FY23 SBIR I: Modification of Nafion® Thermoplastic Precursor to Enable Reprocessing of Fuel Cell Manufacturing Scraps

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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

ROCKYTECH

Project Goals

(1) Modification of Nafion-SO2F to make reprocessible and durable Nafion membranes and dispersions

(2) Modification of recycled manufacturing scraps and end-of-life membranes for their reuse

Overview

Timeline and Budget

Project Start Date: 7/10/2023

Project End Date: 7/9/2024

Total Project Budget: $206,490.00

- -Total DOE Share: $206,490.00
- -Total Cost Share: $0.00
- -Total DOE Funds Spent: $55,999.63
- -Total Cost Share Funds Spent: $0

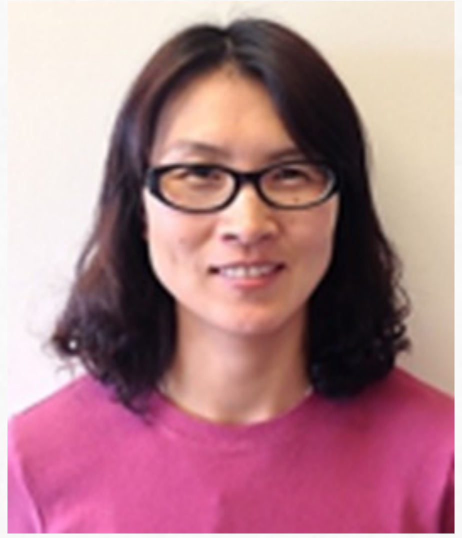
*As of 03/06/2024

Barriers

(1) Lack of suitable recycling mechanism for manufacturing scraps and spent Nafion membranes

(2) Poor reprocessibility of Nafion-ionomers for their reuse or repurpose

Partners



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Potential Impact

Lower Greenhouse Gas Emissions & Criteria Pollutants

- **Enhanced membrane service life:** By introducing dynamic covalent crosslinks, self-healing capability could be endowed to PEMs, which could expand PFSA-PEM lifespan.

Build Clean Energy Infrastructure

- **Improved recyclability:** By modifying PFSA-PEM precursors at the SO2F stage with click chemistry, recyclability can be introduced to the SO3H ionomer using thermal or solvent-based processes.

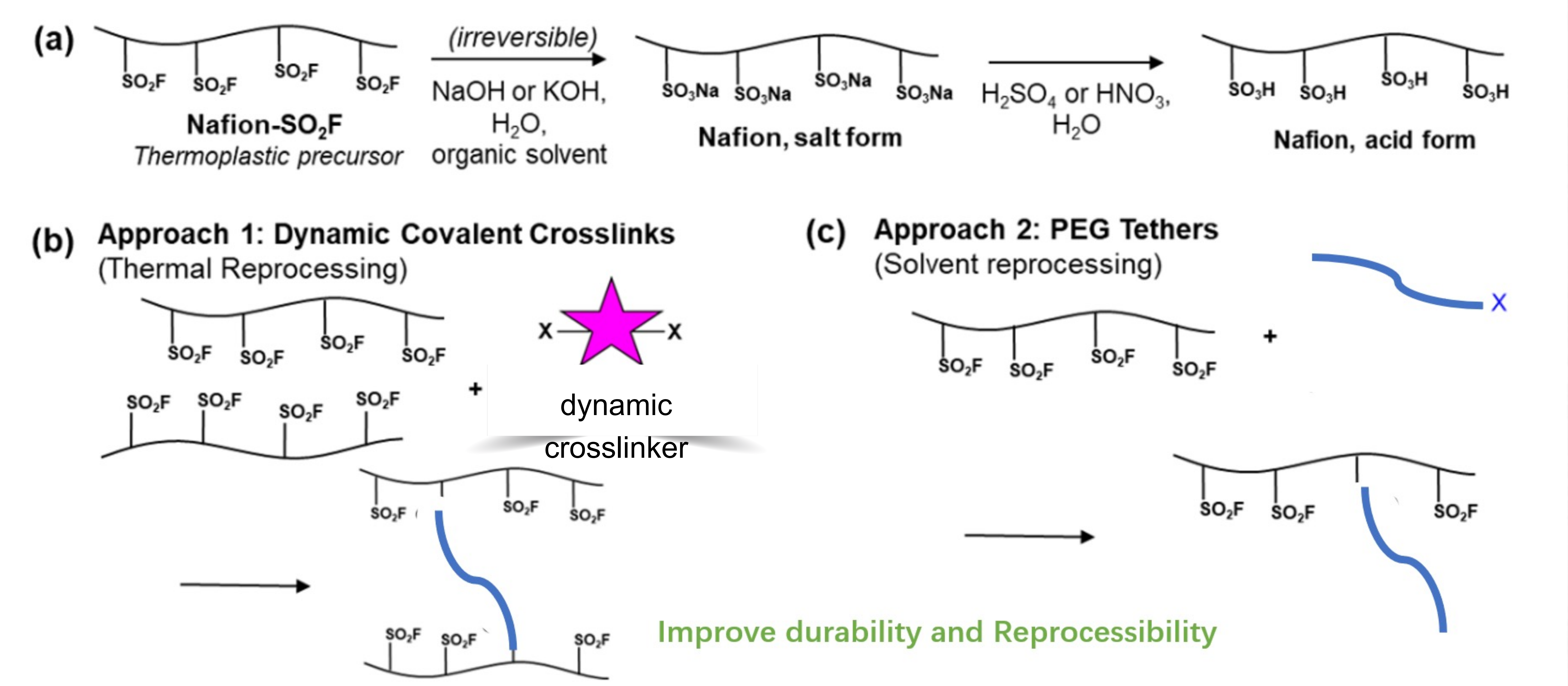
Support and Improve Energy, Environmental, or Social Justice

- **Environmental and social benefits:** Introducing circular PFSA-PEM materials will reduce fluorinated material waste, associated EOL emissions and hazards, as well as those of new manufacturing.

Provide Pathways to Private Sector Uptake

- **Easy integration into existing manufacturing process:** Utilizing rapid click chemistry on the SO2F precursor aligns with current PFSA-PEM production methods, ensuring a smooth transition of this precursor into the ionomer membrane.

