

Development of electrolytes for vanadium redox flow batteries

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FUTURE BATTERY INDUSTRIES
CRC PROJECT REPORT

Development of electrolytes for vanadium
redox flow batteries

A collaborative research project with
Hydrometallurgy Research Group and
Murdoch University.

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EXECUTIVE SUMMARY



To meet increases in energy demand while reducing greenhouse gas emissions associated with electricity generation, distribution, and transmission, the world needs to transition to more environmentally friendly energy sources. One of the main options to achieving this is through the use of vanadium redox flow batteries (VRFBs) to store renewably-generated electricity.

VRFBs are considered durable systems, with an expected lifetime of more than ten years and a cycle life of several thousand cycles. They can be used as an energy storage system for a range of purposes including load-leveling, flex ramping, peak shaving, time shifting, maintaining power quality, long duration energy storage, and frequency regulation. The VRFB is the only redox flow battery that has been used in large-scale applications around the world (e.g., Europe, Southeast Asia, and North America) for extended periods of time. A VRFB is not harmed by repeated discharge or charge rates provided that the maximum rates are not exceeded. VRFBs have the standard RFB components of current collectors, bipolar plates, electrodes, and a membrane.

The use of a single metal element in both half-cells eliminates the cross-contamination issues that plague other redox flow cell chemistries, providing a theoretically indefinite electrolyte life. The solubility of vanadium ions not only determines the achievable energy density but also limits the operational conditions. However, the cost of the electrolyte accounts for a significant portion (about a third) of the total VRFB system cost.

The VRFB electrolyte has been constantly improved, and several generations of VRFB have emerged as a result of research spanning several decades aimed at enhancing performance and solving challenges in operating the batteries. The main differences between these generations are the use of different electrolyte chemistries or the use of a single mixed inorganic acid.

The new technique of mixing chloride ions with sulfate ions in the supporting electrolyte has the potential to

increase the energy density of the battery, improve the electrolyte stability and enhance the solubility of the vanadium species in the catholyte and/or anolyte. This approach has been successful in providing a more stable vanadium electrolyte and higher vanadium concentration. The concentration of vanadium in a mixed acid electrolyte (Gen 3 electrolyte) can reach up to ca. 2.5 M (vs. <1.6 M for Gen1 VRFBs) without any precipitation, and this electrolyte can operate at temperatures ranging from -5°C to 50°C.

Only a few researchers have focused on improving electrolyte stability by the use of stabilising agents and also by looking into the effect of impurities during electrolyte preparation stages. Disagreements persist in identifying the most effective stabilising agents that will allow for increased energy density and operating temperature range in practical systems. Research groups agree on the benefits of using additives to improve thermal stability, yet this technique has challenges because the additives should be compatible with all vanadium ions since the electrolyte will change oxidation state in each half-cell during the charging and discharging processes, and the additive will eventually diffuse into the other half-cell and interact with other vanadium ions. A few groups have tried to develop an impurities specification for VRFB electrolytes, but they are currently insufficient to be considered as a guideline for industry. Further study into impurity specifications is required to ensure the stable operation and long cycle life of a VRFB in commercial installations.

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1. INTRODUCTION

We are currently living in an environmental and energy crisis [1]. Many factors affect the global environment, including the use of fossil fuels as a source of energy [2]. Burning fossil fuels, such as coal, oil, and natural gas, to produce energy causes air and water pollution. Fossil fuels generate large amount of greenhouse gas (GHG) emissions, such as carbon dioxide (CO₂)(in large volume) [3], methane (CH₄) and nitrous oxide (N₂O) which in addition to chlorofluorocarbons (CFC) and water vapour, form the five key greenhouse gases [4]. Their presence traps the sun’s heat in the earth’s atmosphere, and slows down heat loss to space.

To meet increases in energy demand while reducing GHG emissions associated with electricity generation, distribution, and transmission, the world needs to transition to more environmentally friendly energy sources. This transition should be as smooth as possible in order to keep the wheels of the economy turning.

Renewable energy sources such as wind and solar have been developing as the ideal alternative to fossil-fuel based energy sources and are increasingly being integrated into the global energy resource [5], which is helping to reduce the dependency on fossil fuels as the primary source of energy. The transition to renewable energy generation is expected to accelerate significantly in the coming years, with wind and solar increases from 2018 to 2050 predicted to be 14-fold and 30-fold respectively [6]. However, renewable energy sources are

irregular in energy generation, thus there is a real need for reliable energy storage systems (ESS) or electrical energy storage (EES) with high safety and low cost. ESS (or EES) are a method of converting electrical energy from a power generating system into a form that can be stored then converted back to electrical energy when required. ESS store the excess energy generated from renewable sources when it is in surplus and feed it back into the power grid during peak hours [7]. ESS should be regarded as essential infrastructure for the energy transition. A variety of ESS are available to choose from depending on location, demand, capacity, technology, and costs of investment (Figure 1).

The number of photovoltaic panels currently installed in Australian households is very high, and they generate enormous quantities of solar energy. However, energy from these installations feeding into the main power grid is considered a threat to the stability of the grid when the energy share from these resources surpasses 10 – 20% of overall energy production [8]. In recent years, solar farms have been required to shut down, when there is an oversupply of energy, regardless of electricity needs [9]. A substantial network of distributed energy storage systems could solve many of the issues with Australia’s current renewable energy system. Energy storage systems are essential where there is night-time use of electricity from solar PV such as in houses, health and aged care facilities, and any business with night-time operations.

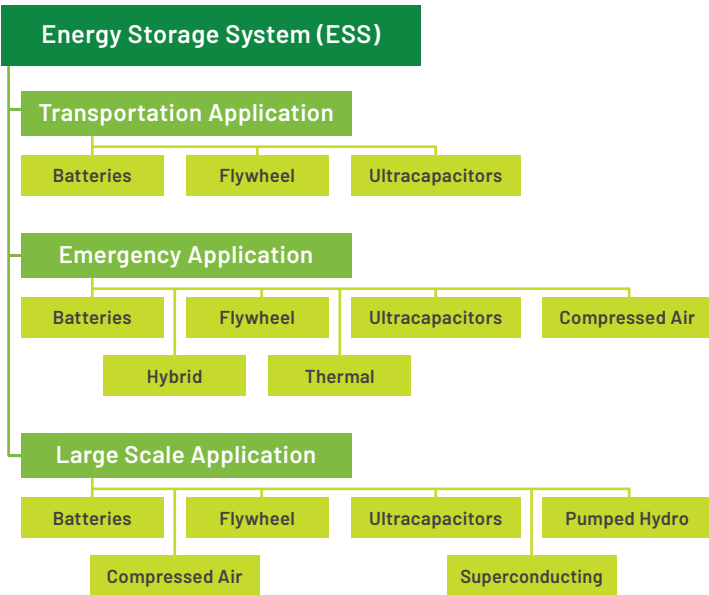
There are several technologies for energy storage (Figure 1) that store electrical energy and later return it to the grid. The classification of energy storage systems is electrochemical (batteries and supercapacitors), chemical, electrical (capacitors and superconducting magnets), thermal, and mechanical (pumped hydro, fly wheel, and compressed air)[10].

Every energy storage system has challenges, but batteries, which are electrochemical storage systems, are the easiest and most flexible form of energy storage. They are very fast to respond to demand for power; and they provide stability when integrated into the main electricity gird better than other energy storage systems. Currently, the calculated return on capital investment for batteries may be ten years or more [11], but this may reduce in future as the cost of battery components reduces.

Increasing demand for storing energy produced from renewables has led to a rapid advancement in battery technology. Flow batteries have future development prospects particularly in the large-scale commercial and grid-scale storage markets [13-15]. The recent installation of Redox Flow Batteries (RFBs) alongside solar PV by Yadlamalka Energy [16, 17], a first of its kind in Australia, is an excellent example of use of this technology. The use of batteries for energy storage has accelerated in recent years in Australia and worldwide. It has been a huge step towards energy independence as it allows for power-on-demand and minimises dependence on the grid. Battery

manufacturers are now making every effort to offer robust commercially available battery solutions. Capital cost analysis indicates that RFBs are cost-effective for long discharge duration applications [18] and long cycle life [19] making them an excellent choice for large-scale energy storage.

Figure 1: Classification of the principal energy storage systems (adapted from [12]).



2. REDOX FLOW BATTERIES (RFBS)

Among energy storage battery systems, RFBs are one of the most recent technologies. Full-scale development of RFBs started in the 1970s. The principle of the RFB system was presented by L. H. Thaller in 1974 based on research conducted at NASA and focusing on the Iron Chromium (Fe/Cr) system [20].

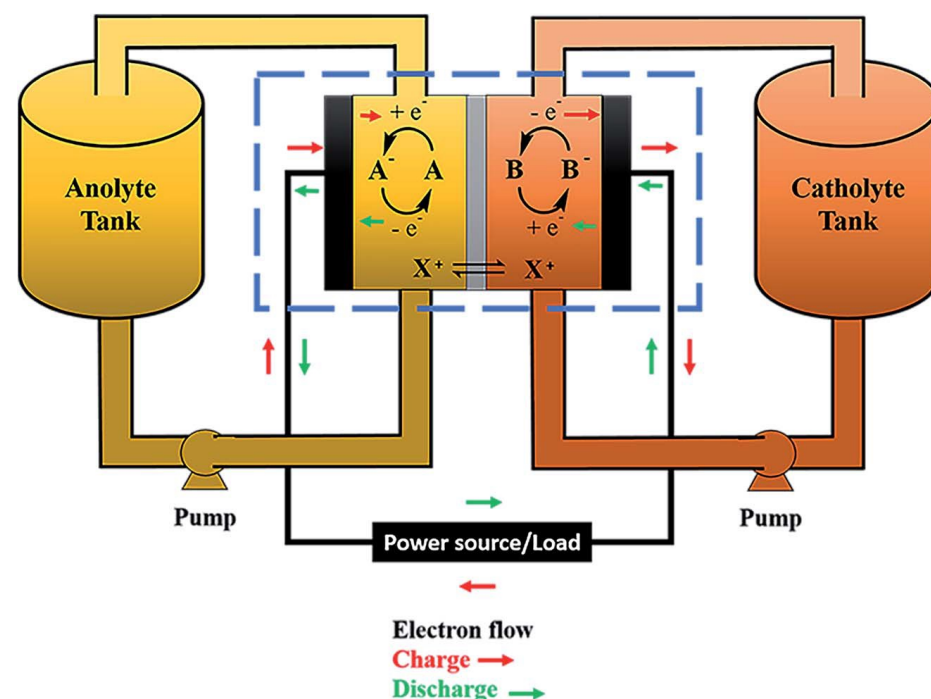
The word “Redox” is an abbreviation for reduction and oxidation reactions. RFB liquid electrolytes contain electroactive redox species dissolved or suspended in a supporting electrolyte which is used to increase conductivity.

The electrolyte is always kept in two separate tanks and is propelled through the electrochemical cell or the battery stack using pumps. A cooling system is also needed as charge and discharge of RFB's involve heat release. Oxidation and reduction reactions between the two electroactive species occur on the surface of

electrodes, where the electrical energy is converted to chemical energy during charge or vice versa during discharge (Figure 2).

During a charge and discharge cycle the battery stores energy in the liquid electrolyte that flows through a stack of electrochemical cells. In the charge part of the cycle, an electron is liberated through an oxidation reaction from a high chemical potential state on the negative or anode side of the cell stacks. This electron reaches the positive or cathode side through an external connection (usually an electric wire) and is accepted through a reduction reaction at a lower chemical potential state, allowing the storage of energy. The reverse process happens in the discharge cycle. Ions cross from one side of the cell to the other side through a membrane to complete the circuit. For every electron transferred from the anolyte to the catholyte, a proton moves across the membrane to maintain electroneutrality.

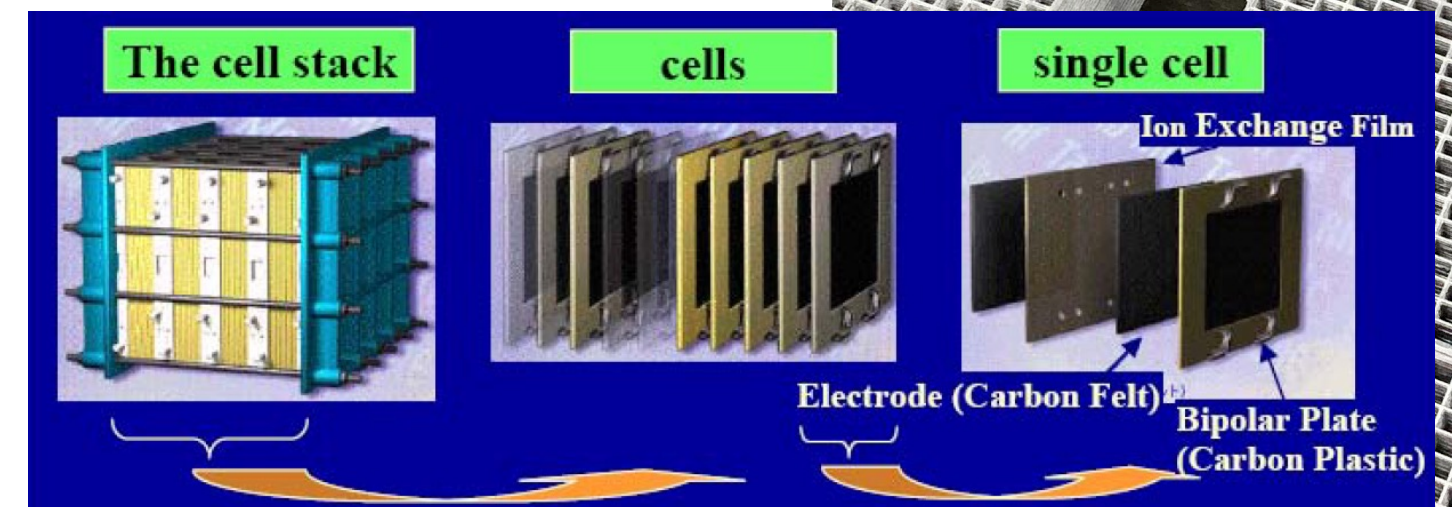
Figure 2: General scheme of an RFB. Redox reactions take place inside the cell (marked with a blue dashed rectangle) on the surface of the electrodes (black rectangle). The electrolyte is continuously renewed by pumping the solution from the tanks. The direction of electron flow (charge or discharge) is managed by the electrical components, acting as a power source or loading the energy from the battery [21].



A flow battery system has a distinctive configuration (Figure 3). It consists of four components: a cell stack (which contains several half-cells of prismatic bi-polar cells (flow-through or flow-by) separated by a membrane (that may be an anionic exchange membrane, or a cationic exchange membrane); two energy storage tanks; a flow system including pumps and a plumbing system through which the electrolyte is circulated from the tanks to the battery stack, and a control system [22].

The energy conversions from electrical energy to chemical potential (for charging) and vice versa (for discharging) take place rapidly at the surface of the electrodes as soon as the liquid electrolytes flowing through each cell flow past one another in the stack.

Figure 3: Vanadium Redox Flow Battery Cell Stack (Courtesy Kansai Electric Power Co) [23].

