

Chapter 6.1 Aqueous organic flow batteries

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Abstract

In the chapter, we provide a brief introduction to organic flow batteries, followed by a discussion of aqueous organic flow batteries and their advantages, challenges and potential opportunities. Key attributes include solubility, viscosity, crossover, lifetime, analytic methods, molecular engineering, cost, membrane, pH imbalance, and toxicity. We review different classes of redox molecules used for aqueous organic flow batteries, corresponding parameters including redox potential, solubility, fade rate, operational pH, decomposition mechanism, and various aspects of cell performance. We provide our perspectives on future directions to advance the commercialization of aqueous organic flow batteries.

Key words

Organic flow battery, aqueous, quinone, lifetime, cost, molecular decomposition.

An organic flow battery is a flow battery that reversibly converts electrical energy into the chemical energy of bond formation and cleavage through redox reactions of organic or metalorganic molecules. The two electrolytes contain redox species with distinct redox potentials: to conveniently distinguish them, hereafter we call the negolyte (negative electrolyte) the electrolyte comprising the lower-potential species and the posolyte (positive electrolyte) the electrolyte comprising the higher-potential species.

Featuring their rich redox chemistry, structural diversity and tunability, and earth-abundance of composing elements, organic molecules are promising as energy-carrier materials. Organic flow batteries (OFBs) are therefore the subject of a great deal of R&D. Depending on whether the redox-active compounds are dissolved in aqueous or non-aqueous solvents, OFBs are further categorized into aqueous organic flow batteries (AOFBs) and non-aqueous organic flow batteries (NAOFBs). Organic solvents typically utilized demonstrate broad stability windows of > 4 V; and therefore, nonaqueous FBs offer opportunities for higher energy density if organic redox couples with high solubility and extreme redox potentials are developed to leverage the broad voltage window of organic solvents.¹ Aqueous electrolytes are highly ion-conductive and offer higher power density; they are also typically nonflammable and have negligible solvent cost. For these reasons we focus on AOFBs.

AOFBs have typically utilized quinones, viologens, phenazine, nitroxide radicals, aza-aromatics, and iron coordination complexes.² They operate in acid, base, or near-neutral pH, typically with ion-selective membranes designed to transport monatomic cations or anions. Great progress has been made on developing organic redox molecules for AOFBs, particularly for negolytes. In contrast, the development of active species for posolytes has lagged behind. Several review articles have been published recently by different groups with their own perspectives on the development of AOFBs.²⁻⁸ For example, Kwabi, Ji, and Aziz recently collected, analyzed, and compared capacity fade rates from all aqueous organic electrolytes that have been utilized in the capacity-limiting side of flow or hybrid flow/nonflow cells; categorized capacity fade rates as being “high” ($>1\%/day$), “moderate” ($0.1-1\%/day$), “low” ($0.02-0.1\%/day$), and “extremely low” ($\leq 0.02\%/day$), and discussed the degree to which the fade rates have been linked to decomposition mechanisms. Because of the aforementioned reviews, here we aim to provide a brief and general overview.

6.1.1 Advantages

Advantageous features of aqueous-soluble redox organics are elaborated below.

1. Organic and metalorganic compounds composed of earth-abundant elements such as C, H, O, N, S, P, and Fe are potentially low-cost. In addition, redox organic molecules could possibly be derived from renewable biomass. In particular, depolymerized biomass can be an important feedstock of redox organic molecules.⁹ Manufacturing organics or metalorganics on a large scale could be advantageous if cost-effective and readily accessible bio-based feedstock is used.
2. Redox organic molecules are able to undergo multiple electron transfers. For example, quinone and phenazine derivatives have demonstrated two-electron transfer in both aqueous and nonaqueous electrolytes. This doubles the volumetric capacity compared to single-electron transfer molecules of the same solubility, and also decreases the concentration of radicals, which tend to undergo undesirable side reactions.
3. Redox organic and metalorganic compounds have much larger molecular sizes than redox inorganic compounds. Crossover rates of redox organics are thus effectively suppressed, leading in some cases to extremely low permeability.¹⁰⁻¹²
4. Molecular engineering is continually being used to improve the performance of AOFBs. Improved molecular design has proven to be powerful in adjusting redox potentials, enhancing molecular solubility, improving molecular stability, and ultimately developing high-performing molecule-based electrolytes with adequate volumetric capacity and extremely long lifetime.
 - a. The redox potentials of molecules can be adjusted by introducing functional groups. For instance, the sulfonate group is electron-withdrawing; hence, the redox potential of anthraquinone-2,7-disulfonic acid (AQDS) is 50 mV higher than that of anthraquinone-2-sulfonic acid (AQS) because of the two sulfonate groups in AQDS and one in AQS.¹³ Similarly, the deprotonated hydroxyl group is electron-donating; hence the potential of 2,3,6,7-tetrahydroxyanthraquinone is found 130 mV lower than that of 2,6-dihydroxyanthraquinone because of the two extra alkoxide groups.¹⁴
 - b. Introducing water-solubilizing functional groups, including ionic groups such as SO_3^- ,¹⁵ O^- ,¹⁴ PO_3^{2-} ,¹⁶ COO^- ,¹⁰ ammonium cations¹⁷; and non-ionic hydrophilic groups, *e.g.*, polyethylene glycol (PEG),¹¹ to hydrophobic redox molecules via covalent bonds can enhance water solubility by several orders of magnitude. For instance, anthraquinone itself is virtually insoluble (< 1 mM) in water; the solubility of 2,6-dihydroxyanthraquinone (DHAQ) in pH 14 KOH reaches 0.5 M; the solubility of AQDS in pH 0 H_2SO_4 reaches 1.5 M; and 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)-ethoxy)anthracene-9,10-dione (AQ-1,8-3E-OH) is completely water-miscible with a molecular concentration of 2.2 M.
 - c. Significant improvements on molecular stability have been made by different groups through rational molecular design,^{1, 2, 18} and extremely stable redox molecules, exhibiting capacity fade rates $< 0.02\%/ \text{day}$ in AOFBs, have been demonstrated recently.^{2, 10, 12, 16, 19}

Figure 1 shows a schematic of redox organic molecule discovery paradigm. Discoveries of important organic redox molecules for OFBs have often been achieved by a multi-disciplinary team. First, guided mainly by chemical insight, organic chemists come up with a molecule pool filled with numerous desirable redox molecules in mind. Second, they select a synthesizable molecule from the pool with retrosynthetic analysis. Sometimes they have to “re-design” or slightly modify molecular structure given the accessible precursors. They explore a series of synthetic conditions to obtain the desired pure product, whose structure is well-characterized by different techniques. Third, electrochemists evaluate and further downselect those molecules with fast electrochemical reaction kinetics, high aqueous solubility, and high stability. Fourth, flow cell experts run the selected molecule-based aqueous flow cells including cell cycling and polarization curves to evaluate metrics of cell performance such as open circuit voltage, area-specific resistance, peak galvanic power density, and capacity fade rate. It is essential to perform post-cycling chemical analyses as, in most instances, redox molecules decompose too rapidly to meet a decadal lifetime criterion: learning the decomposition mechanisms is the first step in re-designing molecules for improved performance. After a few rounds of these iterations, there might be a candidate meeting the critical requirements for commercialization. Once the molecules are determined, organic chemists further optimize the synthetic routes and conditions to make sure the syntheses are environmentally friendly and inexpensive at mass-

production scale. If development goes well, the intellectual property is commercialized by a startup company or licensed to an established company.

