Electrochemical Impedance Modeling of the Proton Conducting Membrane in a PEFC

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ABSTRACT

An electrochemical impedance spectroscopy (EIS) model for water transport in the membrane in a polymer electrolyte fuel cell has been developed. Simulations show that an electrolyte can give a semi-circle in EIS if the resistivity or water concentration changes with current density. The magnitude of the loop is the sum of $i\cdot dR/di$ and $dE_{conc}/di$, where $E_{conc}$ is the potential difference associated with the difference in water concentration between the anode and cathode side. The loop is capacitive for a positive sum and inductive for a negative sum. The characteristic frequency is proportional to the effective diffusivity of water and inversely proportional to the square of the membrane thickness. The model is based on the concentrated electrolyte theory, but similar results have also been obtained with a model for a diluted electrolyte. The influence of $E_{conc}$ is, however, omitted.

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a very powerful tool for elucidation of rate limiting processes in polymer electrolyte fuel cells (PEFC). However, it can sometimes be difficult to distinguish between different processes. Experimental measurements of the EIS on the PEFC working with pure oxygen usually give one semi-circle, resulting from the coupling of the kinetics to the double layer capacitance. Limitations from oxygen diffusion and proton migration in the electrode can also influence the magnitude of the semi-circle. When the cathode gas is diluted with for example nitrogen, a second low frequency loop can appear due to diffusion limitations in the gas diffusion layer. A low frequency loop has, however, also been seen experimentally when pure oxygen has been used [1-3]. Freire et al. [1] studied the impedance with different thickness of the membrane and at different humidities and cell voltages. A low frequency capacitive loop was seen for ambient temperature of the cell and the humidifiers, or when using dry hydrogen, at low cell voltages. This loop was seen with Nafion 117 (180 μm thick), but not with Nafion 112 (50 μm thick). They proposed that this loop was due to flooding of the cathode or water transport in the membrane. Paganin et al. also saw an increasing low frequency loop for increasing thickness of the membrane and assigned this to water transport in the membrane.
Water is transported through the membrane by different processes. When a net current is applied, water is transported from the anode to the cathode by electro-osmotic drag. This gives rise to a gradient in water activity and a resulting back transport of water. The mechanism of this back transport has been modeled as diffusion due to concentration gradients [4-11], as a convective flow due to gradients in the hydraulic pressure [12,13] or as a combination of both processes [14]. Diffusion has been modeled as in a diluted electrolyte with Fick's law [4-6] or as in a concentrated electrolyte [7-11] using Stefan-Maxwell's equation. With the concentrated electrolyte theory, pressure gradients can also be included in the electrochemical potential [11]. Models where only diffusion is taken into account have problems when the membrane is in contact with liquid water and there is no concentration gradient. Models with only hydraulic pressure fail when the water content is low.

Most models of water transport in the membrane are limited to steady state conditions. Chen et al [6] has, however, modeled the transient behavior of the water transport in the membrane as a diluted electrolyte. They showed that the characteristic time for the water transport and the resistance to reach steady state is in the range of 10 seconds. This time constant should be visible in EIS. In this study we propose a theoretical model for the water transport in the membrane that can give rise to a low frequency loop.

EXPERIMENTAL RESULTS

Measurements were performed with a small cell with an electrode area of 0.5 cm². The cell temperature was held constant at 50°C while the temperature of the humidifiers were changed to get different relative humidities. Pure H₂ and O₂ were passed through the cell at a flow rate of 100 and 50 cm³/min, respectively. The MEA used comprised a Nafion 1035 membrane and the electrode ink consisted of 30 wt% Nafion and 70 wt% Pt/C (ratio of 20 wt% Pt on C). The loading was estimated to about 0.2 mg Pt/cm². EIS was performed under galvanostatic control at frequencies ranging from 50 kHz to 5 mHz with an amplitude of 5% of the DC current. For further experimental details, see reference 3.

At low and moderate current densities EIS resulted in one semi-circle at 10² Hz from kinetics, double-layer capacitance and mass transport in the electrode. At high current densities a second low frequency loop appeared at 0.1 Hz, see figure 1. This loop increased with decreasing humidity and could therefore neither be attributed to O₂ diffusion in the gas backing, nor to diffusion in a water film in the active layer. In reference 3, the low frequency loop was instead assigned to water transport in the membrane.
Figure 1. Experimental impedance spectra obtained at 400 mA/cm² for incoming gases with a relative humidity of 75, 50 and 30%. The cell was operated with pure hydrogen and oxygen. The cell temperature was 50°C.