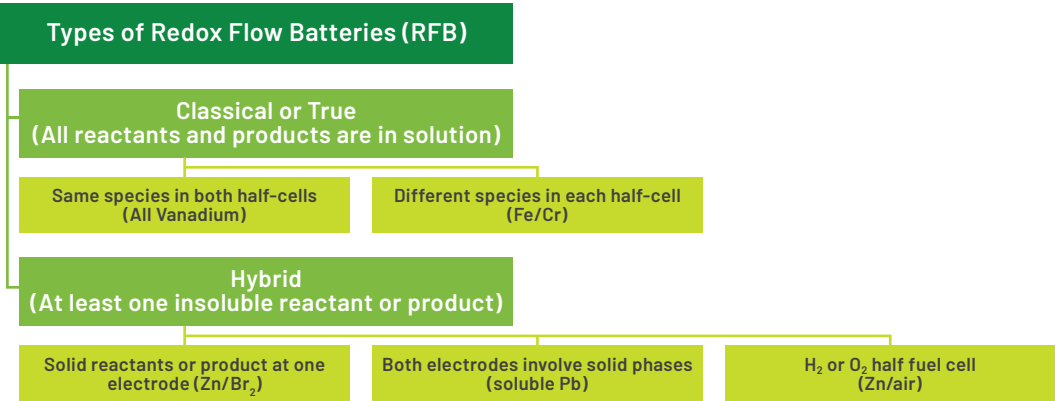


RFBs have a unique design in which the power (kW) and energy storage capacity (kWh) are designed separately. While the size of the tanks (the volume of the electrolyte) decides the energy capacity of an RFB, the size of the electrode and the number of stacks (total surface area of all the cells) control the power of the battery.

A bipolar electrode design can be used to increase the specific energy of the battery. This design allows the current to travel directly through the battery stack, since the electrochemical reactions take place on opposite sides of the bipolar electrodes. Unlike the encased configuration of a lithium-ion battery, where energy is stored in rolled electrode sheets of solid nanoparticles compacted and glued together, a flow battery utilises electroactive species dissolved and freely migrating in liquid electrolytes, present in different oxidation states, with the electrolyte stored in the tanks away from the electrodes.

RFBs can be divided into classical or true RFBs and hybrid RFBs, which are further divided into Type I and Type II [24]. Classical RFBs use inert electrodes and redox species that remain in solution. Examples of classical RFBs are the Iron Chromium (Fe/Cr) system [20], bromine-polysulphide [25, 26] and the Vanadium redox flow battery [27]. Hybrid RFB operation involves a phase change during the cell reaction. An example is the zinc/bromine system in which the plating and dissolution of zinc at the anode occurs upon charge and discharge respectively [28-31].

Figure 4: Classification of redox flow batteries, showing classical (redox/redox) and hybrid (solid layer/redox or gas/redox) types (adapted from [32]).



The system efficiency calculations for all batteries including RFBs involve several parameters and are based on the following calculations.

The Coulombic efficiency, CE, is the ratio of the amount of charge transferred upon discharge to the amount of charge transferred upon charge. Coulombic losses are caused by several phenomena such as ion diffusion processes, irreversible reactions, and shunt currents through the electrolyte.

$$CE = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} \times 100\% = \frac{\int i_{\text{discharge}}(t) dt}{\int i_{\text{charge}}(t) dt} \times 100\%$$

The Voltaic efficiency, VE, is classified as the ratio of the average discharge voltage ($\bar{V}_{\text{discharge}}$) to the average charge voltage (\bar{V}_{charge}). VE losses occur when the average charging voltage is consistently higher than the voltage required to activate the response of the material inside the battery. Another factor that reduces VE is the internal resistance of the battery, which increases with battery size, age, current, and can be dependent on the battery chemistry.

$$VE = \frac{\bar{V}_{\text{discharge}}}{\bar{V}_{\text{charge}}} \times 100\%$$

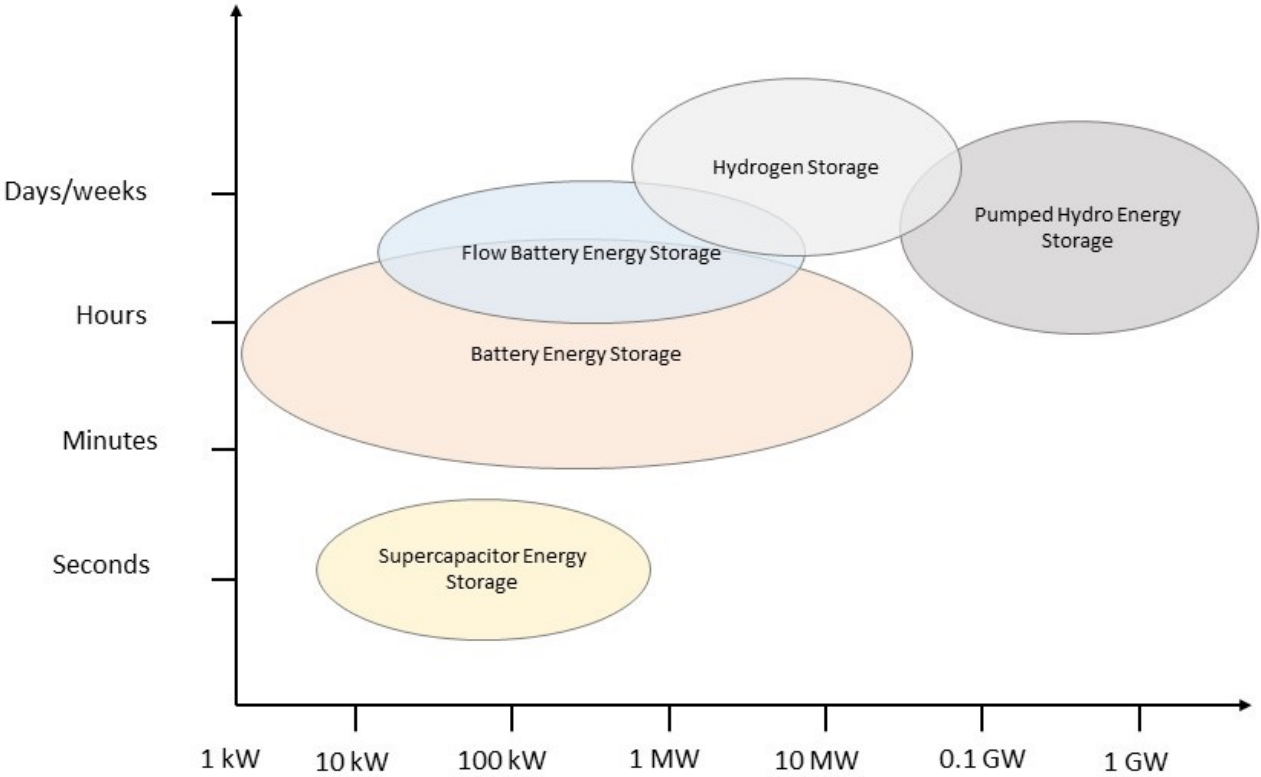
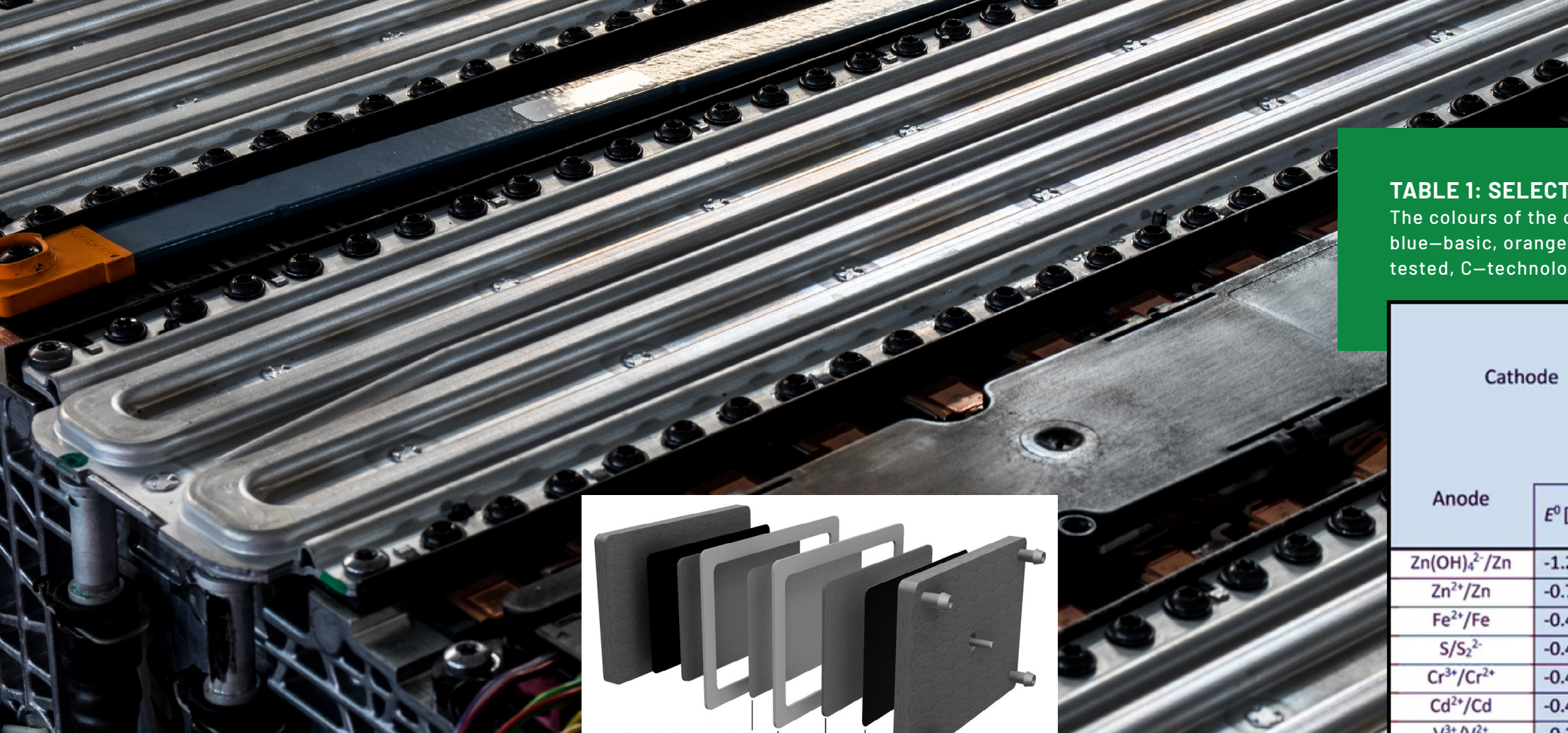


Figure 5: Power duration diagram of some energy systems (adapted from [34][35]).

The Energy efficiency, EE, is calculated as the product of the coulombic efficiency and the voltaic efficiency. The EE indicates how much of the energy that is supplied to the battery during charging can be extracted upon discharge.

$$EE = \frac{\int i_{\text{discharge}}(t) dt}{\int i_{\text{charge}}(t) dt} \times \frac{\bar{V}_{\text{discharge}}}{\bar{V}_{\text{charge}}} \times 100\% = CE \times VE$$

RFBs are well-known for their long cycle life, modular design, excellent electrochemical reversibility, high round-trip efficiency, good scalability and flexibility, safety, independent sizing of power and energy, deep discharge ability, short response times, moderate maintenance cost, and low environmental impact [33]. With these characteristics, RFBs can be used in applications with a range of operational power and discharge times and are suitable for supporting electricity generation from renewable sources (Figure 5).



RFBs can be easily integrated into a range of applications that need energy storage systems for load-leveling, flex ramping, peak shaving, time shifting, maintaining power quality, and frequency regulation [22, 36–38].

Figure 6 shows the structure of a typical redox flow battery: carbon felt or carbon plastic electrodes; bipolar plates usually made from graphite (these prevent direct contact between the electrolyte and current collectors); membranes or a separator; a flow frame (to direct the electrolyte flow through the electrodes); and an end plate with electrolyte fittings and current collector. The details of the flow frame are shown in Figure 7 [39].

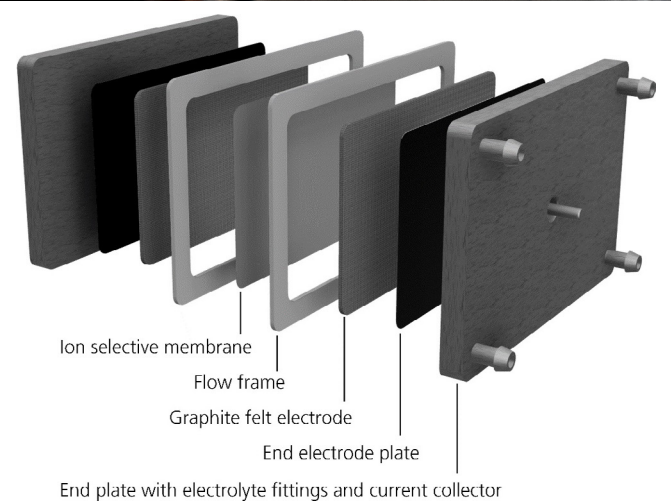


Figure 6: Illustration of the structure of a redox-flow battery cell with designation of the most important components [38].

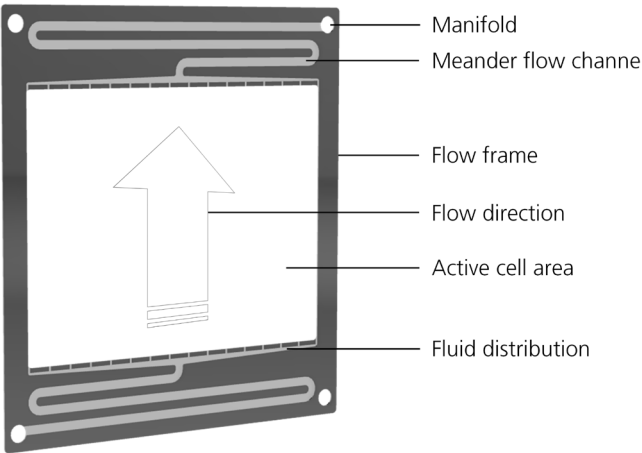


Figure 7: Illustration of the supply channel and distribution geometry in a flow frame of a redox flow battery [38].

TABLE 1: SELECTED EXAMPLES OF INORGANIC REDOX COUPLES FOR RFBs.
The colours of the cells correspond to the pH value of the electrolytes; red—acidic, blue—basic, orange—neutral. Stage of development: A—half cell study, B—prototype tested, C—technology has been commercialised [40].

Cathode	Anode	E° [V]	MnO ₂ /Mn ₂ O ₃	Fe(CN) ₆ ³⁻ /Fe(CN) ₆ ⁴⁻	Cu ⁺ /Cu	Fe ³⁺ /Fe ²⁺	VO ₂ ⁺ /VO ₂ ²⁺	ClBr ₂ ⁻ /Br ⁻	Br ₂ /Br ⁻ [a]	NpO ₂ ⁺ /NpO ₂ ²⁺	IO ₃ ⁻ /I ₂	O ₂ /O ²⁻	HCrO ₄ ⁻ /Cr ³⁺	Cl ₂ /Cl ⁻	PbO ₂ /Pb ²⁺	Mn ³⁺ /Mn ²⁺	Ce ⁴⁺ /Ce ³⁺
			0.15	0.36	0.52	0.77	0.99	1.04	1.09	1.14	1.2	1.23	1.35	1.36	1.46	1.54	1.72
Zn(OH) ₄ ²⁻ /Zn	-1.22	B	B														
Zn ²⁺ /Zn	-0.76						B	B	C					B			B
Fe ²⁺ /Fe	-0.45				A												
S/S ₂ ²⁻	-0.43								C								
Cr ³⁺ /Cr ²⁺	-0.41				C				A				B				
Cd ²⁺ /Cd	-0.40				B												
V ³⁺ /V ²⁺	-0.26				B	C	B					B				B	B
Pb ²⁺ /Pb	-0.13														B		
H ⁺ /H ₂	0				B	B			B					B			
TiO ²⁺ /Ti ³⁺	0.04				A			A						A			
Cu ²⁺ /Cu ⁺	0.15			B													
Np ⁴⁺ /Np ³⁺	0.15									B							
Cu ²⁺ /Cu	0.34														B		
I ₂ /I ⁻	0.54										A						

[a] Or Br₃⁻/Br⁻ 1.06 V (based on formation of polybromide), the potentials can vary according to the composition of the electrolytes because of complex formation.

