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Coupling tetraalkylammonium and ethylene glycol ether side chain to enable highly soluble anthraquinone-based ionic species for nonaqueous redox flow battery

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ABSTRACT: Non-aqueous redox flow batteries (NARFBs) possess promise for the large-scale energy storage with high energy density. Developing advanced active materials is of paramount importance to achieve high stability and energy density. Herein, we adopt the molecular engineering strategy by coupling tetraalkylammonium and ethylene glycol ether side chain to design anthraquinone-based ionic active species. By adjusting the length of the ethylene glycol ether chain, an ionic active species 2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-N-(2-(2-methoxyethoxy)ethyl)-(N,N-dimethylethan-1-aminium)-bis(trifluoromethyl-sulfonyl)imide (AQEG2TFSI) with high solubility and stability is obtained. Paired with FcNTFSI cathode, the full battery provides an impressive cycling performance with discharge capacity retention of 99.96% and 99.74% per cycle over 100 cycles with 0.1 M and 0.4 M AQEG2TFSI, respectively.

1. INTRODUCTION

With the increase in the share of renewable energy sources in electricity generation, the development of advanced and reliable energy storage systems to maintain the stability of the grid has become urgent.^{1,2} Among the various energy storage technologies, redox flow battery (RFB) possesses the unique characteristics of the space-separated electrolyte and electrode, which decouples power and energy units,³ allowing it to be flexibly adjusted to meet different power and energy storage requirements. Aqueous RFB (ARFB) has been developed by leaps and bounds;^{4, 5} however, limited by the electrochemical window of water, ARFB generally has low voltage and therefore low energy density. In contrast, the non-aqueous RFB (NARFB) using organic solvents can provide a wider voltage range,⁶ which provides the possibility to realize a high energy density energy storage system.

Recent research on NARFB has mainly focused on the active materials. Organic materials have diverse structures and adjustable properties, which can be tuned to meet the requirements of NARFB system via function-oriented organic synthesis. Recently, the active species based on anthraquinone (AQ),⁷⁻⁹ methyl viologen (MV),¹⁰⁻¹³ 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO),¹⁴⁻¹⁷ ferrocene (Fc),¹⁸⁻²⁰ and phenothiazine²¹⁻²³ have been reported for NARFB. Among those materials, the study on the AQ-based compounds is extremely limited compared to their aqueous counterparts. The low solubility in organic solvents and the instability of free radicals formed in aprotic solvents during charge/discharge processes have seriously plagued their application in NARFB. Although the oligoether, alkyl or ionic chains have been introduced into the AQ structures,^{7, 8, 24} the resultant compounds still show limited solubility and/or poor charge/discharge cycle performance.

Herein, we show the feasibility of molecular engineering by coupling tetraalkylammonium and ethylene glycol ether side chain to significantly increase the solubility and stability of the AQ-based compounds. Four AQ derivatives, 2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-(N,N,N-trimethylethan-1-aminium)-bis(trifluoromethylsulfonyl)imide (AQTFSI), 2-((9,10-dioxo-9,10-dihydroanthracen-1 -yl)amino)-N-(2-methoxyethyl)-(N,N-dimethylethan-1-aminium)-bis(trifluorome-thylsulfonyl)imide (AQEG1TFSI), 2-((9,10-dioxo-9,10-dihydroanthracen-1-



Scheme 1. (a) Synthetic routes to AQ based ionic species; (b) redox reactions of the anode and cathode active species.

