

VANADIUM REDOX FLOW BATTERIES FOR LONG-DURATION ENERGY STORAGE: RECENT ADVANCES IN ELECTROLYTE STABILITY, POLYMER MEMBRANE SELECTIVITY, ELECTRODE ENGINEERING AND CAPACITY-FADE MITIGATION

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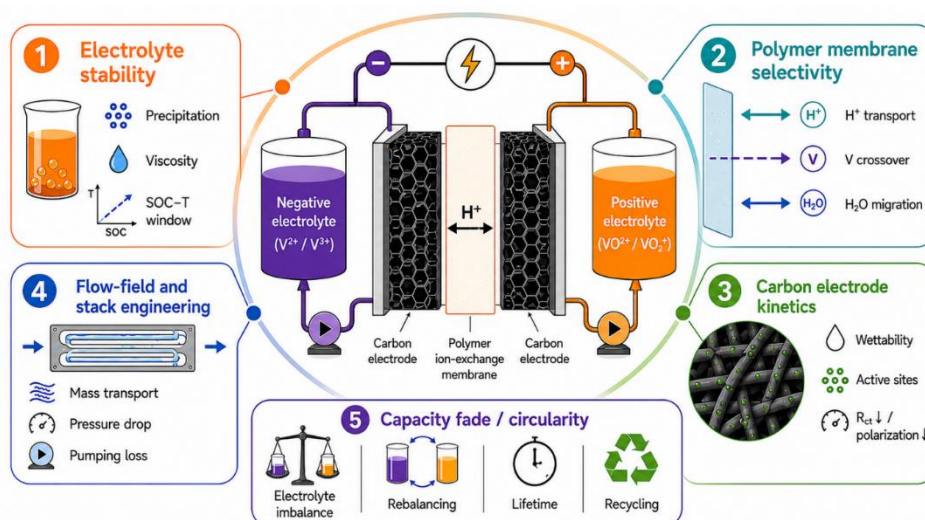
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ABSTRACT

Vanadium redox flow batteries (VRFBs) are promising systems for stationary long-duration energy storage because they use aqueous non-flammable electrolytes, allow independent scaling of energy and power, and offer long cycle life. Their wider deployment, however, remains limited by coupled materials and engineering challenges, including electrolyte instability, V(V) precipitation, vanadium crossover, water migration, sluggish carbon-electrode kinetics, hydraulic losses, capacity decay and vanadium-related cost. This review discusses recent progress in VRFB development with emphasis on the interactions between electrolyte chemistry, polymer membrane selectivity, electrode kinetics, stack design and long-term capacity retention. Particular attention is given to polymeric and polymer-composite ion-exchange membranes, including PFSA/Nafion-type membranes, hydrocarbon cation-exchange membranes, SPEEK-based composites, PBI/PBMI-type membranes, anion-exchange membranes and porous or nanofiltration membranes. Their conductivity-selectivity-stability trade-offs are considered in relation to vanadium crossover, water transport and capacity fade. The review also highlights key performance compromises, such as energy density versus electrolyte stability, membrane conductivity versus crossover suppression, electrode activity versus durability, and mass transport versus pumping loss. Finally, remaining challenges are outlined, including stable high-concentration electrolytes, low-cost selective polymer membranes, durable scalable electrodes, standardized capacity-decay diagnostics, stack-level validation and circular vanadium-electrolyte management.

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Graphical abstract



Introduction

The rapid expansion of solar and wind power increases the demand for efficient energy storage because these renewable sources are inherently intermittent and weather-dependent. Solar generation varies with irradiation, cloud cover and day-night cycles, whereas wind generation depends on wind speed, site conditions and seasonal variability. As a result, renewable electricity generation often does not coincide with electricity demand. Long-duration energy storage is therefore considered a key option for improving renewable integration, reducing curtailment and supporting reliable low-carbon power systems [1],[2].

Energy storage is becoming a central component of modern power systems because it can smooth renewable power fluctuations, shift electricity from low-demand periods to peak-demand periods and support grid stability [2],[3]. Lithium-ion batteries are widely used for short-duration storage because they provide high energy density and high round-trip efficiency. However, in large-scale stationary battery energy storage systems, thermal runaway propagation, gas release and fire-safety management remain important engineering concerns [4]. Therefore, safer and more scalable long-duration storage technologies are needed for stationary and grid-level applications.

Redox flow batteries separate energy storage from power conversion: electroactive species are held in external electrolyte tanks and pumped through an electrochemical stack, where redox reactions occur at the electrode surfaces. Electrolyte volume and concentration primarily determine energy capacity, whereas stack size, electrode area and cell design govern power output. This architecture allows energy and power ratings to be adjusted more independently than in many conventional battery systems [2],[3],[5].

Among redox flow batteries, the all-vanadium redox flow battery, commonly known as the vanadium redox flow battery (VRFB), is one of the most mature systems. It is also one of the most studied redox flow battery technologies. The all-vanadium redox flow cell concept was developed by Skyllas-Kazacos and co-workers in the 1980s [6],[7]. Its key feature is the use of vanadium species in both half-cells. This reduces irreversible cross-contamination. If vanadium ions cross the membrane, the electrolyte can still be chemically rebalanced because both half-cells contain the same element in different oxidation states [5].

A VRFB operates through four vanadium oxidation states. The negative half-cell uses the V²⁺/V³⁺ redox couple. The positive half-cell uses the VO²⁺/VO₂⁺ redox couple. The electrolyte is usually based on vanadium salts dissolved in sulfuric acid. During charge and discharge, electrons move through the external circuit. Ions move through the membrane to maintain electroneutrality.

The main components are electrolyte tanks, pumps, flow channels, carbon-based electrodes, an ion-exchange membrane and a cell stack [5],[8],[9].

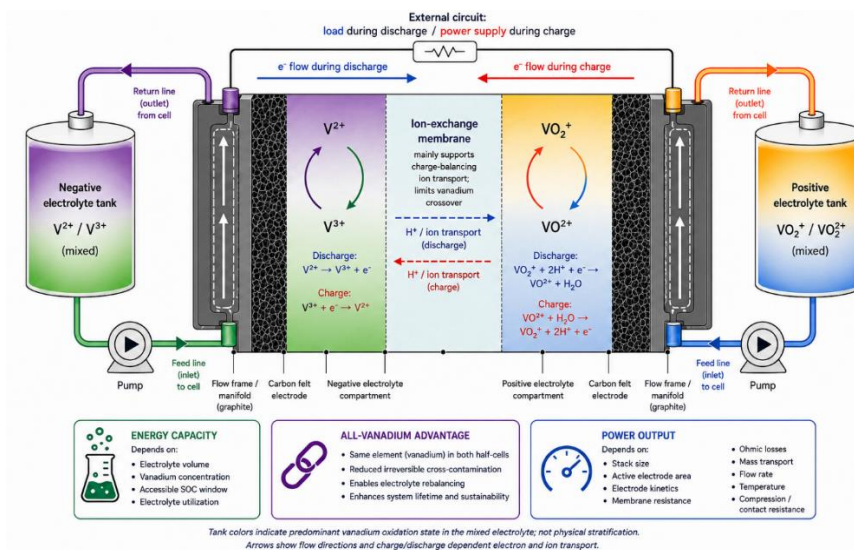


Figure 1. Operating principle and main components of a vanadium redox flow battery

The schematic shows the negative and positive electrolyte tanks, pumps, flow channels, porous carbon electrodes, polymer ion-exchange membrane, and charge/discharge-dependent electron and ion transport. The architecture enables separate scaling of electrolyte-based energy capacity and stack-based power output.

VRFBs have several advantages for grid-scale and stationary storage. First, they use aqueous electrolytes. This reduces flammability risk compared with battery systems based on organic electrolytes [5],[8]. Second, energy and power can be scaled separately. This gives design flexibility for multi-hour storage [2],[5]. Third, VRFBs can provide long service life because the electroactive species are stored in liquid electrolytes rather than in solid insertion-type electrodes [5],[8]. Reported VRFB durability can exceed 12,000 cycles, and recent reviews describe cycle life that can surpass 20,000 cycles under suitable operating conditions [10],[11]. Fourth, capacity loss can be partly recovered by electrolyte rebalancing or remixing when imbalance is caused by crossover, side reactions or faradaic imbalance [12],[13].

However, VRFB technology still faces several scientific and engineering challenges. The first challenge is electrolyte stability. Vanadium ions exist in different oxidation states. Their stability depends on acid concentration, temperature, state of charge and total vanadium concentration. At high vanadium concentration or elevated temperature, precipitation can occur. This is especially critical for the positive electrolyte containing V(V) species. Precipitation limits energy density and complicates long-term operation [14],[15].

Membrane selectivity presents a coupled transport challenge. Ionic conduction must be sufficiently fast to limit resistance, while vanadium crossover and uncontrolled water transfer must remain low enough to suppress self-discharge and electrolyte imbalance. Membrane development consequently requires a balance among conductivity, selectivity, chemical stability and cost, assessed through capacity retention and energy efficiency under relevant operating conditions [16],[17].

The third challenge is electrode reaction kinetics. Carbon felt and graphite felt are commonly used because they are conductive, porous and chemically stable. However, their intrinsic catalytic activity toward vanadium redox reactions is often limited. This causes polarization losses and reduces voltage efficiency. Electrode modification is therefore a major research direction. Common strategies include thermal treatment, acid treatment, oxygen functionalization, heteroatom doping, metal oxide decoration, graphene-based modification, electrografting and biomass-derived carbon coating [18],[19].

The fourth challenge is flow-field and stack-level performance. A VRFB is both an electrochemical system and a hydraulic system. Electrolyte flow rate, pressure drop, pumping loss, flow-field geometry, electrode compression and stack uniformity affect cell performance. A low flow rate can cause mass-transport limitation. An excessive flow rate can increase pumping energy consumption. Therefore, stack design must balance electrochemical efficiency and hydraulic energy loss [20],[21].

The fifth challenge is capacity decay. Capacity decay can result from vanadium crossover, side reactions, water transfer, electrolyte volume imbalance, state-of-charge imbalance and changes in active species concentration. This problem is not controlled by one component alone. It reflects the combined behavior of electrolyte, membrane, electrode, operating voltage window and system management. Accurate state-of-charge monitoring, electrolyte rebalancing and optimized remixing procedures are therefore essential for stable long-term VRFB operation [11],[13].

Table 1

Comparative characteristics of major battery technologies for stationary energy storage.

Battery technology	Safety profile	Cycle life / durability	Scalability for stationary storage	Energy density	Main limitations and suitable applications
Lithium-ion batteries	Organic electrolyte; thermal-runaway risk [4]	~3,000-8,000 cycles; ~8-15 years [22],[23]	High; modular, typically 1-4 h storage [22]	~120-260 Wh kg ⁻¹ [22], [23]	Fire safety, ageing, material cost; short-/medium-duration BESS [4], [22]
Lead-acid batteries	Aqueous acid; H ₂ evolution and acid leakage risk [22]	~300-1,500 cycles [22], [23]	Mature, low-cost; limited for deep cycling [22]	~30-50 Wh kg ⁻¹ [22], [23]	Sulfation, heavy weight, short cycle life; UPS/backup power [22], [23]
Sodium-ion batteries	Chemistry-dependent; generally safer resource profile [24]	~2,000-6,000 cycles [24]	Emerging; promising for cost-sensitive storage [24]	~90-160 Wh kg ⁻¹ [24]	Lower maturity and energy density; stationary storage [24]
Vanadium redox flow batteries	Aqueous, non-flammable electrolyte [22], [23]	~12,000-20,000+ cycles; ~15-25 years [25],[11]	Excellent; energy and power scaled separately [22], [23]	~20-35 Wh L ⁻¹ electrolyte [22], [23]	Low energy density, vanadium cost, crossover, pumping losses; long-duration grid storage [11]

The table compares lithium-ion, lead-acid, sodium-ion and vanadium redox flow batteries in terms of safety, durability, scalability, energy density and application suitability.

Cost is another important limitation. Vanadium electrolyte can represent a large fraction of total system cost. Stack materials, membranes, pumps and balance-of-plant components also contribute to capital cost. Long-term economic performance depends on more than initial electrochemical efficiency. It also depends on electrolyte utilization, capacity fade, rebalancing frequency, service lifetime, recycling and circular use of vanadium resources [26],[27].

Recent VRFB research has developed along several directions. Electrolyte studies focus on high-concentration formulations, thermal stability, additives, impurities and V(V) precipitation control [14],[15]. Membrane studies focus on selectivity, proton transport, vanadium crossover suppression, water migration and low-cost alternatives to perfluorinated membranes [16],[17]. Electrode studies focus on carbon felt and graphite felt activation, oxygen functional groups, heteroatom doping, metal oxide catalysts, graphene-based modification and biomass-derived carbons [18],[19]. Stack studies focus on flow-field optimization, pressure drop reduction, pumping loss control and uniform electrolyte distribution [20],[28]. Capacity decay studies focus on

crossover, side reactions, state-of-charge estimation, electrolyte imbalance and rebalancing strategies [11],[13].

Component improvements can create losses elsewhere in the system. Increasing vanadium concentration may raise energy density while increasing viscosity and precipitation risk; a highly conductive membrane may also accelerate crossover, and a higher flow rate can improve mass transport at the expense of pumping energy. Even an active electrode cannot compensate for severe electrolyte imbalance. These interactions make coordinated optimization of electrolyte chemistry, membrane transport, electrode kinetics and stack operation essential [5],[21].

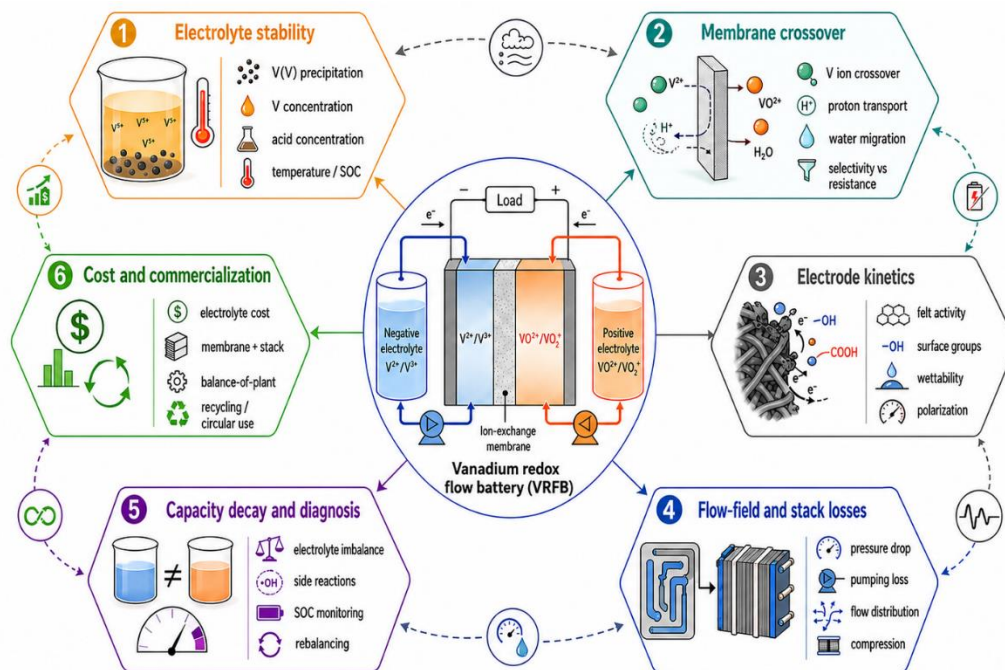


Figure 2. Interconnected scientific and engineering challenges in VRFB development

The framework summarizes the coupled electrolyte-polymer membrane-electrode-stack-operation interactions that control practical VRFB performance, durability and commercialization. It highlights how electrolyte instability, membrane crossover, electrode kinetics, flow-field losses, capacity decay and cost are mutually connected rather than independent limitations.

Unlike many VRFB reviews that discuss electrolytes, membranes, electrodes or stack design as separate research areas, this review argues that the practical limitations of VRFBs originate from their coupled component-system interactions. Electrolyte instability is not only an electrolyte problem because precipitation, viscosity and impurity effects influence membrane transport, flow distribution and capacity retention. Membrane crossover is not only a separator problem because it changes electrolyte composition, state of charge and rebalancing requirements. Electrode activation is not only a kinetic problem because surface modification can also affect wettability, pressure drop, durability and side reactions. Therefore, the main novelty of this review is its integrated perspective linking electrolyte stability, membrane selectivity, carbon-electrode kinetics, flow-field engineering, capacity-fade diagnosis and commercialization barriers. This system-level viewpoint provides a more practical framework for identifying which material advances can realistically improve long-duration VRFB performance.

Although VRFBs are often discussed as electrochemical energy-storage systems, their practical performance is strongly governed by polymer materials, particularly ion-exchange membranes. Polymer membranes determine proton or charge-balancing ion transport, vanadium-species crossover, water migration, swelling, oxidative durability, area resistance and ultimately

capacity retention. Therefore, polymer chemistry is not a secondary materials issue in VRFBs; it is one of the central factors connecting electrolyte composition, cell efficiency, capacity fade and system lifetime. In this review, polymer-based membranes are treated as a key functional component within the broader VRFB system, linking molecular membrane structure to transport selectivity, degradation resistance and long-duration operation.

The aim of this review is to provide a structured analysis of VRFB technology for long-duration stationary energy storage. The review first introduces the fundamental chemistry and cell architecture of VRFBs. It then discusses electrolyte chemistry and stability, membrane selectivity and crossover, carbon-based electrodes and reaction kinetics, flow-field and stack design, capacity decay and performance diagnosis, and cost and commercialization perspectives. The central thesis of this review is that practical VRFB development requires integrated optimization of electrolyte-membrane-electrode-stack interactions rather than isolated improvement of individual components. This approach is essential for improving durability, efficiency, scalability and economic viability of VRFB systems.

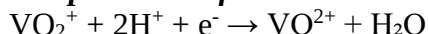
Fundamentals of VRFB chemistry and cell architecture

The vanadium redox flow battery is based on reversible redox reactions of vanadium ions in aqueous acidic electrolyte. Its main feature is the use of vanadium species in both the negative and positive half-cells. This design reduces permanent cross-contamination because the same element is present on both sides of the cell [6],[7],[3]. The negative electrolyte contains the V^{2+}/V^{3+} redox couple. The positive electrolyte contains the VO^{2+}/VO_2^+ redox couple. These four oxidation states make the all-vanadium system possible [29].

