A Systematic Approach to Developing Durable, Conductive Membranes for Operation at 120℃

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University of Tennessee-Knoxville

DOE project award # EE0009246

June, 2022

DOE Hydrogen Program

2022 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID #

FC336

Overview

Timeline and Budget

- Project Start Date: 10/01/2020*

(*actual start date for funding: 3/15/2021)

- Project End Date: 3/31/2024
- Total Project Budget: $1,250,000
  - Total DOE Share: $1,000,000
  - Total Cost Share: $250,000
  - Total DOE Funds Spent*: $330,000
  - Total Cost Share Funds Spent*: $80,000

* As of 03/28/2022

Barriers

- Barriers/targets addressed

1. Low areal specific resistance
2. Low O_2, H_2 crossover
3. 25,000 Hr lifetime

Partners

- Tom Zawodzinski, **UTK**/ORNL
- Tomonori Saito, ORNL,
- John Harvey, Akron Polymer Systems

Akron Polymer Systems
Innovators in High Performance Polymer Technology

THE UNIVERSITY OF TENNESSEE KNOXVILLE

OAK RIDGE National Laboratory

Project Goals

- Develop membranes with sufficient performance and long projected lifetime to meet the requirements of long-term applications in PEM fuel cells for Heavy Vehicles.
- Use background measurements and literature evaluation to inform paths forward for membrane development to meet cell resistance requirements over ranges of temperature and relative humidity that reflect operating conditions in HVs.
- Prepare new membrane materials with side-chain and polymer chemistry tailored to achieve acceptable conductivity/resistance with low water uptake and swelling.
- Demonstrate improved material lifetime by applying DOE-approved tests but also critically assess the lifetime and degradation projection approaches commonly used.

Relevance and Potential Impact

- This project is part of the MMFCT effort
- Fuel Cells for long-range trucks require membranes that:
  - Can provide adequate conductance over a wide range of humidity and temperature
  - Exhibit minimal cross-over
  - Are stable for long periods of time
- This Project:
  - Uses a combination of Data Mining and Investigator Experience-based Hypotheses to Rationally Identify Promising Candidates with high conductance (low ASR) and low cross-over
  - Will incorporate and extend current best practices for durability (e.g. additives)
  - Aims to help identify application-specific statistical approaches to durability assessment
- Addresses DOE Goals by providing paths to
  - Lower greenhouse gas emissions: inherent in FC Truck application
  - Create good-paying jobs in the U.S.: path to manufacturing in US supply chain
  - Build clean energy infrastructure: inherent in FC Truck application
  - Support environmental justice: : Trucking is a blue collar industry

Approach: Dual Paths that Converge…

Membrane performance

- **Goal:** identify paths to acceptable conductivity with **minimal water**
  - Explore a range of materials to mine information on factors that increase efficiency of use of water, control uptake.
- **Goal:** identify paths to acceptable cross-over levels
  - Explore a range of materials, mine information on factors that decrease permeability

Membrane durability

- **Goal:** identify polymer-related factors that control durability
- Examine different chemistry, morphology, mechanical props
- Statistics and testing evolution
- May include additive packages for external testing

Interesting materials can be prepared AT SCALE, enabled by this partnership

Supporting Elements: New testing approaches, statistical underpinnings

Approach: Milestones etc

Milestone #	Project Milestones	Type
Y1Q1	First PPO-Br acquired.	progress
Y1Q2	Functionalization of at least 3 commercially available polymers with TFSI groups.	progress
Y1Q3	Functionalization of first team-synthesized polymers with TFSI groups.	progress
Y1Q4	New durability test (peroxy radical) validated.	progress
Y1Q4	First publication of results.	progress
Y1Q4	At least one membrane achieving < 0.08 Ohm cm^2 at 120 °C assuming 15-micron thick film	SMART progress
Year 1 GNG	Demonstrate at least one membrane that can meet target ASR at 120°C if prepared as a 15-micron thick film.	GNG

Approach to date

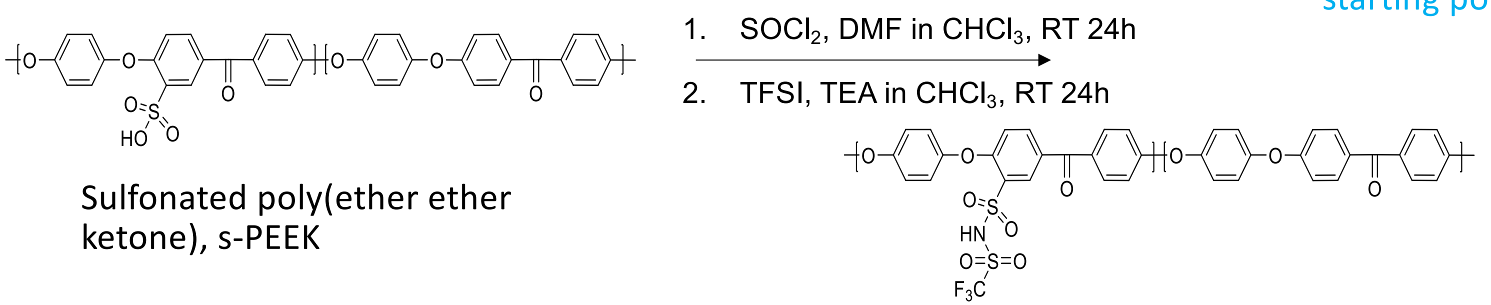
Focus on functionality

1. Extensive measurements on ‘legacy’ polymers and some new types to reveal key trends over range of temperature and RH
2. Lots of synthesis to prepare polymers, modify acid groups
3. Processing into films for testing

