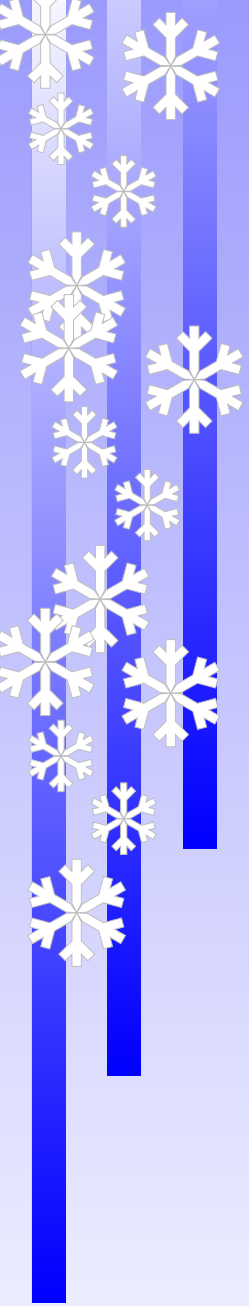

Mathematical Modelling of Membrane Swelling

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Overview

- Question: How can we understand the water content in fuel cell membranes?
- Answer: Very complicated. Many factors play a role:
  - Flux of ions
  - Intermembrane electric field
  - Stress on the membrane
- Goal: Develop a model that takes all effects into account in an appropriate way and is still of practical use.

Features of the model

- Assumptions:
  - One-dimensional continuum model
  - Homogenized (averages over microstructures)
- Predictions:
  - Swelling/Deswelling as a response to changes of the pH of the bath
  - Swelling is slower than deswelling (nonlinear effect)
  - Swelling in response to changes of an exterior electric field

Nernst-Planck equation

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$$\Gamma_H = \phi\left(-\bar{D}_H\frac{\partial \bar{c}_H}{\partial x} + \bar{\mu}_H\frac{z_H}{|z_H|}\bar{c}_H E\right) + \bar{c}_H U \qquad (1)$$

- Coefficients depend on hydration H (ratio of fluid to solid volume) in a *nonlinear* way.
- Examples: Membrane porosity ϕ and diffusivity $\bar{D}_H$:

$$\phi = \frac{H}{1+H}, \qquad \frac{\bar{D}_H}{D_H} = \left(\frac{H}{2+H}\right)^2$$

Continuity condition and chemical reaction

- Continuity condition for the ionic flux

$$\frac{\partial}{\partial t}\left(H\bar{c}_H + H\bar{c}_H^b\right) = -\frac{\partial\left(\alpha\Gamma_H\right)}{\partial\psi}, \tag{2}$$

- Chemical reaction

$$\bar{c}_m = \frac{\bar{c}_{mo}^s}{H} - \bar{c}_H^b = \frac{\bar{c}_{mo}^s}{H}\left(\frac{K}{K+\bar{c}_H}\right). \tag{3}$$

- $\bar{c}_H^b \rightarrow H^+$ ions bound to the PMAA carboxyl groups,
  $\bar{c}_m \rightarrow$ ionized PMAA carboxyl groups.

Equation for H^+ concentration

- Combination of the three equations (Nernst-Planck, continuity, and chemical reaction) leads to (for the convection-free case $U = 0$)

$$\frac{\partial}{\partial t}\left[\bar{c}_H\left(H + \frac{\bar{c}^s_{mo}}{K + \bar{c}_H}\right)\right] = \frac{\partial}{\partial \psi}\left[\alpha\psi\left(\bar{D}_H\frac{\partial \bar{c}_H}{\partial x} - \bar{\mu}_H\bar{c}_H E\right)\right]$$

- ψ is the *Lagrangian* coordinate, accounting for swelling. In the one-dimensional case, we have

$$dx = (1 + H)d\psi$$

The simple case

- Let's assume
  - electrical migration is irrelevant ($E = 0$)
  - instantaneous mechanical equilibrium

$$H = H_{eq} = H_{eq}(\bar{c}_H)$$

- Both, H and $\bar{c}_H$ are functions of (ψ, t). We can eliminate one of them and are left with a highly *nonlinear* diffusion equation, describing the time evolution of both the H^+-concentration and the hydration.