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Cell Resistances of ABPBI-Based HT-PEFC-MEAs: Time Dependence and Influence of Operating Parameters

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Abstract

Time-dependent measurements of cell impedance of a HT-PEFC based on ABPBI were performed at constant frequencies close to the high-frequency (h.f.) intercept of the corresponding Nyquist plots with the real axis. The h.f. impedances approximate the ohmic resistance of the cell and they decrease, when current (140 mA/cm²) is switched on. Steady state values are attained after 10 minutes. *Vice versa*, when current is switched off (OCV), the h.f. impedances instantaneously increase but reach steady state values only after about 1 hour. These values rise with increasing gas flow rates. The results are discussed in terms of hydration/dehydration processes, changing the equilibrium between orthophosphoric and pyrophosphoric acid and thus the conductivity of the electrolyte as well as the mobility of molecules and charge carriers. Impedance spectra were recorded after each time-dependent measurement under OCV conditions. The fit of these impedance data based on an equivalent circuit revealed ohmic resistances corrected by h.f. inductances and low frequency impedances associated with the cathode oxygen exchange reaction. The charge transfer resistances deduced from the low frequency impedances strongly depend on both air and hydrogen flow rates.

1 Introduction

Most of today's high temperature cells (HT-PEFCs) rely on membrane electrode assemblies (MEAs) with phosphoric acid absorbed in PBI (= *poly*(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) as electrolyte [1]. Recently membranes based on the chemically related ABPBI (= *poly*(2,5-benzimidazole) have emerged as a promising alternative [2-4]. Various aspects of the steady-state cell impedance of HT-PEFCs based on PBI as membrane polymer at different operating conditions have already been reported in the literature (e.g. [5-7]). The influence of water activity on the steady-state conductivity of the electrolyte [8,9] as well as the distribution of phosphoric acid within the membrane electrode assembly (MEA) [10,11] are intensively studied at present. We will not only discuss the influence of several testing parameters on the cell resistance of a MEA based on ABPBI instead of PBI, but we will also turn our attention to its time dependence after changes of the operating conditions.

2 Experimental

MEAs (A = 14.4 cm^2) have been assembled from ABPBI membranes (FuMA-Tech) and gas diffusion electrodes (~1 mg Pt/cm^2) produced in-house which have been impregnated with appropriate amounts of phosphoric acid [4]. They have been characterized in a single cell using pure hydrogen and air at ambient pressure as the reactants. Under these conditions reasonable power densities of ~250 mW/cm^2 are obtained at T = 160 °C [4]. We have deduced the time-dependent ohmic resistances from impedance measurements using a symmetric two electrode configuration. The experiments were run at a predefined frequency of 5-10 kHz close to the high-frequency intercept of the corresponding Nyquist plots with the real axis. Two hours prior to the beginning of the time dependent measurements during which the current density was changed from j = 0 to 140 mA/cm^2 and *vice versa* at 160 °C the cell was switched to OCV and the hydrogen and air flow rates were changed from $\lambda_{Anode/Cathode}$ = 2/2, to the values used for the respective experiment (λ_{H_2} = 2/4/6, λ_{air} = 2/4/6). In case of OCV measurements, the indicated air and hydrogen stoichiometries refer to the corresponding flow rates at a current density of 140 mA/cm². Additionally, impedance spectra were performed after the end of each time-dependent experiment in a frequency range of 10^{-2} – 10^4 Hz under OCV steady state conditions. The a.c. signal voltage amplitude was always ± 10 mV. The impedance spectra were fitted on basis of an equivalent circuit (see Fig. 2) using the EQUIVCRT 3.0 Software written by B.A. Boukamp [12]. From the fit data, corrected data of the ohmic resistance, R_Ω, could be obtained. In the following, the original impedance values will be denoted as R'_Ω ('ohmic resistance') and the corrected fit data of the ohmic resistance will be indicated as R_Ω. All the impedance measurements were performed with an IM 6 unit of Zahner Elektrik.