-N-(2-(2-methoxy)ethyl)-(N,N-dimethylevl)amino) than-1-aminium)-bis(trifluoromethylsulfonyl)imide (AQEG2TFSI) and 2-((9,10-dioxo-9,10-dihydroanthracen-1yl)amino)-N-(2-(2-(2-methoxy)ethoxy)ethoxy)ethyl)-(N,N-dimethylethan-1-aminium)-bis(trifluoromethylsulfonyl)imide (AQEG3TFSI) were synthesized (Scheme 1, Figures S1-S4). AQTFSI modified with conventional tetraalkylammonium side chain shows a medium solubility of 0.24 M in acetonitrile (MeCN) (Figure S5). For derivatives modified with tetraalkylammonium and ethylene glycol ether coupled side chains, by adjusting the length of the oligoether chain from a single to two and three ethylene glycol (EG) units, the active species AQEG2TFSI and AQEG3TFSI of viscous oily at room temperature and miscible with MeCN, are obtained. The rationales behind are as follows: The flexible oligoether chain is tethered to the ionic side chain to destroy the crystal packing and thus increase the solubility; the matched counter anion bis(trifluoromethanesulfonyl)imide (TFSI) ensures its high solubility in the electrolyte. The electron-withdrawing characteristics of the quaternary ammonium cation side chain and its Coulomb repulsion maintain the stability of AQ core in the redox process. Despite the introduction of long side chains, thanks to the ionic form of this species, it possesses fast mass and charge transfer kinetics compared to neutral AQ derivatives. Employing AQEG2TFSI as anode and ionic ferrocene derivate (ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide (FcNTFSI) as cathode, the resultant NARFB shows stable cycling performance with discharge capacity retention of 99.96% and 99.74 % per cycle over 100 cycles with 0.1 and 0.4 M active species, respectively.

2. EXPERIMENTAL SECTION

2.1. Materials

1-Chloroanthraquinone (98%), Lithium bis(tetrafluoromethylsulfonyl)amide (LiTFSI, 99.5%) and Tetraethylammonium bromide (TEAB, 99%) were purchased form Meryer, China. N,N-Dimethylethylenediamine (99%), Methyl iodide (99%), and (Dimethylaminomethyl) ferrocene (97%) were purchased form Adamas, China. Ethyl acetate (99%) and Dichloromethane (99%) were purchased from Jiangtian, China. Acetonitrile (MeCN, 99.9%) was purchased form Aladdin, China. All the materials were used as received. 1-iodo-2-methoxyethane, 1-iodo-2-(2-methoxy)ethoxy)ethane and 1-iodo-2-(2-(2-methoxy-ethoxy)ethoxy)ethane were synthesized according to the literature.²⁵ Tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI) was synthesized through simple ion-exchange between LiTFSI and TEAB. Cathode species (ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide (FcNTFSI) was prepared according to the literature.²⁶

2.2. Synthetic procedures

General procedure for the preparation of AO-based ionic species. Compound 2 (1-((2-(dimethylamino)ethyl)amino)anthracene-9,10-dione) was obtained through literature procedures.²⁷ A mixture of compound 2 (1.0 eq) and corresponding iodides (1.5 eq) in MeCN were stirred at 60 °C overnight. After the completion of the reaction, a large amount of ethyl acetate was added to the reaction solution, and the product (compound 3) was precipitated. The precipitate was isolated by filtration and washed with ethvl acetate, followed by vacuum drving for 12 h. The resulting products were directly subjected to the next ion exchange reaction. A mixture of compound 3 (1.0 eq) and LiTFSI (1.5 eq) in a mixed solution of CH₂Cl₂ /DI-H₂O (1:3) was stirred at room temperature for 6 h. After the reaction, the organic layer was collected and washed with DI-H2O for several times, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the products were obtained. The product was determined via nuclear magnetic resonance (NMR) spectra (1H) on a VARIAN INOVA 400 MHz NMR spectrometer with DMSO-d₆.

2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-(N,N,Ntrimethylethan-1-aminium)-bis(trifluoromethylsulfonyl)imide (AQTFSI). General procedure was followed starting from compound 2 (15 mmol, 4.41 g) and methyl iodide (22 mmol, 3.19 g) in MeCN (30 mL). The product compound 3a was further ion-exchanged with LiTFSI. The final product AQTFSI is orange-red solid. Yield: 5.3 g, (60%). 1H NMR (400 MHz, DMSO-d6) δ 9.72 (t, J = 6.1 Hz, 1H), 8.20 – 8.14 (m, 2H), 7.90 (ddd, J = 9.4, 5.0, 1.8 Hz, 2H), 7.76 – 7.68 (m, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 3.94 (q, J = 6.5 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 3.20 (s, 9H).

