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Enhancing the performance of an all-organic non-aqueous redox flow battery

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Abstract

The non-aqueous redox flow battery (NARFB) is a promising device for grid-scale energy storage. However, its electrochemical performance and long-term stability still need to be improved. This work shows that the electrochemical performance of NARFB can be remarkably enhanced by optimizing the supporting electrolyte and separator. The battery with 2,1,3-benzothiadiazole (BzNSN) as anolyte, 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB) as catholyte, tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI) as supporting electrolyte, and porous Daramic 250 separator delivers an average discharge capacity of 1.7 Ah L⁻¹, voltage efficiency of 87.8%, Coulombic efficiency of 89.1%, and energy efficiency of 78.3% over 100 cycles at the current density of 40 mA cm⁻² with 0.1 M active materials. The reasons for the capacity decay over cycling in terms of electrolyte leakage, crossover, and chemical decomposition are discussed.

Keywords: Electrochemical energy storage; Non-aqueous redox flow battery; Supporting electrolyte; Separator; Stability

1. Introduction

Redox flow battery (RFB) is a promising large-scale energy storage device owing to its independent power and energy features, long cycle life, and rapid response. The aqueous RFBs based on all-vanadium and Zn/Br have been commercially demonstrated [1]. However, their further market penetration is hindered by the high cost as well as low energy density originated from the narrow electrochemical stability window of water electrolysis [2]. In contrast, the non-aqueous RFBs (NARFBs) show much wider voltage window and thus can be an alternative to achieve high energy density [3,4]. Correspondingly, numerous efforts have been devoted to the development of NARFBs in recent years focusing on improving the electrochemical performance and long-term stability [5-7].

The anode and cathode active materials are the core components, which determine the energy density and cycling life of NARFBs. Many active materials, including organometallic complexes such as ferrocene [8,9], cobalt complex [10] and vanadium complex [11], and redox-active organic materials (ROMs) such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [12,13], quinones [14,15], alkoxybenzene [16-19] and polymers [20,21] have been proposed. Among those, ROMs are attracting increasing attention because of higher solubility, flexible structure, natural abundance, and low-cost [5,22]. Because there is no bond formation and/or breakage involved and the electron transfer in the reactions proceeds in the form of charged radicals, the reaction kinetics is very fast and thus high rate constant [3,23]. The electrochemical rate constants of $0.9 \times 10^{-2} \text{ cm s}^{-1}$ for reduction of

2,1,3-benzothiadiazole (BzNSN) and $1.0 \times 10^{-2} \text{ cm s}^{-1}$ for oxidation of 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB) have been reported [17]. Such a rapid kinetics contributes to high flow cell efficiencies. The galvanostatic cell with BzNSN anolyte and DBMMB catholyte in lithium bis(trifluoromethylsulfonyl)imide (LiTFSI)/acetonitrile (MeCN) electrolyte showed fairly stable efficiencies over ~150 cycles at 40 mA cm^{-2} , with average Coulombic efficiency (CE) of 95%, voltage efficiency (VE) of 73%, energy efficiency (EE) of 69%, and materials utilization of ~80% [17]. However, the radical ions are reactive and short-lived, which poses significant challenges to the long-term cycling stability of NARFBs [3]. Although theoretical calculation revealed that the negative charges in BzNSN are distributed over their conjugated π -bond systems and thus reducing the excess negative charge in the individual atoms [23], the attack of radical anions by the solvent molecules still happens and should be mainly responsible for the capacity decay [24].

The supporting electrolyte, which serves to enhance the electrical conductivity of the electrolyte, is another important component for NARFBs. The interactions between the active materials, solvent, and supporting electrolyte have significant influences on the electrochemical performance of NARFBs [3,18,19]. The electron spin resonance (ESR) results revealed that the supporting electrolyte salts affects the chemical stability of the charged radical species. The DBMMB $\cdot^+$ shows much better stability in tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI) than in tetraethylammonium tetrafluoroborate (TEABF₄) because of the high reactivity of the

latter with DBMMB $\cdot^+$ [19]. Although LiTFSI is often used as the supporting electrolyte in NARFBs [8,17-19], the strong ion pairing of Li $^+$ ion with other radical ions seriously hampers the long-term stability of NARFBs [19,25]. In contrast, the bulky cation TEA $^+$ in TEATFSI interacts weakly with the radical anions and thus has little effect on the stability of radical anions, which makes TEATFSI a good candidate as the supporting electrolyte for NARFBs [19,25].

