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

Final Technical Report

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Objectives, Barriers and Technical Targets

Insufficient oxidation resistance is a major hindrance to the use of polymeric electrolyte membranes in electrochemical devices such as fuel cells, electrolyzers, and redox flow batteries (RFBs). This problem is especially pronounced for high voltage RFBs that implement a strong oxidant as a part of the positive redox pair. The objective of this project is to develop a new class of anion-exchange membranes (AEMs) with very high oxidation resistance for high-voltage (i.e., 3 V in an aqueous system) cerium RFBs, and other AEM-based electrochemical devices such as fuel cells and electrolyzers. By developing a new oxidation stable AEM, we significantly improve upon the lifetimes of commercial AEM membranes and address the durability, cost and performance technical barriers from the fuel cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan. The most significant milestone of this project is to demonstrate a membrane with less than 20% loss of initial anion conductivity in an accelerated stability test at 55°C for 100 hours in 0.5 M $Ce(IV)(ClO_4)_4$ and significantly improved lifetime over state-of-art commercial membranes in cerium RFB testing.

Executive Summary

In this work, multiple polymer backbones were screened for oxidation resistance and multiple chemistries were explored for tethering tris(2,4,6-trimethylphenyl)phosphonium ($9MeTTP^+$) to the selected polymer backbones. A new tethering strategy through brominated $9MeTTP^+$ cation was developed and used to obtain the desired $9MeTTP^+$–functionalized polysulfone (PSf) and hexafluoro polybenzimidazole (F_6PBI) polymer. The crosslinked $9MeTTP^+$–functionalized hexafluoro polybenzimidazole (9MeTTP–F_6PBI) polymer demonstrated excellent oxidation stability that met the go-no-go milestone of the first year. However, large-scale bromination inevitably involved multi-bromination products, which led to polymer crosslinking in the next tethering. A new synthesis strategy with diiodobutane as linker was developed to overcome the crosslinking problem. The prepared $9MeTTP^+$-F_6PBI membrane without crosslinking showed only 3.58% water uptake and less than 1 mS/cm OH^- conductivity in water at 20°C, possibly due to the hydrophobic $9MeTTP^+$ cation. In order to improve the conductivity, hydrophilic tris(2,4,6-trimethoxylphenyl)phosphonium ($9MeOTTP^+$) cation was tethered to an F_6PBI backbone, and a $9MeOTTP^+$-F_6PBI PTFE reinforced membrane was prepared with 17.4% water uptake to increase the mechanical strength and durability in cerium (IV) solution. A $9MeOTTP^+$-F_6PBI PTFE reinforced membrane had less than 20% conductivity loss during an accelerated stability test in 0.5 M cerium (IV) and 1.3 M $HClO_4$ at 55°C for 100 hours. Moreover, a $9MeOTTP^+$-F_6PBI PTFE reinforced membrane had more than double the lifetime of commercial FAS-30 and FAB-PK-130 AEMs during an accelerated stability test in 0.5 M cerium (IV) and 1.3 M $HClO_4$ at 55°C. Low area specific resistance (ASR) of a $9MeOTTP^+$-F_6PBI PTFE reinforced membrane in the sulfuric acid system was also achieved due to the high acid doping ability of the polymer structure. The cationic $9MeOTTP^+$-F_6PBI PTFE reinforced membrane shows a cerium (IV) permeability that is 27-fold lower than that of Nafion 212. Excellent voltage and energy efficiencies with a $9MeOTTP^+$-F_6PBI PTFE reinforced membrane were demonstrated in an all-vanadium redox flow battery (VRFB).

Introduction

As a reversible fuel cell, redox-flow batteries (RFBs) are one of the most promising electrochemical technologies with great scalability and durability (e.g., 15-20 years) required for intermittent renewable energy storage. In particular, cerium redox pair [Ce(IV)/Ce(III)]-based RFBs are appealing because of their unprecedented high cell voltages (up to 3.08 V with Zn negative pair) in an aqueous system. High cell voltage is a key factor in achieving high energy and power densities, which may lead to low storage cost. An anion-exchange membrane (AEM) is needed as a key component in cerium RFBs to achieve stable cell voltage and high coulombic efficiency. However, existing commercial ammonium cation-based AEMs have very limited stability when working with Ce(IV) electrolytes (e.g., less than 200 hours of durability). The lack of stable AEMs causes cerium RFBs to suffer from either high self-discharge rate or low coulombic efficiency. The development of highly stable and conductive AEMs has become one of the most urgent challenges for cerium RFBs as well as electrolyzers to become a viable electricity storage solution. However, with the prevailing focus on the alkaline stability in the AEM research community for fuel cell applications, the development of oxidation resistance AEMs have so far received limited attention. Herein, we propose to develop highly stable AEMs based on the sterically hindered $9MeTTP^+$ or $9MeOTTP^+$ cation and an oxidation stable backbone.

