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Detection of Solubility, Transport and Reaction Coefficients from Experimental Data by Inverse Modeling of Thin Layer Flow Cells

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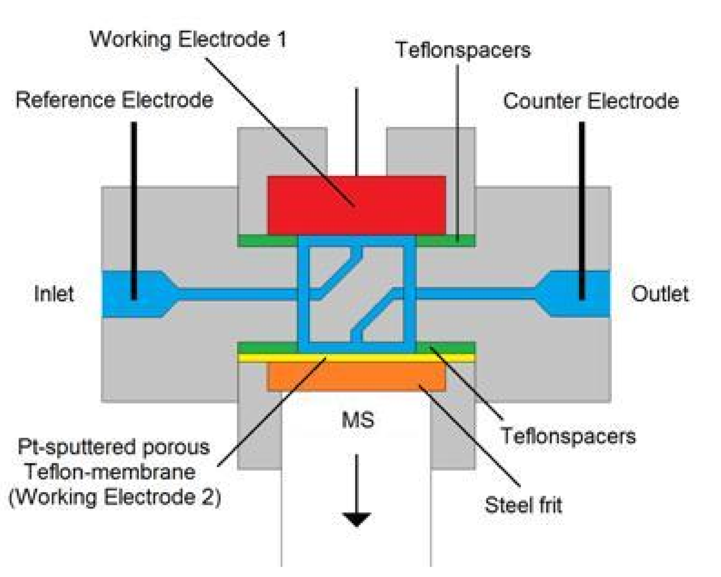
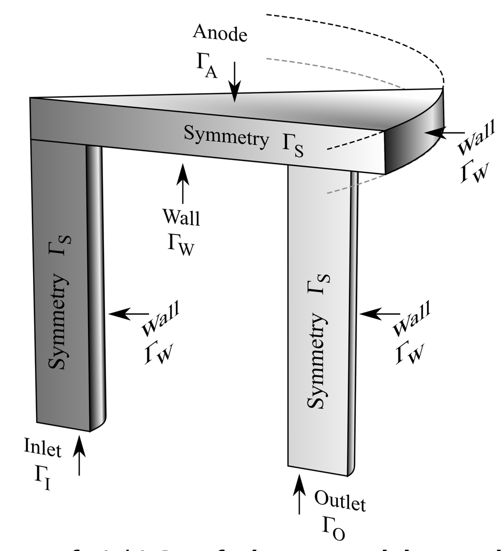
Thin Layer Flow Cell

- Purpose: investigation of electrocatalytic surface reactions under controlled conditions using reasonably small electrolyte volumes
- Coupling to on-line product analysis by differential electrochemical mass spectrometry





Side view of 1/12 of the working chamber

Inverse Modeling

- Result of experimental work: electrical and mass-spectrometry currents for given flow rates and inlet concentrations
- Aim: detection of inlet concentrations, species diffusion coefficients and reaction rates from measurements
- Interpretation of measurement data:
  - State of the art: auxiliary measurements with known characteristics to derive characteristic geometry coefficients
  - Project aim: Precise numerical modeling + data detection by fit procedure

Numerical Discretisation = Navier Stokes + Transport Equations

- Stationary solvent flow with velocity $\vec{u}$, pressure p, dynamic viscosity η and density ϱ inside the flow cell is governed by the incompressible Navier-Stokes equations

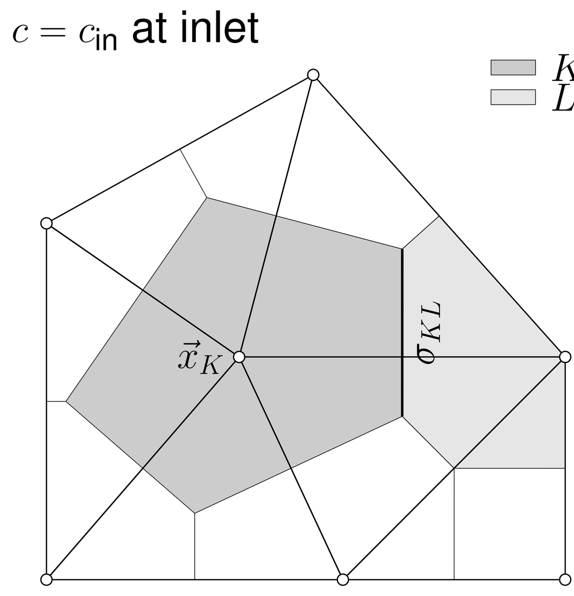
$$-\eta\Delta\vec{u} + \varrho(\vec{u}\cdot\nabla)\vec{u} + \nabla p = 0 \text{ in } \Omega, \quad \nabla\cdot\vec{u} = 0 \text{ in } \Omega$$

