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Nano-scale Monte Carlo study on liquid water distribution within the polymer electrolyte membrane fuel cell microporous layer, catalyst layer and their interfacial region

A. Pournemat[a,*], H. Markötter[b], F. Wilhelm[a], S. Enz[a,1], H. Kropf[b], I. Manke[b], J. Scholta[a]

[a] Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Helmholtzstr. 8, 89081, Ulm, Germany
[b] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109, Berlin, Germany

HIGHLIGHTS

- Mass transport limitations restrict the maximum power density feasible for PEMFCs.
- Water agglomerations within the interfacial region of MPL and CL are critical.
- The interface structure used in simulations is provided by a FIB-SEM tomography.
- Water distribution within the interface is modelled by a Monte Carlo model.
- The pore size distribution and the pore filling degrees are analyzed.

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ABSTRACT

Liquid water saturation of pores in the gas diffusion layer (GDL) and the catalyst layer (CL) of polymer electrolyte membrane fuel cells (PEMFC) hinders the transport of the reactant gases, leading to inhomogeneous current density distribution, reduced overall cell performance, and accelerated material degradation. This effect restricts the PEMFC operation, specifically at high current densities. In this study, the simulation results illustrate how the interplay of wettability and pore sizes influences the water distribution within the CL, microporous layer (MPL) of the GDL, and specifically their interface. The liquid water distribution within the porous material is studied employing a voxel-based Monte Carlo (MC) model reflecting the effect of local thermodynamic boundary conditions and inner surface characteristics. Real material structures obtained with a focused ion beam - scanning electron microscope (FIB-SEM) are employed. Local temperature and relative humidity values required as inputs are obtained from sophisticated computational fluid dynamics (CFD) simulations comprising all relevant effects, including the electrochemical reactions. The results show that avoiding drastic changes in wettability at the CL-MPL interface can help to mitigate the possible detrimental water accumulations. Further developing and exploiting this study will contribute to facilitate the systematic material development for better PEMFC performance and durability.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are efficient electrochemical energy convertors, in which electricity is produced, while water and heat the only products of the electrochemical reaction. Thus, this technology constitutes an important building block for a sustainable energy economy, facilitating carbon dioxide free energy conversion for both automotive and stationary applications. The presence of liquid water in the cell involves some advantages and disadvantages. By hydrating the polymer membrane of the cell, the ionic conductivity is increased [1], thus the cell electrical resistance is lowered. However, liquid water can block the open pores in the catalyst layer (CL) and the gas diffusion layer (GDL) and therefore, obstruct the transport of the reactant gases from the flow channel to the electrodes [2]. This effect can reduce the overall cell performance and durability by fuel starvation and material degradation, such as dehydrophobization. Specifically, inter alia these gas transport limitations constrain cell efficiency at very high current densities, which is a significant problem

* Corresponding author.
E-mail address: anahid.pournemat@zsw-bw.de (A. Pournemat).
[1] Present address: BMW Group, 80807 Munich, Germany.

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for automotive applications, where high current densities of up to 3 A cm^{-2} are pursued [3]. Therefore, optimizing the water transport in PEMFCs is an important research topic. Reaching high current densities with less electrical power loss due to the gas transportation limitations depends strongly on the fuel cell stack design, including all the existing components, such as bipolar plates, GDLs, electrodes and membranes. The focus of this study is on the effect of operating conditions and inner surface wettability properties on the distribution of the liquid water in the microporous layer (MPL), CL and most importantly at their interfacial region (IR), using a Monte Carlo (MC) simulation method.

The spark of this method was triggered in the late 1940's after building the first US electronic computer [4]. This method is based on random sampling in order to obtain numerical results, and depending on whether or not the problems handled by MC methods are directly associated with the outcome of the random processes, they could be grouped in two types: probabilistic or deterministic. In case of the probabilistic problems, it might be easier to grasp that how a solution based on randomness could help to solve a problem, which is directly concerned with the random processes. However, in the case of deterministic problems, e.g. monitoring a system containing a large number of particles to for a long time span, a description in terms of statistical mechanics can provide the macroscopically relevant averaged properties with much lower effort than a complete deterministic description of all single processes involved, if the latter is feasible at all. The MC method is able to use the main strength of the theoretical mathematics in the form of abstraction and generality to define the fundamental behavior of a system. Furthermore, by benefiting from experimental values in terms of boundary conditions and governing physical laws, it is able reduce the generality in order to get numerical results for a particular case of study. Yet defining a problem with the use of theory may help to recognize the underlying random processes, which can be solved by MC simulations [5]. Therefore, this method has shown from the early stages to be a feasible approach to the statistical mechanical problems, which sometimes might not be soluble analytically or in any other way, and on its evolution path reducing the computational efforts was always of interest [6–9].

