

RELAXATION IMPEDANCE AS A MODEL FOR THE DEACTIVATION MECHANISM OF FUEL CELLS DUE TO CARBON MONOXIDE POISONING

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polymer electrolyte fuel cells, carbon monoxide poisoning, electrochemical impedance spectroscopy, 'two-pole' logarithmic Hilbert transform (Z-HIT), porous electrode model

Abstract

The influence of carbon monoxide poisoning on the platinum anode in a polymer electrolyte fuel cell was investigated using electrochemical impedance spectroscopy (EIS). 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 with a 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 in the case for powering electric vehicles. The application of pure hydrogen which possesses the highest performance as fuel in low-temperature fuel cells is restricted due to several reasons. First of all, the storage systems for compressed or liquid hydrogen are heavy and bulky. Next, hydrogen refuelling is expensive and time consuming. At least, an infrastructure to distribute hydrogen to the consumer is hardly existing [1]. To overcome these problems, the in-situ generation of hydrogen directly on board of the electric vehicles either by reforming 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 as one of the most effective catalysts for the 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 of the fuel cell performance is that the carbon monoxide blocks or limits the active sites of the platinum catalyst due to adsorption which leads to an 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 galvanostatic mode of operation is applied to analyse the time dependency of the anode potential decay during poisoning.

2. Experimental

The measurements were carried out in a 23 cm² polymer electrolyte fuel cell with stainless steel sinter plates which exhibit a porosity of 50 percent. 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 in addition with 100 ppm carbon monoxide was used as the anodic fuel and oxygen as the cathodic fuel, both gases 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 eight times 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 in addition with a current sink EL100 under a constant load of 5 A ($\cong 217 \text{ mA}\cdot\text{cm}^{-2}$) within a frequency range between 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 at 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 recognises 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 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 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.

As expected, the evolution of the impedance spectra indicate 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 minutes ¹, 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 ². Nevertheless it is possible, to reconstruct 'quasi steady state' (and therefore 'quasi causal') spectra from drift

¹ Recording 10 points per decade and 10 sine-waves per point.

² The 'steady state' of the system during the measurement.

affected impedance data using enhanced mathematical procedures, provided that the time of acquisition is available for each frequency sample³.

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 Sovova-Stoynov [7] and Stoynov [8,9] and finally the Z-HIT refinement. Also, the comparison of the impedance data obtained from the present fuel cell experiment 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, the evaluation of the obtained impedance spectra of the fuel cell 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, like 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 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. 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.

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. 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 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 physico-chemical model of the cathode - besides 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 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 at non equilibrium potential with a potential

³ This is not a restriction for modern electrochemical workstations.

dependent transfer reaction rate and its time dependent relaxation according to equation 1 [10].

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

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

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

In equation 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 equation 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 ($k=1/\tau_K$) against the potential ε . According to its frequency dependence, Z_K can be splitted into the relaxation-resistance R_K and the relaxation inductivity X_K , with the pseudo-inductance $L_K = \tau_K \cdot R_K$ 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 of the impedance spectra during the experiment are dominated by the changes of 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 m Ω to value of 120 m Ω at 5000 Ks and converges towards a constant value of about 88 m Ω 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 should keep 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 a 'thermodynamically ideal' behaviour⁴. 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 a 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 causes also 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 influence also a change of the charge transfer resistance at the cathode side. Comparing the change of 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 to be small. The value of the charge transfer resistance of the anodic half cell reaction (fig. 6; R_{ctH_2} -circles) increases more than 2 orders of magnitude from initially 3 m Ω to finally 500 m Ω . The by far smaller change of the cathodic charge transfer resistance

⁴ In the sense that, for instance, concentrations must be replaced by activities.

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:

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 $d\ln k/d\varepsilon$ in the denominator of eq. 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 Pt [11] is possible (about 1 h = 3600 s). Now, the oxidation of carbon monoxide to carbon dioxide, followed by a desorption, 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 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.

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

5. Conclusion

The progressive poisoning with carbon monoxide of a fuel cell was monitored using EIS. 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 is observed. For the evaluation of the series measurements, 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 time course of the charge transfer resistances shows that the degradation of the fuel cell performance during the poisoning is dominated by an increase of the anodic resistance by more than two orders of magnitude whereas the cathodic one increases only 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.

