Modelling of Microporous Layers

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Retrospection: Modelling of Gas Diffusion Layers without MPL

First step: Structure Model
- virtually created
- tomography image

Second step: Solve PDE
- Flow (Stokes Equation)
- Diffusion (Laplace Eq.)
- Conduction (Poisson Eq.)

Third step: Upscaling
- Permeability
- Diffusivity
- Conductivity
MPL Modelling - What is the Problem?

Gas diffusion layers (GDL) in technical applications (e.g. automotive) are typically coated with a microporous layer (MPL) to

• improve electrical and thermal contact to catalyst layer.
• protect membrane electrode assembly (MEA) from mechanical stress.
• enhance fuel cell performance and robustness under humid and wet operating conditions by improving water management.

MPL Modelling - What is the Problem?

Pore size distribution of GDL w/ MPL and GDL

Mean pore radii:
• MPL  10..100 nm
• GDL  10..100 µm

→ three orders of magnitude difference

Implications:
• GDL and MPL pores cannot be resolved in the same computational grid to numerically determine effective properties of assembly
• There are different transport mechanisms in GDL and MPL
  • GDL: bulk diffusion (particle-particle collisions dominate)
  • MPL: contribution of Knudsen diffusion (significant particle-wall collisions)
Outline / Approach

A) Modelling of the MPL (stand-alone)
   1. Structure model (resolution ~ 5 nm)
   2. Determination of MPL diffusivity

B) Modelling of GDL plus MPL
   1. Structure model (resolution ~ 1µm) with homogenised MPL
   2. Determination of diffusivity of GDL plus MPL
A) Modelling of the MPL
MPL Structure Model: Material Parameters

Primary particle and particle aggregate data, e.g. acetylene black:
• Particle size 42 nm
• Aggregate size 200 particles
• Surface area 51 m²/g
• Shape parameters

Pore size distribution:
• Shape of pore size distribution
• MPL porosity 55%

SEM images of MPL surface and cross-section → visual plausibility check
MPL Model and SEM Picture

Virtually created model

SEM picture
Diffusion

Macroscopic description (homogenized porous media model)
Fick's first law:

\[ j = -D^* \nabla c \]

- \( D^* \): anisotropic effective diffusivity [m²/s]
- \( j \): diffusion flux [mol/m²/s]
- \( \nabla c \): concentration gradient [mol/m³/m]

Microscopic description (pore structure model)
- \( j \) and \( D^* \) can be calculated
- Depending on the Knudsen number, the diffusion mechanisms in the pores change.

\[ Kn = \frac{\text{mean free path}}{\text{characteristic length}} \]
Diffusion Mechanisms

1) Kn >> 1 (Knudsen diffusion)
Diffusion by particle-wall collisions
Mathematical model: random walk methods

2) Kn << 1 (bulk diffusion)
Diffusion by particle-particle collisions
Mathematical model: Laplace equation

3) Kn ~ 1 (transition regime diffusion)
Both mechanisms are present
**Diffusion at Kn~1: Bosanquet's Formula**

Bosanquet's formula: \[ D = \left( D_{bulk}^{-1} + D_{Kn}^{-1} \right)^{-1} \]

Coefficient \( D_{bulk} \)
- describes diffusion by particle - particle collisions
- scales with \( D_{bulk} = \frac{1}{3} \lambda \bar{v} D_1 \)
- determined by solving Laplace equation

Coefficient \( D_{Kn} \)
- describes diffusion by particle - wall collisions
- scales with \( D_{Kn} = \frac{1}{3} l \bar{v} D_2 \)
- determined by random walk methods

Definitions:
- \( \varepsilon \) porosity
- \( \bar{v} \) mean thermal velocity
- \( \lambda \) mean free path
- \( l \) char length

Remarks:
- \( D_1 \) and \( D_2 \) are dimensionless and independent from \( \lambda, l, \bar{v} \)
- Tortuosity \( \eta_1 = \varepsilon / D_1 \)
- Knudsen tortuosity: \( \eta_2 = \varepsilon / D_2 \)
Determination of $D_{Kn}$

