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Principle, Advantages and Challenges of Vanadium Redox Flow Batteries

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Abstract: Vanadium redox flow batteries (VRFBs) represent one of the most advanced and reliable technologies for large-scale energy storage. This review focuses on VRFBs due to their maturity, excellent cycle life, scalability, and safety features, making them well-suited for grid-scale applications and renewable energy integration. Unlike other flow battery chemistries, VRFBs utilize vanadium in different oxidation states for both electrolytes, which prevents cross-contamination and enhances long-term stability. Although VRFBs face challenges such as high costs and moderate energy density, their proven reliability makes them a leading option for stationary energy storage. This work also compares VRFBs with other types of flow batteries, including zinc-bromine, iron-chromium, and organic flow batteries, to provide a comprehensive understanding of the advantages and limitations of VRFBs in the context of other available technologies.

Keywords: Circulating flow batteries; Renewable energy storage; Molecular engineering; Energy density



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1. Introduction to Circulating Flow Batteries

1.1 The Importance of Renewable Energy Storage

The energy needs of our society are constantly increasing. Today, these needs can still be met using fossil resources as a means of energy production. However, their overuse has led to the depletion of these resources. Furthermore, the use of fossil resources has a considerable impact on the environment. In order to be able to meet our energy needs while limiting the environmental impact of its production and consumption, it is crucial to develop alternative solutions. Producing renewable energy through the use of wind turbines or photovoltaic panels appears to be a promising alternative to fossil fuels. Due to the intermittent nature of renewable

energy production, it is currently not possible to use renewable energy as the sole source of energy, creating a gap between production and consumption. Our society is so used to using energy on demand that it seems inconceivable that we could adjust our energy consumption to coincide with wind and solar production. If it is currently possible to balance the use of fossil resources with the production of renewable energies, with partial energy production from wind and solar energy, the share of renewable energies in the French energy mix remains low, as shown in **Figure 1**. This chart, taken from a report by the General Council for Sustainable Development on French energy key figures, shows that the share of renewable energy in primary energy consumption was about 11% in 2018.

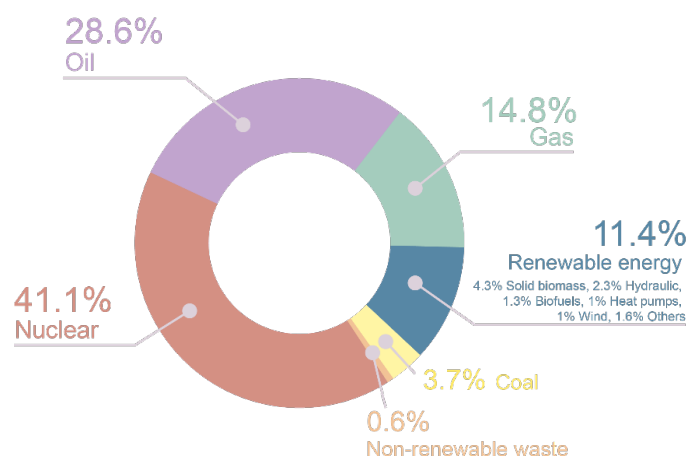


Figure 1. Breakdown of primary energy consumption in France in 2018. Reproduction of the 2019 General Commissioner for Sustainable Development report^[1]

To increase the share of renewable energy, it is crucial to develop energy storage methods that match production and demand. To this end, methods are being developed to store electrical energy in another form of energy (mechanical, chemical, magnetic, thermal, *etc.*). The simplest and most economical is hydroelectric storage, where electricity is stored in the form of gravitational potential energy using a pump system and returned through a turbine, which will again generate electricity. Some systems use the conversion of electrical energy to mechanical energy. Although the hydraulic system is economical, it is not enough to use these storage systems due to geographical restrictions. Other methods also exist, such as flywheels, where the electrical energy generated is used to spin a large cylinder at high speed. The inertia of the device makes

it possible to store this mechanical energy and later recover it in the form of electrical energy. One can also cite the use of gases, where energy is used to compress air (for example), the energy can be recovered by decompression.

Electrochemical energy storage devices store electrical energy in the form of chemical energy. For example, batteries are based on the use of reversible redox reactions between two oxidation/reduction pairs. By circulating an electric current between the negative and positive electrodes, the battery will charge, forming a torque reducer at the negative electrode and an oxidant at the positive electrode. Instead, by connecting the two electrodes of the battery with electrical conductors, a current flow occurs, arising from the reverse spontaneous redox reaction observed during

battery charging.

Electrochemical energy storage stands out as a promising solution for renewable energy storage. Various devices have been realized on an industrial scale as prototypes. Thanks to nearly 30 years of industrial development, lithium-ion technology is

still state-of-the-art. For stationary storage, other technologies are emerging, such as sodium-ion, sodium/sulfur systems and even circulating flow batteries^[2], whose vanadium technology already has a certain number of industrial prototypes (**Figure 2**).

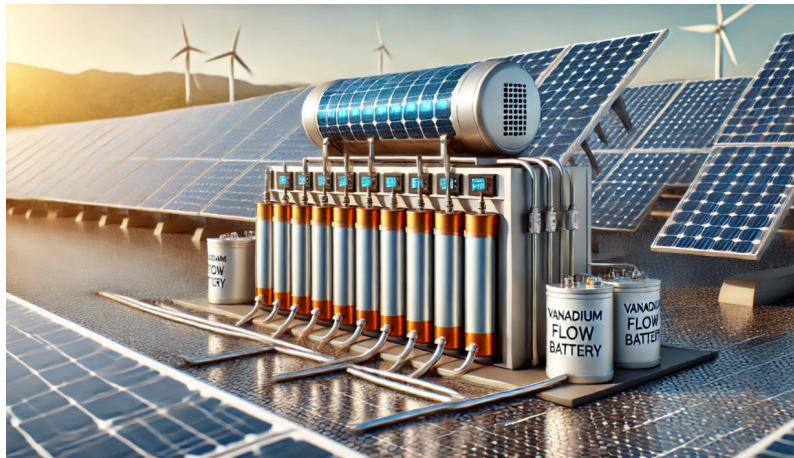


Figure 2. Schematic diagram of a vanadium flow-through batteries storing the energy produced by photovoltaic panels. Reproduction from the article by Walsch *et al.*^[3]

1.2 Principle and Operation of Circulating Flow Batteries

The term “circulating flow battery” is commonly known by its English name “redox flow battery” and includes a range of devices whose characteristics may vary from one configuration to another. If we want to be very strict, it’s hard to simply define “that” how a flow battery works. However, it is generally accepted that the following description corresponds to the general principles of circulating flow batteries and that other configurations are ultimately variations of

the presented technology. A circulating flow battery is an electrochemical energy storage system in which redox species are dissolved in an electrolyte. Two pairs of redox molecules are dissolved in two different electrolytes, one is called the positive electrode, corresponding to the electrolyte in which the higher potential redox pair is dissolved, and the other is called the negative electrode, which contains the lower potential redox pair. These electrolytes are divided into two compartments, separated by a membrane. **Figure 3** explains the operation of these systems.

