ABSTRACT: Bipyridinium derivatives represent the most extensively explored anolyte materials for pH-neutral aqueous organic redox flow batteries, and most derivatives feature two separate electron-transfer steps that cause a sharp decrease in cell voltage during discharge. Here, we propose a strategy to fulfill the concurrent two-electron electrochemical reaction by designing extended bipyridinium derivatives (exBPs) with a reduced energy difference between the lowest unoccupied molecular orbital of exBPs and the β-highest occupied molecular orbital of the singly reduced form. To demonstrate, a series of exBPs are synthesized and exhibit a single peak at redox potentials of $-0.75 \text{ to } -0.91 \text{ V (vs standard hydrogen electrode (SHE))}$, as opposed to the two peaks of most bipyridinium derivatives. Cyclic voltammetry along with diffusion-ordered spectroscopy and rotating disk electrode experiments confirm that this peak corresponds to a concurrent two-electron transfer. When examined in full-flowing cells, all exBPs demonstrate one charge/discharge plateau and two-electron storage. Continuous galvanostatic cell cycling reveals the side reactions leading to capacity fading, and we disclose the underlying mechanism by identifying the degradation products. By prohibiting the dimerization/β-elimination side reactions, we acquire a 0.5 M (1 M e$^-$) exDMeBP/FcNCl cell with a high capacity of 22.35 Ah L$^{-1}$ and a capacity retention rate of 99.95% per cycle.

KEYWORDS: energy storage, aqueous organic redox flow battery, anolytes, multiple-electron storage, bipyridinium derivative

INTRODUCTION

The current electricity supply relies on nonrenewable fossil fuels, which poses serious concerns of energy crisis and environmental benignity. This situation has stimulated the exploration of green electricity generated from renewable resources. Nevertheless, the intermittent nature of renewable energy sources, such as wind and solar photovoltaic power, precludes their massive scale integration into the grid. It is an urgent challenge to balance the relatively constant demand and fluctuating supply of renewable energy. Aqueous redox flow batteries (ARFBs), which store electrical energy through electrochemical reactions and operate by circulating electrochemically active electrolyte solutions to store energy, play vital roles in addressing this challenge, regarding their intrinsic advantages, namely, their decoupled energy and power, easy scale-up, and high safety.

Metal-based ARFBs, represented by vanadium flow batteries, may be eventually restricted by the abundance of vanadium in the Earth’s crust. In contrast, aqueous organic redox flow batteries (AORFBs) employ water-soluble organic electroactive electrolytes, which are composed entirely of earth-abundant elements (C, H, O, N, etc.) while also being inexpensive. In addition, rational molecular engineering on organic electrolytes offers more electrolyte options and tunable electrochemical properties for practical AORFB application.

Reported anolytes include viologens, quinones, fluorenones, phenazines, azobenzenes, phenothiazines, and nitroxide radicals are exploited as catholytes.

Operating an AORFB under neutral pH conditions offers an intrinsic advantage over acidic or basic solutions because these solutions may be corrosive, thereby posing high requirements on the materials contacting the electrolyte. Bipyridiniums, for example, viologen and its derivatives, are the most extensively used anolytes for pH-neutral AORFBs. Methyl viologen (MV), the first of this type applied in pH-neutral AORFBs, stores one electron per molecule in the cell at a redox potential of $-0.45 \text{ V (vs the standard hydrogen electrode, SHE)}$. To unleash the full potential of viologen derivatives as anolytes, rational molecular engineering has been conducted. [(NPr)$_2$V]Br$_4$ (another name of BTMAP-Vi) demonstrates a two-electron storage capability with potentials at $-0.35 \text{ to } -0.72 \text{ V (vs SHE)}$ for the first
and second redox reactions, respectively. However, the broad potential gap (0.37 V) between the separate redox steps may necessitate additional battery management as a sharp voltage difference between the two voltage plateaus during charge and discharge is anticipated. A π-conjugation extended viologen derivative, namely, [(NPr)2TTz]Cl4, delivers a narrow potential gap (0.12 V) and demonstrates two nearly overlapped voltage plateaus during charge and discharge, with an average potential of ~0.44 V (vs SHE).

