Modelling of Microporous Layers

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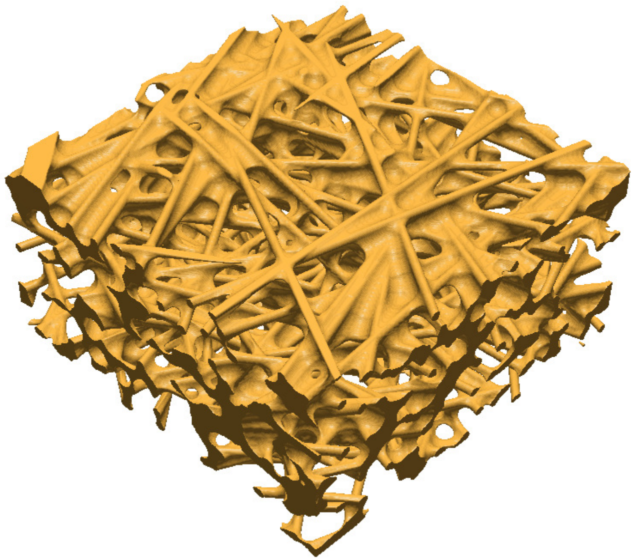
Retrospection: Modelling of Gas Diffusion Layers without MPL

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



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MPL Modelling - What is the Problem?

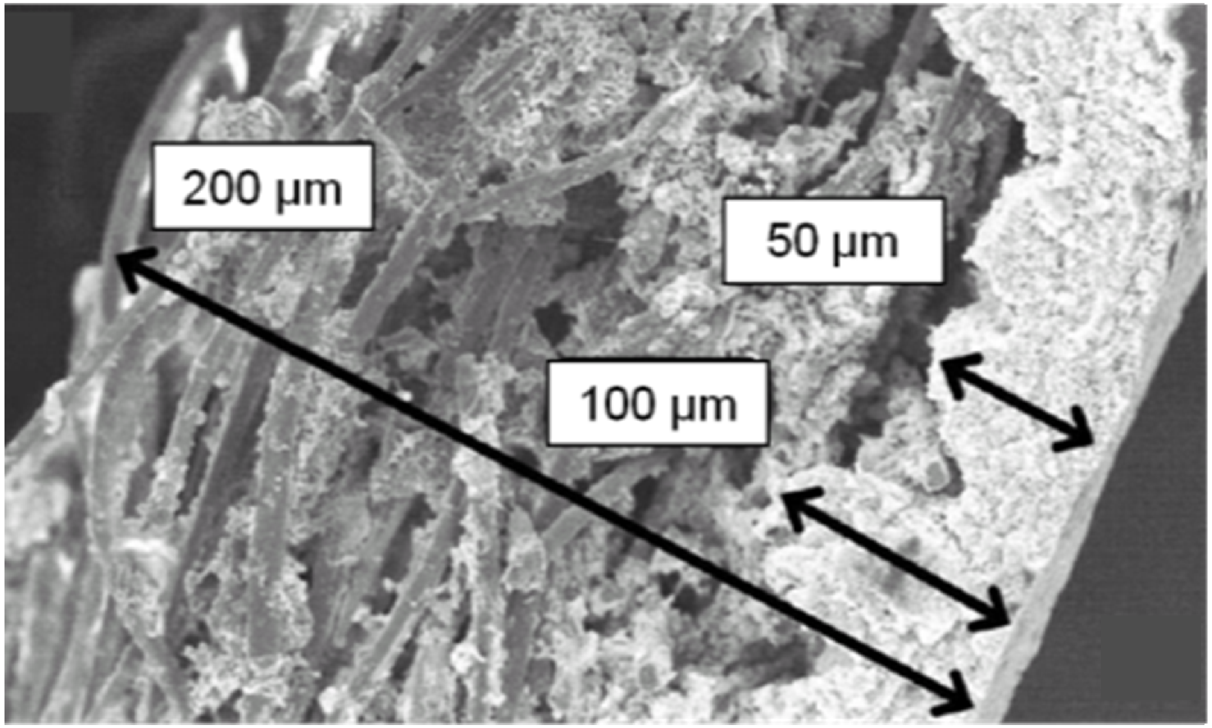

image source: Gostick et al., Journal of Power Sources 156 (2006), p. 375-387

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.

