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# A high-performance all-iron non-aqueous redox flow battery

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**Abstract:** An all-iron non-aqueous redox flow battery (NARFB) based on iron acetylacetonate (Fe(acac)<sub>3</sub>) anolyte and N-(ferrocenylmethyl)-N,N-dimethyl -N-ethylammonium bis(trifluoromethane-sulfonyl)imide (Fc1N112-TFSI) catholyte with an open circuit voltage of 1.34 V is designed. Due to the high electrochemical activity of the active species, the resultant battery demonstrates fairly high cycling performance and rate capability with anion exchange membrane FAP-375-PP. The Coulombic efficiency (CE) of 98.7%, voltage efficiency (VE) of 84.5%, and energy efficiency (EE) of 83.4% are achieved over 100 cycles at the current density of 10 mA cm<sup>-2</sup>. VE and EE can be further enhanced by employing mixed-reactant electrolyte as both anolyte and catholyte, which are 89.2% and 85.2%, respectively. The underlying reasons for the capacity decay are discussed for future optimization.

**Key words:** Electrochemical energy storage; redox flow battery; non-aqueous electrolyte; organometallic materials

## 1. Introduction

The vigorous exploration of clean, renewable but intermittent energy such as solar and wind and their large-scale integration into the existing electrical grid has spurred the development of energy storage technologies to maintain the grid stability and safety[1]. An ideal energy storage technology should be high cycling efficiency and rate capability, safe, scalable and cost-effective. In such context, redox flow batteries (RFBs) stand out as one of the most promising energy storage technologies owing to their unique advantages in terms of independent modular design, long cycle life, rapid response, and environmentally friendliness[2]. By storing the active species in the liquid electrolytes and circulating between external reservoirs and cell compartments to store or release energy, the energy and power of RFBs is completely decoupled and thus can be tailored independently to accommodate different scalability[1, 3]. The traditional aqueous RFBs such as all-vanadium RFBs and Zn/Br RFBs have been commercialized for large scale energy storage[4]. Although the requirement of energy density is not so strict for such applications, the low energy density of aqueous RFBs due to the narrow voltage from water electrolysis jeopardizes its competition with other energy storage technologies. Correspondingly, developing non-aqueous RFBs (NARFBs) with wider electrochemical window is desirable to achieve high energy densities[2].

For NARFBs, the active species in the early research were focused on the organometallics, i.e., metal–ligand complexes such as  $Ru(bpy)_3[5]$ ,  $V(acac)_3[6]$ ,  $Co(phen)_3[7]$ , and  $Cr(acac)_3[8]$ . Due to the multi-electron transfer characteristics, they were used for symmetric RFBs to mitigate the cross-contamination. However, most of those metal complexes show low solubility and exhibit rather poor battery cycling performance. Among the metal-ligand active materials, the iron-based active materials

are earth abundant and have good electrochemical properties[9]. Therefore, in recent years, many hybrid all-iron RFB and complete all-iron RFB for aqueous system have been investigated[10-14]. However, for hybrid all-iron RFB, the deposition of the metallic iron and the hydrogen evolution reaction on the anode will result in decreased battery performance[9, 10]; for complete all-iron aqueous RFB, the Coulombic efficiency (CE) of the battery is usually low due to the cross-over of the active species[10, 13].

Another organometallic, the metallocene family, has been widely studied as the active species for NARFBs owing to its good electrochemical properties and fast kinetics[15, 16]. Especially, ferrocene is extremely attractive considering its high reversibility and low cost[15-17]. Some derivatives have been synthesized to increase its solubility and redox potential and successfully used in NARFBs[18-20]. However, those batteries were assembled with Li-metal as the anode, which shows safety issue. Therefore, their utilization in the RFBs still requires screening for appropriate redox couples.

