Redox Active Polymers for Non-Aqueous Redox Flow Batteries: Validation of the Size-Exclusion Approach

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Non-aqueous redox flow batteries (NRFBs) are emerging technologies that promise higher energy densities than aqueous counterparts. Unfortunately, cell resistance and redox component crossover observed when using ion-exchange membranes (IEMs) hinders NRFB development. The size exclusion approach for polymer-based NRFBs addresses these issues by using macromolecular design to mitigate crossover. Here, we highlight the benefits of this approach using inexpensive nano-porous separators (PS) (Celgard and Daramic). We evaluated these along with an IEM (Fumasep) in a flow cell configuration using a classical redox couple of viologen and ferrocene, both in monomer and polymer forms. High Coulombic efficiencies above 98% and access up to 80% of capacity were observed for the polymer cells. These displayed better performance with PS than with the IEM, which exhibited lower energy efficiencies from higher overpotentials. The monomer equivalent cells with PS resulted in lower efficiencies and rapid decrease in depth of discharge. Post-cycling analysis by ultramicroelectrode voltammetry showed that the small molecules freely crossed PS and to a lesser degree through the IEM. Therefore, here we demonstrate that the combination of redox active polymers and simple PS enables a potential next-generation NRFB system that provides a competitive alternative to the use of IEMs in NRFBs.

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to investigate the feasibility of polymers for size-exclusion applications in general. These polymers were chosen for their simple one-step synthetic design and well characterized electrochemical reversibility and fast charge transfer kinetics.\(^{20,24}\) We chose high molecular weight polymers of 271 kDa (PAF) and 318 kDa (PEV) along with their monomer equivalents for comparison (Scheme 2). These RAPs displayed mean hydrodynamic radii of 19 nm and 9.5 nm in 0.1 M LiBF\(_4\) electrolyte respectively (Figure S1).

**Experimental**

**Materials.**—The polymers and monomers used: PEV, PAF, benzyl ethyl viologen (BEV) were synthesized using reported protocols.\(^{20,25}\) Benzyl(ferrocenylmethyl)dimethylammonium hexafluorophosphate (BAF) was synthesized from (dimethylaminomethyl)ferrocene and benzyl chloride (see Supplementary Information). All chemicals, except for synthesized RAPs and monomers, were purchased from Sigma-Aldrich with the highest available purity and used as received.

**Electrochemical methods.**—All experiments were performed inside of an Ar-filled drybox with stringent control of O\(_2\) and moisture levels. Measurements were done using a CHI601E or Arbin BT-2000. Unless specified, all voltammetric experiments were carried out using a standard three-electrode configuration with 12.5 \(\mu\)m radius Pt ultramicroelectrode (UME) as the working electrode, a non-aqueous reference electrode (CHI112, 0.1 M AgNO\(_3\) in acetonitrile solution), and a Pt wire as counter electrode. Experiments were carried out with a 10 mM concentration (by effective repeating unit for RAPs) in 0.1 M LiBF\(_4\) in acetonitrile solution, and a Pt wire as counter electrode. Experiments were carried out with a 10 mM concentration (by effective repeating unit for RAPs) in 0.1 M LiBF\(_4\) in acetonitrile as supporting electrolyte unless stated otherwise. In UME voltammetry, the steady-state limiting current \(i_0\) is directly proportional to concentration \(C\)\(^*\), diffusion coefficient \(D\), number of electrons transferred \(n\), and the radius of the UME \(a\), according to:

\[
i_0 = 4nFd a DC^*\]

where \(F\) is Faraday’s constant. This equation allows us to directly relate the concentration of species in the solution in crossover studies using the limiting current, \(i_0\).

