Prediction of Diffusivity and Tortuosity in Micro and Nano Pores

Jürgen Becker

GeoDict User Meeting 2012

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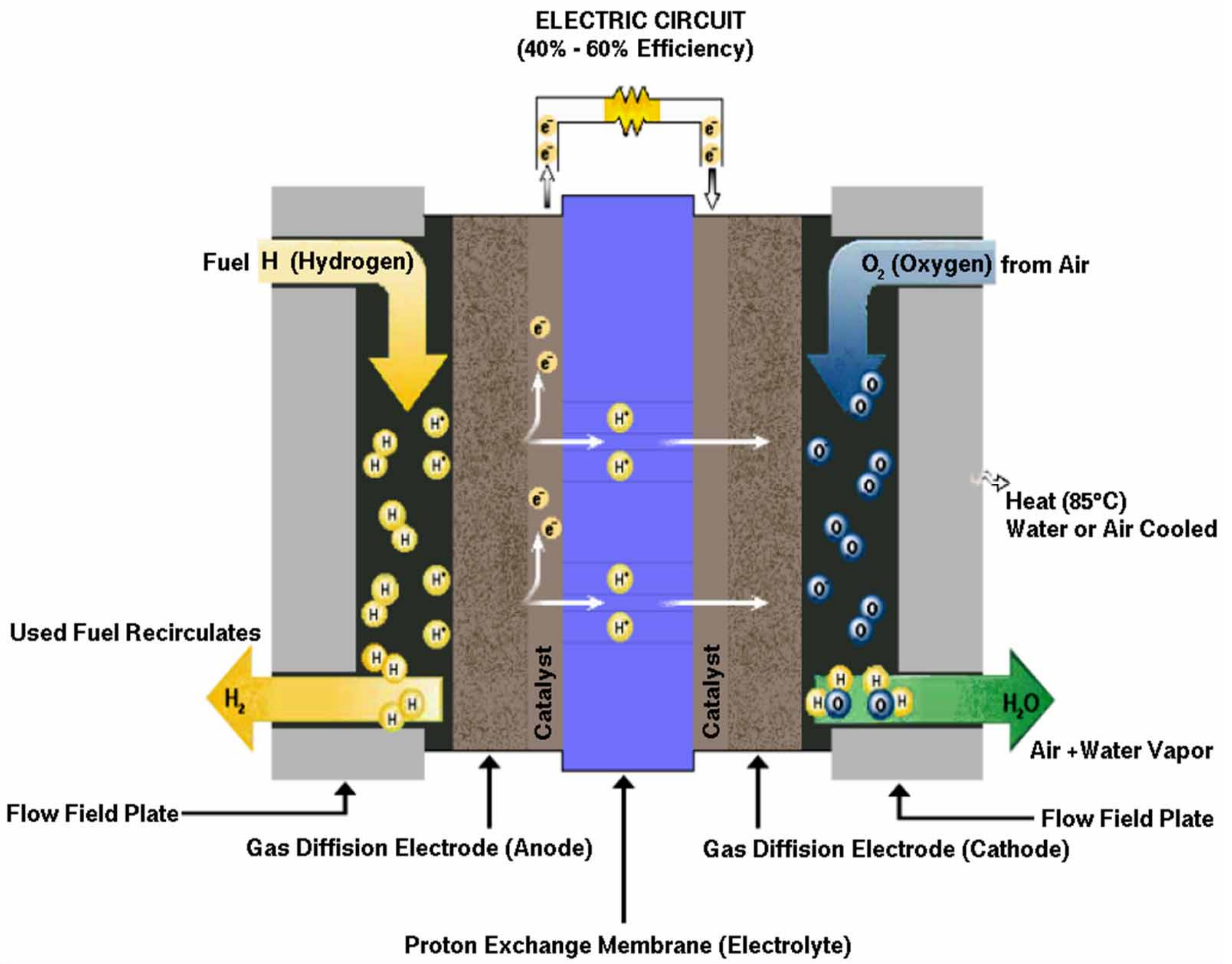
Proton Exchange Membrane (PEM) Fuel Cell



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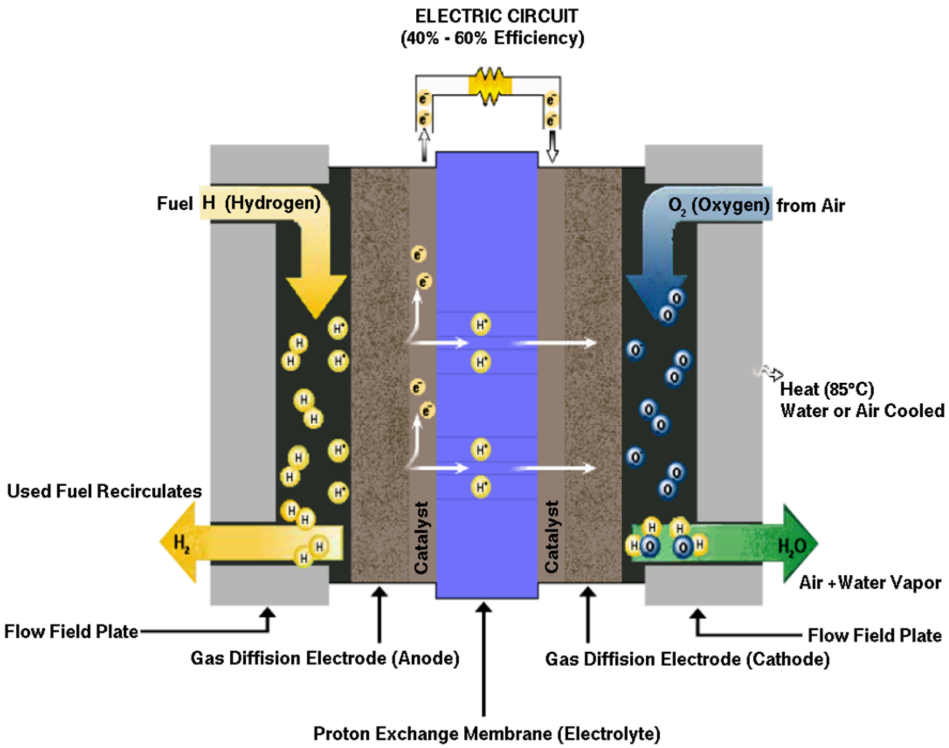
Porous Layers in a PEM Fuel Cell



