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Molecular engineering redox-active organic materials for nonaqueous redox flow battery

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Abstract

Nonaqueous redox flow batteries (NARFBs) have the potential as high-energy-density electrochemical storage systems due to their wider electrochemical windows compared with their aqueous counterpart. Before possible commercial application, three major performance metrics (energy density, power density, and cycling stability) of NARFBs need to be improved. With molecular diversity and scalability, redox-active organic materials (ROMs) are considered as promising redox-active materials for establishing sustainable NARFBs. Reasonable molecular engineering ROMs can obtain desired physicochemical properties, leading to the improvement of battery performance metrics. This mini review comprehensively summarizes the NARFB improvement through molecular engineering ROMs over the recent years, aiming to provide a guideline for the future battery design.

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Keywords: electrochemical energy storage, redox flow battery, nonaqueous electrolyte, molecular engineering, redox-active organic materials.

1. Introduction

With the continuous growth of the global population and the development of social economy, the electricity demand will increase from 23,300 TWh in 2020 to ~42,000 TWh by 2050 according to the World Energy Outlook 2021 (<https://www.iea.org/reports/world-energy-outlook-2021>). Traditional fossil fuels, particularly coal and natural gas remain cornerstones and account for more than 60% of electricity generation in 2020 (<https://www.iea.org/reports/world-energy-outlook-2021>). Their non-renewable nature and the ensuing environmental issues promote the rapid transition from fossil fuels to clean and abundant renewable energy alternatives. More than 256 GW of new renewable power generating capacity was installed in 2019, raising the global total to 2,839 GW by the year end (<https://www.ren21.net/reports/global-status-report/>). Given the highly intermittent nature due to the alternation of day and night and the changing seasons, developing large-scale energy storage technology such as batteries is greatly desirable in grid integration [1]. In such context, redox flow batteries (RFBs) are promising. Unlike other secondary batteries (e.g., lead-acid batteries and lithium-ion batteries), liquid electrolytes of RFBs are stored in two external tanks, and circulated through the porous electrodes, resulting in decoupled energy and power (Figure 1a). The energy capacity and power are determined by the electrolyte volume and cell size, respectively [1].

The first practical RFB was invented by Thaller with Cr(II)/Cr(III) and Fe(II)/Fe(III) as redox-active materials and H₂O as solvent [2]. Subsequently, the aqueous all-vanadium RFBs (VRFBs) were developed and represent the state-of-the-art [3]. Nevertheless, these aqueous RFBs show limited energy density due to narrow electrochemical window of water (1.23 V) [1]. In contrast, nonaqueous RFBs (NARFBs) using organic solvents provide a wider electrochemical window, which allows to increase the open circuit voltage of the battery, and thus achieve a higher energy density [1]. However, NARFBs are still in their infancy and need to be continuously optimized before possible commercial applications. Performance metrics of NARFBs generally include energy density, power density, and cycling stability. The redox-active materials are the core component, their properties substantially determine those metrics (Figure 1b). The redox-active materials for NARFBs

mainly contain metal coordination complexes (MCCs) and redox-active organic materials (ROMs) [4]. MCCs rely on the valence change of the central cations, such as tris (2,2'-bipyridyl) ruthenium tetrafluoroborate ($[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$) and iron acetylacetonate ($\text{Fe}(\text{acac})_3$), leading to expensive component and narrow redox-active materials choices [5, 6]. Instead, ROMs are considered as promising alternatives due to molecular diversity, environmental benignancy, and potentially low cost. More importantly, reasonable molecular engineering ROMs can obtain desirable physicochemical properties for NARFB application. Accordingly, we summarize the recent efforts towards improving the performance of NARFBs through molecular engineering.