Herein, an all-iron NARFB is designed with iron acetylacetonate (Fe(acac)<sub>3</sub>) and N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium bis(trifluoromethane-sulfonyl) imide (Fc1N112-TFSI, Figs. S1 and S2) as anolyte and catholyte, respectively. The electrode reactions of this NARFB are illustrated in Scheme 1. Both catholyte and anolyte contain only one redox couple of Fe<sup>II</sup> and Fe<sup>III</sup>. The resultant RFBs show relatively high cycling performance and rate capability.



Scheme 1. Redox reactions of Fc1N112-TFSI catholyte and Fe(acac)<sub>3</sub> anolyte.

## 2. Experimental

#### 2.1. Materials

Fe(acac)<sub>3</sub> (99%, Dibai, China) was purified by recrystallization from ethanol to remove the impurities. Bromoethane (99%, Bailingwei, China), (dimethylaminomethyl) ferrocene (97%, Adamas, China), lithium bis(tetrafluoromethylsulfonyl)amide (LiTFSI, 99.5%, Meryer, China), tetraethylammonium bromide (TEAB, 99%, Guangfu, China), ether (99.5%, Yuanli, China), and acetonitrile (MeCN, 99.9%, Sigma-Aldrich) were used as received.

#### 2.2. Synthesis of Fc1N112-Br, Fc1N112-TFSI, and TEATFSI

Fc1N112-TFSI was synthesized according to the literature[18]. Bromoethane (3.1 mL, 41.5 mmol) was added to a solution of (dimethylaminomethyl)ferrocene (9.7 g, 39.9 mmol) in 50 mL MeCN, then the mixed solution was stirred overnight. The precipitate was isolated by filtration and washed with ether. The orange product Fc1N112-Br was yielded at 13.2 g, 73.3%. Then LiTFSI (6.42 g, 22.35 mmol) was dissolved in 50 mL deionized water and added in a solution of Fc1N112-Br (7.5 g, 21.3 mmol) in 50 mL deionized water. The mixture was stirred at room temperature for 2 h.

The product Fc1N112-TFSI was filtered and dried under vacuum for 24 h. Yield: 11.2 g, 95.2%. The supporting electrolyte TEATFSI was synthesized according to the literature[21]. A solution of LiTFSI (46 g, 0.16 mol) in 25 mL deionized water was added to a solution of TEAB (35.3 g, 0.17 mmol) in 25 mL deionized water. The mixture was stirred at room temperature for 2 h and the extra deionized water can be added if the mixture was too thick. Then the white product was filtered and washed with deionized water, dried under vacuum for 24 h. Yield: 41.4 g, 63.0%. The synthesized active materials and supporting electrolyte were determined via nuclear magnetic resonance (NMR) spectra (1H) carried out on a Bruker Avance III 400MHz NMR spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard.

# 2.3. Solubility measurement of the active materials

The solubility of Fc1N112-TFSI and Fe(acac)<sub>3</sub> was tested by UV-Vis absorption spectra (Shimadzu UV-2450). A range of standard solutions of different concentration were prepared by dissolving active species in 0.5 M TEATFSI/MeCN and determined by UV-Vis to get the standard curves. Then, the active materials were gradually added to 1 mL of 0.5 M TEATFSI/MeCN solution and dissolved by ultrasonication until the added substances no longer dissolved, resulting in a saturated solution. The saturated solutions were allowed to stand overnight, after which the supernatant was diluted and subjected to UV-Vis test. For Fc1N112-TFSI and Fe(acac)<sub>3</sub>, the peak wavelengths of 435 and 353 nm were selected for calculation, respectively. The absorbance of the active substances at the selected wavelength was recorded and the solubility was extrapolated based on the calculated standard curves.

## 2.4. Cyclic voltammetry (CV) test

The CV test was performed on a VersaSTAT3 electrochemical workstation

(Princeton Applied Research, USA) with a three-electrode cell at room temperature. A glassy carbon (6 mm in diameter, Aidahengsheng, China), graphite plate (5.24 cm<sup>2</sup>), and Ag/Ag<sup>+</sup> (5 mM AgNO<sub>3</sub>/MeCN) were employed as the working, counter, and reference electrodes, respectively. The electrolytes were prepared by dissolving 0.01 M active species and 0.1 M supporting electrolyte in MeCN, which were deoxygenated by bubbling with Argon (99.999%, Liufang, China) for 10 min before test.