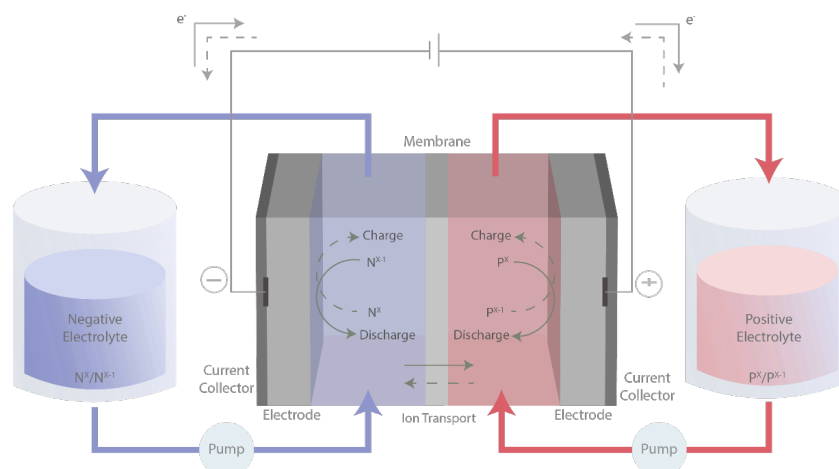


Figure 3. Diagram of the operation of a circulating flow battery

The device consists of an electrochemical cell in which electrochemical reactions will take place on the surface of carbon electrodes. A reservoir external to the electrochemical cell contains a large amount of electrolyte and a pump system will allow continuous delivery of the redox electrolyte in the electrochemical cell. This may be the most important property of a flow battery. As with fuel cells, the reagents are stored outside the electrochemical cell. It is customary to say that for such batteries, the power (battery) is separated from the energy (tank), which constitutes a major asset in terms of modularity and safety.

Finally, the separator is one of the key components

of a flow battery. It must allow the passage of cations or anions (from the carrier salt) contained in the electrolyte to achieve charge balance during charging and discharging of the battery. The membrane must also prevent electroactive species from entering the opposite compartment (a phenomenon known in the literature as “crossover”) to limit the continuous self-discharge and irreversible loss of capacity caused by the electrochemical reaction of charged species together. In a nutshell, we can say that flow batteries correspond to rechargeable fuel cells. Thus, the device sits between a normal battery and a fuel cell, with different characteristics of the two systems (**Figure 4**).

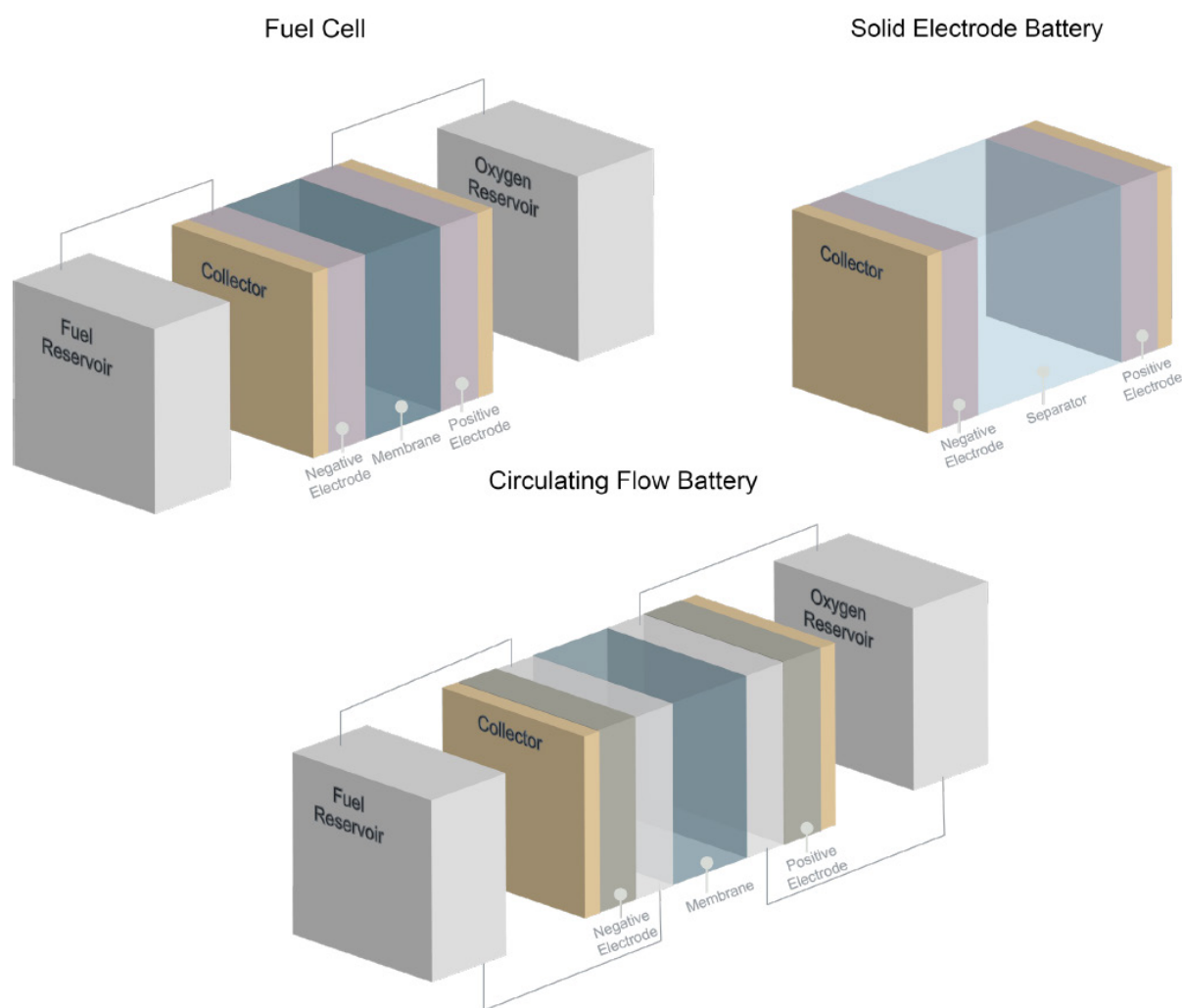


Figure 4. Diagram of the usual device for fuel cells, solid electrode batteries and circulating flow batteries

