New Fluoroionomer Electrolytes with High Conductivity and Low SO_2 Crossover

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Hybrid Sulfur Cycle

- **Thermochemical Water splitting Cycles (High Efficiency)**

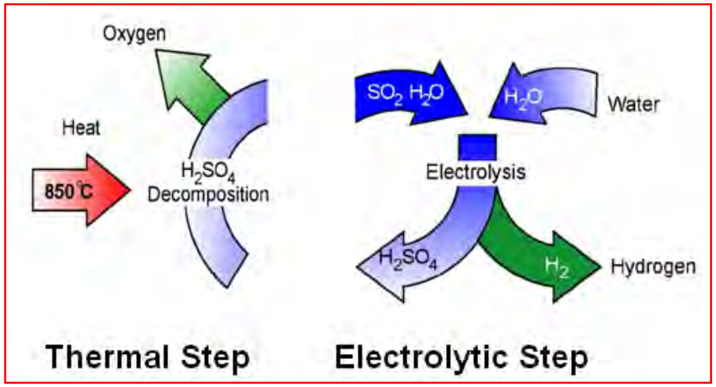
⇩

Surfur-based Cycles

⇩

Hybrid Sulfur(Hys) Process

Figure. Hybrid Sulfur(Hys) Process



1. Thermal Step: 850 ⁰C

$H_2SO_4 \rightarrow SO_2 + 2H_2O$

2. Electrolytic Step: 80-120 ⁰C

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ [at the anode]
$2H^+ + 2e^- \rightarrow H_2$ [at the cathode]
$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ [Overall reaction]

- Uses a **Sulfur Dioxide polarized Electrolyzer(SDE)** to produce hydrogen

- Key attribute of SDE: High energy efficiengy and long operating lifetime

MEA design concept for SDE

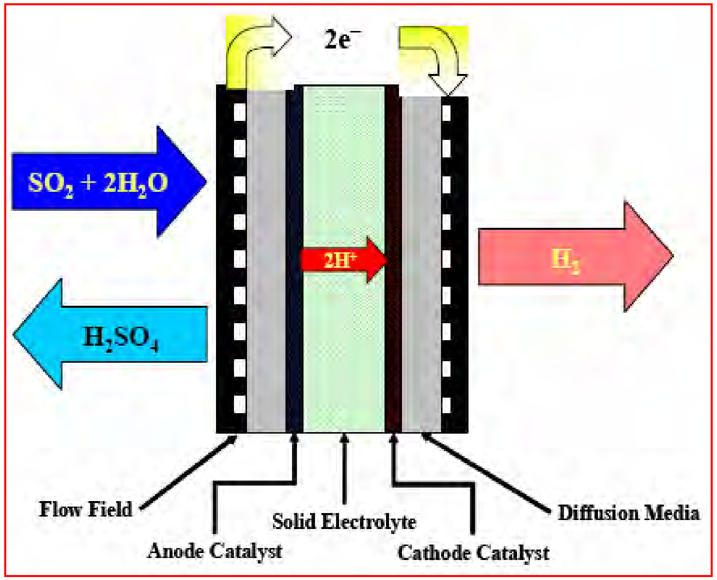
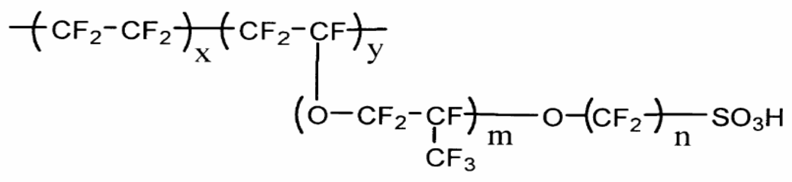


Figure. Schematic Diagram of PEM Electrolyzer

Key PEM Electrolyzer Attributes

- ✓ High ionic conductivity
- ✓ Smaller SO_2 crossover
- ✓ Excellent Chemical Stability

- **Nafion family of perfluorinated sulfonic acid membrane**



Nafion®117 m≧1, n=2, x=5-13.5, y=1000

-High ionic Conductivity

-High Chemical Stability in Strong Acid

-Fairly high SO_2 transport across the membrane to the cathode

- Cost

- **Sulfonated Poly-Etherketones(SPEKs) from Fumatech**

- Good conductivity in water

- Quickly degraded in high sulfuric acid concentration

Objectives

❖ **The overall objective of this project is to produce a new generation of stable ion conductive proton exchange membranes that can facilitate rapid proton transport while suppressing the transport of sulfur dioxide.**

- **Develop new proton-conducting fluoropolymer electrolyte membranes**

  - Sulfonated perfluorocyclobutyl aromatic ether polymer (S-PFCBs) electrolytes.

  - Composite organic/Inorganic proton-conducting membranes of PFSI and S-PFCB electrolytes.

  - Covalent perfulorocyclobuthyl(PFCB)-ZrO_2 hybrid electrolytes type I and II.

✓High ionic conductivity
✓ Smaller SO_2 crossover
✓ Excellent Chemical Stability in SO_2 saturated sulfuric acid solution
✓Lower projected cost than Nafion
✓Synthetic Versatility

- **Characterization of the Membranes**

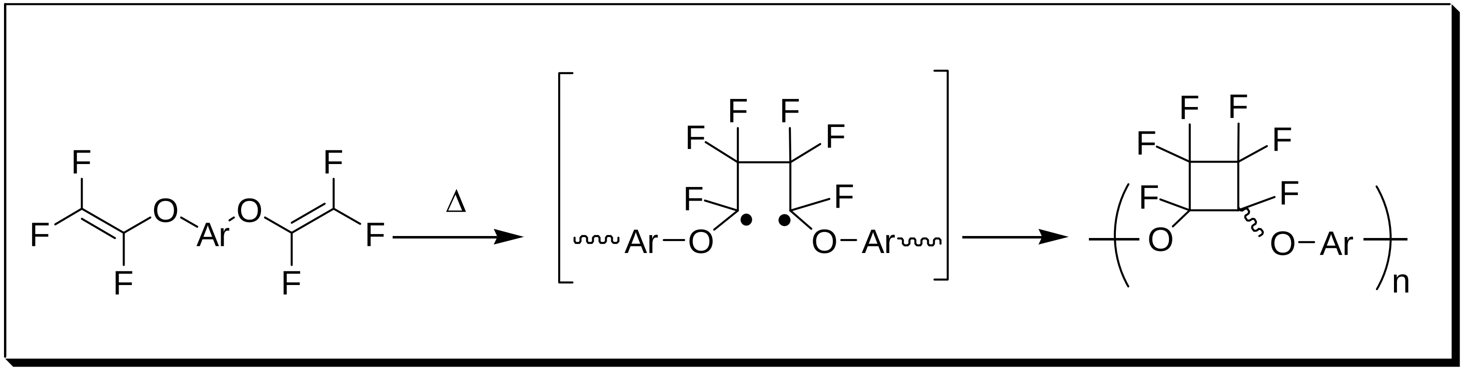
  - Sulfur dioxide transport characteristics at different acid concentration and temperature (SRNL)

  - Evaluating experimental vs. commercially available membranes for ionic conductivity

Ionomer Design Parameters

	Design Parameter	Possible Hypothesis
Ionomer	Ionomer Molecular Weight	Increased entanglement facilitates high volume swell (performance), increases membrane integrity (mechanical/chemical durability)
	Ion Exchange Capacity	Increases water affinity and number of protogenic groups (performance)
	Hydrophobic Domain – block copolymers, blends, etc…	Increases local IEC, reducing spacing between protogenic groups (dry performance), provides pseudo cross-links (mechanical)
Membrane	PEM Thickness	Improves PEM water content under comparable operating conditions, reduces ohmic resistance
	Expanded Supports	Provides Z-plane swelling, limiting XY dimensional change reducing membrane stress
	PEM Architecture	Hygroscopic additives, anhydrous protogenic additives, bi-layers, multi-layers, anti-oxidants, …

Perfluorocyclobutane (PFCB) Aryl Ether Polymers



J. Polym. Sci. Part A: Polym. Chem. **2007**, *45*, 5705.
Polymer Inter. **2007**, *56*, 1142

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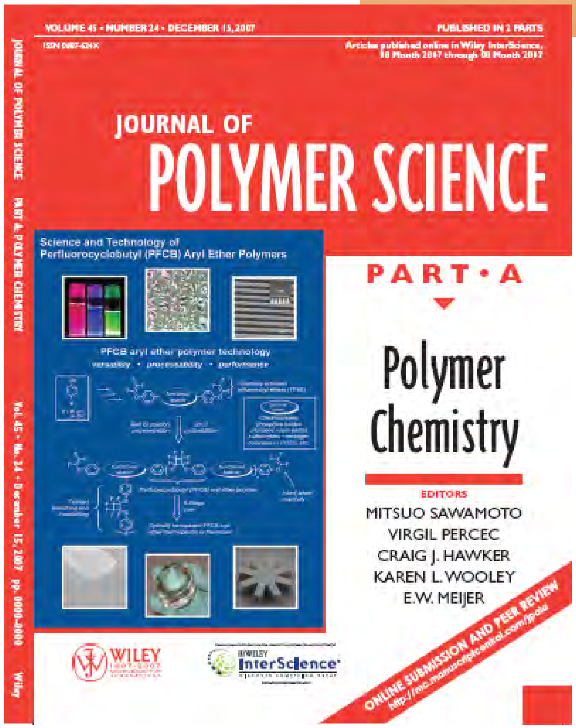
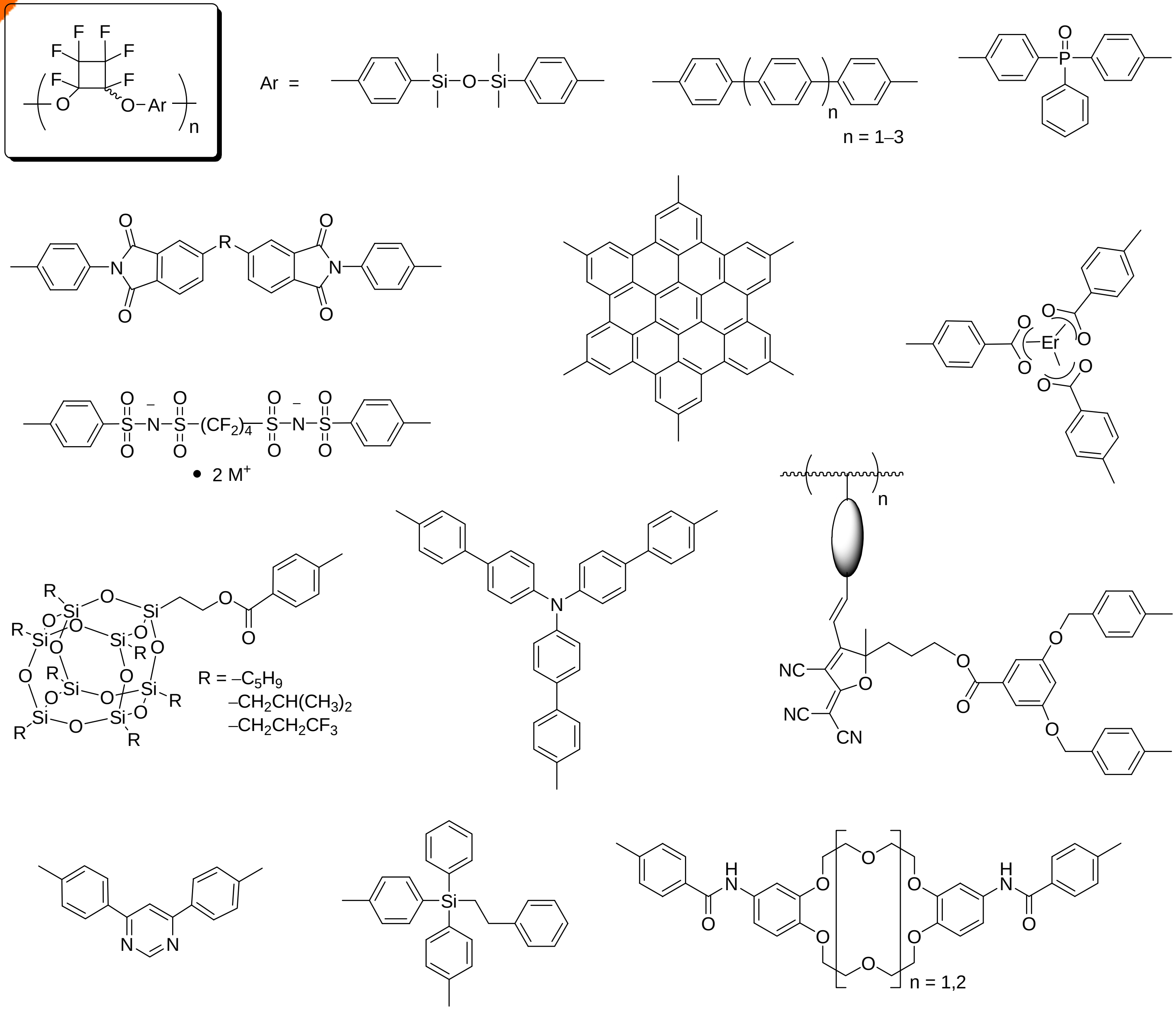
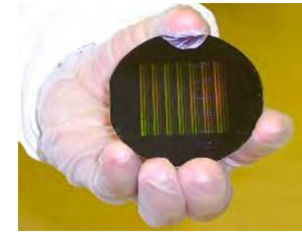
- Recently commercialized at Clemson
- Monomers prepared from phenolics (22 L scale)
- Thermal initiated step-growth cyclopolymerization
- Catalyst & condensate free “Click” polymerization
- Stereorandom PFCB polymer and others
- Typically amorphous (6F homopolymer cryst.)
- High thermal stability decomposition 450–500 °C
- Glass transition temperatures from 150–300 °C
- Low optical loss at telecom wavelengths
- Tunable optical & thermal properties

Property	Range
Mechanical	
Glass transition (DSC or DMA)	110–350 °C
Thermal decomposition (TGA in N_2 & air)	> 450 °C
Tensile strength	50.3–66.0 MPa
Tensile modulus	1770–2270 MPa
Flexural strength	74.0–92.4 MPa
Flexural modulus	1779–2320 MPa
Percent elongation (break)	4.1–12.5 %
Interfacial shear	123–163 MPa
Hardness	175–653 MPa
Processing	
Cure temperature/time (°C)	150–220/0.1–3.0 h
Molecular weight (GPC)	1,200–30,000 M_w
Solution viscosity (RMS)	0.02–100 Pa·s
Crystallinity (WAXD)	0–35 %
Solid content	50–90 %
Patterning technique	μ-molding, RIE, O_2 plasma
Spin coat thickness (μm, single)	1–30
Percent water absorption (wt %) (24 h)	0.021
Optical	
Loss (1550 nm)	< 0.25 dB/cm
Birefringence	< 0.003
Refractive index (1550 nm)	1.442–1.505
dn/dt (1550 nm)	–0.7 to –1.5 ($\times 10^{-4}$)
Insulation	
Dielectric constant (10 kHz)	2.4–2.45
Dissipation factor (10 kHz)	0.0003–0.0004