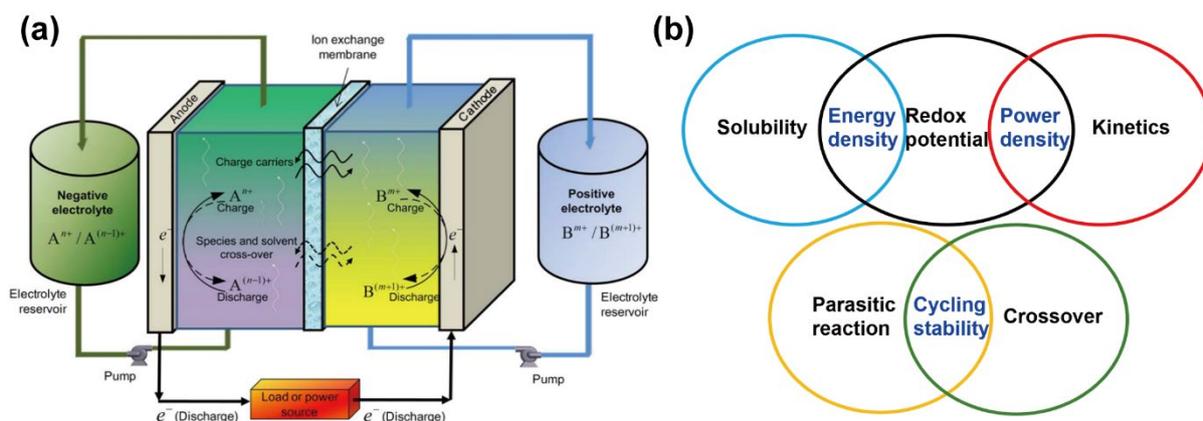


Figure 1. (a) Schematic illustrating the general structure of a typical RFB system. Source: Reproduced with permission from Ref. [1]. (b) Relationship between redox-active materials properties and NARFB performance metrics.

2. Energy density

Energy density is a crucial performance metric of NARFB, which represents the electric energy stored per unit volume. It is determined by eq. 1 according to

$$\text{Energy density} = \frac{nCFV}{\mu_v} \quad (1)$$

where n , C , F , and V represent the number of electrons transferred, the lower concentration of two ROMs, Faraday's constant, and the voltage of the battery, respectively. $\mu_v = 1 + \text{lower/high electrolyte concentration}$. Currently, even the most advanced VRFBs hold the relatively lower energy density than commonly commercialized lithium-ion batteries (max. 40 vs. 700 Wh L^{-1}) [7, 8]. To enhance the energy density of

NARFBs, the open circuit voltage (OCV) and electrolyte concentration should be as high as possible.

2.1. Redox potential

In recent years, ROMs families have continued to expand, mainly including metallocene, nitroxide radical, dialkoxybenzene, heteroaromatics, carbonyl, and nitrobenzene [9-15]. The redox potentials of conventional ROMs used in NARFBs are summarized in Figure 2a. Selecting ROMs with large potential difference is effective to achieve high OCV. In addition, molecular engineering can be employed to modify the redox potential of ROMs. One strategy is to introduce functional groups into the organic molecule to change the electronic properties. Pelzer et al. studied the redox potentials of 4178 molecules through high-throughput screening, where the molecules consisted of base groups and functional groups attached [16]. Figure 2b and 2c shows that the electron-withdrawing/-donating groups tend to increase/decrease the redox potentials. In this regard, Huo et al. attached electron-donating groups including methyl and methoxy to the benzophenone (BP) core [17]. The half-wave potentials of 4, 4'-dimethylbenzophenone and 4, 4'-dimethoxybenzophenone were -2.26 and -2.37 V vs. Ag/Ag⁺, respectively, which were lower than that of BP (-2.17 V vs. Ag/Ag⁺). Paired with 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBB), the resultant NARFBs achieved substantially high OCVs of up to 3.08 V. In a parallel study, as emerging catholyte material, tris(dialkyl)aminocyclopropenium (CP) salts were introduced with electron-withdrawing S atoms to increase the redox potential [18]. Density functional theory (DFT) predicted comparably high redox potentials of these four derivatives based on different substituents on sulfur (Figure 2d). Among them, 2-Me²⁺ showed the lowest NBO charge at C_α and predictably minimal degree of parasitic reaction. Subsequent electrochemical characterization of 2-Me²⁺ showed a quasi-reversible reaction at +1.35 V vs. Fc/Fc⁺. NARFB based on 2-Me²⁺ and phthalimide showed an OCV of 3.2 V, which is the highest value up to date. Furthermore, Yan et al. modified the parent 10-methylphenothiazine through the installation of electron-withdrawing diaminocyclopropenium (DCA) substituents [19]. The final product showed ~300 mV higher redox potential. Two DCA substituents simultaneously stabilized the second oxidation through resonance delocalization of the charged radical.