Beyond picture comparisons, this has practical implications for how to characterize flow battery performance. For these devices, experiments from the battery community have notions of capacity in

amp-hours per liter (**Figure 5a**), but there are also experiments from fuel cell protocols with concepts such as power in area watts was performed as a function of applied current density (**Figure 5b**).

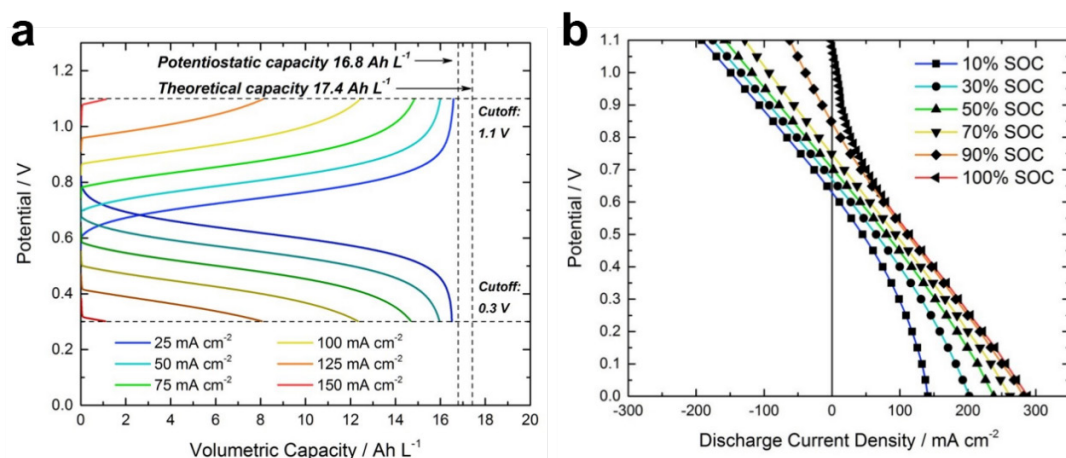


Figure 5. Examples of the electrochemical evaluation of the performance of a redox flow battery (a) Galvanostatic charge/discharge and (b) Cell voltage of the battery for different states of charge depending on the applied current density.

Reproduction of the publication by John *et al.*^[4]

1.3 History of Circulating Flow Batteries

As we just said, circulating flow batteries are often described as rechargeable fuel cells. The reason for this comparison is the continuous supply of reagents to the electrochemical cell and the use of a separator between the positive and negative compartments of the cell. However, the fact that circulating flow batteries are rechargeable separates the two systems nicely. NASA established the Lewis Research Center in 1973 with the goal of developing rechargeable fuel cells, now known as circulating flow batteries^[5]. The project highlights a number of theoretical advantages of such devices compared to fuel cells, such as the long lifetime of these systems, the possibility of use at room temperature and their better energy efficiency. In 1975, NASA patented a chromium/iron circulating flow battery using the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ pair as the highest potential torque and the torque $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$ as the lowest potential torque in acidic medium hydrochloric acid. Many problems with this technology have driven research into other systems. In particular, the $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$ pair requires the use of catalysts (such as bismuth or gold/titanium mixtures) on carbon electrodes to compensate for the poor electrochemical kinetics. Furthermore, the catalysts used must induce an overvoltage associated with the electrochemical reduction of water, since water is thermodynamically easier to reduce than trivalent chromium. In the case of reduced water, hydrogen production, in addition to limiting the energy efficiency of the device, can also cause an imbalance between the states of charge of the two electrolytes during cycling^[6].

Even if larger-scale prototypes are tested, the high cost of the catalysts required for these devices, as well as their low energy density, will limit their development. NASA will propose an alternative device that uses $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{III}}$ as the anode. Although this system is attractive in terms of cost, the limited electrochemical kinetics at the anode side will inhibit its development. Meanwhile, Japanese researchers developed the first organometallic flow battery in 1988 using ruthenium complexes in an acetonitrile medium. These systems exploit the electrochemical stability window of acetonitrile to exploit higher energy densities. However, the high cost of ruthenium combined with the extremely low energy efficiency of 30% to 40% makes these systems unsuitable for the application^[7]. In 1980, the metal/halogen system was patented. Chromium/halogen and iron/chlorine systems were investigated, but the poor electrochemical reversibility of these devices would hinder their development. The vanadium battery, which remains the reference technology for flow devices to this day, was also developed in the 1980s and utilizes the various oxidation states of vanadium^[8,9]. The system claims to avoid species cross-contamination issues because the same element is used in different oxidation states on both sides of the cell. This configuration should allow for a long life of these devices. The system claims to avoid species cross-contamination issues because the same element is used in different oxidation states on both sides of the cell. This configuration should allow for a long life of these devices. The system claims to avoid species cross-

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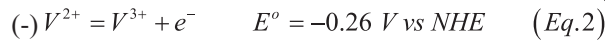
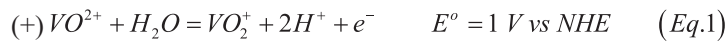
1.4 Advantages and Limitations of Circulating Flow Batteries

The vanadium system, the most used in industry today, was developed using the different oxidation levels of vanadium (Figure 6).



Figure 6. Solution containing vanadium at different oxidation states. From left to right, V^V, V^{IV}, V^{III}, V^{II}. Source: © Periodic TABLE Elements

Use couple V^V/V^{IV} for the positive electrolyte and force couple V^{III}/V^{II} for the negative electrolyte. These two electrolytes consist of a concentrated sulfuric acid solution in which two redox couples are dissolved.



