

Nano structure of NAFION: a SAXS Study

A discussion of

H.-G. Haubold et al., *Electrochimica Acta* 46 (2001)
1559–1563

Outline

❑ **Background on NAFION:**

- Role in DMFCs
- Structure

❑ **Experimental design:**

- The SAXS experiment
- In-situ experimental design

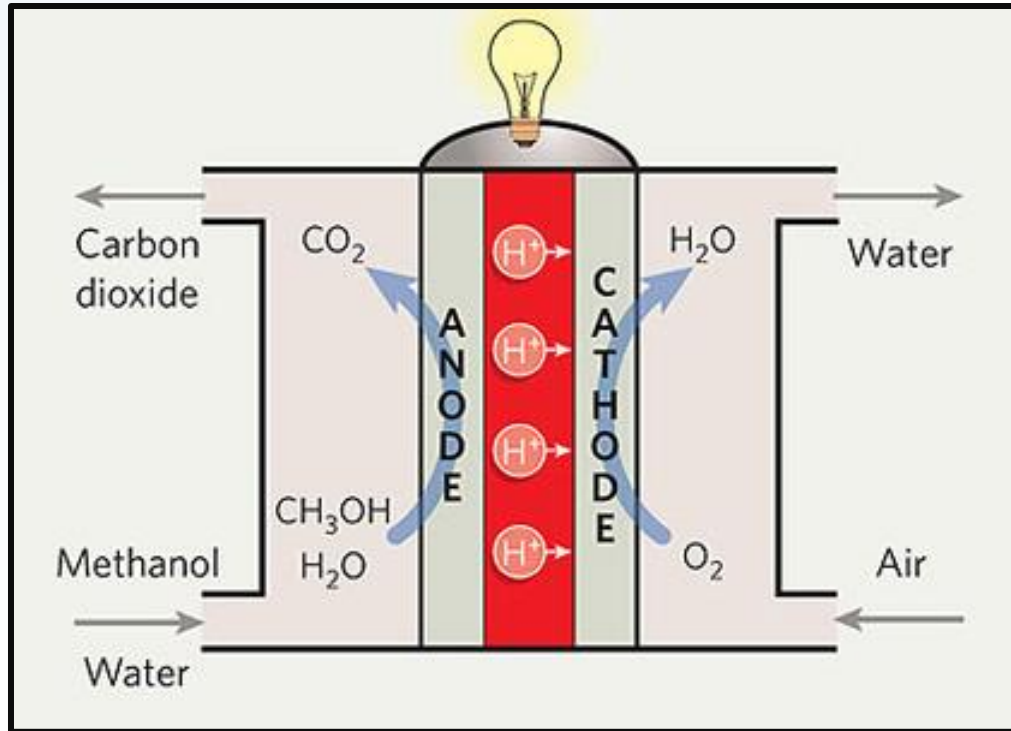
❑ **The fitting model**

❑ **Results and discussion:**

- SAXS data
- Model fit

