A multi-scale approach to material modeling of fuel cell diffusion media

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1. Introduction

Fuel cells electrochemically convert chemical energy to electrical energy at potentially high efficiencies without the efficiency “penalty” of the Carnot process. Hydrogen as a fuel offers the opportunity to be produced in a sustainable manner and generates only water as reaction product. Hence, fuel cells, and specifically polymer electrolyte fuel cells (PEFC), are considered as long-term alternatives to internal combustion engines in automotive applications. Pore-scale simulations utilizing imaging data sets of real materials or virtual model representations provide such diffusivity numbers. However, components like the microporous layer (MPL) or the gas diffusion electrode have not been covered adequately so far by efficient and practical modeling approaches due to the small pore sizes and resulting Knudsen contribution to diffusion. In this publication we report the development of a numerical method which allows for the determination of binary diffusion coefficients for all Knudsen numbers and demonstrate the application to fuel cell diffusion media in a multi-scale modeling approach. For high Knudsen numbers effective diffusivity is determined by tracking a large number of individual molecules that collide with the pore walls. For low Knudsen numbers, effective diffusivity is determined by solving the Laplace equation on the pore space. Both contributions to the overall diffusivity are merged by applying Bosanquet’s formula. The resulting diffusivity can be used as an effective number for a microporous layer coating of a spatially resolved fibrous diffusion medium. As this multi-scale method is also based on a 3D voxel grid, we could study any distribution of the MPL on and inside the gas diffusion layer (GDL) with this model, e.g. cracks, different penetration depths, etc.

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and the generation of virtual material representations as well as experimental model validation and material fabrication, as depicted in Fig. 2.

An exemplary and important material property of interest is the effective gas diffusivity. In fuel cells, for instance, the effective diffusivity of the diffusion medium controls the humidification level of the membrane. Diffusivity as an effective number is the result of experimental material characterization and enters volume-averaging cell simulations. Due to the existence of solid in the porous medium the open pore space is reduced. Furthermore, these pores are not straight across the material thickness but wound and tortuous. The combined effect of porosity and tortuosity reduces the diffusion coefficients in the free space to an effective number, the effective diffusivity \( D_{\text{eff}} \) [4]. This macroscopic, effective material property is important in fuel cells as the porous medium controls the access of oxygen to the catalyst layer and the removal of product water vapor in the opposite direction (Fig. 1). Since the fuel cell membrane needs water to become proton-conductive, dry operating conditions as desired in automotive applications require a well-balanced diffusion resistance of the DM to retain enough water vapor at the membrane/catalyst layer interface in order to keep the membrane humidified but still not hinder access of oxygen from the flow field channel across the DM [5,6].

Fig. 3 shows various views of a typical fuel cell diffusion medium comprised of a hydrophobically treated, fibrous and woven or non-woven gas diffusion layer (GDL) and a so-called microporous layer coating (MPL). The GDL is typically made from 5 to 10 \( \mu \text{m} \) diameter carbon fibers that are chemically or mechanically bound to provide the approx. 150–300 \( \mu \text{m} \) thick sheet with sufficient mechanical integrity. GDL pore sizes range from 1 \( \mu \text{m} \) up to 100 \( \mu \text{m} \) with porosities between 70\% and 90\%. Usually the MPL forms a coating on the GDL based on particle aggregates comprised of tens and hundreds of 10–50 nm sized carbon black primary particles. The resulting mean pore size of the MPL coating is in the order of 10–100 nm with porosities in the 30–70\% range. Depending on the manufacturing process, which in most cases is a wet coating process, the MPL may exhibit mud cracks and form either a distinct layer on the GDL or penetrate deeply into the fiber structure thereby forming an uneven penetration profile. The porous nature of the resulting DM assembly, hence, is complex in terms of the individual pores structure of the GDL and MPL themselves as well as the way they are connected. Both GDL and MPL are usually hydrophobically treated to avoid flooding of the gas-transporting pores with product water of the electrochemical reaction [7]. For a comprehensive introduction to fuel cell gas diffusion media, see [2,8].

