EE-0009245

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Additive Functionalized Polymers for Extended HD Polymer Electrolyte Membrane Lifetimes

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Lab Partners: NREL
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AMR Project ID #FC335

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Project Goal

Project Goal – To develop membranes with enhanced chemical durability to improve the lifetime of PEM fuel cells for heavy-duty vehicles

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Overview

Timeline

Project Start: Q2 2021

Project End: Q3 2023

Budget

Total Project Budget: $1,250,000

Total Recipient share: $250,000

Total Federal Share: $1,000,000

Barriers and Targets

Barriers addressed

- Chemical durability of PEMs
- Shortcomings of current radical scavengers
- Fuel cell stack lifetime

Targets

- Demonstrate membranes with >500 h OCV durability
- Enable DOE target of 25,000 h/1,000,000 mile HD truck lifetime

Partners

NREL – Golden, CO

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Relevance

Objectives:

- Identify novel additives to mitigate chemical degradation of membranes for PEM fuel cells
- Address current radical scavenger shortcomings through immobilization of novel additives
- Improved membrane durability to enable clean energy PEMFC HD vehicles with 1,000,000 mile/25,000 h stack lifetime

Targets for Current Year Project

- Prepare PEMs with impregnated additives designed to improve chemical stability
- Prove efficacy by matching or exceeding state-of-the-art membrane technology in OCV ASTs
- Demonstrate covalent functionalization strategies to be utilized for immobilization within polymer electrolyte

Go/No-Go: *Demonstrate AST chemical stability of equal or greater to cerium doped PFSA. OR demonstrate 3x or greater AST chemical stability vs non-additized sulfonated hydrocarbon PEM*

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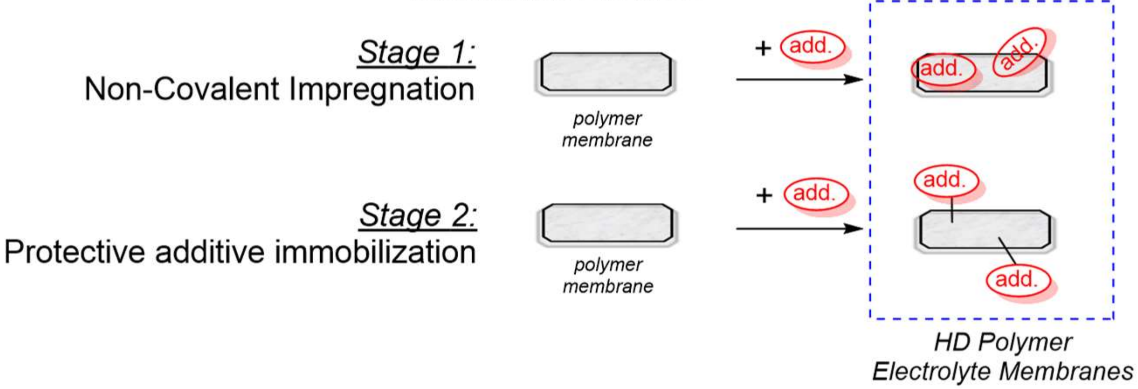
Approach

Membrane durability enhancement will first be evaluated by high throughput OCV screening of PFSA and hydrocarbon ionomers with non-covalent, dispersed additives. High performing additives will be utilized for two proposed covalent functionalization strategies to each ionomer system and membranes will be prepared. Characterization, durability, and performance data will be assessed for functionalized membranes.

Immobilization of additives for Improved HD Polymer Electrolyte Membrane Lifetime



Deliverables

Stage 1: *Non-covalent impregnation*

- Prepare minimum of 8 unique PFSA membranes with impregnated additives.
- Prepare a minimum of 4 unique hydrocarbon base membranes with impregnated additives
- Evaluate membrane durability using established OCV ASTs for additive down selection

Stage 2: *Additive immobilization*

- Prepare a minimum of 4 membranes utilizing diverse polymer functionalization strategies to immobilize additives on PFSA ionomers
- Prepare a minimum of 4 membranes utilizing diverse polymer functionalization strategies to immobilize additives on hydrocarbon ionomers

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Accomplishments + Progress

Hand casting PFSA Membranes

1. Initial conditions resulted in poor film formation

2. Formulation optimization enabled in-tact membrane films

3. Further drying condition optimization afforded pristine membranes

4. System is compatible with most additives to be screened

Evolution of PFSA membrane formulation and casting conditions

Solvent, additive, and ionomer system was identified and successful membrane casting achieved