7. References

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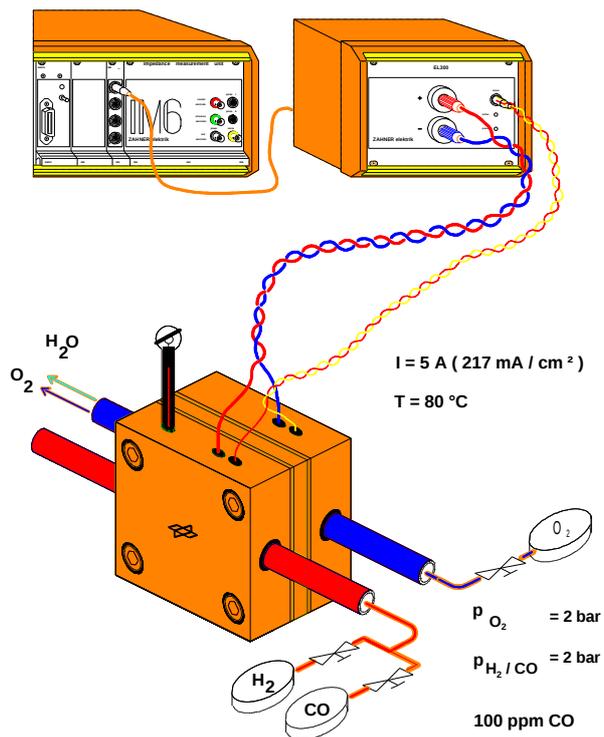