As indicated above, the pore systems of GDL and MPL differ significantly. Fig. 4 shows the pore size distributions of a typical plain GDL and the DM assembly comprised of a hydrophobically treated GDL of the same kind coated with an MPL. These distributions illustrate that the mean pore radii differ in two to three orders of magnitude. Besides that, the secondary axis in Fig. 4 shows the Knudsen number for oxygen at 20\°C calculated for a cylindrical pore of the given radius. From the perspective of the GDL, the Knudsen number is much smaller than 1, and particle/wall collisions can clearly be neglected over particle/particle collisions. Hence, the fluid can be considered a continuum in the GDL, and transport processes can be calculated with continuum mechanical approaches.

In the MPL with pore sizes in the 10–100 nm range, the Knudsen number, defined as mean free path of the diffusing gas divided by a characteristic length of the porous medium, e.g. the mean pore diameter, is in the order of 1 and, thus, right within the transition from continuum to molecular flow. Consequently, particle/wall collisions cannot be neglected any longer, and continuum mechanical models are not valid.

The numerical determination of transport properties such as effective diffusivity and permeability in fibrous GDL by pore scale modeling utilizing samples imaged in 3D, e.g. applying synchrotron radiography, or by using virtual material representations has been demonstrated and validated [9,10]. Despite of the fact,
though, that the occurrence of Knudsen diffusion in the MPL has been widely accepted and considered in volume averaging approaches [11], methodologies for determining the effective diffusivity of MPL and the MPL/GDL sandwich by pore scale modeling are missing. The major challenges are (i) the provision of a computational grid of the MPL and the MPL/GDL sandwich, (ii) the efficient and fast determination of the effective diffusivity of sufficiently large regions in the MPL considering the transition regime, i.e. the particle/wall collisions, and (iii) the combined effective diffusivity of the MPL/GDL sandwich.

In the following, an integrated approach will be introduced to determine the effective diffusivity of realistic micro-porous sandwich layers in fuel cells by construction of 3D multi-scale MPL/GDL models and a hybrid method to efficiently calculate the diffusivity over the full spectrum of Knudsen numbers.

In Section 2 the construction of an MPL/GDL sandwich by resolving the GDL pores but homogenizing the MPL therein is described. A full 3D material representation of the MPL based on measured data is also needed to obtain the homogenized diffusivities of the MPL. In Section 3 the methods are developed and described to efficiently calculate effective diffusivities in the full
range of Knudsen numbers appearing in MPL and GDL. A two-scale upscaling technique is developed to obtain the effective diffusivity tensor for the complete MPL/GDL assembly. The potential of the described ansatz to understand the impact of different MPL/GDL assemblies on effective transport properties like gas diffusivity will be shown in Section 4 with the help of exemplary results.

2. Structure characterization and model generation

As the pore sizes of MPL and GDL differ by at least two orders of magnitude, a single structure model is not capable to both resolve the pores of the MPL and show a sufficiently large part of the GDL. For that reason, two different structure models are needed. The first one is a high-resolution model which only shows the pore structure of the MPL. The second one is a model with a lower resolution showing the whole thickness of the GDL and treating the MPL as a homogenized porous medium.

To construct good models of the pore and material structure of either the GDL or the MPL or the assembly, detailed information on the structure of the porous medium is required. Naturally, the best structure models are obtained by directly transforming a 3D tomography image into a model. While this is a possible approach for gas diffusion layers without MPL [9,12], the resolution of these 3D images is not sufficient to resolve the pore structure of the MPL. Hence, the structure model has not directly been derived from 3D imaging experiments but generated virtually based on characterization data obtained on a representative and commercially available MPL on a GDL as used in technical applications.