#### 2.5. Flow battery test

The flow battery performance was tested with a home-designed flow battery system in the nitrogen-filled glove box with LAND battery testing instrument (Wuhan LAND Electronic Co. Ltd., China). The sandwich-structured flow cells were assembled with centrally located anion exchange membrane (Fumasep FAP-375-PP) or porous membrane (Daramic AA-250), and graphite felt electrodes (Morgan WDF-5) symmetrically distributed on both sides. The electrolytes with 10 mL of 0.1 M Fc1N112-TFSI/0.5 M TEATFSI/MeCN and 10 mL of 0.1 M Fe(acac)<sub>3</sub>/0.5 M TEATFSI/MeCN were employed as catholyte and anolyte, respectively. The electrolytes were circulated between cells and storage tanks by two peristaltic pumps (BT100-1L, Longer Precision Pump Co., Ltd., China) at a flow rate of 50 mL min<sup>-1</sup>. The battery with mixed-reactant electrolyte consisting of 1:1 mixture of Fc1N112-TFSI and Fc(acac)<sub>3</sub> in 0.5 M supporting electrolyte as both anolyte and catholyte was also tested under the same condition. For all the charge/discharge tests, the charge and discharge limited voltages were set at 1.8 and 0.5 V, respectively.

#### 2.6. Cross-over measurement

The cross-over measurement was performed in the H-type cells in which 10 mL of 0.01 M Fc1N112-TFSI/0.1 M TEATFSI/MeCN and 10 mL of 0.01 M Fe(acac)<sub>3</sub>/0.1  $^{6}$  M TEATFSI/MeCN were used as the catholyte and anolyte, respectively. The membranes

were placed in the center of the H-type cells and fixed with the clips to avoid the electrolyte leakage.

## 2.7. Electrochemical impedance spectroscopy (EIS) test

The EIS tests before and after charge/discharge cycling were conducted on the VersaSTAT3 electrochemical workstation at the frequency of  $10^5$ -10 Hz with a perturbation amplitude of 10 mV at the open circuit condition. The intercept with the X-axis at the high frequency is recorded as ASR<sub>HF</sub> (area specific resistance).

#### 2.8. SEM-EDS test

The microstructure of the fresh and cycled membranes and electrodes was observed with field emission scanning electron microscope (FE-SEM, Hitachi, s4800) equipped with an energy dispersive spectroscopy (EDS) unit.

# 3. Results and discussion

The open circuit voltage (OCV) of RFBs is determined by CV with 0.01 M active species in 0.1 M TEATFSI (Fig. S3)/ MeCN at a scan rate of 300 mV s<sup>-1</sup>. As shown in Fig. 1, the half wave potentials of Fc1N112-TFSI catholyte and Fe(acac)<sub>3</sub> anolyte are 0.26 and -1.08 V vs.  $Ag/Ag^+$ , respectively, yielding an OCV of 1.34 V.



**Fig. 1.** CV curves of Fc1N112-TFSI and Fe(acac)<sub>3</sub> (0.01 M in 0.05 M TEATFSI/MeCN) on a glassy carbon electrode (scan rate =  $300 \text{ mV s}^{-1}$ ) at room temperature.