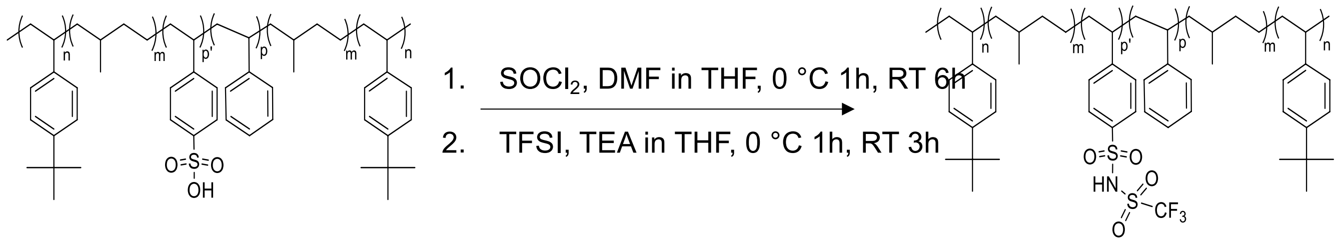
Technical Approach: Nexar-based Model (ORNL)

Spicing up aromatic hydrocarbons with sulfonimides

Also applied to other polymer starting points—e.g. PPO derivatives



Sulfonated poly(ether ether ketone), s-PEEK



Nexar

Nexar-SO3H Conductivity Experiments

		Temperature (◦C)										
Molarity	**Water Activity**	**21**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**	**110**	**120**
0.5M	**0.9828**	14.846	16.064	21.682	25.663	27.169	29.472	25.324	26.063	27.226	15.904	1.810
1M	**0.964**	34.805	30.912	12.098	11.912	10.539	10.301	7.860	6.881	7.584	1.656	0.182
2M	**0.921**	61.652	66.314	73.502	85.355	87.949	95.496	97.044	90.188	96.665	54.958	13.084
4M	**0.8116**	18.787	22.135	25.814	29.333	30.529	32.512	31.861	21.858	23.969	22.103	5.679
6M	**0.6784**	2.438	3.873	11.367	10.116	3.608	4.032	8.754	9.552	10.783	10.207	9.745
8M	**0.5381**	0.958	1.400	1.773	1.980	7.329	8.358	9.536	10.502	11.459	11.146	10.461
10M	**0.4101**	0.765	0.765	1.495	1.818	1.982	2.464	1.999	2.432	2.303	2.626	2.794
11M	**0.355**	0.389	0.526	0.544	0.631	0.667	0.890	1.141	1.194	1.360	1.260	1.400
12M	**0.307**	0.130	0.204	0.279	0.330	0.432	0.547	0.698	0.887	1.036	0.923	1.047
13M	**0.2657**	0.071	0.113	0.159	0.181	0.249	0.279	0.383	0.464	0.578	0.485	0.583

Nexar-TFSI Conductivity Experiments

		Temperature °C										
Molarity	**Water Activity**	**21**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**	**110**	**120**
0.5M	**0.9828**	30.517	31.996	45.216	56.813	61.394	69.049	99.954	122.897	121.119	63.198	21.246
1M	**0.964**	36.247	27.496	34.977	35.078	30.364	33.646	5.383	19.053	18.533	6.995	1.280
2M	**0.921**	14.027	13.047	16.951	23.213	24.848	27.288	65.723	89.795	95.490	67.594	31.166
4M	**0.8116**	0.344	14.607	23.950	25.125	25.008	23.365	26.864	26.782	30.209	27.251	17.565
6M	**0.6784**	2.966	12.190	13.713	14.282	18.175	5.487	5.395	7.005	6.695	7.063	6.808
8M	**0.5381**	2.137	4.593	5.124	5.467	6.409	1.005	1.166	0.999	1.100	1.334	1.422
10M	**0.4101**	0.224	0.255	0.352	0.377	0.448	1.569	0.211	0.241	0.285	0.344	0.398
11M	**0.355**	0.531	0.706	0.092	0.067	0.031	0.033	0.042	0.041	0.091	0.086	0.114
12M	**0.307**	0.037	0.080	0.094	0.002	0.006	0.080	0.013	0.009	0.053	0.062	0.084
13M	**0.2657**	0.025	0.105	0.034	0.025	0.012	0.088	0.019	0.093	0.095	0.142	0.833

Key Results and Trends from Previous Slides

- High T, High RH (T > 80, RH >90)
  1. Polymers tend to dissolve, form gels; difficult to get reliable data
  2. Reasonably high conductivity for TFSI-form
- 50% RH:
  1. SO_3H form: 1 to 10 mS/cm between 21 and 120^{o}C
  2. Imide form: 2.5 mS/cm at 21^{o}C but seems to lose water easily at high
- 25% RH:
  1. Both forms below 1 mS/cm

