

# Flow Batteries

Impact on Fire Safety



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## Flow batteries - Impact on Fire Safety

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## Abstract

The need for sustainable renewable energy has been increasing due to the negative impact of non-renewable energy sources. With the unstable and sporadic nature of sustainable renewable energy, flow batteries show immense potential in mitigating these issues. Traditional vanadium and zinc-based flow batteries, as well as new flow battery systems, are now being researched extensively. Vanadium and zinc-based flow batteries are nearing commercialization, but their low power and energy densities keep them from being used in more businesses and industries.

This thesis examines the effect of flow batteries on fire safety, since battery storage systems have become more popular as a form of energy storage. A literature review is undertaken using the key terms listed below to locate current articles, journals, and research papers that give the most comprehensive answers to flow battery-related concerns. The first section of the thesis discusses the necessity for energy storage systems and how flow batteries may be incorporated into them. The second section discusses the operating principle and idea of a flow battery. The thesis's second half discusses the safety and fire issues connected with flow batteries, including gas development, thermal runaway, and deterioration. These risks are contrasted to those associated with lithium-ion batteries to demonstrate how each storage solutions might contribute to fire safety.

## Keywords

Flow battery, Flow battery types, Flow battery risks, Firefighting, Fire risk analysis, Safety hazards in flow batteries, Fire risks in lithium-ion battery, Safety hazard in lithium-ion battery, Application of battery storage systems, Safety reports.

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This thesis examines the effect of flow batteries on fire safety, since battery storage systems have become more popular as a form of energy storage. A literature review is undertaken using the key terms listed below to locate current articles, journals, and research papers that give the most comprehensive answers to flow battery-related concerns. The first section of the thesis discusses the necessity for energy storage systems and how flow batteries may be incorporated into them. The second section discusses the operating principle and idea of a flow battery. The thesis's second half discusses the safety and fire issues connected with flow batteries, including gas development, thermal runaway, and deterioration. These risks are contrasted to those associated with lithium-ion batteries to demonstrate how each storage solutions might contribute to fire safety.

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# Disclaimer

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Read and approved,

A handwritten signature in black ink, appearing to read 'Ajay Menon', with a horizontal line underneath.

Ajay Menon

May 11<sup>th</sup>, 2022

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## Abbreviations/Nomenclature

ESS	Energy storage system
BESS	Battery energy storage system
FB	Flow battery
RFB	Redox flow battery
HFB	Hybrid flow battery
MHFB	Membranelles hybrid flow battery
VRFB	Vanadium redox flow battery
ZBFB	Zinc-bromine flow battery
NiCd	Nickel-cadmium battery
NiMH	Nickel-metal hydride battery
PHES	Pumped hydro energy system
CAES	Compressed air energy system
SMES	Super magnetic energy system
BOP	Balance of plant
Fe/Cr	Iron-chromium battery
PBS	Polysulfide bromide
NaBr	Sodium bromide
$Na_2S$	Sodium sulphide
IEM	Ion-exchange membrane
ZnBr	Zinc-bromine battery
ORR	Oxygen reduction reaction
OER	Oxygen evolution reaction
HER	Hydrogen evolution reaction
SLF	Single phase co-laminar flow
FSE	Flowing supporting electrolyte
IISS	Ionically inert solid separators
SOC	State of charge
PV	Photovoltaic
PCS	Power control system
BMS	Battery management system
UL	Underwriters laboratory
ASTM	American society for testing and materials
THR	Total heat release
LiB	Lithium-ion battery
LTO	Lithium-titanate oxide
NMC	Lithium nickel manganese cobalt oxide

# 1. Introduction

Amongst the top pressing concerns that we face in the twenty-first century is the challenge to shift to a clean energy future. The efforts of governments, business institutions, and non-profit groups all around the world are aimed to progress in a society that emits fewer harmful emissions. In 2015, the United Nations, a global organization with 193 member states, produced the 2030 Agenda for Sustainable Development, which was unanimously endorsed by all member nations. Sustainability is a societal objective comprising environmental, economic, and social components. Environmental sustainability is interacting with the environment responsibly without depleting or degrading natural resources. Economic sustainability refers to economic development that does not adversely impact the social, economic, and cultural components of a community. Social sustainability refers to the systems, structures, and relationships that promote healthy communities for present and future generations. The agenda includes a roadmap for achieving peace and prosperity for people and the environment. One of its most important components is a call to action for all countries, developed and developing, to make rapid progress toward the 17 sustainable development objectives that make up the core of this framework. Investing in renewable energy resources, emphasizing energy-efficient practices, and deploying clean energy technology and infrastructure helps member states expedite the transition to a more affordable and stable energy system.

