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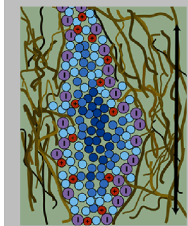

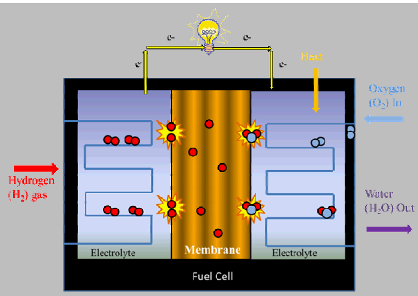

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Characterization of Heterogeneous Diffusion and Degradation in Fuel Cell Polymer Membranes using PFG HRMAS NMR

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U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

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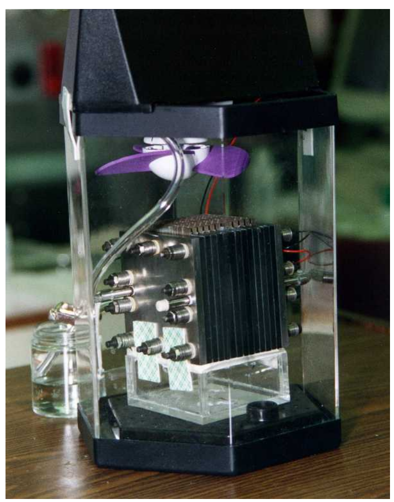
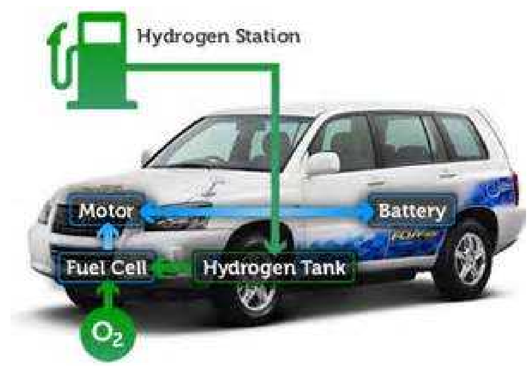
Fuel Cells – Emerging Technology