2.1 Redox flow battery chemistry

Several combinations (more than 30) of redox pairs have been detailed in the literature as a possible RFB electrolytes that contain two redox couples. Noack *et al.* [40] summarised these combinations (Table 1) using data from published articles and/or patents. Only five of those electrolytes are used in RFBs that are produced commercially, as in All-Vanadium (V³⁺/V²⁺ couple and V⁵⁺/V⁴⁺ couple), Iron Chromium (Fe/Cr), Zinc Bromine (Zn/Br₂), All-Iron (Fe²⁺/Fe³⁺ couple and Fe²⁺/Fe⁰ couple) or Polysulphide Bromine (S₂/Br₂) systems. Most battery electrolytes are acidic, because many metal ions, except for zinc, precipitate as insoluble hydroxides at high pH values and are therefore unsuitable for use in RFB electrolytes. Table 2 summarises some selected redox flow batteries with different chemistries and Table 3 details the names and the location of some flow battery companies.

Petrov *et al.* [41] in their review on redox flow batteries classified the RFB batteries into three types: Classical RFBs, Hybrid RFBs (type I) and Hybrid RFBs (type II). Each type contains several battery chemistries. A brief description of classical and hybrid RFBs will be discussed in the next sections.

TABLE 2: SELECTED REDOX FLOW BATTERIES WITH DIFFERENT CHEMISTRIES.

SYSTEM	OPEN CIRCUIT POTENTIAL (OCP) (V)	CURRENT DENSITY (mA/cm ²)	ENERGY DENSITY (Wh/ dm ³)	CHARGE/ DISCHARGE EFFICIENCY (%)	REFERENCE
Fe-Cr	1.18	21.5		95 (coulombic)	[33, 42]
Fe-Ti	1.19	14		44-50 (overall)	[33]
VRB	1.6	10-130		80 at 40 mA cm2	[33]
V-Br	1.4	20	30-70	74 (overall)	[43-48]
V-Fe					[18, 49-51]
V-Mn	1.66	20		63 (overall)	[52-54]
V-Ce	1.5	22		90 (coulombic)	[55-61]
V-glyoxal (O ₂)	1.2	20		66 (coulombic)	[33]
V-polyhalide	1.3	20		83 (coulombic)	[33]
Hybrid V-O ₂ fuel cell	-	2.4		80 (voltaic)	[33]
Zn-Br	1.85	20		45.7 (overall)	[33, 62-64]
Flow-through lead battery	1.62	20		80 (overall)	[65]

2.1.1 Classical or true RFBs

2.1.1.1 All-vanadium RFBs

The VRFB was developed for the first time at the University of New South Wales in Australia by Maria Skyllas-Kazacos and colleagues [27]. By using vanadium redox couples in both half-cells, the issue of cross-contamination with another element caused by ion diffusion across the membrane is eliminated. The VRFB takes advantage of vanadium’s capacity to exist in four different oxidation states and uses this characteristic to create a battery with one electroactive element rather than two. Large stationary storage applications are a great fit for these flow batteries. Each power cell in a VRFB has two half-cells that are separated by an ion-permeable membrane. A VRFB is made up of an assembly of these power cells.

The electrochemical reactions occur on inert carbon felt electrodes in the half-cells, where the current is gathered. Pipes and pumps are the remaining parts that the VRFB needs in order for the electrolyte to flow from the tanks to the stack. The VRFB is not harmed by repeated full discharge or charge rates as high as the maximum discharge rates, according to Skyllas-Kazacos and colleagues [67].

TABLE 3: SOME FLOW BATTERY COMPANIES [66]

COMPANY NAME	LOCATION	SYSTEM
CellCube (Enerox GmbH)	Wiener Neudorf, Austria	VRFB
ESS Tech Inc.	Wilsonville, Oregon, U.S.A.	Fe Flow
Invinity Energy Systems	St. Helier, Jersey	VRFB
Largo Inc.	Toronto, Ontario, Canada	VRFB
Lockheed Martin Corp.	Bethesda, Maryland, U.S.A.	Synthetic metal-ligand
Primus Power Solutions	Hayward, California, U.S.A.	Zn/Br ₂
SCHMID Group	Freudenstadt, Germany	VRFB
Sumitomo Electric Ind., Ltd.	Osaka, Japan	VRFB
UniEnergy Technologies, LLC	Mukilteo, Washington, U.S.A.	VRFB
VRB Energy	Vancouver, British Columbia, Canada	VRFB
Rongke Power	Dalian, China	VRFB
Redflow Technologies Ltd.	Queensland, Australia	Zn/Br ₂
VisBlue	Denmark	VRFB
Vanadis Power	Germany	VRFB
VSUN	Australia	VRFB

Additionally, a VRFB can be cycled from any state of charge or discharge without enduring long-term harm to the cells or electrolytes, provided that it doesn’t exceed the capacity of the electrolytes.

However, there is the issue that the ion exchange membrane deteriorates due to the intense activity of a specific form of vanadium ion, V⁵⁺. The study of vanadium batteries continues to be conducted in-depth by the Skyllas-Kazacos research team at the University of New South Wales (Australia) and by various industrial organizations all over the world [68-70]. The electrolyte has the same acidity as a typical lead-acid battery since it is a vanadium solution combined with diluted sulfuric acid, but in contrast to lead-acid systems, the VRFB electrolyte has an infinite life span and can be reused [71].

Depending on the treatments and conditions exposed to the battery components, moderate efficiency (70-90%) was reported for controlled laboratory setups [70]. Kim *et al.* [72] presented a 1 kW/1 kWh prototype VRFB system, which was experimentally and numerically evaluated, delivered more than 1.1 kW at 15-85% SoC and an energy efficiency of 82%.



The redox flow battery that has received the most attention is the all-vanadium redox flow battery (VRFB). VRFBs are considered to be one of the most promising large, grid-scale energy storage systems and are well suited for integration with renewable energy generation sources. It is a technology that is well suited to use as a long duration, stationary energy storage system due to its robustness under a wide range of operating conditions, the property that power and energy ratings are independent of each other, long maximum discharge and storage times, and safety [73]. The VRFB electrolyte (which is 85% of the weight of a VRFB) can be recycled for reuse in another battery system or converted to useful vanadium compounds [74].

2.1.1.2 Iron chromium RFBs

The iron-chromium redox system was initially investigated by NASA [20]. The hydrochloric acid-acidified aqueous solutions containing a ferric-ferrous redox couple and a chromous-chromic couple, serve as the positive and negative reactants, respectively. Each reactant in this redox flow cell flows at a rate that is consistently higher than the stoichiometric flow requirement, allowing all of the reactants to be used up in one trip through the cell. The two flowing reactant solutions are divided by an anionic and cationic ion exchange membrane in each cell.

In theory, the membrane prevents the cross diffusion of the iron and chromium ions, allowing only the chloride and hydrogen ions to freely move through the cell to complete the electrical circuit. The performance of a Fe-Cr redox flow cell was investigated by a number of researchers and organisations, including NASA [20, 75-77], a study team at the University of Alicante in Spain [75], and Shimada *et al* [78], who reported that the coulombic efficiency of a redox flow cell increased to 95% when the carbon fibres' structure was changed from amorphous to graphite. In a further investigation by Johnson and Reid [79], the Fe-Cr redox system was assessed using electrodes made of 1/8 inch carbon felt.

2.1.1.3 Polysulfide halide RFBs

A polysulphide bromide (PSB) battery is a type of RFB that uses sodium bromide and sodium polysulphide as salt solution electrolytes. To keep the cell electroneutral, sodium ions pass through the membrane. Although Price *et al.* [26] claim that this technology is environmentally friendly, there is concern that toxic bromine vapour could be released in the event of an accident. Some multi-kilowatt batteries have been constructed. Innogy has constructed a 100-kW stack with a 1 m² electrode area and a nett efficiency of approximately 75%. Due to engineering challenges and financial constraints, the construction of two large power (12 MW and 15 MW, at energy rating of 120 MWh) storage plants in the UK and US has been halted. Active PSB development is not currently occurring [80].

2.1.2 Hybrid RFBs

2.1.2.1 Zinc bromine RFBs

The zinc bromine battery (ZBB) is termed a hybrid flow battery because one of its electrodes participates in the reaction after charging. Currently, this technology is being developed primarily for stationary energy storage applications. The system has an excellent specific energy (65-84 Wh/kg).

The ZBB concept originated in the 1880s [81], but due to technical difficulties, particularly with bromine corrosiveness, development was not fully realised until the mid-1970s. ZBBs have piqued the interest of researchers as a rechargeable power source due to

their high energy density, high cell voltage, high degree of reversibility, and use of readily-available, low-cost materials. The electrolyte is dissolved zinc bromide salt in water, and during charging, zinc is plated on the negative electrode, which limits the capacity of the battery.

Bromine is produced at the positive electrode and forms a bromine complex with a quaternary ammonium salt (e.g., N-Ethyl N-methyl pyrrolidinium bromide, N-ethyl-N-methyl-morpholinium bromide [82]) that forms a heavy phase that sinks to the bottom of the positive electrolyte tank.

At the positive electrode, zinc is redissolved to form zinc ions, and bromide ions are formed during discharge. To recirculate the bromine complex, a third pump or extra valve is required. The ZBB efficiency ranges between 60 and 75%. In terms of energy output, ZBBs ranging from 500 kWh to 2 MWh have been built and tested over the years [28-31].

The major drawback of ZBB is the system installed energy cost. The International Renewable Energy Agency (IRENA) reported in 2017 the electricity storage costs including RFBs. The cost of ZBB kWh in 2016 was USD 900 whereas all vanadium was USD 310.

2.1.2.2 Zinc-cerium RFBs

The Zn-Ce system has been developed by Plurion Systems Inc., who have operated a cell at high current densities of 400-500 mA/cm². Their cell voltage during charging was approximately 2.5 V and dropped to below 2 V on the discharge cycle [83].

2.1.2.3 All-Iron RFBs

Hruska and Savinell [84] proposed all-iron RFB in 1981. It employs iron in different valence states for both the positive and negative electrodes and based on iron deposition at the negative electrode [85]. Because of their high solubility, chloride salts have a high theoretical energy density (76 Wh/L). However, at high concentrations of FeCl₂ and FeCl₃, solution resistivity increases dramatically, limiting practical concentrations, but the addition of NH₄Cl and KCl reduces resistivity. A few ligands, including organic diacids, malic acid, malonic acid, amino acids, and dimethylsulfoxide, were tested in an effort to enhance the electrode kinetics of the FeII/FeIII couple and increase iron solubility over a wider pH range [86]. Glycine was found to be the best candidate for use in an all-iron RFB, with faster kinetics and the ability to stabilise 0.5 M iron at pH 2 [86, 87], as the electrolyte containing 1:1 glycine-to-iron ratio showed a reasonable open-circuit potential of 468 mV vs Ag/AgCl. When the anolyte pH was 1 and the catholyte pH was in the range of 3 - 4, the cell performed best. At a discharge power density of 50 mW/cm², the cell had a Coulombic efficiency of 90% but a low energy efficiency (50%). It was discovered that proton reduction during cycling caused an electrolyte imbalance, but at higher cell voltages, hydrogen evolution causes pH to rise and Fe(OH)₂ to precipitate. Currently, companies namely Energy Storage Systems (ESS) and Electric Fuel have become key players in the manufacturing of iron hybrid redox batteries [88].

3. VANADIUM REDOX FLOW BATTERIES (VRFBs)

3.1 General principles and design

Flow batteries suitable for large scale energy storage have currently been developed by various organisations around the world. The VRFB type of flow battery is one of the most mature flow battery systems [89]. VRFBs are a type of rechargeable flow battery that employs vanadium redox couples in both half-cells, thus eliminating the problem of cross contamination by diffusion of ions across the membrane. The vanadium (V) redox couple was first mentioned in a 1933 patent by P.A. Pissort [90] and was suggested for use in batteries by NASA and by Pellegrini and Spaziant in 1978 [91]. The first known successful demonstration and commercial development of VRFBs was carried out in Australia by Skyllas-Kazacos and co-workers at the University of New South Wales (UNSW), who registered a patent in 1988 [92]. VRFBs are well suited to use in Australia as vanadium resources are abundantly. VRFBs have already proven their value, but several research groups around the world are looking to improve their performance and efficiency to achieve higher power outputs.

The VRFB cell consists of two half-cells, with each half-cell consisting of an end plate, an end gasket, a bipolar plate (extruded sheet of carbon polymer material), a porous electrode (usually carbon felt) and a frame gasket. The two halves are separated by a membrane which is usually an ion exchange membrane (Figure 8). Electrical connection to the cells is normally done via a metal current collector (usually copper sheet or mesh) isolated from the battery electrolyte.

VRFBs store energy through a solution of vanadium in sulfuric acid in both half-cells. The negative half-cell contains a V^{3+}/V^{2+} couple (V^{2+} (purple), V^{3+} (turquoise)) and the positive half-cell contains a V^{5+}/V^{4+} couple (V^{4+} (blue), V^{5+} (yellow)) (Figure 9). The membrane separates the two halves, preventing migration and cross-mixing of the two half-cell electrolytes, but it allows the transport of charge balancing ions such as H^+ and HSO_4^- from the supporting electrolyte and H_2O to complete the circuit (Figure 9).