3 Results and Discussion

Fig. 1 shows the time dependent behaviour of the 'ohmic resistance', more precisely the high frequency impedance at constant frequency at Im(Z) part of almost zero, for three different air flow rates. The initial values of 250 - 300 mΩcm^2 under OCV conditions drop down within 10 minutes to about 200 mΩcm^2 when a current of 140 mA/cm^2 is switched on. The 'ohmic resistance' reaches steady state values, which shows only a weak dependence on the air flow rate. These results can be explained by the production of water in the cathode, which increases the conductivity of the electrolyte by increasing the amount of free phosphoric acid compared to its less conductive dehydration products (mainly pyrophosphoric acid $H_4P_2O_7$) [13] in the electrodes (especially the cathode) and the membrane. After 3 hours of operation, the current was turned off. The instantaneous increase of the 'ohmic resistances' indicates a more or less reversible hydration / dehydration process. Indeed, it takes the resistances about 1 hour, to reach steady state values during the dehydration process under OCV conditions. A simple explanation for the much faster hydration process is the *in situ* water production at the cathode, compared to the slow removal of water by diffusion processes in case of dehydration process. The steady state values of the 'ohmic resistances' under OCV conditions exhibit a significant increase with rising air flow rate. This effect is even more pronounced if hydrogen flow rate is also enhanced. These results are consistent with the idea of a dehydration process, which should be promoted by increased gas flow rates at both electrodes.

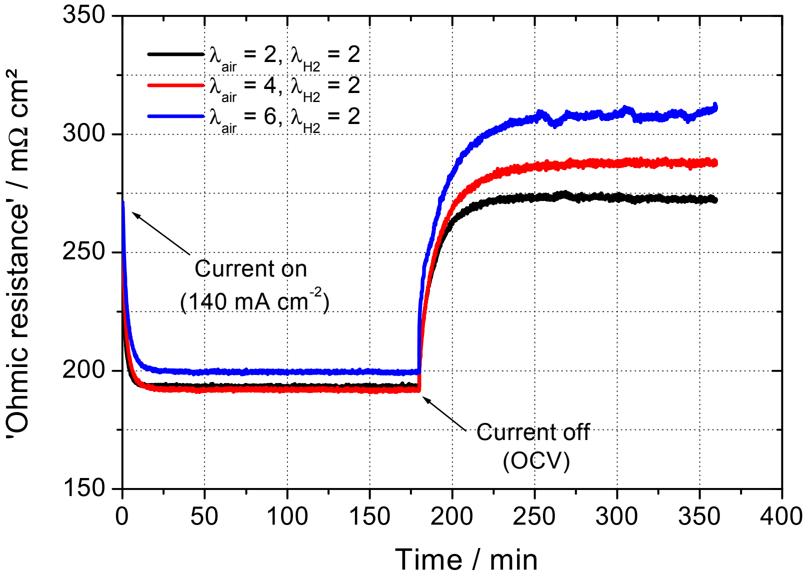

Figure 1: Time dependence of the cell resistance after changing the current density from j = 0 to 140 mA/cm^2 and *vice versa* at 160 °C; Variation of λ_{air} = 2/4/6; λ_{H_2} = 2 (constant).

Besides current density and gas flow rates, cell temperature and humidity of supplied gases should play an important role in the hydration / dehydration process. In future experiments, the influence of these parameters has to be investigated in more detail. First measurements with humidified fuel gas reveal a reversible 10% decrease of the ohmic resistance in presence of 5 vol.% H_2O in H_2 compared to dry hydrogen. This result supports again our reasoning based on a reversible hydration / dehydration process.

After each time dependent measurement, impedance spectra were recorded under OCV conditions in the frequency range of 0.01 Hz to 10 kHz. Fig. 2 shows a Nyquist plot of the MEA impedance at different flow rates of air and hydrogen. The indicated air and hydrogen stoichiometries refer to the corresponding flow rates at a current density of 140 mA/cm². Measured values are marked by closed symbols and fit data are indicated by lines and open symbols. The fit values were obtained by using the equivalent circuit shown in Fig. 2. The measured values and selected fit data are summarized in Table 1.

