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# High Temperature Polymer Membranes for Fuel Cells

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DOE Technical Barriers for Components

O. Stack Material and Manufacturing Cost

P. Durability

Q. Electrode Performance

R. Thermal and Water Management

DOE Technical Target for Fuel Cell Stack System for 2010

Cost $35/kW

Durability 5000 hours

# Hydrogen Safety Measures

Existing facilities

Thorough analysis undertaken with facilities personnel to ascertain expected flow rates of $H_2$ in various test operations

Hydrogen primarily used in test stands

Hydrogen supply will be placed outside building

Appropriate automated emergency shutdown protocol to ensure no large leaks

New Facilities

Additional test stands require enclosure

Consulting with industry ---> new design for enclosure

# Cast of Characters: Research Group and Others

Z-group at Case

Students: Berry Chou, Tom Kalapos, Ram Subbaraman, Derek Lebzelter, Tom Greszler, Mike Bluemle, Felicia Costello, Brian Kienitz, Mike Pelsozy, Jessy Kurasch

Staff: Hayley Every, Chock Karuppaiah, Vlad Gurau, Hossein Ghassemi

Jim McGrath (Va. Tech)

# Role of This Research Group

Lead Lab in High T Membrane Development Efforts

Internal focus: develop new membranes and MEAs for high T applications

External focus: coordinate activities of high T team, provide central resource/facilities to primarily synthesis-oriented team members, lead HTMWG

# Project Elements

Technical

New Membrane Development

Electrodes for High T

MEAs from new Polymer Types

Programmatic

High T Program

High T Working Group

# Development of New Membranes: Rationale and Targets

Development of systems for both:

- 120$^{o}$C: minimally hydrated polymers (Primary Focus)
  - Achieve H+ conductivity approaching that of well-hydrated PFSAs at 80$^{o}$C
  - Focus on new polymers and other scaffolds carrying sulfonic acids or other superacids
  - 25% RH at operating temperature suggested by GM, based on system requirements
  - Need improved durability
- >150$^{o}$C: need to replace water with 'proton mobility facilitator' (Secondary Focus)
  - Focus on different conduction modes, non-volatile molecules to effect proton transfer
  - Durability of any polymeric components also a must

# Development of New Membranes: Approach

## Rational development strategy

- Combine diagnosis and physical chemistry studies with synthetic effort
- Understand functional role of 'significant structures' operating at various length scales
- Synthesis motivated by building block approach to improve or develop functions
- Synthesis sometimes carried out 'just' for insight
- Develop new analytical tools, deploy old tools to maximize insight gained
- Iterate

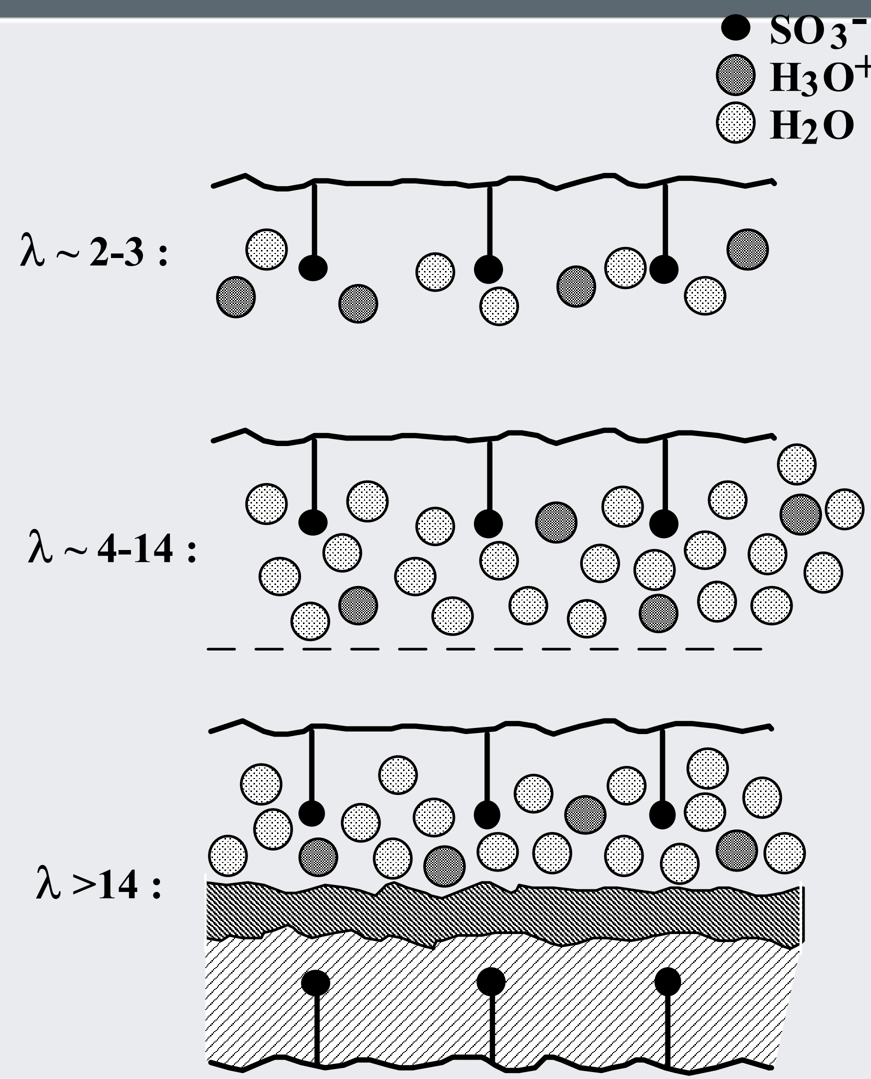
# Proton Conduction in PEMs: A Qualitative Picture

## Steps in the Process

- Dissociate

Escape and ‘Bridge the Gap’

- Plasticize/Network Forming



# What Materials Are We Focused on? Why?

Provide driving force for proton dissociation, carrier for transport and well-connected network

## Multicomponent Systems with Controlled NanoArchitecture

Composites
Blends
Networks
Molecular,Oligomeric Additives

<u>What We Must Build In</u>
Molecular level interactions
Tuned electronic structure
Connected over long range