In a VRFB, liquid electrolytes store the active species in external reservoirs and pumps circulate them through the porous electrodes, where electrochemical conversion occurs [5],[8]. Electrolyte volume and vanadium concentration primarily set energy capacity; stack area, cell count, electrode structure, membrane resistance and operating conditions determine the available power [9]. Separating these functions provides flexibility in storage duration while making the hydraulic and electrochemical subsystems interdependent.

A VRFB operates through four vanadium oxidation states. The negative half-cell uses the V^{2+}/V^{3+} redox couple. The positive half-cell uses the VO^{2+}/VO_2^+ redox couple, where VO^{2+} corresponds to V(IV) vanadyl species and VO_2^+ corresponds to V(V) dioxovanadium species. During discharge, V^{2+} is oxidized to V^{3+} at the negative electrode, while VO_2^+ is reduced to VO^{2+} at the positive electrode [5],[29].

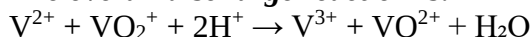
The positive half-cell reaction during discharge is:



The negative half-cell reaction during discharge is:



The overall discharge reaction is:



These notations should be kept consistent throughout the manuscript because VO^{2+} and VO_2^+ represent different vanadium oxidation states and different electrolyte-stability behavior [5],[29].

The acidic supporting electrolyte is usually sulfuric acid. It provides ionic conductivity and stabilizes dissolved vanadium species. It also supplies protons for the positive half-cell reaction. However, the electrolyte composition must be controlled carefully. Vanadium concentration, acid concentration, temperature and state of charge affect solubility and stability. These parameters become especially important at high energy density and long-term operation [14],[15].

The cell stack is the central electrochemical unit of a VRFB. It consists of repeated cells connected electrically and hydraulically. Each cell contains a negative electrode, a positive electrode, a membrane or separator, flow channels and current collectors. The stack determines the

power rating of the system. Increasing the number of cells or the active electrode area can increase power. Increasing tank volume mainly increases energy capacity [8],[9].

The electrolyte tanks store the negative and positive electrolytes separately. Tank size is one of the main factors controlling system energy capacity. Larger tanks can store more electrolyte. Higher vanadium concentration can also increase energy capacity. However, high concentration can increase viscosity and precipitation risk. Therefore, energy density cannot be increased only by adding more vanadium. Electrolyte stability must also be maintained [14],[15].

Pumps circulate the electrolytes from the tanks to the stack and back to the tanks. Flow rate affects reactant supply, mass transport and concentration gradients inside the porous electrodes. A low flow rate can cause reactant depletion and concentration polarization. A very high flow rate can reduce concentration losses but increases pumping energy consumption. Thus, flow management is a key part of VRFB operation [20],[28].

Carbon-based porous electrodes are commonly used in VRFBs. Carbon felt and graphite felt are the most common electrode materials. They provide electrical conductivity, chemical stability and a large surface area for redox reactions. Their porous structure allows electrolyte penetration and contact between vanadium ions and active electrode sites [5],[18]. However, untreated carbon felt may show limited catalytic activity. Its surface chemistry and wettability strongly affect reaction kinetics. For this reason, electrode activation and surface modification are widely studied [19],[30].

The membrane separates the negative and positive electrolytes. It must prevent direct mixing of the two half-cell solutions. It must also allow ionic transport to complete the internal circuit. In most VRFB systems, proton exchange membranes or ion-exchange membranes are used. The membrane affects ohmic resistance, vanadium crossover, water migration, coulombic efficiency and energy efficiency [31],[16]. A highly conductive membrane can reduce internal resistance. However, high ionic conductivity alone is not sufficient. If the membrane allows strong vanadium crossover, self-discharge and capacity decay can increase [11],[16].

A complete VRFB system also includes balance-of-plant components. These include pumps, pipes, valves, sensors, electrolyte reservoirs, power electronics and control units. These components are essential for stable operation. They control electrolyte circulation, temperature, state of charge and operating safety. In large systems, balance-of-plant design affects efficiency, cost and reliability [26],[32].

The performance of a VRFB is usually evaluated by coulombic efficiency, voltage efficiency and energy efficiency. Coulombic efficiency reflects charge losses, mainly related to crossover and side reactions. Voltage efficiency reflects polarization losses, including activation, ohmic and mass-transport losses. Energy efficiency is the product of coulombic and voltage efficiencies. Long-term performance also requires capacity retention and stable operation over repeated cycles [10],[11].

Capacity decay is closely linked to cell architecture and chemistry. Vanadium crossover through the membrane can change the composition of both electrolytes. Water migration can change electrolyte volume and concentration. Side reactions can change the state of charge. Flow maldistribution can increase local concentration gradients. Electrode degradation can reduce active surface area. These factors show that VRFB operation is governed by coupled chemical, electrochemical and engineering processes [11],[21].

This fundamental architecture explains the main advantage of VRFBs. The system can be scaled for long-duration storage by increasing electrolyte volume. It can be scaled for higher power by increasing stack size. This separation gives VRFBs a clear advantage for stationary energy storage. At the same time, it creates a complex optimization problem. Electrolyte stability, membrane selectivity, electrode kinetics, flow distribution, stack resistance, pumping loss and system cost must be considered together [5],[26].

The main operating parameters and performance indicators used to describe VRFB systems are summarized in Table 2. These parameters show that VRFB performance is governed not only

by redox chemistry, but also by electrolyte composition, membrane transport, electrode kinetics, stack design and system-level operating conditions.

Table 2

Typical operating parameters and performance indicators of VRFB systems

Parameter	Typical VRFB range / value	Why it matters	Main limitation	Suggested references
Standard cell voltage	ca. 1.26 V	Defines theoretical voltage window	Practical voltage depends on SOC, concentration and polarization	[5],[29]
Practical energy density	ca. 20-35 Wh L ⁻¹ electrolyte-level; often about 20-25 Wh kg ⁻¹ depending on system basis	Shows why VRFBs are suitable for stationary rather than mobile storage	Lower than Li-ion batteries	[8],[32]
Vanadium concentration	commonly around 1.5-2.0 M in conventional systems	Controls capacity and electrolyte utilization	High concentration increases viscosity and precipitation risk	[14],[15]
Operating current density	commonly 80-200 mA cm ⁻² in many lab/stack studies	Determines power performance	High current density increases polarization and mass-transport demand	[21],[28]
Coulombic efficiency	often high, commonly >90% under optimized conditions	Indicates charge loss and crossover	Can be reduced by crossover and side reactions	[11],[16]
Voltage efficiency	commonly lower than CE	Reflects ohmic, kinetic and mass-transport losses	Reduced by membrane resistance, electrode kinetics and flow limitation	[18],[20]
Energy efficiency	depends on CE × VE; commonly lower than CE	Best single electrochemical efficiency indicator	Does not include all auxiliary losses unless system-level analysis is used	[28],[5]
Membrane vanadium permeability	should be as low as possible; often compared against Nafion benchmark	Directly linked to self-discharge and capacity decay	Low permeability may increase resistance	[16],[17]
Cycle life	can reach very long cycling under suitable conditions	Important for long-duration stationary economics	Depends on crossover, side reactions, electrolyte management and stack design	[10],[11],[27]

These parameters also explain why VRFB optimization cannot be based on a single metric. For example, increasing vanadium concentration may improve theoretical energy density, but it can also increase viscosity and precipitation risk. Similarly, reducing membrane permeability can improve coulombic efficiency, but excessive membrane resistance can reduce voltage efficiency. Therefore, the following section focuses on electrolyte chemistry and stability, which is one of the first constraints controlling practical VRFB energy density and long-term operation.

3. Electrolyte chemistry and stability

The electrolyte stores energy in a VRFB through dissolved vanadium species in an acidic aqueous medium. Sulfuric acid commonly serves as the supporting electrolyte, providing ionic conductivity and influencing vanadium speciation through proton activity and sulfate coordination [33],[29]. A suitable formulation must keep the active species soluble and chemically stable throughout charging, discharging and storage across the intended operating temperature range [14],[34].

A VRFB uses four oxidation states of vanadium. The negative half-cell contains V²⁺ and V³⁺. The positive half-cell contains VO²⁺ and VO₂⁺. These species have different stability windows. They also respond differently to temperature, acid concentration and state of charge [5],[29]. Therefore, electrolyte stability is not a single property. It is controlled by redox chemistry, solubility, acid composition, impurity content and operating conditions [33],[14].

V²⁺ is the strongly reducing species in the charged negative electrolyte. Exposure to oxygen can oxidize it, shifting the state of charge and contributing to imbalance [5]. Although V³⁺ is less reducing, both oxidation states must remain compatible with the electrolyte formulation and

operating environment throughout repeated cycling to preserve capacity and coulombic efficiency [29].

The positive electrolyte is particularly sensitive to the combination of temperature, concentration and state of charge. Charging converts VO^{2+} to VO_2^+ , increasing the proportion of V(V) species that can precipitate or crystallize under unsuitable conditions. High vanadium concentration and elevated temperature intensify this risk, constraining the practical concentration and upper operating temperature of the electrolyte [15],[34].

Sulfuric acid influences conductivity, proton-involved reactions and vanadium speciation [5],[29]. Its concentration must be optimized together with vanadium loading because changes in viscosity, water activity and membrane transport can alter precipitation behavior and long-term component compatibility [33],[14]. Raising acid concentration is therefore a formulation choice with several coupled consequences, rather than an unrestricted route to higher performance.

Vanadium concentration is directly related to energy density. A higher vanadium concentration can increase the theoretical amount of stored charge per unit electrolyte volume [35],[36]. This is important because conventional VRFBs usually have lower energy density than lithium-ion batteries. However, high vanadium concentration also increases the risk of precipitation, viscosity rise and mass-transport limitations [14],[15]. Thus, electrolyte design must balance energy density and stability. The stability behavior of each vanadium species is summarized in Table 3. The table highlights that the negative electrolyte is mainly affected by $\text{V}^{2+}/\text{V}^{3+}$ redox balance and oxygen sensitivity, whereas the positive electrolyte is more strongly limited by VO_2^+ -related precipitation at high SOC, high vanadium concentration and elevated temperature.

Table 3

Vanadium redox species and electrolyte-stability issues in VRFBs

Vanadium species	Oxidation state	Half-cell location	Typical color / SOC meaning	Main electrolyte-stability issue	Role in charge/discharge	Design implication	Refs.
V^{2+}	V(II)	Negative electrolyte	Purple; charged negative electrolyte	Sensitive to air oxidation; oxygen exposure can shift SOC and cause electrolyte imbalance	Oxidized to V^{3+} during discharge; regenerated during charge	Oxygen exclusion and stable negative-electrolyte management are required	[5], [29]
V^{3+}	V(III)	Negative electrolyte	Green; discharged negative electrolyte	Maintaining $\text{V}^{2+}/\text{V}^{3+}$ balance is necessary for reversible negative-electrolyte cycling	Reduced to V^{2+} during charge; produced as V^{3+} during discharge	Stable $\text{V}^{2+}/\text{V}^{3+}$ cycling supports capacity retention and coulombic efficiency	[5], [29]
VO^{2+}	V(IV)	Positive electrolyte	Blue; discharged positive electrolyte	Stability depends on acid concentration, proton activity, sulfate coordination and vanadium concentration	Oxidized to VO_2^+ during charge; produced as VO^{2+} during discharge	Acid and vanadium concentration must be optimized for conductivity and solubility	[14], [29], [34]
VO_2^+	V(V)	Positive electrolyte	Yellow/orange; charged positive electrolyte	Precipitation/crystallization risk increases at high SOC, high vanadium concentration and elevated temperature	Reduced to VO^{2+} during discharge; produced as VO_2^+ during charge	Positive-electrolyte stability often limits practical vanadium concentration and upper operating temperature	[14],[15], [35]

Beyond the species-specific stability issues summarized in Table 3, temperature is another key factor controlling electrolyte performance. Low temperature can reduce solubility and increase viscosity, whereas high temperature can accelerate V(V) instability and precipitation in the positive electrolyte [34],[15].

Both conditions reduce practical operating stability. For grid-scale systems, this is important because batteries may operate under seasonal and daily temperature variations. Electrolyte formulation must therefore be stable not only at room temperature but also over a realistic operating range [14].

The precipitation of V(V) species is one of the most important electrolyte-stability problems. It can block flow channels, reduce active species concentration and increase pressure drop. It can also cause irreversible or partially reversible loss of capacity if the precipitated species are not redissolved [33]. In situ Raman spectroscopy has been used to follow V(V) crystallization behavior and to understand precipitation kinetics in vanadium electrolytes. Such studies are important because precipitation is controlled not only by concentration but also by local chemical environment and time-dependent nucleation processes [15].

Electrolyte additives are widely studied to improve stability. Additives can suppress precipitation, modify vanadium speciation, improve thermal stability or reduce the effect of impurities. Different types of additives have been reported, including inorganic additives, organic compounds and complexing agents [33],[37]. Their role is often related to interaction with vanadium species or modification of the local solvation environment. However, an additive must not only improve solubility. It must also remain electrochemically stable, chemically compatible and cost-effective [14].

Additive concentration is important. A low amount may be insufficient to stabilize the electrolyte. An excessive amount may increase resistance, change viscosity or cause side effects [33],[37]. Therefore, additive design requires systematic optimization. It should consider solubility, conductivity, viscosity, electrochemical window, membrane compatibility and long-term cycling behavior [36]. This is why electrolyte additives should be evaluated under full-cell conditions, not only by static solubility tests.

Impurity ions also affect electrolyte stability. They may come from vanadium raw materials, acid, water, electrode corrosion, current collectors or stack components. Some impurities may accelerate side reactions. Some may affect vanadium redox kinetics. Others may influence precipitation or gas evolution [33],[38]. Therefore, electrolyte purity is a practical issue in VRFB commercialization. A high-purity electrolyte can improve reproducibility, but it may increase cost. A more realistic approach is to identify impurity tolerance limits and purification requirements [38].

Mixed-acid electrolytes are another strategy for improving vanadium solubility and energy density. Sulfuric acid can be combined with other acids to modify vanadium speciation and increase electrolyte stability. High-energy-density mixed-acid formulations have been demonstrated in laboratory and system-level VRFB studies. These studies showed that electrolyte composition can be engineered to increase the practical operating window. However, mixed-acid systems also require evaluation of membrane compatibility, corrosion behavior, safety and long-term operation [35],[36].

Electrolyte state of charge strongly influences stability. At high SOC, the positive electrolyte contains more V(V) species. This can increase precipitation risk. At very low or very high SOC, side reactions may also become more important [39]. Therefore, the operating SOC window must be controlled. A wider SOC window can increase usable capacity, but it may reduce stability and accelerate degradation. Practical operation should therefore balance capacity utilization and electrolyte lifetime [29].

Electrolyte imbalance is closely connected to electrolyte chemistry. Even when both half-cells contain vanadium, crossover can change the oxidation-state distribution. Side reactions can also shift the charge balance. Water migration can change electrolyte volume and concentration. These processes lead to capacity decay and reduce usable energy [39],[11]. Although capacity decay is discussed in detail in Section 7, its origin is partly chemical. Electrolyte composition and stability are therefore central to long-term VRFB performance.

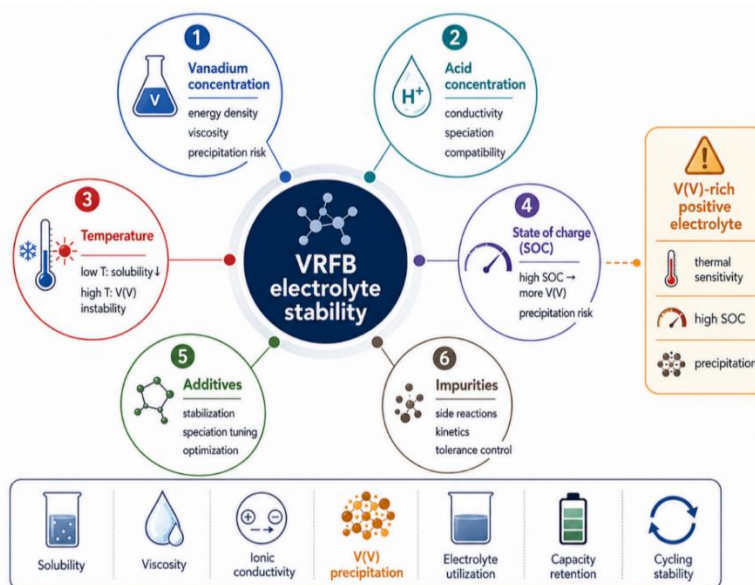


Figure 3. Key chemical and operational factors controlling electrolyte stability in VRFBs

The schematic summarizes how vanadium concentration, acid concentration, temperature, state of charge, additives and impurities jointly affect electrolyte solubility, viscosity, ionic conductivity, V(V) precipitation, electrolyte utilization and long-term capacity retention. Electrolyte engineering has recently become a major research direction. Modern studies do not only aim to increase vanadium concentration. They also focus on thermal stability, impurity tolerance, precipitation control, electrolyte rebalancing and stable operation under practical conditions [11],[34]. This shift is important. A highly concentrated electrolyte is useful only if it remains stable during storage, cycling and temperature variation. Otherwise, the gain in energy density can be lost through precipitation, viscosity increase or capacity decay [15].

Electrolyte performance should be evaluated by several parameters. These include vanadium solubility, ionic conductivity, viscosity, electrochemical stability, precipitation onset, thermal stability, impurity tolerance, cycling stability and compatibility with membrane and electrodes [14]. Static chemical stability tests are useful but insufficient. Flow-cell cycling, long-term storage, temperature-dependent tests and post-cycling analysis are also necessary [34]. This is especially important for translating laboratory electrolyte formulations into real VRFB systems.

A key challenge is the trade-off between energy density and stability. Increasing vanadium concentration improves theoretical capacity. Increasing acid concentration can improve conductivity and speciation control. Adding stabilizers can suppress precipitation. However, these changes may also increase viscosity, affect membrane transport, alter reaction kinetics or increase cost [14],[35]. Therefore, electrolyte optimization must be performed as part of a complete VRFB system, not as an isolated chemical formulation.

In summary, VRFB electrolyte stability depends on the coupled behavior of vanadium redox chemistry, sulfuric acid concentration, vanadium concentration, temperature, additives, impurities and operating SOC. The positive electrolyte, especially V(V)-rich solution, is often the most sensitive to precipitation and thermal instability [34],[15]. Additives and mixed-acid systems can improve stability, but they must be validated under long-term cycling and realistic operating conditions [33],[35]. Future electrolyte research should focus on stable high-concentration formulations, impurity-tolerant systems, reliable precipitation control and compatibility with low-cost membranes and durable electrodes [14].