Two Approaches for Nafion Modification

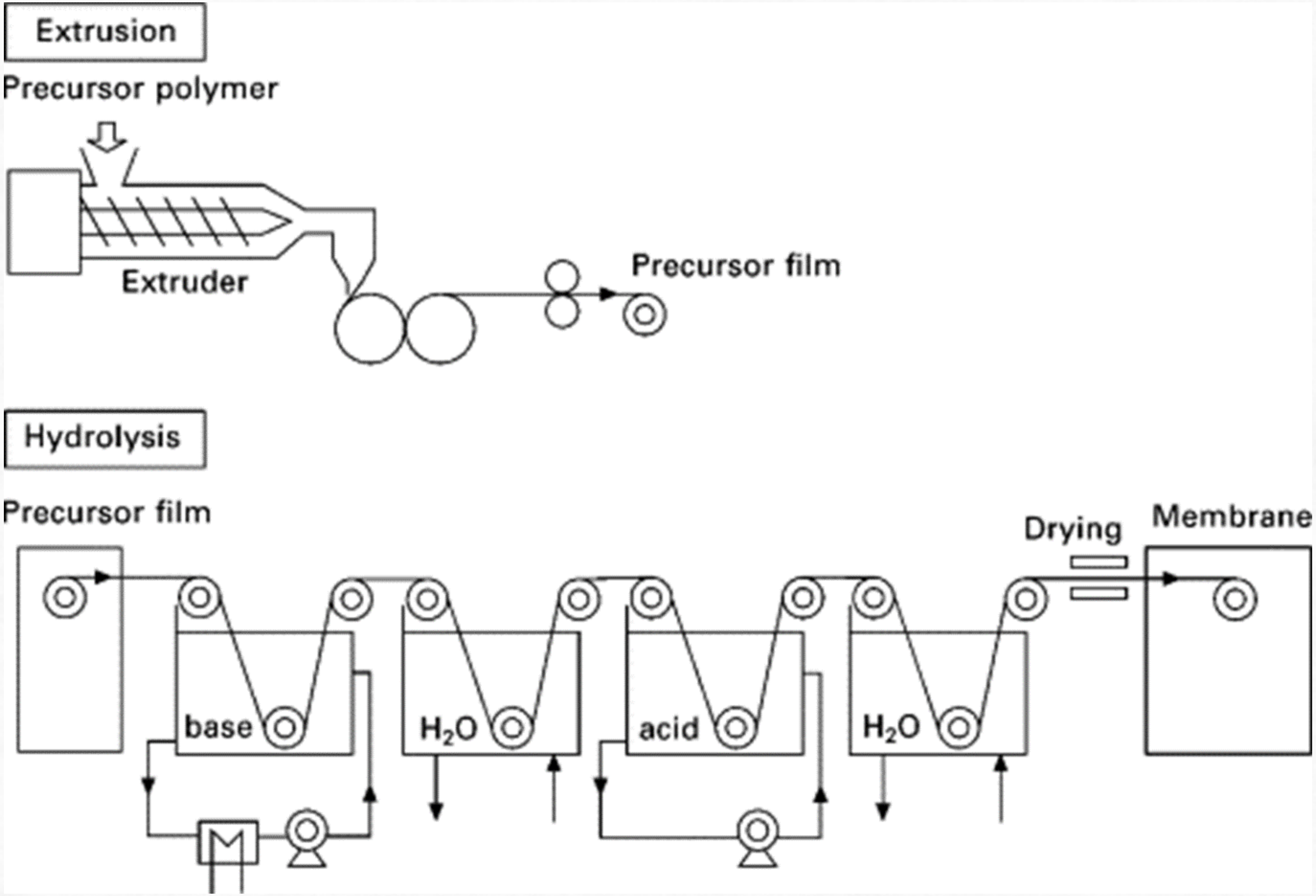


(a) Typical manufacturing process of Nafion®

(b) Our covalent adaptable network approach to recycling

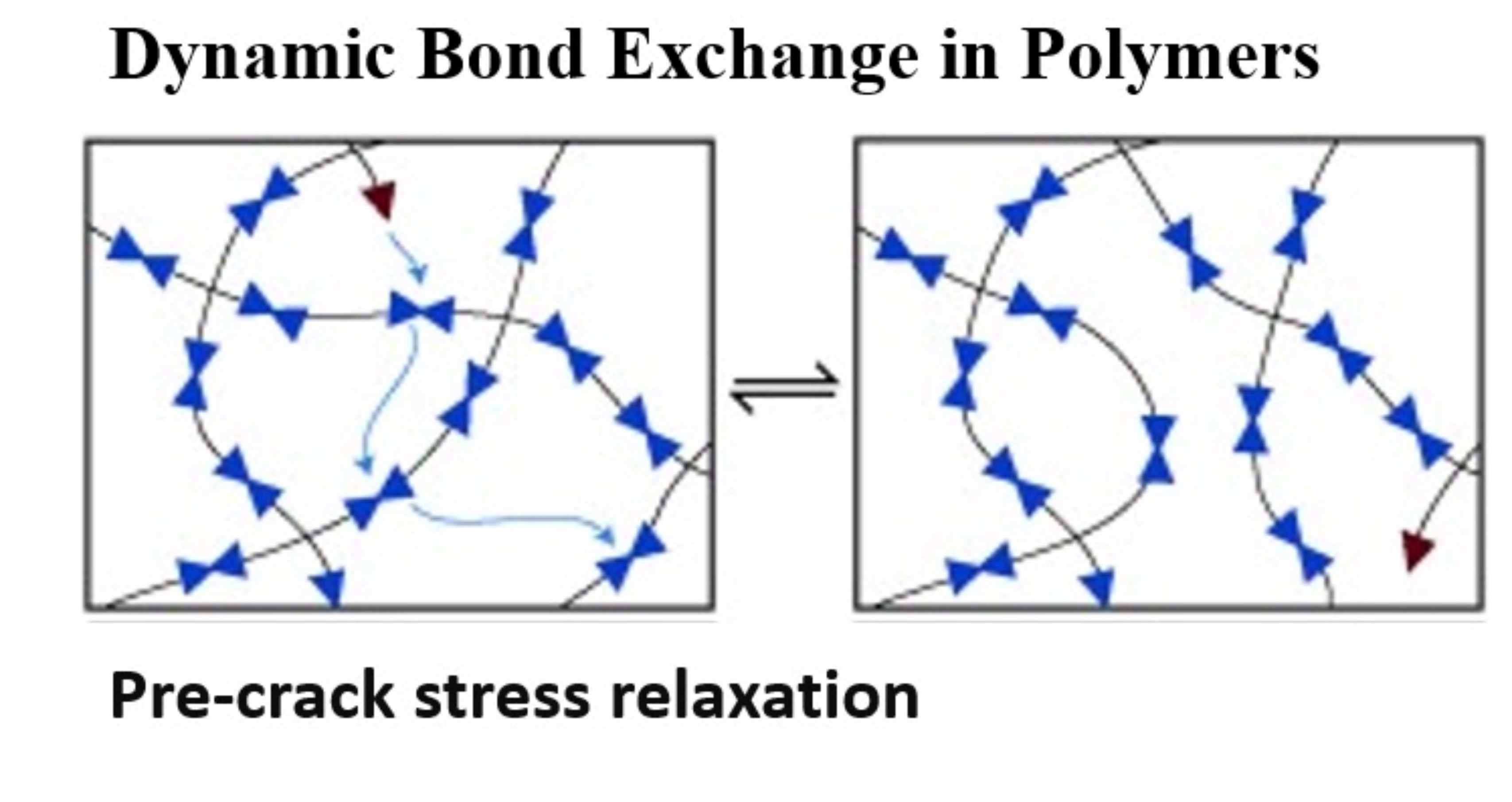
(c) Our hydrophilic modification approach to recycling. (Conversion to SO3H after modification not shown.) The repeat unit of the polymer backbone is CF2CF2.