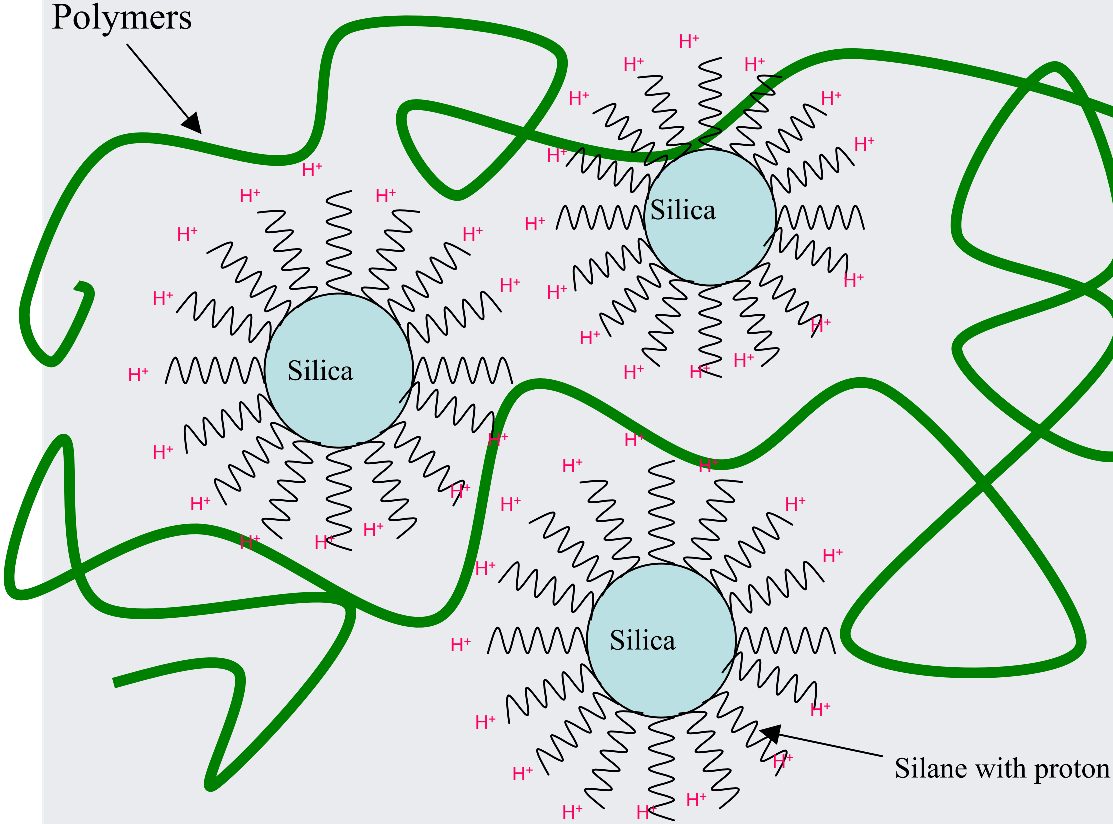
# The Building Blocks

- Polymer System---structural, functional base material
  - High proton density
  - Strong intrinsic proton acidity
  - Phase separation:  organizes acids, stabilizes structure

- Proton acceptor---water is the best but for low RH must augment to achieve transport out of local vicinity of acid group
  - Inorganic:  heteropolyacids
  - Organic:  molecules, oligomers, polymers

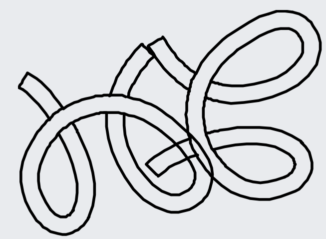
# Network of Acid-modified Silica Particles

