Redox Flow Batteries – concepts and chemistries for cost-effective energy storage

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Abstract: Electrochemical energy storage is one of the few options to store the energy from intermittent renewable energy sources like wind and solar. Redox flow batteries (RFBs) are such an energy storage system, which has favourable features over other battery technology, e.g. solid state batteries, due to their inherent safety and the independent scaling of energy and power content. However, because of their low energy-density, low power-density and the cost of components such as redox species and membranes, commercialised RFB systems like the all-vanadium chemistry cannot make full use of the inherent advantages over other systems. In principle, there are three pathways to improve RFBs and to make them viable for large scale application: First, to employ electrolytes with higher energy density. This goal can be achieved by increasing the concentration of redox species, employing redox species that store more than one electron or by increasing the cell voltage. Second, to enhance the power output of the battery cells by using high kinetic redox species, increasing the cell voltage, implementing novel cell designs or membranes with lower resistance. The first two means reduce the electrode surface area needed to supply a certain power output, thereby bringing down costs for expensive components such as membranes. Third, to reduce the costs of single or multiple components such as redox species or membranes. To achieve these objectives it is necessary to develop new battery chemistries and cell configurations. In this review we focus on a comparison of promising cell chemistries, be they all-liquid, slurries or hybrids combining liquid, gas and solid phases. Aim is to elucidate which redox-system is most favourable in terms of energy- density, power- density and capital cost. Also the choice of solvent and the selection of an inorganic or organic redox couples with the entailing consequences are discussed.

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1. Principles of operation for redox flow batteries

Electrochemical energy storage (EES) devices store energy for later use. To clearly showcase the unique features of redox flow batteries (RFBs), we will contrast them and their principles with three other devices: Electrochemical double layer supercapacitors (EDLSCs), solid-state batteries (SSBs) and fuel cells (FCs). These four archetypes capitalize on different physical and chemical principles, not even all of them employ redox reactions to store energy, and are therefore suitable for diverse EES applications. Examples for these applications are balancing and stabilizing the grid [1], electric vehicles [2,3] and mobile consumer electronics [4,5]. Schematics of these four devices are shown in Fig. 1.

EDLSCs (Fig. 1a) work on the principle that a potential difference ΔU at an electrode-electrolyte interface, which establishes itself due to the different Fermi energies of (metal) electrode $E_{F,Me}$ and electrolyte $E_{F,EL}$, is balanced by accumulating charges. Cations or anions in the electrolyte form an electrochemical double layer, conglomerating in order to keep the electrochemical potential μ_e across the interface constant [6,7]. Charges in the electrode, counterbalanced by charges in the electrolyte form a capacitor with a differential capacitance C_d equal to:

$$C_d = \frac{dQ}{d(\Delta U)} = \frac{\epsilon_r \epsilon_0 A}{d} \quad (1)$$

With accumulated charge Q , distance between charges d , dielectric constant ϵ_r , permittivity of free space ϵ_0 and electrochemically active surface area A .

High specific capacitances of $10 \cdot 10^{-6} \text{ F cm}^{-2}$ are reported in the literature for carbon electrodes in aqueous electrolytes [8], because the first layer of charges is very close to the electrode (some Ångströms). Carbon can have a high gravimetric surface area ($\sim 1000 \text{ m g}^{-1}$) [9–11]. The energy E_{SC} of an EDLSC, which is stored entirely in the electrochemical double layer, is given by:

$$E_{SC} = \frac{1}{2} C_D \Delta U^2 \quad (2)$$

The maximum voltage ΔU is limited by the oxidative and reductive stability of the system comprising electrodes and electrolyte. Organic electrolytes and room temperature ionic liquids can sustain higher voltages than water (approx. 1.23 V) [12,13]. In commercial EDLSCs propylene carbonate or acetonitrile are used as solvent with quaternary ammonium

salts as supporting electrolyte, their maximum voltage is typically 2.8 V. Storage of energy in the double layer as only principle limits the energy density of EDLSCs to some Wh kg⁻¹, however, the build-up of the electrochemical double layers is a very fast process. This enables high power density for EDLSCs, on the order of 10 kW kg⁻¹ [12].

As shown in Fig. 1b, SSBs also comprise two electrodes and an electrolyte (plus separator), but their energy is not stored in the ECDL, but in the electrodes. The energy content in SSBs is given by the product of the charge that can be transferred, the capacity Q , and the potential difference at which electrons flow through the external circuit:

$$E_{\text{Bat}} = Q\Delta U \quad (3)$$

Atom density in condensed matter is roughly 10²³ atoms [14], which entails a high capacity Q for SSB because the active material is present at a very high concentration. This is a significant difference to RFBs, as we will see later. This can be illustrated for the example of a lithium metal electrode [15,16]. At a mass of roughly 7 u, each lithium atom can be oxidised to give a monovalent cation:

The standard potential of this reaction is at -3.04 V vs. the Standard Hydrogen Electrode (SHE). Hence, a lithium anode could store a theoretical specific capacity of $q_{\text{Li}}^{\text{theo,g}} = 3,660 \text{ mAh g}^{-1}$ or $q_{\text{Li}}^{\text{theo,v}} = 2,061 \text{ mAh cm}^{-3}$. Due to the problems associated with Lithium metal anodes [17], graphite is commonly employed as host material for the anode in a lithium ion battery (LIB). Because Carbon is heavier than lithium, and six carbon atoms are required to store one lithium cation, the theoretical capacity of carbon is lower at $q_{\text{C}}^{\text{theo,g}} = 372 \text{ mAh g}^{-1}$.

Cathodes for LIBs are typically lithium metal oxides such as LiCoO₂ ($q_{\text{LCO}}^{\text{theo,g}} = 170 \text{ mAh g}^{-1}$) or LiFePO₄ ($q_{\text{LFP}}^{\text{theo,g}} = 150 \text{ mAh g}^{-1}$). As intercalation reactions into these cathodes take place at a high potential, e.g. 0.7 V vs. SHE for LiCoO₂, the energy density of a LIB can be high (approx. 200 Wh kg⁻¹)[15].

Intercalation reactions are not conversion or alloying reactions, which limits the stress the electrodes experience during charge or discharge. As LIBs rely entirely on the intercalation of lithium ions into interstitial sites of host lattices, high cycle lives are possible.

The combination of high capacity, high voltage and high stability make LIB the premier choice for electric vehicles and consumer electronics. One of the major current challenges is safety, as the employed organic electrolyte has a large combustion enthalpy and can therefore explode violently.

FCs oxidize some fuel (hydrogen, methanol, ethanol, carbon, etc.) at the anode while reducing an oxidant (oxygen) at the cathode, see Fig. 1c [18]. The reaction product (H_2O , CO_2 , etc.) is exhausted. The energy is stored in the chemical bonds of the fuel, which is pumped from external tanks into the power converter and the electrodes contain catalysts which facilitate the oxidation of fuel or the reduction of oxygen. Advantages of FCs are the high energy density of the fuel (ethanol stores 6.4 kWh L^{-1}) and their versatility in accepting various types of fuel. Also, FCs converting hydrogen are local-zero emission, a big advantage for FC electric vehicles when looking at the detrimental impact of internal combustion engine fumes on human health [3]. One of the main challenges are the sluggish redox reactions at anode and cathode. In acidic media on platinum, which is one of the best catalysts for the hydrogen related reaction, the hydrogen oxidation reaction (HOR) has an exchange current density of 1 mA cm^{-2} [19]. Therefore, large over-potentials are required to obtain a substantial current from anode. For the oxygen reduction reaction (ORR) typically no exchange current density but a kinetic current is given [20,21]. It is agreed however, that the activity for the ORR is orders of magnitude lower than that of the HER on platinum. This is thought to be mostly due to the high stability of reaction intermediates such as adsorbed oxygen and adsorbed hydroxyl [22]. To obtain a current density of 200 mA cm^{-2} (at 1 bar O_2 and H_2 pressure) in a low temperature FC, the resting potential of 1.23 V is reduced to 0.78 V [7]. This kinetic limitation renders FCs low power devices.

Fig 1. Schematics of different electrochemical energy storage devices. The location where the active material is stored is highlighted in red. (a) Supercapacitor, (b) solid state battery, (c) fuel cell, and (d) redox flow battery.

RFBs share many characteristics with FCs, as can be seen in Fig. 1c and 1d. Like FCs, RFBs store the active material in tanks which is then pumped to the anode or cathode for charge transfer. One of the differences is that the reaction products are not discarded in a RFB, but kept in their respective streams and pumped back into the anolyte and catholyte tanks. As a RFB is a secondary battery, the discharged species can be re-charged. For that the polarity of the RFB is reversed, the anode is now reducing the anolyte redox species, the cathode is oxidizing the catholyte redox species (against electrochemical conventions). While a FC can use liquid (ethanol, methanol, liquid nitrogen) and gaseous fuels (compressed hydrogen), a RFB will usually operate with dissolved redox molecules, it stores its energy entirely in solution. For the energy density of the RFB equation 3 holds. The charge of the RFB is determined by how many redox molecules are in solution (governed by concentration c), and number of transferred electrons per molecule n :

$$Q = n c F \quad (6)$$

Because typical concentrations are on the order of 1 mole of redox molecules per litre ($6 \cdot 10^{23} \text{ L}^{-1} \approx 6 \cdot 10^{20} \text{ cm}^{-3}$) and only a single electron is transferred for most RFB chemistries ($n = 1$), the charge contained in the liquid electrolyte is approximately two orders of magnitude lower than for SSBs (10^{23} cm^{-3}). However, storing energy in a liquid has many conceivable advantages, some of which are shared with FCs: The electrolyte can be easily exchanged by draining and refilling. This could be employed to replace faulty or aged electrolyte or to upgrade the battery with a more advanced electrolyte, or to instantaneously recharge a battery. Also, it enables the scalability of RFBs: The size of the tanks determines the charge Q that is stored in the battery and therefore the battery's energy content. The power is determined by the size of the membrane electrode assembly (MEA). This means that RFBs can be easily adapted to specific needs, either by changing the size of the tanks, or by altering the size of electrodes and membranes (or the number of cells).