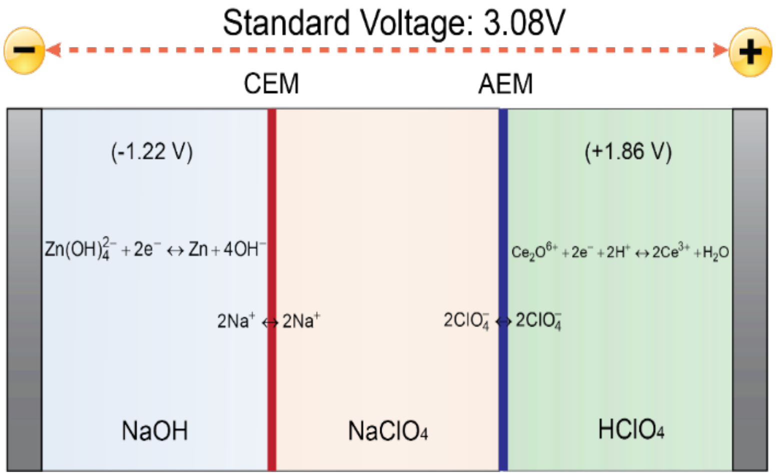

Figure 1. Double-membrane zinc-cerium RFB with 3.08 V standard voltage. An oxidation stable AEM is required by the cerium electrolyte.

Approach

We first examined a number of common polymers that were likely to meet the oxidation resistance and then explored multiple pathways and chemistries for connecting $9MeTTP^+$ to the selected polymers. After recognizing the low conductivity of the $9MeTTP^+$ polymers, believed to be due to the hydrophobic nature of the $9MeTTP^+$ cation, we switched to explore the chemistry of grafting $9MeOTTP^+$ to the thermo-oxidation stable F_6PBI backbone and then examined the performance and stability of the $9MeOTTP^+$-F_6PBI polymer in the cerium (IV) environment. Finally, RFB testing was conducted for the prepared $9MeOTTP^+$-F_6PBI PTFE reinforced membrane.

Results

We screened a number of chemically stable and commercially available polymers and found that polysulfone (PSf), polyether ether ketone (PEEK) and hexafluoro polybenzimidazole (F_6PBI) are oxidatively stable in Ce(IV) solutions with less than 1% weight loss and no appreciable morphology change during a 1000 hours cerium stability test.

Table 1. Stability test of polymer backbone at 40°C for 1000 hours in 0.5 M Ce(IV)(ClO_4)$_4$

	Weight loss (%) at 500 hours	Weight loss (%) at 1000 hours	Morphology change
PS	0 [a]	5	No
PPO	10	30	Cloudy and Brittle
PSf	0 [a]	0 [a]	No
PEEK	0 [a]	0 [a]	No
F_6PBI	0 [a]	0 [a]	No

[a] 0 denotes less than 1% weight loss

Direct tethering through the central phosphorus atom of 9MeTTP to the polymer backbone was proven infeasible due to the high steric hindrance of the 9MeTTP molecule. We devised a new synthesis strategy, tethering through a brominated 9MeTTP$^+$ cation, and obtained the desired 9MeTTP$^+$ −functionalized polysulfone (PSf) (Figure 2) and hexafluoropolybenzimidazole (F_6PBI) (Figure 3).

