

Relaxation impedance as a model for the deactivation mechanism of fuel cells due to carbon monoxide poisoning

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The influence of carbon monoxide poisoning on the platinum anode in a polymer electrolyte fuel cell was investigated using electrochemical impedance spectroscopy (EIS). 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. 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 carbon monoxide on the electrochemical behaviour of the contaminated fuel cell may be interpreted by means of a Faraday impedance in addition to potential-dependent hindrance of the charge transfer.

1. Introduction

Due to the high energy conversion rate and the harmless emission products, polymer electrolyte fuel cells (PEFC) receive more and more attention especially for the powering of electric vehicles. The application of pure hydrogen, which possesses the highest performance as fuel in low-temperature fuel cells, is restricted for several reasons: the storage systems for compressed or liquid hydrogen are heavy and bulky and hydrogen refuelling is expensive and time consuming. An infrastructure to distribute hydrogen to the consumer hardly exists.¹ To overcome these problems, the *in situ* generation of hydrogen on board the electric vehicles by reforming either hydrocarbons or alcohols (*e.g.* methanol) seems to be a suitable procedure. The formation of the unwanted by-product carbon monoxide, which is a catalyst poisoning material for the reforming process of methanol, can be reduced to about 50 ppm using a selective oxidiser.² The performance of platinum, which is known to be one of the most effective catalysts for hydrogen oxidation in polymer membrane fuel cells, is influenced even by traces of carbon monoxide: compared with the use of pure hydrogen, the maximum power density is more than halved in the presence of only 5 ppm carbon monoxide.³ One possible explanation for the decrease in the fuel cell performance is that the carbon monoxide blocks or limits the active sites of the platinum catalyst by adsorption, which leads to inhibition of the hydrogen oxidation reaction.⁴

For the development of improved catalysts which are more insensitive with respect to the presence of carbon monoxide, a mechanistical understanding of the poisoning process of the anode is desirable. Therefore, electrochemical impedance spectroscopy (EIS) in the galvanostatic mode of operation has been applied to analyse the time dependence of the anode potential decay during poisoning.

2. Experimental

The measurements were carried out in a 23 cm² polymer elec-

trolyte fuel cell with stainless steel sinter plates which exhibit a porosity of 50%. The temperature of the cell was kept at 80 °C. The membrane electrode assembly consists of two electrodes with 20 wt.% platinum on charcoal pressed onto a Nafion 117 membrane. Pure hydrogen with 100 ppm carbon monoxide was used as the anodic fuel and oxygen as the cathodic fuel, both gases being at 2 bar absolute pressure. The hydrogen/carbon monoxide mixture flows 'dead end' (the anodic gas outlet was closed) whereas the amount of oxygen exceeds by a factor of eight the stoichiometric requirement for the applied current (see below) to ensure steady state conditions at the cathode side of the cell.

The influence of the carbon monoxide poisoning was investigated by means of EIS. The electrochemical impedance measurements were performed using a Zahner IM6 workstation with a current sink EL100 under a constant load of 5 A ($\cong 217 \text{ mA cm}^{-2}$) within a frequency range of 10 KHz and 50 mHz. A series of measurements at periodic time intervals was recorded during the experiment applying a small sine-wave distortion of 200 mA. The experimental set-up is depicted in Fig. 1. As indicated in the figure, a twisted pair arrangement of the current, as well as of the sensing lines, was used to depress the mutual induction effect which is often observed in the high frequency region of impedance measurements in low-ohmic systems.⁵

3. Results

Representative impedance measurements of the series are depicted in Fig. 2 as Nyquist plots. At the beginning of the experiment (left-hand side of the diagram), one can see a full, depressed (capacitive) semicircle in addition to an onset of a second semicircle at low frequencies. With increasing time (turning to the right-hand side of the diagram), the real, as well as the imaginary, part of the impedance increases and the two semicircles are no longer resolvable visually. In addition, the fuel cell impedance exhibits an enlarged pseudo-inductive

