Investigation of Mass Transport Losses in Polymer Electrolyte Electrolysis Cells

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In polymer electrolyte electrolysis cells different processes contribute to the losses with increasing current. While the contribution of the ohmic overpotential is well characterized and can easily be determined by measuring the high frequency resistance of the cell, the kinetic and mass transport losses are more difficult to characterize and understand.

For determining the mass transport losses, also the kinetic losses need to be characterized, which needs careful analysis in particular when pressure varies over a wide range. The dependence of the mass transport losses is determined as function of the structures employed as current collectors, i.e., possible two-phase phenomena in the porous structures as well as for different operating conditions with respect to pressure and temperature. The results show that over a wide range of current densities a quite significant part of the voltage losses can to be attributed to mass transport.

Introduction

In order to prevent curtailment (1), polymer electrolyte water electrolysis cells (PEECs) are used for storing excess electric energy from renewable sources in hydrogen and oxygen.

In the energy storage application, efficiency of the processes is of particular concern, not to waste precious renewable power. PEECs allow operation up to current densities around 5 A/cm$^2$, however with increasing current density also voltage losses increase. Similar as in fuel cells, different processes contribute to the voltage losses. While the contribution of the ohmic overpotential is well characterized and can easily be determined by measuring the high frequency resistance of the cell (2), the kinetic and mass transport losses are more rarely investigated and more difficult to separate.

At the anode, mass transport takes place in a counter-flow regime where liquid water is transported in the porous structure of the titanium current collector from the channel to the catalyst layer and gaseous oxygen in the opposite direction. It is documented that the structure of the current collector has an influence on the polarization of the cell (3-5), however it is not well understood, what are the influential parameters.

Furthermore, the pressure dependence of the cell voltage often shows an unexpected behavior: with many operating conditions and material combinations, no distinct cell voltage increase is observed with increasing operating pressure. This is a thermodynami-
cally unexpected behavior, because the increase in thermodynamic cell voltage with gas pressure needs to be compensated by reducing either mass transport or kinetic losses.

In this work we carry out experiments to better understand the losses in the electrolysis cell as function of current density and pressure. Experiments are performed with current densities up to 5 A/cm² and 100 bar pressure. The polarization data are then analyzed for the thermodynamic voltage changes and the overpotentials are evaluated for the contributions of the ohmic, kinetic and mass transport losses.

**Experimental**

Experiments have been made with commercial catalyst coated membranes based on Nafion 117 (Greenerity™ E400, SolviCore, D) with an active area of 4 cm². Current collectors from sintered titanium powder (SIKA-T10, GKN Sinter Metals Filters, D) with a thickness of 2 mm and an average pore diameter of 10 µm have been used.

In the anode and cathode loop gases are separated from liquid in gas separators. At the anode the water is circulated by a membrane pump. Temperature control was thus performed by regulating the water inlet temperature at the anode side, which was recirculated with a volume flow of 30 mL·min⁻¹·cm⁻². The cell temperature, used for temperature control, is measured close to the active area in the cell housing, but not directly on the MEA.

Current voltage curves were measured from low to high current with holding time of 10 s at each point using a DC power supply (E3633A, Agilent). The high frequency resistance (HFR) of the cell was measured concurrently at 1 kHz (Model 3566, Tsuruga, J) to obtain the iR-free cell voltage. From the Tafel plot of the iR-free voltage, mass transport losses were obtained as the deviation from the extrapolated voltage of the points below 30 mA/cm². Kinetic losses finally were assumed to be the difference between the Tafel line and the equilibrium cell voltages at the respective operation conditions.

Hydrogen crossover was measured (0.3 mA·bar⁻¹·cm⁻²) using a current compensation technique (6). The total Faraday losses due to crossover were calculated assuming that oxygen crossover rate is half of that of hydrogen (7) and complete recombination at the cathode.