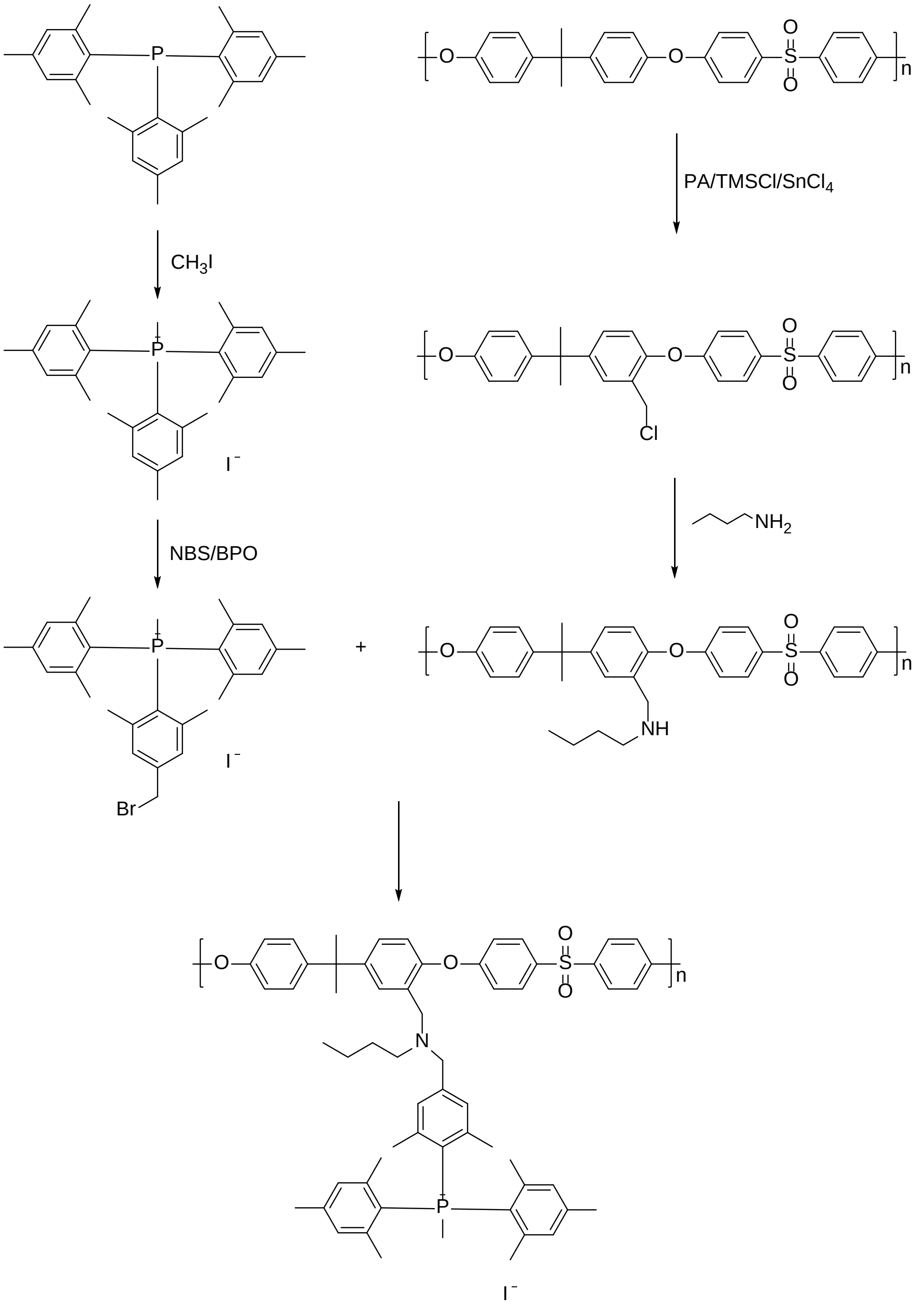

Figure 2. Synthesis route for 9MeTTP−PSf

However, the functionalized PSf was not stable enough due to the presence of cations on the tether, which activated backbone degradation. Therefore, we chose to focus on $9MeTTP^+$−functionalized F_6PBI.