Manufacturing Process for Membrane



Approach 1: Dynamic Covalent Crosslinks

Covalent Adaptable Network (CAN) Rearrangement

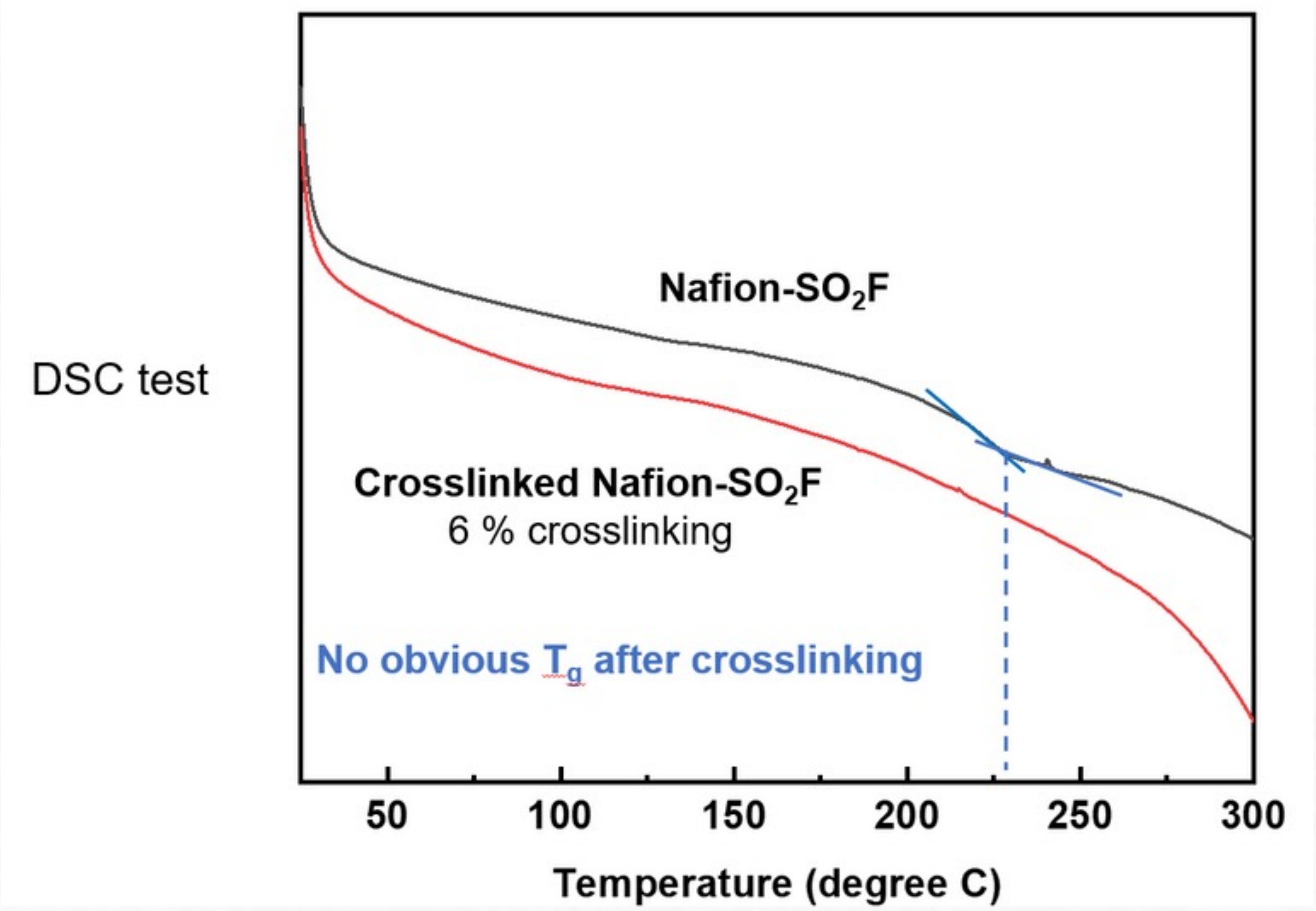


Dynamic bond exchange in polymers enables stress relaxation before crack formation.