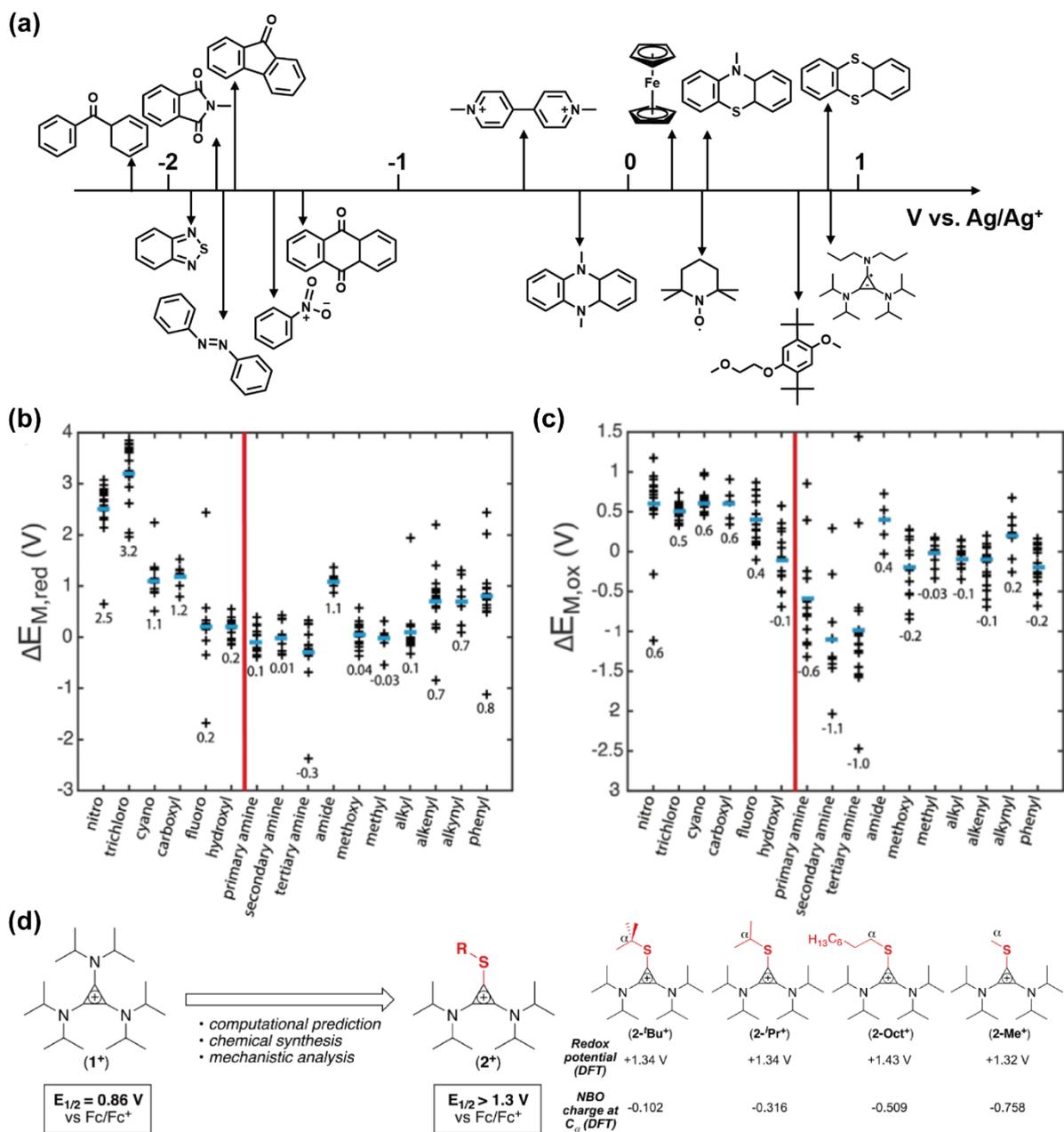


Figure 2. (a) Redox potentials of conventional ROMs used in NARFBs [9-15]. (b, c) The effect of introducing additional functional groups on the potential of organics. (b) $\Delta E_{M,red}$ and (c) $\Delta E_{M,ox}$. The red vertical lines divide the plot into electron-withdrawing functional groups (left) and electron-donating functional groups (right). The mean value of $\Delta E_{M,red/ox}$ for each functional group, given by the number beneath each column of data points, is shown with the blue horizontal line in each column. Source: Reproduced with permission from Ref. [16]. (d) Derivatives to investigate the impact of alkyl substitution on catholyte properties. Source: Reproduced with permission from Ref. [18].

Although introducing functional substituents to the parent ROMs is relatively straightforward, it will

inevitably increase the molecular weight, and also impose possible negative effect on solubility and stability. Dai et al. presented a new method to enhance the redox potential through diluting the electron density in the π -conjugated skeleton of ROMs [20]. Among four N-based heterocyclic compounds, pentatomic carbazole held the highest atomic-dipole-moment-corrected Hirshfeld (ADCH) charge population, indicating the most difficulty to withdraw electrons from the N atom. It led to a higher redox potential of 0.5-0.6 V than other hexatomic compounds. This approach is more effective to increase the redox potential by ~ 0.3 V compared with the introducing functional substituents method. Hu et al. introduced C=C double bond into pentatomic nitroxide radical to increase the redox potential [21]. 