

Proton and Water Transport in Nano-separated Polymer Membranes

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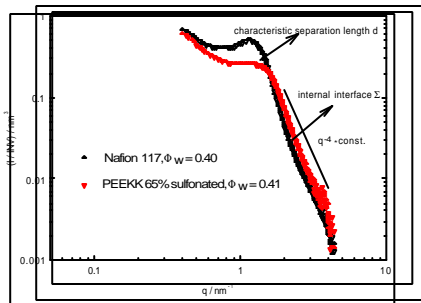
Introduction

Perfluoro-sulfonic polymers (e.g. NAFION) and sulfonated polyaryles (e.g. sulfonated polyetherketones), which are often being used as materials for membranes in fuel cells, show characteristic hydrophilic / hydrophobic nano-separations, especially in the presence of water. While the hydrophobic domain provides the membrane with a certain morphological stability, the hydrated hydrophilic domain is responsible for the transport of both the water of hydration and the acid proton.

This poster addresses the question, in which way the confinement of the water in the hydrophilic domain and the confinement of the acidic functional groups to the interface of the hydrophobic and hydrophilic domain control the macroscopic transport coefficients. NAFION 117 (Du Pont, 1100 g/eq.) and sulfonated polyetherketones S-PEK (Aventis, 650 g/eq.) have been chosen for this case study, since the first shows a pronounced hydrophobic / hydrophilic separation with a well connected hydrophilic domain, while the latter is less separated with a highly branched, poorly connected hydrophilic domain.

Microstructure: Determination and Model

Microstructure from SAXS



- ratio of internal surface to volume:

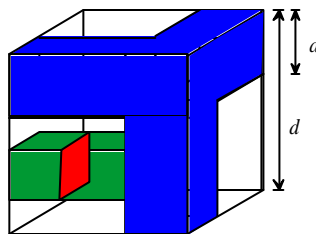
$$\Sigma = \lim_{q \rightarrow \infty} \frac{q^4 I(q)}{INV} \cdot p \cdot \Phi_w \cdot (1 - \Phi_w)$$

with $INV = \int_0^\infty I(q) q dq$ scattering invariant
and Φ_w = volume fraction of absorbed solvent

- characteristic separation length:

$$d = \frac{2p}{q_{max}}$$

Making diffraction (d , Σ) and transport data (D) self-consistent by fitting and modifying a cubic system of hydrophilic channels in a hydrophobic matrix

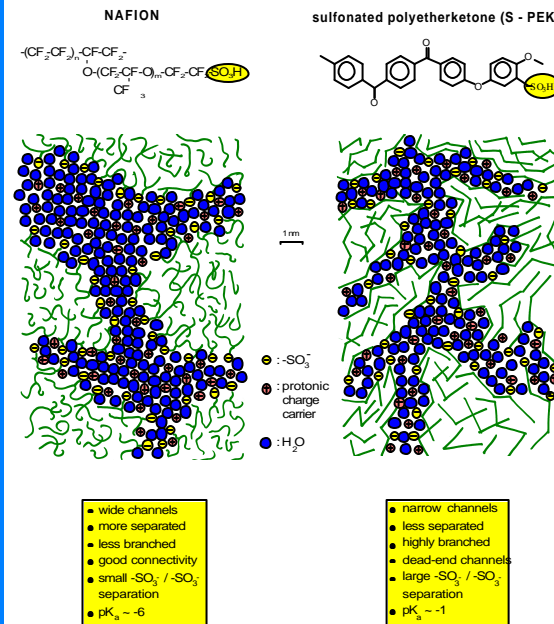


- SAXS, Φ_w → separation length, internal interface

model free !

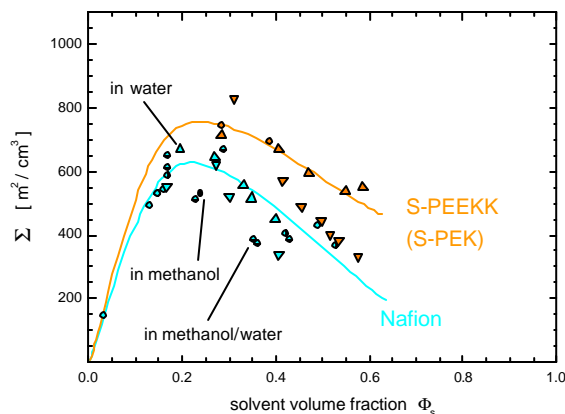
- internal interface Σ , $[-SO_3H]$ → $-SO_3H$ - separation d_{SO_3H}
- fit channel diameter to data a
- if no solution: take away or add channels → branching N
- make microstructure consistent with water diffusion coefficient (percolation) → number of cuts (dead-end channels) c