Throughout this review, numerical values compiled from different studies are treated as condition-specific literature examples rather than as a direct performance ranking. Electrolyte and acid composition, temperature, state-of-charge window, membrane thickness, electrode

compression, current density, flow conditions, cell geometry and cycling protocols vary among reports. Comparisons therefore emphasize material–property relationships and performance trade-offs; a claim of superiority requires matched operating conditions or an explicitly justified normalization. Cell-level CE, VE and EE should also be distinguished from system-level efficiency when pumping and other auxiliary losses are excluded.

4. Polymer membrane selectivity, proton transport and crossover

The membrane separates the two electrolytes while providing an ionic path that maintains charge balance [31],[40]. Its performance reflects the competition between resistance and crossover: rapid ionic conduction reduces ohmic losses, whereas suppression of vanadium transport limits self-discharge and improves charge recovery. A membrane that favors either property at the expense of the other may lower voltage or coulombic efficiency, so both must be evaluated together [16],[17].

In acidic VRFB electrolytes, proton transport is particularly important because protons participate in the positive half-cell reaction involving the $\text{VO}^{2+}/\text{VO}_2^+$ redox couple. Fast proton or charge-carrier transport helps maintain electroneutrality during charge and discharge, reduces polarization and improves voltage efficiency [31],[40]. However, proton conductivity alone is not sufficient. The membrane must also suppress vanadium crossover, control water migration and remain chemically and mechanically stable in strongly acidic and oxidizing vanadium electrolyte [16],[17].

Perfluorosulfonic acid membranes, especially Nafion-type membranes, remain common benchmark materials because of their high proton conductivity, chemical stability and commercial availability [31],[40]. Nevertheless, Nafion is expensive and still permits vanadium crossover to some extent. Crossover promotes self-discharge, changes electrolyte composition, accelerates state-of-charge imbalance and reduces long-term capacity retention [16],[11]. Therefore, Nafion is useful as a reference membrane, but it is not an ideal final solution for low-cost large-scale VRFB deployment [16],[17].

Vanadium crossover is one of the main membrane-related degradation pathways. It occurs when vanadium species move from one half-cell to the other through the membrane by diffusion, migration and convection. The corresponding driving forces include concentration gradients, electric field and pressure difference across the membrane [16],[31]. Different vanadium species show different crossover behavior because they differ in charge, size, hydration structure and chemical form [16],[17]. Crossover not only transfers active species but also changes the oxidation-state distribution of both electrolytes, causing chemical imbalance, self-discharge and usable capacity loss during repeated cycling [11],[16].

Water migration is another important membrane-related process. Water can move between the half-cells by osmosis, electro-osmotic drag and pressure-driven transport [31],[41]. This changes electrolyte volume, vanadium concentration, acid concentration, viscosity and state of charge in the tanks. As a result, water transfer can worsen capacity decay and complicate rebalancing [41]. Therefore, membrane evaluation should include not only proton conductivity and vanadium permeability, but also water-transport behavior.

A useful way to interpret membrane-related degradation is to treat the membrane not as an ideal passive separator, but as a coupled transport interface. In this framework, desired charge-balancing ion transport occurs simultaneously with non-ideal vanadium-species crossover and water migration. Knehr et al. developed a transient VRFB model incorporating vanadium crossover and water transport through the membrane, including diffusion, migration, convection, electrolyte-volume change, interfacial concentration and potential gradients, and crossover-induced side reactions [42]. This coupled-transport view explains why membrane performance cannot be judged only by proton conductivity or vanadium permeability. Instead, the relevant design target is the simultaneous control of proton transport, vanadium crossover, water migration and chemical durability. These pathways are summarized in Figure 4a.

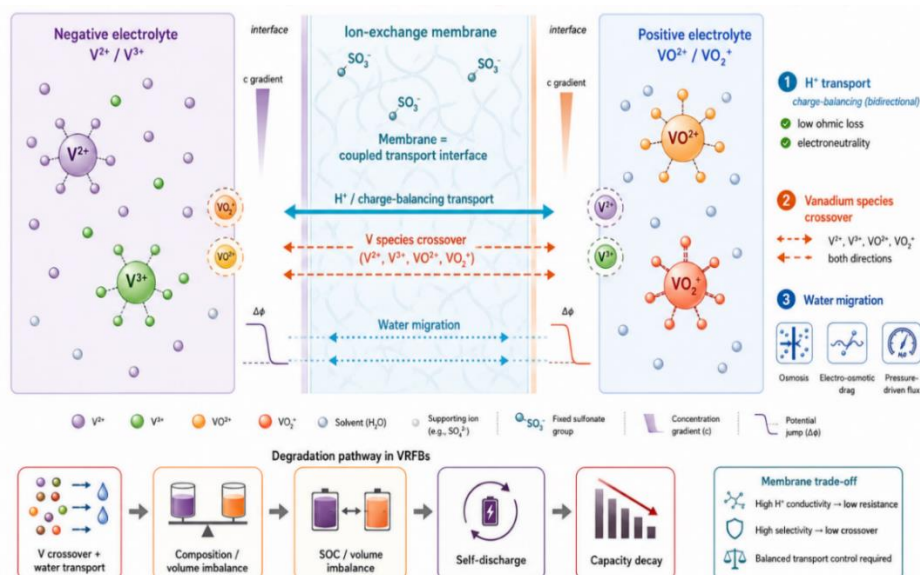


Figure 4a. Coupled transport pathways in polymer membranes governing crossover, imbalance and capacity decay in VRFBs

The schematic illustrates the membrane as a coupled transport interface rather than an ideal separator. Desired H^+ /charge-balancing ion transport occurs together with non-ideal vanadium-species crossover and water migration. Vanadium crossover is driven by diffusion, migration and convection, while water transfer is associated with osmotic, electro-osmotic and pressure-driven mechanisms. These coupled fluxes alter electrolyte composition and volume, producing SOC/volume imbalance, self-discharge and long-term capacity decay.

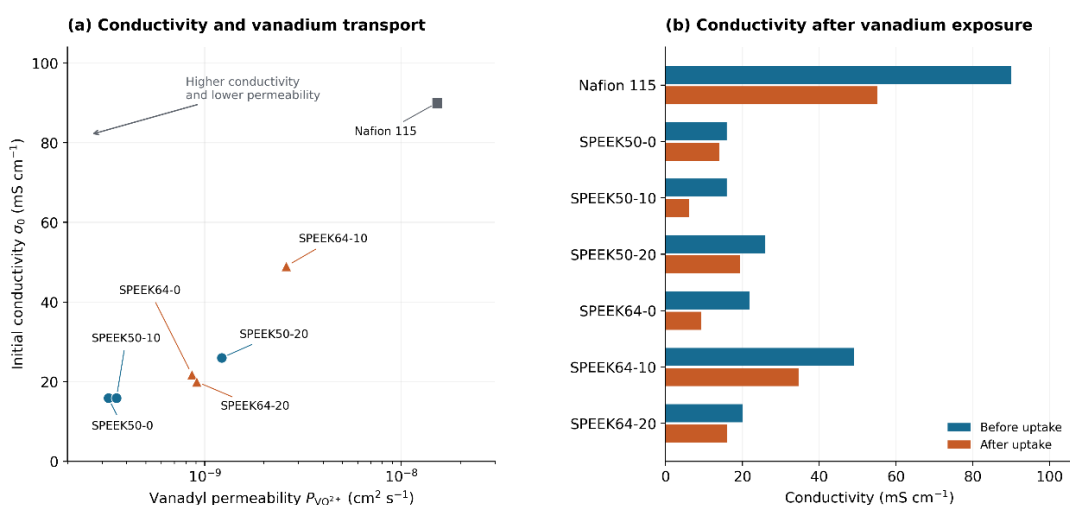


Figure 4b. Experimental membrane transport data. (a) Initial ionic conductivity versus VO^{2+} permeability. (b) Conductivity before and after vanadium uptake. Values are redrawn from Table 1 of Rizzuti et al. [43], licensed under CC BY 4.0. SPEEK50 and SPEEK64 denote 50% and 64% sulfonation; the final number is the reported amino-functionalized silica loading in wt%. Conductivity was measured in-plane at 30 °C and 100% relative humidity. Vanadium uptake used 1 M $VOSO_4$ in 2 M H_2SO_4 for 24 h at room temperature. No uncertainty estimates were tabulated, so error bars are not shown. These ex situ properties do not constitute a full-cell performance ranking

The experimental transport map in Figure 4b illustrates the membrane trade-off within a single study [43]. Nafion 115 combines the highest initial conductivity with the highest measured VO^{2+} permeability. SPEEK50-0 has lower conductivity but substantially lower permeability. Conductivity also changes after vanadium uptake, so the membrane conditioning state must be reported when comparing transport values. The change after uptake should not, by itself, be

assigned to irreversible polymer degradation; ion exchange, hydration and retained electrolyte can also affect the measured response.

This coupled-transport perspective is especially useful for comparing membrane classes because different polymer chemistries control proton conduction, vanadium rejection and water transfer through different structural mechanisms. VRFB membrane performance should therefore not be interpreted only as a static conductivity-permeability trade-off. A more useful interpretation is to treat membrane selectivity as a polymer-structure-controlled kinetic problem. In this view, proton or charge-balancing ion transport, vanadium-species crossover and water migration are coupled processes governed by polymer backbone chemistry, fixed ionic groups, hydration structure, free volume, pore/channel morphology, swelling behavior and membrane–electrolyte interfacial gradients [42],[17],[31].

This interpretation is important because conventional membrane comparison often relies on *ex situ* proton conductivity and vanadium permeability. Although these parameters are essential, they do not fully describe membrane behavior under real VRFB operation. During cycling, ion and water fluxes are driven simultaneously by concentration gradients, electric field, pressure difference, hydration-shell movement and local interfacial concentration changes. Therefore, the same membrane may behave differently depending on SOC, electrolyte concentration, current density, water uptake, swelling state and flow-induced pressure gradients [31],[17]. Membrane selectivity is thus kinetic and dynamic, not only structural and static.

From a polymer-structure viewpoint, PFSA/Nafion-type membranes illustrate both the benefit and limitation of highly connected hydrated ionic domains. Their sulfonic-acid clusters and fluorinated backbone support fast proton conduction and strong chemical stability, but the same hydrated pathways can also support vanadium-species transport and water migration [17],[31]. Hydrocarbon sulfonated polymers such as SPEEK, SPI, SPES and SPAEK offer lower cost and greater structural tunability, but their transport behavior depends strongly on sulfonation degree, hydrophilic-hydrophobic phase separation, swelling ratio and oxidative stability. Excessive sulfonation can improve proton transport, but it can also enlarge hydrated channels, increase swelling and accelerate crossover or polymer degradation [17].

PBI/PBMI-type membranes follow a different kinetic-selectivity strategy. Their dense aromatic backbones, acid-base interactions and restricted free volume can strongly suppress vanadium transport. However, if the polymer network is too dense or acid uptake is insufficient, proton transport becomes kinetically limited and area resistance increases. AEMs and amphoteric membranes use fixed cationic or mixed ionic groups to reject vanadium cations through Donnan exclusion, but their practical value depends on maintaining sufficient charge-balancing ion transport and chemical stability in strongly acidic, oxidizing electrolyte [17],[31].

Composite polymer membranes further show that kinetic selectivity is controlled by multi-scale structure. TiO₂, SiO₂, graphene oxide, carbon-based fillers, MOFs, zwitterionic groups, silica barrier layers and other functional phases can increase transport tortuosity, introduce size-sieving pathways, improve water management or create additional proton-transfer sites. However, these benefits depend on filler dispersion, polymer-filler interfacial compatibility and the continuity of hydrated ion-transport channels. Poor compatibility, aggregation, delamination or interfacial defects can create local crossover pathways, increase resistance or reduce durability [17],[31],[44],[45].

Therefore, next-generation VRFB membranes should be designed by linking molecular structure to transport kinetics and then to cell-level degradation. The relevant design chain can be expressed as: polymer backbone and functional groups → hydrated channel morphology and swelling state → proton/charge-balancing ion kinetics, vanadium crossover and water migration → SOC and volume imbalance → self-discharge, capacity fade and rebalancing demand. This structure-transport-degradation framework explains why the best membrane is not necessarily the one with the highest proton conductivity or the lowest *ex situ* vanadium permeability. The practical target is a stable kinetic selectivity window under operating conditions: fast charge-balancing ion

transport, slow vanadium-species transport, controlled water migration, low swelling, oxidative durability and stable interfacial structure during long-term cycling.

Cation-exchange membranes are widely studied in VRFBs because they contain negatively charged fixed groups and conduct cations, mainly protons in acidic electrolyte. Their main advantage is relatively high proton conductivity, which helps reduce ohmic resistance [31],[40]. However, CEMs may also allow transport of vanadium cations. The design challenge is therefore to maintain fast proton transport while rejecting larger or more highly charged vanadium species [16],[46].

Anion-exchange membranes and amphoteric membranes offer another selectivity mechanism. Their fixed positive or mixed ionic groups can suppress vanadium cation crossover through electrostatic repulsion or Donnan exclusion, which can improve coulombic efficiency and reduce self-discharge [31]. However, AEMs and amphoteric membranes often face challenges related to proton transport, chemical stability in strongly acidic oxidizing electrolyte and long-term durability [16],[17]. Therefore, they remain promising but require careful molecular design and practical full-cell validation.

SPEEK-based membranes are among the most studied hydrocarbon alternatives. Sulfonated poly(ether ether ketone) has lower cost potential than perfluorinated membranes and contains sulfonic acid groups for proton transport [46],[47]. However, pure SPEEK membranes may suffer from excessive swelling, mechanical instability or reduced oxidative stability under harsh VRFB conditions. Blending, crosslinking and incorporation of functional fillers are therefore used to improve the conductivity-selectivity balance [44].

Polybenzimidazole and polybenzimidazolium-type membranes are also attractive because their dense structures and ion-pair interactions can suppress vanadium crossover and improve chemical robustness under acidic conditions [48]. Their main limitation is that proton conductivity and membrane resistance must be optimized. If area resistance is too high, voltage efficiency decreases even when crossover is low [17].

Composite and barrier-layer membranes provide additional routes to improve selectivity. Inorganic nanoparticles, MOF-based components, phosphotungstic-acid hybrids, silica-based barrier layers, sulfonated conductive polymers, graphene oxide and zwitterionic functional groups can create selective ion-transport pathways or physical barriers against vanadium crossover [44],[41]. However, these systems must be evaluated for filler dispersion, acid stability, interfacial adhesion, swelling tolerance and long-term cycling durability. A thin selective layer can reduce crossover without greatly increasing resistance, but it must remain mechanically intact under pressure, swelling and repeated charge–discharge operation [45].

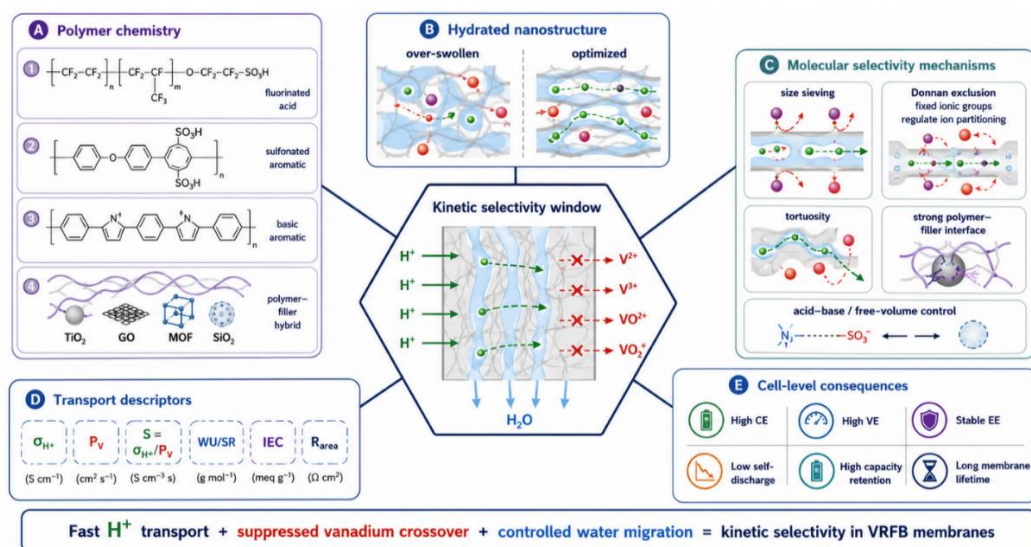


Figure 5. Polymer-structure-controlled kinetic selectivity in VRFB membranes

The schematic links polymer membrane chemistry to transport kinetics and cell-level performance. PFSA/Nafion-type membranes form hydrated sulfonic-acid ionic domains that support fast H^+ transport but may also permit vanadium crossover and water migration. SPEEK and other sulfonated hydrocarbon membranes provide tunable ion-exchange capacity, but excessive sulfonation increases swelling and crossover. PBI/PBMI membranes suppress vanadium transport through dense aromatic backbones and acid-base interactions, whereas AEM/amphoteric membranes use fixed cationic or mixed ionic groups to enhance Donnan exclusion. Composite membranes regulate kinetic selectivity by incorporating fillers, barrier layers, MOF particles, graphene oxide, TiO_2 , silica or zwitterionic groups. The key design target is a stable kinetic selectivity window combining fast charge-balancing ion transport, low vanadium permeability, controlled water migration, low swelling, oxidative stability and mechanical durability.

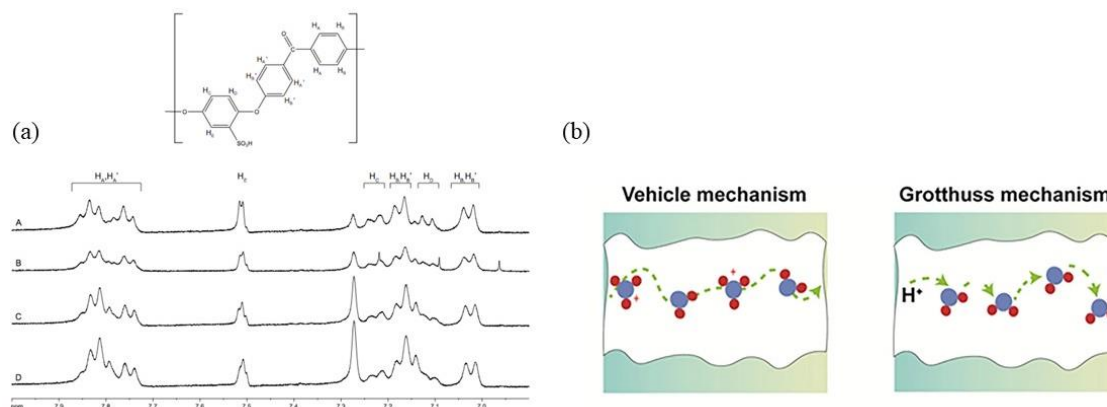


Figure 6. Molecular structure, sulfonation characterization and proton-transport mechanisms in sulfonated polymer membranes. (a) SPEEK repeat-unit structure and ^1H NMR spectra of samples prepared under different sulfonation conditions. The NMR-derived degrees of sulfonation for the original samples A-D are 0.85, 0.73, 0.70 and 0.64, respectively. The image and DS values are reproduced from Figure 1 and Table 1 of [Yee et al. \(2013\)](#) [49], respectively, under the [CC BY 3.0 licence](#). (b) Schematic comparison of vehicle transport (left) and Grotthuss transport (right), adapted from Figure 1b,c of [Huynh et al. \(2025\)](#) [17] under the [CC BY 4.0 licence](#). The selected panels have been rearranged and relabelled. These mechanisms may coexist; their relative contributions under VRFB operating conditions are not quantified by the schematic.