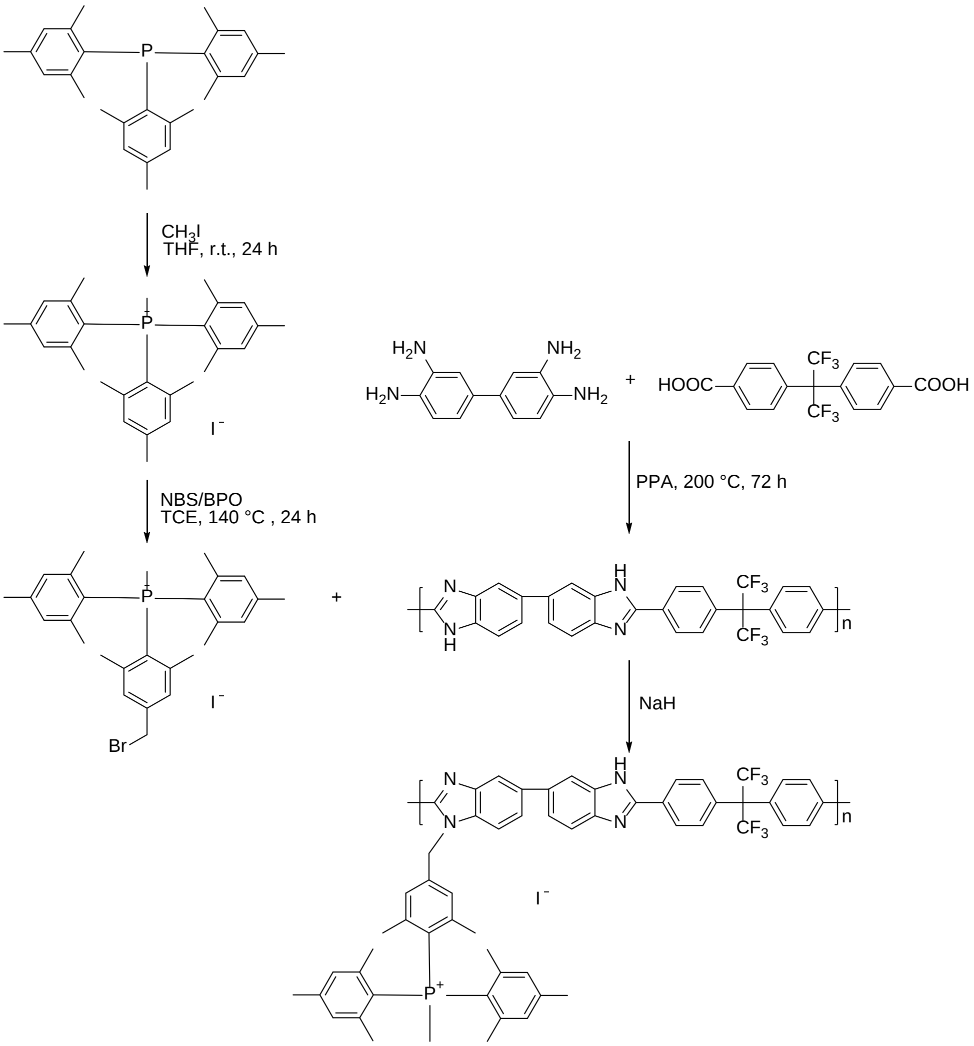

Figure 3. Synthesis route for 9MeTTP− F_6PBI

9MeTTP$^+$−functionalized hexafluoropolybenzimidazole (9MeTTP− F_6PBI) has shown excellent oxidation stability and met the year 1 go/no-go milestone of less than 20% loss of initial IEC at 40°C for 1000 hours in 0.5M Ce(IV)$(ClO_4)_4$ by passing an accelerated stability test at 55°C for 100 hours, based on the Gibbs energy of activation for 9MeTTP+ cation oxidation of 31.0 kcal/mol (from the PhD thesis of Dr. Bingzi Zhang of the Yan group, 2015).

Table 2. 9MeTTP$^+$−functionalized polymer IEC test at 40°C for 1000 hours in 0.5 M Ce(IV)$(ClO_4)_4$

Time (hours)	0	500	1000
9MeTTP−PSf IEC	0.5660	0.3023 (46.59% loss)	
9MeTTP− F_6PBI IEC [a]	0.5591		0.5558(0.59% loss)

[a] The 9MeTTP−F_6PBI polymer was tested via accelerated test at 55°C for 100 hours in 0.5 M Ce(IV)$(ClO_4)_4$. This condition is equivalent as 40°C for 1000 hours in 0.5 M Ce(IV)$(ClO_4)_4$.

$9MeTTP^+$-F_6PBI polymer showed excellent IEC retention (less than 0.59% loss) during accelerated stability test in cerium (IV) (presented in FY 2016 Annual Progress Report). However, the $9MeTTP^+$-F_6PBI polymer tested was crosslinked due to multiple bromination of the $9MeTTP^+$ cation. To overcome the crosslinking problem, a new method of utilizing diiodobutane as a linker molecule was conducted and produced soluble $9MeTTP^+$-F_6PBI polymer for membrane casting. The membrane obtained had OH^- conductivity of less than 1 mS/cm in water at 20°C, likely due to the hydrophobic nature of the $9MeTTP^+$ cation.