Since high diffusion ability of active materials is important to achieve high performance, the diffusion coefficient of active materials was determined by CV at different scan rates. As shown in Fig. 2a and b, the redox peak current ratio of the catholyte and anolyte is roughly 1.0 and 0.9, respectively. The peak separation ( $\Delta E_p$ ) slightly increases with the scan rate from 100 to 600 mV s<sup>-1</sup>. All the results indicate that both anolyte and catholyte redox reactions are quasi-reversible. The linear relationship between the peak current and the square root of the scan rates (Fig. 2c and d) suggests a diffusion-controlled process. The diffusion coefficients, calculated with modified Randles-Sevcik equation for quasi-reversible process, are  $6.15-7.23 \times 10^{-6}$  and  $1.34-1.81 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for Fc(II)1N112-TFSI/Fc(III)1N112-TFSI and Fe(III)(acac)<sub>3</sub>/Fe(II)(acac)<sub>3</sub>, respectively, similar with the results of other active species for NARFBs[16, 22].



**Fig. 2.** CV curves of Fc1N112-TFSI (a) and Fe(acac)<sub>3</sub> (b) at various scan rates (100, 200, 300, 400, 500, 600 mV s<sup>-1</sup>). Peak current densities for Fc1N112-TFSI (c) and Fe(acac)<sub>3</sub> (d) versus the square root of scan rate.

The solubility of both active species in 0.5 M TEATFSI/MeCN was measured by UV-Vis absorption spectra (Figs. S4 and S5), which is 2.1 and 0.28 M for Fc1N112-TFSI and Fe(acac)<sub>3</sub>, respectively. Combined with the OCV (Fig. 1, 1.34 V), a theoretical energy density of 8.9 Wh L<sup>-1</sup> can be derived for such an all-iron NARFB. Considering the much lower solubility of Fe(acac)<sub>3</sub> compared with Fc1N112-TFSI, the theoretical energy density is limited by the solubility of Fe(acac)<sub>3</sub>. It can be optimized through molecular engineering [2] as widely adopted, which will be carried out in our future work.

To evaluate the charge/discharge performance of the all-iron NARFB, a flow cell with 0.1 M Fc1N112-TFSI and 0.1 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN as catholyte and anolyte, respectively, was assembled. Because the properties of separators have a significant influence on the performance of RFBs[23], two types of separators, anion exchange membrane Fumasep FAP-375-PP and porous membrane Daramic AA-250 which are widely used for NARFB[24, 25], were selected to screen appropriate separator for such an all-iron NARFB. The corresponding results are shown in Fig. 3.



**Fig. 3.** Cycling performance of the batteries over 100 cycles (a, c) and galvanostatic charge-discharge profiles from 95<sup>st</sup> to 100<sup>st</sup> cycles (b, d) using FAP-375-PP anion exchange membrane (a, b) and AA-250 porous membrane (c, d) with 0.1 M active species in 0.5 M TEATFSI/MeCN at the current density of 10 mA cm<sup>-2</sup>.

The NARFB with anion exchange membrane Fumasep FAP-375-PP (Fig. 3a and b) exhibits rather stable cycling. The average CE, voltage efficiency (VE), and energy efficiency (EE) are 98.7%, 84.5%, and 83.4%, respectively, over 100 cycles, which are much higher than most non-aqueous systems[22, 26]. The average discharge capacity is 1.50 Ah L<sup>-1</sup>. In contrast, the battery with porous membrane Daramic AA-250 (Fig. 3c and d) shows much higher VE of 91.8% but smaller CE (88.3%), EE (81.1%), and average discharge capacity (1.06 Ah L<sup>-1</sup>). The high VE value can be attributed to the low resistance of the porous membranes, as evidenced by the lower ASR<sub>HF</sub> of 4.9  $\Omega$ 

cm<sup>2</sup> (Fig. S6) compared with its anion exchange membrane counterpart (8.5  $\Omega$  cm<sup>2</sup>).