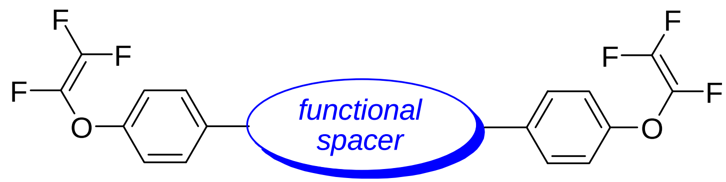
Ar =
n = 1–3
• 2 M+
R = –C5H9
–CH2CH(CH3)2
–CH2CH2CF3
n = 1,2



PFCB Aryl Ether Polymer Technology

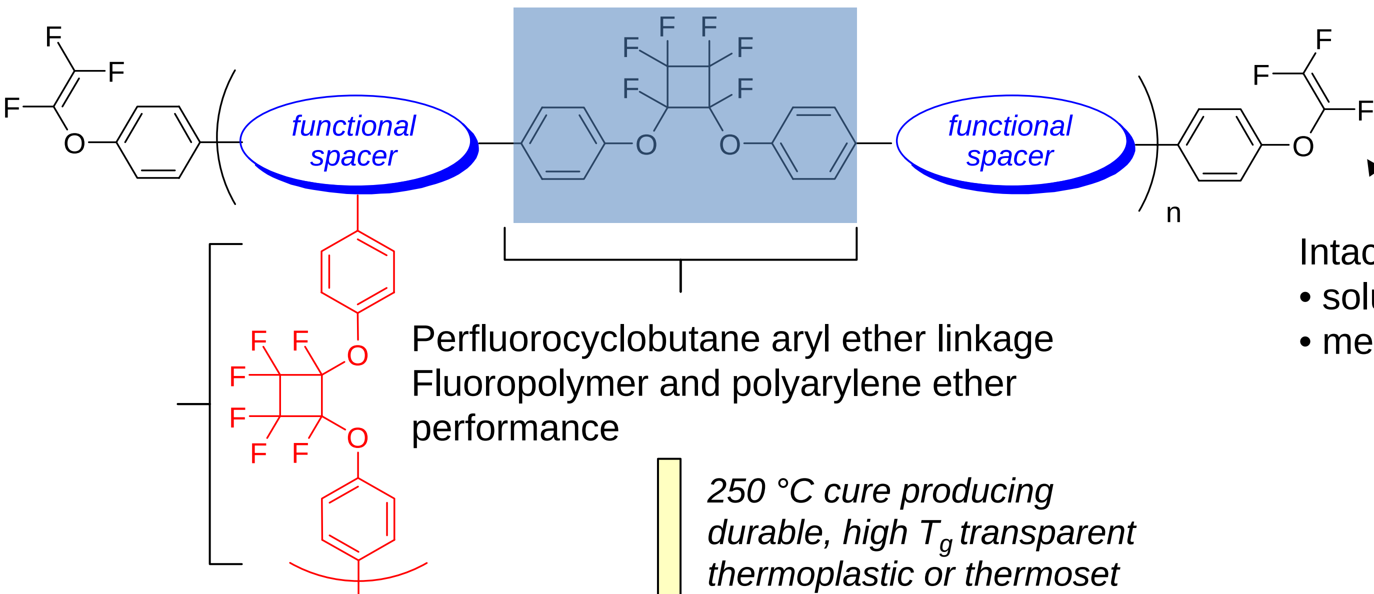
versatility • processability • performance

thermal activated trifluorovinyl ethers →



melt or solution polymerization

- *chromophores (NLO/LED)*
- *phosphine oxides • imides*
- *siloxanes • rare earths*
- *sulfoacids • thiophenes*
- *coronenes • POSS, etc.*



Intact latent reactivity for
- solution or
- melt post-process cure

Perfluorocyclobutane aryl ether linkage
Fluoropolymer and polyarylene ether performance

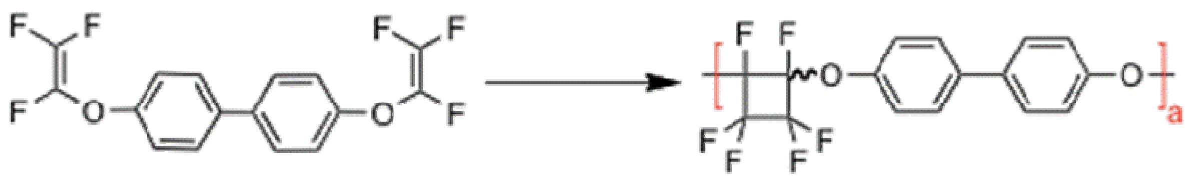
250 °C cure producing durable, high T_g transparent thermoplastic or thermoset (T_g 120-300 C, T_d 400 °C)

***J. Polym. Sci. Part A: Polym. Chem.* 2007, *45*, 5705-5721**

Synthesis of PFCB Ionomers

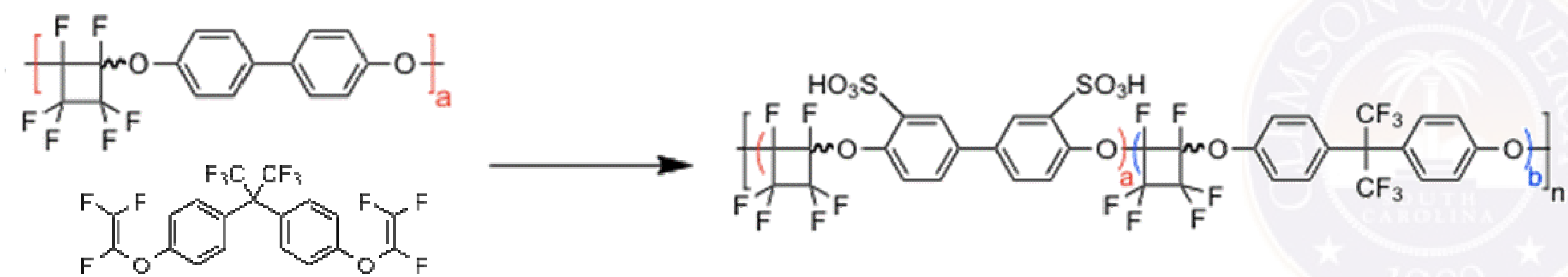
- **Homopolymers of Biphenyl Vinyl Ether (BPVE):**

Synthesis involved the random sulfonation of BPVE homopolymer with a max IEC of ~2-2.3 meq/g resulting in water soluble ionomers.

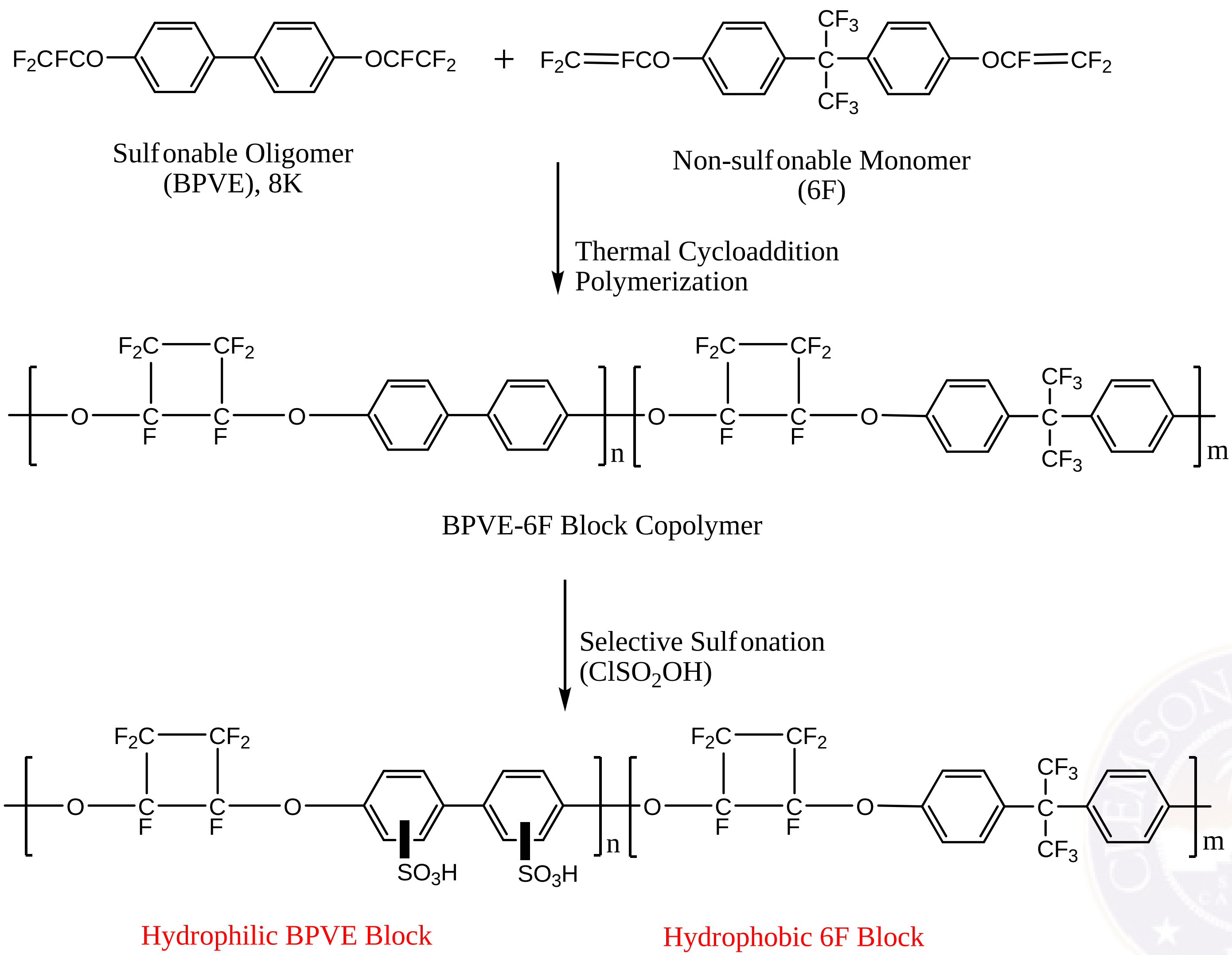


- **Segmented/block co-polymers of oligo-BPVE (Mn=8k, Mw=16k) and hexafluoro biphenyl vinyl ether (6F) monomer:**

Synthesis copolymerized oligomeric BPVE with 6F monomer resulting in segmented block copo lymers. Selective sulfonation of BPFVE segments achieved similar IEC's of ~1.8-2.3 meq/g wit hout dissolving in boiling water.



Synthesis of Sulfonated Block Copolymer



Sulfonated PFCB Membranes

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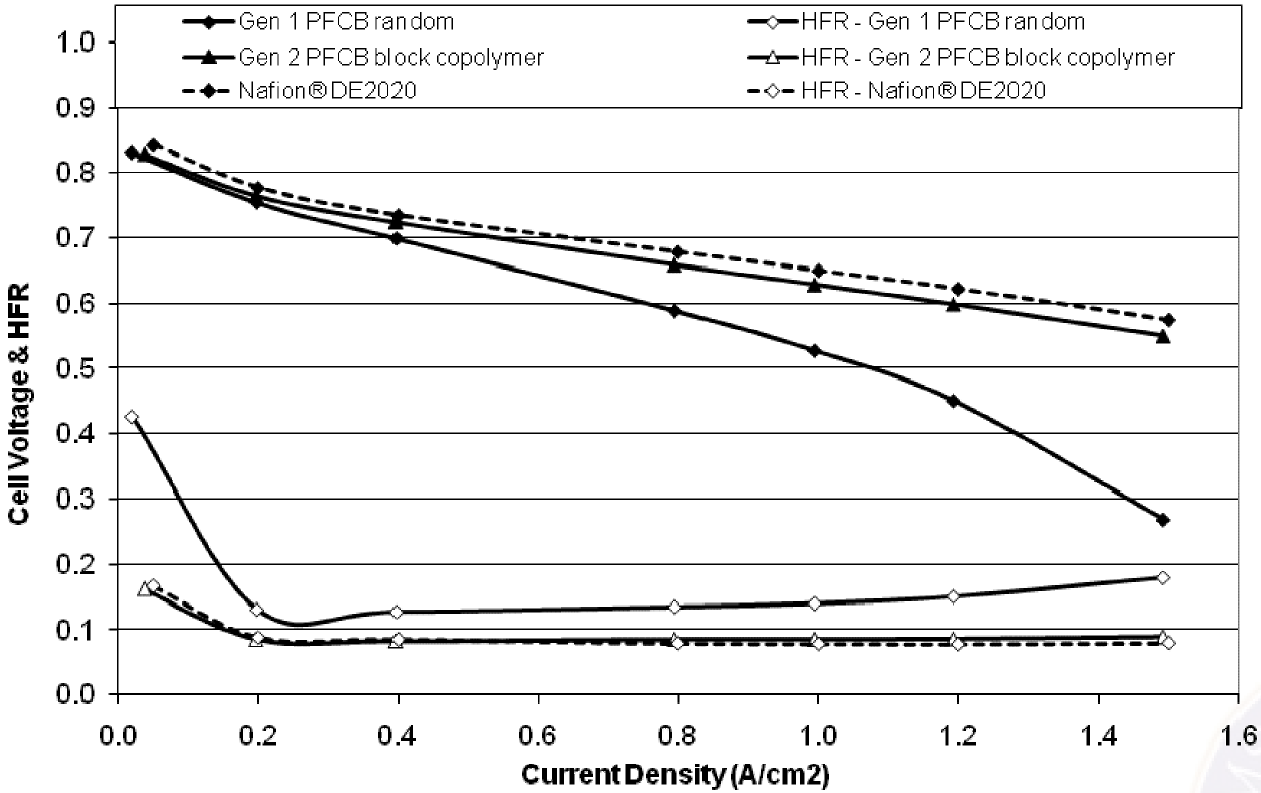
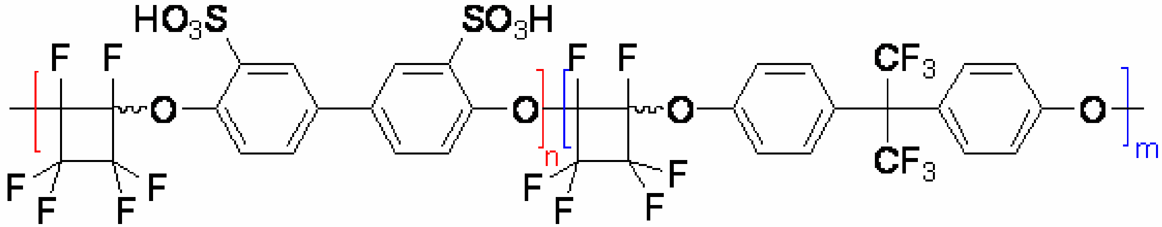
FC Performance of PFCB Ionomers