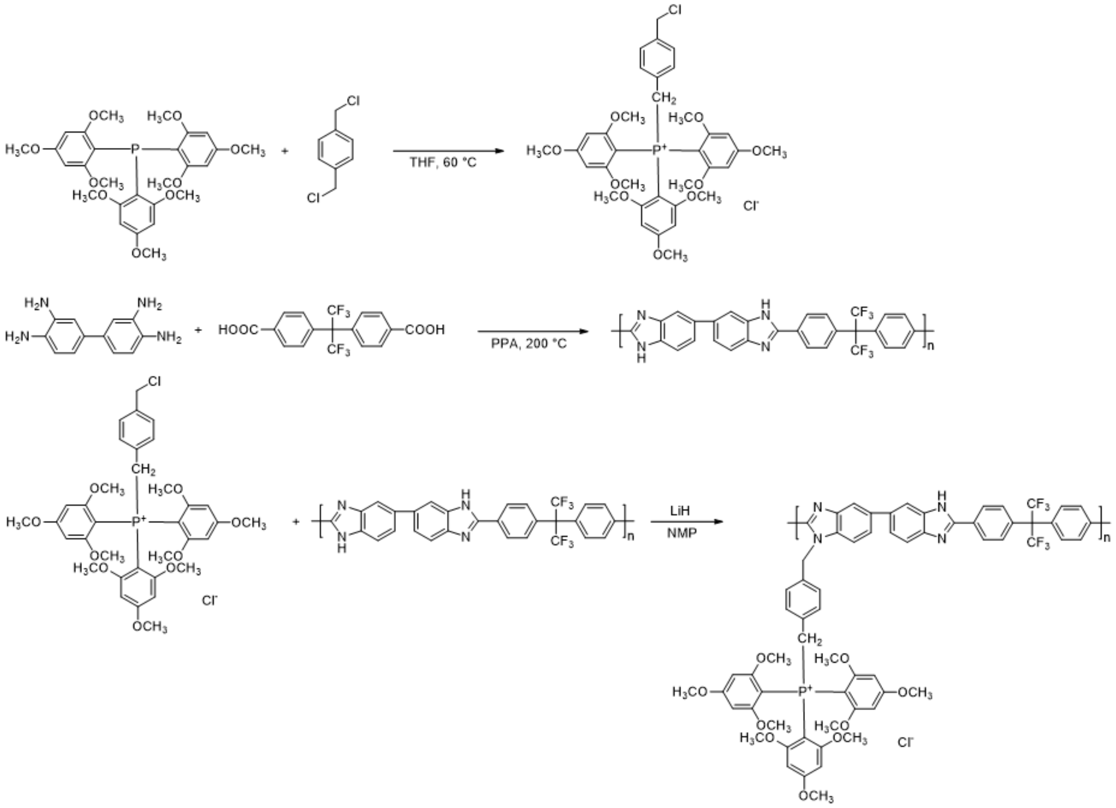

Figure 4. Synthesis route for 9MeOTTP− F_6PBI

In order to solve this problem, a hydrophilic $9MeOTTP^+$ cation was tethered to the F_6PBI backbone. A PTFE reinforced membrane (Figure 5) was prepared to restrict swelling and increase the mechanical strength and durability in cerium (IV) solution. For $9MeTTP^+$-F_6PBI membrane, the OH^- conductivity was less than 1 mS/cm with a water uptake of only 3.58% at 20°C. In contrast, the $9MeOTTP^+$-F_6PBI membrane showed 80% water uptake at 20°C before PTFE reinforcement, and the PTFE reinforced $9MeOTTP^+$-F_6PBI membrane showed ClO_4^- conductivity of 2.7 mS/cm and 17.4% water uptake at 20°C.

Figure 5. Prepared 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane with thickness 20 μm

After the accelerated stability test in 0.5 M Ce(IV) and 1.3 M HClO$_4$ at 55°C for 100 hours, 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane showed 13 - 19% conductivity loss in a temperature range of 20°C to 70°C (Figure 6). This membrane met milestone Q8/7 (i.e., less than 20% loss of initial anion conductivity).

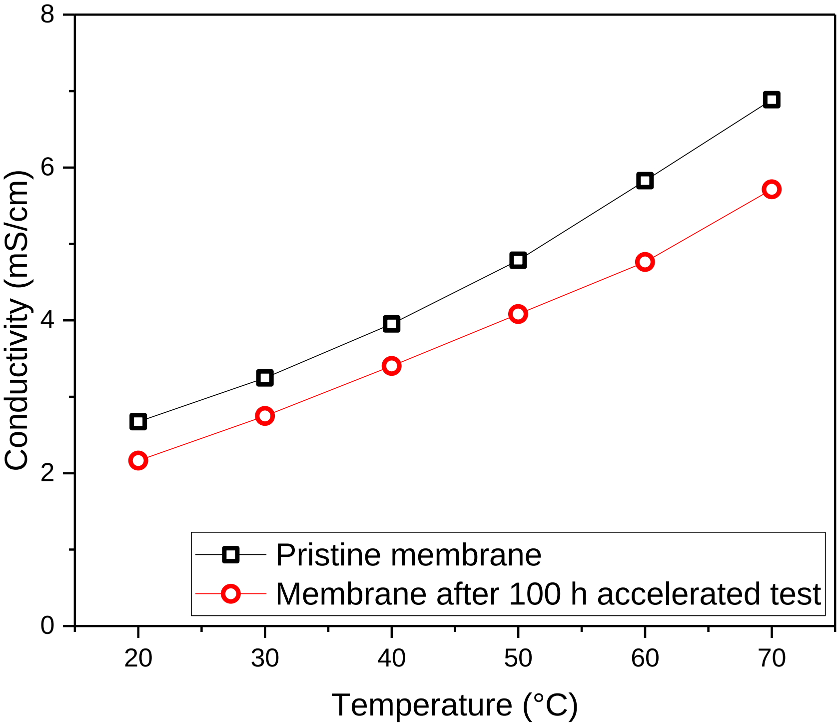

Figure 6. Conductivity (ClO$_4^-$ form) of 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane measured at different temperatures before and after accelerated oxidation stability test in in 0.5 M Ce(IV) and 1.3 M HClO$_4$ at 55°C for 100 hours

In addition, commercial AEM FAS-30 and FAB-PK-130 from fumasep® were also tested by the same procedure and dramatically failed the test in the first 100 hours, while 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane showed no noticeable morphology change during 200 hours of testing as shown in Table 3. Micrographs of FAB-PK-130 and 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane before and after accelerated oxidation stability test were taken (Figure 7). The commercial FAB-PK-130 membrane suffered breakage of the membrane and loss of polymer, while no appreciable change was observed for the 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane.

