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ARTICLE

All-PEGylated Redox-Active Metal-Free Organic Molecules in Non-Aqueous Redox Flow Battery

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Non-aqueous organic material-based redox flow batteries (NAORFBs) possess the advantage of using organic solvents to achieve high electrochemical potential. However, regardless of the great progress made in this regard in the past decade, further development has been restricted by the lack of stable electroactive organic materials and highly selective separators. Here, we present a NAORFB with all-PEGylated, metal-free, organic compounds as electroactive materials. PEGylated phenothiazine and PEGylated viologen are utilized as the catholyte and anolyte, respectively. Combined with a composite nanoporous aramid nanofiber separator, the all-PEGylated NAORFB presents outstanding cyclability, with a capacity retention of 99.90% per cycle and average Coulombic efficiency of 99.7%. By contrast, NAORFBs using half-PEGylated and non-PEGylated electrolytes display inferior cyclability owing to the crossover of non-PEGylated materials. An extended investigation was also performed on the batteries using non-PEGylated or half-PEGylated materials for mechanistic elucidation. This work validates the PEGylation strategy in NAORFBs for enhanced overall performance with respect to solubility, cyclability, and alleviated crossover.

Introduction

Over the past century, there has been a significant increase in demand for electricity. The continually increasing content of greenhouse gases generated from traditional fossil fuels has prompted researchers worldwide to develop clean energy, such as wind and solar energy.¹⁻³ However, the intrinsic intermittence and fluctuation of these renewable energy sources pose serious challenges. Energy storage devices, such as lithium (metal),⁴⁻¹² sodium,^{13,14} aluminum,¹⁵ and magnesium ion batteries,^{16,17} have played an important role in reducing peak shaving and valley filling in electric networks. Among the emerging energy storage devices, redox flow batteries (RFBs) have attracted much attention.¹⁸⁻²¹ RFBs store energy in liquid electrolyte reservoirs, which decouple the energy and power densities.²²⁻²⁵ Non-aqueous organic material-based redox flow batteries (NAORFBs) have been studied in recent years owing to their wide electrochemical window of non-aqueous electrolytes and vast molecular diversity.²⁶⁻³⁸ However, a limiting factor that retards further development of the NAORFBs is the crossover of electroactive compounds through the membrane into the opposite compartments, causing inferior cyclability performance.^{26,39,40} The crossover issue is less severe in the conventional aqueous RFBs because of the availability of ion-exchange membranes, such as the commercially available and widely used Nafion[®], Fumasep[®], AMV[®], and DSV[®] membranes,^{20,41-48} which can suppress the permeability of redox-active species. These ion-exchange membranes usually possess super-

high ionic conductivity (> 100 mS/cm) in aqueous electrolytes,⁴⁸⁻⁵⁰ endowing the aqueous RFBs with superior power densities. Unfortunately, merely using these membranes in non-aqueous electrolytes typically induces new issues, such as inferior stability and high resistance (< 100 mS/cm),^{27,51-53} resulting in low charge/discharge rate and power density. The pretreatment of Nafion[®] membranes to convert the proton of the sulfonic acid to lithium ion⁵² or tetraalkylammonium,⁵⁴ such as tetrabutylammonium or tetraethylammonium, does not substantially improve the performance. Size exclusion-based porous membranes, such as Daramic[®] and Celgard[®] membranes, have been used in some non-aqueous symmetrical batteries or catholyte–anolyte-mixed batteries, but typically in low Coulombic efficiencies (80–95%)^{31,39,40,55-60} and high self-discharge rates, owing to the large pore sizes (20–200 nm). NAORFBs using inorganic glass ceramic separators display high Coulombic efficiencies and high charge/discharge current density.^{29,61} However, their intrinsic brittleness and high cost prevent their wide application.

Two strategies can be adopted to address the aforementioned issues and improve the overall battery performance. One is to increase the molecular size of electroactive compounds to suppress penetration through the membrane based on a physical blocking mechanism. For example, small electroactive compounds can be incorporated on redox-innocent polymer backbones^{24,57,62,63} or decorated with long tails.^{23,64,65} The second strategy is to design novel membranes with high ion selectivity, low resistance, and high solvent compatibility.^{26,66} The porous membrane can be modified with positively or negatively charged ions to introduce ion-exchange features,⁶⁶⁻⁶⁹ thus suppressing crossover by a combination of steric hindrance and Donnan exclusion mechanism.^{53,70} The Sanford group reported a Fumasep[®] anion exchange membrane to separate the positively charged anolyte and catholyte.⁶⁷⁻⁶⁹ Both strategies

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(molecular engineering and membrane decoration) are used in a synergistic manner to improve the overall battery performance.

