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Ferrocene/Phthalimide Ionic Bipolar Redox-Active Molecule for Symmetric Nonaqueous Redox Flow Batteries

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ABSTRACT

Symmetric non-aqueous redox flow batteries (NARFBs) that utilize bipolar redox active organic molecules (BROMs) provide a facile strategy to mitigate the crossover issue. However, their performance has lagged behind due to low solubility of organic redox species and poor high-current operations. To address these technical hurdles, a series of ionic BROMs based on ferrocene (Fc) and phthalimide (Ph) moieties with fast mass and charge-transfer kinetic are synthesized, which show high solubility and ionic conductivity. Both computational and experimental results show that the extended chain length between phthalimide moiety and quaternary nitrogen atom, and the acidity of the solvent act a pivotal part in determining the stability of active materials and thus the cycling stability of NARFB. The assembled symmetric NARFB shows an open circuit voltage of 2.04 V, cycling capacity retention of 99.8% per cycle and energy efficiency of 77.0% over 50 cycles at 20 mA cm\(^{-2}\). Furthermore, the battery yields a peak power density of 110 mW cm\(^{-2}\) at 90 mA cm\(^{-2}\), which outperforms most NARFBs. This work demonstrates a promising molecular engineering strategy to improve the cycling stability of BROMs and to enable the high-current operation of symmetric NARFB.

KEYWORDS

Energy storage, symmetric nonaqueous redox flow battery, bipolar redox active organic molecule, solubility, crossover, ferrocene, phthalimide.
1. INTRODUCTION

Redox flow batteries (RFBs) characterized by decoupled control on energy and power now represent a potential candidate for renewable energy storage technology.\(^1\)\(^,\)\(^2\) Compared with their aqueous counterparts, non-aqueous RFBs (NARFBs) offer potentially high energy density enabled by the wider electrochemical window of organic solvents (up to 5 V).\(^3\)\(^,\)\(^4\) Conventional NARFBs suffer from the electrolyte crossover due to different concentration of two redox couples across the separator.\(^5\) Consequently, self-discharge, low Coulombic efficiency (CE), complex side reactions between the mixed redox couples, and capacity decay tend to occur. In contrast, symmetric NARFBs that utilize bipolar redox active organic molecules (BROMs) for both negative and positive electrode half-reactions have received growing attention because of simpler types of redox-active materials in electrolyte.

Recently, a variety of artificial BROMs have been reported to alleviate the crossover issue in symmetric RFB systems, including bipolar radicals (e.g., 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO),\(^6\) and combined molecule containing the 2,2,6,6-tetramethylpiperidinyl-N-oxyl and phenazine\(^7\)), bipolar quinones (e.g., diaminoanthraquinones\(^5\)) and organometallic molecules (e.g., 1-(4-ferrocenyl-n-butyl)-1’-[3-(trimethylammo)propyl]-4,4'-bipyridinium cation, \(\text{Fc-bipy}^{3+}\)\(^8\), \(\text{N-ferrocenylphthalimide (FcPh)}\), \(\text{N-(a-ferrocenyl)ethylphthalimide (FcEtPh)}\),\(^10\) and 1-(ferrocenylmethyla-mino)-anthraquinone (FcMeAAQ)\(^11\)). However, most of these symmetric systems delivered relatively poor cycling stability with evident capacity loss. For instance, the PTIO-based symmetric NARFB exhibited rapid capacity decay by ~50% after 35 cycles.\(^6\) Similar phenomenon is found for the battery based on FcMeAAQ,\(^11\) whose capacity sharply decreased during 100 cycles. Wei et al. proposed that the instability of redox materials, especially in the charged state, caused the fast capacity decay.\(^12\) It is reported that the close proximity between redox-active centers and other redox unit or backbone moiety often leads
to reduced electrochemical stability of redox materials. Therefore, the instability may be optimized through tuning the distance between different moieties based on deliberated structural engineering.

