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Communication—Sulfonated Poly (ether ether ketone) as Cation Exchange Membrane for Alkaline Redox Flow Batteries

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A sulfonated poly (ether ether ketone) (sPEEK) was tested as the separator in a full alkaline flow battery with 2,6-dihydroxyanthraquinone-ferro/ferricyanide, DHAQ-FeCy, redox couples. Cell performance was compared to that of an identical cell utilizing a perfluorosulfonic acid (PFSA) membrane. Replacement of the PFSA membrane with sPEEK resulted in a 10% power density increase, a 40% decrease in capacity loss per day and an 85-fold decrease in ferricyanide permeation. Though long-term stability of sPEEK in alkaline media requires improvement, these results highlight the potential to produce non-fluorinated membranes with better performance in organic redox flow batteries than the commercially available PFSAs.
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Aqueous organic redox flow batteries (AORFBs) constitute one of the most attractive alternatives to solve the storage problem associated with environmentally friendly, yet intermittent, power sources.[1,2–9] Promising electrolyte compositions have been reported for AORFBs using commercially available cation exchange membranes (CEMs) as the electrode separator. The typical materials of choice for these membranes are perfluorinated sulfonic acids (PFSAs), such as Nafion. One barrier that hinders their widespread adoption is their relatively high cost.[10] Replacement of PFSAs with a non-fluorinated membrane could reduce the cost of the films by a factor of 2.5 and facilitate the commercial implementation of AORFBs.[11] Though inspiring new AORFBs operating at neutral pH have recently been reported,[8,12–14] the majority of the systems developed to date require relatively harsh operation conditions (pH>13 or pH<0). These operating parameters limit the polymer chemistry choices that warrant further exploration. One promising starting point is the sulfonated version of poly ether ether ketone (sPEEK). This material has been previously tested as the CEM in fuel cells and vanadium redox flow batteries.[15,16] Herein we compare the performance of a sPEEK membrane with a 50% degree of sulfonation with that of a commercially available perfluorinated alternative, Nafion NR212. The sPEEK membranes exhibited higher ionic conductivity, higher peak power density, lower capacity loss per cycle, and lower crossover of electroactive species than the PFSA membranes. Though the long-term stability of these non-fluorinated polymers needs to be improved, these results illustrate the potential for producing non-fluorinated membranes with comparable or better performance than the commercially available PFSAs, if the hydrolysis-prone heteroatoms are eliminated from the polymer backbone.

Experimental

The procedures used for membrane preparation and characterization, as well as cell assembly and testing, are included in the supplemental information (SI).

Results and Discussion

Membrane properties relevant for flow cell performance are presented in Table I. The higher conductivity observed for sPEEK is ascribable to its higher ion exchange capacity and higher water uptake. The water uptake differences between sPEEK and Nafion in their corresponding potassium forms are attributed to the presence of solvent-shared ion pairs in the perfluorinated polymer. These solvent-ion interactions decrease the number of water molecules available for cation hydration and limit the overall water uptake.[17] Though sPEEK's higher water uptake may be expected to lead to higher permeabilities of redox-active species, this was not observed for sPEEK, see Table I. This is attributed to differences in the water cluster structure between PFSA and sPEEK.[18] The permeability of potassium ferricyanide (FeCy) was measured because it is the fastest diffusing redox-active species within our system, and will contribute most significantly to capacity loss via reactant crossover. The non-fluorinated membranes exhibited a FeCy crossover rate approximately two orders of magnitude lower than that measured for Nafion NR212. The permeability coefficient P calculations are described in the SI. The variation of normalized concentration in the receiving side as a function of time, for Nafion NR212 and sPEEK, is presented in Figure 1. Figure 2 shows the total accessible capacity over 100 cycles at 250 mA/cm^2. The capacity loss per cycle extracted from these measurements is 0.036% for Nafion and 0.018% for sPEEK; these correspond to capacity loss rates of 3.83%/day and 2.62%/day, respectively (Table II). In accordance with prior work on a quinone-bromide AORFB,[19] we tentatively attribute these capacity losses to a continuous loss of electrolyte from the capacity-limiting side due to a combination of chemical decomposition, electrolyte crossover and leakage from the pumping system. The energy efficiency and round-trip voltage efficiency remained nearly constant over 100 cycles for both sPEEK and Nafion cells. The energy efficiency for the sPEEK and PFSA cells were 66.2% and 59.1%, respectively. The round-trip voltage efficiency at 250 mA/cm^2 was 67% for the sPEEK cell and 59.2% for the PFSA cell. The lower current efficiency observed for the sPEEK cell compared to the Nafion cell is hypothesized to be the result of side-reactions occurring between the functional groups present in the membrane and the reduced version of DHAQ, 2,6-dihydroxyanthraquinone.[20,21] A detailed study of these processes is currently underway.