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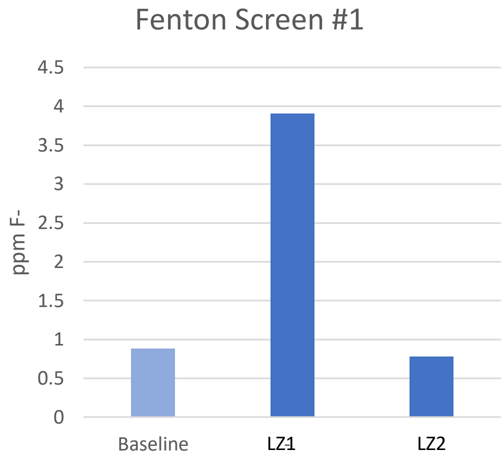
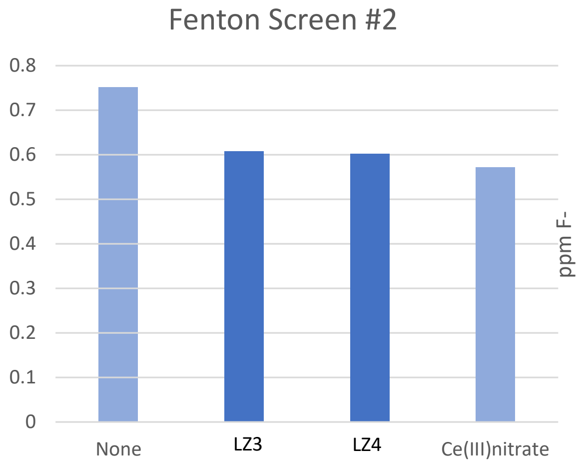
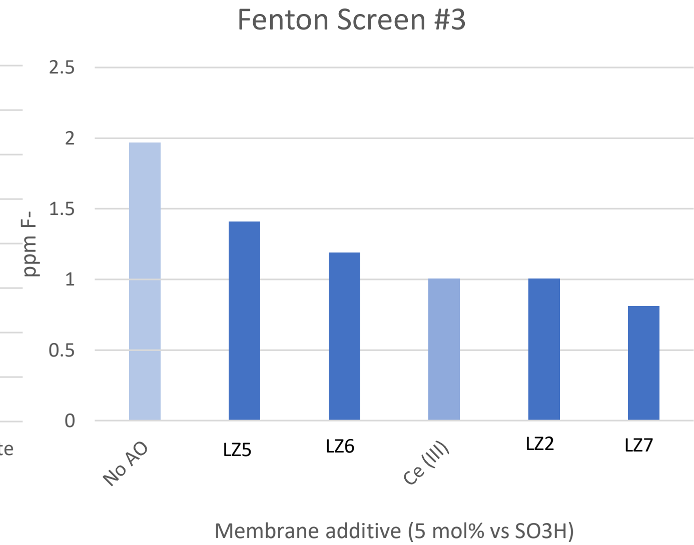
Accomplishments + Progress

Fenton Oxidation Testing

- Fenton Testing to be used as a means to rapidly screen for ionomer stability in a heavily oxidative environment.
  - 10% H_2O_2 + 10 ppm $Fe^{2+} \rightarrow \cdot OH + \cdot OOH$
- On-site testing capabilities confirmed:
  - Repeatability and reliability of method.
  - Established calibration standards appropriate for detection regime.
  - High throughput capacity for rapid screening of lead candidates.







Lubrizol chemistries have positive impact on fluoride release in solution Fenton test

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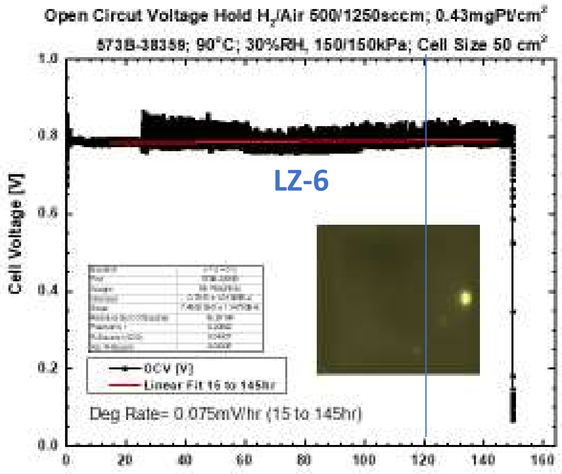
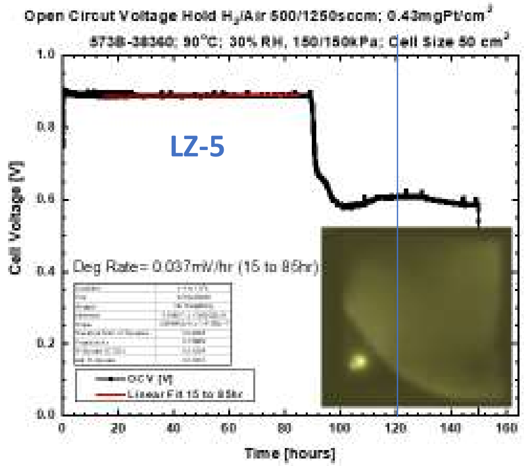
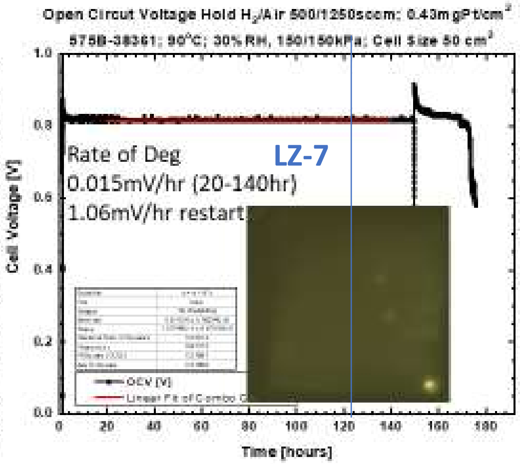
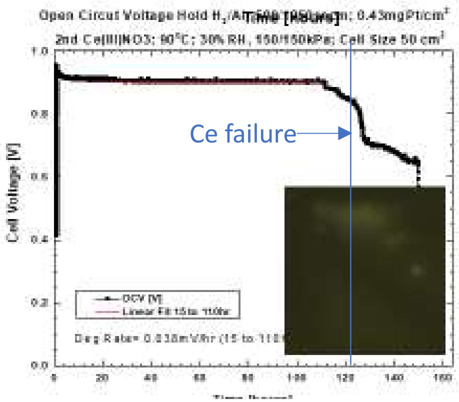
Lubrizol Cast Membranes