- Gas Diffusion Layer
- Micro-porous Layer
- Catalyst Layer
- Membrane

Topic of this talk:
Oxygen transport (diffusion)
from flow channel to catalyst.

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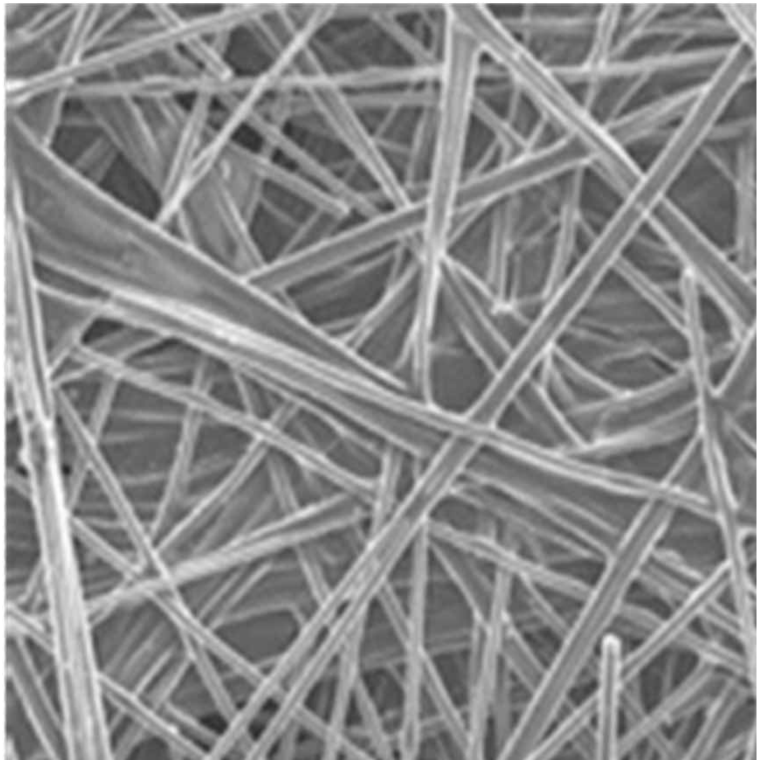
Gas Diffusion Layer (GDL)



- Carbon Fibers (7 µm diam.)
- Teflon Coating
- Pore Sizes ~ 30 µm
- Thickness 200-400 µm

Optional:

- Binder
- Entangled Fibers
- Filling

Alternative:

- Woven Carbon Paper

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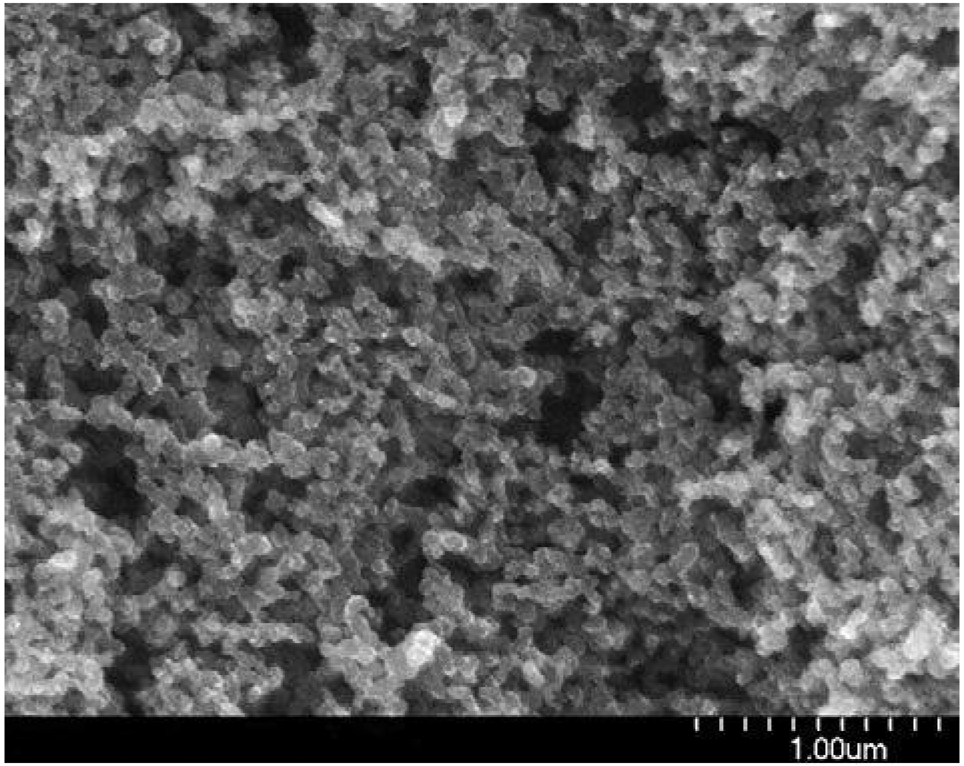
Microporous Layer (MPL)



