

V.C.5 Highly Stable Anion-Exchange Membranes for High-Voltage Redox-Flow Batteries

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in high-voltage cerium RFBs, and other alkaline membrane-based electrochemical devices such as fuel cells and electrolyzers.

FY 2016 Accomplishments

- Screened multiple polymers for oxidation resistance.
- Explored multiple chemistries for tethering 9MeTTP⁺ to selected polymer backbones.
- Developed a new synthesis strategy through brominated 9MeTTP⁺ cation, and obtained the desired 9MeTTP⁺-functionalized polysulfone (PSf) and hexafluoro polybenzimidazole (6FPBI).
- Demonstrated excellent oxidation stability of 9MeTTP⁺-functionalized hexafluoro polybenzimidazole (9MeTTP-PBI) that met the go/no-go milestone.



INTRODUCTION

As a reversible fuel cell, RFBs are one of the most promising electrochemical technologies with the 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) in an aqueous system. High cell voltage is a key factor in achieving high energy and power densities, which lead to low storage cost. An 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 h 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 to become a viable electricity storage solution. We recently developed an oxidation-resistant phosphonium cation (i.e., tris(2,4,6-trimethylphenyl) phosphonium, or 9MeTTP⁺), with the oxidative stability a factor of 1,500+ better than the conventional trimethyl ammonium cation and a factor of 25+ better than our previous-generation phosphonium cation (i.e., tris(2,4,6-trimethoxyphenyl) phosphonium, or 9MeOTTP⁺). The excellent oxidation resistance of 9MeTTP⁺ cation is attributed to protection from substantially improved steric hindrance. Herein we propose to develop highly stable AEMs functionalized with the 9MeTTP⁺ cation.

Overall Objectives

- Develop a new class of anion exchange membranes (AEMs) with very high oxidation resistance for high-voltage cerium redox flow batteries (RFBs), and other alkaline membrane-based electrochemical devices such as fuel cells and electrolyzers.

Fiscal Year (FY) 2016 Objectives

- Demonstrate 9MeTTP⁺-cation functionalized polymers with oxidation stability in 0.5 M Ce(IV)(ClO₄)₄ at 40°C for 1,000 hours or its equivalent.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project aims to develop new AEMs with high oxidation stability. These AEMs are targeted for applications

APPROACH

Our approach is to examine a number of common polymers that are likely to meet the oxidation resistance requirement and then explore multiple pathways and chemistries for connecting 9MeTTP⁺ to the selected polymers.

RESULTS

We have screened a number of polymers and found that PSf, Polyether ether ketone (PEEK) and 6FPBI are stable (Table 1).

TABLE 1. Stability Test of Polymer Backbone at 40°C for 1,000 h in 0.5 M Ce(IV)(ClO₄)₄

	Weight loss (%) at 500 h	Weight loss (%) at 1,000 h	Morphography change
PS	0 ^a	5	No
PPO	10	30	Cloudy and Brittle
PSf	0 ^a	0 ^a	No
PEEK	0 ^a	0 ^a	No
6FPBI	0 ^a	0 ^a	No

^a 0 means that the polymer has less than 1% weight loss
PS - Polystyrene; PPO - Poly(p-phenylene oxide)