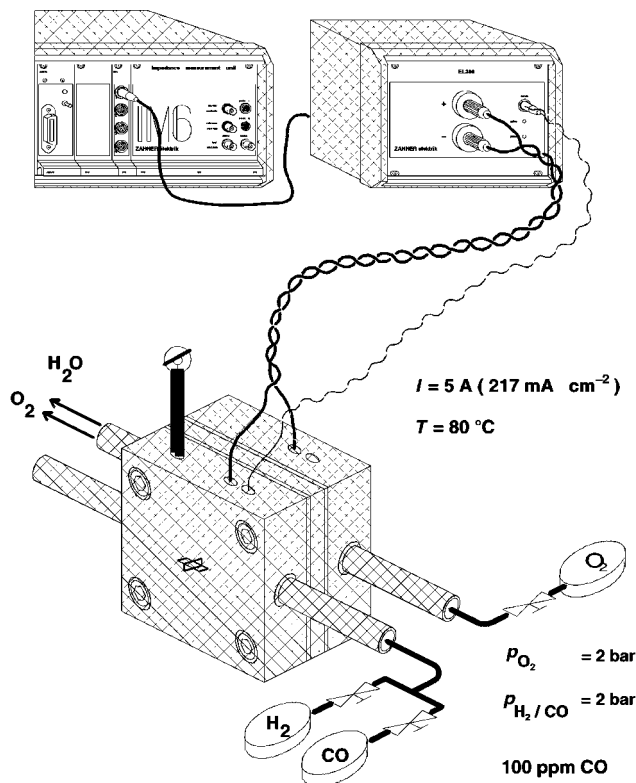


Fig. 1 Experimental set-up. Master-slave configuration of the electrochemical workstation IM6 and the current sink EL 100; twisted pair connection between the EL 100 and the fuel cell; anodic gas outlet closed.

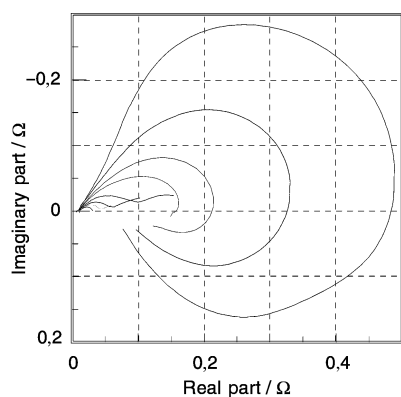


Fig. 2 Nyquist plots of the fuel cell impedance at different times; the influence of the carbon monoxide poisoning leads to an increase in the real and imaginary part of the impedance during the experiment; at short times (left part of the diagram) the anodic and cathodic impedances are separable (two half cycles in the Nyquist plots); with increasing time, the anodic cell impedance increases and becomes more and more dominant, 'hides' the cathodic cell impedance and exhibits an enlarged pseudo-inductive behaviour.

behaviour at the low frequency side with increasing time. At the end of the experiment, the impedance spectrum resembles more a full circle rather than the semicircle which is observed at the beginning of the experiment.

As expected, the evolution of the impedance spectra indicates that carbon monoxide poisoning causes a change in 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 on 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,⁶ a combination of three mathematical procedures can be applied successfully to the interpretation of impedance measurements of fuel cells which exhibit non-steady-state behaviour. These techniques are denoted as the real-time drift compensation, the time-course interpolation, which was first introduced by Savova-Stoynov and Stoynov⁷⁻⁹ and finally the Z-HIT refinement. The latter mathematical procedure, denoted as the 'two-pole logarithmic Hilbert transform' (Z-HIT), is an integral transform like the Kramers-Kronig transform (KK). As in KK, Z-HIT enables the detection (and the compensation) of deviations from causality, which are caused by the drift of the investigated system. In contrast to KK, Z-HIT possesses the advantage that the integration boundaries are finite and therefore, the transformation can be performed within the measured frequency range without the need to extrapolate the experimental data. Comparison of the impedance data obtained from the present fuel cell experiment also demonstrates the improvement which results from the application of these enhanced evaluation techniques. In Fig. 3, the measured (triangles) as well as the calculated (solid line) impedance spectrum of the fuel cell at the end of the overall experiment is depicted in a Nyquist plot. The deviation between the two data sets in the middle frequency region is obvious. This deviation is significantly lowered if the enhanced evaluation techniques are applied (Fig. 4). Therefore, evaluation of the impedance spectra of the fuel cell obtained during carbon monoxide poisoning was performed using these improved numerical techniques.

4. Discussion

As reported in a recent paper,⁶ 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. Therefore, in principle, the half cell impedances should be modelled using the same elements, *i.e.* a porous electrode 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 the modification of the experimental conditions for a distinct investigation, so that a simplification of the equivalent circuit for the interpretation of the impedance spectra obtained is made possible.