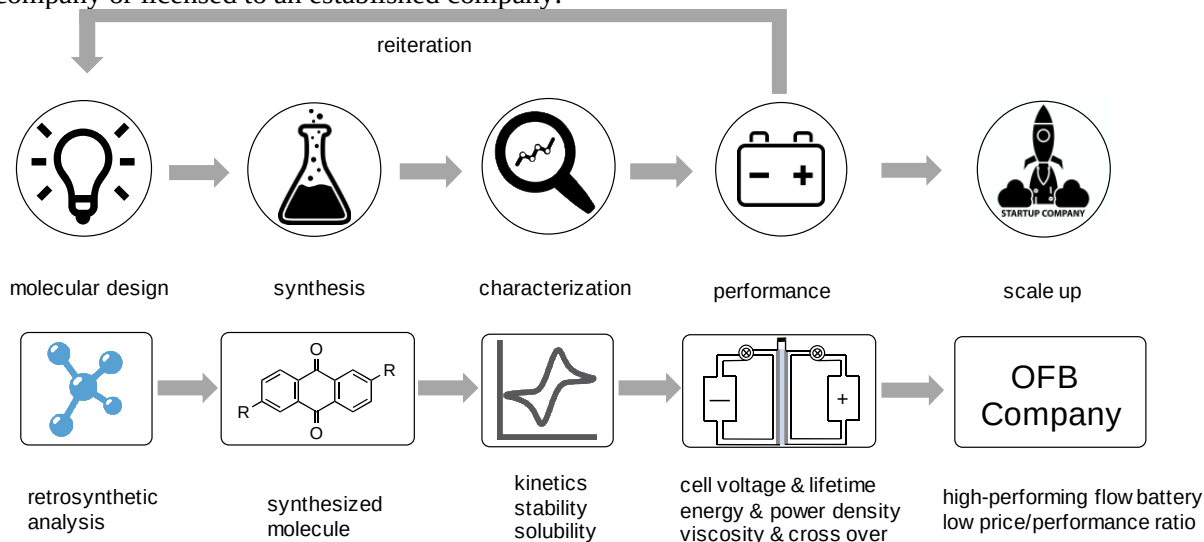


Figure 1. Schematic of redox organic molecule discovery paradigm. The top row presents the logical flow chart in general; the bottom row indicates what needs to be implemented and evaluated in order to move the species toward OFB commercialization. (Source: Yan Jing)

6.1.2 Challenges and opportunities

- Solubility

The aqueous solubility of redox molecules designed for AOFBs is significantly influenced by the type and number of water-solubilizing groups and the choice of supporting salt. Most of the reported water-soluble redox molecules have demonstrated charge-storing capability of more than one mole electrons per liter of electrolyte. The aqueous solubility of redox molecules can be increased by incorporating multiple water-solubilizing groups via covalent bonds.¹⁵ Introducing molecular asymmetry,^{20, 21} or mixing redox organic isomers¹⁹ have been found helpful in raising solubility.

Redox molecules designed for NAOFBs are usually screened in different organic solvents to obtain high solubility. Following the “like dissolves like” principle, a redox molecule with polar groups demonstrated good solubility in a polar organic solvent.²²

It has been found that both quantum-mechanical molecular static²³ and molecular dynamic²⁴ theoretical simulations can reasonably well predict redox potentials of organic molecules in electrolytes; nonetheless, it has been less successful in predicting their solubilities. Unlike the redox potential, the solubility involves a comparison of molecular free energies in solution and in the crystalline form, and predicting the crystal structure has proved elusive.

Compared to dissolving redox species in electrolytes, the suspension of particulates comprising redox species²⁵; alternatively, the utilization of redox-targeting reactions in order to transport charge through liquid electrolytes to solids for storage in tanks,²⁶ transcend the solubility limitations and promise high volumetric capacity. The extent to which electrochemical reaction kinetics or hydrodynamic or mass transfer processes are compromised await further investigation.

- Viscosity

Viscosity of electrolytes containing inorganic compounds may slightly increase with the increased concentration of inorganic compounds. Viscosity of electrolytes containing organic molecules could significantly increase with increasing concentration because of the increased molecular size and the corresponding range of intermolecular interactions. The high energy density of concentrated redox organics may trade off against slow mass transfer and high pumping losses caused by high viscosity in OFBs in ways that are not apparent from the behavior of inorganic FBs.

Many organic molecules used in OFBs possess aromatic systems, which generate π - π interactions. These interactions can be significantly strengthened in concentrated electrolytes where distances between organic molecules are reduced. The associated molecular interactions lead to higher viscosity.

- Crossover

If an OFB is projected to have decades-long operation time, besides the extremely stable redox organic couples, crossover rates of redox molecules in both states through the membrane must be extremely low. Otherwise, the OFB will have a low coulombic efficiency, a fast capacity fade rate, and a short operational lifetime. In vanadium flow batteries (VFBs), although fast vanadium crossover decreases current and energy efficiencies, it does not cause a chemical contamination problem leading to permanent capacity fade, because the posolyte and negolyte can be re-mixed and the states of charge rebalanced. In contrast, crossover of redox species in OFBs can result in irreversible capacity fade even if redox molecules remain intact. Increased molecular size in OFBs compared to inorganic redox species can drastically reduce the crossover rate of active species.¹⁰ Nevertheless, when the molecular size is large enough to make crossover rates virtually negligible, e.g. by forming oligomers or polymers, and the concentrations are raised to useful levels, unacceptably large viscosity increases tend to result.²⁷ Analogously to the operation of VFBs, Winsberg *et al.* demonstrated a symmetric aqueous organic flow battery,²⁸ in which a low potential molecule (phenazine) and a high potential molecule (2,2,6,6-tetramethylpiperidiny-N-oxyl) are covalently bound to form a bipolar molecule composing both negolyte and posolyte active species. In an analogous approach to Fe-Cr FBs utilizing porous separators, Luo *et al.* simply mixed negolyte with posolyte species to minimize the effects of crossover of redox species.²⁹ In both these cases, however, because roughly half of redox-active material is not utilized, the viscosity and cost of the electrolytes are increased. Efforts based on a simple redox molecule intrinsically possessing two widely-separated redox potentials,^{30, 31} so that the single molecule can serve as the redox species of both negolyte and posolyte, have met with limited success. Attaching multiple ionic groups to a redox molecule increases Coulomb repulsion (electrostatic repulsion) against membranes,^{12, 32} thereby reducing crossover of the redox molecule without increasing the viscosity of the electrolyte.

- Lifetime

Evaluating the lifetime of a single redox molecule in full cells is difficult because both molecular decomposition and crossover across the membrane contribute to capacity fade. Goulet and Aziz developed the “unbalanced, compositionally symmetric flow cell method” in which the electrolytes are compositionally symmetric but volumetrically unbalanced. One side is the capacity limiting side during both charge and discharge, and the other side is non-capacity limiting side.³³ Diffusion of redox species through the membrane is virtually eliminated because the oxidized and reduced states of the single redox molecule reside on both sides of the membrane with equal durations, suppressing the influence of crossover on capacity fade.

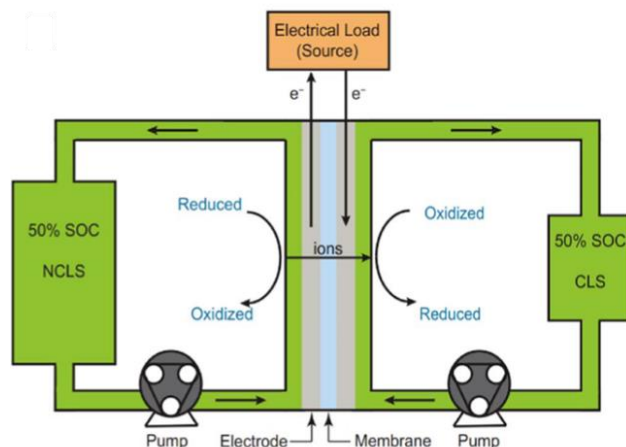


Figure 2. Schematic of volumetrically unbalanced compositionally symmetric cell, with identical electrolytes at identical concentrations at 50% state of charge in reservoirs of different volumes. Active

species crossover is suppressed, and measured capacity fade may be attributed to the state of the capacity limiting side. Reprinted with permission from ref. 32. Copyright 2018 Electrochemical Society. (Fig.1a, A1466)

When the crossover of redox species in an OFB is negligibly small or eliminated in an unbalanced, compositionally symmetric flow cell and precipitation is avoided, molecular instability, i.e., (electro)chemical decompositions of redox molecules become the main reasons leading to capacity fade of an OFB. Electrochemical decomposition involves the electrode as an electron donor or acceptor; its trajectory depends on the history of the electrode potential. Typically, this results in the capacity fade rate being proportional to the charge-discharge cycling rate. Chemical decomposition tends to occur homogeneously throughout the electrolyte at a rate that is independent of cycling. Both electrochemical and chemical decomposition can be strongly influenced by aspects of the chemical environment including concentration, solvent, salt, pH, temperature, electrolyte-contacting materials, etc. Identified chemical decomposition mechanisms include nucleophilic addition/substitution, disproportionation, and dimerization.² Electrochemical decomposition mechanisms including over-reduction or over-oxidation, which can be highly sensitive to the applied potential. When evaluating the capacity fade rate of a cell utilizing a new redox molecule of unknown lifetime and decomposition mechanism, it is important to report both time-denominated and cycle-denominated fade rates (%/day and %/cycle). In the absence of confounding mechanisms such as leakage, the time-denominated fade rate reflects chemical instability and the cycle-denominated fade rate reflects electrochemical instability of the molecule. In virtually all cases exhibiting reasonably long lifetimes reported to date, in which sufficient experimentation has been performed to distinguish between time-denominated and cycle-denominated mechanisms, the capacity fade has been shown to be time-denominated.²