An Artists View

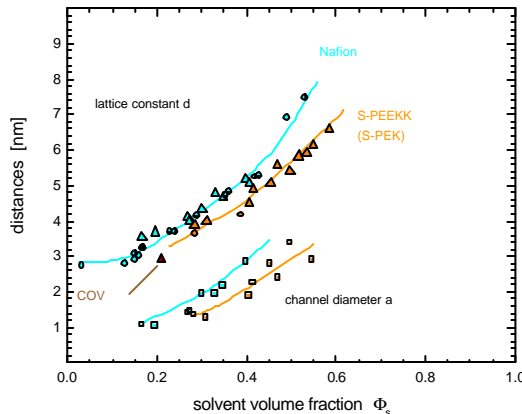


Model Parametrisation

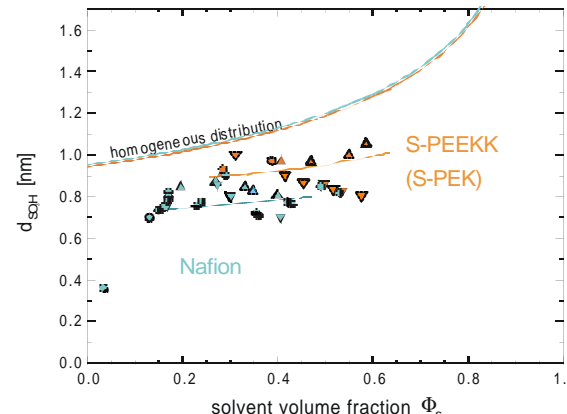
Internal Hydrophobic / Hydrophilic Interface



Separation Length and Channel Diameter



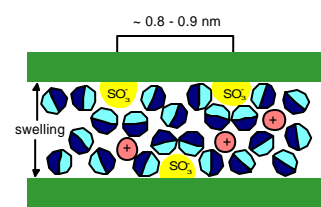
SO₃⁻ / SO₃H Separation on Internal Surface



Relations between Microstructure and Diagonal Coefficients of the Transport Matrix

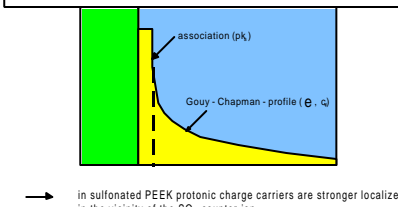
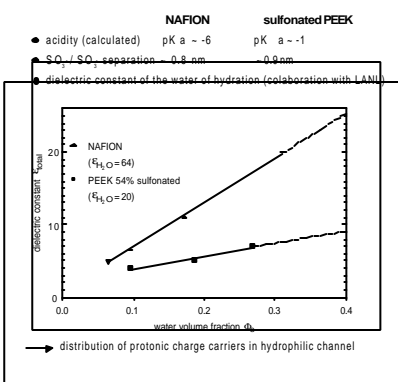
- confinement of water in nano-channels
 - confinement of acid functional groups ($-SO_3H$) to hydrophilic / hydrophobic interface
- size effect
- chemical wall effects (hydrophobic and hydrophilic interactions)
- long-range electrostatic effects (formation of space-charges)
- percolation effects (geometric)

Formation of inner space - charge regions with immobile $-SO_3^-$ and mobile protonic defects being the charge carriers



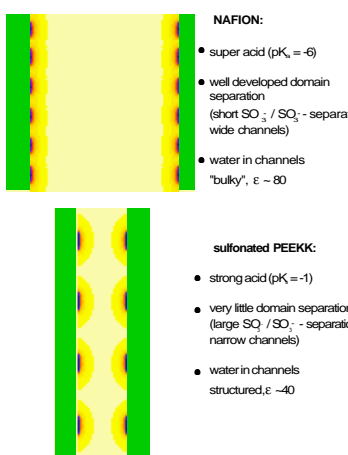
Electrostatic potential distribution and distribution of protonic defects determined by:

- interaction coefficient (pK_a calculated: -6 for NAFION, -1 for PEEKK)
- SO_3^- / SO_3H separation and channel width (microstructure) (microstructures by SAXS)
- dielectric constant of water (dielectric spectroscopy, LANL)



in sulfonated PEEK protonic charge carriers are stronger localized in the vicinity of the SO_3^- counter-ion

numerical solution of Poisson-Boltzmann eq. for different boundary conditions



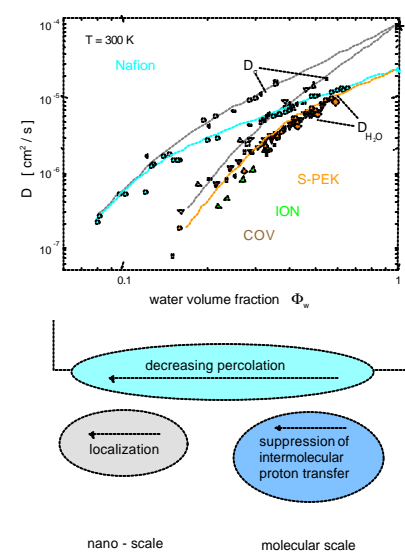
- super acid ($pK_a \sim -6$)
- well developed domain separation (short SO_3^- / SO_3H separation, wide channels)
- water in channels "bulky", $\epsilon \sim 80$

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- strong acid ($pK_a \sim -1$)
- very little domain separation (large SO_3^- / SO_3H separation, narrow channels)
- water in channels structured, $\epsilon \sim 40$

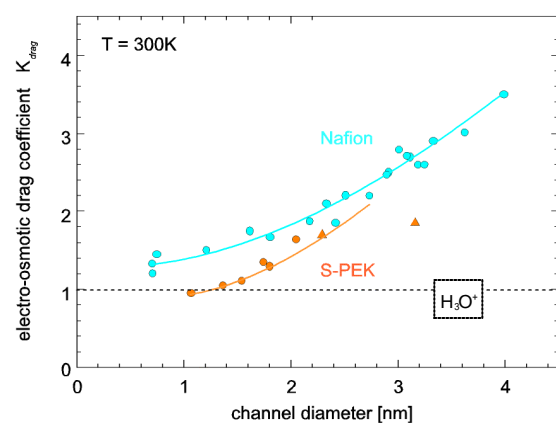
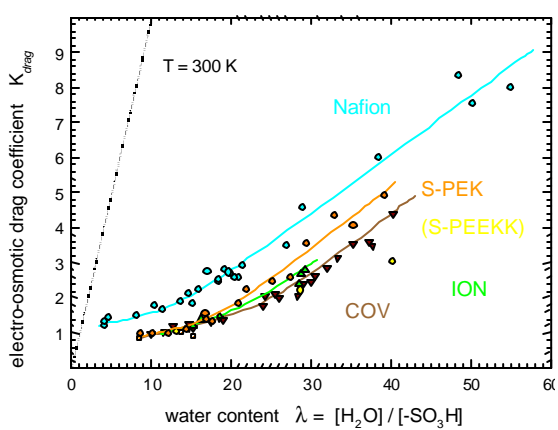
protonic defects more associated with SO_3^- in S-PEK compared to NAFION

long-range transport coefficients as a function of water volume fraction (proton mobility L_{11} and water self-diffusion L_{22})

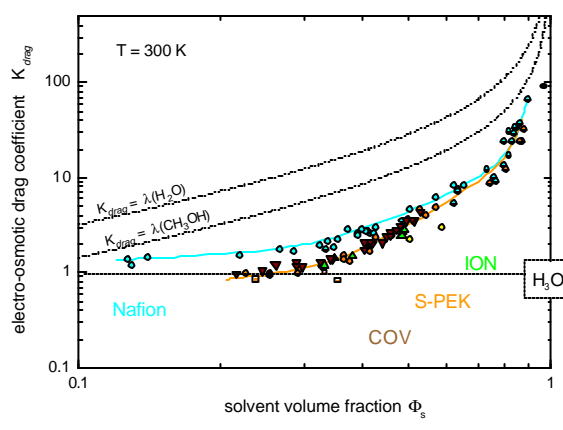


Relations between Microstructure and Cross-Coefficients of the Transport Matrix

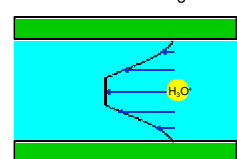
electroosmotic water drag $\left(\frac{L_{12}}{L_{11}} \right)$



electroosmotic water/methanol drag $\left(\frac{L_{12}}{L_{11}} \frac{L_{13}}{L_{11}} \right)$



electroosmotic drag:

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- lower limit given by primary hydration of proton (H_3O^+)
- otherwise electroosmotic drag may be described as hydrodynamic process controlled by water/water and water/polymer interaction, microstructure and swelling

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- reduce hydrophobic/hydrophilic separation
- reduce swelling (methanol, T)
- increase polymer/water interaction