Chun et al, Int. J. Hydrogen Energy 35, 2010

- Carbon Agglomerates
- Pore Sizes ~ 100 nm

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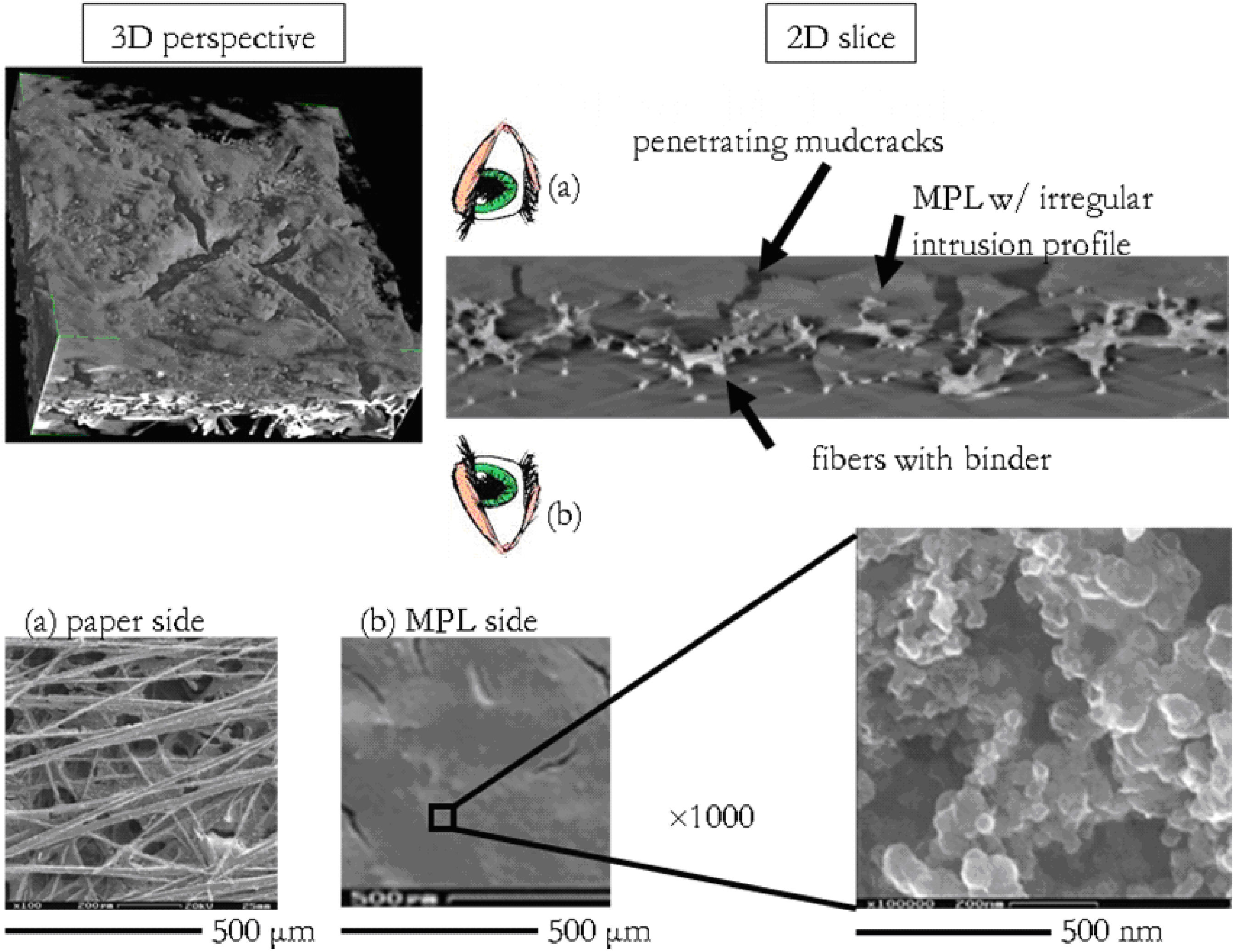
GDL and MPL



Becker, Wieser, Fell, Steiner, Int. J. Heat and Mass Transfer 54, 2011

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Overview / Idea

1. Structure Model
   - GDL model (voxel length ~ 1 µm)
   - MPL model (voxel length ~ 10 nm)
   - Combined GDL + MPL model (voxel length ~ 1 µm)

     (=> material with micro and nano-pores)
2. Diffusivity
   - GDL model
   - MPL model (Knudsen diffusion)
   - Combined GDL + MPL model
3. Outlook: Flow through membranes with nano-pores