- Analytic methods

Galvanostatic and/or potentiostatic methods are commonly used to evaluate cycling stability of OFBs. If an OFB fades rapidly (faster than about 1%/day) then purely galvanostatic cycling is adequate for measuring the fade rate with a reasonable degree of uncertainty. If, however, a FB exhibits a low fade rate (less than ~1%/day), artifacts in the purely galvanostatic cycling method render it inaccurate, as galvanostatic cycling is highly sensitive to fluctuations caused by diurnal temperature changes and drifts in membrane resistance. To overcome the inaccuracy, purely potentiostatic cycling, or galvanostatic cycling followed with a potentiostatic hold at the end of a charging step and of a subsequent discharging step (also known as CCCV or IU mode charging and discharging), is essential for accurate capacity measurements.^{5,}

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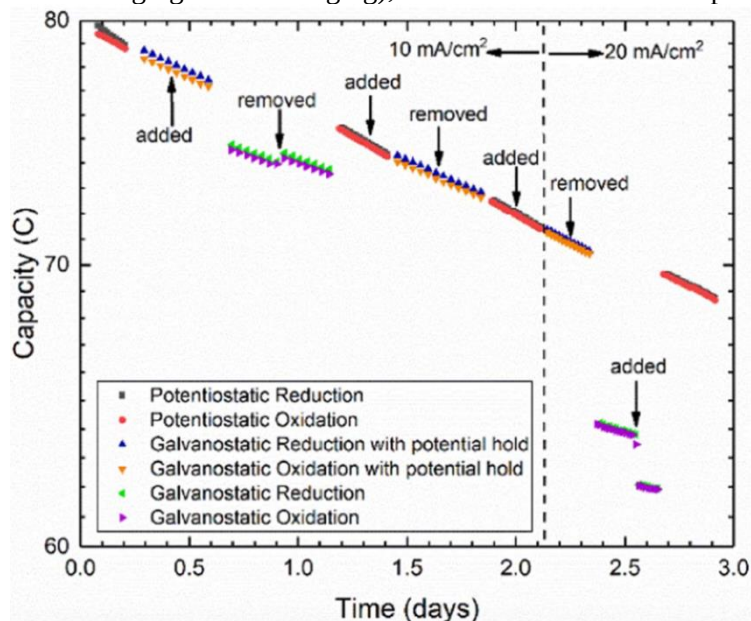


Figure 3. Semi-log plot of volumetrically unbalanced compositionally symmetric cell cycling of 2,6-dihydroxyanthraquinone (DHAQ), showing equivalence of potentiostatic and galvanostatic cycling with same potential holds. In both cases cycling was performed by imposing voltage holds at ± 200 mV and switched when current density dropped to 1 mA/cm^2 . Galvanostatic conditions were started at 10 mA/cm^2 and increased to 20 mA/cm^2 after roughly 2.1 days. Vertical arrows indicate times at which a 0.1Ω resistor was added and removed in series with the cell. The jumps in measured capacity demonstrate the dependence of measured cycling capacity on cell resistance when strictly galvanostatic conditions are used. Reprinted with permission from ref. 32. Copyright 2018 Electrochemical Society. (Fig.11, A1475)

Because molecular decomposition is a major cause of capacity fades of OFBs, it is indispensable to perform post-mortem analysis in order to characterize decomposition compounds in cycled electrolytes. Reported characterization techniques include cyclic voltammetry (CV), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), Fourier-transform infrared spectroscopy (FT-IR), ultraviolet–visible spectrophotometry (UV-Vis), and liquid chromatography–mass spectrometry (LC-MS). Multiple techniques should be employed to examine whether molecular decompositions occur over cycling and to determine decomposition compounds, in particular when decomposition compounds are elusive.³⁴

Of the aforementioned techniques, CV, EPR, UV-Vis, and FT-IR are usually qualitative, but they can determine concentrations quantitatively if suitably calibrated, e.g. with known concentrations. Capacity measurements during cycling are quantitative but are incapable of providing structural information on decomposition products. NMR coupled with LC-MS has been shown to be effective at identifying and quantifying decomposition compounds.³⁵

It is worth noting that each technique has its own instrumental sensitivity limit, i.e. a lower limit of detection. It is possible to extend the cycling time³⁶ or cycle count, or to accelerate fade rates to accumulate appreciable decomposition compounds for post-mortem analysis. Acceleration of fade rates can be achieved by changing cell test conditions, including increasing concentration of redox molecules, cycling cells at elevated temperatures, or holding cells at certain state of charge (SOC).¹⁰ In any event, failing to detect decomposition compounds does not mean there is no molecular decomposition even if the amount of observed capacity loss is large enough for a decomposition product to exceed detection limits. There may be multiple decomposition products, or a single decomposition product may itself decompose into other products, each of which is below the detection limit. It is also possible that decomposition products may precipitate, or may polymerize on the electrolyte-contacting materials.

- Molecular engineering

Molecular engineering involves multiple stages to ultimately achieve high-performing organic molecules for OFBs. When a new redox molecule is first developed for OFBs, it often possesses an appropriate redox potential and an adequately high solubility, but exhibits a fast fade rate. Subsequently, multiple characterizations are conducted to identify the major decomposition compound. With better understanding of the molecular decomposition mechanism from the identification of products, a modified structure is designed and synthesized to protect against the hypothesized or proven decomposition mechanism. Iteration leads to improved performance in cell operation.

Molecular engineering has been employed for both AOFBs and NAOFBs.^{10, 37} For example, the alkaline flow battery using commercially available 2,6-DHAQ in the negolyte shows a fast fade rate of $\sim 5\%/ \text{day}$.^{14, 33} With significant efforts on structural characterization, the decomposition compounds were determined to be redox-inactive 2,6-dihydroxyanthrone or 2,6-dihydroxyantranol, and a corresponding decomposition mechanism was proposed. Theoretical simulations suggest that the anthraquinone negolyte decomposition rate by this mechanism increases with decreasing molecular redox potential, albeit at the cost of a decreased cell voltage.³⁸ Raising the redox potential was thus expected to slow the decomposition rate. Indeed, 4,4'-((9,10-anthraquinone-2,6-diyl)dioxy)dibutyrates (2,6-DBEAQ), whose redox potential is 100 mV higher

than that of 2,6-DHAQ, was synthesized and demonstrated a temporal fade rate 0.04%/day,¹⁰ which is two orders of magnitude lower than that of 2,6-DHAQ. Further experimental studies suggest that 2,6-DBEAQ is susceptible to nucleophilic attack at high pH and elevated temperature, leading to the cleavage of the ether bonds between anthraquinone and the water-solubilizing chains. Carbon-carbon bonds are chemically more resistant against extreme pH or elevated temperature than carbon-oxygen bonds. Thus, 3,3'-(9,10-anthraquinone-diyl)bis(3-methyl-butanoic acid) (DPivOHAQ) and 4,4'-(9,10-anthraquinone-diyl)dibutanoic acid (DBAQ), possessing carbon-linked water-solubilizing groups, indeed demonstrate outstanding thermal stability and extremely low temporal fade rates of < 1%/year.¹⁹

As a general strategy, molecular engineering has been applied to different redox cores with improved molecular stability. However, complicated synthesis and expensive chemicals adversely increase the synthetic cost of targeted molecules. Alternatively, restricting the SOC of an AOFB,³⁸ or chemically regenerating redox-active molecules from decomposition compounds^{19, 38} have been employed to reduce AOFB fade rates.

- Cost

Because organics are composed of earth-abundant elements, organic molecules are potentially inexpensive compared to inorganic compounds; nevertheless, the synthetic cost of a high-performing organic redox molecule must quite low to be commercially viable.