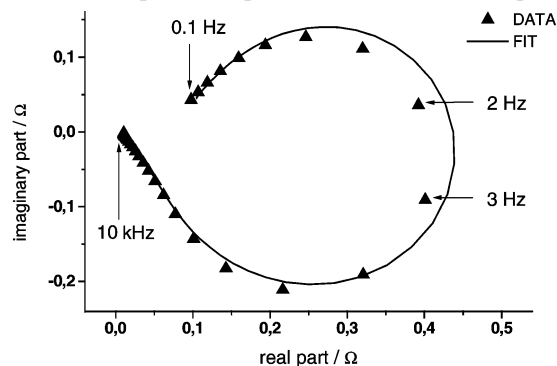


Fig. 3 Measured (triangles) and fitted (solid line, model of Fig. 5) data after 8 h; the markers indicate representative frequencies.

[†] Recording 10 points per decade and 10 sine-waves per point.

[‡] The 'steady state' of the system during the measurement.

[§] This is not a restriction for modern electrochemical workstations.

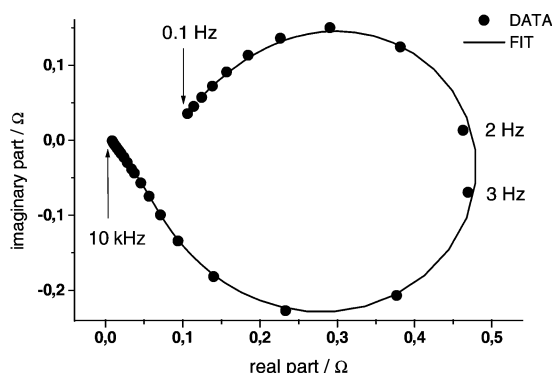


Fig. 4 Drift corrected (circles) and calculated (solid line) data of the measurement depicted in Fig. 3; the markers indicate representative frequencies.

First, in the galvanostatic mode of operation the current density keeps constant at the electrodes. In contrast to the potentiostatic mode of operation, the evaluation of the charge transfer resistances is facilitated, because the values are inversely proportional to the exchange current density. At the same time, the galvanostatic mode forces a constant conversion rate with respect to the (charged) species which are involved in the electrode reactions.

With these experimental conditions it is assumed that the changes in the impedance spectra are dominated by the changes in the anodic half cell reaction. Therefore, the effect of progressive poisoning of the fuel cell with carbon monoxide can be described quantitatively according to the simplified model given in Fig. 5. In series to both half cells, the resistance of the membrane itself—denoted as the electrolyte resistance (R_{el})—as well as a parasitic inductance due to the mutual induction effect has 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 with a constant phase element (CPE). This simple equivalent circuit describes the partial impedance of the cathodic half cell with

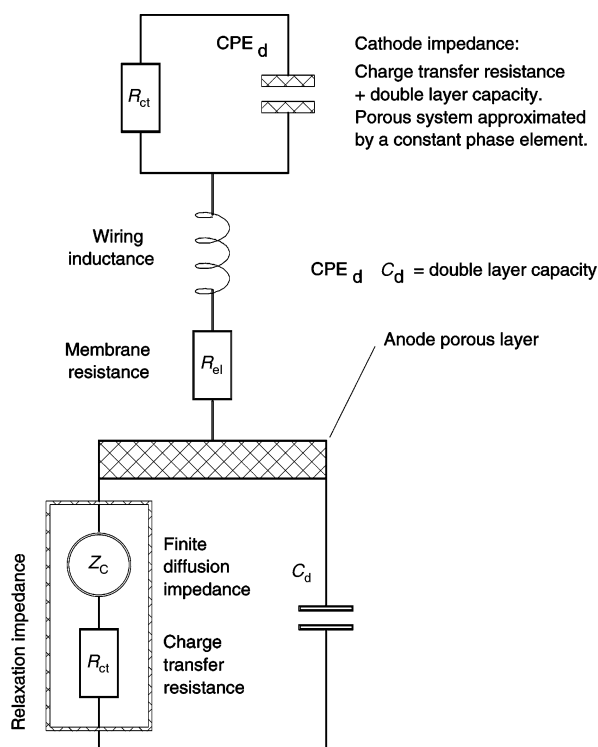


Fig. 5 Equivalent circuit for the evaluation of the impedance spectra of the fuel cell.

sufficient accuracy. For this reason, an accurate description of the physico-chemical model of the cathode, except for its impedance, is neither intended nor necessary.