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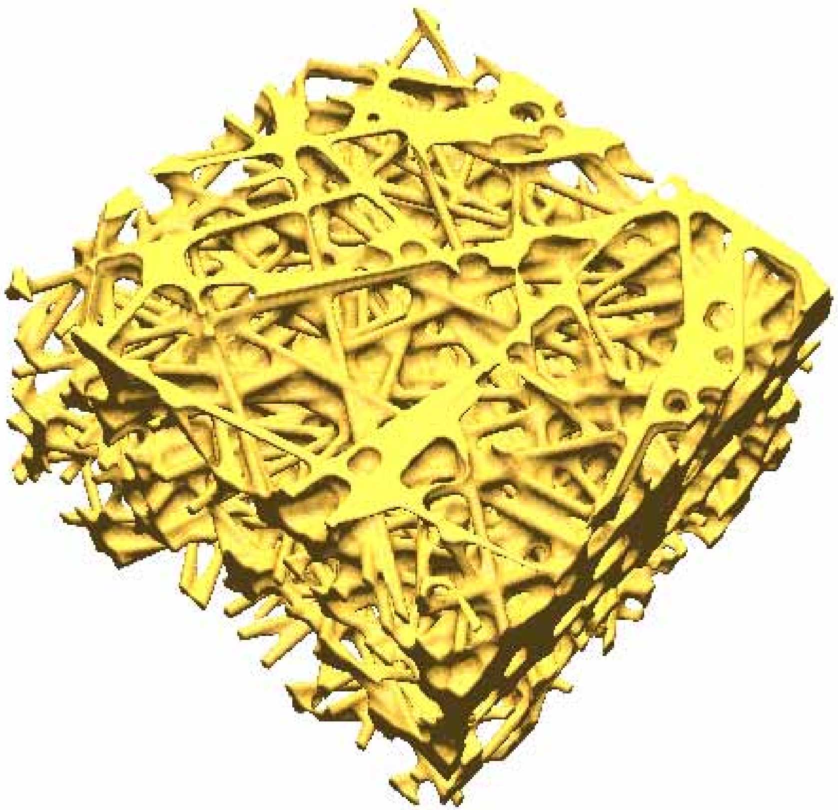
3D Model: Gas Diffusion Layer

FiberGeo:

- Straight, infinitely long fibers
- Circular cross section
- Anisotropic

ProcessGeo:

- Weight% binder



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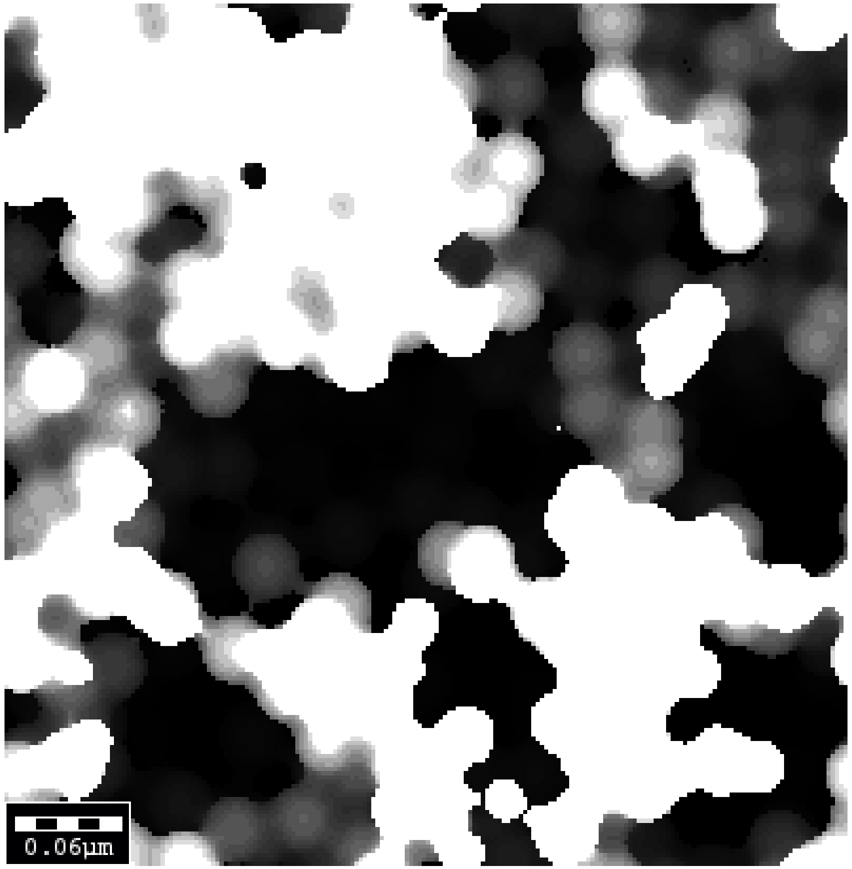
MPL Model

1. Create large pores
   (SinterGeo-Create & Invert)
2. Create carbon particles
   (SinterGeo-Create with 'On current structure' as centre distribution)
3. Glue
   (2x ProcessGeo-Dilate)