The cost of a molecule decreases with the increase of the production scale and will, at sufficiently large scale, approach the cost of raw materials used for the synthesis; therefore, the raw materials should be sufficiently inexpensive. In addition, mild synthetic conditions, fewer synthetic steps, recyclable solvents and catalysts, higher product yields, and minimal waste are favored to further reduce synthetic cost. Both innovation and optimization in synthesis should be accomplished for a promising low-cost high-performing redox molecule. C-H activations simplify synthetic procedures by eliminating intermediate steps; thus it is expected to dramatically reduce synthetic cost if catalysts used for C-H activations can be easily recovered and reused. Electrosynthesis can replace toxic chemicals with clean electrons and possibly synthesize redox molecules in place; hence it can reduce the cost of waste disposal.^{36, 39} Biosynthesis is in its infancy;⁴⁰ it may hold the promise of producing desired molecules with high yields under mild conditions assisted by directed evolution of enzyme catalysts.⁴¹

Note that, under certain scenarios, molecular lifetime does not have to be infinite for an organic chemical when the molecule is extremely cheap.^{5, 42} The up-front capital cost savings of using an inexpensive molecule instead of vanadium can be compared with the present value of a series of future replacement costs, recognizing the time-value of money. The trade-off is quantified by a replacement cost ratio, defined as the annual replacement cost divided by the up-front capital cost savings. The break-even value of the replacement cost ratio depends on the interest rate for discounting and the project lifetime, as shown in Figure 4. When the actual value of the replacement cost ratio is less than this break-even value, organic molecules are potentially lower cost than vanadium.

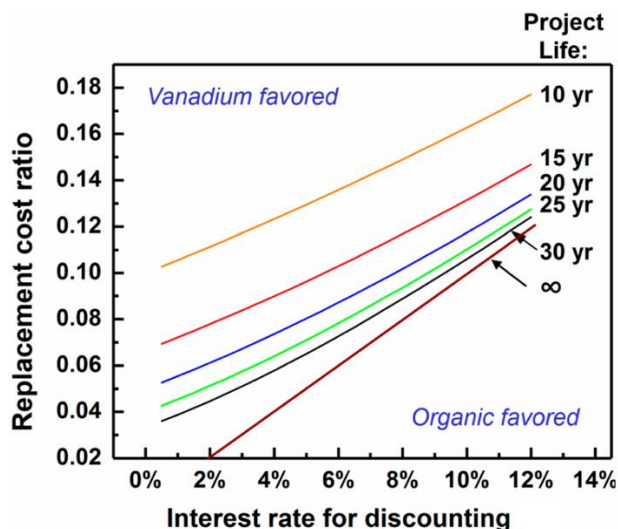


Figure 4. Breakeven value of replacement cost ratio vs. interest rate for discounting, assuming project lifetimes as indicated. Reprinted with permission from ref. 5. Copyright 2020 (Fig. 4, 880) Adapted with permission from ref. 41. Copyright 2017 John Wiley and Sons. (Fig. 8, Yang, Z. *et al. Adv. Energy Mater.* **2018**, 8, 1702056)

- Membrane

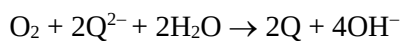
Ion-selective membranes include cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs). Negatively charged sulfonate groups are attached covalently as pendants in typical CEMs, positively charged ammonium groups are attached as pendants in typical AEMs. A cation-exchange membrane selectively allows cations to permeate because of Coulomb attraction (charge attraction) between cations and the sulfonate groups but constrains negatively charged redox molecules from permeation due to Coulomb repulsion between anions and the sulfonate groups. Increasing the degree of sulfonation of a cation-exchange membrane increases the population of sulfonate groups and Coulomb repulsion between membrane and negatively-charged redox molecules, thus reducing the crossover rates of redox molecules.

Size-selective membranes are capable of blocking large redox molecules and conducting ionic or neutral species that are smaller than the pore size of membrane.⁴³ Reducing the pore size of membranes can reduce crossover rates of redox molecules. Because different sterically bulky groups can be incorporated into the repeating unit of a polymer, the pore size of final size-selective polymer membrane is thus adjustable, selectively conducting ions through the polymer membrane. The permeability as a function of molecular size tends to have a somewhat broad transition from high to low with increasing size.

It is extremely challenging to develop a durable membrane maintaining high ionic conductivity and selectivity in a varying electrical field, at extreme pH, and at fluctuating temperatures for decades. Commercially available Nafion® membranes exhibit reasonable stability, moderate ion selectivity and ionic conductivity. However, the cost of Nafion® is still too high because of its per-fluorination.⁴⁴ Developing low-cost, long-lasting membranes with high ionic conductivity and selectivity is as important as developing high-performing redox organic molecules.⁴⁵

- pH imbalance

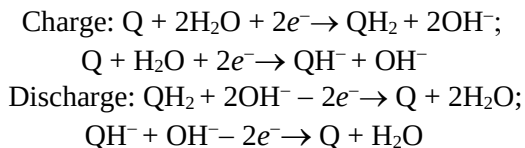
pH imbalance results from side reactions during AOFB cycling including oxygen evolution reactions (OER), oxygen reduction reactions (ORR), and hydrogen evolution reactions (HER). For example, when a charged (reduced) negolyte containing reduced organic molecules (Q^{2-}) is exposed to oxygen, the reduced molecules will become their oxidized forms (Q) and meanwhile oxygen will be reduced to hydroxide, increasing the pH of the negolyte.



The pH gradient produces concentration overpotential, which penalizes energy efficiency. Furthermore, pH imbalance induced by side reactions penalizes Coulombic efficiency and ultimately results in system

imbalance. The pH drift may also bring the electrolyte into a regime in which the molecule is unstable or precipitates.

When one electrolyte involves proton-coupled electron transfer (PCET) whereas the other one does not,¹¹ cycling will induce temporary pH imbalance, which will periodically intensify/relieve during the charge/discharge process.



This cyclic pH imbalance can lead to Coulombic efficiency loss due to proton or hydroxide crossover, which may require engineering to control the losses. Sometimes it can be avoided by increasing the pH of electrolytes to above the pK_a values of the protonated form of the reduced molecule (for example QH_2), so that the AOFB has proton-decoupled electron transfer on both the negolyte and posolyte sides.¹⁰

- Toxicity

When a FB is considered commercially viable, toxicology studies of the redox species need to be conducted. Although VFBs are being deployed, it is worth noting that vanadate (V^{5+}) and vanadyl (V^{4+}) are reproductive and developmental toxicants in mammals.⁴⁶

Polyaromatic hydrocarbons (PAHs) are frequently related to cancers, cardiovascular disease, and poor fetal development.⁴⁷ As one of the typical PAHs, anthracene is the precursor of anthraquinone (AQ), which is the starting material of anthraquinone-based redox molecules. Because of the similarity in structure between anthraquinone and anthracene, concern about the toxicity and carcinogenicity of AQ derivatives used for large-scale electricity storage is sensible. Earlier studies seem to suggest that substituent groups and their positions on AQ can have different effects.⁴⁸ For example, 1-(methylamino)-anthraquinone appears to alleviate toxicity; emodin and 1,8-dihydroxyanthraquinone are two phenolic anthraquinones; both are non-carcinogenic and used as cathartic laxatives.⁴⁹ In contrast, 1-nitro-anthraquinone consistently produced tumors in experimental animals.⁴⁸ Therefore, a conclusive statement on redox-active molecular toxicity should be cautious and it is essential to investigate the toxicity of the redox species before an OFB is deployed on a commercial scale.

It is worth noting that methyl viologen is proven notoriously toxic to mammals.⁵⁰ Toxicology studies should be performed for other viologen derivatives before they are considered for practical AOFB applications.

6.1.3 Classes of aqueous organic redox actives

- Redox aromatic carbonyl compounds (quinones, fluorenones)

Carbonyl groups when connected in a conjugated manner, such as quinones or fluorenones, can reversibly accept and donate electrons, thus being redox-active.

Quinones, including benzoquinones, naphthoquinones, and anthraquinones, are the most studied redox molecular family due to their structural richness and their facile two-electron transfer. As the simplest quinone, benzoquinone derivatives were first studied as posolyte active species because of their high redox potential. Yang *et al.* investigated 1,2-benzoquinone-3,5-disulfonic acid (BQDS) as the posolyte active species which has a potential of 0.85 V vs. SHE at pH 0.⁵¹ Subsequent characterization done by the same group demonstrates that BQDS is susceptible to nucleophilic addition, forming 1,2,4-trihydroxybenzene-3,5-sulfonic acid (THBS), which is still redox-active. THBS can be further oxidized during a charging process and attacked by water, ultimately becoming 1,2,4,6-tetrahydroxybenzene-3,5-disulfonic acid with a much lower potential due to the electron-donating hydroxyl groups.⁵² To avoid the susceptibility of the molecule to nucleophilic addition, the group hypothesized that it is essential to minimize the number of unsubstituted positions on the benzene; therefore, they synthesized 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid (DHDMBS), which indeed does not undergo any more nucleophilic additions. Post-mortem analysis of the cycled electrolytes indicates that it is the crossover of DHDMBS causing the capacity fade.¹⁸

