Highly Stable Anion-Exchange Membranes for High-Voltage Redox-Flow Batteries

2017 DOE Hydrogen and
Fuel Cells Program Review

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FC131

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This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- Timeline

Start: June 1, 2016

End: August 31, 2017

Complete: 80%

- Barriers
  - Durability (Oxidative Stability of Membrane)
  - Performance (Ion conductivity)
- Budget
  - University of Delaware, $500K
  - National Renewable Energy Laboratory (NREL), $100K
  - Total Project Budget $750K ($600K DOE Share + $150K Cost Share)
- Partners
  - University of Delaware (lead)
  - NREL (funded partner)
  - Xergy (new no-cost collaborator)
  - Giner (new no-cost collaborator)

University of Delaware
Yushan Yan, Shuang Gu, Bingjun Xu

National Renewable Energy Laboratory
Bryan Pivovar

Relevance

Objectives & Relevance

- Objectives:
  - Develop anion-exchange membranes (AEMs) with high oxidation resistance for high-voltage cerium redox-flow batteries (RFBs).
- Relevance:
  - *This project was selected from the EERE/FCTO "Incubator" Funding Opportunity Announcement (FOA) to support innovative technologies and solutions that could help meet existing goals but are not represented in a significant way in the current portfolio.*
  - This is an AEM project designed for RFBs but fuel cells (FCs) are considered.
  - Cerium RFBs have a cell voltage that is more than double that of standard all-vanadium RFBs, and thus hold the potential to offer high-performance and low-cost electricity storage solutions for grid storage.
  - Stable AEMs can also be used for hydroxide exchange membrane fuel cells (HEMFCs), which may improve the durability and performance of fuel cells.
  - Stable AEMs are also necessary to achieve highly durable AEM electrolyzers, which will lower the cost for hydrogen production.

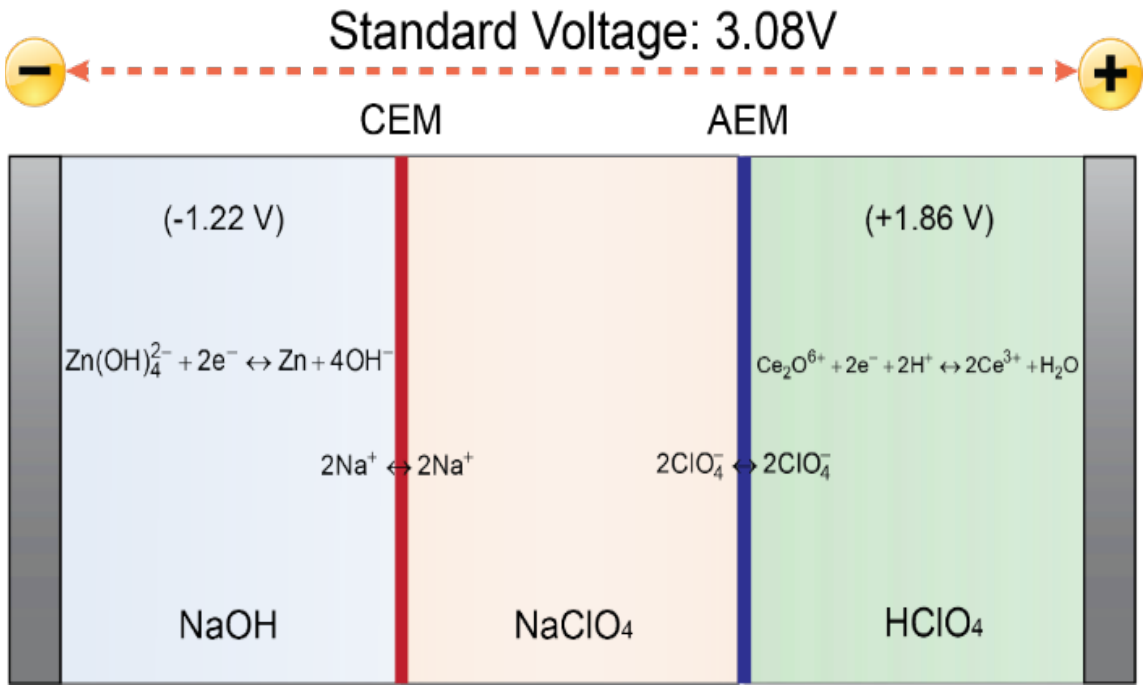
Approach
Project Milestones

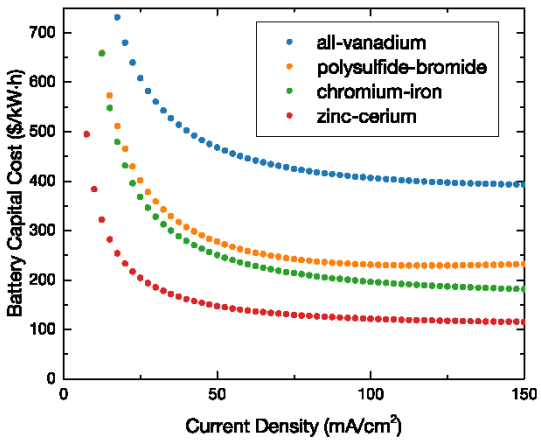
Qtr.	Quarter Due Date	Milestones	Status
Q1	08/30/2015	Less than 10% loss of initial weight for the identified polymer at 40 °C for 1000 h in 0.5 M $Ce(IV)(ClO_4)_4$	Completed on time
Q2	11/31/2016	Less than 5% of multiple brominated $9MeTTP^+$ cation based on ^1H and ^{31}P NMR spectroscopy	Completed on time
Q3	02/31/2016	More than 95% purity for synthesized $9MeTTP^+$ - functionalized polymers based on ^1H and ^{31}P NMR spectroscopy	Completed on time
Q4, GNG	05/31/2016; 06/30/2016	Less than 20% loss of initial IEC for $9MeTTP^+$ - functionalized polymers at an accelerated degradation test at 55 °C for 100 h in 0.5 M $Ce(IV)(ClO_4)_4$**	Delayed 1 month; Complete on 07/31/2016 NCE of 1 quarter is granted
Q5	8/31/2016	More than 10 MPa of tensile strength for prepared $9MeTTP^+$ - functionalized polymer membranes	N/A
Q6/5*	11/30/2016	More than 10 MPa of tensile strength for prepared $9MeTTP^+$ - functionalized polymer membranes	Completed on time
Q7/6*	2/28/2017	At least 10 pieces of $9MeTTP^+$ - functionalized polymer membranes with a size of 3 cm * 4 cm and a thickness of 100 µm	Completed on time
Q8/7*	5/31/2017	Less than 20% loss of initial anion conductivity for $9MeTTP^+$ - functionalized polymers at an accelerated degradation test at 55 °C for 100 h in 0.5 M $Ce(IV)(ClO_4)_4$**	TBD
Q9/8*	8/31/2017	At least 50 pieces of $9MeTTP^+$ - functionalized polymer membranes with a size of 6 cm * 8 cm and a thickness of 100 µm; Report both RFB and fuel cell performance	TBD

*quarter number for original proposed timeline
**approved accelerated oxidation stability test condition, see slide 23 in backup slides

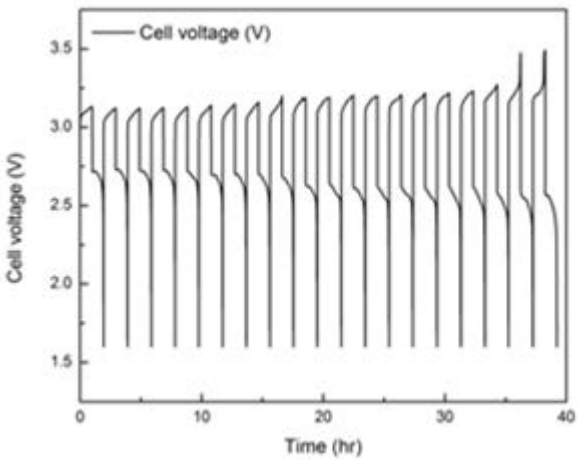
Approach

Zinc-Cerium double membrane redox flow battery (RFB)





- Highest voltage (i.e., ~3V) in all aqueous RFBs, and low battery capital cost.
- Current AEMs have inadequate oxidation stability, and can operate for only 40 hours.