OCV Hold – Lubrizol cast, 3rd shipment, Parallel, Not Conditioned









- All these cells show an improvement of OCV over a long period of time. This may be again related to conditioning.
  - 573B-38359: -75 µV/hr
    - Improving, stable over 150 hrs, promising
  - 573B-38360: -37 µV/hr
    - Improving, stable over 85 hrs, promising, hole developed
  - 573B-38361: -15 µV/hr
    - Improving, stable over 140 hrs, promising, hole developed after restart
  - Ce(III)NO3: 38 µV/hr
    - stable over 110 hrs, hole developed at 115 hrs, not captured well in IR
- AO seem to contribute to effect that improves OCV over time
  - Reason currently unclear.

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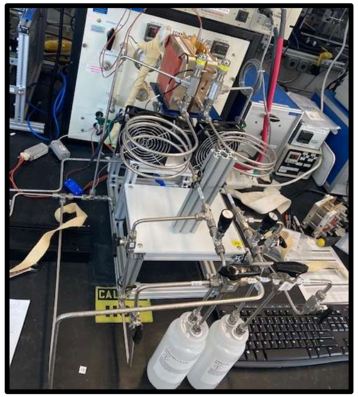
Effluent Water Collection

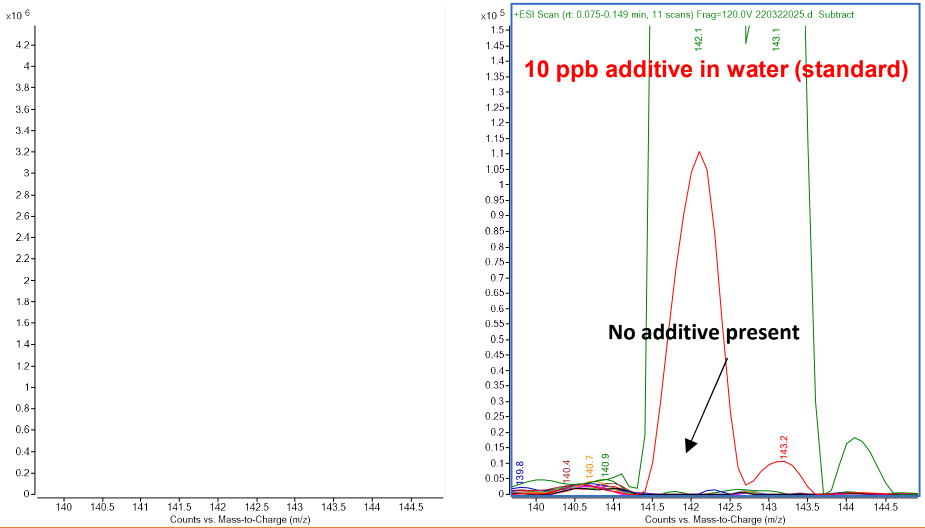
Goals:

- Set up apparatus to collect effluent water on anode and cathode during fuel cell operation
- Analyze water collections for presence of additive due to leaching
- Analyze water collections for fluoride and ionomer degradation products to study rate of degradation.



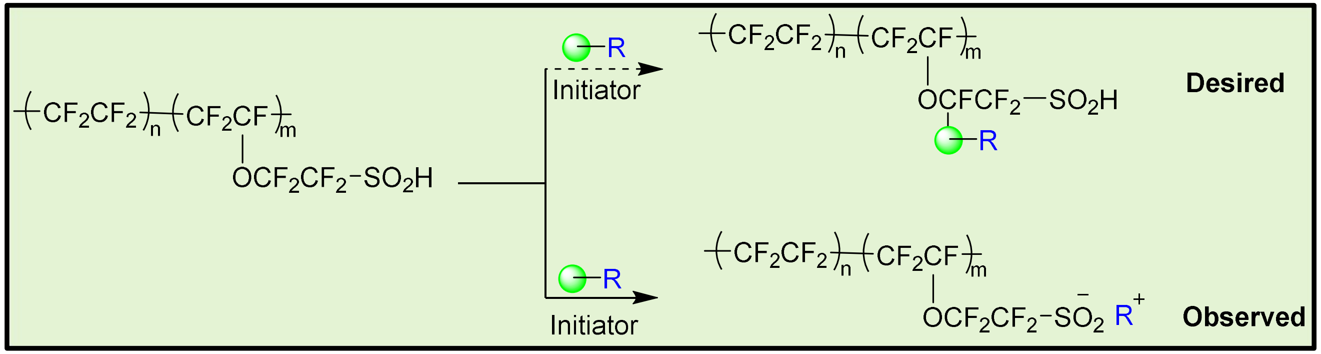
Results:

- NREL set up test station with water collection capabilities
- Lubrizol analyzed water samples from membrane with noncovalent additive ESI-MS
- Fluoride/degradation product analysis ongoing



No additive detected in effluent water collected from non-covalent incorporation strategy