Several types of organic redox-active materials have been reported in NAORFBs, including (but not limited to): (1) Viologens. The most promising feature of using viologens as the anolyte is the two-electron redox activity for higher energy capacity compared to its one-electron-active peers. In comparison to the intrinsically water-soluble viologens,^{19,49,71,72} Liu et. al. reported a highly organic soluble viologen by replacing its halogen anions with less polar bis(trifluoromethanesulfonyl)imide (TFSI) units and successfully applied it in NAORFB;³⁰ (2) Ferrocene (**Fc**). As a highly electrochemically stable organometallic complex, **Fc** is commonly used as a catholyte in NAORFBs.^{29,73} However, the low redox potential of **Fc** (0.69 V vs standard hydrogen electrode) does not take full advantage of the wide electrochemical window of non-aqueous solvents. In addition, the energy density of **Fc** is relatively low owing to the limited solubility in organic solvents [200 mM in acetonitrile (ACN), and even lower in carbonate solvents].^{38,74} Derivatized **Fc**, such as quaternized ferrocene^{30,38,75} and brominated ferrocene,⁷³ were also developed to improve the solubility and/or increase the redox potential; and (3) Phenothiazine (**PTZ**). As catholyte materials,^{44,57,76,77} **PTZs** can undergo facile molecular modification on the N atom and aromatic ring to optimize solubility, stability, and redox potentials, making **PTZs** attractive in NAORFBs.⁷⁷ For practical applications, an electroactive compound in RFB should possess features including (1) high electrolyte stability, (2) wide electrochemical window, (3) high electrolyte solubility, and (4) mitigated crossover (Fig. 1). Few (if any) materials satisfy all four criteria.

Recently, we investigated a PEGylated strategy and used PEGylated viologens as anolytes for the demonstration of proof-of-concept in the NAORFB.⁶⁴ The introduction of poly(ethylene glycol) (PEG) increased the molecular size of viologen and improved solubility in all the charged and discharged states of viologen in the organic solvent. In this paper, we present a PEGylated **PTZ** as the catholyte. PEGylated electroactive materials have been applied in NAORFBs.^{23,58} However, the majority of the reported materials employed lower degree of PEG units with limited capability for crossover suppression. The PEGylated viologen and PEGylated phenothiazine herein possess lower permeability due to the increases molecular size by the introduction of higher degree of PEG chains. Paired with the PEGylated viologen, the all-PEGylated battery exhibited substantially long cyclability. An extended investigation was also conducted on the NAORFBs using partially or non-PEGylated compounds and illustrated that the all-PEGylated system possesses superior cyclability and higher Coulombic efficiency. This study validates that the PEGylation strategy can greatly improve the performance of redox-active materials in NAORFBs.

Experimental section

Materials

Sodium hydride, phenothiazine, sodium sulfate, potassium hydroxide, 1-iodopropane, anhydrous acetonitrile (99.8%), and tetrabutylammonium hexafluorophosphate were purchased from

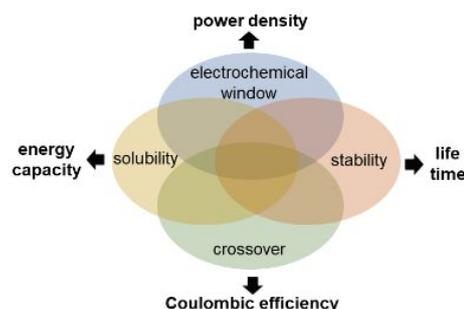


Fig. 1 Venn diagram depicting the four key requirements for redox-active species in NAORFBs.

Sigma-Aldrich. Methylene dichloride and *N,N*-dimethylformamide were obtained from Fisher Chemical. Dimethyl sulfoxide was purchased from TCI Chemicals. The aramid nanofiber was purchased from the Thread Exchange. The Daramic separator was provided by Daramic LLC. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized in absolute ethanol and dried in vacuo. The other materials were used as purchased without any purification. The ¹H NMR and ¹³C NMR analyses were performed at room temperature using a Bruker AV 400 MHz spectrometer. Chemical shifts are based on the ppm unit. Electrospray ionization–mass spectrometry (ESI–MS) analysis was performed on an Orbitrap Fusion Lumos mass spectrometer from Thermo Scientific. Compounds PEGylated viologen (**PEG12-V**, with 12 oxyethylene units),⁶⁴ methyl viologen (**Me-V**)^{30,78} and *N*-propyl phenothiazine (**C3-PTZ**)⁷⁹ were prepared according to reported procedures.

Electrochemical measurement

All the cyclic voltammetry (CV) tests were conducted in 0.1 M TBAPF₆-ACN solution in an argon-filled glovebox. The CV studies were carried on a Bio-Logic potentiostat. For a CV study, a glassy carbon (3 mm in diameter) and a Pt wire electrode were used as the working and counter electrode, respectively. Ag/AgNO₃ electrode with 0.01 M AgNO₃/ACN solution was used as reference electrode.

Linear sweep voltammetry (LSV) studies were carried out using a Pine modulated speed rotator with CHI760e electrochemical workstation. Rotating disk electrode (RDE, diameter: 5 mm), Pt wire electrode and Ag/AgNO₃ electrode were used as the working, counter and reference electrodes, respectively. Before testing, the samples were purged with argon for 10 min to remove the dioxygen. LSV dates were collected at different rotation rates from 100 to 2500 rpm. Diffusion coefficient (*D*) of electroactive material was calculated from Levich plot:^{46,48,80}

$$i = 0.620nFAC_0D^{2/3}\omega^{1/2}\nu^{-1/6}$$

where *i* is limiting current density (A), *n* is the number of electrons in redox process, *F* is Faraday's constant (96,485 C/mol), *A* is the area of the glassy carbon electrode (0.196 cm²), *C*₀ is the concentration of active material (1 × 10⁻⁶ mol/cm³), *D* is the diffusion coefficient (cm²/s), ω is angular rotation rate (rad/s), and ν is the kinematic viscosity of 0.1 M TBAPF₆-ACN (0.00442 cm²/s).

