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Estimation of water distribution and degradation mechanisms in polymer electrolyte membrane fuel cell gas diffusion layers using a 3D Monte Carlo model

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ABSTRACT

Understanding of both water management in PEM fuel cells and degradation mechanisms of the gas diffusion layer (GDL) and their mutual impact is still at least incomplete. Different modelling approaches contribute to gain deeper insight into the processes occurring during fuel cell operation. Considering the GDL, the models can help to obtain information about the distribution of liquid water within the material. Especially, flooded regions can be identified, and the water distribution can be linked to the system geometry. Employed for material development, this information can help to increase the life time of the GDL as a fuel cell component and the fuel cell as the entire system. The Monte Carlo (MC) model presented here helps to simulate and analyse the water household in PEM fuel cell GDLs. This model comprises a three-dimensional, voxel-based representation of the GDL substrate, a section of the flowfield channel and the corresponding rib. Information on the water distribution within the substrate part of the GDL can be estimated.

1. Introduction

One of the main obstacles on the way of polymer electrolyte membrane fuel cells (PEMFCs) towards commercial use is their durability. Thus during the last years a significant amount of research work has been done to investigate PEMFC degradation mechanisms and mitigation strategies. Up-to-date overviews on PEMFC degradation are given in [1–4]. For a long time the focus has been less on GDL ageing but different studies concerning the lifetime of fuel cells have rather investigated reaction layer, membrane and bipolar plate ageing. Nevertheless, recent results show that GDL degradation should not be neglected anymore. For the case of the electrode in [5] it was demonstrated that the degradation of the PTFE results in approximately two times higher performance losses than the catalyst degradation by Pt agglomeration after 1000 operating hours under the operating conditions chosen; this at least implies that an impaired water household caused by the loss of GDL hydrophobicity may have similarly severe effects. Though the correlation between liquid water and GDL degradation has been discussed since quite some time [6], the mechanisms are still not well understood. In principle two reasons of degradation for the PEMFC GDL are presumed:

- Changes of the wetting behaviour of the GDL: The wetting behaviour changes may be induced by PTFE decomposition, see e.g. [7], or depletion caused by oxidation of the PTFE or the carbon, mechanical effects [8] (compression or fibre cracking) or impurities [6]. By these effects the originally hydrophobic GDL becomes more hydrophilic which results in an accumulation of liquid water in the GDL pores and blocking of these pores for reactant transport.
- Changes of the structure of the GDL caused by mechanical effects (compression below the ribs, see [8,9]) or carbon oxidation (for the case of the MEA, see e.g. [10]) could change the electric as well as the heat conductivity of the GDL.

These mechanisms are not limited just to the GDL, but also influence other components of the PEM fuel cell. This phenomenon demonstrates how important the interaction of the different degradation mechanisms is. The changes in the wetting behaviour and the structure of the GDL and thus its durability depend on the operating conditions of the PEM fuel cell. In [11] it is stated that the presence of liquid water, excess reactants and high current densities induces significant degradation of the MEA and the GDL. The authors of [11,12] observe that high humidification and especially liquid water are correlated with PTFE decomposition.

The task of modelling the GDL water household implies two challenges: finding an appropriate description of the porous structure and modelling the dynamic behaviour of water and gas within this structure. In literature, different modelling approaches can be found associated with porous media description and modelling of

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transport phenomena in porous media. On the one hand there are several approaches to find a reasonable description of the porous media, on the other hand there are approaches to model the transport processes in porous media by solving macroscopic transport equations or by describing molecular particle transport. The former can be divided into models representing the real geometry of the porous structure, statistically generated structures, randomly generated structures, abstracted structures representing certain properties of the real material; even continuous material linked with some integral structural parameters as permeability can be used to describe transport properties of porous structures.

1.1. Macroscopic transport models

As an example for a macroscopic modelling approach, computational fluid dynamics (CFD) can be mentioned. This approach can be subdivided into two major categories. The first category is considering the real multi-fluid approach where the entire set of conservation equations for each phase is solved and the coupling of the equations is achieved through pressure and inter-phase exchange coefficients. A successful example of an implementation can be found in [13]. The second category is the multi-phase mixture approach where the mixture momentum equations are solved and the relative velocities are calculated in a post-iterative step. One of the first papers introducing this approach is [14]. In the context of CFD, the porous material can be described both by real geometry data or continuously together with integral structural parameters.