(1) Redox equation for the couple V^V/V^{IV} as a positive electrolyte

(2) Redox equation for the couple V^{III}/V^{II} as a negative electrolyte

The electrochemical reaction of the battery involves only one electron, and the maximum solubility is V²⁺ and V³⁺ on the order of 2 M. This solubility limit, coupled with a potential difference of 1.26 V, enables energy density values between 25 Wh • L⁻¹ and 35 Wh • L⁻¹ (Equations 3 to 5).

$$Q^{+/-} = \frac{n \cdot F \cdot e}{V} = C \cdot F \cdot e \quad (Eq.3)$$

$$Q_{battery} = \frac{Q^+ \cdot Q^-}{Q^+ + Q^-} \quad (Eq.4)$$

$$E = Q_{battery} \cdot \Delta V \quad (Eq.5)$$

(3) Calculation of the volumetric capacity of the

In this context, an ideal membrane that theoretically limits the crossover of electroactive species must be specific and permeable to the anion SO₄²⁻ present in the electrolyte, while preventing the passage of vanadium cations. However, the conductivity of anion exchange membranes is low. Among other things, their chemical stability is limited relative to the strong oxidant VO₂⁺, the charged species in the electrolyte cathode. In fact, these systems therefore use a cation-conducting membrane, the Nafion membrane, which is stable under these conditions.

The use of a cationic membrane induces the long-term passage of vanadium cations. These transfers of cations are due to concentration gradients and electric fields formed during cell cycling. Furthermore, the permeability of vanadium in these different degrees of oxidation is variable, again leading to an imbalance between the two electrolytes. Due to the osmotic pressure in the device, water molecules also cross the membrane, causing a further imbalance between the electrolytes. One of the advantages of using vanadium in two electrolytes is that the two electrolytes can be rebalanced after a certain number of cycles by different methods^[10-12]. This balancing can be effected in particular by mixing and electrolysis of the electrolytes, thus solving the problem of gradual imbalances in the system^[13].

electrolyte (positive or negative), where *C* is the concentration of redox species in mol • L⁻¹, *F* is Faraday's constant equal to 26.8 Ah • mol⁻¹, and *e* is the number of electrons exchanged in the redox half-reaction.

(4) Calculation of the volume capacity of Q⁺, Q⁻ and Q_{battery} batteries is the volume capacity of positive electrode, negative electrode electrolyte and Ah • L⁻¹ battery respectively.

(5) Using *E* to calculate the battery energy, the unit is Wh • L⁻¹, Q_{battery} is the volumetric capacity of the battery, the unit is Ah • L⁻¹, Δ*E* is the potential difference between the redox pair of the positive and negative electrolytes, the unit is V.

The performance of these systems has been well documented, showing excellent cycling stability with little performance loss (provided electrolyte

rebalancing is performed) and a lifetime of up to 20 years^[14]. However, the electrolytes for these systems are expensive, which is directly related to the scarcity of vanadium, which is limited and localized.

The main advantage of circulating flow batteries is that they are highly adaptable and can be flexibly designed and sized. The fact that electroactive materials are flowable allows the separation between capacity and power of storage devices, a characteristic of these systems. The power will depend on the flow of liquid and the configuration of the electrochemical cell, while the capacity will only be related to the stored electrolyte volume^[15]. This property is very interesting for bulk energy storage devices because it allows the easy design of very large capacity devices (by the simple fact of increasing the size of the electrolyte reservoir). Prof. Aziz discusses this difference in solid electrode battery systems^[16]. The study shows that for bulk storage applications, a battery with solid electrodes produces two orders of magnitude more power, too high for the intended application of a circulating flow battery that can be tuned as needed. If this excess power does not prevent the system from operating, it may represent unnecessary additional cost for the equipment. Another interesting application of these devices could be to power unserved areas by transporting charged electrolytes, which transport energy in liquid form in tanks.

The cost of circulating flow batteries is currently estimated to be between \$300 and \$800 kW · h⁻¹^[17]. To compete with lithium-ion batteries, the price of the new system should be at least comparable to that of ~\$100 kW · h⁻¹^[18]. More recently, it's often considered more relevant to talk about cost of normalization (LCOS, or levelized cost of storage). These costs better account for the singularity of each system. During the most recent call for projects (2020), Europe called for the development of energy storage systems at a cost of €0.05 kW · h⁻¹ per cycle in the next few years. It is worth noting that circulating flow batteries again become potentially attractive compared to Li-ion batteries when normalized costs are taken into account.

The cost of circulating flow batteries is related to many parameters that affect the economic profitability of these batteries. The limited cell voltage of 1.23 V associated with the use of aqueous electrolytes and the low solubility of redox species means that the energy

density is very low, 5 to 10 times lower than that of Li-ion batteries^[15,19].

To address these issues and improve the current performance of these devices, many research directions have been investigated and more details on some systems will be provided.

1.5 Overview of Improvement Fields of Circulating Flow Batteries

Given the sheer number of configurations that could be proposed as the flow battery of the future, it is logical that there is much room for improvement in these systems. Nevertheless, in summary, we can remember that there are mainly three components of a battery that can be studied, namely the electrolyte, the separator and the electrodes. **Figure 7** represents the different axes where improvements may be made and the possible impact of these improvements on device performance.

The electrolyte of a circulating flow battery consists of supporting salts, solvents, and electroactive substances. Solvents can be aqueous or organic, a distinction is made between so-called “aqueous” and “non-aqueous” systems. The electroactive species can be of organic origin in the case of redox molecules such as anthraquinone, for vanadium batteries inorganic sources using metal cations or even complexes such as potassium ferrocyanide or ferrocene Organometallic sources. Circulating flow batteries are thus characterized by the nature of the solvent (aqueous or non-aqueous), as well as the nature of the electroactive species used (organic, inorganic, or organometallic). Vocabulary is important here, especially in the case of battery research using organic molecules in aqueous solvents. Then we'll talk about organic aqueous batteries. Aqueous refers to solvents, organic molecules. AORFB for Aqueous Organic Redox Flow Battery will be asked in English literature. Much research has focused on developing highly soluble redox species with suitable redox potentials to generate large potential differences between positive and negative electrolytes. A second major concern of the current research concerns the good chemical and electrochemical stability of the species used. Recently, many studies (as well as Pr. Aziz's research group) have attempted to pinpoint the cause of capacity loss over time in organic aqueous systems^[2,20-22].