- 50 cm^2 single cell, serpentine flow field
- 80°C, 3/3 A/C stoich, 175kPa, 0.4/0.4 mg_{Pt}/cm^2
- PEM 20 μm

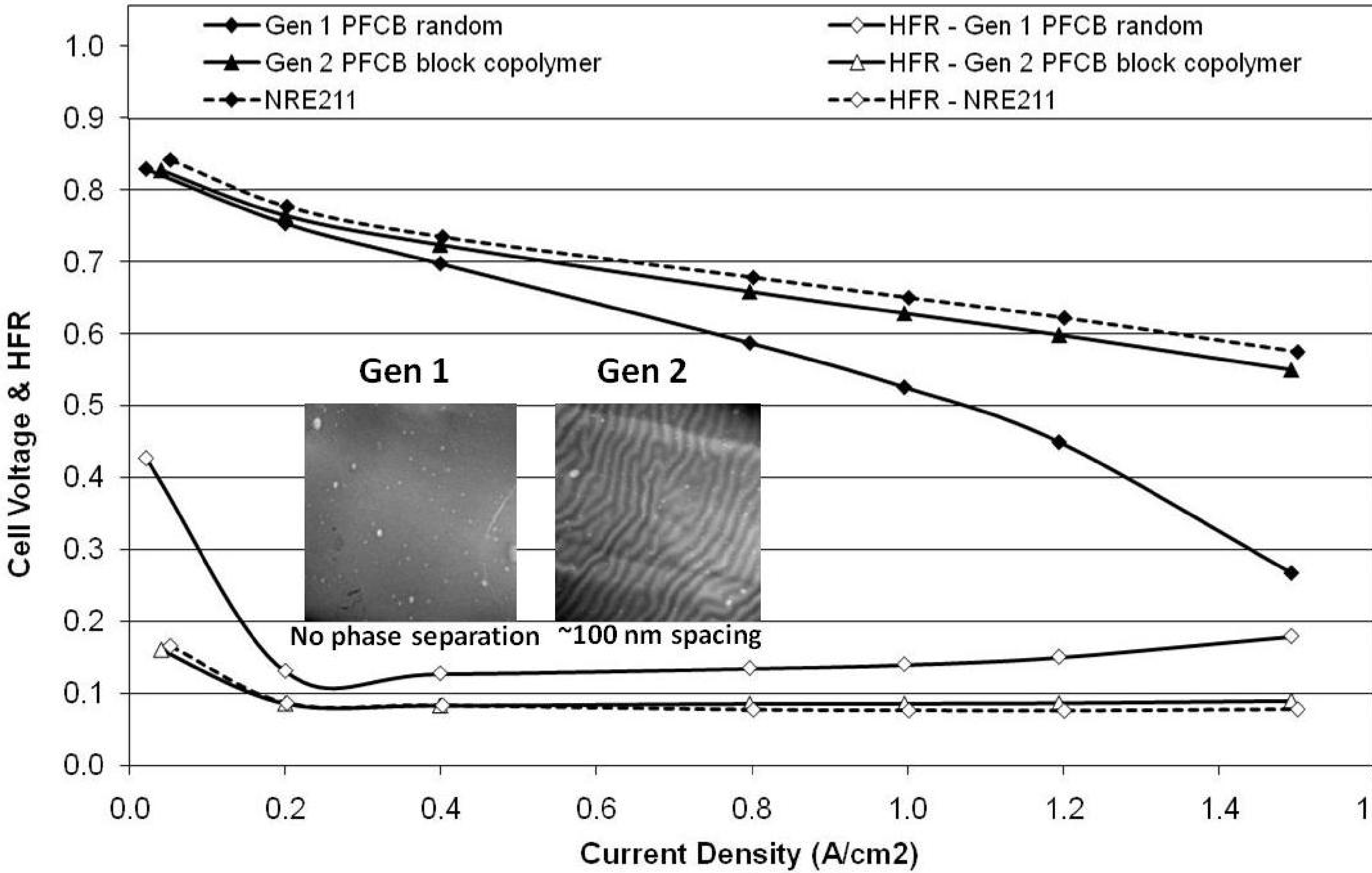


- Improvement over Gen 1 FC performance were observed upon preparation of segregated domains in Gen 2 segmented PFCB copolymers. FC performance approaching Nafion® DE2020.

Asilomar 2009, Pacific Grove, CA

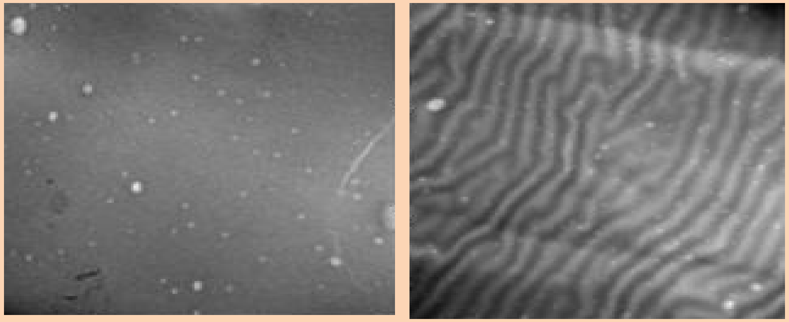


FC performance Gen 1&2 PFCB PEM (85 % RHout, 50 cm^2, 3/3 stoich, 75 kPa, 80°C)



Preparation and Ion Exchange Capacity of Membranes

Sulfonated-PFCB
Block Copolymer membrane



No phase separation
BPVE Homopolymer

~100 nm spacing
S-PFCB Block Copolymer

	Sample Name	Mn (kg/mol)	Thickness (µm)	IEC (meq/g)
1	BPVE Homopolymer	80	18	1.7
2	BPVE-6F (1:1) Block Copolymer	30	16	0.8
3	BPVE-6F (2:1) Block Copolymer	70	19	2

*Ion Exchange Capacity (Degree of Sulfonation): measured by titration

$$\mathbf{IEC(mmol/g)} = \Delta V_{NaOH} C_{NaOH} / W_S$$

ΔV_{NaOH} : consumed volume of NaOH solution
C_{NaOH} : concentration of NaOH
W_S : weight of dry membrane

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Hydrophilic Volume IEC

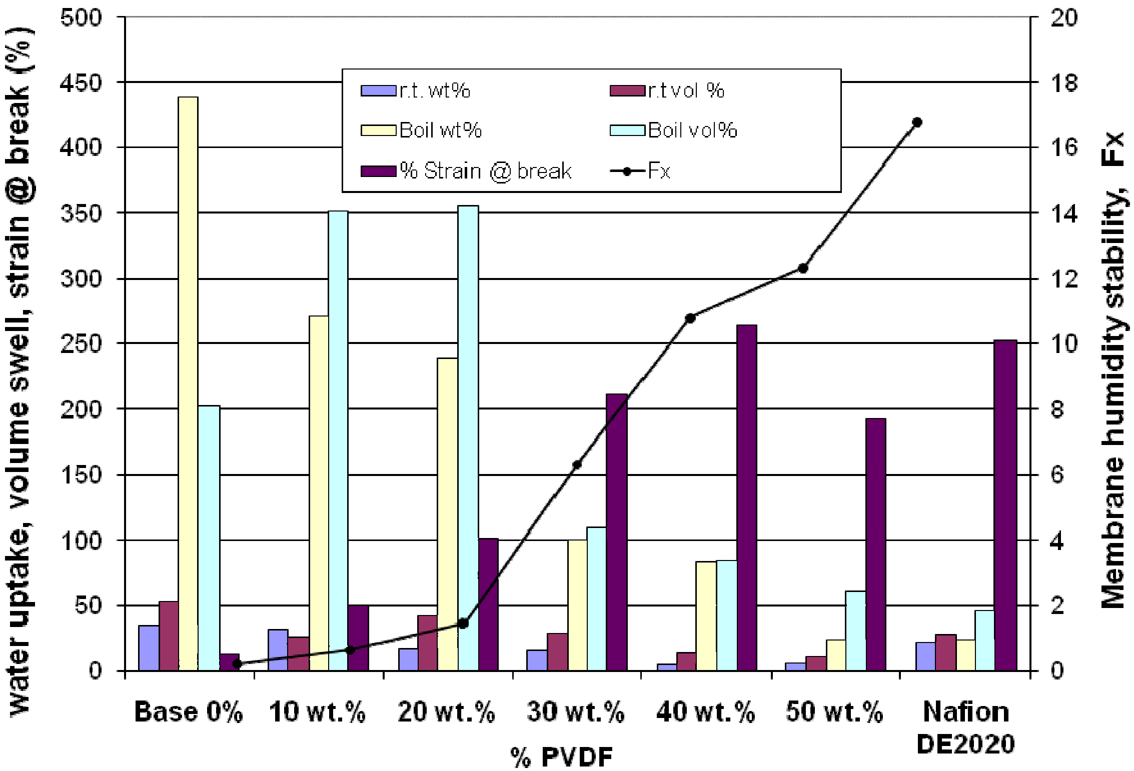
Proton Exchange Membrane	Wt. IEC (meq/g)	Density (g cm^{-3})	Vol. IEC (meq cm^{-3})	100°C Vol. Swell (%)	Vol_{H2O} IEC (meq cm^{-3}_{H2O})
Nafion® NRE111[a]	0.92	1.97	1.81	50	1.83
Cast Nafion® 1000 [b]	1.0	1.97	1.97	102	1.96
Sulfonated PEEK[b]	1.46	1.3	1.90	1000	0.95
Sulfonated polyphenylene [b] (Parmax 1200)	1.6 – 1.7	1.5	2.4 – 2.5	120 – 300	0.8 – 2.0
Gen 3 sulfonated PFCB/PVDF blends [b]	1.0 – 2.0	1.7	1.7 – 3.4	60 – 200	2.0 – 3.4

[a] values taken from NRE111 product data sheet published on DuPont's website

[b] values acquired from membranes cast from commercial materials or prepared in our lab

- Comparison of hydrophilic volume IEC identifies that PFCB based membranes can achieve increased membrane proton concentration prior to becoming water soluble
  as compared to conventional aryl-sulfonated ionomers.

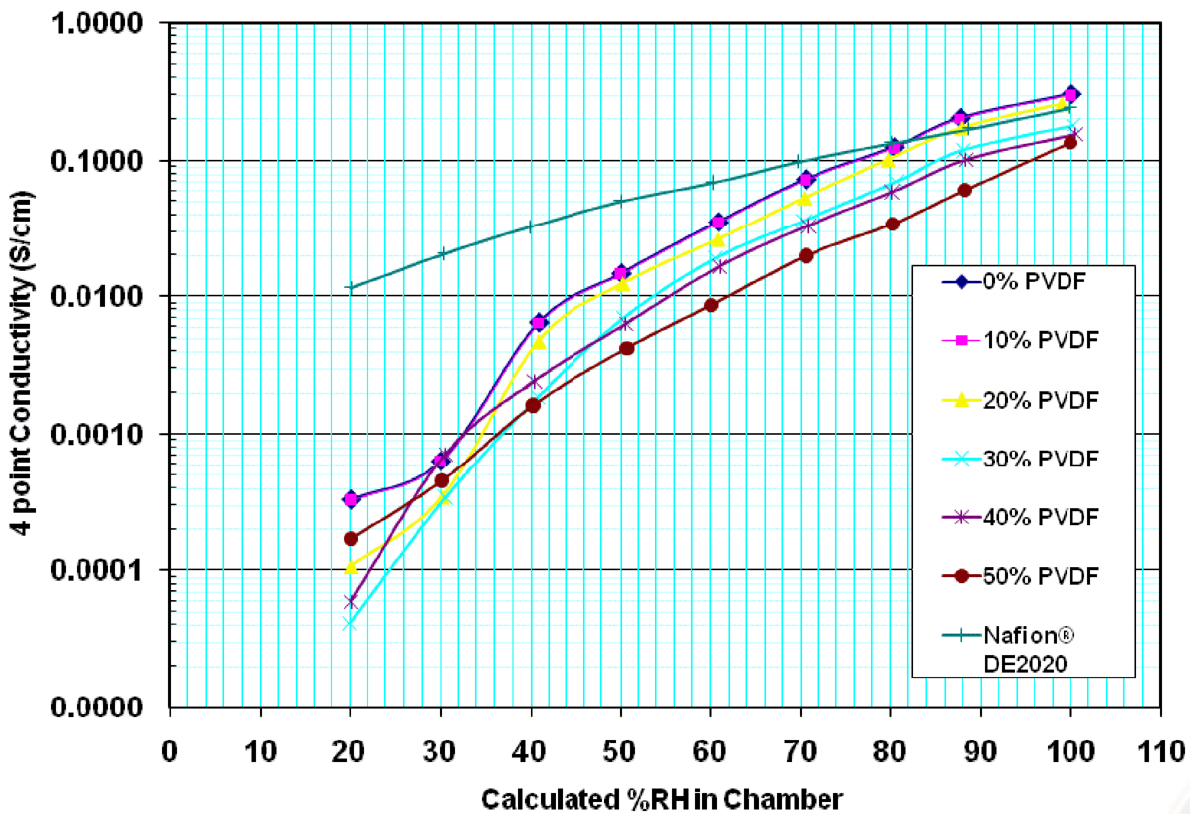
Gen 3 PFCB PVDF Blend Membranes



- Solutions of sulfonated Gen 2 PFCB ionomers are fully miscible with solutions of PVDF over all concentrations and yield transparent Gen 3 membranes.
- Gen 3 membranes exhibit increasing strain @ break and reduced water swell with greater percentages of PVDF. The 50% PVDF membrane displaying *ex-situ* properties and F_x comparable to Nafion® DE2020.