Parameters: radii, volume fractions



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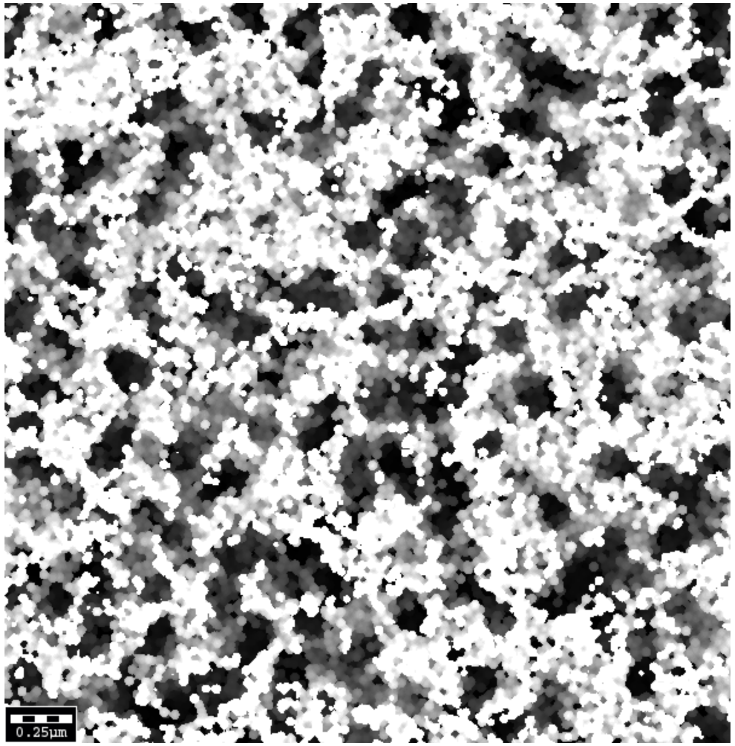
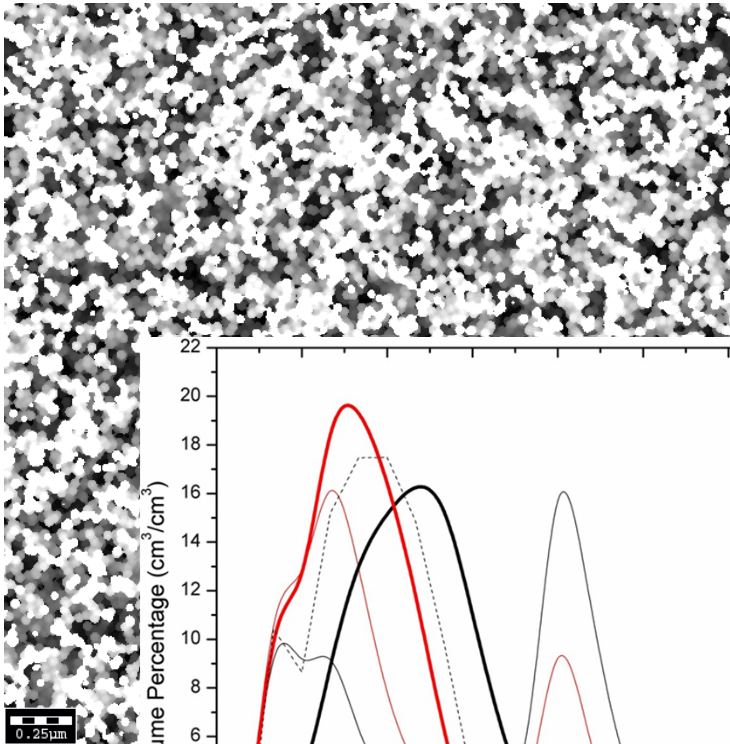
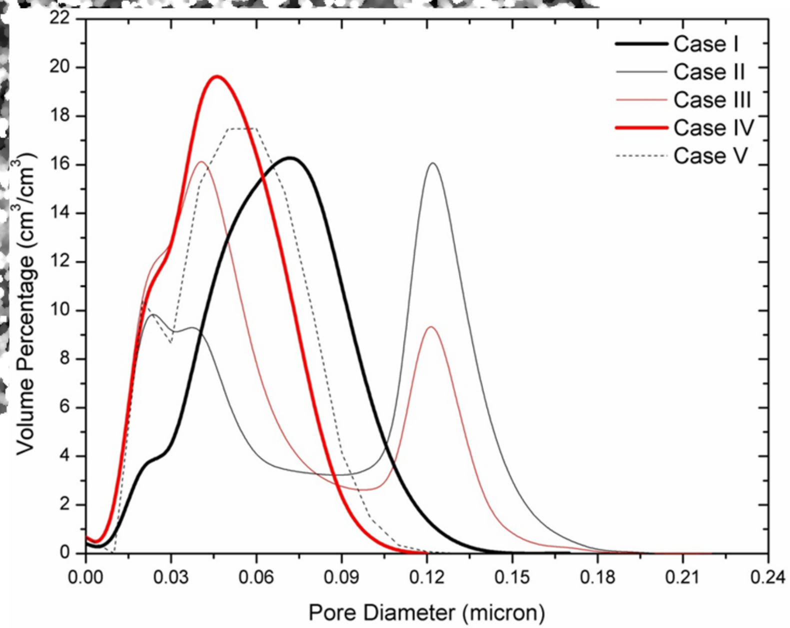
Create Different MPL







- same porosity & carbon particle sizes
- different pore size distributions

Zamel, Becker, Wiegmann, J. Power Sources 207, 2012

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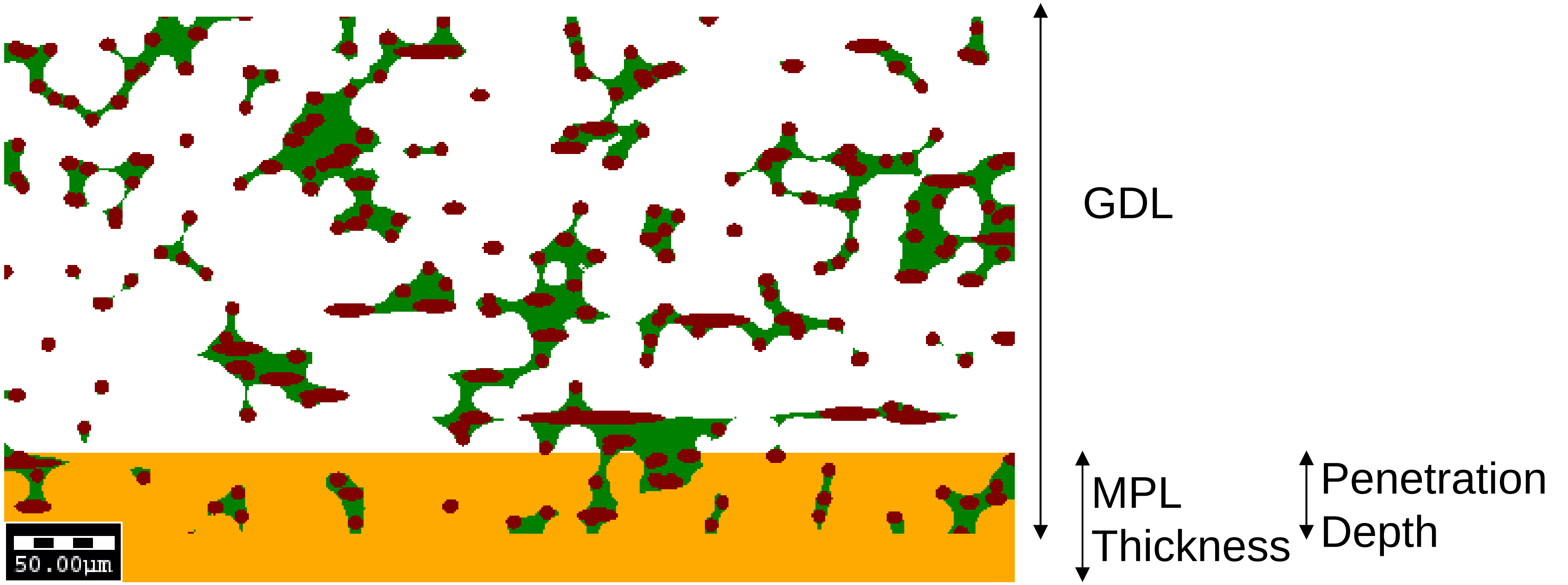
GDL / MPL Assembly