The lower CE, discharge capacity, and material utilization (40% vs. 56%) of battery with Daramic AA-250 membrane is probably associated with more severe cross-over effect. As shown in Fig. S7, the cross-over measurement reveals that the color of the catholyte side in the H-cell becomes deeper with the Daramic AA-250 membrane after 8 h. Furthermore, precipitates are found on the surrounding edges of Daramic AA-250 membrane after 5 days (Fig. S7f) whereas the Fumasep FAP-375-PP membrane remains almost intact (Fig. S7c). Such result is consistent with the changes of the membrane after cycling test. The cells were dissembled after 100 charge/discharge cycling, and the photographs of the membranes are shown in Fig. S8. For FAP-375-PP membrane, deposits are found on the surface that in direct contact with the electrode. In sharp contrast, the surrounding edges of the Daramic AA-250 membrane show serious deposition in addition to the parts in contact with the electrodes, indicating more loss of the active materials, which should be responsible for the lower discharge capacity and material utilization.

Taking all those into consideration, the anion exchange membrane Fumasep FAP-375-PP is more suitable for the present battery system and thus used for the following test. It should be noted that compared with other organometallic NARFBs, the present RFBs show high cycling performance (Table 1).

Electrolyte	Voltage (V)	Cycle number	CE/VE/EE (%)	Initial capacity Ah/L	Current density (mA cm <sup>-2</sup> )	Ref.
0.1 M Cr(acac) <sub>3</sub> /Fe(acac) <sub>3</sub>	1.2	50	99/53/53	~ 0.67	5 (charge) 1 (discharge)	[22]
0.01 M Co(phen) <sub>3</sub> /Fe(phen) <sub>3</sub>	2.1	25	80/48/39	~ 0.1	0.5 (charge) 0.25 (discharge)	[27]
5 mM Co(P <sub>3</sub> O <sub>9</sub> ) <sub>2</sub> /V(P <sub>3</sub> O <sub>9</sub> ) <sub>2</sub>	2.4	100	>90/-/-	~ 0.105	0.21 (charge) 0.0525(discharge)	[28]
0.2 M [Co(bpy) <sub>3</sub> ]Tf <sub>2</sub> /[Fe(bpy) <sub>3</sub> ]Tf <sub>2</sub>	2.0	12	90/21/-	-	0.8	[29]
0.1 M M FeCp <sub>2</sub> PF <sub>6</sub> /CoCp <sub>2</sub>	1.7	30	95/90/85	~ 2.5	0.4C	[16]
0.1 M V(acac) <sub>3</sub>	2.17	10	91/-/80 (for 5 <sup>th</sup> cycle) (TEA <sup>+</sup> -Nafion membrane)	_	10	[30]
	2.2	10	74/-/68 (for 5 <sup>th</sup> cycle) (Daramic membrane)	_	10	
0.1 M Fc1N112-TFSI/Fe(acac) <sub>3</sub>	1.34	100	98.7/84.5/83.4 (FAP-375-PP membrane)	2.47	10	This work
			88.3/91.8/81.1 (Daramic AA-250 membrane)	1.86	10	

 Table 1. Performance comparison of NARFB with organometallics active materials.

The rate capability is another merit for practical application. The rate performance was examined by galvanostatically charging/discharging the battery with 0.02 M Fc1N112-TFSI and 0.02 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN at the current density of 1-20 mA cm<sup>-2</sup> (Fig. 4). Except the initial decline at the current density of 1 mA cm<sup>-2</sup>, the battery cycles stably at other current densities. CE increases gradually with the current density due to the reduced cross-over effect. CE of > 99% is achieved over all the current densities investigated here. By contrary, VE decreases rather quickly due to the increased polarization resistance. Meanwhile, EE decreases with the same trend of VE. When the current density increases from 5 to 20 mA cm<sup>-2</sup>, the discharge capacity decreases from 336.9 to 301.4 mAh L<sup>-1</sup>, indicating rather robust rate capability of the present all-iron NARFB.



**Fig. 4.** (a) Capacity versus cycling numbers from 1 to 20 mA cm<sup>-2</sup> for the battery with 0.02 M active species in 0.5 M TEATFSI/MeCN using FAP-375-PP membrane. (b) Representative charge/discharge profiles of the battery at different current densities.