Building Silica/Polymer composite membrane

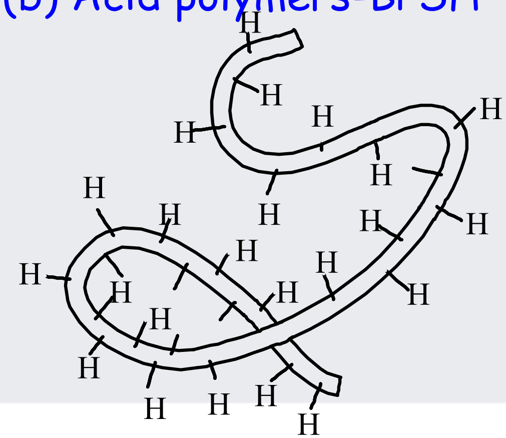



Form network in polymers
Polymer Types

(a) Proton free polymer-PVDF

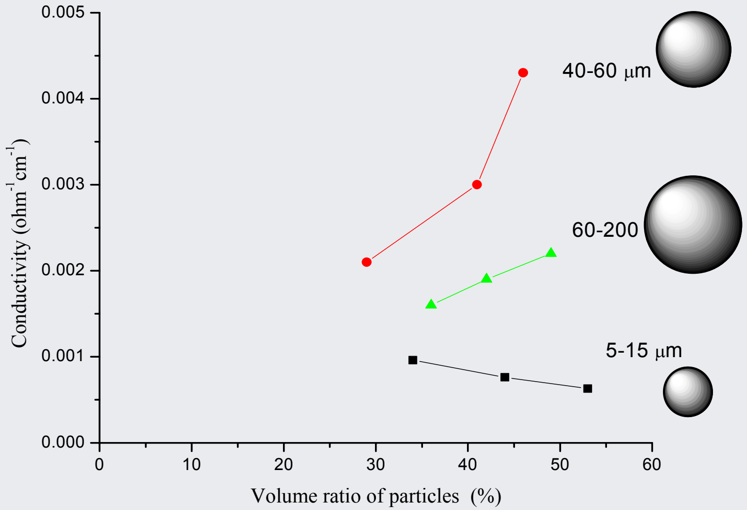


(b) Acid polymers-BPSH



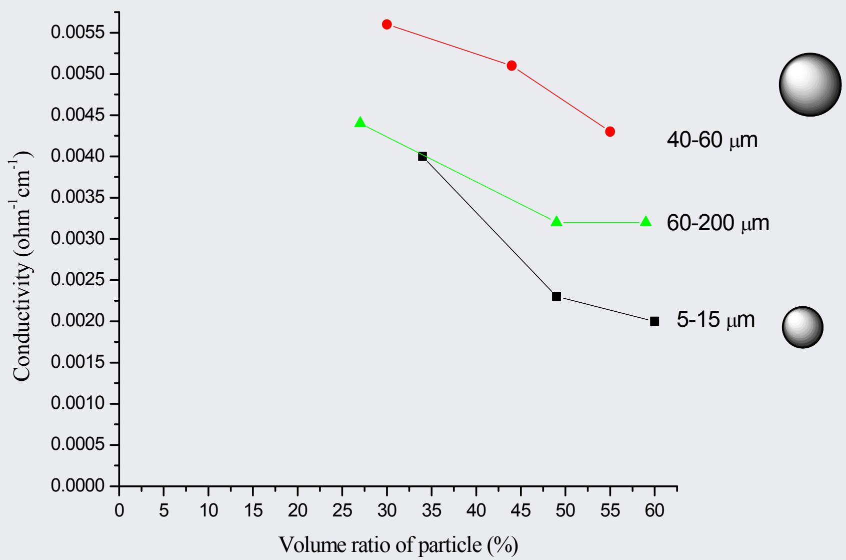
# Conductivity of silica/polymer composite membranes

Binder : PVDF (Insulator)




Binder : BPSH (with intrinsic protons) σ

σ = 8.5 × $10^{-2}$ $\Omega^{-1}cm^{-1}$



# Conduction in Networks: Ratio of conductivity / proton density

PVDF

BPSH

| Membrane | | Conductivity/[Proton] (g/Ω.cm.mol) |
|---|---|---|
| Nafion 117 | | 94.56 |
| BPSH 35 | | 70.83 |
| $SiO_2$/PVDF (34:66) | 5-15 μm | 30.97 |
| $SiO_2$/PVDF (44:56) | 5-15 μm | 25.33 |
| $SiO_2$/PVDF (53:47) | 5-15 μm | 27.39 |
| $SiO_2$/PVDF (29:71) | 40-60 μm | 6.77 |
| $SiO_2$/PVDF (41:59) | 40-60 μm | 9.09 |
| $SiO_2$/PVDF (46:54) | 40-60 μm | 11.94 |
| $SiO_2$/PVDF (36:64) | 60-200 μm | 10.67 |
| $SiO_2$/PVDF (42:58) | 60-200 μm | 10.00 |
| $SiO_2$/PVDF (49:51) | 60-200 μm | 18.33 |
| SiO2/BPSH (34:66) | 5-15 μm | 6.15 |
| SiO2/BPSH (49:51) | 5-15 μm | 4.11 |
| SiO2/BPSH (60:40) | 5-15 μm | 4.65 |
| SiO2/BPSH (30:70) | 40-60 μm | 5.09 |
| SiO2/BPSH (44:56) | 40-60 μm | 5.66 |
| SiO2/BPSH (55:45) | 40-60 μm | 5.37 |
| SiO2/BPSH (27:73) | 60-200 μm | 4.00 |
| SiO2/BPSH (49:51) | 60-200 μm | 4.57 |
| SiO2/BPSH (59:41) | 60-200 μm | 5.00 |

Data suggests that we are not getting full conductivity effect per proton; WHY NOT?

## Next steps

Sort out limiting factors

Smaller particles

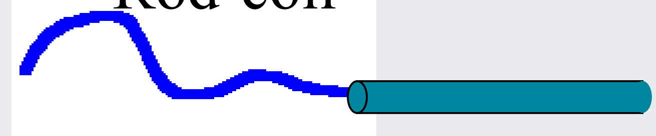
Increased acidity

Increased acid loading

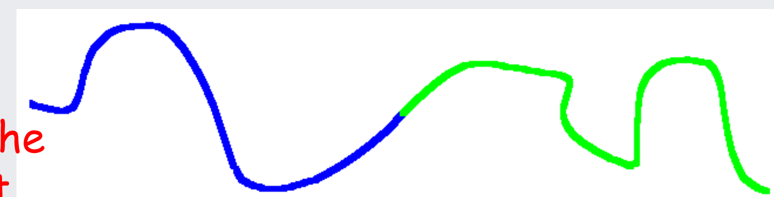
# Multiblock Copolymers

- Multiblock copolymers are fascinating materials exhibiting various phase behaviors.
- They can self-assemble into multiphase domain structures on a nm scale due to the repulsive energetic interaction between the incompatible blocks.
- This unique self-assembling property offers the potential to achieve 1-, 2-, or 3-D confinement of functional materials, such as conducting materials.