**NRFB cycling.**—The flow cell design used consisted of two stainless steel current collectors with a flow-through field where carbon felt (SGL GFA6) electrodes could be inserted. Exposed area of electrodes through PTFE gaskets separating collectors was 4.63 cm\(^2\). One layer of membrane was placed in between gaskets (see Supplementary Information for schematic). Neoprene tubing was used on a calibrated Masterflex L/S peristaltic pump. The cells were tested under flow conditions at a volumetric flow rate of 5 mL/min. 10 mL of solution were prepared for each catholyte and anolyte compartment.

**Membrane choice.**—The IEM chosen for this study was Fumasep FAPQ-375-PP (Fumatech GmbH), an anion exchange membrane, due to the redox chemistry of the viologen-ferrocene pair where an anion leaves the viologen to maintain electroneutrality at the ferrocene compartment undergoing oxidation when charging (Scheme 1). The as-received membrane contains chloride and sulfate anions and has a dry thickness of 70–80 \(\mu\)m;\(^{26}\) thus, the membranes were immersed in 0.1 M LiBF\(_4\) in acetonitrile for a minimum of three days to ensure full ion exchange and swelling prior to use according to previous reports.\(^ {18}\) The porous membranes used in these studies, Celgard 2325 and Daramic 175, are both hydrocarbon polymer-based membranes with differing porosity. Their porosity allows for quick solvent uptake and do not need preconditioning; thus, these were not pre-soaked before use. Celgard 2325 is a trilayer membrane of 25 \(\mu\)m thickness made with polyethylene and polypropylene\(^ {27}\) while Daramic is a polyethylene membrane with amorphous silica and 175 \(\mu\)m thickness.\(^ {28}\) By nitrogen adsorption isotherms (Figure S2), Celgard 2325 showed a narrow distribution of pore radii between 8 and 12 nm, with peak pore radius of 9 nm. Daramic showed a wider distribution of pore radii between 5 and 16 nm. When using the steric partition coefficient\(^ {29}\) as a guide for tailoring RAP molecular weight to pore size, the chosen combination of RAPs and separators theoretically leads to negligible crossover. This coefficient \(K\) relates the probability that a dissolved linear polymer will remain in solution \((K = 0)\) or inside of a cavity \((K = 1)\), therefore potentially leading to crossover. When considering holes of radius \(r\) and a spherical particle of radius \(a\), the steric partition coefficient \(K\) approaches zero when \(a/r > 0.6\) for a spherical pore and when \(a/r > 0.8\) for a cylindrical pore, reflecting sensitivity to pore shape (see Supplementary Information). Our groups have previously shown a decrease in crossover with increasing polymer size for a series of viologen polymers with \(a/r\) values between 0.2 and 0.5, displaying crossover values as low as 7%.\(^ {20}\) For Celgard 2325, with a mean pore radius of 9 nm \(a/r\) values of 2.1 (PAF) and 1.1 (PEV), are obtained when considering the RAP’s hydrodynamic radii (Table S1). These values are theoretically well beyond the required \(a/r\); thus, strongly suggesting that these two polymer species will be size excluded, although experimental uncertainties suggest that a non-zero crossover is expected. These include heterogeneity in pore size and geometry, as well as dissolved polymer structure, and the effects of overlapping distribution of pore and polymer sizes. However, to a first approximation, the large calculated \(a/r\) values give us confidence that the selected polymer sizes are adequate for demonstrating the impact of size-exclusion in a flow battery employing a porous separator.