The MPL structure models show a rectangular area $\Omega$ and are composed of cubic voxels (= volume pixels), where each voxel either represents a solid material or pore space, so

$$\Omega = \Omega_{\text{solid}} + \Omega_{\text{pore}}.$$ 

The GDL structure models can additionally contain voxels representing the porous MPL, which are neither solid nor pore, but represent a porous material, thus

$$\Omega = \Omega_{\text{solid}} + \Omega_{\text{pore}} + \Omega_{\text{porous}}.$$ 

2.1. MPL model

Acetylene blacks which are usually used as a base material typically exhibit primary particle sizes of approx. 40–50 nm forming agglomerates of 200 particles per aggregate on average [13]. Since MPL are usually fabricated as a wet coating onto a GDL, these aggregates might be much smaller in the ink or paste formed by the carbon and a solvent. In the absence of better data, above numbers have been used for the virtual material. MPL both on GDL and non-porous substrates have been characterized for pore size distribution and porosity using the method of standard porosimetry [14]. Fig. 5 shows measured pore size distributions of the GDL fiber substrate coated with an MPL of the underlying plain GDL fiber substrate and of plain MPL material. Since no free-standing MPL of the kind used in the MPL/GDL assembly is available, an MPL of similar composition has been coated onto a non-porous substrate and afterwards removed from that non-porous substrate in order to make it measurable with standard porosimetry. Hence, the MPL material may have experienced changes, and the interpretation of the measured data has to be done with care. On the other hand, the interpretation of the results obtained on the MPL/GDL assembly is difficult, too, since the intrusion of the MPL into the fiber substrate is unknown, and therefore an unknown portion of the sample volume is occupied by both, MPL material and fibers. Nevertheless, given the fact that any pores in the plain fiber substrate have pore radii larger than 1 $\mu$m, it can clearly be said that the mean pore radius in the MPL is between 10 and 100 nm, presumably in the order of 40 nm.

The MPL/GDL assembly results furthermore suggest an MPL porosity of approx. 35%, but since an unknown portion of this region is occupied by GDL fibers, this number is too low. The MPL-only data, on the other hand, suggest porosities of 60% or even up to 80%. It has to be assumed, though, that the appearance of large voids and mud cracks during the MPL manufacturing process as well as the process of removing the MPL from the non-porous substrate introduces some porosity that is not representative of the bulk MPL material itself. Hence, it has been concluded that the actual MPL porosity is between 35% and 60%.

Based on this material characterization an algorithm was designed to construct a virtual 3D model. As the MPL layer consists of particle agglomerates, the model is constructed with agglomerates of spheres. Each agglomerate consists of $N$ spheres, whose centers fulfill the conditions that

(a) any two centers have at least a distance $d_{\text{min}}$ from each other and
(b) for each center exists another center which has a distance less than $d_{\text{max}}$.

In this way, a connected agglomerate of slightly overlapping spheres is constructed by choosing $d_{\text{min}} < d_{\text{max}} < d$, where $d$ is the diameter of a single sphere.
In order to be close to carbons that are typically used for fuel cell MPL, like acetylene black, and to match the desired pore size distributions we chose $N = 200$, $d_{\text{min}} = 30 \text{ nm}$, $d_{\text{max}} = 50 \text{ nm}$ and $d = 52 \text{ nm}$. Agglomerates created with these parameters were added to the model until the desired porosity of 55% was reached. Fig. 6 shows a model created with these parameters.

The consistency of the virtual model and the real media was checked in two ways: first, the pore size distribution of the virtual model was determined numerically and the resulting curve was compared with the experimental findings. Fig. 7 shows a good agreement between experimental and numerical results. Second, as a qualitative cross-check, model images were compared to SEM images of the MPL surface and freeze-fractured cross-sections of the MPL/GDL assembly. Fig. 8 shows the virtually generated MPL with a representative SEM image of the used MPL material.

2.2. GDL model

The whole diffusion layer consists of three materials: fibers, binder and MPL. These three materials are added to the model step by step, as illustrated in Fig. 9.

