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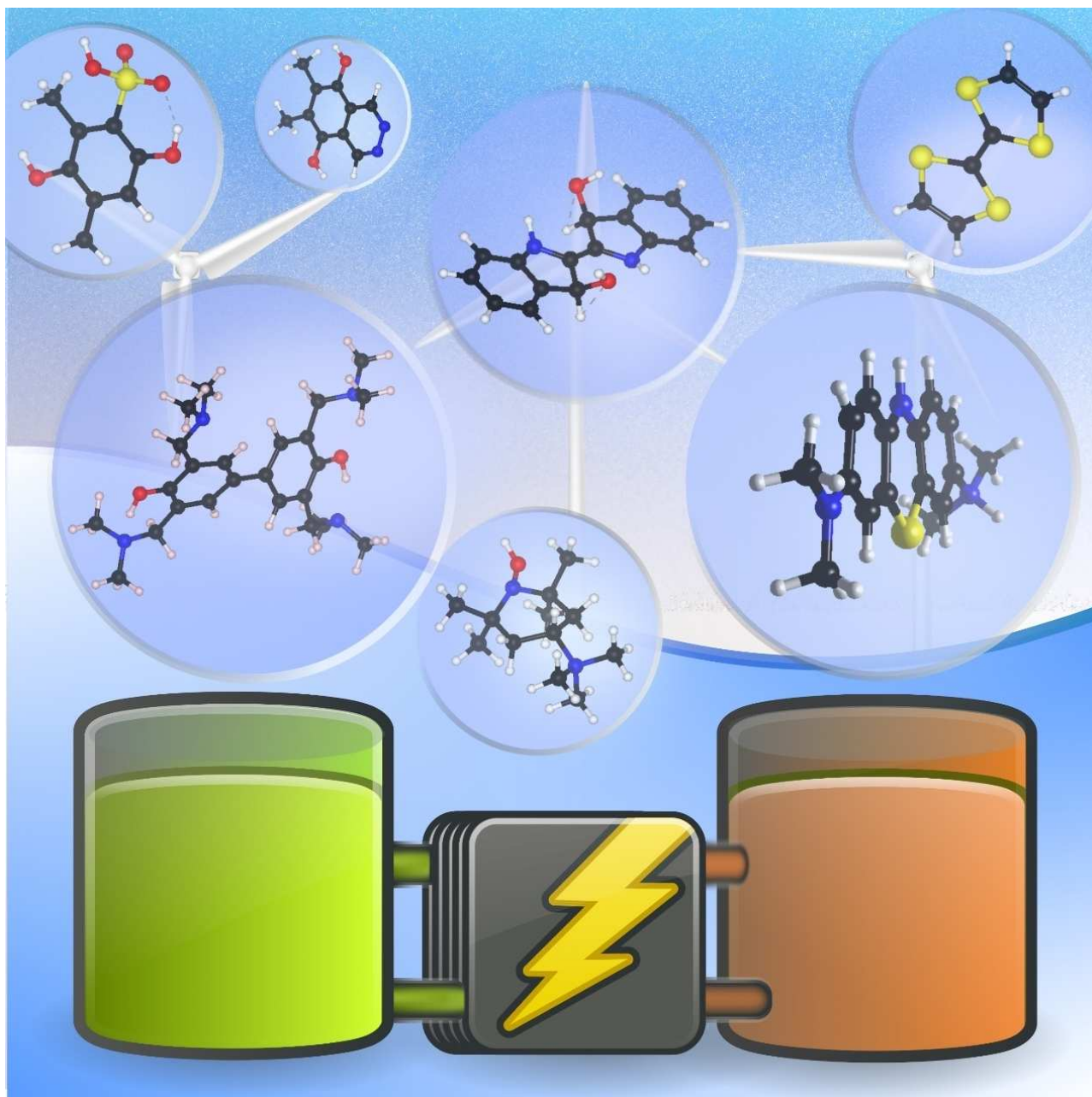


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Aqueous Redox Flow Batteries: Small Organic Molecules for the Positive Electrolyte Species

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There are a number of critical requirements for electrolytes in aqueous redox flow batteries. This paper reviews organic molecules that have been used as the redox-active electrolyte for the positive cell reaction in aqueous redox flow batteries. These organic compounds are centred around different organic redox-active moieties such as the aminoxyl radical (TEMPO and *N*-hydroxyphthalimide), carbonyl (quinones and biphenols), amine (e.g., indigo carmine), ether and thioether (e.g., thianthrene) groups. We consider the key metrics that can be used to assess their performance: redox potential, operating pH,

solubility, redox kinetics, diffusivity, stability, and cost. We develop a new figure of merit – the theoretical intrinsic power density – which combines the first four of the aforementioned metrics to allow ranking of different redox couples on just one side of the battery. The organic electrolytes show theoretical intrinsic power densities which are 2–100 times larger than that of the $\text{VO}^{2+}/\text{VO}_2^+$ couple, with TEMPO-derivatives showing the highest performance. Finally, we survey organic positive electrolytes in the literature on the basis of their redox-active moieties and the aforementioned figure of merit.

1. Introduction

A redox flow battery (RFB) uses redox active species dissolved in electrolytic solvents that are pumped through the cells during charging and discharging in order to continuously replenish redox active species inside porous electrodes.^[1] In contrast to static battery designs, whereby the redox-active species and the cell electrodes have an integrated construction, the RFB disconnects the power of the cell stack from the charge-discharge capacity because the amount of energy the battery is capable of storing depends on the amount of electrolyte in the external tanks, rather than in the cell stack. The dynamic RFB design has the advantage of being scalable to the capacities required for stationary megawatt-hour scale energy storage, necessary for levelling-out energy supply and demand incongruity.^[2] The implementation of grid-connected electrochemical energy storage (EES) is considered an important factor for achieving energy security in a renewable energy dominated market. Researchers, companies, and policy-makers therefore all take an interest in RFB energy storage, and start-ups now exist to develop aqueous soluble redox-active organic molecules (ROM) on one or both sides of the battery.^[3] At present, only RFB electrolytes utilising transition metal ions as the energy carrying species fulfil the performance and stability requirements for commercial use. An RFB that can perform as well as the state-of-the-art aqueous RFB systems of today using organic molecules as the charge carrying species could provide a way to lower the cost of widespread EES.

The recent development of many soluble, redox-active organic molecules has drastically expanded the design space of redox flow battery chemistries. This marks a shift from the previous era of mostly metallic and halide ion chemistries into a budding field of investigations into the tuneable redox properties of organic species, with realistic ambitions for grid-connected energy storage. In the family of all-organic redox couples for aqueous flow battery applications, only the upper strata from the growing array of small, molecular redox couples could be considered to undergo a free energy change significant enough to be appropriate for the positive electrolyte couple.

Although research output within the context of aqueous organic RFBs is growing, and methods of studying electrolytes are developing, knowledge of high potential redox candidates is still fragmentary, and measurement and testing protocols still vary considerably between research groups. To help bring together the research in this space, the underlying key properties of small organic redox couples that should be considered are discussed in Section 2. These key properties are used to appreciate the merits and limitations of specific aqueous organic redox couples from the literature. These specific examples are contextualised in detail in Section 3, in which the very wide range of organic electrolyte materials are sorted into just a few fundamental types. With distinctions based upon the redox-active group (aminoxyl, carbonyl, amine, ether, or thioether) molecules built around organic redox couples can be easily understood.

As the title suggests, we focus on small molecules, generally with a molecular weight of < 500 Da and a potential exceeding 0.5 V vs. SHE, that are aimed at aqueous RFB systems. Compared to non-aqueous RFB electrolytes, the electroactivity of fewer redox couples can be utilised in aqueous media due to the ability of organic solvents to better solvate some otherwise insoluble organic molecules, stabilise radical species, and permit a much wider potential range than the stability window of water.^[4] However, non-aqueous RFB systems are currently at an earlier stage of development due to low solution conductivity and a lack of suitable membrane materials. The overall performance of non-aqueous RFBs, in terms of energy and power densities, is significantly further from commercial EES targets than aqueous organic RFBs. Non-aqueous organic RFBs are therefore considered a separate topic that is not covered here.^[5] However, the use of non-aqueous solvent certainly provides insight into organic redox couples on a molecular level.

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2. Key Properties of Aqueous Organic RFB Electrolytes

2.1. Overview of electrochemical redox reactions in small organic molecules

The removal or addition of an electron via electrochemical oxidation or reduction of a closed shell organic molecule will generate a radical species. Of the persistent radicals that are known, the majority are O, S, or N centred.^[6] Electronegative heteroatoms such as these can also incorporate electrochemical reversibility into the redox characteristics of a molecule if an electron from a lone-pair can be reversibly removed and replaced. These are viable ROM candidate species if the radical is sufficiently persistent such that two oxidation states of the molecule can exist in solution. In a recent study, Sowndarya et al. quantitatively assessed spin density and steric hindrance to predict stability of small organic radicals in water for this application.^[6] Stabilisation of radicals is afforded by lone-pair delocalisation, σ -hyperconjugation, and π -conjugation. Therefore electroactive organic molecules utilised in RFB electrolytes often have a cyclic structure and a conjugated system. Organic molecules that contain two O, S, or N heteroatoms can allow for a reversible two-electron redox process. Rather than forming a diradical, heteroatoms linked by conjugation can increase the total bond number by 1 and reform a closed shell system. In a

flow battery, this also doubles the energy storage capacity per molecule.

A recent study by Wang et al. is a good example to show the redox properties of small organic molecules.^[7] The starting point shown in Figure 1a is the redox couple of triphenylamine (TPA). TPA is well-known to form a relatively stable charged radical species upon oxidation, but in aqueous solution TPA^+ decays by radical quenching, and also to a lesser extent by intermolecular C–C coupling.^[7] The structural modification of adding three electron donating *para*-methoxy groups to TPA successfully stabilised the radical in aqueous media by electron-delocalisation. The reversible redox couple of tri-*para*-methoxy-TPA (TMTPA) is also shown in Figure 1a. The addition of *para*-hydroxy groups to TPA was also investigated, and the presence of both the central nitrogen and the new keto-enol redox couple in the form of a hydroxy substituent enabled a reversible two-electron oxidation of trihydroxytriphenylamine (THTPA) in a mix-and-match of hydroxy-carbonyl and amine-imine mechanisms, shown in Figure 1b. The minimum conjugation associated with completing any two-electron mechanism in redox-active organic molecules is shown in Figure 1b. Many one-electron redox couples also exist in the aqueous organic RFB literature which only utilise one of these redox transformations; for an RFB a high degree of reversibility is required and the two electron steps are not necessarily both reversible in the same electrolyte environment. Molecules built around these redox centres can be polymerised or grafted to create macromole-



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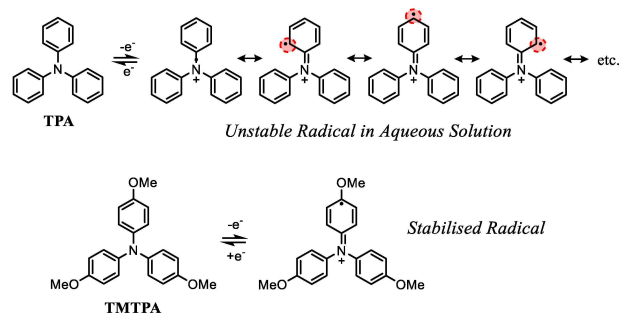


Professor Nigel Brandon OBE FREng FRS received his PhD in electrochemical engineering from Imperial College in 1984. After a 14 year career in industrial research with BP and Rolls-Royce, he joined Imperial College London as a member of academic staff in 1998, where he holds the Chair in Sustainable Development in Energy. His research interests are focussed on electrochemical devices for low carbon applications, with a particular focus on fuel cells, electrolyzers, hydrogen and flow batteries. He is a co-founder of Ceres Power, a UK fuel cell/electrolyser company, and RFC Power, a UK flow battery company.