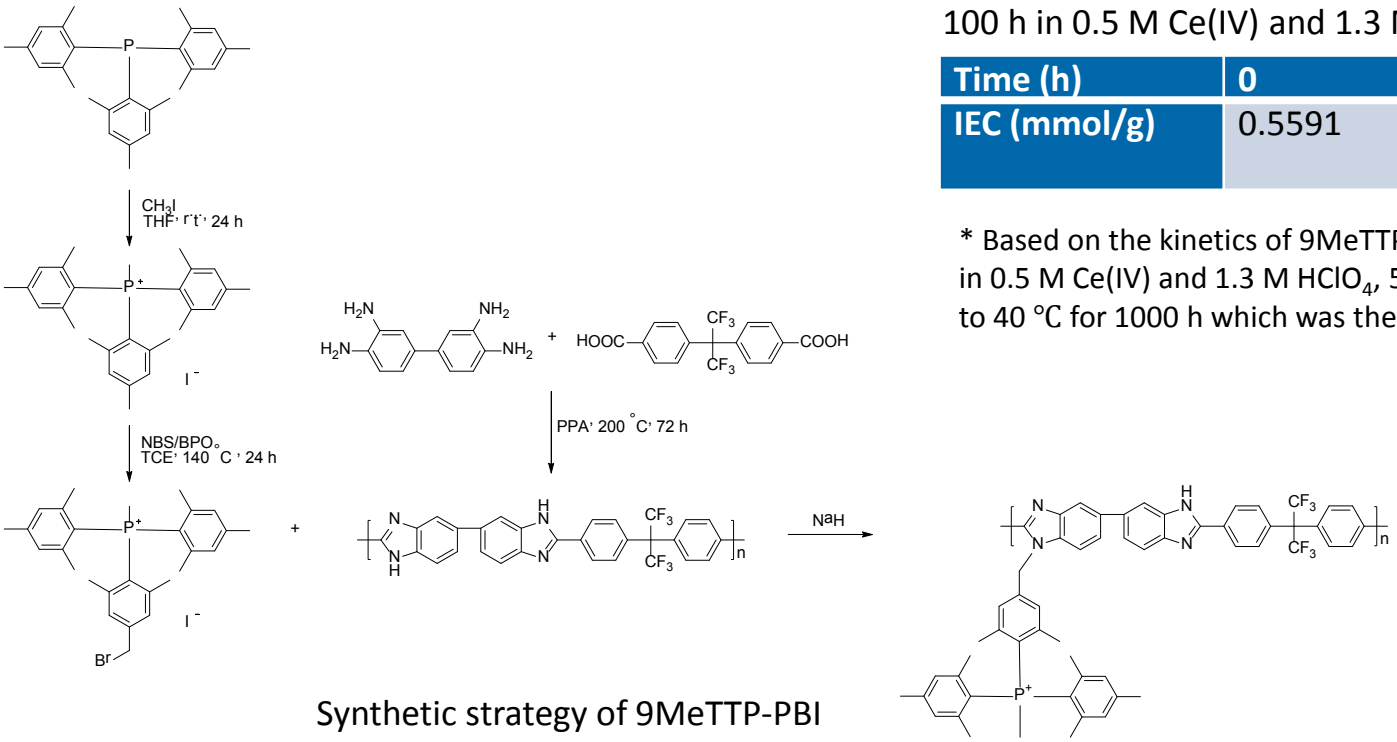
Accomplishments and Progress

Summary of AMR 2016

- 9MeTTP$^+$ cation functionalized polymer membranes
  - 9MeTTP$^+$ tethered to PSf via direct quaternization
    - Did not work due to high steric hindrance of 9MeTTP molecule.
  - 9MeTTP$^+$ functionalized PSf via brominated 9MeTTP$^+$
    - 9MeTTP-PSf polymer was successfully synthesized.
    - During the stability test at 40 ℃ for 1000 h in 0.5 M Ce(IV) and 1.3 M $HClO_4$, 46.59 % loss of IEC in the first 500 h
    - Model reaction showed PSf backbone is not oxidation stable after functionalized with ammonium cation.
  - 9MeTTP$^+$ functionalized PBI via brominated 9MeTTP$^+$
    - 9MeTTP-PBI polymer was successfully synthesized.

Accomplishments and Progress

9MeTTP$^+$ - functionalized PBI via brominated 9MeTTP$^+$



Synthetic strategy of 9MeTTP-PBI

9MeTTP-PBI stability test was operated at 55 °C for 100 h in 0.5 M Ce(IV) and 1.3 M $HClO_4$.

Time (h)	0	100
IEC (mmol/g)	0.5591	0.5558 (0.59% loss)

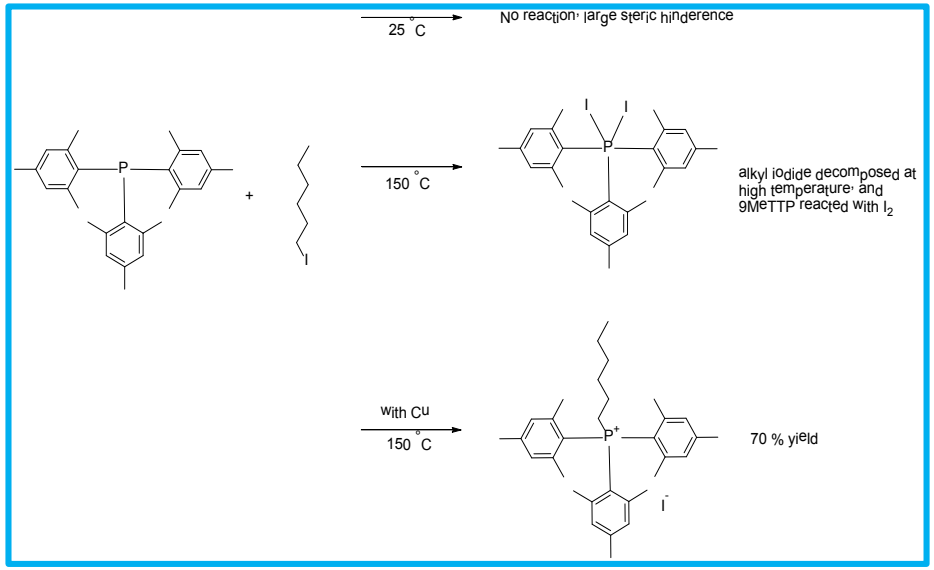
* Based on the kinetics of 9MeTTP$^+$ cation oxidation reaction, in 0.5 M Ce(IV) and 1.3 M $HClO_4$, 55 °C for 100 h is equivalent to 40 °C for 1000 h which was the test condition in proposal.