The power density of a RFB, which is normalized to the geometric surface area of the MEA, is limited by four resistances that introduce a potential drop in the cell:

$$R_{\text{total}} = R_{\text{elec}} + R_{\text{mem}} + R_{\text{CT}} + R_{\text{mass}} \quad (7)$$

The total resistance R_{total} is the sum of the resistances caused by the electronic resistance R_{elec} between the various components (e.g. between current collector and electrode), the membrane resistance R_{mem} , the charge transfer resistances on anode and cathode R_{CT} and the mass transport resistance R_{mass} . Because R_{elec} , R_{mem} and R_{mass} are related to the engineering of the MEA [23,24], we will only briefly cover R_{CT} here:

$$R_{\text{CT}} = \frac{R T}{n F A j_0} = \frac{R T}{n^2 F^2 A k_0 c} \quad (8)$$

With the gas constant R , temperature T , Faraday constant F and electron transfer constant k_0 . Because k_0 can spread over several orders of magnitude, from facile couples such as ferrocene/ferrocenium with $k_0 \approx 1 \text{ cm s}^{-1}$ [25] to sluggish ones such as the $\text{VO}^{2+}/\text{VO}_2^+$ redox reaction with $k_0 \approx 10^{-6} \text{ cm s}^{-1}$ [26,27], this fundamental parameter is of high importance for the power of a RFB. Maximizing it could lead to high-power RFBs, but current technology, such as the all-vanadium RFB (VRFB) provides only about 70 mW cm^{-2} .

With these principles established, the sequence in energy density and power density shown in the Ragone plot (Fig. 2) can be understood: SCs store energy only in the electrochemical double layer, by placing charges in a potential field, which gives small energy densities. RFBs store energy in redox couples in liquid form, which entails a lower density of charge carriers than in SSBs. Lastly FCs store energy in the chemical bonds of either the lightest element (H_2), or hydrocarbons (ethanol, methanol, gasoline) which makes them high-energy density devices. However, because the reactions in a FC are sluggish (ORR, HOR), they are low power devices. The intercalation reactions that take place in LIBs are faster than the redox reactions occurring RFBs, making the latter slower than the former. SCs exhibit the highest power density, because the formation of the double layer is a purely physical process and no electron transfer is taking place.

Fig 2. Ragone plot for four electrochemical devices, supercapacitors, batteries, redox flow batteries and fuel cells.

2. Criteria for technology

A typical RFB cell consists of two electrode compartments divided by a separator. The separator is commonly an ion exchange membrane which prevents the crossover of active species between half-cells but allows the movement of ions between electrode compartments for the balancing of charge. The positive and negative electrolyte are stored in external tanks and are pumped into each half-cell. The electrodes of a RFB are normally inert, serving as the site for the redox reactions of the active species only which remain soluble in the electrolyte. Upon exiting the electrode compartments, the electrolytes are returned to the storage tanks to be recirculated through the cell. Individual RFB cells can be connected in series to produce cell stacks through the use of conductive bipolar plates which connect one cell to another. The array of cell stacks, stored electrolyte and the balance of plant constitute a complete RFB system. The balance of plant includes all other components necessary for operation of a RFB: pumps, plastic plumbing and tanks, a power conditioning system and systems for battery monitoring and control [28].

Fig 3. Figure illustrating the creation of a RFB system through the building up of individual cells into modular stacks. Reprinted with permission from [29].

RFBs can be subdivided into ‘true’ RFBs and hybrid RFBs (see section 3 ‘Various concepts’ for further detail). In short, true RFBs utilise inert electrodes and redox species that remain in solution. Examples of classical true RFBs are the iron-chromium [30], bromine-polysulphide [31] and the VRFB [32]. A schematic of the VRFB is shown in Figure 4. The operation of a hybrid RFB involves a phase change during the cell reaction. An example is the zinc-bromine system in which the plating and dissolution of zinc at the anode occurs upon charge and discharge respectively [33].

Fig 4. A schematic diagram of the all-vanadium RFB in discharge mode.

The efficiency of a RFB can be characterised by several parameters. Firstly, the coulombic efficiency η_{CE} which is the ratio of the current transferred upon discharge to the current transferred upon charge.

$$\eta_{CE} = \frac{Q_{out}}{Q_{in}} \cdot 100\% \quad (9)$$

With Q_{out} the amount of charge during discharge and Q_{in} the amount of charge during charge. Low values indicate a crossover of active species between electrode compartments causing self-discharge, or side reactions that consume charge. Another parameter is the voltage efficiency η_{VE} , defined as the ratio of the average discharging voltage to the average charging voltage.

$$\eta_{VE} = \frac{V_{\text{discharge}}}{V_{\text{charge}}} \cdot 100\% \quad (10)$$

Activation over-potentials deriving from the reaction kinetics, mass transport over-potentials and Ohmic losses are all sources of a discrepancy between the charging and discharging voltage (see equation 6). The coulombic efficiency η_{CE} multiplied by the voltage efficiency η_{VE} yields the energy efficiency η_{EE} of a RFB which indicates how much of the energy that is supplied to the battery during charging can be extracted upon discharge.

$$\eta_{EE} = \eta_{CE} \cdot \eta_{VE} \cdot 100\% \quad (11)$$

RFBs have several benefits over conventional secondary batteries. For instance, external storage of the electrolyte prevents the self-discharge of the stored solutions. Further, as the electrodes are not subjected to continuous plating or intercalation reactions, electrode deterioration is minimised. When a conventional battery undergoes repeated charge/discharge cycles, the electrode materials expand and contract which results in their degradation over time[34]. Thus, lifetime can be much improved when there is no phase change at the electrodes during cycling, as in a RFB. The predicted lifetime for a RFB tends to exceed 10 years and the VRFB is rated at 10 000 cycles [35].

The life-limiting component of a RFB is typically the cell stack. Wearing of the membranes separating the electrode compartments is a source of performance degradation and for the VRFB in particular, the cell stack is expected to have a lifetime of 10 to 15 years for a RFB undergoing 1000 charge/discharge cycles per year [36]. The electrolyte storage tanks, plumbing, structural components, power electronics and controls of a RFB should have longer useful lifetimes [35], but pump replacement may also be required periodically. Crossover of active species between the half-cells due to an inefficiency of the separator is a source of capacity fade and as such, a degree of electrolyte maintenance may be necessary. However, with stack and pump replacement, VRFBs can operate for more than 20 years [36]. Hazards relating to the operation of RFBs include the use of flammable, toxic and/or corrosive electrolytes. While the flowing electrolytes aid heat dissipation and RFBs such as the VRFB classically used aqueous solutions, flammability should be a consideration if a RFB electrolyte is based on a non-aqueous solvent. Further, acidic supporting electrolytes are typically used which necessitates the use of acid-resistant components and toxicity associated with active species is of concern in the event of leakages.

It is often noted that cost is currently prohibitive for the widespread deployment of RFBs for energy storage. The cost of a RFB system includes numerous components: the cell stacks including separators, electrolyte solutions, storage tanks, power-electronics equipment, the control system, pumps, valves and plumbing as well as the cost of assembly and installation costs [34]. A target capital cost of \$100 per kWh has been suggested for large-scale grid storage of energy from renewable sources [37], while a recent cost analysis that considered the VRFB set a base case capital cost of \$380 per kWh for a 1 MW/12 MWh system [38]. Both the electrolyte and the cell stack and membrane are implicated as substantial contributors to the capital cost of VRFBs [38,39]. The cost of the electrolyte is dependent on the price of vanadium per kg, while the acidic and oxidising environment of the VRFB requires the use of hardwearing yet costly Nafion ion exchange membranes. Thus, at the electrolyte level, possible improvements to the capital cost of RFBs relative to the VRFB could come from the use of lower-cost active materials and RFB chemistries that allow less expensive porous separators to be used.

The different RFB chemistries have been summarised in several recent review papers [40–46] and there is a myriad of published reactions for the positive and negative electrode (see Table 1). Aqueous metal-based chemistries are complemented by both reports of non-aqueous RFBs and the emergence of active species based on organic molecules, as alternatives to the traditional and widely tested RFBs are continually devised. The themes of non-aqueous electrolytes versus aqueous electrolytes and non-metallic RFBs versus metal-ion chemistries are discussed herein.

3. Various concepts, all-liquids, gas/liquid, semi-solid, slurries, redox mediators

Since their inception in the 1970s at NASA, various combinations of electrolyte/electrode phases have been investigated for RFBs [40,42,43]. Classic examples, like the Fe-Cr system [47] or the VRFB [32,48,49] use two liquid electrolytes, anolyte and catholyte, to store energy. This all-liquid form exhibits all the advantages and disadvantages related to liquid electrolytes stated in the introduction: Lower concentration of charge carriers than in the solid state but a capacity that is only limited by the size of the tank (and the cost of the electrolyte).

The gaseous phase is lighter than liquid electrolytes and oxygen, if it can be taken from the atmosphere, is almost free of costs. This motivated the design of a V-O₂ RFB or Vanadium/air RFB as presented by Hosseiny *et al.* [50]. This embodiment of a gas/liquid RFB hybrid employs the V²⁺/V³⁺ redox couple as anolyte, and the oxygen evolution reaction (OER) and the ORR as cathode. The battery published suffered from low η_{EE} (27% at 60°C), and the need for catalyst loading on the cathode. As this battery combined the more problematic half-cell of the VRFB [51,52] with the sluggish half-cell of a hydrogen-oxygen FC, the underwhelming performance can be understood.

Combinations of hydrogen electrodes with regular RFB catholytes (H₂/2H⁺-VO²⁺/VO₂⁺ [53], H₂/2H⁺-Fe²⁺/Fe³⁺ [54], H₂/2H⁺-Ce³⁺/Ce⁴⁺ [55]) might have been born from the realisation that the hydrogen evolution reaction (HER) contributed a substantial parasitic current in VRFB and Fe-Cr batteries [56,57]. The replacement of one liquid half-cell by H₂/2H⁺ seems promising from a cost and energy-density perspective, but problems such as Pt catalyst leaching into the cell and carbon corrosion by Ce³⁺/Ce⁴⁺ have to be addressed [55].

Solid-liquid RFBs comprise one liquid half-cell and one metal electrode which typically undergoes a plating reaction [58]. One example is the zinc-bromine battery, that features a Zn or carbon plastic anode on which Zn is deposited during charge [59]. Metal electrodes allow for an increase in energy density as compared to regular flow batteries, however, they also introduce the problems of regular batteries into the RFB: Dendrite formation upon plating reactions that can lead to internal short-circuits and high-self-discharge rates make it questionable whether liquid-solid hybrids are useful.

Slurries of lithium-metal-oxides are well-studied system due to their importance for LIBs. Under the moniker “semisolid flow batteries” they were introduced for RFBs utilizing 20

vol% LiCoO₂ and 10 vol% Li₄Ti₅O₁₂ [60]. This concept allows for very high concentrations of redox species (estimated ranges from 20 to 80 mol L⁻¹) [61]. Conductive slurries are used as electrolyte, in which carbon forms a conductive network. The limited conductivity of these slurries (0.1 mS cm⁻¹) is one of the contemporary challenges of semisolid flow batteries [60,61].