Table 3. Accelerated stability test results in 0.5 M cerium (IV) and 1.3 M $HClO_4$ at 55℃

Membrane	Thickness (µm)	24 hours	100 hours	200 hours
FAS-30	30	Breakage into pieces		
FAB-PK-130	130		Loss of polymer	
9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane	20			No appreciable morphology change

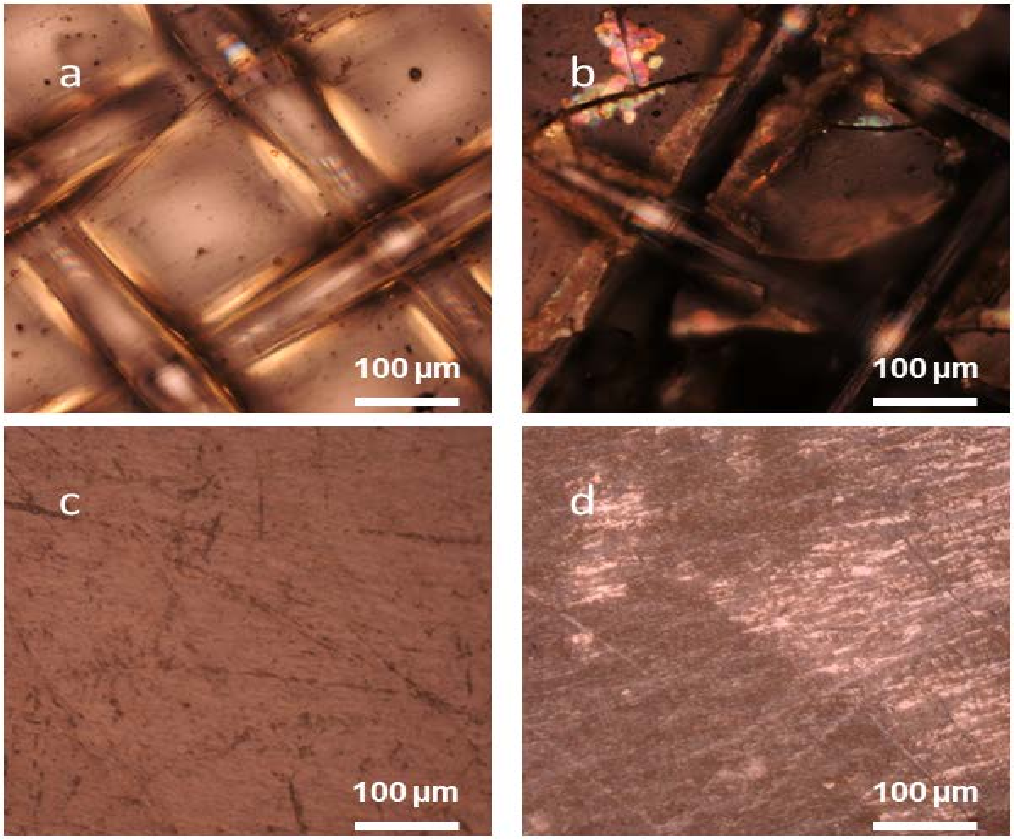

Figure 7. Micrograph of FAB-PK-130 and 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane before and after accelerated oxidation stability test in 0.5 M Ce(IV) and 1.3 M $HClO_4$ at 55°C for 100 hours. (a and b: FAB-PK-130 before and after; c and d: 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane before and after)

Unlike traditional ammonium cations, 9MeOTTP$^+$ is attractive for acid doping because its large cationic group size has space for extra ‘free acids’ and its nine protruding methoxy groups are capable of forming hydrogen bonds with extra ‘free acids’, especially in concentrated acids (illustrated in Figure 8). As shown in Figure 9 a, the area specific resistance (ASR) of the 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane is lower than Nafion 212, F$_6$PBI, FAB and FAS membranes in 3 M sulfuric acid.

