Pore Scale Modelling of Porous Layers in a PEFC

ModVal 7, Lausanne 23.03.2010

Jürgen Becker

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Motivation

- MEA is an assembly of porous layers: GDL, MPL, CL, membrane
- Each layer needs to have optimal properties
- Properties of a porous medium are influenced by
  - Material
  - Pore structure

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Our goal: enable virtual material design!

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Outline

1. *Creation of 3D virtual structure models*
2. Determination of effective properties
3. Validation

GEO DICT

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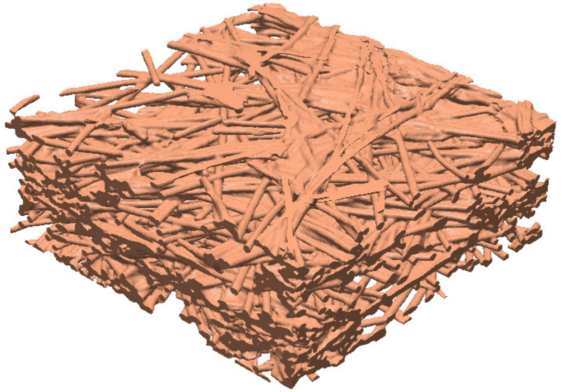
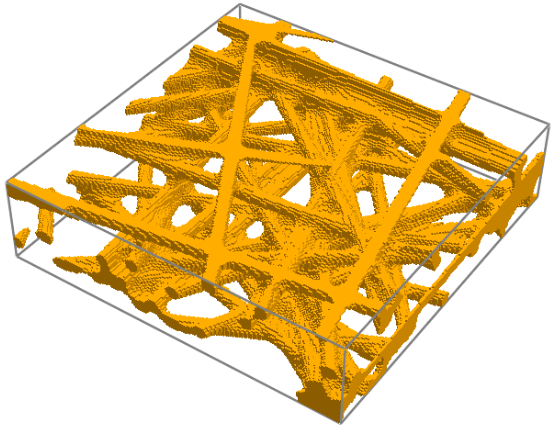
3D Structure Model

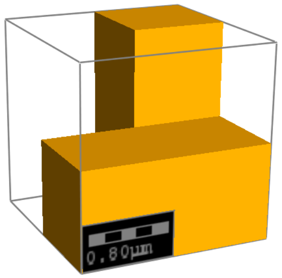
Two sources:

1) tomography image (segmentation)



2) virtually generated (stochastic geometry)





all structure models:
cubic voxels (voxel = volume pixel)

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3D Models: Gas Diffusion Layer (GDL)

Typically: nonwoven fibre structures plus binder

Input:
- Porosity
- Fibre diameter and type
- Anisotropy
- (Weight% binder)
- (Fibre crimp)