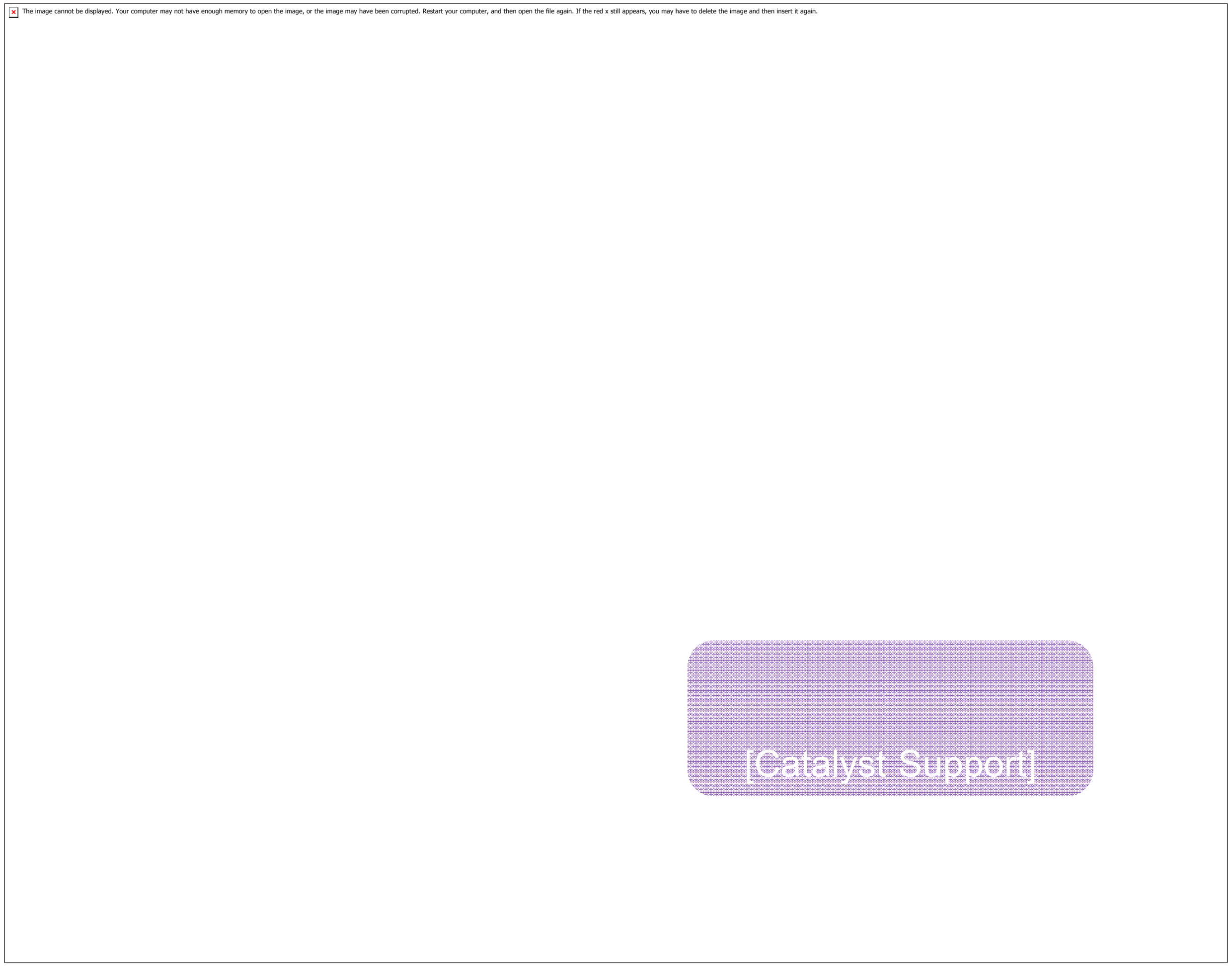
"Old Technology – Material Advances Lead the Way"

- Convert chemical energy (fuel) to electricity using oxygen.
- Different types of fuels (hydrogen, methanol, ethanol…).
- Can produce electricity as long as there is fuel (unlike batteries).
- Power generation (backup), including remote sites, military, automobile.
- Higher efficiency (60 – 85%) that combustion systems (30%).





MeOH Fuel Cells - AEMs



Development of new membranes materials for a wide range of technological applications ultimately based on fundamental understanding of transport.

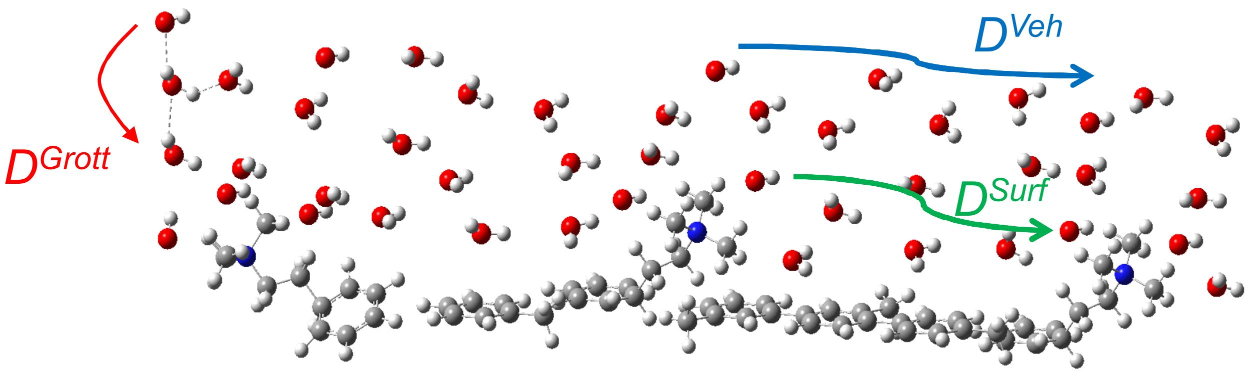
Conductivity Related to Diffusion Properties

via Nernst-Einstein Equation

$$\sigma_i = \frac{F^2}{RT}\left(\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{1}{D_{ij}^{eff}} + \frac{1}{D_{iM}^{eff}}\right)^{-1} C_i$$