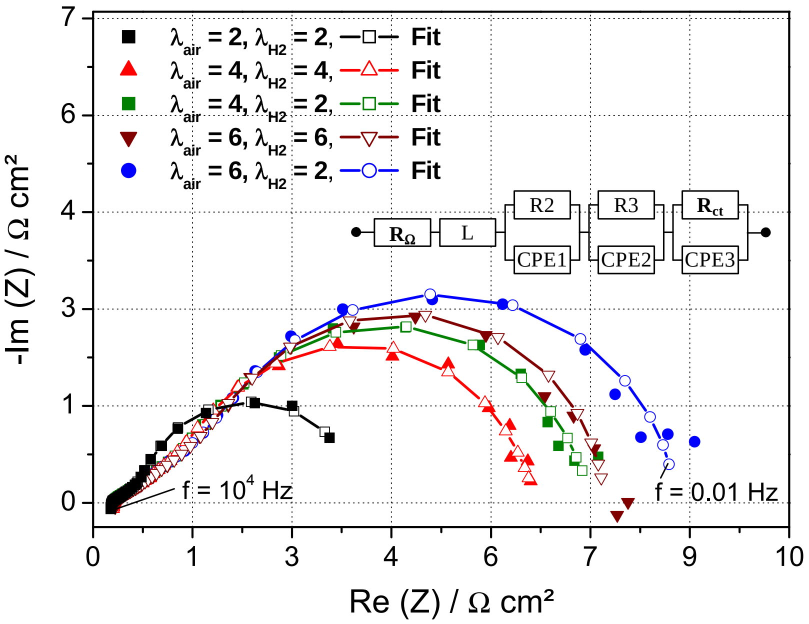

Figure 2: **Nyquist plots of the MEA impedance under OCV conditions; T = 160 °C; Variation of λ_{air} / λ_{H_2}; measured values: closed symbols, fit values: lines and open symbols; frequency range: 10^{-2} – 10^{4} Hz; AC amplitude: 10 mV.**

Table 1: **Ohmic/ charge transfer resistances obtained from impedance measurements (see Figs. 1&2).**

λ_{air} / λ_{H_2}	'Ohmic resistance': Re(Z) @ -Im ≈ 0 / mΩ cm²	Impedance Spectra: Re(Z) @ -Im = 0 / mΩ cm²	Fit of impedance spectra: $\tilde{R}_{\Omega}$ mΩ cm² Fit Code: $R_{\Omega}L(R_2Q_2)(R_3Q_3)(R_{ct}Q_4)$	Fit of impedance spectra: $\tilde{R}_{ct}$ mΩ cm²
2 / 2	272	272	248	3010
4 / 2	289	288	252	4360
4 / 4	306	307	263	4020
6 / 2	311	307	267	6440
6 / 6	333	336	289	5360

In a first approximation, limiting mass transport processes under OCV conditions and limitation of hydrogen reaction rate can be neglected. Under these assumptions, the large semi-arc at medium and low frequencies (see Fig. 2) is mainly attributed to the charge transfer resistance, R_{ct}, of the oxygen exchange reaction. If air flow rate is enhanced (λ=2 to λ=6) at constant hydrogen flow rate (λ=2), R_{ct} increases from 3.0 to 6.4 Ωcm^2 (see Table 1 & Fig. 2). Interestingly, this effect is slightly diminished, if hydrogen flow is also increased, i.e. hydrogen and air stoichiometries are equal: In this case, R_{ct} increases from 3.0 to only

5.4 Ωcm^{-2} (see Table 1 & Fig. 2). On basis of the results presented here, the following tentative explanation may be given: If air flow rate is increased, the water content of the MEA decreases and the amount of pyrophosphoric acid in the equilibrium between $2\ H_3PO_4 \leftrightarrow H_4P_2O_7 + H_2O(g)$ increases. For this reason, the proton conductivity of the MEA decreases, causing a decrease of catalytic activity especially in the outer part of the cathode. Because the solubility of oxygen in H_3PO_4 is much lower than in water [14], the oxygen concentration nearby the platinum catalyst decreases, in spite of the higher air flow rate. Both effects decrease the exchange current density of the oxygen equilibrium reaction and thus increase the charge transfer resistance, R_{ct}, as observed. By increasing the hydrogen flow rate, more hydrogen permeates from the anode through the membrane to the cathode. Although hydrogen 'consumes' a part of the oxygen which is present at the cathode, the increased formation of water causes a much better solubility of oxygen and a more thorough wetting of the inner surface of catalyst layer, leading to an enhanced oxygen concentration respectively a higher activity of the cathode. Hence, the exchange current density of the oxygen equilibrium reaction increases and R_{ct} decreases.

4 Conclusions

It turns out, that time dependent measurements of cell impedance at different operating conditions are crucial since they provide a valuable insight into the hydration / dehydration processes of HT-PEFCs. We attribute the fact that high water production by the fuel cell reaction, high water insertion, and its low removal by the gas flows (i.e. the water content in the cell) lowers the ohmic resistance to the increasing amount of mobile H_3PO_4 in the electrolyte. The hydration process is fast because of the water production inside the cathode, compared to the slow removal of water by diffusion processes through the gas diffusion layer into the channel. In general, ohmic resistances become small when (a) the current density is increased, (b) the gas flows are reduced, (c) the cell is run at elevated temperatures, and (d) when the fuel gas is humidified. Furthermore, the hydration / dehydration processes are believed to influence the local distribution of free phosphoric acid in the cell and thus local physico-chemical properties of the HT-PEFC, like proton conductivity, oxygen gas solubility, and inner active surface of the electrodes. For future studies, it is therefore important to investigate the local distribution and composition of the phosphoric acid electrolyte depending on the operation conditions of HT-PEFC in more detail.

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