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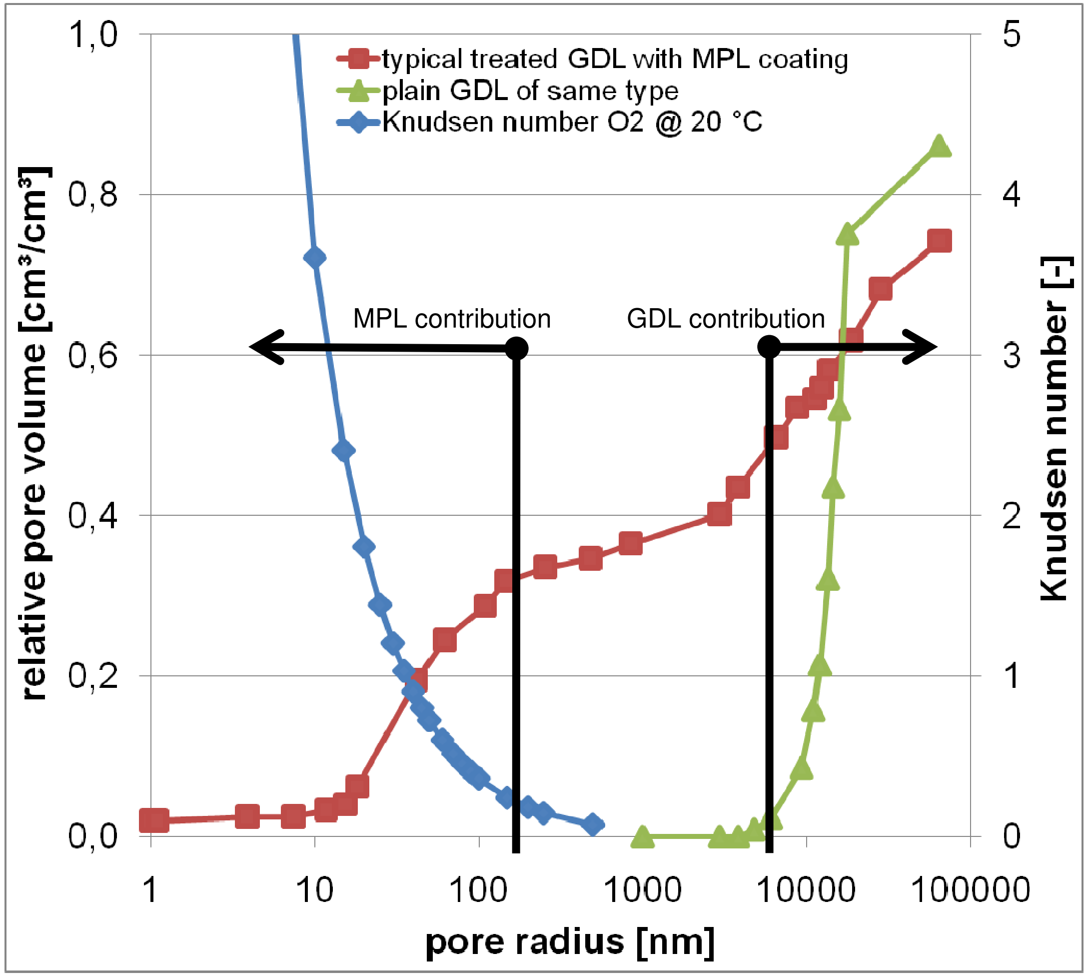