Although the development of viologen electrolytes has made great advancements, there are pressing demands for effective strategies targeting the development of anolytes that have a low redox potential and can store more than two electrons in a single redox step. Here, we present a method to fulfill this target by analyzing and tuning the molecular orbital energy of anolyte materials. We design and synthesize extended bipyridinium derivatives (exBPs) with significantly raised lowest unoccupied molecular orbital (LUMO) energy and a reduced energy difference between the LUMO and β-highest occupied molecular orbital (β-HOMO) of the singly reduced exBPs. Cyclic voltammetry studies, along with diffusion-ordered spectroscopy (DOSY) and rotating disk electrode

**Figure 1.** (a) Schematics show a strategy that narrowing the energy difference between the lowest unoccupied molecular orbital (LUMO) of pristine bipyridinium and the β-highest occupied molecular orbital (β-HOMO) of the singly reduced bipyridinium radical cation transforms the “two-step, one-electron” reduction (the black line) to an apparent “one-step two-electron” reduction (the blue line). (b) By extending the π-conjugation and incorporating electron-donating substituents, the β-HOMO and LUMO energy difference can be reduced, as revealed by DFT calculations. The shadowed aromatic rings signify singly reduced bipyridinium radical cations.
(RDE) tests, confirm that exBPs deliver a low redox potential (−0.75 ~ −0.91 V vs SHE) and enable two-electron storage in a single redox step. In full cells, all of the exBPs exhibit one voltage plateau and accomplish a two-electron capacity. Capacity fading is observed during long-term cycling, and a dimerization product is detected. To suppress side reactions, exDMeBP, which is capable of two-electron storage, is designed following the same strategy. The 0.5 M (1 M e− concentration) exDMeBP/FcNC1 cell achieves a high capacity of 22.35 Ah L−1, a peak power density of 246.4 mW cm−2, and a capacity retention rate of 99.95% per cycle.

## RESULTS AND DISCUSSION

Organic electrolytes that can deliver multiple-electron storage in a single redox step can significantly raise the energy density of an AORFB and ease battery voltage management. To design such electrolytes, we propose that the redox behavior of organic electrolytes is closely related to the electrode potential and their frontier molecular orbital energy.33 By rational molecular engineering, the molecular orbital energy of organic electrolytes can be tuned and one-step multiple-electron transfer may be enabled.

To demonstrate this idea, we choose bipyridinium derivatives that show two reversible redox peaks in the cyclic voltammetry studies but only deliver one electron in pH-neutral AORFBs. For example, at an electrode potential of φ1, electrons flow to the LUMO of 4,4′-bipyridinium, and the first reduction occurs. At a more negative potential (φ2), the second reduction occurs, injecting electrons to the β-HOMO of the singly reduced 4,4′-bipyridinium radical cations. The two reactions correspond to two distinct peaks in the cyclic voltammetry (CV) curves, observed as “two-step, one-
bipyridinium tetrachloride), exBP-Me (1,1′-bis[3-(trimethylammonium)propyl]-4,4′-bipyridinium tetrachloride), and exBP-DMe (1,1′-bis[3-(trimethylammonium)propyl]-4,4′-(2-methyl-1,4-phenylene)-bipyridinium tetrachloride). These potentials are much lower than those reported for BTMAP-Vi and the viologen derivative, namely, [(NPr)2TTz]Cl4. The lowered π-conjugation extended π-electron orbital energy via a π-conjugation strategy and by varying the peripheral substituents. Four extended bipyridinium electrolytes are designed, namely, exBP (1,1′-bis[3-(trimethylammonium)propyl]-4,4′-(1,4-phenylene)-bipyridinium tetrachloride), exBP-Me (1,1′-bis[3-(trimethylammonium)propyl]-4,4′-(2-methyl-1,4-phenylene)-bipyridinium tetrachloride), exBP-DMe (1,1′-bis[3-(trimethylammonium)propyl]-4,4′-(2,5-dimethyl-1,4-phenylene)bipyridinium tetrachloride), and exDBMe (2,2′-methyl-1,1′-bis[3-(trimethylammonium)propyl]-4,4′-(1,4-phenylene)bipyridinium tetrachloride). The molecular orbital energies of these molecules in the pristine form and the singly reduced form are calculated by density functional theory (DFT) (Figure 1b). As expected, the energy difference is significantly reduced compared to that of the well-explored bipyridinium derivatives, represented by the BTMAP-Vi.

We synthesized the extended bipyridinium electrolytes including exBP, exBP-Me, and exBP-DMe via Suzuki coupling reactions from commodity chemicals and the subsequent quaternization reaction (Figure 2a). The 1H NMR spectroscopy and mass spectrometry (MS) results (Figures S1–S7 in the Supporting Information) confirm the products. BTMAP-Vi was also synthesized as a control, according to a reported method with a slight modification (Figure S8).