2,3,5,6-tetrakis((dimethylamino)methyl)hydroquinone (FQH₂) is a fully substituted hydroquinone bearing four (dimethylamino)methyl groups which will become water-soluble ammonium cations in strong acid. The full substitution improves the stability of FQH₂ and the multiple charges and increased molecular size reduce the crossover of FQH₂.³² Similarly, 2,3,5,6-tetrakis(propylsulfanyl-2'-sulfonate)-1,4-hydroquinone tetrasodium salt bearing four longer chains and four negative charges, shows improved molecular stability and inappreciable crossover of redox molecules.⁵³

Naphthoquinone (NQ) has been less studied because of its intermediate redox potential, which is higher than that of anthraquinone but lower than that of benzoquinone.⁵⁴ It can exhibit desired potentials when the structure is properly modified, for example, bislawsone is a dimerized 2-hydroxyl-naphthoquinone with a potential of -0.551 V vs. SHE at pH 14, which was used as a negolyte active species with four-electron transfers per molecule. Post-mortem analysis of the cycled electrolyte indicates that tautomerization of the half-reduced bislawsone is the major reason leading to the capacity fade.⁵⁵

The redox potentials of AQ derivatives are close to but slightly higher than the potential of the hydrogen evolution reaction over a broad pH range; therefore, anthraquinones with water solubilizing groups are ideal negolytes. In general, the more aromatic rings a quinone is fused with, the lower redox potential it will have due to the extended π -electron delocalization. The extended aromatics also stabilize structures over redox reactions; hence, extremely stable anthraquinone negolytes have been reported with projected decades-long lifetimes. Compared to BQ and NQ, AQ has the largest conjugation and the highest molecular weight; the bare AQ core is thus the least water-soluble. Significantly improved solubility of AQ in water has been achieved by introducing water-solubilizing groups to AQ.

Redox-active fluorenone derivatives have been studied as negolyte active species for AOFBs.⁵⁶ For example, 9-fluorenone-2-carboxylic acid shows a solubility of 0.8 M in 1 M KOH with a redox potential of -0.69 V vs. SHE. When paired with the ferro-/ferricyanide redox couple, an open cell potential of 1.18 V was achieved. However, significant capacity loss was observed within the first few cycles. Given that fluorenone is derived from coal tar,⁵⁷ its derivatives are potentially low cost; water-soluble fluorenone derivatives deserve more investigations in the future. Recently, Feng *et al.* synthesized a series of water-soluble fluorenones and reported 4-carboxylic-7-sulfonate fluorenone (4C7SFL) with two electron-transfer and a claimed temporal fade rate of 0.0209%/day.⁵⁸ The 4C7SFL molecule demonstrates significantly improved cell performance and extended lifetime over other fluorenone derivatives. Interestingly, the capacity utilization of 4C7SFL is highly dependent on current density and concentration of redox molecule. For example, at room temperature, 0.5 M 4C7SFL demonstrates 77.5% of theoretical discharge capacity utilization at 2 mA/cm², but only 31% at 20 mA/cm²; at the same current density of 20 mA/cm², 0.5 M 4C7SFL shows a 31% of theoretical discharge capacity utilization, 1.36 M 4C7SFL shows a 72.2% of theoretical capacity utilization. This atypical electrochemical behavior deserves further investigation.

- Aza-/azo-aromatics (alloxazines, phenazines, azobenzenes, and viologens)

Another redox organic family is aza-/azo-aromatics. They are composed of aromatic rings and multiple nitrogen atoms. The nitrogen atoms are the redox-active sites that accept/donate electrons. The nitrogen atoms are incorporated into aromatics in two different manners: 1. nitrogen atoms replace carbon atoms in aromatics and form aza-aromatics, such as (iso)alloxazine,^{59, 60} phenazine,^{20, 21} and viologen;^{12, 17} 2. nitrogen atoms are connected with aromatics through conjugation and form azo-aromatics such as azobenzene.⁶¹

Redox in water-soluble (iso)alloxazine, phenazine, and azobenzene derivatives proceeds by two-electron transfer. Phenazine derivatives undergo proton-coupled electron transfer even in strong alkaline conditions as the pK_a values of 5,10-dihydrophenazine are higher than 14.²⁰

Viologens (C₅H₄NR)₂ⁿ⁺, derived from 4,4'-bipyridyl, undergo stepwise two-electron transfer at near neutral pH, with single-electron reduction potentials separated by ~400 mV.¹² Nevertheless, the 1st electron is mostly utilized in aqueous flow batteries as the 2nd electron transfer is less reversible. Extremely stable viologen molecules have been developed with the utilization of only the 1st electron transfer.^{12, 17}

Recently, through extending π -conjugation of viologens, two-electron transfer in one step has been demonstrated. For example, Luo *et al.* introduced a planar thiazolo[5,4-d]thiazole in between the two pyridiniums, which undergoes 2-electron transfer at -0.44 V vs. SHE.⁶² Hu *et al.* reported a phenylene-

bridged bispyridinium with 2-electron transfer at -0.763 V vs. SHE; however, chain cleavage leads to rapid capacity fade.⁶³

- Nitroxide radicals

Featuring the high redox potentials, fast kinetics, and ease of structural modifications, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, (TEMPO) is a relatively stable radical. It has been substituted with water-solubilizing groups at its 4 position via carbon-heteroatom bonds which then were used as posolyte active species. Water-soluble TEMPO derivatives are pH sensitive as the oxidized TEMPO derivative tends to react with either proton or hydroxide,⁶⁴ and corresponding reversibility and stability are demonstrated mainly at neutral pH.⁶⁵

TEMPO itself is inexpensive for use on a laboratory scale; however, its price is prohibitive at an industrial scale. Instead, 4-hydroxy-TEMPO (TEMPOL), produced from acetone and ammonia via triacetone amine, is less expensive than TEMPO. The hydroxyl group in TEMPOL can be further modified and functionalized with water-solubilizing groups.⁶⁵ Given that developing high-performing organic posolyte active species has been challenging, TEMPOL derivatives deserve further investigation.

- Metal coordination complexes

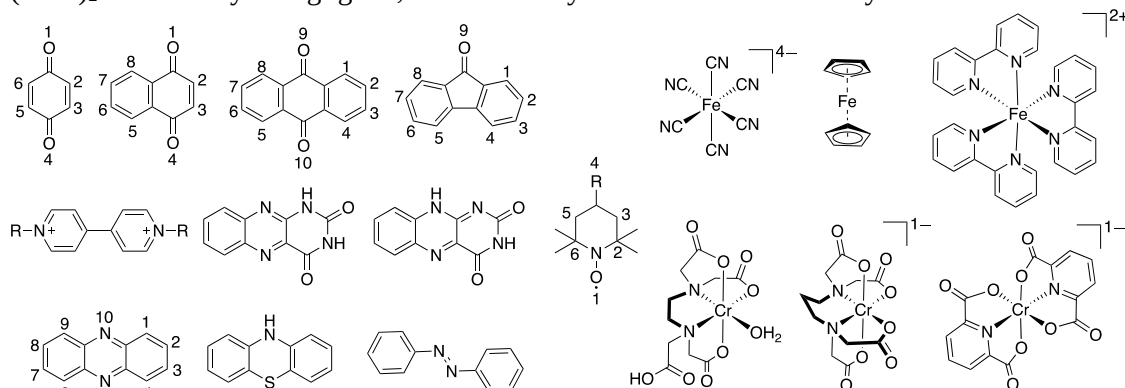
A typical metal complex used for AOFBs consists of a redox-active transition metal and a few ligands. For example, ferrocene comprises an iron atom and two cyclopentadienyl ligands; ferro-/ferricyanides are composed of one iron atom and six cyanide ligands; tri(bipyridyl)iron complexes are composed of one iron atom and three bipyridyl ligands. Compared to bare $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, iron complexes demonstrate faster reaction kinetics and several orders of magnitude lower crossover rates due to the larger complex sizes. The thermodynamic stability of complexes can be affected by their coordination number and the binding constant between the metal center and the donor atoms of the ligands. Side reactions can happen between protons and ligands or between hydroxides and metal centers; neutral pH is often used for metal complexes to avoid unwanted side reactions.

