Change of electrochemical impedance spectra during CO poisoning of the Pt and Pt–Ru anodes in a membrane fuel cell (PEFC)

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Received 16 October 2002; received in revised form 18 February 2003; accepted 7 May 2003

Abstract

The influence of carbon monoxide poisoning on the platinum and platinum–ruthenium anode in a polymer electrolyte fuel cell was investigated using electrochemical impedance spectroscopy (EIS). EIS is a very useful method for the characterisation of fuel cells. Therefore, impedance measurements of the cell under constant load were performed at periodic time intervals. Due to the poisoning effect of the carbon monoxide, the system changes its state during the experiment. The reconstruction of quasi-causal spectra was made possible using enhanced numerical procedures, especially the time course interpolation and the Z-HIT refinement. The reconstructed impedance spectra show a strong time dependence and exhibit pseudo-inductive contributions at the low-frequency part of the spectra which increase during the experiment. The analysis of the spectra suggests that the pseudo-inductive behaviour can be attributed to a surface relaxation process of the anode. Furthermore, the influence of the carbon monoxide on the electrochemical behaviour of the contaminated fuel cell may be interpreted by means of a Faraday impedance in addition to a potential-dependent hindrance of the charge transfer.

Keywords: Electrochemical impedance spectroscopy; Polymer electrolyte membrane fuel cell; CO poisoning; Pt anode; Pt–Ru anode

1. Introduction

Much attention has been paid to fuel cells because they offer a highly efficient and environmentally benign technology for energy conversion. In particular, polymer electrolyte fuel cells (PEFCs) have been receiving more and more attention due to their high energy conversion efficiency and emission-free operation for powering electric vehicles [1]. The highest performance is achieved with hydrogen (H₂) which is the preferred fuel for low-temperature fuel cells. However, H₂ has several limitations. The storage systems for liquid or compressed H₂ are heavy and bulky. Furthermore, H₂ refuelling is costly and takes time. An additional obstacle is the lack of an infrastructure to distribute H₂ to the consumer [2].

An alternative to the use of H₂ as fuel is methanol which is a liquid fuel easy to handle. This can be directly transformed to electrical current in a direct methanol fuel cell (DMFC). DMFC allows a simple system design. However, presently achieved performance data of DMFC is not satisfying and material costs are too high. As another alternative methanol or hydrocarbons (e.g. natural gas, biogas) can be transformed to hydrogen on board of the electric vehicle by a reformation reaction. This allows us to use the H₂-PEFC cell which has a higher level of development. The reformate feed gas may contain up to 2.5 vol.% carbon monoxide (CO), which can be reduced to about 50 ppm CO using a selective oxidiser [3].

Although Pt has proven to be the most effective catalyst for hydrogen oxidation in polymer membrane fuel cells, even small traces of carbon monoxide can cause significant decrease in fuel cell performance. It was reported that only 5 ppm CO in the hydrogen stream leads to a drop of the maximum power density to less than half the value obtained for neat hydrogen [4]. The decrease of the cell performance is caused by the...
adsorption of carbon monoxide on the platinum electrocatalyst. The CO blocks or at least limits the number of the active catalyst sites and inhibits the hydrogen oxidation reaction (HOR) [5–8].

The preparation of an efficient electrocatalyst with high activity for HOR and good tolerance to CO is related to the understanding of reactive mechanisms on its surface. At present new methods for preparing high surface electrocatalyst [9,10] and new bimetallic [11–15] or multimetallic catalysts are investigated.

This paper focuses on the electrochemical characterisation, e.g. time–voltage measurement at constant load and time-resolved electrochemical impedance spectroscopy (TREIS) of PEFCs with two different anodes during operation of the fuel cell with oxygen and H2 + 100 ppm CO, respectively.

TREIS during galvanostatic operation is applied to analyse the time dependency of fuel cell impedance, in particular the time dependency of anode impedance and impedance elements related to the reactions on the anode (hydrogen and CO oxidation) during CO poisoning of the anode. In our experiments, the anode of PEFC was operated “dead end” with a mixture of hydrogen and 100 ppm CO.