Figure 6 connects the molecular structure of a representative sulfonated polymer with its structural characterization and possible proton-transport pathways. SPEEK contains an aromatic poly(ether ether ketone) backbone functionalized with sulfonic acid groups. For the monosulfonation-based description considered here, the degree of sulfonation (DS) represents the fraction of repeat units bearing a sulfonic acid group. The ^1H NMR spectra in Figure 6a provide experimental evidence of sulfonation, while integration of the assigned aromatic proton signals enables DS estimation [49]. These spectra characterize the polymer structure and should not be interpreted as measurements of VRFB performance.

Within hydrated ionic domains, proton transport can involve both vehicle and Grotthuss mechanisms (Figure 6b). Vehicle transport occurs through the motion of solvated proton-bearing species, whereas Grotthuss transport involves successive proton-transfer events and rearrangement of the hydrogen-bond network [17]. Consequently, increasing the density of sulfonic acid groups does not by itself establish improved membrane performance: changes in hydration and conductivity must be evaluated together with swelling, vanadium crossover and mechanical stability. For VRFB applications, molecular design should therefore be assessed through transport measurements and cell testing under clearly defined conditioning and operating conditions.

A comparative overview of the main membrane classes is necessary because membrane performance in VRFBs cannot be evaluated only by proton conductivity or only by vanadium permeability. Different membrane chemistries suppress crossover through different mechanisms, including fixed-charge effects, dense polymer backbones, physical barrier layers, filler-assisted

tortuosity and size-sieving pores. Table 4 summarizes representative membrane classes, selected reported performance indicators, major advantages and key limitations. The listed values should be interpreted as compact literature examples rather than as a direct ranking because testing conditions, electrolyte composition, current density, membrane thickness and cycling protocols differ among studies.

Table 4

Representative polymer and polymer-composite membrane classes and conductivity-selectivity trade-offs in vanadium redox flow batteries

Membrane class / design type	Representative examples	Compact reported indicator	Main advantage	Main trade-off / limitation	Refs.
Nafion / PFSA membranes	Nafion, Nafion/TiO ₂ , Nafion/TiZrO ₄	Nafion/TiZrO ₄ : $\sigma(\text{H}^+) = 75.9 \text{ mS cm}^{-1}$; CE/EE = 99.8/84.1 at 80 mA cm ⁻²	Benchmark conductivity and chemical stability	High cost; vanadium crossover; water transport	[50],[51], [52]
Hydrocarbon CEMs	SPI, SPES, SPAEK, PFSPi-PAA	PFSPi-PAA-25: VO ²⁺ permeability = $0.06 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$; EE = 85.0% at 140 mA cm ⁻²	Lower-cost fluorine-free chemistry; tunable structure	Oxidative stability and swelling must be controlled	[53],[54]
AEMs / AIEMs	QPAPEKK, nanoporous AEM, amphoteric membranes	QPAPEKK-90: EE = 91.4% at 80 mA cm ⁻² ; 80.0% at 220 mA cm ⁻²	Strong vanadium rejection by electrostatic repulsion	Lower proton transport; cationic-group stability concerns	[55],[56], [57]
SPEEK-based composites	SPEEK/TiO ₂ , SPEEK/PVDF, SPEEK/GO, SPEEK/FCB	SPEEK/TiO ₂ : $\sigma(\text{H}^+) = 18.3 \text{ mS cm}^{-1}$; VO ²⁺ permeability = $0.18 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$; EE = 84.8% at 120 mA cm ⁻²	Low cost; easy modification; good processability	Swelling and mechanical/oxidative durability at high sulfonation	[58],[59], [60],[61]
PBI / modified PBI membranes	TM-OPBI, B-PBI, PBI composite membranes	TM-OPBI-12: CE $\approx$ 100%; EE = 68.2% at 160 mA cm ⁻² ; 93.9% retention after 500 cycles	Very low vanadium crossover; robust backbone	Conductivity/resistance requires acid uptake or structural design	ADDIN CSL_CITATION {"citationItems":[{"id":"ITEM-1","itemData":{"DOI":"10.1016/j.jowsour.2023.232858","author":{"droppingleadingparticle":"","family":"Ding","given":"Ling","non-droppingparticle":"","parse-names":false,"suffix":""},"droppingleadingparticle":"","family":"Wang","given":"Lihua","non-droppingparticle":"","parse-names":false,"suffix":""}], "container-title":"Jo

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Inorganic/composite barrier membranes	Nafion/TiO ₂ nanotube, Nafion/GO, CLGO/Nafion	Nafion/TiO ₂ nanotube: CE $\approx$ 98.3%; EE $\approx$ 84.4% at 120 mA cm ⁻² ; discharge-capacity retention $\approx$ 55.7% after 1400 cycles	Physical barrier to vanadium crossover; improved selectivity	Filler aggregation and interfacial defects may reduce conductivity	[51],[65]
Porous / nanofiltration membranes	TMA-5, PPY/PES, PES-based porous membranes	TMA-5: CE/VE/EE $\approx$ 99/90/88.5% at 80 mA cm ⁻² ; 1500 cycles	Low-cost size-sieving strategy; high selectivity possible	Pore-size control and long-term chemical stability	[66],[67], [68],[69]

The comparison in Table 4 shows that each membrane class has a characteristic advantage and a corresponding limitation. Nafion/PFSA membranes remain benchmark materials because of their high proton conductivity and chemical stability, but their high cost, vanadium crossover and water transport remain important drawbacks. Hydrocarbon CEMs and SPEEK-based membranes offer lower-cost and more tunable structures, although swelling and oxidative durability must be controlled. AEMs and amphoteric membranes can suppress vanadium cation crossover through electrostatic repulsion, but proton transport and cationic-group stability remain challenging under strongly acidic and oxidizing VRFB conditions. PBI-based membranes show very low vanadium crossover, but their conductivity and acid uptake must be optimized. Composite, barrier-layer and porous/nanofiltration membranes provide additional routes to improve selectivity, although filler aggregation, interfacial defects, pore-size control and long-term chemical stability remain unresolved issues.

Membrane performance is usually evaluated by proton conductivity, area resistance, vanadium permeability, ion selectivity, water uptake, swelling ratio, chemical stability, mechanical strength, coulombic efficiency, voltage efficiency, energy efficiency and capacity retention. No single parameter is sufficient. A membrane with high conductivity may perform poorly if crossover is high, whereas a membrane with very low vanadium permeability may be unsuitable if resistance is excessive [16],[17]. Thus, membrane quality must be judged by balanced full-cell performance and long-term stability under realistic operating conditions.

Cost and durability are also critical. Nafion-type membranes are effective but expensive, which limits large-scale deployment [16],[17]. Hydrocarbon membranes, SPEEK-based membranes, PBI/PBMI-type membranes and composite membranes are studied partly because they may reduce cost while maintaining acceptable performance [44],[47]. However, low material cost alone is not enough. The membrane must also provide low crossover, low resistance, reproducible fabrication, mechanical integrity and compatibility with industrial-scale stack assembly [17],[26].

Membrane degradation must also be considered because VRFB membranes operate in acidic electrolyte containing strongly oxidizing V(V) species. They also experience swelling, concentration gradients, pressure differences and repeated cycling [16],[17]. Chemical degradation can increase crossover, mechanical damage can create pinholes or cracks, and excessive swelling can change membrane thickness and resistance. These changes reduce efficiency and accelerate capacity decay [11]. Therefore, long-term membrane durability is as important as initial electrochemical performance.

A major limitation in membrane research is inconsistent testing conditions. Different studies use different vanadium concentrations, acid concentrations, current densities, membrane thicknesses, flow rates and cycling protocols [16]. This makes direct comparison difficult. Future

membrane studies should report standardized transport, stability and full-cell data, including membrane thickness, electrolyte composition, current density, flow rate, CE, VE, EE, capacity retention and post-cycling stability. They should also include comparison with benchmark Nafion-type membranes under identical conditions [17].

In summary, membrane selectivity is directly connected to VRFB efficiency, capacity retention and cost. Nafion-type membranes remain useful benchmarks, but their cost, crossover and water-transport limitations motivate the development of lower-cost and more selective polymer membranes [16],[17]. CEMs, AEMs, SPEEK-based composites, PBI/PBMI-type membranes, MOF-containing membranes, porous/nanofiltration membranes and barrier-layer systems each offer specific advantages and limitations [44],[47]. Future progress requires membranes that combine conductivity, selectivity, durability, water-management control and economic viability under practical long-duration cycling conditions. Therefore, VRFB membrane development should be treated as a polymer-structure-transport problem, where backbone chemistry, fixed-charge density, ionic-group distribution, swelling control, filler-polymer interfacial compatibility and oxidative stability jointly determine cell-level selectivity and durability.

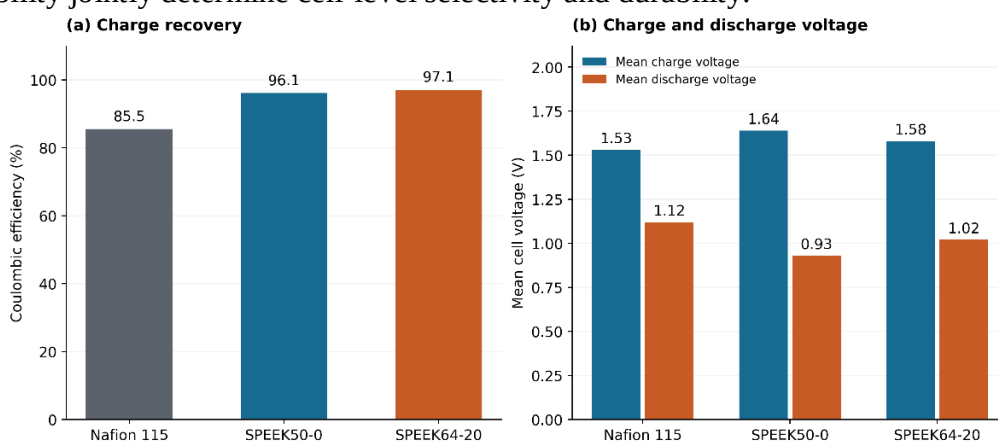


Figure 7. Experimental cell performance showing the distinction between charge recovery and voltage performance. (a) Coulombic efficiency. (b) Mean charge and discharge voltages. Data redrawn from Table 2 of Rizzuti et al. [43], CC BY 4.0. The reported comparison used a 25 cm² single cell, the same STD electrolyte, 20 mA cm⁻² for charge and discharge, and cutoffs of 1.9 and 0.7 V. SPEEK films at this stage were 70 μm thick; Nafion 115 was nominally 127 μm. Membrane chemistry and thickness are therefore not independently isolated. Error bars are omitted because the table does not report dispersion or replicate counts. These are literature measurements, not new experiments by the review authors.

Figure 7 shows why membrane selection cannot rely on coulombic efficiency alone [43]. Relative to Nafion 115, both SPEEK membranes recover a larger fraction of the charging capacity, while their mean charging voltages are higher and mean discharge voltages are lower. The observed benefit in charge recovery thus accompanies a voltage penalty in this configuration. The comparison supports joint assessment of crossover and polarization; it does not establish a universal ranking or isolate polymer chemistry from thickness. Energy efficiency should be taken from directly integrated charge–discharge energy rather than inferred from rounded mean voltages without checking how those averages were defined.

5. Carbon-based electrodes and reaction kinetics

Carbon and graphite felts provide electronically conductive, porous interfaces for vanadium redox reactions [18],[70]. Their three-dimensional fiber networks expose reaction sites to the circulating electrolyte [71], while the active vanadium remains dissolved in solution. Electrode performance consequently depends on surface chemistry, wettability, fiber morphology, pore accessibility and electrical conductivity [19]. Useful modifications must lower charge-transfer resistance without compromising electrolyte access or long-term chemical stability [30].

Graphite felt and carbon felt are similar in function but not identical in structure and surface chemistry. Graphite felt is usually more graphitized and electrically conductive. Carbon felt may contain more disordered carbon and more surface functional groups depending on processing conditions [18],[70]. Both materials can be used in VRFBs. However, their untreated surfaces often show limited catalytic activity for vanadium redox reactions [19]. This limitation increases activation polarization and reduces voltage efficiency [30].

The reaction kinetics in VRFBs are controlled by both half-cell reactions. The positive reaction involves the $\text{VO}^{2+}/\text{VO}_2^+$ redox couple. The negative reaction involves the $\text{V}^{2+}/\text{V}^{3+}$ redox couple [18]. The positive reaction is often discussed more frequently because it is sensitive to surface oxygen groups and electrode oxidation state [72],[73]. However, both positive and negative electrode reactions must be optimized for full-cell performance. Improving only one side may not provide balanced operation [30].

Electrode hydrophilicity is an important factor. Vanadium electrolytes are aqueous and strongly acidic. If the carbon surface is hydrophobic, electrolyte penetration into the porous felt becomes incomplete. This reduces the effective electrochemical area [18],[19]. Improved hydrophilicity enhances electrolyte wetting, reactant transport and contact between vanadium species and active sites [70]. Contact-angle measurements are often used to evaluate wetting behavior after electrode modification [74].

Surface oxygen functional groups can improve electrode activity. These groups include hydroxyl, carbonyl, carboxyl and other oxygen-containing sites [73],[75]. They can increase surface polarity and wettability. They can also influence electron-transfer kinetics for vanadium redox reactions [72],[73]. However, the role of oxygen groups is not always simple. Excessive oxidation may damage the carbon structure or increase resistance [30],[73]. Therefore, oxygen functionalization must be controlled carefully.

Electrode modification must preserve accessible flow pathways while improving wetting and reaction kinetics. Adding functional groups or a catalyst is beneficial only when the gain survives changes in resistance, pore accessibility and surface durability. Figure 8 summarizes the principal strategies for carbon and graphite felt electrodes and the associated trade-offs.

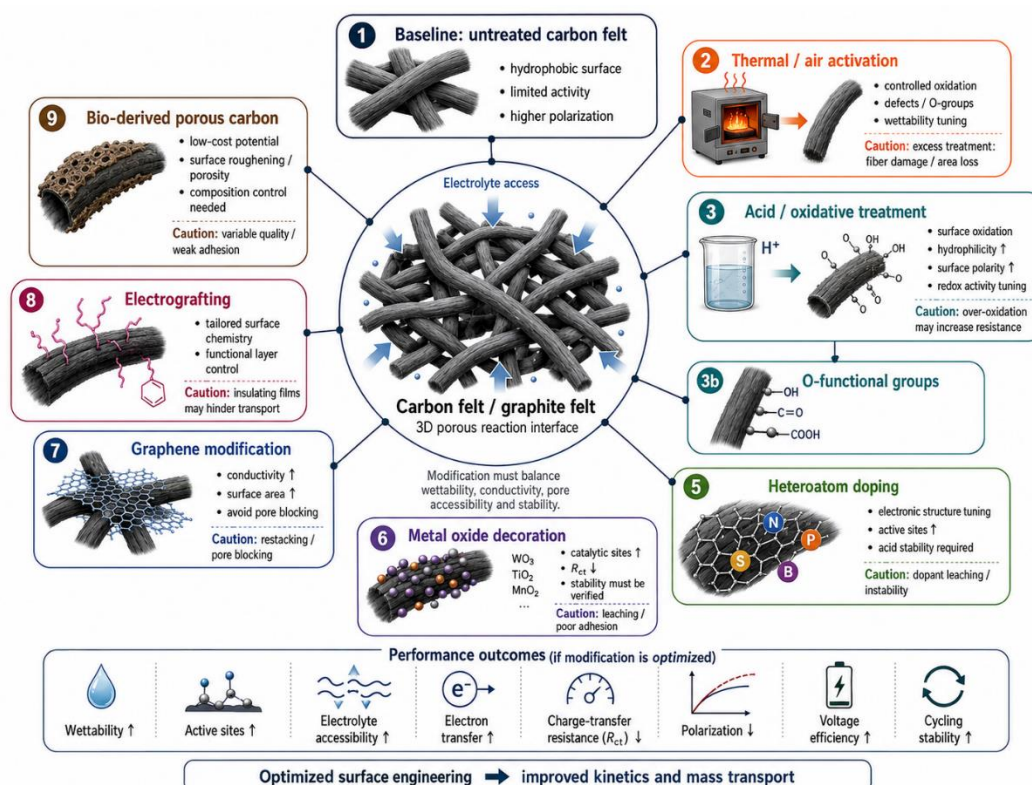


Figure 8. Main surface-engineering strategies for carbon-based VRFB electrodes.

The schematic summarizes representative modification routes for carbon felt and graphite felt electrodes, including thermal/air activation, acid or oxidative treatment, oxygen functionalization, heteroatom doping, metal oxide decoration, graphene-based modification, electrografting and bio-derived porous carbon coating. These strategies aim to improve wettability, active-site density, electrolyte accessibility and electron-transfer kinetics, but over-modification may increase resistance, block pores or reduce long-term stability. Therefore, optimized electrode design requires balancing catalytic activity, conductivity, permeability and durability.

As shown in Figure 8, these strategies can be grouped into activation methods, chemical functionalization routes, conductive/catalytic coatings and controlled interfacial modification. Each route can improve selected electrode properties, but each also introduces possible trade-offs related to resistance, pore blocking, adhesion, durability or scalability.

Thermal treatment is one of the simplest electrode activation methods. It can introduce oxygen-containing groups when performed in air or oxygen-containing atmospheres. It can also remove surface impurities and improve wettability [70]. Thermal activation is attractive because it is relatively simple and scalable. However, its effect depends on temperature, atmosphere and treatment time [19]. Too mild treatment may be insufficient. Too severe treatment may damage fibers or reduce mechanical integrity [30].