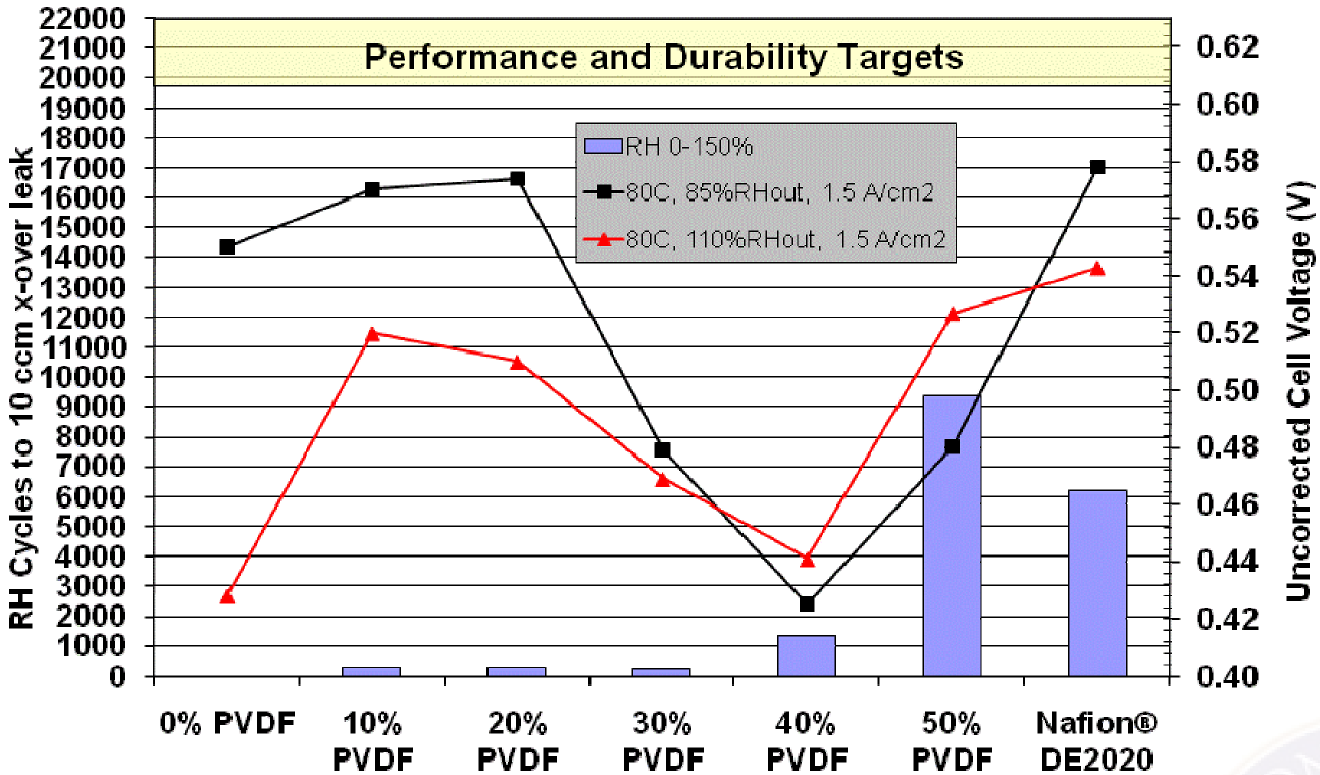
$$Fx = \frac{\text{\% Elongation at Break (25°C, 50\% RH)}}{\text{\% Length Change (100°C, H2O)}}$$

Gen 3 PFCB/PVDF Ex-situ H^+ Conductivity



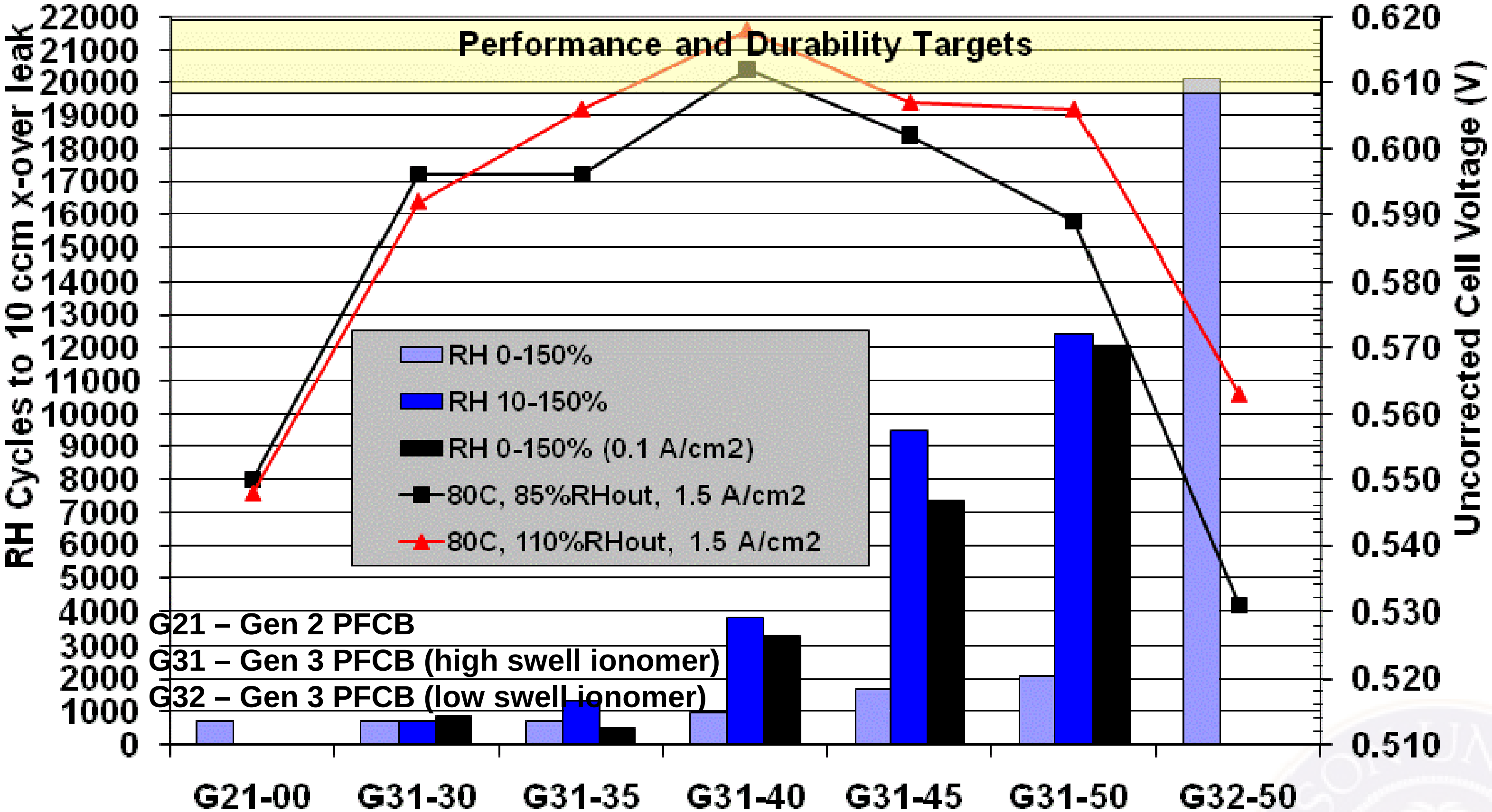
- Increased wt% of PVDF results in the expected decrease in proton conductivity (80°C) as a function of inlet relative humidity, falling well below Nafion® DE2020.

Gen 3 Performance-Durability Trade-off



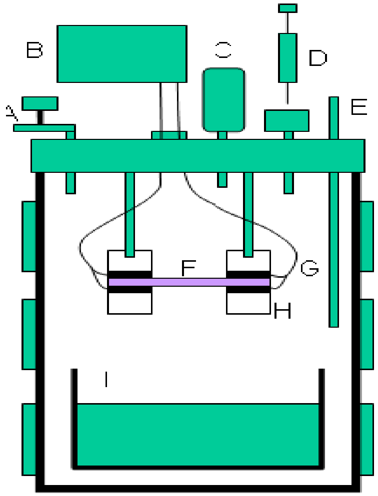
- FC cell voltage of blends does not directly correlate with *ex-situ* H^+ conductivity measurements as the 20% PVDF blend provides ~30 mV improvement compared to 0% PVDF with a drop in *ex-situ* H^+ conductivity.
- The 50% PVDF has improved mechanical durability compared to Nafion® DE2020.

Gen 4 Performance-Durability Trade-off



- The Gen 3 40% PVDF blend (G31-40) displayed optimum performance at 85% and 110% RH_{out} at $1.5 A/cm^2$. All membranes were the same nominal thickness.
- There was only a 20 mV penalty at 85% RH_{out} for a 3x improvement in mechanical/chemical durability from G31-40 to G31-50 PVDF blends.

Ion Conductivity of BPVE-6F as a function of time



Simplified schematic of the ionic conductivity characterization cell

- **A**. Vacuum / gas inlet / outlet.
- **B**. Impedance analyzer
- **C**. Pressure transducer
- **D**. Water injection port and syringe (not needed for this application)
- **E**. Thermocouple
- **F**. Electrolyte membrane
- **G**. Dual platinized platinum foil contacts
- **H**. PEEK open-facedconductivity cell
- **I**. H2O

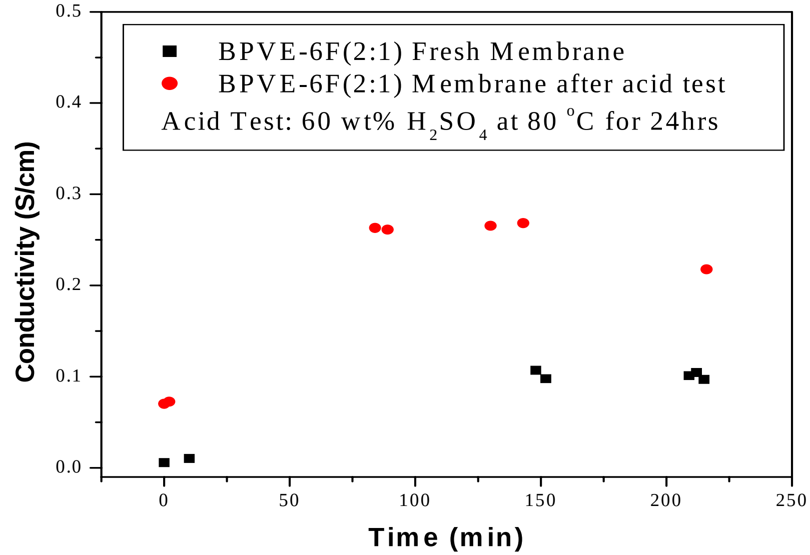


Figure: Ion conductivity of the BPVE-6F membrane as a function of time. (80°C, 100 RH%)

Ionic conductivity(σ) =K/Z_{real}

K: cell constant of the membrane = L/(Width× Thickness)

L: the distance between the electrodes

Width: the width of the membrane

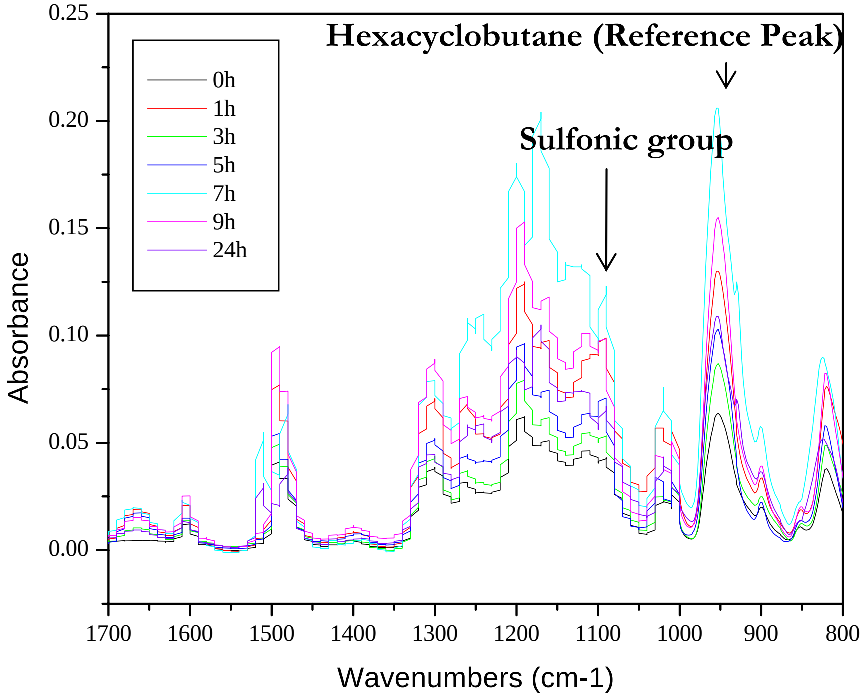
Thickness: the thickness of the membrane

Z_{real}: the real part of the impedance response, when the imaginary impedance = 0

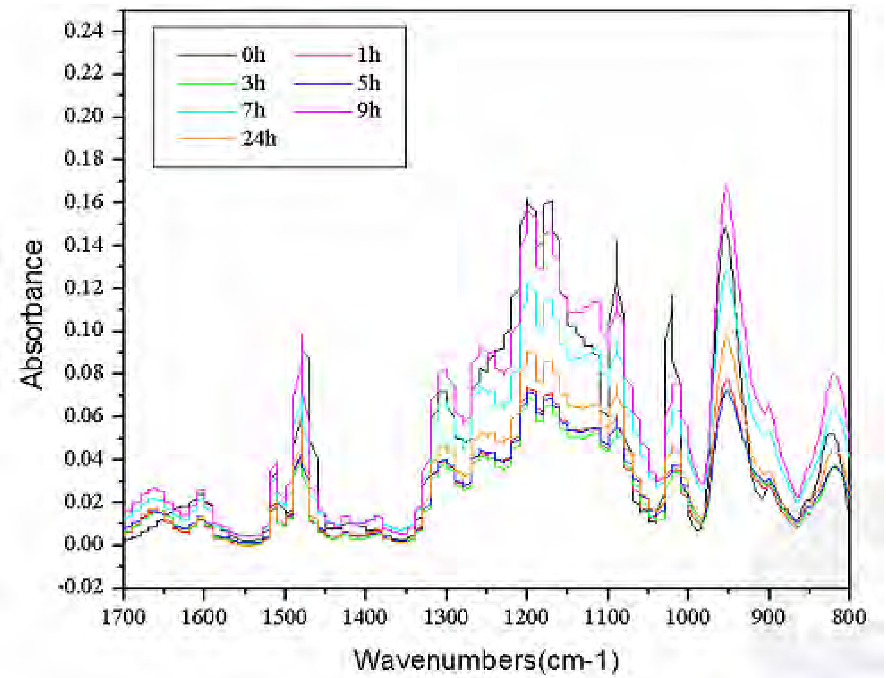
Electrochemical impedance measurements of the BPVE-6F (2:1) polymer membranes showed high proton conductivity (0.1069 S cm $^{-1}$ and 0.2368 S cm $^{-1}$) at 80˚C and relative humidity (RH) of 100%.

