

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

Yushan Yan (Primary Contact), Shuang Gu,
Bingjun Xu

University of Delaware
150 Academy Street
Newark, DE 19716
Phone: (302) 831-2552
Email: yanys@udel.edu

DOE Manager: Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

Technical Advisor: John Kopasz
Phone: (630) 252-7531
Email: kopasz@anl.gov

Contract Number: DE-EE0006964 (Incubator)

Subcontractor:
Bryan Pivovar, National Renewable Energy Laboratory,
Golden, CO

Project Start Date: June 1, 2015
Project End Date: August 31, 2017

(B) Cost

(C) Performance

Technical Targets

This project aims to develop new AEMs with high oxidation stability. These AEMs are targeted for applications in high-voltage cerium RFBs, and other alkaline membrane-based electrochemical devices such as fuel cells and electrolyzers.

FY 2017 Accomplishments

- Synthesized 9MeTTP⁺-F₆PBI polymer without crosslinking and prepared its membranes with 0.52 mmol/g titration ion-exchange capacity and only 3.58% water uptake.
- 9MeTTP⁺-F₆PBI membranes had less than 1 mS/cm OH⁻ conductivity in water at 20°C possibly due to the hydrophobic 9MeTTP⁺ cation.
- Tethered hydrophilic 9MeOTTP⁺ cation to F₆PBI backbone, and prepared 9MeOTTP⁺-F₆PBI PTFE reinforced membrane with 17.4% water uptake to increase the mechanical strength and durability in cerium (IV) solution.
- Demonstrated that cerium (IV) had a 27-fold lower permeability through the cationic 9MeOTTP⁺-F₆PBI PTFE reinforced membrane than Nafion 212.
- Demonstrated that 9MeOTTP⁺-F₆PBI PTFE reinforced membrane had less than 20% conductivity loss during accelerated oxidation stability test in 0.5 M cerium (IV) and 1.3 M HClO₄ at 55°C for 100 h.
- Demonstrated that 9MeOTTP⁺-F₆PBI PTFE reinforced membrane had more than doubled lifetime during accelerated oxidation stability test in 0.5 M cerium (IV) and 1.3 M HClO₄ at 55°C than commercial FAS-30 and FAB-PK-130 anion exchange membranes.



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) 2017 Objectives

- Test poly-tetrafluoroethylene (PTFE) reinforced tris(2,4,6-trimethoxyphenyl) phosphonium (9MeOTTP⁺)-hexafluoro polybenzimidazole (F₆PBI) membrane with oxidation stability in 0.5 M Ce(IV) (ClO₄)₄ at 55°C for 100 h (this condition is equivalent to 40°C for 1,000 h).

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

INTRODUCTION

As a reversible fuel cell, RFBs are one of the most promising electrochemical technologies with the 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 aqueous

systems. 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. Herein, we propose to develop highly stable AEMs based on the 9MeOTTP⁺ cation and F₆PBI backbone.

APPROACH

Our approach is to explore the chemistry of grafting 9MeTTP⁺ and 9MeOTTP⁺ to the thermo-oxidatively stable F₆PBI backbone and then examine the performance and stability of membranes made from these materials in a cerium (IV) environment.

RESULTS

After several attempts that could not tether 9MeTTP⁺ to the polymer backbone using approaches of direct quaternization and use of 7MeTTP⁺ synthesized from Grignard reaction and so on, we were finally able to obtain 9MeOTTP⁺-F₆PBI polymer by quaternization using diiodobutane at 150°C with copper powder to inhibit diiodobutane degradation. The 9MeOTTP⁺-F₆PBI polymer showed excellent ion-exchange capacity retention (less than 0.59% loss) during accelerated oxidative stability tests in cerium (IV) (presented in FY 2016 annual progress report). However, its membrane had less than 1 mS/cm OH⁻ conductivity in water at 20°C, which is possibly due to the hydrophobic nature of 9MeOTTP⁺ cation. In order to solve the problem, a hydrophilic 9MeOTTP⁺ cation was tethered to F₆PBI backbone, and 9MeOTTP⁺-F₆PBI PTFE reinforced membrane (picture shown in Figure 1) with 17.4% water uptake was successfully prepared to increase the mechanical strength and durability in cerium (IV) solution.

Considering the strong acidic environment of the permeation test (0.1 M cerium (IV) and 1 M H₂SO₄), the F₆PBI backbone is also positively charged due to the formation of hydrogen bonds between the acid and nitrogen groups. The repulsion the cerium cations have with the 9MeOTTP⁺ cations and the positively charged basic heterocyclic groups on the polymer backbone creates a high selectivity based on Donnan exclusion. In our test, cerium (IV) had a 27-fold lower permeability through 9MeOTTP⁺-F₆PBI PTFE reinforced membrane than through Nafion 212 (Table 1).