Approach 1: Dynamic Covalent Crosslinks

Material Preparation: Accomplishments & Progress

DSC analysis of crosslinked Nafion-SO2F

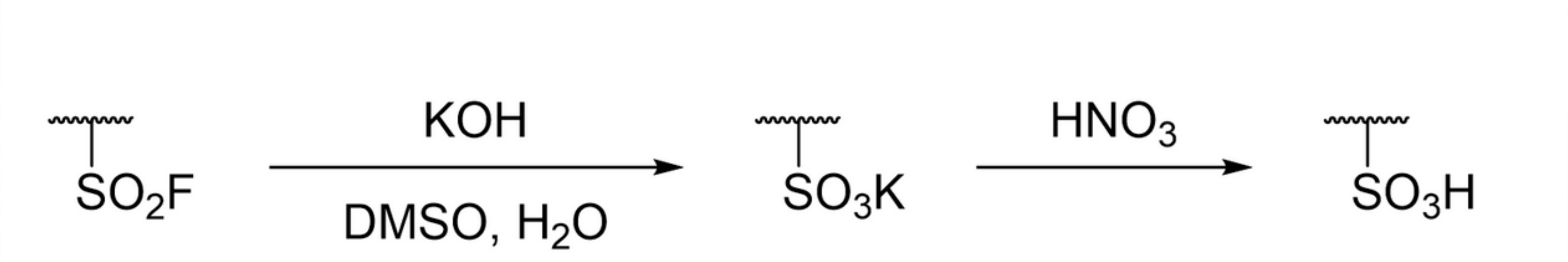


Introduction of crosslinking was successful

Approach 1: Dynamic Covalent Crosslinks

Material Preparation: Accomplishments & Progress

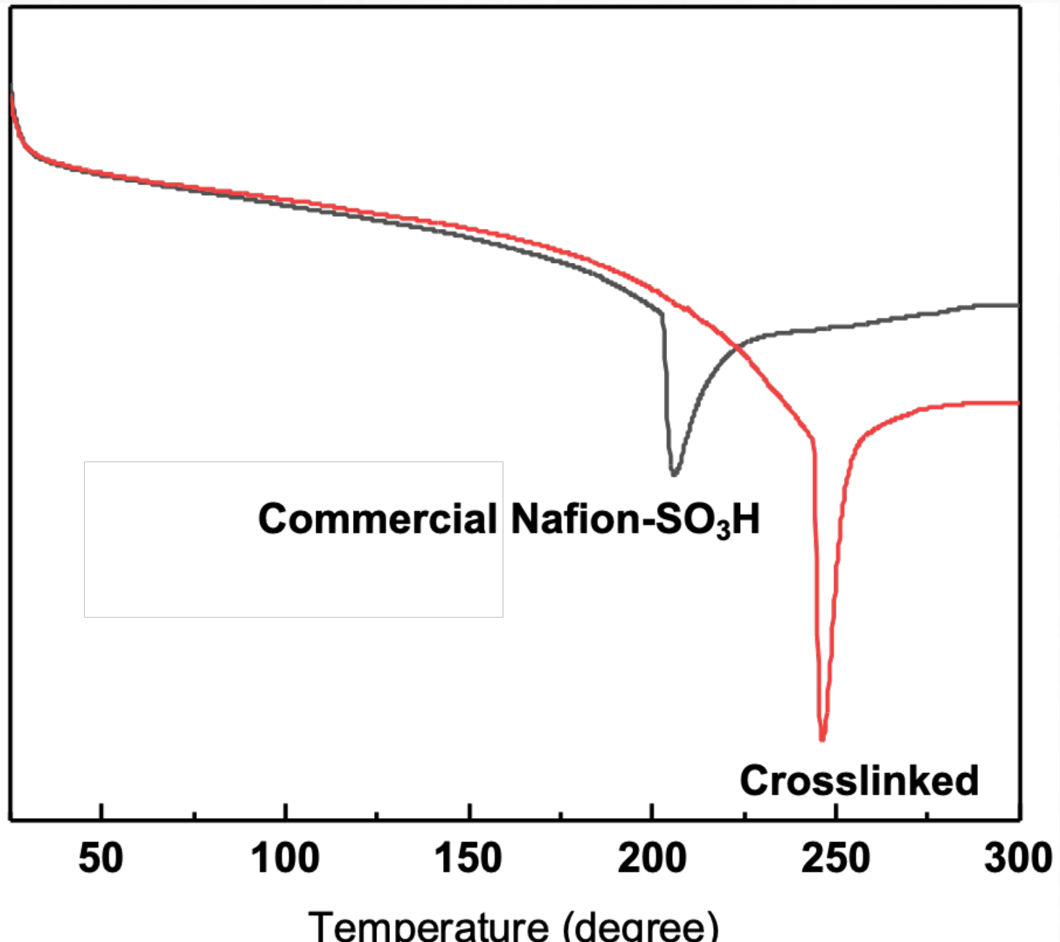
Nafion SO2F Hydrolysis to Nafion SO3H



Crosslinked Nafion-SO3H Comparison

Control Sample: Commercial Nafion-SO_3H membrane (Nafion N-115, Ion Power, Inc.)

Crosslinked sample: Nafion-SO_3H-Crosslinked made from crosslinked Nafion-SO_2F through hydrolysis (6 mol% crosslinking)



Approach 1 Summary

Crosslinkers have been successfully introduced

Evidence:

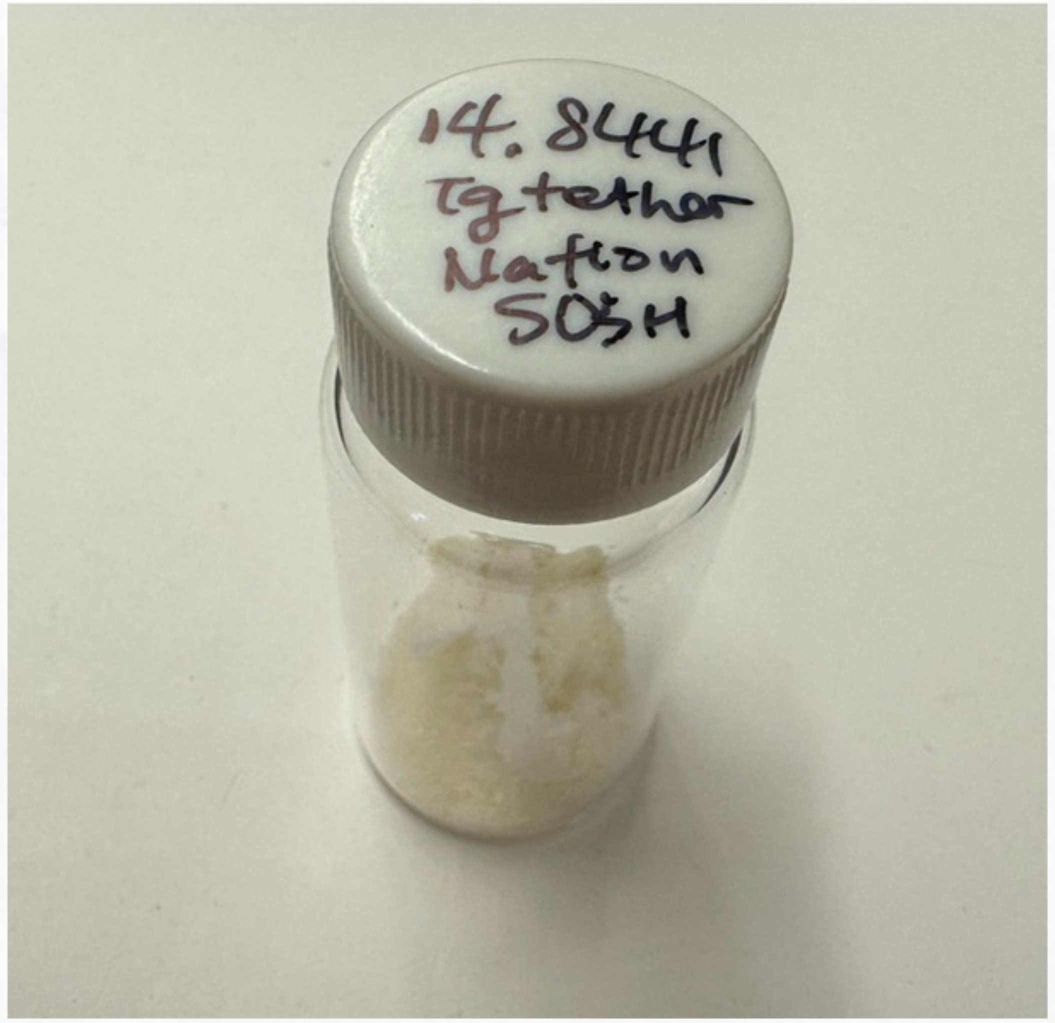
- Small molecule modeling
- Infrared (IR) spectroscopy
- Differential scanning calorimetry (DSC)
- Energy-dispersive X-ray spectroscopy (EDS) mapping