A number of crucial challenges, especially the low solubility of BROMs and low operational current density ($j$), limit the further improvement in performance of symmetric NARFB. Most BROMs demonstrate lower solubility than other redox-active materials for asymmetric flow cell, leading to low theoretical energy density. The low ionic conductivity of non-aqueous electrolytes is mainly responsible for low $j$ (typically 0.1-5 mA cm$^{-2}$). According to the molecular engineering, ionic modification provides a viable solution to address the technical hurdles above. Wei et al. converted ferrocene (Fc) into ionic compound, whose solubility increased by 20 times in the supporting electrolyte. Attanayake et al. synthesized phenothiazine and viologen based ionic redox-active materials with inherent ionic conductivity and established a NARFB without supporting salt. Overall, ionic redox couples are appealing because of their high solubility and ionic conductivity, which contribute to the high energy density and high-current operations.

Herein, we try to explore high-performance ionic BROMs based on Fc and phthalimide (Ph) moieties (Fc$n$Ph-TFSI, $n = 2$, 4 and 6) for symmetric NARFBs. Fc- and Ph-based redox couples were selected due to their excellent electrochemical performance and wide application in NARFBs. FcPh has been reported as a promising BROM. However, it has a limited solubility of 0.64 M in 1,3-dioxolane (1,3-DL) and the FcPh based H-type coin-cell bears a low current density (0.04 mA cm$^{-2}$). FcPh was introduced as an ionic charged tetraalkylammonium moiety with a bis(trifluoromethylsulfonyl)imide anion (TFSI$^-$), leading to relatively high solubility of up to 2.27 M in N,N-dimethylformamide (DMF) and inherent ionic conductivity. FcnPh-TFSI ($n = 2$, 4 and 6) with varied chain lengths of 2, 4, and 6 carbons between the Ph moiety and quaternary nitrogen atom were synthetized. Both computational and experimental results show
that the chain length and the acidity of the solvents act a pivotal part in determining the battery cycling stability. The compound with \( n = 4 \) show impressive battery performance.

2. EXPERIMENTAL SECTION

2.1 Materials. N-(2-bromoethyl)phthalimide (HEOWNS, 98%), N-(4-bromobutyl)phthalimide (HEOWNS, 97%), N-(6-bromoheptyl)phthalimide (Bide Pharmatech Ltd, 96%), (dimethylaminomethyl)ferrocene (Adamas, 97%), lithium bis (tetrafluoromethylsulfonyl)amide (LiTFSI) (Meryer, 99.5%), tetrahydrofuran (THF) (MACKLIN, 99%), ethyl acetate (99% Jiangtian), n-hexane (AR, Jiangtian), and AgNO₃ (Aladdin, 99.8%) were used. N,N-dimethylformamide (DMF) (Aladdin, 99.9%), acetonitrile (Sigma-Aldrich, 99.9%), and propylene carbonate (Aladdin, 99%) were further dried with 3 Å molecular sieves (Acros Organics) at 260 °C for 24 h. Tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI) were synthesized according to the reported procedures.²⁵

2.2 Synthesis of FcnPh-TFSI (\( n = 2, 4 \) and 6). (Dimethylaminomethyl)ferrocene (5.84 g, 24 mmol) was reacted with N-(2-bromoethyl)phthalimide (5.08 g, 20 mmol) in THF (50 mL) under argon atmosphere (Liufang, 99.999%). The mixture was stirred at 55 °C for 24 h, filtered and washed with ether, to obtain Fc²Ph-Br. Fc²Ph-Br (2.49 g, 5 mmol) was dissolved in 500 mL deionized water at 80 °C and then added to the solution of LiTFSI (2.87 g, 10 mmol) in 50 mL deionized water. The mixture was stirred for 2 h, filtered, and dried under vacuum for 24 h. The crude product was purified by precipitation from ethyl acetate (20 mL) and n-hexane (200 mL) to obtain Fc²Ph-TFSI as an orange solid. Fc⁴Ph-TFSI and Fc⁶Ph-TFSI were synthesized with similar procedure. The products were determined by hydrogen nuclear magnetic resonance (¹H NMR spectra, Varian Inova 500 MHz NMR spectrometer).