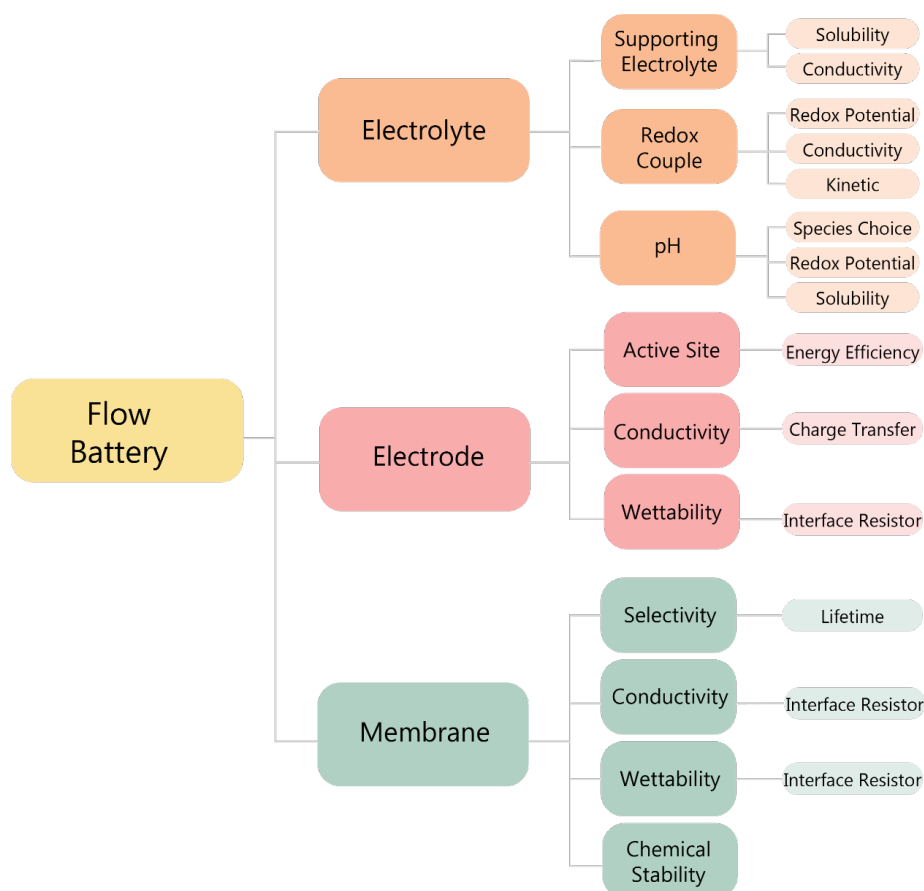


Figure 7. Diagram showing the impact of the different components of the flow battery on the electrochemical performance of the system

The role of the carbon electrode is to allow the transfer of charge from the molecule to the current collector during the redox reaction. The electrodes used in circulating flow batteries are mostly macroporous carbon electrodes, such as GDL (Gas Diffusion Layer) electrodes used in fuel cells. Electrodes are an important part of the battery, and their characteristics affect the power density of the system, as well as the

energy efficiency of the device. These electrodes must have mechanical strength to inhibit the compression required to seal the device and minimize contact resistance with the current collector. Different areas of improvement were investigated. The choice of carbon, its porosity and its morphology are important factors. Different types of carbonaceous materials have been used, such as sheets, felts and even carbon fiber fabrics (Figure 8)^[23].

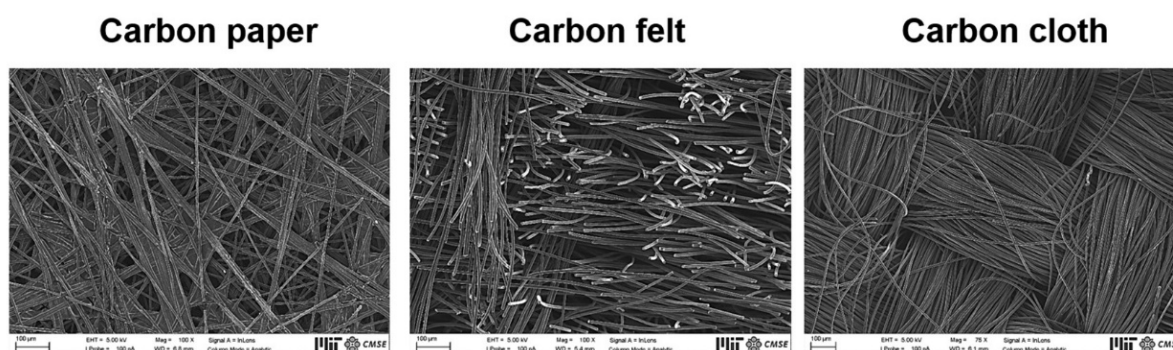


Figure 8. Snapshots obtained by scanning electron microscopy of different virgin carbonaceous substrates. Reproduction of the article by Forner-Cuenca *et al.*^[23]

Many electrode properties are directly related to battery performance. For flow batteries in aqueous media, the hydrophilicity of the electrodes is important to limit the interfacial resistance and improve the wettability of the electrodes by the electrolyte.

The separator is another key component of a circulating flow battery. It is critical to the proper functioning of the battery and accounts for a significant portion of the cost, up to 20% of the price of a vanadium cycle flow battery^[24]. As mentioned above, it acts to be permeable to electrolyte ions while impermeable to electroactive species, but also permeable to water molecules to limit the effects of electrolyte dilution or concentration^[24]. Its performance is directly related to the life of the battery and therefore the profitability of these devices. In addition to this need for selectivity, the membrane must also have good ionic conductivity to guarantee good energy efficiency and good specific power of the system. The membrane must also be chemically resistant to acidic environments, such as vanadium batteries, or alkaline to other systems, and strong oxidizing species that are typically present once the battery is charged in the positive electrolyte. To increase the versatility of available electroactive species, membranes must be developed for both cation exchange membranes (CEMs) and anion exchange membranes (AEMs). Developing these two types of membranes will allow greater flexibility in finding promising redox molecules.