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl showed 100 mV higher redox potential than 3-carbamoyl-2,2,5,5-tetramethyl-pyrrolidine-1-oxyl radical mainly due to the lower the lowest solvation free energy difference (ΔG_{sol}) and charge population sum in N-O. In addition, Liu et al. proposed fused conjugation to construct bipolar molecules [22]. The fused conjugation in QPT-OMe molecular facilitates the redistribution of electron density from the ketone moiety to the quaternary N moiety, leading to broadened voltage gap.

2.2. Solubility

As aforementioned, the energy density of NARFBs partly depends on the concentration of the redox-active materials. Polar solvents such as acetonitrile (MeCN) and N,N-dimethylformamide (DMF) are widely adopted for NARFBs. According to the “like dissolves like” general rule, certain polar functional groups can be attached to ROMs to improve the solubility [23]. Huang et al. introduced the poly ethylene oxide (PEO) chains to the symmetrical DBB molecular [23]. The growth of dipole moments led to improved solubility in the carbonate-based electrolyte. Particularly, developing liquid active materials such as 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB), which has high miscibility with the polar solvent, opens up a new strategy to build high-energy-density NARFBs. Paired with DBMMB, Xu et al. studied a series of liquid nitrobenzene-based anolyte materials [15]. All-liquid electroactive materials achieved a supreme volumetric energy density of 37.8 W h L^{-1} at 1.0 M. Similar strategy was adopted in the non-polar

phenazine molecules [24]. The introduction of alkyl ether chains enhanced the solubility whilst spatially hinders the charged radical from parasitic reactions. The final product, 5,10-bis(2-methoxyethyl)-5,10-dihydrophenazine (BMEPZ) exhibited improved solubility of 0.5 M in MeCN and two reversible single-electron redox reactions. The BMEPZ/9-fluorenone (FL) based NARFB yielded high energy density of 17 Wh L⁻¹ at 0.4 M.