2. Experimental

The electrochemical measurements were carried out in a 23 cm² single cell (Fig. 1) with stainless steel sinter plates having a porosity of 50% as the gas distribution structure [16,17]. In the present work, we used two different membrane electrode assemblies (MEAs): one MEA consists of same two electrodes with 20 wt.% Pt–C (0.4 mg Pt cm⁻²) and the other MEA consists of an anode with 20 wt.% Pt–Ru–C (0.4 mg Pt–Ru cm⁻²) and a cathode with 20 wt.% Pt–C. All electrodes were purchased from E-TEK, hot pressed (1.6 MPa, 10 min, increasing temperature up to 160 °C) onto a proton exchange membrane (Nafion 117, purchased from DuPont).

The cells were run at 80 °C. Pure hydrogen or hydrogen with addition of 100 ppm carbon monoxide were used as the anodic fuel and oxygen as the cathodic gas, both gases at 2 bar absolute pressure. The hydrogen–carbon monoxide mixture flowed “dead end” (the anodic gas outlet was closed), whereas the amount of oxygen was adjusted to the applied current densities, exceeding up to eight times the stoichiometric requirement for the applied current. The influence of the carbon monoxide poisoning was investigated by means of EIS. The electrochemical impedance measurements were carried out using a Zahner IM6 workstation in addition to an external current sink EL100 under a constant load of 5 A (≅ 217 mA cm⁻²) within a frequency range between 10 kHz and 0.050 Hz. All impedance spectra reported herein were measured between the fuel cell cathode and anode. In the galvanostatic mode of fuel cell operation, at constant current density, the impedance of the cathode and the membrane resistance can be assumed to be constant during the course of impedance measurements and the changes in the impedance spectra during poisoning the anode with CO can be attributed exclusively to the impedance of the anode. On the basis of this fact the non-negligible contribution of the cathode impedance

![Fig. 1. Experimental setup of the fuel cell; anodic gas outlet closed.](image)
can be separated from the measured cell impedance. A series of impedance measurements at periodic time intervals was recorded during the experiment applying a small sine wave distortion (AC perturbation) of 200 mA amplitude. A twisted pair arrangement of the current as well as of the sensing lines was used to depress the mutual induction effect (inductance of the wiring) which is often observed in the high-frequency region of impedance measurements at low-ohmic systems [18,19], for instance for the used system at $f > 8$ kHz.

3. Results

3.1. PEFC with Pt–C anode and Pt–C cathode

During galvanostatic mode of operation with $\text{H}_2 + 100$ ppm CO, due to the poisoning of the anode the overvoltage ($E_{\text{i,n}} - E_\text{i}$) of the anode increases with time and therefore the cell voltage decreases (Fig. 2). Representative time-dependent impedance spectra of the series, i.e. time-resolved impedance spectra, are depicted in Fig. 3 as Nyquist plots whereby the experimental data are represented by dots and the solid lines in the figures represents the modelled curves after fitting the experimental data with the equivalent circuit from Fig. 6. The fitting procedure is a complex non-linear least-squares fitting one and is integrated in the evaluation and simulation program of the electrochemical workstation IM6. The fit results in a list of optimised parameters, significance and error of each fitted parameter. In all presented impedance diagrams, the experimental data (dots) and theoretical (simulated) curves (solid lines) are compared graphically and the goodness of the fit (difference between dots and lines) is evident. The quality of the fit is obtained from the errors of the modulus of the impedance and the phase angle (Bode diagram). In addition to the mean error the maximum deviation is given. In general, the deviations are less than 2.5% for the modulus of the impedance and maximum 1.5° for the phase angle.