The mass-transfer-independent kinetic current *i*_k was obtained from the Koutecký-Levich plot for different overpotentials (the reciprocal of the current at overpotentials vs the reciprocal of the square root of the rotation rate).^{20,62} Exchange current *i*₀ can be obtained from the Butler-Volmer equation^{41,62} via a Tafel plot [$\log(i_k)$

vs overpotential], which yields the kinetic oxidation rate constant k_0 (cm/s) from following equation:

$$i_0 = F A k_0 C_0$$

The transfer coefficient (α) was obtained from Tafel analysis:

$$\text{Tafel slope} = (1-\alpha)F/(2.3RT)$$

where R is the universal gas constant (8.314 J/(K mol)) and T is the absolute temperature (298 K).

Permeability measurement

The permeability measurements of active materials were carried out following the procedures in the references.^{20,64} The samples of 15 mL 50 mM active material in 0.1 M TBAPF₆-ACN were added to one side of the H-cells. The blank electrolyte solution without redox-active materials was used in the other side. The H-cell was separated by composite nanoporous aramid nanofiber (CANF) membrane. The concentrations of active materials were calculated from the calibration curve of the peak current density vs concentration. The permeability (P) is calculated from the following equation:²⁰

$$P = \frac{\ln\left(1 - \frac{2C_r}{C_0}\right)\left(-\frac{Vl}{2A}\right)}{t}$$

where C_r is the concentration measured at the receiving side (mol/cm³), C_0 is the active species concentration in the working chambers (mol/cm³), V is the volume (cm³), l is the membrane thickness (cm), A is the membrane area (cm²), and t is the test time (s).

DFT calculation

All calculations were carried out by using Gaussian 09 software for original and one-electron oxidation state.⁸¹ All oxidation states were optimized at ground states with M06-2x functional: Minnesota

'06 2x global hybrid functional with 54% Hartree-Fock exchange and 6-31+G(d) basis sets. The universal solvation model SMD was selected to optimize all geometries in ACN to include the solvation effect to the free energies. The molecular orbitals (MOs) and molar volume calculations were carried out at M06-2x/6-31+G(d) level.

Battery measurement

The flow battery possesses an active area of 28 cm², and is composed of a metal plate, polytetrafluoroethylene plate, copper plate, graphite current collector, polytetrafluoroethylene frame, and graphite-felt electrodes. The CANF membrane was prepared according to reported procedure,^{26,64} which was sandwiched between two graphite-felts. For full batteries, 50 mM cathode materials and 10 mM anode materials were dissolved in 0.5 M TBAPF₆-ACN (8 mL). The battery was galvanostatically charged/discharged at a current density of 2 mA/cm² within a potential range of 0–2.2 V.

Electrochemical impedance spectroscopy (EIS) of the RFBs before and after cycling was conducted on a Bio-Logic potentiostat under a frequency ranging from 200 kHz to 100 mHz and using a 10 mV AC amplitude signal.

Results and discussion

Molecular design and synthesis

A set of four compounds are synthesized for systematic investigation of PEGylation effects on battery performance in an organic solvent (Fig. 2a). Among the four compounds, **PEG12-V** and **Me-V** function as anolytes, and *N*-PEG12 phenothiazine (**PEG12-PTZ**) and **C3-PTZ** as catholytes (Fig. 2b). As the cathode redox material, compound **PTZ** undergoes one-electron oxidation to become a stable radical cation.⁸²

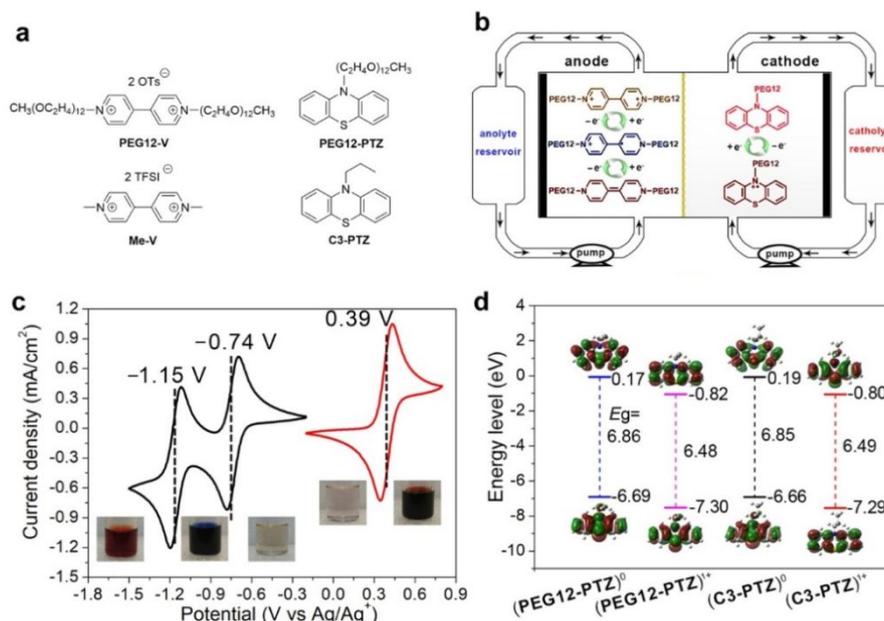


Fig. 2 (a) Molecular structures of compounds **PEG12-V**, **Me-V**, **PEG12-PTZ**, and **C3-PTZ**. (b) Redox reactions at the negative and positive sides during charge and discharge. (c) CV scans of **PEG12-PTZ** and **PEG12-V** (5.0 mM of both) in 0.1 M TBAPF₆-ACN on a glassy carbon electrode at a scan rate of 50 mV s⁻¹. (d) HOMO/LUMO of **PEG12-PTZ** and **C3-PTZ** on the redox-neutral and one-electron oxidized states.