Professor Anthony Kucernak received his PhD in photoelectrochemistry from Southampton University (United Kingdom) in 1991. He became an academic member of staff at Imperial College in 1995 following postdoctoral work at the University of Cambridge (United Kingdom). His research interests focus on electrochemistry and electrocatalysis specifically associated with production and use of electrochemical energy carriers such as hydrogen, redox active molecules and battery materials. This has led to the development of a number of systems based around fuel cells, electrolyser and flow batteries. He is co-founder of Bramble Energy, a UK fuel cell/electrolyser company, and RFC Power, a UK flow battery company.

(a) One-electron Oxidation



(b) Two-electron Oxidation

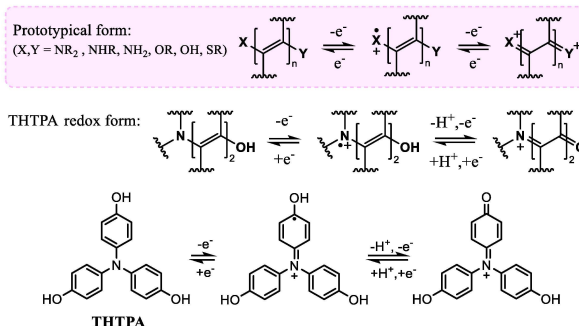


Figure 1. The oxidation state changes of triphenylamine (TPA) and trimethoxytriphenylamine (TMTPA), and (b) the general prototypical form of two-electron organic redox couples and the specific example of trihydroxytriphenylamine (THTPA).

cules with even higher electron transfer numbers per molecule and has led to the development of organic redox switches for use in other electrochemical devices.^[8,9]

Many redox couples that have the necessary redox-active units and associated conjugation still may not exhibit multi-electron reaction in the potential window explored due to poor reversibility. For example, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) undergoes a reversible oxidation, shown in Figure 2, between the highly persistent aminoxyl radical and the oxoammonium ion form.^[10] For TEMPO compounds, although it is reportedly reversible in certain ionic liquid electrolyte solutions, the hydroxylamine-aminoxyl couple is considered electrochemically irreversible and is not utilized in aqueous RFBs.^[3,11–13] Similarly, the *N*-hydroxyphthalimide (NHPI) redox couple switches between the hydroxylamine and aminoxyl radical, and is not thought to utilize the oxoammonium ion state.^[14]

Benzoquinone (BQ) is an example of a two-electron redox couple, and the electrochemical reaction steps are shown in Figure 3a. In the reduced state of BQ, the hydroxy groups can be either protonated or deprotonated. In aprotic organic

solvents voltammetry of BQ shows two defined peaks, indicating the redox process occurs in two distinct one-electron transfer steps between the dihydroquinone, semiquinone, and quinone forms. Gradually adding an increasing amount of water to quinone solutions in aprotic organic solvent increases the amount of hydrogen bonding, and this brings the two peaks closer together. In purely aqueous media BQ undergoes both electron transfers occur in a single wave and the reaction is effectively a two-electron transfer.^[15] Figure 3b shows the redox reaction of BQ in two pH conditions in which the majority of the dihydroquinone is either protonated or deprotonated. When BQ is protonated, the redox reaction is a proton-coupled electron transfer (PCET).

Decomposition of the redox-active organic species is a common issue. Decreasing radical intermediate formation could limit the possible pathways by which the redox-active molecules can decompose in solution. Therefore, switching between stable closed-shell oxidation states may be seen as preferable, from a stability standpoint, as well as doubling the energy storage capacity. Some molecules that form stable aromatic products upon two-electron oxidation are not observed to produce any radical transient species. An example is 9,10-bis(dimethylamino)anthracene (DMA), which undergoes a concerted two-electron transfer step. This phenomenon is known as *potential inversion*: the transient radical is thermodynamically unstable because the oxidation potential of the second electron transfer is lower than the initial.^[16] BQ and DMA are examples of a dicarbonyl and a diamino compound, which are common types of ROMs that have wide ranging structures used in negative and positive electrolytes. The diamine-diimine redox mechanism is the essence of many organic anolytes including isoalloxazine, phenazine, and viologen derivatives, shown in Figure 4. These two-electron ROMs are frequently tested as anolytes for the negative terminal reaction, however there are a handful of similar molecules with sufficiently high redox potential to have been tested as positive electrolytes. These include blue dye chemicals. Indigo dye derivatives are one example, which can exhibit reversible four-electron redox chemistry, observed to occur in two distinct two-electron transformations, as shown schematically in Figure 4. The

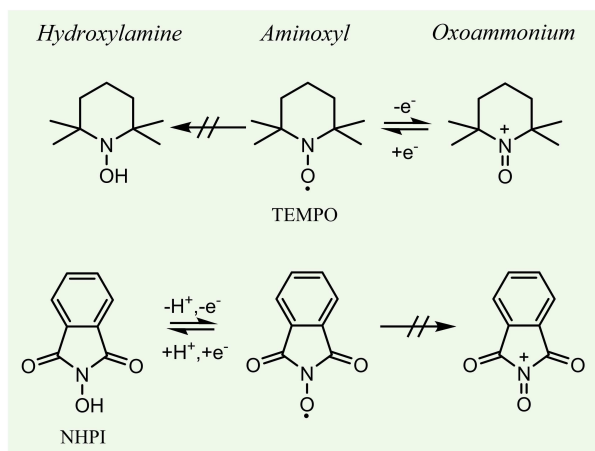


Figure 2. Structures and functional group names for the oxidation states of TEMPO and NHPI in aqueous solution.

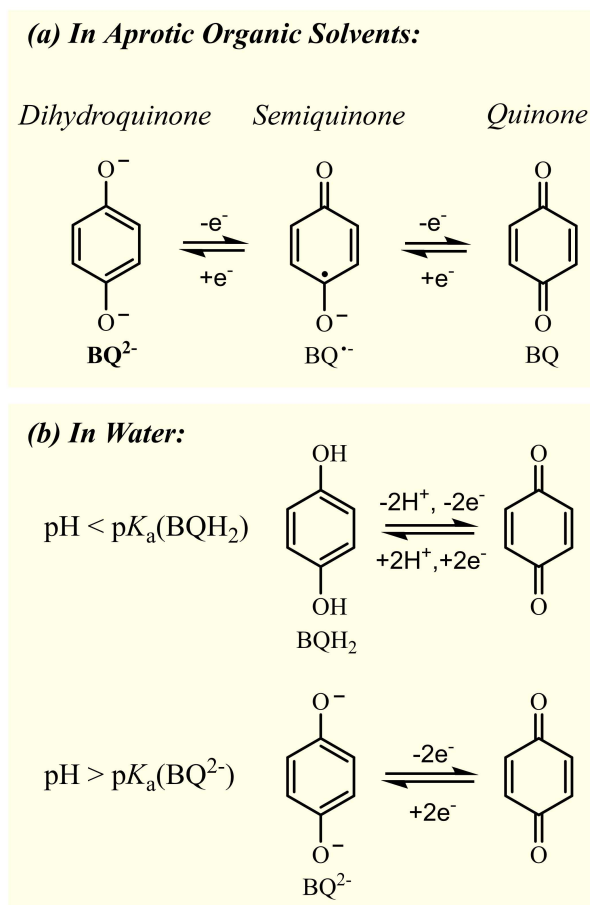


Figure 3. The two-electron redox reactions of benzoquinone in (a) aprotic solvent and (b) aqueous solutions.

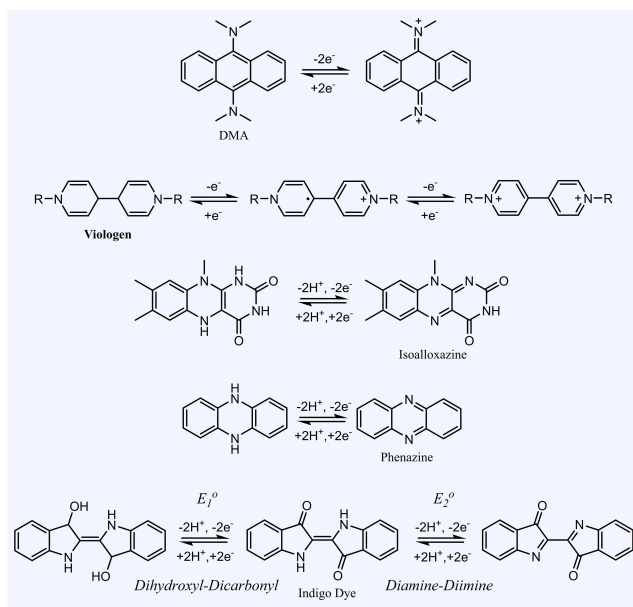


Figure 4. Two-electron redox transformations diamine compounds 9,10-bis-(dimethylamino)anthracene (DMA), viologen, isoalloxazine, phenoxazine, and indigo dye.^[17]

dihydroxyl-dicarbonyl reaction occurs at a lower potential akin to common anolyte species, and the diamine-diimine redox couple occurs at a much higher potential. Indigo can thus theoretically be used on both sides of an RFB, with the diamine-diimine switch used as the positive electrolyte reaction.

In Section 3.3, the amine-imine redox functionality in organic RFB electrolytes is discussed. Some ROMs that have been explored are composed of a phenothiazine (PTZ) sub-structure, which contains a single amine group and can undergo a single electron transfer, with the second electron transfer possibly reliant on electron-donation from the thioether group. This results in a two-step oxidation seen at different potentials.^[18] As for other ether and thioether functionalized ROMs, the stability in aqueous solutions has hindered research, but some possibly promising findings regarding ether and thioether based RFB candidates are discussed in Section 3.4.

2.2. Redox potential

The redox potential (E) reflects the difference in the free energy of formation of the oxidised and reduced states of the molecule within the RFB electrolyte. ROMs have a wide range of redox potentials, and many redox couples can be paired within the stability window of water, but aqueous soluble ROMs generally have potentials lower than 1 V vs the standard hydrogen electrode (SHE). Alongside examples of transition metal ion and inorganic RFB chemistries, selected potentials published in the literature including NHPI, indigo carmine (IC), THTPA and TEMPO-derivatives are presented in Figure 5 to give an overview of the field. The specific ROM examples shown are referenced underneath and are discussed further in Section 3.

