Sustainable Recovery of Fuel Cell and Electrolyzer Materials

PI: Chris Topping
Tetramer Technologies, LLC

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Tetramer Team

Chris Topping (PI)	[chris.topping@tetramer.com]
Matt Wasilewski (Project Manager)	[matthew.wasilewski@tetramer.com]
Margaret Shaughnessy	[margaret.shaughnessy@tetramer.com]
Bogdan Zdyrko	[bogdan.zdyrko@tetramer.com]
Collin Swanson	[collin.swanson@tetramer.com]
Stephen Hudson	[stephen.hudson@tetramer.com]
Manoj Randunu	[manoj.randunu@tetramer.com]
Dana Overman	[dana.overman@tetramer.com]
Earl Wagener	[earl.wagener@tetramer.com]

Project Goals

This Phase I Project seeks to assess cost effective, energy and resource conservative approaches to recycling multiple components of scrap and end of life Catalyst Coated Membranes (CCMs) used in fuel cells and electrolyzers.

A further goal is to future proof recycling routes by incorporating orthogonal output strategies that capture ionomer and PGM catalysts independently to design closed-loop technologies which advance the DOE's goal of sustainably producing hydrogen for $1/kg by 2031.

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Project Overview

AMR Project ID: **MNF-BIL003**

Timeline

- Project Start Date: 10 July 2023
- Project End Date: 09 April 2024

Budget

- Total Project Budget: $ 197,446
- Total DOE Share: $ 197,446
- Cost Share: $ 0
- Total Funds Spent: * $ 163,369

* Through March 2024

Barriers

- Sourcing of spent CCMs limited as existing recycling pathways utilize destructive recovery of PGMs (*incineration or oxy-acid digestion*).
- CCMs are delicate substrates necessitating cautious handling to avoid material loss.
- Membranes are varied, complex matrixes requiring robust analytical techniques to study.
- Solubility parameters for non-PFSA PEM materials under-represented in literature.

Partners

- No subcontractors were involved in this Phase I proof of concept investigation.
- Partners have been identified for Phase II further development of this work.

Potential Impact

- Ionomers and Platinum Group Metal (PGM) catalysts remain the most cost inflexible components in Proton Exchange Membrane (PEM) based Electrolyzers and Fuel Cells.
- This is driven by low abundance and high cost of production.

- **Successful recycling of these components will bolster supplies and reduce the overall cost and environmental impact of clean hydrogen production by electrolysis and fuel cell derived energy.**

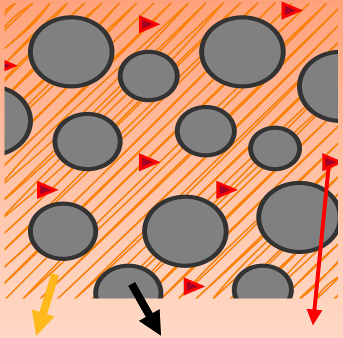
Targets

- **>50% recovery / reuse of scrap membrane material**
- **>90% recovery of PGM content in recycled membranes**
- **>90% performance of recycled membranes relative to virgin material**