The diffusivity matrix can be calculated from the displacement of a set of gas molecules, where for each molecule we

- start at a random position $x^0$
- find the end position at time $t$ by a random walk: $x^t$
- calculate the displacement vector: $\xi = x^t - x^0$

Diffusivity matrix: 

$$D_{Kn} = \frac{\varepsilon}{2t} E \left[ \xi \xi^T \right]$$

( $E[...]$ expectation value, $\varepsilon$ porosity)

Random walk (for a single molecule):

- if molecule hits a wall, choose new velocities $(v, w_1, w_2)$, $v$ orthogonal to wall, $w_1, w_2$ parallel to wall with probability density (Maxwell):

$$p(v, w_1, w_2) = 2\alpha v e^{-\alpha v^2} \sqrt{\frac{\alpha}{\pi}} e^{-\alpha w_1^2} \sqrt{\frac{\alpha}{\pi}} e^{-\alpha w_2^2}$$

- molecule moves with this velocity until it hits a wall.
- speed determined by $\alpha = \frac{4}{\pi v^2}$

Results: Diffusivity of O$_2$ in N$_2$ in the MPL

Gas species parameters for diffusion of O$_2$ in N$_2$ (Input):
- mean thermal velocity: 444.1 m/s
- absolute diffusivity (no obstacles): 20.86 mm$^2$/s
- mean free path: $\lambda = 140.9$ nm

These parameters lead to the following diffusivity values (isotropic) for the MPL:
- Knudsen diffusion: $D_{Kn}$ 3.12 mm$^2$/s
- Bulk diffusion: $D_{bulk}$ 6.40 mm$^2$/s
- Bosanquet formula gives: $D = 2.10$ mm$^2$/s
B) Modelling of GDL plus MPL
GDL Model: Material Parameters

GDL:
• Fibre diameter 7 µm
• Fibre density 1.9 g/cm³
• Binder density 1.7 g/cm³
• GDL thickness 180 µm
• Assumptions:
  • Fibre content 11 vol%
  • Binder content 50 wt%
GDL Model with Homogenised MPL

GDL+MPL model parameters:

- Voxel length 0.625 µm
- Geometry size: 550 x 550 x 304 voxels
- GDL thickness: 180 µm
- MPL thickness: 10 µm +10 µm
- Overall thickness: 190 µm
Results: Diffusivity of GDL/MPL Assembly

Input: (Diffusivities of $O_2$ in $N_2$):
- Pore space (black): 20.86 mm$^2$/s
- MPL (green): 2.10 mm$^2$/s
- Fibres (white): 0
- Binder (red): 0

Solve equation: $\text{div}(d(x)\nabla u) = 0$

<table>
<thead>
<tr>
<th></th>
<th>$D_x$ [mm$^2$/s]</th>
<th>$D_y$ [mm$^2$/s]</th>
<th>$D_z$ [mm$^2$/s]</th>
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</thead>
<tbody>
<tr>
<td>without MPL</td>
<td>11.54</td>
<td>11.73</td>
<td>9.71</td>
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<tr>
<td>MPL</td>
<td>10.30</td>
<td>10.36</td>
<td>5.98</td>
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Conclusions

Summary
• Method to determine diffusivity of MPL and MPL+GDL developed
• Approach can now be used to study different geometrical setups

Challenges / Open Problems
• No tomographical 3D images available for MPL
• Generating realistic MPL models requires MPL-only material data:
  • porosity, pore size distribution...
• Generating realistic MPL+GDL models requires
  • penetration depth, cracks etc.
• Experimental validation of simulated MPL+GDL diffusivities
  • MPL-only, MPL+GDL
Outlook: Pore Scale Material Visualization

Exemplary method:
Dual-beam focused ion beam/scanning electron microscopy nanotomography (FIB/SEM) w/ serial slicing

Major challenges:
• Resolution in slicing direction
• Image processing/segmentation (visibility of pore background)

single FIB/SEM image of typical MPL from image stack obtained by serial slicing