



Short communication

Evaluation of Diels–Alder poly(phenylene) anion exchange membranes in all-vanadium redox flow batteries



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ABSTRACT

Quaternary ammonium functionalized Diels–Alder poly(phenylene)s (QDAPPs) with different ion exchange capacities (IECs) are examined as membranes in all-vanadium redox flow batteries. QDAPP membrane behavior is compared to a standard, Nafion 212, in measurements of cycling efficiencies, areal specific resistance (ASR), vanadium permeation and durability. The IEC of the QDAPPs clearly shows an impact on the cell ASR and vanadium crossover. The results imply a trade-off between performance, indicated by cell voltage loss at a given current density, and rate of cross-over driven capacity loss in the system. Among the membranes studied, QDAPP with moderate IEC represents the best trade-off of these factors and exhibits higher performance and lower capacity loss compared to Nafion 212. All QDAPP membranes are found to be more durable than the analogous cation exchange membrane, sulfonated DAPP (SDAPP), in V^{5+} solution.

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1. Introduction

Increasing the electric grid efficiency and reliance on renewable energy requires large-scale energy storage systems [1]. In this context, redox flow batteries (RFBs) have emerged as leading candidates for large-scale electrochemical energy storage. Among the RFBs, the all-vanadium redox flow battery (VRFB) has attracted considerable attention because cross-contamination is eliminated by employing the same metal in both catholyte and anolyte solutions [2,3].

For commercial success, low cost is a crucial factor and remains an issue for VRFB [4]. In a cell stack, the Nafion separator contributes up to 40% of the total cost [4]. Thus, despite its good performance and durability in a VRFB [5], the high cost of Nafion has driven the development for cheaper alternatives, primarily hydrocarbon membranes [6].

Based on a recent review, the majority of hydrocarbon membrane studies focused on cation-exchange, sulfonated ionomers [7]. Sulfonated hydrocarbon membranes have shown good selectivity and energy efficiencies compared to Nafion. However, the long term stability of such materials exposed to VRFB electrolytes remains an issue [8]. It has been speculated that VO_2^+ oxidizes the membrane upon uptake. The adoption of anion exchange membranes may suppress VO_2^+ transport within the membrane and thus improve cell lifetimes [9].

Sandia National Laboratories has been developing both cation and anion exchange poly(phenylene) membranes, SDAPP and QDAPP respectively, for fuel cell applications [10,11]. Despite their fully aromatic-based structures, some degradation of poly(phenylene)-based cation exchange membranes was observed in VRFBs [12,13]. Nonetheless, potentially promising results, including good conductivity with lowered vanadium cross-over, were observed for SDAPP membranes. To continue to explore the relationship between structure and properties, we prepared AEMs by incorporating quaternary ammonium groups to form QDAPP membranes and evaluated their performance and durability at various IECs in vanadium redox flow batteries.

2. Experimental

The structure of QDAPP is illustrated in Fig. 1a. QDAPP was synthesized and cast into films following the procedure described previously [11]. Water uptake and ion exchange capacities were determined via the protocols reported elsewhere [10].

Vanadium crossover measurements were made using a membrane separated diffusion cell with 1 M $VOSO_4$, and 4 M H_2SO_4 on one side and 5 M H_2SO_4 on the other side. The procedure and calculations used have been reported previously [13].

Vanadium flow battery measurements were conducted in a cell with a single membrane sandwiched between two experimental carbon papers (CP-EXP). The electrodes used had a geometric area of 5 cm², BET surface area of 50 m²/g and porosity of approximately 85%. Two