2D Cross Section

Red: Fibers
Green: Binder
Orange: MPL

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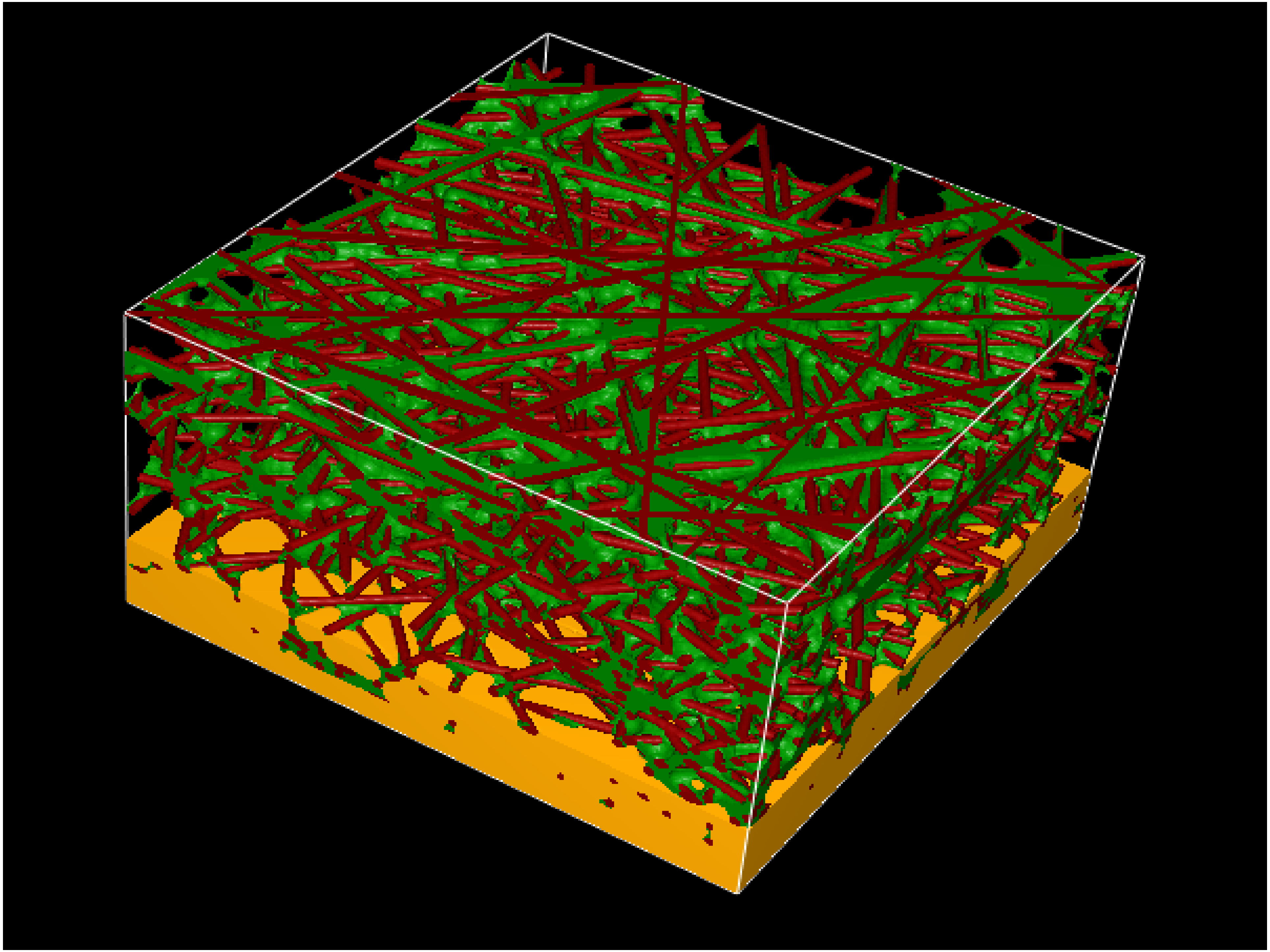
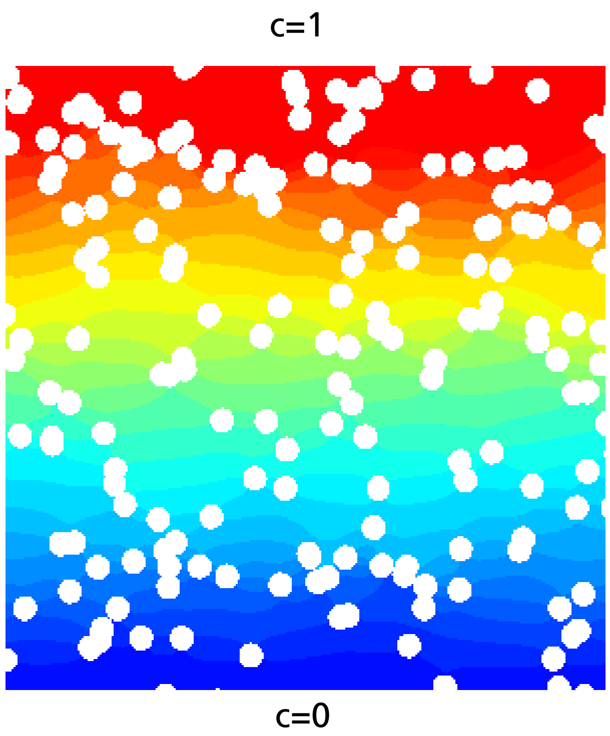


