Rate limiting proton hydration in the anode of the polymer electrolyte membrane fuel cell

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Abstract

We studied the isothermal hydrogen adsorption and reaction at the carbon and platinum (Pt) surface of the humidified E-TEK electrode of a polymer electrolyte fuel cell (PEMFC) with a Nafion® 117 membrane by impedance spectroscopy at 30 and 50 °C. We found three rate-limiting steps, one of them is interpreted as proton hydration, a step that has not been reported previously. We analysed the influence of water transport on the impedance and found that the semicircle for the charge transfer reaction and that of proton hydration are superimposed at 50 °C, but separate at 30 °C. Additional evidence is presented for hydrogen adsorption to the carbon surface prior to charge separation. The surface diffusion coefficient of hydrogen was calculated to $1 \times 10^{-7}$ m$^2$/s.

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1. Introduction

It is well known that water plays an important role in the low temperature polymer membrane fuel cell (PEMFC). High performance of PEMFC requires a continuous supply of water to hydrate the membrane and maintain its proton conductivity. Water is carried by protons that are transported through the membrane from the anode to the cathode, i.e. electro-osmosis. Water is also produced at the cathode. This will induce a diffusional back flow of water in the membrane [1].

But does water affect the anode reaction? To answer this question one can use impedance spectroscopy. This is an experimental technique that can separate phenomena with different relaxation times, and is thus useful for determination of rate-limiting steps at electrode surfaces [2]. It has been used widely, also in studies of rather complicated three-phase contacts [3,4], which are typical for fuel cell electrodes.

The fuel cell electrodes consist of a porous matrix of carbon black that allows gas diffusion up to the catalyst (Pt) particles. The gas reacts at the catalyst, which is in contact with the proton-conducting membrane electrolyte. Three phases must be near each other to allow charge transfer. To describe the events at the three-phase contact-line by thermodynamic variables is a difficult task. The successful agglomerate model [5] describes the production of charges in the interface region in a continuous way. We have chosen to address the problem, taking a Gibbs surface as a starting point [6]. In this picture, the interface region, which in fact has a thickness around $10 \mu$m, is described as a two-dimensional layer. It is a separate thermodynamic system, and we shall refer to this layer as the surface. The thermodynamic variables of this layer are excess properties [1]. In the present case, the surface contains excesses of catalyst material (platinum), gas, adsorbed gas and water, membrane polymer and membrane water. This description leads to discontinuities in the thermodynamic variables at the surface.

We have earlier studied the cell in which both the anode and cathode were hydrogen electrodes. The electrode region was considered to consist of a catalyst interface (i.e. the two-dimensional thermodynamic system), surrounded on one side of a homogeneous phase of gaseous carbon, and on the other side of a homogeneous phase of a water filled membrane, respectively. In order to reach the platinum catalyst and the surface, the gas was allowed to diffuse also along the carbon phase. The electrode region is pictured schematically in Fig. 1. We see the

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two-dimensional surface indicated by two stipled vertical lines, and the surrounding homogeneous phases. The transport pathway for hydrogen is on the right hand side, while the flux of hydrated protons in the membrane is to the left in the figure. In our coarse grained, one-dimensional description, transport takes place along a coordinate normal to the surface of the membrane. All variables are then independent of coordinates parallel to the surface. Using these conditions with this division into subsystems, we were able to derive the electrode impedance for the interface with two rate-limiting steps of charge transfer and of hydrogen adsorption/diffusion on carbon. The present work offers supplementary support for these steps, and includes also a third step, namely proton hydration.

Impedance studies of the hydrogen electrode have mostly been motivated by the need to understand the CO tolerance of this electrode [7,8]. As a background for such studies, it is important to have a good understanding of the elementary steps concerning hydrogen alone. This is why we have chosen to use only hydrogen electrodes here. We have found experimental support for the hypothesis of reversible gas adsorption on carbon black as a first step in the electrode reaction. The adsorption reaction took place most probably in front of the catalyst (Pt) particles. In our previous paper [6] we assumed that water was in equilibrium throughout the system, even if results from the high frequency part of the impedance diagram indicated that this assumption was questionable. In this paper we analyse by theory and experiments how water affects the behaviour of the system, using again two hydrogen electrodes. We shall see, that it is probably not correct to assume equilibrium for water at the surface, not even in the absence of a dc electric current. At low temperatures, we find evidence that hydration of protons can be rate-limiting at high frequencies in the anode reaction of PEMFC, also when the electric current is zero. The membrane electrode assemblies consisted of E-TEK electrodes with 0.5 mg Pt/cm² and a Nafion®117 membrane.

The paper is organised as follows. The model is first described in Section 2. We then give the formulae of the impedance (which is derived in Appendix A) in Section 3. The experiments and the results, which confirm the three-step model, are then described in Sections 4 and 5 and discussed in Section 6.

2. A model with three rate-limiting steps

The model assumes that hydrogen gas is first adsorbed along the pores in the carbon matrix (see Fig. 1):

\[ \frac{1}{2} \text{H}_2(g) \rightarrow \frac{1}{2} \text{H}_2(a) \]  

(1)

Adsorption can happen close to or far from the platinum particle. Once adsorbed, hydrogen proceeds to diffuse along the carbon surface to the platinum, that is located in the electrode interface [9]. The catalyst particle is located in the surface between the porous carbon matrix and the cation exchange membrane (grey area in Fig. 1). During the diffusion process some of the hydrogen molecules desorbs back to form molecular hydrogen in the gas phase. We assumed that the adsorption has a first order
forward reaction in both directions (the superscript a refers to the carbon surface of the anode):

\[ \rho \frac{\partial c}{\partial t} = D \nabla^2 c - \Theta \frac{c - c_d}{\tau} \]

A model using adsorption of atomic hydrogen was also possible [6]. We use a coarse-grained description in which both concentrations are given in mol/m³ for the carbon matrix. The concentration \( c_{H_2} \) is the time and position independent concentration in the pores times the porosity of the layer. The concentration \( c_{H_2}^a \) is the concentration in mol/m² times the area of the pores per unit of volume (in m⁻¹). In most models, the adsorption reaction (1) is assumed to take place on the metal surface, see e.g. [10]. We have shown that the adsorption may take place earlier, and continue working with this hypothesis [6]. Support for this model has recently been given also by Paulus et al. [9].

In the Tafel-Volmer mechanism, the molecule dissociates into protons and electrons in active sites in the electrode surface on the platinum nanoparticles:

\[ \frac{1}{2} \text{H}_2(a) \rightarrow \text{H}^+(s) + e^- (a) \]  (2)

Electrons are eventually transported into the anode carbon phase (see Fig. 1). There are two modes of transport related to water in the fuel cell membrane: (1) the electro-osmotic transport, or (2) diffusion of water. The transport number can be regarded as constant to 1 [11]. In the present case, the membrane is saturated with water, and the transport number can be regarded as constant [12]. We may therefore in good approximation, say that one water molecule is associated with each proton that is moving across the membrane. The protons bind then, on the average, to one water molecule at the surface, before they move into the cation exchange membrane (m) as hydronium ions:

\[ \text{H}^+(s) + \text{H}_2\text{O}(m) \rightarrow \text{H}_2\text{O}(m) \]  (3)

In summary, we have a model where hydrogen is adsorbed as molecular hydrogen/atomic hydrogen on the surface of the carbon pores in a reaction-diffusion layer located before the surface. The hydrogen is then converted into protons and electrons in active sites in the surface on the platinum catalyst in Fig. 1. The electrons move into the carbon phase (a porous matrix), while the protons bind to water at the surface to form hydronium ions which move into the membrane. The thickness of the carbon phase in the experiment is in the order of 0.5 mm, while the thickness of the catalyst layer is in the order of 0.01 mm.