The properties of the separator in terms of conductivity and selectivity also affect the performance of NARFBs [3,5,26]. Both porous separators and anion (cation) exchange membranes are used, which show higher ion conductivity and better selectivity, respectively [3,5,27]. Although the selectivity of the active species is sacrificed, i.e., more serious crossover effect, the porous separators generally show lower area resistance compared to the ion-exchange membrane and thus make it possible to achieve charge/discharge cycling at high current densities [17,18,28]. Wei et al. found that the thickness and pore size of porous separator strongly affect VE and CE of NAFRBs [18,27]. VE increases with separators of smaller thickness and larger pore size due to the decreased area specific resistance whereas CE decreases due to the more serious crossover.

A 0.1% loss in capacity per cycle over 100 cycles was observed for an aqueous system with 2,6-dihydroxyanthraquinone anolyte and ferrocyanide catholyte. Lin et al. [29] proposed three possible loss mechanisms for such capacity decay in terms of chemical decomposition, electrolyte crossover through the membrane, and leakage from the pumping system. Such study will help design high performance RFBs.

However, there are rare systematic study on NARFBs although scattered investigation existed [18,19].

With the purpose to improve the performance of NARFBs, BzNSN and DBMMB are selected as the anolyte and catholyte active materials in the present work considering their outstanding performance [17]. TEATFSI and porous Daramic 250 separator were used as the supporting electrolyte and separator, respectively. The assembled cell delivered a high CE of 89.1% over 100 cycles at the current density (j) of 40 mA cm^{-2} . The loss mechanisms for cycling are proposed based on the results of an in-house designed flow cell (Fig. S1).

2. Experimental

2.1. Materials

MeCN (Sigma-Aldrich, 99.9%) was used as received. TEATFSI (Fig. S2) was synthesized with the procedure in literature [30]. The aqueous solutions of tetraethylammonium bromide (Guangfu, 99%) and lithium bis(trifluoromethanesulphonyl)imide (Meryer, 99.5%) were mixed in a molecular ratio of 1:1 and stirred for 3 h to form crystallites, followed by rinsing with deionized water and drying under vacuum at $60 \text{ }^{\circ}\text{C}$ for 48 h. BzNSN (Aladdin, 98%) was purified by flash column chromatography (silica gel, eluted with n-pentane, Fig. S3). DBMMB (Fig. S4) was synthesized according to the reported procedure [16].

2.2. Electrochemical test

Cyclic voltammetry (CV) tests were performed on a VersaSTAT 3 potentiostat/galvanostat (Princeton Applied Research, USA) at room temperature in

argon with a standard three-electrode system, with glassy carbon, platinum, and Ag/AgNO₃ (0.5 M in MeCN) as the working, counter, and reference electrodes, respectively. The electrolyte is the mixture of BzNSN and DBMMB with TEATFSI as the supporting electrolyte in MeCN. The cell performance was tested in an argon-filled glove box. The flow cells were assembled with graphite felts (Morgan, USA, 5 mm in thickness) at both anode and cathode sides with active area of 2 cm × 2 cm. The Daramic 250 separators (250 μm thick, pore size 150 nm) were cleaned by MeCN and dried under vacuum at 70 °C for 24 h before use. The PTFE gaskets (0.2 mm in thickness) were used to seal the cell assembly. The electrolytes (10 mL on each side) flowed through the felt electrodes at a flow rate of 50 mL min⁻¹ by using BT100-1L peristaltic pump (LONGER, China). The electrolyte solutions were individually purged with ultra-high pure Argon before test. Galvanostatic charge and discharge cycling was conducted on a LAND CT2001A cell test system (LAND, CHINA). The area specific resistance (ASR_{HF}) of the cell was measured by AC impedance in the frequency range of 0.1–10⁶ Hz with a perturbation amplitude of 10 mV.

2.3. Other characterization

For electrolytes analysis, the solvents in the electrolytes after cycling were first removed by natural evaporation. To remove the supporting electrolyte, the sample was diluted with n-hexane followed by centrifugation. Finally, the solvent was once again removed by natural evaporation and replaced with CDCl₃. All the samples were prepared in the argon-filled glove box. The UV-vis absorption spectra were collected

on Shimadzu UV-2450 spectrometer in a 10 mm optical path sealed quartz cell. Nuclear magnetic resonance (NMR) spectra were obtained with Varian Inova 500 MHz spectrometer. For gas chromatography-mass spectroscopy (GC-MS) analyses, liquid samples were loaded on an HP-5MS column using an Agilent Technologies Model 7890 chromatograph equipped with a Model 5977 mass detector. The typical program included a 20 min duration at 50 °C, followed by 20 °C min⁻¹ ramping to 250 °C followed by another 20 min duration.