Electrochemical and spectrosopic studies on these compounds reveal that they undergo reversible two-electron redox reactions that consist of two overlapped one-electron steps. As shown in Figure 2b, exBP, exBP-Me, and exBP-DMe exhibit a single peak at potentials of −0.75, −0.83, and −0.91 V (vs SHE), respectively, whereas two distinct peaks are observed for BTMAP-Vi (Figure S9). These potentials are much lower than those reported for BTMAP-Vi and the π-conjugation extended viologen derivative, namely, [(NPr)2TTz]Cl4. The lowered redox potential is a result of the increased molecular orbital energy (Figure S10). The exBP-Me and exBP-DMe exhibit narrow peak separations of 34 mV, which are consistent with the theory ΔE0 = 58 mV n−1 for n = 2 electrons. Surprisingly, we notice that the peak current density at these potentials is higher than expected for a one-electron reduction. Thus, we simulated the current from two successive reduction steps and compared it with the measured values. Our results confirm that the observed single peak for exBP consists of two overlapped one-electron reduction peaks and that the total current matches perfectly the experimental data (Figure 2c).

The two-electron transfer during this reaction is further confirmed by DOSY and RDE experiments (Figures 2d,e and S11–S14). Similar results are obtained for exBP-Me and exBP-DMe (Table 1), while the number of electrons involved in the reduction of BTMAP-Vi is calculated to be ∼1 (RDE data quoted from the literature).

Other properties of the exBPs reflect that they are potent anolyte candidates for pH-neutral AORFBs (Table 1). RDE experiments are performed to obtain the electron-transfer rate constants (k0) of exBP, exBP-Me, and exBP-DMe, and the values are 4.26, 1.54, and 2.03 × 10−3 cm s−1, respectively. The solubility of exBP, exBP-Me, and exBP-DMe in deionized water is 1.3, 1.1, and 1.0 M (Figures S15–S17), respectively. Yet, their measured permeability across a Selemion DSV membrane decreases from 8.00 × 10−11 to 5.28 × 10−11 cm2 s−1, which is much lower than the permeability of BTMAP-Vi (3.17 × 10−10 cm2 s−1).11

The exBP was evaluated in a flow cell as an anolyte and paired with FcNCl26 ((ferrocenylmethyl)trimethylammonium chloride, Figures S18 and S19) at an electrolyte concentration of 0.1 M (0.2 M e− concentration, with a theoretical capacity of 96.5 C) (Figure 3a). exBP was separated from FcNCl by a commercial Selemion DSV membrane; notably, the exBP side is capacity limiting. The exBP/FcNCl cell exhibits only one voltage plateau during charge or discharge, and the charge capacity is 90.8 C (94.1% theoretical capacity utilization), corresponding to a two-electron transfer. As a control, an otherwise identical cell is assembled with BTMAP-Vi and FcNCl, which shows two distinct plateaus during charge or discharge, and only one electron is delivered at each plateau according to the measured capacity. The advantage of a single two-electron plateau over the two separate one-electron plateaus includes simplified voltage management and a ∼0.36 V increase in cell voltage (Figure 3b).

Polarization curves of the exBP/FcNCl cell were measured by stepwise charging the cell at a constant voltage of 1.6 V, with a 10% increase in the state of charge (SOC). The peak power density is 154.3 mW cm−2 at ∼100% SOC (Figure 3c). The rate performance of the exBP/FcNCl cell at constant current densities of 40, 60, 80, and 100 mA cm−2 (Figure 3d) demonstrates a Coulombic efficiency (CE) of ∼100%, while the average energy efficiency (EE) of the cell reaches 87% at 40 mA cm−2 and remains at 70% at 100 mA cm−2.

Long-term galvanostatic cycling of the exBP/FcNCl cell was performed at 60 mA cm−2 for 300 consecutive cycles with

| electrolyte | E1/2 [V vs SHE] | D0 [cm2 s−1] | n0 (e−) | k0 [cm s−1] | solubility [mol L−1] | permeability [cm2 s−1] |
|-------------|----------------|--------------|---------|-------------|---------------------|------------------------|
| exBP        | −0.75          | 3.53 × 10−6  | 1.7     | 4.26 × 10−3 | 1.3                 | 8.00 × 10−11           |
| exBP-Me     | −0.83          | 3.65 × 10−6  | 1.6     | 1.54 × 10−3 | 1.1                 | 5.31 × 10−11           |
| exBP-DMe    | −0.91          | 4.20 × 10−6  | 1.4     | 2.03 × 10−3 | 1.0                 | 5.28 × 10−11           |

*E1/2 = redox potential. D0 = diffusion coefficient measured by diffusion-ordered spectroscopy. Calculated number of transferred electrons by a combination of diffusion-ordered spectroscopy and rotating disk electrode experiments. k0 = electron-transfer rate constant. Solubility in deionized water. Permeability of the electrolytes across a Selemion DSV membrane.
voltage cutoffs of 1.6 V for charge and 0.5 V for discharge. A potentiostatic hold was conducted at the end of both the charge and discharge processes to access the full capacity. The cell demonstrates a capacity retention rate of 99.85% per cycle, an average CE of ∼100%, and an EE of 78% during cell cycling (Figure 3e).