  - Divergence-constraint: crucial for mass conservation $\Rightarrow$ use divergence-free finite element methods (Scott-Vogelius FEM, novel modified nonconforming Crouzeix-Raviart FEM [4]).
  - Less expensive (non-divergence-free) Taylor-Hood FEM gives comparable results [2, 3].
- Species transport with concentration c, diffusion coefficient D:

$$\nabla\cdot(-D\nabla c + c\,\vec{u}_h) = s \text{ in } \Omega \quad \text{and} \quad c = c_{\text{in}} \text{ at inlet}$$

discretised by an exponentially fitted finite volume method with Voronoi cells as control volumina. On every $\sigma_{KL} := \partial K \cap \partial L$ set

$$u_{\sigma_{KL}} := \int_{\sigma_{KL}} \vec{u}_h\cdot(\vec{x}_L - \vec{x}_K)\, ds / |\sigma_{KL}|$$

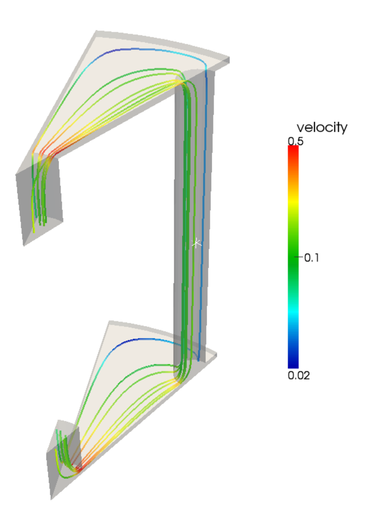


Find $c_h \in P_0(\mathcal{K})$ with $c_K := c_h|_K$ such that

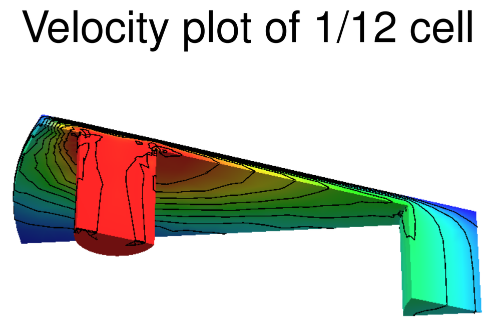
$$\sum_{L \text{ neighbour of } K} |\sigma_{KL}| / |\vec{x}_L - \vec{x}_K| \; g(c_K, c_L, u_{\sigma_{KL}}) = |K|\, s_K \quad \text{for all } K \in \mathcal{K}_0 := \mathcal{K}\setminus\mathcal{K}_D$$

where $g(c_K, c_L, u_{\sigma_{KL}}) := D\Big(B(u_{\sigma_{KL}}/D)c_K - B(-u_{\sigma_{KL}}/D)c_L\Big)$ with $B(z) = z/(1-e^{-z})$.