A concept does not rely on dissolved redox species, but instead on a solid active material that is stored in tanks: Mediated flow batteries. In these, the charge is transferred to the active material via redox-mediators such as ferrocene [62] or cobaltocene [63]. This type of flow battery utilises similar active materials as the semisolid flow batteries, but avoids the high viscosity and poor conductivity of slurries. To avoid losses, the potentials of the redox mediators must closely match the (de-)intercalation potentials of the active material.

Another concept is the addition of a solid energy booster to the tank of a RFB [64]. This approach proposes that the redox transitions of the polymer polyaniline are accessed by a redox mediator, storing charge in the emeraldine-bernigraniline and leucoemeraldine-emeraldine redox transitions of the polymer. As redox-mediator Fe²⁺/Fe³⁺ and V³⁺/VO²⁺ were employed at a concentration of 1 M. When polyaniline was combined with conductive carbon and abovementioned electrolytes the volumetric energy density was increased by a factor of three, compared to the base case with only iron- and vanadium-ions [64]. Current challenges are a “passivation” of polyaniline in certain redox state and sluggish kinetics of the V³⁺/VO²⁺ couple.

Type	Advantages	Challenges
Solid - liquid (e.g. Zn/Br)	<ul style="list-style-type: none"> High energy density due to solid state. 	<ul style="list-style-type: none"> Internal short-circuiting High self-discharge.
Slurries (e.g. LiCoO ₂ / Li ₄ Ti ₅ O ₁₂)	<ul style="list-style-type: none"> High energy density due to high concentration of redox species. 	<ul style="list-style-type: none"> Limited conductivity High viscosities; Potentially sluggish species.
Mediated FB (Ferrocene as shuttle and LiFePO ₄ as storage material)	<ul style="list-style-type: none"> Low viscosity of shuttles Good conductivity 	<ul style="list-style-type: none"> Limited variety of shuttle species Complicated reactions
Liquid-liquid (e.g. Fe/Cr)	<ul style="list-style-type: none"> Capacity that is only limited by the size of the tank. 	<ul style="list-style-type: none"> Lower concentrations in the solid state.

Liquid-gaseous (e.g. V/O ₂ or H ₂ /V)	<ul style="list-style-type: none"> • Low costs for gaseous species; • High concentrations of gaseous species can be reached, therefore high energy density, 	<ul style="list-style-type: none"> • low energy efficiency • self-discharge; • oxygen gas permeation • need for catalyst loading • Pt leaching into the electrolyte
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Table 1: Summary of advantages and drawbacks of various RFB concepts.

4. Solvent: aqueous – non-aqueous

In most of the invented RFB-systems, acidic, aqueous electrolytes are used. One disadvantage of electrochemical application in aqueous solutions is the electrolysis of water. The corresponding half-reactions can be described for acidic and basic solutions:

Cathodic reaction:

Anodic reaction:

The potential at which those reactions occur depends on the used electrode material. The thermodynamic potential window in which no reactions take place is 1.23 V. Out of this range, water electrolysis is promoted which leads to parasitic side reactions and therefore to efficiency loss and capacity imbalance in a full RFB. This limits the selection of electrochemical active species for an aqueous RFB. Furthermore, the application of aqueous electrolytes is restricted by the temperature range of 0 to 100°C. Mostly sulphuric acid is added as supporting electrolyte to enhance the conductivity of the electrolyte without the addition of additional salts as supporting electrolyte.

Often, to ensure higher conductivity, hydrochloric acid is added to the aqueous electrolyte [65]. However, the dissociated chloride ions can promote corrosion processes, thus having a negative effect on the lifetime of the battery attachments. Chloride ions are not oxidizing agents themselves, but, they can influence the corrosive conditions and are able to catalyze the process depending on the used materials, which results in higher maintenance costs [66].

The use of non-aqueous electrolytes is a possibility to enlarge the potential window and the temperature range. An example for an organic solvent that was used in a RFB is acetonitrile [67–70]. To obtain a reasonable conductivity, a supporting electrolyte like tetrabutylammonium hexafluorophosphate (TBA PF₆) or sodium perchlorate (NaHClO₄) has to be added to the electrolyte, which can limit the potential window because of decomposition reactions [71]. Furthermore, these supporting electrolytes increase capital costs. The potential windows of acetonitrile with 0.1 M additive on a platinum electrode are from +3.0 V to -2.6 V vs. Saturated Calomel Electrode (SCE) in the case of TBA PF₆ and from +1.8 V to -1.6 V vs. SCE in the case of sodium perchlorate NaHClO₄ [72]. This suggests, that the potential window can be enlarged in non-aqueous media but is limited by the decomposition of the additive. The useable temperature range of acetonitrile (anhydrous) is between -43.8 and 81.7°C which is beneficial for low temperature applications. In general, solvents with nitrile groups have a good stability towards oxidizing and reducing conditions in electrochemical cells [72].

Another example for non-aqueous electrolytes are organic carbonates like propylene carbonate (PC), ethylene carbonate (EC) and methyl ethyl carbonate (EMC), which are well studied due to their application in LIBs [71,73]. Those solvents have the capability to dissolve salts such as tetrabutylammonium trifluoromethanesulfonate (TBAOTf) and lithium hexafluorophosphate (LiPF₆) to function as supporting charge carrier in the electrolyte.

The use of organic solvents could potentially require complex maintenance operations, especially if the organic solvent is hygroscopic and prone to water intake from the atmosphere which would lead to a decreased potential window. Acetonitrile for example is strongly hygroscopic, and will readily absorb water from air if not stored under inert conditions. For technical application, this would mean that the battery would have to run under nitrogen or argon gasping which would result in higher maintenance costs compared

to the aqueous system. Also non-aqueous solvents like acetonitrile corrode rubber and polymer materials which could damage the tubes the electrolyte is pumped through and the innards of the cell which would reduce the lifetime of the battery[66].

While intensifying maintenance requirements, electrolytes such as PC, EC, EMC and others also carry a significant safety risk. This is aggravated in LIBs because they contain besides the flammable electrolyte also oxidizing material in the form of the lithium-metal oxides that typically make up the cathode [5]. Therefore, two of the three elements of the combustion triangle (fuel and oxidant) are present in LIBs, addition of a heat source can lead to catastrophic failure. In a large scale RFB application of organic electrolytes the fuel would be present in a much higher quantity than in a LIB, surrounding oxygen in the atmosphere could function as oxidizer. Organic solvents are in most cases ecologically questionable, and their application should be reduced as much as possible because, in spite of safety measures, solvents are released into the environment and have a polluting impact. For the synthesis of PCs, dichloromethane is used for which carcinogenic effect is suspected and it harms aquatic organisms (H-351, H-373) [74]. Acetonitrile as a solvent should also be considered critically as well. Acetonitrile is absorbed by the digestive system, the skin and the lungs and releases cyanide in the human body. Hence, poisoning symptoms of cyanide exposure occur [75]. Due to these properties, the toxicity of the used solvent must be taken into account when developing a battery [76].

The selection of a suitable solvent for conducting experiments requires careful consideration, as the solvent can have a significant influence on the electrochemical properties of the redox couples. The standard potential of a reaction like

depends on the solvent or on the solvation energy of the metal ion. For instance, the standard potential is shifted to more negative values in solvents in which the metal ion is solvated more strongly [66]. In some cases, solvents have the capability to change the whole reaction mechanism, which affects the electrochemistry of a redox system. For example, a one-step reaction in water could be a two-step reaction in an organic solvent. Copper in the oxidation state I+ is unstable in water but is stabilized in acetonitrile, which means the reduction of Cu(II)

to Cu(0) in water occurs at another potential than in acetonitrile. Also the permittivity and Lewis acidity of a solvent affects the standard potential of metal ions significantly. The electron transfer constant k_0 , an important factor in electrochemistry, is affected by the solvent, too, due to its influence on the reorganization energy.

Another type of electrolyte that receives more and more attention to enhance the energy density of RFBs are room temperature ionic liquids (RTILs) [77]. They are solvents that consist entirely of ions, are non-volatile, non-flammable, chemically stable and highly conductive [78]. Furthermore, if free of water they make a huge potential window and temperature range accessible [79,80]. RTILs offer environmentally friendly properties and can be used as green solvents in electrochemical application, especially RFBs. There are two main types of RTIL: one is a mixture of AlCl_3 and quaternary ammonium chloride (R^+Cl^-) and the other type are salts of cations like 1-butyl-3-methylimidazolium (BMI^+), 1-ethyl-3-methylimidazolium, and 1-butyl-pyridinium and anions like BF_4^- , PF_6^- , CF_3COO^- , CF_3SO_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. The potential window depends on the acidity and basicity of the solution, respectively. In the case of 1-butyl-3-methylimidazolium - PF_6^- the potential window is 7.1 V [66]. Some properties can be adjusted by the anion and in which way the ligand coordinates to the metal centre. The group of Anderson *et al.* investigated aforementioned properties in copper ionic liquids [81]. $\text{Cu}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_6[\text{BF}_4]_2$ showed the best results regarding viscosity, conductivity and electrochemical reversibility and was liquid at 25°C, whereas the copper complex with one anion exchanged with triflate was solid at RT. Also the conductivity changes with the anion. With one 2-ethylhexanoate anion instead of tetrafluoroborate, the conductivity decreases from 6.8 to 0.586 mS cm^{-1} . [82]

Membranes in RFBs are used to separate the liquid electrolyte compartments and are permeable ions to enable charge balancing [83,84]. The most important properties of those membranes are high ionic conductivity and low permeability towards the electrochemical active species to inhibit crossover of the catholyte into the anolyte and vice versa. In aqueous systems a cation exchange membrane like Nafion is usually used [85]. However, also anion exchange membranes [86–88] or porous membranes [89] have been used. In non-aqueous media polyethylene-based porous separators [73], anion exchange membranes [68] and cellulose-based dialysis membranes [90] are reported.

Electrolyte	Advantages	Challenges
Aqueous	<ul style="list-style-type: none"> • Environmental friendly; • Inexpensive; • High conductivities; • Often high solubilities for redox species 	<ul style="list-style-type: none"> • Small potential window • Restriction by temperature range • Corrosion processes by chloride ions
Non-Aqueous	<ul style="list-style-type: none"> • Larger potential window than aqueous electrolytes; • Larger temperature range than aqueous electrolytes; 	<ul style="list-style-type: none"> • Potential window limited by decomposition additives; • Safety risks; • Low conductivity; • Environmental hazards; • Higher (maintenance) costs.
Room temperature ionic liquids	<ul style="list-style-type: none"> • Non-volatile; • Non-flammable; • Highly conductive; • Chemically stable; • Wide potential window; • Environmental friendly? 	<ul style="list-style-type: none"> • High viscosity; • High (maintenance) costs; • Low conductivity.

Table 2: Summary of advantages and challenges of various types of electrolytes used in RFBs.