2.3 Flow cell tests. A home-designed sandwich-structure flow cell with Daramic-250 membrane and two graphite felt electrodes (Morgan WDF-5, 4 cm²) was assembled in an argon-filled glove box. 5 mL
electrolytes on each side were circulated at a flow rate of 50 mL min⁻¹ by two peristaltic pumps (BT100-1L, LONGER, China). The flow cell test was measured by LAND CT2001A cell test system (LAND, CHINA). The polarization curves (current-voltage curves) were also collected on VersaSTAT 3.

2.4 Other characterization. The solubility of FcnPh-TFSI (n = 2, 4 and 6) in DMF was evaluated by cyclic voltammetry (CV) tests. A series of calibration curves were measured with 1–5 mM FcnPh-TFSI/DMF. Based on the calibration curves, the solubilities of FcnPh-TFSI in DMF can be obtained. The inherent ionic conductivity was measured with a conductivity for 0.1 M active species (FcnPh-TFSI) and the widely used supporting electrolyte tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI) in DMF. The details for CV test, diffusion coefficients (D) and electrochemical kinetics (k₀) calculation, and computational methods can be found elsewhere.

3. RESULTS AND DISCUSSION

As shown in Scheme 1, three ionic BROMs (FcnPh-TFSI, n = 2, 4 and 6) were synthesized via a nucleophilic substitution of dimethylaminomethyl ferrocene with bromine-substituted phthalimide-based compound, followed by ion exchange of Br⁻ with TFSI⁻. The successful synthesis of ionic BROMs is confirmed by ¹H NMR (Figures S1-S3). The ionic BROMs exhibit high solubility, 2.17, 2.21 and 2.27 M for Fc₂Ph-TFSI, Fc₄Ph-TFSI and Fc₆Ph-TFSI, respectively, in DMF (Figures S4), which is comparable with, or even superior to some reported BROMs, for example, 2.6 M for PTIO in acetonitrile (MeCN), 0.64 M for FcPh in 1,3-DL, and 0.017 M for FcMeAAQ in DMF. Moreover, the inherent high ionic
conductivity of ionic BROMs in DMF is an additional advantage, which (665, 659, and 655 μS cm⁻¹ for 0.01 M Fc2Ph-TFSI, Fc4Ph-TFSI, and Fc6Ph-TFSI, respectively) approximates to the widely used supporting electrolyte tetraethylammonium bis(trifluoromethylsulfonyl) imide (TEATFSI, 859 μS cm⁻¹ for 0.01 M TEATFSI). Such high inherent ionic conductivity is expected to enhance the conductivity of the nonaqueous electrolytes and thus enable desirable performance at high current densities.

**Figure 1.** a) Electrode reactions of the ionic BROMs FcnPh-TFSI during charge/discharge. b) CV curves of 5 mM FcnPh-TFSI (n = 2, 4, or 6) in 0.5 M TEATFSI/DMF at a scan rate of 100 mV s⁻¹.

CV was first performed to evaluate the electrochemical behavior of the three ionic ROMs. The redox reactions of FcnPh-TFSI during charge/discharge are schematically shown in Figure 1a and the corresponding CV curves are shown in Figure 1b. Three redox molecules show half-wave potential of 0.15 ~ 0.17 V vs. Ag/Ag⁺ for the Fc moiety and -1.81 ~ -1.89 vs. Ag/Ag⁺ for the Ph moiety, leading to open circuit voltage (OCV) of 1.96~2.06 V. The DFT calculation results indicate that the linker length affects the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energetics (Figure 2). The oxidation potential is linearly correlated with the HOMO energies and the reduction potentials are dominated by the LUMO energetics (Figure S5). Fc4Ph-TFSI and Fc6Ph-TFSI show similar HOMO/LUMO energetics and redox potentials, which are different from that of Fc2Ph-TFSI. Considering that the variable is only the distance between different moieties, we infer that
the difference of Fc2Ph-TFSI is due to the inadequate distance between different moieties. The ferrocene and quaternary ammonium salt part is an electron withdrawing group. The closer to the Ph moiety, the greater the impact on the LUMO energy level.  