Figure 1

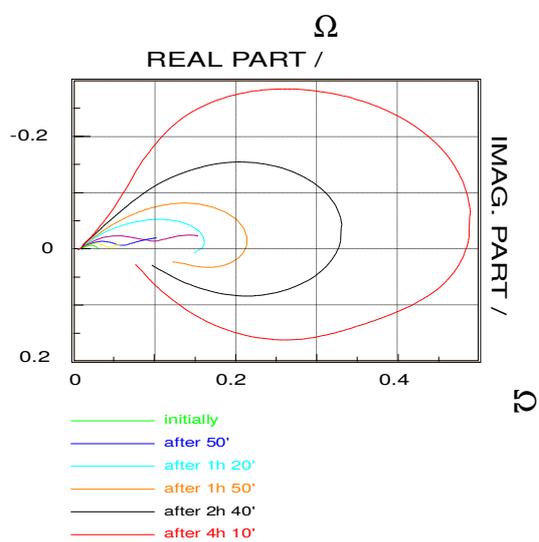


Figure 2

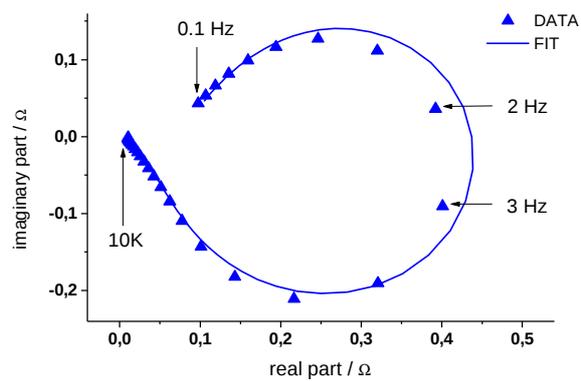


Figure 3

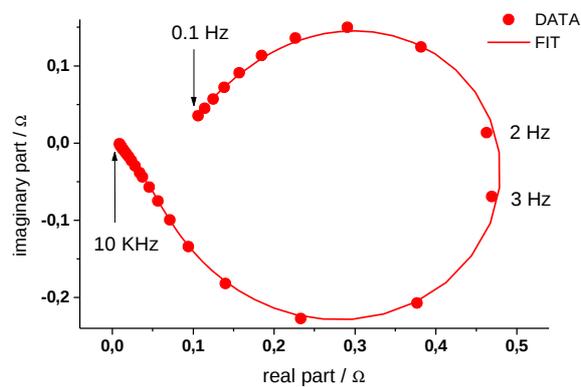


Figure 4

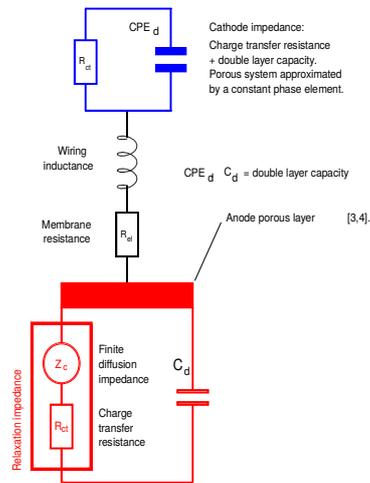


Figure 5

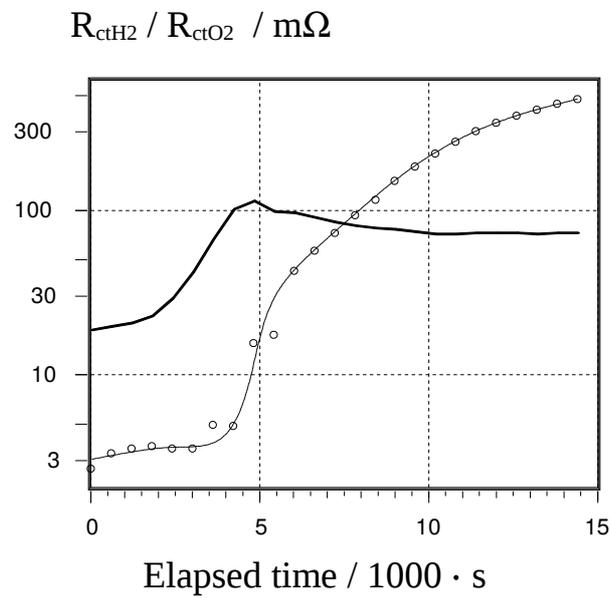


Figure 6

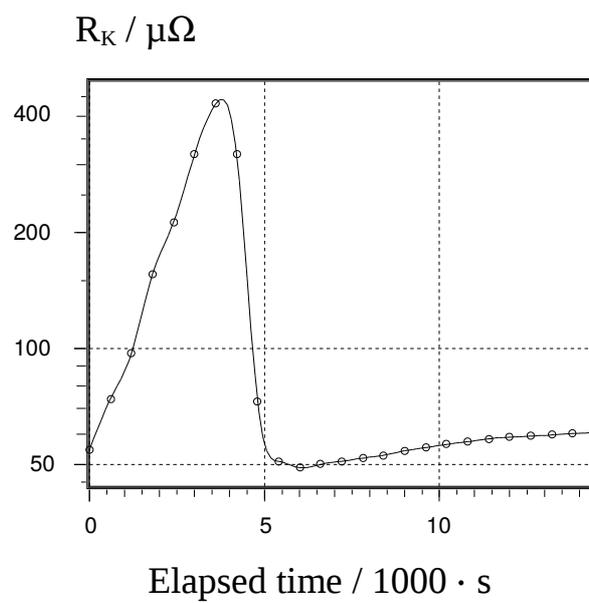


Figure 7

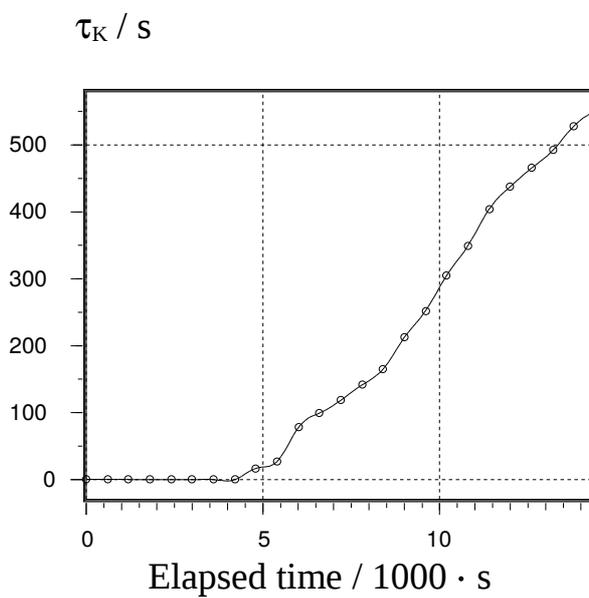


Figure 8

Figure captions

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 of 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

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

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

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

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

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