Chemical oxidation is another common strategy. Acid treatment can introduce oxygen groups and increase surface hydrophilicity [70],[76]. Nitric acid, sulfuric acid and mixed acid treatments have been used in many studies [18],[19]. These treatments can improve vanadium redox activity. However, they may also create defects, reduce conductivity or generate unstable surface groups [73]. Therefore, chemical oxidation should be evaluated not only by initial activity but also by long-term cycling stability [30].

Graphene oxide and reduced graphene oxide have been used to modify carbon felt surfaces. Graphene-based layers can increase surface area and introduce oxygen-containing functional groups. They can also improve electron-transfer pathways when well connected to the carbon fiber network [76]. However, graphene-based modification must avoid blocking pores or increasing mass-transport resistance. A uniform and stable coating is more important than simply increasing the amount of graphene-based material [75].

The role of oxygen groups introduced by graphene oxide has been compared in vanadium and anthraquinone flow batteries [75]. This is useful because it shows that surface chemistry may affect different redox chemistries in different ways. For VRFBs, oxygen functional groups can improve wettability and catalytic activity, but their exact contribution depends on group type, surface density, electronic structure and cycling conditions [72],[73]. This means that electrode design should not treat all oxygen groups as equally beneficial.

Heteroatom doping is another important route. Nitrogen, sulfur, phosphorus and other heteroatoms can modify the electronic structure of carbon materials [30]. They can change charge distribution, defect density and surface polarity. These changes may improve redox kinetics and electrolyte affinity [77].

Biomass-derived carbons are attractive because they combine porous structure, heteroatom content and low-cost precursor availability [19]. Their main weakness is variability: precursor composition, carbonization temperature and activation chemistry can strongly change conductivity, pore structure and surface functionality. For this reason, biomass-carbon modifiers should be evaluated with reproducible synthesis protocols and benchmarked against conventional carbon-felt activation [77].

Metal oxide decoration introduces catalytic sites and improves surface polarity, but its practical value depends on acid stability and adhesion under flowing electrolyte [19],[78]. The key design question is not only whether the oxide increases initial activity, but whether it remains attached and electrochemically useful during long-term cycling [30].

Electrografting offers a more molecularly controlled route than thermal or acid oxidation because functional groups can be attached directly to the carbon surface. Its future value lies in mechanistic design: selected grafted groups should be linked to charge-transfer resistance, wettability and durability rather than reported only as improved peak currents in cyclic voltammetry [79].

Three-dimensional electrode design is also important. Felt electrodes already have a 3D structure, but their pore size distribution, fiber diameter, compression and permeability strongly influence performance. A good 3D electrode should provide high active area and short ion-transport pathways. It should also allow uniform electrolyte flow and low pressure drop [71]. If pores are too small or blocked by modifiers, mass transport can become limited. If pores are too large or poorly connected, the effective surface area may be low [80].

Electrode compression affects both electrochemical and hydraulic behavior. Compression can improve contact between electrode, current collector and flow field. This can reduce contact resistance [36]. However, excessive compression can reduce porosity and permeability. This increases pressure drop and pumping energy consumption [80]. Therefore, electrode structure must be optimized together with flow-field design. Electrode engineering and stack engineering are not independent problems [20].

Table 5 summarizes representative carbon-electrode modification strategies, their reported benefits and their limitations. The performance indicators are condition-specific literature examples and do not establish a direct ranking: cell geometry, electrolyte composition, current density, electrode compression, flow rate and cycling duration differ among studies. Improvements should therefore be assessed against the corresponding unmodified electrode tested under the same conditions.

Table 5

Modification strategies for carbon-based electrodes in VRFBs

Modification strategy	Representative examples	Compact indicator / evidence	Main benefit	Main limitation	Refs.
Thermal / air activation	Heat-treated carbon felt/graphite felt	EE up to 86.2% at 60 mA cm ⁻²	Better wettability; lower polarization	Fiber damage if over-treated	[70],[74],[76]
Chemical oxidation	HNO ₃ , H ₂ SO ₄ , mixed-acid treatment	More O-groups and hydrophilic sites	Improved redox kinetics	Conductivity loss; unstable defects	[70],[73],[76]
Graphene-based coating	GO, rGO, graphene-coated felt	O-groups affect VRFB redox activity	Higher area; better electron transfer	Pore blocking; coating instability	[75],[76]
Heteroatom doping	N-, S-, P-doped carbon	Doped sites improve charge transfer	Tuned electronic structure	Reproducibility issue	[30],[77]
Biomass-derived carbon	Porous biomass carbon coating	Hierarchical pores + heteroatoms	Low-cost; sustainable modifier	Precursor variability	[19],[77]
Metal oxide decoration	TiO ₂ , MnO ₂ , CeO ₂ , LTO/TiO ₂	EE = 82.89% at 80 mA cm ⁻²	Catalytic/polar active sites	Acid stability; detachment	[19],[78]
Electrografting	Molecularly grafted carbon surfaces	Controlled functional groups	Defined surface chemistry	Scale-up still limited	[79]
3D structure / compression control	Optimized felt porosity and compression	Higher limiting current; lower pressure drop	Better mass transport	Excess compression increases pumping loss	[71],[80]

As shown in Table 5, electrode modification must balance activity, wettability, conductivity, permeability and durability. Simple activation methods are scalable, while graphene, biomass-carbon, metal-oxide and electrografted modifiers can improve surface activity. However, excessive modification may block pores, increase resistance or reduce long-term stability.

Electrode degradation is another key issue. Carbon materials can undergo surface oxidation, loss of functional groups, structural changes or catalyst detachment during long-term cycling. Degradation may increase charge-transfer resistance and reduce voltage efficiency. It may also change wettability and active surface area. Therefore, initial electrode activity is not enough. Long-

term stability under realistic current density, acid concentration and flow conditions is required [30].

The catalytic activity of graphite electrodes is still debated. Some studies show that oxygen functional groups and defects can improve activity. Other studies suggest that the relationship between surface oxygen and catalytic performance is complex. The origin of catalytic activity may involve edge-plane sites, defect sites, surface functional groups, carbon hybridization and local electronic structure [72],[73]. This complexity explains why different modification methods sometimes produce inconsistent results [30].

Electrochemical characterization is essential for evaluating electrode performance. Cyclic voltammetry can show redox peak separation and reversibility. Electrochemical impedance spectroscopy can estimate charge-transfer resistance and ohmic resistance. Polarization curves can show performance under different current densities. Full-cell charge-discharge tests are necessary to determine coulombic efficiency, voltage efficiency, energy efficiency and capacity retention [18]. Surface characterization is also needed. SEM can show fiber morphology and coating distribution. XPS can identify surface functional groups and heteroatoms. Raman spectroscopy can evaluate carbon disorder and graphitization [19],[30].

A major problem in electrode research is the gap between half-cell activity and full-cell performance. A modified electrode may show improved cyclic voltammetry response in a small electrochemical test. However, this does not always translate into better full-cell cycling [18],[30]. Full-cell performance depends on electrode kinetics, membrane resistance, electrolyte composition, flow rate, compression and current density [20]. Therefore, electrode materials should be tested under practical VRFB conditions.

Another problem is over-modification. Increasing the amount of catalyst, graphene or biomass carbon does not always improve performance. Excess coating can block pores. It can reduce permeability. It can increase pressure drop. It can also detach during operation [30],[78]. Therefore, the best electrode is not the one with the highest amount of modifier. It is the one with the best balance between active sites, conductivity, wettability, permeability and durability [71],[80].

Carbon-based electrode development should also consider sustainability and cost. Thermal treatment is simple but may consume energy. Chemical oxidation is effective but may require acid handling and waste treatment. Metal oxide and graphene-based modifications can improve performance but may increase material and processing cost [19],[78]. Biomass-derived carbons may offer lower-cost and more sustainable modifiers, but reproducibility remains a challenge [77]. Therefore, electrode design should be evaluated by performance, durability, cost and scalability together.

In summary, carbon felt and graphite felt remain the main electrode platforms for VRFBs because they combine conductivity, porosity and chemical stability [18],[70]. Their main limitation is insufficient intrinsic catalytic activity and incomplete wetting in untreated form [19]. Surface modification can improve hydrophilicity, active site density and vanadium redox kinetics [78]. However, each modification route has trade-offs. Excessive oxidation can damage carbon. Excess catalyst loading can block pores. Unstable coatings can degrade during cycling. Therefore, future electrode research should focus on durable, scalable and low-cost modifications that improve reaction kinetics without sacrificing permeability, conductivity and long-term stability [78].

6. Flow-field, stack design and system engineering

Flow-field and stack design determine how effectively the circulating electrolyte supplies reactants to the electrode surface. Local kinetics, membrane resistance and electrolyte chemistry operate within a hydraulic system whose flow distribution, pressure drop and pumping demand influence the delivered power and energy efficiency [20],[21].

The electrolyte flow must deliver vanadium species uniformly to the porous electrodes. If the flow is poorly distributed, some electrode regions receive enough reactant while other regions

become underutilized. This produces local concentration gradients and mass-transport losses [20],[81]. Non-uniform flow can also increase local current density. This may accelerate side reactions and capacity imbalance during long-term cycling [21],[11]. Thus, flow design is directly connected to efficiency, durability and capacity retention.

Flow-through designs force electrolyte through the porous felt, improving electrode–electrolyte contact and, under suitable conditions, reducing concentration polarization [20]. The corresponding hydraulic resistance can raise pumping demand [82]. In flow-by designs, electrolyte travels along adjacent channels and penetrates the felt through the combined effects of convection and diffusion; this can reduce pressure drop, but poor channel design may leave parts of the electrode underutilized [20],[82]. The appropriate configuration depends on electrode thickness and compression, flow rate, channel geometry and current density [21],[81].

Flow-field-assisted designs are used to improve the balance between mass transport and pumping loss. Common flow-field patterns include serpentine, interdigitated, parallel and mixed designs [20],[21]. Serpentine channels can enhance electrolyte penetration and reactant distribution. However, they may also produce higher pressure drop. Parallel channels can reduce pressure drop, but they may suffer from flow maldistribution. Interdigitated designs can force electrolyte through porous electrodes, improving mass transport but increasing hydraulic resistance [83].

Pressure drop is a key engineering parameter. It represents the hydraulic resistance experienced by the circulating electrolyte. A high pressure drop requires higher pump work. This reduces net system efficiency [20]. Pressure drop depends on flow rate, electrolyte viscosity, channel geometry, electrode permeability, compression and stack dimensions [81]. Therefore, pressure drop should be considered together with electrochemical performance. A design with high power density may not be practical if it requires excessive pumping energy [28].

Pumping loss is especially important in long-duration systems. VRFBs use external tanks and continuous electrolyte circulation. Pumps consume auxiliary power. If pumping loss is high, the overall energy efficiency decreases [84]. Increasing the flow rate can reduce concentration polarization. However, it also increases pumping power. Therefore, the optimal flow rate is not always the highest flow rate. It is the flow rate that gives the best compromise between electrochemical efficiency and hydraulic energy consumption [28].

Mass transport limitation occurs when reactants cannot reach active electrode sites fast enough. It becomes more serious at high current density, low flow rate or poor electrolyte distribution [20]. In VRFBs, mass transport is influenced by convection in channels, flow through porous electrodes, diffusion inside pores and reaction at carbon fiber surfaces [21]. Electrode compression also changes mass transport. Moderate compression can improve electrical contact. Excessive compression can reduce porosity and permeability [81].

The qualitative differences among common VRFB flow-field configurations are summarized in Figure 9. These designs differ not only in the visual pathway of electrolyte flow, but also in the degree of electrolyte penetration into the porous electrode, flow uniformity, pressure drop and pumping-energy demand. Therefore, flow-field comparison should be interpreted as a transport trade-off rather than a simple ranking of best and worst designs.

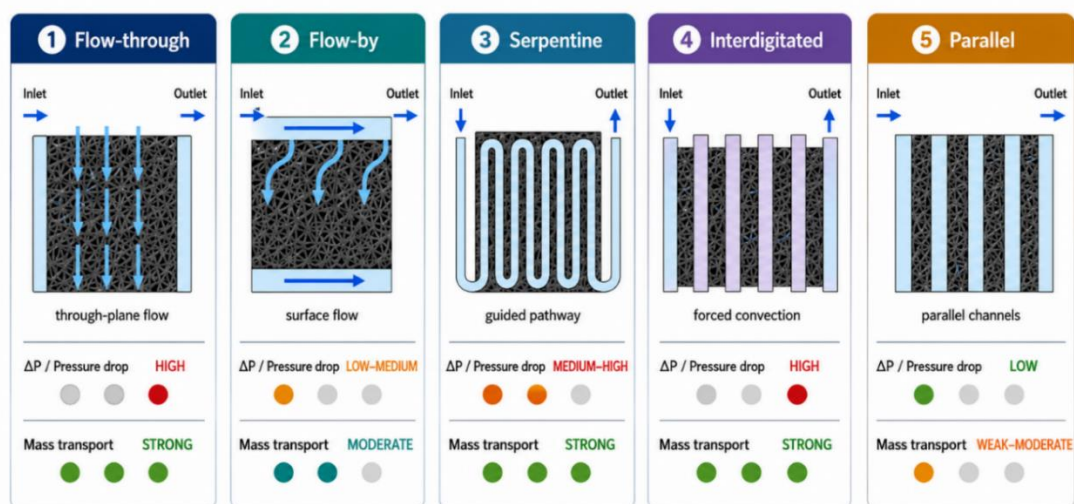


Figure 9. Main flow-field configurations and transport trade-offs in VRFB stacks

The trends shown in Figure 9 are consistent with experimental and modelling studies on flow-field effects in redox flow batteries. Flow-through operation can enhance electrolyte-fiber contact because electrolyte is forced through the porous electrode, but this usually increases hydraulic resistance. Flow-by operation reduces direct through-plane hydraulic resistance, although electrolyte penetration and utilization of the full electrode thickness may be less uniform. Serpentine and interdigitated flow fields can improve reactant distribution and forced convection in the electrode, but their pressure-drop penalty depends strongly on channel and land geometry, active area and flow rate. Parallel channels usually offer lower pressure drop, but they can suffer from flow maldistribution and underutilized electrode regions. These results support the view that no single flow-field design is universally superior; the optimal design depends on the balance between mass transport, pressure drop and pumping energy.

Electrode compression is a coupled electrochemical and hydraulic factor. It affects contact resistance, electrode thickness, porosity and permeability [80]. Higher compression can improve contact between electrode, current collector and flow frame. This can reduce ohmic losses. However, high compression can block pores and increase pressure drop. It can also change local flow distribution. Therefore, compression should be optimized together with flow-field geometry and electrode structure [81].

Stack design determines the power scale of the VRFB system. A stack contains multiple cells connected electrically and hydraulically. Increasing the number of cells can increase voltage and power. However, larger stacks create more complex flow-distribution problems [21]. Each cell should receive a similar electrolyte flow rate. Uneven flow distribution can cause different local SOC, different polarization behavior and uneven thermal profiles [32]. This reduces stack efficiency and long-term reliability [85].

Kilowatt-scale stack studies show that scaling a VRFB is not only a matter of increasing cell number or active area [85]. Large stacks require careful design of manifolds, channels, seals, compression plates, current collectors and flow distribution paths [32]. Hydraulic balance becomes more difficult at larger scale. Electrical resistance and shunt currents also become more important [32]. Therefore, stack engineering is a separate research area, not only an extension of single-cell testing.

Computational fluid dynamics is widely used to study VRFB flow behavior. CFD models can predict velocity fields, pressure distribution, concentration gradients and reactant utilization [20]. They can also compare different channel patterns before experimental fabrication. This reduces trial-and-error design. CFD-based studies have shown that optimized flow fields can

improve performance and reduce system cost by lowering pressure drop and improving electrolyte distribution [83].

Topology optimization is a modern approach for flow-field design. Instead of selecting a traditional channel pattern, the channel geometry is computationally optimized for target functions such as low pressure drop, uniform concentration distribution and high electrochemical performance. Three-dimensional flow-field optimization is especially important because transport inside VRFB electrodes is not purely two-dimensional. This approach may help design next-generation flow fields with better reactant distribution and lower pumping loss [86].

Flow-rate control is another important system-level strategy. Fixed flow rate is simple, but it may not be optimal during the whole charge–discharge cycle [84]. The reactant concentration and SOC change during operation. Therefore, the required flow rate also changes. Output feedback control and optimized flow-rate control can reduce power losses and improve efficiency [28]. This is important for long-duration VRFB systems where auxiliary energy consumption accumulates over many hours [32].

Thermal management must also be considered. VRFB performance is temperature-dependent. Temperature affects electrolyte viscosity, ionic conductivity, redox kinetics and precipitation risk [34],[15]. Heat can be generated by ohmic losses, pumping work and electrochemical polarization. In large stacks, temperature gradients may develop if heat removal is insufficient [20],[32]. High temperature can improve kinetics but may reduce electrolyte stability. Low temperature can increase viscosity and reduce mass transport. Therefore, thermal management links electrolyte chemistry with stack engineering [34],[32].

System engineering also includes balance-of-plant components. These include pumps, reservoirs, pipes, valves, sensors, heat exchangers, power electronics and control systems [87],[32]. These components do not directly store energy. However, they affect reliability, efficiency and cost. Poor pump selection can increase parasitic loss. Poor sensor control can lead to SOC imbalance. Poor thermal control can accelerate electrolyte instability [84]. Therefore, practical VRFB design requires both electrochemical and mechanical optimization [28].

Efficiency analysis must include coulombic efficiency, voltage efficiency and system energy efficiency. Coulombic efficiency is mainly affected by crossover and side reactions. Voltage efficiency is affected by activation, ohmic and mass-transport losses. System energy efficiency also includes pumping loss and auxiliary consumption [84],[28]. This means that cell-level efficiency can be higher than real system efficiency. For practical systems, hydraulic and balance-of-plant losses must be included [32].

Flow-field design is linked to membrane and electrode behavior. A highly selective membrane can reduce crossover, but it may increase ohmic resistance [16],[17]. A highly active electrode can reduce activation loss, but poor flow distribution can still cause concentration polarization [19]. A thick felt electrode can provide larger surface area, but it may increase pressure drop under compression [80],[85]. Therefore, stack performance is controlled by interactions among membrane, electrode, electrolyte and flow design [16],[21].

A frequent limitation in flow-field studies is the use of small laboratory cells. Small cells are useful for understanding basic trends. However, they do not fully represent stack-scale flow distribution, manifold losses, shunt currents or thermal gradients [21],[85]. This creates a scale-up gap. A flow design that works well in a small cell may not perform the same way in a large stack. Therefore, single-cell studies should be followed by stack-level validation [32].