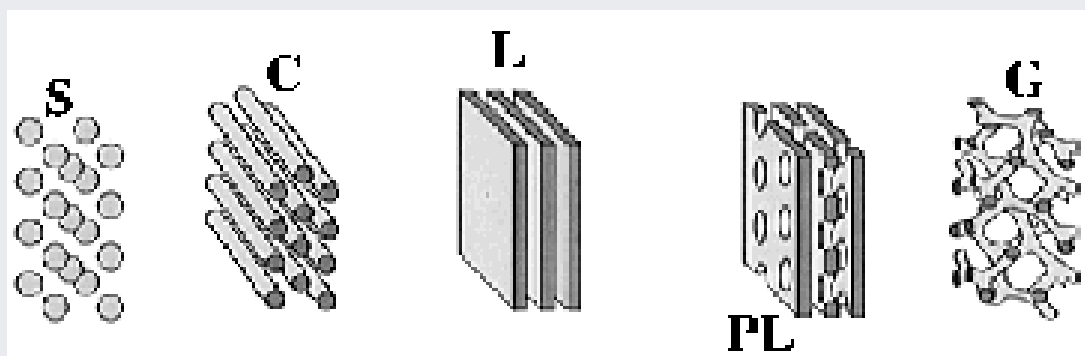
Rod-coil



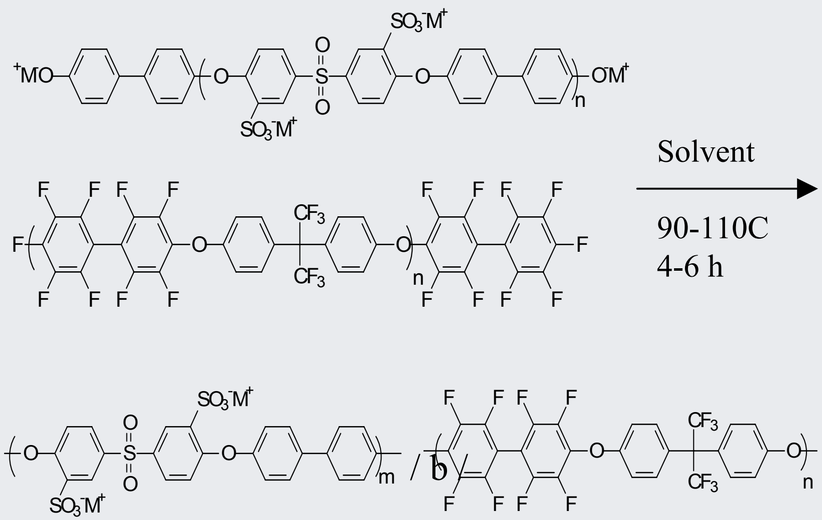
Coil-coil



*Schemes for different multiblock copolymer morphologies : spheres (S), columns (C), lamellae (L), perforated layers (PL), gyroid (G).*

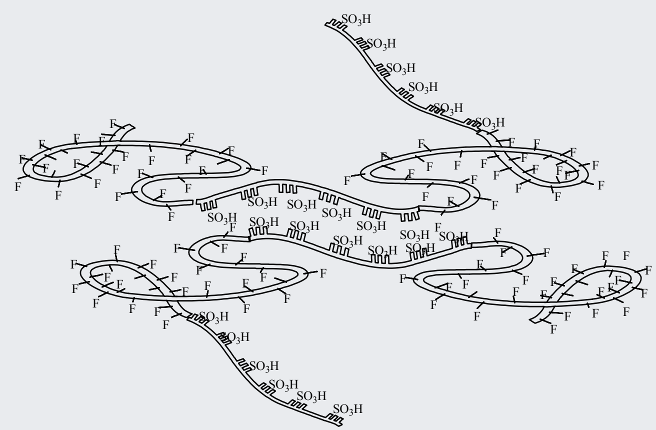


# Mixed Hydrophilic and Hydrophobic Block Copolymers as H+ Conductors




Several compositions prepared to date

Organized structures yield higher conductivity at low RH ($\sigma \sim 10^{-1}$ S/cm)



<u>Next Steps: Designed Materials!!</u>

- Huge array of possible polymers, acid groups, morphologies
- Introduce compatibilizers
- Tailor acid group orientation
- Introduce small molecule additives

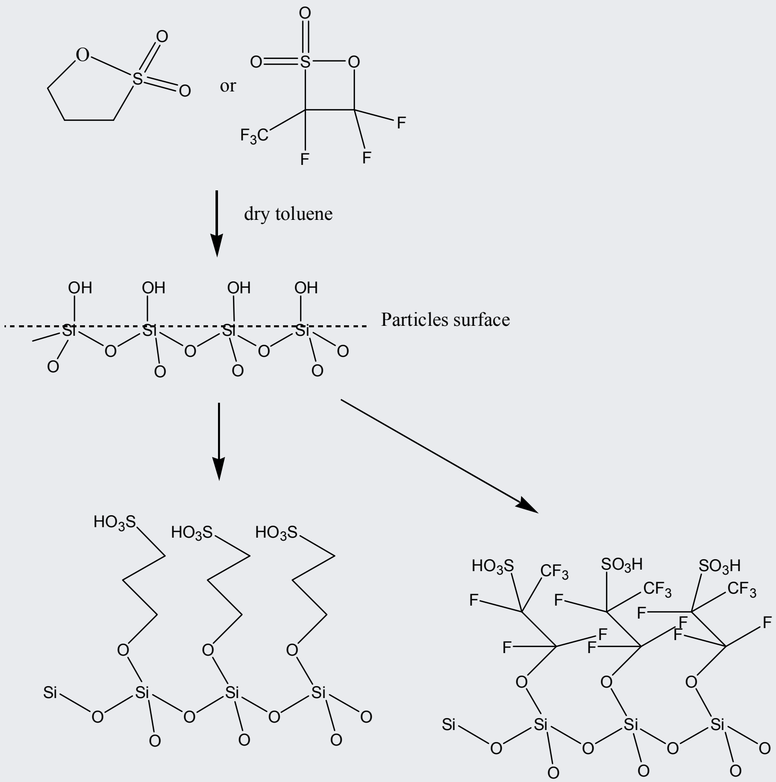
**NB: In this talk, <u>**Next Steps**</u> refers to future plans.