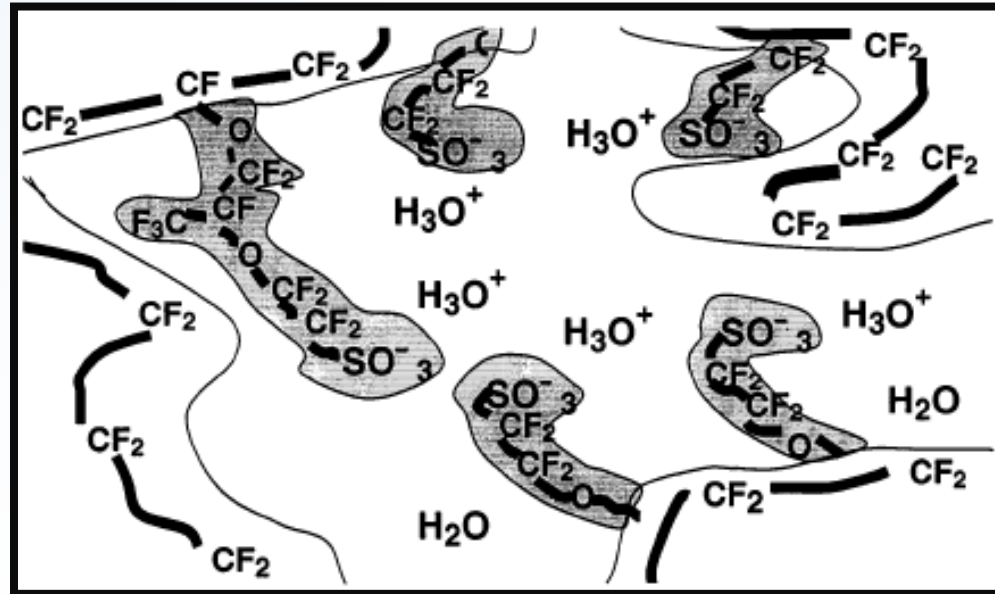
❑ **Conclusion**

Role of NAFION in DMFCs

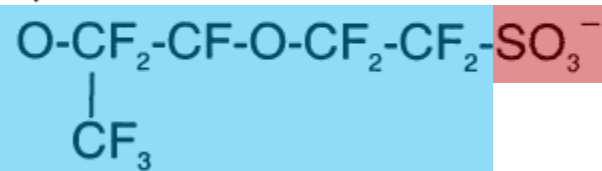
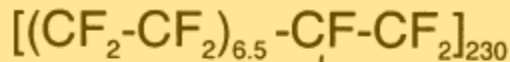


- ❑ **Solid Polymer electrolyte** : ionic conduction
- ❑ **Separator** between methanol-water environment and air environment

NAFION: Structure



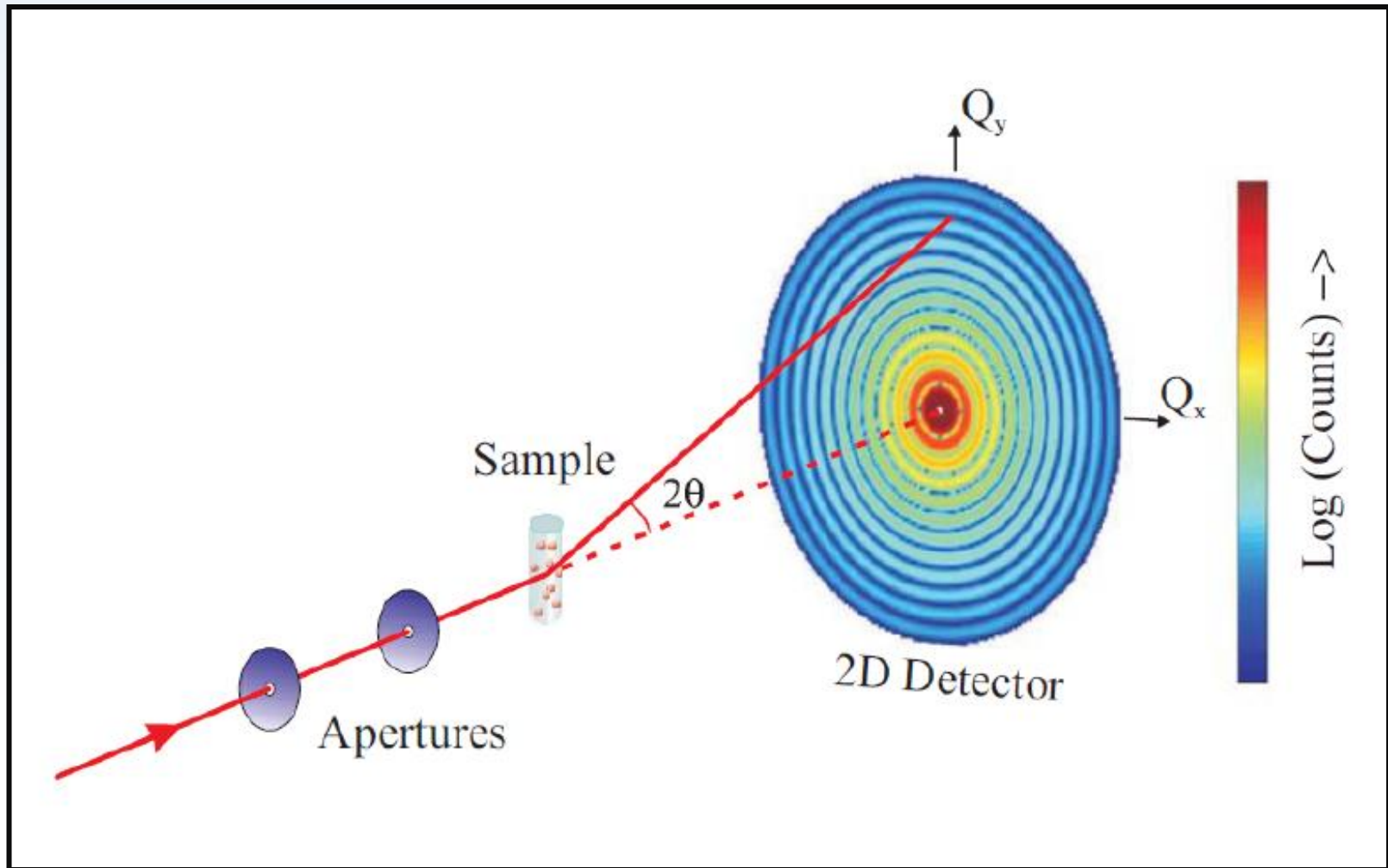
PTFE backbone
(Hydrophobic)