**Results and Discussion**

**Polymer flow batteries.**—Although viologen-based RAPs exhibit a solubility in excess of 1 M,\(^ {20}\) this proof of concept study used NRFB cells with 10 mM effective concentration (based on repeat unit for RAPs) in 0.1 M LiBF\(_4\) in acetonitrile. This concentration was suitable
due to the limited solubility of PAF, as well as to remain within a polymer dilution regime where polymer chains behave as individual coils in solution. The expected open circuit voltage for the cell was 0.95 V, therefore an upper maximum limit of 1.1 V was set for these cells as to prevent irreversible cycling. Cycling of the PEV/PAF RAP NRFB cells was done at 1C (0.9 mA/cm²) for all the membranes studied. The porous separators demonstrated similar performance for the RAP NRFBs, as expected from the size-exclusion mechanism (Figure 1). While a minimal difference in cycling performance was observed when comparing Celgard and Daramic separator cells in the first cycle, by the 15th cycle both cells had completely overlapping behavior (Figures 1d–1e). This slight difference arises likely due to conditioning stages of the RAPs and wetting of the separator. Both Celgard and Daramic RAP cells showed voltage plateaus close to the...
theoretical voltage of the couple, averaging 0.94 ± 0.07 V and leading to voltage efficiencies of 92.0 ± 0.4% and 93.0 ± 0.6%, respectively (Fig. 1b). Stable Coulombic and energy efficiencies above 98% and 91%, respectively in both cells (Fig. 1c) were observed during the long-term cycling (50 cycles), all suggesting low resistance across the porous membranes.

The PEV/PAF RAP NRFB cell cycled using Fumasep FAPQ membrane showed similar capacity access and Coulombic efficiencies to the porous separator cells, yet the charge/discharge profile and voltage and energy efficiencies differed. The widening overpotentials of the charge/discharge curves (Figures 1d–1e) led to lower average voltage and energy efficiencies over the 50 cycles. When compared to porous separators, the Fumasep FAPQ cell resulted in approximately a 10% decrease in voltage and energy efficiencies at 82.5 and 82.0 ± 1.0%, respectively. Therefore, the NRFB cell with Fumasep FAPQ showed indications of higher resistance as expected from lower conductivity of IEMs than porous separators in organic solvents.16

Figure 2. Performance of symmetrical PEV NRFB cell. (a) Pre-charging of the positive compartment was confirmed by UME CV. (b) Voltage vs. capacity plots of cycles 2–20. Dotted line represents theoretical capacity of cell at 180.5 mAh/L. (c) Coulombic efficiency of the symmetrical cell. Inset: comparison of depth of discharge over cycle number for the symmetrical and mixed polymer cells using Celgard 2325.

Figure 3. Performance of monomer NRFB cells as compared to RAP equivalents. (a-b) Discharge capacity of cells over 20 cycles for membranes studied in cells of monomers (a) and RAPs (b). Dotted line represents theoretical capacity of cell at 268 mAh/L. (c) Voltage vs. capacity at cycles 1 and 15 for both monomer and RAP cells using Celgard 2325 charging/discharging at 1C (0.58 mA/cm²).
Figure 4. Summary of monomer and RAP NRFBs tested. (a) Maximum depth of discharge achieved with each membrane used. (b) Average coulombic (CE), energy (EE) and voltage (VE) efficiencies observed with each membrane for both RAP (solid) and monomers (line pattern).

The similar behavior observed with all three membranes allowed us to conveniently troubleshoot the performance of these devices. While the cells showed a steady discharge capacity c.a. 200 mAh/L for the first 15 cycles, capacity loss was observed at long-term cycling (Figure S3). To investigate this observation, ultramicroelectrode cyclic voltammetry (UME CV) experiments were done at the end of each run to assess the condition of the RAPs after continuous cycling. Since RAPs adsorb strongly to electrodes, transient voltammetry complicates the decoupling of the adsorbed species from those in solution. Therefore, we chose UME steady state voltammetry, as we have established it as a suitable technique for assessing RAP solution state of charge and concentration.\textsuperscript{20} UME CVs of the PAF catholyte compartments displayed the evolution of a secondary redox process at 0.05 V vs. Ag/Ag\textsuperscript{+} as well as lower limiting currents than expected, indicating loss of active material for PAF (Figure S4). We hypothesize that the quaternary amine linkage may be susceptible to cleavage\textsuperscript{31} while charged. Such process occurring at the quaternary amine would detach ferrocene units from the polymer backbone, consequently releasing free ferrocene into solution, which has an \( E_{1/2} \) at 0.05 V vs. Ag/Ag\textsuperscript{+}.\textsuperscript{32}