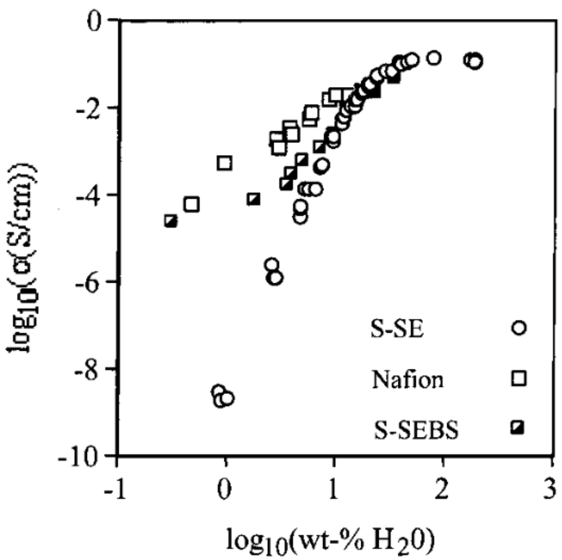
Trends for Nexar

- Both Nexar and Nexar-TFSI show similar poor behavior overall in the RH range targeted.
- Conductivity vs. RH: drops off precipitously below ~60% RH (3 to 4 orders of magnitude too low at ~25% RH)
  - By contrast, PFSAs show a large (but not as large) drop below 15%
- Activation energy for proton transport: ~32 kJ/mol @ 40% RH, ~53 kJ/mol @ 25% RH
  - Double that for PFSAs
- Significant water loss at high RH as temperature increases
  - Limits advantage of increasing temperature

Do these trends hold for all aromatic-types?

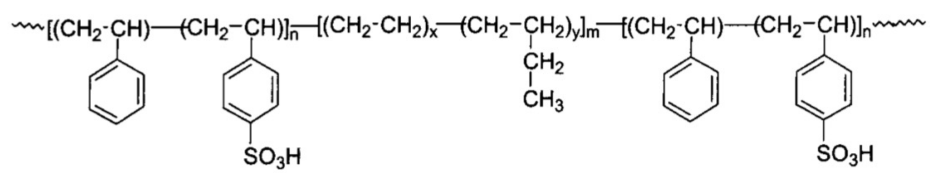
--investigating effects of electronic structure, clustering, multiblock co-polymer

A Perspective: How Difficult is it to get needed conductivity with non non-PFSA Acids?



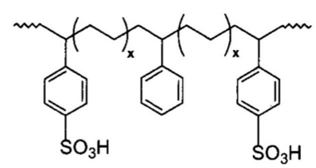
Serpico et al

b S-SEBS



c SE Series

Structure of partially sulfonated styrene-ethylene interpolymer (S-SE), x = 9, 2.5, and 1.2 for S-SE1, S-SE2, and S-SE3 respectively.



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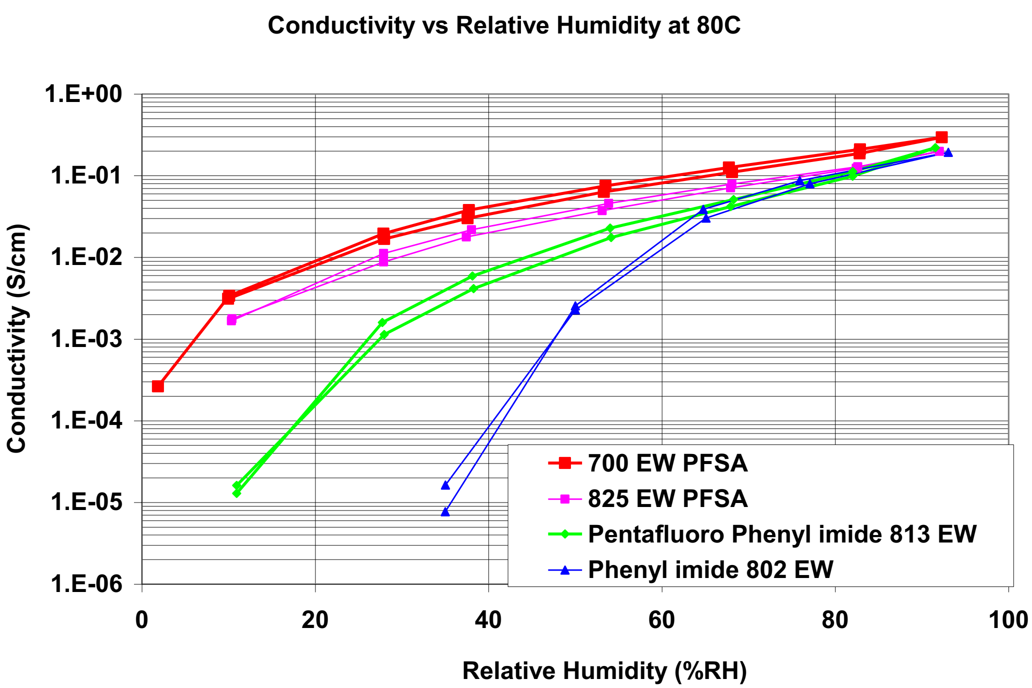
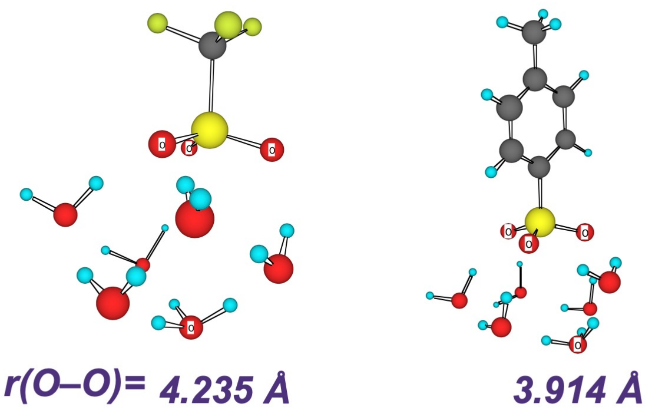
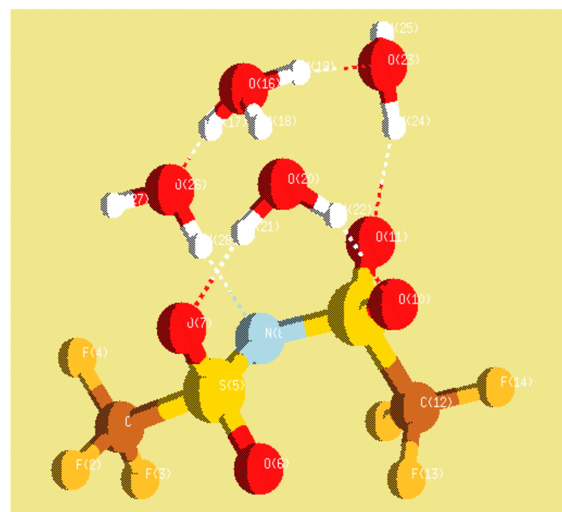