# Ongoing Work/Next Steps: Higher Acidity Functional Groups

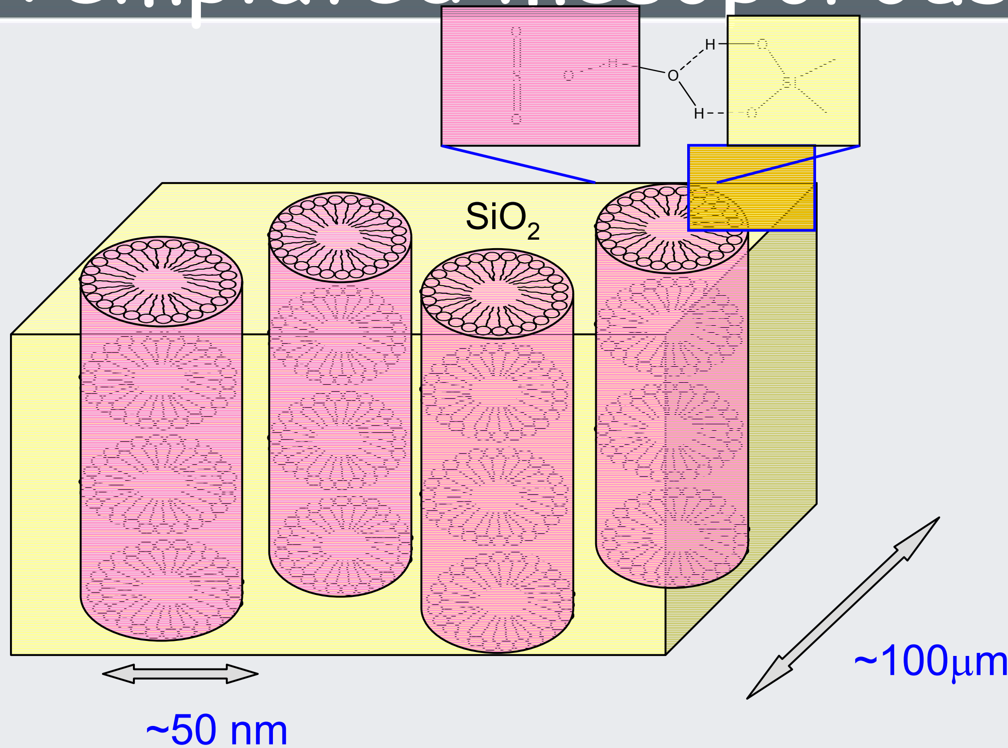
(1) Perfluorosultone chemistry--attached to many different starting materials.

(2) Stability of bis (sulfonimides) on aromatics

(3) Other groups structured to 'trap' water



# Ongoing Work/Next Steps: Templated mesoporous membranes




- Create interfacial structure to promote dissociation and transport of protons
- Fluorocarbon sulfonic acid surfactants--strong acids
- Makes maximum use of limited available water

Use Block Co-polymer and/or polymer solution processing approaches to make this structure without silica

Introduce additional layers (monolayers?) of conducting phases to tailor acid/inorganic interface

# Characterization Methods: Focusing on Critical Information

- NMR Methods explicitly designed to separate transport influences occurring at different length scales
    - 'Restricted Diffusion'
    - Comparison of Relaxation, Diffusion

- Spectroscopic Probes of water interaction with polymers, other components, each other

- Thermal Analysis to study strength of interaction between water and components and model compounds

# NMR Probes of Interactions and Transport over Various Length Scales

NMR Relaxation: Measure of Mobility at Nanometer scale

- Water in Aromatic Sulfonate dramatically slower motion than Nafion--tighter binding

NMR Diffusion: Micron-Scale Mobility; 'Restrictions' to Translation

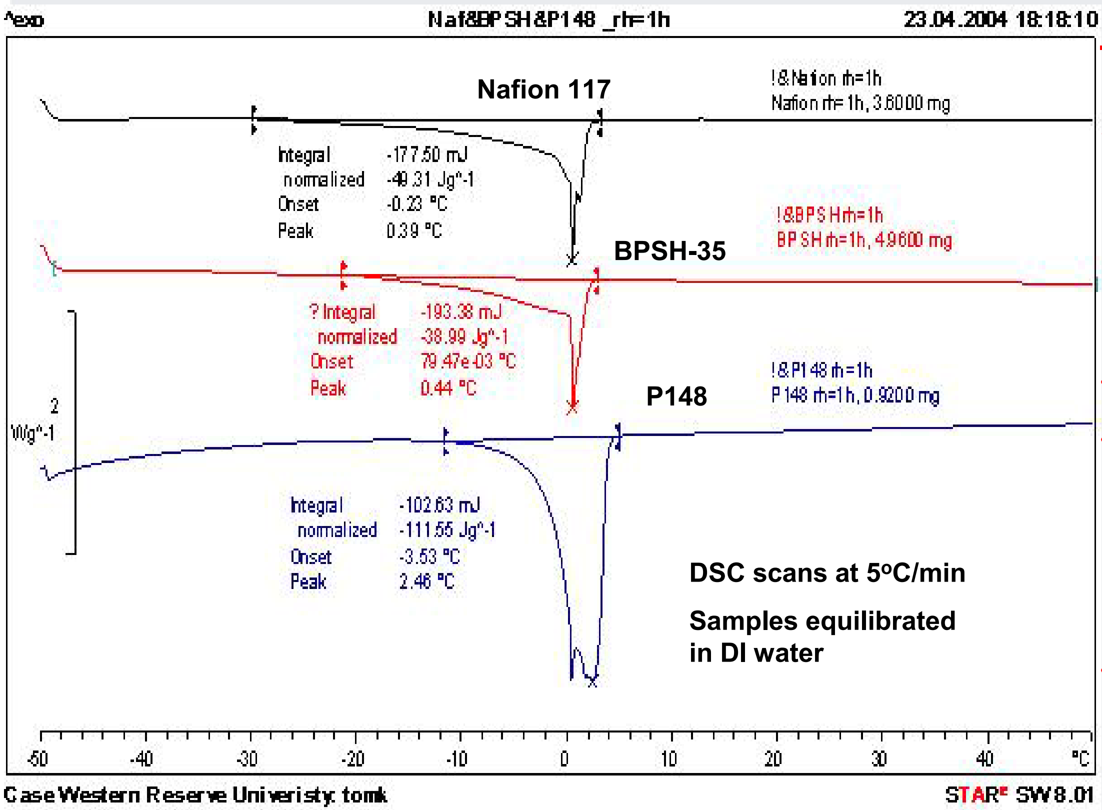
- BPSH sample shows effect of 'grain-boundary' at ~ 2um

NMR Relaxation-Diffusion Comparison

- Reveals the relative importance of local scale interactions vs long-range structure effects in controlling transport

- Results: Much slower transport in Ar-$SO_3H$ than in PFSAs

# Thermal Analysis: How Tightly is water bound?




For different polymer types:

Substantial differences in freezing fraction of water (well humidified)

All water is non-freezing for samples equilibrated below saturated water vapor

Only Nafion, P148 (multiblock) have freezable water for saturated vapor

Results of NMR, DSC experiments clearly illustrate:

- Weaker acid groups hold water more tenaciously, lowering overall transport rates
- Strong influence of controlled morphology for multiblocks; easier to hydrate