Usually, the fiber structure consists of long, straight carbon fibers and it can be assumed that the fibers are long compared to the sample size and that the crimp is negligible. Thus it is possible to model the fiber structure using a stochastic process which adds fibers randomly until a desired volume fraction is reached. To model the high anisotropy between in-plane and through-plane direction of the medium, the directions of the fibers are not distributed uniformly. Rather, the probability density of the direction is given in polar coordinates as [15]

$$
p(\theta) = \frac{1}{4\pi} \sin(\theta) \left(1 + \left(\frac{b^2}{C^2} - 1\right) \cos^2(\theta)\right)^{-3/2}.
$$

Here, the parameter $b$ describes the anisotropy of the structure. For isotropic media $\beta = 1$ holds, whereas for increasing $\beta$ the fibers tend to be more and more parallel to the $xy$-plane. Here, choosing $\beta = 20$, round cross-sectional shapes and a fiber diameter of 7 $\mu$m, fiber structures similar to a Toray TGP H60 paper were created (see [9] for a comparison with tomography data).

Typically, a GDL consists of a large amount of carbonaceous binder. When applied, the binder basically behaves like a wetting fluid, therefore filling small pores first. To follow that idea algorithmically, the pore size of the 3D geometry was determined using granulometry [16], i.e. the size of a pore is determined by the radius of the largest sphere that fits inside. So each voxel in $\Omega_{\text{pore}}$ is as-

Fig. 7. Comparison of pore size distributions: model data are averaged over three random realisations of the MPL layer; measurement data are from Fig. 5, where only pores smaller than 300 nm are considered as MPL pores.

Fig. 8. Comparison of a cross section of the virtually generated MPL from Fig. 6 (left) with an SEM image of an MPL surface (right).
signed a pore size and $\Omega_{\text{pure}}$ can be ordered by this. Then the voxels with the lowest pore sizes are assigned to $\Omega_{\text{solid}}$ as binder until the desired volume fraction is reached (note that $\Omega_{\text{pure}}$ is still empty). Here, we assumed that the GDL consists of 50 wt% binder (specific weights 1.70 g/cm³) and 50 wt% fibers (spec. weight 1.90 g/cm³).

In the third step, the MPL layer is added to the model. In the production process, the MPL is added onto the GDL, but usually intrudes into the fibrous structure. This is reflected by the model: the MPL is added on top of the layer but also intrudes into it by a constant factor.

It is of course also easily possible to modify the model e.g. by using variable intrusion depths or by adding cracks into the MPL layer, but such modifications are not part of this publication.

3. Numerical determination of diffusivity values

The diffusion mechanism of gas molecules through a porous medium is dependent on the Knudsen number. For small Knudsen numbers $Kn$ the pore sizes of the medium are much larger than the mean free path of the gas, and diffusion is driven by collisions of gas molecules with each other. This type of diffusion is called bulk diffusion and it can be modeled mathematically by the classical continuum mechanics approach.

For large Knudsen numbers pore sizes of the medium are much smaller than the mean free path of the gas. Thus, particle–particle collisions happen only rarely and the diffusion is driven mainly by collisions between the gas molecules and the pore walls. This type of diffusion is called Knudsen diffusion and has to be modeled mathematically by random walk methods.

In case of intermediate Knudsen numbers both diffusion mechanisms contribute. Tomadakis and Sotirchos [17,18] proposed an algorithm to calculate the diffusivity matrix $D$ directly by a random walk method. In their method a particle moves on a straight line into a random direction by a random walk length $l$, where $l$ is exponentially distributed with the mean free path $\lambda$ as expectation value. After having traveled the distance $l$, it is assumed that another particle is hit, and a new direction and length is chosen. If a particle hits a wall during its travels, it is reflected diffusively, i.e. it leaves the wall with a new random direction and walk length. From the displacements of a set of particles, the diffusivity can then be calculated. Unfortunately, this algorithm can diverge for $Kn \rightarrow \infty$, i.e. the Knudsen diffusion coefficient in a tube should converge for $Kn \rightarrow \infty$ to $D = \frac{4d^2}{\pi^2} \nu$ [19], where $d$ is the diameter of the tube and $\nu$ is the mean thermal velocity of the gas, but the algorithm as stated in [17,18] gives $D \rightarrow \infty$.