At the beginning of the experiment ($t = 0$), one recognises a full, depressed (capacitance) semicircle in addition to an onset of a second semicircle at low frequencies, uncovered, for example, in Fig. 3, curve 2. With increasing time, the real as well as the imaginary parts of the impedance increase and the two semicircles are no longer resolvable visually. In addition, the fuel cell impedance exhibits an enlarged pseudo-inductive behaviour at the low-frequency side ($f < 3$ Hz) with increasing time. At the end of the experiment, the impedance spectrum resembles more a full circle than a semicircle which is observed at the beginning of the experiment.

The evolution of the impedance spectra indicates that the carbon monoxide poisoning causes a change of the state of the system under investigation. One has to assume that the system changes its state not only between two measurements but also during the recording of a single spectrum. The latter fact causes problems for the evaluation of the spectrum, because the recording of an impedance spectrum one frequency after each other requires a finite time, while the measurement at high frequencies requires less time than the measurement at low frequencies. Due to the fact that the recording of a single spectrum in the frequency range mentioned above requires about 20 min, the influence of the changing state to the measured spectrum is not negligible. For this reason, one of the fundamental prerequisites for the evaluation of impedance measurements is violated. Nevertheless, it is possible to reconstruct “quasi-steady-state” (and therefore “quasi-causal”) spectra from drift-affected impedance data.
using enhanced mathematical procedures, provided that the time of acquisition is available for each frequency sample.

As recently shown [20], a combination of three mathematical procedures can be applied successfully to the interpretation of time-dependent impedance measurements of fuel cells which exhibit non-steady-state behaviour (time drift). These techniques are denoted as the real-time drift compensation, the time course interpolation, which was first introduced by Savova-Stoynov and Stoynov [21] and Stoynov and coworker [22–24], and finally the Z-HIT refinement [25,26].

The first technique, the real-time drift compensation, is performed online during recording the impedance spectra and is essential if during measuring at a given frequency, in particular at low frequencies given by the use of several sine waves used for averaging in time domain, the system shows a drift. A detailed theoretical explanation with illustration of the real-time drift compensation and the effect of the other two used techniques is given by Schiller et al. [20].

### 3.2. PEFC with Pt–Ru–C anode and Pt–C cathode

A promising CO-tolerant electrocatalyst for the HOR in PEFC [27–30] and for the oxidation of methanol [31–38] is Pt–Ru. It is generally accepted that the action of ruthenium as co-catalyst for the oxidation of adsorbed CO is the generation of oxygen-containing species (e.g. OH) on the surface at lower potentials than Pt itself [39–52].

Similar to the measurements performed on the fuel cell with Pt–C anode series of impedance spectra (Fig. 4) were measured on the fuel cell with Pt–Ru anode and Pt–C cathode during CO poisoning. The experiment started with pure hydrogen ($i_0$). In both experiments we used the same experimental conditions (temperature, gas flow, etc.) and the same ion-exchange membrane and cathode so that the observed differences can be attributed exclusively to the different anodes under investigation. Like expected, during load at 217 mA cm$^{-2}$ a decrease of the cell voltage (Fig. 5) due to poisoning of the anode was observed. The decrease of cell voltage is lower compared to the decrease of cell voltage with Pt–C anode.

### 4. Discussion

As reported in a recent paper [17], the separation of the anodic and the cathodic contributions is the main problem for the analysis of the impedance spectra of the fuel cell. Both half cells consist of a porous system separated by the membrane. In principle, the half-cell impedances should be modelled using the same elements, like a porous electrode (PE) and a (finite) diffusion impedance. The results presented here are based on a more general concept for the improvement of fuel cells by means of EIS. This concept involves that the experimental conditions for a distinct investigation are modified, so that a simplification of the equivalent circuit for the interpretation of the obtained impedance spectra is made possible. First of all, in galvanostatic mode of operation the current density keeps constant at the electrodes. At the same time, the galvanostatic mode forces a constant conversion rate with respect to the uncharged (reaction gases) and charged species (ions) which are involved in the electrode reactions.