Surface **Grotthuss** **Vehicular**

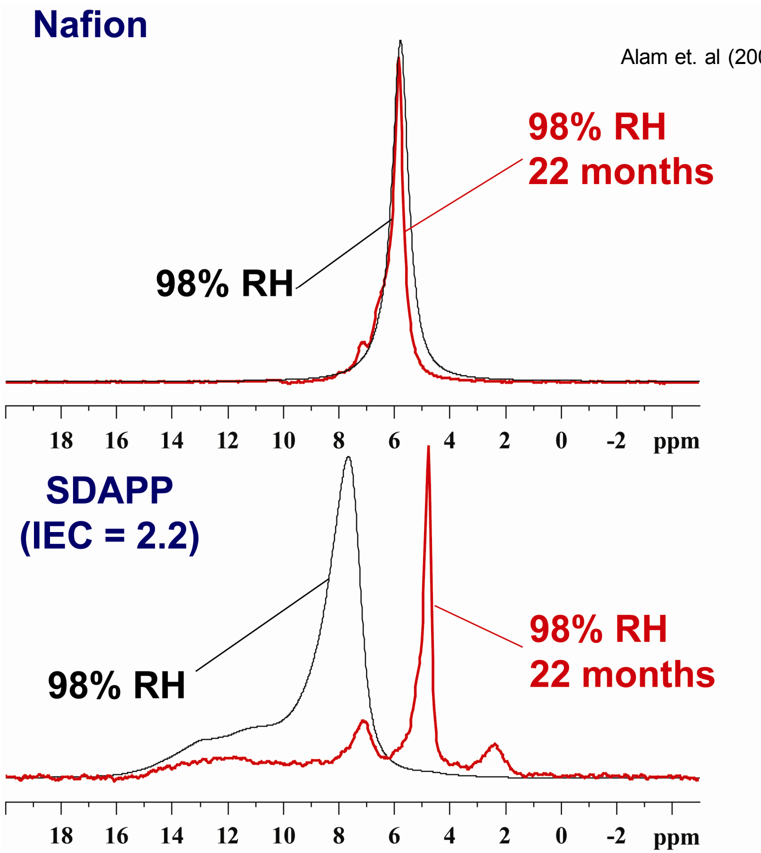
$$\sigma = \frac{F^2}{RT}\left(D_{OH^-}^{Surf}C_{OH^-}^{Surf} + D_{OH^-}^{Grott}C_{OH^-}^{Grott} + D_{OH^-}^{Veh}C_{OH^-}^{Veh}\right)$$



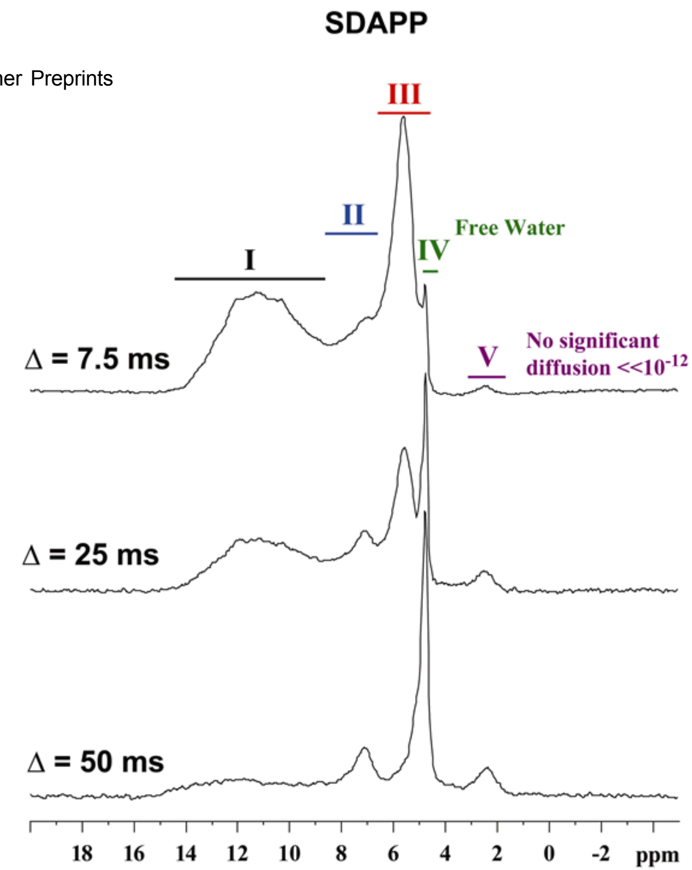
The transport of MeOH can also be discussed in terms of different diffusion environments.