Chemical Stability under 60 wt% H_2SO_4 at 80˚C

- Measured by ATR-IR



BPVE Homopolymer Membrane



BPVE-6F(2:1) Block copolymer Membrane

ATR-IR analysis showed no change for the block copolymer, while BPVE homopolymer membranes showed increased intensity at 1030 cm^{-1} corresponding to sulfonic acid group that indicates sulfonation occurred during the chemical stability test. Copolymer membranes were found to be fairly stable during acid test.

SO_2 Crossover of Sulfonated PFCB Membrane

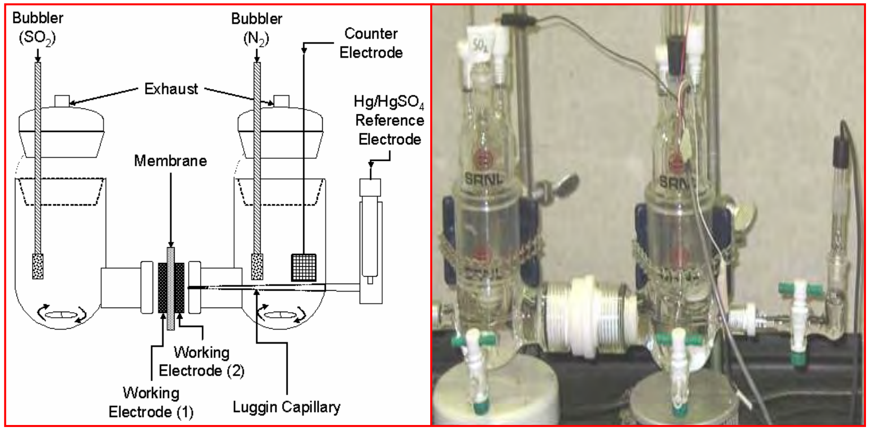
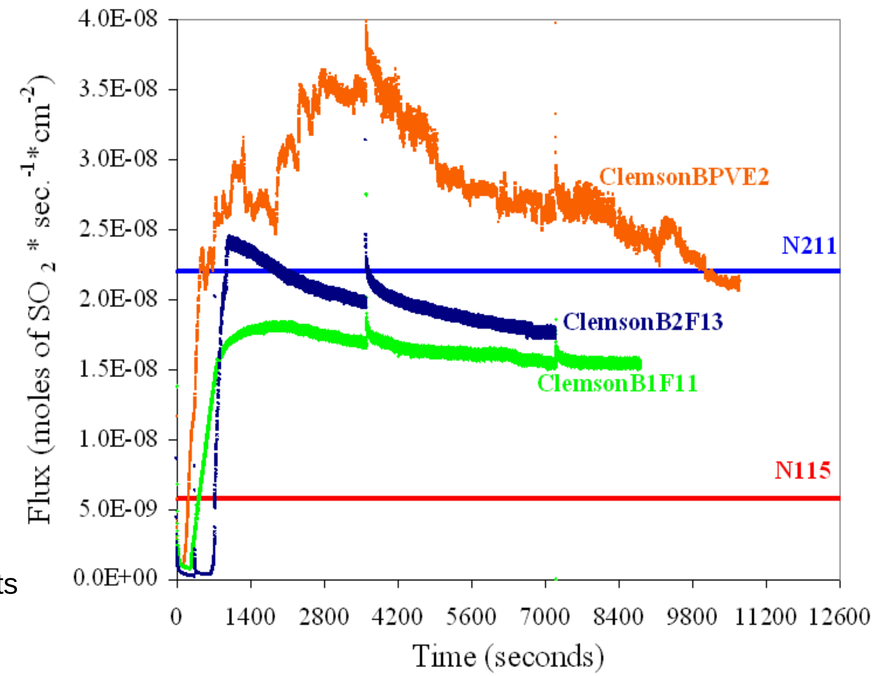


Figure. Simplified schematic of the SO_2 transport characterization cell

Working electrode (1) : used during the ionic conductivity measurements
Working electrode (2) : used during the SO_2 transport measurements
*designed by SRNL

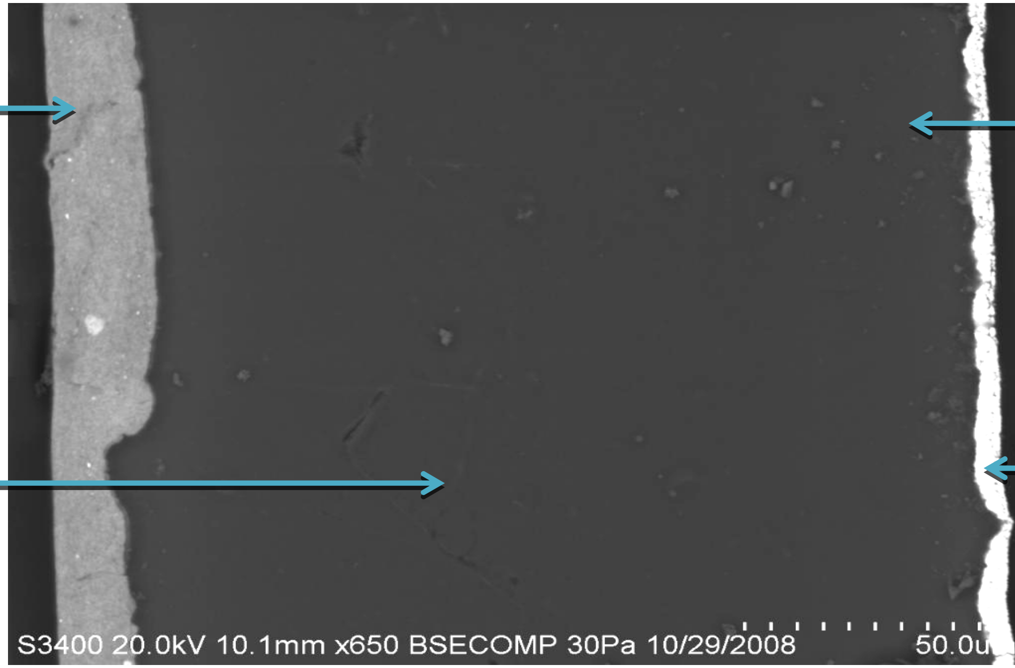


Sample Name	Thickness (μm)	IEC (meq/g)	I_{ave} (mA)	SO_2 flux (mol $SO_2 s^{-1} cm^{-2}$)	SO_2 transport ($cm^2 s^{-1}$)
BPVE Homopolymer (80K)	18	1.7	8.17	2.12E-08	3.50E-08
BPVE-6F (1:1) Block Copolymer (30K)	16	0.8	6.24	1.62E-08	2.37E-08
BPVE-6F (2:1) Block Copolymer (70K)	19	2	6.8	1.76E-08	3.07E-08
Nafion 115	127	-	2.02	5.23E-09	6.10E-08
Nafion 112	50.8	-	5.25	1.36E-08	6.34E-08
Nafion 211	25.4	-	8.43	2.18E-08	5.09E-08

SEM and EDX of Fresh N117 MEA

C: 63.12 %
O: 8.25 %
F: 4.00 %
S: 5.20 %
Pt: 19.43 %

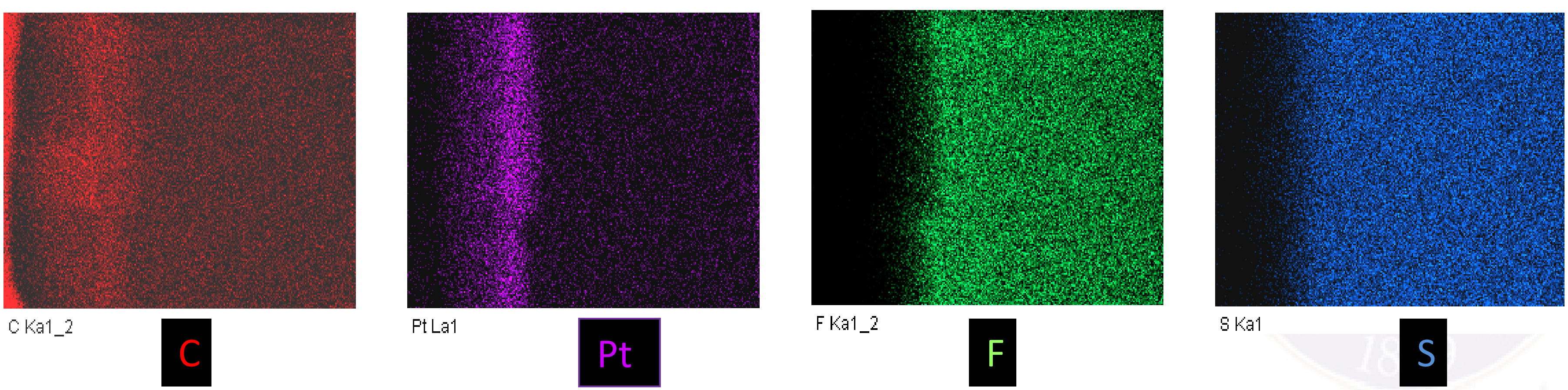
C: 39.74 %
O: 8.95 %
F: 38.53 %
S: 11.92 %
Pt: 0.87 %



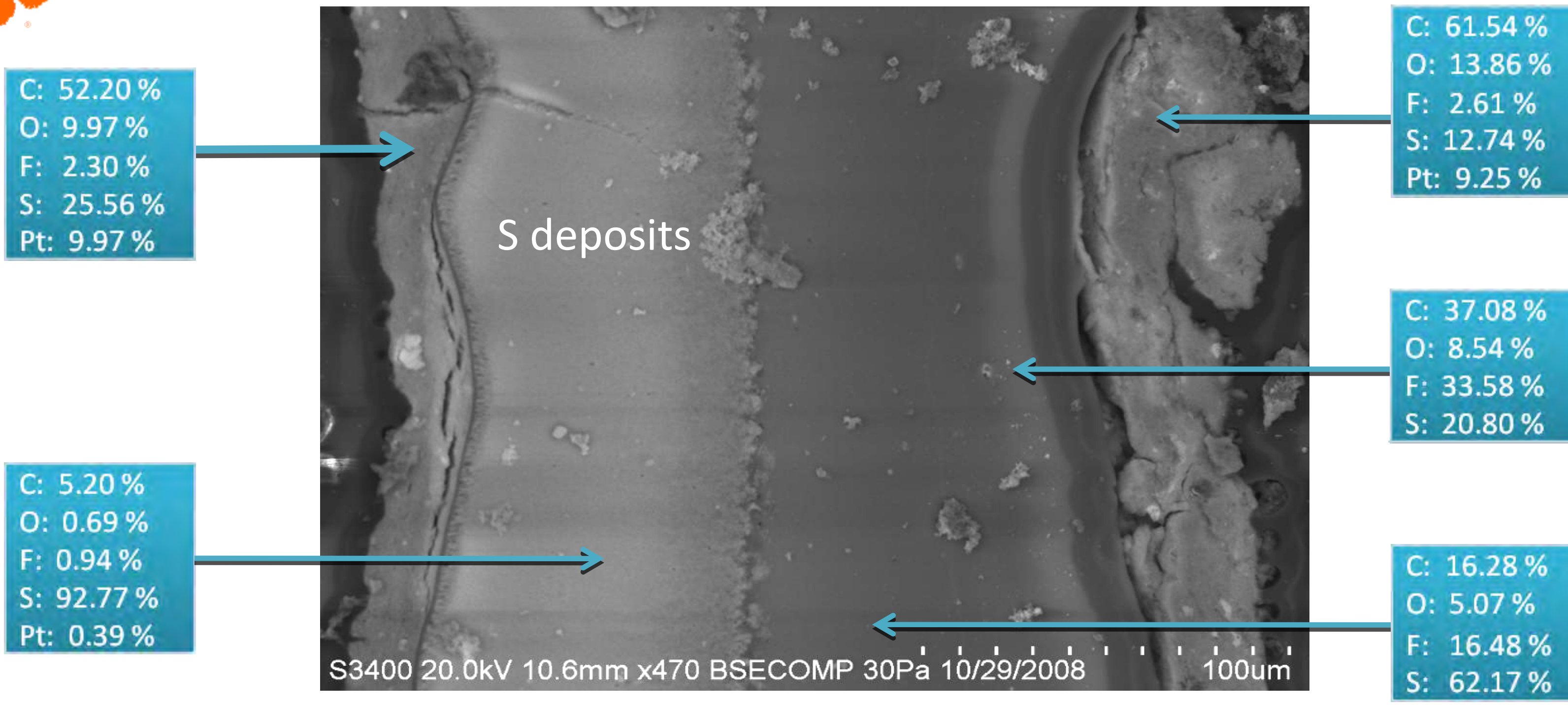
C: 56.96 %
O: 13.21 %
F: 16.40 %
S: 11.64 %
Pt: 1.80 %