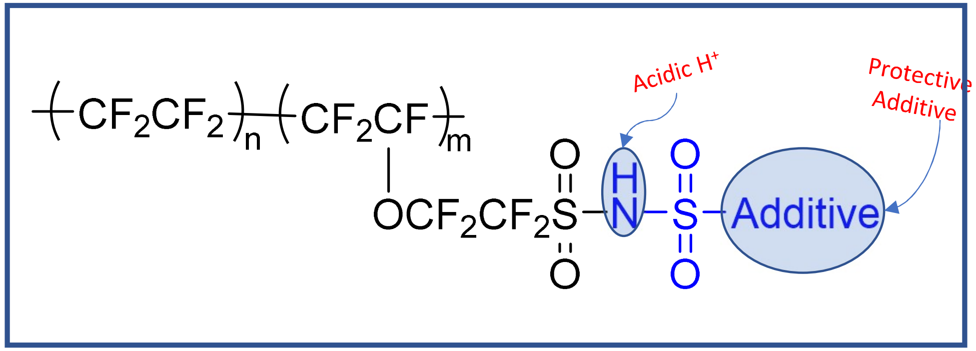
Synthetic Strategy I

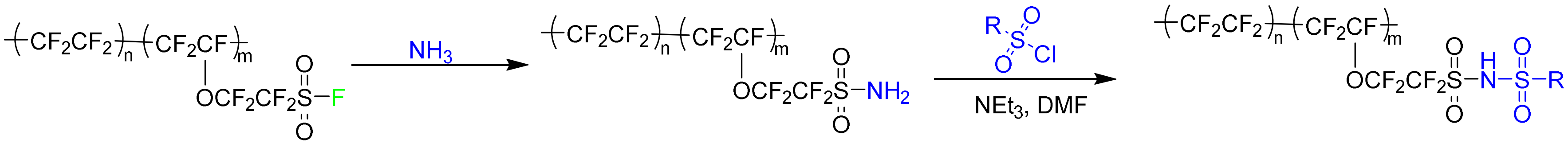


- Functionalization Strategy I relies on grafting of the functional group to the PFSA polymer backbone via a reactive linker
- A number of conditions were explored (initiators, solvents, temperatures)
- While the reactive linker used is typically acid stable, the extreme acidity of PFSA has lead cleavage of the functional group and linker in some instances
- The cleaved functional group is observed ionically bound with the sulfonic acid, while the linker is washed out during precipitation

Grafting via reactive linker proved unsuccessful with reasonable reaction conditions for scaling chemistry

Synthetic Strategy II





- Converted SO_2F intermediate to sulfonamide through amidation with ammonia
- Synthesized functional SO_2Cl coupling partners from Lubrizol chemistries and readily available starting materials (1-2 step process).
- Prepared, purified, and isolated additive functionalized perfluorosulfonimide polymer
- Characterized polymer to confirm identity (NMR, IR, APC-UV, pyrolysis-MS, TGA)

Functionalized ionomer structure confirmed by (NMR, IR, APC-UV, pyrolysis-MS, TGA)

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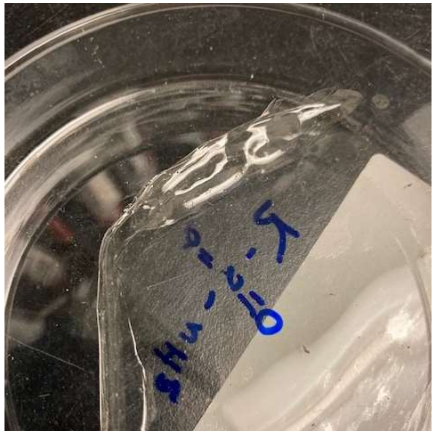
Dispersing and Casting

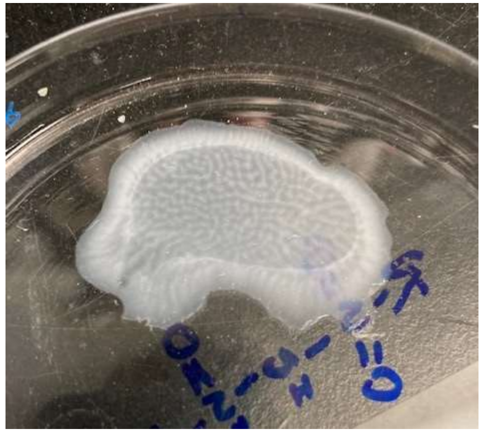
SO_2NH_2 form of polymer is soluble in DMF, but fully functionalized polymer gives hazy suspension. Casting the suspension leads to brittle, inhomogeneous solid. DMAc provides significant improvement in solubility of functionalized polymer. Film casting TBD

Functionalized polymer in DMF

Functionalized polymer in DMAc



Aquivion SO_2NH_2 (10%) blended with conventional PFSA



Aquivion SO_2NHSO_2R (10%) blended with conventional PFSA

Functionalized polymer is more difficult to disperse and cast

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2021 AMR Reviewer Comments

Reviewer comment: “Goals should be set higher than the go/no-go of only equal durability to state-ofthe-art PFSA materials. In fact, the team should use a Chemours NC700 as the benchmark, or at least a Nafion™ XL membrane, to determine whether improvement over the state of the art is made”
Response: The aim of this project is to identify the additive that will enable the improvement over the state of the art. We are not experts in membrane manufacturing, and therefore do not anticipate producing membranes with this performance in the course of this

Reviewer comment: It would be good to collaborate with OEMs sooner rather than later
Response: We are now currently engaged with numerous OEMs and regularly discuss opportunities to collaborate

Reviewer comment: There is no mention of consideration as to whether the impregnated additives, if liquid or low-melting, will plasticize the membrane, thereby depressing the glass transition of the polymer, which may limit cell operation temperature
Response: glass transition determination is routinely done ant Lubrizol and will be carried our for any promising membranes going forward