Crosslinked Nafion-SO3H: Reprocessible from powder to film, but mechanical properties of the film needs to be investigated

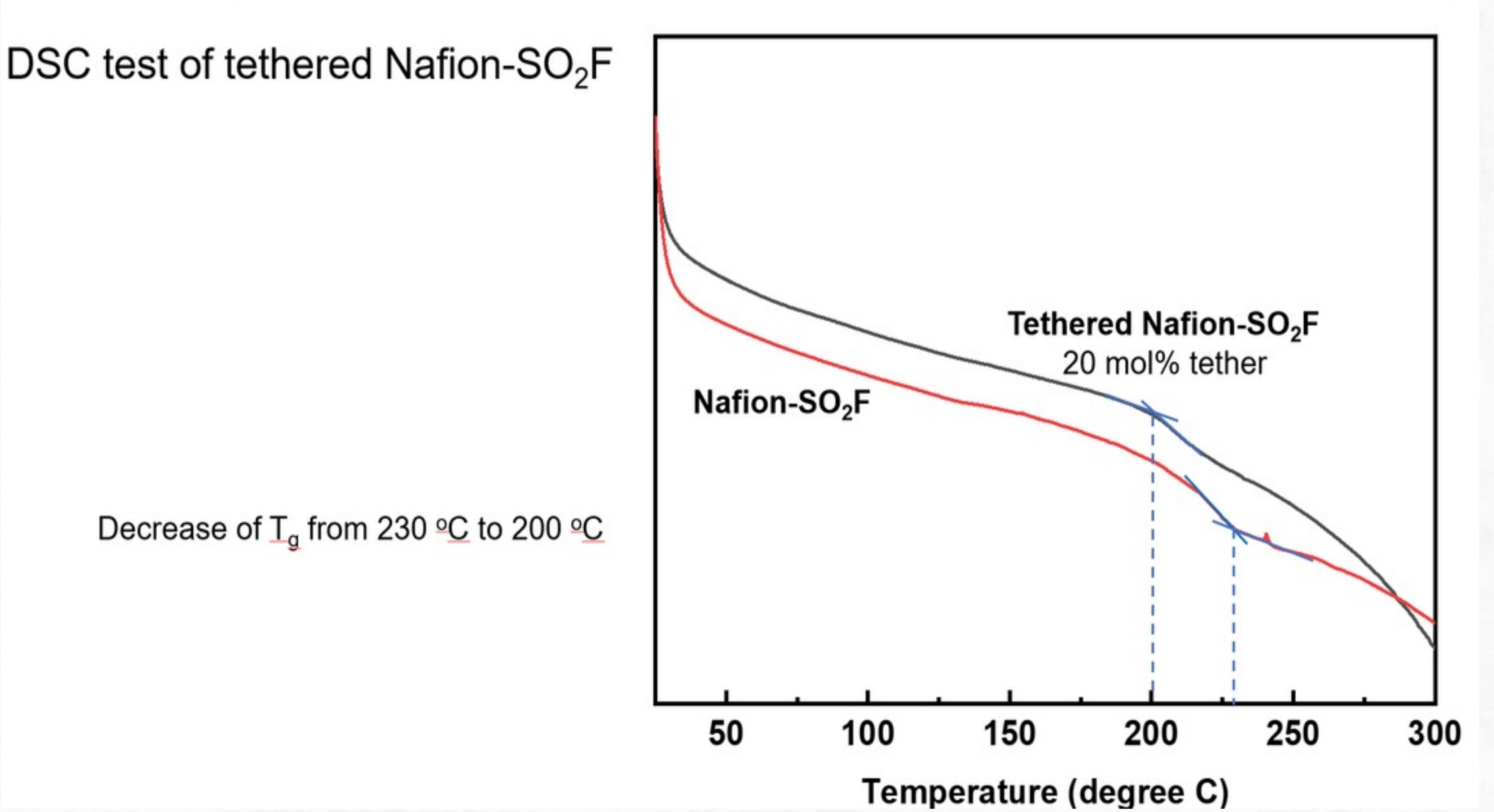
Approach 2: PEG Tethers

Material Preparation: Accomplishments & Progress

Preparation of Tethered Nafion-SO3H



Tethered Nafion-SO2F Shown with a DSC Test

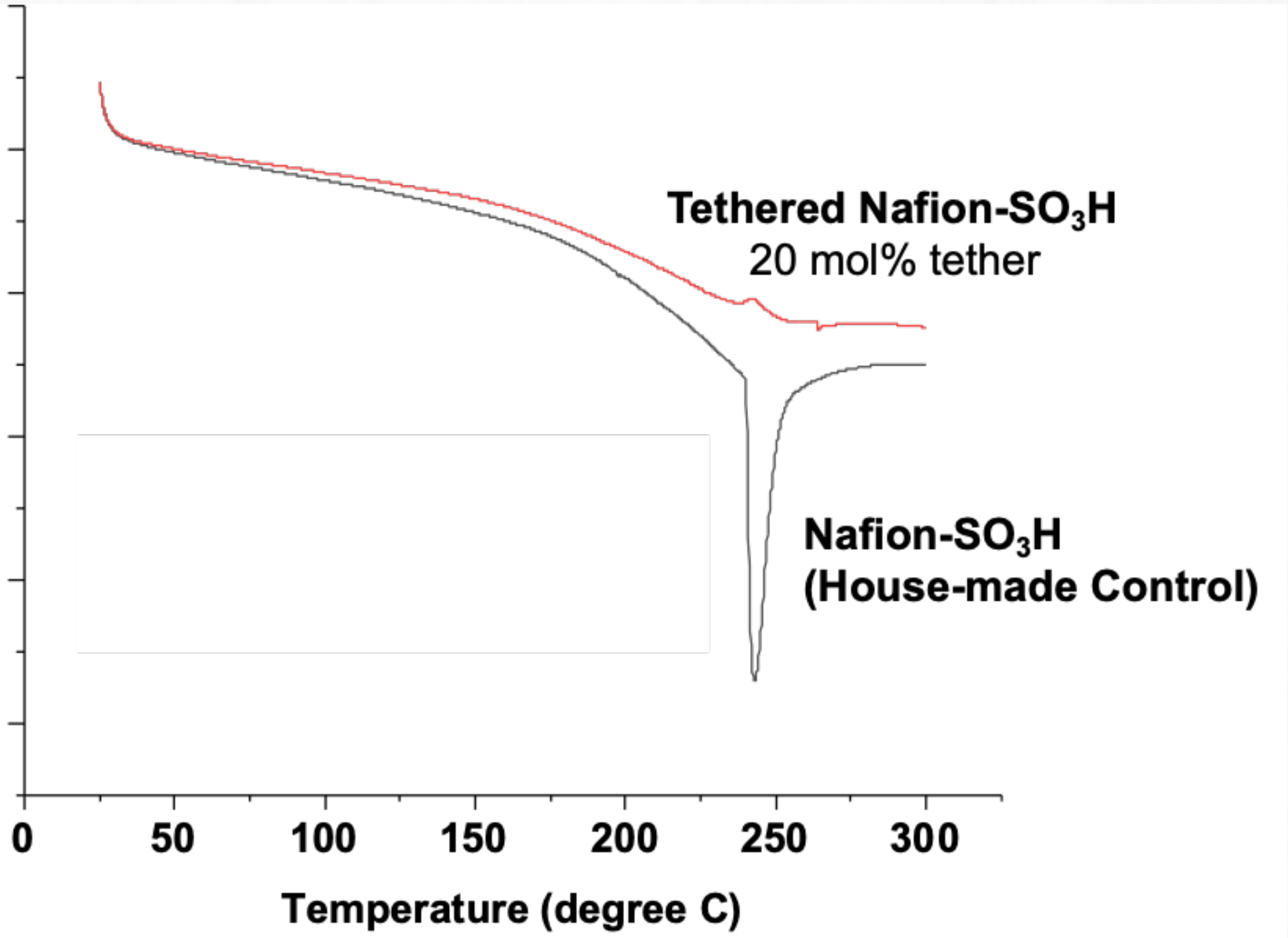


Approach 2: PEG Tethers

Material Preparation: Accomplishments & Progress

Tethered Nafion-SO3H

Tethered sample: Nafion-SO_3H-Tethered made from Tethered-Nafion-SO_2F through hydrolysis (20 mol% tethers)



Approach 2 Summary

Tethers have been successfully introduced

Evidence:
- Small molecule modeling
- Infrared (IR) spectroscopy
- Differential scanning calorimetry (DSC)

Tethered Nafion-SO3H:
- Reprocessable from powder to film, though discoloration occurs. The cause of this discoloration warrants investigation.