2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-N-(2methoxyethyl)-(N,N-dimethylethan-1-aminium)-bis(trifluoromethylsulfonyl)imide (AQEG1TFSI). General procedure was followed starting from compound 2 (15 mmol, 4.41 g) and 1iodo-2-methoxyethane (22 mmol, 4.18 g) in MeCN (30 mL). The product compound 3b was further ion-exchanged with LiTFSI. The final product AQEG1TFSI is red solid. Yield: 5.8 g, (61%). 1H NMR (400 MHz, DMSO-d6) δ 9.68 (t, J = 6.1 Hz, 1H), 8.16 (dt, J = 13.0, 1.9 Hz, 2H), 7.90 – 7.84 (m, 2H), 7.71 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 7.3 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 3.92 (q, J = 6.7 Hz, 2H), 3.84 – 3.77 (m, 2H), 3.72 – 3.62 (m, 4H), 3.33 (s, 3H), 3.21 (s, 6H).

2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-N-(2-(2-methoxyethoxy)ethyl)-(N,N-dimethylethan-1-aminium)bis(trifluoromethylsulfonyl)imide (AQEG2TFSI). General procedure was followed starting from compound 2 (15 mmol, 4.41 g) and 1-iodo-2-(2-methoxyethoxy)ethane (22 mmol, 5.17 g) in MeCN (30 mL). The product compound 3c was further ion-exchanged with LiTFSI. The final product AQEG2TFSI is dark red viscous oil. Yield: 6.9 g, (68 %). ¹H NMR (400 MHz, DMSO-d₆) δ 9.70 (t, J = 6.1 Hz, 1H), 8.19 (dd, J = 7.7, 1.4 Hz, 1H), 8.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.95 – 7.87 (m, 1H), 7.87 – 7.80 (m, 1H), 7.71 (dd, J = 8.6, 7.4 Hz, 1H), 7.51 (d, J = 7.3 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 3.93 (q, J = 5.7, 4.0 Hz, 4H), 3.76 – 3.65 (m, 4H), 3.65 – 3.60 (m, 2H), 3.53 – 3.46 (m, 2H), 3.26 (s, 8H), 3.21 (s, 1H).

2-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-N-(2-(2-(2-methoxy)ethoxy)ethyl)-(N,N-dimethylethan-1aminium)-bis(trifluoromethylsulfonyl)imide (AQEG3TFSI). General procedure was followed starting from compound 2 (15 mmol, 4.41 g) and 1-iodo-2-(2-(2-methoxyethoxy)ethoxy)ethane (22 mmol, 6.16 g) in MeCN (30 mL). The product compound 3d was further ion-exchanged with LiTFSI. The final product AQEG3TFSI is dark red viscous oil. Yield: 4.5 g, (42 %). ¹H NMR (500 MHz, DMSO-d₆) δ 9.72 (t, J = 6.1 Hz, 1H), 8.21 (dd, J = 7.7, 1.3 Hz, 1H), 8.15 (dd, J = 7.6, 1.4 Hz, 1H), 7.93 (td, J = 7.5, 1.4 Hz, 1H), 7.87 (td, J = 7.5, 1.4 Hz, 1H), 7.73 (dd, J = 8.6, 7.4 Hz, 1H), 7.53 (dd, J = 7.4, 1.0 Hz, 1H), 7.37 (dd, J = 8.7, 1.0 Hz, 1H), 3.93 (dt, J = 18.1, 5.6 Hz, 4H), 3.70 (q, J = 7.3, 5.6 Hz, 4H), 3.62 (dd, J = 6.0, 3.1 Hz, 2H), 3.55 (dd, J = 5.8, 3.2 Hz, 2H), 3.52 – 3.48 (m, 2H), 3.41 – 3.37 (m, 2H), 3.21 (s, 6H).

2.3. Solubility measurements

A 0.01 M solution of the active species in MeCN was prepared and diluted to different concentrations to obtain standard solutions, which was tested by UV-Vis absorption spectra (Perkin Elmer, Lambda 750, USA). Then a standard curve was obtained by recording the absorbance of the peak wavelength of each concentration at 480 nm. The saturated solution was prepared and left standing overnight. After diluting the supernatant, UV-Vis test was performed, and the solubility was extrapolated according to the calculated standard curve.

2.4. Electrochemical characterizations

All electrochemical tests were performed at room temperature. The electrolyte samples were deoxygenated by bubbling with Argon (99.999%, Air Liquide, China) before the electrochemical test.