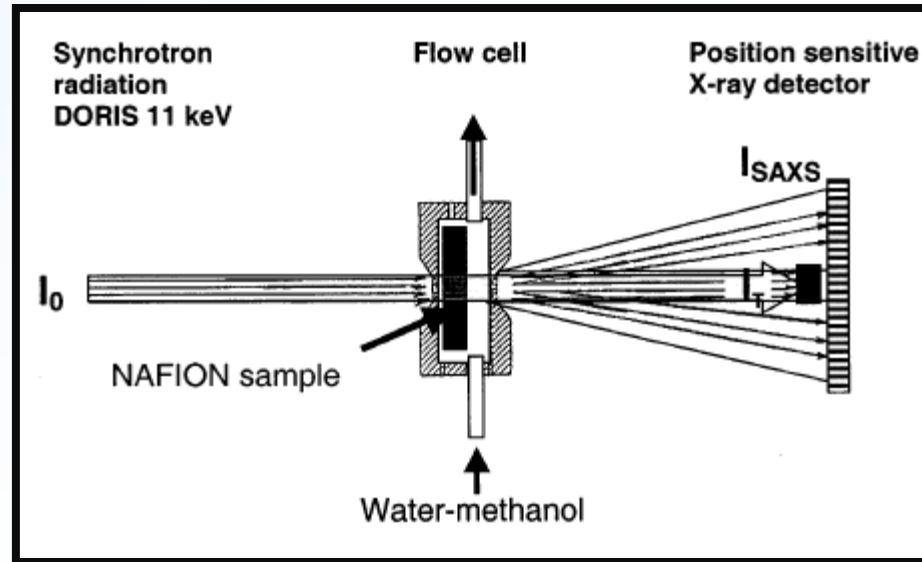
perfluorovinyl ether
side chain

sulfonate ionic group
(Hydrophilic)