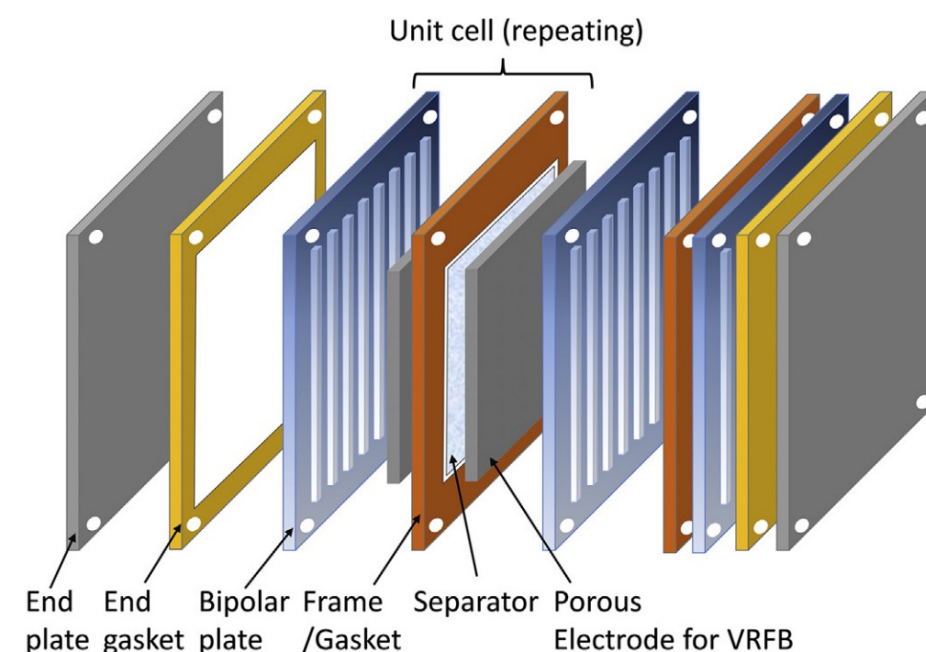


Figure 8: Vanadium redox battery stack (2 cells) assembly [93]



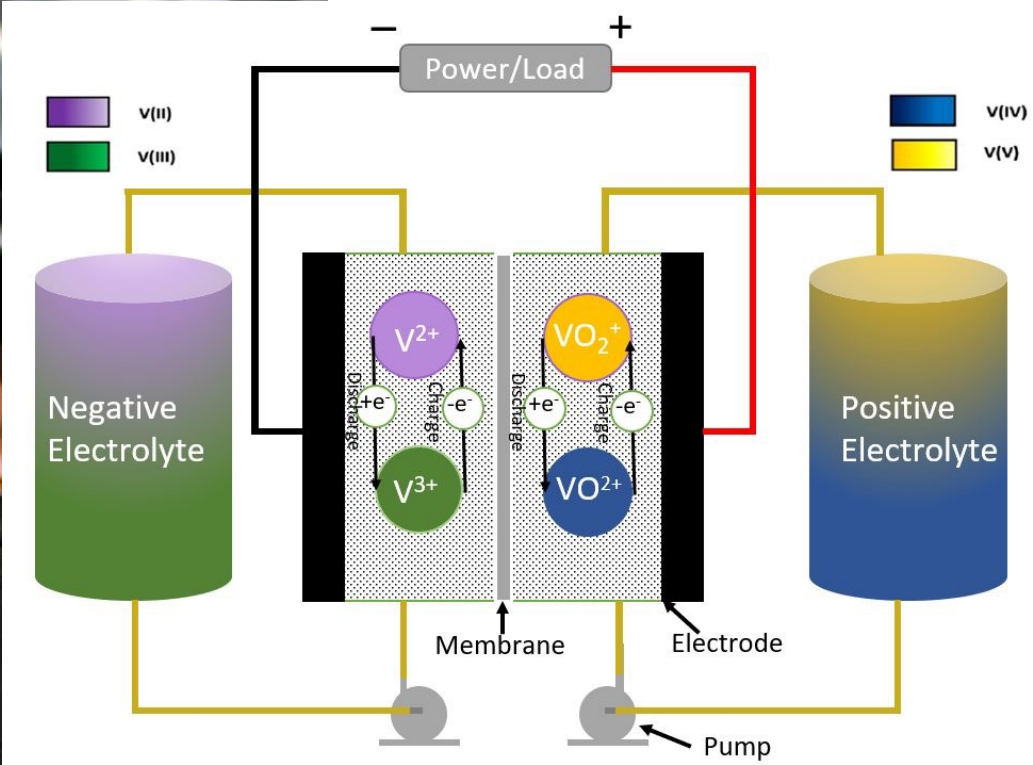
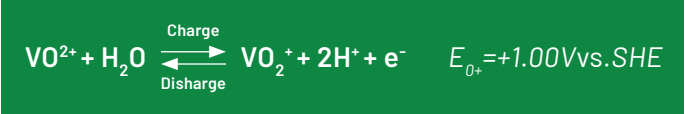


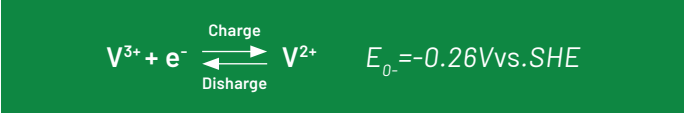
Figure 9: Schematic diagram of a vanadium redox flow battery

The main reactions that occur in the battery during charge and discharge cycles are:

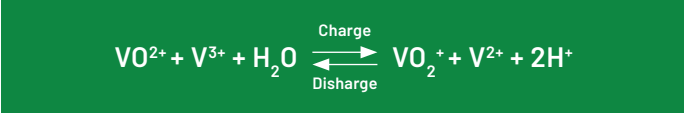
Positive electrode:



Negative electrode:



Overall reaction:



Note: $\text{VO}_2^{2+} = \text{V}^{4+}$; $\text{VO}_2^{+} = \text{V}^{5+}$

The single cell voltage is between 1.4 and 1.6 V. VRFB net efficiency can be as high as 85%. Like other flow batteries the power and energy ratings of VRFBs are independent of each other. A typical charge–discharge curve for the VRFB bipolar electrode is shown in Figure 10 for a battery with 80% voltaic efficiency (VE) and 91% coulombic efficiency (CE)[94]. The water (H_2O) and protons (H^{+}) are required in the positive reaction to maintain the charge balance and the stoichiometry.

The discharged electrolyte contains an equal amount of V^{3+} and V^{4+} ions in single or mixed acid. It is usually termed a $\text{V}^{3.5+}$ electrolyte. During the charge cycle V^{4+} oxidises to V^{5+} in the positive compartment and V^{3+} reduces to V^{2+} in the negative compartment, and vice versa on discharge (Table 4). H^{+} ions are exchanged through the ion selective membrane. VRFBs have discharge duration times up to 24 hours. The technology has a quick response (faster than 0.001 s) and can operate for (10,000–16,000+) cycles. The VRFB is the only redox flow battery that has been used in large-scale applications around the world (e.g., Europe, Southeast Asia, and North America) for extended periods of time [35, 38, 68, 89, 95–101].

Figure 10: Typical charge discharge behaviour in a vanadium battery based on Gen 1 electrolyte (charge and discharge current = 40 mA/cm²)[94].

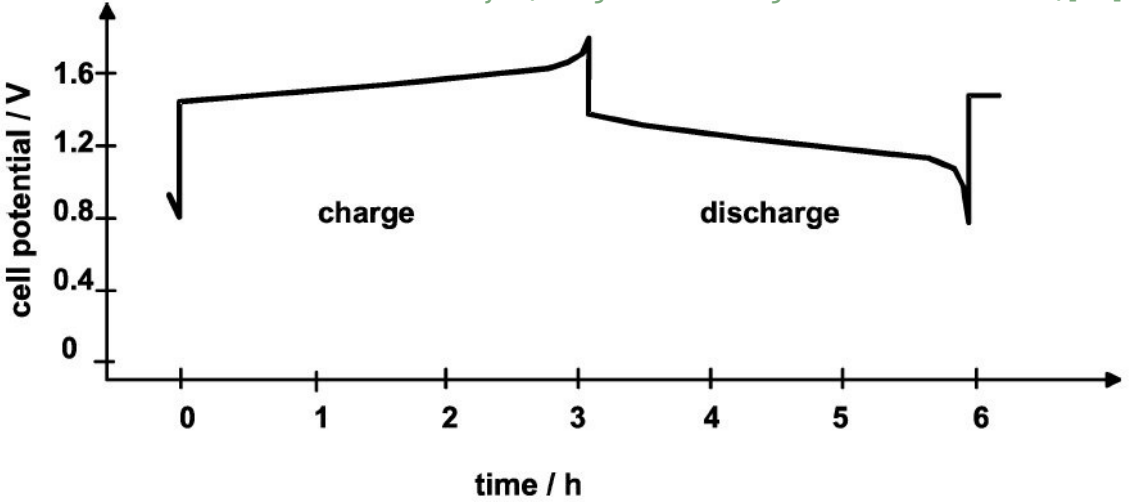


TABLE 4: VANADIUM IONS WITH THEIR CORRESPONDING SALT, THEIR CORRESPONDING BATTERY AND THE ELECTROLYTE STATE AND CONCENTRATION VARIATION OF VANADIUM IONS DURING THE CHARGE AND DISCHARGE CYCLE.

SPECIES	SALT	BATTERY STATE	ELECTROLYTE	CHARGE	DISCHARGE
V^{2+}	VSO_4	Charged	Anolyte	↑	↓
V^{3+}	$\text{V}_2(\text{SO}_4)_3$	Discharged	Anolyte	↓	↑
$\text{VO}_2^{2+} (\text{V}^{4+})$	VOSO_4	Discharged	Catholyte	↓	↑
$\text{VO}_2^{+} (\text{V}^{5+})$	$(\text{VO}_2)_2\text{SO}_4$	Charged	Catholyte	↑	↓

Kim *et al.* [102] lists some technical challenges for VRFBs including low electrolyte stability and solubility leading to low quality of energy density [102], and vulnerability of the storage systems to sealing and leakage issues [103].

The other major challenge for VRFB systems is their capital cost, roughly \$550–600 per kWh, which is still high for broad market penetration. The high cost is, in part, due to the use of relatively expensive vanadium [104], but the high initial cost can be recouped as VRFBs can operate for over 10,000 full cycles and their lifespan can exceed 20 years [103].

The International Renewable Energy Agency (IRENA) reported the advantages and disadvantages of VRFBs (Table 5) [103].

VRFB flow battery technology provides for a very long operational life, low lifetime costs and low greenhouse gas emissions. The battery technology is mature, and it can be considered to be at the commercial stage for fixed applications. The technology is well proven and is undergoing demonstration as a load levelling battery for electricity utility zone sub-stations and other transmission and distribution applications [105]. VRFBs providing MWs in power and MWhs in energy-storage capacity have been demonstrated, and recently a 200 MW / 800 MWh VRFB was built and partially operated at 100 MW / 400 MWh in northeast China in Dalian [106]. H₂ Inc., a South Korean vanadium flow battery company, has installed several VRFB systems and has begun construction of a factory with 330 MWh annual manufacturing capacity [107].

3.2 Different VRFB generation chemistries

Since the first development of VRFBs in the 1980s at the University of New South Wales (UNSW) by Professor Maria Skyllas-Kazacos (as mentioned in section 2.1.1.1), the VRFB electrolyte has been constantly improved [108]. Several generations of VRFB have emerged over decades of work aimed at enhancing performance and solving challenges in operating the batteries. The main differences between these generations are the use of different electrolyte chemistries or the use of a single mixed inorganic acid (Table 6).



TABLE 5: ADVANTAGES AND DISADVANTAGES OF VRFB ELECTRICITY STORAGE SYSTEMS [103].

ADVANTAGES	DISADVANTAGES
<ul style="list-style-type: none">Long cycle life (10 000+ full cycles)Relative high energy efficiency (up to 85%), but lower than Li-ionOne of the most mature flow batteries with multiple demonstration and deployed at MW scaleDesign E/P ratio can be optimised to suit specific applicationLong-duration (1-20 hours) continuous discharge and high discharge rate possibleQuick response timesSame element in active materials on electrolyte tanks limits ion cross-contaminationElectrolyte can be recovered at end of project lifeHeat extraction due to electrolyte prevents thermal runaway	<ul style="list-style-type: none">Low electrolyte stability and solubility limit energy density, and low specific energy limits use in non-stationary applicationsPrecipitation of V₂O₅ at electrolyte temperatures above 40°C can reduce battery life and reliability, although this can be managedHigh cost of vanadium and current membrane designsUnoptimised electrolyte flow rates can increase pumping energy requirements and reduce energy efficiency

TABLE 6: COMPARISON OF EACH GENERATION OF VRFBs [109, 110]

	GEN1	GEN2	GEN3
Electrolyte	V/sulfate in both half-cells	V/HBr/HCl solution in both half-cells	V/H ₂ SO ₄ /HCl in both half-cells
Negative couple	V ³⁺ /V ²⁺	V ³⁺ /V ²⁺	V ³⁺ /V ²⁺
Positive couple	V ⁵⁺ /V ⁴⁺	Br/ClBr ₂	V ⁵⁺ /V ⁴⁺
Maximum vanadium concentration	1.5 – 2 M	2.0 – 3.5 M	2.0 – 2.7 M
Supporting Electrolyte	H ₂ SO ₄	HBr and HCl	H ₂ SO ₄ and HCl
Specific energy	15 – 25 Wh kg ⁻¹	25 – 50 Wh kg ⁻¹	25 – 40 Wh kg ⁻¹
Energy density	20 – 33 Wh L ⁻¹	35 – 70 Wh L ⁻¹	35 – 55 Wh L ⁻¹
Operating temperature range	10 – 40°C	0 –50°C	0 – 50°C

3.2.1 Generation 1 electrolyte

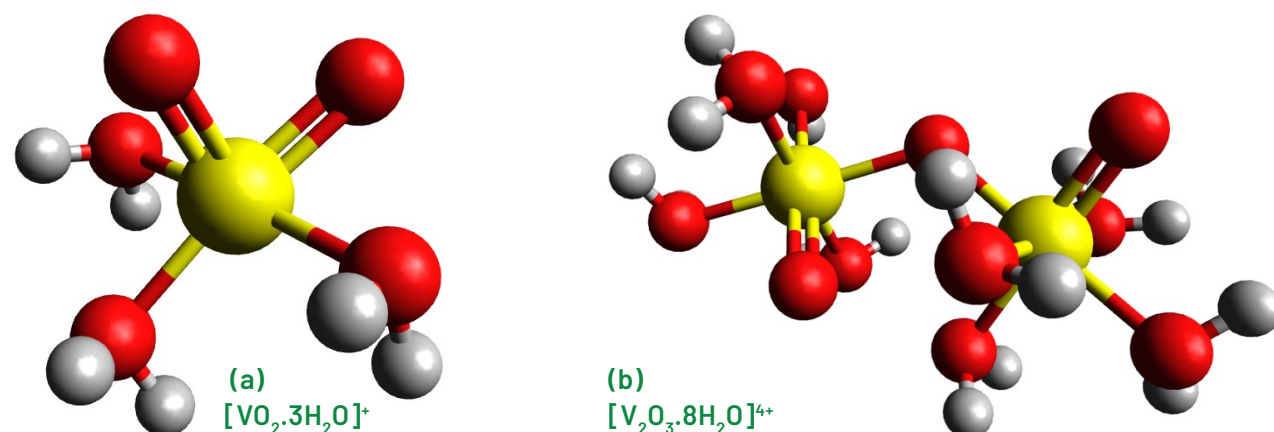
The first all-vanadium VRFB generation (Gen 1) was introduced by Skyllas-Kazacos *et al.* in the 1980s [27, 92, 111], with an electrolyte containing V^{3+} and V^{4+} vanadium oxidation states in concentrated sulfuric acid as a supporting electrolyte. Sulfuric acid was selected after testing a number of other supporting electrolytes. The cheapest vanadium salt available in the market is vanadium pentoxide (V_2O_5), but its very low solubility in sulfuric acid required Skyllas-Kazacos *et al.* to find another route to prepare the electrolyte. This was done via dissolution of $VOSO_4(V^{4+})$ (a more expensive salt) in sulfuric acid to achieve 2 M V^{5+} . This concentration reflects the solubility limit of the V^{2+} and/or V^{3+} ions in the sulfuric acid supporting electrolyte at temperatures below 5°C and the stability of the V^{5+} ions at temperatures above 40°C [112], which limits the battery energy density and operating temperature range. The maximum specific energy achieved using this type of electrolyte was 25 Wh.kg⁻¹, and this was low because vanadium salts have low solubility in sulfuric acid [113]. According to Kazacos *et al.* [112], the limited range of operating temperature of Gen 1 VRFBs (15 to 40°C) can be expanded by reducing the vanadium concentration in the electrolyte, thus reducing the specific energy. Later, a cheaper method for preparing Gen 1 electrolyte was developed by the same team using an electrochemical technique involving a suspension of V_2O_5 powder in sulfuric acid in one tank and sulfuric acid

in the other compartment separated by a membrane [114]. Other starting materials such as ammonium metavanadate were also considered [115]. This invention was nevertheless a major development in proving the commercial viability of VRFBs [116–118].