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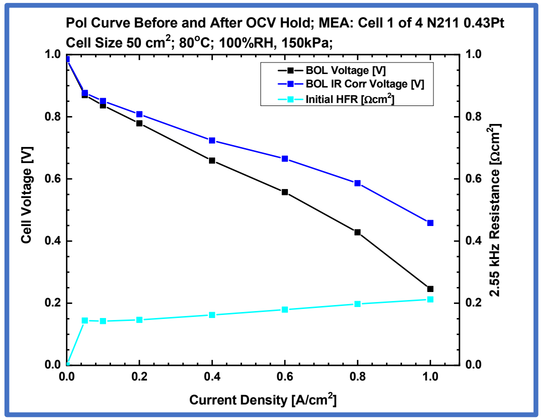
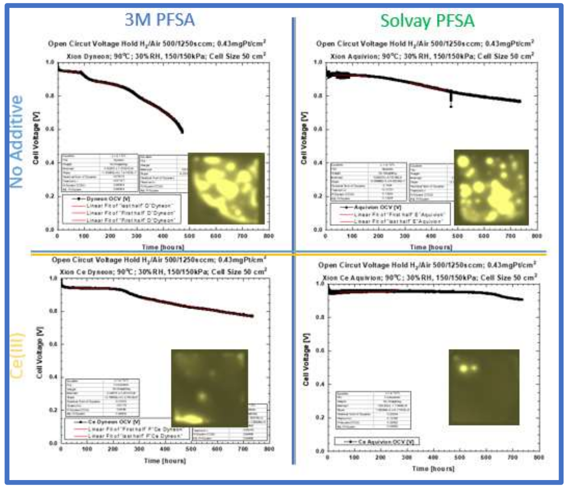
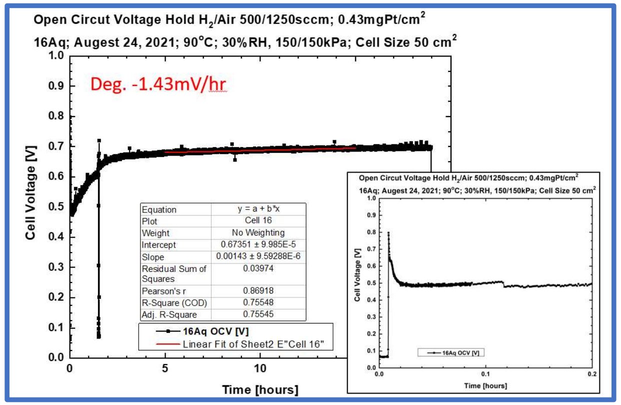
Collaboration with NREL



BOL Polarization curves for membranes with non-covalent additives



4-cell test station design, build, and validation for OCV AST



Identification of unexpected behavior for certain Lubrizol additives

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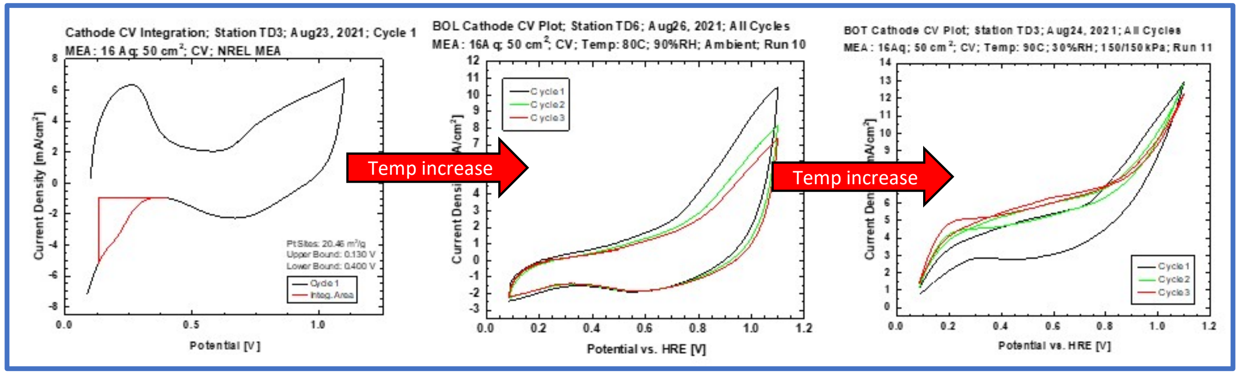
- Assembles MEAs
- Performs fuel cell durability ASTs
- Runs performance and diagnostic tests



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Remaining Challenges and Barriers

Technology challenges for project advancement

- Optimization of covalent immobilization synthesis
    - Controlling degree of functionalization
- Converting functionalized ionomer into membrane
    - Identify appropriate casting solvent
    - Preparing non-brittle membranes
- Potential electrochemical interference from non-covalent additives
- Proof of covalent membranes demonstrating superior durability and equal performance to incumbents

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Proposed Future Work

- Expand scope of coupling partners for covalent functionalization
- Explore techniques to control degree of functionalization
- Further investigate membrane samples showing odd electrochemical behavior (full BOL profiling, analysis of collected water for additive migration and F^- release)
- Analyze components of EOT MEAs to investigate migration of additive
- Process synthesized functional perfluorosulonimide polymers to membranes for performance and durability evaluation in fuel cell
  - Solvent and casting condition screening
  - Explore blends of functionalized ionomer and conventional monomer
- Explore functionalization strategies for hydrocarbon-based membranes