It is clear there is often room to increase the redox potential, particularly of those studied in strong acid. As such, high potential molecules ($E > 0.5$ V vs SHE) are a key area of research, and many have been tested in lab-scale RFB cells. The reversible potential of the cell (V_{cell}) at 50% state-of-charge (SOC) of a RFB is the difference between the redox potentials of the two redox-active electrolytes.^[39,40] A V_{cell} of 1.5 V is commonly seen as a benchmark for aqueous RFBs with a viable energy and power density, although these performance figures are also dependent on other aspects such as how facile the redox couple is, its transport properties, and its solubility.^[2] The V_{cell}° is defined in Equation (1), where $E_{\text{RHE},+}^{\circ}$ and $E_{\text{RHE},-}^{\circ}$ are the redox potentials of the positive and negative electrolytes respectively, referenced to the RHE scale and measured under standard conditions (298 K and unit activities of all redox active species).

$$V_{\text{cell}}^{\circ} = E_{\text{RHE},+}^{\circ} - E_{\text{RHE},-}^{\circ} \quad (1)$$

The ability to modify the chemical structure of organic molecules and their surrounding environment allows the redox potential of organic molecules to be adjusted. A higher electron density in the vicinity of the redox centre will lead to a lower redox potential, and vice versa, although the stratification of redox potentials in the literature may not be typical of this trend due to effects such as hydrogen-bonding, protonation, and

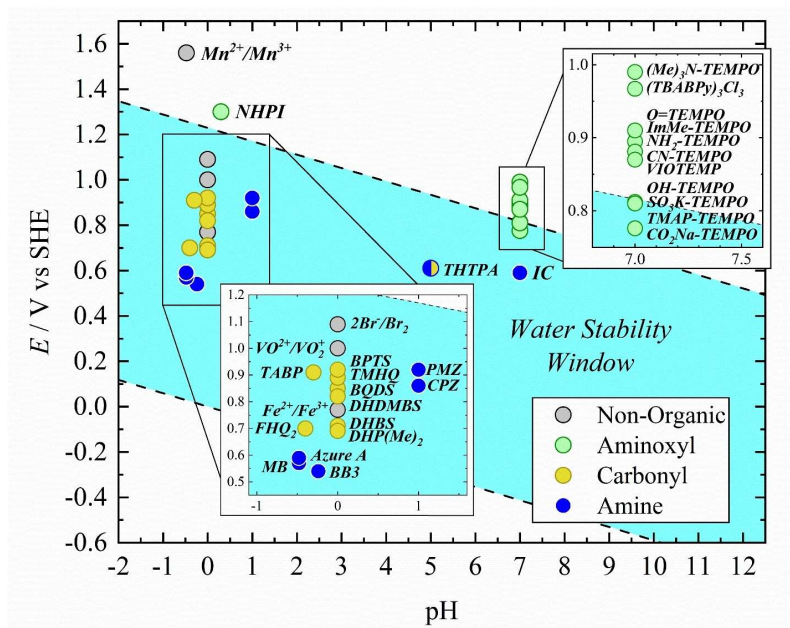


Figure 5. An E-pH diagram with selected redox potentials from the literature referenced to standard hydrogen electrode (SHE) versus the pH conditions used for each redox couple, including the thermodynamic water stability window.^[19–22] (Abbreviations: IC^[23] = indigo carmine, TEMPO^[8] = 2,2,6,6-tetramethylpiperidine-1-oxyl, NH₂-TEMPO = 4-amino-TEMPO^[24], CO₂H-TEMPO = 4-carboxyl-TEMPO^[24], CO₂Na = 4-carboxyl-TEMPO^[25], OH-TEMPO = 4-hydroxy-TEMPO^[24], O = TEMPO = 4-oxo-TEMPO^[26], CN-TEMPO = 4-cyano-TEMPO^[24] ImMe-TEMPO^[27], SO₃K-TEMPO = TEMPO-4-sulfate^[28], N^{Me}-TEMPO = 4-trimethylamino-TEMPO^[29], TMAP-TEMPO^[30] = 4-[3-(trimethylammonio)propoxy]-TEMPO, VIOTEMP^[31] = 1-(4-(((1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)oxy)carbonyl)benzyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium-chloride, (TBABPy)₃Cl₃^[32] = 1-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-1-(3-(trimethylammonio)propyl)-4,4'-bipyridinium, THTPA^[7] = trihydroxytriphenylamine, NHPI^[14] = N-hydroxyphthalimide, BB3^[33] = basic blue 3, MB^[18] = methylene blue, FQH₂^[34] = 2,3,5,6-tetrakis((dimethylamino)methyl)hydroquinone, DHBS^[35] = 1,4-dihydrobenzoquinone-3-sulfonic acid, DHDMS^[36] = 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid, BQDS^[35] = 1,2-dihydrobenzoquinone-3,5-disulfonic acid, TABP^[37] = 3,3',5,5'-tetramethylaminemethylene-4,4'-biphenol, 4,4'-BPTS^[38] = 4,4'-biphenol-3,3',5,5'-tetrasulfonic acid, QZ^[23] = quinizarin, CPZ = chlorpromazine and PMZ = promethazine^[18]).

inter- or intra-molecular functional group interactions.^[40,41] As a general trend, electron-donating groups (EDG) such as alkyl, alkoxy, amine, and hydroxyl groups, and fused aromatic rings reduce the redox potential, whereas an electron-withdrawing group (EWG) such as a halogen atom, carboxyl, sulfonate, cyano or a nitro substituent can serve to increase the redox potential. The higher redox potential molecules therefore have a high electron affinity and are vulnerable to nucleophilic attack and decomposition. This is exasperated in alkaline environments as the hydroxide ion (OH⁻) is a very good nucleophile.

For many aqueous organic redox couples there is a pH range in which the redox transformations are also proton-coupled. Electron-transfer into and out of molecules is the central mechanism of the organic RFB. The increase in the acidity as a result of oxidation is the origin of PCET reactions.^[42] For organic molecules this is often obvious from the solution pH and the pK_a of dissociable protic groups for each state. This differs crucially from hydrogen atom transfer, in which the proton and electron are transferred from the same orbital. The organic molecules discussed here often have extensive delocalization, and the interaction between orbitals allows simultaneous H⁺/e⁻ transfer from the molecule, and hydrogen bonding to heteroatoms (e.g., O or N) can pre-form the reaction pathway.^[42] Proton-transfer is a shorter range process than electron-transfer, and the redox potential is dependent on the pH of the external solution with which the H⁺ ions are

exchanged. Within the proton-coupled pH region, the pH-dependence of *E* is predicted by the Nernst equation: for a redox reaction at a given pH involving *m* protons and *n* electrons, the reversible potential, *E*^{rev} (in units of V), at 25 °C can be found from the standard potential (*E*_{SHE}⁰) as shown below.

$$E^{\text{rev}} = E_{\text{SHE}}^0 - \frac{0.059m}{n} \text{pH} \quad (2)$$

The *E*^{rev} of pH-dependent reactions, such as the scheme shown in Figure 3b between BQH₂ and BQ, increases at lower pH due to the greater thermodynamic preference to protonate the basic hydroxyl groups upon reduction. The decomposition of water occurs in hydrogen and oxygen evolution reactions, which when measured on the RHE potential scale have pH-independent thermodynamic reaction potentials of 0.000 and 1.229 V respectively. These potentials define the thermodynamic stability window of water depicted in Figure 5. Here, the potentials (vs SHE) of organic redox candidates are shown for comparison, at the pH conditions of the supporting electrolytes in which they were tested. The oxidation and reduction potentials of water impose a fundamental limitation on the cell voltage that is attainable with the conventional aqueous RFB design. The need to limit electrolyte solution decomposition-supports the use of the RHE reference scale as appropriate for

these aqueous electrolytes. There is the possibility of the parasitic hydrogen evolution reaction (HER) if the potential of the negative redox couple decreases to below the hydrogen equilibrium potential of 0.000 V vs RHE. For instance, in the vanadium redox flow battery, $E_{\text{RHE},-}^0$ of the negative electrode reaction $\text{V}^{2+}/\text{V}^{3+}$ is -0.255 V, and this can be tolerated, but care has to be taken to avoid electrode and electrolyte compositions which include species that may catalyse the HER. The slow kinetics of oxygen evolution allows electrolyte redox potentials to fall far above the upper 1.229 V vs RHE limit, and therefore candidates with redox potentials above the water stability region in Figure 5 are usable provided the kinetics of oxygen evolution remain slow. The maximum positive operating electrode potential can be extended up to 1.5–1.6 V vs RHE, at which point the oxidation of carbon electrode materials, rather than water, will often become the limiting factor.^[41] That being said, as we can see from Figure 5 most of the relevant organic compounds that have been studied so far are within the water stability window, particularly in acid. The type of redox couple is classed by the redox centre (aminoxyl, carbonyl, or amine), and these compounds are discussed in further detail in Section 3. Their redox potentials are all situated in similar ranges for each type. However, in both neutral and acidic systems the aminoxyl redox centre compounds have the highest E° values vs RHE.

2.3. pH value

As we have already said, the redox potentials of certain ROMs have a region of pH-dependence. pH can therefore change the cell voltage when using positive and negative cell reactions with different degrees of proton-coupling; if the positive electrolyte has a proton independent reaction and the negative electrolyte is proton dependent then the cell potential could be increased by using a higher operating pH. Similarly, the cell potential will increase if the positive electrolyte reaction is pH dependent and the negative electrolyte is pH independent when shifting to a lower pH, within the region of proton-coupling. The pK_a of the organic redox molecule in all oxidation states is important to be aware of, as PCET reactions may cause the pH to be dynamic during cycling. Considering the electrolyte and RFB as a whole, the pH at which the system is chosen to operate at can greatly affect the longevity, efficiency, power density, and energy storage capacity of the system. Double membrane architectures have been explored to take advantage of the wider window of aqueous stability that can be possible using a pH-differential system.^[34]

Neutral pH is commonly used because it is a safe, non-corrosive, and stable environment for many organic molecules as well as for polymer electrolyte materials. Issues that arise with alkaline electrolytes are firstly that long-term operation would require protection from CO_2 in the atmosphere to prevent carbonation, and secondly the high concentration of hydroxide ions can be unsuitable for some organic active species that are susceptible to nucleophilic attack. Another issue that affects both alkaline and acidic systems is the

susceptibility of some ion-exchange polymers to degradation at high or low pH, whereas almost all are stable under neutral pH conditions. The issue of stability may also apply to other components such as metallic or ceramic materials, and the risks when using corrosive electrolytes need to be considered for long-term use. During RFB operation, the Ohmic resistance of charge conducting components, including the electrolyte solution (R , $\Omega \text{ cm}^2$), is an energy loss that should be minimised in order to optimise the power density and round-trip efficiency (ϵ), shown by the relation below.

$$\text{Maximum power density} \approx \frac{V_{\text{cell}}^0 \left[(1 - \epsilon)^{\frac{1}{2}} - (1 - \epsilon) \right]}{R} \quad (3)$$

The ionic conductivity of the electrolyte must therefore be as high as possible, as this maximises the power density at constant efficiency. As shown in Figure 6, the ionic conductance of acid and alkaline solutions at 1 mol L^{-1} supporting electrolyte surpass near-neutral electrolytes by a factor of approximately 3:1 and 2:1 respectively.