The CV tests were carried out using a three-electrode cell with 1.0 mM active species in 0.1 M TEATFSI/MeCN on a VersaSTAT3 electrochemical workstation (Princeton Applied Research, USA). A glassy carbon (3 mm in diameter, Ai-dahengsheng, China), graphite plate, and Ag/Ag^+ (0.5 M AgNO₃/MeCN) were employed as the working, counter, and reference electrodes, respectively. The CV tests of the electrolyte after charge/discharge cycling was conducted in argon-filled glove box (Mikrouna, China). To obtain the diffusion coefficient *D*, CV curves at different sweep speeds (0.04-0.36 V s⁻¹) were recorded and then calculated according to modified Randles-Sevcik equation:²⁸

$$\mathbf{i}_{p} = (2.69 \times 10^{5}) A C D^{1/2} v^{1/2} \mathbf{K}(\Lambda, \alpha)$$
(1)

where i_p is the peak current density, A the electrode surface area (0.07 cm²), C the concentration of the active species (1.0 mM), v the scan rate, and K(Λ, α) is the parameter associated with electrochemical irreversibility (K(Λ, α) =0.8 when the transfer coefficient α delivered as 0.5).

The LSV tests were performed using a three-electrode cell on a CHI 660D Electrochemical Workstation (Shanghai Chenhua Instruments Co., Ltd., China). A glassy carbon disk electrode (5 mm Teflon encased), platinum net, and Ag/Ag⁺ were employed as the working, counter, and reference electrodes, respectively. The working electrode was rotated from 400 to 2500 rpm using a modulated speed rotator (AFMSRCE 061906, PINE), and the LSV curves were recorded from -0.8 to -1.6 V at a scan rate of 10 mV s⁻¹. The diffusion coefficient can also be obtained from Levich equation:

$$i_l = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C$$
(2)

where *n* is the number of electrons involved in an electrode reaction (1), *F* the Faradaic constant (96485 C mol⁻¹), A the electrode area (0.2 cm²), *D* the diffusion coefficient, ω the rotation speed, ν the kinematic viscosity (5.07 ×10⁻³ cm² s⁻¹ for 0.1 M TEATFSI in MeCN, measured with Ubbelohde viscometer), and *C* is the concentration of the active species (1.0 mM).

To obtain the rate constant k^0 , the kinetic-controlled current i_k was first calculated according to Koutecký-Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l}$$
(3)

where i_l is the diffusion-controlled limiting current and *i* the apparent current. Then, according to the Tafel equation, the linearly fitted plots of $\log i_k$ versus η can be obtained to calculate the exchange current i^0 :

$$\eta = -\frac{2.3RT}{anF}\log i^0 + \frac{2.3RT}{anF}\log i_k \tag{4}$$

Finally, k^0 can be calculated according to the following equation:

$$C^{0} = nFAk^{0}C \tag{5}$$

Electrochemical impedance spectrum was recorded on the VersaSTAT3 electrochemical workstation with the frequency range of 10^{5} -1 Hz and a perturbation amplitude of 10 mV. The area specific resistance (ASR_{HF}) was recorded by the intercept with the X-axis at the high frequency in the Nyquist plot. The polarization curves were recorded by LSV at 100 mV s⁻¹ after the battery was charged to certain state of charge (SOC).

2.5 Flow battery tests

The battery tests with a home-designed flow cell engraved with a serpentine flow field were conducted by LAND battery test instrument (Wuhan LAND Electronic Co. Ltd., China) in argon-filled glove box. Two pieces of graphite felts (2 mm) were used as the electrodes with a compression ratio of 20% and placed on both sides of the membrane. The electrolytes (5 mL on each side, deoxygenated by bubbling with Argon for 10 min before putting in the glove box) were pumped by two peristaltic pumps (BT100-1L, Longer Precision Pump Co., Ltd., China) at a flow rate of 30 mL min⁻¹. For symmetric flow battery test, the charged species AQEG2TFSI- was first prepared through bulk electrolysis, in which the reticulated vitreous carbon (RVC) was used as working and counter electrode, and the Ag/Ag⁺ were employed as the reference electrode. Then the 1:1 mixed AQEG2TFSI and AQEG2TFSI was employed as the electrolyte. For full flow battery test, the same anolyte and catholyte with mixed-reactant electrolyte was utilized, in which the concentration of the cathode species, FcNTFSI, was 1.2 times that of the anode species to ensure that the anode side acted as a capacity limiting species.