The impedance that follows from these steps is derived in Appendix A. The impedance was derived following a systematic procedure, starting with the mass and energy balances of the steps, and using the entropy production of the surface to define the relation between the surface potential drop and the electric current as a function of frequency.

3. Equations for data reduction

We show in Appendix B, by combining Eqs. (A.18) and (A.22)–(A.24), that the impedance of the whole surface is

\[ Z' = \frac{\rho_{cm}^e + Z_{ct}}{1 + i\omega C_{H_2O}^c} \]  (4)

In this equation, \( Z_{ct} \) is the impedance of the charge transfer step

\[ Z_{ct} = \frac{\rho_{ct}^e + Z_{ad}}{1 + i\omega C_{H_2O}^c} \]  (5)

and the capacitance and the resistivity of the proton hydration are given by \( C_{H_2O}^c \) and \( \rho_{cm}^e \). The relaxation time for the proton hydration reaction, \( \tau_{cm} \), is

\[ \tau_{cm} = \rho_{cm} C_{H_2O}^c \]  (6)

We find that the proton hydration, Step 3, modifies the impedance of the charge transfer step. The impedance of Step 1, the step for adsorption and surface diffusion was given by [6]

\[ Z_{ad} = \frac{RT}{2F^2 C_{H_2O,eq} \sqrt{2D_{H_2O}^c (1 + i\omega \tau_{ad})}} \]  (7)

where the relaxation time in the absorption process was

\[ \tau_{ad} = \left( \frac{c_{H_2O,eq}^d}{c_{H_2O,eq}^c} \right) \]  (8)

The hydrogen pressure in the pores was assumed constant in the derivation of this equation, giving a constant gas concentration, \( c_{H_2O}^c \) and therefore also a constant value for the concentration of absorbed gas at equilibrium, \( c_{H_2O,eq}^c \). The impedance \( Z_{ad} \) was the impedance of a Gerischer element. Experimental results fitted this impedance better than a finite length Warburg element, so it shall be used also here, see Section 5 below.

The equivalent circuit that can be put up on the basis of Eqs. (4) and (5) is given in Fig. 2. In this context it is important to note that the sequencing of the contributions to the total spectrum is fixed. There is no possibility to switch the elements of the circuit in Fig. 2. When \( \omega \rightarrow \infty \), we see that:

\[ Z_{\omega \rightarrow \infty} = 0 \]  (9)

In the present experiments, we measure the response of two identically made electrodes plus membrane electrolyte. When a dc current is passing the cell, one electrode will be a sink for hydrogen, while the other will be a source for hydrogen. The impedances of the two electrodes are the same, however. Both electrodes therefore give the same contribution to the measurement, also when the electrodes are polarised. In terms of
The expression for the relaxation time, $\tau^*$, and the membrane impedance, $Z_{\text{mem}}$, the impedance of one electrode is then:

$$Z^* = \frac{1}{2} (Z_{\text{cell}} - Z_{\text{mem}})$$  \hspace{1cm} (10)

The membrane impedance is found by assuming $Z_{\text{mem}} = Z_{\text{cell}}$ as $\omega \rightarrow \infty$. The results that are calculated for $Z^*$ from Eq. (10), can now be fitted to formulas (4) and (5) using Eq. (7) for $Z_{\text{ad}}$.

A constant phase element (CPE) shall be used for the charge transfer step in Eq. (4), rather than one capacitance in parallel with the resistance. The CPE is defined as:

$$Z_{\text{CPE}} = \frac{1}{T_{\text{CPE}}(\omega)^{\alpha}}$$  \hspace{1cm} (11)

The phase angle of the CPE impedance is constant and independent of the frequency. When $\alpha$ equals 1, CPE is identical to $C_{\text{ct}}$. The more depressed the semi-circle is, the lower is the $\alpha$-value. We found $\alpha$ to be typically 0.82. The relaxation time for the charge transfer reaction is

$$\tau_{\text{ct}} = \left(T_{\text{ct}}(\omega)\right)^{1/\alpha}$$  \hspace{1cm} (12)

Eq. (5) then becomes:

$$Z_{\text{ct}} = \frac{\rho_{\text{ct}}^* + Z_{\text{ad}}}{1 + T_{\text{ct}}(\omega)^{\alpha}(\rho_{\text{ct}}^* + Z_{\text{ad}})}$$  \hspace{1cm} (13)

The limiting behaviour $\omega \rightarrow 0$ gives

$$Z_{\omega \rightarrow 0} = Z_{\omega \rightarrow 0, \text{ad}} + \rho_{\text{ct}} + \rho_{\text{cm}}$$  \hspace{1cm} (14)

The fit of the experimental results to the theoretical expressions gave $Y_0$ and $\tau_{\text{ad}}$ in the following expression for $Z_{\text{ad}}$:

$$Z_{\text{ad}} = \frac{1}{Y_0 \sqrt{\tau_{\text{ad}}^{-1} + i\omega}}$$  \hspace{1cm} (15)

The expression for the relaxation time, $\tau_{\text{ad}}^{-1} = k_{\text{H}_2}^d$, was given in Eq. (8) while the other variable is:

$$Y_0 = \frac{2F^2}{RT} c_{\text{H}_2, \text{eq}}^2 \sqrt{2Dk_{\text{H}_2}^d \tau_{\text{ad}}} = \frac{2F^2}{RT} c_{\text{H}_2, \text{eq}}^2 \sqrt{2D}$$  \hspace{1cm} (16)

We see that the admittance $Y_0$ is proportional to the hydrogen concentration in the gas phase, that is the hydrogen pressure. Knowledge of the diffusion constant for hydrogen along the pores gives $c_{\text{H}_2, \text{eq}}^2$ from this equation. Such calculations were performed earlier.

4. Experimental

4.1. The membrane-electrode assembly

The electrodes were E-TEK Elat/Std/DS/V2 gas diffusion electrodes with a loading of 0.5 mg Pt/cm². The catalyst was 20 wt.% Pt supported on Vulcan XC-72. To obtain a better ionic contact between the layers in the membrane- and electrode assembly (MEA), the electrodes were sprayed with a 5% Nafion® solution to give 0.6–0.8 mg/cm². This was done with a Badger Airbrush Pistol (model 200). The airbrush was operated at an air pressure of about 200 kPa (2 bar). The electrode was weighed before and after the spraying so the amount of Nafion® could be calculated. The electrodes were then dried in a heating cabinet at 125 °C for 30 min. The electrodes were stored at least 48 h before they were used in the fuel cell.