2.4. Solubility

The solubility of active species defines the limit for the theoretical capacity (Q_t) of the electrolyte tank, which is commonly expressed in Ah L^{-1} and is defined in Equation (4), where n is the number of electrons per molecule involved in the redox couple, c_{max} is the maximum solubility, and F is the Faradaic constant.^[1]

$$Q_t [\text{Ah L}^{-1}] = \frac{c_{\text{max}} n F}{3600} \quad (4)$$

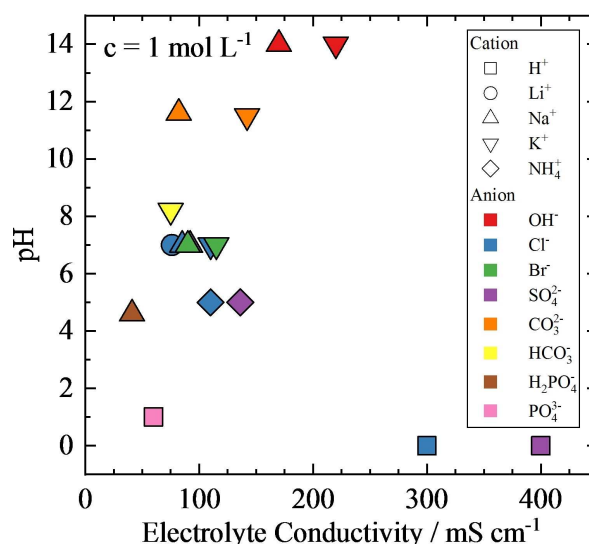


Figure 6. The ionic conductivity and pH of selected ionic solutions including common aqueous RFB supporting electrolytes at 25°C and 1 mol L^{-1} molarity.^[43,44]

The theoretical volumetric energy density (E_v) of an RFB has units J m^{-3} although is typically expressed in Wh L^{-1} and is half of the average electrolyte tank capacity multiplied by the cell voltage.

$$E_v[\text{Wh L}^{-1}] = \left(\frac{Q_{t,+} + Q_{t,-}}{4} \right) V_{\text{cell}}^{\circ} \quad (5)$$

An equivalent electron concentration ($c_{\text{max}}n$) of 1 mol L^{-1} is often cited as a minimum benchmark for the capacity. Two tanks of 26.8 Ah L^{-1} (1 mole L^{-1}) of electrolyte creating a 1.5 V cell potential leads to an energy density benchmark E_v of 20.1 Wh L^{-1} .^[28] The ability to tune the properties of organic structures allows the solubility to be improved with the addition of functional groups to otherwise non-polar, hydrophobic structures. Sulfonate and phosphate groups are both highly polar across the pH range, and sulfonate is an especially common ROM substituent, the counter-ion usually being H^+ , Na^+ , or K^+ . The pH at which substituents ionise can be predicted from the pK_a of the functional groups that the molecule contains. The supporting electrolyte pH can therefore also be tailored to increase the capacity of the electrolyte. Carboxylic acid groups tend to dissociate only above a pH of approximately 4.5, and so in acidic solutions their solubilisation effect is less dramatic.^[45] Quaternary amine groups and sodium ions are isoelectronic, which may help explain the high solubilisation often seen for aminated ROMs.^[44] A quaternary amine substituted TEMPO has a water solubility of 3.2 mol L^{-1} , compared to 2.5 mol L^{-1} for TEMPO with a sodium carboxylate substituent at the same position.^[25,29] Primary and secondary amine functionalized compounds also display good solubility, for example the solubility of 4- NH_2 -TEMPO was measured to be nearly 5.8 mol L^{-1} in water.^[24] Furthermore, amine groups can be bifunctional by also adding redox reversibility into the compound through their electron-donating properties, as discussed in Section 3.3.

For organic electrolytes to attain energy densities that are adequate for flow batteries a second organic material referred to as a cosolvent or solubility promoter is sometimes added to the electrolyte solution to increase the concentration of a hydrophobic ROM in aqueous electrolyte. Cosolvent is a broad term to describe organic solvents that are miscible with water, with examples being ethylene carbonate or acetic acid. Solubility promoters include hydrotropes, which are small amphiphilic organic molecules, such as nicotinamide and urea, and have been used in flow batteries to successfully achieve high concentrations of ROMs in aqueous electrolytes. Cheng et al. investigated the effect of five hydrotropic additives in the range 0–20 wt% on the aqueous solubility and electrochemical properties of five aqueous ROMs.^[46] Similar to previous studies, it was shown that hydrotropes can raise the solubility of ROMs without severely altering the electrochemical properties, although there are no accurately defined common principles to describe the mechanism of solubilisation upon their addition.^[46,47] Creating a high energy density electrolyte solution is preferable as this can increase the overall efficiency by requiring a lower volume to be pumped while still maintaining

a high concentration of reactant in the electrodes.^[48] The trade-off is that although a practical E_v can be attained, adding a significant volume of inactive organic material to improve the solubility can have a negative impact on the conductivity and rheological properties of the electrolytes containing the ROMs of small molar mass.^[46] The conductivity of acidic and alkaline aqueous solutions depends on the ionic strength and ionic mobility.^[4] Water is a small and polarisable molecule that can form small solvation shells, allowing for highly concentrated solutions that do not have overwhelmingly high viscosity and good ionic conductivity. For this reason, it is preferable to design electrolyte formulations with high ROM concentrations within a purely aqueous solvent, and with a supporting electrolyte composition that maximises the conductivity of the solution.

2.5. Redox kinetics

The redox kinetics summarises the ease with which the charge transfer reactions between the redox-active species and the electrode surface occur. Fast reaction rates will increase the power density that is attainable, as well as the efficiency of the RFB as a whole.^[4] Electrodes are typically porous conductive carbon materials and therefore an inexpensive component, and ideally the ROM reaction kinetics should be facile on these materials without the aid of an expensive catalyst. The reorganisation energy of conjugated systems is usually low compared to solvated metal ions, and in such instances the fast kinetics of ROM oxidation and reduction lead to the major advantage of having a lower charge transfer overpotential. For example, the electron transfer rate constant (k_e) of the $\text{VO}_2^+/\text{VO}^{2+}$ couple is on the order of $10^{-6} \text{ cm s}^{-1}$, which is multiple orders of magnitude slower than many of the aqueous-soluble organic redox couples discussed here.^[49] k_e is dependent on not only the redox species but also the electrode material, so some care must be taken when making comparisons between different experiments, although carbon is the most common electrode material because of the ease in production of high surface area carbon electrodes. It is typical to assume the Butler-Volmer equation to describe the electrokinetic properties of the reaction, assuming that they take place under outer sphere electron transfer conditions only and there is no adsorption of the redox species on the surface.

2.6. Diffusivity

Conventional RFB electrodes are three-dimensional structures of conductive carbon with a flow-by or flow-through design, generating a considerable electrode-electrolyte interfacial area, designed to maintain short distances between the dissolved active species and the electrochemically active surface. The pressure drop incurred by flowing electrolyte through RFB electrodes adds to the pumping energy required, which ultimately is an efficiency loss in the overall system. The pressure drop (ΔP) is inversely proportional to the Darcian

permeability (K), as shown in Equation (6), where μ is the dynamic viscosity of the electrolyte and L is the length of the electrode over which ΔP is measured.^[50] A higher value of K implies more efficient fluid flow at a given electrolyte velocity.

$$K = \frac{v \cdot \mu \cdot L}{\Delta P} \quad (6)$$

The linear velocity (v) of an incompressible fluid through an RFB electrode is simply the volumetric flow rate (Q_v) divided by the porosity (ϵ) and cross-sectional area (A_x) of the electrode.^[50]

$$v = \frac{Q_v}{\epsilon \cdot A_x} \quad (7)$$

Flow field design, electrode microstructure, temperature, and pumping power can therefore all be varied to improve mass transfer or efficiency, but the diffusivity of both oxidation states of the molecule or ion in the electrolyte solution is also important, as faster diffusion of the redox-active molecule to the electrode surface will reduce the mass transport overpotential and increase the efficiency. Sections 2.1–2.4 have outlined the parameters that are used to define the energy density. The kinetics and diffusivity are then two key metrics of specific redox couples that can be used to assess comparative performance by quantifying the properties required for high power output. The diffusion coefficient (D) is a constant of proportionality that correlates the chemical potential gradient to the flux of active species across the Nernst diffusion layer. The D values of small organic molecules are on the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The mass-transfer coefficient (k_m) describes the steady-state transport of the active species across the diffusion layer, from the bulk electrolyte to the electrode surface within the pores of RFB electrodes. k_m combines not only the diffusion coefficient but also the Nernst diffusion layer thickness, and hence is dependent on the flow rate. If the RFB electrolyte is not pumped, mass transport is reliant on diffusion only, and k_m can be expressed as $2D/d_p$ using the diffusion coefficient of the species and the pore diameter (d_p), where it is assumed that the pore radius is an adequate representation of the Nernst diffusion layer thickness.^[51] To facilitate an adequate supply of reactant to the surface of RFB electrode surface requires pumping the electrolyte solution, and mass transport in RFB electrode pores becomes an advective-diffusive process during operation. Therefore, k_m can provide a complete description of the transport rate in real systems. The volumetric surface area of the electrode (A_e) and k_m define the performance under mass transport control. This condition is attainable in an RFB cell experimentally.^[52] Milshtein et al. quantified the volumetric mass transport of reactants with the variation in these parameters, extracted using a one-dimensional model for single cell polarization measurements with iron chloride.^[53] The volumetric mass-transfer coefficient $A_e k_m$ is a performance factor that may be used to understand contemporary electrode functionality.^[54]

Noting that k_m is proportional to $D^{2/3}$ of the redox species, relative values of k_m can be determined in a known config-

uration, using a well characterised redox couple to estimate what k_m should be if we used an alternative redox couple. This approach assumes that other factors such as the changes in viscosity between electrolytes do not have a substantial effect, which is reasonable. Hence the determination of k_m for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple as a model mass transport limited active species is applicable to correlate values for organic and metallic ion redox couples at representative flow rates which allow for constant convective mass transfer (see supplementary material).^[51] It is then possible to combine the electron transfer and mass-transfer rate constants into a single rate constant ($k_{\text{composite}}$ units m s^{-1}), as in Equation (8).

$$\frac{1}{k_{\text{composite}}} = \frac{1}{k_e} + \frac{1}{k_m} \quad (8)$$

This composite rate constant takes into account that the reaction is composed of two serial processes. The first of these is the mass transfer of the active species to the surface, which is followed by electron transfer once the redox active molecule is close to the surface. The process may be either limited by electron transfer kinetics ($k_m \gg k_e$), mass transport ($k_e \gg k_m$), or in a mixed regime. Many papers focus on the energy density of the electrolyte as the primary metric and somewhat fewer papers consider the electrokinetics, and therefore relatively little has been done in the past to understand the intrinsic power production capability of the RFB. Producing higher power densities at low overpotentials is important as this allows the RFB to operate at higher efficiency and to utilise the minimum amount of material in the RFB stack, thus contributing to a low capital cost of the system. As a result, we introduce the concept of the theoretical intrinsic power per unit electrode surface area ($P_{\text{intrinsic}}$), with units of W cm^{-2} , which scales with the product of the composite rate constant multiplied by the specific energy of the electrolyte. $P_{\text{intrinsic}}$ is a notional power that represents the power generated at a defined overpotential (η) of $\pm 25 \text{ mV}$ and $\alpha = 0.5$ (see Supporting Information) in the absence of Ohmic losses and using the full electrolyte capacity, and the voltage of the ROM coupled to an (infinitely fast) hydrogen electrode as the counter reaction. It takes into account the balance between mass transfer, electron transfer kinetics, and the volumetric energy density of the positive electrolyte as shown in Equation 9.

$$P_{\text{intrinsic}} = 3.6 \cdot k_{\text{composite}} \cdot E_v \quad (9)$$

Figure 7 shows how $k_{\text{composite}}$ and the E_v vary for different redox couples using available literatures data. We also plot lines of constant $P_{\text{intrinsic}}$. As shown in Figure 7, the value of $k_{\text{composite}}$ varies by over one order of magnitude, from $1.7 \times 10^{-3} \text{ cm s}^{-1}$ for THTPA (trihydroxytriphenylamine) down to $8.8 \times 10^{-5} \text{ cm s}^{-1}$ for BB3 (basic blue 3). The volumetric energy density (E_v) of also varies by almost one order of magnitude, ranging from a maximum value of 180 Wh L^{-1} for BQDS (1,2-dihydrobenzoquinone-3,5-disulfonic acid) to only 3.4 Wh L^{-1} for NHPI, the largest effect being due to the electrolyte capacity.

