



Weierstraß-Institut für Angewandte Analysis und Stochastik

J. Fuhrmann, K. Gärtner

A Detailed Numerical Model for DMFC: Discretization and Solution Methods



Leibniz
Gemeinschaft

Joint work with J. Divisek and R. Jung, Jülich Research center

- ▷ Stefan-Maxwell diffusion for gas mixture in porous layer
- ▷ Two phase gas/water flow in diffusion layers
- ▷ Darcy type flow of water in membrane
- ▷ Transport of dissolved species in water
- ▷ Proton/Electron transport
- ▷ Energy transport
- ▷ Evaporation/condensation reactions
- ▷ Electrochemical reactions via catalytic reaction chains

11 PDEs nonlinearly coupled, valid in different regions of the model

additional algebraic equations for catalyst coverings

1/2/(3) dimensional unstructured meshes

Finite Volumes:

- ▷ focus on conservation laws
- ▷ control volume \equiv representative elementary volume (REV)
- ▷ well suited for transport and diffusion phenomena
- ▷ can be regarded as a discrete model of the physics
- ▷ well known approaches to upwinding and stabilization can be carried over to unstructured grids

Subdivision of polygonal domains into triangles/tetrahedra.

Boundary conforming Delaunay property of triangular mesh:

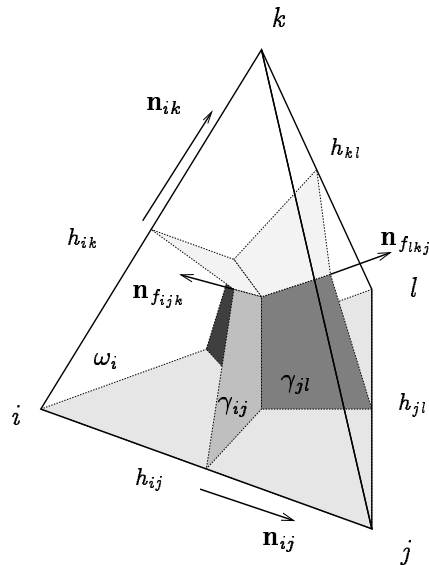
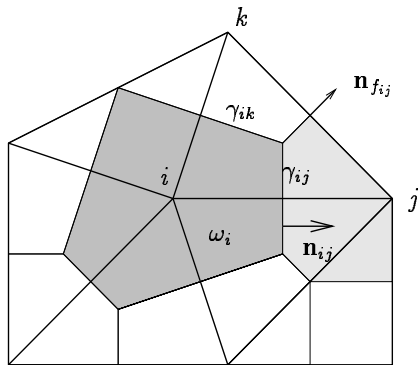
Sum of angles opposite to an interior triangulation edge $\leq \pi$,

angles opposite to boundary edge $\leq \pi/2$

More involved condition in 3D.

- ▷ 2D: J.R. Schewchuk, CMU/UC Berkeley: [triangle](#) – uses proven algorithm to create boundary conforming Delaunay meshes from a geometry description made of linear segments
- ▷ Problem still open. (like 3D quality mesh generation in general)
Current work: Hang Si, WIAS Berlin: [tetgen](#) (under development) Attempt to generalize the Shewchuk approach.

Voronoi Finite Volumes



Given: computational domain

$$\Omega = \bigcup_{m \in \mathcal{M}} \Omega_m$$

Delaunay mesh conforming to interior and exterior boundaries.

Control volumes \equiv Voronoi boxes are defined by joining the circumcenters of simplices adjacent to given node.