In contrast, the impedance of the anodic part (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 porous electrode (PE) in series with 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 at non-equilibrium potential with a potential-dependent transfer reaction rate and its time dependent relaxation according to eqn. (1).¹⁰

$$Z_F = \frac{R_{ct} + Z_C}{1 + (R_{ct}/Z_K)} \quad (1)$$

$$Z_K = \frac{1 + j\omega\tau_K}{I_F d \ln k/d\varepsilon} \quad (2)$$

with

$$R_K = \frac{1}{I_F d \ln k/d\varepsilon} \quad \text{and} \quad X_K = j\omega\tau_K R_K = j\omega L_K$$

In eqn. (1), R_{ct} denotes the charge transfer resistance of the anode (R_{ctH_2} in Fig. 6), Z_K is defined as the relaxation impedance according to eqn. (2), where I_F denotes the Faraday current, τ_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 ($k = 1/\tau_K$) vs. the potential ε . 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 $L_K = \tau_K R_K$ which is proportional to the relaxation time constant τ_K . At least, for the finite diffusion impedance Z_C in Fig. 5, the well-known Nernst impedance was chosen for the evaluation of the impedance spectra.

On the basis of this model, the changes in the impedance spectra during the experiment are dominated by the changes in the charge transfer resistance (mainly R_{ctH_2}) and the surface relaxation impedance (R_K, τ_K). The evolution of the charge transfer resistances (R_{ctH_2} and R_{ctO_2}) are depicted in Fig. 6 as a function of the elapsed time (1 ks = 1000 s). One recognises that the cathodic charge transfer resistance (R_{ctO_2} , solid line) increases from an initial value of 20 mΩ to a value of 120 mΩ at 5 ks and converges towards a constant value of about 88 mΩ at the end of the experiment. Therefore, the overall change is only about a factor of 4. In a first approximation, one would expect that the cathodic charge transfer resistance

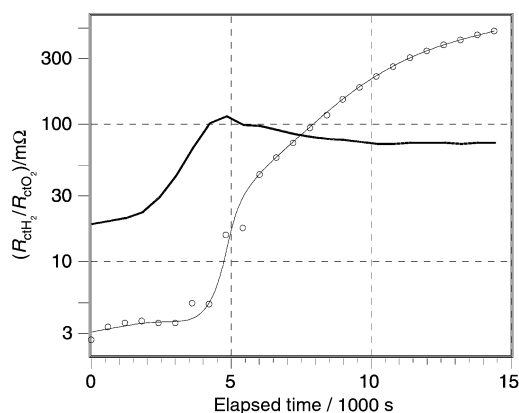


Fig. 6 Evolution of the cathodic charge transfer resistance R_{ctO_2} (solid line), the anodic charge transfer resistance R_{ctH_2} (circles) for $I = \text{const.} = 217 \text{ mA cm}^{-2}$ as a function of time.

should remain constant during the experiment. However, one has to take into account that the effective charge transfer reaction is influenced by the concentrations of the charged as well as of the uncharged species (water). Moreover, the volume of the fuel cell is very small and therefore, the system is far away from 'thermodynamically ideal' behaviour.¶ Considering these two aspects one can suppose that the poisoning of the anode side causes a local, inhomogeneous distribution of the generated protons and hence an inhomogeneous distribution of the protonated and associated water molecules at the anode side including the membrane. It is safe to assume that this inhomogeneous distribution also causes a local, inhomogeneous distribution of these species at the cathode side. From this point of view, it seems not surprising that the changes at the anode side also influence a change in the charge transfer resistance at the cathode side. Comparing the change in the cathodic charge transfer resistance (dR_{ctO_2}/dt) with that of the anodic charge transfer resistance (dR_{ctH_2}/dt), one can denote the change of the former as small. The value of the charge transfer resistance of the anodic half cell reaction (Fig. 6; R_{ctH_2} , circles) increases by more than 2 orders of magnitude from 3 m Ω initially to 500 m Ω finally. The much smaller change in the cathodic charge transfer resistance suggests that the (absolute) value of the cathodic potential can be considered to be nearly constant during the whole experiment.