- The material disperses easily in a water/isopropyl alcohol co-solvent

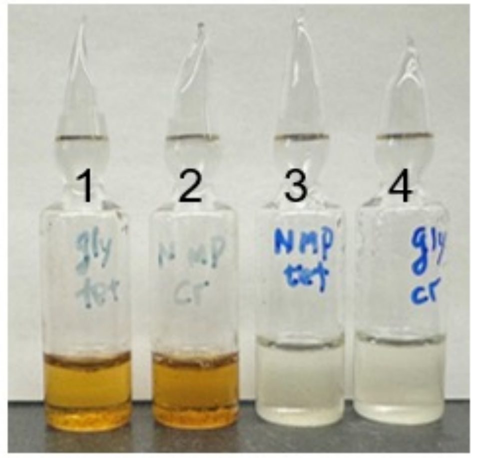
Approach 2: PEG Tethers

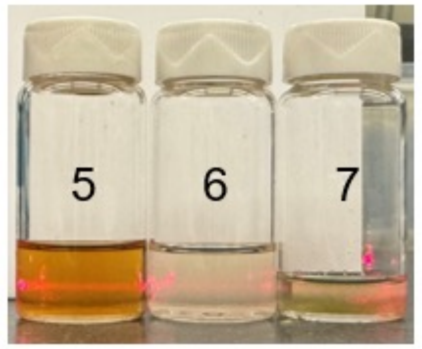
Reprocessibility: Accomplishments & Progress

Dispersibility of Tethered Nafion-SO3H

Trials	Source	Form	Solvent	Condition	Results
1	Tethered powder	$-SO_3Na$	Glycerin	210 °C for 3 h	A lot of polymer left
2	Crosslinked powder	$-SO_3Na$	Glycerin	210 °C for 3 h	A lot of polymer left
3	Tethered powder	$-SO_3Na$	NMP	100 °C for 1 h	A lot of polymer left
4	Crosslinked powder	$-SO_3Na$	NMP	100 °C for 1 h	A lot of polymer left
5	Commercial	$-SO_3Na$	H_2O/IPA	250 °C, overnight	Dissolved
6	Made from commercial Nafion-SO_2F	$-SO_3K$	H_2O/IPA	250 °C, 3 h	A lot of polymer left
7	Tethered powder	$-SO_3H$	H_2O/IPA	250 °C, 3 h	Dissolved