Figure 2. DFT calculation results for molecular orbital energy level of FcnPh-TFSI (n = 2, 4 and 6).

The mass- and charge-transfer kinetics of the ionic BROMs was further explored by CV study at different scan rates (Figure S6). The D and k0 were estimated according to the Randles-Sevcik equation and the Nicholson method, respectively. The resultant values of three species (Table 1) are comparable to, and even higher than, those of some redox couples used in asymmetric NARFBs. The overpotential is related to the mass- and charge-transfer kinetics, the viscosity of the electrolyte, the concentration polarization, etc. Relatively fast mass- and charge-transfer kinetics can help minimize overpotential and achieve high operational j.

Table 1. Electrochemical properties and diffusion coefficients for ionic BROMs

<table>
<thead>
<tr>
<th>BROM</th>
<th>E$_{1/2}$ Fc (V vs. Ag/Ag$^+$)</th>
<th>E$_{1/2}$ Ph (V vs. Ag/Ag$^+$)</th>
<th>D Fc (cm$^2$ s$^{-1}$)</th>
<th>D Ph (cm$^2$ s$^{-1}$)</th>
<th>k$_0$ Fc (cm s$^{-1}$)</th>
<th>k$_0$ Ph (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc2Ph-TFSI</td>
<td>0.15</td>
<td>-1.81</td>
<td>2.69-3.10$\times 10^{-6}$</td>
<td>2.10-2.15$\times 10^{-6}$</td>
<td>3.66$\times 10^{-3}$</td>
<td>4.19$\times 10^{-3}$</td>
</tr>
<tr>
<td>Fc4Ph-TFSI</td>
<td>0.17</td>
<td>-1.87</td>
<td>2.66-3.00$\times 10^{-6}$</td>
<td>3.10-3.11$\times 10^{-6}$</td>
<td>3.63$\times 10^{-3}$</td>
<td>4.58$\times 10^{-3}$</td>
</tr>
<tr>
<td>Fc6Ph-TFSI</td>
<td>0.17</td>
<td>-1.89</td>
<td>2.63-2.81$\times 10^{-6}$</td>
<td>2.50-2.55$\times 10^{-6}$</td>
<td>3.50$\times 10^{-3}$</td>
<td>4.05$\times 10^{-3}$</td>
</tr>
</tbody>
</table>
CV analysis of three ionic BROMs shows promising metrics of relatively high OCV and fast mass- and charge-transfer kinetics. The cycling stability is another imperative parameter, which determines the lifetime of NARFBs. To assess the robustness, three ionic BROMs were subjected to cycling test in flow cells with Daramic-250 as the porous separator. The flow cells were evaluated for 50 cycles at 7.5 mA cm\(^{-2}\) employing voltaic limits to reach the achievable maximum state-of-charge (SOC). Figure 3 displays that the symmetric NARFB based on Fc2Ph-TFSI shows enormously rapid capacity decay. In sharp contrast, extension of the linker to Fc4Ph-TFSI and Fc6Ph-TFSI leads to a significant improvement in cycling stability. The capacity retention for Fc4Ph-TFSI and Fc6Ph-TFSI-based symmetric NARFB is 84.1% and 83.8%, respectively, after 50 cycles.

![Figure 3](image)

**Figure 3.** Cycling discharge capacity retention of the flow cell based on 10 mM FcnPh-TFSI (n = 2, 4, or 6) in 0.5 M TEATFSI/DMF at 7.5 mA cm\(^{-2}\).

To explore the reasons for the different cycling stability of ionic BROMs, the DFT calculations were carried out. When the linker length n = 2, the HOMO/LUMO isosurfaces show interaction between Fc and Ph moieties (Figure 2). As the linker length increases, the interaction decreases, corresponding to more localized charge transfer at the redox center, which is also confirmed by the spin density surfaces for the radical dictation after reduction (Figure 4). When the linker length is short (n = 2), the spin density is not only confined to Ph moiety, but also extended onto the quaternary nitrogen atom and Fc moiety,
which indicates the electronic communication. As the linker length increases (n = 4 and 6), the spin density becomes more localized within the redox centers, which contributes to the radical stability.