Different pairings of the four electrolytes give four battery systems for thorough investigation. Instead of using KOH as the base for the deprotonation of PTZ to prepare C3-PTZ,⁷⁹ a stronger base, sodium hydride, was used to afford a stronger PTZ nucleophile to react with PEG methyl ether tosylate (Scheme S1 and Fig. S1), for the synthesis of compound PEG12-PTZ; 66% yield of PEG12-PTZ was obtained in high purity. The PEG12-PTZ compound is a purple liquid and is miscible with ACN in any proportion, to be compared to C3-PTZ as white crystal powders (Fig. S2). The density of PEG12-V and PEG12-PTZ was 1.16 g/mL and 1.17 g/mL, corresponding to a concentration of 0.79 M and 1.72 M, respectively. For two-electron-active viologen, the electron concentration of PEG12-V is 1.58 M. The high solubility of PTZ is required to improve the energy density of the NAORFBs.

Electrochemical properties

The electrochemical properties of the electrolytes were characterized by CV in ACN with 0.1 M TBAPF₆ as the supporting electrolyte (Fig. 2c). The single-electron oxidation of PEG12-PTZ exhibits a reversible redox couple at 0.39 V vs Ag/Ag⁺. The compound PEG12-V presents two redox peaks at -0.74 V and -1.15 V vs Ag/Ag⁺. The pairing of PEG12-V and PEG12-PTZ gives a potential difference as high as 1.54 V. Moreover, the introduction of the PEG chain had negligible effect on the redox potential of the electroactive materials (Fig. S3). Molecular orbital (MO) Density Functional Theory (DFT) calculations for PEG12-PTZ and C3-PTZ in the two oxidation states were performed to evaluate the corresponding redox potentials during the electrochemical processes. The results show that for both C3-PTZ and PEG-PTZ, the HOMOs and LUMOs are almost identical and mapped through three PTZ rings symmetrically (Fig. 2d). Owing to the electron delocalization and

conjugation, the HOMO orbitals show stable structures for C3-PTZ and PEG12-PTZ. The **Table 1.** Molecular sizes and permeability properties of the four compounds.

Compound	Charge state ^b	Molecular diameter (nm)	Permeability (cm ² /s × 10 ⁹)
PEG12-PTZ	0	1.20	1.31
C3-PTZ	0	0.82	16.46
PEG12-V ^a	+2	1.43	0.35
Me-V ^a	+2	0.78	2.60

^a Data for PEG12-V and Me-V were derived from ref.⁶⁴

^b The charge state refers to the viologen cations.

energy gaps (E_g) for the different redox states of C3-PTZ and PEG12-PTZ are almost identical, further confirming that the presence of the PEG unit does not affect the electrochemical properties. The E_g for the original oxidation state of both C3-PTZ and PEG12-PTZ is higher than that for the one-electron oxidation state, indicating higher energy is needed for electron transfer in redox reactions. The crossover issue is one of the long-standing challenges in NAORFBs.^{26,83} One of the advantages of PEGylation is that it can increase the molecular size of organic electroactive compounds and alleviate the crossover issue. A three-day permeability experiment was conducted by monitoring the concentration of active materials in the test chamber of a H-cell (Fig. S4). Compound PEG12-PTZ presented a significant decreased crossover rate for the CANF membrane (1.31×10^{-9} cm²/s), a tenth lower than that of C3-PTZ (16.46×10^{-9} cm²/s, Fig. S5) owing to its bigger molecular size (Table 1). A similar trend was observed for viologens.⁶⁴ It is worth noting that with similar molecular diameters (PEG12-PTZ vs PEG12-V, and C3-PTZ vs Me-V), viologens presented a lower permeability owing to their two positive charges and the Donnan exclusion of the CANF separator.⁶⁴