Energy supply capacity and security improvements, on the other hand, face major barriers because current fossil fuel-based energy infrastructures are struggling to meet the standards for long-term sustainability. It is therefore vital to study green and effective renewable energy sources, and to increase their use in current energy supply infrastructures. However, renewable energy sources like solar and wind are highly dependent on environmental and geographical factors, causing unstable and intermittent electricity production that impacts power grids. As a solution to the existing predicament, large-scale energy storage technologies and high-capacity storage devices are required, which allows power grids to better regulate their response to the volatile nature of renewable energy sources. Advantages offered by flow batteries is amplitude and frequency modulation which increases efficiency of renewable power sources.

Flow batteries can store electrical energy in the form of chemical energy, which could subsequently be transformed back into electric energy as needed. Flow battery technologies, in a nutshell, have the potential to accelerate the use of renewable energy sources. To effectively use large-scale energy storage systems, the battery technology used must be safe, environmentally benign, and cost effective, which makes a flow battery a feasible alternative. It is worth noting that this type of technology may prove to be extremely advantageous in the areas of load leveling and peak shaving, among other things. During times of low demand, a load leveling system stores energy or power and only releases it when huge demand is present. This can be a substitute to resources that could harm the environment or raise questions about long-term sustainability. Peak shaving, on the other hand, is a method for lowering the power consumption spikes that are experienced by all users. In order to avoid peak loads, natural gas providers will reduce the amount of electricity utilized in small increments during periods of high demand. Companies will either reduce output or rely on a backup power source until the power is restored, a process known as load shedding in the industry. Figure. 1 illustrates the power and

energy density of capacitors, batteries, and flow batteries. This illustrates their versatility and scalability while also providing an understanding of their cost-effectiveness.

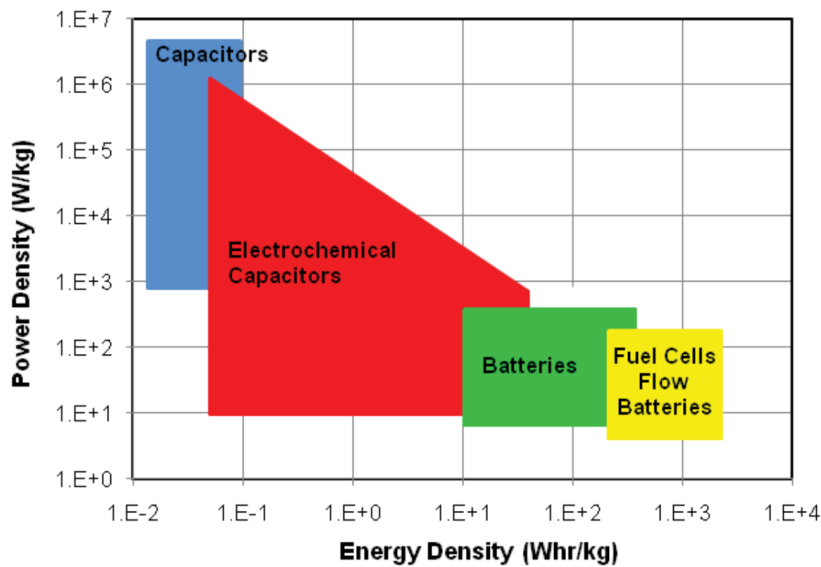


Figure 1 Power Vs energy density of ESS, copied with permission (Nguyen and Savinell 2010)