So instead of using this algorithm, we recall that the overall diffusivity can be approximated by Bosanquet’s formula [20]:

$$D = \left( D_{\text{bulk}}^{\frac{3}{2}} + D_{\text{Kn}}^{\frac{3}{2}} \right)^{-\frac{1}{3}},$$

and determine $D$ indirectly by determining $D_{\text{bulk}}$ and $D_{\text{Kn}}$. Typically Bosanquet is applied to the scalar diffusion coefficients of an unary gas to derive a scalar combined diffusion coefficient. In this work it is assumed that Bosanquet can also be applied to determine the combined anisotropic 3D diffusion coefficient. Pollard and Presence [20] compare their results for gas diffusion of an unary gas to Bosanquet’s approximation and find a good agreement. Other diffusion models like the Dusty Gas Model aim at considering multi-species transport. As shown by Keil [21], the derivation of the Dusty Gas Model from the Stefan–Maxwell equations results in a Bosanquet-type formulation of the combined Knudsen and binary diffusion coefficient for the individual species. The errors in the derivation of the Dusty Gas Model as shown by Kerkhof [22] relate to the viscous term and may not matter for our considerations here. This derivation and the closeness of the gases oxygen and nitrogen considered here in the context of PEM fuel cells justify the approach. Furthermore, the values of the diffusion matrices $D_{\text{bulk}}$ and $D_{\text{Kn}}$, and, hence, of $D$, are dependent on the gas species and the pore structure of the medium as well as on the gas condition (e.g., composition, pressure, temperature). Consequently, for the latter derived effective diffusion coefficient it has to be kept in mind that this coefficient is species-specific.

The bulk diffusivity $D_{\text{bulk}}$ can be written as

$$D_{\text{bulk}} = D_{\text{bulk}}^0 \cdot D_{\text{bulk}}^{\text{eff}},$$

(1.3)

where $D_{\text{bulk}}^0$ is then a dimensionless diffusivity matrix depending only on the pore geometry of the porous media and being independent of the gas species. The dimensionless diffusion matrix $D_{\text{bulk}}^{\text{eff}}$ describes the reduction of the free bulk diffusion $D_{\text{bulk}}^0$ to the effective bulk diffusion $D_{\text{bulk}}$ by the porous medium. In case of an unary gas, $D_{\text{bulk}}^0$ is the self-diffusion coefficient, with $D_{\text{bulk}}^0 = \frac{1}{2} \frac{k}{m} \nu$ with mean free path $\lambda$ and mean thermal velocity $\nu$. In case of a binary gas mixture, e.g. O₂ in N₂, $D_{\text{bulk}}^0$ is the (measurable) binary diffusion coefficient. Thus, it suffices to determine $D_{\text{bulk}}$ numerically for one gas type and then use (1.3) to instantly get the result for any other gas species, temperature or density.

Similarly, we can define a dimensionless $D_{\text{Kn}}^0$ through

$$D_{\text{Kn}} = D_{\text{Kn}}^0 \cdot D_{\text{Kn}}^{\text{eff}},$$

(1.4)

where the coefficient $D_{\text{Kn}}^0$ is given by $D_{\text{Kn}}^0 = \frac{1}{2} \frac{k}{m} \nu$. Here, $\nu$ is the mean thermal velocity of the gas which is given by

$$\nu = \sqrt{\frac{8kT}{\pi m}},$$

(1.5)

with temperature $T$, Boltzmann number $k$ and molecular mass $m$. $l$ is a characteristic length of the porous medium, typically the mean pore diameter or the mean chord length. When comparing the Knudsen diffusion matrices of the same porous medium for two different gases, $l$ cancels out and

$$D_{\text{Kn}2} = \frac{D_{\text{Kn}1}}{D_{\text{Kn}1}},$$

(1.6)

holds. Thus it suffices to determine $D_{\text{Kn}}$ for one gas type. Then, for any other gas species, temperature or density, the diffusivities can be calculated using (1.6).