A Perspective: How Difficult is it to get needed conductivity with non-PFSA Acids?

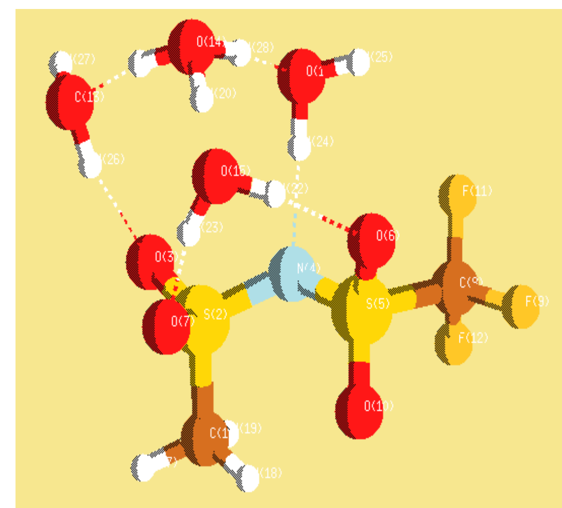


Ar-SO_3H hold water more tightly than PFSAs

Perfluorinated Imide



Partially fluorinated Imide



Imides hold water less tightly than PFSAs

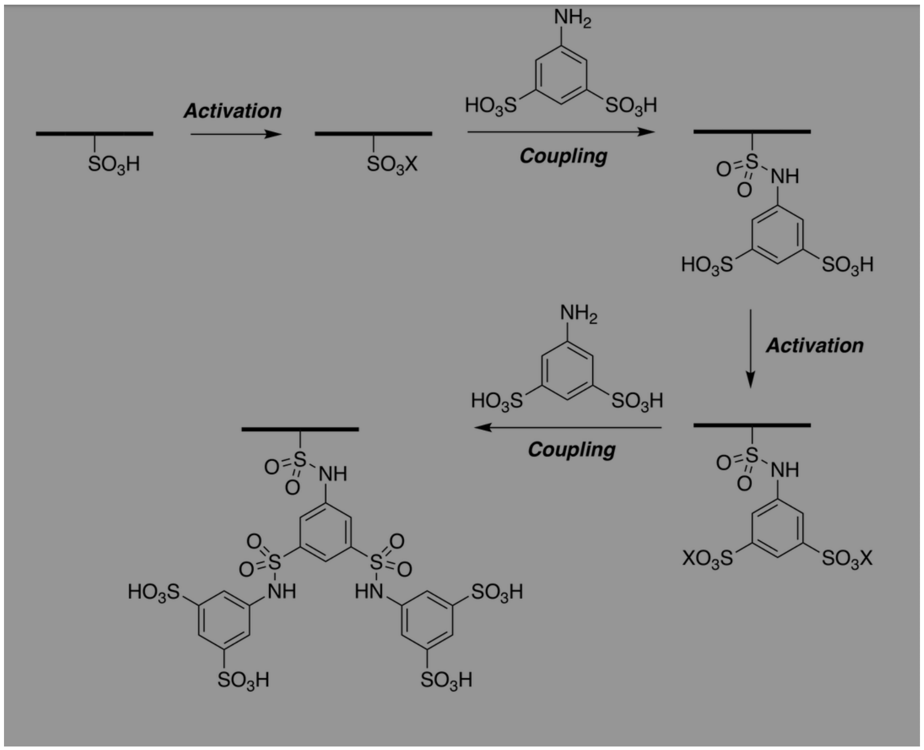
Partly fluorinated: water shifts away from perfluorinated site