\mathbf{x}_i	i -th node of discretization
ω_i	Voronoi box around \mathbf{x}_i
$\gamma_{ij} = \overline{\omega_i} \cap \overline{\omega_j}, \quad i \neq j$	interior Voronoi box faces
$\mathbf{n}_{ij}, \quad i \neq j$	outward unit normal to interior Voronoi box face
$h_{ij} = \mathbf{x}_i - \mathbf{x}_j , \quad i \neq j$	edge lengths

Scalar convection-Diffusion problem

$$b(x, \cdot), r(x, \cdot), k(x, \cdot) : \mathbb{R} \rightarrow \mathbb{R}$$

$$\mathbf{j}(x, \cdot), \mathbf{q}(x, \cdot) : \mathbb{R} \rightarrow \mathbb{R}^d$$

piecewise constant space dependency: $\xi(x, \cdot) = \xi^m(\cdot)$ on Ω_m .

$$\partial_t b(x, u) + \nabla \cdot \mathbf{j}(x, u) + r(x, u) = 0$$

$$\mathbf{j}(x, u) = -k(x, u) \nabla u + \mathbf{q}(x, u).$$

Boundary conditions:

- ▷ Neumann: $\mathbf{j}(x, u) \cdot \mathbf{n} = f$
- ▷ Dirichlet: $u|_{\Gamma} = u_0$
- ▷ Equilibrium Flow: $\mathbf{j}(x, u) \cdot \mathbf{n} = \mathbf{q}(x, u) \cdot \mathbf{n}$

Problems in this class:

- ▷ Saturated/unsaturated flow in porous media (Richards equation)
- ▷ Nonlinear heat conduction
- ▷ Advection-diffusion equation

Implicit Euler Finite Volume Discretization

Introduce the numerical flux $g_{\mathbf{h}}^m(u, v)$. Let $\omega_i^m = \omega_i \cap \Omega^m$.

Space-Time balance over control volume $\omega_i \times [t^n, t^{n+1}] = \bigcup_{m \in \mathcal{M}} \omega_i^m \times [t^n, t^{n+1}]$:

$$\begin{aligned}
 0 &= \int_{t^n}^{t^{n+1}} \int_{\omega_i} \left(\frac{\partial b(x, u)}{\partial t} + \nabla \cdot \mathbf{j} + r(x, u) \right) d\omega d\tau \\
 &= \int_{\omega_i} (b(x, u^{n+1}) - b(x, u^n)) d\omega + \int_{t^n}^{t^{n+1}} \int_{\omega_i} r(x, u) d\omega d\tau + \int_{t^n}^{t^{n+1}} \int_{\partial\omega_i} \mathbf{j} \cdot \mathbf{n} d\gamma \\
 &\approx \sum_{m \in \mathcal{M}} |\omega_i^m| \left(b^m(u_i^{n+1}) - b^m(u_i^n) \right) + \\
 &\quad + \tau^n \sum_{m \in \mathcal{M}} |\omega_i^m| r^m(u_i^{n+1}) + \tau^n \sum_{m \in \mathcal{M}} \sum_{j \in \text{nb}_{\mathcal{N}}(i)} \frac{|\gamma_{ij}^m|}{h_{ij}} g_{\mathbf{h}_{ij}}^m(u_i^{n+1}, u_j^{n+1}) \\
 &\quad + \tau^n \sum_{m \in \mathcal{M}} \sum_{f \in \text{nb}_{\mathcal{B}_E}(i)} |\gamma_{if}^m| g_{\mathbf{n}_f}^m(u_i^{n+1}, u_i^{n+1}).
 \end{aligned}$$

Smoothness: $g_{\mathbf{h}}^m(\cdot, \cdot) \in C^1(\mathbb{R} \times \mathbb{R}), \quad b^m \in C^1(\mathbb{R})$

Mass conservation: $g_{\mathbf{h}}^m(v, v') = -g_{-\mathbf{h}}^m(v', v)$

Flux consistency: $g_{\mathbf{h}}^m(v, v) = \mathbf{h} \cdot \mathbf{q}^m(v)$

Diffusion consistency: $\forall v, v' \exists \lambda \in [v, v'] : g_0^m(v, v') = k^m(\lambda)(v - v')$

Weak isotonicity: $\frac{g_{\mathbf{h}}^m(v, v') - g^m(\mathbf{h}, v, v)}{v' - v} \leq 0$

Isotonicity: $\partial_1 g_{\mathbf{h}}^m(v, v') \geq 0, \quad \partial_2 g_{\mathbf{h}}^m(v, v') \leq 0$

For $e_{ij} = (\mathbf{x}_i, \mathbf{x}_j)$ and $\xi \in [0, h_{ij}]$,

let $\mathbf{x}(\xi) := \mathbf{x}_i + \xi \mathbf{n}_{ij}$

and $u_{e_{ij}}(\xi) := u(\mathbf{x}(\xi))$.