C: 38.57 %
O: 7.86 %
F: 3.66 %
S: 2.80 %
Pt: 47.10 %

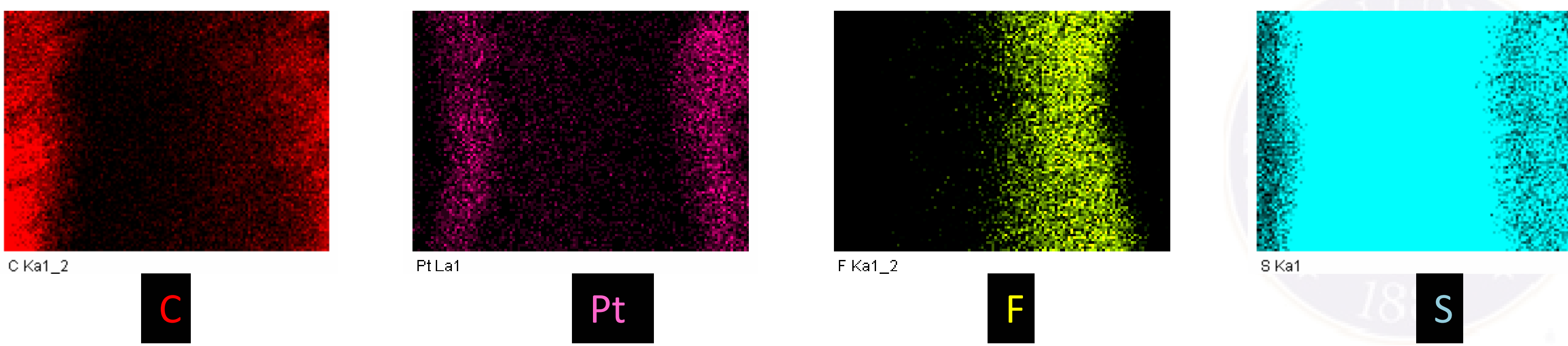
EDX Map



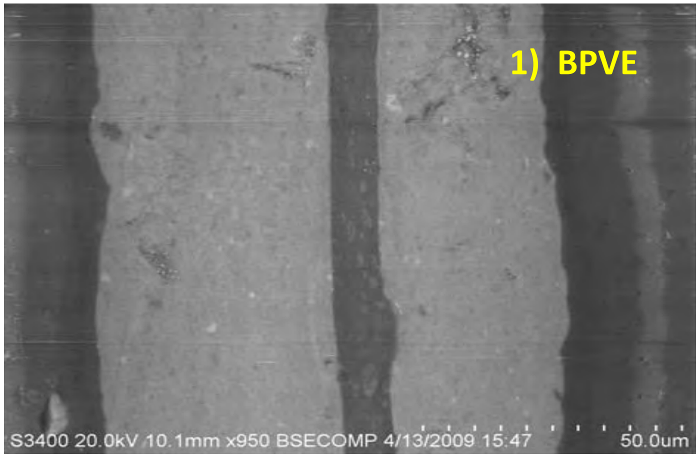
Sulfur Deposition of N117 after SO_2 Crossover Test

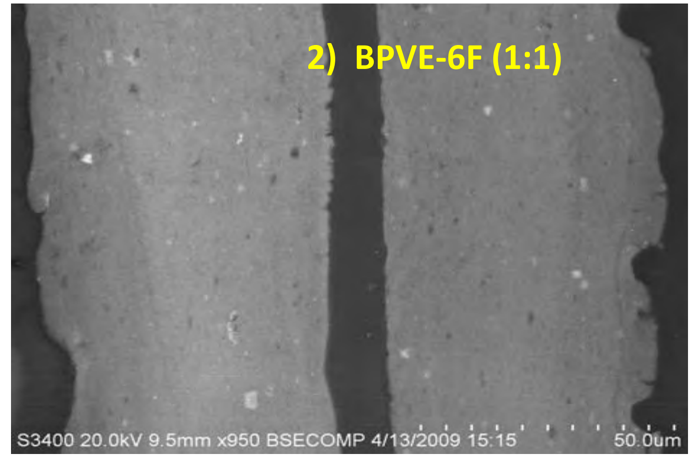


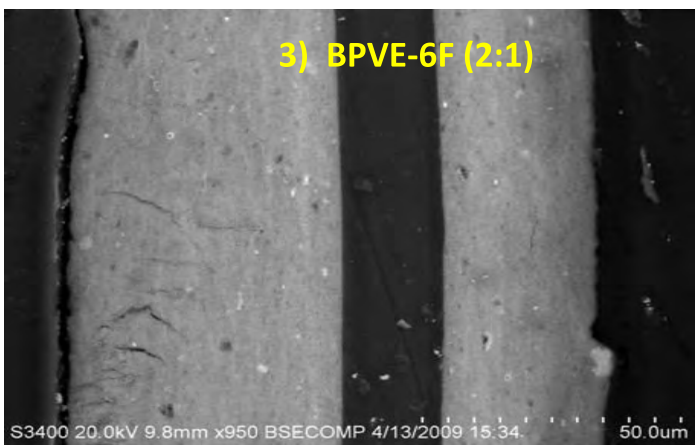
EDX Map



MEA for SO_2 Crossover and Ion Conductivity







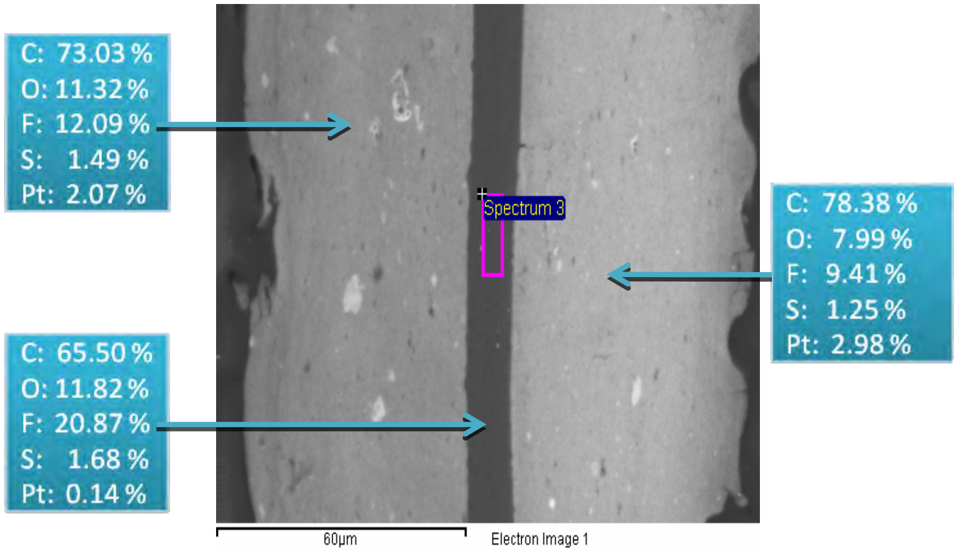
Membrane Electrode Assembly
1)BPVE homopolymer
2)BPVE-6F (1:1) block copolymer
3)BPVE-6F (2:1) block copolymer

- Pt loading on the anode: 1.8 mg
- Pt loading on the cathode: 0.9 mg
- Nafion loading: ~25 wt%
- Catalyst for both sides: 45 wt% Pt/C **(SRNL)**

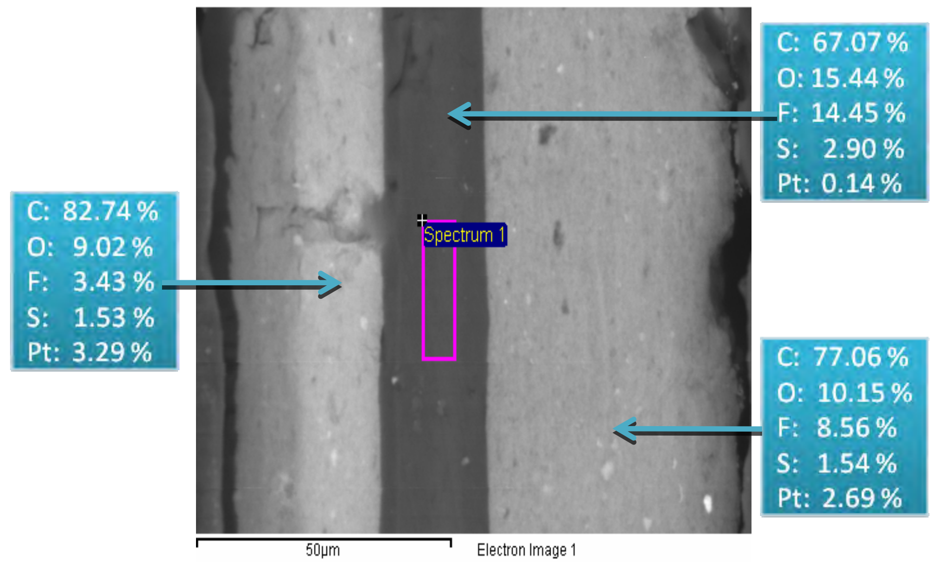
No Sulfur layer in Clemson Membrane has been shown after SO_2 Crossover Test

SEM and EDX of BPVE-6F Block Copolymer MEA

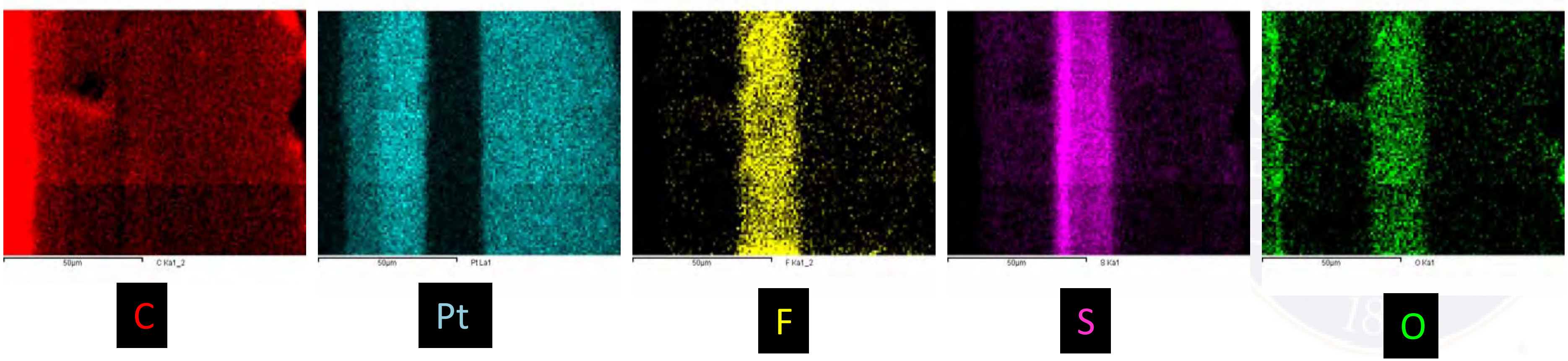
BPVE-6F (1:1)



BPVE-6F (2:1)



EDX Map of BPVE-6F(2:1) MEA



Future Work

- **Design Fluoroionomer for Low SO_2 Crossover and High Conductivity**

- Optimization of Sulfonated BPVE-6F Block Copolymer

- Block Copolymer / PVDF Blends

- Organic-Inorganic Composites (Zirconia / POSS)

- Cross-linking

- PFSI / PFSA / PFCB blends

- Electro-spun architectures

- **Characterization**

- Measurement of the membrane SO_2 transport : Effect of Degree of Sulfonation

- Evaluation of the membrane conductivity in H_2O and under electrolyzer conditions

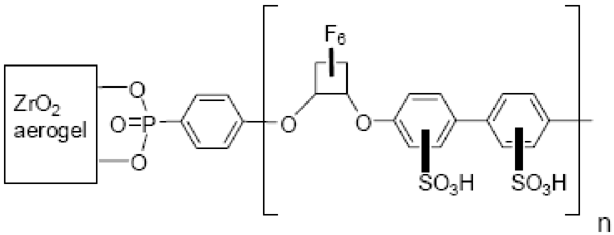
- Chemical Stability in Sulfuric acid and Water uptake dimension changes of membrane

- Phase Separation of the membrane(AFM) : Hydrophilic and Hydrophobic region

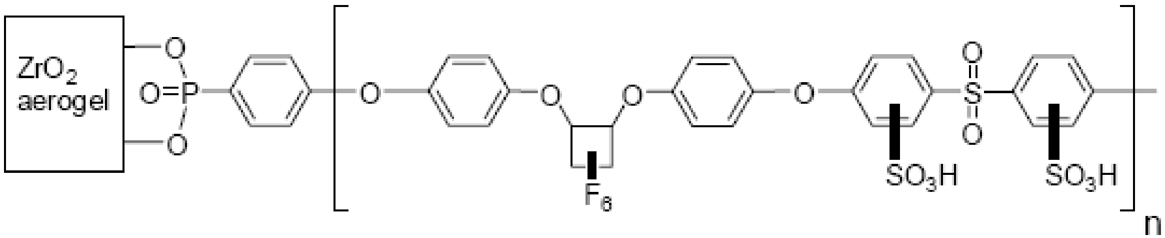
- Preparation of Membrane Electrode Assembly (MEA)

(S-PFCB)-ZrO_2 Hybrid Electrolytes Type I and II

(S-PFCB)-ZrO_2 hybrid electrolytes Type I



(S-PFCB)-ZrO_2 hybrid electrolytes Type II



Advantages of the (S-PFCB)-ZrO_2 hybrid electrolytes

-Low SO_2 transport (Stiffer backbones)

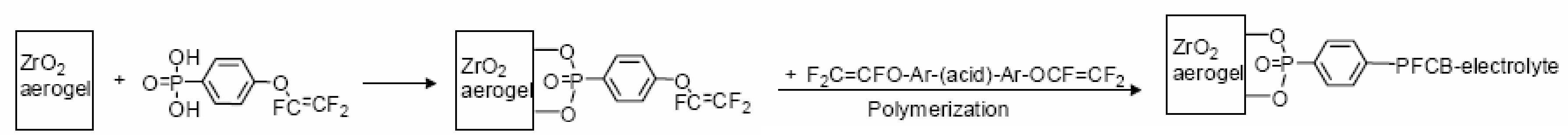
-High conductive under the aggressive electrolyzer conditions

-Improved mechanical properties: mere addition of Zr aerogel (ZrO_2) or ZrP caused the same polymer to become very stable

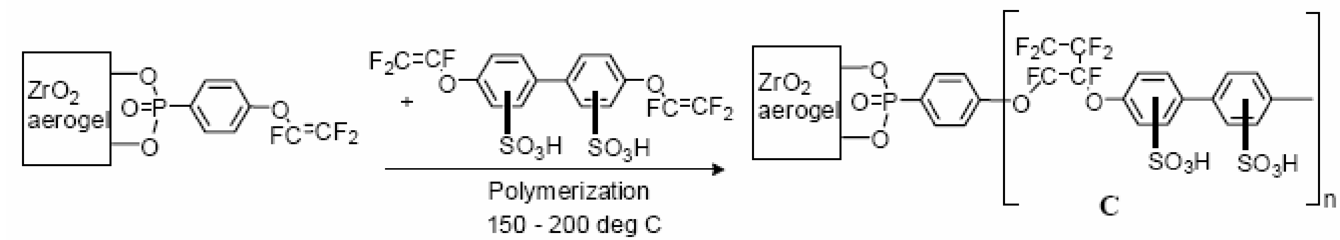
: Good dimensional stability and long life: Covalent combination of a rigid inorganic framework (Zirconia areogel) with a very stable and durable integrated S-PFCB

