IN-PLANE RESOLVED IN-SITU MEASUREMENTS OF THE MEMBRANE RESISTANCE IN PEFCs

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ABSTRACT

The in-situ resistance of Nafion® membranes with different thickness was measured in H2/O2 fuel cells as function of current density and gas humidity. The resistance distribution across the thickness of membranes was determined by using membranes composed from several thin sheets with interlaying thin gold wires as potential probes. The same method was used to measure the resistance at different in-plane locations (i.e. at gas inlets and outlets). It was found that with increasing current density the resistance at the anode side of the membrane is increasing. When oxygen was fed dry, then complex in-plane patterns of membrane hydration distribution were observed.

INTRODUCTION

Polymer Electrolyte Fuel Cells (PEFCs) are a promising candidate as power plant for many future applications [1]. In this type of fuel cell, a thin organic proton exchange membrane plays the dual role as electrolyte and gas separator. Per-fluorinated polymer membranes from DuPont de Nemours (Fayetteville, USA) sold under the trademark of Nafion® are the most common membrane materials used in PEFCs. Only after swelling with water the membrane becomes a reasonable proton conductor (= 10 Ωcm at 20 °C) because the membrane bulk separates in at least two phases, a hydrophobic phase containing the backbone and hydrophilic phase containing the sulfonic acid groups and water [2]. In the fuel cell application the protons move through the hydrophilic membrane phase from anode to cathode.

A low electrolyte (membrane) resistance is one of the key parameters for attaining high power densities in PEFC. The specific resistance of the membrane-electrolyte is determined by the concentration of the charge carrier (proton) and its mobility. The most
important parameter for the mobility of the protons in the membrane is its water content [3], often expressed as \( \lambda = \) number of \( \text{H}_2\text{O}/\text{SO}_3\text{H} \). In the range \( \lambda = 1 \) to \( \lambda = 20 \) the specific conductivity varies by more than an order of magnitude. The proton mobility is also influenced by the temperature, but in the operating range of PEFCs of 20 to 80 °C, the variation of the water content has a much stronger influence on the membrane resistance than the variation of the temperature.

A high water content of the membrane in the fuel cell is therefore of importance for attaining high power densities. Hence, the water management of the fuel cell, aiming at retaining the highest possible water content in the membrane is one of the most critical operating aspects. To understand the phenomena of membrane water content during fuel cell operation research was carried out investigating the ex-situ membrane properties like water-sorption [3-5], water-diffusion [6] and ex-situ conductivity [3, 7-9] under well controlled conditions. Model calculations [10-13] have given insight into the complex water management of PEFCs where for the determination of the membrane water content additional parameters, such as current density, dew-point of gases on cathode and anode side, mass-transport in the electrodes, and gas-crossover have to be accounted for. It was established, that the water distribution in the membrane is determined on the one hand by the osmotic drag of water from the anode to the cathode and on the other hand by the back transport of water to the anode.

In earlier work we have investigated the resistance of Nafion® 117 in-situ as function of different operating conditions and found, that the resistance increases considerably with current density [14]. However, no efforts have been made to localize the increase of the resistance and the corresponding water loss within the membrane. I.e., the nature of the evolving water profile with current density was not investigated. In order to elucidate the membrane hydration profile Watanabe et al. [15] have performed experiments with very thin layers of recast Nafion (ca. 15 \( \mu \text{m} \)) and interlaying Pt-wires as potential probes. In contrast to our previous measurements they have found a decreasing membrane resistance with current density [15]. Using very thick membranes Bellows et al. [16] have recently used neutron scattering and detected a decrease of the water content at the anode with increasing current density.

In this study we present data for the resistance- and water-content distribution across the thickness and in-plane of membranes in PEFCs with respect to current density and gas humidity.

EXPERIMENTAL

The Nafion® membranes (N112, N115, N117, N105) were pretreated by heating for 1 hour in half concentrated nitric acid, subsequent washing with pure water (18 MΩ, from Seralpur C90 System) and then boiling for 1 hour in water. The membranes were...
stored in pure water in the dark. The membrane thickness was measured in the swollen state using a digital thickness gauge (Heidenhain). The following thicknesses were obtained for the swollen membranes, which have, after the described pretreating procedure, a water content of $\lambda=21-22 \text{ H}_2\text{O}/\text{SO}_3\text{H}$: \begin{itemize} 
  \item N112: 58 - 62 $\mu$m; 
  \item N115: 145 - 150 $\mu$m; 
  \item N117: 200 - 205 $\mu$m; 
  \item N105 ($\lambda=27-28$): 160 - 165 $\mu$m. 
\end{itemize} For fuel cell experiments ELAT-electrodes from E-Tek (Natick, USA) with a Pt-loading of 0.6 mg/cm$^2$ (20% Pt on C) have been used. To extend the three phase boundary the electrodes were impregnated (0.6 - 0.7 mg/cm$^2$ dry mass) with solubilized Nafion (1100 EW, Solution Technology, USA).