Pore size distribution of GDL w/ MPL and GDL

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)

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Outline / Approach

A) Modelling of the MPL (stand-alone)

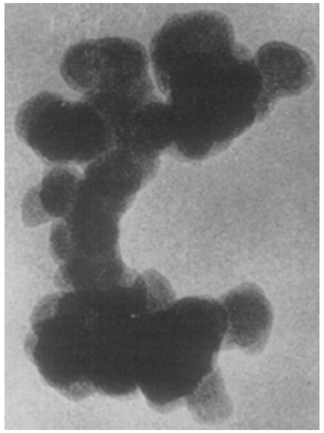
1. Structure model (resolution ~ 5 nm)
2. Determination of MPL diffusivity

B) Modelling of GDL plus MPL

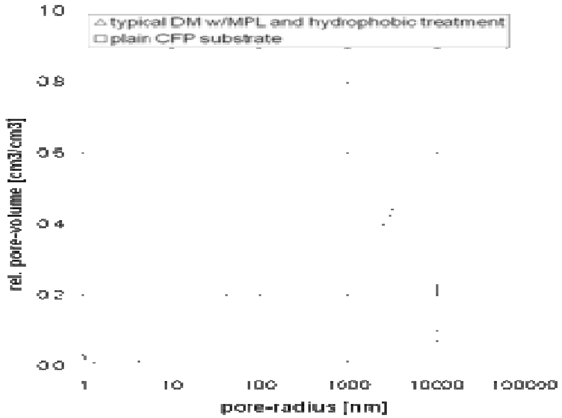
1. Structure model (resolution ~ 1µm) with homogenised MPL
2. Determination of diffusivity of GDL plus MPL

A) Modelling of the MPL

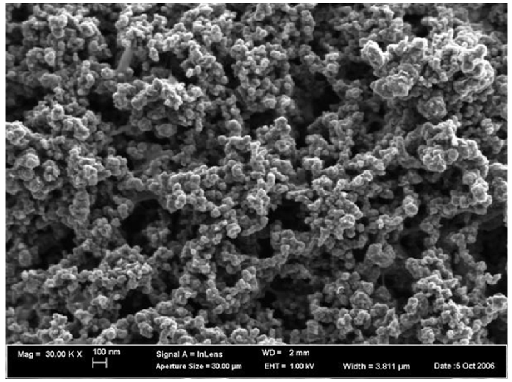
MPL Structure Model: Material Parameters