The SAXS experiment



In-situ Experimental design

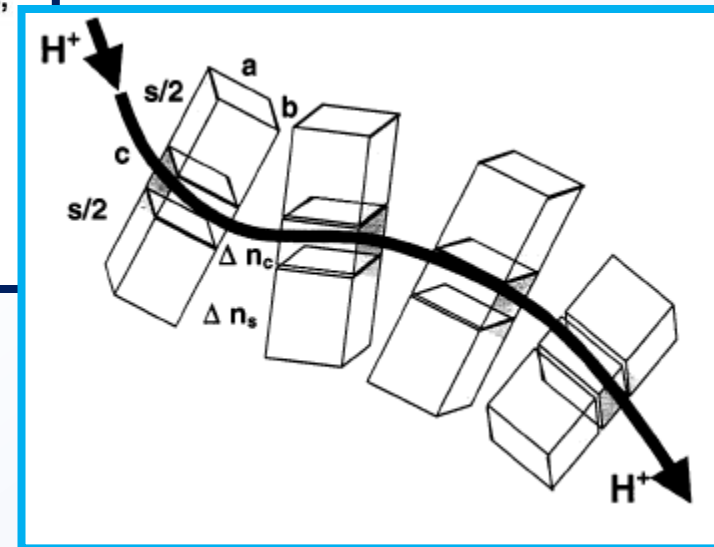
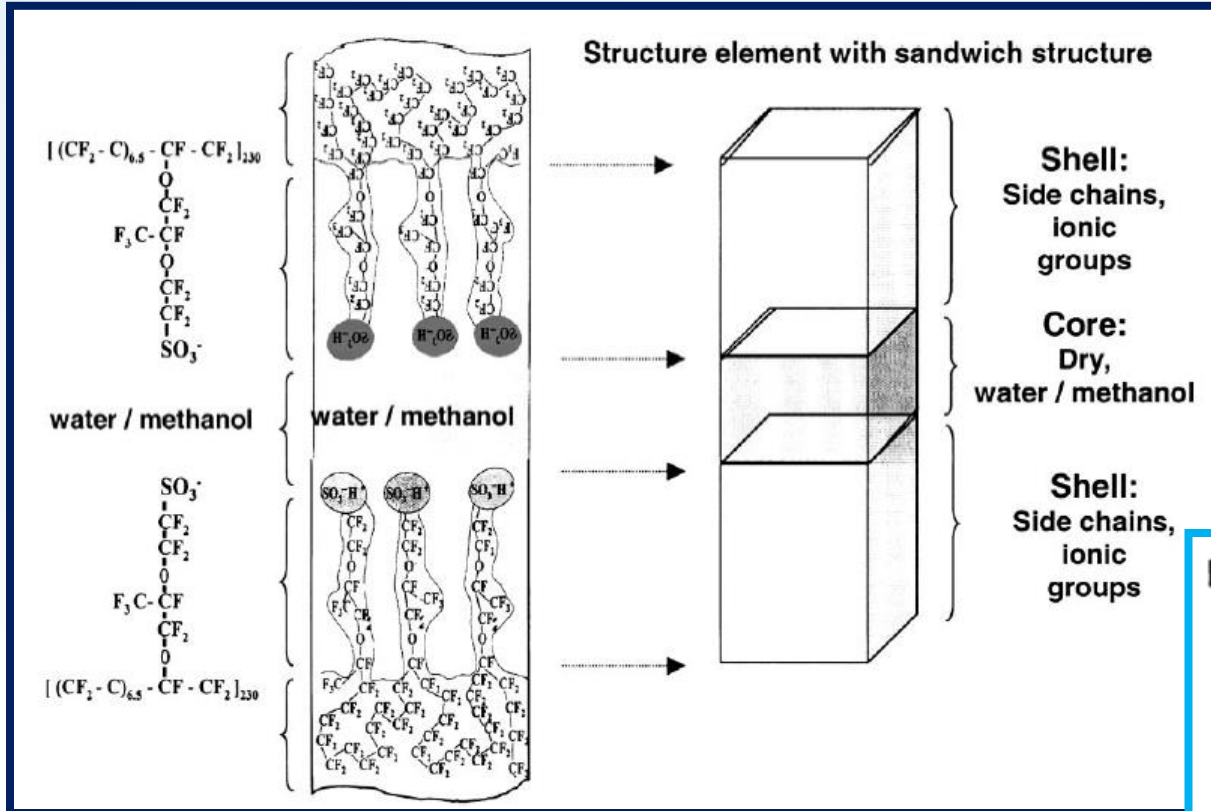


Sample characteristics:

- 175 μ m thickness
- Molecular wt. : 250000
- 8 wt% sulfonic groups

- In-situ in a flow cell
- Working conditions simulated:
 - Dry
 - In water
 - In water-methanol mixture
 - Pure methanol

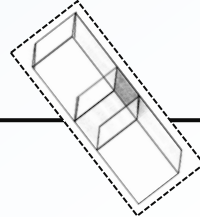
The fitting model : Discrete structure elements



The fitting model : Model equations

$$\frac{d\Sigma}{d\Omega} \sim \Delta n_p^2 S^2(\vec{Q})$$

$$S^2(Q) = \left(\frac{\sin(Q_x a/2)}{Q_x a/2} \frac{\sin(Q_y b/2)}{Q_y b/2} \frac{\sin(Q_z c/2)}{Q_z c/2} abc \right)^2$$

