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Membranes and MEAs at Freezing Temperatures

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Freezing Fuel Cells: Impact on MEAS

Below 0^oC

•Transport processes/motions slow down: *questions re:* lower conductivity,water mobility etc

•Residual water will have various physical effects in different portions of the MEA

questions re: durability of components

3 'States' of Water in Proton Conductors ?

Freezing (bulk), bound freezable, bound non freezable water states claimed based on DSC

- Freezing water more mobile, allegedly important for high conductivity

Analysis common for porous systems

Does the presence of these states matter? Why?

'State of Water' in PEMs

At T < 0^oC

•'Liquid-like' water freezes

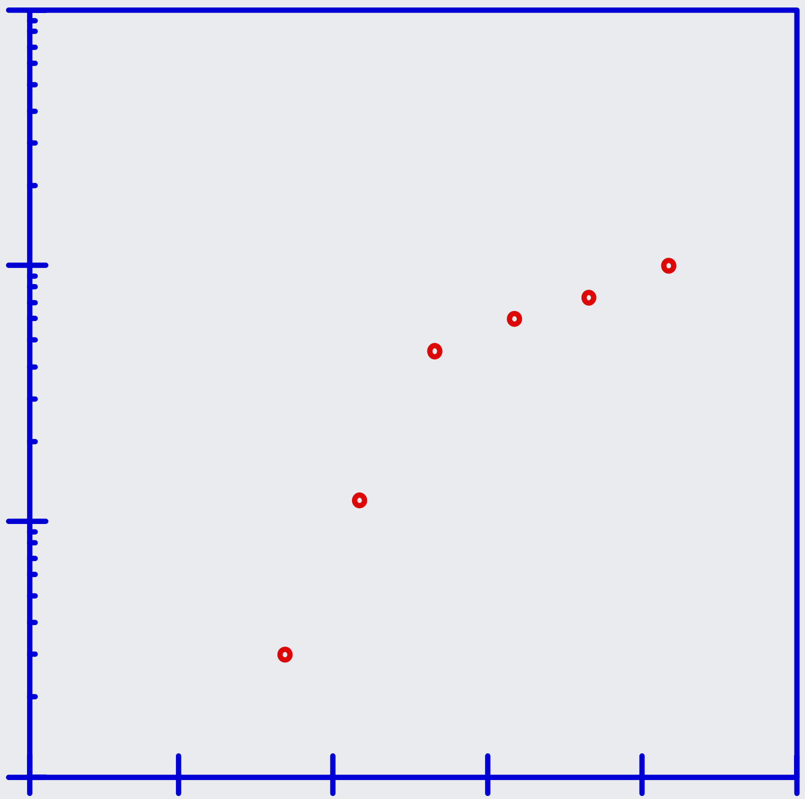
•'Non-freezing' fraction: water of solvation at pore wall; in some sense, this water is 'already frozen'

At T > 0^oC

•Water freely interchanges between environment on sub-nanosecond timescale; all observed properties of water are population weighted averages

•At this T: 1 'state' = average

Conductivity of Membrane at Low T



Conductivity drops dramatically below freezing point

Note that's a log scale!

NB: sample fully hydrated

Water binding

- 'Freezing' vs. 'non-freezing' fractions of water
  - derived from thermal analysis; Pure phenomenology