The most widely used cationic and anionic membranes are Nafion and Selemion respectively, such as CEM and AEM. Currently, CEM seems to be more suitable for this application. In fact, AEM has low chemical stability, especially in alkaline media and oxidizing conditions. In addition, their ionic conductivity is low, partly due to the large size of the transported anions^[25].

2. Examples of Post-Vanadium Research Axes

The focus of this review is on vanadium redox flow batteries (VRFBs), given their maturity in the field of flow battery technology and their proven applicability in large-scale energy storage solutions. VRFBs are recognized as one of the most

reliable technologies for grid-scale energy storage, mainly due to their excellent cycle life, scalability, and safety features. Unlike other flow battery technologies, VRFBs utilize the same element-vanadium-in different oxidation states for both the positive and negative electrolytes. This approach not only prevents cross-contamination but also ensures long-term stability and durability of the battery system.

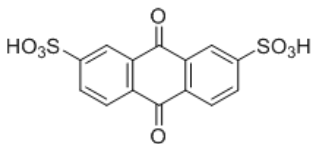
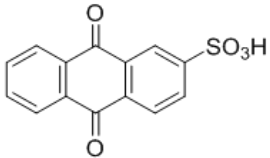
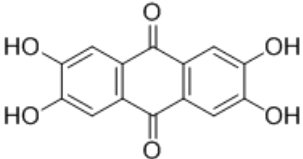
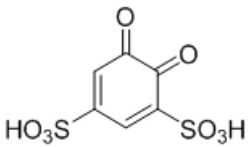
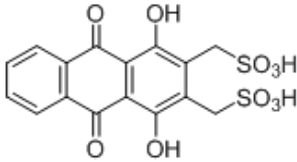
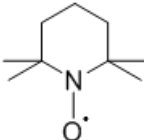

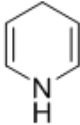
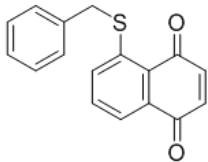
VRFBs have demonstrated significant advantages over other types of flow batteries, particularly in terms of operational stability and safety. The use of vanadium as the redox element on both sides of the battery reduces the risk of electrolyte degradation and cross-contamination, which are common issues in other flow battery chemistries. This makes VRFBs especially suitable for applications requiring consistent and reliable energy output, such as renewable energy integration and grid stabilization.

While VRFBs face challenges, such as relatively high costs due to the price of vanadium and moderate energy density compared to other flow battery technologies, they remain a preferred option for stationary energy storage due to their long cycle life, typically exceeding 10,000 cycles. The robustness and modularity of VRFB systems make them ideal for large-scale implementations where safety and reliability are of utmost importance.

2.1 A Range of Possibilities Brought About by Molecular Engineering

Organic aqueous flow batteries have experienced significant growth over the past decade. Using organic molecules that can be synthesized in large quantities from biomass is attractive from the standpoint of cost and the potentially low environmental footprint of production^[2]. Another major advantage of these systems is that new redox molecules can be synthesized or existing molecules modified by molecular engineering to adapt their properties to needs^[26]. Redox potential, solubility of molecules and their stability can be altered by functionalization of these. In the case of redox molecules, functionalization with electron-withdrawing groups near the redox center can increase the redox potential of the initial pair, while electron-donating groups will have the opposite effect (**Table 1**).

Table 1. Potential applications of multifunctional redox molecules in aqueous flow batteries

Molecule	Redox potential (V)	Electrolyte	Reference
	0.22	1 M H ₂ SO ₄	[27]
	0.15	1 M H ₂ SO ₄	[28]
	-0.8	1 M KOH	[29]
	0.87	1 M H ₂ SO ₄	[28]
	0.02	1 M H ₂ SO ₄	[30]
	0.8	3 M KCl	[31]
	0.4	0.1 M NaClO ₄	[32]
	-2.6	0.25 M Ce ₂ CO ₃	[33]
	-0.4	0.15 M NaOAc	[34]

TEMPO is a stable organic free radical molecule that has attracted much attention in flow batteries due to its good electrochemical stability, high redox potential and reversible redox reaction. TEMPO is usually used in neutral or alkaline media and exhibits a high redox potential. Through functionalization, such as the

introduction of hydrophilic groups, the solubility and electrochemical performance of TEMPO are further enhanced, making it a strong competitor for aqueous organic flow batteries. Ferrocene and its derivatives are widely used in electrochemical systems due to their high redox potential and electrochemical reversibility.

Functionalized ferrocene, such as the addition of amino or carboxyl groups, greatly increases its solubility in aqueous solution. This modification makes ferrocene have potential application value in aqueous flow batteries, especially in acidic and neutral media.

1,4-Dihydropyridine is a reversible organic molecule with a low redox potential and good water solubility. It is stable in acidic or neutral media, and its redox properties can be changed by structural adjustment. In flow batteries, it has the advantages of low cost and environmental friendliness. Quinoneimines are another class of potential redox molecules that can achieve redox reactions in a wide potential range by changing the position and type of substituents. They have good stability in both acidic and alkaline media and are suitable as alternative redox molecules for aqueous flow batteries.

To increase the solubility of organic molecules in aqueous electrolytes, certain hydrophilic groups such as ammonium groups^[35] have been used to functionalize redox molecules. In particular, the functionalization of ferrocene made it possible to achieve a solubility of 4 M in pure water, whereas unmodified ferrocene is practically insoluble in water. The use of ammonium groups is compatible with the use of AEM. In the case of CEM, functionalization is typically performed using sulfonate^[31] or carboxylic acid^[36] groups. For example, the functionalization of anthraquinones with carboxylic acid groups^[36] resulted in a solubility of 1.1 M in alkaline media, whereas unfunctionalized anthraquinones were practically insoluble in the same media. A consequent increase in solubility can thus be obtained. Organic molecules provide chemists with an important field of action and make it possible to imagine more efficient and cheaper solutions. The stability of these molecules is one of the main issues in developing circulatory systems using organic molecules as redox species^[22]. A large part of the research on the development of organic molecules for use in aqueous circulating flow batteries is the phenomenon of molecular degradation during their electrochemical cycling. For example, study these mechanisms by NMR or UV spectroscopy to understand the degradation reactions involved and to find ways to functionalize the molecules to improve their stability^[37]. Prof. Aziz's group studied the degradation of quinone and anthraquinone derivatives in aqueous

media for application in circulating flow batteries. The functionalization of these derivatives aims to make them more stable^[38] and to enable their use at neutral pH, for example a phosphonate-functionalized quinone redox flow battery, it has a very high-capacity retention rate at near-neutral pH condition^[39].