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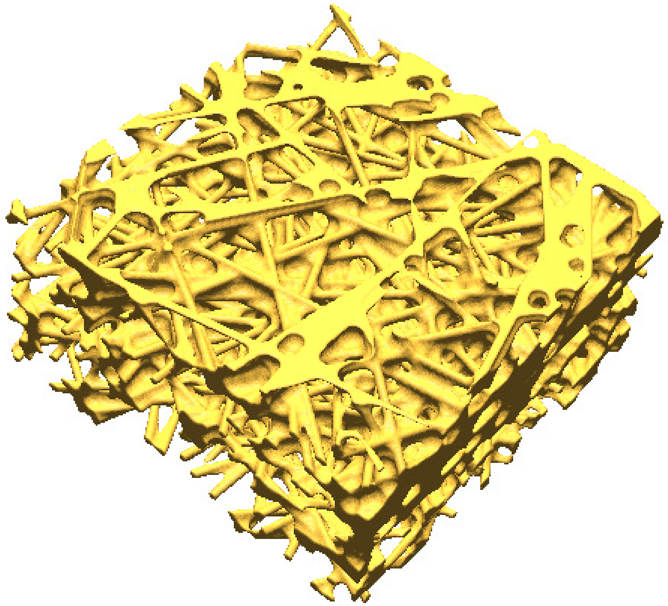
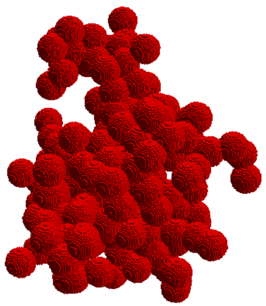
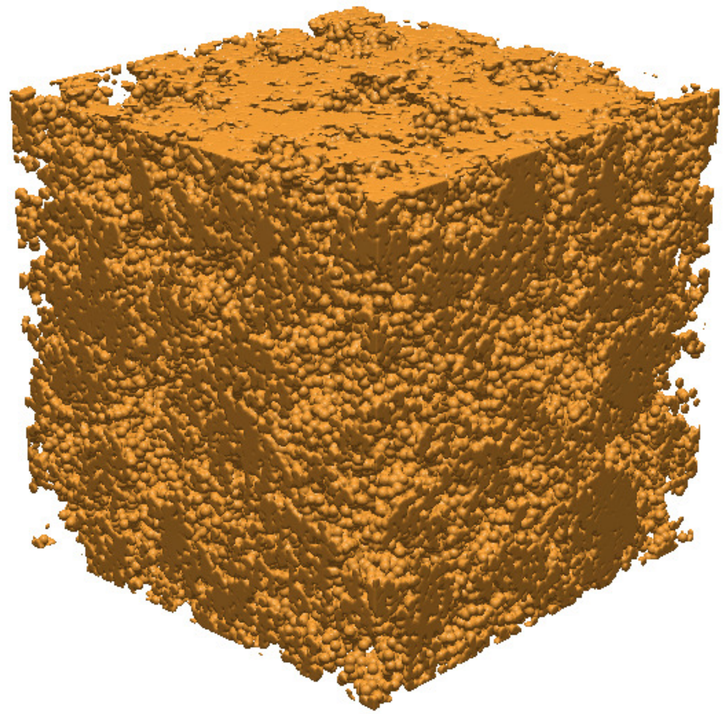


3D Models: Microporous Layer (MPL)

Typically: carbon agglomerates

Input:
- Particle size
- Particles per Agglomerate
- Porosity





Becker, Wieser, Fell, Steiner, 2010, submitted

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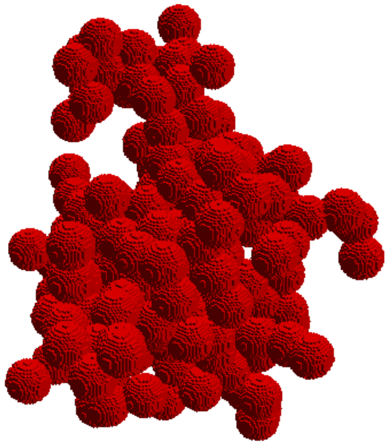
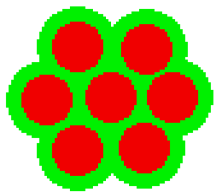
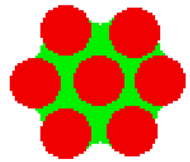
3D Models: Catalyst Layer (CL)