**Results and Discussion**

The voltage of the electrolysis cell can be defined according to equation [1] as the sum of the thermodynamic voltage $E^0(p,T)$ and the three main overpotentials processes:

$$E = E^0(p,T) + R \cdot j + b \cdot \log(j) + \eta_{mtx}$$  \[1\]

where the second term denotes the ohmic, the third term the kinetic and the fourth term the mass transport overpotential, respectively. In equation [1] the thermodynamic cell voltage $E^0(p,T)$ is calculated from the Nernst equation:
with \( a \) denoting the activity of the species and \( E^0(T) \) representing the approximately linear temperature dependent (8) equilibrium potential as:

\[
E^0(T) = \frac{\Delta G}{2F}
\]  

Then clearly the activity of the gaseous species can be defined according to their partial pressure divided by the standard pressure (assuming ideal gas behavior). For liquid water generally an activity of one is assumed, even if it also changes when the pressure in the cell is increased. It is not obvious that the assumption of using a constant activity for water is reflecting the real physics. Table I shows the calculated thermodynamic equilibrium cell voltage increases for different assumptions of water activity and cell pressure.

### TABLE I. Change of Nernst voltage in [mV] of a water electrolysis cell at 50 °C for a pressure increase of a factor of 10, for different assumptions. For the case of “Hydrogen pressure only”, the activity of oxygen is assumed as unity.

<table>
<thead>
<tr>
<th>Activity of liquid water</th>
<th>Balanced Pressure</th>
<th>Only Hydrogen Pressurized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unity (( a=1 ))</td>
<td>48.1</td>
<td>32.1</td>
</tr>
<tr>
<td>Function of pressure (( a=p ))</td>
<td>16.0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1 shows the polarization curves for 1, 30 and 100 bar balanced gas pressures at 50 °C. For low current densities, the expected influence of pressure is observed (see lower inset in Figure 1). Interestingly, at higher current densities, the cell voltage is not increasing with pressure (see also upper inset in Figure 1).

According to Table I for the pressure increase of two orders of magnitude, from 1 to 100 bar, a cell voltage increase of the balanced pressure cell between 32 to 96 mV would be expected, based on the change of the Nernst voltage and the definition of the activity of liquid water. The thermodynamically unexpected behavior of the cell voltage has also been reported in other work (9-11).

The fact that the cell voltage is not increasing with gas pressure at high current densities needs to be interpreted that the undisputed thermodynamic increase of the cell voltage must be compensated by a decrease of one of the overpotentials defined in equation [1]. The ohmic overpotentials may be easily calculated from the HFR of the cell. As shown in Figure 2a, HFR is about constant, slightly decreasing with the current density and is independent of the gas pressure. The decrease of the HFR can be attributed to an increase in cell temperature due to heat production at high current densities.
Since measuring the actual cell temperature directly in the catalyst layer or membrane is challenging, it is possible to estimate the temperature increase due to the waste heat production, using an Arrhenius approximation. The HFR, measured at 1 A/cm² at different temperatures can be plotted vs. the inverse temperature, see Figure 2b. Using this Arrhenius plot a temperature increase in Figure 2 a) can be estimated to be about 18 °C for current densities at 5 A/cm².

When the iR-free polarization curves are plotted semi-logarithmic vs. the current density, the so called Tafel plot is obtained. For the ideal case without any transport
resistance and with a pressure independent electrochemical reaction mechanism, linear Tafel lines are predicted to be shifted to higher cell voltages, according to Table I for the balanced pressure case, by 16 to 48 mV per order of magnitude. For the pressure increase from 1 to 100 bar a shift of 32 to 96 mV is expected at 50 °C.

Figure 3 shows the experimental Tafel plots. For current densities below about 30 mA/cm², indeed a linear behavior is noted, while at higher current densities a voltage increase is observed which is attributed to mass transport. The mass transport losses increase from about 70 mV at 0.5 A/cm² to over 250 mV at current densities above 2 A/cm². Above 3 A/cm², the transport losses do not increase significantly, anymore.

![Figure 3: Tafel plot of the iR-free voltage at 50 °C for 1, 30 and 100 bar balanced pressure operation. Mass transport losses are defined as the voltage difference between Tafel lines and experimental points.](image)

It is evident, and somehow surprising, that the transport losses are independent of pressure. Though it is not clear what are the underlying effects for the losses, it may be speculated that this is in some form due to the two-phase behavior in the current collector and/or catalyst layer.