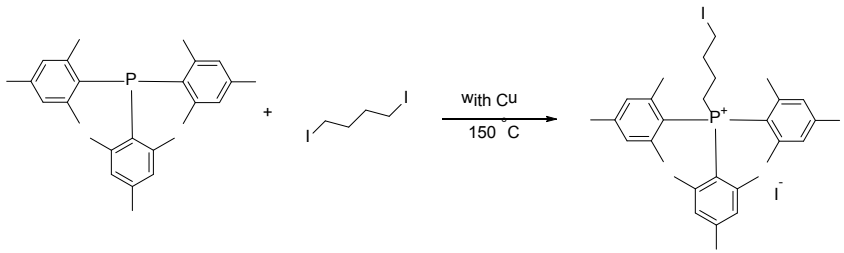
- 9MeTTP-PBI polymer **met the GNG milestone** and has less than 20% loss of initial IEC after durability test.
- 9MeTTP-PBI polymer was crosslinked due to multiple bromination of 9MeTTP$^+$ in large scale synthesis, making membrane preparation difficult.
- IB9Me-PBI will be explored (see next page)

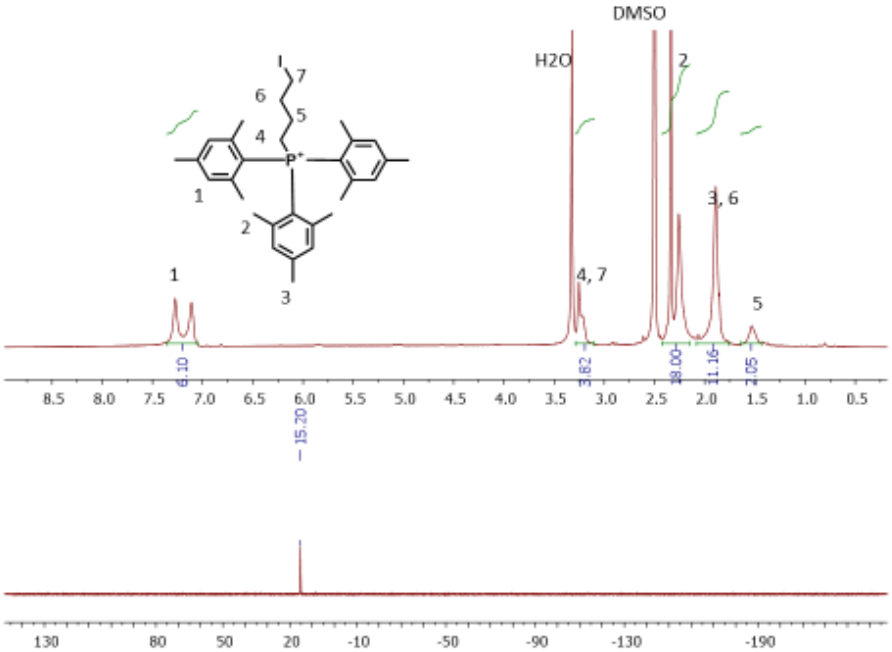
Accomplishments and Progress

9MeTTP$^+$ - functionalized polymer synthesis via IB9MeTTP$^+$

Model reaction between 9MeTTP and alkyl iodide.



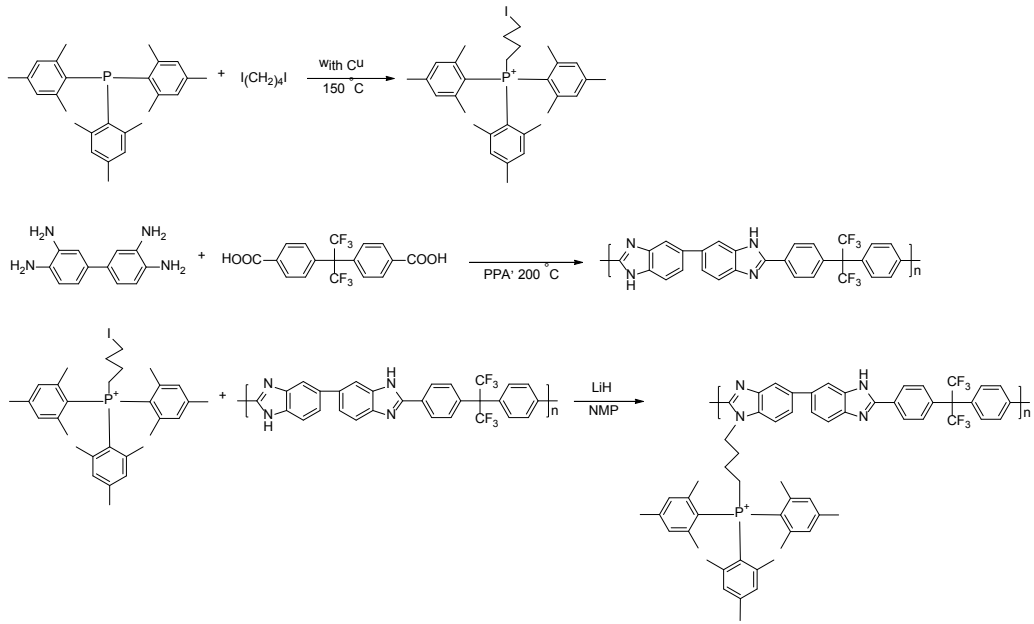




- Copper could inhibit the decomposition of alkyl iodide during the reaction.
- IB9MeTTP$^+$ cation was successfully synthesized.