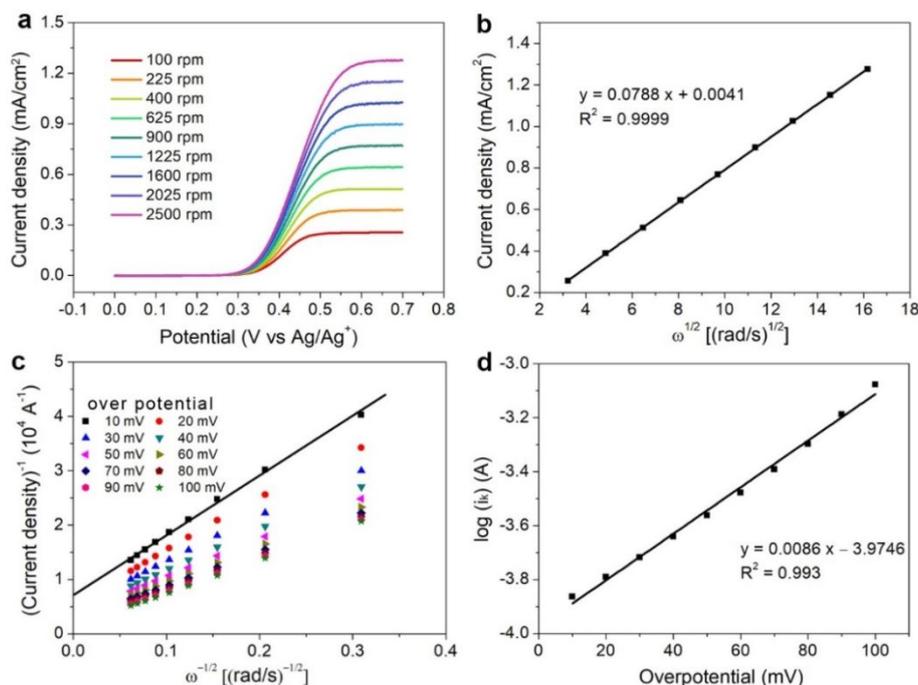


Fig. 3 (a) Linear sweep voltammetry of 1 mM of PEG12-PTZ in 0.1 M TBAPF₆-ACN at different rotation rates from 100 to 2500 rpm. (b) Levich

plot from the obtained limiting currents. (c) Koutecký–Levich plot (i^{-1} vs $\omega^{-1/2}$) of 1 mM of PEG-PTZ. (d) Plot of $\log(i_k)$ vs overpotential.

To investigate the effect of PEGylation on the stability of PTZ, we repeated CV scans of PEG12-PTZ and C3-PTZ in 0.1 M TBAPF₆-ACN for 500 cycles. The overlapped traces showed the electrochemical stability of PEG12-PTZ in a non-aqueous electrolyte (Fig. S6a). Meanwhile, C3-PTZ presented the same stability property (Fig. S6b). In addition, the PTZ and viologen CV scans at different charge states showed that the redox potential and peak current density had almost no change after 5 days (Fig. S7), which concluded that PEGylation did not affect their electrochemical stability.

The electrochemical kinetics of PEG12-PTZ in 0.1 M TBAPF₆-ACN were studied by the RDE method (Fig. 3a). The diffusion coefficient (D) of PEG12-PTZ was calculated from Levich plot (Fig. 3b),^{46,48,80} which yielded a diffusion coefficient of 1.23×10^{-5} cm²/s, consistent with that from the Randle–Sevcik equation ($D_O = 1.10 \times 10^{-5}$ cm²/s and $D_R = 9.88 \times 10^{-6}$ cm²/s) (Fig. S8 and Table S1). The diffusion coefficient of PEG12-PTZ is slightly lower than that of C3-PTZ (1.61×10^{-5} cm²/s) (Fig. S9), presumably owing to the increased viscosity from the PEG chains. Application of the Koutecký–Levich plot gave the mass-transfer-independent kinetic current i_k from the intercept of linear fitting (Fig. 3c).^{20,62} The Butler–Volmer equation^{41,62} via a Tafel plot yielded the exchange current i_0 , and then provided the kinetic oxidation rate constant k_0 ($k_0 = 5.64 \times 10^{-3}$ cm/s) via $i_0 = FAK_0C_0$ (Fig. 3d). The kinetic oxidation rate constant of C3-PTZ in 0.1 M TBAPF₆-ACN is 9.88×10^{-3} cm/s, slightly higher than that of PEG-PTZ, indicating that the introduction of PEG reduces the reaction rate constant of PTZ. However, the transfer coefficient (α) of C3-PTZ, obtained from the Tafel analysis, is only 0.315, which is lower than that of PEG12-PTZ ($\alpha = 0.492$). The latter value is close to 0.5, which is the value for an ideally reversible redox reaction.⁶²

Battery performance

The battery was assembled for rate performance and long cyclability tests using 50 mM PEG12-PTZ and 10 mM PEG12-V as catholyte and anolyte, respectively. The excess PEG12-PTZ was used to ensure the two-electron utilization of PEG12-V. The investigation of the all-PEGylated RFB was initiated with open circuit voltage (OCV) measurements at various states of charge (SOC) (Fig. S10). The resulting all-PEGylated PEG12-PTZ/PEG12-V battery presented an OCV increasing nearly linearly from 0.97 V at 5% SOC to 1.17 V at 45% SOC, and from 1.42 V at 50% SOC to 1.59 V at 95% SOC. The two charge platforms correspond to the two redox peaks of PEG12-V in CV scans. Similarly, the discharge plot showed two platforms. Additionally, the polarization voltage was as small as 75 mV, indicating the low internal impedance of the all-PEGylated PEG12-PTZ/PEG12-V battery.

As the power density of a RFB is directly related to the rate property, a PEG12-PTZ/PEG12-V battery was galvanostatically charged/discharged at different current densities from 1 to 5 mA cm² with an interval of 1 mA/cm² (Fig. 4a). At a current density of 1 mA/cm², the battery displayed a capacity of 5.03 mAh (93.4% of the theoretic capacity) with a Coulombic efficiency of 97.7% and energy efficiency of 88.3%. With increased current density, the overpotential increases and discharge capacity decreases owing to the intrinsic internal impedance of the battery. However, even at a current density as high as 5 mA/cm² the battery still presented a discharge capacity of