5. Redox centre: metallic – non-metallic

There are two types of metal-based batteries: It can be distinguished between Me/Me^{z+} and $\text{Me}^{z+}/\text{Me}^{(z+1)+}$ systems (with integer z). An example for Me/Me^{z+} system is the Zn/Br_2 battery in which metallic Zn is deposited on the cathode during charging and Br^- ions are oxidised to elementary bromine simultaneously [33,59]. In this system the metal is an electrochemically active species and forms part of the electrode as well [91]. A problem that often occurs with this kind of battery is the formation of dendrites, which can lead to a short circuit when these protrusions pierce the separator [92,93].

An example for a $\text{Me}^{z+}/\text{Me}^{(z+1)+}$ system is the VRFB [94]. In this battery the redox couples $\text{V}^{3+}/\text{V}^{2+}$ and $\text{VO}^{2+}/\text{VO}_2^+$ are used. During charging V^{3+} is reduced to V^{2+} and VO^{2+} is oxidised to VO_2^+ simultaneously. During the entire process, the ions remain dissolved and are not part of the electrode. Disadvantages of this type of system is the crossover of the ions across the membrane into the other half-cell which decreases the efficiency. In the case of different elements, the capacity is significantly reduced by the crossover and the associated irreversible contamination. Another point which limits the application is the limited

solubility of the used metal salts. In the case of the VRFB the maximum concentration of the VRFB electrolyte is 1.7 to 2 M vanadium if only sulphuric acid is used as supporting electrolyte [95]. It should also be mentioned that at higher concentrations the V^{3+} and V^{2+} ions precipitate in the negative electrolyte if the temperature is lower than 10°C. While the solubility of V^{2+} , V^{3+} and VO^{2+} increases with increasing temperature, thermal precipitation of the VO_2^+ species into V_2O_5 occurs when the positive electrolyte is over 40°C [96]. The electrolyte of non-aqueous system contains a concentration of electrochemically active species from 0.01 M [68] to 2 M [73].

The locus of the redox reaction is the electrode surface and this is why the selection of the right electrode plays an important role. The electrode requirements for all systems are in general high conductivity, good resistance towards the chemical environment, mechanical stability towards compression and inexpensive costs. In $Me^{z+}/Me^{(z+1)+}$ systems commonly carbon-felt materials are used because they do not undergo any redox reaction within the stability window of water [26]. The surface of the electrode should be active towards the desired redox reactions and simultaneously inhibit unwanted side reaction such as the HER.

6. Review of battery chemistries

The development of novel chemistries for RFBs is a research area that attracts a tremendous amount of attention at the moment. Therefore, it is impossible to present a holistic compendium of all the investigated (half-cell) chemistries. The present article should be seen complimentary to recently published reviews on the topic of chemistries for RFBs [40–46]. In our selection, we focus on chemistries that target the capital costs of RFBs which is currently the main inhibitor for their wide-spread application. Avenues to achieve these cost-savings are high capacity chemistries that allow for a reduction in footprint of the battery, high power chemistries that allow for a reduction in size of the cells and therefore reduce the footprint and costly materials such as membranes and low-cost molecules.

6.1 High energy density all-vanadium RFBs

6.1.1 VRFBs with increased concentration

As described, for VRFBs, V^{2+} and V^{3+} species in the negative half-cell precipitate below 10°C while VO_2^+ precipitates as V_2O_5 above 40°C in the positive half-cell which allows a maximum vanadium concentration of 2 M in the sulphuric acid electrolyte and limits the energy density to 25 Wh kg⁻¹ [96]. Reformulation of the electrolyte is a possible way to access higher vanadium concentrations and increase energy density. Indeed, Li *et al.* demonstrated use of a mixed sulphate and chloride electrolyte that allowed a 2.5 M concentration of vanadium to be achieved [97]. This represented about a 70% increase in energy density relative to current sulphate-only systems. It was found that vanadium in all four oxidation states was stable in a solution of 2.5 M SO_4^{2-} and 6 M Cl^- from -5 to 40°C, and a subsequent study demonstrated the stability of VO_2^+ in solution at 50°C. The mixed electrolyte could therefore provide an extended operational temperature range of -5 to 50°C, compared to the 10 to 40°C temperature window that is allowable for VRFBs that use a supporting electrolyte of sulphuric acid only. The enhanced stability of V(V) is attributed to the formation of soluble, neutral vanadium-containing complexes of formula $VO_2Cl(H_2O)_2$ as the temperature approaches 20°C [97]. This was evidenced by use of the Amsterdam Density Functional program and by ⁵¹V and ³⁵Cl NMR analysis. Quantum calculations also indicated that in sulphate solution, V(V) exists as $[VO_2(H_2O)_3]^+$ which is converted to insoluble V_2O_5 -

3H₂O at elevated temperatures. The solubility and stability of V³⁺ and VO²⁺ is also thought to be increased by the lower sulphate concentration of the mixed electrolyte relative to standard sulphate concentrations for VRFBs. When a 2.5 M vanadium solution in the mixed sulphate-chloride electrolyte was tested in a RFB cell, a stable performance with 87% energy efficiency over 20 days was achieved. Energy densities of > 36 Wh L⁻¹ were demonstrated for 2.5 M vanadium solutions in mixed electrolyte compared to around 22 Wh L⁻¹ for 1.6 M vanadium solutions in 4.5 M sulphate electrolyte [96,97]. The formation of Cl₂ gas during cycling is a concern, but it was reported that no significant gas evolution was observed. Our group was able to show that k_0 of the VO²⁺/VO²⁺ reaction in 1 M H₃PO₄ is up to 67 higher than in 1 M H₂SO₄, which was attributed to a different chemical coordination in the electrolytes [98].

Electrolyte additives are also a possible measure that can be implemented to increase vanadium concentration and achieve higher energy densities for the VRFB. For instance, Roe *et al.* recently investigated various stabilising additives for the purpose of preventing the thermal precipitation of VO₂⁺ species [97,99]. Several inorganic additives were studied as it was noted that finding effective organic additives that have long-term stability is a challenge due to the high oxidising power of VO₂⁺. Sodium pentapolyphosphate, K₃PO₄, H₃PO₄ and (NH₄)₂SO₄ were thus screened as stabilisers for 3 M supersaturated VO₂⁺ solutions. H₃PO₄ (1 wt%) was found to be most effective at maintaining VO₂⁺ concentration at 30°C while a 1 wt% H₃PO₄ + 2 wt% ammonium sulphate formulation performed best at 50°C and was investigated further in cell cycling tests. Such stabilising behaviour could be attributed to the formation of V(V)-phosphate complexes and the increase in H⁺ concentration due to phosphoric acid addition causing thermal precipitation of V(V) as V₂O₅ to become disfavoured. A 3 M VO₂⁺ solution with 5 M total sulphate concentration and containing 1 wt% H₃PO₄ + 2 wt% ammonium sulphate demonstrated stable efficiencies over 90 charge/discharge cycles with a slight decrease in cell capacity observed [99]. No precipitation was evident during the experiments. A viable 3 M vanadium electrolyte could allow a 60-90% increase in energy density relative to the practical concentrations of 1.6 M–1.8 M that are currently used in VRFBs.

A number of organic additives were proposed [100] and researchers found that amino acids [101], couler dispersant [102], polyacrylic acid and its mixture with CH₃SO₃H [103] as well

as fructose, mannitol, glucose, and D-sorbitol [104] and other [105] organic compounds could improve the temperature stability of the catholyte in the VRFB. However, Nguyen *et al.* studied the effect of additives glucose and ascorbic acid, and found that they only lead to an apparently enhanced stability [105]. They claim that the catholyte with organic molecules is more stable because these molecules are oxidised by the VO^{2+} ions, thereby reducing the state of charge (SOC) of the VRFB. As precipitation occurs at high SOC, when the catholyte is mostly present at VO_2^+ and these additives effectively diminish the concentration of VO_2^+ , the time until precipitation occurs is prolonged.

Fig 5. a) Coulombic, voltage and energy efficiencies vs. cycle number and b) Capacity vs. cycle number for a vanadium redox flow cell with 3 M V concentration in 5 M total sulphate electrolyte and 1 wt% H_3PO_4 + 2 wt% ammonium sulphate additives. Reprinted from [99], licensed under CC BY (<https://creativecommons.org/licenses/by/4.0/>)

6.1.2 VRFBs with increased cell voltage

The energy density of a RFB is proportional to the cell voltage, but for aqueous electrolytes the voltage is limited by the electrochemical window of water. In light of this, Liu *et al.* have investigated a non-aqueous electrolyte for application in RFBs [67]. Vanadium(III) acetylacetonate ($V(acac)_3$) was dissolved in acetonitrile with tetraethylammonium tetrafluoroborate ($TEABF_4$) as the supporting electrolyte. The stability window for the system was approximately 4 V (-2.5 V to 1.5 V vs. Ag/Ag^+) and within this voltage range, analysis of $V(acac)_3$ by cyclic voltammetry (CV) showed peaks corresponding to V^{2+}/V^{3+} and V^{3+}/VO^{2+} redox couples. From the potentials of these reactions, a useful cell potential of 2.2 V for a RFB was calculated. The charge-discharge performance for a non-aqueous V^{2+}/V^{3+} - V^{3+}/VO^{2+} system was tested in an H-type glass cell. The separation between charging voltage and discharging voltage was around 3 V and coulombic efficiencies η_{CE} near 50% were obtained for a 0.01 M $V(acac)_3$ solution. Nonetheless, the 4 V stability window of acetonitrile indicates the higher electrochemical window offered by non-aqueous solvents and it is noteworthy that both the V^{2+}/V^{3+} and V^{3+}/VO^{2+} redox couples revert to the same V^{3+} species upon discharge. This system saw further evaluation focusing on kinetics [106], degradation mechanisms [107] and the influence of different solvents and supporting electrolytes [108,109].

Fig. 6 Cyclic voltammograms recorded at 0.5 V s^{-1} at a glassy carbon electrode in 0.5 M $TEABF_4$ in CH_3CN (dashed line) and 0.01 M $V(acac)_3$ and 0.5 M $TEABF_4$ in CH_3CN (solid line). Measurements were taken at room temperature. Reprinted with permission from [106].