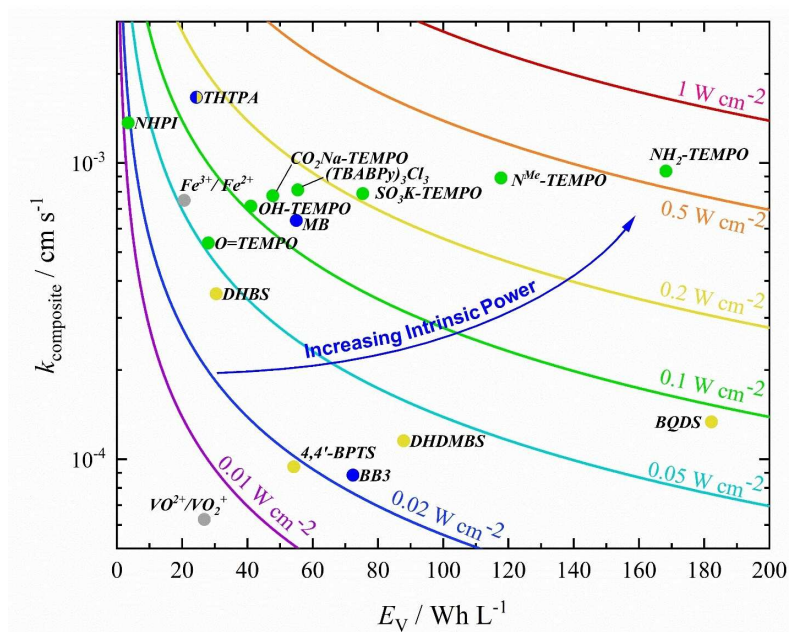


Figure 7. Comparison of composite serial rate constant and theoretical energy density relative to the hydrogen reaction. The lines represent curves of surface area normalized power density at a representative electrolyte velocity of 1 cm s^{-1} , and overpotential of 25 mV (see the mass-transfer-coefficients-calculation Section in the Supporting Information for description). (Abbreviations: $\text{NH}_2\text{-TEMPO}$ = 4-amino-TEMPO^[24], $\text{CO}_2\text{Na-TEMPO}$ = 4-carboxyl-TEMPO^[25], OH-TEMPO = 4-hydroxy-TEMPO^[24], O=TEMPO = 4-oxo-TEMPO^[26], $\text{SO}_3\text{K-TEMPO}$ = TEMPO-4-sulfate^[28], $\text{N}^{\text{Me}}\text{-TEMPO}$ = 4-trimethylamino-TEMPO^[29], $(\text{TBABPy})_3\text{Cl}_3$ = 1-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-1-(3-(trimethylammonio)propyl)-4,4-bipyridinium, THTPA ^[7] = trihydroxytriphenylamine, NHPI ^[14] = N-hydroxyphthalimide, BB3 ^[33] = basic blue 3, MB ^[18] = methylene blue, DHBS ^[35] = 1,4-dihydrobenzoquinone-3-sulfonic acid, DHDMS ^[36] = 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid, BQDS ^[35] = 1,2-dihydrobenzoquinone-3,5-disulfonic acid, $4,4'\text{-BPTS}$ ^[38] = 4,4'-biphenol-3,3',5,5'-tetrasulfonic acid).

Combining the kinetic and mass-transfer coefficients creates a parameter for dynamic performance, which directly feeds through to the CAPEX and OPEX of an RFB system, we see that the materials with the highest performance for one of the parameters k and D are not necessarily those with the highest values for $P_{\text{intrinsic}}$ as it is ones for which the product of the two factors is maximised. We find that there is a factor of 25 difference between the worst and best performers, with the best performers being in the class of TEMPO based systems.

2.7. Stability

Maintaining a high proportion of the original capacity over the course of at least 20 years will be necessary for RFBs to be commercially attractive.^[30] The two major technical difficulties that cause irreversible capacity loss in organic RFBs are i) permeation and crossover through the separator or membrane, and ii) the chemical degradation of the electrolyte.

The mixing of the positive and negative electrolytes is highly undesirable but is tolerable to a low extent, further depending on whether the capacity loss due to crossover is recoverable or not. The conventional form of RFB separators is an ion-exchange membrane (IEM).^[55] An IEM is a polymeric material with fixed charged functional groups along interior channels to allow the exchange of anions or cations. Crossover can also be reduced by tailoring the chemistry of the ligands or molecule or of the membrane itself to install a significant

permanent charge of the redox species alike to the internal electric charge of the membrane, reducing the transport of active species transport through the membrane due to Coulombic repulsion, known as the Donnan exclusion effect.^[56] Microporous separators are used in lithium-ion and lead acid batteries but are not the conventional membrane technology of RFBs. They are however a low-cost alternative to many IEM materials that are currently in production.^[57] The ion selectivity in microporous separators is due to the unequal rate of ion transport, and therefore depends on the pore size and thickness, combined with the specific RFB electrolyte chemistry. These materials are also usually prepared from inherently hydrophobic polymers, but the wettability can be increased with the incorporation of ceramic particles, which also are used to adjust the pore size and void volume.^[57] In order to totally eliminate capacity loss from ROM crossover, electrolyte compositions may be identical. This can be achieved by using bipolar ROMs (molecules with two or more redox potentials) or with mixed electrolytes (both tanks containing both the positive and negative species). As a consequence of the mixed electrolyte approach, the energy and power densities of the RFB can suffer, as neither electrolyte is truly optimised. Hybrid-RFBs using a gas on one side, H_2 or O_2 for example, offer an effective means of minimising capacity loss by allowing the liquid crossover to be collected on the gas side and be returned to the liquid side, thus recovering the capacity loss due to crossover. Important too is the stability of the IEM or separator, which must withstand long-term usage in an oxidising environment, and

resistant to chemical attack from strong acid or alkaline electrolytes depending on the electrolyte pH, and retain their physical integrity. They must also be resistant to fouling, which is the hindrance of membrane functionality via interaction with the electrolyte and is already a known problem for some organic species.^[58,59]

Capacity loss due to the chemical degradation of ROMs is usually irrecoverable. Electron-deficiency in the oxidised state of ROMs such as quinones and viologens can lead to nucleophilic attack from water and hydroxyl anions.^[3] Organic species will eventually generally degrade to non-redox active products.^[26] On the contrary, it is sometimes possible to regenerate metal-based active species that have undergone chemical degradation without a need to replace the electrolytic solution. Therefore, capacity fade in many organic RFBs is considered permanent and for ROMs tested in full systems the stability is a parameter of equal importance as the energy storage capacity and electrochemical properties. In the literature, stability is generally reported as capacity fade per cycle. This can provide an indication of the level of chemical degradation but can overcomplicate the determination of RFB longevity and differs depending on the timescale of the experiment. It is worth emphasizing that analysing stability by capacity fade is more relevantly measured by also considering the molecular stability of the reduced and oxidised forms independently and on a temporal basis.^[60] Cycling protocols, which are conventionally applicable to deposition and intercalation batteries to study the reversibility of electrode processes, often provide little or inaccurate comparative information for permanently solvated molecules in a reduced or oxidised form that fade primarily due to molecular degradation in the aqueous electrolyte rather than during the actual reduction or oxidation processes. Therefore, the timescale of RFB cycling tests should always be noted, and capacity fade per hour or per day stated alongside the fade per cycle. This will provide more information about the stability of organic electrolytes in conditions that reflect the needs of their real-world application.^[60]

2.8. Cost

The final key parameter that is mentioned here is the cost, which is an ultimate determinant of whether any functional energy storage technology will be of service to consumers. The applications of flexible EES installation include frequency regulation, peak shaving and arbitrage, and black start support.^[61] At present, the primary method of grid-connected energy storage, with a 96% share of the total storage capacity worldwide, is pumped hydropower.^[62] Of the remaining share, lithium-ion batteries is the most popular.^[61] Due to the demand for other EES options, the cost of aqueous flow battery installation has been the subject of several techno-economic analyses, and the cost is a common criticism of current state-of-the-art RFB technology, generally referring to the vanadium RFB specifically.^[2,63,64]

Small redox-active molecules in aqueous media are often recognised as possible low-cost alternatives to systems using

transition metal ions such as vanadium, which currently dominates the redox flow battery market. The much more advanced state of aqueous RFB development over non-aqueous systems allows more predictable evaluation of organic RFBs at a system level.^[2] The system cost of an RFB can be separated into the stack and the electrolyte, which represent the power and energy needs of the system respectively. These two factors scale independently, and with increasing storage capacity the system cost per kWh decreases.^[2] Darling et al. concluded that \$5 kg⁻¹, equivalent to \$0.75 (mole⁻¹) or \$28 (kAh)⁻¹, is the requirement for cost-effective active species in 2014. This is considering performance targets of 2 mol L⁻¹ and a cell potential of 1.5 V.^[2] All of the compounds discussed here use abundant elements, and a commercial ROM could be produced from petrochemical or biomass precursors, and therefore the cost of the electrolyte could be independent from the wavering and expensive prices of transition metals.^[2,65]

3. Organic Molecules for Energy Storage

3.1. Aminoxyl compounds

TEMPO compounds were introduced in Section 2.1. To reiterate, the persistent aminoxyl radical group of TEMPO undergoes a highly reversible one-electron oxidation reaction in organic and neutral aqueous media. Unfunctionalized TEMPO has been predominantly studied in non-aqueous electrolytes, but numerous TEMPO derivatives now constitute the most studied radical species for aqueous-organic electrolytes due to the stability of both the neutral radical (reduced) and oxoammonium (oxidised) forms.^[66,67] TEMPO derivatives are a popular redox couple for the positive terminal in neutral aqueous solution because the redox potentials are usually in the region 0.8–1.0 V vs SHE, which is near the standard potential of water oxidation (0.817 V vs SHE at pH 7). Although high, this could still be increased significantly to maximise the cell voltages of an aqueous RFB system before oxygen evolution occurs.^[30]

The neutral TEMPO radical structure is persistent firstly due to electron delocalization within N–O bond and secondly by the steric hindrance from the four alpha-methyl substituents. Upon oxidation, an electron is taken from the singly occupied molecular orbital, creating a formally positive charge on the molecule, as shown in Figure 8a.^[69] Crucially, TEMPO-based electrolytes are restricted to use in near-neutral pH solutions. The redox reaction is effectively irreversible at high pH because TEMPO⁺ self-discharge rapidly occurs via a parasitic side reaction with hydroxyl anions, shown in Figure 8b. TEMPO-compounds are also unable to function well in acidic conditions, even when the pH is only mildly acidic, due to the degradation reaction shown in Figure 8c.^[66,69]

Functionalized TEMPO molecules have presented exciting opportunities for neutral high potential candidates with high energy density.^[70] Increasing the solubility of TEMPO for aqueous systems requires polar or hydrophilic substituents. The research concerning TEMPO-based ROMs for aqueous RFBs has focused on adding various substituents to the 4-position of the

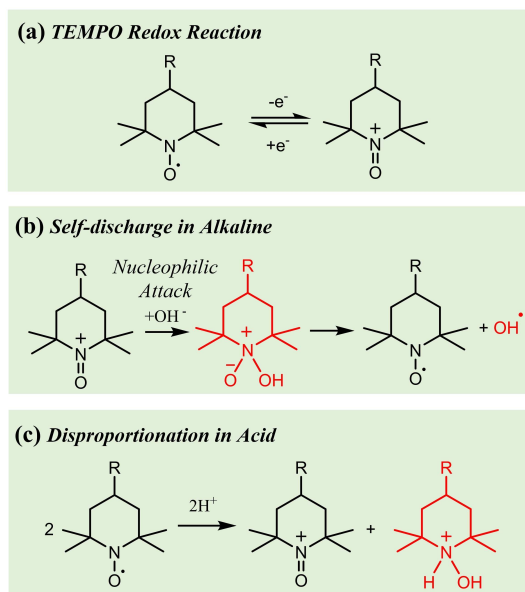


Figure 8. (a) Redox reaction between the neutral TEMPO radical and the oxoammonium ion, and the known degradation reaction schemes of (b) TEMPO⁺ in acid and (c) the TEMPO radical in alkaline solutions.^[65,68]

ring (shown by the R group in Figure 8). Due to its high solubility, OH-TEMPO has been studied for multiple RFB systems.^[68,71] The findings however revealed significant chemical degradation, which is often attributed to self-oxidation of the alcohol group.^[65,71,72] A study by Zhou et al. investigated multiple derivatives of TEMPO, and those with a sufficient solubility for RFB systems were tested in a symmetric cell arrangement at 60 °C. It was revealed that OH-TEMPO and NH₂-TEMPO retained only 44.6% and 23.1% of their original capacity after 200 cycles.^[24] The aqueous solubilities of CN-TEMPO and CO₂H-TEMPO were found to be unsuitably low. Interestingly, Liu et al.

synthesised CO₂Na-TEMPO, the sodium salt equivalent of CO₂H-TEMPO studied by Zhou et al., and discovered it is soluble up to 1.5 M in 1.5 M NaCl.^[25] This shows the difference in ROM solubility by increasing the amount of ionisation, as during the testing of this compound they identified the formation of a precipitate, which was identified as CO₂H-TEMPO.^[25] The precipitation and another degradation mechanism of CO₂Na-TEMPO, initiated by nucleophilic attack, are both shown in Figure 9a.