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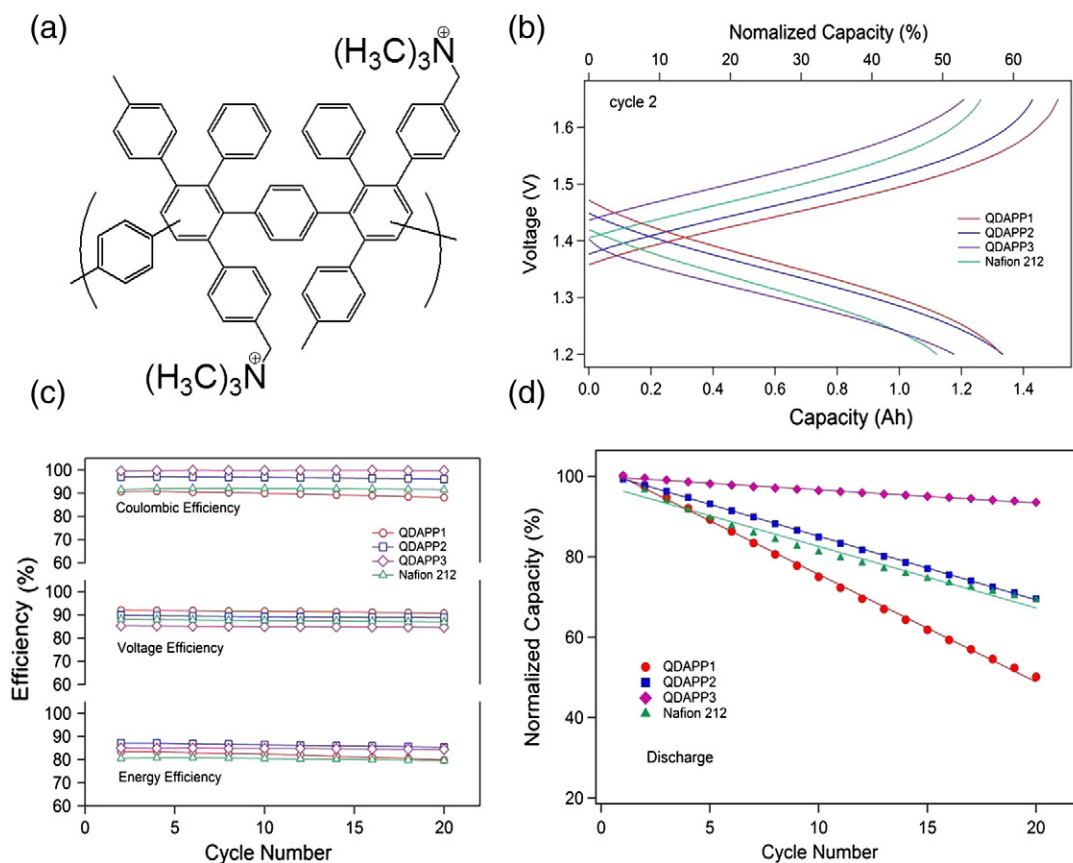


Fig. 1. (a) Structure of quaternized Diels–Alder poly(phenylene) (QDAPP); (b) charge and discharge curve of QDAPPs and Nafion 212 at cycle 2, top axis indicates the percentage normalized by the total solution capacity (2.28 Ah); (c) cycling efficiencies of QDAPPs and Nafion 212; and (d) normalized capacity (normalized by the capacity of 1st cycle) of QDAPP and Nafion 212 vs. cycle number. The solid line represents the linear fit.

reservoirs containing 50 mL of 1.7 M vanadium with 5 M total sulfate electrolyte each were blanketed by nitrogen in a temperature chamber held at 30 °C for area specific resistance (ASR) and cycling measurements. ASR was obtained using the high frequency intercept of the electrochemical impedance spectrum at a given polarization [14]. Cycling was performed at 200 mA/cm², with a solution flow rate of 90 mL/cm². A relative narrower voltage cycling window, between 1.65 V and 1.2 V, was used to minimize the previously observed side reactions [15].

Ex-situ soaking of an immersed 0.5" × 1" membrane sample in 0.1 M VO⁵⁺ solution with a 5 M total sulfate at 40 °C [13] was used to probe membrane susceptibility to oxidation.

