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A novel membrane transport model for polymer electrolyte fuel cell simulations

L. Karpenko-Jereb [a,*], P. Innerwinkler [a], A.-M. Kelterer [a], C. Sternig [a], C. Fink [b], P. Prenninger [b], R. Tatschl [b]

[a] Institute of Physical and Theoretical Chemistry, Graz University of Technology, Graz, Austria
[b] AVL List GmbH, Graz, Austria

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ABSTRACT

This work presents the development of a 1D model describing water and charge transport through the polymer electrolyte membrane (PEM) in the fuel cell. The considered driving forces are electrical potential, concentration and pressure gradients. The membrane properties such as water diffusion and electro-osmotic coefficients, water sorption and ionic conductivity are treated as temperature dependent functions. The dependencies of diffusion and electro-osmotic coefficients on the membrane water concentration are described by linear functions. The membrane conductivity is computed in the framework of the percolation theory under consideration that the conducting phase in the PEM is formed by a hydrated functional groups and absorbed water. This developed membrane model was implemented in the CFD code AVL FIRE using 1D/3D coupling. The simulated polarization curves at various humidification of the cathode are found in good agreement with the experiments thus confirming the validity of the model.

Introduction

Currently, hydrogen Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are one of the most promising devices as high efficient sources of electric power for electric vehicles. The main advantages of the fuel cells are their high energy conversion efficiency and low noise, as well as their high power and energy density even under consideration of the H_2-tank [1–4]. The main goal of the PEMFC modeling is to calculate the cell potential and its efficiency. For this purpose it is necessary to find out which processes contribute to the potential losses and the extent of their contribution. If Ohmic voltage drops across GDLs and bipolar plates are neglected, the PEMFC potential is expressed by the equation:

$$U_{cell} = U_{oc} - \eta_c - \eta_a - \eta_{mem} \quad (1)$$

U_{cell} – cell potential; U_{oc} – open-circuit voltage; η_c, η_a – potential losses at cathode and anode; η_{mem} – membrane over-potential.

The main purpose of a membrane transport model is to calculate the membrane over-potential. Fig. 1 depicts the most important processes in the proton exchange membrane coated with a catalyst layer (PEMCC) taking place in a fuel cell at operation. These are the proton and electro-osmotic transports, the water generation resulted by the electro-

* Corresponding author. Tel.: +43 316 873 32241; fax: +43 316 873 32202.
E-mail address: larisa.karpenko-jereb@tugraz.at (L. Karpenko-Jereb).
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chemical reaction, the water diffusion and convection. Water diffusion arises due to a water concentration difference between the cathode side and the anode side. Usually the cathode has a higher water concentration caused by water formation as a result of the chemical reaction between H^+ and O_2. The electro-osmosis (often called electro-osmotic flux or water drag) is caused by the conjugated transport of the water molecules with the protons in the electric field: the water molecules mainly move in the protons' solvation shells. The convective flux of water is caused by a pressure gradient.

Theoretical modeling of the transport in an ion-exchange membrane (IEM) is based usually on structural and transport models [2,5,6]. The *structural models* give a simplified concept of the inner structure of the membranes. Currently, the following structural models of the IEMs are known: cluster-network [7,8], dusty-fluid [9,10], capillary [11,12], micro-heterogeneous two-phase [13,14] and percolation [15–17]. The *transport models* describe the transport of ions, water and gases through the membrane.

Table 1 displays a comparison of several membrane transport models published in the scientific papers [18–28]. Based on the governing equations used for calculating membrane overpotential, the membrane transport models can be separated into three main groups: first – Stefan–Maxwell equation based models [18,19]; second – Nernst–Planck equation based models [20,21]; third - Ohm's law based models [6,22–28]. Most of the models are known in the third group. From experimental investigations it is known that the temperature and pressure gradients have a weak influence on fuel cell voltage. Therefore most of the membrane transport models only consider two driving forces: the gradients of water concentration and those of electrical potential. Models such as those from of Rowe et al. [21], Senn and Poulikakos [24] additionally take into account the pressure gradient. Table 1 also displays the approaches to the description of the membrane transport properties (water diffusion and electro-osmotic coefficients) and the proton concentration as a function of the membrane water concentration as well as approximations in the calculations of the total water flux through the membrane. Most of the models take into account the dependencies of the water diffusion and electro-osmotic coefficients on the membrane water concentration. The simplified model of Berg et al. [20] sets the electro-osmotic coefficient (C_{drag}) in the perfluorinated membrane equal to unity and considers the dependence of the proton concentration on the membrane hydration level. Usually, the total water flux via the membrane is considered as a sum of diffusion and electro-osmotic flows. Kulikovsky proposed [6,22] a description of the transport phenomena in PEM based on the approximation that the water back diffusion is completely compensated by the electro-osmotic transport. This approach allows calculating the total water flux through the membrane analytically. But this model is not able to predict electrode water flooding effects. The membrane transport models differ also in the formulation of boundary conditions and in the definition of the water concentration at interfaces of PEM/CL, CL/GDL as well as in the calculation of the water concentration profile in the fuel cell. In Berg's model [20] the water sorption isotherm is used for the calculations of the water concentrations at the interfaces GDL/CL (Fig. 1), C_w^{a*}, C_w^{c*}, while in other models [6,22,24,28] it is used for the computation of the water concentrations at the membrane boundaries with CLs, C_w^a and C_w^c. Whereas the influence of temperature on water sorption properties of the membrane is described insufficiently in the models [6,18–33], however the experimental investigations [34–36] showed the temperature effect on the membrane water sorption isotherm, which is especially pronounced for the equilibrium of the membrane with the saturated water vapor and liquid water.

The aim of this present work was the development of a membrane transport model for PEMFC simulations, which describes water and charge transports through the polymer electrolyte membrane, and considers the influence of temperature and water concentration on the important membrane properties such as the water sorption isotherm, the water diffusion and electro-osmotic coefficients as well as on ionic conductivity.

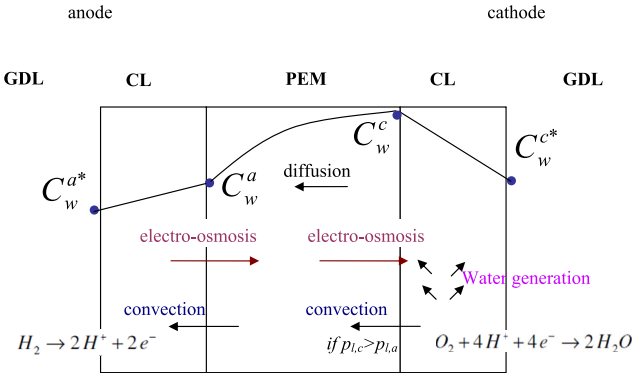

Fig. 1 – Transport and chemical phenomena in proton exchange membrane coated by catalyst in an operating PEMFC. These phenomena are considered in the developed membrane transport model.

Membrane transport model

Approximations

The developed membrane transport model is based on the approximations summarized below:

1. The transport of water and protons is considered only in one dimension.
2. It is a steady-state model.
3. Three driving forces are considered to describe the transport: gradients of electrical potential, concentration and pressure.
4. The model is an isothermal model, i.e. it does not take into account an effect of temperature gradient across the membrane on the water transport. For the calculations in the membrane transport model an average value between the temperatures at the membrane interfaces at the cathode and anode sides is taken.
5. Four types of water motions are considered in the model, as shown in Fig. 1: water formation at the cathode, water diffusion, electro-osmosis and water convection.