The major challenge with Gen 1 electrolyte is the precipitation of V^{5+} as V_2O_5 , this is due to the thermal instability of V^{5+} . V_2O_5 precipitates with increasing temperatures and state of charge (SoC), typically around 40°C for a 1.6 M vanadium solution at 100% SoC [119]. V^{5+} solution in diluted sulfuric acid has a yellow colour related to the $VO_2^+(aq)$ ions (which exist as hydrated penta-coordinated vanadate ions $[VO_2 \cdot 4H_2O]^+$ [120, 121]) or the more energy favourable $[VO_2 \cdot 3H_2O]^+$ cations [122]. The ability of this ion to form a dimer is highly dependent on the concentration of the acid. V^{5+} cations in concentrated sulfuric acid exist as di-nuclear $[V_2O_3 \cdot 8H_2O]^{4+}$ cations which are created via a dimerization reaction of $VO_2^+(aq)$ ions [120]. These di-nuclear cations undergo subsequent hydrolysis via a de-protonation reaction which leads to V_2O_5 precipitation [122].

The structure of a $[VO_2 \cdot 3H_2O]^+$ cation [122] (Figure 11a) and a di-nuclear $[V_2O_3 \cdot 8H_2O]^{4+}$ cation [123] (Figure 11b) are presented in Figure 11. These were created using Avogadro software (an open-source molecular builder and visualization tool) [124].

Figure 11: The structures of V^{5+} cation in diluted sulfuric acid (a) and the dimer in concentrated sulfuric acid (b). The yellow, red, and grey spheres represent vanadium, oxygen, and proton ions, respectively.



3.2.2 Generation 2 electrolyte

Vanadium-based Generation 2 VRFBs, “the vanadium bromide redox flow battery” (Gen 2) were developed by Skyllas-Kazacos *et al.* [125] in the early 2000s. The aim was to overcome the limited solubility of V^{5+} in the system. Bromine (as Br^-/Br_2) was used in the positive compartment instead of V^{5+}/V^{4+} , and vanadium V^{3+}/V^{2+} couple was used in the negative compartment [43, 44, 47, 126]. The solubility of vanadium ions in Gen 2 electrolytes increased by ca. 40% thus increasing the energy density by ca. 80%. The presence of bromine in this electrolyte introduced the new challenge of finding an appropriate material for the tanks, plumbing and the pumps, as bromine is a strong oxidiser and is more corrosive than vanadium. A vanadium chloride/polyhalide redox flow battery has also been suggested with a VCl_3/VCl_2 couple in the negative compartment and a $Br^-/ClBr_2^-$ couple in the positive compartment [125, 127]. Solubilities of V^{2+} and V^{3+} in hydrochloric acid as high as 4 M have been reported for this system. The high solubility of V^{2+} and V^{3+} in hydrochloric acid compared to sulfuric acid greatly increases the energy density of the electrolyte and is the main motivation to introduce hydrochloric acid into the system.

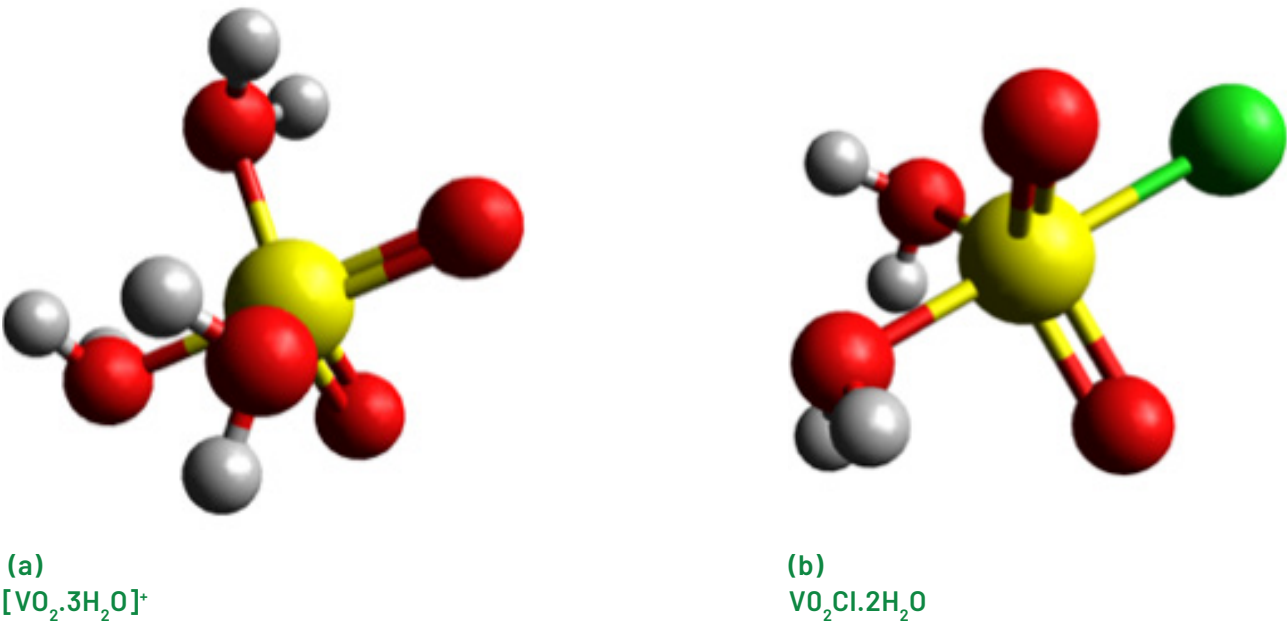
3.2.3 Generation 3 electrolyte

In 2011 Li *et al.* [128] from Pacific Northwest National Laboratory (PNNL) were the first to introduce a Gen 3 electrolyte. In a novel method they employed chloride ions together with sulfate ions in the supporting electrolyte. They added hydrochloric acid into a sulfuric acid Gen1 electrolyte to form a mixed acid electrolyte. The mixed acid electrolyte has the potential to increase the energy density of the battery, improve the electrolyte stability [129] and enhance the solubility of the vanadium species in the catholyte and/or anolyte [130, 131]. This approach was successful in providing a more stable vanadium electrolyte and higher vanadium concentration.

The concentration of vanadium in a mixed acid electrolyte (Gen 3 electrolyte) can reach up to ca. 2.5 M (vs. <1.6 M for Gen 1 VRFBs) without any precipitation, and this electrolyte can operate at temperatures ranging from -5°C to 50°C. The improved electrolyte stability is related to the formation of a soluble neutral species $VO_2Cl \cdot 2H_2O$, with V^{5+} [128] instead of $[VO_2 \cdot 3H_2O]^+$ (in sulfate media). Structures of vanadium sulfate (Figure 12a) and sulfate-chloride mixed electrolyte (Figure 12b) are presented in Figure 12 [124].

Vijayakumar *et al.* [123] from PNNL, analysed the V^{5+} cation structures in mixed acid electrolytes using computational modelling based on density functional theory (DFT) supported by ⁵¹V and ³⁵Cl nuclear magnetic resonance (NMR) spectroscopy. As V^{5+} cations exist as di-nuclear $[V_2O_3 \cdot 8H_2O]^{4+}$ compounds at higher vanadium concentrations (<1.75 M) in concentrated sulfuric acid, they undergo a ligand exchange process at high temperatures (>295 K) with chloride ions to form the energetically favourable chlorine bonded $[V_2O_3Cl_2 \cdot 6H_2O]^{2+}$ compound. The formation of the chlorine bonded compound might be the key to the higher thermal stability of mixed acid V^{5+} electrolytes as it prevents V_2O_5 precipitation by inhibiting the de-protonation reaction.

Figure 12: The structures of V⁵⁺ complexes in the sulfate and the sulfate–chloride mixed solutions. The yellow, green, red, and grey spheres represent vanadium, chloride, oxygen, and proton ions, respectively.



Another approach that involved incorporating chloride ions into a VRFB electrolyte was introduced by Kim *et al.* [104]. The authors used only chloride ions in the electrolyte without any sulfate. The vanadium concentrations in the chloride solutions were more than 2.3 M for all vanadium species and remained stable for >20 days between 0–50 °C. At –5 °C only V³⁺ was stable for 96 hours at a concentration of 2.3 M, but this species was stable for >20 days at 1.5 M [130]. The improved stability of the electrolyte was also related to the formation of the vanadium di-nuclear compound. Chlorine gas evolution was prevented by using proper voltage control during charging [132], but further development of the mixed acid VRFBs should take into account the possible formation of chlorine gas or the VCl₃ toxic powder.

3.3 Composition and operation of VRFBs

VRFBs have the standard RFB components of current collectors, bipolar plates, electrodes, and a membrane. A recent review by Iwakiri *et al.* [110] summarised the state-of-the-art in RFBs used in research between 2015 and the middle of 2021. They focused on the main innovations being investigated in materials and designs, the main drawbacks identified, and future prospects for each technology. Table 7 summarises the most common VRFB components used since 2016.

TABLE 7: THE MOST RELEVANT VRFB COMPONENTS REPORTED SINCE 2016 [110].

YEAR	ELECTROLYTE	ELECTRODES	BIPOLAR PLATES	MEMBRANE	REFERENCE
2016	3 M H ₂ SO ₄ + 1 M V + varying concentrations of CuSO ₄	Graphite felt	Graphite plate with serpentine	Nafion 212	[133]
2016	3 M H ₂ SO ₄ + 1 M V	Carbon paper with KOH activation of the fibres	Graphite plate with serpentine flow-field	Nafion 212	[134]
2017	3 M H ₂ SO ₄ + 1.5 M V	Graphite felt	IrOx-coated TiO ₂	Nafion 117	[135]
2018	3 M H ₂ SO ₄ + 1 M V	Electrospun carbon fibres	Not specified	Nafion 212	[136]
2019	3 M H ₂ SO ₄ + 1.5 M V	Carbon felt	Low-carbon-content design based on the bridging effect of graphene	Nafion 212	[137]
2019	3 M H ₂ SO ₄ + 1.7 M V	Carbon nanofoam free standing sheets	Graphite plate with serpentine flow-field	Nafion 117	[138]
2020	2 M H ₂ SO ₄ + 1.6 M V	Composite material based on nickel manganite and carbon nanofibers	Graphite plate	Fumasep F-930-RFD	[139]
2020	3 M H ₂ SO ₄ + 1.1 M V	Graphite felt treated at 500 °C for 8 h	Graphite plate with serpentine flow-field	Nafion 211	[140]
2020	3 M H ₂ SO ₄ + 1.5 M V	Not specified	Low carbon content with hybrid conductive materials of graphene, carbon fibres and graphite powders	Nafion 212	[141]
2021	3 M H ₂ SO ₄ + 1.5 M V	Carbon felt	Graphite plates	Derived from pyridine-containing poly(aryl ether ketone ketone)	[142]
2021	3 M H ₂ SO ₄ + 1.5 M V	Carbon felt	Not specified	Hybrid membrane prepared using a casting method	[143]
2021	3 M H ₂ SO ₄ + 1 M V	Carbon felt	Graphite plates with serpentine flow-fields	composite polybenzimidazole	[144]

3.3.1 Electrolytes

The electrolytes in VRFBs consist of vanadium ions in an acid-aqueous solution. Sulfuric acid is the most common acid used as a supporting electrolyte, but limitations of using sulfuric acid includes the solubility of vanadium species in the solution and the limited operating temperature range. The concentration of vanadium ranges between 1.5 – 2.0 M in a sulfuric acid-based electrolyte, and the operating temperature is between 10 and 40°C. At low temperatures the viscosity of the electrolyte increases, which makes it more difficult to flow through the system and below 10°C, V²⁺ and V⁴⁺ precipitate out as a solid phase. At a high temperature above 40°C, V⁵⁺ precipitate out as solid V₂O₅ in the positive electrolyte.

It is critical to minimise or eliminate impurities in the electrolyte for a battery to perform well [145, 146]. Numerous methods to prepare a pure VRFB electrolyte have been investigated throughout the years. A number of vanadium oxidation states can be produced by either chemical or electrochemical methods using vanadium salt in the supporting electrolyte. In the early stages of VRFB development, the vanadium salt used was

the expensive vanadium (IV) sulfate. Later vanadium pentoxide V₂O₅ was used as a precursor salt as it is much cheaper than vanadium (IV) sulfate.

While suspended V₂O₅ is used as a starting chemical in sulfuric acid-based electrolytes, V₂O₃ is used in hydrochloric acid electrolytes which results in a mixture of V⁴⁺ and V³⁺ ions.

To produce the electrolyte through a chemical method, a range of reducing agents such as SO₂ are utilised in order to reduce V⁵⁺ from vanadium pentoxide V₂O₅ to V⁴⁺. Further addition of reducing agent plus a catalyst will produce a mixture of V⁴⁺ and V³⁺ known as a V³⁻⁵⁺ electrolyte. On the other hand, producing the electrolyte via an electrochemical method uses suspended V₂O₅ in sulfuric acid in the anolyte tank and sulfuric acid in the catholyte tank, and after passing a current through the system, the VRFB electrolyte is ready.

Table 8 provides a summary of the chemicals used in producing commercial electrolytes. Researchers conducting fundamental studies on potential electrolytes have investigated other electrolyte formulae and these are summarised in Table 9.

TABLE 8: A SELECTION OF COMMERCIAL ELECTROLYTE VENDORS.

CHEMICAL	ENIENERGY TECHNOLOGIES [147]	OXKEM VANADIUM [148]	HIGHVELD VRB [149]	US VANADIUM [150]	ELECTROCHEM TECHNOLOGIES & MATERIALS INC. [151]
Vanadium III Chloride	1-25%	-	-	-	-
Hydrochloric acid	2-25%	-	-	-	-
Vanadyl dichloride	1-25%	-	-	-	-
Vanadium dichloride	0-20%	-	-	-	-
Sulphuric Acid	0-10%	10-20%	5-20%	< 20%	10-20%
Vanadyl sulfate	0-10%	10-20%	NotSpec	< 15%	5-15%
Vanadium trisulfate	0-5%	10-20%	-	< 15%	10-15%
Orthophosphoric acid	-	1-10%	-	-	≤ 1%
Water	NotSpec	NotSpec	NotSpec	NotSpec	50-70%



TABLE 9. A FEW RESEARCH LABORATORY VRFB ELECTROLYTE FORMULAE.

VANADIUM PRECURSOR	CONCENTRATION (M)	SUPPORTING ELECTROLYTE	CONCENTRATION (M)	REFERENCES
V ₂ O ₃	2.3	HCl	10	[104]
VO ₂ SO ₄	2	H ₂ SO ₄ + HCl	2 and 5	[72]
VO ₂ SO ₄ VCl ₃	1.0	H ₂ SO ₄ + HCl	1 and 2	[152]
V ₂ O ₅ oxalic acid dihydrate	1.0 1.0	H ₂ SO ₄ + HCl	2 and 5	[152]
V ₂ O ₅	1.0	H ₂ SO ₄ + HCl	2 and 5	[152]
VO ₂ SO ₄		H ₂ SO ₄	3	
VO ₂ SO ₄	1.5	H ₂ SO ₄	2.6	[153]
VO ₂ SO ₄	1.5	H ₂ SO ₄	3	[154]
VO ₂ SO ₄	1.5	H ₂ SO ₄	2	[155]

The performance of VRFBs is impacted by capacity reduction, which is caused by a variety of effects that result in various types of imbalances between the positive and negative electrolytes, necessitating rebalancing procedures. During long-term cycling, three types of electrolyte imbalances can occur: concentration imbalance; oxidative imbalance; and reductive imbalance [156-159]. All three imbalances result in a decrease in battery capacity over time [160]. The concentration imbalance is the most reversible and is distinguished by a difference in vanadium

concentration between electrolytes. The concentration, pressure, and potential gradients between the positive and negative half-cells cause water and vanadium species to cross through the cell membranes. The oxidative and reductive imbalances are caused by side reactions that occur within the battery, and these imbalances are irreversible [160].