Polarization curves at different SOC are shown in Figure 3 and Figure 4 for cells constructed using a sPEEK or a Nafion membrane. As expected for this combination of electrolytes, the polarization curves show no signs of redox kinetics limitations, which would be manifested by curvature near zero current density. The peak power density for the sPEEK cell was 0.47 W/cm^2 at 0.72 A/cm^2 and that for the PFSA cell was 0.42 W/cm^2 at 0.6 A/cm^2. These results are consistent with the lower ASR values for sPEEK compared to the PFSA, as determined by EIS.

To gain insight into the long-term chemical stability of the sPEEK membranes, the polymer molecular weight was measured before and after cell cycling by GPC. Changes in the molecular weight distribution were observed after 3 weeks of cycling and were attributed to loss of macromolecules in the low end of the molecular weight

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Table I. Area Specific Resistance and conductivity from EIS, IEC, water uptake, and K_3FeCN_6 permeability coefficients for Nafion 212 and sPEEK, in the potassium sulfonate form. ASR_{hf} is measured in 0.4 M $K_4Fe(CN)_6$ + 0.03 M $K_3Fe(CN)_6$ in 1 M KOH | 0.5 M DHAQ in 2 M KOH. Permeability is measured in 0.3 M $K_3Fe(CN)_6$ in 1 M KOH | 1.9 M KOH.

Membrane	Thickness (μm)	ASR_{hf} (Ω cm^2)	Conductivity (mS/cm)	IEC (mEq/g)	Water uptake (%wt)	Permeability coefficient for $FeCN_6$ cm^2/s
sPEEK	45.88 ± 8.75	0.515 ± 0.003	9.13 ± 1.70	1.67	13.1	5.3×10^{-12}
Nafion NR212	50 ± 2	0.758 ± 0.013	6.61 ± 0.26	0.95	5	4.5×10^{-9}

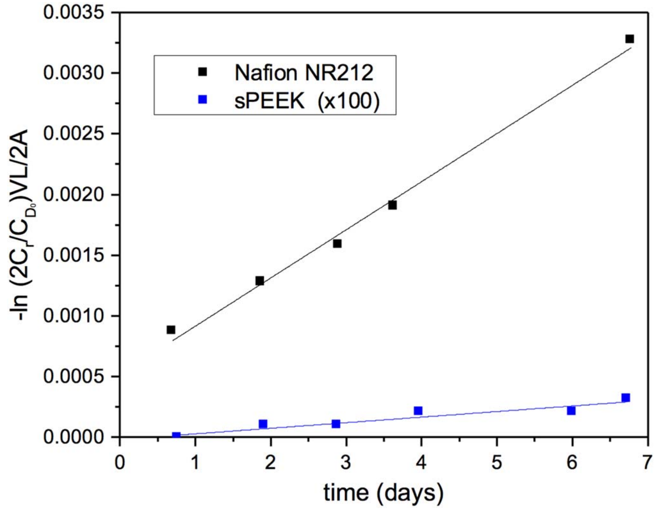

Figure 1. Normalized receiving side concentration (C_r) of Ferricyanide as a function of time for Nafion 212 and sPEEK. Permeability is measured in 0.3 M $K_3Fe(CN)_6$ in 1 M KOH | 1.9 M KOH.

distribution. See Figure S1 in the SI. HPLC-MS analysis of the electrolyte solutions showed fragments consistent with the hydrolysis of the sPEEK backbone at the aryl ether sites, as has been observed in previous literature reports.[22] See Figure S2 in the SI.

Exposure to the alkaline electrolyte solutions produced a decrease in the storage modulus of sPEEK of approximately 20% (from 1.1 GPa before cycling to 0.88 GPa after cycling), but did not result in the mechanical failure of the polymer films. The cell performance using sPEEK membranes, along with the observed changes in polymer properties upon exposure to strongly alkaline media, highlight the need to develop macromolecules without hydrolysis-prone heteroatoms in their backbone. Elimination of alkaline-labile aryl ether bonds has already produced promising anion exchange membranes for alkaline fuel cells.[23] Our results indicate that adoption of a parallel synthetic approach may be an attractive pathway toward low-cost, non-perfluorinated, ion exchange membranes for AORFBs.

Table II. Capacity loss per cycle and per day for Nafion 212 and sPEEK. Negolyte: *7 mL 0.5 M DHAQ in 2 M KOH*; Posolyte: *42 mL* 0.4 M $K_4Fe(CN)_6$ + 0.03 M $K_3Fe(CN)_6$.