Carbon agglomerates plus elektrolyte

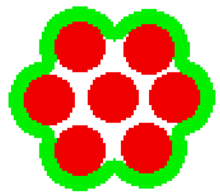




Elekt. surrounds C.Partikels



Elekt. between C.Partikels



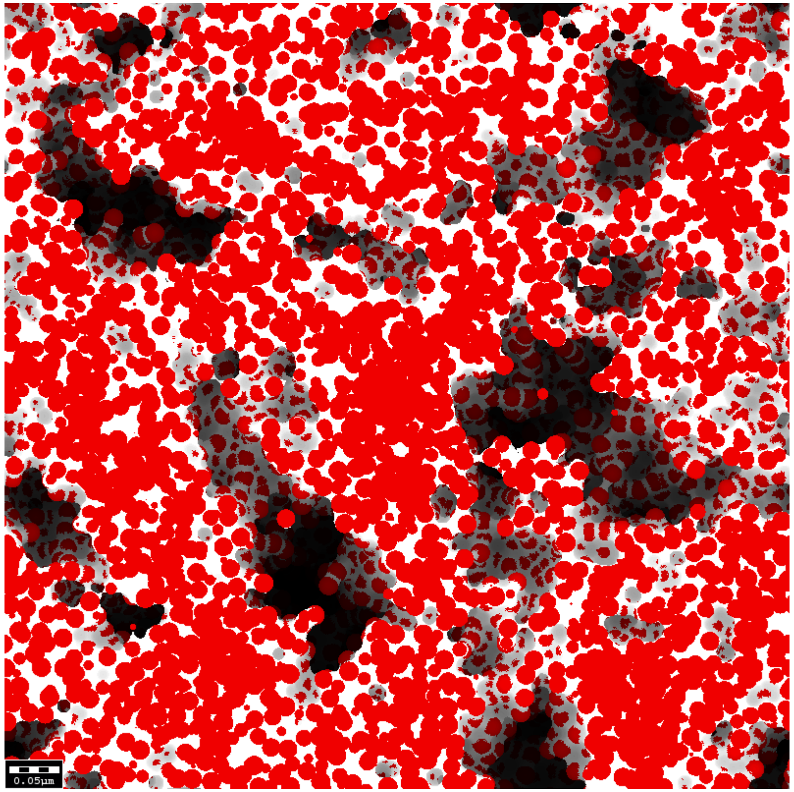
Elekt. surrounds C.Partikels but not in between

3D Models: Catalyst Layer (CL)

Model example:

Porosity 33.3 %
Carbon/Pt 50.1 vol%
Elektrolyte 16.6 vol%

Size: (800 nm)³, voxel length 1 nm



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Outline

1. Creation of 3D virtual structure models
2. ***<u>Determination of effective properties</u>***
3. Validation

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Determination of Effective Properties

Common approach:

1. Start with a 3D voxel structure given

2. Find effective properties based on the geometrical structure
   a) Geometrical properties:
      - pore size distribution, pore morphology, surface area
   b) Transport properties:
      i. Solve PDE on the voxel grid
      ii. Find effective property by upscaling / averaging

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]

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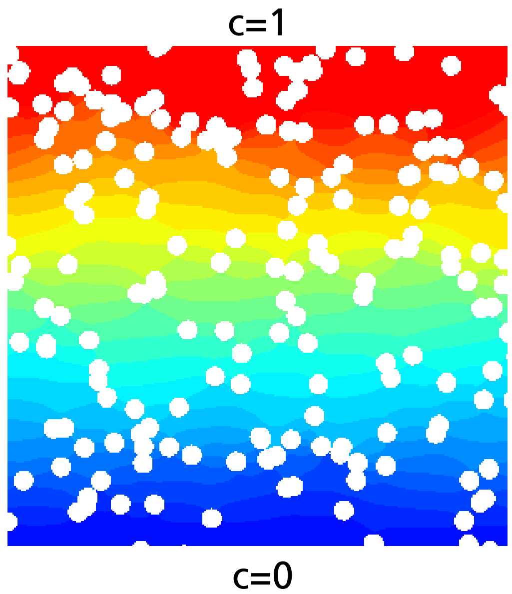
j : diffusion flux [mol/m²/s]
c : concentration [mol/m³]

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

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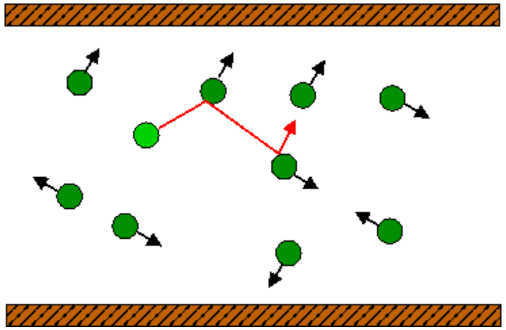
Knudsen Diffusivity



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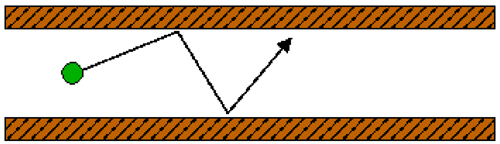
Diffusion mechanisms