# Progress This Year and Status: Membrane Development

Fully implemented rational development strategy

- Required synthetic and characterization tools in place

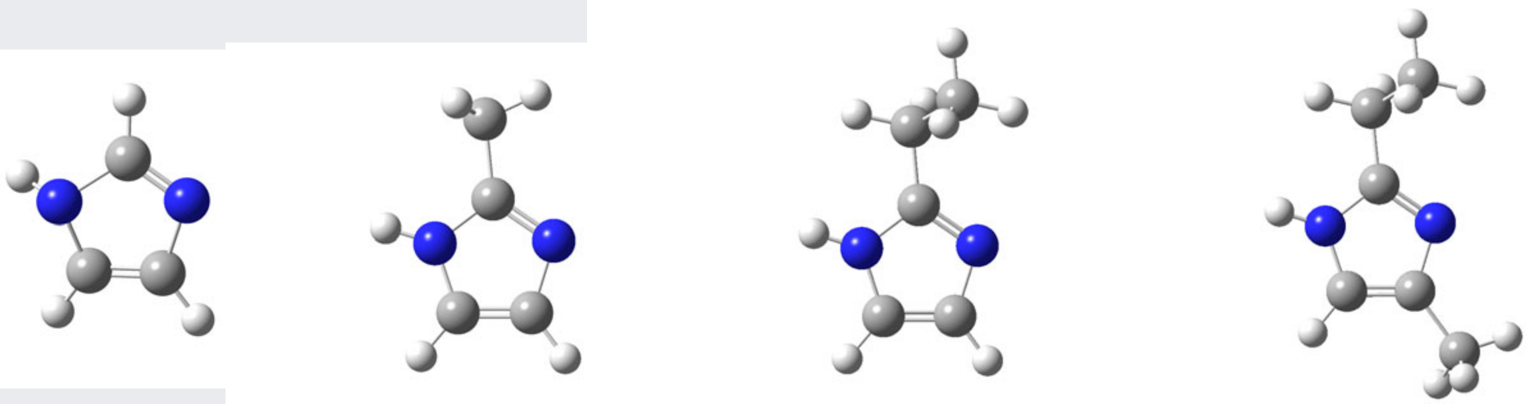
Synthesis or Preparation of multiple new material sets

- Focused on development of 'controlled nano-architectures'
- ~15 new materials synthesized (not all reported on here)

Themes

- Importance of phase segregation
- Key factors in improving percolating network structures
- Stability of new material classes

# Computational Studies of Substituent Effects on Imidazole Proton Affinity



| Imidazole | 2-methylimidazole | 2-ethylimidazole | 2,4-ethylmethylimidazole |
|---|---|---|---|
| mp=89-91°C | mp=142-143°C | mp=85-86°C | mp=47-54°C |
| 224.2kcal/mol | 228.9 | 230.8 | 233.9 |

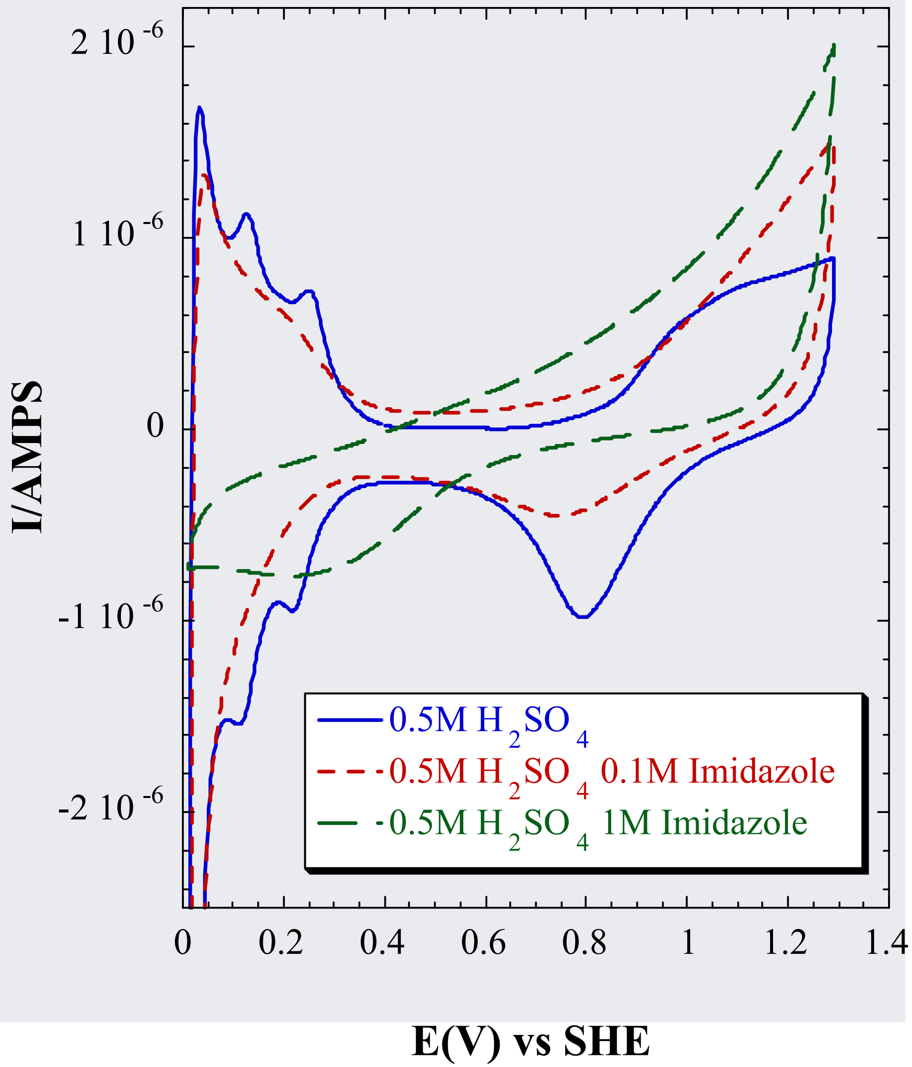
Increasing basicity, increasing proton affinity