FIGURE 1. Prepared 9MeOTTP⁺-F₆PBI PTFE reinforced membrane with thickness 20 μm

TABLE 1. Cerium (IV) Permeability Results

Membrane	Thickness (μm)	Cerium Permeability (m ² s ⁻¹)
Nafion 212	50±2	3.64*10 ⁻¹³
9MeOTTP ⁺ -F ₆ PBI PTFE Reinforced Membrane	20±2	1.36*10 ⁻¹⁴

After the accelerated oxidation stability test in 0.5 M Ce(IV) and 1.3 M HClO₄ at 55°C for 100 h, 9MeOTTP⁺-F₆PBI PTFE reinforced membrane showed 13% to 19% conductivity loss across 20°C to 70°C (results in Figure 2). This membrane met the milestone Q8/7 (i.e., less than 20% loss of initial anion conductivity). In addition, commercial anion exchange membranes FAS-30 and FAB-PK-130 from Fumasep[®] were also tested in the same procedure, and all failed the test in the first 100 hours. As shown in Figure 3 and Table 2, FAB-PK-130 membrane suffered significant loss of polymer, while 9MeOTTP⁺-F₆PBI PTFE reinforced membrane has no breakages or holes. (Note that in 3b and 3b', the color difference is due to the different background brightness.)

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has achieved all milestones scheduled within the reporting period:

- 9MeOTTP⁺-F₆PBI membrane was prepared and tested, but has insufficient conductivity likely due to the hydrophobic 9MeOTTP⁺ cation.

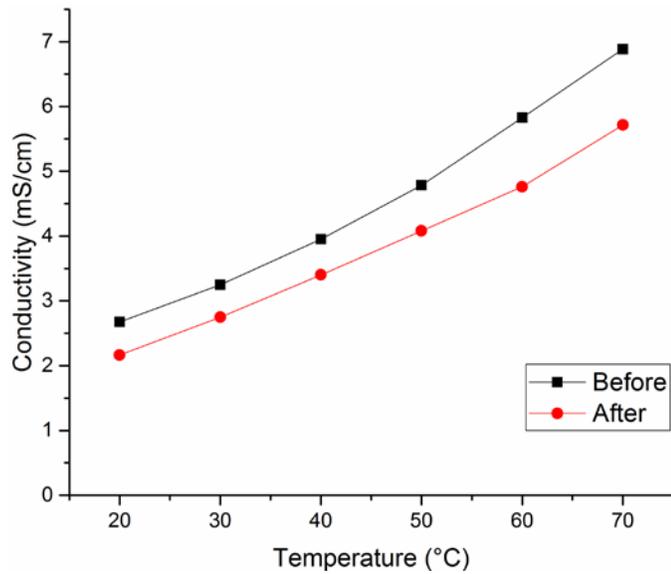


FIGURE 2. Conductivity (ClO_4^- form) of 9MeOTTP⁺-F₆PBI PTFE reinforced membrane measured at different temperatures before and after accelerated oxidation stability test in cerium (IV)

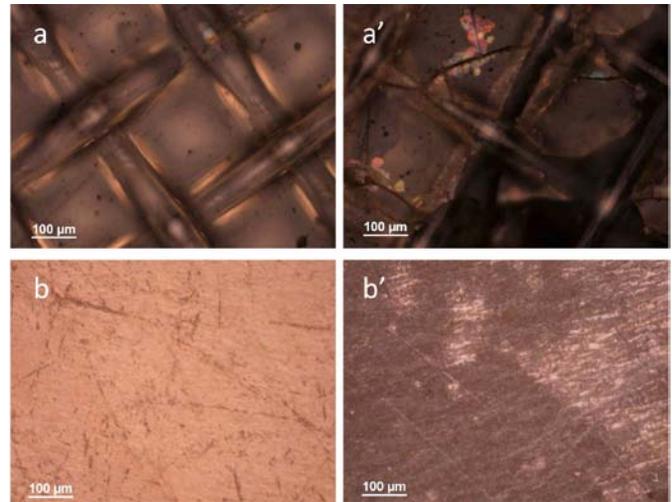


FIGURE 3. Microscopy image of FAB-PK-130 and 9MeOTTP⁺-F₆PBI PTFE reinforced membrane before and after accelerated oxidation stability test in 0.5 M cerium (IV) and 1.3 M HClO₄ at 55°C for 100 h (a and a': FAB-PK-130 before and after; b and b': 9MeOTTP⁺-F₆PBI PTFE reinforced membrane before and after)

TABLE 2. Accelerated Stability Test Results in 0.5 M Cerium (IV) and 1.3 M HClO₄ at 55°C

Membrane	Thickness (μm)	24 h	100 h	200 h
FAS-30	30	Break into pieces		
FAB-PK-130	130		Loss of polymer	
9MeOTTP ⁺ -F ₆ PBI PTFE reinforced membrane	20			No appreciable morphological change

- 9MeOTTP⁺-F₆PBI PTFE reinforced membrane showed excellent oxidative resistance against cerium (IV) solution.

Upcoming activities include:

- Membranes and ionomers shipped to the National Renewable Energy Laboratory for membrane electrode assembly preparation and tests.
- Collaborate with Xergy to prepare reinforced membranes.
- Collaborate with Giner to prepare reinforced membranes using their dimensionally stable membrane technology.