The MEA consisted of two identical electrodes separated by a Nafion®117 membrane. The membranes were pretreated in several steps as described for instance by Møller-Holst [14]. This procedure included hydrogen-peroxide (5%) to oxidize organic impurities, sulfuric acid (0.05 M) to remove metallic impurities and rinsing in distilled water several times. All was done at temperatures around 90 °C. The prepared membranes were stored in distilled water until use.

The mechanical pressure over the MEA was 4.2 bar gauge, controlled by a pneumatic piston. The hydrogen gas pressure on the two sides of the MEA were the same and varied between 1 and 4 bar. The pressure and temperature were constant during each experiment. The hydrogen flow into the cell was controlled by Brooks 5850S mass flow controllers.

The MEA’s were tested in a test-station developed by Møller-Holst [14] and Vie [15]. The fuel cell was a circular single cell with 4.91 cm² active area. The fuel cell housing was made of stainless steel (SS-316) and was supported by two pistons (SS-316). At the top of the pistons there were serpentine patterned flow fields. These pistons also served as current collectors. Each piston contained a heating element. Thermocouples inside the cell housing measured the temperature at the electrode backings. The temperature was controlled by a PID controller (Eurotherm 2408) and a Pt-100 thermistor to 30.0 ± 0.1 and 50.0 ± 0.1 °C.

4.2. The gas humidifying system

The hydrogen gas (AGA 99.999%) was humidified at 80 °C before it entered the cell, making sure that gas was always saturated with water. The dry gas entered at the top of the humidifier tank and was preheated in a heating coil. The gas was then bubbled through a glass-sieve and finely dispersed into an 800 ml internal container filled with water at a given temperature. The small internal container was placed inside a larger 101 tank also filled with water. This outer tank was heated with an electrical heating tape. This ensures a stable temperature of the gas. The humidified gas left the humidifier at the top of the internal container and entered then the fuel cell system. Saturation of the gases at the given temperature can then be assumed. The humidifying temperature was always minimum 20 °C higher than the cell temperature to prevent the MEA to drying out when electric current was passing the cell.

4.3. The water condensers

The water condensers were designed by Vie [15]. They remove the water by condensing the water in the gas flow. The outer container has a volume of 101 and is filled with cooling water. Gas enters at the top of the container, goes through a condensing coil and into a smaller (500 ml) condensate tank. The gas escapes at the top of the tank and water at the bottom. The condensers are able to operate at an elevated pressure and the condensing medium is tap water (5–8 °C). There are two condensers in the system, one for the anode side and one for the
cathode side. The gas from each condenser enters a pressure control valve (Brooks 5866). The valves are controlled from the computer.

4.4. Impedance measurements (EIS)

The impedance diagrams were recorded using a PAR 263A/94 potentiostat and a Solartron 1260 FRA. Z-plot software from Scribner Ass. Inc. was used to run the experiments. Measurements were made in a two-electrode set-up on freshly prepared membrane-electrode samples, unless otherwise is stated. The impedance was obtained by sweeping over the frequencies from 10 kHz to 10 mHz, recording 12 steps/decade, for each pressure. An amplitude of 5 mV was used in all experiments.

The impedance was first measured at 30°C, with zero dc voltage across the cell, and with the varying gas pressure. Five different hydrogen pressures were used: 1.0, 1.56, 2.25, 3.06 and 4.0 bar.

The impedance was next measured, with constant gas pressure (1 bar) at different dc voltages. The applied dc voltages were 10, 20, 30, 50, and 60 mV. The temperature was then 30 and 50°C.

5. Results

5.1. Data reductions

The results are shown in Figs. 3–8. At all pressures at low temperature and no dc voltage (Figs. 3, 4, 6 and 7), the EIS showed three relaxing phenomena, as expected from the theoretical model. All data were therefore interpreted using this model. All spectra were fitted using the software Z-View (Scribner Associated Inc.) and are given as Nyquist plots of $Z_{cell}$. The results of the fits of these as well as those from the previous article [6] are given in Appendix B, Tables A.1–B.4. The two high frequency arcs became superimposed at the highest temperature, 50°C, see Fig. 5.

The relaxation times for all three processes are presented in Tables 1–3. The relaxation time for adsorption/diffusion $\tau_{ad}$ followed directly from the measurements. The relaxation time for the charge transport, $\tau_{ct}$, was calculated using Eq. (12) and the relaxation time for the proton hydration reaction, $\tau_{cm}$, was found using Eq. (6).
Fig. 7. The impedance spectrum for the unpolarised symmetric cell at $T = 30^\circ C$. (a) Nyquist plot. (b) Phase shift plot. Points are experimental data and lines are data fitted with the equivalent circuit of Fig. 2.

Fig. 8. The admittance of Eq. (16) as a function of the hydrogen concentration in the gas phase. The error-bars of the single experiments are shown.

5.2. The membrane area resistance

A constant membrane area resistance, $R_m$, was observed. For the experiments done at $30^\circ C$, the membrane area resistance was $0.50 \pm 0.02 \ \Omega \ cm^2$ and when the cell temperature was raised to $50^\circ C$, the value was $0.40 \pm 0.02 \ \Omega \ cm^2$. These values are in good agreement with results reported in the literature for the same membrane and temperatures [16,3], and are taken as evidence for a good measurement technique. The resistances did never vary more than 5% for a given MEA. This was seen as long as freshly prepared MEA’s were used. Gas pressure changes (Table A.1) or changes in applied potential (Tables B.1 and B.3) did not change this.

The high reproducibility in the measured membrane resistance (± 5%), indicates also that the humidifying conditions were good. If the MEA was drying out, $R_m$ would be increasing. We can thus conclude that the membrane at all times is saturated with water at the given temperature. The reproducibility of experiments makes this conclusion reliable.

5.3. The ageing effect

An ageing effect was observed in the spectra after prolonged use. After a few days or after 10–30 experiments, a change was seen in the spectra. It was therefore important that the experiments were done as soon as a new system was mounted and shown to be stable. When two experiments were done after each other within about 24 h, the results were identical. When the time interval between the experiments grew, an ageing effect was seen. Fig. 3 shows the ageing effect in one EIS experiment, repeated after 5 days with about 30 measurements. The resistance of the high frequency arc (proton hydration step) increased from 0.030 to 0.074 $\ \Omega \ cm^2$ (150%) and the resistance of the middle frequency arc (charge transfer step) increased with 100% from 0.023 to 0.046 $\ \Omega \ cm^2$.

Table 1

<table>
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<th>$p_{H_2}$ (bar)</th>
<th>$\tau_{cm}$ ($10^{-4}$ s)</th>
<th>$\tau_{ct}$ ($10^{-3}$ s)</th>
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$\Delta \phi_{dc}$ (mV) | $j$ (A/cm$^2$) | $\tau_{cm}$ ($10^{-4}$ s) | $\tau_{ct}$ ($10^{-3}$ s) | $\tau_{ad}$ (s) |
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$T = 30^\circ C$ and $E = 0 \ V$. $\tau_{cm}$ and $\tau_{ct}$ were calculated using Eqs. (6) and (12). $\tau_{ad}$ followed directly from the data fitting.