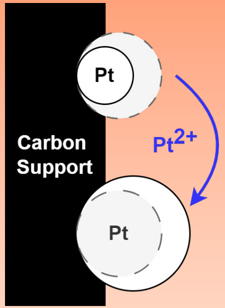
Approach

- **PGM content in CCM is localized to carbon-supports.**

Spray Coated CCM

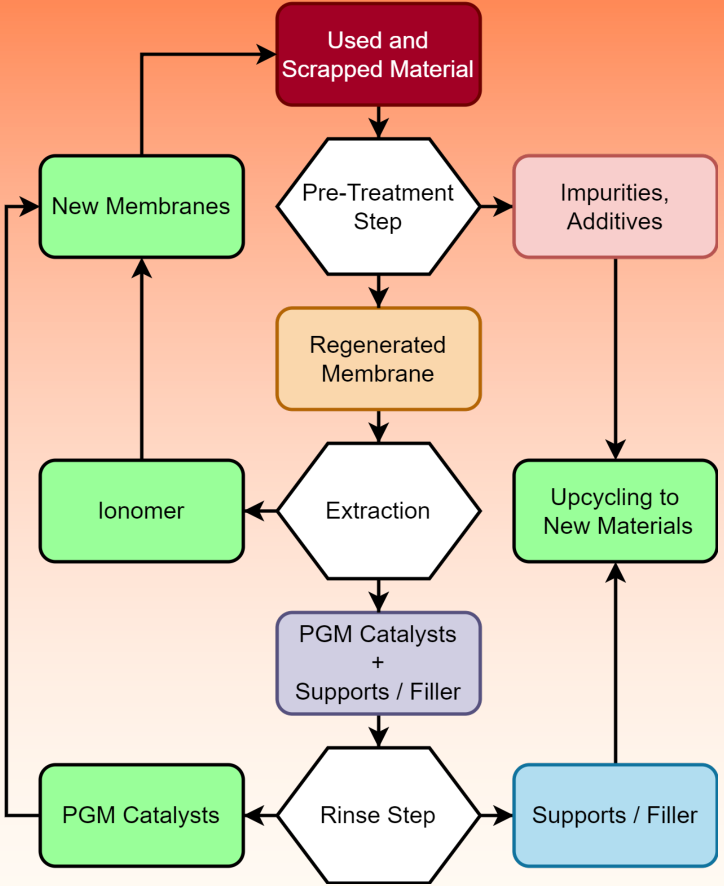


Ionomer **PGM / Carbon** **Additives / Impurities**



Ostwald Mechanism

- **PGM migration is limited by Ostwald Ripening** - *Dissolved PGM structures redeposit onto larger PGM structures.*
- **Capturing carbon recovers bulk of PGM content of a CCM and concentrates it for further processing.**
- **Extracting the ionomer simplifies PGM / C isolation and allows potential recycling vs landfill or incineration.**



Safety Planning and Culture

Culture of Prioritizing Safety

- Preliminary start-up safety reviews (**PSSRs**) performed prior to any labwork at Tetramer.
- Quality Management System is ISO 9001:2015 certified with Paradigm 3 tracking for safety documentation.
- Tetramer has established safety practices which are available to all team members.
- Safety training conducted annually for all team members.

Incident Review and Best Practices

- Weekly lab inspections to review potential hazards.
- Monthly safety meetings address near-misses, incidents, issues arising and required policy changes.
- Regular process review prevents scope-creep induced hazards from becoming blind spots.
- Systems are in place for reporting safety concerns, fostering a culture of awareness and amnesty.

Specific Safety Considerations of this Project →

Prioritizing non-toxic solvent choices for extractions
Utilizing conditions that minimize pyrophoric hazards
Avoidance of analytics relying on oxidizers / explosive acid
Ergonomic considerations for equipment placement

This project was not required to submit a Safety Plan for review

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Work Plan and Objectives

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Objective 1: Baseline Film Composition and Processing

Task 1.1: Membrane Content Determination

Task 1.2: Exploration of Pre-Treatments to Reduce Contaminant Interference

Objective 2: Extraction of Film Components

Task 2.1: Ionomer Isolation

- Identify optimum solvent(s) to selectively extract ionomer
- Soxhlet extraction
- Agitated mixing

Task 2.2: PGM catalyst isolation

Task 2.3: Support material recovery

Objective 3: Yield Confirmation and Recycling Stream Integrity

Task 3.1: Yield Confirmation and Recycling Stream Integrity

- Quantitative and qualitative evaluation of reclaimed materials
  - PGM Catalysts
  - Ionomers
  - Mechanical Supports

Progress & Accomplishments

- **Achieved simultaneous determination of ionomer and support in commercial PEM.**

Multi-step TGA analysis of e-PTFE supported PFSA membrane

500-550 °C (support decomposition)

400-500 °C (ionomer decomposition)

Bound water loss allows ionomer identification and IEC prediction

360 °C isotherm (bound water)

100 °C isotherm (free water)