# Effect of Imidazole on Pt voltammetry in Acid

Imidazole added to 0.5M $H_2SO_4$

At low imidazole contents, a slight loss in Pt activity (imidazole all protonated)

High imidazole concentrations affect activity significantly (imidazole free base present)

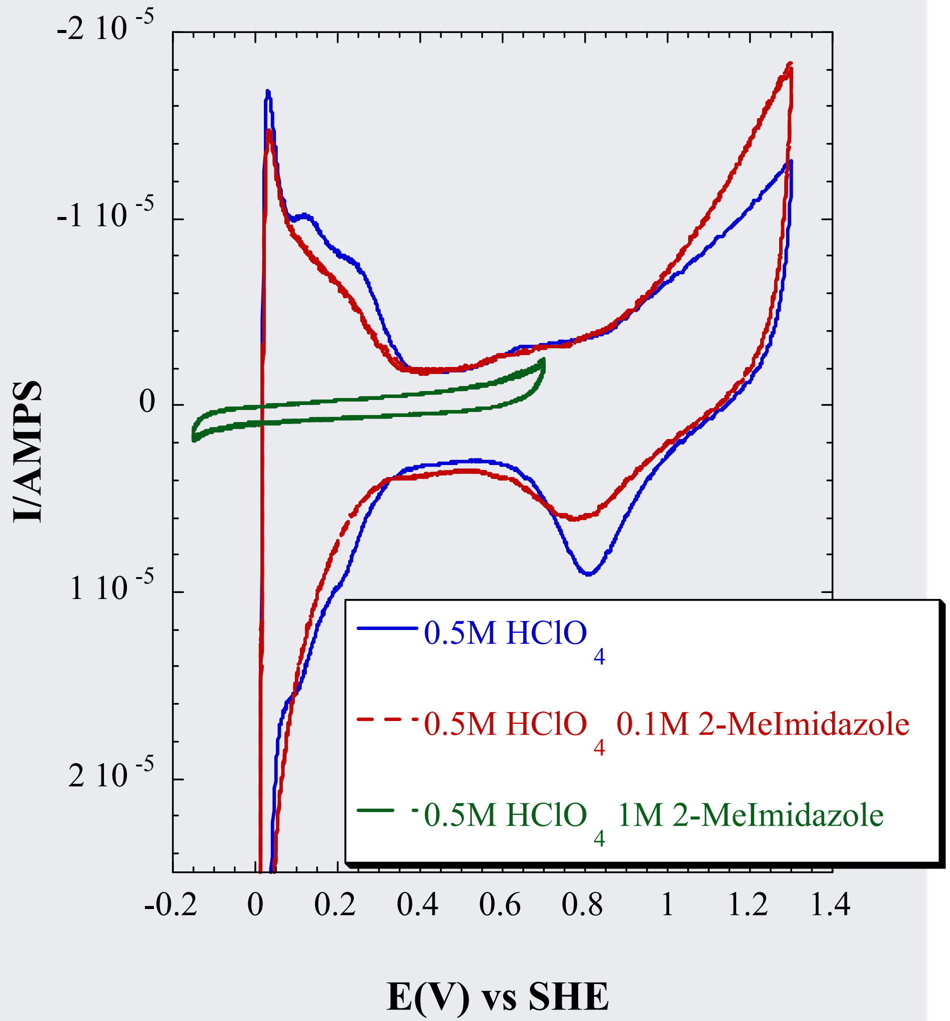


# Effect of 2-Me-Imidazole on Pt voltammetry in Acid

2-methyl Imidazole added to 0.5M $HClO_4$

At low 2MeIm contents, less loss in Pt activity cf Imidazole

Substantial loss in activity at high concentrations



# Progress This Year: High Temperature Proton Conductors

Limited activity

- Secondary focus

Studying Properties of Alternative Proton Acceptors

- Tuning electronic structure of imidazole
- Emphasized IP as determining factor

Imidazole in Electrodes

- Electrochemical studies show that impact of imidazole in acid less than that in base
- Protonation induces ring puckering, interferes with Im adsorption on Pt

# Electrode Studies: Approach and Objective

Study the ORR at High Temperature, low RH conditions in an operating Fuel Cell

- Aid in identifying the critical material parameters by studying their impact on ORR
- Will provide a point of comparison engineering of new electrode materials for use in High Temperature Electrodes

# Factors to be decoupled

Resistive and gas phase mass transport losses at high temperature and low RH

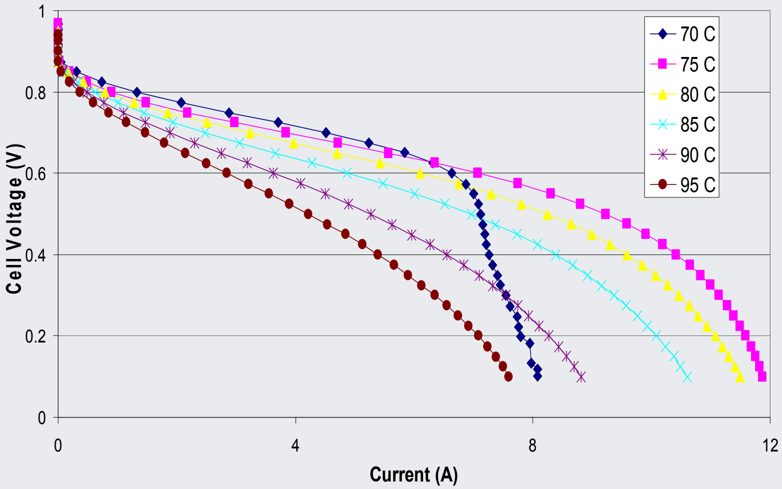
Once the resistive and mass transport corrections are done, the kinetics is affected by:

- Available/Accessible Area
- Proton conductivity
- Oxygen Permeability and Gas Phase mass transport
- ORR Kinetics devoid of the above limitations (involves the electron and proton transfer step)