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

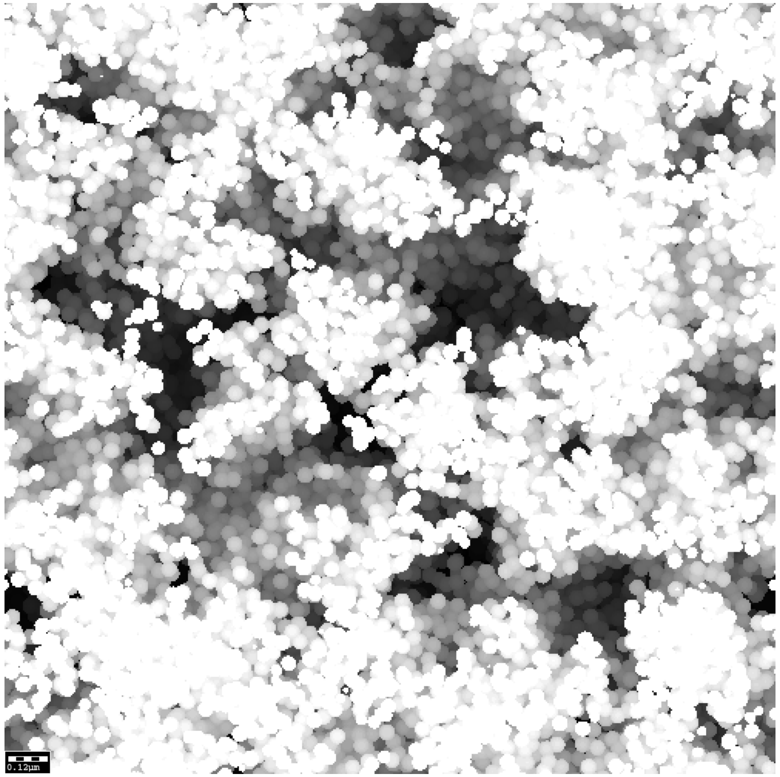


Pore size distribution:
- Shape of pore size distribution
- MPL porosity 55%

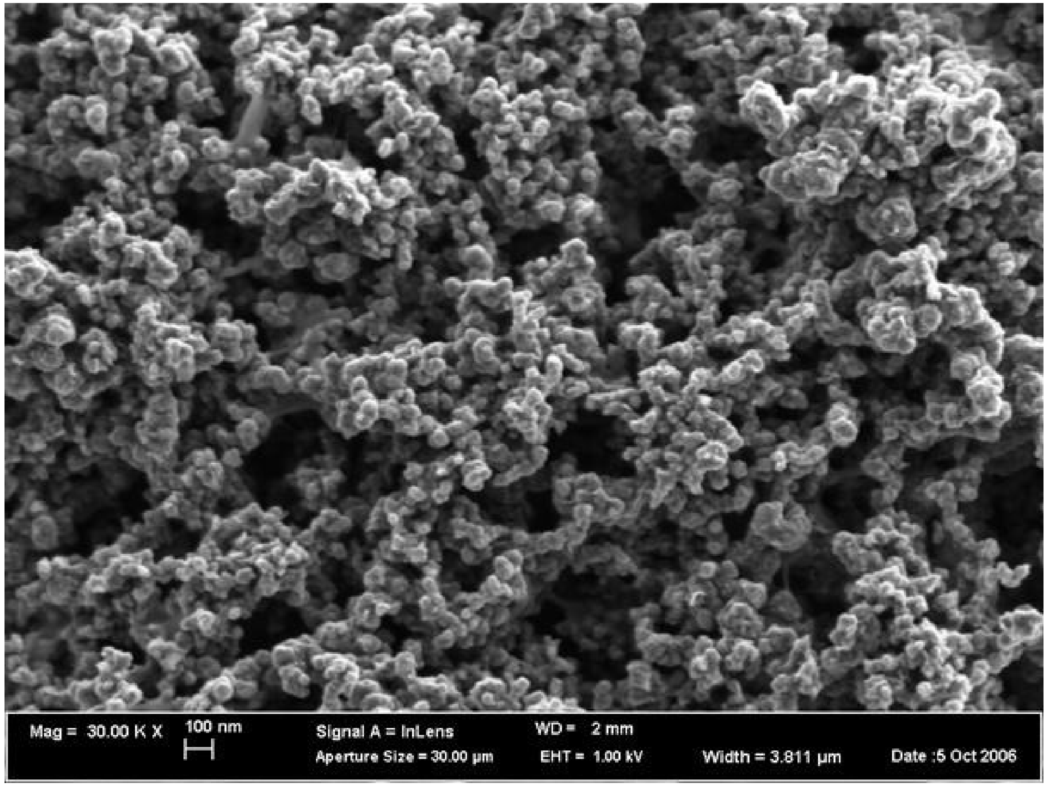


SEM images of MPL surface and cross-section
→ visual plausibility check

MPL Model and SEM Picture



Virtually created model



SEM picture

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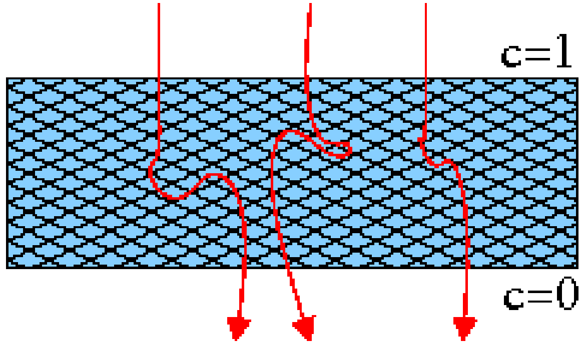
Diffusion