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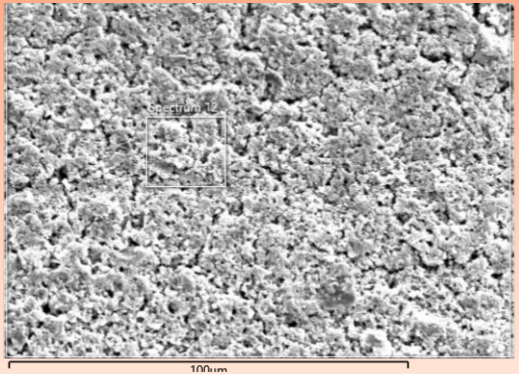
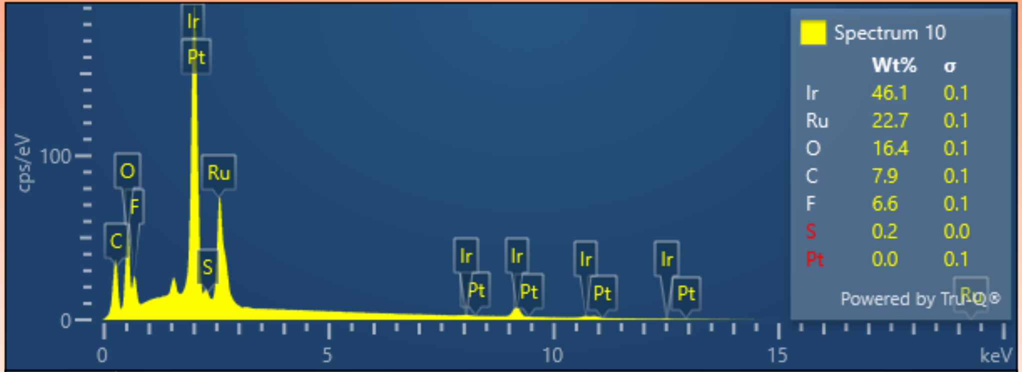
Progress & Accomplishments

SEM (scanning electron microscopy) and EDS (energy dispersive X-ray spectroscopy)

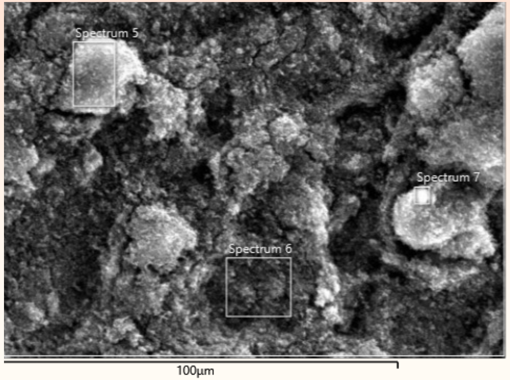
- Verification of catalyst-particle size pre- and post-extraction.
- Identity and abundance of PGM metal species facilitates downstream sorting and processing.

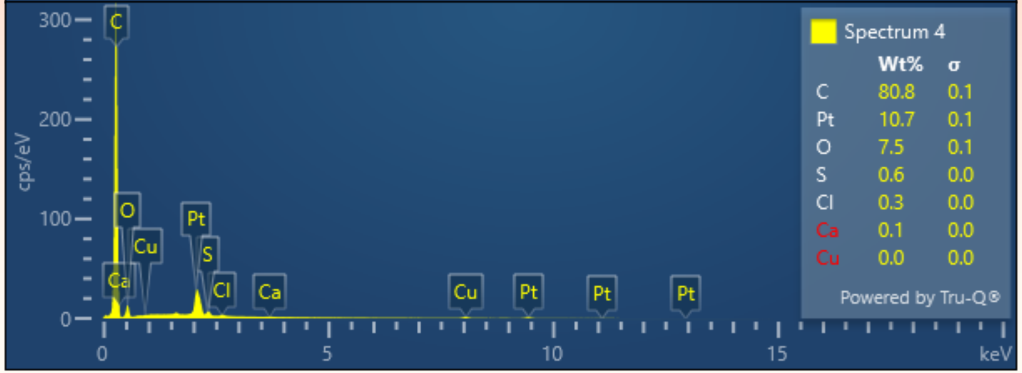
Fine structure of Ir/Ru Oxide catalyst layer