Then $\mathbf{j}^m(u_{e_{ij}}(\xi)) \cdot \mathbf{n}_{ij} = k^m(u_{e_{ij}}(\xi))u'_{e_{ij}}(\xi) + \mathbf{q}^m(u_{e_{ij}}(\xi)) \cdot \mathbf{n}_{ij}$

A **canonical** flux function $g_{\mathbf{h}_{ij}}^m(u, v)$ can be defined as the flux of the solution w of the one-dimensional Dirichlet defined by the projection of the main part of the equation onto the edge \mathbf{h}_{ij} :

$$\begin{aligned} (k^m(w)w' + \mathbf{q}^m(w) \cdot \mathbf{n}_{ij})' &= 0 \\ w(0) &= u \quad w(h_{ij}) = v \end{aligned}$$

Sometimes, an exact solution can be obtained, but in many cases we would use an approximation.

Examples of Flux Functions

Basically, any reasonable one-dimensional difference formula can be taken.

$0 = u_t - \dots$	flux function $g_{\mathbf{h}}(v, v')$	
$\nabla(k\nabla u)$	$k(v - v')$	isotone, canonical
$\nabla(k(u)\nabla u)$	$k\left(\frac{v+v'}{2}\right)(v - v')$	weakly isotone
$\nabla(k(u)\nabla u)$	$K(v) - K(v')$	isotone, canonical
$\nabla(k\nabla u - \mathbf{q}u)$	$k\left(B(q/k)v - B(-q/k)v'\right)$	isotone, canonical (Allan-Southwell, Il'in, Scharfetter-Gummel)
$\nabla(k\nabla u - \mathbf{q}u)$	$k\left(U(q/k)v - U(-q/k)v'\right)$	isotone ("simple upwind")
$\nabla\mathbf{q}(u)$	$q^+(v) - q^-(v')$	isotone (Enquist-Osher)

$$q(v) = \mathbf{q}(v) \cdot \mathbf{h}$$

$$q^+(v) = q(0) + \int_0^v \max(q(s), 0) ds$$

$$q^-(v) = \int_0^v \min(q(s), 0) ds$$

$$K(v) = \int_0^v k(\xi) d\xi$$

$$B(\xi) = \frac{\xi}{e^\xi - 1} : \text{Bernoulli function}$$

$$U(\xi) = \begin{cases} 1 - \xi, & \xi \leq 0 \\ 1, & \xi > 0, \end{cases}$$

Properties ($r = 0$, scalar case)

Write time step equations as

$$B(u^{n+1}) + A(u^{n+1}) = B(u^n)$$

No flow bc \Rightarrow global mass conservation:

$$\sum_{i \in \mathcal{N}} \sum_{m \in \mathcal{M}} |\omega_i^m| b^m(u_i^{n+1}) = \sum_{i \in \mathcal{N}} \sum_{m \in \mathcal{M}} |\omega_i^m| b^m(u_i^n)$$

No flow, isotonicity, $b(\cdot) \uparrow\uparrow$, $A(0) = 0 \Rightarrow$ existence, uniqueness, L^1 stability

$$\|MB(u^{n+1})\|_1 \leq \|MB(u^n)\|_1$$

Equilibrium flow/Dirichlet BC, weak isotonicity, $A(u) = K(u)u$ with $K(u)$ having row sum zero \Rightarrow existence, L^∞ stability, local maximum principle

$$\|u^{n+1}\|_\infty \leq \max(\|u^n\|_\infty, \|u_D\|_\infty); \quad u_i^{n+1} \leq \max\{u_i^n\} \cup \{u_j^{n+1}\}_{j \in \text{nb}(i)}$$