Macroscopic description (homogenized porous media model)

Fick's first law:

$$j = -D^{*}\nabla c$$



D^{*} : ansiotropic effective diffusivity [m²/s]

j : diffusion flux [mol/m²/s]

∇ c : concentration gradient [mol/m³/m]

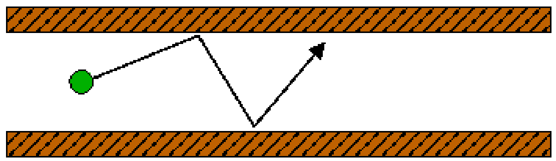
Microscopic description (pore structure model)

• j and D* can be calculated

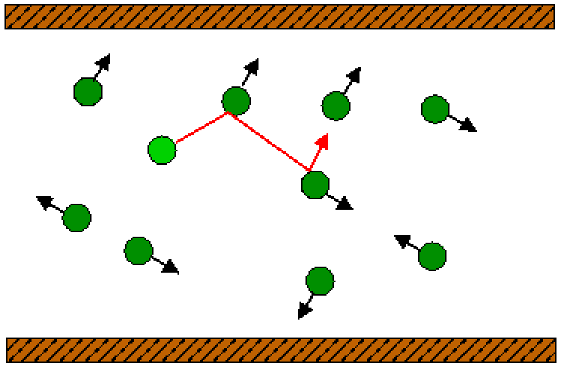
• Depending on the Knudsen number $Kn = \frac{\text{mean free path}}{\text{characteristic length}}$ the diffusion mechanisms in the pores change.

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

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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:
- ε porosity
- v mean thermal velocity
- λ mean free path
- l char length

Remarks:
- D_1 and D_2 are dimensionless and independent from λ, *l*, *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: $D_{Kn} = \frac{\epsilon}{2t} E\left[\xi\xi^T\right]$

(E[...] expectation value, ε 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 $\alpha = \frac{4}{\pi \bar{v}^2}$

H. Babovsky, On Knudsen Flows within Thin Tubes, J. Stat. Physics 44, pp 865--878, 1986.

Results: Diffusivity of O_2 in N_2 in the MPL

Gas species parameters for diffusion of O_2 in N_2 (Input):

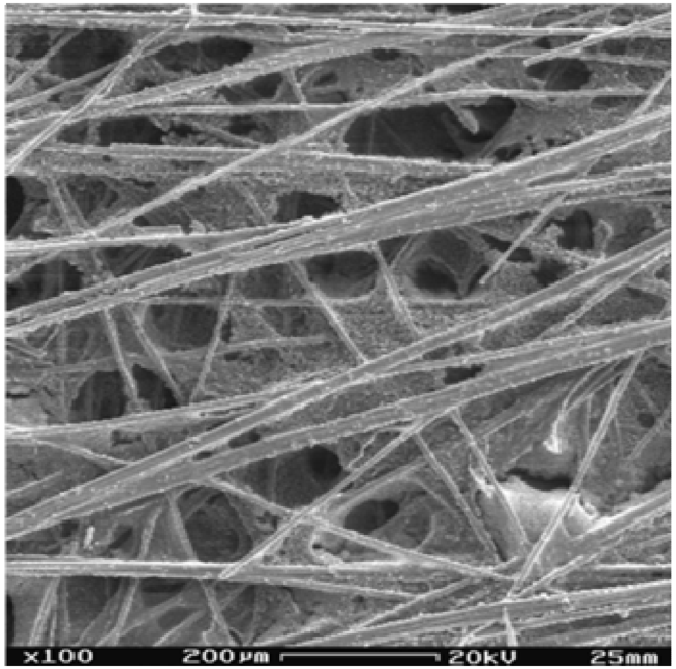
- mean thermal velocity: 444.1 m/s
- absolute diffusivity (no obstacles): 20.86 mm^2/s
- mean free path: λ = 140.9 nm

