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Cardo-polyetherketone anion exchange membranes with suitable chemical/mechanical stability and performance for all-vanadium redox flow battery

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Introduction

As sustainable energy sources have been developed and commercialized over the past decade, redox flow battery (RFB) technology has been received more attention as an applicable energy storage system. RFBs employ redox species for storing energy like an ordinary battery but with continuous flow of active species through the electrodes. The storage of active species in external tanks permits the independent manipulation of capacity, energy and power densities. Among them, all-vanadium RFBs (VRFB) are preferred mostly because the intermixing of positive and negative solutions does not cause irreversible damage of the battery (the electrolytes can be regenerated electrochemically).

Perfluorosulfonic cation exchange membranes (i.e. Nafion®) have been traditionally used as separators in VRFB because of their high proton conductivity and excellent chemical stability. However, Nafion® has some drawbacks as their elevated cost and permeation of active species (vanadium cations) that result in self discharge of the battery. Anion exchange membranes (AEM) based on aromatic hydrocarbon polymers have advantages over Nafion®, including lower cost, and good thermal, chemical, and mechanical stability. Cation crossover is also reduced as a consequence of Donnan exclusion (cations are excluded of the membrane because of the presence of quaternary ammonium groups fixed in the polymer backbone). However AEMs are not extensively employed in VRFB because it is assumed the quaternary ammonium group (cationic site of AEMs) degrades in the presence of strong oxidizing vanadium solutions.(1)

In this work we will study the stability of cardo-polyetherketone (PEK-C) based AEMs under RFB working conditions. We will study the chemical and mechanical stability by immersion in vanadium (V) solutions (strong oxidizing), and during charge/discharge cycling to get more insight of how membrane behavior during RFB operation.

Experimental

PEK-C was purchased from Xuzhou Vat Chemical Company in China. Chlorotrimethylsilane and tin tetrachloride (Sigma Aldrich) were used for chloromethylation of PEK-C.(2) The chloromethylated PEK-C (CMPEK-C) was then reacted with trimethylamine (TMA) to obtain quaternary ammonium anion exchange membrane (QPEK-C/TMA$^+$).

Vanadium (IV) permeability was measured in a 20mL Frank diffusion cell (Permegear, Inc). The membrane conductivity was measured using 4 electrode conductivity cell immersed in DI water (Bekktech). Tensile tests (50°C and 50% relative humidity) were done in a Q800 dynamic mechanical analyzer (TA instruments). Redox flow battery (5 cm^2 single cell) testing was carried out in an acid-resistant fuel cell hardware (Fuel Cell Technologies, Inc). The MEA was assembled by sandwiching an AEM between two carbon felt electrodes activated by heating in air at 400°C for 36 h (Alfa Aesar).

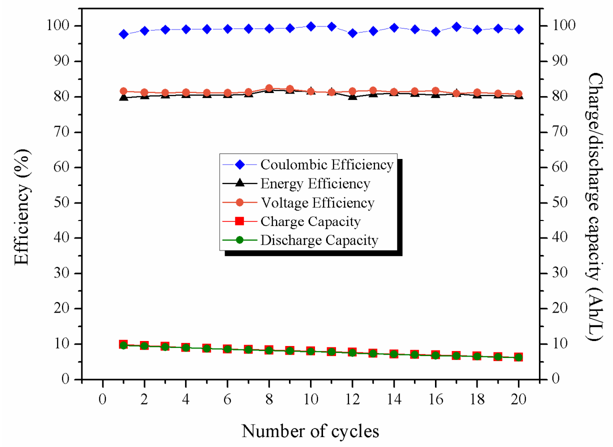

Figure 1. Coulombic, energy and voltage efficiencies, and battery capacity during RFB charge-discharge cycling (30 mA cm^{-2}) using QPEK-C/TMA$^+$ AEM as separator. 1.5 M vanadium solutions in 3 M H_2SO_4 solution.

Table 1. The effect of exposure of QPEK-C/TMA$^+$ AEM to 1.5 M VO_2^+ (in 3M H_2SO_4 at 30°C) on the ionic conductivity and ultimate tensile strength

Time of exposure to VO_2^+ (days)	Sulfate ionic conductivity (mS cm^{-1})	Ultimate tensile strength (MPa)
0	5.6 ± 0.2	19 ± 2
2	5.7 ± 0.3	20 ± 1
7	4.3 ± 0.5	18 ± 1
14	4.4 ± 0.4	19 ± 1
30	4.4 ± 0.6	21 ± 1

Results and discussion

QPEK-C/TMA$^+$ was prepared with a degree of chloromethylation of 0.9 which resulted after quaternization in an ion exchange capacity of 1.54 mmol/g. The structure of CMPEK-C and QPEK-C/TMA$^+$ were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, two-dimensional NMR correlation spectroscopy (COSY), and ^{1}H-^{13}C heteronuclear multiple quantum correlation (HMQC) spectroscopy. The same spectroscopic tools were employed to investigate the polymer structure before and after exposure to VO_2^+ solution and identify any possible degradation products.

Water absorption isotherms (VTI-SA, TA instruments) showed moderate water uptake. PEK-C, CMPEK-C and QPEK-C/TMA$^+$ SO_4^{2-} uptook (at 95% RH) 2%, 2% and 30%, respectively. The VO^{2+} permeability of QPEK-C/TMA$^+$ membrane (8.2 ±0.2 $\times 10^{-9}$ cm^2 s^{-1}) was 35 times lower than for Nafion® membranes (2.9 ±0.2 $\times 10^{-7}$ cm^2 s$^-$1).

We did not observe any changes in the tensile strength after 1 month immersion in the oxidizing solution (Table 1). The initial drop in the ionic conductivity could be explained by the penetration of the lower mobility vanadium ions into the membrane. HMQC (2D NMR) and RFB testing (Figure 1) also confirmed the absence of any chemical or mechanical degradation. The stability of the membrane under RFB operating conditions is a promising result that can lead to the widespread use of AEM as separators in RFBs.

References

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