC anode, an increase in potential is obviously followed by an increase in current with a phase delay, $\varphi < 90°$. This inductive behaviour can now be rationalized by postulating slowness of $(CO)_{\text{ads}}$ coverage relaxation: The $(CO)_{\text{ads}}$ coverage decreases with increasing potential [10] but it takes some time after a potential perturbation before the new steady-state coverage is established and the corresponding current flows. It is this phase-delay which leads to the observed inductive behaviour of DMFC anode impedance. R_0 serves to modify the phase-delay according to the reaction scheme, and the R_∞ arm of the circuit is associated with the part of the current response which occurs without change in coverage [4]. Consequently, these results

provide further support for the mechanism of methanol electrooxidation according to Eq. (1).

The capacitor C_d also requires explanation. From the frequencies of the maxima in the impedance plots (cf. Fig. 1) and from the results of parameter-fitting during modelling of the impedance behaviour (Figs. 3 and 4), the magnitude of this capacitance is known to be in the order of 0.1–1 F/cm^2, depending on parameters such as current density. This is too high to be explained by double-layer capacitances of the DMFC anode and cathode, since double-layer capacitance values for similar electrodes have been reported to be in the 0.001–0.01 F/cm^2 range [11,12]. Instead, this capacitance is believed to be associated with the redistribution of charge at the anode: The modulation of current density during the impedance experiment implies a modulation of the current distribution profile on our large electrodes, as suggested in Ref. [13].

4. Conclusion

The impedance behaviour of a DMFC anode was studied with and without mass-transport limitations. The faradaic impedance was successfully modelled using a kinetic theory based on the most widely accepted reaction mechanism for methanol electrooxidation. A simple equivalent circuit was suggested whose elements are linked to kinetic parameters of the reaction and which explains the characteristic inductive behaviour of the DMFC anode working without diffusion control.

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