Diffusivity

Macroscopic description
(homogenized porous media model)
Fick's first law: $j = -D^* \nabla c$

D^* : effective diffusivity [m²/s] ***unknown***
j : diffusion flux [mol/m²/s]
c : concentration [mol/m³]

Microscopic description (pore structure model)
Laplace equation: $-\Delta c = 0$



Boundary conditions:
no-flux on fibre surface, concentration drop

D^* can be determined from the solution!

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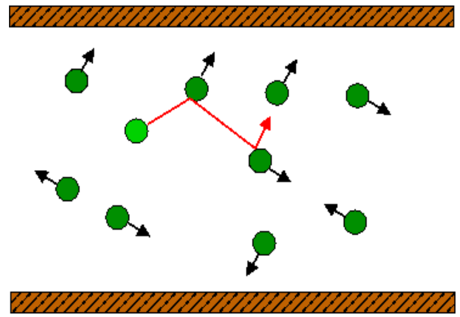
Knudsen Diffusivity

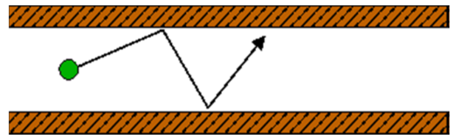
Macroscopic description
(homogenized porous media model)
Fick's first law: $j = -D^{*}\nabla c$



D : effective diffusivity [m²/s] ***unknown***
j : diffusion flux [mol/m²/s]
c : concentration [mol/m³]

Diffusion mechanisms

1. Kn << 1 (bulk diffusion)
   - Diffusion by particle-particle collisions
   - Mathematical model: Laplace equation
2. Kn >> 1 (Knudsen diffusion)
   - Diffusion by particle-wall collisions
   - Mathematical model: random walk methods
3. Kn ~ 1 (transition regime diffusion)
   - Both mechanisms are present, Bosanquet:



$$D_{Kn} = \frac{\varepsilon}{2t} E[(x_t - x_o)(x_t - x_o)^T]$$

$$D = \left(D_{bulk}^{-1} + D_{Kn}^{-1}\right)^{-1}$$

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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} unit: m²/s
- particle - particle collisions
- scales with $D_{bulk} = \frac{1}{3}\lambda\bar{v}D_{b*}$
- determined by solving Laplace equation

Coefficient D_{Kn} unit: m²/s
- particle - wall collisions
- scales with $D_{Kn} = \frac{1}{3}l\bar{v}D_{k*}$
- determined by random walk method

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

Remarks:
- D_{b*} and D_{k*} are dimensionless and independent from λ, *l, v*
- Tortuosity $\tau_b = \varepsilon/D_{b*}$
- Knudsen tortuosity: $\tau_k = \varepsilon/D_{k*}$

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Determination of D_{Kn}

The diffusivity matrix is calculated from the displacement of a set of molecules.

For each molecule:

- start at a random position x^0
- find end position x^t at time *t* by random walk
- calculate 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 (single molecule):

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

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

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

H. Babovsky, J. Stat. Physics 44, pp 865--878, 1986.

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Procedure

1. Load MPL model
2. DiffuDict: determine "Bulk (Laplace) Diffusion"
   - get a dimensionless effective diffusivity
3. DiffuDict: determine "Knudsen Diffusion"
   - get a dimensionless effective Knudsen diffusivity

4. DiffuDict: use "Bosanquet Approximation"
   - use *.gdr files from 2. and 3. as input
   - mean thermal velocity: 425 m/s
   - mean free path: 63.3 nm

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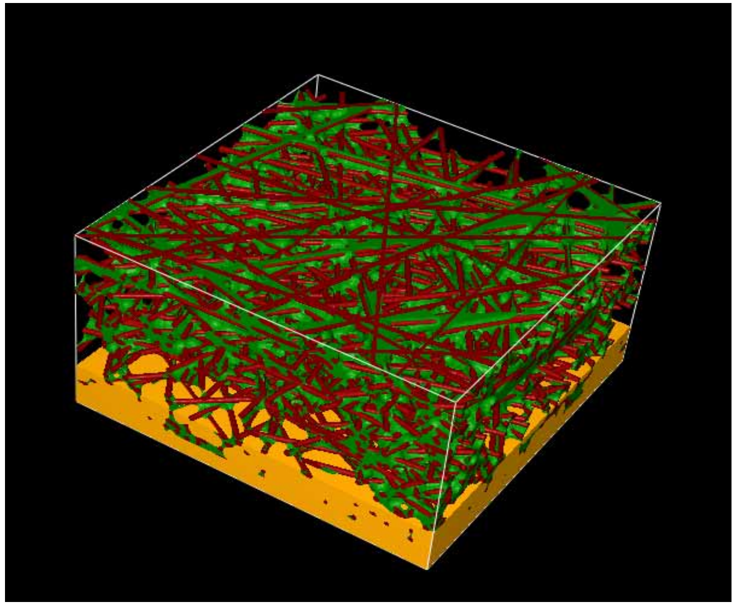
Procedure