2.2 Hybrid Systems to Increase Energy Density

The solubility of molecules, although it can be improved by molecular engineering, is limited and leads to low energy density. To achieve higher energy densities, the use of metal electrodes in one of the battery compartments has been explored. The coupling of solid electrodes with large specific volume compartments can achieve remarkable energy densities. However, the use of aqueous electrolytes greatly limits the use of certain metals, such as lithium, sodium, or aluminum, in batteries. Zinc appears in this configuration as the material of choice. Zinc plating is well known in the industry for different applications including anti-corrosion properties. Zinc can be used in both acidic and alkaline media, and its use in mixed systems seems promising. A number of systems have been studied, mainly using zinc in acidic media, with $Zn^{2+}/Zn(s)$ coupling in the negative compartment and Br_2/Br^- coupling in the positive compartment. Due to the very low cost of the components, the zinc-bromine system is probably the most studied hybrid system^[40-42]. Due to the high solubility of potassium iodide, systems using iodine as the catholyte have been developed in acidic and alkaline media and have shown high energy densities^[19,43].

A certain number of industrial prototypes already exist, and research on these systems is important. One problem with the use of metal electrodes is the appearance of dendrites during battery cycling, which is caused by the formation of concentration gradients during charging, which cause uneven deposition of metals during battery charging. Convection due to flux in cells with cyclic flux can limit the formation of concentration gradients that inhibit dendritic growth due to more uniform deposition of zinc. This phenomenon can prolong the lifetime of zinc systems^[44] compared to static applications. Despite more uniform deposition, the control of zinc electrodeposition remains a major issue associated with the use of metallic zinc as an anode material.

2.3 Development of Systems That Do Not Require the Use of Ion Exchange Membranes

The separator in a circulating flow battery is one of the most expensive parts of the device. To reduce the cost of circulating flow batteries, systems have been developed that can dispense with the use of ion-exchange membranes. Significant cost reductions can be achieved by using simple porous separators, such as those used in lithium-ion batteries or dialysis membranes.

Different approaches have been considered to overcome the use of ion exchange membranes and even develop systems that do not require the use of membranes.

The first axis is the development of electroactive species large enough to be blocked by steric membranes. The use of oligomers or polymers significantly facilitates the use of dialysis membranes^[45]. In Prof. Schubert's research, polymers are synthesized from redox molecules. The polymer consists of a redox group and a hydrophilic ammonium group to enhance its solubility. The degree of polymerization was studied so that crossover through the dialysis membrane could be limited while simultaneously limiting the viscosity of the electrolyte formulated therefrom. The developed system functions normally, and the author demonstrates that the system has certain stability. The problem with this setup is the low energy density developed at $15 \text{ Wh} \cdot \text{L}^{-1}$ due to the low solubility of the redox polymer.

A second, more exploratory approach uses immiscible electrolytes and uses ionic liquids^[46,47]. This concept is still poorly studied in the literature, existing research is fundamental and implements static configuration far away from the application. The idea here is to use a common cation or anion between the two electrolytes, which will achieve charge balance during the redox reaction. Redox species must be insoluble in the opposite electrolyte to limit self-discharge through diffusion of charged species between them and spontaneous electrochemical reactions. The use of immiscible electrolytes can completely eliminate the use of membranes. An important issue with this system is self-discharge at the interface of the two electrolytes, which has been observed under static conditions and can be even more problematic under flow conditions that may favor exchange at the interface.

A third approach is to use micron-sized solid

electroactive particles dispersed in a solution. This structure that forms a suspension between solid electroactive particles and electrolyte is called a semi-solid structure. This type of system is described in detail in the next paragraph. Due to the large particle size, this configuration allows the use of steric membranes.

2.4 Comparisons with Other Types of Flow Batteries

To provide a comprehensive understanding of VRFBs and their position in the flow battery landscape, this review also includes comparisons with other types of flow batteries, such as zinc-bromine, iron-chromium, and organic flow batteries. These comparisons highlight the unique strengths of VRFBs while acknowledging the potential benefits and limitations of alternative flow battery technologies. By understanding these distinctions, it becomes clear why VRFBs are often chosen for long-term, grid-scale energy storage applications.

Vanadium redox flow batteries are the most mature type of flow batteries and have been extensively studied and commercialized^[48]. VRFBs have moderate energy density (25-50 Wh/L) and excellent cycle life, typically exceeding 10,000 cycles. The use of different oxidation states of vanadium on the positive and negative electrodes prevents cross-contamination, a common problem in other flow battery types, thereby achieving long-term stability. VRFBs are also known for their safety and scalability, which makes them ideal for large-scale stationary energy storage, such as grid balancing and renewable energy integration^[15].

Zinc-bromine flow batteries Zinc-bromine flow batteries have higher energy density (up to 70 Wh/L) compared to VRFBs, which makes them more suitable for applications that require higher energy storage in limited space^[49]. These batteries typically have a cycle life of 2,000-3,000 cycles. A key challenge of zinc-bromine batteries is the formation of zinc dendrites during charging, which can cause short circuits and shorten cycle life. In addition, bromine is highly reactive and toxic, so it requires careful handling and safety measures during operation^[50].

Iron-chromium flow batteries are one of the earliest types of flow batteries developed, and they use iron and chromium as the active redox species^[51]. These batteries have a relatively low energy density (15-

30 Wh/L) and a moderate cycle life (3,000-5,000 cycles). However, the use of chromium presents safety challenges as it is toxic and needs to be carefully managed to prevent environmental contamination. In addition, the electrochemical performance of the iron-chromium system is less efficient than other flow batteries, resulting in lower energy density^[52].

Similar to VRFBs, all-vanadium flow batteries use vanadium as the redox active element on both sides of the cell^[53]. The main advantage of this configuration is that the energy output is stable and cross-contamination is prevented, resulting in a longer cycle life of more than 10,000 cycles. These batteries have a moderate energy density of 25-50 Wh/L, making them well suited for stationary energy storage applications. However, like VRFBs, the high cost of vanadium remains a significant limitation, which affects their economic viability, especially for large-scale projects^[54].