Due to these experimental conditions it is assumed that the changes in the impedance spectra are dominated by the changes of the anodic half-cell reaction. Therefore, the effect of the progressive poisoning with carbon monoxide of the fuel cell can be described quantitatively according to the simplified model given in Fig. 6. In series to both half cells, the resistance of the membrane itself—denoted as the electrolyte resistance ($R_{el}$)—as
well as a parasitic wiring inductance due to the mutual induction effect have to be taken into account. The impedance of the cathodic half cell (oxygen reduction) is approximated using a charge transfer resistance ($R_{ct}$) in parallel to a constant phase element (CPE). This simple equivalent circuit describes the partial impedance of the cathodic half cell with sufficient accuracy. For this reason, an accurate description of the physicochemical model of the cathode—besides its impedance—is neither intended nor necessary in these investigations.

In contrast, the impedance of the anode (hydrogen oxidation) is more complicated due to processes within the pores of the anodic material which are influenced by the carbon monoxide poisoning. The anodic impedance is modelled using a PE in series to a double-layer capacity ($C_d$) which is in parallel to a surface relaxation impedance. As will be shown below, the latter impedance contribution explains the development of the pseudo-inductive behaviour in the impedance spectra of the fuel cell. The surface relaxation impedance represents a Faraday impedance ($Z_F$) at non-equilibrium potential with a potential-dependent transfer reaction rate $k = k(\varepsilon)$ and its time-dependent relaxation according to Eq. (1) [53,54].

$$Z_F = \frac{R_{ct} + Z_C}{1 + (R_{ct}/Z_K)} = \frac{1 + j\omega\tau_k}{I_F(d \ln k/d\varepsilon)}$$

with $R_K = \frac{1}{I_F(d \ln k/d\varepsilon)}$ and $X_K = j\omega\tau_k R_K$

$$Z_K = \frac{1 + j\omega\tau_k}{I_F(d \ln k/d\varepsilon)}$$

In Eq. (1), $R_{ct}$ denotes the charge transfer resistance of the anode ($R_{ct}$ in Fig. 6), $Z_K$ is defined as the relaxation impedance and is schematically shown as the box surrounding the series combination of $R_a$ and $Z_C$ in Fig. 6, according to Eq. (2), where $I_F$ denotes the Faraday current, $\tau_k$ the time constant of relaxation and the expression $d \ln k/d\varepsilon$ is the first derivative of the logarithm of the reciprocal relaxation time constant ($k = 1/\tau_k$) against the potential $\varepsilon$. According to its frequency dependence, $Z_K$ can be split into the relaxation resistance $R_K$ and the relaxation inductivity $X_K$, with the pseudo-inductance $L_K = \tau_k R_K$ and which is proportional to the relaxation time constant $\tau_K$. In the low-frequency region ($f < 3$ Hz) of the impedance spectra the shape of the impedance spectra is determined mainly by the pseudo-inductance $L_K$. For the finite diffusion impedance $Z_C$ in Fig. 6, the well-known Nernst impedance ($Z_N$) was chosen for the evaluation of the impedance spectra. To avoid confusion with the two inductances—the parasitic wiring inductance visible in the high-frequency range of the spectra and the “kinetic” pseudo-inductance $L_K$—visible in the low-frequency range of the impedance spectra—the later one was not represented explicit in Fig. 6. The relaxation impedance is schematically shown in Fig. 6 as a box closing about the other impedance elements ($R_{ct}$ and $Z_C$) of the Faraday impedance. An equal representation of the relaxation impedance $Z_K$ is a series combination of the relaxation resistance $R_K$ and the pseudo-inductance $L_K$ (Eq. (2)).

On the basis of this model, the changes and differences, depending on the used anode in the fuel cell (Pt–C or Pt–Ru–C), the impedance spectra during the experiment are dominated by the changes of the charge transfer resistance of the anode, the surface relaxation impedance ($R_K$, $\tau_k$) and the finite diffusion impedance $Z_N$, or more general $Z_C$ like those used in Fig. 6.