The effect of subsequent carbon monoxide poisoning during the experiment can be best represented by plotting the resistance of relaxation R_K (Fig. 7) and the relaxation time constant (Fig. 8) as a function of time. Proceeding on the assumption that the potential of the cathodic half cell remains constant, the evolution of R_K can be explained as follows: initially, the carbon monoxide begins to block active sites of the catalyst

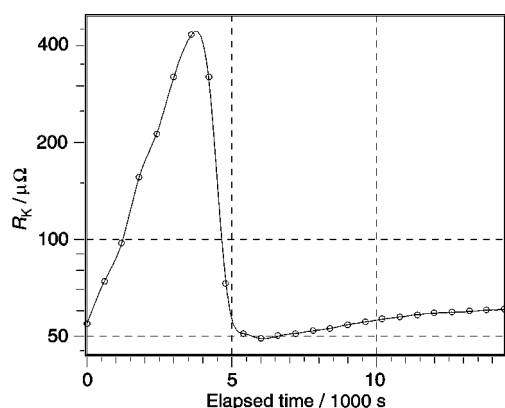


Fig. 7 Evolution of the (cathodic) relaxation resistance R_K during progressive carbon monoxide poisoning.

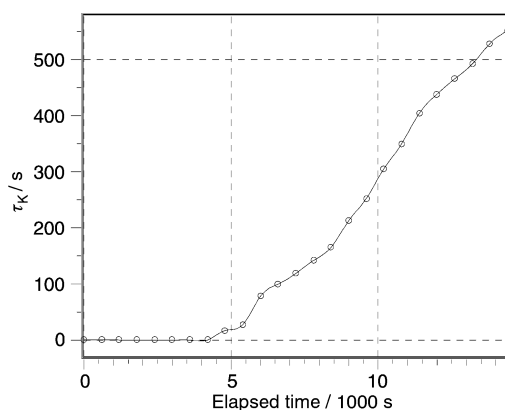


Fig. 8 Evolution of the (cathodic) relaxation time constant τ_K during progressive carbon monoxide poisoning.

¶ In the sense that, for instance, concentrations must be replaced by activities.

which causes a decrease in the cell voltage. As a consequence, R_K increases due to the term $\ln k/\varepsilon$ in the denominator of eqn. (2). Simultaneously, the potential ε 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 Pt¹¹ is possible (about 1 h). Now, the oxidation of carbon monoxide to carbon dioxide, followed by desorption, leads to 'reactivation' of the blocked catalyst and therefore, is responsible for the decrease in R_K . From a chemical point of view, this reaction-sequence, the adsorption of carbon monoxide, oxidation at the Pt catalyst which requires the diffusion of water molecules to the adsorbed carbon monoxide and finally desorption of the generated carbon dioxide, is in competition with the 'normal' oxidation of hydrogen which also requires the presence of water for the desorption of the generated H⁺ ions. From a more mechanistic point of view, this sequence causes a periodical change in the coverage of the electrode surface, which has to relax to enable further reaction at this site.

In total, the resulting increase in the relaxation time constant τ_K (Fig. 8) at times > 5 ks is responsible for the increasing pseudo-inductive contributions which are observed in the impedance spectra of Fig. 2.

5. Conclusion

The progressive poisoning with carbon monoxide of a fuel cell was monitored using EIS with measurements being made at distinct time intervals during the experiment. The poisoning causes a change in the state of the fuel cell which is reflected in the recorded impedance spectra. Besides an increase in the total impedance of the fuel cell, the occurrence and increase of a pseudo-inductive behaviour is observed. For evaluation of the series of measurements, enhanced mathematical procedures, such as real-time drift compensation, time-course interpolation and an additional Z-HIT refinement were applied to reduce the influence of the changing state of the fuel cell on the obtained spectra. Due to the experimental conditions, the evaluation of the spectra can be considerably simplified. The time course of the charge transfer resistances shows that degradation of the fuel cell performance during the poisoning is dominated by an increase in the anodic resistance by more than two orders of magnitude whereas the cathodic resistance increases only by about a factor of four. The increasing pseudo-inductive behaviour can be explained by means of a surface relaxation process due to the competitive oxidation of hydrogen and carbon monoxide at the anode.

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