MODEL

In this study, we have chosen to model the membrane with the concentrated electrolyte theory, since it is the most general approach to describe mass transport and because the membrane is far from diluted. Similar results would, however, be obtained if the transport processes were described by the dilute electrolyte theory. This study is focused on the membrane and the response from the electrodes is assumed to be fast enough to be separated in frequency. It is also assumed that the membrane is isotherm.

In a polymer electrolyte membrane the concentrated electrolyte theory takes account for the interactions between protons and water, protons and sulphonic acid groups and between water and sulphonic acid groups. This can be described by a multicomponent diffusion equation, equation 1, similar to the Stefan-Maxwell equation [15].

$$c_i \nabla \mu_i = \sum K_{ij} (v_j - v_i) = RT \sum \frac{c_i c_j}{c_T D_{ij}} (v_i - v_j)$$  \[1\]
where \( c_i \) is the concentration of species \( i \), \( \mu_i \) is the electrochemical potential for species \( i \), \( K_{ij} \) is the friction coefficient of species \( i \) and \( j \), \( v_i \) is the velocity of species \( i \) and \( D_{ij} \) is the binary diffusion coefficient of species \( i \) and \( j \). The electrochemical potential gradient can be written as in equation 2 where \( \phi \) is the potential in the electrolyte, \( f_i \) is the activity coefficient of species \( i \) and \( z_i \) is the charge number of species \( i \). The total concentration, \( c_T \), is given by equation 3.

\[
\nabla \mu_i = RT \nabla \ln(f_i c_i) + z_i F \nabla \phi \tag{2}
\]

\[
c_T = \sum c_i = c_{H_2O} + c_{H^+} + c_{R SO_3^-} = 2c_{H^+} + c_{H_2O} \tag{3}
\]

To derive expressions for the water concentration gradient and the potential gradient in the membrane the velocity of the polymer with sulphonic acid groups is set equal to zero. It is also assumed that the proton concentration in the membrane is uniform and that the water activity coefficient is constant. The velocity of the protons can be expressed in terms of current density and proton concentration, equation 4, while the velocity of water can be expressed in terms of net water flux and water concentration, equation 5.

\[
v_{H^+} = \frac{i}{F c_{H^+}} \tag{4}
\]

\[
v_{H_2O} = \frac{N_{H_2O}}{c_{H_2O}} \tag{5}
\]

Equation 1 to 5 can now be combined to give the gradient of the water concentration, equation 6, and the electrical potential, equation 7.

\[
\nabla c_{H_2O} = \frac{i}{F} \frac{c_{H_2O}}{c_T D_{H^+H_2O}} - \frac{N_{H_2O} c_{H^+}}{c_T} \left( \frac{1}{D_{H^+H_2O}} + \frac{1}{D_{H_2ORSO_3^-}} \right) \tag{6}
\]

\[
\nabla \Phi = \frac{RT}{F} \left[ \frac{N_{H_2O}}{c_T D_{H^+H_2O}} - \frac{i}{F} \frac{1}{c_T} \left( \frac{c_{H_2O}}{c_{H^+} D_{H^+H_2O}} + \frac{1}{D_{H^+ORSO_3^-}} \right) \right] \tag{7}
\]

At the boundaries, the water concentration in the membrane is assumed to be in equilibrium with the gas phase. With this assumption the water profile and the net water flux through the membrane can be solved numerically with a Newton Raphson method.
Thereafter the potential profile can be calculated with the potential arbitrarily set to zero at the anode side.

**Impedance**

When a small AC-current is superimposed on the steady state current the water concentration, electric potential and net water flux will get a frequency dependent term, equation 8,

\[
i = i_{st} + i = i_{st} + i_{a} e^{j\omega t}
\]

\[
c_{H_2O} = c_{st} + c = c_{st} + c_{a} e^{j\omega t}
\]

\[
\Phi = \Phi_{st} + \Phi = \Phi_{st} + \Phi_{a} e^{j\omega t}
\]

\[
N_{H_2O} = N_{st} + N = N_{st} + N_{a} e^{j\omega t}
\]

where the variables with subscript st and a are the steady state solution and the complex amplitude of the perturbation respectively. \(\omega\) is the angular frequency and \(j\) represents the unit of imaginary numbers. To calculate the variations of the water flux a mass balance for water is used, equation 9.