Accomplishments and Progress

9MeTTP$^+$ - functionalized polymer synthesis via IB9MeTTP$^+$



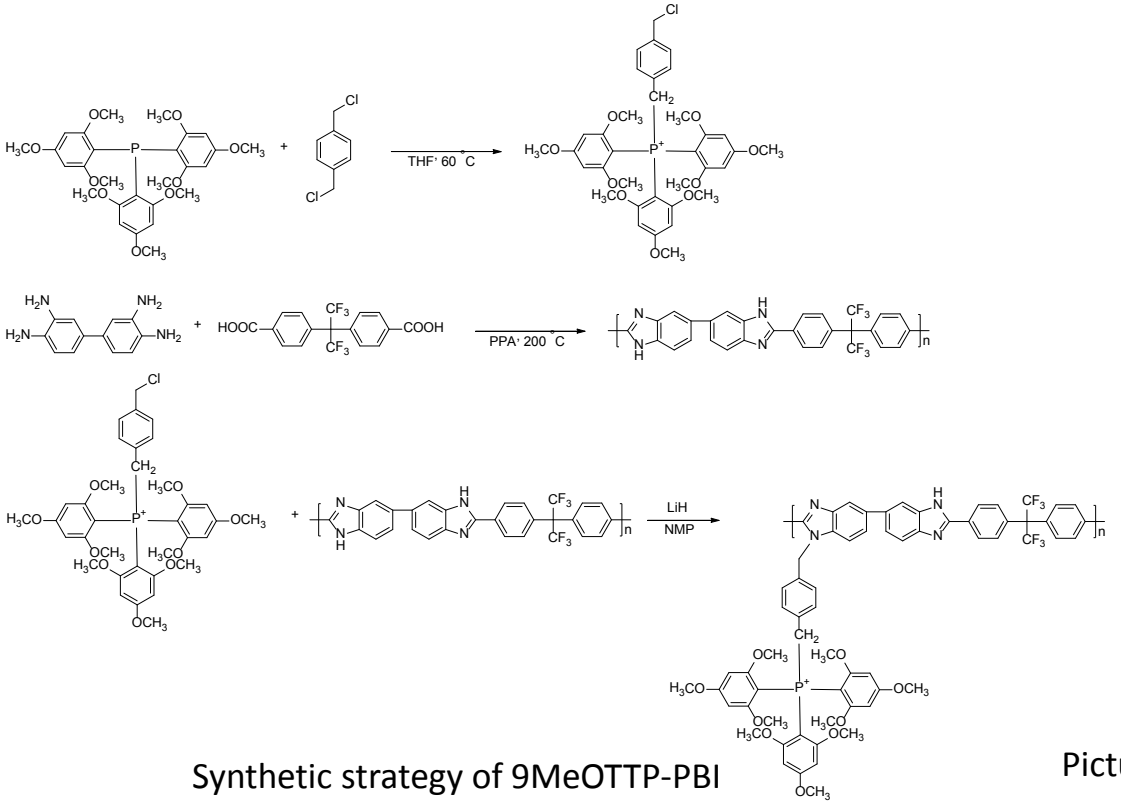
Picture of 9MeTTP-PBI membrane

Membrane	9MeTTP-6FPBI
Tensile stress	26.2 Mpa
Elongation	1.7 %
IEC (titration)	0.52 mmol/g
Water uptake	3.58 %
Swelling ratio	3.02 %
Conductivity (OH^-) in water at 20 °C	1 mS/cm

- Obtained 9MeTTP-PBI membrane successfully
- Overcame crosslinking by new synthesis strategy
- Achieved insufficient conductivity of 9MeTTP-PBI membrane likely due to the hydrophobic 9MeTTP$^+$ cation
- Explored more hydrophilic cation (see next page)

Accomplishments and Progress

9MeOTTP$^+$ - functionalized polymer based on PBI backbone



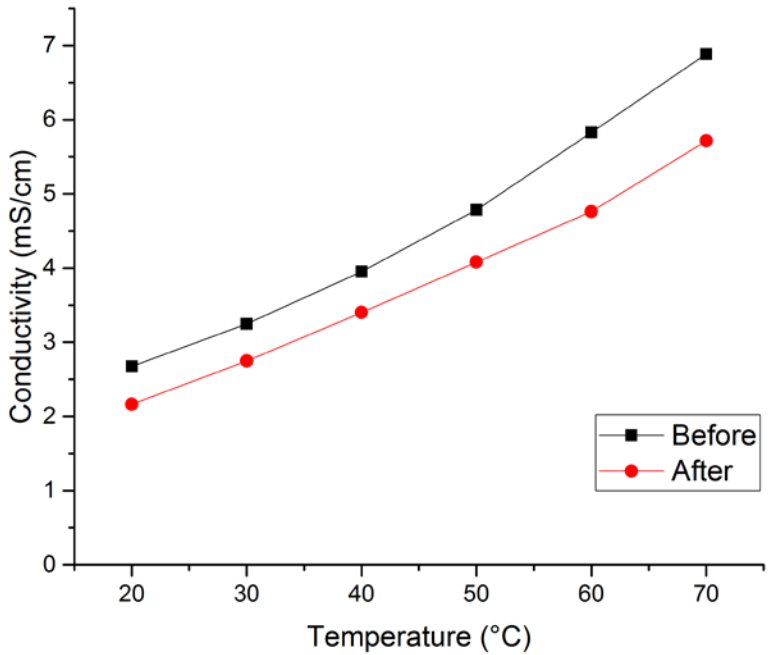
Synthetic strategy of 9MeOTTP-PBI

Picture of 9MeOTTP-PBI PTFE reinforced membrane

- 9MeOTTP-PBI polymer was successfully synthesized.
- 9MeOTTP-PBI PTFE reinforced membrane was successfully prepared to increase the mechanical strength and durability in Ce(IV) solution.
- 9MeOTTP-PBI PTFE reinforced membrane shows 17.4 % water uptake, which is much higher than 9MeTTP-PBI membrane.

Accomplishments and Progress

9MeOTTP – PBI PTFE reinforced membrane stability test



- Oxidation stability test condition: 0.5M Ce(IV) in 1.3 M $HClO_4$ at 55 °C for 100 h
- Conductivity measured in DI water
- ~13-19% of conductivity was lost across all temperatures tested

Conductivity (ClO_4^- form) of 9MeOTTP-PBI PTFE reinforced membrane measured at different temperatures before and after accelerated oxidation stability test

- 9MeOTTP-PBI PTFE reinforced membrane **met the milestone Q8/7** (i.e., less than 20% loss of initial anion conductivity).

Accomplishments and Progress

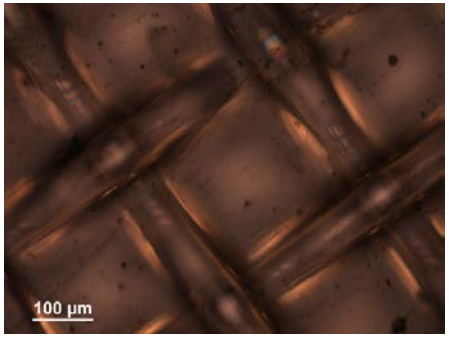
9MeOTTP – PBI PTFE reinforced membrane compared with fumasep® membranes

FAS-30: broke into pieces in 24 h

Non-reinforced, 30 µm, with high conductivity, selectivity and high stability in acidic and basic environment.

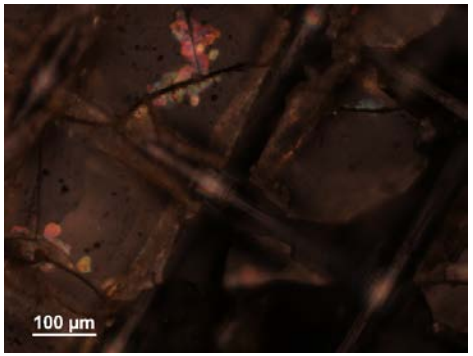
FAB–PK-130: loss of polymer

PEEK-reinforced, 130 µm, with high proton blocking capability, high selectivity, high mechanical stability, and high stability in acidic and basic environment.