Table 2

<table>
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<tr>
<th>$\Delta \phi_{dc}$ (mV)</th>
<th>$j$ (A/cm$^2$)</th>
<th>$\tau_{cm}$ ($10^{-4}$ s)</th>
<th>$\tau_{ct}$ ($10^{-3}$ s)</th>
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$T = 30^\circ C$ and $E = 0 \ V$. $\tau_{cm}$ and $\tau_{ct}$ were calculated using Eqs. (6) and (12). $\tau_{ad}$ followed directly from the data fitting.

Table 3

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$T = 50^\circ C$ and $p_{H_2} = 1 \ bar$. $\tau_{cm}$ and $\tau_{ct}$ were calculated using Eqs. (6) and (12). $\tau_{ad}$ followed directly from the data fitting.
adsorption/diffusion step did not change; however, pointing to its independence of the catalyst layer.

5.4. Effect of temperature

The cell temperature was either 30 or 50 °C. Three arcs were seen at 30 °C (see Fig. 4). At 50 °C, two of the arcs overlapped (Fig. 5). The membrane area resistance, \( R_m \), the proton hydration resistance, \( \rho_{cm} \), and the charge transfer resistance, \( \rho_{ct} \), all decreased by increasing temperature, see Tables B.1–B.4. \( R_m \) decreased with 25% when raising the temperature, and both \( \rho_{cm} \) and \( \rho_{ct} \) decreased with approximately 75% when the temperature increased from 30 to 50 °C, see Fig. 6. The capacitance for the proton hydration, \( C_{H_2O^+} \), increased 1500% when the temperature increased in the unpolished cell.

Data were reduced with the three-step model described in the theory. The relaxation time for the proton hydration (\( \tau_{cm} \)) increased with increasing temperature, the relaxation time for the charge transfer reaction (\( \tau_{ct} \)) was almost constant with the temperature, while the relaxation time for the adsorption/diffusion process (\( \tau_{ad} \)) decreased (see Tables 2 and 3).

5.5. Proton hydration as rate limiting step

The first arc (highest frequency) in the impedance diagram is, according to the model, related to proton hydration when the proton passes from the catalyst surface into the membrane. It was only possible to fit this arc using a pure capacitance and a resistance, and not a constant phase element. When the gas pressure increased, \( C_{H_2O^+} \) and \( \tau_{cm} \) decreased and \( \rho_{cm} \) increased slightly. The same was observed when the applied dc potential increased at constant gas pressure (1 bar) and 30 °C, but here \( \tau_{cm} \) remained almost constant. The results are given in Tables 1, 2, and B.1. When the temperature increased to 50 °C and the gas pressure was constant (1 bar), \( C_{H_2O^+} \) and \( \rho_{cm} \) were approximately constant while \( \tau_{cm} \) decreased. The results are given in Tables 3 and B.3.

5.6. The charge transfer step

The second arc in the impedance diagram is, according to the model, related to the charge transfer step at the catalyst surface. As expected, it depended more on the applied dc potential than the other steps, see Tables A.2 and B.2. The relaxation time in these tables, \( \tau_{ct} \), increased with applied dc-potential and also with increased gas pressure. It is likely that the heterogeneity of the Pt surface can cause a depression like the one we observe. This was also the motivation for us and others [7] to fit this second arc to a constant phase element. The results in Tables A.2 and B.2 show that the resistance, \( \rho_{ct} \), was not so sensitive to changes in applied dc-potential or gas pressure.

The value of \( \alpha_{ct} \) decreased with increasing hydrogen gas pressure, see Table A.2. The value did not vary with the applied dc-potential at 30 °C (see Table B.2). The average value was 0.82. When the temperature in the system was raised to 50 °C, the value of \( \alpha_{ct} \) increased (see Table B.4). The value approached one within the accuracy for all potentials given in Table B.4. When \( \alpha_{ct} \) equals one, the CPE is a pure capacitance.

5.7. Rate-limiting adsorption/diffusion

The third arc was already related to an adsorption/diffusion step in the carbon backing in front of the catalyst [6]. The results from the present and previous experiments on this arc are given in Tables A.2, B.2, and B.4. The admittance, \( Y_0 \), decreased with the increasing dc-potential. It is now shown that \( Y_0 \) are a function of the hydrogen concentration in the gas phase, the equilibrium concentration (see Eq. (16)) in Fig. 8. Only a small variation was seen, but the trend was systematic. The gradient of the straight line was found, and the diffusion coefficient was calculated to \( 1 \times 10^{-7} \) m²/s. This value fits very well with the estimate we made earlier for surface diffusion, represented for the porous material as a whole, \( 3 \times 10^{-7} \) m²/s and with a corresponding value of \( C_{H_2} \text{eq} = 260 \) mol/m³. The relaxation time, \( \tau_{ad} \), remained constant when the gas pressure as well as the applied dc-potential was changed.

As an alternative interpretation, we considered also the finite-length Warburg element for the impedance of this layer. This element has the form

\[
Z_{ad} = \frac{R_W \tanh \sqrt{\frac{\omega}{T_W}}}{\sqrt{\frac{\omega}{T_W}}} \tag{17}
\]

giving here the impedance

\[
Z_{ad} = \frac{RT}{4F^2 c_{H_2\text{eq}} W \sqrt{\frac{\omega}{T_H}} \sqrt{D_{H_2\text{W}}}} \tanh \left( \frac{\sqrt{\frac{\omega}{T_H}} \sqrt{D_{H_2\text{W}}}}{W^2} \right) \tag{18}
\]

and the admittance

\[
Y_0 = \frac{4F^2}{RT} c_{H_2\text{eq}} \sqrt{D_{H_2\text{W}}} = \frac{\sqrt{T_W}}{R_W} \tag{19}
\]

where \( T_W \) and \( R_W \) are given directly from the fit of experiments to the Warburg element. The diffusion coefficient from this formula is \( D_{H_2\text{W}} = \frac{d^2}{T_W} \), where \( d \) is the thickness of the carbon matrix (200 μm) and \( T_W \) is from the fit (7.5 s). The fitted parameter \( R_W \) was 0.01 Ω cm². This gave the very small diffusion coefficient \( 5 \times 10^{-9} \) m²/s, a reduction of two orders of magnitude compared to the aforementioned value. When this value is used in Eq. (19), the equilibrium concentration was calculated to 2700 mol/m³ at 30 °C. This value is ten times the value calculated before and corresponds to a fully occupied monolayer of gas on carbon [6]. So, in addition to the fit giving a less good description of the observation, the properties derived from the finite-length Warburg element are also less realistic for a hydrogen adsorption step. It was not possible to assign this part of the spectrum to a rate-limiting step in the membrane.

6. Discussion

6.1. Three, not two steps

The theoretical model (Section 2) had three rate limiting steps, i.e. three arcs in the Nyquist plot. We allocated these
in the Section 5 to (1) gas adsorption/diffusion in the electrode backing, (2) charge transfer at the catalyst, and (3) a step that involved proton hydration at the catalyst surface. Evidence for the first step was presented and discussed in our earlier work [6]. The present data give further support to this step, by the data that can be derived from Fig. 8. The second step is adopted in all similar investigations [7], while the third proposal about rate-limiting proton transfer at high frequencies is new. The experimental results gives support to the total model.