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

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Permeability

Macroscopic description (homogenized porous media model)

Darcy's law : $$u = -\frac{1}{\mu}\kappa\nabla p$$

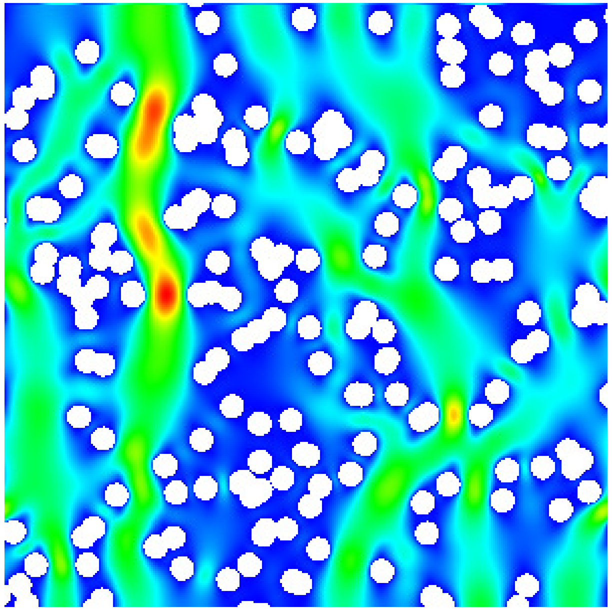
u : average flow velocity
κ : permeability tensor *unknown*
μ : viscosity
p : pressure

Microscopic description (pore structure model)

Stokes equation: $-\mu\Delta u + \nabla p = 0$

Boundary conditions: no-slip on fibre surface, pressure drop

κ can be determined from the solution!



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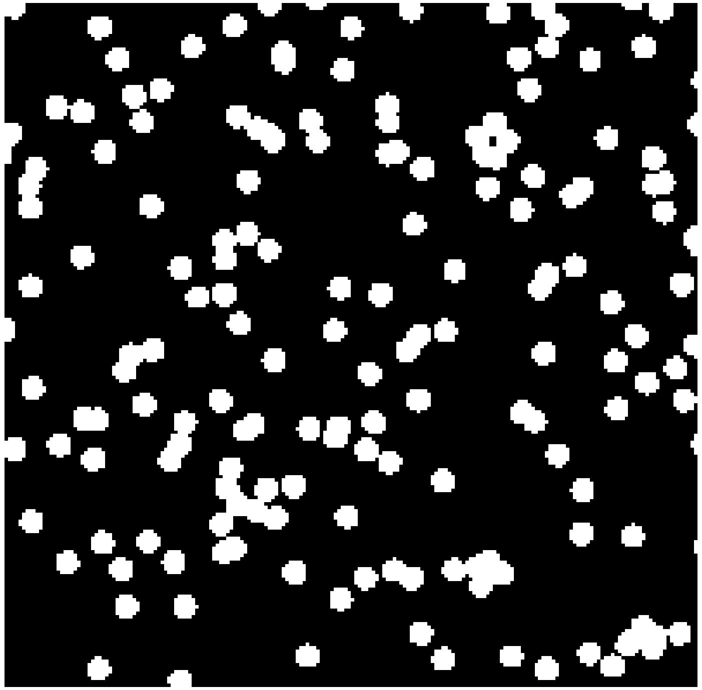
Relative Permeability

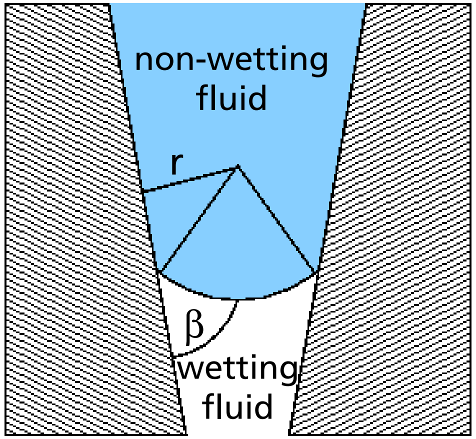
Two-step approach:

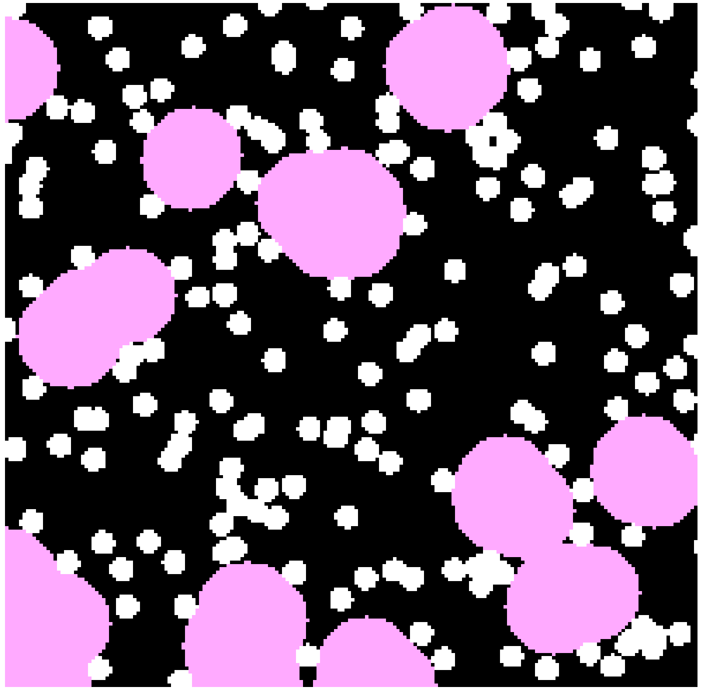


Relative Permeability

Two-step approach:

1. Use pore morphology method (Hilpert, 2001) to determine distribution of air and water phase.
   - Idea: a pore is filled with the non-wetting fluid (=water), if $p_c \geq \frac{2\sigma}{r} \cos\beta$





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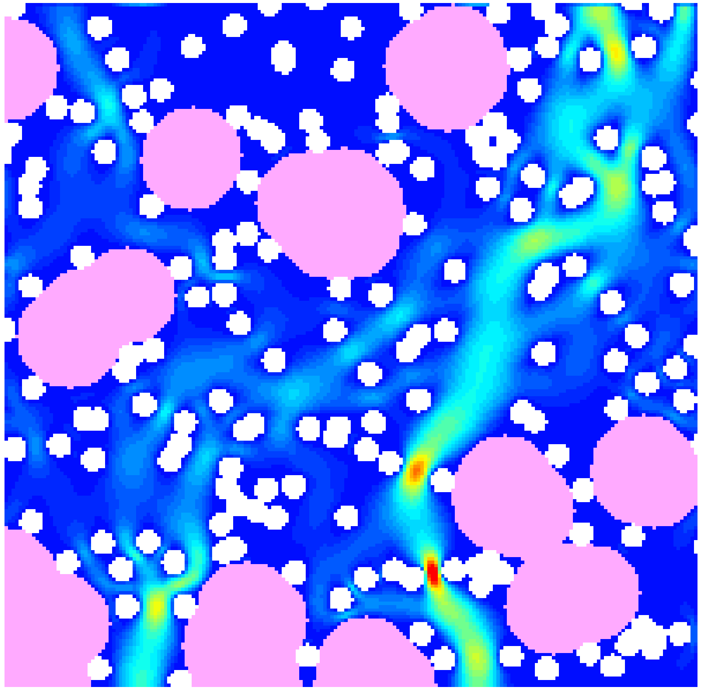
2. Solve Stokes equation on the remaining pore space to determine wetting phase (=air) permebility



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Properties Overview

GDL:
• (saturation dependent) diffusivity, (saturation dependent) permeability, electric conductivity, heat conductivity
• pore size distribution

MPL
• (Knudsen) diffusivity, electric conductivity, heat conductivity
• pore size distribution

CL
• pore size distribution, surface or contact areas, contact lines
• protonic conductivity, electronic conductivity, (Knudsen) diffusivity

Results cannot be better than the 3D structure model permits.