3. Results and discussion

3.1. Impact of IEC

Table 1 summarizes the QDAPP properties for IECs of 1.2, 0.8 and 0.4 meq/g. Similar properties of Nafion at comparable thickness (212) were included for comparison. Evidently, the water uptake and

vanadium permeability are proportional to IEC, whereas areal specific resistance exhibits the opposite trend. This behavior is expected since the water affinity to the membrane is enhanced at higher IEC, resulting in higher ion permeability and conductivity. In addition, the higher ion content leads to larger ionic agglomeration, and the larger hydrophilic domains facilitate ion transport [16]. QDAPP1, with the highest IEC, possessed the largest water uptake and VO²⁺ permeability but the lowest ASR at 0.18 Ω cm². QDAPP3, with the lowest IEC, exhibited the smallest water uptake and VO²⁺ permeability but the highest ASR. QDAPP2 with IEC at 0.8 meq/g had both lower VO²⁺ permeability and area surface resistance compared to Nafion 212 [1.4×10^{-6} vs. 2.1×10^{-6} cm²/min; 0.21 vs. 0.32 Ω cm² respectively]. Although QDAPP should resist cation permeation through Donnan exclusion due to electrostatic repulsion of positively charged co-ions, this barrier typically breaks down at high salt concentrations [17].

3.2. Vanadium flow battery performance

The charge–discharge curves of QDAPPs and Nafion 212 at cycle 2 are plotted in Fig. 1b. The observed overvoltage was in direct agreement

Table 1
Physical properties of QDAPP samples.

Sample	IEC (meq/g)	Water uptake %	VO ²⁺ permeability (cm ² /min)	Area specific resistance (Ω cm ²)
QDAPP1	1.2	99	2.5×10^{-6}	0.18
QDAPP2	0.8	77	1.4×10^{-6}	0.21
QDAPP3	0.4	48	1.8×10^{-7}	0.54
Nafion 212	0.99	35	2.1×10^{-6}	0.32

with the ASRs listed in Table 1. QDAPP1 showed the lowest overvoltage due to the lowest membrane resistance, while QDAPP3 with the highest membrane resistance showed the largest polarization during constant current cycling. However, the highest crossover rate of QDAPP1 reduced its discharge capacity the most, and resulted in the lowest Coulombic efficiency. Furthermore, all QDAPPs reached higher discharge capacities than Nafion 212. QDAPP1 and QDAPP2 achieved higher charging capacities mainly due to their low membrane resistance, whereas QDAPP3 displayed a slightly higher discharge capacity than Nafion 212 due to its lower crossover rate.

As shown in Fig. 1c, high Coulombic efficiencies (CEs) between 90 and 100% were obtained with QDAPPs. QDAPP3 had the highest CE at 99%, due to its low vanadium crossover, while QDAPP1 displayed the poorest CE at 90%, even lower than that for Nafion (93%). These results are in agreement with the VO^{2+} permeability data in Table 1. Voltage efficiencies (VEs) of QDAPPs ranged between 85 and 93% at 200 mA/cm² cycling current indicating high cell performance. QDAPP3 with the highest ASR (0.54 Ω cm²) displays the lowest VE at 85% and QDAPP1 exhibits the highest VE at 93%. The balance between vanadium crossover and membrane resistance resulted in overall energy efficiencies (EEs) of the QDAPPs between 80% and 90%, which were similar to or higher than Nafion 212 (80%).

Fig. 1d shows the capacity decay as a function of cycle number for QDAPPs and Nafion when capacity to the 1st cycle was normalized. To analyze the rate of the capacity decay in this case, one has to consider both ASR and vanadium permeation of the membrane. For example, a cell with lower ASR would require a longer cycling period to reach the fixed cut-off voltage, resulting in a more significant capacity decay due to the prolonged time for each cycle. As a result, QDAPP1, combining the lowest ASR and highest vanadium permeation rate among the samples, exhibits the fastest capacity decay (2.5% cycle⁻¹). On the other hand, QDAPP3 with the highest ASR and the lowest vanadium permeation shows merely 0.3% capacity loss each cycle.

3.3. Ex-situ degradation studies

Membrane durability is of vital importance in VRFB for commercial use, and the ability to withstand +10,000 charge–discharge cycles is desired. Unfortunately, hydrocarbon membranes typically have lower durability compared to Nafion. As reported by Kim et al. [18], S-Radel showed good initial performance compared to Nafion. However after 40 cycles a catastrophic failure occurs, with severe decay in Coulombic and energy efficiencies. Chen and Hickner [8] have suggested possible membrane decomposition induced by V^{5+} oxidation of the polymer. We recently reported that sulfonated Diels–Alder poly(phenylene)s (SDAPPs) can withstand over 400 cycles with stable energy efficiencies [13]. We expect that the employment of an anion exchange membrane would prevent V^{5+} permeation and extend the membrane lifetime further, as suggested by Zhang et al. [9].