In contrast, the anolyte compartments did not show any degradation of PEV, indicating the stable reversibility and size-exclusion of the anolyte material. To explore this hypothesis, a symmetrical\textsuperscript{33} PEV NRFB cell (Figure 2) was assembled with Celgard 2325. In this cell, both compartments contained PEV. The catholyte compartment contained PEV charged by bulk electrolysis before cell assembly, while the anolyte compartment contained uncharged PEV (see Supplementary Information). Symmetrical cycling of PEV at 1C demonstrated a more stable capacity access as compared to the mixed PEV/PAF cells (Figure 2c), as well as very low overpotentials with voltage cutoffs at ±100 mV. This improvement in capacity access during cycling indicated that the long-term losses observed in the PAF/PEV cell were likely due to PAF instability, thereby reinforcing that size-exclusion RAP NRFBs are deployable with appropriate chemistries.
Small molecule flow cells.—To compare and contrast the effectiveness of the size-exclusion strategy to that of small molecule NRFBs, equivalent monomer-based NRFBs were assembled (monomers BEV and BAF in Scheme 2). In contrast to their polymeric equivalent cells, monomer NRFBs displayed a dramatically lower maximum capacity access as well as a sharp decline in depths of discharge (Figure 3). Monomer cells only reached a maximum 50% discharge capacity access with a decrease to less than 9% capacity access by the 50th cycle for the porous separators. The monomer cell with Fumasep FAPQ maintained a higher depth of discharge than those with the porous separators, but its depth of discharge had decreased to 23% by the 50th cycle (Figure S5). The overall performance comparison of the RAP and monomer NRFBs studied are summarized in Figure 4. In general, we observed that monomer NRFBs demonstrated lower Coulombic and energy efficiencies than their polymer equivalent cells as well as lower depths of discharge. There we also observe that the cells with Fumasep FAPQ (both monomer and polymer) display similar metrics (Figure 4b), confirming a lower degree of crossover for the membrane since both monomer and polymer cells have similar coulombic efficiency. Nevertheless, the Fumasep FAPQ cells all displayed lower energy and voltage efficiencies than the polymer cells with porous separators, reinforcing the effect of lower conductivity of IEMs in organic solvents when compared to porous separators. Overall, the results from the Fumasep FAPQ cells demonstrate that IEMs could be utilized, but would incur a cost of lower voltage and energy metrics as compared to polymer cells that utilize porous separators.

UME CVs of the catholyte and anolyte compartments post-cycling served to quantify the degree of overall crossover for these cells (Figure 5). These revealed that the small molecules had freely crossed the porous membranes. Especially in the case of Celgard 2325, the compartments had similar final concentrations of the monomers. In the case of Fumasep FAPQ, the crossover was much lower than in the case of porous separators, yet demonstrates that given a longer timescale the monomers could reach equal mixing and cell shutdown. The capacity loss observed over the 50 cycles (Figure S5) was likely due to deleterious mixing at the opposite electrodes, which was predominant with the porous membranes. These effects of materials crossover are a common challenge in small molecule RFBs that has yet to be fully resolved. Overall, crossover in the monomer cells was much higher than that in the polymer cells (Table 1).

Self-discharge experiments.—To further highlight the benefits of a size-exclusion flow battery, both polymer and monomer NRFB cells were charged at 1C and allowed to flow for one hour while tracking the open circuit voltage (Figure 6). To compensate for possible instabilities of the ferrocene polymer or monomer, symmetrical cells with viologen monomer (BEV) and polymer (PEV) were also assembled. These cells were run using Celgard 2325 and demonstrate the deleterious crossover problem for small molecules over time. In Figure 6, it is observed that in both the mixed and symmetrical cells, polymer NRFBs hold a steady potential over the 1 hour period observed as compared to the monomer cells. These monomer cells demonstrated a marked gradual decline in potential. This decline can be associated to a Nernstian response to changes in concentration where the ratio of oxidized to reduced species will have a direct impact in the observed potential of the system. Therefore, over time the crossing of charged species to opposing compartments caused discharge upon mixing. In the case of the mixed monomer cell the drop was 60 mV within an hour, indicating a decade difference in the ratio of charged to discharged states of the active material. For the symmetrical cell, we observed only a 20 mV drop, reinforcing the greater stability of the viologen species over the mixed ferrocene-viologen environment. In contrast, the polymer cells showed decreases lower than 2 mV within the same timeframe, highlighting the operational robustness of the size exclusion approach.