Developing redox species used in posolytes is fundamentally more challenging because high-potential molecules have lower electron density around molecular skeletons, and their oxidized forms become energized electron-deficient electrophiles vulnerable to nucleophilic attack by hydroxide or even water. Ferro-/ferricyanide solutions, $([\text{Fe}(\text{CN})_6]^{4-/3-})$, have been the most studied posolyte active species in alkaline or near neutral media. The solubility of $\text{K}_4\text{Fe}(\text{CN})_6$ is 0.76 M in water and the solubility of $\text{Na}_4\text{Fe}(\text{CN})_6$ is 0.56 M in water. A total concentration of $\text{Fe}(\text{CN})_6^{4-}$ is up to 1.5 M when sodium ferrocyanide and potassium ferrocyanide are mixed with 1:1 ratio;⁶⁶ the solubility of $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ in water could be up to 1.6 M (Fig. 7a, vide infra).²⁹ Recently, Gregory et al. estimated that the mass production cost of $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_4\text{Fe}(\text{CN})_6$ are 16, 25, 21 \$/kAh, respectively.⁶⁷

Beh et al. introduced (3-trimethylammonio)propyl dichloride to the 1, 1' positions of ferrocene and synthesized bis((3-trimethylammonio)propyl)-ferrocene dichloride (BTMAP-Fc).¹⁷ The solubility of BTMAP-Fc in water is approximately 2 M. More important, BTMAP-Fc demonstrates a low temporal fade rate of 0.031%/day.

Because the redox potential (0.77 V vs. SHE) of bare $\text{Fe}^{2+}/\text{Fe}^{3+}$ is close to that of the oxygen evolution reaction, iron coordination complexes are developed as posolyte active species.^{17, 68, 69} In contrast, the redox potential of $\text{Cr}^{2+}/\text{Cr}^{3+}$ is -0.41 V vs. SHE; chromium (Cr) coordination complexes have been studied as negolyte active species. Ethylenediaminetetraacetic acid (EDTA) is a commonly used chelating agent that has been found to coordinate with Cr in conjunction with water to form $\text{Cr}(\text{EDTA})(\text{H}_2\text{O})$, which has a redox potential of approximately -1.10 V vs. SHE, which is lower than the thermodynamic potential of the HER. Consequently, the ligand water molecule can be reduced by the Cr, releasing hydrogen gas. 1,3-propylenediaminetetraacetic acid (PDTA) allows the formation of a CrPDTA complex instead of being ligated to one water molecule in $\text{Cr}(\text{EDTA})(\text{H}_2\text{O})$. PDTA provides six donor atoms that fully surround the Cr center, serving as a molecular barrier to prevent the reaction between Cr^{2+} and water. The difference between EDTA and PDTA is the number of methylene groups ($-\text{CH}_2-$) in between two adjacent nitrogen atoms (Scheme 1): there are two methylene groups in EDTA and three in PDTA. The extra methylene group in PDTA extends the chain length and thus enables full coordination of Cr metal center.⁷⁰ In a separate

work, two deprotonated dipicolinic acid (DPA) coordinate with Cr to form $\text{Cr}(\text{DPA})_2$, whose redox potential (-0.7 V vs. SHE) is 300 mV lower than that of $\text{Cr}^{2+}/\text{Cr}^{3+}$, but 300 mV higher than that of $\text{Cr}(\text{PDTA})$ or $\text{Cr}(\text{EDTA})(\text{H}_2\text{O})$. Due to the sluggish kinetics of the HER in the absence of a catalyst, the HER side reaction in a $\text{Cr}(\text{DPA})_2$ flow battery is negligible, as reflected by its Coulombic efficiency of $>99.5\%$.⁷¹



Scheme 1. Redox organics and metalorganics used for aqueous organic flow batteries. (Source: Yan Jing)

6.1.4 Properties of aqueous organic redox actives

- Range of redox potential

Generally, the potentials of negolyte active species are close to but slightly higher than that of HER; the potentials of posolyte active species are close to but slightly lower than that of OER. As such, an AOFB can deliver an open circuit voltage of ~ 1.0 V. Sometimes, the potentials of redox species are either lower than that of the HER or higher than that of the OER; overall cell voltages of AOFBs can thus be slightly higher than the water stability window of 1.23 V due to the overpotentials of the OER and the HER. For example, $\text{Cr}(\text{PDTA})^{2-/1-}$ is reported as a negolyte active species and its redox potential is -1.10 V vs. SHE, 582 mV lower than that of the HER (-0.528 V vs. SHE) at pH 9; and when ferro-/ferri-cyanide is used as the posolyte active species whose potential is 0.45 V vs. SHE, the full cell thus demonstrates an open circuit voltage of 1.55 V, which is 320 mV higher than 1.23 V.⁷⁰

- Range of solubility

Because of the incorporation of water-solubilizing groups, redox organics or metalorganics can store electrons ranging from ~ 1 M up to 5 M; corresponding volumetric capacities range from below 20 to above 100 Ah/L.¹¹ Mixing counter ions for a redox species can be helpful to increase its solubility. For instance, the solubility of potassium ferrocyanide and sodium ferrocyanide in water is 0.5 M and 0.3 M respectively, whereas the solubility of potassium and sodium ferrocyanide with 1:1 molar ratio can reach up to 1.5 M at pH 7. That is because the mixed cations frustrate recrystallizations of ferrocyanide.⁶⁶

- Range of fade rate

A redox core can be introduced with different functional groups at different positions; consequently, the temporal fade rates of the modified redox molecules could vary by orders of magnitude. For example, the temporal fade rates of 2,6-DHAQ,¹⁴ 1,8-PEGAQ,¹¹ 2,6-DBEAQ,¹⁰ and 2,6(7)-DPivOHAQ¹⁹ are $\sim 5\%$ /day, 0.5% /day, 0.04% /day, and 0.0018% /day, respectively. Similarly, order of magnitude improvements in lifetime have been achieved for redox aza-aromatic compounds: in particular, viologen and phenazine derivatives have demonstrated extremely low fade rates ($<0.02\%$ /day) after judicious molecular modifications.^{2, 12, 17, 20, 21, 72, 73}

- General decomposition mechanisms

Generally, but not always,¹⁰ the “energized” state of a redox molecule is susceptible to chemical or electrochemical decompositions. “Energized” states are the reduced form of the redox molecule in the negolyte and the oxidized form of the redox molecule in the posolyte. Reported chemical decompositions include nucleophilic addition, nucleophilic substitution, disproportionation, dimerization, and

tautomerization.² Electrochemically induced decompositions can also happen during the charge-discharge process.^{30, 34, 35}

- Range of operation pH

Reported AOFBs operate with a broad pH range, from below 0 to above 14. An appropriate operational pH should be chosen because pH influences solubility, potential, reversibility, and stability of a redox molecule. For instance, the reduced viologen derivatives¹⁷ and the oxidized TEMPO derivatives⁶⁵ are susceptible to both acid- and base-induced decompositions, thus (near) neutral operation pH (7±2) should be used to minimize the decomposition rate.

In general, a mild or near neutral pH is advantageous because electrolytes with extreme pH tend to be highly corrosive, requiring costly acid- or base-resistant electrolyte-contacting materials; corrosive electrolyte leakage may raise safety concerns. Therefore, when a redox molecule exhibits similar properties within a broad pH range, a milder pH would be chosen for cell operations. For example, PEGAQ demonstrates similar electrochemical reversibility, solubility, and redox potentials from pH 7 to 14, and pH 7 is chosen for the cell cycling.¹¹ Similarly, DBEAQ exhibits the same reversibility and redox potential, and similar solubility at pH 12 and 14, hence pH 12 is preferred.¹⁰

Solubility of redox species is often dependent on pH, and sometimes active species of negolyte and posolyte may reach their maximum solubilities at different pH values. Because a pH differential across the membrane is not viable over long time periods, negolyte vs. posolyte solubility may need to be traded off via pH selection for maximizing the energy density.