Technical Approach
Steps for New or Modified Polymers

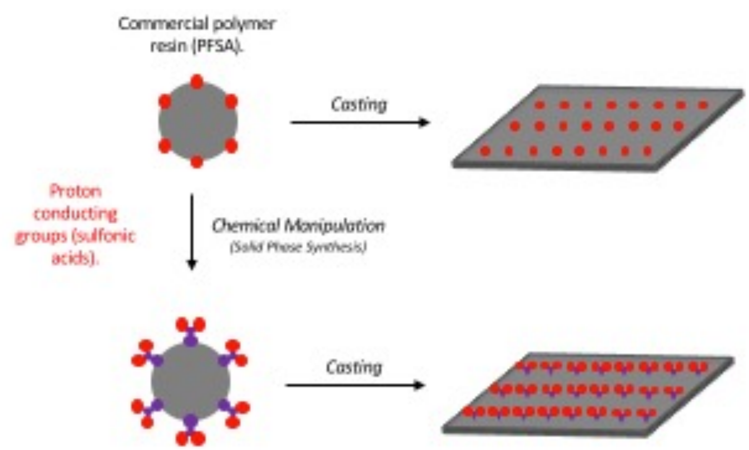
- Synthesis conditions: Solid or solution? Solvent choice?
- Reaction, purification, analysis
- Solubility profile for casting
- Preliminary casting-film quality? Swelling? Water soluble?
- Need to cross-link?
- Casting conditions
- Membrane treatment before use
- Testing

Technical Approach: Examples

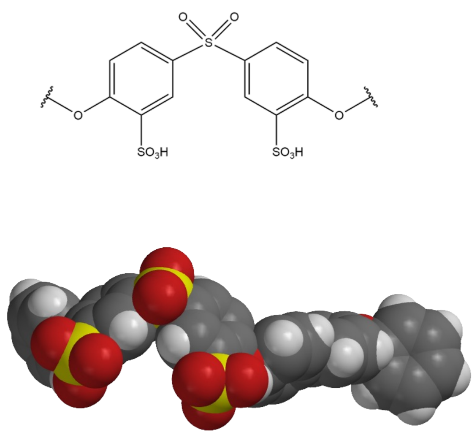
Introducing clusters of sulfonates

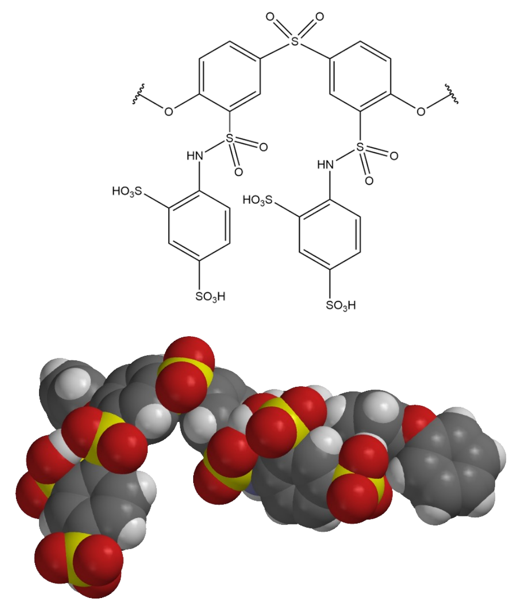


- Applied to both aromatic and PFSA materials



Multi-acid systems arranging to create water ‘bridging’ systems

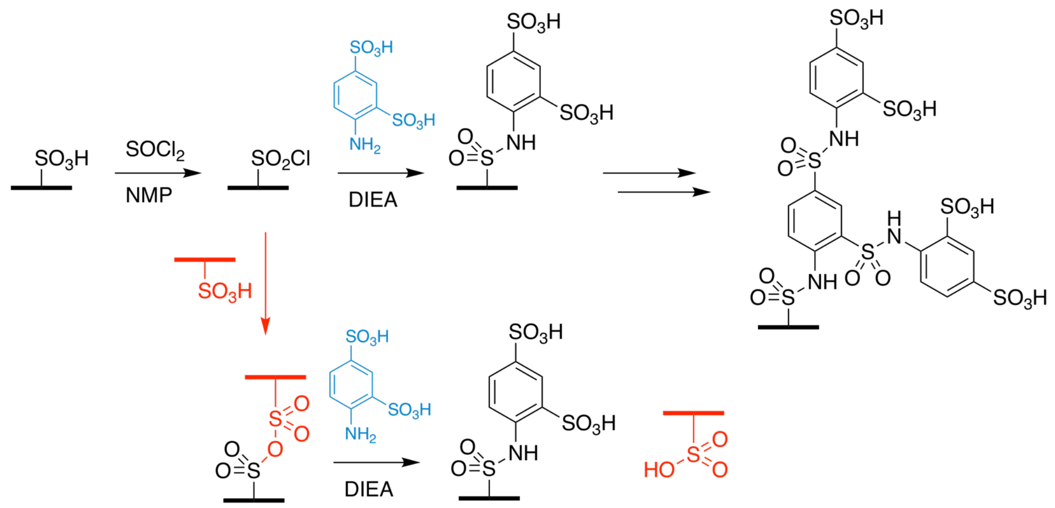




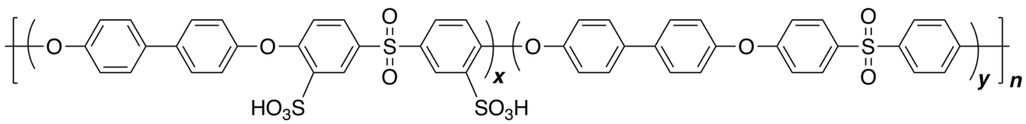
BoS First Generation

'Ball of Sulfonates' (BoS) is a strategy to chemically modify sulfonic acid groups of PEMs for efficient use of water to increase conductivity @low RH.