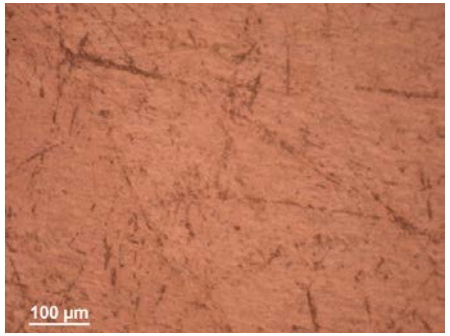
0.5M Ce(IV) in 1.3 M $HClO_4$ →

at 55 °C for 100 h



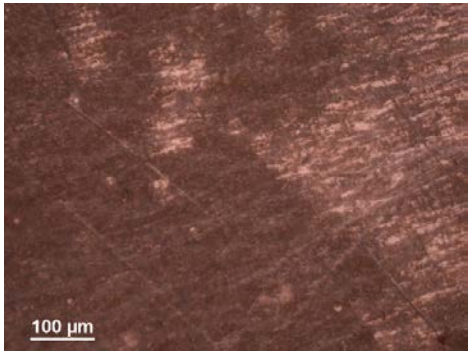
9MeOTTP-PBI PTFE reinforced membrane: no loss of polymer

20 µm.



0.5M Ce(IV) in 1.3 M $HClO_4$ →

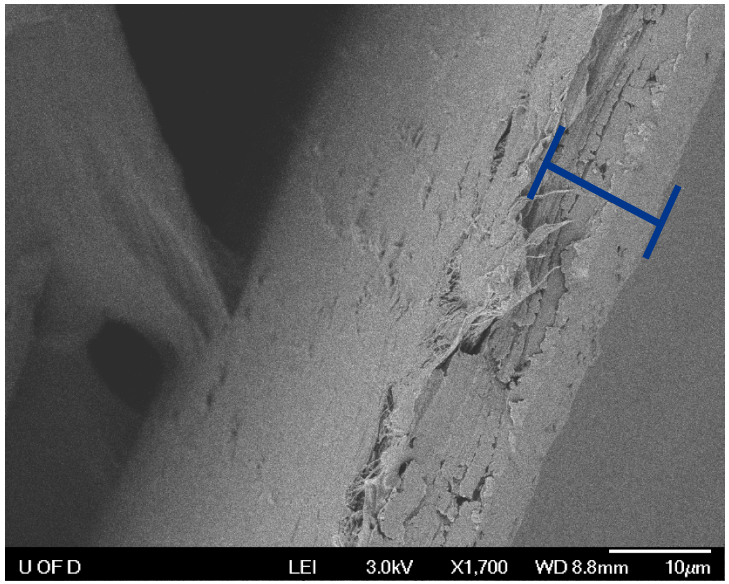
at 55 °C for 100 h



- 9MeOTTP-PBI PTFE reinforced membrane is superior to FAS/FAB membranes in oxidation stability

Accomplishments and Progress

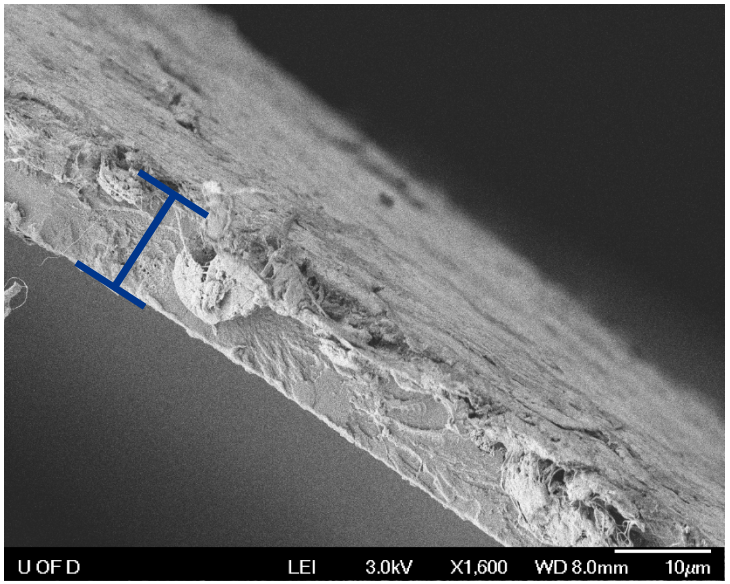
9MeOTTP – PBI PTFE reinforced membrane cross-section SEM



0.5M Ce(IV)
in 1.3 M HClO4

→

at 55 °C for 100 h



9MeOTTP-PBI PTFE reinforced membrane SEM image before and after oxidation stability test.
9MeOTTP-PBI PTFE reinforced membrane is not suitable for freeze fracturing with liquid nitrogen, cross-sections are prepared by cut.

- 9MeOTTP-PBI polymer was fully through the PTFE porous substrate.
- Cross-section and surface had no morphological change after oxidation stability test.

Accomplishments and Progress

Response to previous year (2016 AMR) reviewer's comments

"The project is narrowly focused on ionomer development for alkaline membranes, and it appears that good progress is being made in developing the proposed synthetic pathway, but a clear justification of how these results represent progress toward the overall project goals and DOE goals is lacking."

> This project focuses on the development of a new class of highly stable AEMs tailored for high-voltage cerium RFBs, which might potentially have applications on fuel cells and electrolyzers.

"The project has a nice systematic approach to developing stable phosphonium cation-based AEMs. It is unclear why phosphonium is preferred over ammonium cations. The cost projections based on the high-voltage redox chemistry show the value in pursuing this approach. The project highlighted a specific redox chemistry using a bipolar membrane or a pair of polymer electrolyte membranes (PEMs)/AEMs, but the bulk of the presentation outlined the synthesis of the AEM ionomer. It is unclear whether the project is to develop the RFB chemistry and membrane, or just the membrane."

> Our previous experiments have proven that ammonium cation (BTMA) is the least stable among the three cations considered here ($9MeTTP^+$, $9MeOTTP^+$ and BTMA). This result has certain support in a paper by Dr. Vijay Ramani, *Phys. Chem. Phys.*, 2016, **18**, 19705. This project focuses on the development of a new class of highly stable AEMs tailored for high-voltage cerium RFBs, not new redox chemistries.

"Timely progress was made against project milestones. Durability and synthesis is improving. Conductivity of materials is unclear."

> The initial test suggest that 9MeOTTP-PBI membranes have decent conductivity while the conductivity of 9MeTTP-PBI membrane is not satisfactory, due likely to its strongly hydrophobic property.

Accomplishments and Progress

Response to previous year (2016 AMR) reviewer's comments

"There is no evidence of collaboration with NREL, the only partner on this project"

> The synthetic optimization took longer than expected. We have since sent samples to NREL to be tested in fuel cells. In terms of new partnerships, we are also working with Xergy and Giner as no-cost collaborators to make reinforced membranes and electrolyzers.

"Stability tests should entail some more sophisticated diagnostics, such as testing leachate for organic residue or for P. Color changes can be misleading, and weight changes can be difficult with substituted materials because water adsorption can change and drying to the same state of hydration is not always easy."

> The initial color based stability tests were from our preliminary data before the project started. We have since used rigorous quantifiable tests like conductivity, IEC, water uptake, and mechanical stress-strain curves.

"The synthetic approach appears solid. It would be beneficial to see at least some focus on conductivity/resistance measurements in addition to stability. This project would greatly benefit from some analysis as to what is required for specific applications. It is not clear why milestones are limited to 40 °C. It is not clear how the ex situ stability tests correlate with in situ degradation. Methods for backbone and functional group down-selection are unclear."