3. Results and Discussion

CV of the ROMs was tested to determine the theoretical open circuit voltage (OCV) of the NARFBs. The CV curves of a mixed-reactant electrolyte of 10 mM BzNSN and 10 mM DBMMB in 0.5 M TEATFSI/MeCN are shown in Fig. 1a. Both redox materials exhibit well-defined redox peaks, and the half-wave redox potentials of BzNSN/BzNSN^{•-} and DBMMB^{•+}/DBMMB couples are -1.90 and 0.70 V vs. Ag/Ag⁺, respectively, delivering a theoretical OCV of 2.60 V. Compared to the case with LiTFSI as the supporting electrolyte [17], the OCV with TEATFSI is larger (2.60 vs. 2.36 V). Further analysis reveals that the increased OCV is mainly derived from the more negative reduction potential of BzNSN/BzNSN^{•-} (-1.90 vs. -1.58 V), which is probably due to the weaker ion pairing of TEA⁺ with BzNSN^{•-} compared with Li⁺ [25]. The increased OCV is beneficial to approach the cost target of \$100 per kWh according to the technoeconomic cost analysis [4].

Figure 1b shows the CV results of DBMMB and BzNSN at various scan rates (10–200 mV s⁻¹). The positions of the redox peaks remain almost constant with the

scan rates. The peak current ratios are close to unity. All those results indicate that the redox reactions of anolyte and catholyte are quasi-reversible. The peak current exhibits linear relationship with the square root of scan rate (Fig. 1c), indicating a diffusion-controlled behavior. The diffusion coefficients of DBMMB and BzNSN were calculated to be 1.45×10^{-5} and $1.95 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively, by the quasi-reversible Randles-Savcik equation [31].

Fig. 1. CV results of (a) 10 mM BzNSN and 10 mM DBMMB in 0.5 M TEATFSI/MeCN at a scan rate of 100 mV s^{-1} , (b) 5 mM DBMMB in 0.5 M TEATFSI/MeCN and 5 mM BzNSN in 0.5 M TEATFSI/MeCN at various scan rates, (c) linear relationship between peak current densities versus $(\text{scan rate})^{1/2}$.

The electrochemical performance of flow batteries assembled with 0.1 M mixed-reactant electrolyte in 1 M TEATFSI/MeCN and Daramic 250 membrane was examined with a galvanostatic charge/discharge cycling test. The mixed-reactant electrolyte was used to mitigate the crossover effect. The charge/discharge curves (Fig.

2a) at $j = 20 \text{ mA cm}^{-2}$ show a discharge voltage plateau of 2.48 V, very close to the theoretical OCV of 2.60 V (Fig. 1a). The battery cycles within the cut-off voltage window of 2.10-2.85 V over 100 cycles. An average discharge capacity of 1.8 Ah L^{-1} is achieved. This cell delivers fairly stable efficiencies with average VE of 94.0%, CE of 85.7%, EE of 80.6%, and material utilization of $\sim 80\%$ (Fig. 2b). When j increases to 40 mA cm^{-2} , the cell still demonstrates high efficiencies, with average VE of 87.8%, CE of 89.1%, and EE of 78.3% over 100 cycles. Meanwhile, the cell shows an average discharge capacity of 1.7 Ah L^{-1} . Such performance is remarkably better than most reported NARFBs (Table 1).

Fig. 2. Electrochemical performance of the cell with 0.1 M BzNSN/DBMMB in 1 M TEATFSI/MeCN and Daramic 250 membrane. (a) Voltage profiles at 20 mA cm^{-2} , efficiency and capacity at (b) 20 mA cm^{-2} and (c) 40 mA cm^{-2} , (d) EIS of the cell before and after 100 cycles at 40 mA cm^{-2} .

Table 1. Comparison of the electrochemical performance of NARFBs.