Covalent (S-PFCB)-ZrO2 Hybrid Electrolytes

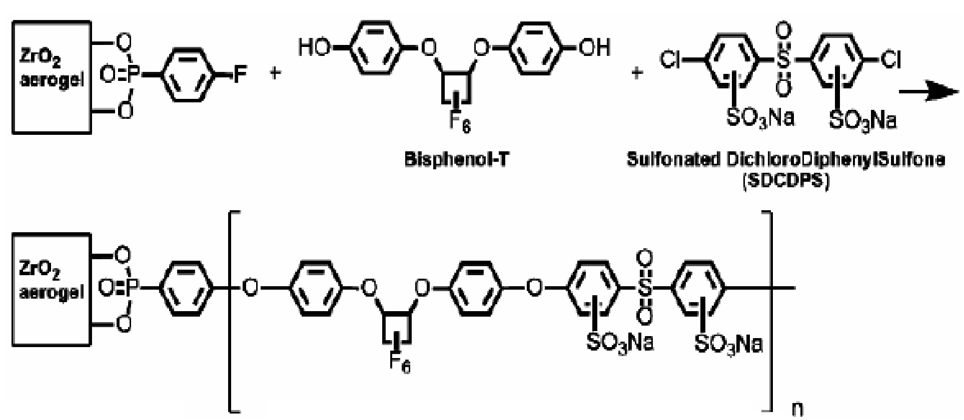
Scheme 1. Preparation of electrolyte-impregnated zirconia aerogel using aryl TVE acids and phosphonates



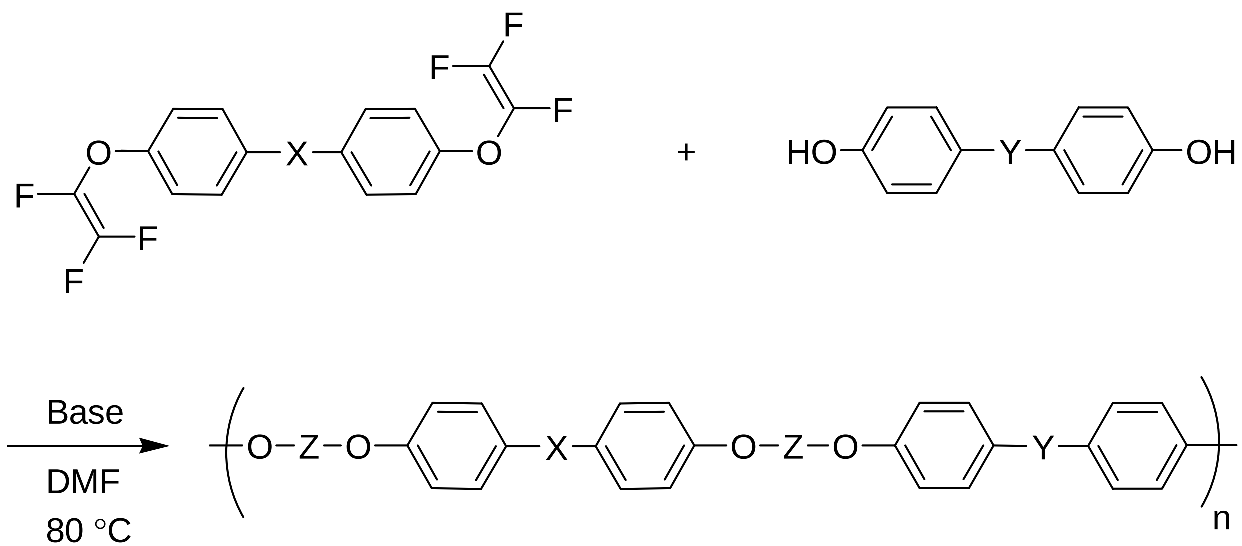
Scheme 2. Proposed reaction pathway for (PFCB)-ZrO2 hybrid electrolytes Type I



Scheme 3. Proposed reaction pathway for (PFCB)-ZrO2 hybrid electrolytes Type II



Fluoroethylene/vinylene aryl ether polymers



Base = NaH, Cs_2CO_3 Z = CF=CF, $CHFCF_2$

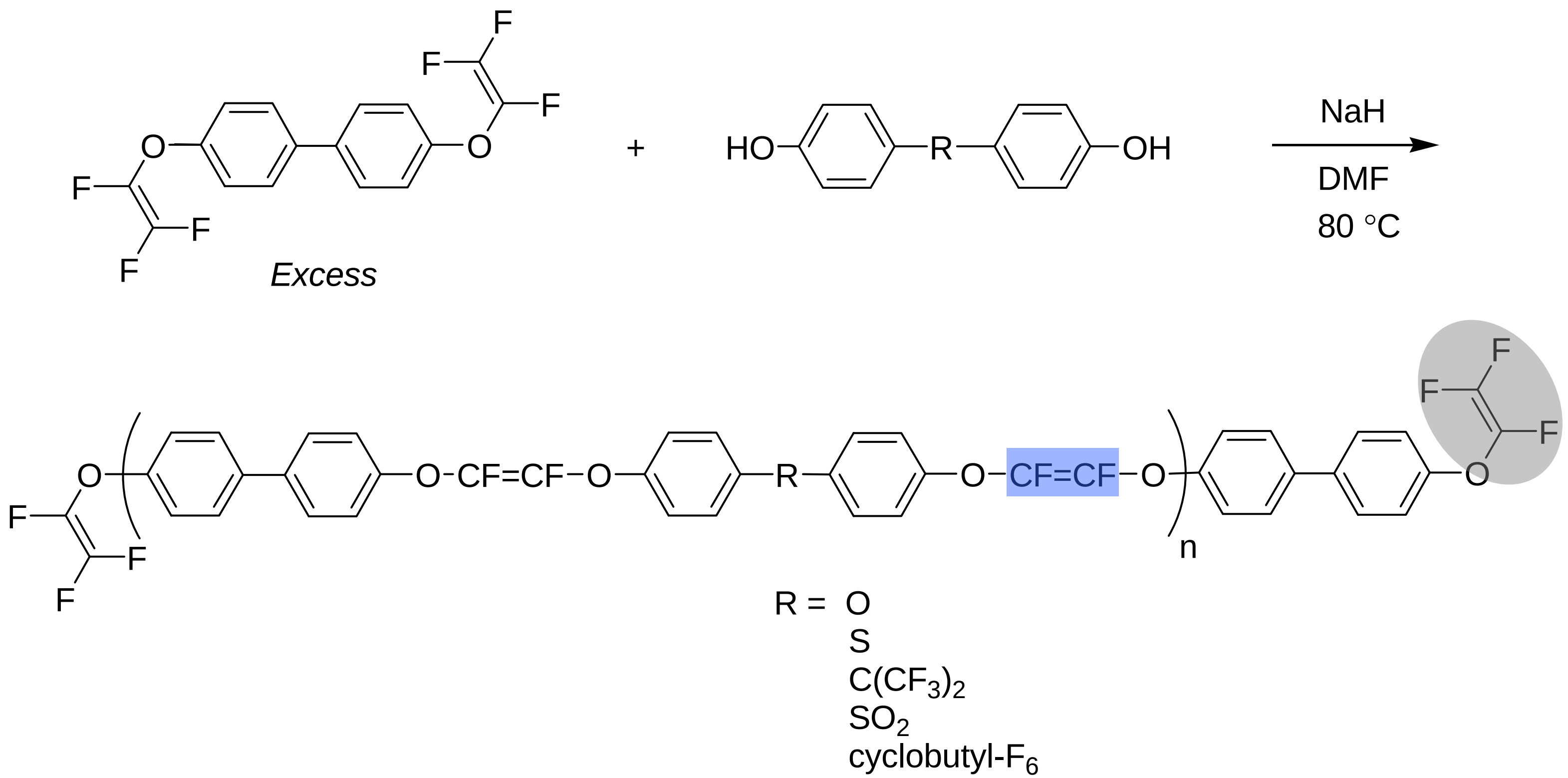
X, Y = —, $C(CF_3)_2$, $C(CH_3)_2$

- Applying 1:1 feedstock of monomers
- High yield (> 85%)
- M_n = 12–35k (PDI = 2–3)
- Produces transparent, flexible films

- Tunable T_g (50–160 °C)
- Capable of crosslinking
- T_d = 512–632 °C (air)
- *Compatible crosslinking additives*

Iacono, S. T.; Budy, S. M.; Smith, D. W., Jr. *Chem. Commun.* **2006**, *46*, 4844
Iacono, S. T.; Ewald, D. E.; Sankhe, A.; Rettenbacher, A.; Smith, D. W., Jr. *High Perform. Polym.* **2007**, *19*, 581

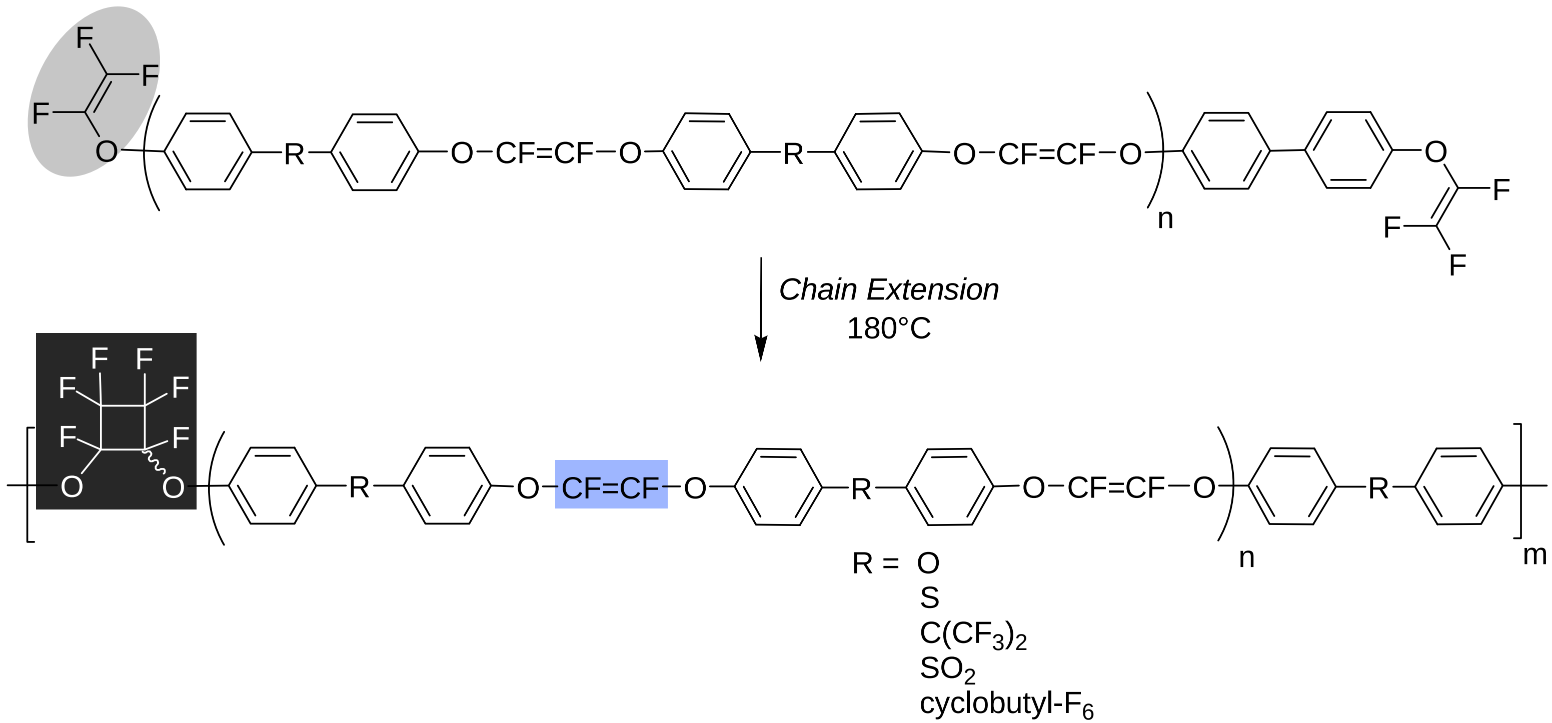
Fluoroethylene/vinylene aryl ether telechelics with duel thermal reactivity

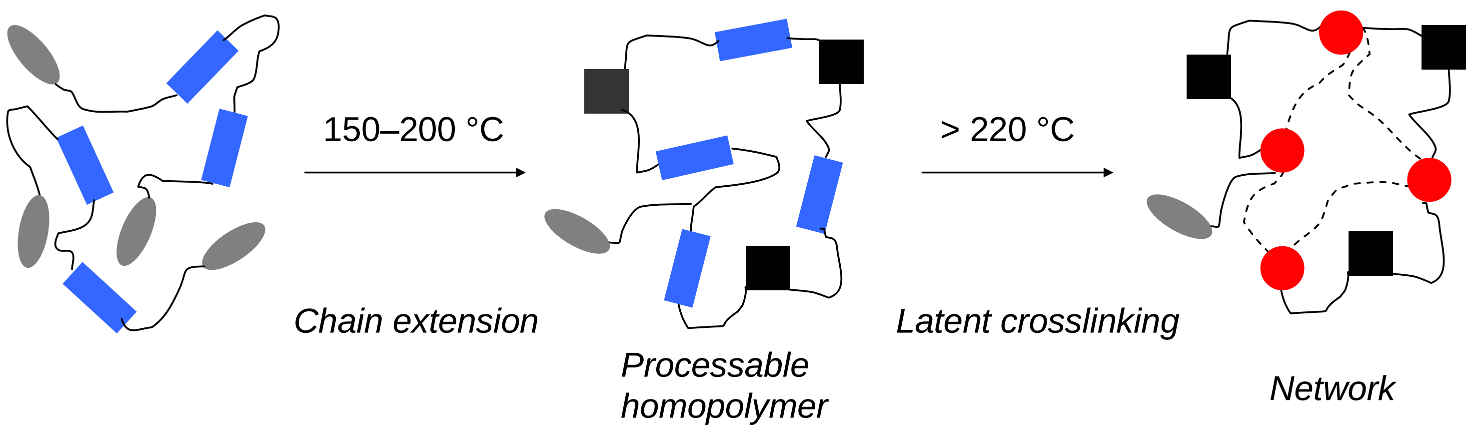


- New FAVE telechelomers by controlling monomer feedstock
- Up to 95% –CF=CF– enchainment
- Telechelomers exhibit duel thermal reactivity