2.6. Computation methods

The density functional theory (DFT) calculations were performed with the Gaussian 09 program package.²⁹ All the calculation were carried out at the Lee–Yang–Parr exchange correla-

3. RESULTS AND DISCUSSION

To improve the solubility of AQ-based species in organic solvent, different cationic side chains were designed, because their preferential solvation can enhance the interaction between the solute and the solvent and thus increase the solubility.³⁰ Although the solubility of AQ-derivative AQTFSI increases compared with the pristine AQ $(0.24 \text{ M vs.} < 5 \text{ mM})^7$ by modifying with conventional tetraalkylammonium side chain, it is still rather low for its application in NARFB. Considering that the flexible oligoether side chain can increase the polarity and thus possible to improve the solubility in polar solvents, the oligoether unit is coupled to the cationic side chain. Surprisingly, when a single EG unit is introduced (AQEG1TFSI), the solubility decreases slightly (0.19 M). The optimized geometric structures of AQTFSI and AQEG1TFSI were calculated by density functional theory (DFT) (Figure 1). For AQTFSI, the amino proton forms a plane six-membered ring with N, O and three C in the AQ structure, and the distance between it and the carbonyl oxygen is 1.75 Å, forming a typical intramolecular hydrogen bonding (N-H···O=C), which can induce the polarization of its neighboring atoms.³¹ Accordingly, the charge tends to distribute asymmetrically (Table S1), leading to increased solubility.³² In sharp contrast, the amino group of AQEG1TFSI was rotated, which cannot form intramolecular hydrogen bonding. In addition, the short-chain ether group has limited solubil-



Figure 1. (a) Molecular structure, (b) calculated geometry-optimized structure by DFT and (c) photos of AQTFSI, AQEG1TFSI, AQEG2TFSI and AQEG3TFSI. The polarization caused by hydrogen bonding is marked in the AQTFSI molecule. The rotated amine protons are yellow-circled.

tion function with Grimme dispersion correction (B3LYP-D3) level considering implicit solvation model based on solute electron density (SMD). The Pople basis set 6-31G(d) and 6-311G(d, p) was used for geometry optimizations and single point energy calculation, respectively.

ization ability, so its solubility may be slightly lower than that of AQTFSI. Considering the significantly promoted effect of prolonging ether chain on solubility,²² two EG units were further introduced to exert the advantages of the flexible long oligoether chain. Interestingly, the resultant AQEG2TFSI is viscous oily at room temperature and miscible with MeCN (Figure 1c), which is due to the increased flexibility of the extended oligoether chain, further reducing the ion packing and



Figure 2. (a) CV curves of 5 mM AQTFSI, AQEG1TFSI, AQEG2TFSI, and AQEG3TFSI in 0.1 M TEATFSI/MeCN, respectively. (b) The frontier orbitals of AQ and its derivatives in MeCN solvent calculated by DFT method.

significantly decreases the melting temperature.³³ An ionic species with three EG units (AQEG3TFSI) were also synthesized, which shows the same physical state as AQEG2TFSI. It should be noted that no intramolecular hydrogen bonding was observed for the amino protons of AQEG2TFSI and AQEG3TFSI. The significant influence of the long oligoether chain compensates for the weak solubility loss caused by the rotated amino group.

The electrochemical properties of four AQ-based species were investigated first by CV. In the electrolyte system based on MeCN/TEATFSI, all the materials exhibit two reversible redox couples (Figure 2a), corresponding to the conversion of radical anions and dianions. For the first redox event, the redox potential first decreases and then increases as the length of the coupled side chain increases (-1.26, -1.28, -1.30 and -1.29 V for AQTFSI, AQEG1TFSI, AQEG2TFSI and AQEG3TFSI, respectively). For structurally related substances, the reduction potential is linearly related to the lowest unoccupied molecular orbitals (LUMO) energy.³⁴ A smaller LUMO value indicates a lower electron affinity, making the redox potential more negative. As the length of the coupled side chain increases, the LUMO energy first decreases from -2.954 to -2.924, further to -2.922 eV, and then increases to -2.924 eV (Figure 2b), consistent with their redox potential. It also indicates that different coupling side chains have different effects on the electronic

structure. In addition, the highest occupied molecular orbitals (HOMO) and energy gap (ΔE) were also calculated. All four AQ derivatives show a smaller ΔE (2.96, 3.15, 3.16 and 3.15 eV) compared to the pristine AQ molecule (4.29 eV), indicating that the modification of cation side chain increases the intrinsic electronic conductivity.