2.5 wt% dispersion





Tyndall Effect

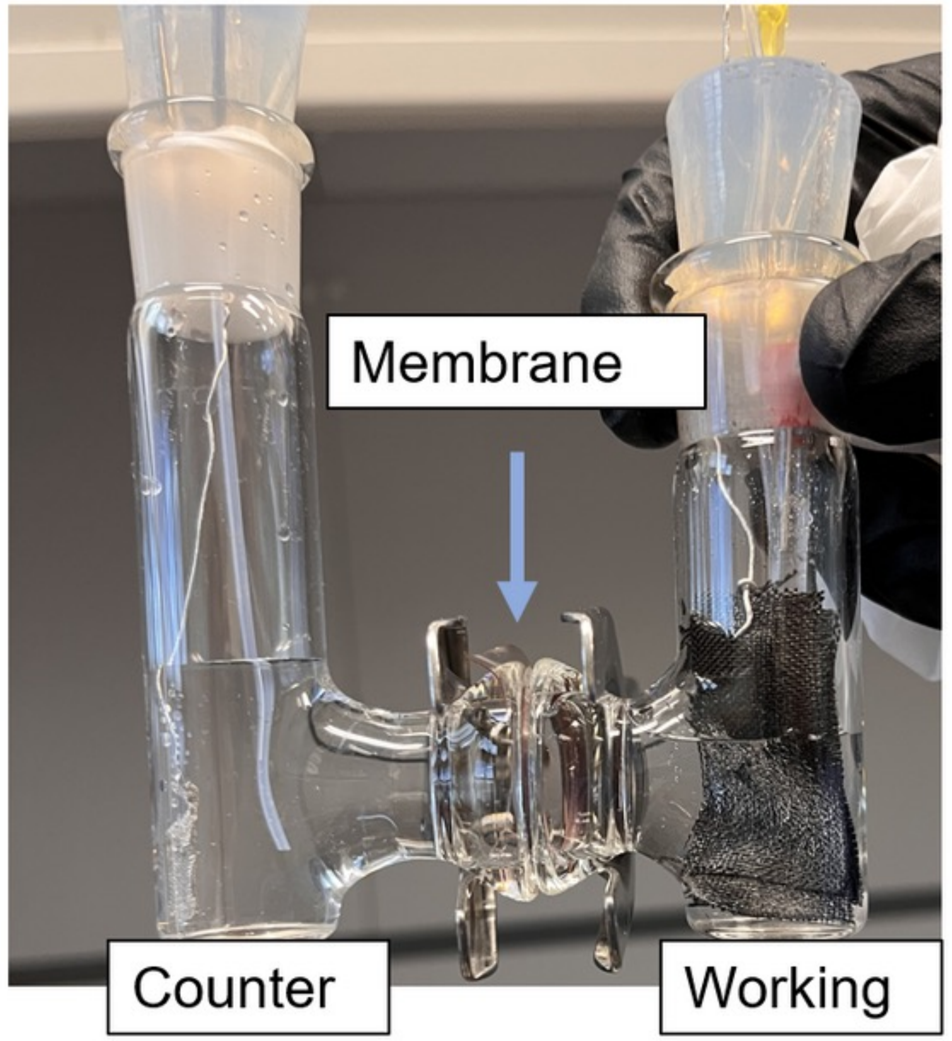
7 in larger scale

- Tethered powder can be dispersed
- The material disperses easily in a water/isopropyl alcohol co-solvent

Cell Testing Conditions

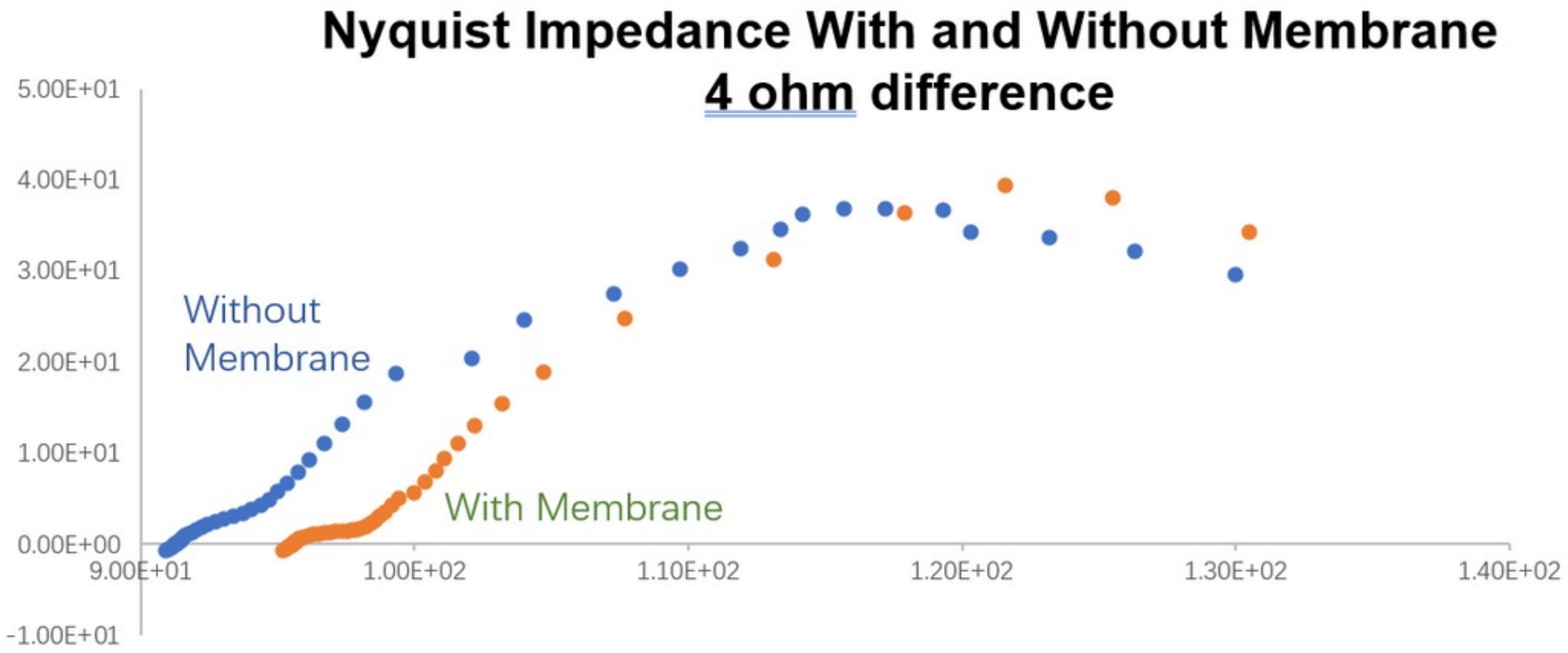
Performance: Accomplishments & Progress

Cell Set-up and Nyquist Impedance



H-cell configuration

-Platinum electrodes
-Membrane separating chambers
-Impedance measured across



Cell Testing

Performance: Accomplishments & Progress

Proton Conductivity and Swelling Rate

Proton Conductivity Experimental

-Applied 10mV
-Ambient temperature or heated
-72 hour pre-soak
-Measure potentiostatic electrical impedance