Derivation using Perron-Frobenius theory

- ▷ Upwinding \equiv ensuring the isotonicity properties of the flux functions
- ▷ positive solutions stay positive
- ▷ “Nonphysical” oscillations are suppressed independent of grid spacing
- ▷ Flux function \equiv “user subroutine” describing main part of the equation
- ▷ “user” subroutines: $r^m(u)$, $b^m(u)$, $g_{\mathbf{h}}^m(u, v)$ specified together with analytical derivatives
- ▷ sparse structure of nonlinear operator \Rightarrow sparse structure of analytical Jacobian which can be assembled using supplied problem data
- ▷ direct and iterative sparse matrix solvers can be applied to solve linearized equations

Systems of Reaction-Diffusion Equations

ν : the number of components, vector, resp. tensor valued functions:

$$b(x, \cdot), r(x, \cdot), k(x, \cdot) : \mathbb{R}^\nu \rightarrow \mathbb{R}^\nu ; \mathbf{j}(x, \cdot), \mathbf{q}(x, \cdot) : \mathbb{R}^\nu \rightarrow \mathbb{R}^{\nu d}$$

piecewise constant space dependency: $\xi(x, \cdot) = \xi^m(\cdot)$ on Ω_m .

System:

$$\partial_t b(x, u) + \nabla \cdot \mathbf{j}(x, u) + r(x, u) = 0$$

$$\mathbf{j}(x, u) = -k(x, u) \nabla u + \mathbf{q}(x, u).$$

l th equation:

$$\partial_t b_l(x, u_1 \dots u_\nu) + \nabla \cdot \mathbf{j}_l(x, u_1 \dots u_\nu) + r_l(x, u_1 \dots u_\nu) = 0$$

$$\mathbf{j}_l(x, u_1 \dots u_\nu) = -k_l(x, u_1 \dots u_\nu) \nabla u_l + \mathbf{q}_l(x, u_1 \dots u_\nu).$$

Boundary conditions given component-wise as in scalar case.

Discretization of Systems

Formal generalization of scalar approach.

Introduce the vector valued numerical flux

$$g_{\mathbf{h}}^m(u, v) = \left(g_{\mathbf{h};1}^m(u_1 \dots u_\nu; v_1 \dots v_\nu) \dots g_{\mathbf{h};\nu}^m(u_1 \dots u_\nu; v_1 \dots v_\nu) \right)$$

l th equation in i th node:

$$\begin{aligned} 0 &= \int_{t^n}^{t^{n+1}} \int_{\omega_i} \left(\frac{\partial b_l(x, u)}{\partial t} + \nabla \cdot \mathbf{j}_l + r_l(x, u) \right) d\omega d\tau \\ &\approx \sum_{m \in \mathcal{M}} |\omega_i^m| \left(b_l^m(u_i^{n+1}) - b_l^m(u_i^n) \right) + \\ &\quad + \tau^n \sum_{m \in \mathcal{M}} |\omega_i^m| r_l^m(u_i^{n+1}) \\ &\quad + \tau^n \sum_{m \in \mathcal{M}} \sum_{j \in \text{nb}_{\mathcal{N}}(i)} \frac{|\gamma_{ij}|}{h_{ij}} g_{\mathbf{h}_{ij};l}^m(u_i^{n+1}, u_j^{n+1}) \\ &\quad + \tau^n \sum_{m \in \mathcal{M}} \sum_{f \in \text{nb}_{\mathcal{B}_E}(i)} |\gamma_{if}^m| g_{\mathbf{n}_f;l}^m(u_i^{n+1}, u_i^{n+1}). \end{aligned}$$

- ▶ Problem specification by the discretization mesh and the callbacks $g_{\mathbf{h}}^m(u, v)$ for flux functions, $r^m(u)$ for reaction terms and $b^m(u)$ for storage terms. All these are vector functions depending on vectors and need to be specified together with their derivatives.
- ▶ Solution of time step problems by Newton's method with analytical Jacobian of discrete nonlinear operator. Solution up to roundoff error (detection by monitoring the functional of a solution). Utilization of quadratic convergence allows for highly accurate mass conservation at low additional cost.
- ▶ Different choices for linear solvers: preconditioned Krylov subspace methods with point block ILU, PARDISO direct solver (Schenk/Gärtner), development of algebraic multigrid preconditioners;
- ▶ Sets of species can vary from subdomain to subdomain. Implementation currently facilitated by dummy equation approach.
- ▶ Time step control in weighted norm via error estimator $\|Wu^{n+1} - Wu^n\|_{\infty}$ and by number of Newton iterations.
- ▶ UI based on Lua extension language, OpenGL graphics
- ▶ Implementation on top of *pdelib* toolbox