RFBs that discharge to the same active species in both half-cells mitigate the issue of cross-contamination of half-cells resulting from active species crossover. In a similar way, a non-aqueous chromium acetylacetonate RFB has also been investigated [110]. A cell potential of 3.4 V was indicated for a one-electron disproportionation reaction of $\text{Cr}(\text{acac})_3$ in which $\text{Cr}^{\text{III}}(\text{acac})_3$ is oxidised to $[\text{Cr}^{\text{IV}}(\text{acac})_3]^+$ and reduced to $[\text{Cr}^{\text{II}}(\text{acac})_3]^-$. The charge-discharge performance in an H-type cell of 0.05 M $\text{Cr}(\text{acac})_3$ in acetonitrile with a 0.5 M TEABF_4 supporting electrolyte was evaluated. Cycling between 0 to 50% of the theoretical SOC yielded η_{CE} of 53-58% and η_{EE} of 21-22%. A non-aqueous RFB utilising manganese acetylacetonate was also later investigated [68]. A 1.1 V cell potential was indicated for a RFB based on $\text{Mn}^{\text{III}}(\text{acac})_3/[\text{Mn}^{\text{II}}(\text{acac})_3]^-$ and $\text{Mn}^{\text{III}}(\text{acac})_3/[\text{Mn}^{\text{IV}}(\text{acac})_3]^{1+}$ redox couples. A cell containing 0.05 M $\text{Mn}(\text{acac})_3$ in 0.5 M $\text{TEABF}_4/\text{acetonitrile}$ supporting electrolyte showed a discharge plateau at around 0.3 V over 10 cycles. An increase in η_{CE} from $\sim 74\%$ to $\sim 97\%$ was attributed to an unknown side reaction, while the η_{EE} remained at around 21% during cycling.

6.1.3 VRFBs with novel reactor design

A co-laminar flow cell (CLFC) is a microfluidic device with a 'membrane-less' design: achieving laminar flow in adjacent liquid streams allows two solutions to flow side by side with mixing occurring only by diffusion of active species between streams [111,112]. The prevention of turbulent mixing thus allows the two electrolytes to flow side by side in a CLFC, with ionic conduction still permitted but no requirement for a membrane, thereby omitting a significant cost contribution [38] and source of overvoltage through membrane resistance. A high power density RFB that utilises vanadium chemistry has been presented in the form of a CLFC by Goulet *et al.* [112]. The high power density was mainly attributed to a novel *in operando* deposition method of carbon nanotubes (CNTs) that was applied to the flow-through porous carbon paper electrodes of the CLFC. This involved suspending the CNTs directly in the electrolyte that was to be flowed through the cell. The deposition of CNTs enhanced the electrochemical active surface area by adhering to the carbon paper electrodes and forming a conducting nanoporous layer. Further, an improvement in mass transport was indicated which was attributed to both the deposition of material directly in

the reactant flow path and a reduced average pore size of the electrodes. The power density of the flow cell subjected to CNT deposition was 2 W cm^{-2} (a typical power density for a RFB cell is 0.1 W cm^{-2} [34,112]). CLFCs are classed as microfluidic electrochemical cells and as such, it is noted that the cell is limited in scale. However, the addition of CNTs directly to the redox electrolyte presents as a simple and inexpensive method that lead to an enhancement of both the surface area and mass transport properties of the electrodes.

Fig 7. a) A real-time image of the CLFC discharging with colour changes indicating the different vanadium ion oxidation states. b) A schematic of the construction of the cell. The flow-through cross-sectional area of the electrode is highlighted in red. Reprinted with permission from [112].

A tubular vanadium redox flow cell was presented by Ressel *et al.* [113]. This approach was chosen to enable reduced manufacturing costs and less shunt currents in a cell stack. The

tubular cell was constructed from extruded current collectors and a welded tubular membrane, it was able to produce 70 mA cm^{-2} at an η_{EE} of 55%.

6.1.4 Vanadium chloride/polyhalide RFB

In order to avoid the precipitation of V_2O_5 at high temperatures a RFB which uses a polyhalide solution in the catholyte and a vanadium(II)/vanadium(III) chloride redox couple in the anolyte was developed [114]. The occurring reactions are:

During the charging process, the bromide ions in the positive half-cell are oxidised to the polyhalide ion Br_2Cl^- ; the reaction between Br_2 and Cl^- leads to the Br_2Cl^- ion, while Cl_2 dissolved in a Br^- solution generates the Cl_2Br^- ion that has high oxidation potential. The application of those compounds in a vanadium chloride/polyhalide redox flow cell would lead to cell potential of around 1.3 V. A CV was conducted on a graphite electrode and the authors claimed that the redox reaction of $\text{VCl}_3/\text{VCl}_2$ was reversible [114]. A correction for the high surface area and porosity of the electrode, which could elucidate k_0 [26], was not performed. A higher chloride ion concentration apparently shifts the peak potentials. In 8.48 M Cl^- supporting electrolyte the anodic peak appears at a potential of -0.27 V vs SHE (recalculated from SCE) and the corresponding cathodic peak at -0.33 V vs. SHE . Another advantage is that no hydrogen evolution is observed at potentials below the V(III) reduction peak which is favourable for the charging process in RFBs. A short-term cell test was conducted and the composition of the negative half-cell electrolyte was 1 M VCl_3 in 1.5 M HCl , while that of the positive half-cell electrolyte was 1 M NaBr in 1.5 M HCl . The η_{CE} and η_{VE} values were calculated as 83 and 80%, respectively. The long-term experiments to investigate the crossover across the membrane of electrolyte and the stability tests of the bromine–polyhalide mixture have to be conducted.

6.2 Bromine-polysulphide RFB

The bromine-polysulphide RFB was patented in 1984. [31]. Upon charge, bromide ions are oxidised to bromine at the positive electrode, which are complexed as the tribromide ion Br_3^- in solution, and the S_4^{2-} anion is reduced to S_2^{2-} at the negative electrode. Upon discharge the reverse occurs, with S_2^{2-} anions oxidised to the polysulphide anion S_4^{2-} at the anode and bromine reduced to bromide ions at the cathode. The catholyte and anolyte originally reported were an aqueous 1 M NaBr solution saturated with bromine and a 2 M Na_2S solution, the optimal pH for the electrolytes being neutral or slightly basic pH , while a cation exchange membrane separated the half-cells to allow the transfer of Na^+ ions between the electrodes to complete the circuit[31]. The open circuit voltage of the system is around 1.5 V [43].

Anolyte:

Catholyte:

The bromine-polysulphide RFB was investigated extensively by Regenesys Technologies Ltd. in the 1990s and early 2000s, leading to the production of three scales of bromine-polysulphide modules with 5 kW, 20 kW and 100 kW power output and a 1 MW pilot scale facility that was built at Aberthaw power station near Cardiff, United Kingdom [115]. Interest in the system culminated in the construction of a 15 MW/120 MWh demonstration plant at Little Barford power station, also in the United Kingdom. However, the plant was never fully commissioned and the funding for the technology was later withdrawn [116]. Problems encountered with the bromine-polysulphide system include cross-contamination of electrolyte solutions due to membrane inefficiency, possible deposition of sulphur species in the membrane as well as concern over the formation of H_2S and Br_2 gases [43].

6.3 Zinc/polyiodide hybrid RFB

On the subject of higher energy density RFBs, Li *et al.* presented a zinc/polyiodide hybrid flow battery [117]. The aqueous electrolyte, a ZnI₂ solution in both compartments, was ambipolar; both the cationic and anionic ions were redox active which eliminated the need for counterions. Further, the Zn²⁺ species also functioned as a charge carrier so a supporting electrolyte was not needed. Upon charge, zinc is deposited at the anode and polyiodide ions are formed in solution at the cathode while the reverse reactions occur upon discharge:

Anolyte:

Catholyte:

A high η_{CE} of 99% was demonstrated in charge/discharge cycling using concentrations of ZnI₂ from 0.5 M to 3.5 M. Over 40 cycles, a 3.5 M ZnI₂ electrolyte showed no obvious efficiency or capacity decay. While η_{EE} was shown to decrease with higher ZnI₂ concentration due to increasing electrolyte resistance, a 5 M ZnI₂ solution reached an energy density of 167 Wh L⁻¹ based upon the discharge energy density which approaches the energy density of some LIBs. An electrolyte stability window of -20 to 50°C is reported. However, as discussed in a previous section for the zinc-bromine RFB, an issue with the operation of the Zn/Zn²⁺ redox couple is the formation of dendrites when zinc is deposited at the anode during charging which was observed in the zinc-polyiodide flow battery.

6.4 Semi-solid lithium slurry RFBs

Optimisation of the VRFB remains a compelling topic, but alternative RFB chemistries also garner attention in the pursuit of improved energy densities. For instance, concepts of LIBs are naturally carrying over into flow battery research. As well as the increased cell voltages allowed by the use of a non-aqueous electrolyte, LIB operation involves ionic transport within solid electrodes which allows greater storage of active species and higher energy densities. As such, a semi-solid flow cell utilising Li-ion chemistry and slurries of suspended electrode material was presented by Duduta *et al.* [60]. The electrolytes were semi-solid

suspensions containing a nanoscale conducting carbon network that was formed by Ketjen black in alkyl carbonate/LiPF₆ solution, with micrometre-scale particles of electrode material (e.g. LiCoO₂) distributed throughout the network. The flowable suspensions that were demonstrated had up to 12 M active material concentration. A full-cell test using intermittent flow mode in which a single volume of the semi-solid suspensions was pumped into the cell, discharged and later displaced by a new volume gave a first demonstration of a fully operational semi-solid flow cell. Suspensions containing LiCoO₂ were utilised at the cathode (20 vol% (10.2 M), 1.5% Ketjen black) and suspensions containing Li₄Ti₅O₁₂ were active at the anode (10 vol% (2.3 M), 2% Ketjen black), both in 1 M LiPF₆ in dimethyl carbonate. η_{CE} of 73% and 80% were achieved in the first and second cycles. A calculated theoretical energy density for a semi-solid system utilising LiCoO₂ and Li₄Ti₅O₁₂ with 40 vol% solid in each suspension at an average discharge voltage of 2.35 V was 397 Wh L⁻¹. More generally, it was estimated that optimised semi-solid flow cells utilising lithium intercalation compounds could have energy densities of 300 to 500 Wh L⁻¹. However, higher viscosity electrolytes are associated with increased parasitic energy losses, owing to the additional energy that is required to pump the electrolyte.

6.5 Redox active polymers for RFBs

The use of organic molecules or polymers as the active materials in RFBs is also gaining prominence in RFB research as such species can be synthesised from inexpensive organic raw materials. An all-polymer RFB utilising a polymer bearing the TEMPO moiety at the cathode and a viologen-based polymer at the anode was presented by Janoschka *et al.* [90]. The TEMPO unit (2,2,6,6-tetramethylpiperidine-1-oxyl) is a heterocyclic, stable radical nitroxide molecule that can be oxidised to an oxammonium cation, while viologens are dicationic 4,4'-bipyridine derivatives that can be reduced to monocationic radicals. Both polymers also contained quaternary ammonium units to aid solubility. A study of the redox properties of the polymers by CV indicated the TEMPO-containing polymer underwent oxidation to TEMPO⁺ at 0.7 V vs. Ag/AgCl while the viologen polymer underwent a reduction at around -0.4 V vs. Ag/AgCl which corresponded to the formation of a monovalent radical Viol^{•+} species. The electrolyte for the all-polymer battery was an aqueous sodium chloride solution and a low-cost cellulose-based dialysis membrane was used to prevent crossover of the polymeric species but allow the movement of ions between half-cells.