PFG NMR and Site Resolution

Pulse Field Gradient (PFG) NMR used to measure solvent diffusion.



Alam et. al (2008) ACS Polymer Preprints



Under static PFG NMR we have occasionally observed different water environments, but the lack of resolution was never considered an issue!

Site Resolution in MeOH Fuel Cell Membranes

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Different water environments in polymers

- Water in hot pressed Nafion, Jeong and Han, Bull. Korean Chem. Soc. (2009), 30, 1559.
- Water in PEEK, Baias *et al,* Chem. Phys. Lett. (2008), 456, 227; (2009) 473, 142. MAS with SSB with no chemical shift resolution.
- Mele *et al*., J. Incl. Phenon. Macrocycl. Chem. (2011), 69, 403. HRMAS resolution.

HRMAS PFG NMR and Site Resolution

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T_1 = 850 ms
D = 5.4 x 10^{-10} m^2/s

T_1 = 1.13 s
D = 2.3 x 10^{-10} m^2/s

T_1 = 2.0 s
D = 1.8 x 10^{-9} m^2/s

T_1 = 2.1 s
D = 1.6 x 10^{-9} m^2/s

Resolution is always exciting! Can ask questions about differences between MeOH and water association with the membrane.

AEM Membranes Investigated

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Alkane spacers (C_6) added for higher mobility, increased water content, alkaline stability.

What is impact on diffusion and types of environments?

^{1}H HRMAS NMR of Different AEM Membranes

2D ^1H-^1H Exchange/NOESY Studies

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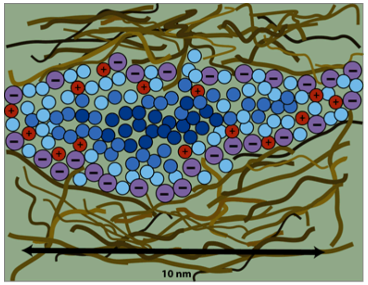
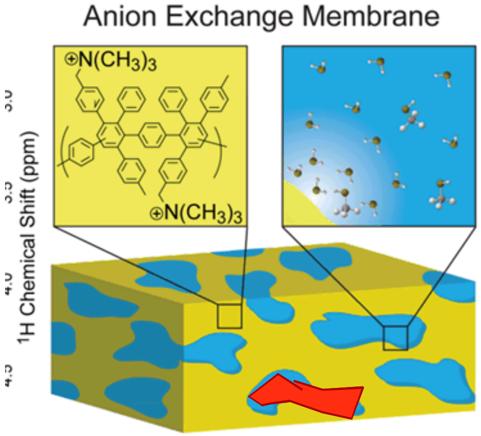


- Free and associated domains exist.
- These domains show some exchange.
- Associated water and MeOH in close contact with membrane.