Coarseness of bulk carbon support and relative Pt abundance





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Progress & Accomplishments

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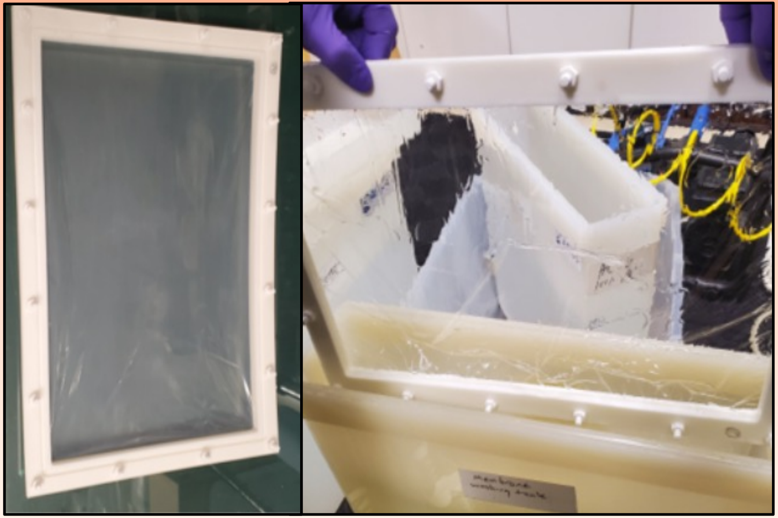
Proprietary membrane treatment employed

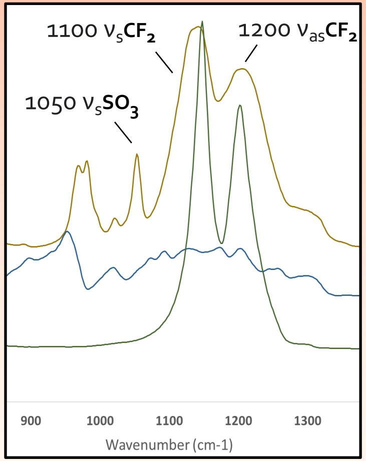
- Successfully restored IEC in depleted and poisoned membranes.

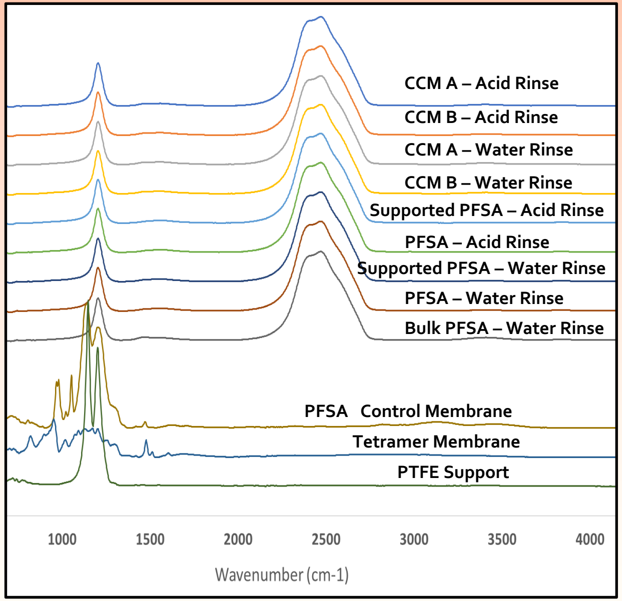
IEC Recovery (Measured by Titration)	Control Dilute Acid Treated	After 1M KOH	Treated	After 14 % NH_4OH	Treated
PFSA (Unsupported)	1.03	0	1.05	0.06	1.03
PFSA (e-PTFE Supported)	0.96	0	0.92	0	1.07
Tetramer Membrane	1.01	0	0.99	0.04	0.93



- Robust HDPE frames manufactured in house allow scalable film treatment without degradation or damage.
- Multi-batch treatments in tandem reduce aqueous waste and facilitate soluble additive capture.

FTIR of Treatment Effluents





No detectable fluorinated fragments or fluoride release in effluents.

Progress & Accomplishments

Initial Ionomer Solubility Screening

(i) Commercial Perfluorosulfonic Acids (PFSAs)

- **Commercial PFSA materials exhibited low solubility in all common solvents used.**
  - Common dispersions prepared from IPA/water and EtOH/water mixtures would not pass through 5 μm filter.*
- **Phase II will revisit the use of mixed solvents with more aggressive conditions and use of specialty (e.g., fluorinated) solvents.**

(ii) Tetramer Non-PFSA Hybrid Hydrocarbons

- **Numerous promising solvents were found that could fully solvate Tetramer ionomers.**

⬇

- **IPA was selected as a low toxicity, readily recyclable solvent with moderate boiling point.**
- **DMAC selected due to enhanced solvating properties.**