Active materials	Concentration (mol L ⁻¹)	Theo. OCV (V)	<i>J</i> (mA cm ⁻²)	CE (%)	VE (%)	EE (%)	Cycles	Utilization (%)	Ref.
DBMMB/BzNSN	0.1	2.6	20	85.7	94.0	80.6	100	~80	This work
DBMMB/BzNSN	0.1	2.6	40	89.1	87.8	78.3	100	~75	This work
DBMMB/BzNSN	0.1	2.36	40	95	73	69	150	~80	[17]
DBMMB/MePh	0.3	2.3	35	90	77	69	50	77	[18]
DBMMB/F-FL	0.1	2.37	10	95	85	81	50	–	[19]
PTIO	0.1	1.73	20	~96	75	~72	35	–	[28]
TEMPO/Li	0.1	3.5	5	99	87	86	100	–	[12]
MVTFSI/FcNTFSI	0.1	1.05	30	~95	~77	73	100	–	[9]
[V(mnt) ₃] ²⁻	0.02	1.1	16	~90	–	–	16	–	[11]
Fc1N112-TFSI/Li	0.1	3.6	3.5	99	88	87	100	–	[8]
Polymeric H ₂ TPP	–	2.83	1	>99	~41	~41	200	92	[20]
Polymeric TEMPO/Zn	0.01	1.8	1.4	>99	~72	~72	500	–	[21]

Note: MePh: N-methylphthalimide; F-FL: 2-fluoro-9-fluorenone; PTIO: 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; MVTFISI: methyl viologen bis(trifluoromethanesulfonyl)imide; FcNTFSI: (ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide; Fc1N112-TFSI: ferrocenylmethyl dimethyl ethyl ammonium bis(trifluoromethanesulfonyl)imide; H₂TPP: 5,10,15,20-tetraphenylporphyrin.

CE is slightly higher for cycling at 40 mA cm⁻² compared with that at 20 mA cm⁻² (89.1% vs. 85.7%), which indicates that the crossover effect becomes weaker at

higher current densities due to the shorter cycle duration [8]. It also suggests that although a mixed-reactant electrolyte was employed, the crossover effect cannot be completely eliminated, which should be responsible for the capacity decay as discussed later. Nevertheless, the crossover effect weakens with cycling because the duration for charge/discharge cycle shortens [8] rooted from the capacity degradation. For example, it is 18 and 11 min for the 1st and 100th cycles, respectively, at the current density of 40 mA cm⁻². Accordingly, the gap between charge and discharge capacity reduces with cycling, i.e., CE increases (Fig. 2c). In contrast, VE is determined by the ohmic resistance and electrochemical polarization resistance which generally increase with cycling [32], leading to declined VE. Correspondingly, although VE is slightly higher than CE at the very beginning (89.2% and 82.4%, respectively, at the 1st cycle), it is lower than CE after 50 cycles (Fig. 2c).

The improved performance of the present NARFB can be attributed to two factors. The first one is the separator. The Daramic 250 porous separator has a larger pore size of 150 nm [17] and thinner thickness of 250 μ m [33], which is beneficial for the ion transport. As shown in Fig. 2d, the intercept of EIS with the real axis at the highest frequency (ASR_{HF}) [29], which is dominated by the ohmic resistance of separator, is $\sim 4.1 \Omega \text{ cm}^2$. Such a low ASR_{HF} renders high efficiency even at high j of 40 mA cm⁻² without obvious compromise in efficiencies and output. The second one is the supporting electrolyte. As aforementioned, the radical cation DBMMB^{•+} is rather stable in the TEATFSI electrolyte [18,19,25]. However, the radical anion BzNSN^{•-} is sensitive to the supporting electrolyte [25,34]. Compared with Li⁺, the weaker ion

pairing of TEA^+ in TEATFSI with $\text{BzNSN}^{\cdot-}$ has little impact on the stability of radical anions, leading to improved cycling stability, as shown in Scheme 1. The results obviously show that the performance of NARFBs can be enhanced by optimizing the key components.

Scheme 1. Interaction of radical ions of the BzNSN active material with the TEATFSI and LiTFSI supporting electrolytes.

Cycling stability is always a great concern for NARFBs [3,5-7]. As shown in Fig. 2b and c, the discharge capacity declines with cycling. It decreases from 2.0 mAh L^{-1} at 1st cycle to 1.4 mAh L^{-1} at 100th cycle at $j = 40 \text{ mA cm}^{-2}$, similar with that reported [17]. The EIS results (Fig. 2d) show that ASR_{HF} , which mainly comes from the contribution of the separator, maintains constant after 100 cycles. It suggests that the separator is stable, at least over the duration of 100 cycles ($\sim 22 \text{ h}$, 40 mA cm^{-2} ; $\sim 49 \text{ h}$, 20 mA cm^{-2}). The graphite felt, which is widely used in the RFBs [1,12,17,35,36], is employed as the electrode. It provides the location for, but does not take part in, the electrochemical reactions. Castañeda et al. reported that graphite felt exhibits good stability as the electrode of flow battery [37]. Similar conclusion is probably applicable to the present work although further examination is needed.

