A1203

Evaluation of Performance and Chemical Degradation Phenomena in Reinforced PFSA Membranes: A Theoretical Study

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Abstract

For proton exchange membrane fuel cell (PEMFC) performance, electrolyte materials need to exhibit two main properties: (i) high proton conductivity and (ii) good gas separation. When it comes to durability, the latter is most important because it is the main source for chemical degradation of the membrane.

To study the cell performance and to evaluate the chemical degradation under various operating conditions, a transient, macroscopic, two-dimensional multi-physics cell model has been developed. It describes the miscible two-phase flow of liquid water and gases in the gas diffusion- (GDL) and catalyst layers (CLs). The electrochemical reactions are modeled with Butler-Volmer-equations and a physical description of Schroeder's paradox [1] is incorporated into the coupling conditions between the porous CLs and the membrane. A schematic overview of the processes of the degradation model is shown in the left hand side of Figure 1: H_2O_2 is formed via two electron transfer reactions of O_2 with H^+ in the electrodes (see Figure 1 right) and reacts with iron impurities in the membrane forming radical species. Two possible radical attack mechanisms are considered: "unzipping" of the backbone and scission of the side chains.
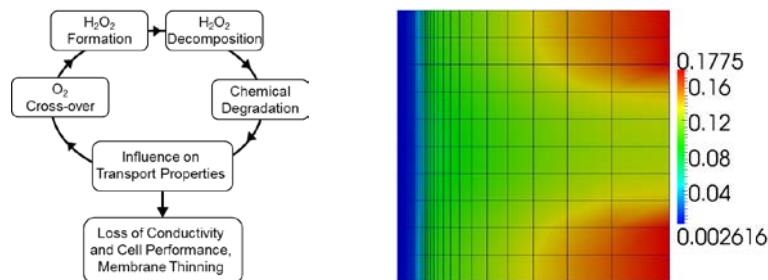
Fig 1 Left: Processes incorporated into the chemical degradation model. Right: the mole fraction of O_2 in the gas phase of the cathode GDL and CL with gas channels positioned at the upper and lower part of the left boundary and a rib in the middle.

Introduction

To compete with the internal combustion engine, the costs for PEMFCs need to be reduced. Further, the performance and durability of the cells needs to be improved to meet the EU or DOE targets. Concerning performance, the degradation of the catalyst is most severe. However, when it comes to safety and longevity the membrane is of utmost importance as its degradation causes catastrophic cell failure. Among thermal, mechanical and chemical membrane degradation the latter is most severe and the mechanisms leading to chemical degradation are only poorly understood. To identify the most relevant mechanisms involved and to find a way for their mitigation is therefore desirable. This is hindered by the complexity of the fuel cell system and by the fact that all processes in a PEMFC occur on extremely small length scales making reliable measurements difficult. Therefore, to interpret the experimental results the development of physical, numerical models able to predict the fuel cell behavior is necessary.

1. Scientific Approach

The aim of this work is to develop a state-of-the-art physical macroscopic cell model for low temperature PEMFCs incorporating the effects of chemical membrane degradation. Based on this model, the identification of advantageous operating conditions under automotive cycling will be derived.

2. Modeling Software

The model is incorporated into the numerical framework of DuMu^X [2,3] which is based on DUNE [4]. DuMu^X is open source software featuring transient simulations in up to three spatial dimensions, multi-physics- and multi-scale simulations, grid adaptivity and the use of different discretization schemes. The multi-domain functionality is used to divide the computational domain into three subdomains: the two electrodes and the polymer electrolyte membrane (PEM). In each of these domains, a separate set of equations can be solved.

