Modeling the Electrochemical Impedance of the Proton Conducting Membrane in a PEFC

Katarina Wiezell, Göran Lindbergh,
Dept. of Chemical Engineering and Technology, Applied Electrochemistry
The Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden

Introduction

Electrochemical impedance spectroscopy (EIS) is a very powerful tool for elucidation of rate limiting processes in a polymer electrolyte fuel cell (PEFC). However, it can be difficult to distinguish between different processes. The membrane is usually assumed to give a pure resistive impedance. In this study an EIS-model for a proton conducting membrane has been developed, which shows that the behavior can be much more complex due to water gradients induced by the current.

Model

The model of the proton conducting membrane is based on the concentrated electrolyte theory with 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 similar to the Stefan-Maxwell equation [1]. With this equation transport of water in the membrane by diffusion and water drag, and the potential distribution in the membrane can be described. In the simulations shown, the water concentration at the boundaries of the membrane is assumed to be in equilibrium with the gas phase. For the EIS model a mass balance for water is added. The steady state model results in a non-linear equation system and the EIS model in a linear equation system, which are solved in MATLAB.

Results

The resistance of a polymer electrolyte membrane often changes with current density due to changes in water content, as in figure 1. The model shows that when the resistance changes with current density, one loop will appear in EIS, see figure 2. The loop has a high frequency intercept equal to the membrane resistance, R, which is often used experimentally to measure the resistances in a cell. The low frequency intercept is equal to the derivative of the iR-drop, dE/dI. A graph of R and dE/dI is shown in figure 3, with the high and low frequency intercepts from figure 2 marked. The EIS-loop can be either capacitive or inductive, depending on whether the membrane resistance increases or decreases with current density. The size of the loop is I*dR/dI. The model shows a characteristic frequency of the loop proportional to the effective diffusivity of water and inversely proportional to the square of the membrane thickness.

These simulations have shown that when measuring EIS, it is important to be aware that a semicircle will appear from the membrane if the resistance is depending on the current density.

References

1. J.S. Newman, Electrochemical systems, by Prentice Hall, Inc., 1973, p. 239.

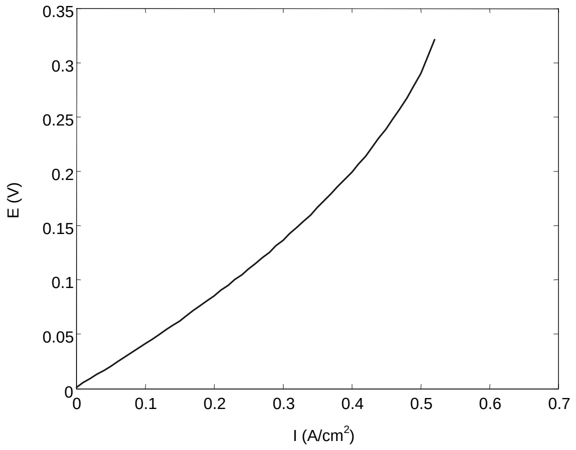

Figure 1. Modeled potential drop through a membrane at different current densities.

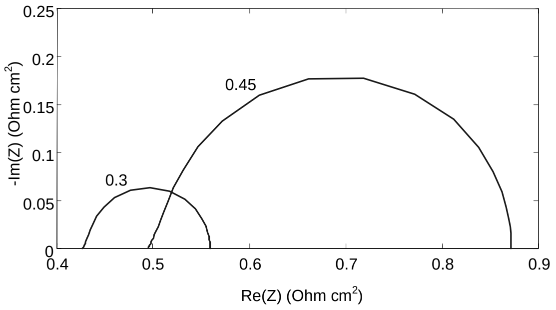

Figure 2. Modeled Nyquist plots for EIS on a membrane at two different current densities, 0.3 and 0.45 A/cm^2.

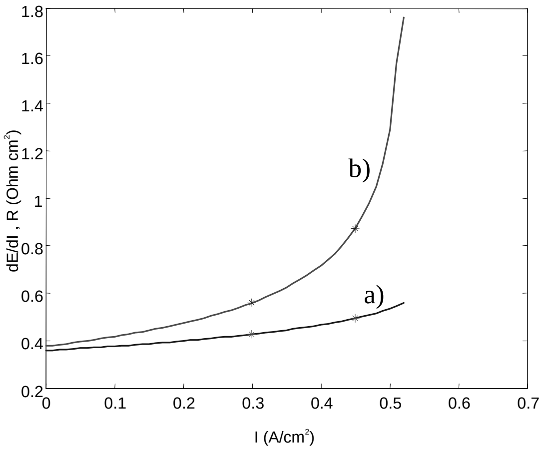

Figure 3. Modeled membrane resistance, curve a), and dE/dI, curve b), vs. current density. The high and low frequency intercepts from the Nyquist plot in figure 2 are marked.