Nafion Type	Temperature(°C)	Proton Conductivity(mS/cm)
Nafion 115	25+/- 2	40.3
Nafion 115	70 +/- 5	52.3
Recast	25+/- 2	37.6
Recast	70+/- 5	71.9

Swelling Rate Horizontal

Nafion 115- 10%
Recast- 5%

Swelling Rate Width

Nafion 115- 38%
Recast- 8%

- Recast tethered Nafion has a significant jump in proton conductivity at elevated temperature—very promising.
- The swelling rate for the recast Nafion is decreased
- The recast membrane likely exhibits enhanced durability due to its reduced swelling.

Milestones & Summary

- **Milestone 1: Material Preparation.** Crosslinkers and tethers have been successfully integrated into the Nafion-SO2F thermoplastic precursor, leading to the successful preparation of the modified Nafion-SO3H ionomer. This method was confirmed through model reactions utilizing small molecule model compounds. Characterization of the materials was performed using IR spectroscopy, DSC, and EDS.
- **Milestone 2: Reprocessibility.** The reprocessing of crosslinked Nafion-SO3H and tethered Nafion-SO3H has been examined by employing heat press techniques and dispersion methods.
  - The crosslinked Nafion-SO3H can be reprocessed from powder to film, although the mechanical properties of the resulting film require further investigation.
  - Tethered Nafion-SO3H can be reprocessed from powder to film, but it experiences significant discoloration. Investigating the cause of this discoloration is essential, and thermogravimetric analysis (TGA) would be an excellent technique to assess potential decomposition.
  - The material easily disperses in a co-solvent of water and isopropyl alcohol.
- **Milestone 3: Performance.** The electrochemical properties have been evaluated, and the initial results are highly promising. Tethered Nafion-SO3H membranes prepared via heat press, albeit the discoloration, demonstrate less swelling and higher conductivity at 70°C compared to commercial Nafion 115.
- **Go/no-go decision:** We have validated the chemical modification method and the reprocessibility and performance enhancement of modified Nafion-SO3H. Based on the promising results we plan to continue the development in Phase II.

Accomplishments and Progress:
Responses to Previous Year Reviewers' Comments

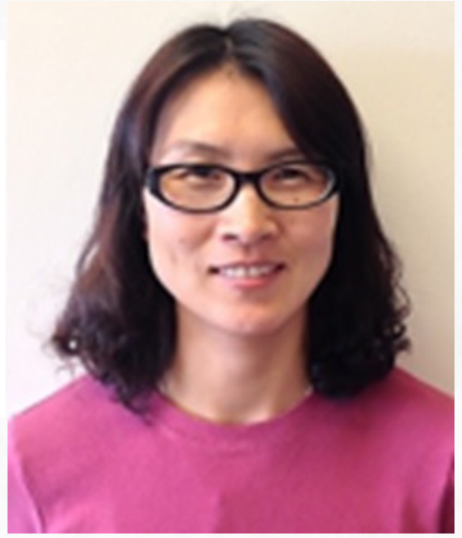
This project was not previously reviewed at an AMR.

Safety Planning and Culture

- **Safety Training**: Annual safety training is required for all employees which covers but is not limited to: handling of hazardous materials, emergency procedures, and proper use of PPE.
- **Personal Protective Equipment (PPE)**: PPE is required for all employees within the lab space, which includes gloves, goggles, and a lab coat at a minimum.
- **Emergency Preparedness**: Eyewash station, Safety shower, first aid kit, and chemical spill skit are readily accessible in the lab space.
- **Communication**: When transferring novel materials from one sub-contractor to another, potential hazards and risks of the material are clearly communicated.

A safety plan was not required for this project.

Collaboration and Coordination



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DEIA/Community Benefits Plans and Activities

RockyTech is committed to supporting and advocating for underrepresented communities in the field of science.

RockyTech's team is:
67% female
78% minorities
11% persons with disabilities

This project is not required to have a CBP or DEIA plan.

Remaining Challenges and Barriers

(1) Fabrication of robust and durable membrane made of modified Nafion-SO3H

(2) Upcycling of end-of-life membrane and manufacturing scraps through similar chemical modification approach

(3) Integration of chemical modification step into the existing manufacturing process

Proposed Future Work

Phase I

- Production of films from crosslinked and tethered Nafion-SO3H, which are derived from Nafion-SO2F thermoplastics, through methods such as heat pressing or drop casting.
- Surface reaction of Nafion-SO2F films for more seamless integration into current Nafion membrane production.
- Electrochemical testing of in-house materials to compare them with commercial membranes in terms of water uptake, swelling ratio, proton conductivity at various temperatures, hydrogen crossover current density, and gas permeability.

Phase II

- Fabrication of Membrane Electrode Assemblies (MEAs) and conducting their performance tests
- Membrane properties refinement through the use of various crosslinkers and tethers (Structure-properties relationship study).
- Scale up possibility and collaboration
- Evaluation of end-of-life Nafion membranes to explore the possibility of recycling, repairing, and reusing them by restoring their properties through crosslinking or tethering methods. This feasibility will depend on the amount of residual SO2F groups present in the end-of-life membranes.

Summary

- **Material Preparation**: Crosslinkers and tethers have been successfully integrated into the Nafion-SO2F thermoplastic precursor, leading to the successful preparation of the modified Nafion-SO3H ionomer. This method was confirmed through model reactions utilizing small molecule model compounds. Characterization of the materials was performed using IR spectroscopy, DSC, and EDS.

- **Reprocessibility**: The reprocessing of crosslinked Nafion-SO3H and tethered Nafion-SO3H has been examined by employing heat press techniques and dispersion methods.
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    - The material easily disperses in a co-solvent of water and isopropyl alcohol.

- **Performanc**e: The electrochemical properties have been evaluated, and the initial results are highly promising. Tethered Nafion-SO3H membranes prepared via heat press, albeit the discoloration, demonstrate less swelling and higher conductivity at 70°C compared to commercial Nafion 115.