3.3.2 Electrodes

Electrodes provide active solid-electrolyte interface sites for the electrochemical reactions of the vanadium redox couples and thus play a key role in determining the power density as well as the life cycle of a battery. The kinetics and mechanism of the vanadium redox couple reactions are strongly dependent on the electrode surface. The electrochemical performance and stability of a range of new electrode materials, used as positive and negative electrodes in VRFBs, have been evaluated by many researchers using classic voltammetry curves (cyclic and linear voltammetry), charge-discharge cycles and morphology studies of the electrode.

It is essential for an electrode material to demonstrate high electrical conductivity with high active surface area, low cost, good stability against acids, and electrochemical stability in the operation potential window of the VRFB.

Graphite is preferable to metals (unless they are coated) as the material for bipolar plates (BPPs) in the acidic environment of a VRFB, because it is conductive and has high electrochemical and chemical stability. However, pure graphite substrates are brittle and susceptible to electrolyte penetration due to their porosity.

In order to produce better BPPs, conductive carbon-polymer based composites have been used and they offer some significant advantages over pure graphite plates, including greater mechanical strength, resistance to electrolyte permeation, and corrosion resistance.

Graphite felts (GFs) are another popular electrode material in VRFBs due to their high surface area, chemical stability, low toxicity, low cost and good electrical conductivity. However, the main barriers to using pristine GF in VRFB applications are its hydrophobicity and limited electrochemical activity [161].

Carbon-based materials, including graphite plates, glassy carbon, PAN-type carbon felt or graphite felt, carbon paper, graphene oxide, carbon nanowires/nanotubes, carbon cloth, carbon-polymer composite etc., are intriguing battery electrode material candidates because in general they are resistant to acid corrosion. It has been reported that they can be used safely for the negative compartment (V²⁺/V³⁺), but also that they degrade and mechanically disintegrate during charging at the positive electrode due to oxygen evolution. A historical flow chart for research on electrodes for VRFBs is shown in Figure 13.

For the positive electrolyte, whose kinetics appear to be more complex due to the oxygen transfer between V⁴⁺ and V⁵⁺, a treatment is required to form oxygenated surface groups that are capable of increasing electrode responses (V⁵⁺). There are numerous electrode treatment methods including metal doping, structural modification, heat treatment, and acid treatment.

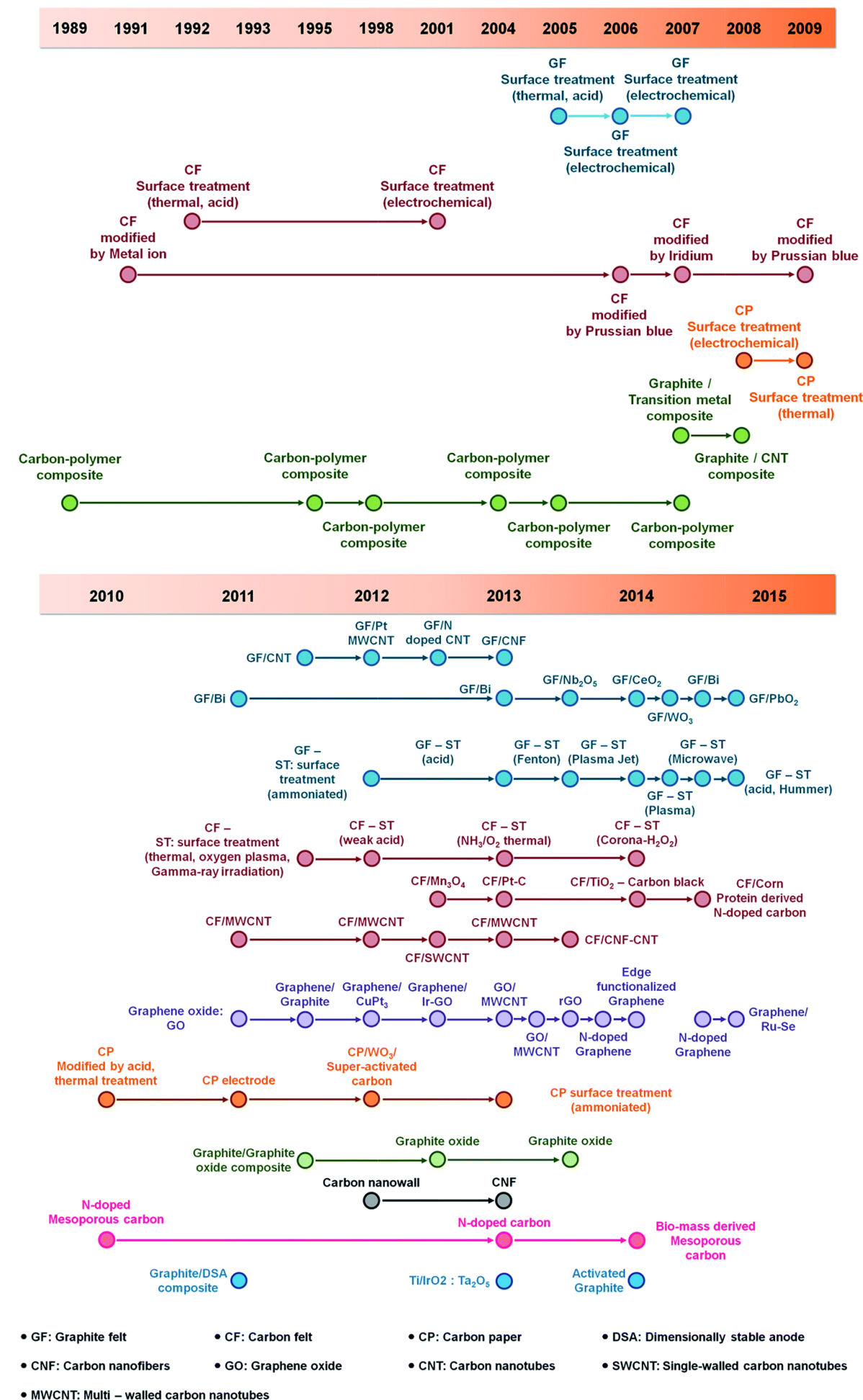


Figure 13: Historical flow chart for research on electrodes for VRFBs [102].

3.3.3 Membranes

The membrane or separator is a key component of VRFBs, as it plays the role of separating the positive and negative electrolytes and keeping the vanadium ions in their respective positive and negative compartments. In this way, membranes prevent cross-mixing of the vanadium ions, while passing ions such as protons, sulfate or chloride ions during the charge-discharge cycle in order to complete the electrical circuit.

High ion selectivity, ion conductivity, and chemical and mechanical stability are all desirable properties in membranes. Perfluorinated sulfonic acid polymers such as Dupont's Nafion have traditionally been used

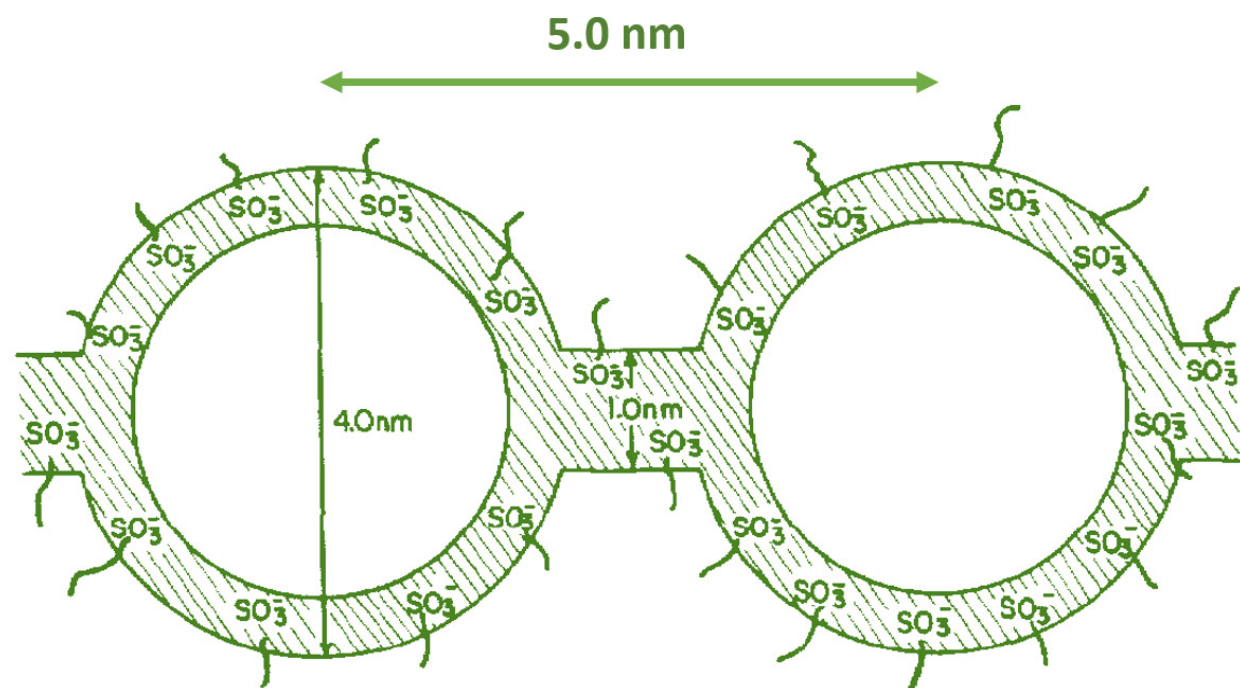
in VRFB membranes. Although these membranes have high proton conductivity and chemical stability, their extremely high cost and low ion selectivity (high vanadium crossover) have limited their commercial use. As a result, new ion exchange membrane (IEM) materials are being sought.

Recently, various types of IEMs, such as anion or cation exchange membranes and even blend membranes, have been investigated for VRFB applications [121]. Under normal operating conditions, a VRFB membrane should have low vanadium ion permeability to minimise self-discharge, low cost, and long-term chemical stability. It is well known that high proton conductivity and low vanadium ion crossover improve the efficiency of VRFBs [162].

TABLE 10. DIFFUSION COEFFICIENT, STOKES RADIUS AND IONIC RADIUS FOR THE VANADIUM SPECIES (DATA ARE FROM[163-166].

SPECIES	DIFFUSION COEFFICIENT (cm ² /s) [163]	STOKES RADIUS (nm) [163]	IONIC RADIUS (6-COORDINATE) (pm) [165]
V ²⁺	1.1 × 10 ⁻⁶	0.32	79
V ³⁺	0.57 × 10 ⁻⁶	0.32	64
VO ²⁺ (V ₄ ⁺)	1.0 × 10 ⁻⁶	0.21	58
VO ²⁺ (V ₅ ⁺)	1.0 × 10 ⁻⁶	0.28	54
Hydrated Vanadium ions	-	0.60 [164]	-
Hydrated V ³⁺ ion	-	-	65 [166]

Figure 14: Cluster-network model for the morphology of hydrated Nafion membranes [167].



Hsu *et al.* [167] (Figure 14) presented a nafion membrane cluster-network model in which the polymeric ions and absorbed electrolyte are separated from the fluorocarbon backbone and form roughly spherical clusters connected by short narrow channels. They have proposed that the polymeric charges are most likely embedded in the solution near the electrolyte-fluorocarbon backbone interface. In this way, the hydrophobic interaction of water with the backbone is minimised, as is the electrostatic repulsion of proximate sulfonate groups.

Mohammadi *et al.* [168] investigated the chemical stability of Daramic (microporous polymer), modified Daramic, and commercial ion exchange membranes during charge-discharge cycling by monitoring membrane resistivity and permeability for changes caused by fouling or degradation. It was discovered that chemical degradation of the membranes is related to catholyte oxidation of the polymeric membrane material.

Sukkar and Skyllas Kazacos [169] also investigated membrane stability and discovered that membrane resistivity decreased after prolonged exposure to a 0.1 M V^{5+} + 0.25 M H_2SO_4 solution, possibly due to polymeric material erosion. The ion exchange capacity (IEC) of membranes was found to increase with soaking time, which could be attributed to SO_4^{2-} and HSO_4^- from the solution being embedded in the membrane pores. The V^{4+} ion diffusivity of membranes was also found to increase with prolonged exposure to this solution. The results of the long-term stability tests indicated that the faster rate of ion transfer was most likely responsible for the decrease in membrane resistance, and that, despite the low weight loss and degree of oxidation, all of the membrane properties gradually deteriorated over time.

Huang *et al.* [170, 171] investigated the degradation of sulfonated polyimide (SPI) membranes in VRFBs. They discovered that the SPI membrane was visibly fractured after 800 cycles, resulting in VRFB failure. Studies on membranes revealed that the surface facing the positive electrode contained significant microdefects, whereas the surface facing the negative electrode did not change. The highly oxidative V^{5+} species and the strong acidic environment were thought to be responsible for membrane degradation, as evidenced by the generation of V^{4+} (the reduction product of V^{5+}) observed alongside degradation. According to their findings, the higher the concentrations, the faster the membrane degrades.

Kim *et al.* [172, 173] investigated the chemical degradation of a sulfonated poly(sulfone) membrane during charge-discharge cycling in a VRFB cell. They discovered that the membrane delaminated on the surface facing the positive electrode, similar to the findings of Huang *et al.* Near the degraded surface, vanadium rich and sulfur deficient regions were observed [174].

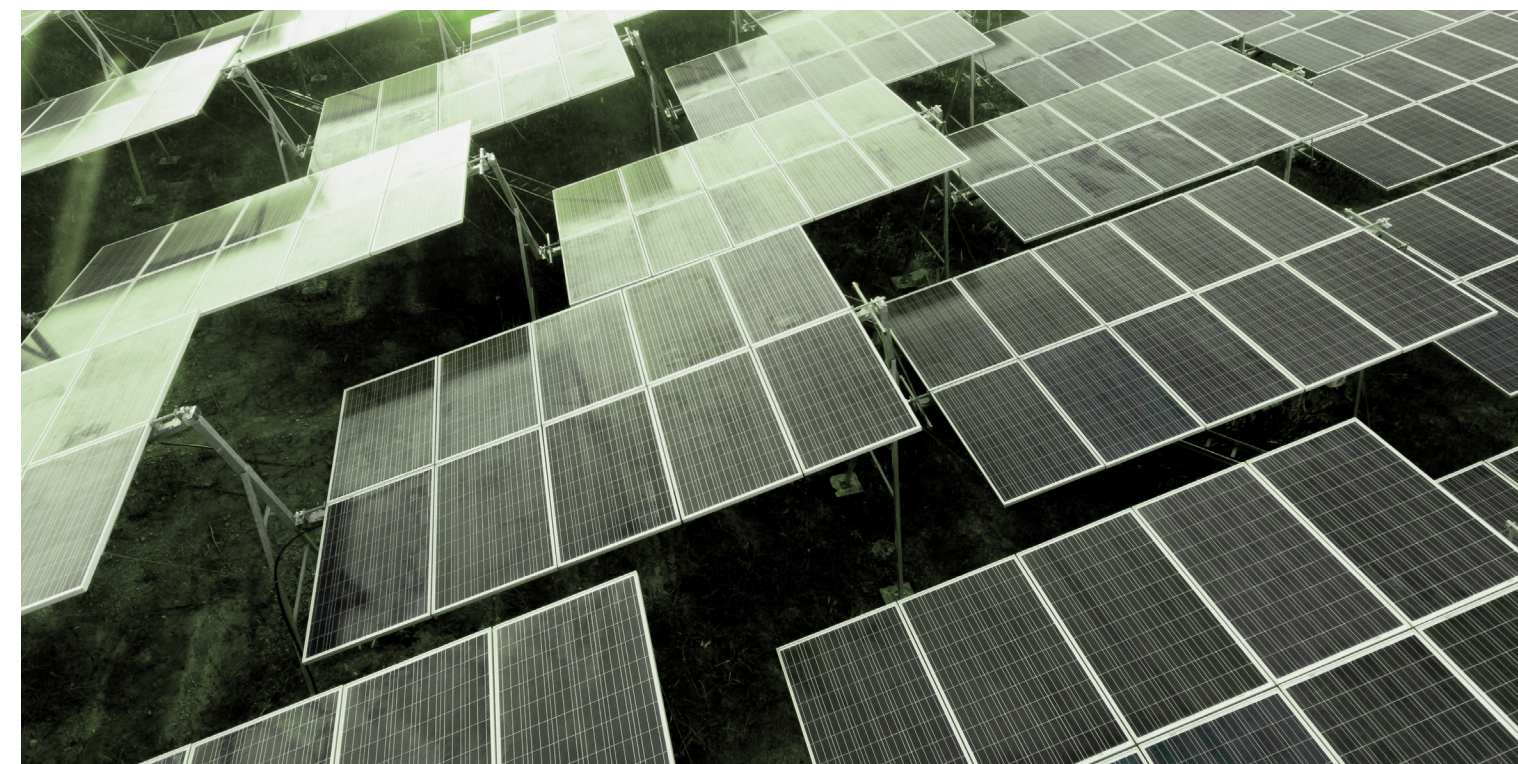
Choi *et al.* [175] studied a series of sulfonated poly(ether sulfone) copolymers to study the degradation mechanisms of hydrocarbon membranes. They discovered that polymers with electron-accepting sulfone linkages were significantly more stable than those with electron-donating thioether linkages. The linkage groups in the latter membrane were thought to be more flexible, allowing the V^{4+} ions to pass through the membrane more easily. There are relatively few publications that describe the degradation mechanism of hydrocarbon membranes. These studies have reported that V^{5+} attacks positively charged functional groups, neutralising the membrane and shifting the electrophilic centre to the polymeric backbone, where further attack occurs, eventually leading to the scission of the main chain.