We may first note, that the results for the membrane resistance, \( R_m \) (Tables A.1, B.1 and B.2), confirm earlier investigations. The value is within a few percent reported earlier. The reduction in \( R_m \) with an increase of temperature from 20 to 45 °C, was explained by Sone et al. [17] by the loss of water from the membrane at higher temperatures (see next section). The reproducibility of the experiments (cf. Sections 5.2 and 5.3) allow several conclusions to be drawn.

The relaxation time of the third arc or the Gerischer element, did again (see [6]) not depend on the applied potential (see Tables B.2 and B.4) and it was also independent of the ageing effect. We expect that adsorption and diffusion of the hydrogen molecules along the surface of the carbon pores, is independent of ageing (or the Pt surface area, see below), and this is indeed observed, giving credence to this part of the interpretation. The hydrogen pressure variation in \( Y_0 \) is small (Fig. 8), and has a large uncertainty. Nevertheless, it is interesting to find that the diffusion coefficient that can be derived from the slope is very near the one we estimated earlier [6], and which was used to support that reaction (1) takes place in the carbon matrix. The value, \( 1 \times 10^{-7} \text{ m}^2/\text{s} \), is a likely value, as it is comparable with diffusion in the gas phase, and consistent with a fractional coverage of hydrogen on the carbon surface. A finite-length Warburg element, which give a similar mathematical form of the impedance, did not give a likely alternative explanation. The new evidence confirms our hypothesis of this step, that there is surface diffusion of hydrogen to the catalyst.

Support for the interpretation of next two steps is given from (1) the fits themselves, (2) the observed ageing effect, (3) the pressure effect, under the experimental conditions used.

The first arc (with highest frequency) had few signs of depression and the relaxation time was independent of the applied dc-potential. We had to use an ordinary capacitance and a resistance to model this arc. The fit was not perfect, but it was the only element that did not give an unphysical result (an \( \alpha_{ct} \) value larger than unity in a fit to a constant phase element). In the fit of the second arc (the charge transfer step), a constant phase element was essential, however. It is likely that the charge transfer step, and not so much the proton hydration step, is affected by the surface heterogeneity and the applied potential. It is also likely that the heterogeneous nature of the surface becomes less important as the temperature rises, as evidenced by \( \alpha_{ct}=1 \) for 50 °C. So these variations are as expected for the chosen model.

We expect that an increase in the hydrogen pressure leads to an increased concentration of protons at the catalyst surface. The results in Table 1 support this idea because the charge transfer relaxation and the proton hydration relaxation depend on the hydrogen pressure. More protons at the surface may explain why both \( \rho_{ct} \) and \( T_{ct} \) increase in Table A.2. We have no clear explanation for the simultaneous reduction of \( \rho_{cm} \) and \( C_{m,H^+} \) in Table A.1. The formation of \( H_3O^+ \) is facilitated by the increased \( J_{l4} \), and this may have a bearing on \( \rho_{cm} \).

We find it reasonable to relate the observed ageing effect to a reduction of the active catalyst (Pt) surface area. Such a reduction has been allocated to sintering or Pt particle agglomeration in the literature [18,19]. Agglomeration and coalescence of Pt particles into larger ones will lower the surface-to-volume ratio. The sintering rate is strongly affected by the temperature [18,19], and is therefore not so likely with the low temperatures used here. Another explanation for a reduced active area may be the withdrawal of polymers from the surface sites.

Proton hydration as well as charge transfer, but not adsorption/diffusion, should depend on the catalyst surface area. A reduction of the surface area must make it more difficult for the reaction to proceed; and accordingly the resistance will increase. This is indeed seen in the data: the resistances of the two first steps increased with the number of experiments (Fig. 3). Further support to this interpretation may come from molecular dynamics simulations. These indicate that a water molecule has to be in the right position to catch the proton before it goes into the membrane [20].

Three arcs were observed also by Paganin et al. [3], Kim et al. [8], Freire et al. [16] and Schneider et al. [21] in the PEMFC, and water has also earlier been mentioned as playing a rate-limiting role. These authors assign the role of water to the low-frequency arc, however. They explain that water becomes rate-limiting because of diffusion of water through the membrane and support this by showing that this low-frequency arc disappears when a thinner membrane, as Nafion®115, is used. Our experimental conditions are such that concentration gradients in water are unlikely (see below). We have shown here and earlier [6] that the low-frequency arc support a Gerischer element for the carbon matrix. A finite-length Warburg element could not be equally well fitted and understood. Our interpretation of the low-frequency arc therefore different from that of others [3,8,16]. The third arc is more sensitive to the temperature and hydrogen pressure than the other arcs.

In conclusion, we have presented theoretical and further experimental evidence to support rate-limiting surface diffusion of hydrogen to the catalytic site before charge transfer, and a rate-limiting step for proton hydration of water. A closer look on the state of water in the fuel cell membrane is now interesting.

6.2. Water in the fuel cell membrane

The performance of the polymer electrolyte membrane fuel cell depends on the water management in the system. The condition of the Nafion® membrane is an important factor for this performance. Nafion® is a proton conducting membrane based on a perfluorosulfonic acid (PFSA) polymer. It consists of a polytetrafluoroethylene (PTFE) backbone with side chains terminating in \( \text{SO}_3^- \cdot \text{H}^+ \) groups. The water content in
the membrane, $\lambda$, is given by the number of water molecules per sulfonic acid group [22]. The water uptake in the Nafion® membrane depends strongly on the pre-treating procedure [23] and operational procedures. Nafion®117 membranes used in these experiments were rinsed and then boiled in pure water. The membranes were always stored in water and they never dried out. That gave us an expanded uniform membrane that was filled with water at all times (E-form) before mounting the MEA.

The MEA’s were exposed to a varying applied potential. The small current densities that were used in Tables 2 and 3, can not cause a significant variation in the water content around the electrodes in one experiment, however. Diffusion of water is therefore not important for the experiment, since the water concentration can be expected to be uniform. This was one reason why we were able to allocate the high frequency arc to proton hydration, and exclude water diffusion as an explanation for the low frequency arc.

Two different states for water have been found in the membrane [24,25]. When the membrane surface is in contact with saturated water vapour, the membrane can be treated as a single homogeneous phase, in which water dissolves and can move due to a concentration gradient [24]. When the membrane surface is in contact with liquid water, the membrane can be treated as a heterogeneous porous medium in which water can move also by convection, for instance in the presence of hydraulic pressure gradient [25]. In the present case with hydrogen electrodes only, we can regard the membrane phase as being homogeneous. This was the background for using the hydronium ion in the theoretical model, equivalent to a water transferance number of unity [11]. This does not mean that exactly one water molecule will hydrate the proton. We have taken only one water along in our derivations, since the method is not good enough to tell the exact number of waters that are carried along.