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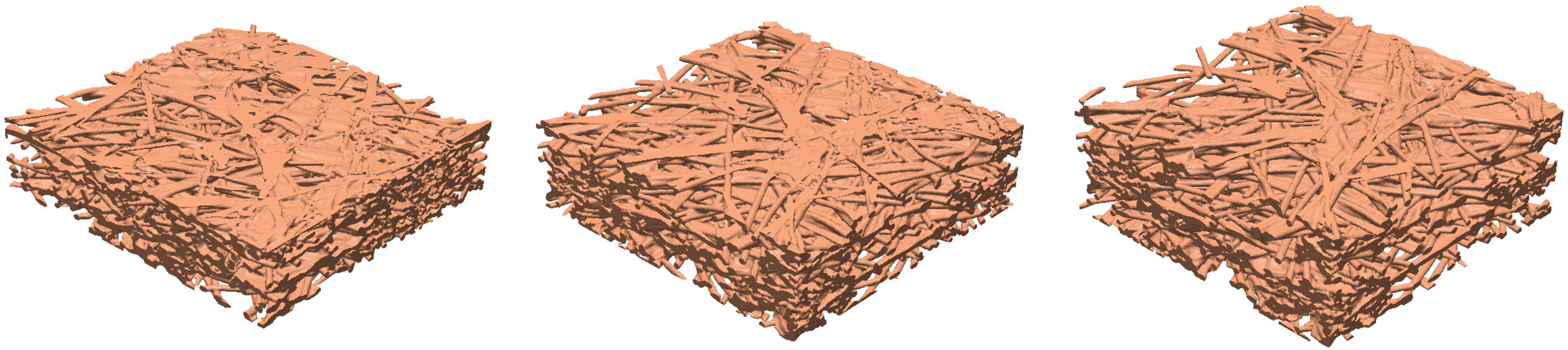
Validation: Toray TGP H 060 Gas Diffusion Layer

Data from PSI:
• Tomography images of Toray TGP H 060 at different compression levels
• Diffusivity, permeability and conductivity were measured at different compression levels experimentally

Now: compute diffusivity, permeability and conductivity numerically and compare results



Becker, Flückiger, Reum, Büchi, Marone, Stampanoni, 2009, J. Electrochem. Soc. 156

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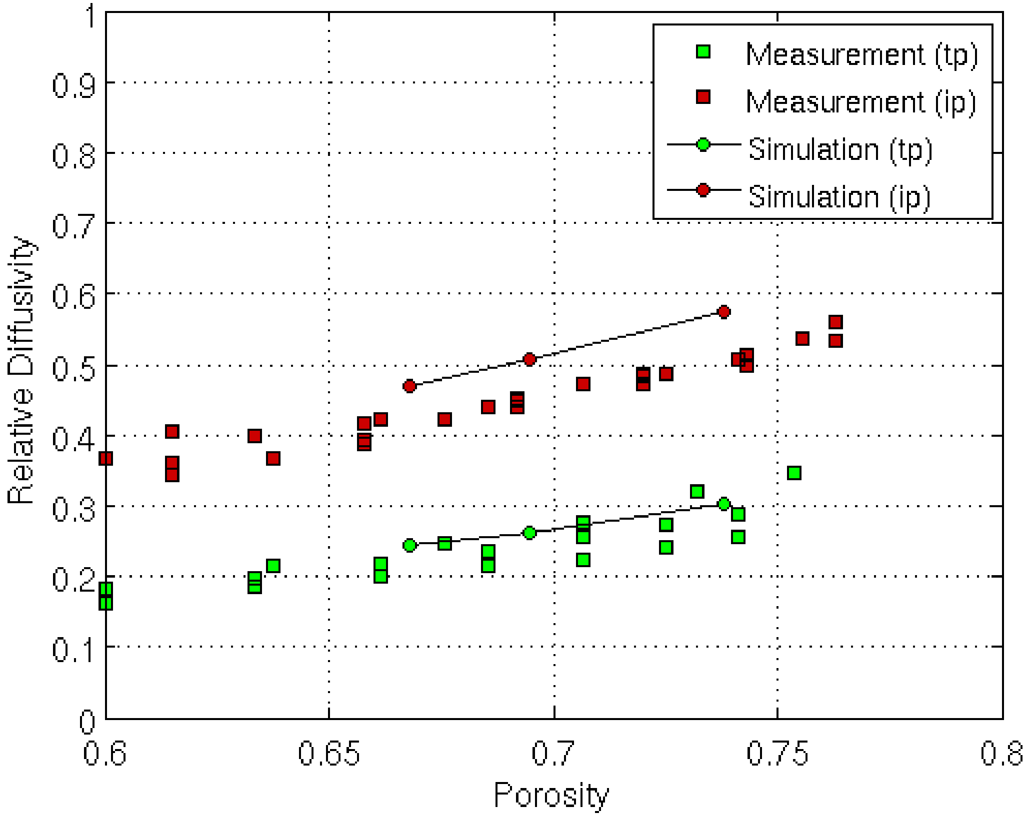
Diffusivity