Before further analysis, the cycling stability of the 2e⁻ transfer reaction was first evaluated. Compared with the single electron transfer process, the cycling stability of 2e⁻ event is more unstable at the CV time-scale (Figure S6). Furthermore, preliminary charge/discharge experiment also shows that the battery capacity decays rapidly during cycling with the 2e⁻ process. The CV curve of the cycled anolyte shows a significant degradation of the second redox couple (Figure S7). In addition, the increase in concentration exacerbates the capacity fading (Figure S8). Considering the single electron transfer process exhibit stable cycling performance, here we focus on the first redox process.

The diffusion coefficient (D) and kinetic rate constant (k^0) were calculated through CV and LSV. The CV tests were conducted at different scan rates from 0.04 to 0.36 V s⁻¹ (Figure S9). The diffusion coefficients of AOTFSI, AOEG1TFSI, AOEG2TFSI and AOEG3TFSI were calculated to be 2.35~2.47×10^5, 2.00~2.04×10^5 , 1.33~1.50×10^5 and 1.43-1.52×10⁻⁵ cm² s⁻¹ according to the modified Randles-Sevcik equation,²⁸ respectively. The LSV tests were carried out at the rotation rate from 400 to 2500 rpm (Figures S10-S13). The diffusion coefficients of four AO derivatives calculated from Levich equation were 1.56×10⁻⁵, 1.49×10⁻⁵, 1.20×10⁻⁵ and 9.45×10^{-6} cm² s⁻¹, respectively. The diffusion coefficients obtained from the two methods are slightly different, but generally decrease with the increase of the side chain length. The kinetic rate constants of the corresponding four materials are 2.47×10⁻ ², 2.36×10⁻², 2.59×10⁻² and 2.10×10⁻² cm s⁻¹, respectively. It should be noted that although AQEG1TFSI, AQEG2TFSI and AQEG3TFSI have longer side chain due to the attached EG group, the D and k^0 (i.e., mass- and charge-transfer kinetics) values are still high, which is comparable to or greater than that of state-of-the-art active materials,^{22, 35-39} more importantly, superior to those of neutral materials modified with long oligoether chain.9, 40-42 It is mainly attributed to their ionic structure, where the redox active sites mounted on the ionic groups are



Figure 4. (a) CV curve of mixed AQEG2FSI/ FcNTFSI in TEATFSI/MeCN. (b) Cycling performance of the battery with 0.1 M AQEG2FSI/0.12 M FcNTFSI in 0.5 M TEATFSI/MeCN over 100 cycles at 25 mA cm⁻². (c) Galvanostatic charge/discharge curves. (d) CV curves of the electrolyte before and after battery tests. (e) ¹H NMR spectra of the electrolyte before and after cycling tests (the peak around 5.7 ppm is the residual solvent CH₂Cl₂ in the product).

electro-adsorbed on the electrode surface, leading to facile Faraday reaction.⁴³

Although both AQEG2TFSI and AQEG3TFSI possess remarkable solubility (miscible with MeCN), AQEG2TFSI was chosen for further evaluation considering its lower molecular weight and higher D and k^0 values. The symmetric flow battery test at the current density (*j*) of 5 mA cm⁻² was utilized to examine the stability during cycling (Figure 3). The 1:1 mixed 0.02 M AQEG2TFSI and 0.02 M AQEG2TFSI⁻ in 0.2 M TEATFSI/MeCN was utilized as the electrolyte, and the porous membrane Daramic-250 as the separator. The cell exhibits an excellent galvanostatic charge/discharge performance with overall capacity retention of 96% after 400 cycles, indicating the remarkable electrochemical stability of AQEG2TFSI. The average Coulombic efficiency (CE) is close to 100%. Some CE values that higher than 100% may be caused by the uneven mass transfer of the active materials¹⁴. The ¹H NMR spectra of the