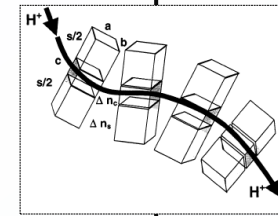


$$\frac{d\Sigma}{d\Omega} \sim \left(\frac{\sin(Q_x a/2)}{Q_x a/2} \frac{\sin(Q_y b/2)}{Q_y b/2} ab \right)^2 [\Delta n_s(S(Q_z, t) - S(Q_z, c)) + \Delta n_c S(Q_z, c)]^2$$

$$S(Q_z, t) = \frac{\sin(Q_z t/2)}{Q_z t/2} t, \quad S(Q_z, c) = \frac{\sin(Q_z c/2)}{Q_z c/2} c$$

Assumptions:

- Random distribution of particles
- Equally sized particles



Fitting parameters:

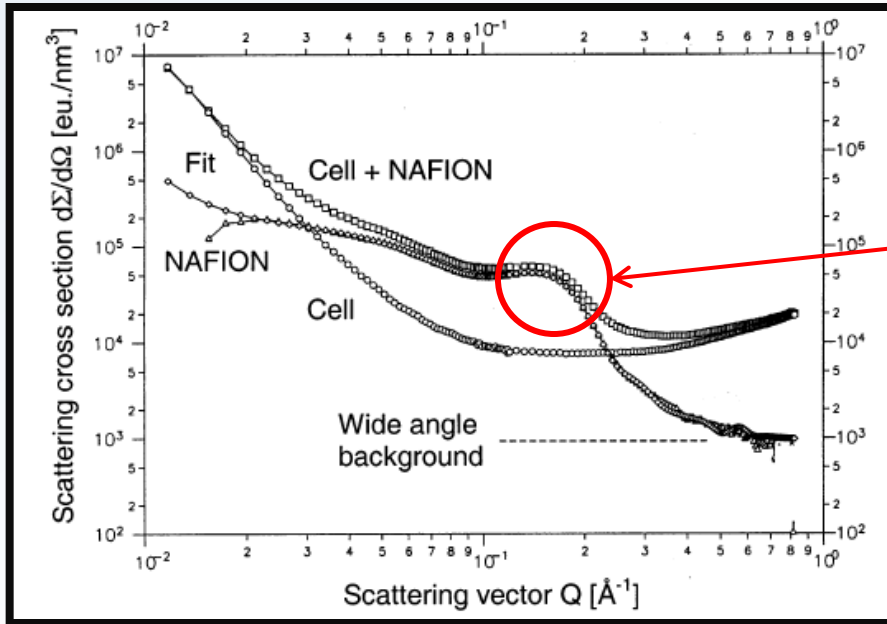
- Core thickness - c
- Total shell thickness - s
- Scattering contrasts - $\Delta n_c, \Delta n_s$
- Lateral dimensions of core and shell - a, b

$$\left\langle \frac{d\Sigma}{d\Omega} \right\rangle \sim \int_0^1 \frac{2}{\pi} \int_0^{\pi/2} S^2(a, b, \phi, u) d\phi [\Delta n_s(S(t, u) - S(c, u)) + \Delta n_c S(c, u)]^2 du$$

$$S(a, b, \phi, u) = \frac{\sin(Qa \cos(\phi) \sqrt{1-u^2/2})}{(Qa \cos(\phi) \sqrt{1-u^2/2})} \frac{\sin(Qb \sin(\phi) \sqrt{1-u^2/2})}{(Qb \sin(\phi) \sqrt{1-u^2/2})} ab$$