Detection of O_2 diffusion coefficients in various solvents

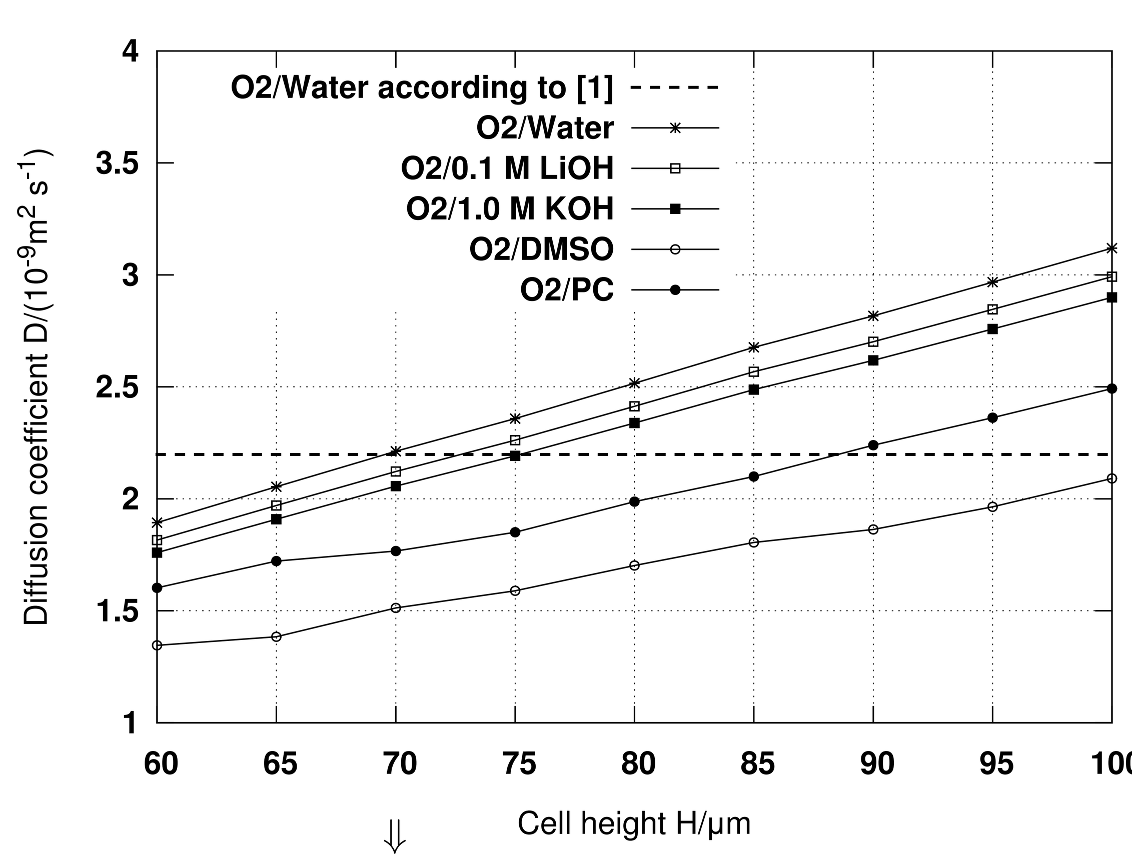


Velocity plot of 1/12 cell



Concentration plot

- Experiment:
  - Detection of relation between mass flow and mass spectrometric current by independent experiment
  - Detection of mass spectrometric current I from O_2 diffusing through the membrane of the measurement chamber for flow rates $u = 0.1\ldots 80\, mm^3/s$
- Intepretation:
  - Detection of inlet concentration from lowest flow rate under the assumption that no O_2 remains in the outlet (strongly diffusion dominated case)
  - Levenberg-Marquardt fit of diffusion coefficient D using coupled flow+transport simulation as forward solver
  - Detection of working chamber height (uncertain due to experimental construction) based on known solvents (O_2/H_2O, [1])
  - Use fit procedure with known cell height to detect diffusion coefficient for new solvents



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$D_{O_2/\text{0.1M LiOH}} = 2.12\cdot 10^{-9} m^2/s \qquad D_{O_2/\text{DMSO}} = 1.51\cdot 10^{-9} m^2/s$

$D_{O_2/\text{1.0M KOH}} = 2.06\cdot 10^{-9} m^2/s \qquad D_{O_2/\text{PC}} = 1.77\cdot 10^{-9} m^2/s$

References

[1] P. Han and David M. Bartels. Temperature Dependence of Oxygen Diffusion in H2O and D2O. *The Journal of Physical Chemistry*, 100(13):5597–5602, 1996.

[2] J. Fuhrmann, A. Linke, H. Langmach, and H. Baltruschat. Numerical calculation of the limiting current for a cylindrical thin layer flow cell. *Electrochimica Acta*, 55:430-438, 2009.

[3] J. Fuhrmann, H. Langmach, and A. Linke. A numerical method for mass conservative coupling between fluid flow and solute transport. *Appl. Numer. Math.*, 61(4):530–553, 2011.

[4] A. Linke. On the role of the Helmholtz decomposition in mixed methods for incompressible flows and a new variational crime. *Comput. Methods Appl. Mech. Engrg.*, 268:782–800, 2014.

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