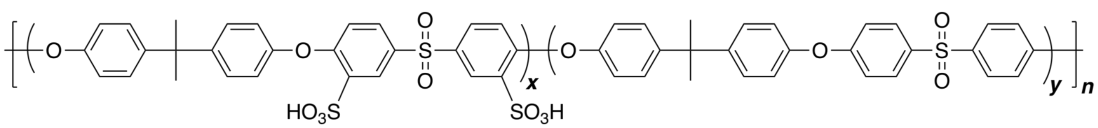
- Chemistry (***First Pass***):
  - Thionyl chloride/NMP or DMF for conversion of sulfonic acids to acid chlorides.
    - *Unintended formation of anhydrides reduces yield of sulfonamides.*
  - Sulfonamide derived from reaction with aniline di-sulfonic acid building block.
    - *This building block is not a great nucleophile.*



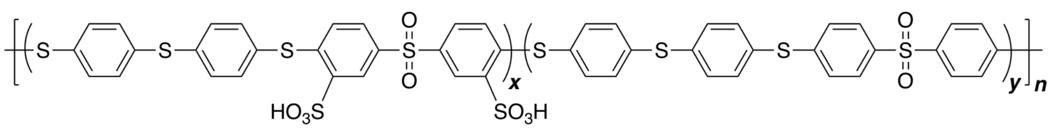
Polymers to be Modified (APS provided; UTK mod)



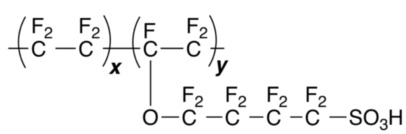
Biphenyl-Based Polysulfones



Bisphenol A-Based Polysulfones



Sulfonated Polythioether Sulfones



3M Ionomer

Synthetic Parameters

- The ***solubility*** of the polymers shown at left was evaluated in different solvents compatible with the BoS scheme: DME, 1,4-dioxanes, DCM, DCE, *DMAC*, *DMF*, and *NMP*.
- NMP was selected owing to its ***high boiling point*** (high temperatures can be used to improve reactivity of aniline building block) and its ***utility as a casting solvent*** (crude polymer solutions can be cast and by-products removed from membranes.

Casting Parameters

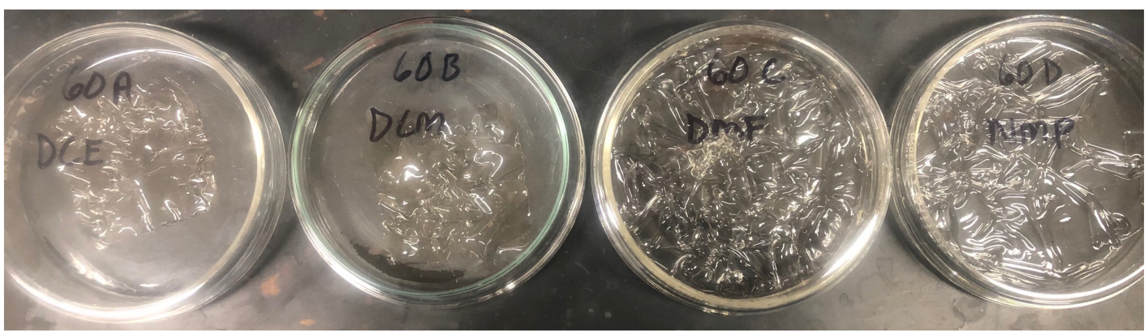
- Highly sulfonated aromatic polymers dissolve partially or completely in water.
- Control over thickness is possible by varying concentration of casting solution and thickness of solution applied (Dr. Blade).

Post-Casting Modification of 3M Membranes

Shown below are (5cm X 5cm) pieces of 3M825 PEMs suspended in different organic solvents for 1 hour under ambient conditions.

Both 60A (dichloroethane) and 60B (dichloromethane) maintain their dimensions; however they do show bending/folding which is not reversed on exposure to aqueous solution.

Both 60C (dimethylformamide) and 60D (N-methylpyrrolidone) showed swelling which resulted in loss of mechanical stability.



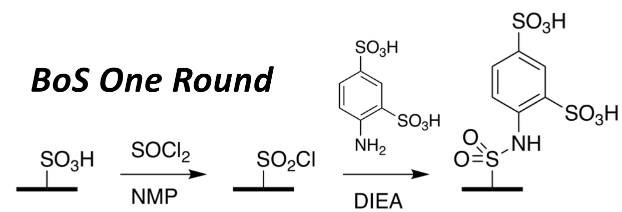
Several other organic solvents were examined using 3M825 membranes; however, none were suitable for heterogenous reactions.