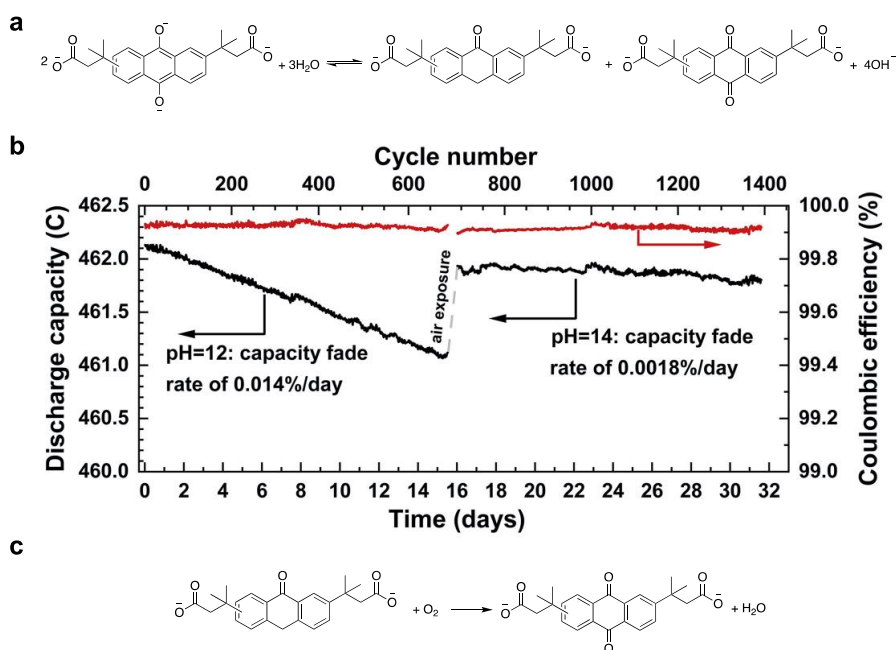


Figure 5. Influence of operation pH on molecular decomposition rate and temporal fade rate of DPivOHAQ electrolyte and possible capacity recovery via aeration. (a) The reversible disproportionation of DPivOHAQ in alkaline conditions (Source: Yan Jing). (b) DPivOHAQ cell cycling at pH 12 and 14. The negolyte was exposed to air (thereby reversing much of the decomposition) and the pH of both negolyte and posolyte were raised to 14 (thereby suppressing the decomposition rate) by adding KOH pellets. Reprinted with permission from ref. 19. Copyright 2020 (Fig.3A, 1437) (c) Chemical oxidation of the redox-inactive anthrone derivative to the redox-active DPivOHAQ (Source: Yan Jing).

When the hydroxide ion is involved in decomposition of a redox molecule, the concentration of hydroxide ions affects the decomposition rate. As a consequence, operation pH influences the fade rate of the organic electrolyte. For example, two reduced DPivOHAQ molecules can reversibly disproportionate to one DPivOHAQ in its oxidized state and one anthrone derivative, producing four hydroxide ions (Fig. 5a). Because the hydroxide ions are a product of this reversible reaction, increasing the hydroxide concentration, i.e., increasing the pH of electrolyte, suppresses the disproportionation reaction. Consequently the temporal fade rate of DPivOHAQ electrolyte decreases from 0.014%/day at pH 12 to 0.0018%/day at pH 14 (Fig. 5b).¹⁹

- Re-composition of redox active molecules

With better understanding of decomposition mechanisms, one can re-compose redox-active molecules from their decomposition products *in situ*. For example, anthrone derivatives are known to be the products of the major decomposition reactions in some anthraquinone-based electrolytes. Anthrone is over-reduced and redox-inactive compared to the corresponding anthrahydroquinone. O₂ is capable of chemically oxidizing anthrones back to anthraquinones in high yields. As shown in Fig. 5b, most of the lost capacity of DPivOHAQ electrolyte was recovered after air exposure on day 16.¹⁹

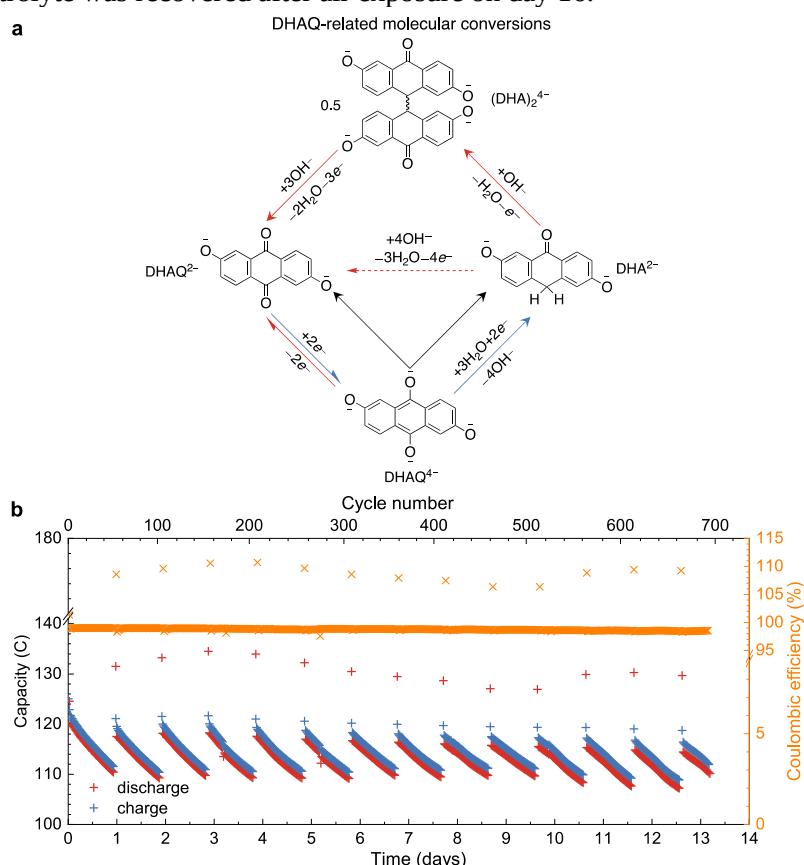


Figure 6. Electrochemically rejuvenating a DHAQ | Fe(CN)₆ flow battery. (a) Potential-driven DHAQ-related molecular conversions at pH 14. The reduction of DHAQ⁴⁻ to DHA²⁻ proceeds either chemically via a “disproportionation” of DHAQ⁴⁻ (2DHAQ⁴⁻ + 3H₂O → DHAQ²⁻ + DHA²⁻ + 4OH⁻) or electrochemically. The red arrows indicate electrochemical oxidations; the blue arrows indicate electrochemical reductions; the black arrows indicate chemical reactions. The equilibrium arrows indicate reversible reactions. Adapted with permission from ref. 74 Copyright 2021. (Scheme 1a, Jing, Zhao, Goulet *et al.* *ChemRxiv*. **2021**, 10.33774/chemrxiv-2021-x05x1) (b) Long-term cycling of DHAQ^{2-/4-} | [Fe(CN)₆]^{3-/4-} flow battery with repeated daily capacity recovery by electrochemical regeneration of the negolyte. Reprinted with permission from ref. 74 Copyright 2021 (Fig. 3a, Jing, Zhao, Goulet *et al.* *ChemRxiv*. **2021**, 10.33774/chemrxiv-2021-x05x1)

Another well-studied example is DHAQ, which is characterized by a fast temporal fade rate of ~5%/day. This is caused by the instability of the reduced DHAQ (DHAQ^{4-}), which disproportionates to form redox-inactive 2,6-dihydroxyanthrone (DHA).³⁸ Instead of increasing the operation pH of the electrolyte as shown in Fig. 5b, Goulet and Tong *et al.* reduced the fade rate by restricting the negolyte SOC, thereby limiting the percentage of DHAQ^{4-} in the electrolyte, thereby reducing the rate of DHAQ^{4-} disproportionation. Additionally, a significant fraction of the redox-inactive DHA in the cycled DHAQ electrolyte was converted back to DHAQ via aeration, extending the overall lifetime of the battery.

Redox-active anthraquinones can even be re-generated *electrochemically* from their decomposition products. Zhao *et al.* demonstrated that DHAQ^{4-} can be electrochemically reduced to DHA^{2-} .³⁵ Soon after, we found that DHA^{2-} can be electrochemically oxidized to the dimer $(\text{DHA})_2^{4-}$ by one-electron transfer, and the dimer can be electrochemically oxidized to DHAQ^{2-} by three-electron transfer (Fig. 6a).⁷⁴ Furthermore, electrochemical regeneration rejuvenates not only DHAQ, but also the positive electrolyte, thereby rebalancing the states of charge of both electrolytes without introducing extra ions. We demonstrated repeated capacity recovery with a DHAQ | potassium ferro-/ferricyanide flow battery in basic conditions (Fig. 6b). The average ratio of capacity recovered to capacity lost in the preceding 50 cycles was 94.7%. The average recovery in Figure 6b leads to an overall fade rate of 0.38%/day, which is more than an order of magnitude improvement over the initial instantaneous fade rate of 6.45%/day in this experiment. In addition, preliminary studies with AQDS show the feasibility of electrochemical regeneration in acidic electrolytes.⁷⁴ Similar strategies may also be applicable for other redox-active organic molecules.