Membrane	Thickness (μm)	Capacity loss (%/cycle)	Capacity loss (%/day)
sPEEK	45.88 ± 8.75	0.018	2.62
Nafion NR212	50 ± 2	0.036	3.83

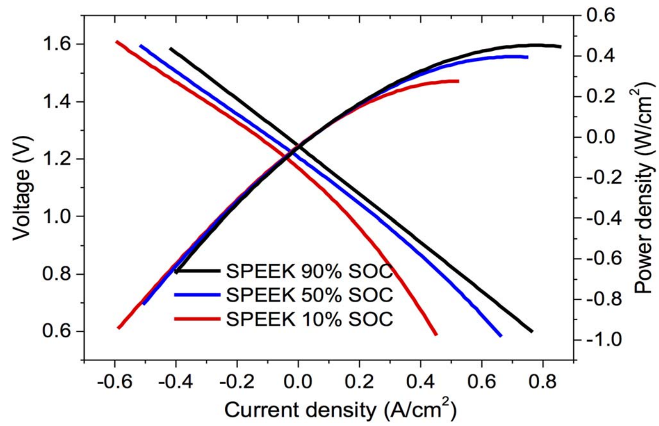

Figure 3. Polarization curve and power density of sPEEK membrane. Negolyte: *7 mL 0.5 M DHAQ in 2 M KOH*; Posolyte: *42 mL* 0.4 M $K_4Fe(CN)_6$ + 0.03 M $K_3Fe(CN)_6$.

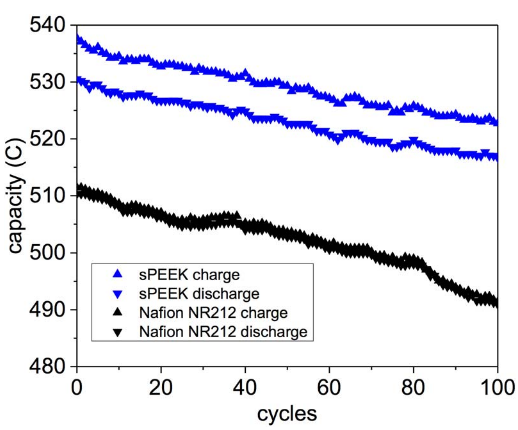

Figure 2. Charge and discharge capacity during cycling at 250 mA/cm^2 for Nafion 212 and sPEEK membranes. Negolyte: *7 mL 0.5 M DHAQ in 2 M KOH*; Posolyte: *42 mL* 0.4 M $K_4Fe(CN)_6$ + 0.03 M $K_3Fe(CN)_6$.

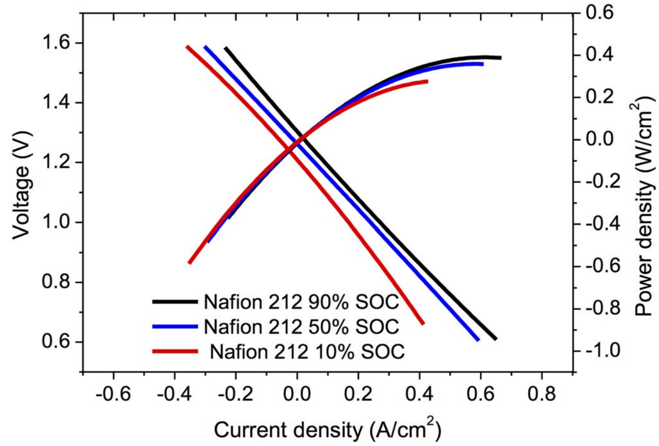

Figure 4. Polarization curve and power density of Nafion 212 membrane. Negolyte: *7 mL 0.5 M DHAQ in 2 M KOH*; Posolyte: *42 mL* 0.4 M $K_4Fe(CN)_6$ + 0.03 M $K_3Fe(CN)_6$.

Summary

The performance of sPEEK as the CEM in AORFBs was evaluated and compared to a PFSA membrane. The hydrocarbon-based membranes showed lower area specific resistance, and lower crossover rates of the redox-active species of highest permeability, FeCy. Alkaline DHAQ-FeCy flow batteries using sPEEK membranes exhibited higher peak power density (0.47 W/cm^2 vs 0.42 W/cm^2) and lower capacity loss per cycle (0.018%/cycle vs 0.036%/cycle) and per day (2.62%/day vs 3.83%/day). Three weeks of continuous sPEEK membrane exposure to the electrolyte solution decreased its molecular weight and storage modulus, but did not cause membrane or cell failure. Despite the limited long-term stability of sPEEK in alkaline solutions, these results demonstrate that the use of non-fluorinated polymers is a promising avenue to produce low-cost, high-performance AORFBs. We anticipate that the cell performance described herein will drive further development of non-fluorinated, low cost, polymer backbones with higher stability in alkaline conditions.

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