Any proposed future work is subject to change based on funding levels

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Proposed Future Work

Future Milestones		
Milestone	**Description**	**% Complete**
1 (FY '21)	Prepare a minimum of 8, active area ≥50 cm^2 additive embedded PFSA membranes for durability AST. A minimum of one additive will be evaluated at two different concentrations in the range from 1-20 mol% vs. the sulfonic acid concentration).	100
2 (FY '21)	Prepare a minimum of 4, active area ≥50 cm^2 non-covalent additive doped sulfonated hydrocarbon membranes for durability AST. A minimum of one additive will be evaluated at two different concentrations in the range from 1-20 mol% vs. the sulfonic acid concentration).	100
1 (FY '22)	Prepare a minimum of four, active area ≥50 cm^2 PFSA membrane covalently functionalized with additive	15
2 (FY '22)	Prepare a minimum of four, active area ≥50 cm^2 hydrocarbon membranes covalently functionalized with additive	0
End of Project Goal	Deliver a minimum of 6 additive functionalized membranes with active area ≥50cm^2 to M2FCT for independent evaluation	0

Any proposed future work is subject to change based on funding levels

NREL to perform all fuel cell performance characterization

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Summary Slide

- Additive dispersed membranes have been prepared and screened by ex-situ Fenton oxidation testing
- Preliminary OCV results of hand casted membranes demonstrate durability surpassing Ce doped membrane
- Effluent water collected from non-covalent additive membranes show no trace of additive
- Synthetic strategy I failed to produce covalently immobilized additive on ionomer
- Synthetic strategy II proved successful in covalently immobilizing additive on ionomer
- Functionalized ionomer membrane fabrication optimization is ongoing

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Acknowledgements

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- Punkaj Ahuja (Lubrizol)
- Chris Rasik (Lubrizol)

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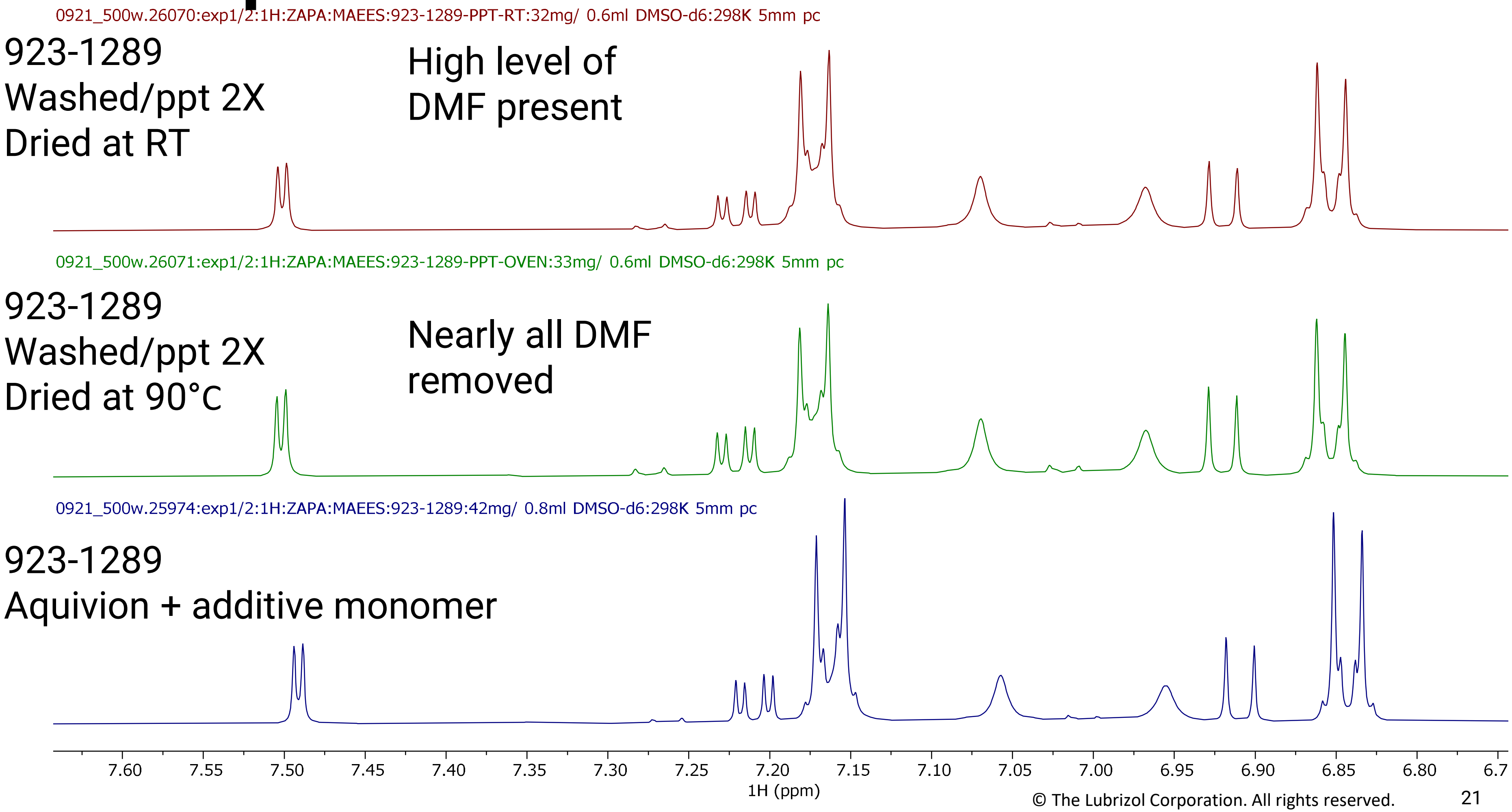
Technical Backup and Additional Information