5. Load GDL+MPL model
6. ConductoDict:
   - Pore space: $D_{pore} = \frac{1}{3}\lambda\overline{v} = 8.96E-6$
   - MPL: value as calculated in 4.
   - Fibers / Binder : D=0

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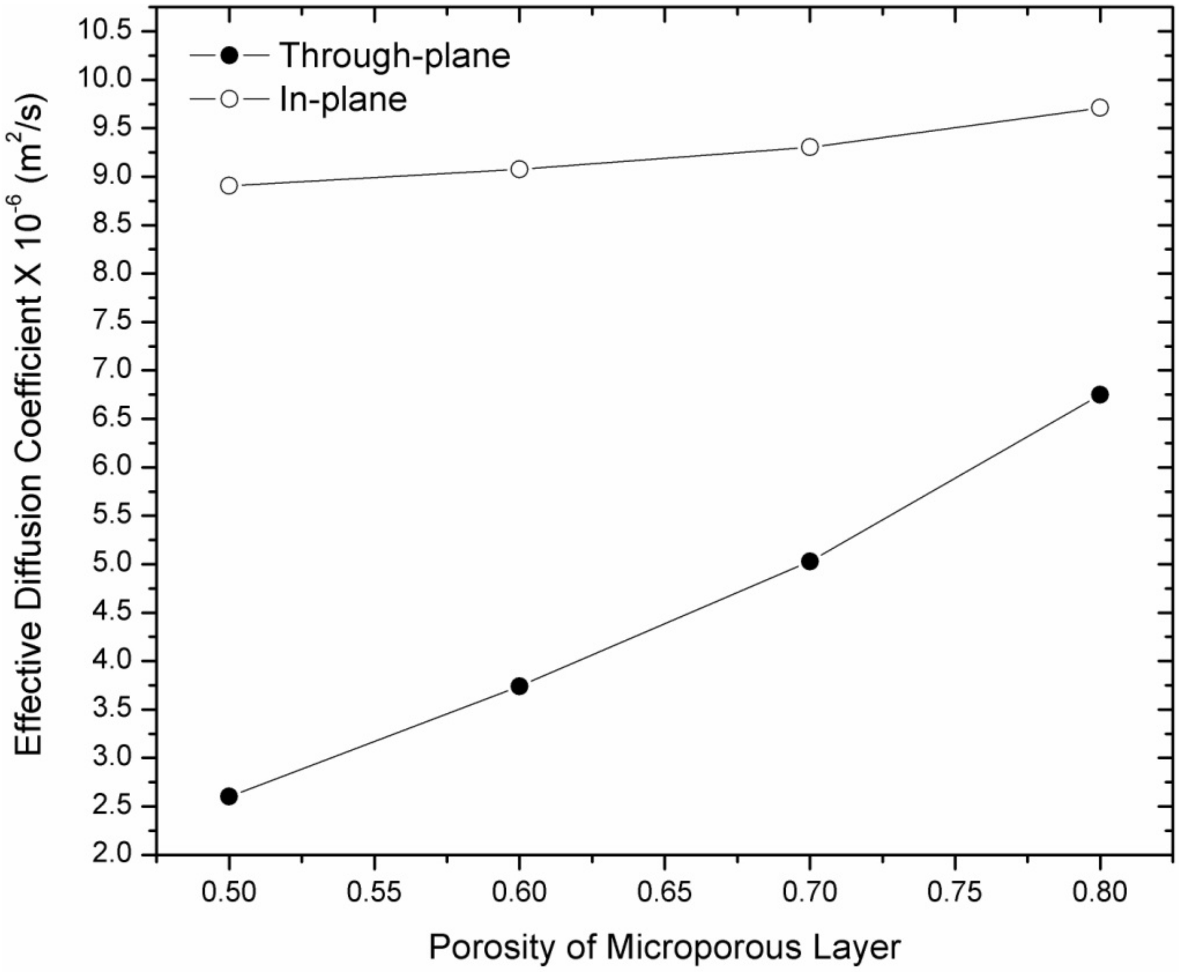
Variation of MPL Porosity



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Summary

- Material with pores from nm to µm range
- Create two models with different resolution
- Determine values for small-scale model first, use these as input in large-scale model.
- Diffusion on small scale has to consider Knudsen diffusion

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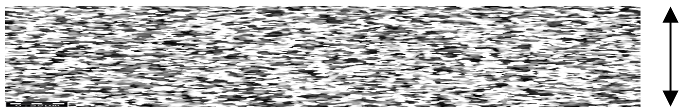
Outlook: Flow through Membrane

$$N = \frac{p}{RT}\left(\frac{\kappa}{\eta}\frac{p_1 - p_2}{L} + D_{Kn}\frac{1}{L}\ln\left(\frac{p_1}{p_2}\right)\right)$$



N: flux through membrane [mol/s/m²]
T: temperature
R: gas constant
η: dynamic viscosity

κ: through-plane permeability as calculated with FlowDict [m²]
$D_{Kn} = \frac{1}{3} l \bar{v} D_{k*}$: through-plane Knudsen diffusivity [m²/s]

L. Pant, S. Mitra, M. Secanell, J. Power Sources, 2012

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