Perfect in tp-direction

Small differences in ip-direction

- ip-measurememts performed on a stack of GDLs
- tomography image shows single layer between sample holder

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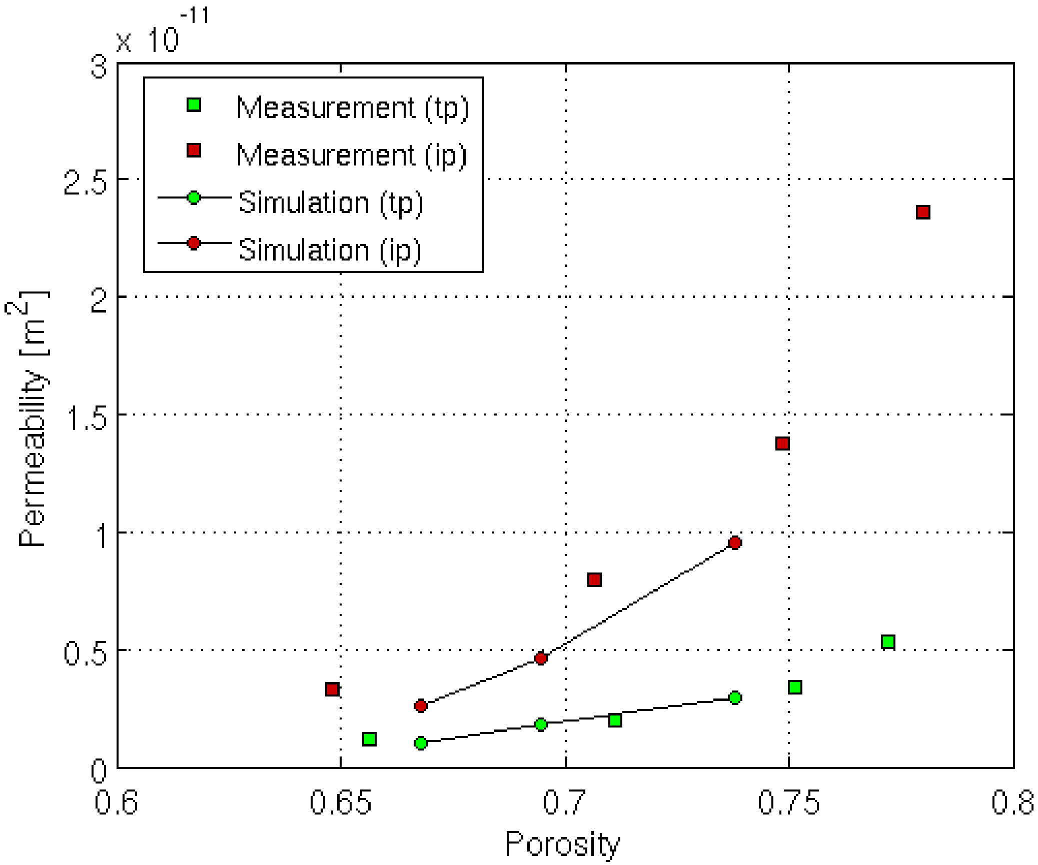
Permeability



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Thank You !

GEO DICT

Geometry generator,
property predictor and
virtual material designer

www.geodict.com

BMBF project PemCaD

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