Solubility Trials (70 °C Roller 24 Hrs)					
Type	Solvent	bpt °C	PFSA A	PFSA B	Tetramer Ionomer
Alcohols	MeOH	64.7	X	X	~5wt%
	EtOH	78.4	X	X	~5wt%
	Isopropanol (IPA)	82.3	X	X	~5wt%
	Propanol	97.2	X	X	~5wt%
	50/50 nPa / Water			X	~5wt%
Aprotic Low BP	Acetonitrile	81.6	X	X	~5wt%
	THF	66	X	X	X
	Chloroform	61.2	X	X	X
	Acetone	56.2	X	X	
	MEK	79.6		X	~5wt%
Aprotic High BP	DMF	153	X		
	DMAC	165.1	X	X	>10wt%
	DMSO	189	X	X	~5wt%
	NMP	202	X		
Fluorous	hexafluorobenzene	80.1	X	X	
	perfluoro-1,2-dimethylcyclohexane	102	X	X	
	Perfluorooctane	103	X	X	
	octafluorotoluene	104	X	X	
	Perfluorodecalin	142	X	X	

Progress & Accomplishments

Soxhlet Extraction

- **Soxhlet extraction was selected as a potential low waste approach to separating CCM components for recycling.**
- **Tetramer Ionomer A (non-PFSA) was used to cast a neat control membrane.**
- **Composite Tetramer PEMs were also cast from Ionomer A incorporating ePTFE mechanical supports and PVDF resin to enhance physical properties.**
- **Initial trials indicated 55-65% ionomer recovery (after 2-8 hrs cycling).**
- **Extracted ionomer retained original IEC.**

Pre and Post IEC of Extracted Ionomer					
Sample	**Membrane Type**	**Ionomer Content**	**Recovered Ionomer**	**IEC Pre Extraction**	**IEC Post Extraction**
Neat Ionomer A membrane	**Unsupported, 100% Ionomer**	**100%**		**2.07**	
Composite PEM	**E-PTFE supported, 40% PVDF**	**60%**	**64.80%**	**1.34***	**2.01**

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Progress & Accomplishments

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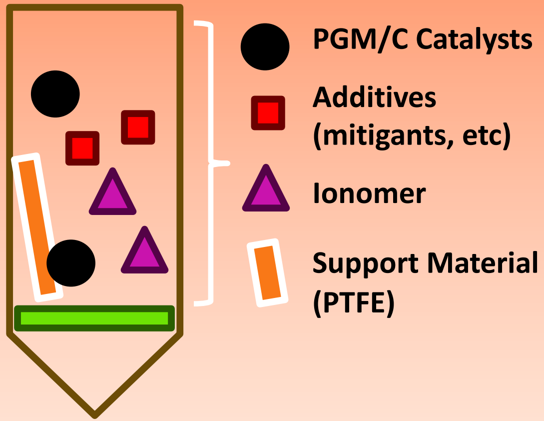
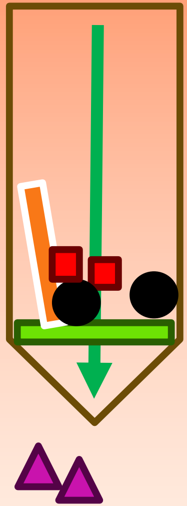
Multiple Component Isolation



Composite Matrix
(Ionomer, PVDF, Support)

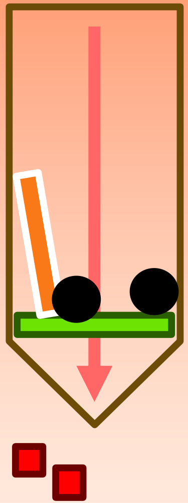
Separation via sequential extractions / washes to remove:
(i) ionomer,
(ii) additives
(iii) catalysts