**Figure 4.** DFT calculation results for spin density surfaces of FcnPh-TFSI (n = 2, 4 and 6) after reduction.

The stability of the electrolyte was further evaluated with CV tests after 50 cycles. New unknown peaks appear for the electrolyte of Fc2Ph-TFSI (Figure S7), which infers some possible parasitic reactions. In contrast, Fc4Ph-TFSI and Fc6Ph-TFSI show similar redox peaks with Figure 1, implying a relatively high stability of the electrolyte. Overall, those results demonstrate a requirement of linker length of at least 4 (n = 4) to achieve stable cycling. Therefore, Fc4Ph-TFSI was selected for further research.

The rate performance was evaluated by flow cell tests with the electrolyte of 50 mM Fc4Ph-TFSI in 1.0 M TEATFSI/DMF from 10 to 40 mA cm\(^{-2}\), 5 cycles at each \(j\). Except the slight decline at \(j = 10\) mA cm\(^{-2}\), the capacity is almost constant at other \(j\), indicating the relatively high stability of the flow battery (Figure 5a). The average discharge capacities decrease with \(j\), 0.76, 0.56, 0.46 and 0.34 Ah L\(^{-1}\) for \(j\) of 10, 20, 30 and 40 mA cm\(^{-2}\), respectively. The rather low capacity at 40 mA cm\(^{-2}\) is originated from the increased polarization loss at high current densities such as ohmic polarization loss of the electrolyte and membrane, and concentration polarization from the active materials. When \(j\) increases from 10 to 40 mA cm\(^{-2}\), CE slightly increases due to reduced unavoidable crossover effect. The different concentration of different charged species will lead to the crossover reactions.\(^9\) In contrast, voltage efficiency (VE) and
energy efficiency (EE) decrease from 91.8% and 84.4% to 57.4% and 55.6%, respectively, due to increased polarization resistance (Figure 5b).

**Figure 5.** a) Rate capability of the battery with $j = 10$ to 40 mA cm$^{-2}$. b) Efficiencies at different current densities. c) I-V polarization curves. d) Cycling efficiency and capacity at 20 mA cm$^{-2}$ for the battery with 50 mM Fc4Ph-TFSI in 1.0 TEATFSI/DMF.

Given the high cycling stability and relatively high EE, the charge/discharge properties of the symmetric NARFB based on Fc4Ph-TFSI were further examined with long-term cycling at 20 mA cm$^{-2}$. The cell exhibits an OCV of ~2.1 V, similar with the CV result (Figure 5c). The flow cell achieves a peak power density of 110 mW cm$^{-2}$ at 90 mA cm$^{-2}$, which outperforms most reported NARFBs and even rivals some aqueous RFBs.\textsuperscript{11, 22, 26, 30-32} Figure 5d presents the cycling efficiency and capacity of 50 mM Fc4Ph-TFSI flow cell at 20 mA cm$^{-2}$. The initial charge and discharge capacities are 1.01 and 0.98 Ah L$^{-1}$, respectively, corresponding to charge and discharge energy density of 2.23 and 1.76 Wh L$^{-1}$, respectively.
The average CE, VE, EE, and discharge capacity are 94.6%, 81.4%, 77.0%, and 0.94 Ah L\(^{-1}\), respectively. Benefited from the high ionic conductivity and fast mass- and charge-transfer kinetics of Fc4Ph-TFSI, the flow battery shows excellent performance, especially EE of \(~80\%\) even at high \(j\) of 20 mA cm\(^{-2}\). Furthermore, the battery achieves a relatively high discharge capacity retention of 99.8% per cycle over 50 cycles. The cycle stability of the battery surpasses the reported symmetric NARFBs (Table 2).\(^6,9-11,33\).
Table 2. Comparison of the electrochemical performance of NARFBs.