Conventional batteries such as lithium-ion and lead-acid are currently the most attractive solution due to their high energy density (more useful for mobile applications) and the majority of components are contained within a single package and do not require recirculation, in contrast to flow batteries, which contain huge amounts of moving parts such as pipes, tanks, and pumps that are at risk of damage or could affect performance. However, flow batteries offer the advantage of efficient scaling, particularly because the power and energy capacities are independent; increasing the concentration of active species in the electrolyte or the volume of the tanks increases the energy capacity, while increasing the amount of reaction sites using electrodes increases the power capacity. The ability to store the liquid electrolyte tanks away from the cell stack, where the electrochemical processes take place, is another significant physical benefit of the power and energy generation units being independent (simpler cooling systems to dissipate heat being generated). Redox Flow Batteries (RFB) have emerged as a viable long-term energy option. Their ability to keep power and energy generating systems separate from each other, allows for flexible design, ability to scale-up easily based on requirements, low maintenance costs, and extended life cycles.

The following chapters provide additional information regarding flow batteries and its composition, as well as the potential fire risks associated with flow batteries along with its advantages and disadvantages compared to other energy storage technologies. Furthermore, the next section covers the methodology, how the data was acquired, and the report's limitations.

## **1.1 Research Objective**

The goal of this report is to offer an overview of flow batteries, including an explanation of how they function, the many kinds of electrolytes, and an assessment of the risks associated with their usage, specifically in terms of fire and safety issues. This report also attempts to achieve the following goals:

- Recognize many instances involving normal occurrences and hazards linked with the usage and refilling phases, as well as situations involving secondary fires that may threaten the existing installation.
- Compare flow batteries to Li-ion batteries in terms of safety advantages and disadvantages.
- Determine the gaps and constraints of flow battery technology, as well as prospective future research.

## **1.2. Limitations**

The findings of this literature review must be interpreted within the context of certain limitations. Limitations of this report relies on previous research works that has been published, along with the accessibility of these studies according to the research method outlined on the methodology section, and on their relevance to the selection/exclusion criteria. Since no experiments were conducted, there is limited data available for reporting. Additionally, access to material is restricted to papers that are publicly available or found in online databases. The information offered by private firms are also limited, and despite the fact that these organizations were approached, the majority of them were unable to provide conclusive study findings due to privacy and company policies. As a result, statistical evidence and experimental results are constrained.

## 2. Methodology

The purpose of this report is to provide an overview of flow batteries, as well as the risks associated with them in terms of fire safety and their use. To acquire a better knowledge of flow batteries, this report utilizes a semi-systematic review or a narrative review approach. This review aims to discover and identify all studies related to flow batteries and their implications on fire safety. To identify and study potential applications of flow batteries as a substitute for non-renewable energy sources, a rigorous content analysis is used as a form of qualitative research. Using this methodology, this work seeks to give relevant analyses and theoretical insights, as well as the challenges encountered by the authors cited in this literature review and the potential for future research.