Pahlevaninezhad *et al.* [176] have investigated a novel composite Nafion-based membrane that significantly improves VRFB performance. Using appropriate analytical techniques, the chemical, structural, and thermal properties of the composite membrane were determined. The results show that using the composite membrane increased energy efficiency from 51% to 63%. Furthermore, charge-discharge capacity and capacity retention improved by approximately 200% and 25%, respectively. This improvement can be attributed to the composite membrane's higher proton conductivity and lower vanadium permeability.

Mu *et al.* [177] presented a series of low-cost and high-performance VRFBs with blend membranes made of polyvinylpyrrolidone (PVP) and cardo-poly(etherketone) (PEKC). The PEKC network provides excellent mechanical rigidity to the membrane, whereas PVP provides superior sulfonic acid uptake due to the presence of N-heterocycle and carbonyl groups in PVP, resulting in low area resistance. In addition, the electrostatic repulsion effect of protonated PVP polymer chains towards vanadium ions results in low vanadium ion permeability in blend membranes.

As a result, the 50% PVP-PEKC membrane had a high ionic selectivity of 1.03×10^6 S min cm^{-3} , whereas Nafion 115 has a nearly 17 times lower selectivity (6.03×10^4 S min cm^{-3}). At current densities of 80–180 mA/ cm^2 , the VRFB with a 50% PVP-PEKC membrane had high coulombic efficiencies (99.3–99.7%), voltaic efficiencies (84.6–67.0%), and energy efficiencies (83.9–66.8%), as well as excellent cycle constancy, indicating that low-cost 50% PVP-PEKC blend membranes have great potential for use in VRFBs.

Most research groups studying membranes for VRFB applications have used chemical stability tests as a standard. However, most have reported binary results: i.e., either the membrane degraded, or it did not. Only a small percentage of researchers appear to have conducted in-depth studies to determine the mechanisms of membrane degradation. As a result, there is still much to learn and discover in this field.



3.4 VRFB applications and installations

The Australian Energy Market Operator (AEMO) has identified multiple storage technologies that can help address the challenges in the uptake of variable renewable energy (VRE) in the National Electricity Market (NEM). These technologies include Pumped Hydro Energy Storage (PHES), large-scale lithium-based battery storage, and vanadium flow battery storage. When AEMO compared VRFB with other storage technologies, VRFBs were found to provide medium-duration storage without the geographic limitations and long lead times of PHES, and storage for a large number of charge-discharge cycles without the significant degradation found with lithium batteries, as well as a better safety profile [178].

Absolute reports (<https://www.absolutereports.com/>) produced an extensive study on the “Global All-Vanadium Redox Flow Batteries Market 2020”. They predicted the global average price of a VRFB would decrease, and the market size was projected to reach USD 6186 million by 2026, up from USD 884 million in 2020 [41].

The number of VRFB installations around the world is growing rapidly (Figure 15) [35, 38, 89, 97-101, 179], as the demand for storing the energy generated from renewables increases. The numbers and combined power rating of installed VRFB storage systems for the five countries with the largest use of this technology in 2019 are summarised in Table 11 [179].

TABLE 11. INSTALLED VRFB STORAGE SYSTEMS IN JANUARY 2019 [179].

COUNTRY	VRFB SYSTEMS	POWER (kW)
China	14	310,755
USA	14	4,348
Germany	14	1,480
Australia	7	945
Japan	5	2,330

There are many companies already producing VRFB systems around the world, including Sumitomo, WattJoule, Invinity Energy Systems, Rongke Power, Cellcube Energy Storage Inc., Prudent Energy VRB Systems, Volterion, Pinflow, VRB Energy, and Delectrik [96]. Currently, commercial systems in the megawatt range are being built.

In Australia, and specifically in Western Australia, VSUN Energy, and Ultra Power systems (UPS) offer VRFB products. UPS is currently building the “V40” module that will deliver 6 kW (40 kWh) [180].

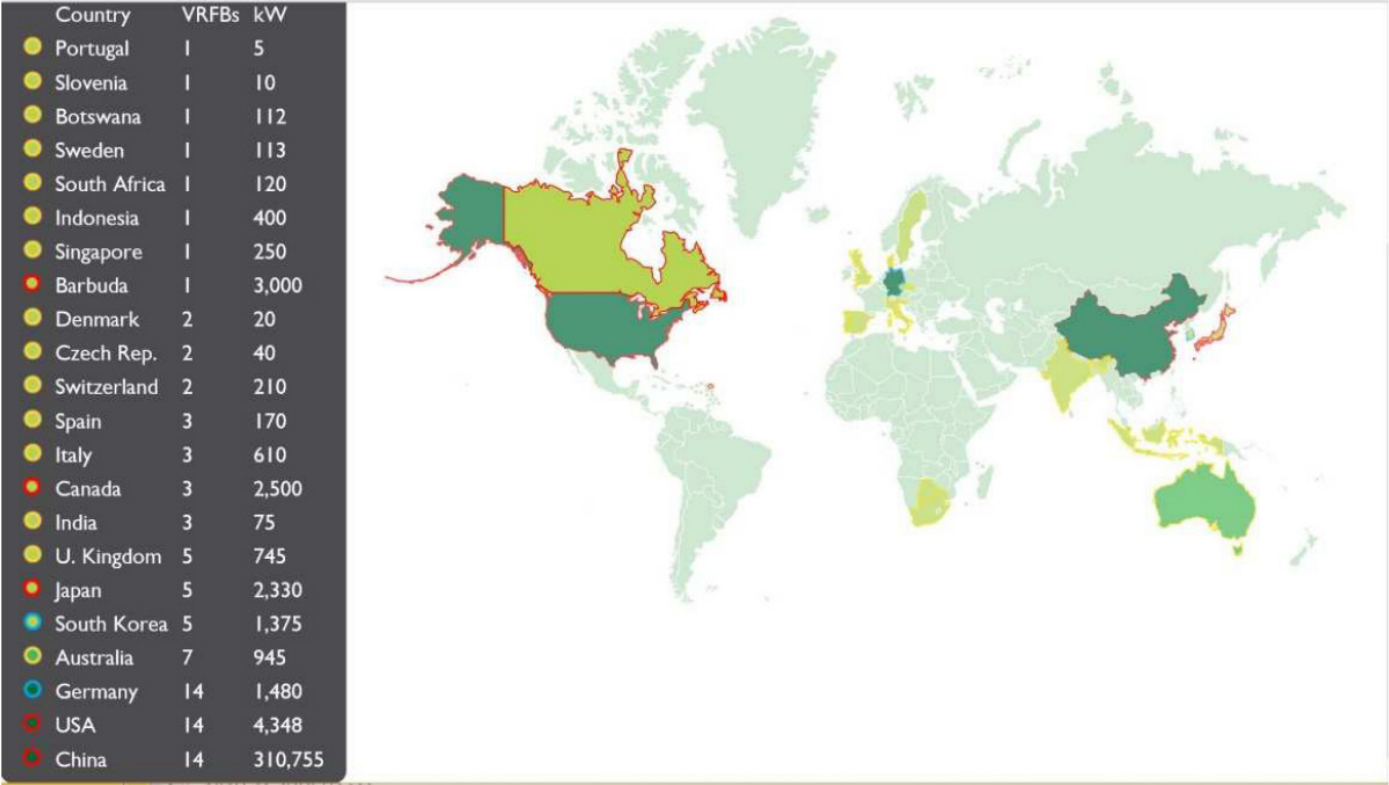


Figure 15: Numbers and combined power rating of installed VRFB storage systems around the world in January 2019 [179].

The first phase of the Dalian Flow Battery Energy Storage Peak-shaving Power Station went online in October 2022. This large-scale chemical energy storage demonstration project will eventually produce 200 megawatts (MW)/800 megawatt-hours (MWh) of electricity. The first phase will produce 100 MW/400 MWh [181].

As the capital cost of large VRFB systems is very high, in order to make VRFBs more competitive, electrolyte suppliers are considering leasing electrolyte to VRFB customers instead of selling it. Of the total system cost, 32% is the VRFB electrolyte [182]. Renting electrolyte is a new business model that may lower the price for VRFBs, which could make VRFBs price competitive with lithium-ion batteries. In 2020, Invinity Energy Systems (a VRFB manufacturer) partnered with minerals company and vanadium producer Bushveld Minerals to form Vanadium Electrolyte Rental Limited (VERL) [183] which allows customers to rent VRFB electrolyte over the lifetime of a project, helping them to balance their initial capital cost. Additional opportunities for VRFB cost reductions include increased manufacturing scale, increased energy densities, and plug and play (e.g., turnkey) units to keep EPC costs down.

3.5 Additives as stabilising agents

Several research groups are reconsidering the use of additives that are expected to improve the stability of supersaturated electrolytes as well as their electrochemical performance in order to increase the energy density of the Gen1 VRFBs. At high temperatures, the pentavalent vanadium ion in the electrolyte crystallises easily, limiting its concentration in the electrolyte. This effect can be mitigated by the addition of additives. These additives can be added to the electrolyte to improve its long-term stability, material compatibility, and thermal stability. The additives should be compatible with all vanadium ions present during the charging and discharging processes (V^{2+} , V^{3+} , V^{4+} and V^{5+}) as the additives can move across the membrane over time.

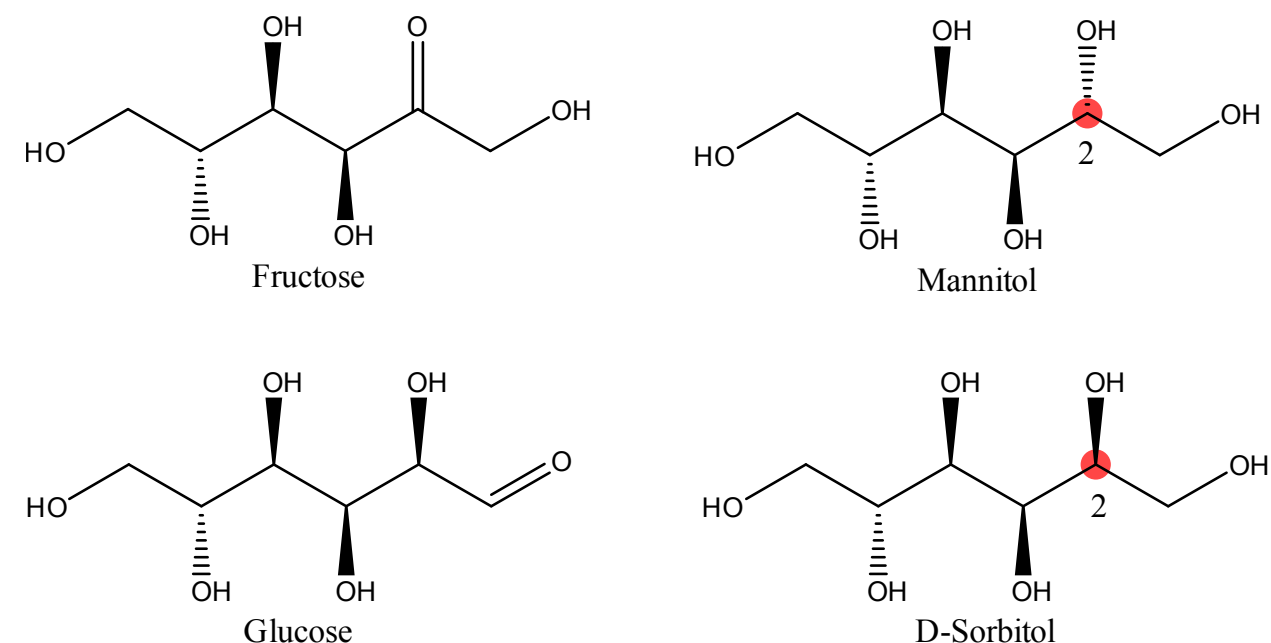
The term “stabilising agent” first coined by Skyllas-Kazacos and co-workers [184, 185] refers to compounds that can be added to vanadium electrolytes to prevent precipitation when supersaturation occurs at high or low temperatures, allowing for a higher practical vanadium electrolyte concentration and/or a wider operating temperature range. The stabilising additives increase precipitation induction time rather than increasing solubility.

To date, the majority of the work reported in the literature has focused on the stability of the positive electrolyte (V^{4+} and V^{5+} containing solutions), with little research on the stability of the negative electrolyte (V^{2+} and V^{3+} containing solutions). Several researchers have previously investigated a wide range of additives as stabilising agents such as surfactants with straight chains consisting of $-OH$, $-NH_2$ and $-SH$, phosphonates and phosphoric acid compounds, carbohydrates, carboxylic acids, oxo-acids, and ammonium compounds [68, 186]. Kazacos and Skyllas-Kazacos presented hundreds of potential additives in a 2002 patent [187]. They discussed the effect of these additives on the performance of VRFBs which varied from harmful to

effective. The effects of various inorganic and organic stabilisers on the stabilities of vanadium ions in sulfuric acid solutions in the -5 to 50°C temperature range were investigated by Zhang *et al.* [188]. By adding some stabilisers, they found that the additives marginally improved the stability of vanadium ions in both positive and negative electrolytes in a sulfuric acid supporting solution. Potassium cations, phosphate, and polyphosphate anions have a negative effect on the stability of positive vanadium solutions due to the formation of insoluble $KVSO_6$ or VPO_4 with V^{5+} ions. While polyacrylic acid was discovered to be a potential negative electrolyte stabilising agent, a mixture of polyacrylic acid and methane sulfonic acid (CH_3SO_3H) appeared to be suitable for the positive electrolyte.