<table>
<thead>
<tr>
<th>BROMs</th>
<th>Electrolyte</th>
<th>Battery type</th>
<th>Voltage (V)</th>
<th>j (mA cm(^{-2}))</th>
<th>CE/VE/EE (%)</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M PTIO</td>
<td>1.0 M TBAPF/MeCN</td>
<td>Flow cell</td>
<td>1.7</td>
<td>20</td>
<td>96/75/72</td>
<td>35</td>
<td>[6]</td>
</tr>
<tr>
<td>0.1 M FcPh</td>
<td>1.0 M TBAPF/1,3-DL</td>
<td>H-type Coin-cell</td>
<td>1.94</td>
<td>0.04</td>
<td>97.3/-/-</td>
<td>50</td>
<td>[9]</td>
</tr>
<tr>
<td>0.6 M FcEtPh</td>
<td>1.0 M TBAPF/1,3-DL</td>
<td>H-type Coin-cell</td>
<td>1.98</td>
<td>0.04</td>
<td>97.8/-/-</td>
<td>50</td>
<td>[10]</td>
</tr>
<tr>
<td>0.01 M FcMeAAQ</td>
<td>0.1 M TEATFSI/MeCN</td>
<td>Flow cell</td>
<td>1.42</td>
<td>2</td>
<td>90.8/90.1/81.8</td>
<td>50</td>
<td>[11]</td>
</tr>
<tr>
<td>0.1 M Me-TEG-DAAQ</td>
<td>1.0 M TEATFSI/DME</td>
<td>Flow cell</td>
<td>1.8</td>
<td>2</td>
<td>99.3/-/-</td>
<td>100</td>
<td>[33]</td>
</tr>
<tr>
<td>0.04 M Verdazyl radical</td>
<td>0.5 M TBAPF/MeCN</td>
<td>Static cell</td>
<td>0.98</td>
<td>0.12</td>
<td>94/68/64</td>
<td>50</td>
<td>[34]</td>
</tr>
<tr>
<td>0.01 M nitronyl nitroxide</td>
<td>0.5 M TBAPF/MeCN</td>
<td>Flow cell</td>
<td>1.62</td>
<td>3</td>
<td>80/80/63</td>
<td>-</td>
<td>[35]</td>
</tr>
<tr>
<td>0.05 M Fc4Ph-TFSI</td>
<td>1.0 TEATFSI/DMF</td>
<td>Flow cell</td>
<td>2.04</td>
<td>20</td>
<td>94/68/77.0</td>
<td>50</td>
<td>This</td>
</tr>
<tr>
<td>0.5 M Fc4Ph-TFSI</td>
<td>1.0 TEATFSI/DMF</td>
<td>Flow cell</td>
<td>2.04</td>
<td>40</td>
<td>87.3/57.9/50.3</td>
<td>20</td>
<td>work</td>
</tr>
</tbody>
</table>

Note: Me-TEG-DAAQ: 1,4-bis((2-(2-(methoxyethoxy)ethoxy)ethyl)amino)anthracene-9,10-dione; TBAPF\(_6\): tetrabutylammonium hexafluorophosphate; TBAP: tetrabutylammonium perchlorate; DME: 1,2-Dimethoxyethane.