\[
\nabla N_{H_2O} = - \frac{dc_{H_2O}}{dt} = - j\omega c
\]

When equation 6 to 9 are combined and linearised, a linear system of equations for the amplitude of the perturbation of water concentration, water flux and electrical potential is achieved, equation 10 to 12.

\[
\nabla c_{a} = c_{a} \left( \frac{2c_{H^+} i_{H^+}}{F(2c_{H^+} + c_{H_2O})} + \frac{N_{H_2O} c_{H^+}}{2c_{H^+} + c_{H_2O}} \left( \frac{1}{D_{H_2O}} + \frac{1}{D_{H_2O, ORSO}} \right) \right) + i_{a} \left( \frac{c_{H^+}}{F(2c_{H^+} + c_{H_2O})} - N_{H_2O} \frac{c_{H^+}}{2c_{H^+} + c_{H_2O}} \left( \frac{1}{D_{H_2O}} + \frac{1}{D_{H_2O, ORSO}} \right) \right)
\]

\[
\nabla N_{a} = - j\omega c_{a}
\]

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\[ \nabla \Phi_s = \frac{RT}{F} \left[ c_a \left( \frac{N_a}{(2c_{\text{H}^+} + c_a)^2 D_{\text{H}^+H_2O}} - \frac{i_a}{F(2c_{\text{H}^+} + c_a) c_{\text{H}^+} D_{\text{H}^+H_2O}} \right) \right. \\
+ \left. \frac{i_a}{F(2c_{\text{H}^+} + c_a)^2 \left( c_{\text{H}^+} D_{\text{H}^+H_2O} + \frac{1}{D_{\text{H}^+\text{RSO}_3^-}} \right)} \right] \\
+ N_a \left( \frac{1}{(2c_{\text{H}^+} + c_a) D_{\text{H}^+H_2O}} - \frac{1}{F(2c_{\text{H}^+} + c_a) c_{\text{H}^+} D_{\text{H}^+H_2O} + \frac{1}{D_{\text{H}^+\text{RSO}_3^-}}} \right) \]

The linear system of equations is solved assuming that the equilibrium between water in the membrane and in the gas phase is fast and that the water concentration in the gas phase is constant. This means that \( c_a \) is zero at the interface membrane-gas phase. The amplitude of the electrical potential is also set to zero at the anode. From this the electrochemical impedance, \( Z \), can be calculated from the potential amplitude at the cathode and the amplitude of the current density, equation 13, where \( L \) is the membrane thickness.

\[ Z = \frac{\Phi_s(x = L)}{i_a} \quad [13] \]

MODELLING RESULTS AND DISCUSSION

For steady state, a potential difference over the membrane as a function of current density can be modeled, see figure 2.

Figure 2. Modeled potential difference through the membrane vs. current density. The potential difference due to differences in water concentration between anode and cathode side and the iR-drop are marked.

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A small potential difference can be seen even at zero current if the humidities are not the same on the anode and cathode side. This potential difference, $E_{\text{conc}}$, can be expressed as in equation 14. The rest of the potential difference is the iR-drop. It can also be seen that the potential difference is not exactly linearly dependent on the current density, due to water drag.

$$E_{\text{conc}} = \frac{RT}{F} \left[ \frac{c_{\text{H}_2\text{O}}/c_{\text{H}^+}}{1 + \frac{D_{\text{H}^+\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}}} \right]_{\text{cathode}} - \left[ \frac{c_{\text{H}_2\text{O}}/c_{\text{H}^+}}{1 + \frac{D_{\text{H}^+\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}}} \right]_{\text{anode}}$$  

[14]

The EIS model for the same conditions gives one semicircle in a Nyquist plot, figure 3. The characteristic frequency for this semi circle, $\omega_{\text{ch}}$, is proportional to the effective diffusivity of water and inversely proportional to the square of the membrane thickness, equation 15. This gives a characteristic frequency in the order of 0.01-0.1 Hz, which corresponds well with the experimental data in figure 1 and with the modeled time constant from reference 6.

$$\omega_{\text{ch}} \propto \frac{2c_{\text{H}^+} + c_{\text{H}_2\text{O}}}{c_{\text{H}^+}} \frac{D_{\text{H}^+\text{H}_2\text{O}}}{D_{\text{H}_2\text{O}}} \frac{D_{\text{H}_2\text{O}}}{D_{\text{H}_2\text{SO}_4}} \frac{1}{L^2} = \frac{D_{\text{eff}}}{L^2}$$  