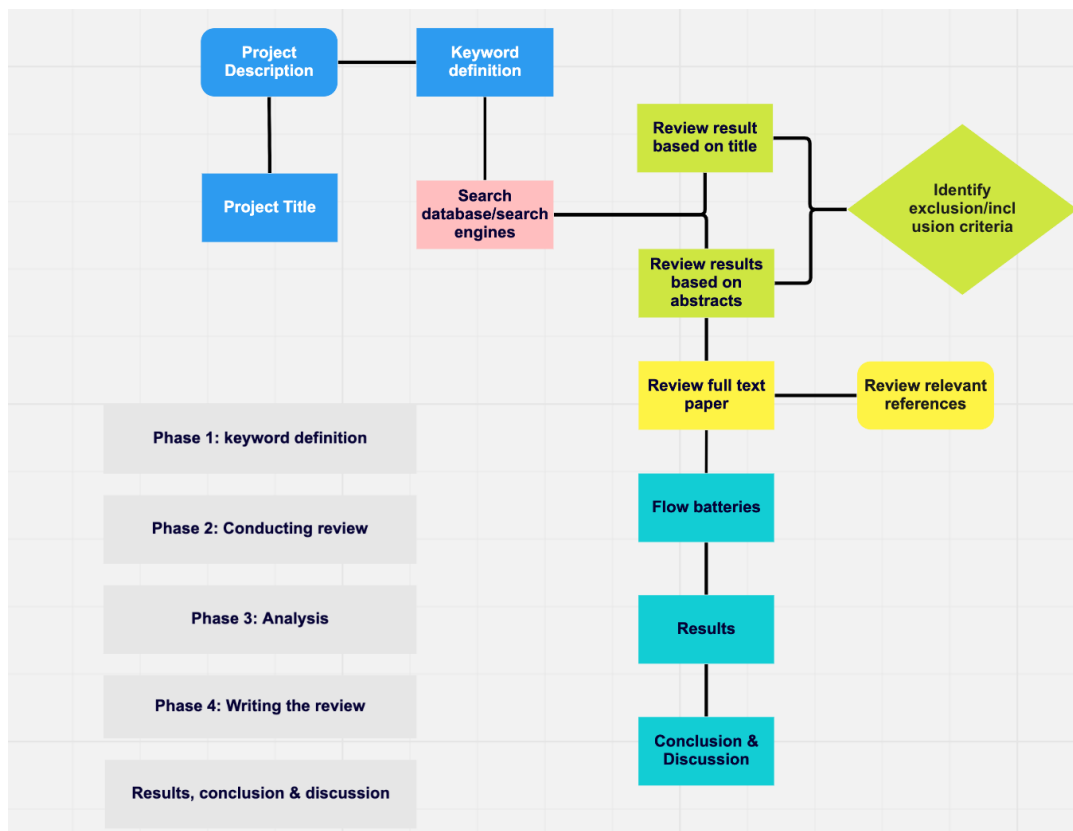


Figure 2 Flow chart depicting the methodology used

Figure 2 shows the overall methodology followed in this report. There are a number of measures that must be taken in order to perform a successful literature review. First, determine important search phrases, best databases, and search criteria limitations. Based on the identification of this phase, research papers are evaluated for their findings. These are carried out in stages, starting with an examination of the title and abstracts, followed by a selection of relevant research papers, and ultimately an examination of the entire content of the research paper. Relevant references cited in these selected research publications are also reviewed to see if they add anything to the research questions in the thesis.

## 2.1 Keyword Definition

The keywords identified on this report came from the problem statement and objectives mentioned. Search keywords are specified as follows:

Table 1 Keywords used for this literature review

Keyword	Refined with	Search Results
Flow Battery	Battery types	45
Flow Battery	Risks	10
Flow Battery	Safety Hazards	10
Flow Battery	Safety Reports	5
Battery Storage Systems	Applications	15
Lithium-ion Battery	Risks	15
Lithium-ion Battery	Safety Hazards	20

## 2.2 Database Search

Finding relevant articles based on the keywords defined are accomplished through the use of databases on search engine websites such as LUB search, Google or Google scholar. Search engine websites are the most popular method of discovering research papers and articles that are published, assist in directing to scientific database websites where the collection of papers may be located.

## 2.3 Article Review (Inclusion and Exclusion Criteria)

110 articles are chosen for further review and analysis. Abstracts of articles, along with the research titles that are highly relevant to the topic area are read and classified further. The search results are then narrowed by defining an exclusion and inclusion condition. With each article read and new data obtained, the criterion is continually updated.

Table 2 Inclusion & Exclusion Criteria

Inclusion Criteria	Exclusion Criteria
Articles mentioning flow battery in the abstract	Non-commercialized flow battery is excluded
Titles that cover a working concept about flow batteries	If the article focuses more on the chemistry and energy of flow batteries, then it is excluded
Articles related to improvements on flow battery safety	Articles related to performance characteristics of chemicals used in flow batteries
Flow battery risks related to fire safety	Risks related to supply chain, logistics, and safety handling of flow batteries are excluded
Fire risks of flow battery components	Performance characteristics of flow battery components
Titles that cover a working concept about lithium-ion batteries	Comparison of different types of lithium-ion batteries
General overview of safety and fire risks in lithium-ion batteries	In depth analysis and chemistry related to evolution of gas are excluded
Product portfolios from private firms related to flow battery	Performance characteristics are not included



## 2.4 Full-text Review

A total of 80 relevant articles are selected for full text review from the first search conducted using the identified keywords together with inclusion and exclusion criteria. These articles serve as the foundation for the findings in chapters 3 to 10 of this report. The articles are then subjected to meta-analysis and evaluation in accordance with the following guidelines:

- Overview of flow batteries, including their different types and how they work.
- Potential risks of flow batteries in terms of fire safety and usage.
- Infrastructure required and the type of electrolytes that can be used.
- Limitations and gaps of the existing battery flow technology and its potential future applications

After the assessment of safety concerns and fire dangers associated with flow batteries, the hazards are compared to lithium-ion batteries. The study of the threats and their effects on life and property are presented in the discussion section to establish a comprehensive picture.