It has to be noted that the actual choice of $l$, although irrelevant in our case, decides whether $D_{\text{bulk}}$ and $D_{\text{Kn}}$ are different or not. Since both matrices describe the effect of the pore structure on the diffusion process it would be counterintuitive if they were different. And in fact, the differences are not a physical phenomenon,
but – as Zalc et al [23] correctly pointed out – simply caused by a sloppy definition of the characteristic length $l$. Unfortunately, the correct characteristic length $l$ which assures $D_{	ext{bulk}} = D_{	ext{por}}$ cannot be calculated by simple geometric means, which would enable us to skip either the calculation of $D_{	ext{bulk}}$ or $D_{	ext{por}}$. So the complexity of the problem cannot be reduced by the knowledge that such a characteristic length $l$ exists.

3.1. Bulk diffusivity of the MPL

The MPL model consists of solid material ($\Omega_{\text{solid}}$) and pores ($\Omega_{\text{pore}}$). In the bulk regime, diffusion is governed by Laplace’s equation

$$-\Delta c = 0 \quad \text{in} \quad \Omega_{\text{pore}}, \quad (1.7)$$

where $c$ is the gas concentration. We solve this equation numerically using Neumann boundary conditions on the solid surface and a concentration drop in one space direction as boundary conditions. Thus, the total diffusion flux is determined. With Fick’s law

$$j = -D_{\text{bulk}} \Delta c. \quad (1.8)$$

and the calculated diffusion flux $j$ we can determine $D_{\text{bulk}}$. To obtain the full diffusivity matrix $D_{\text{bulk}}$, the problem has to be solved for concentration drops in each space direction. This was done using the software package GeoDict [24], which includes solvers optimized for large voxel grids. Here, the explicit jump finite volume solver by Wiegmann and Zemitis [25], which determines $D_{\text{bulk}}$ using homogenization theory [26], was applied.

3.2. Knudsen diffusivity of the MPL

In the Knudsen regime, the continuum mechanical approach (1.7) is no longer valid. Now, the diffusion tensor has to be determined from the molecular movement. Let $x_0 \in \Omega_{\text{pore}}$ be the starting position of a molecule, $x' \in \Omega_{\text{pore}}$ be the position of a molecule after a time $t$ and $\xi = x' - x_0$ be the displacement. Then the diffusion matrix can be calculated by (see [18] and references therein):

$$D_{\text{Kn}} = \frac{\nu}{2} \hat{\xi}^T \hat{\xi} e^{e_\xi^2}, \quad (1.9)$$

where $\hat{\xi}^T \hat{\xi}$ is the expectation value of the correlation matrix $e^{e_\xi^2}$ and $\nu$ is the porosity of the structure.

Babovsky [27] developed an algorithm to model the movement of a single molecule in capillary tubes in the Knudsen regime. In the following, the methodology and its application to fuel cell MPL will be described. A start position $x_0$ and a start velocity $v$ are chosen randomly. The position is chosen uniformly distributed in the pore space. The velocity of the gas molecule has a Maxwellian probability distribution

$$p(v) = \left( \frac{\nu}{\pi} \right)^{\frac{1}{2}} e^{-\frac{\nu v^2}{2}}, \quad (1.10)$$

where $\nu$ is given by $\nu = \frac{m}{kT}$ and $k$ is the mean thermal velocity of the gas. Now the molecule moves with the velocity $v$ until it hits a wall. Then, the particle is reflected diffusely and a new velocity is chosen with components $v_r$ orthogonal to the wall and $v_t$ parallel to the wall with a probability density of

$$p(v_r, v_t, w_2) = 2\pi w_2 e^{-\frac{\nu v_r^2}{2}} \left( \frac{\nu}{\pi} \right)^{\frac{1}{2}} e^{-\frac{\nu w_2^2}{2}} e^{-\frac{\nu w_2^2}{2}}. \quad (1.11)$$