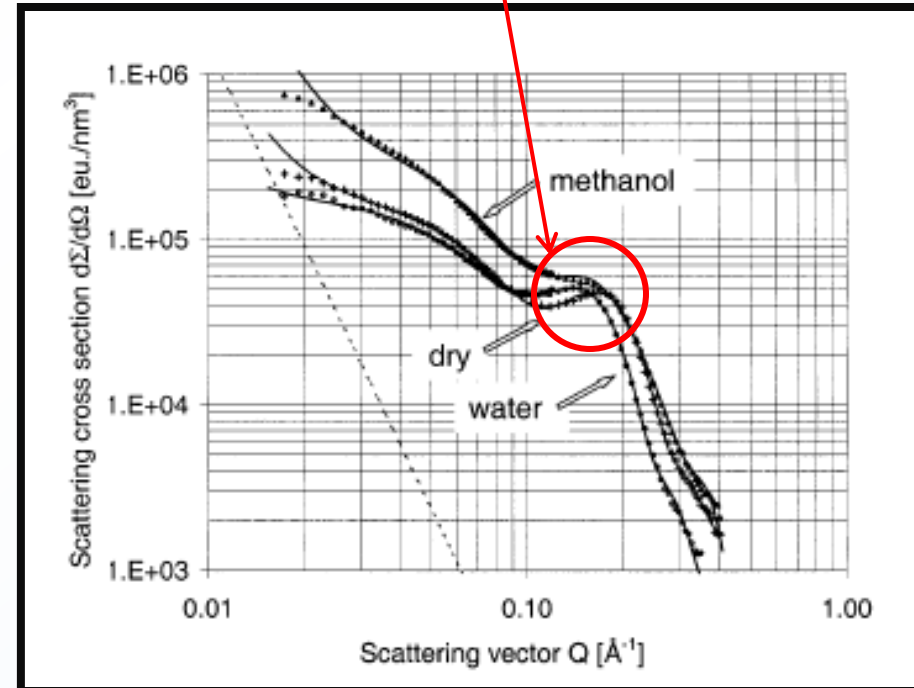
$$S(t, u) = \frac{\sin(Qtu/2)}{(Qtu/2)} t, \quad S(c, u) = \frac{\sin(Qcu/2)}{(Qcu/2)} c$$

Results and discussion

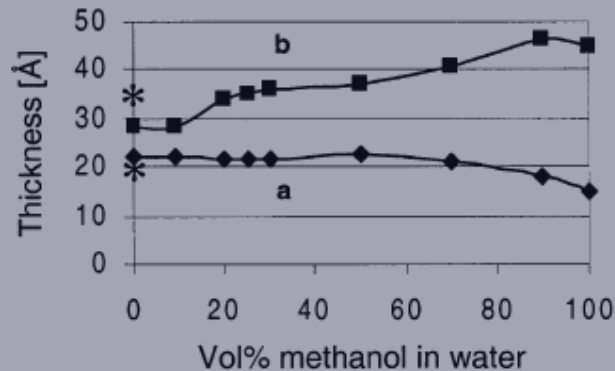
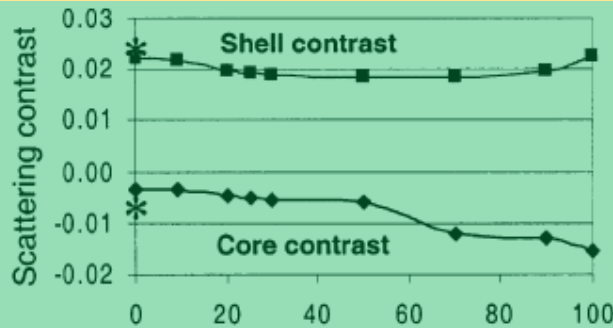
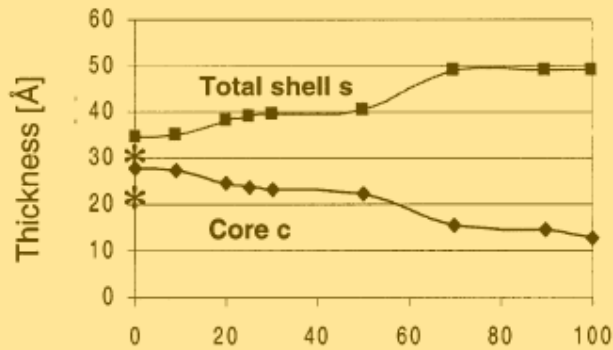


Ionomer peak : $Q \sim 0.15 \text{ \AA}^{-1}$
 $d = 2\pi/Q \sim 40 \text{ \AA}$

- Q^{-4} contribution points to very large structures.



Information from model fit



□ Scattering from small particles of $a=15\text{\AA}$, $b=45\text{\AA}$, $(c+s)=60\text{\AA}$.

□ Core is key to proton transport. Demonstrated by doubling of core contrast for dry membrane compared to water flooded state.

□ Strongly dependent on volume concentration of methanol.
□ Macroscopic swelling in water from difference in volume between dry and water swollen sample.

Conclusion

- ❑ Simple structure models shown to successfully describe nano-structure of ionomers.
- ❑ Model assumptions validated:
 - Core channels key to proton transport
 - Side chains unaffected by water
- ❑ Higher methanol concentration found to :
 - Reduce core volume
 - Dehydrates the ionic shell