Stainless steel fuel cells with 1-dimensional geometry [14] (the gases are fed from the back of the current collector) and cells with a graphite channel-type flow field (channel length 370 mm), both with an active area of 28 cm$^2$ were used. In cells with multiple Nafion$^\circledR$ membranes, a 25 $\mu$m gold wire was placed as potential sensor in between the individual membrane sheets. For some experiments more than one gold wire was placed between two membrane sheets at different locations.

The resistance of the membranes was measured \textit{in-situ} by the auxiliary current pulse technique [14, 17]. With this technique very fast 5A-pulses are injected into the cell and the voltage change at the end of the pulse is measured in a 1 $\mu$s time window. This procedure allows for accurate membrane resistance measurements over the entire current density range. In multiple membrane cells, a fast 4-channel digital oscilloscope (LeCroy 9304) was used to measure simultaneously the voltage change at the end of the current pulse of the entire cell and in-between the gold wire potential probes and the anode. The resistance of the individual membranes was then calculated from the differences of the respective voltage changes. The average water content of an individual membrane sheet was calculated from the resistance by comparison to the \textit{ex-situ} determined resistance, using impedance spectroscopy, of membranes with known water content [9].

\section*{RESULTS AND DISCUSSION}

\subsection*{1-Dimensional Cell}

In the 1-dimensional cell (variation in the direction of the membrane thickness, 1-D) [14], the gases are homogeneously fed from the back of the current-collector to the entire active area. Unlike in cells where the gases flow along the backside of the electrodes humidity, gas composition, temperature, current-density, and membrane resistance are therefore homogeneous over the entire active area.

The membrane resistances as function of current-density @ at 60 °C for 1100 EW Nafion$^\circledR$ membranes of different thickness are shown in Figure 1. Except for the cell with a single N112 membrane an increase of the membrane resistance with current...
density is observed. This increase is a strong function of the membrane thickness. The thicker the membrane in the fuel cell, the stronger is the increase of the resistance with current density. In the current density range from 0 to 0.5 A/cm², the increase of the resistance for the cell with a N115 membrane (= 150 μm) is 8 mΩcm² (ca. 5 %) for the cell with 4x N112 membranes (= 240 μm) it is 55 mΩcm² (25%) and for the cell with 2x N117 membranes (= 400 μm) it is approx. 130 mΩcm² (35 %).

The results displayed in Figure 1 reveal only the resistance of the entire membrane. It is now interesting to investigate how the increase of the resistance is developing across the thickness of the membrane. This can be measured in cells with multiple N112 membranes, as the resistance of every individual membrane can be measured separately. Figure 2 displays the resistance of the individual N112 membranes in a cell with 4 membranes at 60 °C as a function of current density. For 3 of the membranes the open circuit resistance is fairly close in the range of 60 - 70 mΩcm². For one of the membranes (the third one, counted from the anode side) the open circuit resistance is only about 40 mΩcm². We observe such differences for the membrane in the center in most multi-membrane cells. Probably this difference has a geometric explanation: with a diameter of 25 μm the potential sensing wire has a non negligible size as compared to the thickness of the individual membranes, with a swollen thickness of 58 - 62 μm each.

![Figure 1](image_url)

**Figure 1**: In-situ resistance of Nafion® membranes (in 1-D cell) with different thickness as function of current density at 60 °C. The thicknesses and nature of the membranes are as indicated.
Figure 2 : Resistance of the individual N112 sheets, in a H₂/O₂ fuel cell (1-D) with 4 sheets, as function of current density at a cell temperature of 60 °C.

Figure 3 : Resistance of Anode side Nafion® 112 membrane sheet, in cells (1-D) with 2, 3, and 4 N112 membranes, and 2 N117 & 2 N112 membranes as function of current density. Cell temperature 60 °C.
A further indication that the difference is of geometric nature, is that the difference remains unchanged even after the cell has been operated for a considerable time (3 hours) at zero current and humidified gases are fed on both sides. Due to this geometric uncertainties the resistance data do not provide accurate absolute resistance values of the individual membranes. However, changes in the resistance can be measured accurately and are significant.

The only significant resistance change, as function of current density, is observed for the anode side membrane. In fact, the entire increase of the resistance, observed for the fuel cell with 4 N112 membranes takes place within the anode side membrane. The resistance of the anode side membrane is increasing by more than a factor of 2 for the current density increase from 0 to 0.7 A/cm². The resistance of the other three membranes is not changing significantly.

The observation that the resistance is confined to anode side is valid for all multi-membrane cells measured (2, 3, 4 x N112). However, as expected from the thickness-dependence of the resistance increase in Figure 1 and as shown in Figure 3 (resistance of anode side membranes in cells with 2, 3, and 4 N112 membranes, and 2 N117 & 2 N112 membranes), the extent of the increase is a function of total membrane thickness. The thicker the total membrane in the fuel cell, the stronger is the increase in resistance observed at the anode side.