By comparing the time dependencies of the cell voltages (Fig. 7) at constant load at 217 mA cm$^{-2}$ at $t = 0$ (uncontaminated anode) one can observe that the cell voltage of the fuel cell with the Pt–C anode is 740 mV and thus higher than the cell voltage of the fuel cell with the Pt–Ru–C anode (709 mV). These differences were also found in the value of the charge transfer resistances (Fig. 8). From these results we can conclude that the Pt–C anode is more active for HOR than the Pt–Ru–C anode. During constant load at 217 mA cm$^{-2}$ the cell voltages decrease with time due to the poisoning of the anodes with CO from the fuel gas.
(H₂ + 100 ppm CO). The cell voltage decrease is more pronounced in the case of the fuel cell with the Pt–C anode. For example, after 12 000 s constant load, the cell voltage of the cell with the Pt–C anode was 242 mV and that of the cell with the Pt–Ru–C anode was 363 mV. This different behaviour of the two electrodes can be explained by the formation of oxygen-containing species (e.g. OH) on the Pt–Ru–C anode surface at lower potentials (higher cell voltage) than in the case of the Pt–C anode. At the initial state of the experiment, the carbon monoxide begins to block active sites of the catalyst, which causes a decrease of the cell voltage. As a consequence, \( R_K \) increases due to the term \( d \ln k / d e \) in the denominator of Eq. (2). Simultaneously, the potential \( e \) of the anodic electrode shifts towards that of the cathodic potential and therefore to more positive values, until the potential reaches a size, where the oxidation of carbon monoxide at Pt and Pt–Ru, respectively, is possible [55]. Now, the oxidation of carbon monoxide to carbon dioxide, followed by the desorption of CO₂, leads to a “reactivation” of the blocked catalyst and therefore is responsible for the decrease of \( R_K \). From a chemical point of view, this reaction sequence, the adsorption of carbon monoxide, oxidation at the Pt and Pt–Ru catalyst which requires the diffusion of water molecules to the adsorbed carbon monoxide and a final desorption of the generated carbon dioxide, is in competition to the “normal” oxidation of hydrogen which also requires the presence of water for the desorption of the generated H⁺ ions. From a more mechanistical point of view, this sequence causes a periodical change of the coverage of the electrode surface, which has to relax to enable a further reaction at this site. However, the CO coverage changes with time and can lead to oscillations of the cell voltage during galvanostatic operation; for instance, the voltage oscillation of the fuel cell with Pt–Ru–C anode, operated at 80 °C, with a mixture of H₂ and 100 ppm CO in galvanostatic mode at 217 mA cm⁻² is shown in Fig. 9. The oscillation started at a cell voltage of 580 mV with an amplitude of 240 mV (between 580 and 340 mV) and with a frequency of 0.33 Hz. Such oscillations are also observed in the case of oxidation of methanol or oxidation of formic acid where CO is formed as intermediate and oxidised finally to CO₂ [56–67].

The evolution of the charge transfer resistances of the anodes are depicted in Fig. 8 (Pt–C anode (●) and Pt–Ru–C anode (■)) as a function of the elapsed time. One recognises that the charge transfer resistances of both anodes are primarily low and increases from an initial value of about 10 mΩ to a value of 325 mΩ for the Pt–C anode and 103 mΩ for the Pt–Ru–C anode after 12 000 s of operation. The concentration impedance (Z_C) and the Nernst impedance (Z_N) show the greatest difference between the two anodes. The Nernst impedance Z_N [68] contains two parameters: the Warburg parameter \( W \) (“diffusion resistance” at low frequencies) and a diffusion time constant \( (k_N) \), determined by the constant of diffusion \( (D_k) \) and diffusion layer thickness \( (d_N) \). The Nernst impedance is calculated by Eq. (3):

\[
Z_N = \frac{W}{\sqrt{j \omega}} \tanh \left( \frac{j \omega}{k_N} \right)
\]

with:

\[
k_N = \frac{D_k}{d_N}
\]