Attempt to Remove Unreacted Monomer



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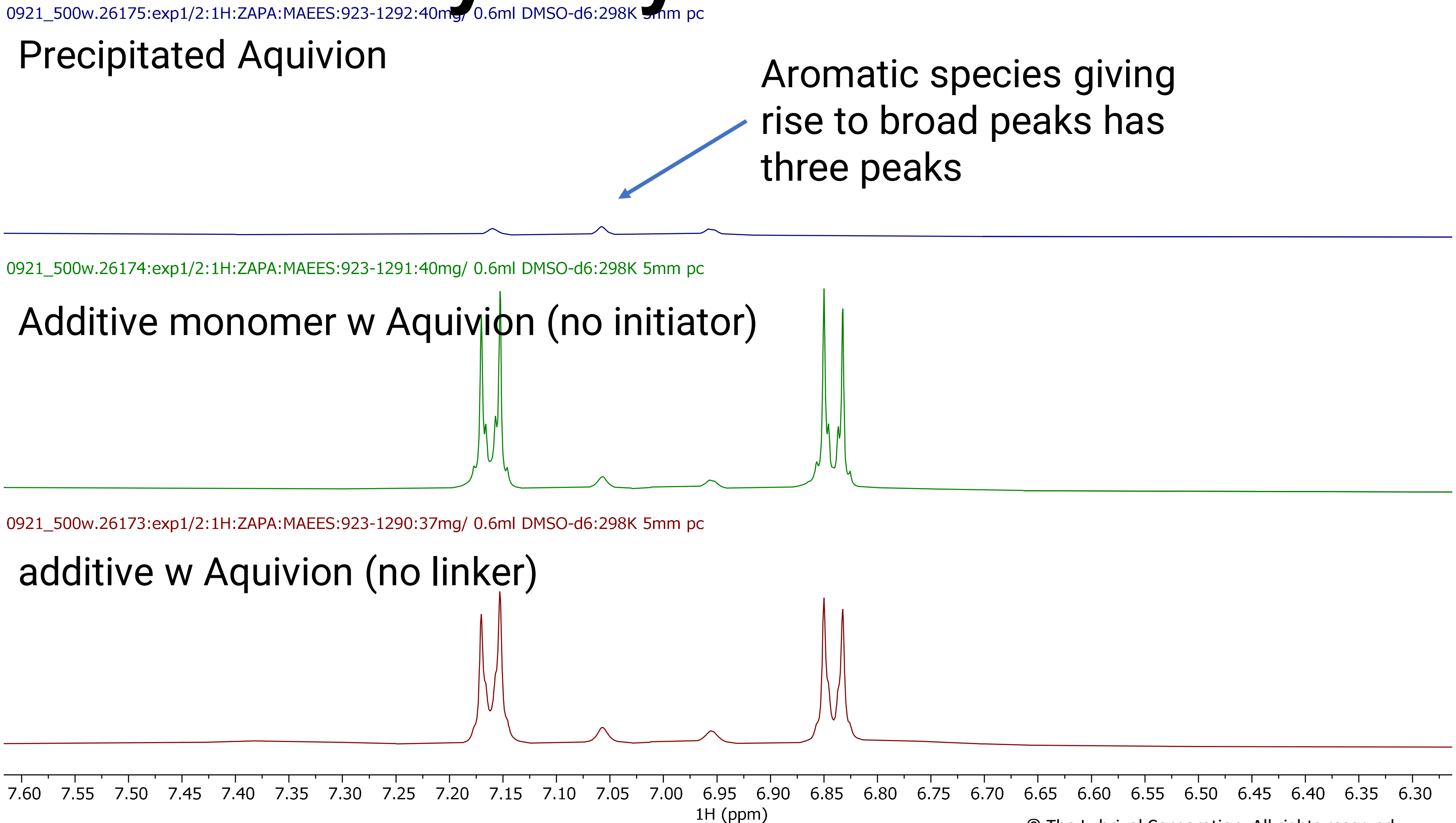
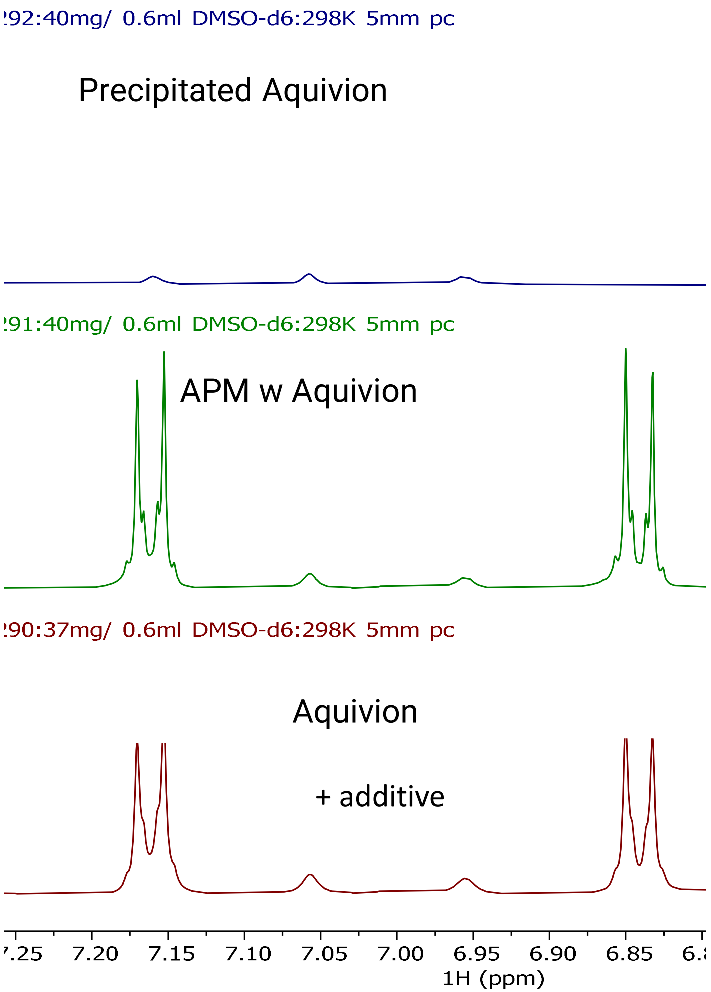
Monomer Hydrolysis