The cycling performance of the AQEG2FSI in full flow battery was further evaluated. With FcNTFSI cathode and TEATFSI/MeCN solution, a cell with open circuit voltage of 1.57 V is obtained (Figure 4a). Since the membranes have a significant impact on the battery performance, different membranes were employed to screen the appropriate membrane for the present active materials. An anion exchange membrane AFP-375-PP was chosen considering the electrostatic repulsion between positively charged membrane and redox active moieties (AQEG2⁺ and FcN⁺). An asymmetric cell with 5 ml of 0.1

periments. Bulk electrolysis experiments were per-formed to prepare 50% SOC electrolytes followed by charge/discharge cycles. NMR measurements were per-formed after 200 cycles. According to the NMR spectra (Figure S15), the cycled electrolyte with H₂O shows similar impurity peaks with that without H₂O except that the signal of impurity peaks becomes stronger, which indicates that H₂O promotes only the original side reactions, no other parasitic reaction happens. The peaks of by-products (7.07, 7.05 and 5.37 ppm) disappear after the addition of D₂O. Accordingly, the impurity peaks are probably resulted from the active proton or protonated moiety in the residual H₂O or the MeCN solvent⁴⁴. In fact, similar studies have demonstrated that compounds containing carbonyl moieties are easily protonated.44, 45 For anthraquinone derivatives, the carbonyl group is converted to a negatively charged phenolate oxygen during charging process, which is highly reactive and thus more prone to be protonated⁸.

M AQEG2FSI/0.5 M TEATFSI/MeCN as anolyte and 10 ml of 0.1 M FcNTFSI/0.5 M TEATFSI/MeCN as catholyte was assembled. The charge/discharge test shows a rapid capacity decay during 30 cycles (Figure S16a, b), and VE and EE decrease, indicating increased polarization. The membrane surface was severely altered after cycling (Figure S17a), suggesting sever undesired interaction between electrolyte and the membrane, implying that FAP-375-PP membrane is not compatible with the current electrolyte system.

Alternatively, the porous membranes, Celgard 4560, was employed for the battery test. To avoid the crossover, a symmetric cell with mixed-electrolyte of 0.1 M AQEG2FSI/0.12 M FcNTFSI in 0.5 M TEATFSI/MeCN as both anolyte and catholyte was constructed. The battery with Celgard 4560 membrane shows very poor cycling performance, the capacity was almost halves by the 6th cycle (Figure S16c, d), and VE and EE decrease sharply during 10 cycles, which may be due to the blockage or collapse of the pores caused by the interaction between the electrolyte and the membrane. In addition, the membrane surface also changed significantly (Figure S17b). Therefore, the Celgard 4560 membrane is also not suitable for this system.

The Daramic porous membranes are widely used in NARFBs and are relatively stable in organic solvents.⁴⁶ Impressively, the battery with Daramic-250 shows overall discharge capacity retention ~96% after 100 cycles at *j* of 25 mA cm⁻², corresponding to capacity retention of 99.96% per cycle. The average CE, VE and EE are 92%, 87% and 80%, respectively (Figure 4b). The galvanostatic charge/discharge curves of the battery maintain basically constant during 100 cycles (Figure 4c), confirming the outstanding stability of the active species. In addition to the two aromatic rings in the AQ core to promote the delocalization of negative charges and thus maintain stability, the cationic side chain attached to the AQ structure provides Coulomb repulsion and steric hindrance, further protecting the active center from being attacked by other compounds. The cycling tests of the



Figure 6. High-concentration battery performance with 0.4 M AQEG2FSI/ 0.48 M FcNTFSI in 1.0 M TEATFSI/MeCN over 100 cycles at 40 mA cm⁻². (a) Efficiency and charge/discharge capacities versus cycle number. (b) Galvanostatic charge/discharge curves of selected cycles.

species and the postmortem analysis demonstrates the excellent stability of AQEG2TFSI during battery cycling.

The rate capability of the battery with 0.1 M AQEG2FSI/0.12 M FcNTFSI in 0.5 M TEATFSI/MeCN is shown in Figure 5a and b. CE increases from 91% to 97% as *j* increases from 25 to 65 mA cm⁻² due to reduced crossover. VE and EE decrease gradually (from 87% and 79% to 66% and 63%, respectively) owing to the increased polarization resistance. A discharge capacity of 2.55 Ah L⁻¹ is delivered at *j* of 25 mA cm⁻², which is equivalent to 95.1% of the theoretical capacity (2.68 Ah L⁻¹). When *j* is increased to 65 mA cm⁻², the battery displays a discharge capacity of 1.78 Ah L⁻¹, corresponding to 66.4% of the



Figure 5. (a) Cycling performance of the battery with 0.1 M AQEG2FSI/ 0.12 M FcNTFSI in 0.5 M TEATFSI/MeCN using Daramic-250 membrane at different current densities. (b) Galvanostatic charge/discharge curves of the battery from 25 to 65 mA cm⁻². (c) Polarization curves of the battery charged to different SOCs.

flow battery with AQTFSI and AQEG1TFSI also confirm the stability of the molecules modified by the cationic side chain (Figure S18).