Conclusions

We evaluated the feasibility and performance of novel size-exclusion non-aqueous flow batteries in comparison to the traditional approach using ion-exchange membranes. By utilizing simple porous separators that allow the free exchange of charge-balancing ions in a non-aqueous environment, we were able to suppress detrimental redox component crossover by using high molecular weight polymers as redox active material. These cells also cycled successfully using an anion exchange membrane demonstrating that the polymer systems work with either type of membrane, but with increased resistance when relying on ion exchange. Polymer based flow batteries with porous membranes exhibited Coulombic, voltage, and energy efficiencies above 98%, 92%, and 90%, respectively. Symmetrical cells showing excellent stability for the viologen polymer were operated for up to four days. Small molecule equivalent cells were also studied with porous separators or the IEM, which demonstrated that crossover...
in those cases caused significant underutilization of the material and terminal capacity losses for the NRFBs. The much higher rates of crossover in monomer cells reinforces the favorability of implementing polymers for size exclusion RFBs to mitigate these effects in working systems. As highlighted by discharge experiments, polymer exclusion flow batteries were able to retain the open voltage of the battery steadily while the use of monomers led to changes in cell voltage of up to 60 mV/h which suggests significant self-discharge of the battery. Future investigations from our laboratory focus on tailoring of the polymer redox pendants to increase the voltage and rate capabilities of the battery as well as to design a more stable catholyte polymer that withstands long-term cycling without degradation. In sum, the size-exclusion concept together with the use of RAPs encourages a renewed approach for exploring diverse NRFB chemistries.