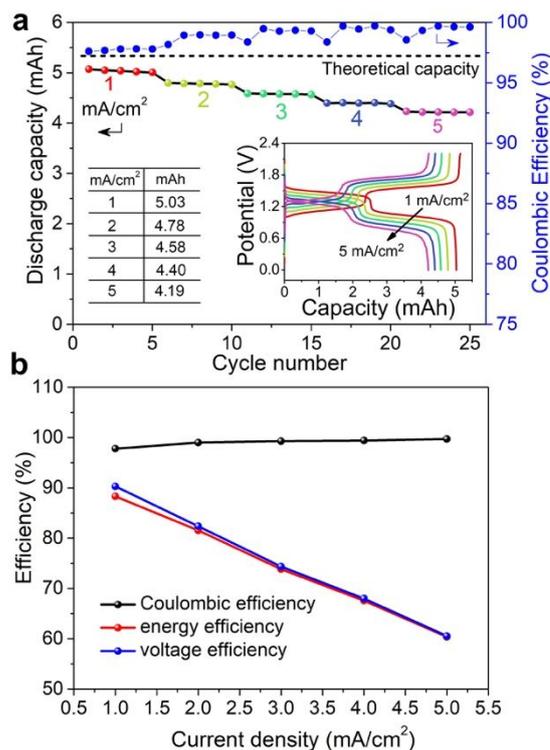


Fig. 4 (a) Discharge capacity and Coulombic efficiency of the PEG12-PTZ/PEG12-V battery at varied current densities. Inset: charge/discharge profiles. (b) Average Coulombic efficiency, energy efficiency, and voltage efficiency at different charge/discharge current densities.

4.19 mAh, corresponding to 78.2% of the theoretical capacity. It should be noted that the Coulombic efficiency increased from 97.7% at 1 mA/cm² to 99.7% at 5 mA/cm² (Fig. 4b). The excellent rate performance was rooted in the high diffusion coefficient and kinetic oxidation rate constant of organic redox species in non-aqueous electrolytes.

Given that the Coulombic efficiency of the battery is up to 99.0% at a current density of 2 mA/cm² (Fig. 4) and that the utilization of active materials exceeded 91.4%, the PEG12-PTZ/PEG12-V battery was galvanostatically charged/discharged at a current density of 2 mA/cm² to investigate long cyclability. The battery possessed a capacity of 4.84 mAh with a capacity retention of 69.0% after 300 cycles (99.9 % per cycle) (Fig. 5a) and an average Coulombic efficiency of 99.7% (Fig. 5b). In addition, no evident change was observed for the charge/discharge profiles at different cycle numbers (Fig. S11), except for a slight reduction in capacity, exhibiting a stable energy efficiency of 72.7%. CV scans after 300 cycles indicated that the crossover of PEG12-PTZ through the CANF separator was negligible (Fig. 5c). EIS plots of the battery before and after the 300 cycles showed that there was a slight increase in the high-frequency impedance (Fig. 5d). However, the charge transfer impedance of the battery⁴⁸ showed an evident decrease presumably because of the prolonged soaking time of the CANF separator in the electrolyte. The stable impedance caused stable charge/discharge profiles and a long

operating lifetime.