Therefore most of the changes in overpotential as function of pressure seem to originate from catalyst kinetics. In the linear section of the Tafel lines between 5 and 30 mA/cm² a separation of the lines between 1 and 100 bar of less than 50 mV is observed. This leads to the conclusion that either the activity of liquid water does not stay constant at unity, or a more complex, pressure dependent electrochemical reaction mechanisms takes place, than assumed.

A reduction of the slope of the Tafel line is observed with increasing pressure. Figure 4 shows that in the pressure range between 1 and 100 bar, the slope is decreasing linearly with the logarithm of pressure. When considering the Tafel equation as:

\[
\eta = a + b \log \left( \frac{i}{i_0} \right) \quad \text{with} \quad i_0 = r_f \cdot i_{0,5} \quad \text{and} \quad b = \frac{2.3RT}{\alpha F} \quad [4]
\]
where $\eta$ is the overpotential, $i_0$ the apparent exchange current density which depends on the specific exchange current density $i_{0,S}$ (in terms of A/cm$^2$ of catalyst surface) and $r_f$ the roughness factor. $\alpha$ is called transfer coefficient, a term depending on the mechanism of the electrochemical reaction. In the simple Tafel model approach the only open parameter affecting the slope is this transfer coefficient $\alpha$, a change of which would mean that the reaction mechanism is influenced by pressure. With the oxygen evolution reaction being a series of complex steps, this cannot be decided based on this simple analysis.

However, it may be speculated that increasing the pressure of about two orders of magnitude may have an influence on the oxygen desorption process and the gas bubble formation at the surface of the commonly used porous catalysts. No more detailed interpretation can be given at the time, more investigations are necessary.

Even if the mechanism of the oxygen evolution reaction on pressure is not well understood, the contribution of the mass transport losses to the total overpotential is considerable. In Figure 5 the relative contributions of the different losses according to equation [1] as well as the Faraday losses due to gas crossover are plotted as function of current density for 1 and 100 bar balanced pressure. Even if the mass transport losses are almost independent of pressure (see Figure 3), the relative contribution increases slightly with increasing the pressure due to lower kinetic losses as a result of higher thermodynamic voltages, according to equation [2]. Figure 5 shows that above of 1 A/cm$^2$ mass transport losses contribute between 20 and 25 % to the total overpotential, both for 1 and 100 bar. The Faraday losses due to crossover are important at current densities below 1 A/cm$^2$ and high pressure.
Figure 5: Analysis of data shown in Figure 1: relative contributions of kinetic, ohmic, mass transport and Faraday losses at a) 1 bar and b) 100 bar for a thermodynamic voltage of 1.208 and 1.304 V (assuming unity for the activity of liquid water).

In the commercially interesting operating range of 1 to 2 A/cm$^2$, the ohmic losses contribute 20 to 35% and become even more dominant when further increasing the current density. This ratio is obviously influenced by the membrane thickness, and would be lowered by using a thinner membrane, at the expense of a higher gas crossover.

**Conclusions**

The voltage of the electrolysis cell can be defined as the sum of the thermodynamic voltage $E^0(p, T)$ and the overpotentials of the three main losses (i.e. kinetic, ohmic and mass transport). The experimental data show that in the range between 1 and 100 bar, the cell voltage is almost independent of pressure. The analysis of the data reveals that because the ohmic losses are independent of pressure the sum of mass transport and kinetic losses need to decrease with increasing gas pressure, because the thermodynamic voltage increases. A Tafel plot analysis shows that it is rather the kinetic losses which decrease with increasing pressure than the mass transport losses.

The present results show that in the commercial operating range of 1 to 2 A/cm$^2$, mass transport losses contribute between 20 and 25% of the total overpotential, both for 1 and 100 bar. It is therefore of interest to further investigate these losses, i.e. as function of temperature, pressure (difference), catalyst layer and current collector structure. A more thorough interpretation of the losses as function of pressure will require more detailed data, i.e. from electrochemical impedance spectroscopy or other diagnostics.

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References