Ionic modification is another method to improve the solubility of ROMs, which was first reported by Wei et al [25]. The ferrocene molecule permitted high electrochemical reversibility and stability, while the introduction of tetraalkylammonium moiety with a bis(trifluoromethylsulfonyl)amide anion (TFSI⁻) would lead to 20 times increase in solubility of ferrocene in the carbonate-based electrolyte. A combined nuclear magnetic resonance (NMR) and DFT study revealed that the tetraalkylammonium ionic moiety preferred to interact with solvent molecules and counter ions. Very recently, Zhen et al. synthesized a series of ionic-derivatized anthraquinone compound through the incorporation of the acetamide and tetraalkylammonium ionic moiety [26]. The different counter anions had a significant influence on the solubility of ROMs. Especially, 2-(N,N,N-trimethylamino)-N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)-bis(trifluoromethylsulfonyl)imide (AQNTFSI) had the highest electronic binding energy and relatively long ion-pair distance, resulting in the highest solubility of 0.91 M in MeCN. The resultant NARFB based on 0.1 M AQNTFSI and 0.2 M (ferrocenylmethyl)trimethylammonium bis(trifluoromethanesulfonyl)imide (FcNTFSI) delivered stable cycling with 78.5% discharge capacity retention over 100 cycles and a practical energy density of 4.6 Wh L⁻¹.

Constructing eutectic systems with low-temperature polynary ionic or metallic mixtures is an effective strategy to increase the mole fraction of redox-active materials in the electrolyte. Zhang et al. prepared deep eutectic solvents (DESS) by mixing metal salts (FeCl₃ or AlCl₃) and hydrogen-bond donors (urea), resulting in a hybrid Fe-Al RFB with a high energy density of 166.2 Wh L⁻¹ [27]. Zhang et al. also used biredox eutectic as the electrolyte, obtained from anode and cathode ROMs (N-butylphthalimide and 1,1-dimethylferrocene), which can obviously alleviate the crossover issue and achieve high concentration of up to 3.5 M [28].

Figure 3a shows the theoretical and demonstrated max. energy density capacity of the recently reported high-dense NARFBs [15, 24, 28-34]. After the improvement on redox potential and solubility of ROMs, related NARFBs can achieve ultrahigh proof-of-principle theoretical energy density ($> 100 \text{ Wh L}^{-1}$). However, practical high-concentration electrolyte will deteriorate due to increased viscosity, polarization resistance, solid precipitation, etc. These problems prevent the practical value from approaching the theoretical value, which need to be well addressed in the future.

Recently, a new strategy based on “solid capacity booster” was proposed to enhance the electrolyte capacity [35]. In the battery system, the solid charge storage materials, as the major charge storage media, are indirectly charged/discharged via a soluble redox mediator. Zanzola et al. developed a RFB with polyaniline as a solid charge storage material and Fe(III/II) and V(IV/III) as potential redox mediators, which achieved a high specific capacity of 64.8 mA h g^{-1} at 38.5 mA cm^{-2} [36].

3. Power density

Power density is another important metric closely related to the capital cost of NARFBs. Commercialized VRFBs deliver a cost of $\$320 \text{ kWh}^{-1}$, still much higher than the target of the U.S. Department of Energy ($\$100 \text{ kWh}^{-1}$) [37]. Enhancing power density can reduce the area of the battery stack, resulting in a lower capital cost.

The power density is determined by eq. 2

$$\text{Power density} = \frac{I \times V}{S} \quad (2)$$

where I , V , and S are the discharge current, the output potential, and the surface area, respectively. When the operating current density (j) increases, the voltage loss (including activation loss, ohmic loss and concentration loss) subsequently increases, leading to lower electrolyte utilization and voltage efficiency (VE). In order to increase the power density, it is necessary to enhance OCV and rate capability of NARFBs. The methods of increasing OCV have been discussed in section 2.1.