The differing substituents and their interaction with the solvent and electrolyte leads to the wide variation in solubility, diffusion, redox kinetics, and stability of TEMPO derivatives. For example, a 1-methylimidazolium functionalized TEMPO (ImMe-TEMPO) synthesised by Chang et al. showed an improved voltage and stability compared to OH-TEMPO.^[27] Winsberg et al. synthesised SO₃K-TEMPO and showed that it decayed at a rate of only 0.72% per day.^[28] At 1.0 M concentration of 4-sulfo-TEMPO, the oxidised form is zwitterionic and was found to precipitate, but this could be mitigated by increasing the chloride ion concentration up to 5 M to shield the positively charged region and prevent aggregation. Liu et al. demonstrated a -(CH₂)₃N(CH₃)₃⁺Cl⁻ substituted 4-[3-(trimethylammonio)propoxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (TMAP-TEMPO), which made the structural modification of electronically separating the charged ammonium group from the six-membered ring.^[30] The OH-TEMPO reference cell capacity was found to fade at a rate of 5.28% per day, compared to only 0.624% per day for TMAP-TEMPO. Janoschka et al. synthesised a quaternary -N(CH₃)₃⁺Cl⁻ substituted derivative (N^{Me}-TEMPO), which contains a permanent positive charge. N^{Me}-TEMPO showed minimal capacity fade over 100 cycles at 2.0 M concentration, which indicates that it is considerably more stable than the other derivatives discussed so far.^[72] Some reasons for the capacity fade of TEMPO-based compounds have been suggested, including H-abstraction and dimerization, but more detailed understanding of the degradation pathways of

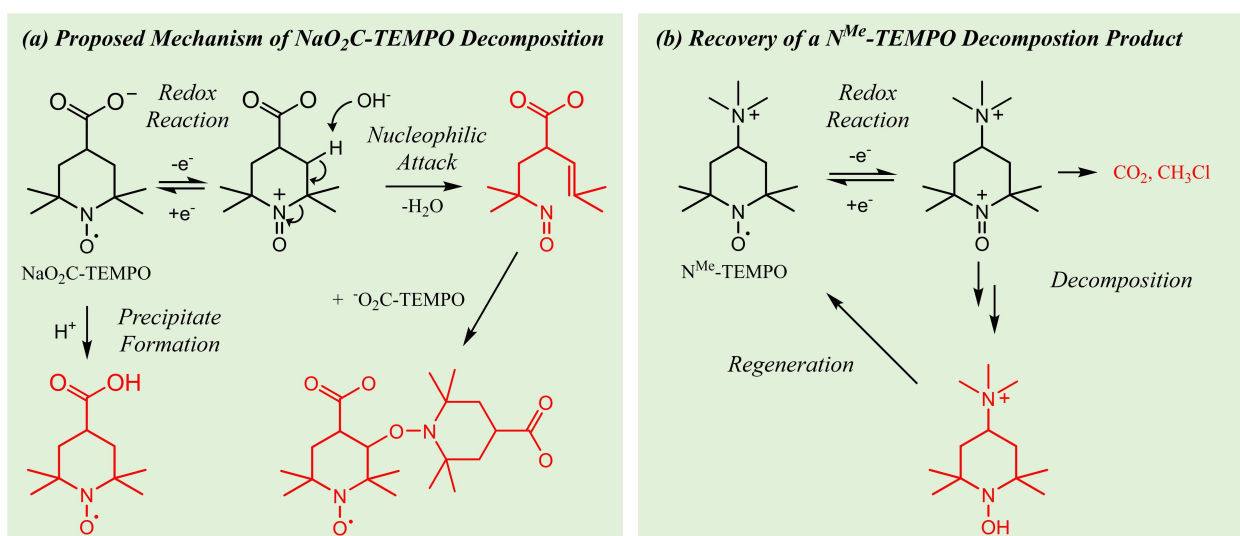


Figure 9. (a) Proposed decomposition pathway and products of NaO₂C-TEMPO^[25] and (b) and partial regeneration of N^{Me}-TEMPO.^[11]

small TEMPO derivatives is needed to further improve the stability of aqueous TEMPO electrolytes.^[3,30] Recent work has attempted to answer this question in greater detail, with several mechanisms of N^{Me} -TEMPO molecular decomposition suggested.^[11] Nolte et al. suggest that capacity loss is mainly due to formation of the hydroxylamine, which can be re-oxidised to TEMPO as shown in Figure 9b, and is a rare example of capacity recovery within organic RFBs.^[11] N^{Me} -TEMPO is regenerated during over-charging the electrolyte. The regeneration is thought to occur indirectly via a comproportionation reaction with an oxoammonium ion.

Research into molecular TEMPO electrolyte species has now also extended beyond simple functional group substituents to assemble more complex molecules. The addition of a viologen molecule as a substituent has been shown to increase the redox potential, due to its electron-withdrawing effect, and can increase the solubility of TEMPO due to the polarity of the three quaternary nitrogen atoms. A novel viologen-functionalized TEMPO (TPABPy)Cl₃ shown in Figure 10 was prepared by Hu et al. which had a reported the redox potential of 0.97 V vs SHE and a solubility in excess of 1 M.^[32] Janoschka et al. synthesised a bipolar ROM to also utilise the redox couple functionality in the viologen substituent. The novel VIOTEMP molecule created a theoretical 1.16 V potential difference in a symmetric RFB using 1.5 M VIOTEMP and without the need for any supporting electrolyte, although the loss of polarity upon electrochemical reduction of the viologen group led to a maximum solubility of only 25 mM. However, cosolvents such as ethylene carbonate, acetonitrile, and dimethyl sulfoxide were incorporated and a symmetric RFB of 0.1 M VIOTEMP was demonstrated.^[31] This cell mimics vanadium-RFB design with a potentially lower cost, however the occurrence of irreversible side reactions in water such as acidification caused by reaction with OH⁻ ions even at neutral pH may impose intrinsic limitations on the calendar lifetimes of TEMPO-based molecules.^[26]

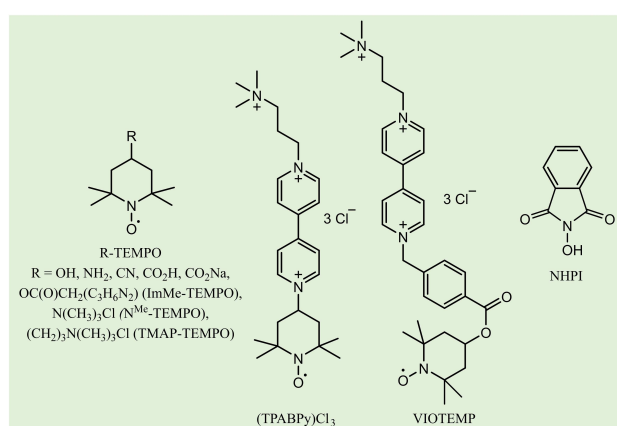


Figure 10. Examples of aminosyl-based ROMs shown are R-functionalized TEMPO molecules, specific viologen-derivatised TEMPO structures ((TPABPy)Cl₃ = 1-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-1-(3-(trimethylammonio)propyl)-4,4-bipyridinium trichloride, and VIOTEMP = 1-(4-((1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)oxy)carbonyl)benzyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium-chloride)^[31,32, 67] and NHPI (N-hydroxyphthalimide).^[14]

The high potential redox behaviour of *N*-oxyl compounds has been employed in organic synthesis as selective oxidative catalysts.^[73] Other than TEMPO compounds, *N*-hydroxyphthalimide (NHPI) shows particularly high potential redox behaviour.^[14] The hydroxylamine to *N*-oxyl radical transformation (see Figure 2) is the redox couple utilised in the case of NHPI. Tian et al. have demonstrated a reversibly cyclable NHPI-anthraquinone RFB with a semi-aqueous electrolyte of 0.1 M NHPI dissolved in 1.0 M H₂SO₄ and acetonitrile, which operates with a cell voltage that overlies the aqueous electrochemical stability window in acid to a significant extent.^[14] The N–O bond of NHPI is relatively electron-deficient and the PCET reaction occurs with a reported potential of 1.30 V vs SHE. Further assessing the capability of this high potential redox mechanism in aqueous systems could present a great advancement of *N*-oxyl compounds beyond TEMPO-based electrolytes.

3.2. Carbonyl compounds

Carbonyl groups can operate as redox centres via an enolization mechanism; hydroxyl groups can be formed by the reversible PCET reduction of electroactive carbonyl groups. Electroactive carbonyl-containing ROMs cover a major sub-section of experimentally tested ROMs, although high potential carbonyl-based ROMs have been dogged by chemical instability under operating conditions. However, research has shown that rational molecular engineering can yield high capacity carbonyl-based redox couples that display cycling performances among the most stable of all reported ROMs. Some examples of high redox potential hydroxyl ROMs (the reduced form) are shown in Figure 11 and are discussed in this section.