Algebraic equations from catalytic reaction chain are part of $r^m(u)$ and are solved by inner Newton iteration within each discretization point during each global Newton step. Catalyst coverings are stored in extra variables.

Upwinding

- ▷ Multiphase flow needs special upwinding yielding maximum principle in saturation, instead of pressures
- ▷ Upwinding in transport terms, drag coefficients, thermal convection parts

Solution process control

- ▷ stationary solution of auxiliary boundary value problem (Laplace + simple reactions) in order to obtain smooth initial value with boundary conditions of first bias
- ▷ Time dependent solution of first bias until stationarity is reached (after several hours of system time)
- ▷ parameter variation from bias to bias (with optional time embedding for to solve bias problems).

Derivation from standard two phase porous media flow model.

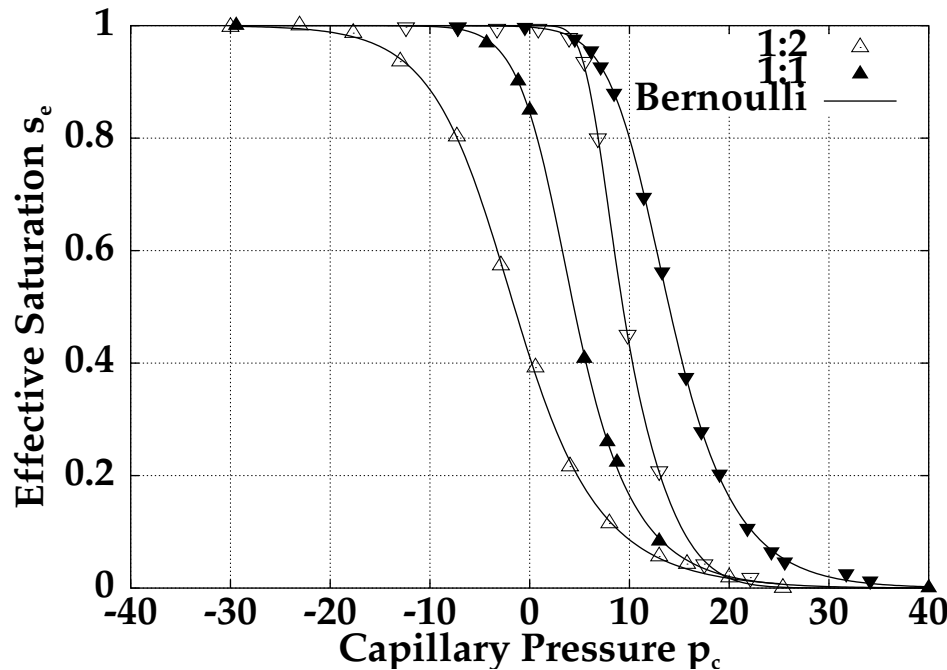
$$\partial_t \frac{\rho_w s_w \phi}{M_w} - \nabla \cdot \mathbf{N}_w = R_w^{ev} + R_w^{chem}$$

$$\mathbf{N}_w = \frac{\rho_w k_f k_{rw}}{M_w \mu_w} (\nabla p_w + n_{drag} \mathbf{N}_{H^+})$$

p_w	water pressure ($p_c = p_{gas} - p_w$)
\mathbf{N}_w	molar flux of water
k_f	hydraulic permeability
ϕ	porosity
$s_w(p_c)$	water saturation
p_c	capillary pressure
$k_{rw}(s_w)$	rel. permeability
ρ_w	water density
μ_w	water viscosity
M_w	molar mass of water
n_{drag}	drag coefficient
\mathbf{N}_{H^+}	molar flux of H^+
R_w^{ev}	evaporation reaction
R_w^{chem}	chemical reactions

For s_w, k_{rw} , we need a modification of standard models to take into account mixed wettability.