Broka and Ekdunge [26] found that water uptake in a membrane exposed to saturated water vapour decreased with increasing temperature, and that the decrease was dramatic in the temperature range 25–50 °C. Also Hinatsu et al. [27] published water sorption data that showed lower water uptakes at 80 °C ($\lambda = 10$) than at 18–30 °C (Zawodzinski et al. [28]). Rieke et al. [29] measured water content and reported that the membrane had the highest water content at 30 °C ($\lambda = 15$) and lower at 50, 75 and 95 °C (9, 6, and 11, respectively). We can therefore expect a dramatic change in water content when the temperature changes from 30 to 50 °C in our experiments. The change in the properties $C_{H_2O}$ and $\rho_{cm}$ with temperature may reflect this change.

We need to explain why proton hydration becomes considerably slower (Tables 2 and 3) at the higher temperature. The large variation in water content may explain this. The smaller the water content is, the more difficult becomes the hydration step, and the higher is the relaxation time for this step. The data in Tables 2 and 3 have such a variation. The relaxation time, $\tau_{cm}$, shows only a very weak dependence on the current density at 50 °C, and no dependency at 30 °C. A reduction in water content, may thus explain why the third rate-limiting step, $H^+ \cdot (H_2O\cdot H_2O)$, became less visible in the Nyquist diagram 50 °C.

### 7. Conclusion

Electrochemical impedance spectroscopy was performed of the fuel cell electrode E-TEK, Elat/Std/DS/V2 0.5 mg Pt/cm², 20% Pt/C, with 0.6 mg Nafion®/cm² (5 wt.% solution). The membrane contact was Nafion®117 and the cell area was 4.91 cm². The electrode was studied at 30 and 50 °C. The pressure was varied between 1 and 4 bars and the applied dc potential varied from 0 to 0.06 V. The results were interpreted by three reaction steps. The first is a slow adsorption/diffusion step supported by a best fit to a Gerischer element, independent of ageing and applied potential, with a surface diffusion coefficient of hydrogen of $1 \times 10^{-7}$ m²/s. The second, the well established charge transfer step, depends on ageing (catalyst surface area) and temperature as expected. The third step was given a new interpretation, as a rate-limiting proton hydration step. A large reduction in membrane water content at high temperatures increases the relaxation time of this step, and can explain why it then coincides with the second semicircle. By extending the temperature range of the investigation, one may earn more about the mechanism of the electrode reaction.

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### Appendix A. The surface impedance

#### A.1. Mass and energy balances of the three steps

The mass balances and the polarisation of the surface follow from the three steps presented in Section 2.

At the surface there is an adsorption of protons, $\Gamma_{H^+}$, hydronium ions, $\Gamma_{H_3O^+}$, and electrons, $\Gamma_e^-$. We take the catalyst surface to be electroneutral, by choosing its thickness such that the total adsorptions (in mol/m²) of positive ions is equal to the adsorption of electrons:

$$\Gamma_{H^+} + \Gamma_{H_3O^+} = \Gamma_e^- \quad (A.1)$$

In the discussion of the properties of the surface it is convenient to use the polarisation of the surface. In this case there are two contributions to this polarisation, one is due to proton-electron pairs and the other is due to hydronium ion-electron pairs. As mentioned before, the extension of the surface is such that these pairs are contained. Together they make the interface electroneutral. The number of moles of the proton-electron dipoles per unit of surface area is given by $\Gamma_{H^+}$ and for the hydronium ion-electron dipoles by $\Gamma_{H_3O^+}$.

The charge transfer (ct) reaction, Eq. (2), increases the number of adsorbed dipoles of the first kind while the proton hydration (cm), Eq. (3), reaction decreases it. We therefore have

$$\frac{d}{dt} \Gamma_{H^+} = \Gamma_{ct} - \Gamma_{cm} \quad (A.2)$$
where \( r^{s}_{ct} \) and \( r^{s}_{cm} \) refer to the reaction rates. Superscript \( s \) indicates a property of the surface. Similarly the cm reaction increases the number of dipoles of the second kind while the electric current decreases it. This gives

\[
\frac{d}{dt} \Gamma_{H_2O^+} = r^{s}_{cm} = \frac{j}{F} \tag{A.3}
\]

where \( F \) is Faraday’s constant. The surface polarisation in the direction normal to the surface is equal to the sum of the polarisations due to the two dipole layers. These polarisations are equal to the dipole concentration times Faraday’s constant times the average distances, \( d_{H^+}^{c} \) and \( d_{H_2O^+}^{c} \), between the charges

\[
P^{s} = P^{s}_{H^+} + P^{s}_{H_2O^+} = Fd_{H^+}^{c} \Gamma_{H^+} + Fd_{H_2O^+}^{c} \Gamma_{H_2O^+} \tag{A.4}
\]

There is no reason to assume that the average distance between both kind of positive ions and the excess electron layer is the same. For the interface, we assume that these average distances are constants independent of the ion densities. It therefore follows from Eqs. (A.2)–(A.4) that

\[
r^{s}_{ct} = r^{s}_{cm} = \frac{1}{F} \left( \frac{d_{H^+}^{c}}{d_{H_2O^+}^{c}} \right) \frac{d}{dt} P^{s}_{H_2O^+} \tag{A.5}
\]

The surface polarisation divided by the surface thickness gives a corresponding potential difference times a capacitance. For the two contributions to the total polarisation we have: \( C_s^{c} \) and \( C^{s}_{H_2O^+} \), of these two dipole layers

\[
\frac{P^{s}_{H^+}}{d_{H^+}} = C^{s}_{H^+} \Delta_{s,m} \phi \quad \text{and} \quad \frac{P^{s}_{H_2O^+}}{d_{H_2O^+}} = C^{s}_{H_2O^+} \Delta_{s} \phi \tag{A.6}
\]

Hydronium ions are present inside the surface as well as in the membrane. The potential difference between the membrane phase and the electron layer is the full potential difference \( \Delta_{s} \phi \) across the surface. The protons are closer to the electron layer, so that the potential difference between this layer and the electron layer \( \Delta_{s,m} \phi \) is smaller.

The rates of the three steps become, using Eq. (A.5),

\[
r^{s}_{ct,dc} = r^{s}_{ct,ac} = \frac{1}{F} j_{dc} \tag{A.7}
\]

and

\[
r^{s}_{ct,ac} = \frac{r^{s}_{cm,ac}}{d_{H_2O}} = \frac{1}{F} \left( \frac{d_{H_2O}}{d_{H_2O^+}} \right) \left( \frac{d}{dt} P^{s}_{H_2O^+} \right) \tag{A.8}
\]

We shall need the reaction Gibbs energy of the adsorption reaction (1):

\[
\Delta_{e} G_{ad}^{s} = \frac{1}{2} \left( \mu^{a}_{H_2} - \mu^{a}_{H_2} \right) = \frac{1}{2} \mu^{a}_{H_2} (x = 0) - \frac{1}{2} \mu^{x}_{H_2} \tag{A.9}
\]