Park et al. presented a method to enhance the rate-capacity through a combination of computational tools and experimental methods [38]. The isomeric effect between 5,12-naphthacenequinone (NAQ) and

1,2-benzanthraquinone (BAQ) were studied, which revealed that BAQ showed lower redox potential due to an asymmetric spin density distribution and a lower lowest unoccupied molecular orbital (LUMO) energy level (-3.82 vs. -3.56 eV). In addition, BAQ showed a lower difference between highest occupied molecular orbital (HOMO) and LUMO (-1.98 vs. -2.25 eV), leading to higher electrical conductivity and thus better rate performance, especially at high current density (~ 300 vs. ~ 100 Wh Kg $^{-1}$ at 6 C) of the BAQ based battery. Besides, ROMs should have fast mass- and charge-transfer kinetics to maintain high performance at high j . Figure 3b compares the kinetic rate constant (k_0) and diffusion coefficient (D) of the recent reported redox-active materials [6, 11, 15, 24, 29, 39, 40]. Generally, ROMs possess smaller molecular size than MCCs and polymer-based redox molecules (PRMs), leading to faster mass- and charge-transfer kinetics. In addition, high electrolyte conductivity and low membrane resistance are required to achieve high-rate performance.

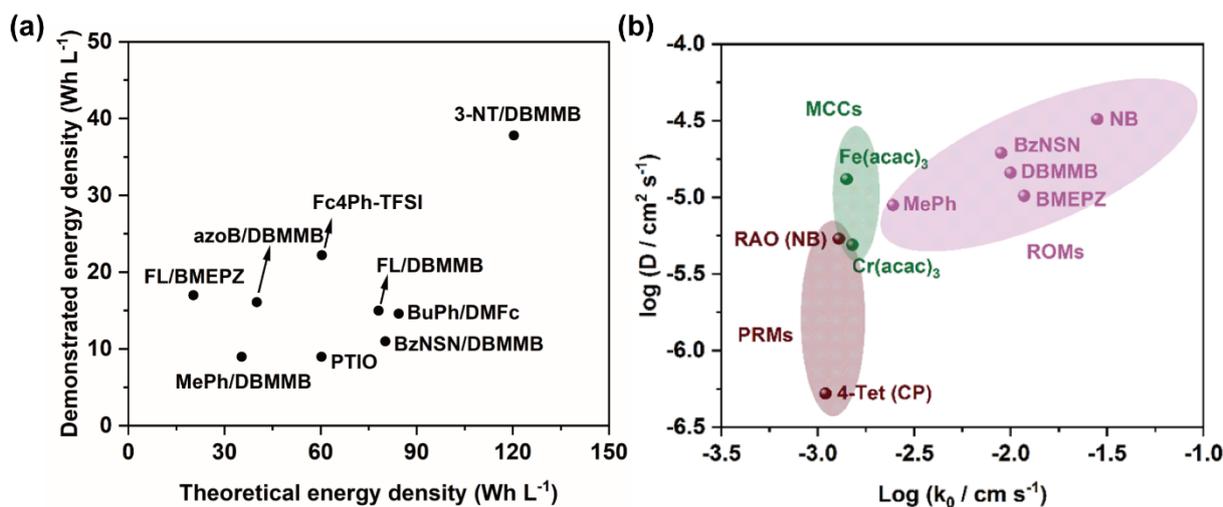


Figure 3. (a) The theoretical and demonstrated max. energy density capacity of the recently reported high-dense NARFBs [15, 24, 28-34]. (b) Comparison of the kinetic rate constants (k_0) and diffusion coefficients (D) of typical ROMs, MCCs, and PRMs reported in the literature [6, 11, 15, 24, 29, 39, 40].

4. Cycling stability

4.1. Parasitic reaction

Cycle stability of NARFBs is the most important metric, which guarantees long-term electrochemical energy storage devices for grid integration. The capacity loss mainly originates from parasitic reactions and crossover issue. Among them, performance degradation caused by parasitic reaction is more harmful due to the

unrecoverable capacity. The way to enhance the stability of ROMs can be categorized into two types. One is through intermolecular interaction such as tuning the Van der Waals interaction among ROM, solvent molecule, supporting electrolyte and additives. For example, to explore the capacity loss mechanisms, Wei et al. studied the system based on DBMMB and FL with different supporting electrolytes and solvents [32]. The electrolyte environment would affect the stability of the redox-active material especially in the charged state, which determined the cycling stability of NARFBs. The other is through intramolecular interaction such as expanding the conjugation and protecting the redox center by steric effect. To improve the stability of the ROMs, Ahn et al. proposed a method according to the bioisosteres strategy in the medicinal chemistry field [41]. 1,3-azole heterocycle was introduced into the pyridinium core and an extended π -conjugated system was established, which stabilized the charged radical after one-electron reduction. Paired with ferrocene derivatives, the resultant NARFB delivered high stability of 65.7% capacity retention after 500 cycles at 0.1 M.