Fig 8: *a*) A schematic representation of the polymer-based RFB, consisting of an electrochemical cell and two electrolyte reservoirs. A semipermeable size-exclusion membrane separates the anolyte and catholyte. *b*) The fundamental electrode reactions of the TEMPO and viologen radicals. Reprinted with permission from [90].

The open-circuit voltage in cell testing was 1.1 V and energy densities of around 10 Wh L⁻¹ are reported for the polymer solutions. After 10 000 cycles, 80% of the initial capacity was retained in a static, unpumped cell. A faster capacity fade was observed in a pumped cell, thought to be attributable to oxidation of the viologen radical species by oxygen entering the electrolyte. The cytotoxicity of the redox-active polymers was also tested and compared with the cytotoxicity of VCl₃, VOSO₄ and two other cationic polymers, poly(L-lysine) and branched poly(ethylene imine), materials chosen because of their wide use. The TEMPO polymer showed less toxicity than the viologen polymer, while both polymers were less cytotoxic than poly(L-lysine), poly(ethylene imine) and the vanadium salts.

The use of size-exclusion membranes that prevent polymeric active species from crossing into the adjacent electrode compartment instead of more costly Nafion ion exchange membranes illustrates a promising aspect of RFBs that utilise polymers. However, as the

concentration or the molecular weight of a dissolved polymer increases, so too does the viscosity of a polymer solution. While for any RFB a higher concentration of active species leads to a greater energy density, increasing the concentration of a polymer solution may be problematic as viscous solutions increase the energy cost of pumping the electrolytes. Thus the advantage of the use of a size-exclusion membrane in a polymer RFB could be counterbalanced by the viscosity that is intrinsic to polymer solutions.

The use of TEMPO and viologen as small organic molecules in a RFB is an alternative to TEMPO and viologen-based polymers. For instance, a RFB that used aqueous solutions of TEMPTMA (*N,N,N*-2,2,6,6-heptamethylpiperidinyloxy-4-ammonium chloride) (a TEMPO derivative) and methyl-viologen (*N,N'*-dimethyl-4,4'-bipyridinium dichloride) had an energy density of 38 Wh L⁻¹ for a theoretical cell voltage of 1.4 V and excellent capacity retention over 100 cycles [118].

Winsberg *et al.* presented a polymer-based RFB that utilised two polymers bearing the boron-dipyrromethene (BODIPY) unit [119] in propylene carbonate as solvent. CV of the monomer containing the BODIPY group showed two redox reactions at -1.51 V vs. AgNO₃/Ag and 0.69 V vs. AgNO₃/Ag which corresponded to reduction of the monomer to BODIPY⁻ and oxidation to BODIPY⁺ respectively. The BODIPY monomer was copolymerised with either TAST ((vinylbenzyl)trimethylammonium perchlorate) or TEGSt ((vinyl-benzyl)-triethylene glycol monomethyl ether) to generate two different polymers that could be used as the anolyte and catholyte in cell testing. Two static cell tests were performed. One employed poly(BODIPY-*co*-TEGSt) as anolyte with a further polymer that bore the TEMPO group used as the catholyte (poly(TEMPO-*co*-PEGMA). The second cell utilised poly(BODIPY-*co*-TAST) and poly(BODIPY-*co*-TEGSt) as the catholyte and anolyte respectively. A size-exclusion membrane separated the half-cells and a solution of 0.5 M tetrabutylammonium perchlorate (Bu₄NClO₄) in propylene carbonate was used as the supporting electrolyte. The TEMPO/BODIPY battery outperformed the all-BODIPY battery, with an average discharging voltage of 1.82 V and η_{VE} and η_{EE} of 89% and 88% respectively. A η_{CE} of 99% was achieved over 100 cycles, with 70% of the initial discharge capacity preserved. The all-BODIPY system had a charging plateau at 2.06 V while the mean discharge voltage was 1.28 V leading to η_{VE} and η_{EE} of 62% and 55% respectively, with η_{CE} reaching 89%. The energy density of the electrolyte was 0.5 Wh L⁻¹ for both polymer RFBs.

Fig 9. a) Representative charge/discharge curves of an all-organic polymer RFB using poly(TEMPO-co-PEGMA) and poly(BODIPY-co-TEGSt) operating in the range of 1.4 V and 2.15 V, showing cycles 3 to 5. b) Long-term battery cycling at a constant current of 0.25 mA. An electrolyte of propylene carbonate with 0.5 M Bu_4NClO_4 was used. Reprinted with permission from [119].

6.6 Polyoxometalate RFB

Pratt *et al.* presented a flow battery containing vanadium- and tungsten-polyoxometalates (POMs), in which the POMs undergo multi-electron reactions [120,121]. POMs are suitable for electrochemical energy storage applications because they are often stable over a wide range of temperatures, exhibit multi-electron transfer with high kinetics [122]. Also, oxidation or reduction of POMs is usually accompanied by proton or cation transfer, a mechanism that avoids the generation of highly charged radicals [123]. In the publication by Pratt *et al.* two three-electron POM redox couples $[SiV(V)_3W(VI)_9O_{40}]^{7-} / [SiV(IV)_3W(VI)_9O_{40}]^{10-}$ and

$[\text{SiV(IV)}_3\text{W(VI)}_9\text{O}_{40}]^{10-}$ / $[\text{SiV(IV)}_3\text{W(V)}_3\text{W(VI)}_6\text{O}_{40}]^{13-}$) were investigated for application as electrolyte in aqueous or non-aqueous media for RFBs.

The η_{CE} in aqueous solution was greater than 95% with low capacity loss observed during more than 100 charge-discharge cycles and no decomposition of the molecule was reported [120]. The POM also dissolved in a non-aqueous electrolyte (0.5 M TBAOTf in propylene carbonate) and the non-aqueous system had a higher operating voltage (1.1 V, 0.3 V higher than the aqueous system) but a drop of η_{CE} (initially 87%, after 10 cycles dropped by half) occurred. With a concentration of 20 mM POM and 0.5 M H_2SO_4 , the observed current densities were one order of magnitude lower than in conventional RFBs. A reasonable approach to increase the current would be to enhance the POM concentration. Stability and costs are not reported. In the paper the dimerization and eventual deposition of POMs containing W-ions at negative potentials was not discussed [120]. Keita and Nadjo reported that at negative potentials (approx. 1 V vs. SHE) in acidic solutions POMs will modify the electrode surface [124]. The deposited material is usually a catalyst for the HER, thereby reducing the stability window of the electrolyte [125]. For $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, the precursor for the redox active material used in [120], electrode coverages of 33 to 120 monolayers are reported [124].

We have reported a potential candidate for a POM catholyte: $[\text{Mn}^{\text{II}}_3\text{SiW}_9\text{O}_{34}]^{7-}$ [122,126]. While this molecule was able to transfer six electrons at high potentials, by oxidising three Mn(II) to Mn(IV), the POM adsorbed on the electrode and was too difficult to synthesise to make upscaling reasonable.

Another symmetric POM RFB was presented by Liu *et al.* [127]. They employed $\text{H}_6[\text{CoW}_{12}\text{O}_{40}]$ in both anolyte and catholyte of an aqueous battery. The reactions for the anolyte were two two-electron waves at -0.04 V vs. SHE and -0.16 V vs. SHE (in 1 M H_2SO_4 , recalculated from the SCE) [128]. As catholyte the single one-electron redox reaction of the Co(II)-heteroatom at 1.1 V vs. SHE was used. The POM was exceptionally soluble, up to 0.8 M, and 14 Ah L^{-1} were reached as capacity. However, for that result four times more catholyte volume than anolyte volumes was used (and above volumetric capacity is given for the anolyte) which is necessitated by the imbalance in charge transfer reactions at low and high potential.

6.7 Metal-free organic-inorganic aqueous RFBs based on anthraquinones

A RFB with quinones as aromatic redox-active organic molecules instead of redox-active metals was developed with the main objective to reduce capital costs [129]. The used molecule in the anolyte was 9,10-anthraquinone-2,7-disulphonic acid (AQDS) dissolved in 1 M H₂SO₄. According to the authors, AQDS can be synthesized from cheap, conventional educts.

Fig 10. Chemical structure of 9,10-anthraquinone-2,7-disulphonic acid. Reprinted with permission from [129].

In the positive half-cell the redox couple was Br₂/Br⁻ complementing the quinone/hydroquinone redox couple in the anolyte. For this type of battery a tremendous power density of 1 W cm⁻² was reported at a relatively low cell voltage of 0.86 V [130,131]. The reached storage capacity retention was more than 99% per cycle (99.90% per cycle over 40 cycles). These losses are thought to originate from leakage of the anolyte, crossover of bromide and destruction of redox species [132].

The theoretical capacity of 35 Wh L⁻¹ cannot be reached in the cell, only 23 Wh L⁻¹ could be realized. A possible explanation was provided by Carney *et al.*, who found intermolecular dimerization of AQDS at concentrations greater than 10 mM [133]. This behaviour is *pH* dependent and might reduce the electrons that can be carried per AQDS molecule from 2 to 1.5 in acidic media.

A further advantage is that the chemical and electrochemical properties of the AQDS molecules can be engineered by adding functional groups. Addition of a hydroxyl group reduces the standard potential of the redox reaction, thereby increasing the open circuit potential U_{OCV} . A CV of 1 mM solution of AQDS in 1 M sulphuric acid on a glassy carbon disk working electrode was conducted and a fast reversible two-electron two-proton redox reaction occurred. The peak separation was 34 mV and corresponds to a two-electron process. The kinetic reaction rate constant k_0 was calculated to 7.25 x 10⁻³ cm s⁻¹ which is greater than that found for other components used in for RFBs such as V³⁺/V²⁺ (compare table 1). The main advantages of the AQDS/Br system are low electrolyte costs and fast

kinetics. The crossover of bromine into the negative half-cell could affect the lifetime and the stability of the organic compound should be investigated. The array of π -aromatic redox-active organic compounds constitutes a new opportunity for low-cost large-scale energy storage.

Another cell chemistry employing quinones is the 2,6-dihydroxyanthraquinone (DHAQ)/ $\text{Fe}(\text{CN})_6$ system in alkaline media [134]. At $\text{pH } 14$ the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ avoids the use of the problematic Br_2/HBr employed in the acidic quinone chemistry [129], and the cell reaches a higher cell voltage of 1.2V. The modest solubility of both DHAQ and $\text{Fe}(\text{CN})_6$, however, limits the theoretical energy density to 9.2 Wh L^{-1} , of which 74% have been shown experimentally [134].