This continues until time $t$ is reached and the displacement $\xi = x' - x_0$ is determined. To calculate the diffusivity according to (1.9) a large number of molecules have to be tracked. The resulting diffusivity scales indeed linearly with $\nu$, so that Eq. (1.6) holds for the solution of this method.

3.3. Diffusivity of the GDL/MPL assembly

The GDL model consists of fibers and binder ($\Omega_{\text{solid}}$), pores ($\Omega_{\text{pore}}$) and the MPL ($\Omega_{\text{pore}}$). The diffusion flux through the whole GDL/MPL assembly is described by the equation

$$-\text{div}(D(x)\nabla c) = 0 \quad \text{in} \quad \Omega,$$

where $c$ describes the concentration of the gas species. The local diffusivity $D(x)$ is given by

$$D(x) = \begin{cases} D_{\text{bulk}} & \text{for} \ x \in \Omega_{\text{bulk}}, \\ D_{\text{por}} & \text{for} \ x \in \Omega_{\text{pore}}, \\ \left( D_{\text{bulk}}^{-1} + D_{\text{por}}^{-1} \right)^{-1} & \text{for} \ x \in \Omega_{\text{pore}}. \end{cases} \quad (1.13)$$

where $D_{\text{bulk}}$ and $D_{\text{por}}$ are determined as described in Sections 3.1 and 3.2 from a corresponding pore-scale model of the MPL. As these values are dependent on the Knudsen number, the solution of (1.12) differs for different gas species. The effective diffusivity of the whole layer is found by applying Fick’s law (1.8) similar to the determination of the bulk diffusivity. Again, the software package GeoDict [24] and the explicit jump finite volume solver [25] were used to solve this equation.

4. Exemplary results

It is the aim of this section to demonstrate the use of methods described in the previous sections by calculating the diffusion coefficient for the diffusion of $O_2$ in $N_2$. Necessary input parameters for this task are the binary diffusion coefficient $D_{\text{bulk}} = 20.86 \text{mm}^2/\text{s}$ and the mean thermal velocity $v = 444.1 \text{m/s}$ at standard conditions ($25\, ^\circ\text{C}, 101.3 \text{kPa}$) [28].

First, the effective diffusivity of the MPL has to be determined. For this purpose we created three MPL structure models as described in Section 2.1, using the same stochastic input parameters but different random seeds. Each model consists of $500 \times 500 \times 500$ grid points using a voxel length of $5 \text{nm}$. The construction process is isotropic, hence it is expected that the material properties are isotropic as well. This means that theoretically all diffusivity values on the principal diagonal of the diffusivity tensors are identical, and all secondary diagonal values are zero if we have a representative elementary volume (REV). Thus we averaged over three space directions and three models when determining the diffusivities. As result we received $D_{\text{bulk}} = 6.40 \text{mm}^2/\text{s}$ (standard deviation $0.11 \text{mm}^2/\text{s}$) and $D_{\text{por}} = 3.12 \text{mm}^2/\text{s}$ (standard deviation $0.16 \text{mm}^2/\text{s}$), or in dimensionless form $D_{\text{bulk}} = 0.307$ and $D_{\text{por}} = 0.386$ with a characteristic length $l = 54.6 \text{nm}$. The small deviations in the course of the averaging may indicate that the REV has been met. Using (1.2), we then get $D = 2.10 \text{mm}^2/\text{s}$ as diffusivity of $O_2$ in $N_2$.