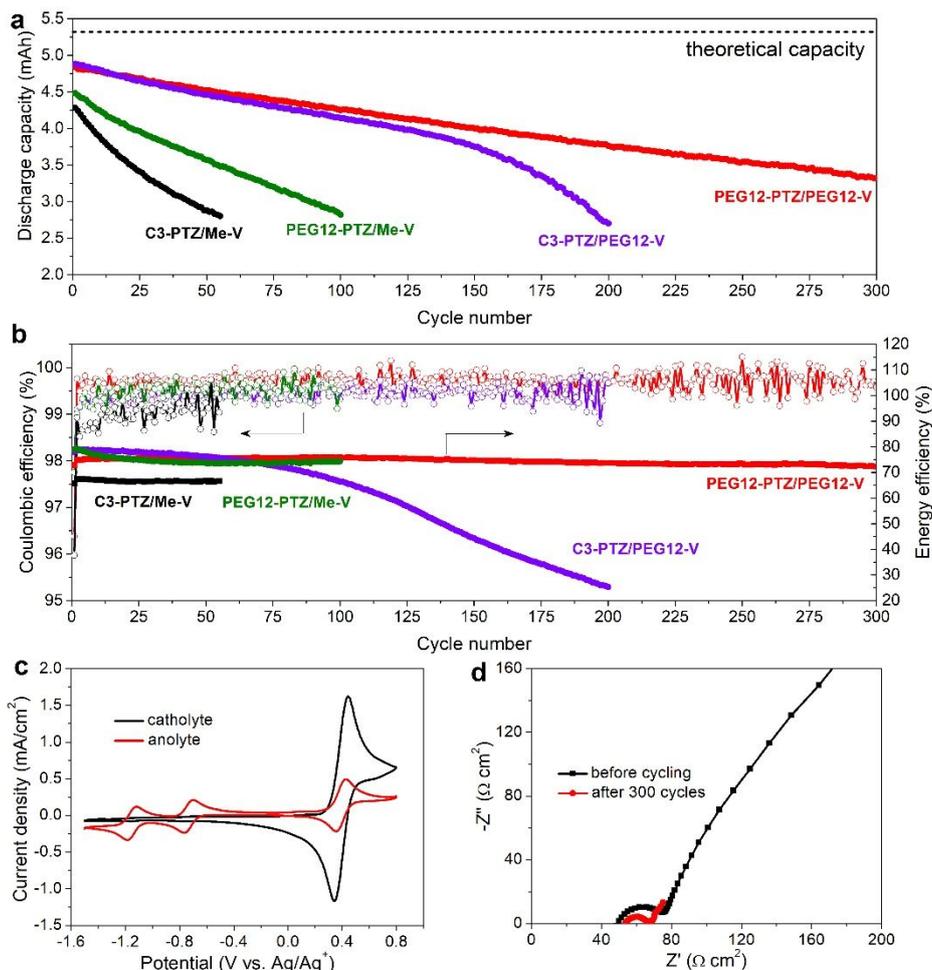


Fig. 5 (a) Discharge capacity vs cycle number of the **PEG12-PTZ/PEG12-V** (red), **C3-PTZ/PEG12-V** (blue), **PEG12-PTZ/Me-V** (green), and **C3-PTZ/Me-V** (violet) batteries. (b) Coulombic and energy efficiencies vs cycle number. (c) CV scans of catholyte and anolyte for **PEG12-PTZ/PEG12-V** battery after 300 cycles. (d) AC impedance spectra of **PEG12-PTZ/PEG12-V** battery before cycling and after 300 cycles.

To investigate the structure–performance relationship, we studied the half-PEGylated batteries (**C3-PTZ/PEG12-V** and **PEG12-PTZ/Me-V**) and non-PEGylated battery (**C3-PTZ/Me-V**). The **C3-PTZ/PEG12-V** battery exhibited good capacity retention in the first 125 cycles (Fig. 5a), but with poor energy efficiency, especially after 100 cycles (Fig. 5b). The poor energy efficiency was attributed to the gradually increasing polarization during the charge/discharge process (Fig. S12a). The redox peak for the catholyte **C3-PTZ** was observed in the anolyte side (Fig. S12b) at almost the same current intensity as that of the same species in the catholyte, consistent with the permeability findings that **C3-PTZ** had a much higher permeability than **PEG-V**. The catholyte **C3-PTZ** may react with anolyte **PEG12-V** in the pores of the CANF membrane, resulting in increased internal resistance of the battery (Fig. S12c). The **PEG12-PTZ/Me-V** and **C3-PTZ/Me-V** batteries displayed a stable energy efficiency but rapid capacity fading (Figs. 5a, 5b, S12d, and S12g). The same batteries also showed relatively low Coulombic efficiency (Table 2) due to the serious crossover of **Me-V** and **C3-PTZ**, which was confirmed by the CV scans after battery cycling (Fig. S12e and S12h). The **PEG12-PTZ/Me-V** and

C3-PTZ/Me-V batteries were charged/discharged for 100 and 50 cycles, respectively. Despite the fewer cycle numbers **Table 2**. Average Coulombic efficiency and capacity retention of the four batteries.

Battery	Average Coulombic efficiency (%)	Capacity retention per cycle (%)	Overall capacity retention
PEG12-PTZ/PEG12-V	99.71	99.90	68.6% after 300 cycles
C3-PTZ/PEG12-V	99.41	99.78	55.3% after 200 cycles
PEG12-PTZ/Me-V	99.48	99.63	62.9% after 100 cycles
C3-PTZ/Me-V	98.99	99.37	65.4% after 50 cycles

compared to those in the all PEGylated (300 cycles) and **C3-PTZ/PEG12-V** (200 cycles) batteries, an evident internal impedance increase of both batteries was still observed (Fig. S12f and S12i). The

increase of impedance was presumably owing to the precipitates formed from the reaction of **PTZs** with viologens on the membranes during the charge/discharge processes.

Mechanistic analysis

The pre- and post-cycling anolyte and catholyte solutions of all the four batteries were analyzed by proton nuclear magnetic resonance (^1H NMR, Fig. S13–S16) and CV to elucidate the possible degradation mechanism. The anolyte solutions were comprised of the anolyte species (**PEG12-V** or **Me-V**) and various amounts of catholyte species from the crossover; no additional ^1H NMR signals were observed, indicating that both the anolyte and catholyte species were electrochemically stable in the anolyte chamber. By contrast, besides the anolyte species from the crossover, unexpected proton signals (panels a in Fig. S13–S16) were detected in the catholyte chamber, suggesting that side reactions occurred in the electrochemically oxidizing catholyte chamber. We hypothesized three possible side reactions: (A) the catholyte molecules (**PEG12-PTZ** and **C3-PTZ**) underwent oxidative decomposition during the charging process; (B) viologen compounds crossed from the anolyte side, decomposing under the oxidizing conditions in the catholyte chamber; and (C) the reduced viologens (radical anion) reacted with oxidized **PTZs** (radical cation) in the catholyte chamber to form a new chemical species, rather than returning to their neutral, original states. Extensive experiments were conducted to confirm or eliminate the hypotheses. (1) CV scans of **PTZs** for repetitive 500 cycles (Fig. S6) indicated that the pure **PTZs** were electrochemically stable for single-electron oxidation, thus eliminating hypothesis A. (2) Repetitive CV scans of **PEG12-V** in different potential ranges were conducted. Though the interconversion between **PEG12-V** and its radical anion is reversible (Fig. S17) from -1.5 to -0.2 V vs Ag/Ag^+ , an evident current decrease was observed in the more positive scan range (from -1.5 to 0.8 V vs Ag/Ag^+), indicating the instability of **PEG12-V** under oxidizing conditions, which supports hypothesis B. (3) Separate

electrolysis of **PEG12-PTZ** and **PEG12-V** formed their corresponding radical anion and radical cation, respectively, and then the two radical species were mixed in a stoichiometric ratio. The ^1H NMR spectrum of the resultant solution is the sum of the spectra of **PEG12-V** and **PEG12-PTZ** (Fig. S18), suggesting neat redox neutralization of the two radicals without forming side products. This experiment result is against hypothesis C. Overall, the stability issue of viologen molecules under oxidizing conditions is a possible cause of battery degradation. The mechanistic analysis here not only provides an explanation for the battery capacity decay, but also emphasizes the importance of addressing the crossover issue by designing the next generation of redox-active molecules and suited membrane separators.