In Nafion, we set $s_w, k_{rw} = 1$. Need better understanding.



Measured values for drying and wetting branches of $s_e(p_c)$ for Quartz sand/Teflon mixture with different compositions (Ustohal/Stauffer/Dracos 1998); least squares fit to **Bernoulli function based ansatz**

Bernoulli function: $B(x) = \frac{x}{e^x - 1}$

$$p_c^\delta = \alpha(p_c - p_{1/2})$$

$$s_e(p_c) = -B' \left(B(p_c^\delta)^{\beta_w} + B(-p_c^\delta)^{\beta_n} \right)$$

$$s_w(p_c) = s_w^{res} + (s_g^{res} - s_w^{res})s_e(p_c)$$

More appropriate than van Genuchten or Brooks/Corey ?

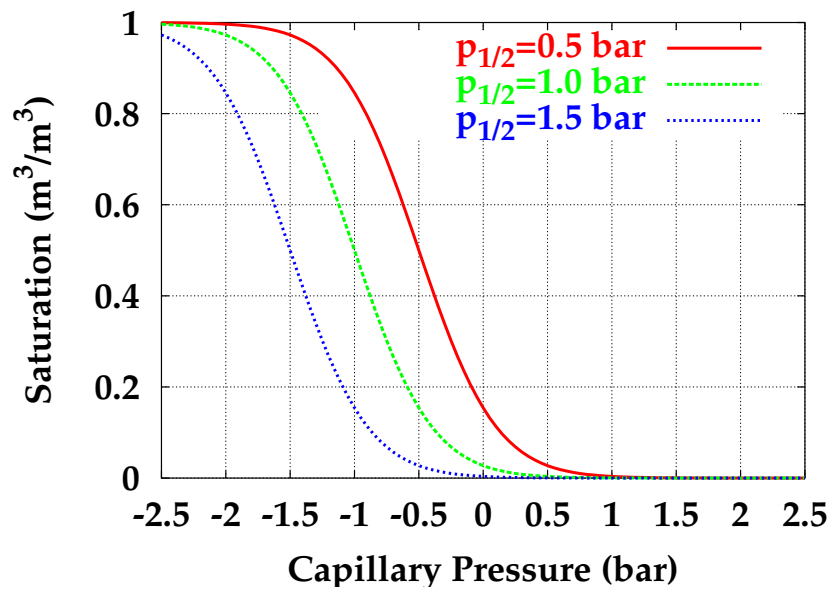
Stefan–Maxwell mean transport pore model for a mixture of n_g gases empirically combined with two phase flow

$$\partial_t \left(\phi(1 - s_w) \frac{p_{gi}}{RT} \right) - \nabla \cdot \mathbf{N}_{gi} = R_{gi}^{chem} + R_{gi}^{ev}$$

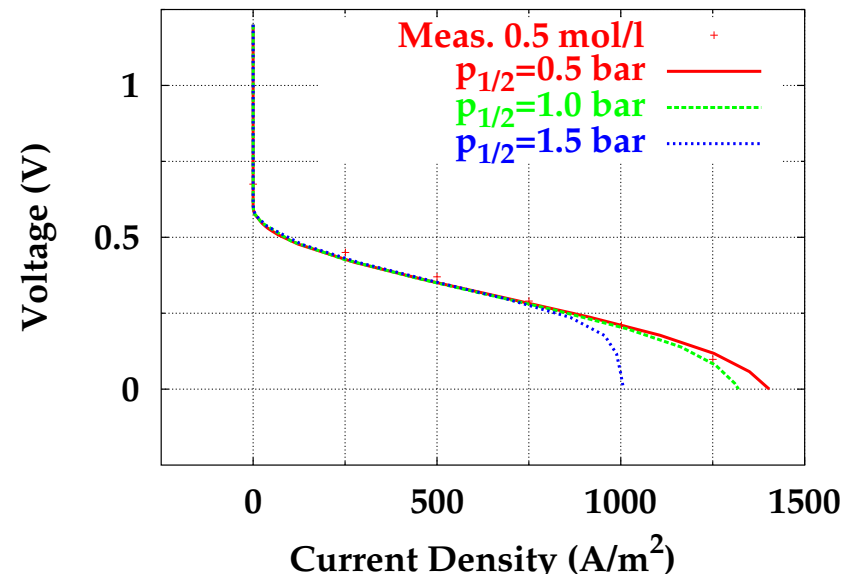
$$\mathbf{N}_{gi} = k_{rg} \sum_{j=1}^{n_g} D_{ij}^{SM}(p_1, \dots, p_{n_g}) \nabla p_{gj}$$