Several authors studied the stability of the positive electrolyte after adding various additives to the VRFB electrolyte [189-196]. Huang *et al.* [197] investigated the effect of adding Mn^{2+} ions to the anolyte of Gen1 VRFBs and discovered that when Mn^{2+} ions are added at a concentration of 0.04 – 0.13 g L^{-1} , there is an improvement in the reversibility and electrochemical activity of the V^{4+}/V^{5+} couple as well as an increase in the vanadium ion diffusion coefficient value. However, when the concentration was less than 0.04 g L^{-1} , the interfacial resistance of the V^{4+}/V^{5+} couple at the electrode surface increased. As a result, different concentrations of Mn^{2+} are expected to have different effects on cell performance. In a recent study, Chang *et al.* [195] investigated Coulter dispersants (an aqueous dispersant from Beckman Coulter Company, USA) as positive electrolyte additives. The electrolytes were tested with various dispersants and studied in terms of electrolyte stability and electrochemical performance. The addition of Coulter IIIA dispersant significantly delayed precipitate formation while also increasing energy efficiency [195]. Li *et al.* [196] studied the effect of the organic additives fructose, mannitol, glucose, and d-sorbitol on the positive electrolyte in VRFBs.

Figure 16: The molecular structures of organic additives investigated by Li *et al.*



The authors found that incorporating d-sorbitol into the electrolyte is an effective method for improving the electrochemical properties of the electrolyte. Based on results from Cyclic Voltammetry (CV), charge-discharge technique, and electrochemical impedance spectroscopy (EIS), the addition of d-sorbitol increases the electrochemical activity of the electrolyte. This was attributed to the ease of vanadium ion adsorption on the surface of the electrode due to the increased availability of hydroxyl groups, which provide active sites for electron transfer. In addition, the orientation of the hydroxyl group on carbon 2 makes d-sorbitol superior to its isomer mannitol. Peng *et al.* [194] investigated the cycling and electrochemical stability of a VRFB using tris(hydroxymethyl) aminomethane (Tris). The addition of Tris to the positive electrolyte improved charge discharge behaviour and resulted in a lower discharge capacity fade rate. Peng and co-workers [198] also investigated the thermal stability and electrochemical activity of the Gen1 VRFB electrolyte using Tris as an additive and discovered that adding 2–4% Tris improved the stability of the V^{5+} electrolyte at 40°C . There was also an increase in voltage and energy efficiencies.

Only Wu *et al.* [199] have investigated quaternary ammonium salt as an additive. They added hexadecyl trimethyl ammonium bromide (CTAB) to the vanadium redox flow battery electrolyte. By interfering with the interaction of the quaternary ammonium salt and V^{5+} ions, CTAB inhibited V^{5+} ion polymerisation and V_2O_5 precipitation.

Only a few authors have explored the stability of the negative electrolyte [186, 200, 201]. A number of inorganic and organic additives were studied by Mousa and Skyllas-Kazacos [186], who investigated the effect on the low temperature stability of the negative half-cell electrolyte of several inorganic acids and salts, low-molecular-weight organic compounds, polymeric organic compounds, and polyphosphate-based compounds as additives. They found that the additives improved the stability of solutions containing $2\text{M } V^{2+}$ ions and 5M total sulfates against precipitation over several days at 5°C compared to a stability duration of 16 h for the solution without additives. Adding ammonium phosphate to the negative electrolyte showed no precipitation or electrolyte blockage from V^{3+} sulphate, as happened in the additive-free solution, even after 250 cycles. In contrast to the V^{2+} , a $2\text{M } V^{3+}$ solution in 5.0M total sulphate was found to be very stable against precipitation.

However, as Skyllas-Kazacos and co-workers [108, 185] previously demonstrated, the effect of organic compounds as stabilising agents for the VRFB electrolyte is usually only temporary because most organic compounds are slowly oxidised by the strongly oxidising V^{5+} species in the charged positive half-cell electrolyte. Compounds like glycerol slowly oxidise to CO_2 plus water, with the V^{5+} in the electrolyte being reduced to V^{4+} . Because inorganic compounds are not attacked by V^{5+} , they have a longer lasting stabilising effect on V^{5+} .

3.6. Effect of different impurities

As mentioned in section 3.2.1 the main starting chemical in preparing VRFB electrolyte is V_2O_5 . The main sources of V_2O_5 are vanadium ores, concentrates, iodide thermal decomposition products, metallurgical slags, petroleum residues, and fly ash [202–204]. These sources can introduce impurities into the electrolytes and understanding what impurities are present is important for a number of reasons. As the electrolyte purity is directly proportional to the performance of the battery, determining the maximum allowable concentration of impurities present in the starting chemicals of the VRFB electrolyte and during the process of making the electrolyte facilitates stable battery performance. Because impurity ions have a large influence on the electrolyte’s properties that greatly affect the electrolyte stability, electrochemical kinetics, energy density, and overall cell performance [205], vanadium electrolyte raw materials such as $VOSO_4$ and V_2O_5 must be highly pure, resulting in a higher cost for VRFB production. In contrast, if low-impurity raw materials such as rich vanadium liquid can be used directly to prepare the electrolyte, the cost of VRFBs can be significantly reduced. Furthermore, when the impurity ions in the electrolyte reach a certain concentration limit, the electrolyte loses activity and must be regenerated. Unfortunately, there are very few published reports of investigations into the effect of electrolyte impurities, and studies of the individual effects of different impurities are extremely rare in the literature.

The main reasons impurities are present in the electrolyte are [184]:

- Using vanadium pentoxide (V_2O_5) as the raw material to produce the VRFB electrolyte due to its lower cost.
- The choice of chemical reductants used in producing the electrolyte could potentially introduce impurities.
- Using Dimensionally Stable Anodes (DSA) in the electrolysis cells to produce electrolyte, over time noble metal impurities leach out into the electrolyte and increase hydrogen evolution during charge and catalyse the oxidation of V^{2+} .

Commercial vanadium pentoxide, which is usually the precursor for the VRFB electrolyte, is available with purities between 95% and 99.6%. The impurity percentage differs from one source to another. Impurities in various concentration like total iron, silicon, manganese, chromium, sulfur, phosphorus, alkali metals (lithium, sodium and potassium), magnesium, cobalt, nickel, copper, zinc, molybdenum and arsenic [146, 206] affect the performance and efficiency of VRFB during charge-discharge cycles. Skyllas-Kazacos group and co-workers conducted preliminary research on the effects of some potential impurities on the hydrogen evolution reaction [207]. However, more detailed research is needed to develop a reliable electrolyte specification for VRFB developers.

The presence of some impurities in low concentration may enhance the battery operation. For example, researchers have reported that the addition of Li^{3+} ions can improve the electrochemical activity and kinetics of the V^{4+}/V^{5+} redox couple [208], and Cr^{3+} can affect the electrochemical performance of the V^{4+}/V^{5+} redox reaction, including reaction activity, reversibility of the electrode reaction, and vanadium ion diffusivity, although excessive amounts will increase cell impedance [209]. The presence of Mn^{2+} in the electrolyte has a similar effect to Cr^{3+} [197]. Iron (Fe^{2+}) impurities in concentrations less than 1.0 wt% had little effect on VRFB performance.

Combinations of Si and NH_4^+ impurities have been shown to have a significant impact on VRFB lifetime [205, 210] particularly due to the significant coverage of the electrode surface with Si. Their presence can decrease the voltaic efficiency and discharge capacity as the impurity concentration increases. Kubata *et al.* [210] from Sumitomo Electric Industries proposed specifying maximum allowable concentrations of NH_4^+ and Si to prevent these contaminants from clogging the carbon electrodes, but they did not present any evidence regarding the mechanism of performance degradation or whether the presence of NH_4^+ had an impact on the effect of Si.

Some metal ions have been shown to improve the redox reaction via interaction with the felt electrode [211]. To facilitate the V^{2+}/V^{3+} redox reaction, bismuth and antimony ions (Bi^{3+} and Sb^{3+}) can be electrodeposited onto the surface of the negative electrode [212, 213].

Park *et al* [146] after investigating the influence of a wide range of potential metal impurities on the electrochemical activity, diffusion of vanadium ions, and battery performance, suggested a specification to manage the quality of the vanadium electrolyte (Table 12).

TABLE 12. SUGGESTED SPECIFICATIONS FOR METAL IMPURITIES IN THE VRFB ELECTROLYTE BASED ON THE RESULTS OBTAINED FROM [146].

SPECIES	CONCENTRATION, M	EFFECT ON VANADIUM REACTIONS
Li^+	0.005	Retarding the kinetics of the V^{2+}/V^{3+} redox reaction
Na^+	-	Negligible effect
K^+	0.05	Decreasing the diffusion rate of V^{3+} ions
Mg^{2+}	-	Negligible effect
Cr^{3+}	0.005	Retarding the kinetics of the V^{2+}/V^{3+} redox reaction and decreasing the diffusion rate of V^{3+} ions
Mn^{2+}	0.02	Decreasing the diffusion rate of V^{3+} ions
Fe^{2+}/Fe^{3+}	0.05	Decreasing the diffusion rate of V^{3+} ions
Co^{2+}	0.05	Decreasing the diffusion rate of V^{3+} ions
Ni^{2+}	0.005	Retarding the kinetics of the V^{2+}/V^{3+} redox reaction and H^+ evolution
Cu^{2+}	0.001	Sedimentation in the negative electrolyte
Zn^{2+}	0.10	Decreasing the diffusion rate of V^{3+} ions
Mo^{6+}	0.001	Sedimentation in both the positive and negative electrolytes

4. CONCLUSIONS

The most studied and currently most promising RFB technology is VRFBs, it is considered as a durable system. They are suitable for a range of applications that need energy storage systems for load-leveling, flex ramping, peak shaving, time shifting, maintaining power quality and frequency regulation. The VRFB is the only redox flow battery that has been used in large-scale applications around the world (e.g., Europe, Southeast Asia, and North America) for extended periods of time. The VRFB is not harmed by repeated entire discharge or charge rates as high as the maximum discharge rates. VRFBs have the standard RFB components of current collectors, bipolar plates, electrodes, and a membrane

The use of a single metal element in both half-cells eliminates the cross-contamination issues that plague other redox flow cell chemistries, providing a theoretically indefinite electrolyte life. The solubility of vanadium ions not only determines the achievable energy density but also limits the operational conditions. However, the cost of the electrolyte accounts for a significant portion of the total VRFB system cost.

The VRFB electrolyte has been constantly improved, and several generations of VRFBs have emerged as a result of decades of work aimed at enhancing performance and solving challenges in operating the batteries. The main differences between these generations are the use of different electrolyte chemistries or the use of a single mixed inorganic acid.

The new technique of mixing chloride ions with sulfate ions in the supporting electrolyte offers the potential to increase the energy density of the battery, improve the electrolyte stability and enhance the solubility of the vanadium species in the catholyte and/or anolyte. This approach has been successful in providing a more

stable vanadium electrolyte and higher vanadium concentration. The concentration of vanadium in a mixed acid electrolyte (Gen 3 electrolyte) can reach up to ca. 2.5 M (vs. <1.6 M for Gen1 VRFBs) without any precipitation, and this electrolyte can operate at temperatures ranging from -5°C to 50°C. The stability is related to the formation of a soluble neutral species $\text{VO}_2\text{Cl}\cdot 2\text{H}_2\text{O}$, with V^{5+} instead of $[\text{VO}_2\cdot 3\text{H}_2\text{O}]^+$ (in sulfate media).

Only a few researchers have focused on improving electrolyte stability by the use of stabilising agents or have studied the effect of impurities during electrolyte preparation stages on VRFB performance. Disagreements persist in identifying the most effective stabilising agents that would allow for increased energy density and operating temperature range in practical systems. Research groups agree that using stabilising agents or additives can improve thermal stability, as long as the additives are compatible with all vanadium ions in the system because the additives will eventually diffuse from one half-cell to the other. A few groups have tried to develop an impurities specification for VRFB electrolytes, but these are not sufficient to be considered as a guideline for industry. This aspect requires further study to develop an impurity specification that would ensure the stable operation and long cycle life of VRFBs in commercial installations.

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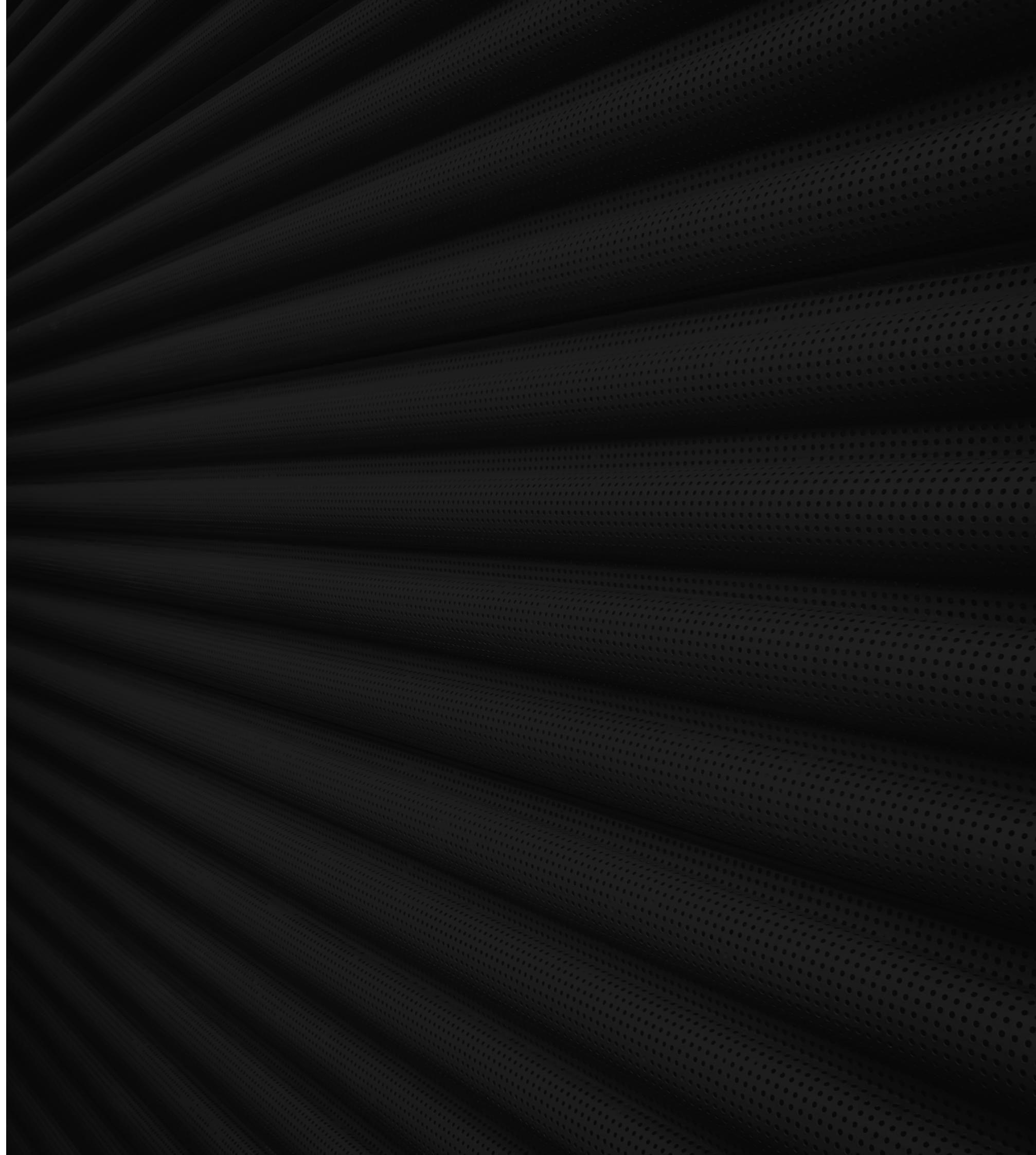
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