[15]

The magnitude of the impedance loop can be explained by studying the iR-drop and the slope of the iR-drop in figure 2. In figure 4 curve a is the resistance, $R$, calculated as in equation 16. It can be seen that this value is the same as the high frequency intercept in the Nyquist plot. Curve b is the slope of the polarization curve, $dE/di$, and has the same value as the low frequency intercept. The high and low frequency intercepts from the

Figure 3. A modeled Nyquist plot at the current density $i = 1\text{A/cm}^2$

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Nyquist plot in figure 3 are marked with stars in figure 4. In equation 17 the magnitude of the loop, $d$, is calculated. The magnitude of the loop is $i \cdot dR/di + dE_{conc}/di$. In the simulations presented in this work the concentrations at the boundaries has been assumed to be constant, resulting in that $dE_{conc}/di$ is zero. A more general case is discussed in a later paragraph. Therefore, the membrane will give a loop when there is a net current and the resistivity changes with current density. The loop can be either capacitive or inductive, depending on whether the resistance increases or decreases as a function of current density.

$$
R = \frac{E - E_{conc}}{i} \quad [16]
$$

$$
d = \frac{dE}{di} - R = \frac{d}{di}(E_{conc} + iR) - R = \frac{dE_{conc}}{di} + i \frac{dR}{di} + \frac{R}{di} - R
= \frac{dE_{conc}}{di} + i \frac{dR}{di} + R - R = \frac{dE_{conc}}{di} + i \frac{dR}{di} \quad [17]
$$

iR-correction can be used to elucidate the potential drop through the membrane and other pure resistances from the total potential drop. As seen from simulations the high frequency intercept from the membrane impedance gives the resistive part of the potential drop, $(E - E_{conc})/i$, which is the same resistance as is acquired by current interrupt. In ref 6, however, it has been claimed that the high frequency intercept from EIS gives $dE/di$ and can only be used for iR-compensation if $R$ and $dE/di$ are the same. In other words, when
the resistance is constant with current density. The current interrupt technique is said to be the only technique that can be used for iR-correction. However, from our simulations it is shown that if dE/di and R are not the same, a semicircle will appear with R as the high frequency intercept. So, contradictory to what is said in reference 16, EIS should give the same result as current interrupt. In both EIS and current interrupt the whole potential drop through the membrane cannot be achieved if there are different humidities at the anode and cathode, since there is a potential difference through the membrane due to the water concentration.

The simulations presented in this work have been limited to the case with constant water concentrations on the membrane boundaries. However, in a real fuel cell the water concentrations at the membrane boundaries depend on the current density. For example, water is produced at the cathode and dragged with protons from the anode. Simulations where the water concentrations in the gas channels changes with current density have been performed. These simulations show that the magnitude of the loop is still i·dR/di + dEconc/di. In this case Econc is not constant with current density and the membrane can give a loop even at zero current density. In this case the characteristic frequency can also depend on the rate of change of humidity in the gas channels and the loop is not necessarily a perfect semicircle. The binary diffusion coefficients have also been assumed to be constant. When concentration dependent diffusion coefficients are used the impedance loop becomes larger.

Similar simulations were also performed using the dilute electrolyte theory with a constant water diffusion coefficient and with water drag coefficient and conductivity linearly dependent on water concentration. These simulations gave similar results, except for the omitted difference in potential associated with differences in water concentration at the anode and cathode side.

The simulated EIS curve is smaller than the experimental curve in figure 1. More experimental data is needed to decide if the low frequency loop in figure 1 comes from the membrane. It could also come from for example the anode, which is sensitive to dehydration, or a combination of both membrane and anode. It is experimentally difficult to measure EIS on only the membrane, since the response of the electrodes is also seen. To separate the membrane from the electrodes, functioning reference electrodes are needed.

CONCLUSIONS

The modeling results show that the proton conducting membrane in a PEFC can give rise to a small loop in EIS. The loop is a result of varying resistivity or changing water concentrations with current density. The size of the loop is the sum of i·dR/di and dEconc/di, where the high frequency intercept is the membrane resistance and the low frequency intercept is dE/di. The loop is capacitive if the sum is positive and inductive if the sum is negative. The characteristic frequency for the loop is proportional to the effective diffusivity and inversely proportional to the square of the membrane thickness.
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