STEP I
Solvent A extracts ionomer



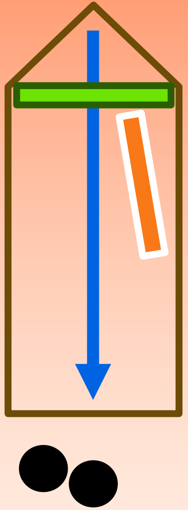
Recovered Ionomer

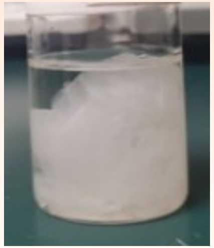
STEP II
Solvent B extracts additives



Recovered PVDF

STEP III
Water rinse removes PGM/C from support





Recovered ePTFE

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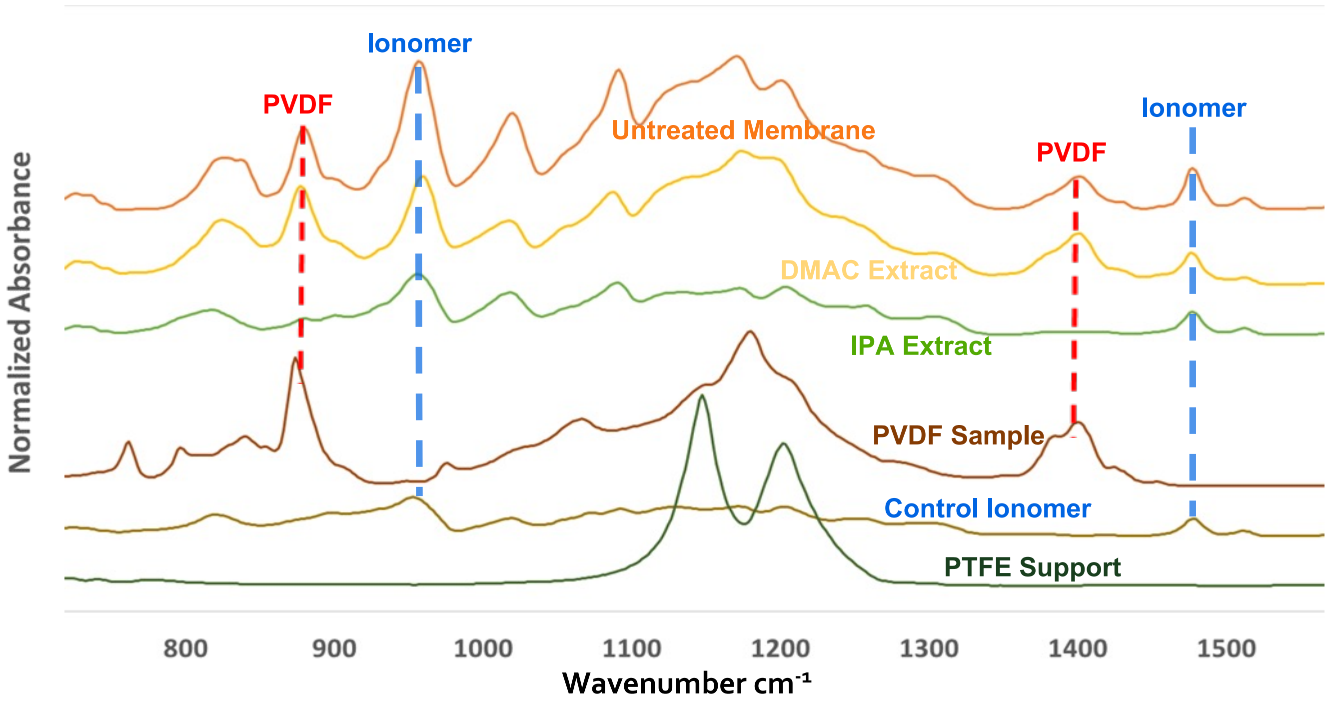
FTIR of Obtained Extracts Compared to Baseline Material



IEC of Pre/Post Extraction Membrane Material	
Sample	IEC
Untreated Membrane	**1.34***
IPA Extract	**2.01**
DMAC Extract	**0.99**
Recovered PTFE	**0.00**

IPA selective for ionomer

DMAC non-selective: recovers ionomer + PVDF

After both washes no ionomer or PVDF present

- **Selective extraction conditions determined for ionomer - yield optimization is under way.**

Progress & Accomplishments

Model CCMs Fabricated to Test Extraction Conditions

- PGM/C particles fully dispersed in membrane to mimic surface coated and hot-pressed catalyst layers.

In house fabricated model CCMs [7-14% C dispersed in 20-60 μm PEMs]

- Initial tests carried out with carbon (Vulcan-XC) alone (PGM free) to validate procedure.
- Ionomer-extraction efficiency from model CCM was found to be comparable with catalyst free PEM (52-68% yield).
- Experiments are currently progress using PGM/C (20% Pt on Vulcan-XC) loaded model CCMs.