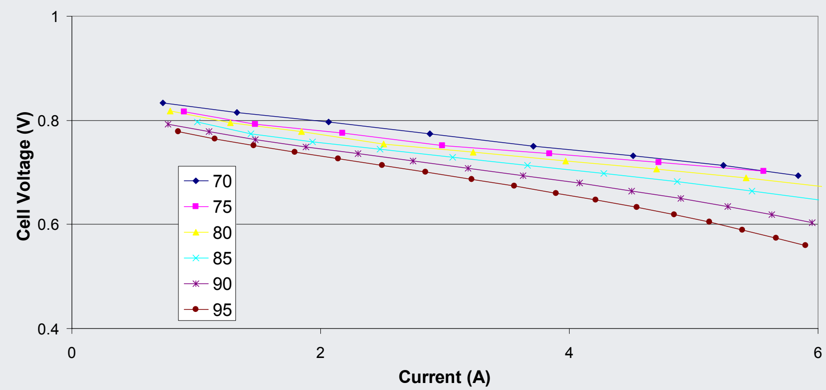
# Experimental Observations at Different Sub-saturation Conditions

Impact of FC Performance at low RH from 70 to 95 C at ambient pressure

Polarization Curves

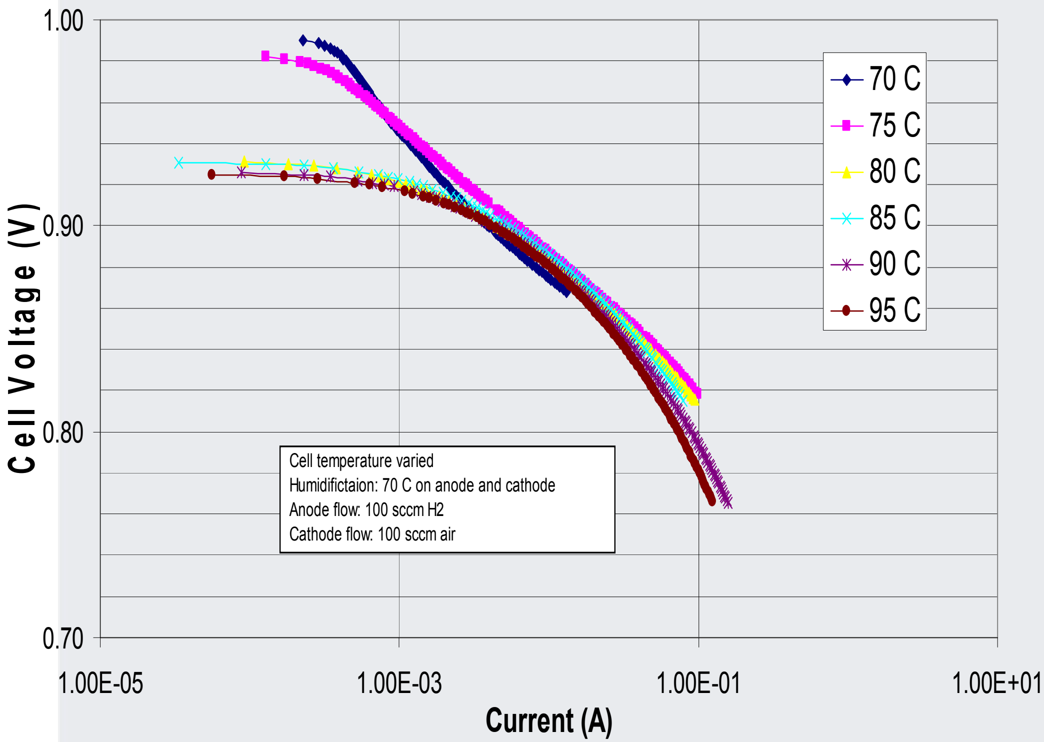



Kinetic region




- Marked decline in electrode kinetics with increasing sub-saturation
- Drop in OCV with low RH condition

# Electrode Kinetics: Tafel Plots




Local mass transport effect is observed. Need to decouple for kinetic analysis.

Change in OCV observed with sub saturation. Possibly due to change in hydrogen/oxygen permeation through the membrane

# Electrodes: Next steps

- Hydrogen permeation test to understand the drop in OCV with low RH
- Operation at 120 C with 25% RH – Follow the performance with continuous diagnostics
- Decoupling of RH effect and partial pressure effect – carryout test with sufficient drying gradient at low operating temperature
- Study the performance as a function of the ionomer fraction in the catalyst layer
- Introduce new materials into catalyst layer to enhance performance

# Progress This Year: Electrode and MEA Development

Electrodes: diagnostics and preliminary

- Diagnostics
  - Working with Pine Instruments to develop high T RRDE
- New Structures
  - Introduced modified carbons to improve CL conductivity and water retention
  - Preparing new carbon supports with different 'topology'

MEA Development

- Coating New Polymers
- Investigation of Compatibilizing Interlayers

# The DOE High Temperature Membrane Program

## Program Focus/Evolution

- This project primarily focuses on new concepts to deliver functionality with limited focus on complete 'development'
- Seed funding (2 years, 100 k$) with continuous turn-over; **Goal:** get beyond the 'usual suspects' to engage best and brightest from polymer science community;
- FY04: 6 new projects funded; all new faces from polymer or materials community; seek to educate this community on needs and transport aspects of fuel cell membranes

## Available Central Facilities/Capabilities at Case

- Electrolyte Characterization at High T
- MEA Preparation and Fuel Cell Testing
- Modest Scale-up
- Polymer Characterization

# High Temperature Membrane Working Group

- Roadmap, Technical Targets under continual revision

- HTMWG bi-annual meetings
  - Going International: meeting held in Paris; EU coordination expected
    - Researcher exchange program proposed
  - Discussion on Characterization Methods
  - Next meeting: Hawaii

- Website:

# Future Work

1. Continue development of tailored nano-materials
   a) Develop block co-polymer/inorganic composites
   b) Network structures
   c) New small molecule or oligomeric additives
   d) High acidity functionality
   e) Develop realistic stability test-->aromatic imides
2. More emphasis on MEAs, electrodes
   a) Coating methods
   b) Use modified C's to improve layer properties
   c) GDLs to control water
3. High Temperature conductors
   a) Begin to test alternative conductors in membranes
   b) Hybridized materials?