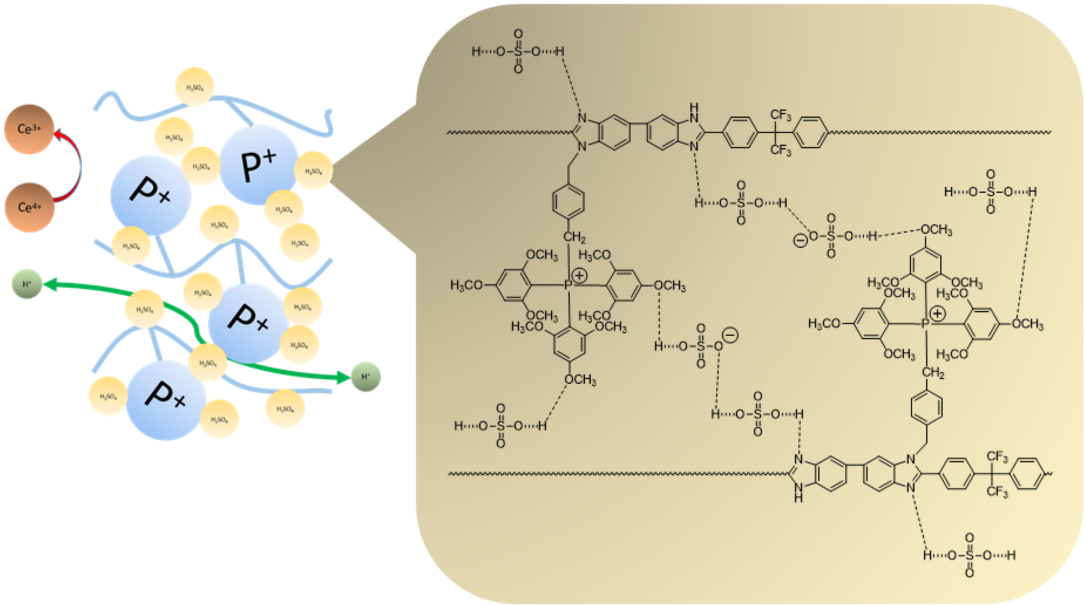

Figure 8. (left) schematic principle of the designed membrane with large phosphonium 9MeOTTP$^+$-sulfuric acid conducting channel; (right) acid doping and proton conducting mechanism of 9MeOTTP$^+$-F$_6$PBI membrane.

Considering the strongly acidic environment of the permeation test (0.1 M cerium (IV) and 1 M H_2SO_4), it is likely that the F$_6$PBI backbone is also positively charged due to the formation of hydrogen bonds between the acid and nitrogen groups. The 9MeOTTP$^+$ cations combined with the positively charged basic heterocyclic groups in the F$_6$PBI backbone repulse the cerium ions leading to a high selectivity based on Donnan exclusion. In our test, cerium (IV) had a 27-fold lower permeability through the 9MeOTTP$^+$-F$_6$PBI PTFE reinforced membrane than through Nafion 212.

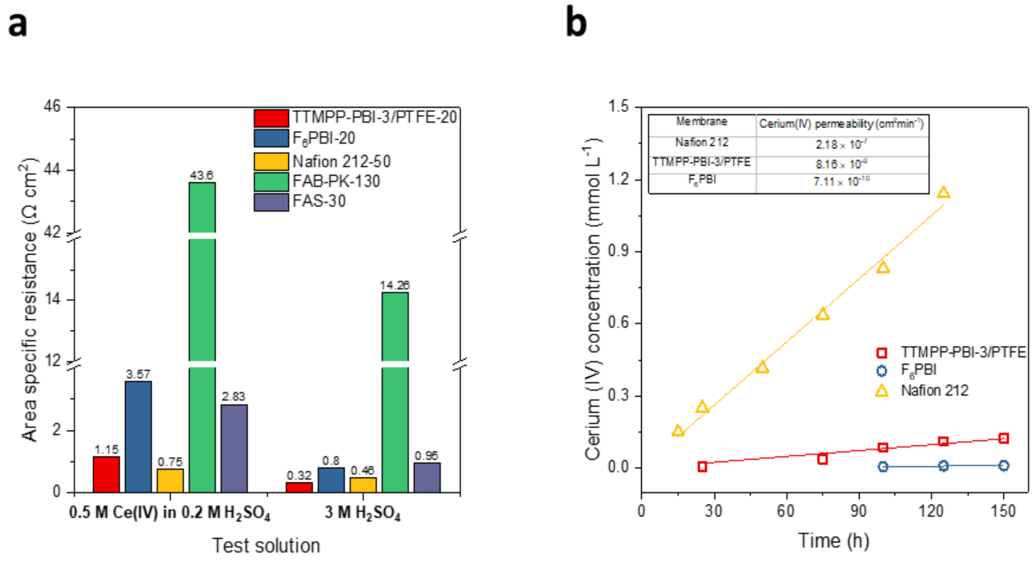

Figure 9. Characteristics of the prepared 9MeOTTP$^+$-F_6PBI PTFE reinforced membrane, F_6PBI membrane and Nafion 212 membrane. (a) Area specific resistance of TTMPP-PBI-3/PTFE, F_6PBI, Nafion 212, FAB-PK-130 and FAS-30 in different test solutions; (b) cerium (IV) concentration versus time at the deficient side using TTMPP-PBI-3/PTFE, F_6PBI and Nafion 212, with calculated cerium (IV) permeability in table.