A further approach which has been successfully applied to the field is the Lattice Boltzmann (LB) method which indirectly solves the Navier–Stokes equation by dealing with the Boltzmann equation for fluid particle movement [15]. It works on a lattice consisting of equally shaped unit volumes (so-called lattice sites, or cells), which are either solid or filled with fluid.

Pore network models are designed to capture the transport properties, but not the morphology of porous media, i.e. they use abstracted structures to represent the properties of the pore space. The use of networks of capillary tubes to model porous media was first suggested in [16].

1.2. Nano- and microscopic models

Models based on macroscopic liquid properties may be useful up to at least the μm scale. Going to even smaller structures, e.g. the nm-scale pores within the MPL material of a fuel cell GDL, the model assumptions break down and fluid flow must be described on the basis of appropriate particle interactions. Molecular dynamics (MD) modelling is one of the principal tools to theoretically study fluid flow based on molecular interactions. This computational method describes the time dependent behaviour of a molecular system, thereby calculating particle interactions either using empirical forcefields or even quantum mechanical methods. Commonly, to describe particle movement, the classical equations of motion are integrated based on an adequate discretization in time. The MD method has been routinely used to investigate the structure, dynamics and thermodynamics of fluids. With MD simulations one can, e.g. study both thermodynamic properties and/or time dependent (kinetic) phenomena such as fluid flow in porous material (for a review, see [17–20]).

A further method which has been commonly used on the molecular scale is the Monte Carlo (MC) method, which was first described in [21]. Since then, MC simulations have been used in several fields of scientific modelling. Concerning fluid behaviour, some authors focus on phase change as [22] or on two phase flow without phase change as for example [23]. But also percolation theory [24] and diffusion, including Knudsen diffusion, [25] are considered. For all of these models, a proper representation mirroring the structure of the porous medium has to be found first. Therefore, depending upon the physical model to be used, simple 2D cylindrical pores as in [22] or spherical clusters as in [25] are employed.

Furthermore, the MC method has been used to gain a representation of the structure of porous media and the associated effective properties (see [22–29]). Some of the MC models also focus on the determination of general parameters of porous media, e.g. in [28] and [29], the MC simulation is used to compute the effective diffusivities in randomly overlapping fibres and filament bundles representing a porous medium. Further articles especially focus on fuel cell topics: in [26], electrical conduction aspects are examined, in [27], the MC method is used to generate the geometry for a lattice Boltzmann calculation of the permeability.

There are further particle-based models using not explicitly molecular, but small-scale descriptions of material behaviour. These include randomly distributed, overlapping grains such as oblate and prolate spheroids. They are known to quite accurately describe the pore space in sandstone, foams and fibre networks [30–33].

The novel approach presented in this article employs the MC method not on the molecular, but on the μm scale to describe water behaviour within randomly generated porous material on a statistical basis, i.e. without the need of numerically solving transport equations. Also real geometry data could be used.

1.3. Experimental visualization of water in PEMFC GDLs

Experimental in situ visualization of liquid water within PEMFCs has been approached using, e.g. optical imaging [34], neutron radiography and tomography [35], synchrotron radiography or tomography. Combined optical imaging and neutron radiography studies have been performed [36], but the spatial resolution of this technique is too low to gain insight into inner-GDL processes. Employing synchrotron radiography, e.g. Manke et al. [37] and Hartnig et al. [38] have shown that in situ water distributions within fuel cell GDLs of appropriate resolution can also be obtained in through-plane direction. Unfortunately, to our knowledge, so far no according experimental data dealing with ageing or variation of PTFE coverage is available.

Clearly, the experimental progress on the field opens new perspectives concerning water household analysis. Nevertheless, further effort on the field of theoretical modelling is required to provide and facilitate deeper understanding and to relieve material improvement by predicting the consequences of changing parameters. The MC model described in the following is intended to complement the established tools in this field.

This article is structured in the following way: first the MC model developed to study the water distribution in fuel cells will be described. Also model specific properties as the handling of porous media and the steady state as approximation of real fuel cell conditions will be presented. The results part is discussing fuel cell systems of different PTFE content which represent different ageing situations. Several approaches to analyse the simulations are presented and discussed. The article will be completed by a conclusions and outlook section.

2. Monte Carlo model

2.1. Description of the MC model

In contrast to the commonly known MC models, the model presented in the following does not work on the molecular level, but on the μm scale. MC models working on the molecular scale often use a (N, V, T)-ensemble to simulate a system at equilibrium. This