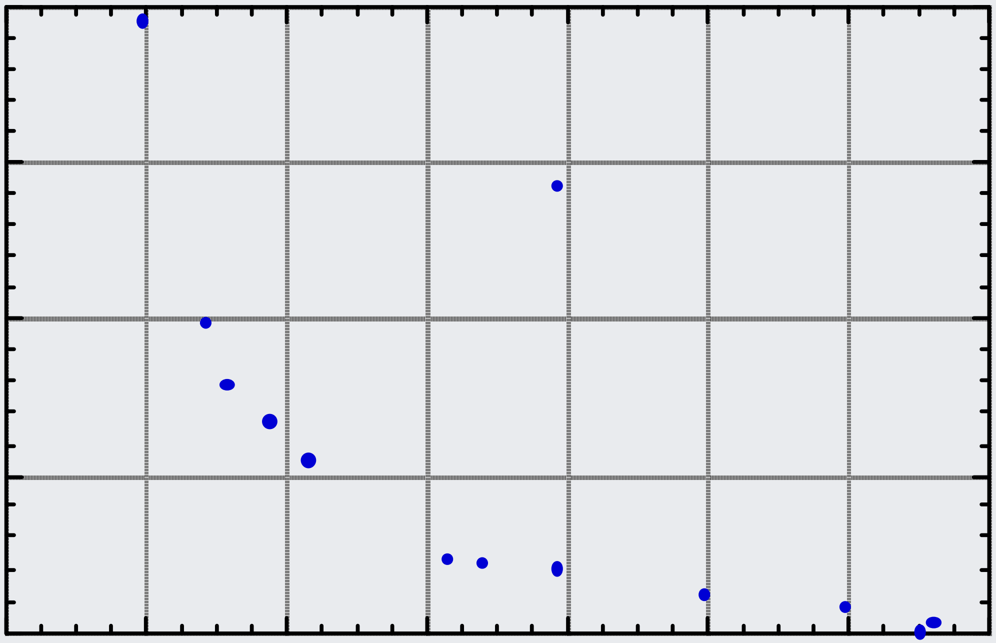
- We prefer to think in terms of physical parameters:
  - Chemical or physical forces associated with water interaction in polymer--thermodynamics, mobility measurements etc.

- Two approaches are basically similar, but focus on physical parameters allow us to hypothesize and predict properties (i.e. do science)

Effect of Water Content

	Water Content	
	Low (a_w < 0.75)	High (a_w > 0.75)
Mechanical Properties	Minimal swelling; constrictions against conduction	Maximum swelling; greater connectivity in conduction network
Proton Transport Mechanism	Vehicular (water moves with H^+)	Grotthuss (hopping)
Proton Conductivity	Low (σ < 0.01 S/cm)	High (σ > 0.04 S/cm)
Controlling Phenomena	Enthalpy of Solvation	Entropy of Swelling
λ, water molecules Per sulfonate	< 6	> 6

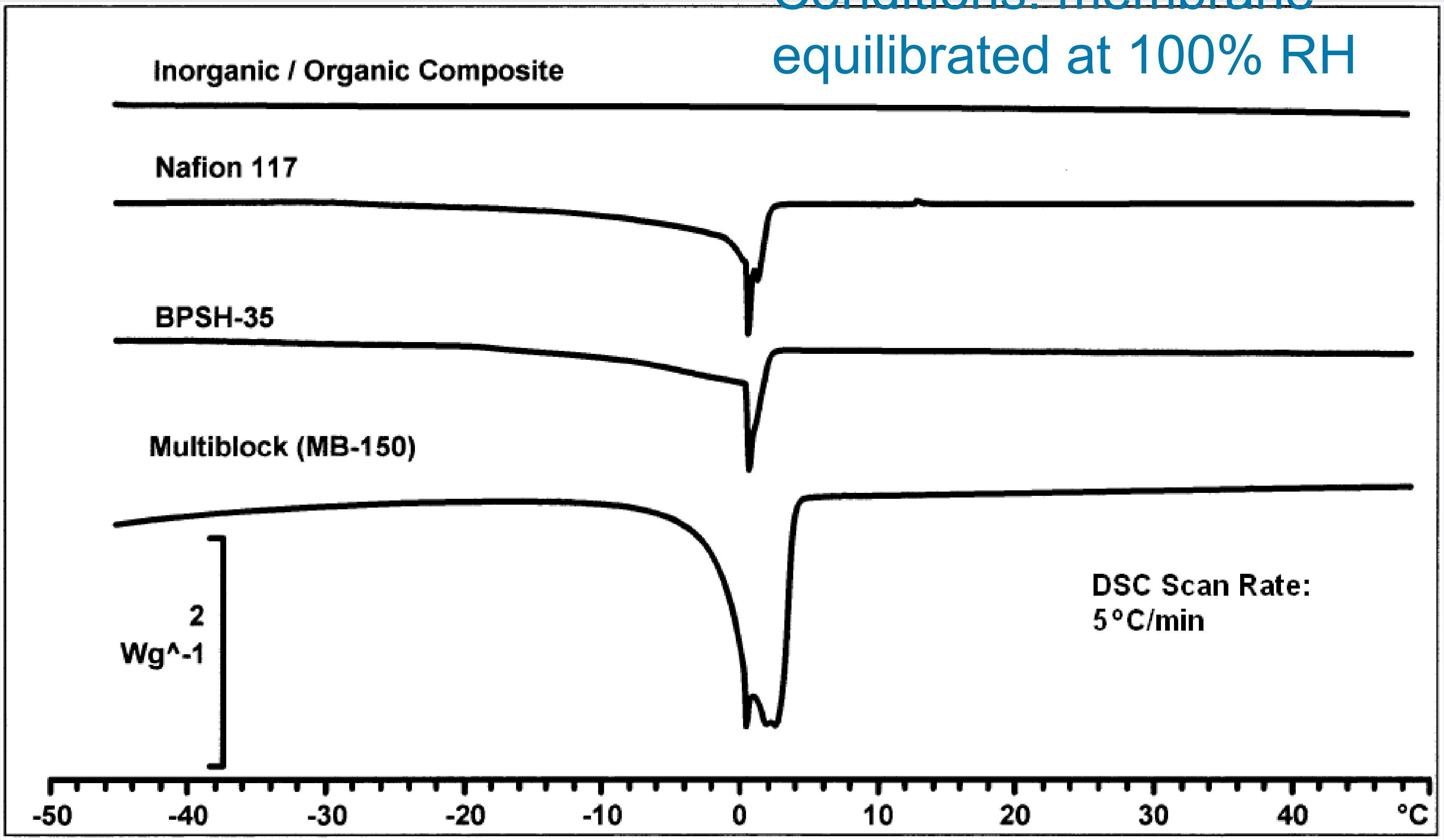
Energetics of Water Uptake by Nafion (Typical for all Ionomers)