In this work, a canonical MC model, which was established to study the steady-state water distribution in GDL and MPL of the PEMFCs [10,11], is used and further developed to be capable of performing simulations in the CL, MPL and their IR, with additional components in the structure. The model includes water movement driven by surface energies, as well as condensation and evaporation based on local boundary conditions. It employs a 3D lattice structure for computation and is capable of choosing an appropriate voxel size. Furthermore, it includes periodic boundary conditions, which can be lifted by introducing walls. Walls represent neutral structures with no contribution in the energy calculations. The change in the liquid water distribution and amount in the porous structure could take place by movement, evaporation and condensation. The decision for this change in the position or phase of the water is based on surface energy and chemical potential calculations. The results include both qualitative and quantitative information on water distribution in the porous media for different boundary conditions and surface characteristics. Furthermore, information on the correlation of porous structure, wettability and the pore filling degree, which could be obtained by the combination of tomography and the MC simulations employed here, is investigated with a new pore analysis method.

2. Simulation inputs

2.1. Structure acquisition of an MPL-CL interface by FIB-SEM tomography

For the MC simulations in this study, real material structures are used, including the MPL structure of a pristine SGL 25 BC “DECODE” GDL (SGL CARBON GmbH, Meitingen, Germany) and a CL supplied by Johnson Matthey (JM) Fuel Cells (Swindon, UK). Therefore, a focused ion beam - scanning electron microscope (FIB-SEM) tomography was applied to an MPL-CL interface region of a membrane electrode assembly (MEA) from a fuel cell operated for 2592 h. This reference MEA, which was a project specific MEA and not representative of a JM commercial product, was a symmetrical one with 0.2 mg cm^{-2} Pt on both anode and cathode side. The mean Pt particle size was 4–5 nm and the carbon support was XC72R, which had a surface area of ~230 $m^2 g^{-1}$. A small cut-out of the MEA and the neighboring MPL region was fixed on a standard SEM sample holder using conducting silver glue. It was decided not to embed the sample into resin to prevent the possible pore space alteration due to the high capillary forces. The complete sample was sputtered with ~10 nm gold and transferred into the vacuum chamber of the FIB-SEM device.

Prior to acquiring a tomography, the ion beam is used to remove the material around the volume of interest in order to gain a proper view on it [12]. The material removal takes place then slice by slice with the ion beam. Subsequent to cutting each slice, the cut face is imaged with the scanning electron microscope detectors.

The ion beam current was set to 700 pA (@30 kV) and the thickness of the milled slices was 10 nm. The electron beam was accelerated with 1 kV and a resolution of 10 nm for scanning the cut face was used, resulting in a 3D voxel resolution of 10 nm. In order to achieve a proper segmentation of the pore space as well as the CL and the MPL, during imaging two different signals were recorded: a secondary electron (SE2) detector, which attracted the electrons with a positive voltage of 400 V, and in addition to that, an In-Lens detector recorded the back scattered electrons (BSE). Both signals provide different characteristics of the acquired images. Due to the sideways position of the SE2 detector, it delivers a signal, which is sensitive to the topology of the sample surface, and hence, it was well suited for the detection of pores at the cut face (Fig. 1, left). The In-Lens detector on the other hand, gives a material contrast due to the atomic numbers of the elements distributed in the material, and therefore, it was appropriate for identifying different material compositions (Fig. 1, right).

The reconstruction of the three dimensional structures was conducted via Fiji [13] along with an adapted algorithm in a self-written software coded in IDL® version 8.4 (Exelis Visual Information Solutions, Boulder, Colorado). The aim was segmentation of the MPL, the CL and the pore spaces. Firstly, the inevitable sample movement during tomography was detected and the images were shift-corrected in order to align the images in the volume. Subsequently, a gradient in the signal strength from top to bottom from each image slice was removed. The segmentation of pores was conducted with an algorithm based on anisotropic filters using the SE2 signal [14]. Fig. 2a) and c) show the MPL-CL intersection with the SE2 signal and the segmented result, respectively. Fig. 2d) and e) illustrate reslices of the MPL and the CL.

During the slice by slice removal of the material, the background of the pore spaces became gradually more visible as the cut plane approached towards it, until it was finally removed by the ion beam. The result was a rising signal when observing the pore background. In the reslice (Fig. 2d) and e)), the rising signal inside the pore spaces is visible. The segmentation here exploited this circumstance. Similar to the approach presented by Salzer et al. [14], anisotropic filters detecting the rising signal are used to identify the pore background, in order to segment the material from void. This step needed a sophisticated choice of the segmentation parameters, such as signal smoothing and threshold values. The best segmentation was achieved by having the focus on the MPL and the CL individually. This could be accomplished in one single step, but the results would not be as accurate as the separated segmentation for MPL and CL as used in this work. The allocation of the material to the MPL and the CL was done with the In-Lens detector signal, which showed a strong contrast on the material (see Fig. 2 b)). In the end, the segmented MPL and CL are combined into one dataset (see Fig. 2 c)). This three dimensional dataset with a voxel size of 10 nm is then rotated to align the MPL-CL interface with the y-z plane. The volume is then scaled to a voxel size of 50 nm, in order to