Conventional cycling is the best indicator for membrane durability. However, the time and equipment required to examine each separator in this manner are relatively inefficient. To inspect the durability of QDAPPs, we performed an ex-situ membrane lifetime soaking test proposed by Skyllas-Kazacos et al. [5,13]. During the period of soaking, a solution color change from yellow (VO_2^+) to blue (VO^{2+}) was observed, indicating that V^{5+} was reduced upon reaction with QDAPP, as shown in Fig. 2. The cation exchange membrane analog, SDAPP with an IEC of 2.2 meq/g and Nafion 212 were also tested as a reference. After soaking the films for 117 h, the SDAPP sample begins to break apart while all QDAPP samples and Nafion remained intact. This observation indicates that the QDAPPs have longer lifetimes than SDAPPs, presumably due to electrostatic repulsion between the fixed positive charges and V^{5+} ions. However, obvious color changes were observed for QDAPP1 and QDAPP2 at 676 h, whereas the solutions for QDAPP3 and Nafion 212 remained unchanged. The intensity of the color change for QDAPP appears to be proportional to the sample IEC, which is consistent with previous work [19].

4. Conclusions

Several quaternary ammonium functionalized Diels–Alder poly(phenylene)s (QDAPPs) were studied as anion exchange membranes in a vanadium flow battery. The vanadium permeation rate of the QDAPP was proportional to the membrane IEC, while the cell ASR exhibited the opposite trend, implying a trade-off between capacity decay and cell performance. In cycling tests, high IEC QDAPP (1.2 meq/g), with the lowest ASR at 0.18 Ω cm² showed the smallest overvoltage, but its highest vanadium permeation rate resulted in the lowest CE at 90%. High CE (99%) could be obtained when the IEC was reduced (0.8 meq/g), leading to lower capacity decay, 0.3% cycle⁻¹, compared to Nafion 212 at 1.4% cycle⁻¹. Overall, the energy efficiencies of QDAPPs (80–90%) were similar to or higher than that of Nafion 212 (80%). In ex-situ soaking studies, the anion exchange membrane, QDAPP, is more stable than its cation exchange analog, SDAPP. The rate of degradation of QDAPP was proportional to IEC, and it appeared that little to no oxidation occurred over the time of the experiment with QDAPP3 and Nafion. These observations indicate a trade-off between cell performance, system capacity decay, and membrane durability. This study suggests one possible pathway toward membrane optimization for VRFB application.

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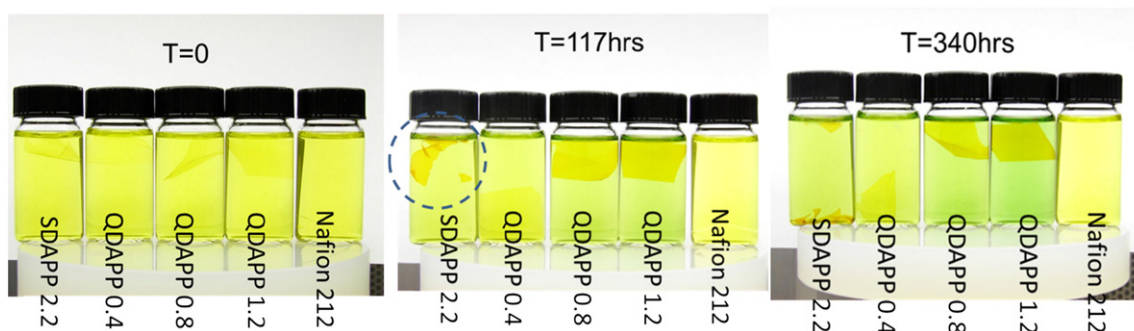


Fig. 2. V^{5+} soaking of QDAPP at 40 °C.

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