> We have since used rigorous quantifiable tests like conductivity, IEC, water uptake, and mechanical stress-strain curves. The choice of 40 °C was based on the expectation that the RFB will be operated at this temperature

Collaborations

- **University of Delaware (lead)**
  - Yushan Yan, Shuang Gu, Bingjun Xu
- **NREL (proposal partner)**
  - Bryan Pivovar
    - Membranes and ionomers shipped to NREL for MEA preparation and tests
- **Xergy (new no-cost collaboration)**
  - Bamdad Bahar
    - In progress to prepare reinforced membranes
- **Giner (new no-cost collaboration)**
  - Hui Xu
    - In progress to prepare reinforced membranes using their DSM technology

Remaining Challenges and Proposed Future Work

- Remaining Challenges
  - 9MeOTTP-PBI polymer synthesis
    - Small batch size (~3 grams/batch)
    - Larger batches are desirable for optimizing reinforced membrane fabrication conditions
  - 9MeOTTP-PBI PTFE reinforced membrane
    - Thickness uniformity of 9MeOTTP-PBI PTFE reinforced membrane needs improvement

- Proposed Future Work
  - 9MeOTTP-PBI polymer synthesis
    - Investigate conditions for large batch production of 9MeOTTP-PBI polymers
  - 9MeOTTP-PBI PTFE reinforced membrane preparation
    - Improve thickness uniformity of 9MeOTTP-PBI PTFE reinforced membrane
    - Work with Xergy to prepare PTFE reinforced membranes
    - Work with Giner to prepare electrolyzers
  - 9MeOTTP-PBI PTFE reinforced membrane characterization
    - More comprehensive tests of reinforced membranes including oxidation stability, conductivity, IECs, water uptake, and mechanical properties
  - RFB/fuel cell test
    - Test 9MeOTTP-PBI PTFE reinforced membrane in cerium RFBs and fuel cells

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

Summary

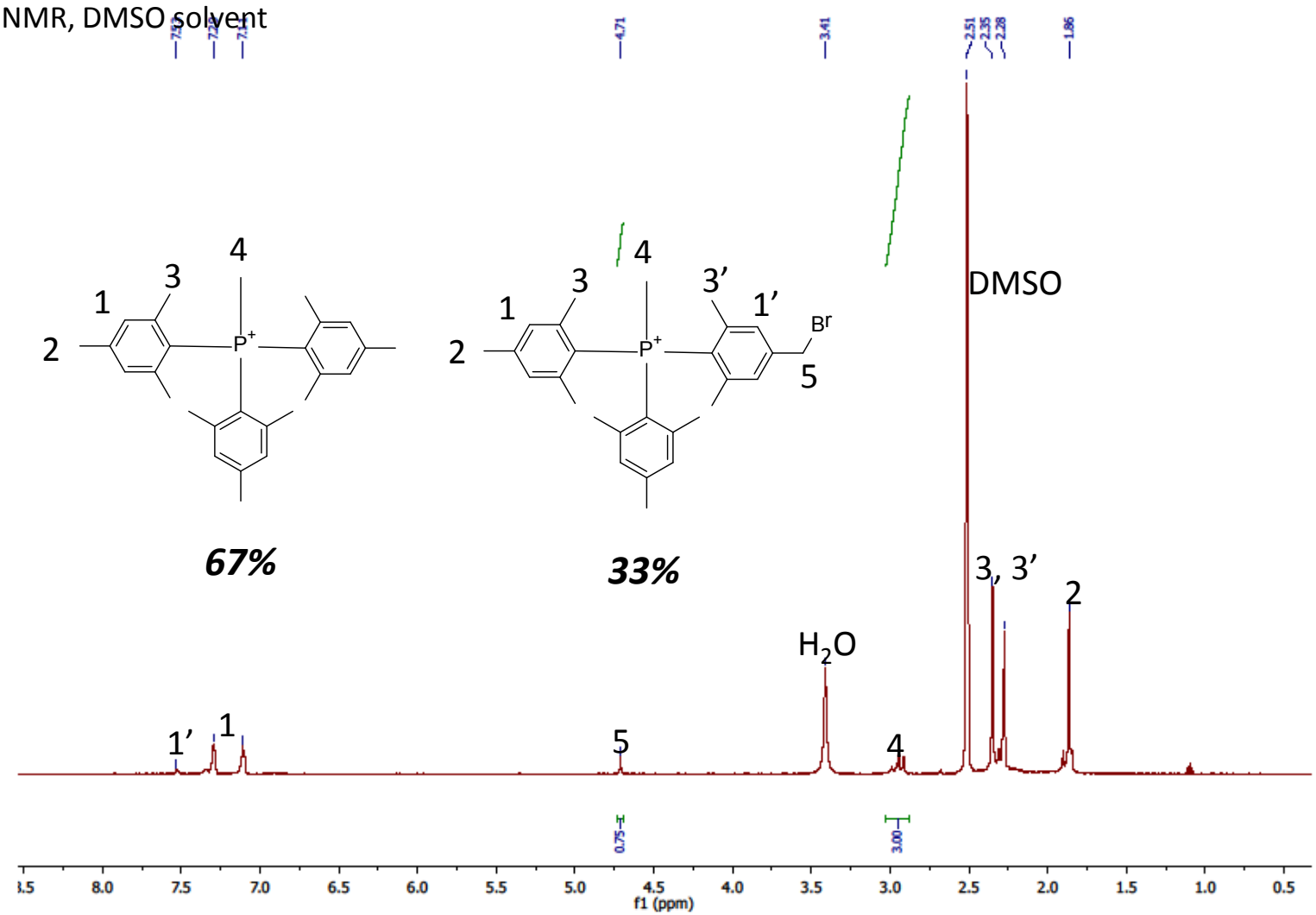
- 9MeOTTP-functionalized PBI polymer was synthesized.
- 9MeOTTP-PBI PTFE reinforced membrane was developed.
- 9MeOTTP-PBI PTFE reinforced membrane met the stability milestone of Q7/6.
- Partners are engaged and necessary new no-cost collaborations are established and engaged.
- All past project milestones have been met and the remaining ones are expected to be met on schedule.

Technical Backup Slides

Backup Slides

Bromination of 9MeTTP$^+$ cation in small scale (0.1 g)