3. Transport Model

In the porous parts of the cell, miscible multi-phase flow is modeled with Darcy flow [5]. A sketch of the simulated channel/rib setup is depicted in Figure 2, the water distribution under load is shown in Figure 3.
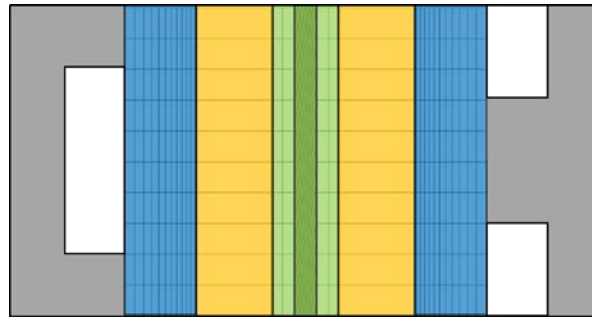
Fig 2 Scaled geometry of the modelling domain: GDLs are in blue, CLs in yellow and the PEM in green. Dark green indicates the location of the reinforcement layer. Gas channels are not yet included. The left electrode is the anode, the right one the cathode.
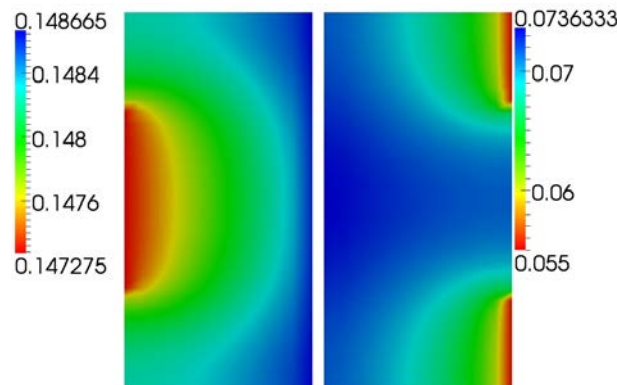

Fig 3 Water distribution in the GDLs and CLs. Left: mole fraction of H_2O in the gas phase. Right: Liquid water saturation.

To determine membrane water sorption from the gas phase, thermodynamic equilibrium is assumed and the model of Meyers and Newman [6] is employed. In the PEM domain, the model of Weber and Newman [7] is applied to describe the details of the water/proton/polymer-interactions and gas cross-over. The influence of a PTFE reinforcement layer on transport in the membrane is incorporated via a simple Bruggemann approach. To incorporate Schroeder's paradox, a macroscopic approach is chosen stating that the fraction of expanded channels in the membrane [7] is the same as the liquid water saturation in the adjacent CLs.

The model is designed to simulate potentiostatic operation. To determine the current density from the prescribed cell potential, a charge balance is solved in the Cls and PEM domain.

4. Electrochemical- and Degradation Model

To describe the chemical reactions in the anode and cathode CL, Butler-Volmer equations are employed. In the anode, the approach of [8] is used for the hydrogen oxidation reaction (HOR) while in the anode the model presented in [9] is applied for the oxygen oxidation reaction (ORR). In both electrodes, H_2O_2 may form due to two-electron-transfer:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E_0 = 0.695 \text{ V}$$
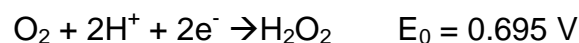
The potential dependent description of H_2O_2-formation is derived from [10]. From H_2O_2 and iron impurities highly reactive radical species are formed in the Fenton's reactions. Based on the work of [11] the steady state concentration of OH radicals is directly calculated from the iron ions and H_2O_2 concentration (Figure 4 left).
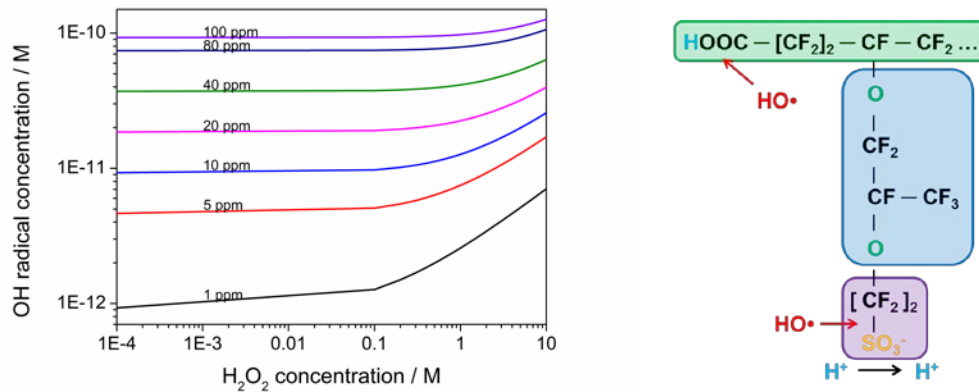

Fig 4 Left: Steady state OH radical concentration as a function of H_2O_2 and iron ion concentration. Right: Polymer structure of Nafion and its coarse-grained simplification. Unzipping and side chain scission are considered as degradation mechanisms [11].