The electrolyte after charge/discharge test was further analyzed (Figure 4d). The CV curve of the cycled anolyte remains almost unchanged, which illustrates the good stability of the anode active material AQEG2TFSI. However, the redox peak currents of both FcNTFSI and AQEG2TFSI decrease for cycled catholyte, which infers that the positive side should be mainly responsible for the capacity degradation. No obvious peaks of protonated by-products were observed in the ¹H NMR spectrum of the cycled anolyte (Figure 4e), probably due to the high concentration of active species, the weak impurity peaks are not easily observed. However, the ¹H NMR spectrum of the cycled catholyte shows obvious impurity peaks at 5.4~7.2 ppm. It may be due to the interaction between the charged cathode (FcNTFSI⁺) and neutral anode (AQEG2TFSI) in the electrolyte during cycling, which promotes the occurrence of side reactions. Nonetheless, this study focuses on the anode active theoretical capacity. When *j* returns to 25 mA cm⁻², the discharge capacity rose back to 2.60 Ah L⁻¹ with no capacity decay during subsequent 20 cycles, indicating the battery is robust enough to bear the current fluctuation. In addition, the battery exhibits high power density of 134.0 and 102.5 mW cm⁻² at 100% and 50% state of charge (SOC), respectively. They are superior to those of other NARFBs with 0.5 M supporting electrolyte^{39, 47} and even comparable with the aqueous RFBs,⁴⁸⁻⁵⁰ which is attributed to the high intrinsic conductivity of the ionic active species (Figure 2) and the relatively low area specific resistance (ASR) of the porous membrane (3.77 Ω cm², Figure S19). The power density can be further improved through optimization of membrane and supporting electrolyte.

Considering that AQEG2FSI is miscible with MeCN, a highconcentration flow battery with 0.4 M AQEG2FSI/0.48 M FcNTFSI in 1.0 M TEATFSI/MeCN was assembled, which delivers an energy density of ~16.8 Wh L⁻¹. Although the increased viscosity and crossover of the electrolyte are harmful for the battery performance inevitably, the cycling test was successfully demonstrated at *j* of 40 mA cm⁻² with average CE of 96% over 100 cycles (Figure 6a). The discharge capacity of the first cycle is 9.5 Ah L⁻¹, which is 88.6% of the theoretical capacity (10.72 Ah L⁻¹). The discharge capacity retention of 74% is obtained after 100 cycles, corresponding to an impressive capacity retention of 99.74% per cycle (Figure 6b). Owing to the greatly increased polarization, the battery exhibits relatively low VE and EE of 60% and 57%, respectively (Figure 6a). Nonetheless, this performance is still superior to most NARFBs with such high concentration electrolyte ^{35, 36, 51} (Table S2).

4. CONCLUSIONS

In summary, the anthraquinone derivatives carrying both a PEG chain and a tetraalkylammonium ion chain were successfully synthesized through the strategy of side-chain coupling. By adjusting the length of the EG chain, an anthraquinone ionic liquid AQEG2TFSI with high solubility and stability was obtained. Benefiting from the ionic form, this active species possesses fast mass- and charge-transfer kinetics although the long side chain was introduced. Assembled with Daramic 250 porous membrane, the NARFB shows impressive cycling performance with discharge capacity retention of 99.96% per cycle over 100 cycles with 0.1 M AQEG2TFSI, and demonstrates robust rate capability and high power density comparable to aqueous systems. The high-concentration battery test with 0.4 M AQEG2FSI exhibits discharge capacity retention of 99.74% per cycle over 100 cycles, which also validate the remarkable stability of AQEG2TFSI in such condition. Although this battery system needs to be further optimized, the modification strategy of side-chain coupling provides an effective way to design active materials with high solubility and high stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

NMR spectra, UV-vis spectra, CV, RDE, EIS, battery performance, DFT calculation results and a table of reported anode materials for NARFB.

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Notes

The authors declare no competing financial interest.

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