p_{gi}	partial pressure of i th component
\mathbf{N}_{gi}	molar flux of i th component
R	gas constant
T	temperature
$k_{rg}(s_w)$	rel. permeability
D_{ij}^{SM}	Stefan Maxwell Diffusion matrix
R_{gi}^{ev}	evaporation reaction
R_{gi}^{chem}	chemical reactions

Influence of anodic saturation curve

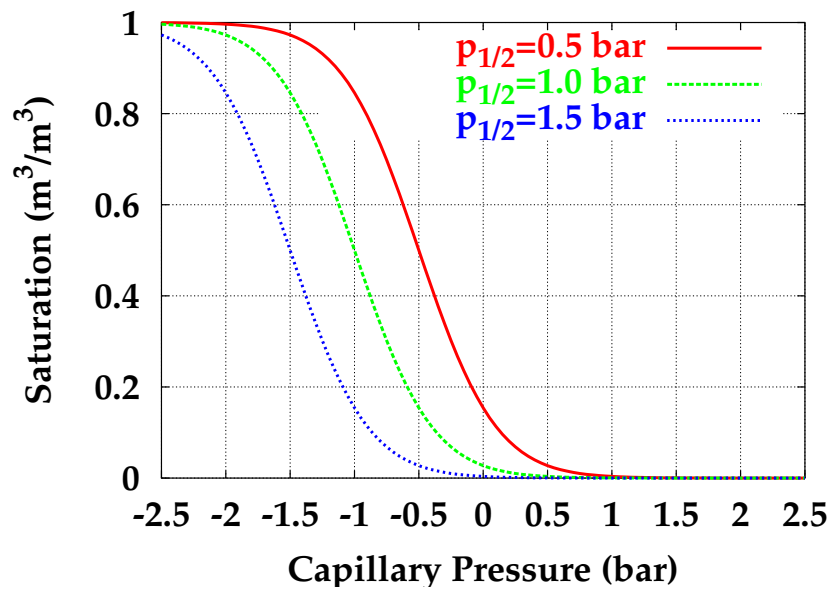


Capillary pressure vs. saturation