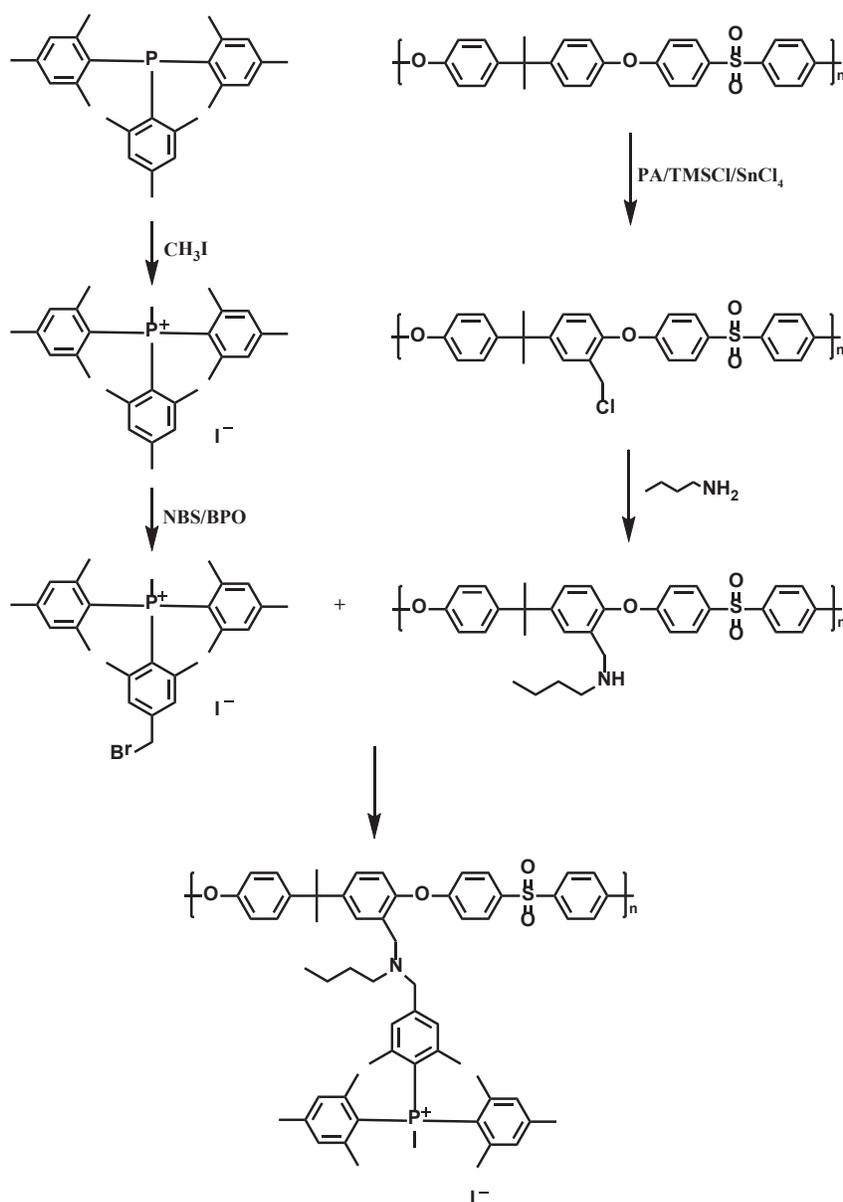


FIGURE 1. Synthesis route for 9MeTTP-PSf

As for tethering of the 9MeTTP⁺ to the polymer backbone, direct attachment through the central phosphorus atom proved infeasible due to the high steric hindrance of the 9MeTTP molecule. We then devised a new synthesis strategy through the brominated 9MeTTP⁺ cation, and obtained the desired 9MeTTP⁺-functionalized PSf and 6FPBI. Synthesis routes for 9MeTTP-PSf and 9MeTTP-PBI are shown in Figure 1 and Figure 2 respectively. The functionalized PSf was not stable enough due to the presence of cations on the tether, which activate the backbone degradation. Therefore, we chose to work on 9MeTTP⁺-functionalized 6FPBI.

9MeTTP-PBI has shown excellent oxidation stability. In an accelerated ageing test in 0.5M Ce(IV) ClO₄ at 55°C, the 9MeTTP-PBI lost only 0.59% of its ion exchange capacity

after 100 hours (equivalent to 1,000 hours at 40°C based on the activation energy of decay of the 9MeTTP⁺ cation) and met the Year 1 go/no-go milestone (Table 2).

TABLE 2. 9MeTTP⁺-Functionalized Polymer Ion Exchange Capacity (IEC) Test at 40°C for 1,000 h in 0.5 M Ce(IV)(ClO₄)₄

Time (h)	0	500	1,000
9MeTTP-PSf IEC	0.5660	0.3023 (46.59% loss)	
9MeTTP-PBI IEC ^a	0.5591		0.5558 (0.59% loss)

^a 9MeTTP-PBI polymer was tested via accelerated test at 55°C for 100 h in 0.5 M Ce(IV)(ClO₄)₄ (this condition is equivalent as 40°C for 1,000 h in 0.5 M Ce(IV)(ClO₄)₄)