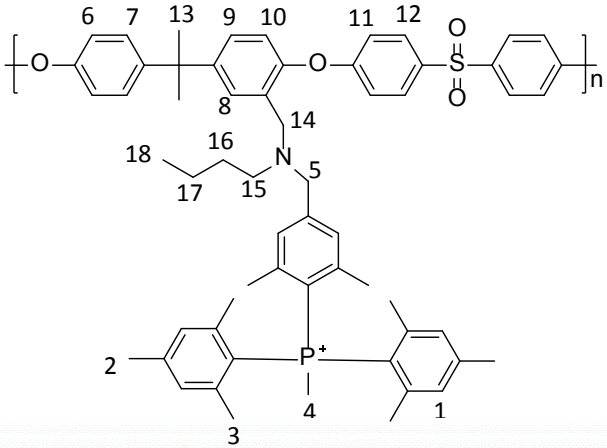
^{1}H NMR, DMSO solvent

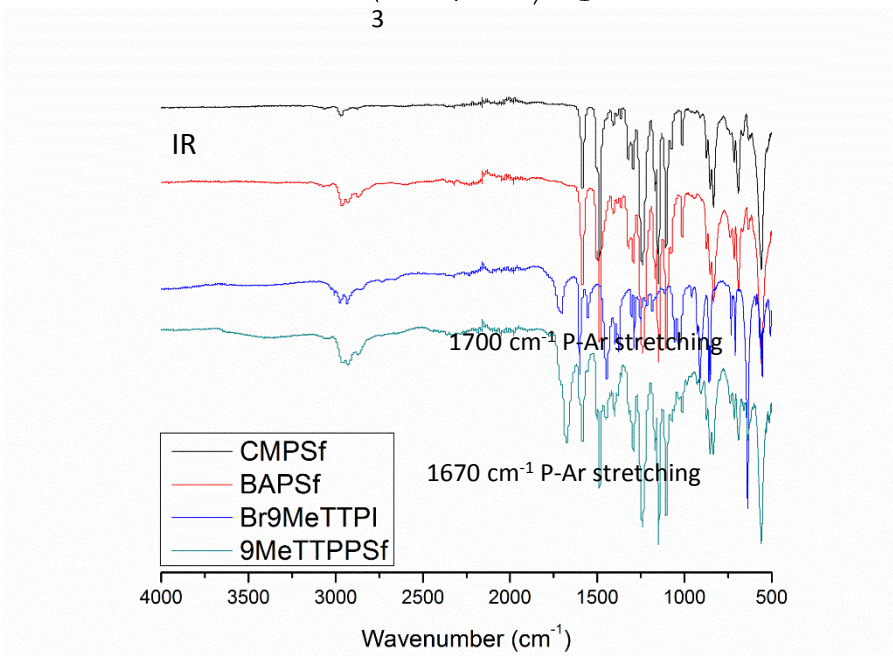


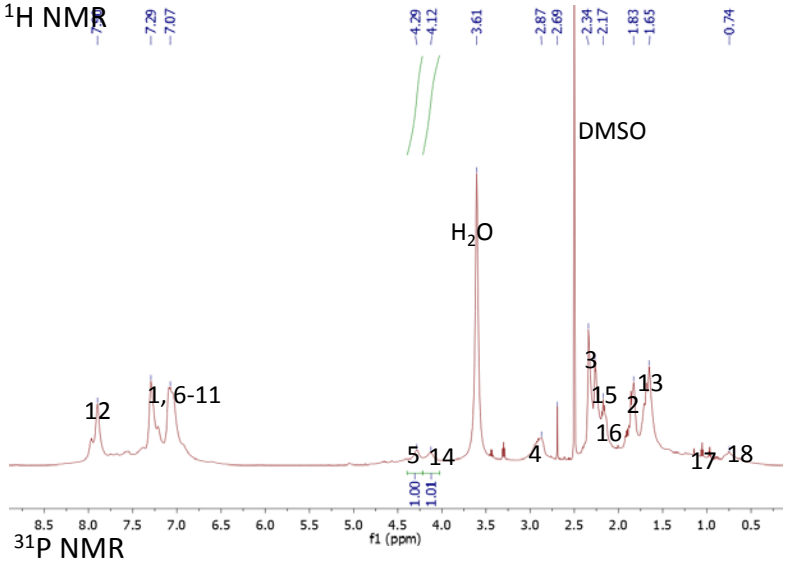
- 33 % single bromination with no multiple bromination was achieved in small scale (0.1 g).

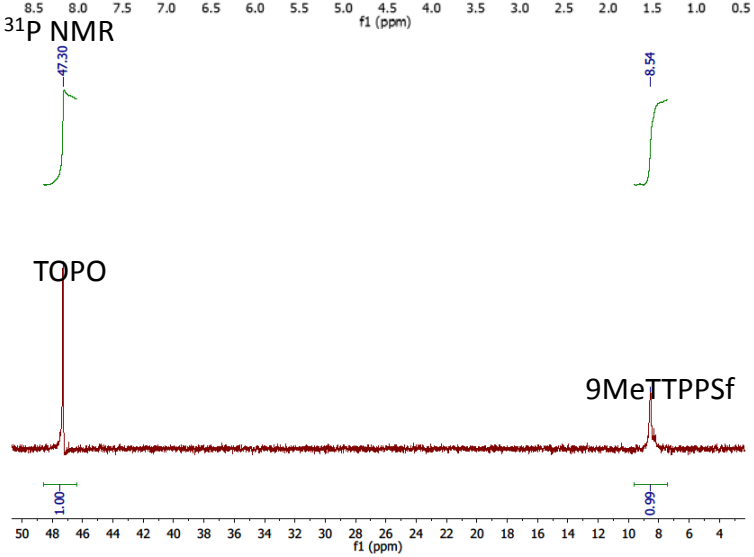
Backup Slides

9MeTTP – PSf synthesized from brominated 9MeTTP+









- 9MeTTP-PSf polymer was successfully synthesized and purified.

Backup Slides

Arrhenius equation for cation oxidation

$$k = \mathrm{K}\frac{k_B T}{h} e^{-\frac{\Delta G^{\neq}}{RT}}$$

k_B = 1.3806e-23 J · K^{-1}
h = 6.6261e-34 J · s
R = 1.9859 cal · K^{-1} · mol^{-1}
K = C mol · L^{-1} (C is a constant)