Another limitation is inconsistent reporting of hydraulic data. Many studies report current density, voltage efficiency and energy efficiency. Fewer studies provide detailed pressure drop, pumping energy, electrolyte viscosity, electrode permeability and flow distribution data [20],[83]. This makes comparison difficult. Future studies should report both electrochemical and hydraulic metrics. This will make it easier to identify designs that are truly efficient at system level [28].

In summary, flow-field and stack design determine how efficiently the electrolyte is delivered to active electrode sites. Flow-through designs can improve reactant access but may

increase pressure drop. Flow-by and channel-based designs can reduce hydraulic resistance but require careful control of flow distribution [20],[82]. Pumping loss, electrode compression, stack size and temperature strongly affect system efficiency [32],[28]. Future VRFB stack engineering should focus on low-resistance flow fields, uniform electrolyte distribution, optimized compression, adaptive flow-rate control, thermal management and stack-level validation under practical long-duration operating conditions [21],[84].

7. Capacity decay and performance diagnosis

Usable discharge capacity can decline during cycling or storage even when the principal vanadium redox reactions remain reversible [10]. Crossover, side reactions, water transfer and state-of-charge mismatch can alter the balance and composition of the two electrolytes [11]. This loss must be distinguished from efficiency: a cell can retain a high short-term coulombic efficiency while its accessible capacity decreases over longer operation [11],[12]. Capacity retention should therefore be tracked together with CE, VE, EE and electrolyte composition [10].

Coulombic efficiency is related to charge loss during cycling. It is usually defined as the ratio between discharge capacity and charge capacity. Low coulombic efficiency can indicate crossover, side reactions or parasitic reactions [11]. Voltage efficiency reflects voltage losses during charge and discharge. It is affected by activation polarization, ohmic resistance and mass-transport limitation [10]. Energy efficiency is the product of coulombic efficiency and voltage efficiency. It is therefore affected by both charge loss and voltage loss [88].

The basic relationships are:

$$CE = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}}$$

$$VE = \frac{V_{\text{discharge}}}{V_{\text{charge}}}$$

$$EE = CE \times VE$$

These indicators are useful but not sufficient alone. CE mainly reflects charge balance. VE mainly reflects polarization. EE reflects overall electrochemical energy conversion. Capacity retention reflects how much usable capacity remains after cycling [10],[11]. A complete diagnosis must therefore consider all four parameters.

Vanadium crossover is one of the most important causes of capacity decay. It occurs when vanadium species pass through the membrane from one half-cell to the other [16]. Crossover changes the oxidation-state distribution in both electrolytes. It also creates self-discharge reactions and chemical imbalance [10],[11]. Over repeated cycles, this reduces the usable capacity even if the total amount of vanadium in the system remains nearly constant [12].

Different vanadium species have different crossover behavior. Their transport depends on charge, size, hydration structure, membrane type, concentration gradient and electric field [31]. Cation-exchange membranes can conduct protons efficiently but may also allow vanadium cations to pass. Anion-exchange membranes can suppress cation crossover by electrostatic repulsion, but they may have higher resistance or lower acid stability [16],[17]. Therefore, membrane crossover is directly linked to both capacity decay and efficiency trade-offs [11].

Water transfer also contributes to capacity decay. Water can migrate through the membrane by osmosis, electro-osmotic drag and hydraulic pressure difference [31]. This changes electrolyte volume in the positive and negative tanks. As a result, vanadium concentration, acid concentration and state of charge become unbalanced [11],[12]. Water imbalance can also affect viscosity, conductivity and precipitation risk [33]. Thus, water management is part of capacity-decay control.

Side reactions are another important cause. Hydrogen evolution can occur at the negative electrode under unsuitable conditions. Oxygen evolution can occur at the positive electrode at high

potentials [10],[88]. These reactions consume charge without contributing to useful energy storage. They also change the oxidation-state balance between the two electrolytes [11],[88]. Side reactions may become more severe at high current density, high upper voltage, high SOC or poor electrode kinetics [89].

The upper voltage limit strongly affects VRFB reliability. Operating at a higher voltage can increase usable capacity in the short term. However, it can also increase side reactions and accelerate performance degradation [88]. Reliability studies show that the upper-limit voltage should be selected carefully. A wider voltage window is not always beneficial if it reduces long-term stability [89]. Therefore, operating protocol is as important as material selection.

These mechanisms show that capacity decay in VRFBs should be interpreted as a coupled degradation process rather than as a single-component failure. Membrane crossover, water transfer, side reactions and SOC imbalance can reinforce one another during cycling, leading to earlier voltage cutoffs and lower usable capacity. Therefore, capacity-decay diagnosis should combine efficiency analysis with electrolyte monitoring, volume tracking, SOC estimation and rebalancing tests.

Electrolyte imbalance is a central concept in capacity decay. It means that the two half-cell electrolytes no longer have matched state of charge, volume or active-species distribution [11],[12]. Imbalance can result from crossover, side reactions and water migration. It can also result from unequal flow, poor mixing or operating errors. Once imbalance develops, the cell reaches the charge or discharge cutoff earlier. The apparent capacity decreases even if active material is still present [13].

State of charge monitoring is essential for diagnosing capacity decay. In VRFBs, SOC is not only a battery-management parameter. It is also a chemical descriptor of electrolyte composition [11]. SOC can be estimated by voltage, electrolyte potential, spectroscopy, density, conductivity, titration, model-based methods or charge balance. Each method has advantages and limitations. Voltage-based methods are simple but may be inaccurate near flat voltage regions or under polarization. Model-based methods require reliable parameters and validation [12].

The cumulated charge method can be used to estimate capacity and SOC under rebalancing conditions. This approach connects charge throughput, electrolyte volume and capacity behavior [12]. It is useful because VRFB electrolytes are external and can be sampled, mixed or rebalanced. However, SOC estimation must account for crossover, side reactions and volume change. Otherwise, calculated SOC may differ from the real chemical state of the electrolytes [11].

Capacity decay may be reversible, irreversible or partially reversible. Reversible capacity loss is often related to electrolyte imbalance. It can be recovered by remixing, rebalancing or correcting SOC mismatch [12]. Irreversible capacity loss may result from severe precipitation, electrolyte contamination, component degradation or permanent loss of active material [11],[90]. In practice, both types may occur together. Therefore, diagnosis should identify whether the lost capacity can be recovered [13].

Electrolyte rebalancing is an important recovery strategy. It aims to restore the correct oxidation-state distribution and volume balance between the two electrolytes. Rebalancing can be done by controlled mixing, electrochemical correction, chemical adjustment or optimized remixing procedures [12]. The correct method depends on the cause of imbalance. If imbalance is caused mainly by faradaic imbalance, optimized remixing can recover capacity without replacing the electrolyte. If side reactions or contamination dominate, additional correction may be required [11].

Initial electrolyte imbalance can also be used strategically. Some studies show that intentional initial SOC imbalance may help mitigate capacity decay under selected operating conditions. This approach is based on controlling the direction and effect of crossover or imbalance development. However, it must be optimized carefully. An incorrect initial imbalance can reduce usable capacity or accelerate instability [91]. Therefore, such strategies require system-specific validation.

Impurities can increase capacity fade. They may come from electrolyte raw materials, acid, water, stack components or corrosion products [38]. Some impurity ions can influence redox kinetics, side reactions or electrolyte stability. Recent studies show that capacity fade can be sensitive to electrolyte impurity content. Therefore, electrolyte quality control is important for long-term VRFB operation. At the same time, very high purity can increase cost. Practical systems need impurity tolerance limits and purification standards [90].

Side reaction validation is important because not every capacity loss mechanism is directly visible from cycling curves. Experimental studies can identify whether capacity fade is linked to hydrogen evolution, oxygen evolution, crossover or electrolyte imbalance [88]. This requires combining electrochemical cycling with electrolyte analysis, gas analysis, SOC measurement and post-test characterization. A simple CE/VE/EE plot may not reveal the full degradation mechanism [11].

Performance diagnosis should be performed at both cell and system levels. At the cell level, CE, VE, EE, polarization behavior and capacity retention are important. At the electrolyte level, SOC, vanadium concentration, oxidation-state distribution, volume and impurity content should be monitored [11],[12]. At the system level, flow rate, temperature, pressure drop, upper voltage limit and rebalancing history must be considered [12]. This combined approach is necessary because capacity decay is a coupled electrochemical and engineering problem [11].

A common limitation in VRFB studies is short cycling duration. Many laboratory reports show improved performance for tens or hundreds of cycles. This is useful but not enough for long-duration storage applications [10]. Capacity decay can appear slowly. Membrane crossover, water imbalance, impurity effects and side reactions may become significant only after extended operation [11]. Therefore, future studies should include longer cycling tests and periodic electrolyte diagnostics [90].

Another limitation is inconsistent reporting of rebalancing procedures. Some studies report capacity recovery after remixing. Others do not clearly describe electrolyte volumes, SOC, crossover direction or rebalancing conditions [12]. This makes comparison difficult. Future reports should include clear information on initial electrolyte composition, tank volume, SOC range, voltage limits, current density, flow rate and rebalancing protocol [11],[13]. This will improve reproducibility and practical relevance.

Capacity decay is closely connected to membrane, electrode and electrolyte design. A selective membrane reduces crossover but may increase ohmic loss [16],[17]. A stable electrolyte reduces precipitation and side reactions but may have lower energy density [33]. An active electrode reduces polarization but may promote side reactions if the voltage window is not controlled [18],[88]. Therefore, capacity retention cannot be optimized by one component alone. It requires integrated system design [11].

In summary, capacity decay in VRFBs results from crossover, side reactions, water transfer, electrolyte imbalance, SOC mismatch, impurities and operating conditions [10]. CE, VE and EE are useful performance indicators, but they do not fully explain long-term capacity loss [11]. Reliable diagnosis requires electrolyte monitoring, SOC estimation, volume tracking, side-reaction analysis and rebalancing evaluation [12],[13]. Future VRFB research should focus on distinguishing reversible and irreversible capacity loss, developing standardized diagnostic protocols, improving SOC monitoring and validating rebalancing strategies under practical long-duration operation.

8. Cost, scalability and commercialization perspective

Commercial competitiveness requires the technical advantages of aqueous electrolytes, long service life and separate scaling of energy and power to translate into favorable system economics [8],[32]. The cost boundary must include electrolyte, tanks, stack materials, pumps, power electronics, thermal management and control equipment [26]. Electrolyte cost depends on feedstock price, concentration, purity requirements and the inventory needed for the specified energy

capacity; increasing storage duration at a fixed power rating generally increases that inventory, making vanadium price a major economic variable [26],[27].

The stack cost is also important. The stack contains membranes, porous carbon electrodes, bipolar plates, flow frames, seals and current collectors. The stack mainly determines power output. High power systems need larger electrode area or more cells. This increases material and manufacturing cost [26]. Therefore, VRFB cost has two different dimensions. Energy cost is strongly linked to electrolyte and tank size. Power cost is strongly linked to stack size and balance-of-plant components [27].

This separation of energy and power is a major advantage of VRFBs. In many conventional batteries, increasing storage duration requires adding more battery cells. In VRFBs, storage duration can be increased by increasing electrolyte volume while keeping the same stack power rating [8],[32]. This makes VRFBs attractive for multi-hour and long-duration storage. The economic advantage becomes more relevant when storage duration increases beyond short-duration applications [26].

However, VRFBs usually have lower energy density than lithium-ion batteries. This limits applications where space and mass are critical. Therefore, VRFBs are not ideal for electric vehicles or portable electronics. Their main target is stationary storage. Suitable applications include renewable energy integration, grid balancing, peak shaving, microgrids, backup power and industrial energy management [8]. In these applications, safety, lifetime and scalability can be more important than compactness [32].

Techno-economic assessment is necessary because cell performance alone cannot determine commercial viability. A high-efficiency cell may still be expensive if membrane cost, electrolyte cost or balance-of-plant cost is high [26]. Similarly, a low-cost material may not be useful if it reduces efficiency or lifetime. Therefore, techno-economic analysis should include capital cost, operating cost, efficiency, lifetime, capacity fade, rebalancing, replacement cost and recycling value [27].

Capacity fade has a direct effect on levelized cost. If usable capacity decreases during operation, the system delivers less energy over its lifetime. This increases the levelized cost of storage. Rebalancing can recover part of the lost capacity when the loss is caused by electrolyte imbalance [13]. However, rebalancing also has operational cost and complexity. Therefore, capacity fade and rebalancing must be included in economic models [27].

Electrolyte leasing is often discussed as a possible business model. The reason is simple. Vanadium electrolyte retains material value because vanadium is not consumed during normal operation [26]. Instead of purchasing the full electrolyte inventory, the user may lease it from a supplier or service company. This can reduce upfront capital cost. It can also support electrolyte recovery, reuse and circular management. However, leasing requires stable supply chains, clear ownership models, electrolyte quality control and reliable recovery infrastructure [92].

Electrolyte recycling is another important commercialization pathway. At the end of system life, vanadium electrolyte can potentially be recovered and reused in new VRFB systems [93]. This differs from many battery chemistries where active-material recovery requires complex solid-state recycling. The liquid nature of VRFB electrolyte can simplify recovery and reconditioning [92]. However, recycling still requires control of contamination, oxidation-state balance, concentration and acid composition [38].

Circular economy approaches can improve the sustainability of VRFBs. They can reduce demand for primary vanadium resources. They can also reduce waste and improve lifecycle value [93]. Life cycle assessment studies show that environmental performance depends strongly on electricity mix, material sourcing, vanadium production route, battery lifetime and electrolyte reuse [94]. Therefore, VRFB sustainability should not be judged only by operating safety. It must be assessed over the whole lifecycle [92].

Vanadium supply is a strategic issue. Vanadium is used not only in batteries but also in steel and other industrial sectors [26]. Competition between these markets can influence price and supply

stability. This creates uncertainty for VRFB deployment. Electrolyte leasing, recycling and second-use electrolyte strategies can reduce exposure to raw-material price fluctuations. These approaches are therefore not only environmental strategies. They are also economic risk-management tools [92].

The economic value of a membrane depends on its service life as well as its purchase price. Hydrocarbon ionomers, composites and selective barrier layers offer alternatives to costly PFSA benchmarks [17],[47]. but their benefits depend on control of swelling, oxidative damage, water transport and mechanical failure in acidic vanadium electrolyte. Initial savings can be offset by increased resistance, crossover, rebalancing demand or replacement frequency. Cost comparisons should therefore connect polymer chemistry and fabrication with measured durability and lifecycle performance [27].

Electrode and stack durability are also cost factors. Carbon felt and graphite felt are relatively robust, but modification methods can add cost [19],[26]. Thermal treatment is simple and scalable. Chemical treatment may require acid handling and waste management. Metal oxide, graphene-based or electrografted modifications may improve activity but can increase processing complexity [79],[78]. Therefore, electrode modification should be judged by cost-normalized performance and long-term durability, not only by initial electrochemical improvement [30],[26].

Pumps, tanks, valves, sensors, pipework, thermal management and power electronics contribute to both capital and operating costs [32]. Pumping consumes part of the delivered energy, while inadequate temperature or state-of-charge control can accelerate electrolyte instability and imbalance [84],[28]. Economic evaluation must capture these effects alongside the performance of the stack itself [26].

Scalability is one of the strongest arguments for VRFBs. The technology is well suited for stationary systems where large tanks and external pumps are acceptable [8],[32]. Energy capacity can be increased by adding more electrolyte and larger tanks. Power can be increased by adding more stack area or more cells [5]. This modularity supports deployment at different scales, from microgrids to utility-scale storage. However, scale-up also increases the importance of flow distribution, shunt currents, thermal gradients and maintenance strategy [85].

Large projects are important because they demonstrate technical feasibility beyond laboratory cells. Commercial and demonstration VRFB systems show that the technology can be built at multi-kilowatt, megawatt and multi-hour scale [85],[32]. However, large projects also reveal practical challenges. These include electrolyte management, stack reliability, pump efficiency, maintenance, safety standards, supply-chain stability and cost control [26]. Therefore, commercialization depends on field performance, not only laboratory efficiency.

Although VRFBs have clear advantages for long-duration stationary storage, commercialization depends on more than electrochemical performance alone. The main barriers are connected to electrolyte cost, vanadium supply, membrane crossover, stack durability, pumping losses, capacity fade and field validation. Table 6 summarizes the major commercialization barriers and the corresponding improvements required for practical VRFB deployment.

Table 6 is a qualitative synthesis of commercialization barriers, not a harmonized techno-economic comparison. Indicative values and cost statements depend on the stated system boundary, power and energy rating, discharge duration, operating conditions and source assumptions. They should not be interpreted as a direct ranking of technologies or components.

Table 6

Commercialization barriers and required improvements for VRFB technology

<i>Issue</i>	<i>Current status / indicative data</i>	<i>Main barrier</i>	<i>Required improvement</i>	<i>References</i>
Vanadium electrolyte cost	Electrolyte is a major cost component; vanadium price strongly affects system cost	High CAPEX and price volatility	Electrolyte leasing, reuse, recycling and better electrolyte utilization	[26],[27],[92]
Low energy density	Typical VRFB electrolyte-level energy density is about 20-35 Wh L ⁻¹	Large tank volume and larger footprint	Stable high-concentration electrolytes and wider usable SOC window	[8], [14], [15],

Membrane cost and crossover	Nafion-type membranes are effective but costly; crossover causes self-discharge	Capacity fade, electrolyte imbalance and high membrane cost	Low-cost selective membranes with low resistance and low vanadium permeability	[16], [17], [31]
Stack cost and durability	Stack cost depends on membrane area, electrodes, bipolar plates, flow frames and seals	High power requires larger stack area or more cells	Durable low-cost stack hardware, reliable sealing and uniform compression	[21],[26],[81],[85]
Electrode performance	Carbon/graphite felt electrodes are stable but often kinetically limited	Polarization loss and reduced voltage efficiency	Scalable electrode activation with stable wettability and catalytic activity	[18],[19],[30],[78],[79]
Pumping and balance-of-plant loss	Pumps, tanks, sensors, valves and thermal control are required	Auxiliary energy loss and higher system complexity	Optimized flow fields, pump control and low-pressure-drop stack design	[20],[28],[83],[84]
Capacity fade and rebalancing	Capacity fade results from crossover, side reactions, water transfer and SOC imbalance	Lower lifetime energy output and higher LCOS	SOC monitoring, electrolyte diagnostics and optimized rebalancing/remixing	[10], [11], [12], [13], [27]
Recycling and circular use	Vanadium electrolyte can retain residual material value after system life	Recycling infrastructure and electrolyte quality control are needed	Electrolyte recovery, purification, reuse and circular business models	[92],[93],[94]
Field validation	VRFBs are promising for stationary multi-hour storage	Laboratory results do not always translate to field performance	Long-term stack testing, standardized reporting and real-system validation	[8],[26],[85]

As shown in Table 6, the commercialization of VRFBs requires simultaneous progress in materials, stack engineering and business models. Reducing vanadium-related cost, improving membrane and stack durability, minimizing capacity fade and developing electrolyte recycling or leasing strategies are especially important for lowering lifetime system cost.