Quinones are conjugated cyclic dione molecules formed by the two-electron oxidation of the corresponding hydroquinone. Natural quinones act as redox mediators in biological systems and show rich electrochemistry.^[74–76] Conjugated quinone systems are also often chromophoric and they have been extracted or synthesised for their use as red, orange, and bright yellow pigments and dyes.^[77] Different quinones have been utilised for positive and negative electrolytes in RFBs because the redox

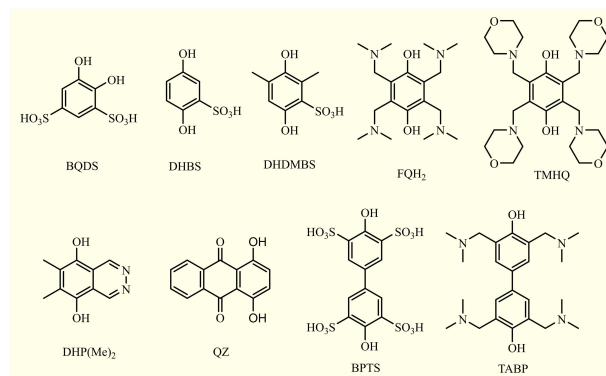


Figure 11. Chemical structures of selected carbonyl-centred organic redox couples in the reduced (hydroxyquinone) states.

potential is widely variable with the molecular structure of the quinone molecule. Naphthoquinone and anthraquinone compounds have relatively low potentials and are common negative electrolytes, whereas benzoquinones have been identified as positive electrolyte redox couples.^[39] The distinctly lower electronic stabilisation of benzoquinones, compared to fused aromatic ring structures, evidently leaves the central benzoquinone ring vulnerable to nucleophilic attack.^[78] The redox reaction of benzoquinone was presented in Figure 3 (see Section 2.1) and occurs at 0.67 V vs SHE.^[79] At least one benzylic hydrogen atom must be substituted for a hydrophilic group to increase the aqueous solubility.^[80] Since 2009, the research interest in organic molecules for RFBs has grown dramatically. Xu et al. first reported the use of aqueous soluble organics for the positive electrolyte by dissolving the molecules 1,2-dihydrobenzoquinone-3,5-disulfonic acid (BQDS) and 1,4-dihydrobenzoquinone-3-sulfonic acid (DHBS) in sulfuric acid solutions.^[35] The sulfonate groups attached to the central hydroquinone redox moiety increased the solubility compared to unfunctionalized hydroquinone, but the electron deficiency of BQDS destabilises the quinone form. The BQDS system showed a large coulombic efficiency drop in the initial charging cycle, which was not seen for DHBS. This indicated that the BQDS redox couple was unstable, but produced a lower energy molecule that continued to cycle, albeit with an approximately 0.2 V lower cell voltage thereafter.^[35,81] The BQDS degradation hypothesis was affirmed by Yang et al. who demonstrated an all-organic RFB utilising BQDS to find the initial charge-discharge cycle displayed a coulombic efficiency (CE) of only 33 %, but was then consistently ~100 % due to the cyclability of the hydroxylated by-product, namely 1,2,4,6-tetrahydroxybenzene-3,5-disulfonic acid, which continues to function as the positive electrolyte but undergoes another reaction with water as shown in Figure 12.^[81]

To overcome this undesired hydrolysis side-reaction of high potential benzoquinones, Hooper-Burkhardt and co-workers synthesised 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid (DHDMBS), which has two *ortho*-methyl groups to slightly increase the electron density and steric protection of the ring, making the 1,4-addition with water less favourable.^[36,82] Considering the inherent instability of benzoquinone ROMs, the current focus in the literature appears to have shifted to

synthesising fully (tetra-) substituted benzoquinones, such as the tetra-amine functionalized hydroquinone (FQH₂) synthesised by Park et al. which demonstrated good cycling stability in a pH-differential hybrid RFB cell.^[34] Drazevic et al. synthesised tetramorpholinohydroquinone (TMHQ) in order to block all four unsubstituted positions with EWGs, with the intention of making a high potential and stable benzoquinone. However, an unintended knock-on effect of adding these groups was an impedance of the two-electron and two-proton redox reaction under acidic conditions, which had a redox a peak separation of 650 mV at pH 0 on carbon, classifying the redox reaction as irreversible.^[83] This may be due to a highly unfavourable dissociation of protons from the basic morpholino substituents upon oxidation of TMHQ⁴⁺. Other than total C–H blocking, other novel molecules have been made that endow the quinone form greater resonance stabilisation. Hofmann et al. synthesised molecules based on the 2,3-diaza-9,10-anthraquinone substructure, which has a fused heterocyclic ring to stabilise the benzoquinone centre and a formal potential 0.796 V vs SHE. This is an estimated +0.46 V higher than the more electron-rich homocyclic 9,10-anthraquinone.^[84] The structure of the demethylated dihydroxyphthalazine DHP(Me)₂ is shown in Figure 11. The protection from nucleophilic attack due to the presence of the two methyl groups is comparable to the modification of BQDS to form DHDMBS. This was a follow-up to previous work on diaza-anthroquinone candidates.^[85] The quinizarin (QZ) structure also has an electron-withdrawing annulated ring. Furthermore, the affixed naphthoquinone group undergoes a separate redox transformation at low potential. QZ structures are therefore candidates for quinone-based bipolar electrolytes.

Beyond quinones, biphenolic compounds are promising high potential carbonyl-based ROMs because their structures allow a greater extension of the electron delocalization than is possible with benzoquinones. Lantz et al. synthesised 4–4'-biphenol-3,3',5,5'-tetrasulfonic acid (BPTS), but in a similar manner to many quinones it also underwent a parasitic Michael reaction with water in the first 10–15 cycles, converting the quinone species to 2,2'-dihydroxy-4,4'-BPTS.^[38] Similar to observations in some of the quinone literature, the hydroxylated by-product of BPTS was still able to reversibly charge and discharge for the rest of the 100 cycle stability test.^[38] Liu et al.

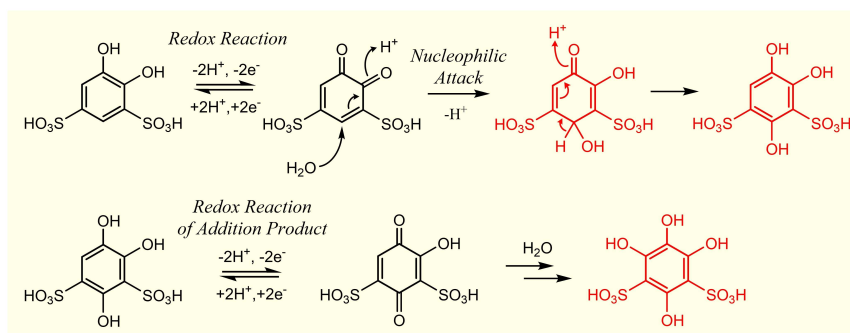


Figure 12. Decomposition reactions of BQDS in acidic solution.^[81]

have recently reported the study of 3,3,5,5-tetramethylaminemethylene-4,4-biphenol (TABP), emphasising that the aqueous TABP electrolyte need not require inertization and possesses a high potential of 0.91 V vs SHE in 2 M HCl solution, and has produced cycling data that is among the most stable to date for an aqueous ROM, showing no significant degradation and capacity loss over an 8 day/900 cycle test of 0.1 M TABP.^[37]

3.3. Amine compounds

This section concerns positive electrolyte molecules that undergo oxidation facilitated by an amine group. Some important amine-centred electrolytes for RFBs are shown in Figure 13. Indigo carmine (IC) is featured here as an example of an emergent promising ROM. As was introduced in Section 2.1, a diamine-diimine redox mechanism in indigo dyes has been observed, as well as a dihydroxyl-dicarbonyl redox functionality at a much lower potential. Therefore IC could be used to create single bifunctional positive and negative electrolyte ROM, since the redox transformations of IC were shown to occur at -0.24 V and 0.59 V vs SHE in buffered aqueous solution at pH 7.^[23] The presence of the sulfonate groups on IC allowed for a solubility of up to 0.76 M and raised the redox potentials by approximately 80 mV compared to the indigo dye substructure. Triphenylamine (THTPA) was also introduced in Section 2.1, which showed how the central tertiary amine group with three para-phenol substituents enables a reversible two-electron reaction. THTPA performs with good temporal and cycling stability of over 99% capacity retention per cycle.^[7]

Other heterocyclic redox mediators containing imine groups such as quinoxaline, phenazine, and alloxazine derivatives have been well-studied.^[86–89] These are annulated derivatives of pyrazine, and the substructure allows for a two-electron redox mechanism to take place, often forming aromatic oxidation products. Fewer have been studied for the positive electrolyte species because the redox potentials are generally low. However, the replacement of one nitrogen atom from the central ring in the phenazine structure for a more electro-negative heteroatom such as O or S elevates the redox potential to >0.5 V vs RHE at low pH and therefore makes

phenoxazine and phenothiazine compounds suitable candidates. The literature so far surrounding this class of molecules infers they can be incredibly stable in aqueous media.^[18,33] Li et al. studied a phenoxazine dye compound known as basic blue 3 (BB3), with a redox potential of 0.54 V vs SHE in 3.5 M H_2SO_4 but the redox reaction was shown to be kinetically slow on carbon in the absence of a *N*-doped graphene catalyst.^[33] Zhang et al. studied methylene blue (MB), which had a reported redox potential of 0.57 vs SHE in 3.5 M H_2SO_4 and extremely facile kinetics on glassy carbon.^[18] The tertiary amine groups greatly increased the solubility compared to unfunctionalized phenothiazine, however the water solubility of MB was still only 0.12 M. Acetic acid was incorporated as a cosolvent to attain higher concentrations. Even at high concentration there was minimal capacity fade over time and the reduced and oxidised forms could be stably retained in ambient conditions for 120 days.^[18] MB is therefore a promising structure and warrants attempts to further improve its properties without compromising its stability and fast reaction kinetics. Another phenothiazine dye molecule Azure A has two H groups on one of the substituent amines, compared to CH_3 groups in MB, and the redox potential increases to 0.59 V in 1.0 M H_2SO_4 , as does the solubility compared to MB, but still only reached approximately 0.9 M in water and 0.6 M in 1.0 M H_2SO_4 .^[18,90] At low pH, the redox mechanism of phenothiazines is a two-electron, two-proton PCET reaction. Although the central tricyclic structures of BB3, MB, and Azure A are phenoxazine and phenothiazine, these also contain amine groups positioned such that they can complete the two-electron transfer without relying on the O or S atoms. The compounds chlorpromazine (CPZ) and promethazine (PMZ) included here are *N*-substituted phenothiazines that have high redox potentials of 0.86 V and 0.92 V at pH 1, as well as high aqueous solubilities of 2.5 M and 2.3 M respectively.^[18] Interestingly, both of these species are also used as treatments in humans: chlorpromazine is used to treat psychotic disorders such as schizophrenia or manic-depression in adults, and promethazine a first-generation antihistamine and antiemetic used to treat allergies, insomnia, and nausea.^[91–93]

The initial one-electron oxidation of CPZ and PMZ generates a radical cation at much higher redox potentials than the aforementioned PTZs. These molecules are both share the same substructure as the stable radicals phenothiazine and *N*-ethyl phenothiazine.^[6] However, the loss of the second electron can be critically destabilising.^[66] The compounds BB3, MB, and Azure A are all able to possess diimine character in the oxidation product and the central heterocyclic O or S atoms could be seen as simply a neighbouring EWG. In these instances the functionalization of the PTZ substructure with a secondary amine *para* to the central nitrogen atom therefore has the effect of allowing a good two-electron redox reversibility, but this electron donation effect leads to a lower redox potential. The effect of adding the *N*-alkyl substituents present on CPZ and PTZ may be fairly inconsequential, and the source of high potential oxidation and instability in the *N*-PTZ compounds chlorpromazine and promethazine may be linked to the absence of diimine character in the dication oxidation products. From Figure 14a, it can be seen that the resonance structures of

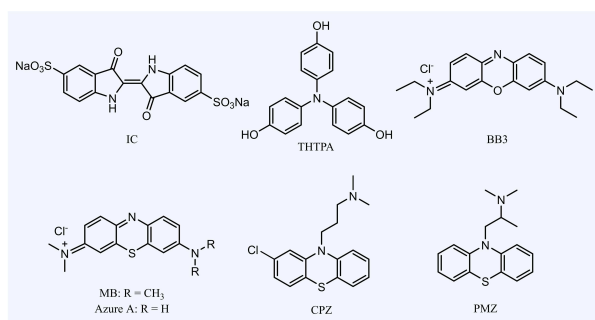


Figure 13. Chemical structures of selected imine-centred organic redox couples.