![Figure 4: Resistance of N115 and N105 membranes in H₂/O₂ fuel cell (1-D) as function of current density at 60 °C.](image)

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Figure 4 shows the membrane resistance as function of current density for the N115 and N105 membranes. The two membranes have approximately the same thickness (148 µm and 155 µm, respectively) but due to the lower equivalent weight, N105 has a considerably higher water content after swelling in water of $\lambda(N105) = 25 - 26$ vs. $\lambda(N115) = 21 - 22$. Due to the higher water content N105 has a lower protonic resistance at zero current, $r_{N105} = 130 \text{ mQcm}^2$ and $r_{N115} = 145 \text{ mQcm}^2$ at 60 °C. From these resistances membrane water contents of $\lambda(N105) = 21 - 22$ and $\lambda(N115) = 13 - 15$ respectively may be calculated by comparison to ex-situ measurements [9]. No increase of the membrane resistance is observed for N105 up to 1.0 A/cm². The small decrease in resistance with current density is attributed to an increase in cell temperature at the higher current densities.

The above observations of the dependence of the membrane resistance as function of current density on the membrane thickness and on the equivalent weight may be explained by the following hypothesis: The transport of water back to the anode is the limiting mechanism of water transport in the membrane. Therefore in thicker membranes the anode needs to dry more (having a higher resistance) to provoke a sufficient water gradient for the transport of water back to the anode in the steady state.

For the transport of water back to the anode two mechanisms are possible: (i) solution-diffusion [10-13] and (ii) convection [19]. The steep gradients in water concentration at the anode side of the membrane and the dependence on the equivalent weight (which is in fact a dependence on the water content of the membrane) require a model in which the water transport is strongly dependent on the local membrane hydration. This is true for the model based on convection of water in the nano-pores of Nafion® and D'Arcy's law [19]. The solution-diffusion models do not predict the observed phenomena correctly. If the experimental results would have to be explained by diffusion, then the water diffusion coefficient $D_{\text{H}_2\text{O}}$, needed to be strongly dependent on $\lambda$ as reported i.e. in [17]. But this dependence is not implemented in the diffusion models.

Quasi 2-Dimensional Cell

In cells with a gas flow field, in which the gases flow along a channel along the surface of the electrode backing, volume flow, temperature and humidity of the gases vary along the flow path. Therefore differences in membrane hydration also occur with respect to the in-plane location of the MEA. With respect to the width of the channel the parameters in the MEA is assumed to be homogenous, therefore the cell is quasi 2-D.
The membrane resistance of a cell with two Nafion® 117 membranes was measured at the gas-inlets and gas-outlets as shown in the upper part of Figure 5. In case both gases are humidified to a dew-point which is at least as high as the cell temperature, the MEA is in a well humidified condition. As shown in the lower part of Figure 5, the hydration of the anode and cathode side membranes are similar at both ends of the channel when no current is drawn form the cell. A constant membrane hydration of approximately 12 - 14 H₂O/SO₃H is calculated from the resistance measurements. When a current of 0.5 A/cm² is drawn from the cell, then the anode side membrane is drying and an average water content of 8 - 9 H₂O/SO₃H is observed. At the cathode side of the membrane no changes in hydration are detected. No significant differences of the membrane hydration between the gas-inlets and gas-outlets are observed, indicating, that the membrane hydration is uniform over the entire active area under these well humidified conditions.

When oxygen is fed dry at a volumetric flow rate (stoich.(O₂)=10) which is representative for operation with air, then a more complex membrane hydration behavior may be observed, as shown in Figure 6. At the ending of the channel, where oxygen is entering dry, the membrane at the cathode side is dry (λ ≈ 6). The anode side membrane in this location however is well humidified (λ = 20). Probably because of the strong water gradient across the membrane, water is diffusing readily into the anode side membrane from the hydrogen gas phase. At the other end of the channel humidified hydrogen is entering and the oxygen has become humid due to the product water. Therefore at this end of the channel the difference in membrane water content is less.

![Figure 5](image-url)
Again when current is drawn from the cell the major change is observed in the anode side membrane, which becomes dryer as observed in the 1-D cell and in Figure 5.

This experiment shows clearly, that when the cell is operated with dry oxygen and as a consequence the membrane is not in a well humidified condition, then gradients of membrane hydration across the active area evolve.

Figure 6: Profile of hydration of the anode and cathode side membranes along the channel length (dotted line at 0 A/cm²; solid line at 0.5 A/cm²) at T_{cell} = 60 °C, hydrogen humidified at 80 °C and oxygen dry. Stoich.\( \text{O}_2 \) =10, stoich.\( \text{H}_2 \) =6.

CONCLUSIONS

The resistance of Nafion® membranes in PEM fuel cells was investigated. Experiments with multiple membranes have shown that the resistance increase (and corresponding water loss) is confined to the anode side of the membrane when current is drawn from a well humidified cell. If the cell is well humidified, then the hydration of the membrane across the active area is uniform. However, in case the reactant gases are not fully humidified, then a complex water distribution in the membrane over the active area of the fuel cell is observed. The quantitative understanding of this observation will need more work of locally resolved resistance measurements within the active area of the cell.

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