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

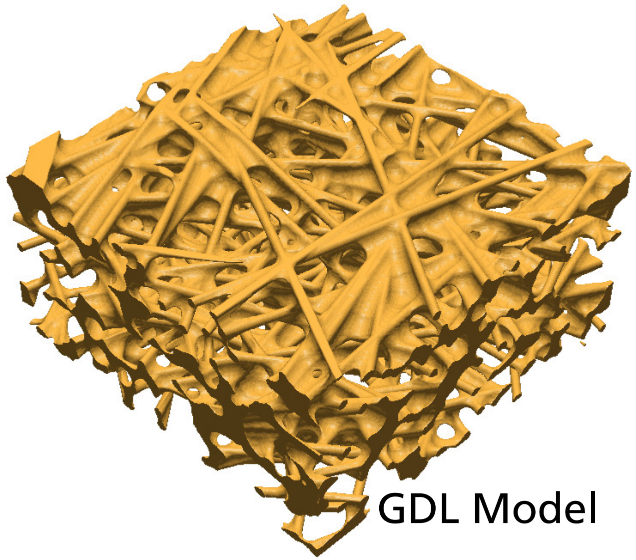
B) Modelling of GDL plus MPL

GDL Model: Material Parameters



SEM Picture

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%



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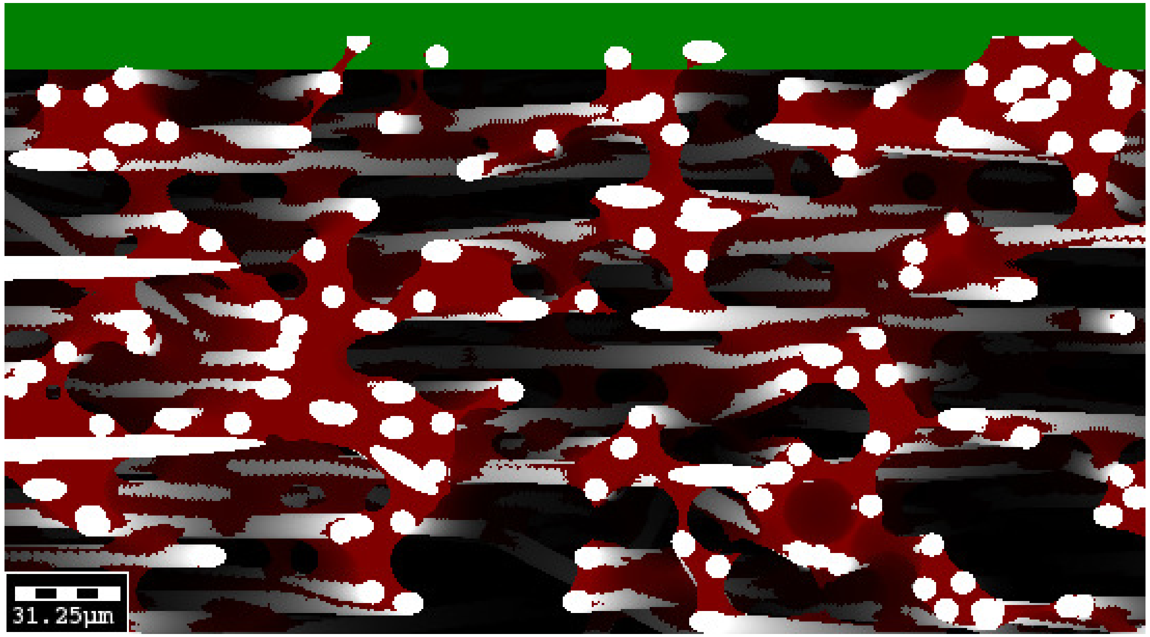
GDL Model with Homogenised MPL