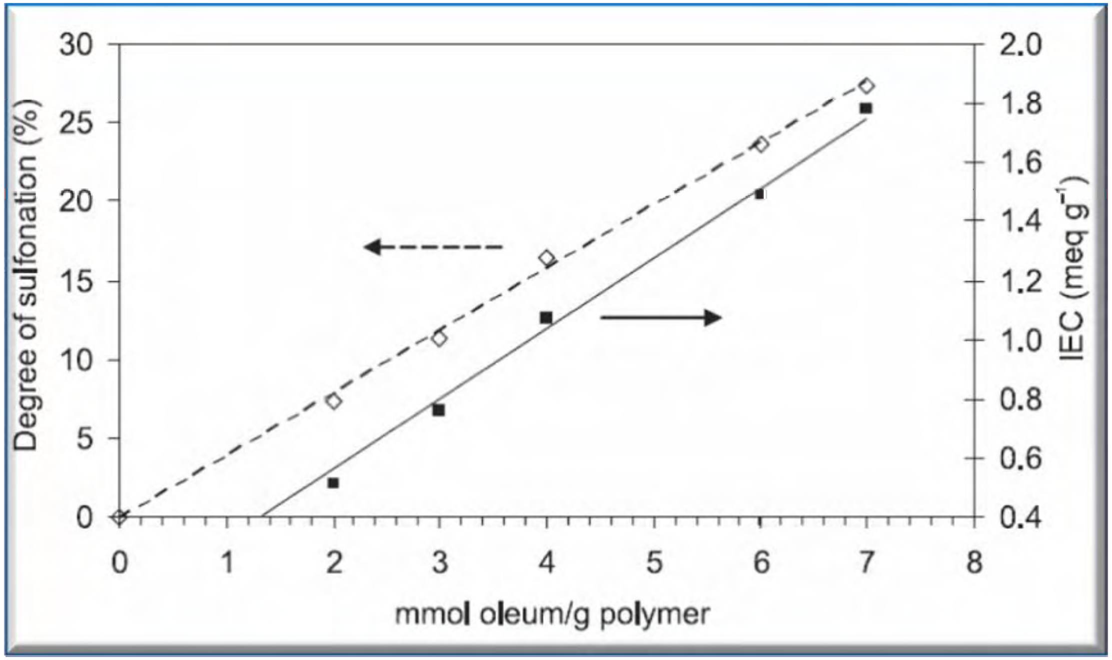
Iacono, S. T.; Budy, S. M.; Smith, D. W., Jr. *Chem. Commun.* **2006**, *46*, 4844. *Macromolecules*, in press.
Iacono, S. T.; Ewald, D.; Sankhe, A.; Smith, D. W., Jr. *High Perform. Polym.* **2007**, *19*, 581

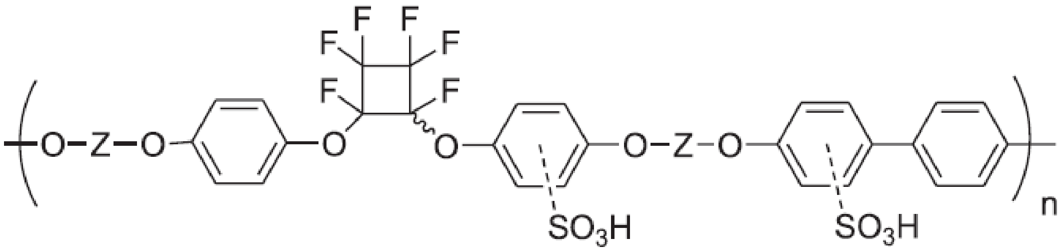
Dual thermal reactivity of telechelomers





Effect and Correlation as a Degree of Sulfonation





Z = $CHFCF_2$ (or) CF=CF (50:50 *cis:trans*)

High Performance Polymers, **19:** 581–591, 2007

Effect of the Backbone of the Polymer

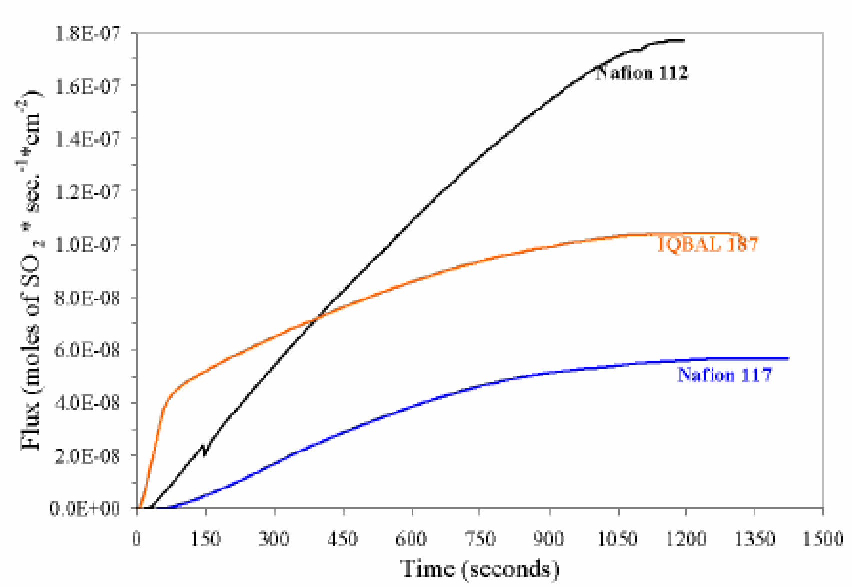
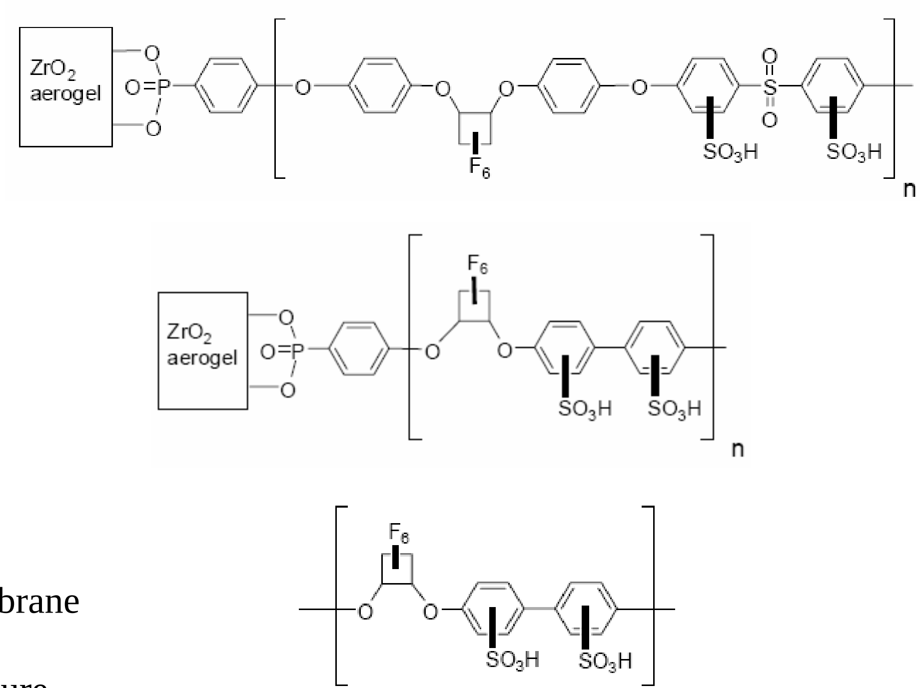


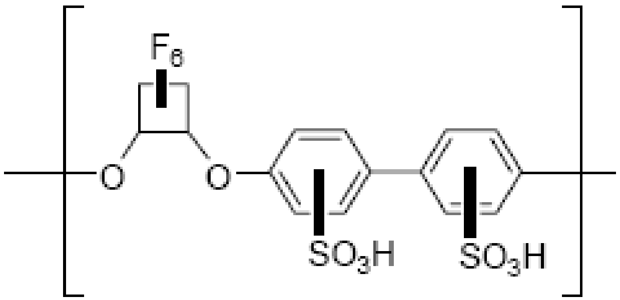
Figure. SO_2 transport through a Clemson produced membrane (Sulfonimide/PTFE blend, EW 1318, **thickness: 1 mil**) Immersed in 30 wt% saturated with SO_2 at room temperature



- ✓ Develop a technology by embedding zirconia nano-particles at the membrane pores in PFSI-based membranes
- ✓ Stiffer backbones: Balance of excellent proton conductivity, chemical stability under conditions and a very low SO_2 permeability

(S-PFCBs) Homopolymer Electrolytes

Sulfonated perfluorocyclobutyl aromatic ether homopolymer (S-PFCBs)



S-PFCBs

- ✓ Low SO_2 permeability!
- ✓ High proton conductivity
- ✓ Improve mechanical properties

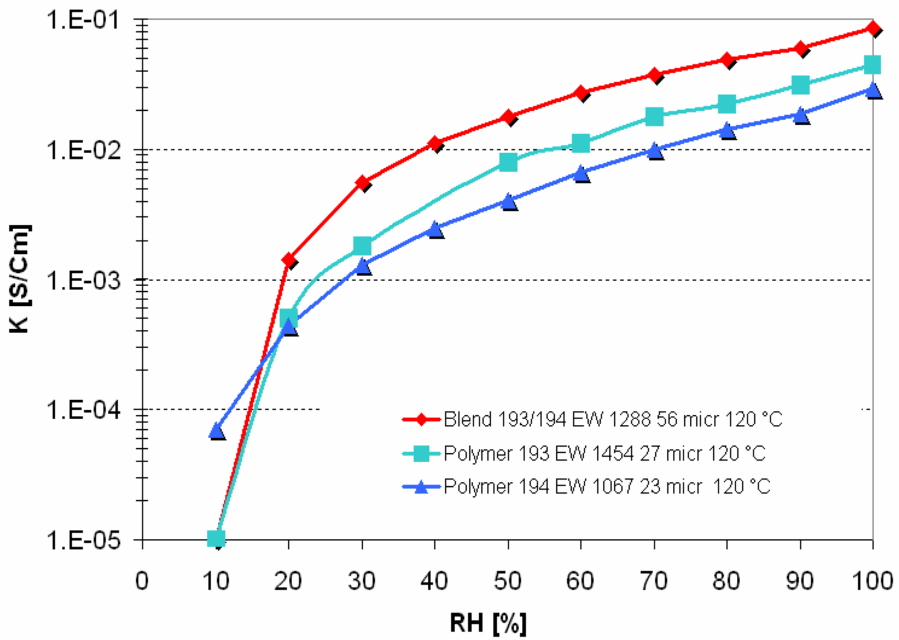
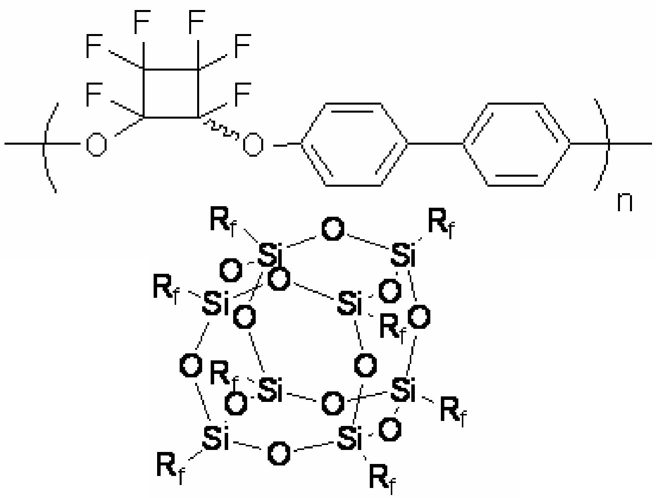


Figure. Conductivity *vs.* RH of a blend of two PFSI polymers at 120 ^{0}C compared to single polymers.

<u>Pproton conductivity for S-PFCB = 0.17 S/cm (Ew=546)</u>

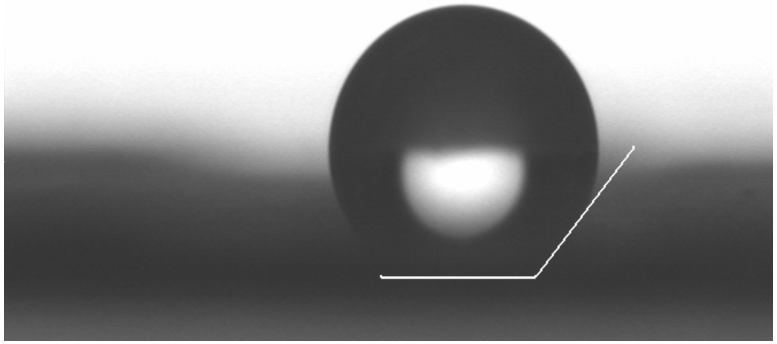
- Mn:60,000
- Voltage:20Volts
- Flow rate:10ml/hr
- Distance:12.2cm
- Concentration of polymer:11.2%
- Concentration of POSS:2.5%
- Solvent:THF

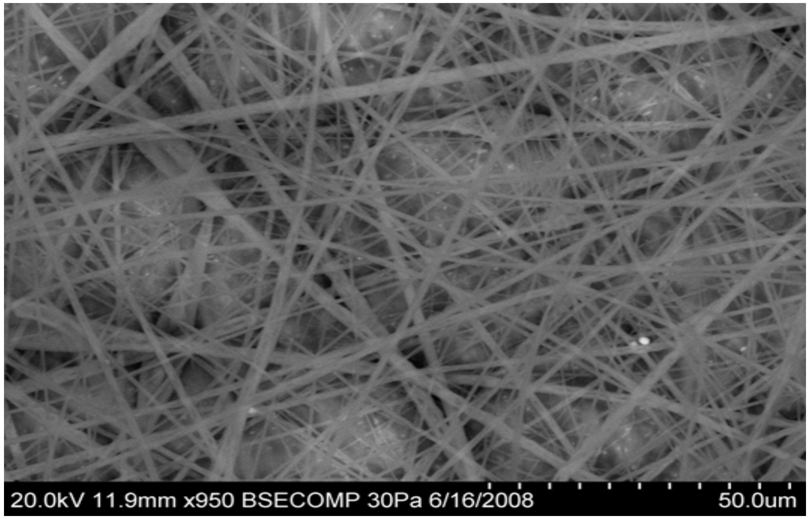


$R_f = CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$

Flurodecyl$_8$T$_8$ (FD$_8$T$_8$)

CA: 133°





Thank You

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