Under identical conditions, the capacity loss is more prominent for exBP-Me and exBP-DMe, which have lower redox potentials (Figures S20a and S20b). Similar results are obtained even if we lower the voltage cutoffs during the charge and discharge processes (Figure S20c). This agrees with the findings of Aziz et al.35 The exBP-DMe/FcNCl lost almost all
of its capacity after the first 100 cycles. The fast capacity fade may be caused by the methyl groups on phenylene, which weaken the π-conjugation between the phenyl and pyridinium rings. The electron-donating capability of methyl groups may also promote the attack of electron-rich pyridinylidene on the positively charged pyridinium ring (Figure 4a). Post-mortem analysis of the exBP-DMe side after cell cycling reveals dimers as the major product of anolyte degradation (Figure S21). This decomposition mechanism is different from the alkyl-chain cleavage of BTMAP-Vi and exBP and the dimerization/disproportionation of methyl viologens. The 1H NMR results after cell cycling also show the chemical degradation of the designed molecules (Figures S22–S24). Overall, exBP manifests the best performance. Yet, its capacity loss during cell cycling is considerable.

To further increase the electrochemical stability of the extended bipyridinium anolytes, exDMeBP was designed and synthesized (Figures S25 and S26). Two methyl groups are added to the pyridinium rings, prohibiting the dimerization reaction and OH⁻ attack, as shown in Figure 4a. The synthetic route of exDMeBP is presented in Figure 4b. Cell cycling under identical conditions validates the improvement in the capacity retention rate. As shown in Figure 4c, a cell assembled with 0.1 M exDMeBP (0.2 M e⁻) and excess FcNCl in 1 M...
NaCl aqueous solution demonstrates superior cycling stability compared with the other cells, exhibiting a capacity retention rate of 99.94% per cycle (93.6% of the theoretical two-electron capacity is utilized during cell cycling).

In addition to the improved electrochemical stability, exDMeBP demonstrates electrochemical and physicochemical properties similar to those of other anolytes (Figures S27–S30). These properties include a one-step, two-electron storage capability (transfer of \(\sim 2\) electrons per molecule according to the DOSY and RDE measurements), low reduction potential (\(-0.81\) V vs SHE), fast kinetics (the rate constant \(k_0\) is \(5.20 \times 10^{-3}\) cm s\(^{-1}\)), and low membrane permeability (permeability of exDMeBP across the Selemion DSV membrane is \(8.32 \times 10^{-11}\) cm\(^2\) s\(^{-1}\)). The measured solubility of exDMeBP is 0.7 M in deionized water.

The performance of a more concentrated exDMeBP/FcNCl cell at 1.0 M e\(^-\) concentration is shown in Figure 5. The peak power density of this cell increases to 246.4 mW cm\(^{-2}\) at \(\sim 100\%\) SOC (Figure 5a). A high capacity of 22.35 Ah L\(^{-1}\) (83.4% of the theoretical capacity) is achieved at 40 mA cm\(^{-2}\) (Figure 5b). Continuous cell cycling with potential holds at 80 mA cm\(^{-2}\) reveals a moderate capacity fade rate of 0.17% per cycle, whereas by controlling the SOC of the cell during cell cycling, a suppressed capacity fade rate of 0.05% per cycle is realized (Figure S31a). Our preliminary results based on postmortem analysis imply that the electrolyte may undergo elimination reactions induced by solution pH changes (Figures S31–S33). The addition of trimethylamine can further suppress such degradation, enhancing the capacity retention rate of the 0.1 M exDMeBP/FcNCl cell to 99.96% per cycle (Figure S34). We believe by controlling the solution pH, long-lived pH-neutral AORFBs can be achieved.

**CONCLUSIONS**

In summary, this work presented a novel strategy. By quantitatively regulating the molecular orbital energy difference, anolytes that have a low redox potential and store two electrons could be obtained for pH-neutral AORFBs. This strategy was exemplified by a series of extended bipyridiniums we designed and synthesized, including exBP, exBP-Me, exBP-DMe, and exDMeBP. These molecules realized one-peak, two-electron storage at the lowest potential ever reported for bipyridiniums. We performed CV, DOSY, and RDE experiments to verify the transfer of two electrons. Full-flowing cells assembled with these anolytes (against FcNCl) exhibited...
“two-electron” voltage plateau during cycling. Reasons causing capacity loss during cell cycling were attributed to alkyl-chain cleavage and dimerization, which were suppressed by introducing steric hindrance. Finally, with the best anolyte, the exDMeBP/FcNCl cell (0.5 M, 1 M e⁻ concentration) demonstrated a capacity of 22.35 Ah L⁻¹ with a capacity retention rate of 99.83% per cycle when deeply cycled. The capacity retention rate was further improved to 99.95% per cycle by controlling the SOC.

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