Here \( x = 0 \) indicates the position of the surface. The chemical potential of hydrogen molecules just outside the surface and at the surface are the same, \( \mu^{a}_{H_2} = \mu^{a}_{H_2} (x = 0) \). The hydrogen gas in the experiment has a constant (position and time independent) pressure, leading to a constant \( \mu^{x}_{H_2} \) as well as constant \( \mu^{x}_{H_2} \). In the description of the electrochemical processes at the surface, we use the change in Gibbs energy at the surface due to the neutral species. For the ct reaction (Eq. (2)) we have:

\[
\Delta_{e} G_{ct}^{s} = - \frac{1}{2} \mu^{a}_{H_2} = - \frac{1}{2} \mu^{a}_{H_2} (x = 0) \tag{A.10}
\]

and for the cm reaction (3) we have:

\[
\Delta_{e} G_{cm}^{s} = - \mu^{x}_{H_2} = - \mu^{m}_{H_2} (x = 0) \tag{A.11}
\]

For the total electrode reaction, the contribution becomes:

\[
\Delta_{e} G^{s} = \Delta_{e} G_{ad}^{s} + \Delta_{e} G_{ct}^{s} + \Delta_{e} G_{cm}^{s}
\]

\[
= \frac{1}{2} \mu^{a}_{H_2} - \mu^{m}_{H_2} (x = 0) \tag{A.12}
\]

A.2. The entropy production and the impedance

In order to derive the impedance of the model in Section 2, we consider again our surface in Fig. 1. The excess entropy production rate of the surface, \( \sigma^{s} \), contains the information about the surface dynamics. For isothermal conditions, the contributions to \( \sigma^{s} \) due to the alternating fields are [13]:

\[
\sigma^{s}_{ac} = - j_{ac} \Delta_{s,m} \phi_{ac} + \frac{\epsilon_{0} P^{s}_{H_2O^+,ac} \left( d^{s}_{H_2O^+,ac} \right)}{d^{s}_{H_2O^+,ac}} \left( \frac{d^{s}_{H_2O^+,ac} - d^{s}_{H_2O^+,ac}}{\epsilon_{0}} \right)
\]

\[
+ \frac{\epsilon_{0} P^{s}_{H^+,ac} \left( d^{s}_{H^+,ac} \right)}{d^{s}_{H^+,ac}} \left( \frac{d^{s}_{H^+,ac} - d^{s}_{H^+,ac}}{\epsilon_{0}} \right)
\]

\[
- \frac{\epsilon_{0} P^{s}_{H^{+,ac}} \left( d^{s}_{H^{+,ac}} \right)}{d^{s}_{H^{+,ac}}} \left( \frac{d^{s}_{H^{+,ac}} - d^{s}_{H^{+,ac}}}{\epsilon_{0}} \right)
\]

\[
- \frac{\epsilon_{0} P^{s}_{H^{+,ac}} \left( d^{s}_{H^{+,ac}} \right)}{d^{s}_{H^{+,ac}}} \left( \frac{d^{s}_{H^{+,ac}} - d^{s}_{H^{+,ac}}}{\epsilon_{0}} \right)
\]

where \( D^{s}_{H^{+,ac}} \) and \( D^{s}_{H^{+,ac}} \) are the displacement fields for the distribution of the two dipoles and \( \epsilon_{0} \) is the dielectric constant of vacuum. The equilibrium displacement fields are zero for free charges, \( D^{s}_{H^{+,ac}} = D^{s}_{H_2O^+,ac} = 0 \). The displacement fields are given by

\[
D^{s}_{H^{+,ac}} = - \epsilon_{0} \frac{\Delta_{s,m} \phi_{ac}}{d^{s}_{H^{+,ac}}} \quad \text{and} \quad D^{s}_{H_2O^+,ac} = - \epsilon_{0} \frac{\Delta_{s,m} \phi_{ac}}{d^{s}_{H_2O^+,ac}}
\]

The reaction Gibbs energies were defined above, Eqs. (A.9)–(A.12). For ac conditions we have:

\[
\Delta_{e} G_{ad,ac}^{s} = \Delta_{e} G_{ct,ac}^{s} = \frac{1}{2} \mu^{a}_{H_2} (x = 0)
\]

\[
\Delta_{e} G_{cm,ac}^{s} = \Delta_{e} G_{ac}^{s} = 0
\]
Using Eq. (A.8) for the ac contributions one obtains
\[ Fr_{ct,ac}^{s} = Fr_{cm,ac}^{s} + \frac{ioF}{d_{H^+}} \]
and
\[ Fr_{cm}^{s} = \frac{ioF}{d_{H^+}} \Delta n_{cm,ac}^{s} \]
Substituting this into Eq. (A.13) and using Eq. (A.15) we obtain
\[ T^{s}_{r,ac} = -r_{cm,ac}^{s} (F\Delta_{s}^{p} \phi_{ac} - F\Delta_{s}^{p} \phi_{ac}) \]
\[ -r_{ct,ac}^{s} (F\Delta_{s}^{p} \phi_{ct} - \Delta r_{G_{ad,ac}}^{s}) \]
(\(A.16\))
Since the two reactions occur consecutively, the coupling of the reactions may be neglected. The theory of non-equilibrium thermodynamics then prescribes that the forces and the fluxes are related by
\[ \Delta s_{m} \phi_{ac} = \frac{1}{F} \Delta n_{G_{ad,ac}}^{s} = -\rho_{ct}^{s} Fr_{ct,ac}^{s} \]
\[ -\Delta s_{m} \phi_{ac} = -\rho_{cm}^{s} Fr_{cm,ac}^{s} \]
(\(A.18\))
where \(\rho_{ct}^{s}\) and \(\rho_{cm}^{s}\) are the resistivities of the ct and cm reactions. The electrochemical reaction rates are normally not related to their driving forces by linear relations. In this experiment, the alternating contribution to the forces are small (±5 mV), however, so that we can use the linear theory. Adding the two relations in Eq. (A.18) one obtains
\[ \Delta s_{m} \phi_{ac} = \frac{1}{F} \Delta n_{G_{ad,ac}}^{s} = -\rho_{ct}^{s} Fr_{ct,ac}^{s} \]
\[ -\Delta s_{m} \phi_{ac} = -\rho_{cm}^{s} Fr_{cm,ac}^{s} \]
(\(A.19\))
The adsorption-diffusion layer has an impact on \(\Delta s_{m} \phi_{ac}\), because this layer determines the chemical potential of hydrogen at position \(x = 0\). The resistivity is independent of the driving force, but can depend on the temperature and the polarisation induced by the dc-field.