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References

1. I. Gyuk, M. Johnson, J. Vetrano, K. Lynn, W. Parks, R. Hands, L. Kannberg, S. Hearne, K. Waldrip, and R. Braccio, Grid Energy Storage, U.S. Department of Energy, Washington D.C. (2013).
2. M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, and M. Saleem, J. Electrochem. Soc., 158 (8), R55 (2011).
3. A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, J. Appl. Electrochem., 41 (10), 1137 (2011).
4. R. M. Darling, K. G. Gallagher, J. A. Kowalski, S. Ha, and F. R. Brushett, Energy Environ. Sci., 7 (11), 3459 (2014).
5. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, and J. Liu, Chem. Rev., 111 (8), 3577 (2011).
6. W. Wang, Q. T. Luo, B. Li, X. L. Wei, L. Y. Li, and Z. G. Yang, Adv. Funct. Mater., 23 (8), 970 (2013).
7. F. R. Brushett, J. T. Vaughney, and A. N. Jansen, Adv. Energy Mater., 2 (11), 1390 (2012).
8. S. H. Shin, S. H. Yun, and S. H. Moon, RSC Adv., 3 (24), 9095 (2013).
9. P. Aalto, M. R. Jobe, and F. Moro, Renew. Sust. Energ. Rev., 29, 325 (2014).
10. K. X. Lin, Q. Chen, M. R. Gerhardt, L. C. Tong, S. B. Kim, E. Rosenach, A. W. Valle, D. Hardee, R. G. Gordon, M. J. Aziz, and M. P. Marshak, Science, 349 (6255), 1589 (2015).
11. K. Gong, Q. Fang, S. Gu, S. F. Y. Li, and Y. Yan, Energy Environ. Sci., 8 (12), 3515 (2015).
12. M.谍, A. Parasuraman, S. Winardi, T. M. Lim, and M. Skyllas-Kazacos, Membranes, 2 (2), 275 (2012).
13. L. Su, R. M. Darling, K. G. Gallagher, W. Xie, J. L. Thelen, A. F. Badel, J. L. Barton, K. J. Cheng, N. P. Balsara, J. S. Moore, and F. R. Brushett, J. Electrochem. Soc., 163 (1), A5253 (2016).
14. X. Li, H. Zhang, Z. Mai, H. Zhang, and Y. Vankelecom, Energy Environ. Sci., 4 (4), 1147 (2011).
15. M. Doyle, M. E. Lewittes, M. G. Roelofs, S. A. Perussia, and R. E. Lowrey, J. Membr. Sci., 184 (2), 257 (2001).
16. N. S. Hudak, L. J. Small, H. D. Pratt, and T. M. Anderson, J. Electrochem. Soc., 162 (10), A2188 (2015).
17. H. Lee, M. Yanilmaz, O. Topraksi, K. Fu, and X. Zhang, Energy Environ. Science, 7 (12), 3857 (2014).
18. X. Hu, J. Solid State Electrochem., 15 (4), 649 (2011).
19. R. Dmello, D. M. Milstein, F. R. Brushett, and K. C. Smith, J. Power Sources, 330, 261 (2016).
20. N. Nagarjuna, J. Hui, K. J. Cheng, T. Lichtenstein, M. Shen, J. S. Moore, and J. Rodriguez-Lopez, J. Am. Chem. Soc., 136 (46), 16309 (2014).
21. E. C. Montoto, G. Nagarjuna, J. Hui, M. Burgess, N. M. Sekerak, K. Hernandez-Burgos, T.-S. Wei, M. Kuehn, J. Grolman, K. J. Cheng, J. A. Lewis, J. S. Moore, and J. Rodriguez-Lopez, J. Am. Chem. Soc., 138 (40), 13230 (2016).
22. T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager, and U. S. Schubert, Nature, 527 (7576), 78 (2015).
23. J. Winsberg, T. Hagemann, S. Muench, C. Friebe, B. Haupler, T. Janoschka, S. Morgenstern, M. D. Hager, and U. S. Schubert, Chem. Mater., 28 (10), 3401 (2016).
24. M. Burgess, K. Hernandez-Burgos, B. H. Simpson, T. Lichtenstein, A. Avetian, G. Nagarjuna, K. J. Cheng, J. S. Moore, and J. Rodriguez-Lopez, J. Electrochem. Soc., 163 (4), H3006 (2016).
25. M. Burgess, K. Hernandez-Burgos, K. J. Cheng, J. S. Moore, and J. Rodriguez-Lopez, Analyst, 141 (12), 3842 (2016).
26. Technical Data Sheet fumasep FAPQ-375-PP, FumaTech BWT GmbH, Bietigheim-Bissingen, Germany.
27. Data Sheet Celgard 2325, Celgard LLC, Charlotte, NC, USA.
28. Product Specification BS-P-6000-2, Daramic SLI Application FlatSheet Membrane, Daramic LLC, Coralyn, IN, USA.
29. E. F. Casassa, J. Polym. Sci. B Polymer Lett., 5 (9PB), 773 (1967).
30. A. V. Dobrynin, R. H. Colby, and M. Rubinstein, Macromolecules, 28 (6), 1859 (1995).
31. J. S. Mayell and A. J. Bard, J. Am. Chem. Soc., 85 (4), 421 (1963).
32. Y. Wang, E. I. Rogers, and R. G. Compton, J. Electroanal. Chem., 648 (1), 15 (2010).
33. D. Milstein, J. L. Barton, R. M. Darling, and F. R. Brushett, J Power Sources, 327 151 (2016).
34. R. Darling, K. Gallagher, W. Xie, L. Su, and F. Brushett, J. Electrochem. Soc., 163 (1), A5029 (2016).