At the beginning, the Warburg parameter (diffusion resistance) from the Nernst impedance of the Pt–C anode (curve (●) in Fig. 10) is 5 and 6200 mΩ s⁻¹/² at the end of the experiment (12 000 s). In the case of the Pt–Ru–C anode (curve (■) in Fig. 10), the value of the Warburg parameter increases from 3 mΩ s⁻¹/² at the beginning to 124 mΩ s⁻¹/² at 12 000 s. From these results we can conclude that the charge transfer resistance of the HOR and the finite diffusion impedance are the most sensitive elements of the proposed model for the HOR with a mixture of H₂ and 100 ppm CO. Considering these two aspects one can suppose that the catalytic effect of the Pt–Ru–C anode is not only to
facilitate the formation of oxygen-containing species on the electrode surface at lower potentials, but also to enhance the diffusion process prior to the CO oxidation reaction. It is known that CO surface diffusion occurs on the catalyst’s surface \([69\text{–}71]\) so that the lower diffusion impedance in the case of the Pt–Ru–C anode can be explained by the higher concentration of OH species on the surface and thus lowering the effective diffusion length.

The interpretation of EIS is complicated by the porous structure of the “technical” electrodes. The theoretical approach is a simplified view of the mechanism of competitive oxidation of hydrogen and CO on Pt–C and Pt–Ru–C electrodes. However, more complicated reaction mechanisms for the kinetic of the electrochemical oxidation of CO and for the reaction mechanism including competition between hydrogen and CO oxidation on well-defined electrode surfaces (single-crystal electrodes) in liquid electrolytes were reported in literature \([72]\).

Similar EIS, with inductive behaviour in the low-frequency range of the spectra, are also reported for the methanol oxidation in the case of DMFC (e.g. in Ref. \([73]\)). The inductive behaviour and the Faraday impedance are explained using the kinetic theory derived by Harrington and Conway \([74]\) for reactions involving intermediate adsorbates, during the hydrogen evolution reaction on Ni electrodes, similar to Eq. (1).

5. Conclusion

The progressive poisoning with carbon monoxide of fuel cells with Pt–C and Pt–Ru–C anodes was monitored using TREIS. Therefore, measurements at distinct time intervals during the experiment were performed. The poisoning causes a change of the state of the fuel cell which is reflected in the recorded impedance spectra. Besides an increase of the total impedance of the fuel cell, the occurrence and the increase of a pseudo-inductive behaviour at frequencies lower than 3 Hz is observed. For the evaluation of the series measurements, recorded on fuel cells with time-changing states, enhanced mathematical procedures, like the real-time drift compensation, the time course interpolation and an additional Z-HIT refinement were applied to reduce the influence of the changing state of the fuel cell in the obtained spectra. Due to the experimental conditions, the evaluation of the spectra can be considerably simplified. The evaluation of the time course and implicit dynamic response of the fuel cell impedances shows that the degradation of the fuel cell performance during the poisoning with CO is dominated by an increase of anodic charge transfer.

Fig. 9. Fuel cell voltage oscillation during galvanostatic mode of operation, with Pt–Ru–C anode, at 217 mA cm\(^{-2}\), 80 °C and H\(_2\)+100 ppm CO.

Fig. 10. Evolution of the Warburg parameter \(W\) (diffusion resistances) from the finite diffusion impedance \(Z_e\): (●) Pt–C anode and (□) Pt-Ru–C anode as a function of time.
resistances and an increase of the finite diffusion impedance. In the case of the Pt–Ru–C anode, the increase of the anodic resistance and diffusion impedance during CO poisoning is much lower than in the case of the fuel cell with Pt–C anode. The increasing pseudo-inductive behaviour can be explained for both anodes by means of a surface relaxation process due to the competitive oxidation of hydrogen and carbon monoxide at the anode.

Acknowledgements

The financial support of the German Bundesministerium für Bildung und Forschung in the project “Entwicklung von Katalysatorsystemen für Anoden der DMFC” is gratefully acknowledged.

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