Diffusion Analysis of Individual Species

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$$\left\langle R^2(\Delta) \right\rangle = -6 \ln\left[E(q,\Delta) / E(0,\Delta) \right] / q^2$$

$$\left\langle R^2 \right\rangle = 6Dt$$

$$\left\langle z_M^2(\Delta) \right\rangle = -2 \ln\left[E(q,\Delta) / E(0,\Delta) \right] / q^2$$

$$\left\langle z_M^2 \right\rangle = 2D_\alpha t^\alpha$$

- **Associated diffusion is an order of magnitude slower than free species (Water and MeOH).**
- **MeOH diffusion slower than Water in both environments.**
- **The ratio of D_{assoc}/D_{free} is much smaller for MeOH, suggesting preferential association with membrane.**

Diffusion Analysis of Individual Species

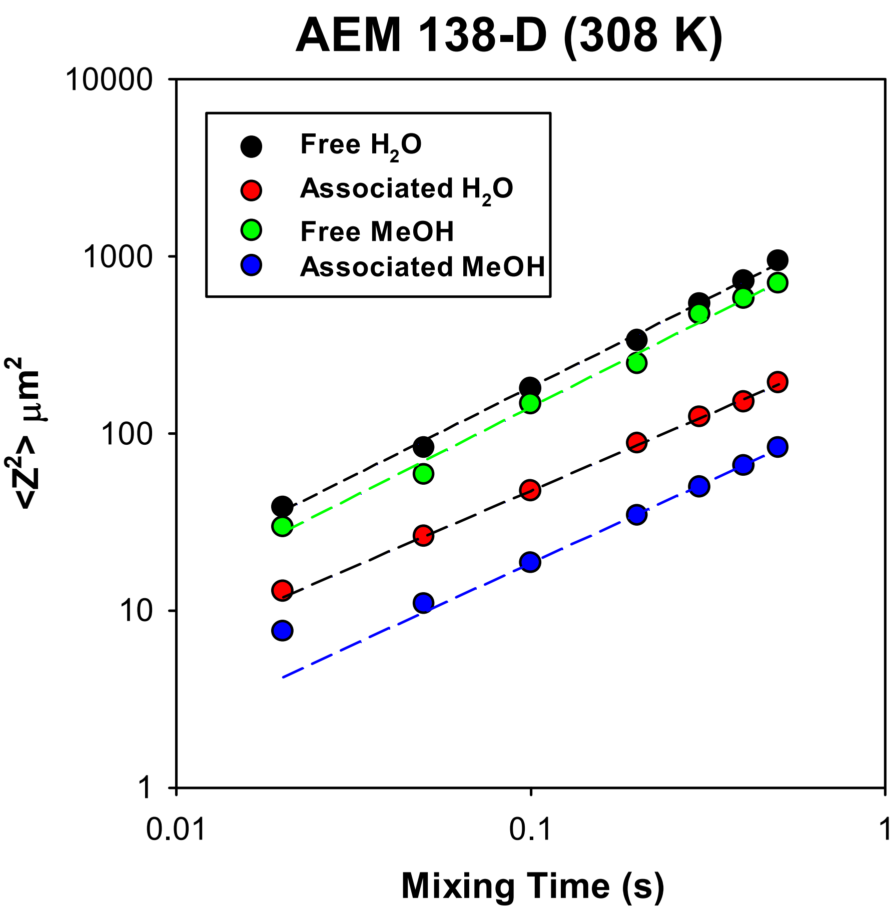
- Extract Δz2 from multiple different
- Δ delays in PFG NMR

- Evaluate possibility of anomalous diffusion ($\alpha \neq 1$).

- Most systems show normal diffusion. As expected in these membranes.

- Associated water environment reveal fractal diffusion at lower hydration/temperatures.

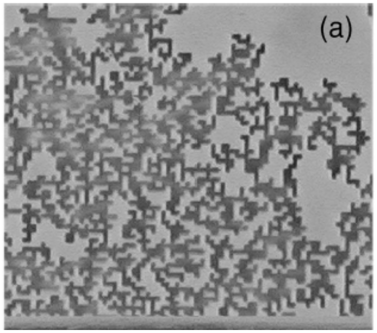
Anomalous Diffusion in Associated Environments?