Concentration dependence

The **PEG12-PTZ/PEG12-V** batteries with higher concentrations were investigated to pursue higher energy density. The battery was initially assembled with 480 mM **PEG12-PTZ** and 200 mM **PEG12-V** mix electrolytes using a macroporous Daramic membrane as the separator. Before cycling, the battery displayed an impedance of $17.5 \Omega/\text{cm}^2$ (Fig. 6a). The battery was galvanostatically charged/discharged at a current density of $20 \text{ mA}/\text{cm}^2$ and presented undesirable polarization and low Coulombic efficiency (55%, Fig. 6b). Then electrolytes were diluted to $\frac{3}{4}$ and afforded 360 mM **PEG12-PTZ** and 150 mM **PEG12-V** mix electrolytes. Both impedance and polarization of the battery reduced with the decreased concentration with a Coulombic efficiency of 72%. Different concentrations of electrolytes impose different viscosity effects on battery impedance; the higher electrolyte concentration, the more viscous the electrolyte solution is; therefore, batteries with higher electrolyte concentration present higher impedance. After further diluted to concentrations of 240 mM **PEG12-PTZ** and 100 mM **PEG12-V**, the battery presented a stable Coulombic efficiency of 92% (Fig. 6c). The gradual decay of energy and voltage efficiencies were

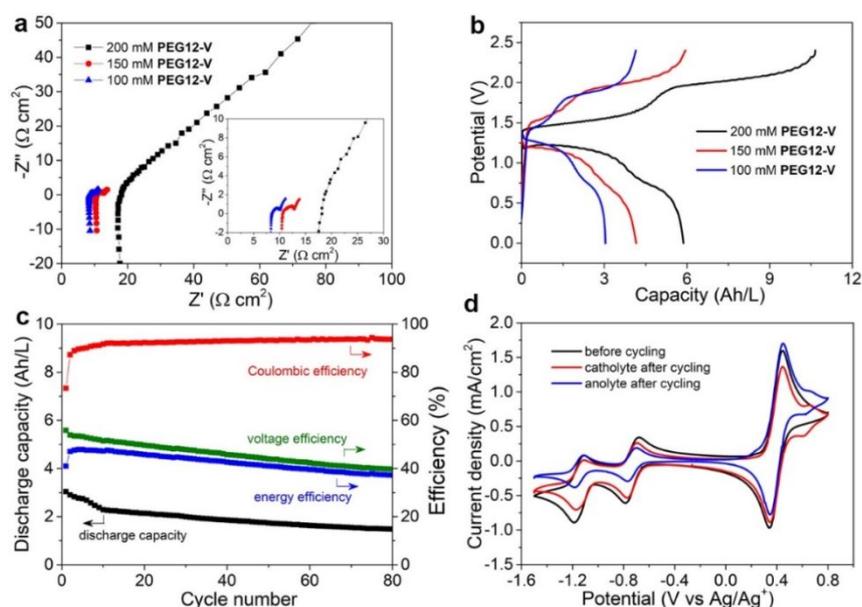


Fig. 6 (a) EIS of the **PEG12-PTZ/PEG12-V** batteries at different concentrations. (b) First charge/discharge curves. (c) Discharge capacity and

efficiencies of battery with 240 mM PEG12-PTZ and 100 mM PEG12-V mix electrolytes. (d) CV scans of catholyte and anolyte after cycling and mix electrolyte before cycling.

observed during cycling. CV scans of the post-cycling electrolyte indicated current density decrease for anolyte presumably due to the interaction of PEG12-PTZ and the reduced viologen species. The concentration-dependence study suggests that the high viscosity of PEG units and the possible side reaction of the anolytes and catholytes could be the two barriers to enhancing the energy density.

Conclusions

In summary, this study demonstrated that PEGylation of organic redox-active materials is a promising strategy to enhance the performance of NAORFBs by increasing the molecular size of compounds without sacrificing their electrochemical properties and alleviating the permeability of active materials in catholyte and anolyte for long cyclability. Combined with the CANF separator, the all-PEGylated battery (PEG12-PTZ and PEG12-V) delivered an excellent capacity retention of 99.9% per cycle and an average Coulombic efficiency of 99.7% after 300 charge/discharge cycles. The half-PEGylated (C3-PTZ/PEG12-V and PEG12-PTZ/Me-V) and non-PEGylated (C3-PTZ/Me-V) batteries were also investigated for structure–function relationship and mechanistic studies, and the instability of viologen molecules under oxidizing conditions was presented. This work highlights the importance of molecular engineering in NAORFBs and opens a new avenue for utilizing the PEGylation strategy in future redox flow battery technology.

Conflicts of interest

There are no conflicts to declare.

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