Organic flow batteries use organic molecules such as quinones or anthraquinones as the redox species^[55]. These batteries are attractive because of their potential for low cost and sustainable materials, as organic

molecules can often be extracted from biomass. Organic flow batteries have a modest energy density (20-50 Wh/L) and a cycle life of between 1,000-2,000 cycles, depending on the stability of the organic molecules used. One of the main challenges facing organic flow batteries is that the organic molecules degrade over time, which limits their long-term stability and increases maintenance costs^[56].

Polysulfide bromide flow batteries (PSBs) use a combination of polysulfides and bromine as redox-active materials^[57]. These batteries have an energy density in the range of 40-60 Wh/L and a modest cycle life of around 1,500-2,500 cycles. PSBs are known for their relatively simple chemistry and modest cost, making them potential candidates for certain medium-scale energy storage applications. However, they face significant challenges related to membrane fouling and the high reactivity of bromine, which complicates their operation and reduces overall safety. Membrane fouling causes efficiency to decrease over time, and the use of bromine requires strict safety measures to prevent leaks and exposure^[58].

Table 2. Comparison of the performance of VRFBs and other types of flow batteries

Type	Energy Density (Wh/L)	Cycle Life (cycles)	Advantages	Disadvantages	Reference
Vanadium Redox (VRFB)	25-50	> 10,000	Long cycle life, safe chemistry	High cost of vanadium	[15]
Zinc-Bromine	50-70	2,000-3,000	High energy density, cost-effective	Zinc dendrites, toxic bromine	[50]
Iron-Chromium	15-30	3,000-5,000	Low cost	Low energy density, toxicity issues	[52]
All-Vanadium (AVFB)	25-50	> 10,000	Stable operation, long cycle life	High cost of vanadium	[54]
Organic	20-50	1,000-2,000	Sustainable materials, low cost	Limited stability of organics	[56]
Polysulfide Bromide (PSB)	40-60	1,500-2,500	Moderate energy density	Membrane fouling, bromine reactivity	[58]

This comparison highlights that vanadium flow batteries are one of the most mature technologies, with excellent cycle life and safety. But other types of flow batteries, such as zinc-bromine and organic flow batteries, also have potential advantages in terms of energy density and cost. However, these alternatives also face significant challenges, such as stability issues, toxicity and processing complexity.

3. Future Directions of Circulating Flow Batteries

The future development of circulating flow batteries

will largely depend on advancements in the core components: electrolytes, membranes, and electrodes. To fully unlock the potential of these batteries for large-scale renewable energy storage, it is necessary to overcome current challenges and leverage new technologies to enhance performance and reduce costs.

One of the most promising directions for future research is in electrolyte optimization. Advances in molecular engineering can help to design new redox-active species that offer higher solubility, stability, and energy density. Organic aqueous electrolytes, which are cost-effective and can be sourced sustainably, are

a major area of interest^[2]. The functionalization of redox molecules with specific groups, such as electron-donating or electron-withdrawing groups, can help tune redox potential and improve the solubility of these species, thereby increasing the overall energy density of the battery. Furthermore, hybrid systems incorporating solid metal electrodes in combination with flowable electrolytes can potentially enhance energy density beyond the current limitations^[26].

Membranes play a critical role in the performance of flow batteries by controlling ion transport and minimizing crossover between the positive and negative electrolytes^[24]. The development of advanced membrane materials that offer high ionic conductivity, low permeability to electroactive species, and chemical stability in both acidic and alkaline environments is essential. New ion-selective membranes with enhanced resistance to fouling and degradation will help improve the longevity and efficiency of flow batteries. A significant area of research is reducing the cost of membranes while maintaining performance, which could involve innovations such as nanocomposite materials or porous separators that bypass the need for expensive ion-exchange materials^[25].

In Battery Components, the carbon-based electrodes used in flow batteries need improvements to optimize power density and overall energy efficiency^[23]. The porosity, surface area, and hydrophilicity of carbon materials significantly affect battery performance. Research into novel carbon structures, such as carbon nanotubes and graphene-based materials, aims to enhance reaction kinetics, improve current collector integration, and minimize resistive losses. Developing cost-effective and scalable electrode manufacturing processes will also be a key trend^[16].

The separator must balance selectivity and conductivity to maintain system efficiency while preventing the crossover of redox species. This crossover, known as “crossover loss,” leads to reduced battery efficiency and lifetime. Future developments will likely focus on creating membranes that achieve better ion selectivity while maintaining high conductivity. Additionally, exploring the use of non-ion-selective porous separators as a lower-cost alternative could be an important trend, especially if paired with electrolyte systems that minimize the

impact of crossover.

One of the main advantages of circulating flow batteries is their scalability. However, practical implementation at a large scale presents unique challenges. Future research should focus on optimizing the entire system, including the design of flow configurations and the integration of energy management systems that allow better responsiveness to varying energy demands. Advanced modeling and AI-based optimization techniques could play a major role in improving system performance and economic feasibility.

The future of circulating flow batteries depends on addressing the challenges associated with their core components. Innovations in electrolyte and membrane technologies, combined with advancements in electrode design and system integration, will determine the feasibility of these batteries as a sustainable solution for large-scale energy storage. As research progresses, the focus will continue to be on improving efficiency, reducing costs, and ensuring scalability, ultimately supporting the widespread adoption of renewable energy systems.

4. Conclusion

Vanadium redox flow batteries (VRFBs) have established themselves as a leading solution for large-scale energy storage due to their scalability, safety, and long cycle life. This work has highlighted the distinct advantages of VRFBs, including their ability to prevent cross-contamination by utilizing vanadium in both electrolytes, which enhances their stability and reliability. Although VRFBs face challenges related to high costs and moderate energy density, their proven robustness makes them highly suitable for stationary energy storage applications, particularly in renewable energy integration and grid stabilization.

Through a detailed comparison with other flow battery technologies, such as zinc-bromine, iron-chromium, and organic flow batteries, it is evident that VRFBs offer a unique balance of safety, reliability, and operational efficiency. The analysis underscores the strengths of VRFBs, especially in applications where consistency, safety, and durability are critical. Moving forward, ongoing research and development focused on reducing costs and improving energy density

will be crucial in further enhancing the viability of VRFBs as a cornerstone of the future energy storage landscape.

Conflict of Interest

The authors declare no conflict of interest.

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