Long-duration storage is the key market for VRFBs. The technology becomes more attractive when storage duration is long enough to benefit from independent energy-power scaling [32],[26]. For short-duration applications, lithium-ion batteries can be more competitive because of mature manufacturing and high efficiency. For longer-duration stationary applications, VRFBs can become more competitive if electrolyte cost, stack lifetime and system efficiency are optimized. This is why VRFB commercialization should focus on use cases where safety, lifetime and duration are valued.

The economic value of VRFBs also depends on service stacking. A single VRFB system can provide renewable smoothing, peak shaving, load shifting, backup power and grid support [8],[32]. Combining several services can improve revenue and reduce payback time. However, service stacking requires reliable control algorithms and accurate state-of-charge estimation [87],[12]. It also requires operating strategies that avoid accelerated capacity fade [10],[11]. Therefore, economics and control strategy are closely linked.

Lifecycle assessment provides a broader view of commercialization. Environmental impact depends on raw materials, manufacturing, operation, lifetime, recycling and electricity source [93],[94]. A VRFB with long lifetime and reusable electrolyte can show sustainability advantages. However, these advantages depend on real operating duration and recycling practice. If lifetime is short or electrolyte is not recovered, the environmental benefit is reduced [92]. Therefore, sustainability claims must be supported by lifecycle data.

In summary, VRFB commercialization is controlled by cost, durability, scalability and lifecycle management. The vanadium electrolyte is a major cost driver, but it also has residual value and can support leasing or recycling models [26],[92]. Stack components and balance-of-plant systems also affect both capital and operating cost [32]. VRFBs are most promising for stationary long-duration storage, where safety, long lifetime and independent energy-power scaling are valuable [26]. Future commercialization should focus on reducing electrolyte and membrane cost,

improving stack durability, minimizing capacity fade, lowering pumping losses, developing circular electrolyte business models and validating performance in large practical systems [92].

Relevance to Uzbekistan

Uzbekistan offers a relevant setting for linking vanadium resources with stationary energy storage. The Tebinbulak deposit contains vanadium-bearing titanomagnetite ore, and process assessments have considered vanadium recovery alongside steel production [95]. This establishes a resource-development opportunity, although a mineral occurrence or an iron-ore reserve should not be equated with an established supply of battery-grade vanadium electrolyte. On the demand side, the Uzbekistan Solar and Renewable Energy Storage project provides a concrete example of storage integration: in May 2024, the World Bank Group announced financing for a 250 MW solar plant with a 63 MW battery energy storage system in Bukhara [96]. This project demonstrates the policy and investment relevance of storage; selecting VRFBs for a particular application still requires a separate assessment of discharge duration, site conditions, grid services and lifetime cost.

Local research also provides a basis for circular electrolyte development. Iskandarov and co-workers at the Arifov Institute of Ion-Plasma and Laser Technologies investigated the reuse of V_2O_5 recovered from a catalyst previously employed in sulfuric-acid production for vanadium flow-battery electrolyte [97]. An actionable next step is to compare such recovered feedstock with a high-purity reference under identical electrolyte composition and cell conditions, including trace-metal analysis, precipitation tests, side-reaction monitoring and cycling before and after a defined rebalancing step. For Uzbekistan and the wider Central Asian supply chain, this would connect resource recovery and purification with measurable electrolyte quality and system performance, rather than assuming that local mineral availability alone guarantees a cost advantage.

9. Future outlook and research gaps

Progress in VRFB materials should be judged by whether a component improvement remains useful after its effects on resistance, crossover, auxiliary energy and maintenance are included. We propose seven linked research priorities that turn the component–system perspective of this review into measurable tests. The experimental examples in Figures 4b and 7 illustrate the need for this approach: a reduction in vanadium transport or an increase in coulombic efficiency does not by itself establish an improvement in delivered energy [43].

1 Separate membrane chemistry from geometry

Use a two-stage design in which sulfonation degree, crosslinking or filler chemistry is first varied at matched conditioned thickness, followed by a thickness series for the most promising chemistry. Keep electrolyte composition, temperature, SOC window and current density fixed, and document swelling, acid uptake and defects. Report in-plane conductivity and through-plane area resistance separately. A useful material improvement should remain evident in full-cell energy and capacity retention after resistance and crossover have both been considered [31],[46],[47].

2 Define an electrolyte operating envelope

Evaluate candidate formulations across a matrix of temperature, SOC and residence time that includes both circulation and idle storage. Measure precipitation onset, viscosity, conductivity and vanadium speciation, and compare impurity-containing or recovered feedstocks with a high-purity reference. Test whether a wider stability window is offset by slower mass transport, membrane swelling or greater side-reaction currents. Report the stable operating envelope rather than a single maximum vanadium concentration [14],[15],[33],[97].

3 Measure the durability of electrode benefits

Compare a modified felt with an identically compressed untreated control using both electrochemical and hydraulic measurements before and after extended cycling. Link changes in polarization to surface chemistry, wetting, pore accessibility, pressure drop and any catalyst loss. If an initially active coating increases pumping demand or loses material into the electrolyte, assess that penalty explicitly. The decision criterion is sustained net performance at a stated treatment and replacement cost [19],[30],[77],[79].

4 Connect membrane selection to stack hydraulics

After selecting a membrane–electrode pair, vary flow rate and compression in a controlled cell-to-stack scale-up study. Track pressure drop, flow maldistribution, temperature and cell-voltage spread alongside stack energy and pump electricity. A lower resistance measured in a small cell should not be accepted as a scale-up benefit until sealing, shunt-current and distribution losses are quantified under the intended duty cycle [21],[81],[84],[85].

5 Quantify what rebalancing actually recovers

Measure discharge capacity immediately before and after a defined rebalancing procedure under the same reference conditions. Report the recovered fraction together with electrolyte volume, SOC, vanadium concentration and relevant gas or impurity measurements. Residual loss should trigger further diagnosis of inaccessible active material, continuing imbalance and component deterioration; it should not automatically be labeled irreversible degradation. This distinction connects a maintenance action with a testable capacity-loss mechanism [10]–[13].

6 Evaluate lifetime value at the required storage duration

Compare candidate systems at matched power rating, discharge duration and usable energy delivery. Include membrane and stack replacement, electrolyte rebalancing, pumping, availability and end-of-life electrolyte value, with sensitivity ranges for vanadium price and service life. For locally recovered vanadium, add purification yield, reagent demand and waste treatment to the cost boundary. A lower material price is beneficial only if it survives these operational and processing costs [26],[27],[91],[97].

7 Make results transferable between laboratories

Report a common minimum dataset covering electrolyte formulation, membrane pretreatment and conditioned thickness, electrode compression, active area, SOC and voltage limits, current density, flow conditions, pressure drop, auxiliary energy, cycle duration and the rebalancing procedure. Include independent specimen or cell replicates and distinguish measurement scatter from fitting uncertainty. Publishing the numerical data behind comparison figures would permit recalculation of transport ratios and efficiency metrics without estimating values from images.

These priorities place polymer chemistry at the center of a reproducible validation sequence: molecular design and conditioning are connected first to transport and cell response, then to stack operation and lifetime value. For Uzbekistan, the same framework provides a route from vanadium recovery and electrolyte preparation to a demonstrable storage capability. The practical objective is to identify combinations that deliver stable energy under a defined duty cycle, with transparent evidence for the source of each improvement.

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Declaration of generative AI and AI-assisted technologies

During the preparation of this manuscript, the authors used ChatGPT (OpenAI, GPT-5.6 Sol) to assist with text translation and the creation of selected schematic figures. All AI-assisted text and graphical content was critically reviewed, checked for scientific accuracy, and revised as necessary by the authors. Particular attention was paid to scientific terminology, chemical notation, figure labels, and consistency with the cited literature. The authors take full responsibility for the accuracy, integrity, and final content of the manuscript and its figures.

References

- [1] M. Staadecker, J. Szinai, P. A. Sánchez-Pérez, S. Kurtz, and P. Hidalgo-Gonzalez, “The value of long-duration energy storage under various grid conditions in a zero-emissions future,” *Nat. Commun.*, vol. 15, no. 1, p. 9501, 2024, doi: 10.1038/s41467-024-53274-6.
- [2] A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, “Redox flow batteries: a

- review,” *J. Appl. Electrochem.*, vol. 41, no. 10, pp. 1137–1164, 2011, doi: 10.1007/s10800-011-0348-2.
- [3] P. Leung, X. Li, C. Ponce de León, L. Berlouis, C. T. J. Low, and F. C. Walsh, “Progress in redox flow batteries, remaining challenges and their applications in energy storage,” *RSC Adv.*, vol. 2, no. 27, pp. 10125–10156, 2012, doi: 10.1039/C2RA21342G.
- [4] M. He, D. Chartouni, D. Landmann, and S. Colombi, “Safety Aspects of Stationary Battery Energy Storage Systems,” 2024. doi: 10.3390/batteries10120418.
- [5] A. Parasuraman, T. M. Lim, C. Menictas, and M. Skyllas-Kazacos, “Review of material research and development for vanadium redox flow battery applications,” *Electrochim. Acta*, vol. 101, pp. 27–40, 2013, doi: <https://doi.org/10.1016/j.electacta.2012.09.067>.
- [6] M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, and M. A. Green, “New All-Vanadium Redox Flow Cell,” *J. Electrochem. Soc.*, vol. 133, no. 5, p. 1057, 1986, doi: 10.1149/1.2108706.
- [7] M. Skyllas-Kazacos and F. Grossmith, “Efficient Vanadium Redox Flow Cell,” *J. Electrochem. Soc.*, vol. 134, no. 12, p. 2950, 1987, doi: 10.1149/1.2100321.
- [8] A. Aluko and A. Knight, “A Review on Vanadium Redox Flow Battery Storage Systems for Large-Scale Power Systems Application,” *IEEE Access*, vol. 11, pp. 13773–13793, 2023, doi: 10.1109/ACCESS.2023.3243800.
- [9] A. Barzigar and E. Ebadati, “A Comprehensive Review of Vanadium Redox Flow Batteries: Principles, Benefits, and Applications,” *Next Res.*, p. 100767, 2025, doi: 10.1016/j.nexres.2025.100767.
- [10] X.-Z. Yuan *et al.*, “A review of all-vanadium redox flow battery durability: Degradation mechanisms and mitigation strategies,” *Int. J. Energy Res.*, vol. 43, pp. 6599–6638, 2019, doi: 10.1002/er.4607.
- [11] Y. Wang, A. Mu, W. Wang, B. Yang, and J. Wang, “A Review of Capacity Decay Studies of All-vanadium Redox Flow Batteries: Mechanism and State Estimation,” *ChemSusChem*, vol. 17, p. e202301787, 2024, doi: 10.1002/cssc.202301787.
- [12] H. Jung and S. Lee, “A Study on Capacity and State of Charge Estimation of VRFB Systems Using Cumulated Charge and Electrolyte Volume under Rebalancing Conditions,” *Energies*, vol. 16, p. 2478, 2023, doi: 10.3390/en16052478.
- [13] T. Puleston, A. Trovò, G. Marini, M. Serra, R. Costa-Castelló, and M. Guarnieri, “Design and experimental validation of an optimal remixing procedure for vanadium flow batteries affected by faradaic imbalance,” *J. Power Sources*, vol. 624, p. 235487, 2024, doi: <https://doi.org/10.1016/j.jpowsour.2024.235487>.
- [14] Z. Yu *et al.*, “Electrolyte engineering for efficient and stable vanadium redox flow batteries,” *Energy Storage Mater.*, vol. 69, p. 103404, 2024, doi: <https://doi.org/10.1016/j.ensm.2024.103404>.
- [15] Z. Wan *et al.*, “Unravel crystallization kinetics of V(V) electrolytes for all-vanadium redox flow battery by in situ Raman spectroscopy,” *Adv. Compos. Hybrid Mater.*, vol. 6, no. 3, p. 119, 2023, doi: 10.1007/s42114-023-00635-2.
- [16] J. Ye, L. Xia, H. Li, F. P. G. de Arquer, and H. Wang, “The Critical Analysis of Membranes toward Sustainable and Efficient Vanadium Redox Flow Batteries,” *Adv. Mater.*, vol. 36, no. 28, p. 2402090, Jul. 2024, doi: <https://doi.org/10.1002/adma.202402090>.
- [17] T. T. K. Huynh, T. Yang, N. P. S. Y. Yang, J. Ye, and H. Wang, “Construction of High-Performance Membranes for Vanadium Redox Flow Batteries: Challenges, Development, and Perspectives,” *Nano-Micro Lett.*, vol. 17, no. 1, p. 260, 2025, doi: 10.1007/s40820-025-01736-x.
- [18] K. J. Kim, M.-S. Park, Y.-J. Kim, J. H. Kim, S. X. Dou, and M. Skyllas-Kazacos, “A technology review of electrodes and reaction mechanisms in vanadium redox flow batteries,” *J. Mater. Chem. A*, vol. 3, no. 33, pp. 16913–16933, 2015, doi: 10.1039/C5TA02613J.
- [19] L. Li *et al.*, “Recent advances and perspectives of practical modifications of vanadium redox flow battery electrodes,” *Green Chem.*, vol. 26, no. 11, pp. 6339–6360, 2024, doi: 10.1039/D4GC00584H.
- [20] I. Aramendia, U. Fernandez-Gamiz, A. Martinez-San-Vicente, E. Zulueta, and J. M. Lopez-Guede, “Vanadium Redox Flow Batteries: A Review Oriented to Fluid-Dynamic Optimization,” *Energies*, vol. 14, p. 176, 2021, doi: 10.3390/en14010176.
- [21] J. Sun, Z. Guo, L. Pan, X. Fan, L. Wei, and T. Zhao, “Redox flow batteries and their stack-scale flow fields,” *Carbon Neutrality*, vol. 2, no. 1, p. 30, 2023, doi: 10.1007/s43979-023-00072-6.
- [22] K. Mongird *et al.*, “Energy Storage Technology and Cost Characterization Report,” Pacific Northwest National Laboratory, Richland, WA, 2019. doi: 10.2172/1573487.
- [23] B. Dunn, H. Kamath, and J.-M. Tarascon, “Electrical energy storage for the grid: a battery of choices,” *Science (80-.)*, vol. 334, no. 6058, pp. 928–935, 2011, doi: 10.1126/science.1212741.
- [24] International Renewable Energy Agency (IRENA), “Sodium-ion batteries: A technology brief,” International Renewable Energy Agency, Abu Dhabi, 2025. [Online]. Available: <https://www.irena.org/Publications/2025/Nov/Sodium-ion-batteries-A-technology-brief>
- [25] H. R. Jiang, J. Sun, L. Wei, M. C. Wu, W. Shyy, and T. S. Zhao, “A high power density and long cycle life vanadium redox flow battery,” *Energy Storage Mater.*, vol. 24, pp. 529–540, 2020, doi: 10.1016/j.ensm.2019.07.005.
- [26] N. Poli, C. Bonaldo, M. Moretto, and M. Guarnieri, “Techno-economic assessment of future vanadium flow batteries based on real device/market parameters,” *Appl. Energy*, vol. 362, p. 122954, 2024, doi:

- 10.1016/j.apenergy.2024.122954.
- [27] K. E. Rodby, T. J. Carney, Y. A. Gandomi, J. L. Barton, R. M. Darling, and F. R. Brushett, "Assessing the leveled cost of vanadium redox flow batteries with capacity fade and rebalancing," *J. Power Sources*, vol. 460, p. 227958, 2020, doi: 10.1016/j.jpowsour.2020.227958.
- [28] N. Ra, A. Dutta, and A. Bhattacharjee, "Optimizing vanadium redox flow battery system power loss using particle swarm optimization technique under different operating conditions," *Int. J. Energy Res.*, vol. 46, no. 12, pp. 17346–17361, Oct. 2022, doi: <https://doi.org/10.1002/er.8402>.
- [29] A. Bourke *et al.*, "Review—Electrode Kinetics and Electrolyte Stability in Vanadium Flow Batteries," *J. Electrochem. Soc.*, vol. 170, Mar. 2023, doi: 10.1149/1945-7111/acbc99.
- [30] N. Remmler and M. Bron, "Recent Progress in our Understanding of the Degradation of Carbon-Based Electrodes in Vanadium Redox Flow Batteries – Current Status and Next Steps," *ChemElectroChem*, vol. 11, no. 15, p. e202400127, Aug. 2024, doi: <https://doi.org/10.1002/celc.202400127>.
- [31] Y. Yang, Q. Wang, S. Xiong, and Z. Song, "Research progress on optimized membranes for vanadium redox flow batteries," *Inorg. Chem. Front.*, vol. 11, pp. 4049–4079, 2024, doi: 10.1039/D4QI00520A.
- [32] V. V. Viswanathan *et al.*, "An Overview of the Design and Optimized Operation of Vanadium Redox Flow Batteries for Durations in the Range of 4–24 Hours," 2023. doi: 10.3390/batteries9040221.
- [33] L. Cao, M. Skyllas-Kazacos, C. Menictas, and J. Noack, "A review of electrolyte additives and impurities in vanadium redox flow batteries," *J. Energy Chem.*, vol. 27, pp. 1269–1291, 2018, doi: 10.1016/j.jechem.2018.04.007.
- [34] T. D. Nguyen *et al.*, "Advanced Electrolyte Formula for Robust Operation of Vanadium Redox Flow Batteries at Elevated Temperatures," *Small*, vol. 20, no. 27, p. 2311771, Jul. 2024, doi: <https://doi.org/10.1002/smll.202311771>.
- [35] L. Li *et al.*, "A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage," *Adv. Energy Mater.*, vol. 1, no. 3, pp. 394–400, May 2011, doi: <https://doi.org/10.1002/aenm.201100008>.
- [36] S. Kim *et al.*, "1 kW/1 kWh advanced vanadium redox flow battery utilizing mixed acid electrolytes," *J. Power Sources*, vol. 237, pp. 300–309, 2013, doi: <https://doi.org/10.1016/j.jpowsour.2013.02.045>.
- [37] W. Tian *et al.*, "A Review of Electrolyte Additives in Vanadium Redox Flow Batteries," *Materials (Basel)*, vol. 16, p. 4582, 2023, doi: 10.3390/ma16134582.
- [38] H. Zhou, W. Liu, D. Hao, and others, "Recent Advances and Perspectives of Impurity Ions and Additives for the Electrolyte of Vanadium Redox Flow Battery," *Energy & Fuels*, vol. 38, 2024, doi: 10.1021/acs.energyfuels.4c04194.
- [39] Z. Wang *et al.*, "An Electrolyte with Elevated Average Valence for Suppressing the Capacity Decay of Vanadium Redox Flow Batteries," *ACS Cent. Sci.*, vol. 9, no. 1, pp. 56–63, Jan. 2023, doi: 10.1021/acscentsci.2c01112.
- [40] D. Dürkop, H. Widdecke, C. Schilde, U. Kunz, and A. Schmiemann, "Polymer Membranes for All-Vanadium Redox Flow Batteries: A Review," 2021. doi: 10.3390/membranes11030214.
- [41] S. Zhai *et al.*, "Highly selective proton exchange membranes for vanadium redox flow batteries enabled by the incorporation of water-insoluble phosphotungstic acid-metal organic framework nanohybrids," *J. Memb. Sci.*, vol. 645, p. 120214, 2022, doi: <https://doi.org/10.1016/j.memsci.2021.120214>.
- [42] K. K. W. Knehr, E. Agar, C. R. Dennison, A. R. Kalidindi, "A Transient Vanadium Flow Battery Model Incorporating Vanadium Crossover and Water Transport through the Membrane Membrane," vol. 159, no. 9, pp. A1446–A1459, 2012, doi: 10.1149/2.017209jes.
- [43] A. Rizzuti *et al.*, "Optimized Sulfonated Poly(Ether Ether Ketone) Membranes for In-House Produced Small-Sized Vanadium Redox Flow Battery Set-Up," *Membranes (Basel)*, vol. 14, no. 8, 2024, doi: 10.3390/membranes14080176.
- [44] Y. Zhang, M. Liu, H. Liu, and others, "High ion-selective SPEEK-based composite membrane containing zwitterionic polymer-modified MOFs for vanadium redox flow battery," *Chem. Eng. J.*, vol. 516, p. 164246, 2025, doi: 10.1016/j.cej.2025.164246.
- [45] M. Cecchetti, T. A. Ebaugh, L. Bonville, R. Maric, A. Casalegno, and M. Zago, "Development of a Vanadium Redox Flow Battery Operating with Thin Membrane Coupled with a Highly Selective and Stable Silica-Based Barrier Layer," *Energy Technol.*, vol. 12, no. 8, p. 2400410, Aug. 2024, doi: <https://doi.org/10.1002/ente.202400410>.
- [46] P. Qian, H. Wang, Y. Jiang, Y. Zhou, and H. Shi, "High-performance composite membrane based on synergistic main-chain/side-chain proton conduction channels for the vanadium redox flow battery," *J. Mater. Chem. A*, vol. 9, pp. 4240–4252, 2021, doi: 10.1039/D0TA11037J.
- [47] S. Jiang, Y. Li, H. Wang, L. Li, Q. Wei, and H. Shi, "High-performance SPEEK composite membrane with ultrahigh selectivity enabled by sulfonated PANI for vanadium flow battery," *J. Memb. Sci.*, vol. 699, p. 122663, 2024, doi: <https://doi.org/10.1016/j.memsci.2024.122663>.
- [48] J. C. Duburg, B. Chen, S. Holdcroft, T. J. Schmidt, and L. Gubler, "Design of polybenzimidazolium membranes for use in vanadium redox flow batteries," *J. Mater. Chem. A*, vol. 12, no. 11, pp. 6387–6398, 2024, doi:

- 10.1039/D3TA07212F.
- [49] R. S. L. Yee, K. Zhang, and B. P. Ladewig, "The Effects of Sulfonated Poly(ether ether ketone) Ion Exchange Preparation Conditions on Membrane Properties.," *Membranes (Basel)*, vol. 3, no. 3, pp. 182–195, Aug. 2013, doi: 10.3390/membranes3030182.
- [50] C. Sun, J. Chen, H. Zhang, X. Han, and Q. Luo, "Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery," *J. Power Sources*, vol. 195, no. 3, pp. 890–897, 2010, doi: 10.1016/j.jpowsour.2009.08.041.
- [51] J. Ye *et al.*, "Hybrid Membranes Dispersed with Superhydrophilic TiO₂ Nanotubes Toward Ultra-Stable and High-Performance Vanadium Redox Flow Batteries," *Adv. Energy Mater.*, vol. 10, no. 22, p. 1904041, 2020, doi: 10.1002/aenm.201904041.
- [52] M. A. Aziz, D. Han, and S. Shanmugam, "Ultrahigh Proton/Vanadium Selective and Durable Nafion/TiZrO₄ Composite Membrane for High-Performance All-Vanadium Redox Flow Batteries," *ACS Sustain. Chem. Eng.*, vol. 9, pp. 11041–11051, 2021, doi: 10.1021/acssuschemeng.1c02466.
- [53] B. Yin, Z. Li, W. Dai, L. Wang, L. Yu, and J. Xi, "Highly branched sulfonated poly(fluorenyl ether ketone sulfone)s membrane for energy efficient vanadium redox flow battery," *J. Power Sources*, vol. 285, pp. 109–118, 2015, doi: 10.1016/j.jpowsour.2015.03.102.
- [54] J. Li *et al.*, "Stable covalent cross-linked polyfluoro sulfonated polyimide membranes with high proton conductance and vanadium resistance for application in vanadium redox flow batteries," *J. Mater. Chem. A*, vol. 9, pp. 24704–24711, 2021, doi: 10.1039/D1TA07248J.
- [55] B. Zhang *et al.*, "Advanced anion exchange membranes with selective swelling-induced ion transport channels for vanadium flow battery application," *J. Memb. Sci.*, vol. 642, p. 119985, 2022, doi: 10.1016/j.memsci.2021.119985.
- [56] L. Liu *et al.*, "An overview of amphoteric ion exchange membranes for vanadium redox flow batteries," *J. Mater. Sci. Technol.*, vol. 69, pp. 212–227, 2021, doi: 10.1016/j.jmst.2020.08.032.
- [57] Y. Ma *et al.*, "Cyclodextrin templated nanoporous anion exchange membrane for vanadium flow battery application," *J. Memb. Sci.*, vol. 586, pp. 98–105, 2019, doi: 10.1016/j.memsci.2019.05.055.
- [58] X. Lou *et al.*, "Highly Efficient and Low Cost SPEEK/TiO₂ Nanocomposite Membrane for Vanadium Redox Flow Battery," *J. Nanosci. Nanotechnol.*, vol. 19, no. 4, pp. 2247–2252, 2019, doi: 10.1166/jnn.2019.16467.
- [59] L. Zhao *et al.*, "SPEEK/PVDF binary membrane as an alternative proton-exchange membrane in vanadium redox flow battery application," *High Perform. Polym.*, vol. 29, no. 2, pp. 127–132, 2017, doi: 10.1177/0954008316631595.
- [60] W. Dai, Y. Shen, Z. Li, L. Yu, J. Xi, and X. Qiu, "SPEEK/Graphene oxide nanocomposite membranes with superior cyclability for highly efficient vanadium redox flow battery," *J. Mater. Chem. A*, vol. 2, pp. 12423–12432, 2014, doi: 10.1039/C4TA02124J.
- [61] X. Lou *et al.*, "Functionalized carbon black modified sulfonated polyether ether ketone membrane for highly stable vanadium redox flow battery," *J. Memb. Sci.*, vol. 643, p. 120015, 2022, doi: 10.1016/j.memsci.2021.120015.
- [62] L. Ding and L. Wang, "Preparation of novel structure polybenzimidazole with thiophene ring for high performance proton conducting membrane in vanadium flow battery," *J. Power Sources*, vol. 564, p. 232858, 2023, doi: 10.1016/j.jpowsour.2023.232858.
- [63] Y. Wan, J. Sun, H. Jiang, X.-Z. Fan, and T. Zhao, "A highly-efficient composite polybenzimidazole membrane for vanadium redox flow battery," *J. Power Sources*, vol. 489, p. 229502, 2021, doi: 10.1016/j.jpowsour.2021.229502.
- [64] D. Chen *et al.*, "Polybenzimidazole membrane with dual proton transport channels for vanadium flow battery applications," *J. Memb. Sci.*, vol. 586, pp. 202–210, 2019, doi: 10.1016/j.memsci.2019.05.076.
- [65] D. Zhang, Q. Wang, S. Peng, X. Yan, X. Wu, and G. He, "An interface-strengthened cross-linked graphene oxide/Nafion212 composite membrane for vanadium flow batteries," *J. Memb. Sci.*, vol. 587, p. 117189, 2019, doi: 10.1016/j.memsci.2019.117189.
- [66] Q. Dai *et al.*, "Thin-film composite membrane breaking the trade-off between conductivity and selectivity for a flow battery," *Nat. Commun.*, vol. 11, no. 1, p. 13, 2020, doi: 10.1038/s41467-019-13704-2.
- [67] H. Zhang, H. Zhang, X. Li, Z. Mai, and J. Zhang, "Nanofiltration (NF) membranes: The next generation separators for all vanadium redox flow batteries (VRBs)?," *Energy Environ. Sci.*, vol. 4, pp. 1676–1679, 2011, doi: 10.1039/C1EE01117K.
- [68] Z. Yuan, Q. Dai, Y. Zhao, W. Lu, X. Li, and H. Zhang, "Polypyrrole modified porous poly(ether sulfone) membranes with high performance for vanadium flow batteries," *J. Mater. Chem. A*, vol. 4, pp. 12955–12962, 2016, doi: 10.1039/C6TA05655E.
- [69] W. Lu, Z. Yuan, M. Li, X. Li, H. Zhang, and I. F. J. Vankelecom, "Solvent-induced rearrangement of ion-transport channels: a way to create advanced porous membranes for vanadium flow batteries," *Adv. Funct. Mater.*, vol. 27, no. 9, p. 1604587, 2017, doi: 10.1002/adfm.201604587.
- [70] C. Ding, Z. Shen, Y. Zhu, and Y. Cheng, "Insights into the Modification of Carbonous Felt as an Electrode for Vanadium Redox Flow Batteries," 2023. doi: 10.3390/ma16103811.

- [71] L. Ye *et al.*, “Vanadium Redox Flow Battery: Review and Perspective of 3D Electrodes,” *ACS Nano*, vol. 18, no. 29, pp. 18852–18869, Jul. 2024, doi: 10.1021/acsnano.4c06675.
- [72] H. Radinger, A. Ghamlouche, H. Ehrenberg, and F. Scheiba, “Origin of the catalytic activity at graphite electrodes in vanadium flow batteries,” *J. Mater. Chem. A*, vol. 9, no. 34, pp. 18280–18293, 2021, doi: 10.1039/D1TA04316A.
- [73] A. Hassan, A. S. Haile, T. Tzedakis, H. A. Hansen, and P. de Silva, “The Role of Oxygenic Groups and sp³ Carbon Hybridization in Activated Graphite Electrodes for Vanadium Redox Flow Batteries,” *ChemSusChem*, vol. 14, no. 18, pp. 3945–3952, Sep. 2021, doi: <https://doi.org/10.1002/cssc.202100966>.
- [74] S. J. Park, M. J. Hong, Y. J. Ha, J.-I. Choi, and K. J. Kim, “Two-in-one strategy for optimizing chemical and structural properties of carbon felt electrodes for vanadium redox flow batteries,” *Sci. Technol. Adv. Mater.*, vol. 25, no. 1, p. 2327274, Dec. 2024, doi: 10.1080/14686996.2024.2327274.
- [75] A. Molina-Serrano *et al.*, “Comparison of the Influence of Oxygen Groups Introduced by Graphene Oxide on the Activity of Carbon Felt in Vanadium and Anthraquinone Flow Batteries,” *ACS Appl. Energy Mater.*, vol. 7, Mar. 2024, doi: 10.1021/acsaem.3c03223.
- [76] J. Xu, Y. Zhang, Z. Huang, C. Jia, and S. Wang, “Surface Modification of Carbon-Based Electrodes for Vanadium Redox Flow Batteries,” *Energy & Fuels*, vol. 35, no. 10, pp. 8617–8633, May 2021, doi: 10.1021/acs.energyfuels.1c00722.
- [77] Y. Chen *et al.*, “Heteroatom-Rich Hierarchical Porous Biomass Carbon for Vanadium Redox Flow Batteries,” *ACS Sustain. Chem. Eng.*, vol. 12, no. 28, pp. 10567–10576, Jul. 2024, doi: 10.1021/acssuschemeng.4c03266.
- [78] Z.-J. Huang *et al.*, “Enhanced Electrochemical Performance of Vanadium Redox Flow Batteries Using Li₄Ti₅O₁₂/TiO₂ Nanocomposite-Modified Graphite Felt Electrodes,” *ChemElectroChem*, vol. 12, no. 2, p. e202400477, Jan. 2025, doi: <https://doi.org/10.1002/celec.202400477>.
- [79] M. Kogler *et al.*, “Unveiling the Role of Electrografted Carbon-Based Electrodes for Vanadium Redox Flow Batteries,” *ChemSusChem*, vol. 17, no. 12, p. e202301659, Jun. 2024, doi: <https://doi.org/10.1002/cssc.202301659>.
- [80] H. Hu *et al.*, “Strategies for improving the design of porous fiber felt electrodes for all-vanadium redox flow batteries from macro and micro perspectives,” *Energy Environ. Sci.*, vol. 18, no. 7, pp. 3085–3119, 2025, doi: 10.1039/D4EE05556J.
- [81] S. Saha, K. K. Maniam, S. Paul, and V. S. Patnaikuni, “Hydrodynamic and Electrochemical Analysis of Compression and Flow Field Designs in Vanadium Redox Flow Batteries,” 2023. doi: 10.3390/en16176311.
- [82] Q. Xu, T. S. Zhao, and C. Zhang, “Performance of a vanadium redox flow battery with and without flow fields,” *Electrochim. Acta*, vol. 142, pp. 61–67, 2014, doi: <https://doi.org/10.1016/j.electacta.2014.07.059>.
- [83] E. Prumbohm, M. Becker, S. Flaischlen, G. D. Wehinger, and T. Turek, “Flow field designs developed by comprehensive CFD model decrease system costs of vanadium redox-flow batteries,” *J. Flow Chem.*, vol. 11, no. 3, pp. 461–481, 2021, doi: 10.1007/s41981-021-00165-2.
- [84] M. Pugach, S. Parsegov, E. Gryazina, and A. Bisch, “Output feedback control of electrolyte flow rate for Vanadium Redox Flow Batteries,” *J. Power Sources*, vol. 455, p. 227916, 2020, doi: <https://doi.org/10.1016/j.jpowsour.2020.227916>.
- [85] R. Gundlapalli and S. Jayanti, “Comparative Study of Kilowatt-Scale Vanadium Redox Flow Battery Stacks Designed with Serpentine Flow Fields and Split Manifolds,” 2021. doi: 10.3390/batteries7020030.
- [86] T. Lin, S. Baker, E. Duoss, and V. Beck, “Topology Optimization of 3D Flow Fields for Flow Batteries,” *J. Electrochem. Soc.*, vol. 169, May 2022, doi: 10.1149/1945-7111/ac716d.
- [87] A. Clemente and R. Costa-Castelló, “Redox Flow Batteries: A Literature Review Oriented to Automatic Control,” 2020. doi: 10.3390/en13174514.
- [88] Z. Huang *et al.*, “Experimental Validation of Side Reaction on Capacity Fade of Vanadium Redox Flow Battery,” *J. Electrochem. Soc.*, vol. 171, Jan. 2024, doi: 10.1149/1945-7111/ad1ec8.
- [89] R. Patel *et al.*, “Reliability studies of vanadium redox flow batteries: upper limit voltage effect,” *RSC Adv.*, vol. 14, no. 46, pp. 34381–34389, 2024, doi: 10.1039/D4RA04713C.
- [90] R. Pichugov, P. Loktionov, D. Verakso, A. Pustovalova, D. Chikin, and A. Antipov, “Sensitivity of Capacity Fade in Vanadium Redox Flow Battery to Electrolyte Impurity Content,” *Chempluschem*, vol. 89, no. 12, p. e202400372, Dec. 2024, doi: <https://doi.org/10.1002/cplu.202400372>.
- [91] M. Cecchetti, G. Nicosia, A. Casalegno, and M. Zago, “Mitigation of capacity decay in vanadium redox flow batteries through initial imbalance of electrolytes state of charge,” *Electrochim. Acta*, vol. 517, p. 145750, 2025, doi: <https://doi.org/10.1016/j.electacta.2025.145750>.
- [92] N. Blume, T. Turek, and C. Minke, “Sustainability Development of Stationary Batteries: A Circular Economy Approach for Vanadium Flow Batteries,” 2024. doi: 10.3390/batteries10070240.
- [93] N. Blume, M. Becker, T. Turek, and C. Minke, “Life cycle assessment of an industrial-scale vanadium flow battery,” *J. Ind. Ecol.*, vol. 26, pp. 1796–1808, 2022, doi: 10.1111/jiec.13328.
- [94] S. Weber, J. F. Peters, M. Baumann, and M. Weil, “Life Cycle Assessment of a Vanadium Redox Flow Battery,” *Environ. Sci. Technol.*, vol. 52, pp. 10864–10873, 2018, doi: 10.1021/acs.est.8b02073.
- [95] M. Bodley, M. Sidawi, S. Thakurdin, Y. M. Gordon, G. Dressel, and S. Kumar, “Green Steel And Vanadium

- Production In Uzbekistan,” in *9th ECIC European Coke and Ironmaking Congress*, Sep. [Online]. Available: <https://www.hatch.com/About-Us/Publications/Technical-Papers/2024/10/Green-Steel-And-Vanadium-Production-In-Uzbekistan>
- [96] World Bank, “Uzbekistan to Build New Solar Plant and First Battery Energy Storage System with World Bank Group Support,” Sep. , *World Bank*. [Online]. Available: <https://www.worldbank.org/en/news/press-release/2024/05/21/uzbekistan-to-build-new-solar-plant-and-first-battery-energy-storage-system-with-world-bank-group-support>
- [97] Ш. Ч. Искандаров, Б. М. Абдурахманов, И. Х. Ашуров, У. Ф. Бердиев, Г. М. Хамдамов, and Т. К. Турдалиев, “Электролит для ванадиевых проточных аккумуляторов,” *«Узбекский физический журнал»*, vol. 25, no. 2, 2023, doi: 10.52304/.v25i2.421.