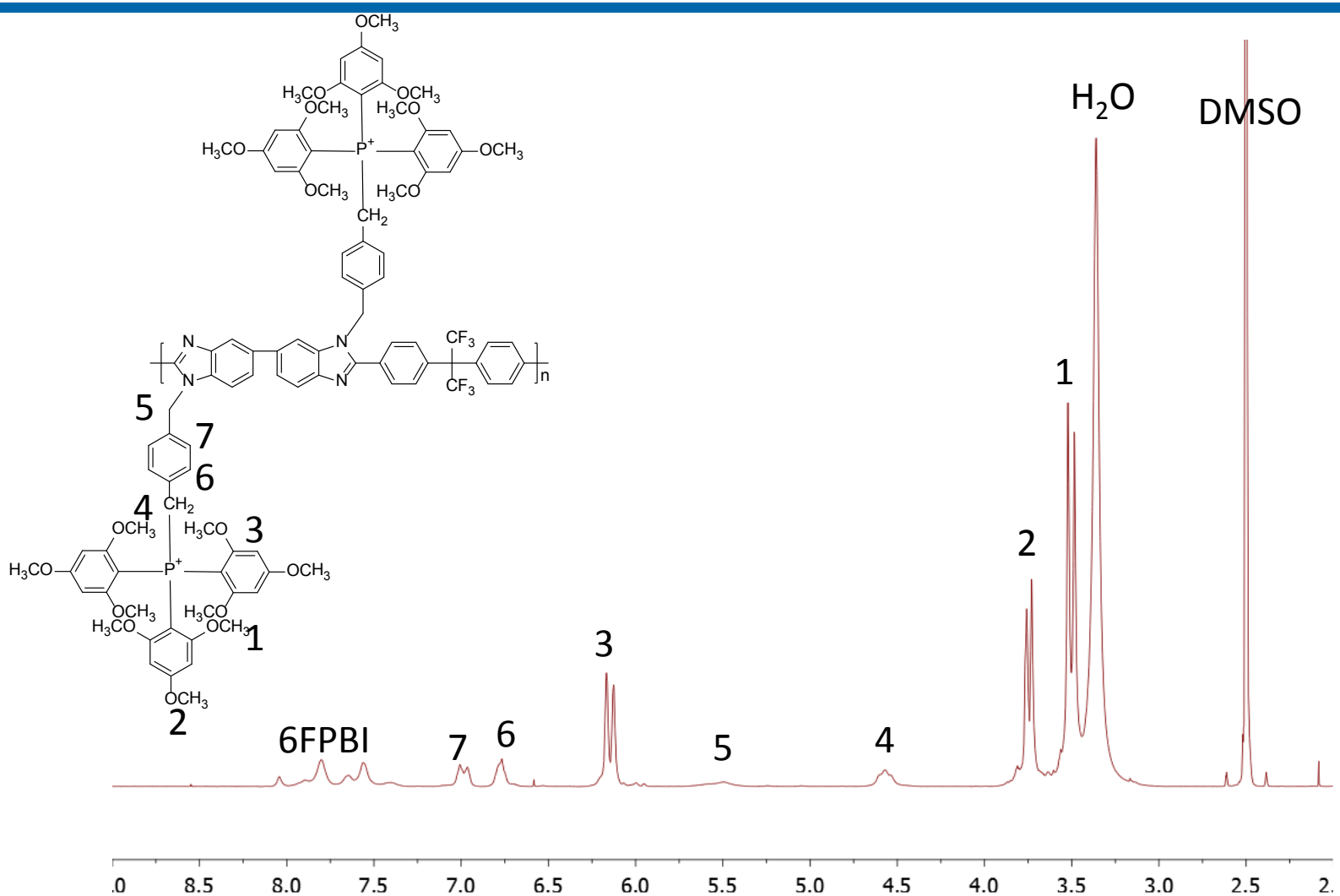
- Assumptions:
  - Zero-order kinetics for polymer degradation
  - PBI backbone is stable during the test, and only TTP^+ cation oxidation happening during stability test
  - Activation energies of cation oxidation are from the thesis of Dr. Bingzi Zhang from Yan group. http://search.proquest.com/pqdtlocal1006271/docview/1708646894/90D7289985F64862PQ/1?accountid=10457

- For $9MeTTP^+$ cation, $\Delta G^{\neq}$ = 31.0 Kcal·mol^{-1}
  - T_1 = 313.15 K, k_1 = 1.4643e-9/C mol · L^{-1} · s^{-1};
  - $k_2 = 10 \cdot k_1$, T_2 = 327.993 K = 54.843 °C
- For $9MeOTTP^+$ cation, $\Delta G^{\neq}$ = 30.9 Kcal·mol^{-1}
  - T_1 = 313.15 K, k_1 = 1.7198e-9/C mol · L^{-1} · s^{-1};
  - $k_2 = 10 \cdot k_1$, T_2 = 328.045 K = 54.895 °C

Yan et al. Exploring the structure-alkaline stability relationship of quaternary phosphonium cations. *pending*

Backup Slides

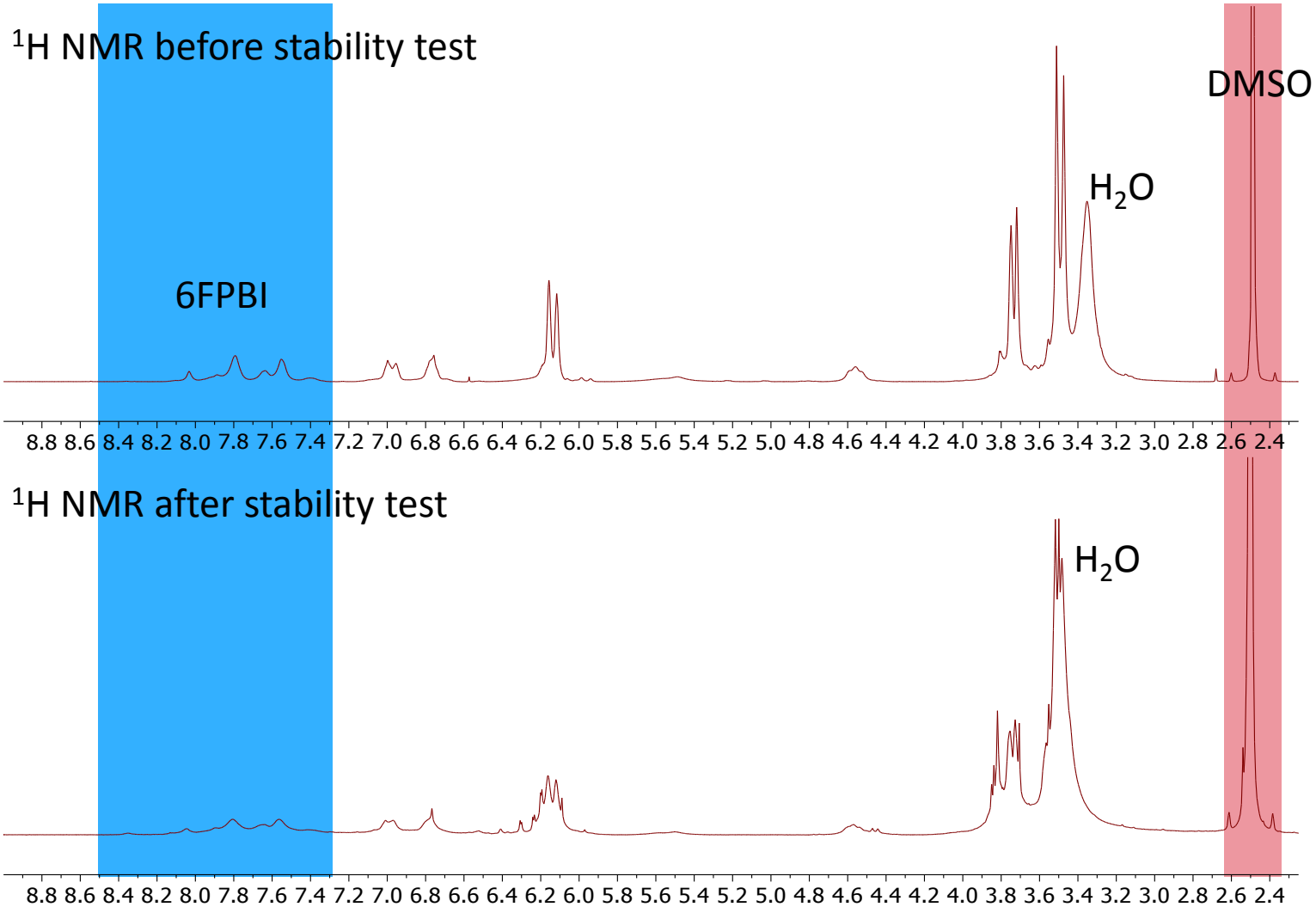
9MeOTTP – PBI, DS = 200 %



- 9MeOTTP-PBI polymer was successfully synthesized and purified.

Backup Slides

9MeOTTP – PBI PTFE reinforced membrane, ^{1}H NMR change



- 9MeOTTP-PBI polymer has noticeable degradation after stability test. Detailed degradation mechanism remains to be studied.