Anomalous diffusion can be expressed can be expressed through the power law.

$$\left\langle z^2 \right\rangle = 2D_\alpha \Delta^\alpha$$

α = 1, normal diffusion
α < 1, sub-diffusive
α ~ 0.7 2D fractal



Klemm, Metler, Kimmich, *Phys. Rev. E* (2002), 65, 021112

Disappears with increasing temperature and hydration.

Solvent Diffusional Activation Energies

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Sample (IEC)	E_a (kJ/Mol)			
	F-H_2O	A-H_2O	F-MeOH	A-MeOH
1N MeOH	26.0	--	27.0	--
ATMPP (1.48)	20.0	44.0	28.3	23.6
ATMPP (1.79)	29.7	24.5	26.2	29.4
ATMPP (2.35)	26.7	28.7	27.0	29.2
$TMAC_6PCC_6$ (2.13)	37.6	33.3	38.6	30.6
$TMAC_6PCC_6$ (2.27)	--	23.2	--	16.5
$TMAC_6PCC_6$ (2.60)		37.4		37.5

- Results similar to Nafion and Nafion composites.
- No direct comparison because individual sites not investigated.

Ratios of Diffusion Rates

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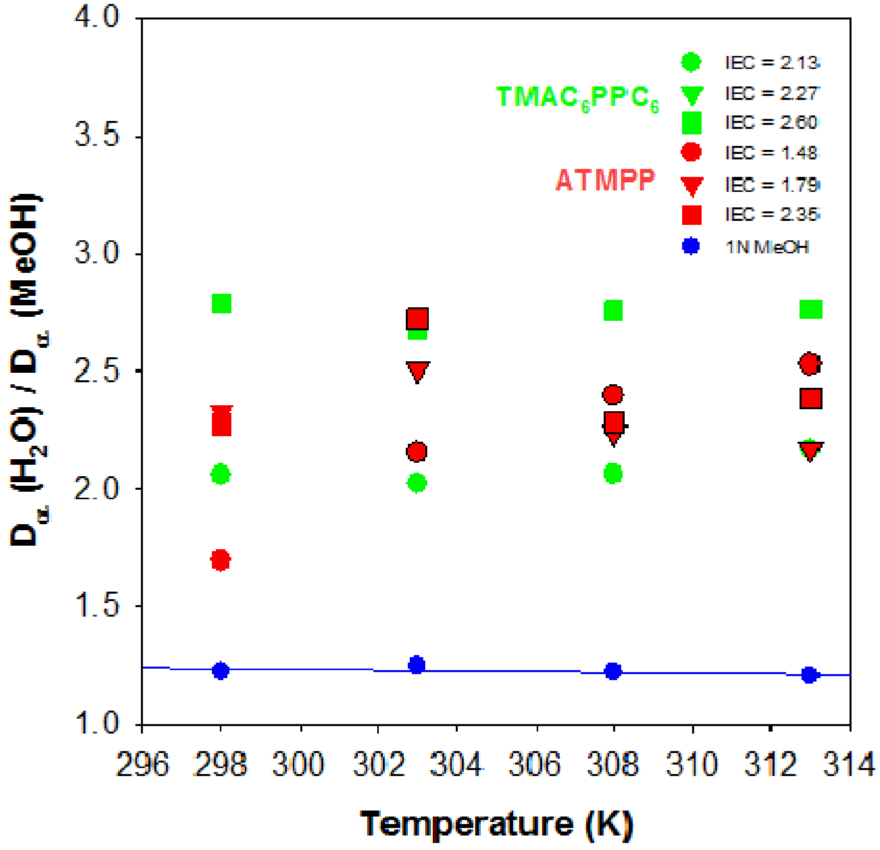
Associated Sites ~5 times slower than 1N MeOH.

ATMC_6PPC_6 higher diffusion.

“Free Sites” NOT really like Bulk 1N MeOH!