We utilized the superior low ASR of our 9MeOTTP$^+$-F_6PBI PTFE reinforced membrane in 3 M sulfuric acid in the most developed VRFB system. The VRFB assembled with 9MeOTTP$^+$-F_6PBI PTFE reinforced membrane showed excellent coulombic, voltage and energy efficiency (Figure 10).

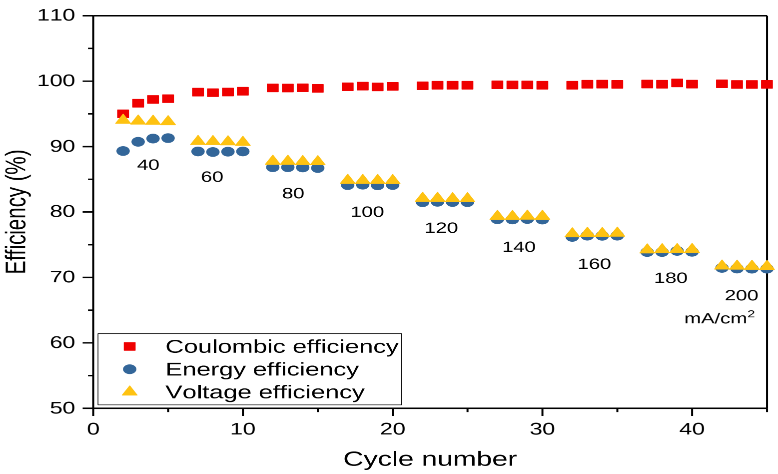

Figure 10. VRFB efficiency test results (electrolyte: 1.5 M vanadium and 3 M sulfuric acid; Membrane: 9MeOTTP-PBI PTFE reinforced membrane (20 µm); Electrolyte volume: 15 ml; Temperature: 20°C; Flow rate: 30 ml/min; Cut off voltage: 1.7 V to 1.0 V)

Conclusions

The project has explored multiple chemistries for connecting 9MeTTP$^+$ to different polymer backbones. The direct quaternization method through the central phosphorus atom has proven to be infeasible due to the high steric hindrance of the 9MeTTP molecule. 9MeTTP-PSf and 9MeTTP-PBI were synthesized from brominated 9MeTTP$^+$. However, during large-scale production, these tend to crosslink due to multiple bromination. PSf was proven to be unstable in the highly oxidative Ce(IV) environment after functionalization by ammonium. A 9MeTTP-PBI crosslinked polymer synthesized from brominated 9MeTTP$^+$ had 0.59% IEC loss during a 100-hour 0.5 M Ce(IV) test at 55^{o}C. This performance exceeded the GNG milestone.

7MeTTP was proposed and synthesized to achieve single brominated phosphonium, but multiple brominations still occurred and the overall degree of bromination was low. We improved the synthesis strategy through the iodobutane-9MeTTP$^+$ cation and obtained the desired 9MeTTP-PBI membrane. However, this 9MeTTP-PBI membrane had no conductivity due to the hydrophobic 9MeTTP$^+$ cation.

To improve the water uptake, hydrophilic 9MeOTTP$^+$ was used to synthesize 9MeOTTP-F$_6$PBI polymer. In order to improve the long term mechanical strength of 9MeOTTP-PBI membrane, a reinforced membrane based on PTFE substrate was developed. 9MeOTTP-PBI PTFE reinforced membrane showed less than 20% conductivity loss during a 100-hour, 0.5 M Ce(IV) test at 55^{o}C. This test condition is equivalent to the 1000-hour, 0.5 M Ce(IV), 40^{o}C test condition.

The 9MeOTTP-PBI PTFE reinforced membrane has fulfilled all the stability requirements listed in the proposal. 9MeOTTP-PBI PTFE reinforced membrane showed excellent conductivity after acid doping in 3 M sulfuric acid aqueous solution. 9MeOTTP-PBI PTFE reinforced membrane was tested in an all-vanadium RFB. The high voltage RFB with cerium electrolyte was not tested due to corrosion of the graphite block and carbon felt electrode during cerium flow cycling. Fuel cell performance was not tested due to the low OH$^-$ conductivity of 9MeOTTP-PBI PTFE reinforced membrane in an alkaline environment. During this project, new no-cost collaborations were established and partners continue to be engaged in future research to further improve membrane properties.

Project Milestones

Quarter	Quarter End Date	Milestones	Status
Q1	08/30/2015	Less than 10% loss of initial weight for the identified polymer at 40°C for 1000 hours 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 hours in 0.5 M $Ce(IV)(ClO_4)_4$**	Delayed 1 month; Completed 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 hours in 0.5 M $Ce(IV)(ClO_4)_4$**	Completed on time
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	Vanadium RFB tested

*quarter number for original proposed timeline
**approved accelerated oxidation stability test condition