6.8 A RFB with an alloxazine-based organic electrolyte

In this work an aqueous RFB utilizing an organic redox compound was reported. As electrochemically active molecule alloxazine, which is a tautomer of the isalloxazine backbone of vitamin B₂ was used [135]. It can be obtained by a single-step coupling of *o*-phenylenediamine derivatives and alloxan with a yield of 95% at room temperature. The synthesis route was inspired by nature and the educts are reported to be inexpensive.

Fig. 11 *Alloxazine 7/8-carboxylic acid, ACA.*

The alloxazine was functionalized with a carboxylic acid group (alloxazine 7/8-carboxylic acid, ACA, see Fig. 10) to increase its solubility in aqueous solution. ACA was investigated by CV and the standard potential is -0.62 V vs. SHE . The rate constant was calculated from rotating-disc electrode measurement and determined to be $k_0 = 1.2 \pm 0.2 \times 10^{-5} \text{ cm s}^{-1}$, which is an order of magnitude higher than that of the reactions of the VRFB [26]. The full-cell test was conducted using 0.5 M ACA (1.5mmol) as the negative electrolyte and 0.4 M ferrocyanide (4.5mmol) + 40 mM ferricyanide (0.46mmol) as the positive electrolyte. Both solutions were adjusted to $\text{pH } 14$ by KOH. An excess concentration of the positive electrolyte was used to determine the electrochemical stability of the negative electrolyte.

The resulting alkaline aqueous RFB exhibited an OCV of 1.2 V and η_{CE} and capacity retention reaching 99.7% and 99.98% per cycle, respectively. The alloxazine redox centre demonstrates high electrochemical and chemical stability and high solubility. It was shown in theoretical studies that structural modification such as adding electron-donating groups to the alloxazine could increase the battery voltage. This aza-aromatic molecule undergoes reversible redox reaction in aqueous electrolyte and constitutes a class of radical-free redox-active compounds for application in RFBs with high power density and low costs.

6.9 TEMPO-Based Catholyte for non-aqueous RFBs

Although only a catholyte was presented, due to its potential it is included in this review. A lithium hybrid flow battery containing TEMPO, a stable, heterocyclic nitroxide radical, as the organic active material was developed [73]. CVs were conducted in an electrolyte of 0.005 M TEMPO and 1.0 M LiPF₆ dissolved in EC/PC/EMC (4:1:5 by weight) and clear redox peaks in the potential range of 2.5–4.0 V of TEMPO were obtained. The peak separation of 61 mV at 10 mV s⁻¹ corresponds to a one-electron-transfer between the nitroxide radical and the oxoammonium cation.

Fig. 12 Redox reactions in the negative and positive electrolyte during charge and discharge.

The electrochemical performance was tested in a non-aqueous hybrid RFB with a polyethylene-based porous separator. The anode was a hybrid anode consisting of lithium foil and graphite felt and as cathode a graphite felt was used. Both electrodes were compressed by 15%. An additive, fluoroethylene carbonate (FEC) was added to protect the Li anode. TEMPO was dissolved in a solution containing EC/PC/EMC (weight ratio of 4:1:5) and LiPF₆ as supporting electrolyte. The TEMPO based electrolyte was static within the anode compartment and was not flowed, whereas in the cathode compartment the electrolyte was

circulated through the graphite felt at a flow rate of 50 mL min⁻¹. Galvanostatic charge/discharge cycling with various concentrations of TEMPO (0.8/1.2 M, 1.5/1.8 M, and 2.0/2.3 M) were conducted. Charge and discharge experiments were conducted and 100 cycles were obtained with a η_{CE} of 99%, an η_{VE} of 87% and an η_{EE} of 86% and an average capacity retention of 99.8 % per cycle were achieved. Due to high viscosities of the electrolytes, the flow cells were cycled at current densities of 2.5 mA cm⁻² at 1.5 M and 1.0 mA cm⁻² at 2.0 M.

The theoretical energy density of the system with 2.0 M TEMPO is 126 Wh L⁻¹ and is much higher than for a conventional VRFB. Due to the high energy density and overall voltage of 3.5 V, TEMPO is a promising candidate for flow batteries.

7. Overview of some redox reactions of importance for RFBs

Redox couples	U^0 vs. SHE	Aqueous/ non-aqueous	k_0 / cm s ⁻¹	Concentration	Number of electrons
Br ⁻ /Br ₂	1.09 V	Aqueous			
Zn/Zn ²⁺	-0.76 V	Aqueous	-		
Fe ²⁺ /Fe ³⁺	0.77 V	Aqueous	6 10 ⁻⁵	2M	
Cr ²⁺ /Cr ³⁺	-0.41	Aqueous	2.2 10 ⁻⁵	2 M	
VO ²⁺ /VO ₂ ⁺	1.0 V	Aqueous	10 ⁻⁶	1.6 – 2M	
V ²⁺ /V ³⁺	-0.25 V	Aqueous	10 ⁻⁶	1.6 – 2M	
Br ₃ ⁻ /Br ⁻	+1.09 V	Aqueous	4 x 10 ⁻⁵	1 M NaBr saturated with Br	
S ₄ ²⁻ /S ₂ ²⁻	-0.265 V	Aqueous	3 x 10 ⁻⁶	2 M Na ₂ S	
I ₃ ⁻ /I ⁻	+0.54 V	Aqueous	-	5.0 M ZnI ₂	
Zn/Zn ²⁺	-0.76 V	Aqueous	-	5.0 M ZnI ₂	
Ce ³⁺ /Ce ⁴⁺	+1.28 to +1.72 V	Aqueous	-	0.2 M Ce(III) methanesulfonate	

				(0.5 M methanesulfonic acid)	
Zn/Zn ²⁺	-0.76 V	Aqueous	-	1.5 M zinc methanesulfonate (0.5 M methanesulfonic acid)	
Mn ²⁺ /Mn ³⁺	+1.3 V vs Ag/AgCl	Aqueous	-	1 M MnSO ₄ + 1.5 M TiOSO ₄ (3 M H ₂ SO ₄)	
Ti ³⁺ /TiO ₂ ²⁺	~0.09 V vs Ag/AgCl	Aqueous	-	1 M MnSO ₄ + 1.5 M TiOSO ₄ (3 M H ₂ SO ₄)	
Fe ²⁺ /Fe ³⁺	+0.77 V	Aqueous	6 10 ⁻⁵	1 M FeCl ₂ + 0.5 M CdSO ₄ (3 M HCl)	
Cd/Cd ²⁺	-0.40 V	Aqueous	-	1 M FeCl ₂ + 0.5 M CdSO ₄ (3 M HCl)	
NiOOH/Ni(OH) ₂	0.490 V	Aqueous	-	1 M ZnO (10 M KOH)	
Zn/Zn(OH) ₄ ²⁻	-1.215 V		-	1 M ZnO (10 M KOH)	
V ^{III} (acac) ₃ /[V ^{IV} (acac) ₃] ⁺	+0.45 V vs. Ag/Ag ⁺	Non-aqueous	1.3 10 ⁻⁴	0.01 M (0.5 M TEABF ₄ /acetonitrile)	
V ^{III} (acac) ₃ /[V ^{II} (acac) ₃] ⁻	-1.8 V vs. Ag/Ag ⁺	Non-aqueous	-		
Ru ^{III} (acac) ₃ /[Ru ^{IV} (acac) ₃] ⁺	+1.0 V vs. SCE	Non-aqueous	3.4 10 ⁻³	0.1 M (0.5 M TEABF ₄ /acetonitrile)	
Ru ^{III} (acac) ₃ /[Ru ^{II} (acac) ₃] ⁻	-0.85 V vs. SCE	Non-aqueous			
Mn ^{III} (acac) ₃ /[Mn ^{IV} (acac) ₃] ⁺	+0.7 V vs. Ag/Ag ⁺	Non-aqueous	-	0.05 M	

$\text{Mn}^{\text{III}}(\text{acac})_3/[\text{Mn}^{\text{II}}(\text{acac})_3]^-$	-0.4 V vs. Ag/Ag ⁺	Non-aqueous	-	(0.5 M TEABF ₄ /acetonitrile)	
$\text{Cr}^{\text{III}}(\text{acac})_3/[\text{Cr}^{\text{IV}}(\text{acac})_3]^+$	+1.2 V vs. Ag/Ag ⁺	Non-aqueous	-	0.05 M	
$\text{Cr}^{\text{III}}(\text{acac})_3/[\text{Cr}^{\text{II}}(\text{acac})_3]^-$	-2.2 vs. Ag/Ag ⁺	Non-aqueous	-	(0.5 M TEABF ₄ /acetonitrile)	
$[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}/[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$	+1.0 V vs. Ag/Ag ⁺	Non-aqueous	-	0.02 M	
$[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}/[\text{Ru}^{\text{I}}(\text{bpy})_3]^+$	-1.6 V vs. Ag/Ag ⁺	Non-aqueous		(0.1 M Et ₄ NBF ₄ /acetonitrile)	
$[\text{V}(\text{mnt})_3]^{2-}/[\text{V}(\text{mnt})]^-$	0.856 V	Non-aqueous	-	0.02 M	
$[\text{V}(\text{mnt})_3]^{2-}/[\text{V}(\text{mnt})_3]^{3-}$	-0.227 V	Non-aqueous	-	(0.1 M TBAPF ₆ /acetonitrile)	
Fc/Fc ⁺ (Fc = ferrocene)	0.041 V vs. Ag/Ag ⁺	Non-aqueous	-	0.01 M	
Cc/Cc ⁺ (Cc = cobaltocene)	-1.290 V vs. Ag/Ag ⁺	Non-aqueous	-	(1 M TEAPF ₆ /acetonitrile)	
$\text{Co}^{\text{II}}(\text{acacen})/[\text{Co}^{\text{I}}(\text{acacen})]^-$	-0.2 V vs. Ag/Ag ⁺	Non-aqueous	-	0.01 M	
$\text{Co}^{\text{II}}(\text{acacen})/[\text{Co}^{\text{III}}(\text{acacen})]^+$	-2.2 V vs Ag/Ag ⁺	Non-aqueous	-	(0.1 M TEAPF ₆ /acetonitrile)	
QCl ₄ /QH ₂ Cl ₄ (QCl ₄ = Tetrachloro- <i>p</i> -benzoquinone)	0.71 V	Aqueous	-	0.5 M CdSO ₄	
Cd/Cd ²⁺	-0.402	Aqueous	-	(1 M (NH ₄) ₂ SO ₄ + 0.5 M H ₂ SO ₄)	
BQDS/H ₂ BQDS (BQDS = 1,2-benzoquinone-3,5-disulfonic acid)	0.85 V	Aqueous	1.55 x 10 ⁻⁴	0.2 M (1 M H ₂ SO ₄)	
AQS/H ₂ AQS (AQS = anthraquinone-2-sulfonic acid)	0.09 V		2.25 x 10 ⁻⁴	0.2 M (1 M H ₂ SO ₄)	