Water is very weakly bound above λ ~ 6 and increasingly tightly bound as λ decreases

DSC thermograms of PEFC membranes (water melting region)

Conditions: membrane equilibrated at 100% RH



Summary of DSC data, water melting region

Sample	wt% Water	Melting Peak (°C)	ΔH_f (J/g sample)	ΔH_f (J/g water)	freezing water (wt%)	Non-freezing water (wt%)
Nafion	19.9	-0.41	35.21	-176.9	10.6	9.3
BPSH35	32.8	0.36	32.53	99.2	9.77	23.03
MB150	35.7	3.71	84.07	-235.5	25.24	10.46
I/O	6.97	none	--	--	--	6.97

$\Delta H_{f(water)}$ = 333 J/g

Conclusions

If free water state is somehow critical to transport, we should see sharp transitions in properties due to its presence. Freezing or free water is only present at very high water contents

We only see significant effect for EO drag (for some membranes); conductivity and water mobility vary smoothly with water content.

Sharp transition for conduction at very low water contents associated with tight binding of water and protons--revealed by isopiestic curve

When is 'Water State' Limiting?

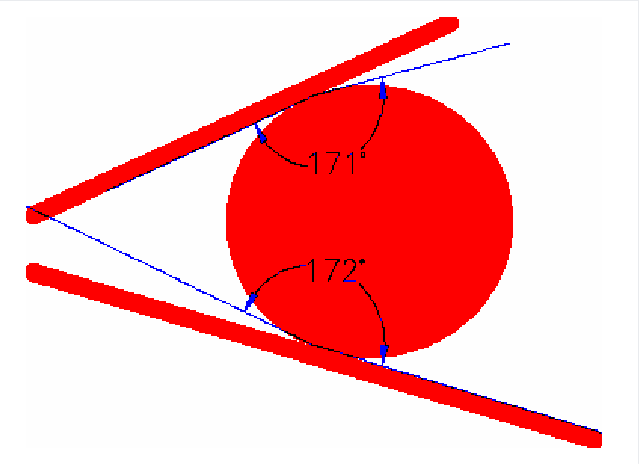
Conduction processes influenced by water content , but not strongly, until below 5 or so waters per sulfonate-->this regime may be key for conduction at with low RH.

EO drag strongly affected by presence of 'free' water--> avoid for passive DMFC

Freezing Effects: Material Properties

Presence of water droplets in MEA components could lead to significant mechanical stresses upon freezing

Likely difficulties: delamination of catalyst later; physical break-up of GDL; some polymers susceptible upon thermal cycling.



Cartoon Depicting Droplet Between GDL Fibers

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