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



Substrate with MPL layer

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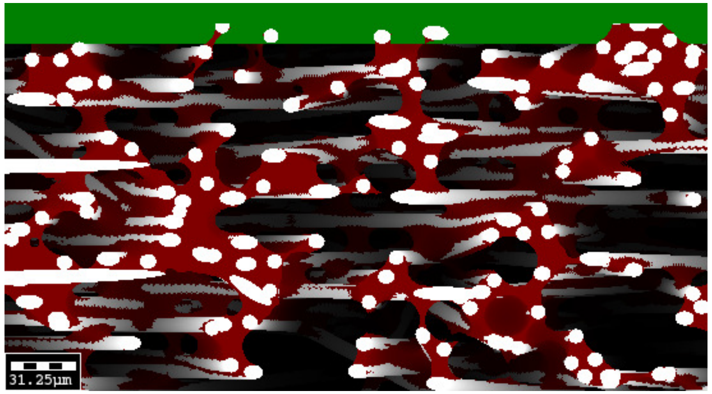
Results: Diffusivity of GDL/MPL Assembly

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: $\mathrm{div}(d(x)\nabla u) = 0$

	D_x [mm^2/s]	D_y [mm^2/s]	D_z [mm^2/s]
without MPL	11.54	11.73	9.71
MPL	10.30	10.36	5.98

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Conclusions

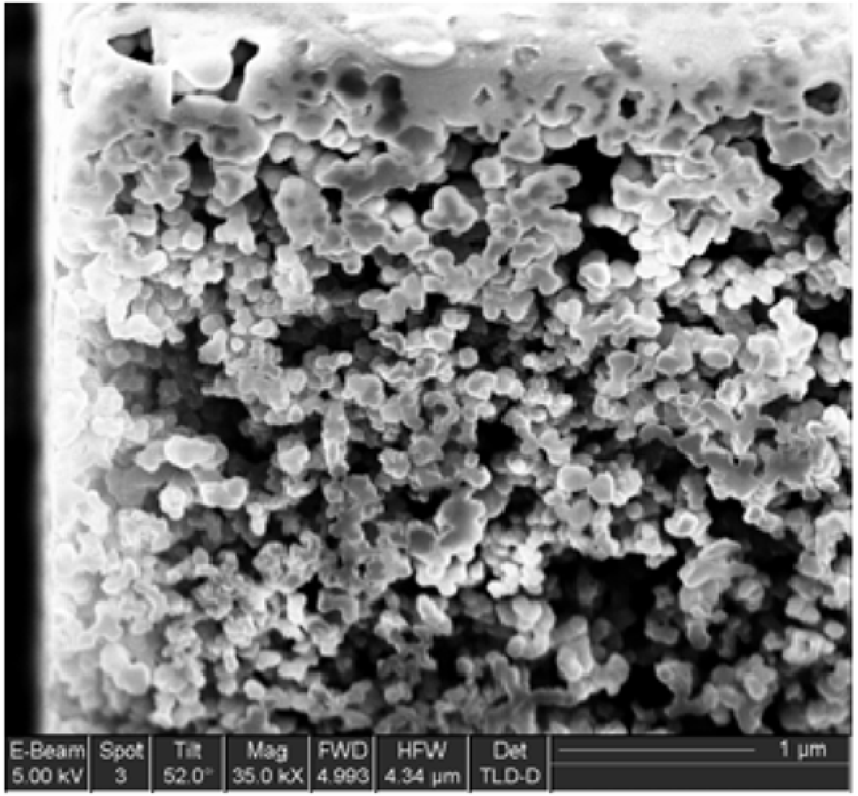
Summary

- 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

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