Computational chemistry provides a new path for the study of parasitic reactions. Assary et al. performed the first-principles simulations to compute the thermodynamic feasibility and activation barriers of parasitic reactions (deprotonation, dimerization, hydrolysis, and demethylation) of a series of 1,4-dimethoxybenzene (DMB) derivatives in the charged state [42]. Taking the study of demethylation in propylene carbonate (PC) as an example, DFT results showed that 2,5-dimethyl DMB corresponded to higher free energies changes ($\Delta G(\text{CH}_3^+)_{\text{PC}}$) and activation enthalpies ($\Delta H^\ddagger(\text{CH}_3^+)_{\text{PC}}$) than those DMB derivatives, indicating the higher stability. Similar work has also been done to study the parasitic reactions of 2,1,3-benzothiadiazole (BzNSN) and paraquat derivatives [43, 44].

4.2 Crossover

Conventional NARFBs are always hindered by the electrolyte crossover, leading to self-discharge, complex side reactions between the mixed electrolyte, low Coulombic efficiency (CE), and capacity decay. One reason is the employment of different concentration of anolyte and catholyte active materials. Another reason is the utilization of porous membranes. The large pore size of the porous membranes is beneficial for the high ion

conductivity, but it also results in low ion selectivity, leading to serious crossover. Although the ionic exchange membranes and/or ceramic membranes can significantly alleviate the crossover issue, their high area-specific resistance seriously limits the power of NARFBs. [45]. To alleviate the crossover issue, several strategies have been developed: (1) Tailoring the size of ROMs with compatible size-exclusion separators. (2) Employing bipolar ROMs to construct symmetric NARFBs. (3) Physically mixing the anode- and cathode-active ROMs [15]. (4) Constructing eutectic mixture [28].

Hendriks et al. provided a general method to establish effective size-exclusion [39]. Electrochemical characterization of CP dimers revealed that the linker length of four carbons was necessary for electrochemical reversibility and stability of redox dimers. Subsequently, a series of n-butyl-linked CP oligomers were synthesized and evaluated in H-cell with cross-linked PIM-1 membranes. The results showed that the growth of oligomer size from monomer to tetramer led to decreased crossover of the batteries. The final NARFB based on tetramer exhibited excellent cycling stability without observable crossover over 2 days. In the parallel work, Milton et al. invented two nanoscale macromolecular ROMs based on perylene diimide and ferrocene, respectively [46]. Paired with the size-exclusion dialysis membrane, the final battery avoided crossover and successfully cycled 450 cycles (74 days) with a high CE of 99.868%. Furthermore, Baran et al. attached the redox centers to the oligoethylene oxide scaffold, which not only bonded the redox centers together, but also served to modify the solubility [40]. The resultant liquid oligomers exhibited infinite miscibility with organic solvents and the increased size could minimize membrane crossover.

The most intensively studied VRFBs employ the same vanadium in catholyte and anolyte, which mitigates the electrolyte crossover [3]. In addition, the capacity loss caused by crossover can be regenerated by remixing the electrolyte or regulating the pressure. Based on that, bipolar ROMs through molecular engineering can be designed for symmetric NARFBs. In the work of Hwang et al., electroactive ferrocene group was attached to substitute H atom at the N-site of phthalimide, resulting in a bipolar redox-active material with redox potential difference of 1.94 V [47]. The resultant symmetric coin-type cell delivered a high average CE of 97.3% without