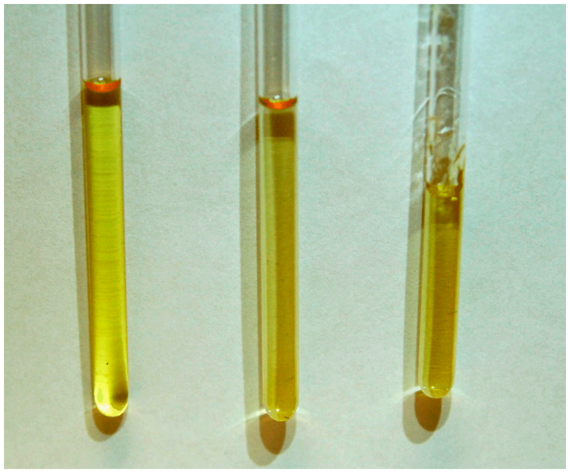
Ratios of Diffusion (H_2O/MeOH)



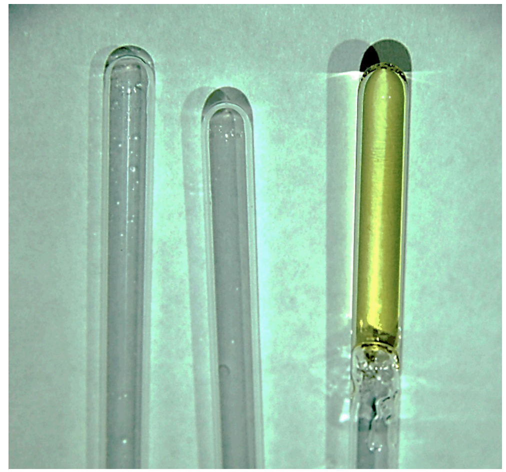
- All of these membranes show a preferential reduction of MeOH.
- Helps reduce MeOH cross-over in membranes.

Why Use HRMAS For Aged Membranes

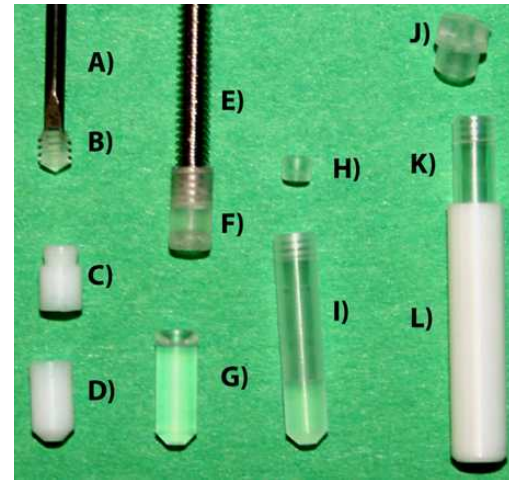
Aged ATMPP (4M KOH) swollen in DMSO



0 days **1 days** **10 days**



0 days **1 days** **10 days**



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- Aged samples not longer dissolve in DMSO, become gels. AEMs also become brittle with aging.
- Solution NMR becomes broad….can address with HRMAS NMR.
- “Liquid like samples” need to retain liquid under MAS.
- Need to consider centrifugation effects under MAS.

HRMAS NMR For Degradation Studies

Solution NMR

Aged ATMPP (4M KOH) swollen in DMSO

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HRMAS NMR

10-Day Aged ATMPP (4M KOH) swollen in DMSO

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- HRMAS removes magnetic susceptibility at low MAS speeds (> 1 kHz).
- Solution like resolution obtained at RT.
- Lower S/N as 30 μL inserts used for HRMAS.

HRMAS NMR For Degradation Studies

2D NOESY ^{1}H HRMAS (τ_{mix} = 100 ms)

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Conclusions

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- **HRMAS NMR provides increased resolution in MeOH fuel cell membranes.**
- **Combined with PFG resolves diffusion for 4 unique solvent environments.**
- **This system may represent a special case, not a generalized solution for all membrane systems.**
- **The diffusion measurements of low water content membranes reveals associated water and MeOH have sub-diffusion process (motion on membrane surface).**
- **There is a large membrane influence on the MeOH versus water species.**
- **Synthetic modification improved solvent diffusion with respect to original AEM membranes.**
- **HRMAS PFG NMR does provide a novel tool to study these heterogeneous diffusion processes in polymer membranes.**

Thanks for your attention!