Although the all-iron NARFB exhibits high efficiency and rate capability, its capacity decreases rather quickly with cycling. The cycling stability is always a serious concern for NARFBs[31]. The main cause of capacity decay is the consumption and volatilization of the electrolyte, which can be easily observed by changes in the electrolyte volume after cycling, decreased by ~50% (Fig. S9), and electrolyte leakage to the battery mold (Fig. S10). The cross-over of the electrolyte should also be responsible for the capacity decay. The CV curves of the electrolyte with 0.02 M active species in 0.5 M TEATFSI/MeCN after 200 charge/ discharge cycles were recorded (Fig. 5a). Compared with Fig. 1, the redox peaks of  $Fe(III)(acac)_3/Fe(II)(acac)_3$  couple appear the CV of 200 in cycled-catholyte, of Fc1N112-TFSI(II)/Fc1N112-TFSI(III) those and appear in the CV curve of 200 cycled-anolyte. It indicates that cross-over of the electrolyte happens during cycling and leads to decrease in CE and capacity.

The EIS of the flow battery after different cycles was recorded (Fig. 5b). The

semicircles at the high frequency are related to the charge transfer process at the interface between electrodes and electrolytes. The charge transfer resistance increases with cycling, which is probably due to the deposition at the electrodes[30] as revealed by SEM (Fig. S11). The semicircles at the medium to low frequencies are probably assigned to the adsorption process at the surface of the electrodes. The resistance of this process also increases with cycling, which is believed to be related with the deposition at the electrodes. In addition, ASR<sub>HF</sub>, which is dominated by the membrane resistance, increases with cycling, which is probably originated from the increasing deposition on the membrane (Figs. S12 and S13, Tables S1 and S2). The total resistance increases with cycling, leading to cycling performance



**Fig. 5.** (a) CV curves of the catholyte and anolyte after 200 charge/discharge cycles. (b) Nyquist plots for the battery after different cycles. Anion exchange membrane FAP-375-PP was used for the battery.

To further investigate the composition of the deposits on the membrane, the 100 charge/discharge cycled anion exchange membrane FAP-375-PP was immersed in 0.05 M TEATFSI/MeCN and sonicated to accelerate the dissolution of the deposition. The soaking solution was then subjected to CV test. Fig. 6 shows strong Fe(acac)<sub>3</sub> redox peaks but weak Fc1N112-TFSI redox peaks, indicating that Fe(acac)<sub>3</sub> is the dominant component of the deposition, which is probably due 14

Similar results are found for the case of porous membrane Daramic AA-250 (Fig. S14). The membrane is exposed to both anolyte and catholyte active materials in the battery. During long-term charge/discharge cycling especially with high concentration electrolyte, due to the volatilization of the solvent, the Fe(acac)<sub>3</sub> with low solubility (0.28 M for Fe(acac)<sub>3</sub> vs. 2.1 M for Fc1N112-TFSI) gradually separates out and precipitates on the membrane. In addition, the solvent uptake of the membrane also makes the active species to permeate through the membrane and precipitate on it[32]. The increasing deposits on the membrane results in decreased capacity and increased membrane resistance (Fig. 5b).



**Fig. 6.** CV of the soaking solution of the FAP-375-PP membrane after 100 cycles with 0.1 M active species in 0. 5 M TEATFSI/MeCN.

As aforementioned, the cross-over is an important factor responsible for the capacity decay and CE reduction for both anion exchange membrane and porous membrane. Mixed-reactant electrolyte is widely employed to alleviate this issue[33, 34]. Correspondingly, a flow battery with mixed-reactant electrolyte (0.1 M Fc1N112-TFSI/0.1 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN) as both anolyte and catholyte was assembled. The anion exchange membrane FAF-373-PP was used. Fig. 7 shows the charge/discharge performance of the battery at the  $^{15}$ 

mA cm<sup>-2</sup> over 100 cycles. The average CE, VE, EE, discharge capacity, and material utilization are ~95.5%, 89.2%, 85.2%, 1.93 Ah L<sup>-1</sup>, and 72%, respectively, which are improved compared with the case with unmixed electrolyte except CE (Fig. 3, 98.7%, 84.5%, 83.4%, 1.50 Ah L<sup>-1</sup>, and 56%, respectively). Similar improvement is also found in the battery with porous membrane Daramic AA-250 (Fig. S15).