obvious capacity loss over 50 cycles at 2.0 C. Subsequently, Zhen et al. designed a bipolar ROM of 1-(ferrocenylmethyl-amino)-anthraquinone (FcMeAAQ) based on ferrocene and anthraquinone. The high stability involving one-electron redox reaction was proved by the electrochemical characterization and DFT calculation [48]. The resultant symmetric NARFB exhibited an OCV of 1.42 V, CE of 90.8%, and energy efficiency of 81.8% over 100 cycles at 2 mA cm^{-2} . Very recently, Our group proposed a series of ionic BROMs composed of ferrocene (Fc) and phthalimide (Ph) moieties with high solubility of up to 2.27 M and inherent high ionic conductivity approximating to the widely used supporting electrolyte in DMF [34]. The resultant symmetric NARFB showed excellent cycling stability with capacity retention of 99.8% per cycle over 50 cycles at 20 mA cm^{-2} .

Table 1 summarizes crucial parameters in terms of cycling stability and rate capability of the recent advanced NARFBs.

5. Conclusions and perspectives

In this work, we summarize the general strategies through molecular engineering the redox-active organic materials to improve the performance of NARFBs in terms of energy density, power density, and cycling stability. The structural diversity and high scalability of ROMs render fine-tailoring of the desired properties for NARFB application. The well-developed function-oriented organic synthesis can promote the development of novel ROMs with wide potential difference, high solubility, multi-electron transfer reaction, leading to higher energy density. Fast mass- and charge-transfer kinetics of ROMs meets the requirements of high-rate capability. Cycling stability can be improved through increasing stability of ROMs in the charged state and alleviating the crossover issue. The rapid development of computational chemistry promotes the molecular design of ROMs, which provides a viable path to screen ROMs. Combining computational tools and experimental methods is believed to facilitate the development of high-performance active materials and thus to accelerate the application of NARFBs.

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Competing interests

The authors declare no competing financial interest.

Table 1. Crucial parameters of the recent advanced NARFBs in terms of cycling stability and rate capability.

Active materials	OCV (V)	Theo. Capacity (Ah L ⁻¹)	Cycling stability			Rate performance		Ref.
			<i>J</i> (mA cm ⁻²)	CE/VE/EE (%)	Discharge capacity retention (%)/Cycle number	<i>J</i> (mA cm ⁻²)	discharge capacity (Ah L ⁻¹)	
PTIO (0.1 M)	1.7	2.68	20	96/75/72	48.3/35	20	0.88	[30]
BzNSN/DBMMB (0.1 M)	2.36	2.68	40	95/73/69	82.7/160	40	0.92	[31]
TMAPBTP-TFSI/BTMAPFc-TFSI (0.1/0.15 M)	1.16	2.68	18	99/74/73	60/500	4.5/9/18/27	2.45/2.40/2.32/2.10	[41]
BuPh/DMFc (0.1 M)	1.8	2.68	60	93/55/51	72/500	20/40/50/60/80	1.27/1.21/1.16/1.06/0.93	[28]
3-NT/DBMMB (0.1 M)	2.25	2.68	60	93.7/76.6/71.8	83.6/50	50/60/70/80	2.6/2.1/1.5/0.9	[15]
NI-TFSI/Fc-TFSI (0.1 M)	1.89	2.68	40	97.0/79.6/77.2	90.3/100	40/60/80/100/120	2.34/2.00/1.70/1.42/1.24	[49]
AQNTFSI/ FcNTFSI (0.025 M/0.05 M)	1.53	1.34	10	96.8/85.2/82.4	86/200	10/40/80	1.04/0.92/0.44	[26]
PI- PF ₆ /CPS-PF ₆ (0.1 M/0.05 M)	3.2	1.34	10	83/74/70	23/30	10	1.24	[18]
FL/BMEPZ (0.1/0.05M)	1.61	2.68	20	96/73/70	88/200	20	2.08	[24]
azo/DBMMB (0.05 M)	2.5	1.34	80	92/75/70	64.5/50	60/70/80/90/100	1.13/1.1/0.97/0.88/0.85	[33]
Fc4Ph-TFSI (0.05 M)	2.04	1.34	20	94.6/81.4/77.0	90/50	10/20/30/40	0.76/0.56/0.46/0.34	[34]

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