To further explore the probable reasons, the cell was tested at $j = 20 \text{ mA cm}^{-2}$ with 50 mM BzNSN/DBMMB in 0.5 M TEATFSI/MeCN. This concentration was used because the intrinsic lifetime of the radical ions is independent of the concentration in the range of 20–100 mM [38]. After 100 cycles, the volume level of electrolyte in the reservoir decreases obviously. Similar phenomenon has been reported [29]. Small amount of solid white precipitates is found in the junction between the gaskets (Figs. 3a and b, and S5). After disassembling the cell, colored liquid is observed on the gaskets and graphite plate (Fig. 3c and d). Furthermore, the membrane becomes darkened especially at the edge of the active areas (Fig. 3e and f). The mass of the

Fig. 3. Leakage of electrolyte into the junction between the gaskets at the bottom of the cell (a) before and (b) after cycling. Leakage of the electrolyte into the gaskets (c) before and (d) after cycling. The images of the Daramic 250 membrane (e) before and (f) after cycling.

membrane increases by ~35%, which indicates that the membrane may be filled with active materials and supporting electrolyte. All those results obviously show the leakage of the electrolyte during cycling, leading to decreased capacity. It indicates that the cell design must be optimized in order to further enhance the performance.

The cycled electrolyte (50 mM solutions of both ROMs) was tested with ^1H NMR after removing the supporting electrolyte. The results reveal that it is composed of BzNSN and DBMMB (Fig. S6). However, the integral area ratio of the peak of BzNSN and DBMMB decreases to 0.3:1 from 1:1 for the fresh electrolyte, indicating the loss of BzNSN anolyte, which is deposited on the junction, gasket and membrane (Figs. 3 and S5). Such deposition is probably due to the lower solubility of BzNSN $\cdot^-$ radical ions [6,7]. UV-Vis was employed to examine the cycled electrolyte after cycling. Compared with the fresh anolyte and catholyte, both active materials change only slightly after the 1st cycle. However, new absorption peaks at ~260 nm appear after 50th and 100th cycles (Fig. 4a and c) and the peak intensity increases with cycling, indicating more new compounds were formed with cycling. The electrolyte, after removing the supporting electrolyte, was then subjected to GC-MS analysis. As shown in Fig. 4b and d, besides the main BzNSN anolyte and DBMMB catholyte, a few by-products are generated. According to the mass spectra (Fig. S7), they are postulated to be compounds labeled with P1, P2 and P3 (inset in Fig. 4b and d), respectively. The exact mechanism for the side reactions remains unclear yet. Nevertheless, the decomposition of electrolyte, mainly the cathode active material

DBMMB during the charge/discharge cycling, reduces the content of active materials and thus leading to capacity degradation.

Similar with the aqueous RFBs [29], the present results confirm that crossover, electrolyte leakage, and chemical decomposition of the active materials also exist in the non-aqueous RFBs. Such mechanistic study is believed to help design high performance non-aqueous RFBs. Improving the performance of non-aqueous RFBs based on the results here is in progress in our group.

Fig. 4. UV-Vis absorption spectra of initial and after 50th and 100th cycled a) anolyte and c) catholyte, and corresponding GC spectra of 100th cycled b) anolyte and d) catholyte. Molecular structures of postulated by-products labeled with P1-P3 are inset.

4. Conclusions

The electrochemical performance of NARFB with BzNSN anolyte and DBMMB catholyte can be improved by employing appropriate supporting electrolyte and

separator. The TEATFSI supporting electrolyte and commercial Daramic 250 porous separator show high compatibility with the active materials and low area specific resistance, respectively, which contribute to the enhanced performance of the resultant NARFB, with an average discharge capacity of 1.7 Ah L⁻¹, VE of 87.8%, CE of 89.1%, and EE of 78.3% over 100 cycles at the current density of 40 mA cm⁻² with 0.1 M active materials. The electrolyte leakage, crossover, and chemical decomposition of the active materials should be responsible for the capacity decay during cycling. Further optimization of the cell design and key components of the battery is required to improve the performance of NARFB.

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