As degradation mechanisms, the unzipping of the polymer backbones and scission of side chains are considered. For simplification, the coarse-grained polymer structure proposed in [11] is used in the degradation model (Figure 4 right).
Depending on the kinetics of the two degradation reactions, the equivalent weight (EW) defined as the mass of polymer per sulfonic acid group may increase. This increase in EW influences the sorption isotherm which is depicted in Figure 5.
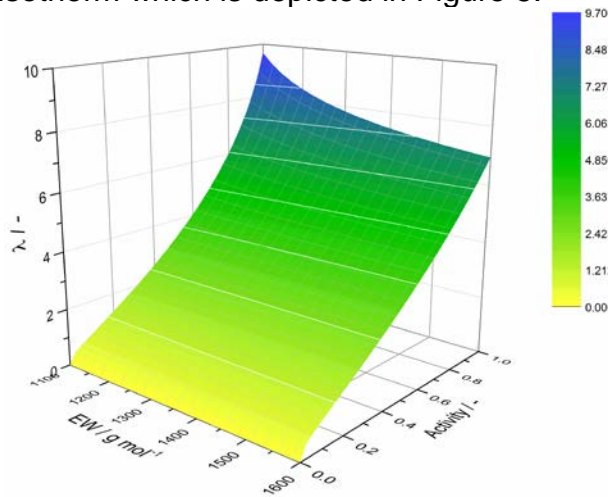

Fig 5: λ as a function of water activity and equivalent weight of the membrane [6].

Additionally, transport parameters in the membrane like the conductivity of the membrane deteriorate, influencing transport in the cell and therefore, performance. From the degradation reactions, the fluorine emission rate (FER) and the loss of membrane mass, leading to thinning of the membrane can be estimated (Figure 6).
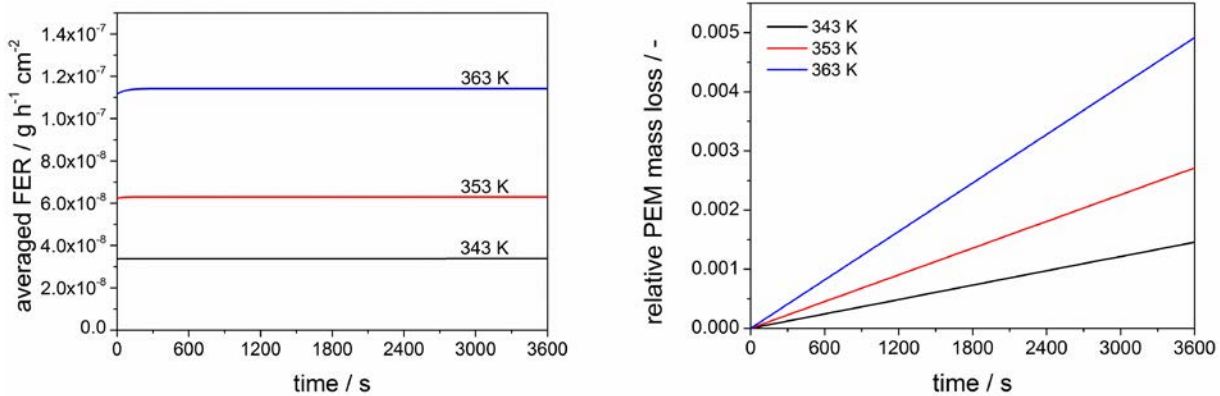
Figure 6: Left: Averaged FER at 343, 353 and 363 K. Right: relative membrane mass loss at 343, 353 and 363 K.

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