Pre-Casting Modifications– Optimized

Membranes have been successfully cast using ***one round*** of BoS chemistry for biphenyl-based polysulfones (BP20, BP33, and BP35), bisphenol A-based polysulfones (BPA20 and BPA25), and 3M800.

These membranes were prepared by casting crude reaction mixtures of polymers on glass plates with a blade. The membranes were washed with peroxide, water, and sulfuric acid before use. The thickness of the membranes obtained ranged from 15 μm (3M800-BoS1) to 70 μm (BPA-BoS1).

BoS One Round



BOS Conductivity

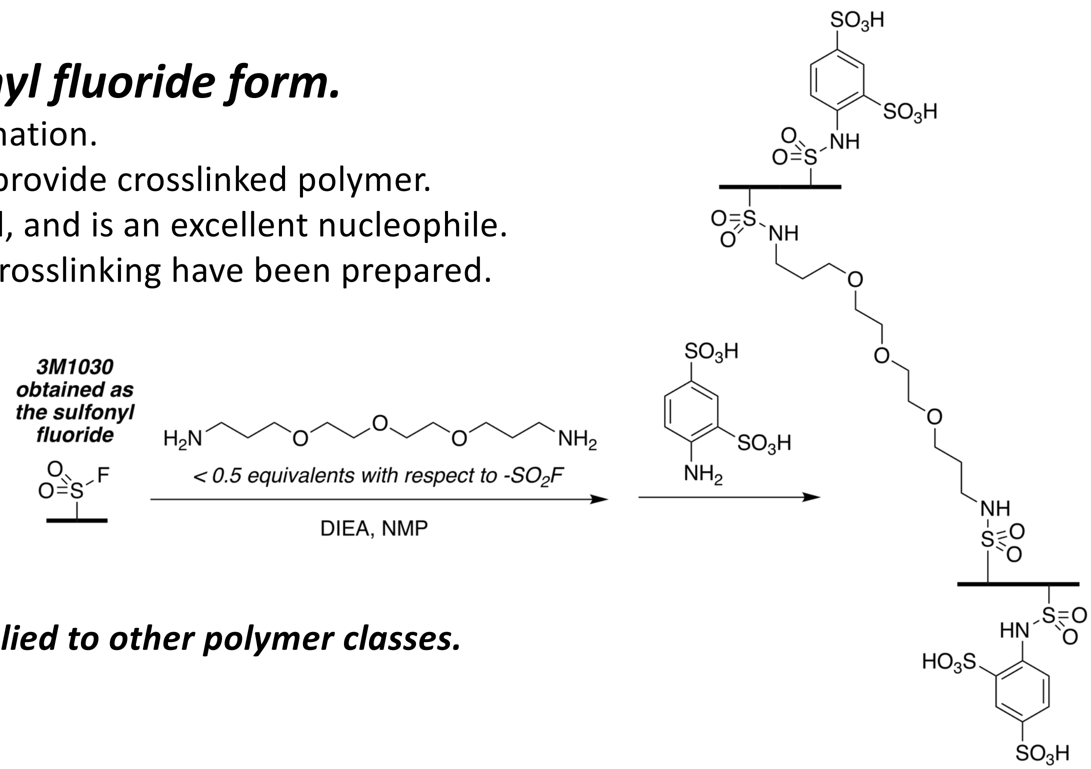
- Clearly need to have a minimum starting level of sulfonation to approach target conductivity

Membrane	Conductivity (mS/cm) @ RT
BP-20	6.6
BP-20-BOS-1	7.7
BP-33-BOS-1	42.6
BP-35-BOS-1	64.1

Pre-Casting Modification of PFSAs– Current Work

3M1030 was obtained in sulfonyl fluoride form.

- This removes issue with anhydride formation.
- Allows two-step, one-pot sequence to provide crosslinked polymer.
- Hydrophilic diamine cheap, commercial, and is an excellent nucleophile.
- Membranes with different degrees of crosslinking have been prepared.

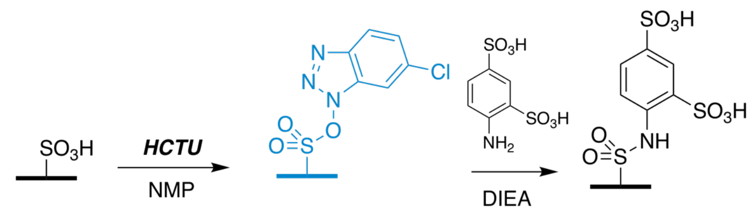


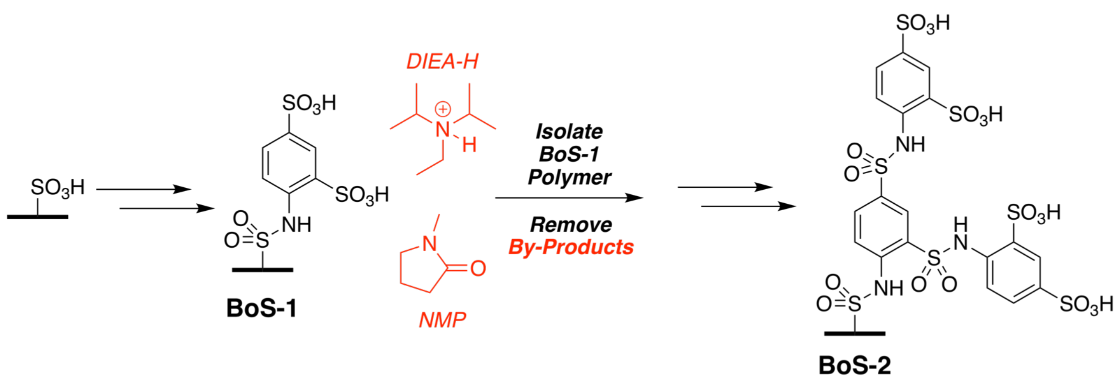
Similar crosslinking strategy could be applied to other polymer classes.