This result now serves as input parameter for the next step: the diffusivity calculation for the whole GDL/MPL layer. Here, we created three structure models of the GDL fiber structure using identical stochastic parameters but different random seeds of the Poisson line process. Each model uses $550 \times 550 \times 288$ grid point and a voxel length of $0.625 \text{μm}$, thus showing an area of the GDL with side length $343.75 \text{μm}$ and the whole layer thickness of $180 \text{μm}$.

Three setups were considered:

(a) GDL without any MPL.
(b) MPL with an overall thickness of $20 \text{μm}$ was added to the GDL, intruding $10 \text{μm}$ into the layer. So the resulting model sized $550 \times 550 \times 304$ grid points and the layer had an overall thickness of $190 \text{μm}$.
(c) MPL with overall thickness of $100 \text{μm}$ was added which intrudes $90 \text{μm}$ into the GDL. As in (b) the overall layer thickness was still $190 \text{μm}$. 


By construction, we can expect different in-plane and through-plane diffusivities, but both in-plane directions give on average the same result. The local diffusivity \( D(x) \) which serves as input for (1.12) is given by

\[
D(x) = \begin{cases} 
2.10 \text{ mm}^2/\text{s} & \text{for } x \in \Omega_{\text{porous}}, \\
20.86 \text{ mm}^2/\text{s} & \text{for } x \in \Omega_{\text{per}}, \\
0 & \text{for } x \in \Omega_{\text{solid}}
\end{cases}
\]

(1.14)

where the value for \( \Omega_{\text{porous}} \) is the result of the above calculation. The results are summarized in Table 1; we observe that the MPL causes a strong reduction of the through-plane diffusivity and a moderate reduction of the in-plane diffusivity. The reason for the latter is that a strong reduction of the through-plane diffusivity and a moderate reduction of the in-plane diffusivity. The reason for the latter is that even in the case of the deeply penetrating MPL (MPL thickness 100 \( \mu \)m) still almost half of the GDL cross-section is dominated by the comparatively high effective diffusivity of the GDL.

5. Conclusion and outlook

We have developed a numerical method which allows for the determination of binary diffusion coefficients for all Knudsen numbers. The method is not restricted to a certain type of porous media (fibrous structures, sphere packing, cylindrical pores), as no assumptions about the structure have entered the numerics. Rather, the method can use any 3D structure model as input, thus allowing to use both virtually generated structures or 3D images. This makes it possible to evaluate the influence of various structural parameters on the diffusivity, e.g. to vary the porosity of the virtual MPL model structures or the agglomerate size and form and study the effect. The method is in principle not limited to MPL, but applicable to any porous media. For PEM fuel cells, it may also be used in catalyst layer modeling. As demonstrated, the resulting diffusivity values can be used as input parameters to obtain the diffusivity of the GDL/MPL assembly using a multi-scale approach. Basing the multi-scale method on a 3D voxel grid allows for considering any distribution of the MPL on and inside the GDL with this model, e.g. cracks, different penetration depths, etc. Again, the multi-scale approach is in principle not restricted to MPL/GDL assemblies but applicable to any porous media.

Future work comprises the validation of the modeling approach with experimental results. On the one hand, validating the MPL model requires the availability of diffusivity measurements of the MPL. Ideally, this utilizes free-standing MPL samples or, if free-standing MPL are not available, MPL that have been coated onto a GDL, which do not penetrate into the pore space of the GDL but form a distinct layer the diffusion properties of which can be back-calculated [29]. On the other hand, the realistic structure of the MPL has to be provided to the simulation in order to compare calculated and measured diffusivity results. Either imaging experiments and image processing methods have to be developed and applied to provide computational domains based on the real material with nm resolution, or virtual model representation based on reliable MPL characterization data (pore and particle size distribution, particle and aggregate morphology, etc.) have to be utilized. A further challenge is to provide the appropriate data in order to realistically model the MPL/GDL sandwich considering the MPL penetration profile and crack area density, shape and penetration depth, for instance.

Finally, a validated modeling approach would be ready and mature to serve the material development by means of virtual material design and provide material design guidelines and recommendations.

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References