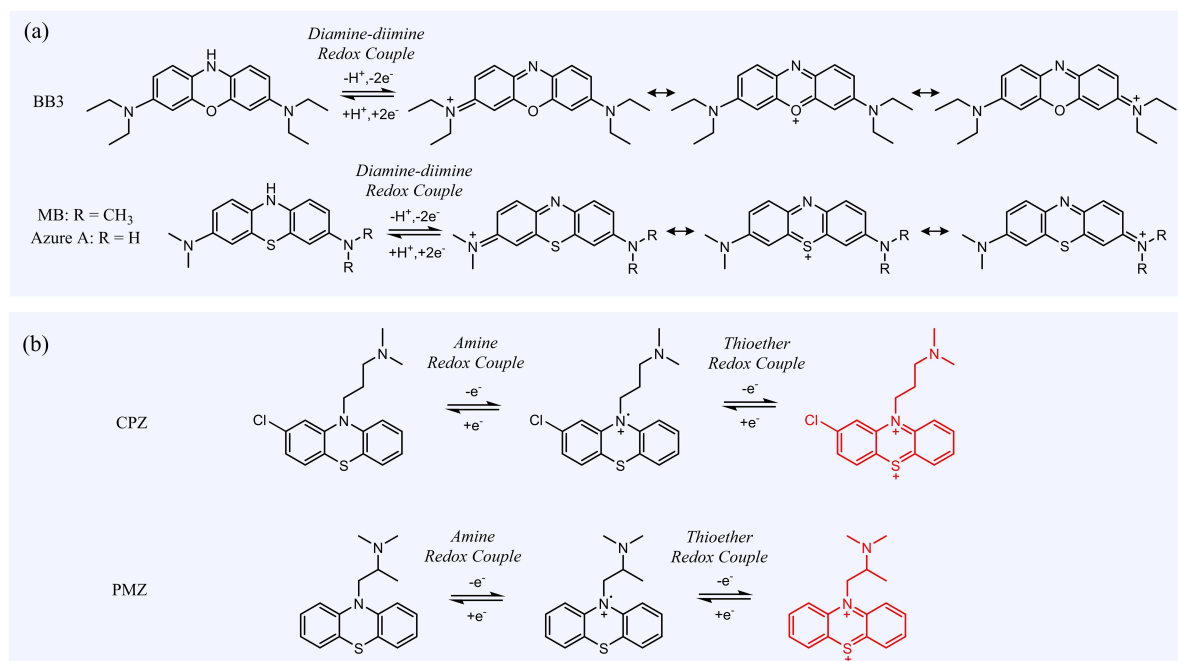


Figure 14. Redox reactions in acid of (a) the amine-functionalized dye molecules basic blue 3 (BB3), methylene blue (MB) and Azure A (including resonance structures), and (b) of chlorpromazine (CPZ) and promethazine (PMZ) and the formation of the unstable oxidation product shown in red.^[18,33]

the amine-substituted phenothiazines BB3, MB, and Azure A have diimine character, whereas analogous two-electron oxidation products of CPZ and PMZ do not. These *N*-PTZ compounds produce a single radical upon oxidation, and it is likely that the second electron-transfer is reliant on electron donation into the ring from the thioether group in order to complete the two-electron oxidation, leading to a high redox potential but also instability. However, successfully stabilising this group may be a strategy to produce a higher potential than typical amine-centred ROMs.

3.4. Ether and Thioether compounds

Many ROMs outside the realm of aqueous RFBs are unstable radical species or have low redox potentials suitable only as negative electrolytes, and we are unlikely to directly benefit from their application in aqueous systems. However, further to the compounds discussed so far, there are a vast number of known redox-active ether and thioether compounds that are worth consideration. The formation of stable dications from the two-electron oxidation of these molecules in aqueous media could present extremely promising opportunities, and this section briefly covers these two classes of ROMs.

Alkoxybenzenes have been used as overcharge protection in lithium-ion batteries due to their sufficiently high potentials and easy one-electron oxidation.^[94] As we also have seen previously, radical cations can be stabilised by the alkoxybenzene group.^[65] The one-electron redox couple of 1,4-dimethoxy-2,5-di-*tert*-butyl benzene (DDB) in Figure 15a has been shown to occur at a very high potential of 4.32 V vs Li/Li⁺, and similar

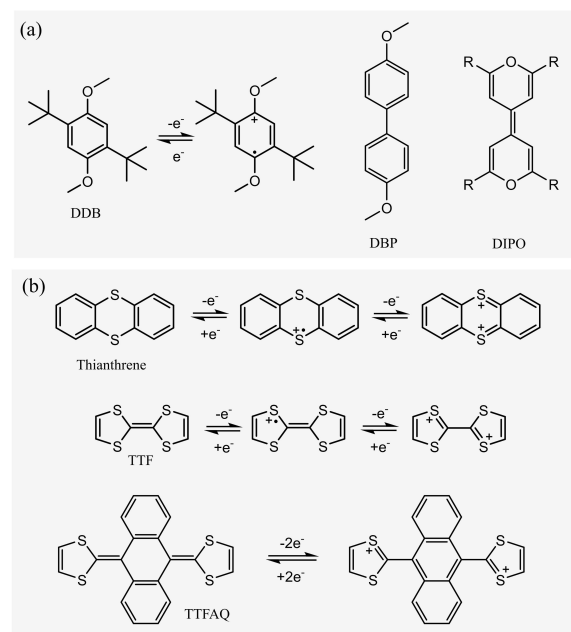


Figure 15. Possible small molecule ROM structures and substructures containing (a) oxygen and (b) sulfur heteroatoms.

alkoxybenzene structures have been employed in non-aqueous RFBs.^[95] Cyclic voltammetry of 4,4'-dimethoxybiphenyl (DBP) in acetonitrile shows two redox peaks at approximately 1.2 and 1.5 V vs the saturated calomel electrode (SCE), and indicates a highly reversible two-electron oxidation.^[96] Similarly, derivatives of the dipyranylidene (DIPO) structure have also been shown to produce dications via two one-electron steps at high potentials,

ranging between 0.24–0.50 V vs Fc/Fc⁺, depending on the identity of the R groups.

Sulfur-centred heterocyclic redox couples are extremely interesting for future organic electrolytes. Explored since the 1970s, the electrochemistry of 2,2'-bis(1,3-dithiolyldine), also called tetrathiafulvalene (TTF), has been the basis of almost all so-called *organic metals*.^[16,97] In acetonitrile, the oxidation of the neutral TTF molecule to the radical and then the subsequent oxidation to the aromatic dication occur at redox potentials of 0.34 V and 0.78 V vs Ag/AgCl. Derivatives of TTF incorporate ring substituents or even exchange the heteroatoms for selenium or tellurium.^[15] TTF-based positive electrolytes have indeed recently been tested in a non-aqueous flow battery, with reported high stability of the dication, showing only ~1 % capacity loss per day.^[98] Without increasing the molecular size beyond the norm of aqueous RFB electrolyte species, the TTF conjugated system can be extended to create TTF-acenes such as 9,10-bis(1,2-dithiol-2-ylidene) (TTFAQ), also shown in Figure 15b. Hundreds of TTF-acenes have been synthesised that almost exclusively exhibit redox inversion, with a two-electron oxidation observed in a single wave. In DCM solvent the two-electron oxidation and reduction of TTFAQ shown in Figure 15b occurs in a single wave centred at 0.44 V vs SCE.^[16] In acetonitrile, cyclic voltammetry of Thianthrene shows two reversible oxidation peaks at approximately 1.3 and 1.8 V vs SCE.^[9,96] In a recent research article, Etkind et al. have explicitly investigated thianthrene electrolytes for non-aqueous RFBs.^[99] Although the redox potentials of many alkoxybenzenes, and oxygen- or sulfur-containing heterocycles are therefore expected to be reasonably high, their use thus far appears to be limited to non-aqueous RFBs.^[94,100–102] To our knowledge improving the solubility and building greater π -extension of thioether compounds via functionalisation, possibly with the addition of redox-active carbonyl or amine groups, to facilitate a reversible two-electron oxidation in aqueous media has not yet been achieved. Studies to understand the properties and outlook of these ROMs will help to fill a gap in the literature.

4. Concluding Remarks

In this quickly growing field of aqueous organic RFBs, key challenges include maintaining long-term molecular stability as well as achieving competitive energy and power densities. This review has assessed different classes of aqueous ROMs in the current literature that have potentials greater than 0.5 V vs SHE to highlight the most exciting research in this area and understand the structure-property relationships of high potential ROMs. It appears that varying substituents on molecules has a large effect on the solubility of the molecule but a small effect in terms of the potential, unless the substituent also changes the type of redox centre, which is the key to achieving a major increase in the potential. As for the research to date, the progress of molecular design work has been described for different types of redox-active species, with the general trend of increasing stability since earlier works.

Regarding their stability, many TEMPO-derivatives have already been shown to operate successfully in aqueous media, with published data for full cell systems showing that the capacity fade of TEMPO-derivatives is generally 0.01–1 % decay per day. As we have highlighted, progress is now being made to better understand the specific degradation mechanisms, and functionalization has extended to creating bipolar redox species, which eliminates some issues associated with ROM crossover. The energy density could also be improved with further research into other soluble and high potential compounds utilising the aminoxyl redox states. From the list of organic compounds considered here, in both neutral and acidic conditions aminoxyl radical species have the highest redox potentials.

In the same way TEMPO derivatives are well-studied in neutral electrolyte, carbonyl-group based ROMs are perhaps the most thoroughly studied for acidic electrolyte RFBs. Protection from nucleophilic attack by the total substitution of vulnerable C–H ring positions and has proved effective in limiting the degradation of the benzoquinone state in water, and the literature indicates only the total substitution of benzoquinones can provide stability. Biphenolic compounds are also highlighted here, as they have a more extensive conjugated structure that appears to improve resistance to nucleophilic attack in water compared to benzoquinones. The biphenols discussed (TABP and BPTS) also have higher redox potentials than quinones.

Limited data exist for amine-centred redox couples such as the blue dye compounds shown (IC, MB, Azure A and BB3), which are promising classes of stable heterocyclic ROMs across a reasonably broad pH range, from negative pH up to pH 7, although currently with relatively low potentials. Similar heterocyclic redox couples are worth exploring due the reportedly stable findings for these redox couples in both acidic and neutral conditions.

Addressing the prospect of aqueous organic RFBs at a cell or system level, the key parameters related to power density include mass transfer, electron transfer, and energy storage capacity. These figures are usually reported separately but are all determinants of the overall performance. By plotting k_{comp} vs E_v for different organic and non-organic positive electrolytes, comparable values of $P_{\text{intrinsic}}$ can be found. $P_{\text{intrinsic}}$ combines these considerations for quickly assessing the notional performance. The differences that prove the most important for the overall $P_{\text{intrinsic}}$ of TEMPO derivatives are solubility and kinetics, which is why in Figure 7, NH₂-TEMPO has approximately factor of ten higher $P_{\text{intrinsic}}$ than O=TEMPO, despite having a comparable value of E° . The biggest effect is the capacity, as the solubility of NH₂-TEMPO in 0.5 M KCl is 4.80 M, a six-fold increase compared to O=TEMPO (0.79 M).^[24] Other types of all-organic molecules will also hopefully be identified for use in aqueous electrolytes and expand the design space, with the aim of stabilising much higher potential redox couples than those that have been demonstrated to date, displaying fast kinetics and a high theoretical capacity. For example, redox potentials of approximately 4 V vs Li/Li⁺ are already known for thianthrene and alkoxybenzene derivatives.^[103,104] Therefore the

evaluation of less studied aqueous soluble redox-active molecules with promising performance characteristics should be pursued.

Supporting Information

Additional references cited with the Supporting Information.^[105–114]

Additional Information

Supporting Information file provides table of information about redox couples described in the review; derivation of mass transport coefficient and specific power.

Author Contributions

C.C. and A.K. conceived the publication; C.C. wrote the publication; all authors contributed to editing the publication.

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Conflict of Interests

The authors declare no conflict of interest.

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