Pre-Casting Modification of PFSAs– Next Steps

Synthetic Adaptations to BoS-1 Scheme

- HCTU is a widely used peptide coupling reagent that can yield ***activated esters*** for reaction with amines.
- The greater bulk of the ester might offer some resistance to anhydride formation.





BoS-2 Synthetic Scheme

- NMR of BoS-1 membranes showed *traces* of ammonium salt and NMP.
- Isolation of the BoS-1 polymer by precipitation and subsequent aqueous washes to remove by-products provides starting materials for BoS-2.
- BoS-2 schemes are underway for BP, BPA, and 3M polymers.

Accomplishments and Progress Beyond Nexar

- Prepared 'BOS' systems based on aromatic and PFSAs
- Promising conductivity and water uptake obtained for Ar-BOS systems
- Synthesis and especially work-up are tricky and take time
- Need to get the EW just right to avoid solubility
  - PFSA-based systems are especially prone to dissolving
- Measurements are incomplete at this stage

Collaboration and Coordination

Partner	Top Level Role	Activities in Project
University of Tennessee	Prime	Polymer modification, processing, characterization
Oak Ridge National Lab	Sub	Polymer modification with TFSI
Akron Polymer Systems	Sub	Polymer syntheis, scaling as needed

- The team is work with commercial starting materials and substantial batches of materials from APS to allow preparation of test films of sufficient level of processing to be relevant.
- APS is capable of expanding polymer batch size toward commercial levels and scaling synthesis of promising candidates
- Planned continued interactions with Kodak coating facilities to prepare rolls of films; APS also and option.

Remaining Challenges and Barriers

- **Simple sulfonated aromatics are a non-starter for this application**
  - **Root cause: comparatively low acidity of this class of materials**
  - **Morphology can help somewhat but not at RH < 35%**
- Need to complete evaluation of BOS systems, TFSI side-chains
  - 'Multi-generation' BOS
  - Increase in testing throughput
  - Increase in synthesis throughput—challenging because of resources available plus slow delivery of reagents etc.
- Increase side-chain acidity
  - Challenging synthetically
- More emphasis on durability needed

Proposed Future Work

Next directions

1. Compare sulfonated aromatics with different electronic structure
   a. Can we eliminate the entire class? What then?
2. More extensive BOS-modified polymer synthesis and testing
   i. Broader range of backbone chemistry
   ii. Increased number of 'generations' of BOS additives
   iii. Controlling solubility and swelling
3. Increasing acidity
   i. TFSI BOS?
   ii. Evaluating possibilities of using fluorinated side chains on aromatic backbones to increase acidity
4. Increased emphasis on durability

Review Criteria

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter) Original Planned	Revised Planned	Actual	Percent Complete	Progress Notes
Y1Q1	First PPO-Br acquired.	progress	1/1/21	6/30/21	4/1/21	100%	UTK now has a supply of PPO-Br
Y1Q2	Functionalization of at least 3 commercially available polymers with TFSI groups.	progress	4/1/21	9/30/21		80%	Delays in obtaining some commercial materials
Y1Q3	Functionalization of first team-synthesized polymers with TFSI groups.	progress	7/1/21	12/31/21	1/31/22	100%	PPO-(SO2)$_2$NH has been prepared
Y1Q4	New durability test (peroxy radical) validated.	progress	10/1/21	3/31/22	--		Not started
Y1Q4	First publication of results.	progress	10/1/21	3/31/22		60%	Nexar results—MS in preparation
Y1Q4	At least one membrane achieving < 0.08 Ohm cm^2 at 120 °C assuming 15-micron thick film	SMART progress	10/1/21	3/31/22		60%	Eliminated 1 class; In progress
Year 1 GNG	Demonstrate at least one membrane that can meet target ASR at 120^{o}C if prepared as a 15-micron thick film.	GNG	10/1/21	3/31/22		60%	Need more time

Note: Project Just started at time of last review so no reviewer comments to address

Summary Slide

- Prepared modified Nexar systems
  - These fall short of goals
- Prepared ‘BOS’ systems based on aromatic polymers and PFSAs
- Promising conductivity and water uptake obtained for some Ar-BOS systems
- Synthesis and especially work-up are tricky and take time
- Need to get the EW just right to avoid solubility
  - PFSA-based systems are especially prone to dissolving
- Measurements are incomplete at this stage

Technical Backup and Additional Information Slides

Technology Transfer Activities

- Early stage for patenting
  - Focused on open sharing of information
  - Need something worth patenting!
- As noted, scale-up contingencies with APS and Kodak already part of project plan
- Beginning to have discussions/work with with other funded M2FCT participants; could implement durability strategies from their work