6.1.5 Performance of AOFBs

A high-performing AOFB is expected to have high energy and power density, to have decadal operational lifetime, and low active materials cost. So far, the investigations of AOFBs have been focused primarily at the single electrolyte level, with different cell components and electrolyte compositions and volumes designed to investigate different aspects of the redox organic. For example, different membranes might be used when studying molecular decomposition and cell power density; different electrolyte volumes might be used when studying the properties of a single molecule as the capacity-limiting side, and when studying the performance of a capacity-balanced cell. These studies have facilitated the development of redox molecules with proper redox potentials, high solubility, high stability, and potential low-cost production. Studies on cell-level performance are not yet systematic and simultaneously reporting all important performance parameters for a system-level optimized cell or stack, with a unique cell build (e.g. membrane choice) and a unique choice of posolyte and negolyte composition. Cell voltage has been reported as high as 2.13 V (Fig. 7b);⁷⁰ power densities have been reported as high as 1.0 W/cm² (Fig. 7c);⁷⁵ energy densities have been reported as high as 25–27 Wh/L (Fig. 7d);^{11, 76} capacity fade rates have been reported as low as 0.66–0.88%/year (Fig. 5b);^{19, 72} and combined active species costs have been reported as low as \$41.25/kWh;⁶⁷ however, these attributes have not been approached simultaneously in any single system. Simply collecting those parameters from the reported AOFBs and comparing different AOFB systems would not be particularly informative at this stage. Optimization of system-level performance will be easier once promising redox molecules are well investigated.

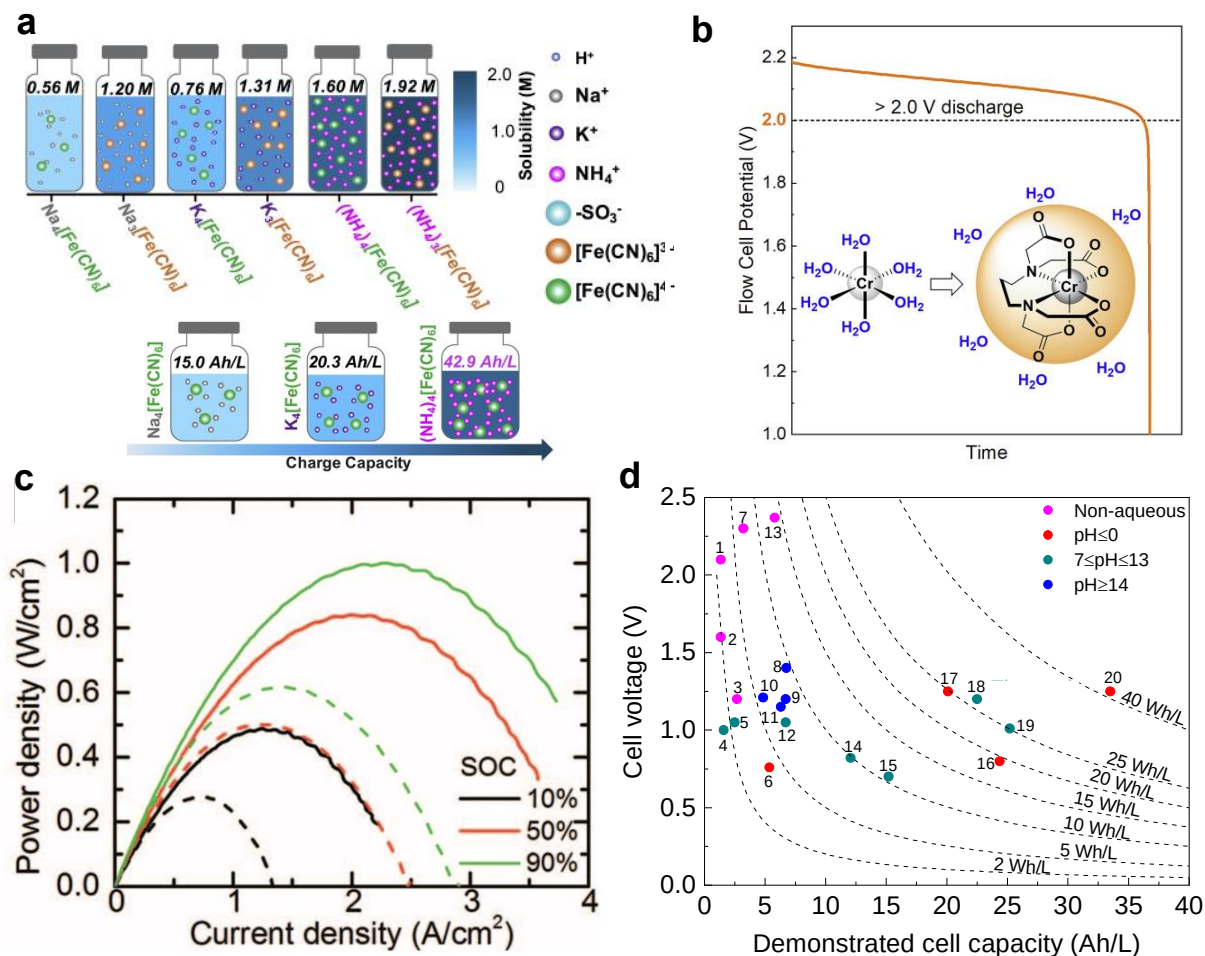


Figure 7. Selected measures of performance of redox species used for aqueous organic flow batteries. (a) Aqueous solubilities of ferro/ferricyanide with different counter cations, and volumetric capacity of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, and $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$. Adapted with permission from ref. 29. Copyright 2019 (Fig.1a and graphical abstract) (b) CrPDTA | Br_2 cell discharge voltage at 10 mA/cm². Reprinted with permission from ref. 70. Copyright 2019 (graphical abstract) (c) AQDS | Br_2 in 1 M H_2SO_4 modified cell performance at 10, 50 and 90% SOC, power density vs. current density. For comparison, the power density curves in the base case are plotted as the dashed lines. Reprinted with permission from ref. 75. Copyright 2016 (Fig.5, A5013) (d) Energy density contours on cell voltage vs. volumetric capacity plot of different flow battery systems. The pink dots (No. 1, 2, 3, 7, and 13) represent non-aqueous organic redox batteries. The red dots (No. 17 and 20) represent all-vanadium flow batteries with different supporting electrolytes (No. 17: H_2SO_4 ; No. 20: $\text{H}_2\text{SO}_4/\text{HCl}$ mixture). The red dots (No. 6 and 16) represent aqueous acidic organic flow batteries. The dark green dots (No. 4, 5, 12, 14, 15, 18, and 19) represent aqueous near-neutral organic flow batteries. The blue dots (No. 8, 9, 10, and 11) represent aqueous alkaline organic flow batteries. Adapted with permission from ref. 11. Copyright 2019 ACS Publications. (Fig. 2, Jin, S. *et al.* *ACS Energy Letters*. **2019**, 4, 1342–1348).

6.1.6 Outlook for AOFBs

Commercialization of AOFBs requires long lifetime of the battery and all its components, low mass-production cost of active species, and competitive power density and energy density. Significant improvement in either of the following two directions, or some combination thereof, might enable successful commercialization:

1. Innovations in molecular synthesis are important to reduce the mass production cost of the extremely stable negolyte species that have recently been reported, or tweaks to molecular design enabling cost reductions without unacceptably compromising other properties. Optimizations on synthetic methods, conditions, reaction temperature, pressure, yields, waste disposal *etc.* should also be conducted to further reduce the cost.

2. Innovations are important to extend the molecular lifetime, over the expected range of operation temperatures, of redox species that are known to be low-cost at mass-production scale, or to re-compose them *in situ* from their decomposition products, so that the total active cost -- including the present value of the cost of periodic future replacements⁵ -- is competitive.

Additionally, progress in a number of additional directions would facilitate AOFB development:

1. The development of extremely stable posolyte species currently lags behind that for negolytes. Currently, ferri-/ferrocyanide appears to offer the best combination of properties for weakly to strongly basic electrolytes. Functionalized ferrocenes appear promising for near-neutral pH. For acidic pH and as alternatives at any pH, inorganic redox couples such as bromide/tribromide and may be utilized in a hybrid organic/inorganic FB,¹⁵ if issues such as crossover can be managed.

2. It has been proven that potentials and water solubility of redox molecules can be readily adjusted by molecular engineering, improving molecular stability requires longer time and more efforts. Multiple characterization techniques should be employed to determine decomposition compounds and reveal decomposition mechanisms, thereby informing molecular design strategies.

3. Ion-exchange membranes should possess high ionic conductivity and selectivity, as well as outstanding stability at the relevant (possibly extreme) pH environment. An important direction particular to AOFBs is to develop low-cost, robust ion-selective membranes with a high ratio of monatomic ion conductivity to bulky organic permeability. A combination of charge exclusion and size exclusion may be exploited to this end.

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