Fig. 7. Charge/discharge cycling performance of the battery over 100 cycles using anion exchange membrane FAP-375-PP with mixed-reactant electrolyte 0.1 M Fc1N112-TFSI/0.1 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN at the current density of 10 mA cm<sup>-2</sup>.

It is worth noting that CE of the batteries with mixed-reactant electrolyte using both membranes decreases compared with their unmixed counterparts. Since cross-over is reduced by using mixed-reactant electrolyte, the relatively lower CE is probably originated from the side reactions. To prove that, the mixed-reactant electrolytes after charge/discharge cycling tests were measured by CV. As shown in Fig. 8a, besides the redox peaks of Fc1N112-TFSI catholyte and Fe(acac)<sub>3</sub> anolyte, a third redox couple at 0 V vs. Ag/Ag<sup>+</sup> appears, which is assigned to the redox of ferrocene (Fc). Such assignment is verified by the CV result of 0.5 mM Fc/10 mM Fc1N112-TFSI in 0.1 M TEATFSI/MeCN (Fig. 8b). The appearance of Fc in the mixed-reactant electrolyte indicates the severe decomposition of Fc1N112-TFSI when it is mixed with Fe(acac)<sub>3</sub>, which should be mainly responsible for the decreased CE. The CV results (Fig. S16) of the soaking solution of both FAP-375-PP membrane and Daramic AA-250 membrane after charge/discharge cycling tests further show the deposition of side reaction product Fc along with anolyte and catholyte active materials. The mechanism of the severe decomposition of Fc1N112-TFSI in the mixed-reactant electrolyte remains to be explored.



Fig. 8. (a) CV curves of the catholyte and anolyte of the mixed-reactant electrolyte after 100 charge/discharge cycles. (b) CV curve of 0.5 mM Fc/10 mM Fc1N112-TFSI in 0.1 M TEATFSI/MeCN.

## 4. Conclusions

A high performance NARFB based on all-iron active materials Fc1N112-TFSI catholyte and Fe(acac)<sub>3</sub> anolyte is proposed. Benefit from the excellent electrochemical activity of the active species, a flow battery using 0.1 M Fc1N112-TFSI in 0.5 M TEATFSI/MeCN as catholyte and 0.1 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN as anolyte demonstrated a high cycling performance with CE of 98.7%, VE of 84.5%, and EE of 83.4% at the current density of 10 mA cm<sup>-2</sup> during 100 cycles with the 17 anion

exchange membrane Fumasep FAP-375-PP. The battery performance can be further enhanced with mixed-reactant electrolyte 0.1 M Fc1N112-TFSI/0.1 M Fe(acac)<sub>3</sub> in 0.5 M TEATFSI/MeCN as both catholyte and anolyte. The average VE and EE are 89.2% and 85.2%, respectively. However, the decomposition of the Fc1N112-TFSI in mixed-reactant electrolyte lead to decreased CE of 95.5%. Although this flow battery exhibits relatively high efficiency, the cycling performance analysis reveals that evaporation and cross-over of the electrolyte, deposition of the active materials on the membrane and electrodes, and decomposition of the active species in the mixed-reactant electrolyte should be responsible for the capacity degradation during long-term cycling. Nevertheless, this work demonstrates that an all-iron NARFB is potentially feasible, its energy density can be further increased by molecular engineering through increasing solubility and OCV. Furthermore, by screening appropriate membrane and optimizing the active materials, supporting electrolyte and solvents, better performance of all-iron NARFB can be expected. **Acknowledgements** 

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