The dc contribution to the excess entropy production rate is found using \(\omega = 0\) and \(j_{dc} = Fr_{ct,dc}^{s} = Fr_{cm,dc}^{s}\). This gives
\[ T^{s}_{\phi,dc} = -j_{dc} \left[ \Delta s_{m} \phi_{dc} + \frac{1}{F} (iH_{2}O \Delta n_{G_{cm,dc}^{s}} + \Delta n_{G_{ct,dc}^{s}}) \right] \]
(\(A.20\))
For small dc-currents the linear law is thus:
\[ \Delta s_{m} \phi_{dc} + \frac{1}{F} (iH_{2}O \Delta n_{G_{cm,dc}^{s}} + \Delta n_{G_{ct,dc}^{s}}) \]
\[ = - (\rho_{ct}^{s} + \rho_{cm}^{s}) j_{dc} \]
(\(A.21\))
The impedance of the charge transfer and the proton hydration steps is defined as:
\[ Z^{s} = \frac{\Delta s_{m} \phi_{ac}}{j_{ac}} \]
(\(A.22\))
We find the surface impedance by adding \(\Delta s_{m} \phi_{ac} = -\Delta n_{G_{ct,ac}} = -Z_{ad} F^{2} r_{ct,ac}^{s} \Delta n_{G_{ct,ac}}^{s} \) to Eq. (A.19). This gives:
\[ \Delta s_{m} \phi_{ac} + \frac{1}{F} \Delta n_{G_{ad,ac}}^{s} = \Delta s_{m} \phi_{ac} \]
\[ = - (\rho_{ct}^{s} + Z_{ad}^{s}) Fr_{ct,ac}^{s} = -\rho_{cm}^{s} Fr_{cm,ac}^{s} \]
(\(A.23\))
where we used Eq. (A.15). It furthermore follows from Eqs. (A.5) and (A.6) that
\[ Fr_{ct} = Fr_{cm}^{s} + i\omega C_{H^+}^{s} \Delta s_{H^+} \phi \]
and
\[ Fr_{cm}^{s} = j_{ac} + i\omega C_{H_2O}^{s} \Delta s_{H_2O} \phi \]
(\(A.24\))
These equations can now be combined to give the impedance presented in Section 3.

**Appendix B**

Table B.1
Fitted results for the first arc for the symmetric cell at $T = 30\,^\circ\text{C}$, 1 bar hydrogen gas pressure and different applied voltages

<table>
<thead>
<tr>
<th>$\Delta \varphi_k$ (mV)</th>
<th>$R_m$ ($\Omega,\text{cm}^2$)</th>
<th>$C_{H_3O^+}$ (s/Ω cm$^2$)</th>
<th>$\rho_{ad}$ ± 0.001 ($\Omega,\text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.51</td>
<td>0.0071 ± 0.0004</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>0.53</td>
<td>0.0061 ± 0.0003</td>
<td>0.038</td>
</tr>
<tr>
<td>20</td>
<td>0.53</td>
<td>0.0057 ± 0.0003</td>
<td>0.041</td>
</tr>
<tr>
<td>30</td>
<td>0.53</td>
<td>0.0053 ± 0.0002</td>
<td>0.044</td>
</tr>
<tr>
<td>50</td>
<td>0.53</td>
<td>0.0049 ± 0.0003</td>
<td>0.047</td>
</tr>
<tr>
<td>60</td>
<td>0.54</td>
<td>0.0047 ± 0.0002</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Table B.2
Fitted results for the second and third arc for the symmetric cell at $T = 30\,^\circ\text{C}$, 1 bar hydrogen gas pressure and different applied potentials

<table>
<thead>
<tr>
<th>$\Delta \varphi_k$ (mV)</th>
<th>$T_0$ ($s/\Omega , cm^2$)</th>
<th>$\alpha_i$</th>
<th>$\rho_s$ ($\Omega,\text{cm}^2$)</th>
<th>$Y_0$ ($s^{1/2}/\Omega , cm^2$)</th>
<th>$\tau_{ad}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.46 ± 0.10</td>
<td>0.83 ± 0.06</td>
<td>0.020 ± 0.002</td>
<td>194 ± 21</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>0.49 ± 0.11</td>
<td>0.80 ± 0.05</td>
<td>0.023 ± 0.002</td>
<td>181 ± 16</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>0.41 ± 0.08</td>
<td>0.84 ± 0.05</td>
<td>0.023 ± 0.001</td>
<td>156 ± 11</td>
<td>8</td>
</tr>
<tr>
<td>30</td>
<td>0.47 ± 0.09</td>
<td>0.82 ± 0.05</td>
<td>0.025 ± 0.001</td>
<td>154 ± 11</td>
<td>8</td>
</tr>
<tr>
<td>50</td>
<td>0.47 ± 0.12</td>
<td>0.82 ± 0.06</td>
<td>0.026 ± 0.002</td>
<td>131 ± 11</td>
<td>8</td>
</tr>
<tr>
<td>60</td>
<td>0.50 ± 0.12</td>
<td>0.82 ± 0.06</td>
<td>0.026 ± 0.002</td>
<td>122 ± 10</td>
<td>8</td>
</tr>
</tbody>
</table>

Table B.3
Fitted results for the first arc for the symmetric cell at $T = 50\,^\circ\text{C}$, 1 bar hydrogen gas pressure and different applied voltages

<table>
<thead>
<tr>
<th>$\Delta \varphi_k$ (mV)</th>
<th>$R_m$ ($\Omega,\text{cm}^2$)</th>
<th>$C_{H_3O^+}$ ± 0.01 (s/Ω cm$^2$)</th>
<th>$\rho_{ad}$ ± 0.001 ($\Omega,\text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.39</td>
<td>0.11</td>
<td>0.009</td>
</tr>
<tr>
<td>10</td>
<td>0.40</td>
<td>0.11</td>
<td>0.009</td>
</tr>
<tr>
<td>20</td>
<td>0.40</td>
<td>0.10</td>
<td>0.009</td>
</tr>
<tr>
<td>30</td>
<td>0.41</td>
<td>0.09</td>
<td>0.009</td>
</tr>
<tr>
<td>50</td>
<td>0.42</td>
<td>0.08</td>
<td>0.010</td>
</tr>
<tr>
<td>60</td>
<td>0.42</td>
<td>0.06</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Table B.4
Fitted results for the second and third arc for the symmetric cell at $T = 50\,^\circ\text{C}$, 1 bar hydrogen gas pressure and different applied potentials

<table>
<thead>
<tr>
<th>$\Delta \varphi_k$ (mV)</th>
<th>$T_0$ ($s/\Omega , cm^2$)</th>
<th>$\alpha_i$</th>
<th>$\rho_s$ ($\Omega,\text{cm}^2$)</th>
<th>$Y_0$ ($s^{1/2}/\Omega , cm^2$)</th>
<th>$\tau_{ad}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.9 ± 0.8</td>
<td>0.86 ± 0.14</td>
<td>0.005 ± 0.001</td>
<td>221 ± 10</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>1.5 ± 0.6</td>
<td>0.83 ± 0.14</td>
<td>0.005 ± 0.002</td>
<td>184 ± 6</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>1.2 ± 0.5</td>
<td>0.87 ± 0.13</td>
<td>0.005 ± 0.002</td>
<td>170 ± 5</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>0.73 ± 0.14</td>
<td>0.97 ± 0.06</td>
<td>0.006 ± 0.001</td>
<td>163 ± 3</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>0.79 ± 0.19</td>
<td>0.97 ± 0.07</td>
<td>0.006 ± 0.001</td>
<td>147 ± 4</td>
<td>5</td>
</tr>
<tr>
<td>60</td>
<td>0.75 ± 0.19</td>
<td>0.97 ± 0.07</td>
<td>0.007 ± 0.001</td>
<td>138 ± 4</td>
<td>5</td>
</tr>
</tbody>
</table>

References