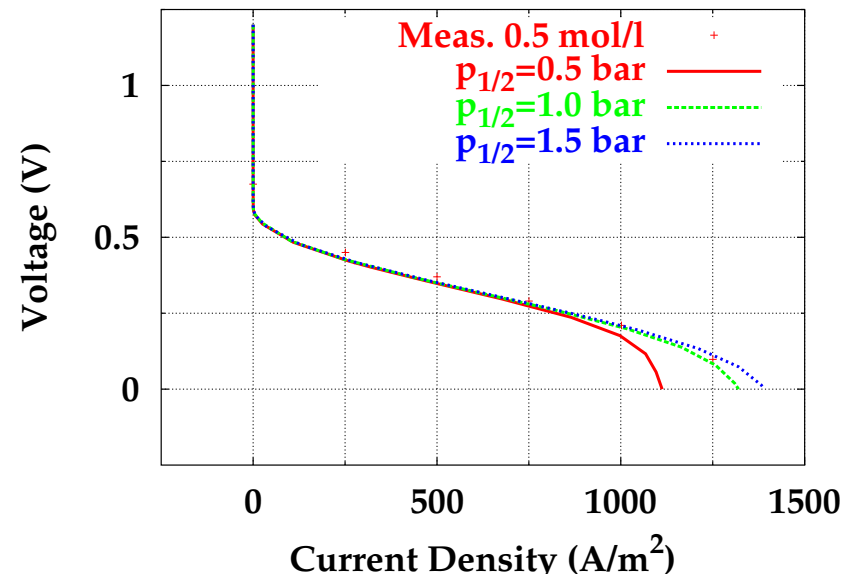


polarization curves

Influence of cathodic saturation curve

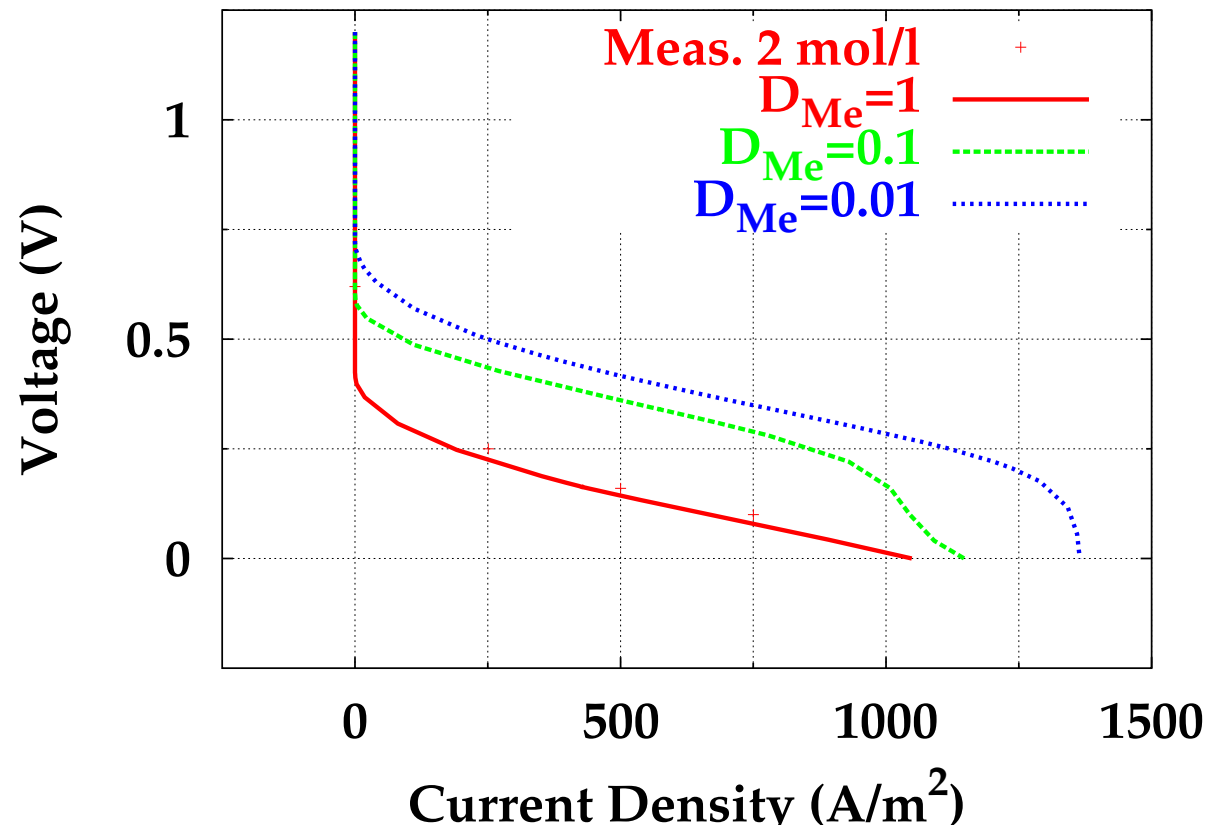


Capillary pressure vs. saturation



polarization curves

Influence of reduced Methanol crossover



Influence of reduction of the diffusion coefficient of Methanol in Nafion by a certain factor.