To make full use of the high solubility of Fc4Ph-TFSI (2.27 M in DMF), a flow cell with 0.5 M Fc4Ph-TFSI in 1.0 M TEATFSI/DMF was assembled and tested at 40 mA cm\(^{-2}\). As shown in Figure 6, the average CE, VE, and EE are 87.3%, 57.9%, 50.3%, respectively. The initial charge and discharge capacities are 9.4 and 6.8 Ah L\(^{-1}\), respectively, corresponding to charge energy density of 22.2 Wh L\(^{-1}\) and discharge energy density of 10.9 Wh L\(^{-1}\). The material utilization is 70.2% (theoretical capacity of 13.4 Ah L\(^{-1}\)) considering the initial charge capacity. The batteries exhibit more serious cycling degradation in the high-concentration systems probably due to crossover, electrolyte leakage and parasitic reaction. The crossover is still a serious issue even for symmetric battery due to the concentration gradient between different charged species in the two sides during cycling. Similar with our previous work, the electrolyte leakage can lead to the capacity loss, which can be mitigated by optimizing the battery configuration in the future. In this work, the parasitic reaction must be mainly responsible for the capacity loss. The
electrolyte after high-concentration battery test was examined by CV and the results are shown in Figure S8. The CV curves are quite different from those of fresh and low-concentration electrolyte (Figure 1). The reversibility of the redox active substance seriously decreases and new redox peaks appear for the anolyte at -2.0 and 0.2 V, respectively. The reasons for such substantial change of high-concentration electrolyte remain to be explored. Now we propose that the parasitic reaction involving radicals probably worsens for high-concentration electrolyte.
Figure 6. Cycling efficiency and capacity at 40 mA cm$^{-2}$ for the battery with 0.5 M Fc4Ph-TFSI in 1.0 TEATFSI/DMF.

As shown in Figure 1a, the redox reactions of Fc4Ph-TFSI involve free radical anion at the anode side. Radicals are usually chemically reactive and thus their chemical stability in the solvent may affect the cycling stability of the battery. The radical anion has a tendency to degradation via protonation to be electrically neutral by the solvent. For instance, 9-fluorenone radical anion ($\text{FL}^\cdot$) can remove H$^+$ from MeCN, leading to protonation and further dimerization. The parasitic reaction via protonation of the negatively charged radical anion probably causes the new redox peaks and capacity decay. Accordingly, we hypothesize that the acidity of solvent has a significant effect on the cycling stability of the present symmetric NARFB based on Fc4Ph-TFSI. To prove that, we selected three typical solvents with an acidity sequence of propylene carbonate (PC) $>$ MeCN $>$ DMF to perform flow battery test. As shown in Figure 7, the battery based on DMF maintains 84.1% of its initial capacity over 50 cycles, much higher than 59.8% for MeCN and 12.8% for PC, which confirms our hypothesis. For NARFBs, the parasitic reaction is always a serious issue and harms the battery performance, which needs to be addressed in future work.
Figure 7. Cycling discharge capacity retention of the 10 mM Fc4Ph-TFSI based flow cells using different solvents (DMF, MeCN, or PC) at 7.5 mA cm$^{-2}$.

4. CONCLUSIONS

In summary, we have proposed a new class of ionic BROMs based on ferrocene (Fc) and phthalimide (Ph) moieties for symmetric NARFBs. Benefit from the high solubility and considerable ionic conductivity, the resultant battery delivers a high theoretical energy density and excellent high-current performance. The linker length of n methylene groups ($n = 2, 4$ and $6$) has a significant influence on the electrochemical properties. A minimum of $n = 4$ is required to achieve stable electrochemical performance. The flow cell based on Fc4Ph-TFSI shows OCV of 2.04 V, CE of 94.6%, EE of 77.0%, and cycling capacity retention of 99.8% per cycle over 50 cycles at 20 mA cm$^{-2}$ and delivers a peak power density of 110 mW cm$^{-2}$, which is competitive with the demonstrated NARFBs reported so far. In addition, the acidity of the solvent affects the stability of organic radical ions and thus the cycling stability of flow batteries.

ASSOCIATED CONTENT
Supporting Information. 1H NMR spectra, CV curves at different scan rates, calibration curves for solubility, and CV curves of the catholyte and anolyte after battery tests are shown in Supporting Information.

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Notes

The authors declare no competing financial interest.

Author Contributions

Donghan Xu: Conceptualization, Methodology, Investigation, Writing – original draft, Formal analysis.

Cuijuan Zhang: Conceptualization, Methodology, Formal analysis, Writing – review & editing, Supervision. Yihan Zhen: Discussion. Yongdan Li: Resources, Supervision, Funding acquisition.

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