TEMPO/TEMPO ⁺	0.30 V vs. Ag	Non-aqueous	-	0.1 M (1 M NaClO ₄ /acetonitrile)	
N-methylphthalimide/ N-methylphthalimide [•]	-1.30 V vs. Ag	Non-aqueous	-	0.1 M (1 M NaClO ₄ /acetonitrile)	
TEMPTMA/TEMPTMA ⁺	0.79 vs. AgCl/Ag	Aqueous	4.2 x 10 ⁻³	2 M (in NaCl)	
Methyl Viol ²⁺ /Methyl Viol ^{•+}	-0.63 V vs. AgCl/Ag		3.3 x 10 ⁻³		
Polythiophene/Polythio phene ⁺	+0.5 V vs. Ag/Ag ⁺	Non-aqueous	-	Suspension of polythiophene (0.1 eq. L ⁻¹ of thiophene repeating units) (1 M TEABF ₄ /propylene carbonate)	
Polythiophene/Polythio phene ⁻	-2.0 V vs. Ag/Ag ⁺	Non-aqueous	-		
TEMPO/TEMPO ⁺	+0.7 V vs. Ag/AgCl	Aqueous	(4.5 ± 0.1) x 10 ⁻⁴	polymer solutions (2 M NaCl)	
Viol ²⁺ /Viol ^{•+}	~0.4 V vs. Ag/AgCl		(9 ± 2) x 10 ⁻⁵		
Poly(BODIPY)/Poly(BOD IPY) ⁺	0.69 V vs. AgNO ₃ /Ag	Non-aqueous	-	polymer solution (0.5 M Bu ₄ NClO ₄ /propylene carbonate)	
Poly(BODIPY)/Poly(BOD IPY) ⁻	-1.51 V vs. AgNO ₃ /Ag	Non-aqueous	-		

Table 3 Overview of redox reactions of importance for RFBs. If approximate realised energy density is given then the energy content is calculated from the given publication. Chemistries not demonstrated in flow batteries were usually tested in a stationary cell configuration.

8. Conclusion: What would be the ideal RFB?

The primary properties of the ideal RFB chemistry are high energy- and power-density, long-time stability and low capital costs. Secondary features are high efficiencies and safety, and low toxicity of the chemistries. However, we will not go into detail in these secondary features, because efficiencies are very much related to the issues power density and stability, and the ideal toxicity level is easily assessed: The ideal RFB chemistry is not harmful to health of humans or the environment, such as claimed by the nanoFlowcell Holdings Ltd. for their undisclosed nanoFlowcell technology [154], which, due to its unverified claims, is regarded very sceptical by the scientific community.

Energy density: The (volumetric) energy density E for a RFB is given by the combination of equations 3 and 6. There are three parameters that can be adjusted to increase E : Number of transferred electrons per molecule n , concentration c and cell voltage ΔU . For most molecules discussed in this paper $n = 1$, with some exceptions such as the AQDS and Br_2/Br^- systems which transfer $n = 2$ electrons [43,129,140] and POM systems with $n \geq 3$ [120,127]. In the latter case, this property is achieved only by employing heavy molecules (molar mass larger than 2000 g mol^{-1}). Due to the high solubility of POMs, this can increase the volumetric energy density, but hardly the gravimetric energy density. Highly charged species are often not stable, therefore multi-electron transfer is usually accompanied by proton transfer [122,123,155]. While this prevents the formation of radicals, balancing of protons adds an additional challenge to the system, if it does not operate at very low pH . As shown in section 4, the question of maximum cell voltage ΔU is intricately connected to the question of aqueous or non-aqueous chemistry. While the limit of ΔU in water is roughly 1.6 V, this value can be significantly higher in organic electrolytes. However, as the use of non-aqueous electrolytes comes with a serious penalty in terms of costs (as we will show later) and ease of operation, the cell voltage has to be increased at least to 3 V in order to warrant drastic step [156].

Concentration c is probably the most freely adjustable parameter that determines the energy density. Employing slurries of Lithium ion battery cathode materials concentrations as high as 12 M for the active material are reported [60]. Classical RFBs such as the VRFB reach concentrations of 1-3 M, often with the use of stabilisers or in concentrated acids. Looking at the discussion of the three parameters above, we can define something like the

expected value in terms of volumetric energy density for an aqueous RFB: This cell transfers one electron $n = 1$ per molecule, anolyte and catholyte are present as $c = 2$ M solutions and the cell voltage takes maximum advantage of the stability window of carbon electrodes in water, $\Delta U = 1.6$ V. The result is a battery with energy density $E \approx 43$ Wh L⁻¹. Any RFB chemistry that features a higher volumetric energy content, while simultaneously satisfying the other constraints (power, cost, safety, efficiency) would be desirable.

Power density: The power that can be drawn from a battery is limited by the overvoltage $R_{\text{total}}I$ that has to be applied to reach a certain current I . This total resistance R_{total} , often given as area-specific resistance (ASR) of the power converter, comprises the single resistances R_{elec} , R_{mem} , R_{CT} and R_{mass} as given in equation 7. R_{elec} and R_{mass} are from the realm of power converter design and electrochemical engineering, and are therefore not discussed here [23,24,43,115]. The membrane resistance R_{mem} is determined by the used membrane or separator, but that is pre-determined by the used chemistry [83,157]. Ideally size-exclusion membranes [90] or fluorinated exchange membranes with high proton concentrations are used to keep R_{mem} low. In non-aqueous solvents or in neutral aqueous electrolytes the membrane can have a significant contribution to the ASR. One major factor is the charge transfer resistance R_{CT} that depends on the employed redox couple. The electron transfer constant k_0 which determines R_{CT} (see equation 8) spreads over more than three orders of magnitude for different redox couples used for RFBs (see table 1). With $c = 2$ M L⁻¹, $n = 1$ and $k_0 = 0.001$ cm s⁻¹, the $R_{\text{CT}} = 0.1$ Ω cm² would contribute only minimally to the ASR for which an upper bound of 1.5 Ω cm² was given [156]. Therefore, the ideal RFB chemistry has an electron transfer constant of $k_0 \geq 0.001$ cm s⁻¹.

Long-time capacity stability is an obvious criterion for an RFB. In terms of the chemistry this can be subdivided into cycling stability and chemical stability. The former is diminished by side-reactions during charge and discharge, and cross-over through the membrane. Only the fraction of electrolyte volume in the power converter is subjected to it. The latter, chemical stability, concerns either individual oxidation states or redox molecules themselves. For most of these phenomena mitigation strategies can be found. For example, in a VRFB hydrogen evolution takes place [57], ion-specific cross-over through the membrane occurs [158] and V²⁺ is oxidized by O₂. All these effects lead to an imbalance in the electrolyte, anolyte and catholyte are not at the same SOC during battery operation. Re-mixing of the

electrolytes or electrochemical rebalancing can be employed to mitigate this capacity loss [159]. More problematic is chemical instability, if the employed redox shuttles react to form other species. This is because even if the temporal capacity fade, such as for the bis((3-trimethylammonio)propyl)-ferrocene dichloride / bis(3-trimethylammonio)propyl viologen tetrachloride seems extremely low, at the reported 99.90%/day [160] the capacity has dropped to 70% of its initial value after one year.

Degradation effects that do not stem from the electrolytes can be due to membrane fouling [161], bipolar plate corrosion and electrode ageing [51,162]. These are serious issues, but they could be remedied by replacing the cell stack which might be cheaper than replacing the electrolyte.

The ideal RFB chemistry features high coulombic efficiency, however, ion cross-over and side reactions can be tolerated if the battery is symmetric as in the case of the VRFB, and viable rebalancing strategies exist. Chemical instability cannot be tolerated, as even tiniest decay rates add up very quickly.

The discussion of costs for a RFB is dominated by the goal set by the United States' Department of Energy's (DOE's) Advanced Research Projects Agency-Energy (ARPA-E) to limit the capital cost to US\$100 per kWh for widespread adoption from 2010 [163,164]. Since then a number of cost calculations for RFBs have appeared [38,156,163], comparing the costs for the various components. For the VRFB, Zhang *et al.* found that the electrolyte and the membrane are the major cost contributors [38]. However, it is also reasonable that when the main application of RFBs shifts from frequency regulation to grid storage, the ratio of power (kW) to energy content (kWh) will decrease, favouring longer storage times over power output. In that case, the contribution of the power converter will decrease in importance, and the main cost factor will be the electrolyte. The cost for battery grade V_2O_5 , a convenient benchmark, fluctuated a lot over the last decade, with maximum costs of US\$28 kg⁻¹ and minimum costs of US\$8 kg⁻¹ [165]. Assuming a cost of US\$21.13 kg⁻¹ for vanadium, the capital cost price tag for a 1MW/12MWh VRFB battery was put at US\$400 kWh⁻¹ [38]. Acknowledging that even at a power to energy ratio of 1:12, this value greatly exceeds the DOE's target, there are two conceivable pathways for capital cost reduction: First, it is considered that the employed vanadium does not degrade over the course of the battery's lifetime. Therefore, it can be fully recuperated at end of operation, potentially with

minimal purification necessary, the spent capital costs is therefore not lost but is merely an investment. With respect to recycling, the VRFB, and RFBs in general, have a clear advantage over LIBs in which the single components are more intimately entangled and cannot be separated easily.

Second possibility is to replace vanadium as active element by cheaper molecules.

Substitution of vanadium by organic molecules that only contain cheap elements [90,119,129] is envisioned, or by replacing it with cheaper metals such as iron and chromium [166] or manganese [143]. Whatever the strategy, Darling *et al.* concluded that the active species should not cost more than US\$5 kg⁻¹ and the electrolyte not more than US\$0.1 kg⁻¹ (for aqueous systems) assuming a weight of not more than 150 g per mole of electrons stored [163]. They further concluded that while the design space for non-aqueous systems seems wider than for aqueous chemistries, the additional costs for the electrolyte (must not cost more than US\$5 kg⁻¹) imposes additional hurdles that need to be taken by the chemistry such as $\Delta U > 3 \text{ V}$ and $c > 4 \text{ M}$. Therefore, our conclusion is that the ideal system in terms of cost is either a combination of two aqueous redox couples that can be easily produced large-scale and are cheaper than US\$5 kg⁻¹, or that there is rethinking regarding the VRFB system, with the electrolyte not seen as something that is spent after the battery's operation, but as an investment that keeps its value, or might even increase in value during the operation of the battery.

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