Remaining Challenges & Barriers

- **Recycling Dispersion Forming Substrates (e.g., PFSAs)**
  - **Many of the most promising candidates for recycling form dispersions rather than solutions (ie Nafion™), making filtration and separation challenging:**
    - We are currently exploring approaches to isolate carbon supported PGMs from micron-scale dispersions.
    - Future approaches may include:
      - Alternative (e.g., specialty/fluorinated) solvents and mixtures.
      - More aggressive agitation.
      - Use of solvothermal cells to bridge the gap between dispersive and hydrothermal approaches.
- **Translation of Techniques to Scrap and End of Life (EoL) Materials**
  - **More variety in substrate sources will enhance relevance and adoptability.**
    - Understanding of recyclability parameters for other developing non-PFSA based PEMs and CCMs needed.
- **External validation of performance of recycled and recast materials.**
  - **This will be addressed with commercial fuel cell and electrolyzer partners during Phase II.**
- **Assess Alternative PGM Detection Methods for Sensitivity and Accessibility**
  - **Current techniques are informative but lengthy (TGA) or inaccessible to manufacturers (SEM).**
    - AA / ICP were attempted but complications with the matrix (non-digestible fluoro-polymers) limited viability.
    - XRF techniques will be further explored
    - Electrochemical approaches may be explored since these can be performed on both surfaces and solutions.

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Collaboration and Coordination

- **Life Cycle Analysis [LCA]**
  - **A full LCA of Tetramer's hybrid hydrocarbon based ionomers and PEMs is currently pending with a leading industrial partner – we anticipate that this will be a major component of our Phase II Work Plan.**

- **Recycling / Refurbishment of used Materials (→ Closed Loop Manufacturing)**
  - **Parallel to this project, multiple parties are currently testing Tetramer PEMs and ionomers for electrolyzer, fuel cell and non-energy applications.**
  - **Collaborators are interest in developing approaches recover scrap and end of life materials.**
  - **Used materials from performance and durability trials will be used during Phase II to allow the further development and evaluation of extraction and re-use approaches.**
  - **Recycled / refurbished materials will be compared against virgin materials by end users with direct feedback.**

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

Proposed Future Work

- **Life Cycle Analysis (LCA)**
  - **A full life cycle analysis is planned for Tetramer developmental fuel cell and electrolyzer ionomers.**
- **Performance Testing**
  - **Phase II work will focus on testing the performance of recycled ionomer and PGM catalysts in recast CCMs to verify post-recycling component integrity.**
- **Treatment Analysis Expansion and Optimization**
  - **Expand analysis to consider at Freshwater and Hard Water Poisoning (Ca, Mg, Zn, etc).**
  - **Expand analysis to remediate MEA corrosion poisons (Fe, Cu, Al).**
- **Ionomer Cycling Studies**
  - **Repeatedly recycle and recast ionomer to observe limits on recyclability and mechanisms for degradation.**
- **Enhance Catalyst Retention and Recovery**
  - **Explore conditions to promote easier isolation of carbon supported PGMs intact.**
  - **Examine reverse Ostwald approaches to regenerate PGM catalyst activity.**
  - **SEM analysis to confirm PGM content and substrate remains unchanged through treatment processes.**
- **Scale Up and Throughput Testing**
  - **Optimizing efficiency for high volume batches or flow processes.**
- **Additive Capture and Concentration**
  - **Examine what valuable additives can be recaptured during treatment or ionomer recycling.**
  - **Recovery and upcycling of structural supports.**

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

Summary

- **A successful approach to extracting materials and potentially re-using valuable materials from PEM-CCM mimics was demonstrated using Tetramer Ionomers.**
- **Highlights include:**
  - Developed protocol for membrane composition analysis that simultaneously quantifies ionomer, PGM and PTFE support content.
  - Demonstrated scalable, mild pre-treatment for CCMs which regenerates ionomer IEC without chemical degradation or fluoride release.
  - Achieved > 90% IEC retention in extracted ionomers with consistent yields.
  - Stepwise extraction yielded a selective separation of ionomer, additive and support.
  - Surrogate CCMs can be reliably prepared, allowing further analysis of compositional studies and their impact on extraction.
  - PGM catalyst recovery is being validated by ongoing studies with Pt/C to quantify PGM retention throughout the treatment process.