Radical Grafting Conclusion



Additive-monomer reaction

- The three small resonances in 1H NMR are present in the baseline Aquivion and are unrelated to functionalization reactions
- Monomers undergo reaction in aqueous persulfate grafting conditions

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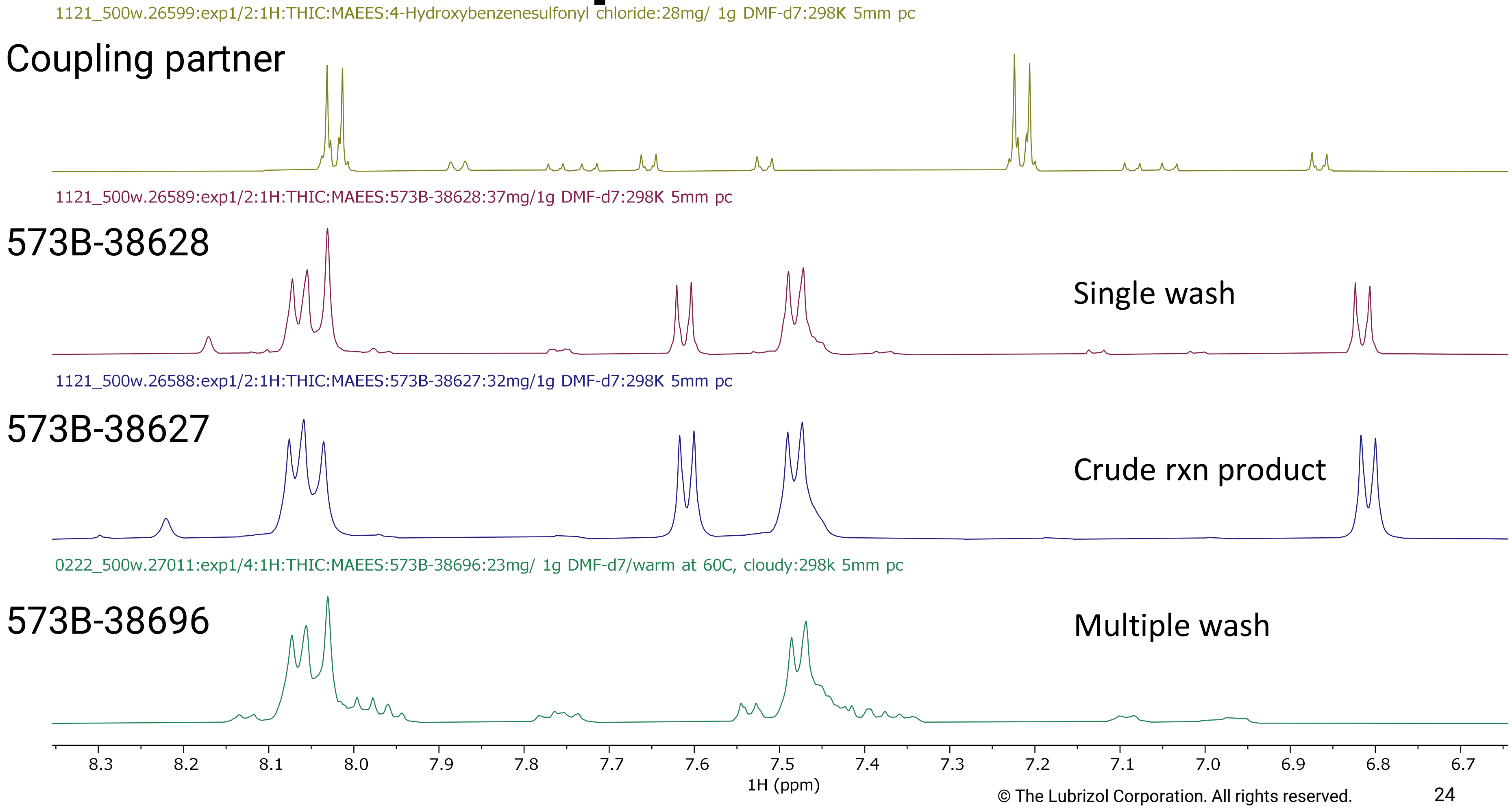
SuFEx

^{1}H NMR: All samples



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Technology Transfer Activities

- In conversation with a number of fuel cell manufacturers to test and potentially integrate technology into devices
- In conversation with membrane manufacturers to integrate and scale membranes