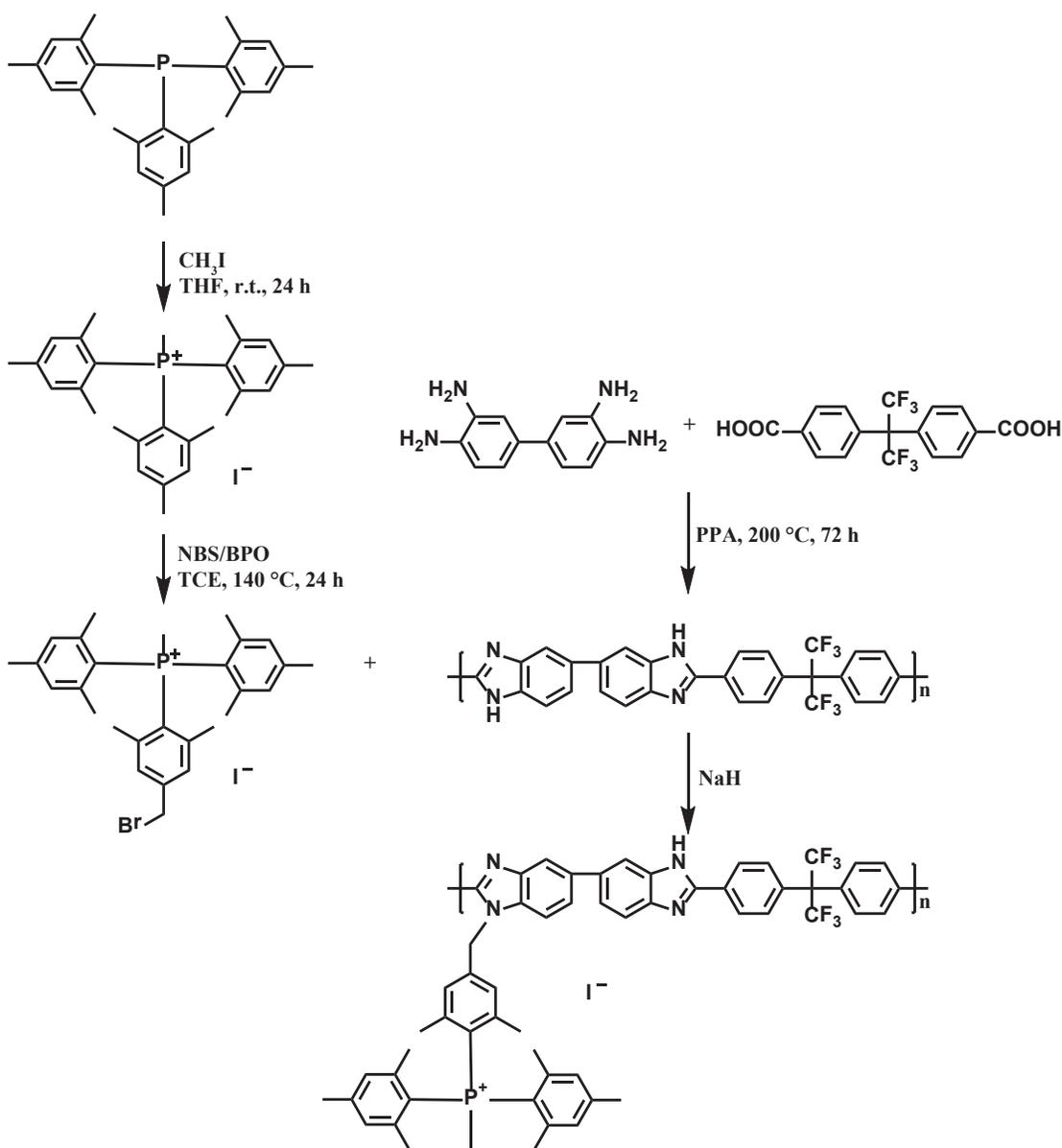


FIGURE 2. Synthesis route for 9MeTTP-PBI

CONCLUSIONS AND FUTURE DIRECTIONS

Although the project is still ongoing, several conclusions can be drawn.

- The direct quaternization method through the central phosphorus atom proved infeasible due to the high steric hindrance of the 9MeTTP molecule.
- The new bromination method proved feasible and led to a 9MeTTP-PBI polymer that met the year one durability target.

Future work includes:

- Development of a membrane preparation method for 9MeTTP⁺-functionalized polymers.
- Development of alternative P⁺-functionalized polymers that have higher yield.
- Testing the stability of 9MeTTP⁺-based polymer membranes against Ce(IV) ions.
- Testing of the membrane in both RFB and fuel cell.