## 3. Flow Batteries

NASA developed the first flow battery in 1970 with the goal of developing an energy storage system capable of powering a lunar settlement. The iron-chromium flow battery was developed as a result of this idea. Exxon and NASA built the zinc bromine flow battery as a hybrid flow battery in the 1970s, while the University of New South Wales in Australia produced the first prototype of the vanadium redox flow battery in 1984, which employed similar chemical components in both half cells. Although many various kinds of flow batteries were examined, constructed, and prototypes developed between 1970 and 2015, vanadium and zinc-bromine flow batteries were the most widely explored and commercialized.

A flow battery is a kind of battery designed to provide high power and high storage capacity. Commercialization of flow batteries such as vanadium and zinc redox flow batteries has already occurred. Sumitomo Electric will complete the construction of a 17MW/51MWh vanadium redox flow battery in Japan this year, while Invintiy will construct a 2MW/8MWh vanadium redox flow battery for solar energy in Australia and Redflow is installing a 2MWh zinc-bromine flow battery in California which helps to store energy produced from a Waste plant.

The duration required for energy to be released and the amount of energy it can store are two major distinctions between flow batteries and regular batteries or flywheels. Energy storage systems such as flywheels are used when high power and a fast discharge rate are required, while standard batteries have longer discharge times but lower power storage capacities. Flow batteries, on the other hand, may be employed in higher-power and high-capacity storage situations as seen in Table 3 which shows important characteristics of flow batteries versus other storage systems, making them one of the best grid-connected energy storage systems which work quite well with renewable sources of power like wind energy, solar energy etc.

The primary distinction between flow batteries and conventional batteries is the operating principle. For instance, lead-acid batteries house their electrodes and electrolyte in the same compartment, which limits their scalability. In contrast to flow batteries, the electrolyte and

electrodes are housed separately, making them more flexible in terms of design and use (surface areas of the electrodes may be increased/decreased, as can the volume of electrolytes). Because flow batteries work on the idea of chemical reactions producing electricity at the cell stack, the design and configuration of the cell stack (where liquid electrolyte flows into the cell) is critical in determining the power rating whereas the energy capacity depends on the size of the tank that holds the electrolyte volume.

Table 3 Comparison of flow batteries with existing battery technology (de Boer and Raadschelders 2007)

	Typical power	Typical energy	Typical discharge duration
<b>Batteries (lead-acid, NiCd, NiMH, Li-ion)</b>	kW - 500 kW	MWh - 100 MWh	1 - 8hours
<b>Flywheels</b>	500 kW - 1 MW	100 kWh – 100 MWh	< 5 minutes
<b>Pumped hydro</b>	100 MW – 4000 MW	500 MW – 15GWh	4 – 12 hours
<b>CAES (Compressed air energy storage)</b>	25 MW – 3000MW	200 MWh – 10GWh	1 – 20 hours
<b>NaS (Sodium sulfur batteries)</b>	1 MW	1 MWh	1 hour
<b>SMES (Superconducting magnetic energy storage)</b>	10 kW – 10 MW	10 kWh – 1 MWh	1 – 30 minutes
<b>Supercapacitors</b>	< 250 kW	10 kWh	< 1 minute
<b>Flow batteries</b>	100 kW – 10 MW	1 – 100 MWh	10 hours

Because the power and energy of flow batteries are separated, it is relatively simple to create a scalable system that meets the needs of the application. Increasing the amount of electrolyte stored in big tanks improves the capacity, whilst increasing the number of cell stacks helps to offer greater output power, allowing power to flow continuously as long as there is new electrolyte available. Table 4 illustrates a typical range of flow battery sizes and power output levels from two different manufactures.

Table 4 Flow battery typical weight, geometric, capacity and power output (for all vanadium system) (Cell Cube, n.d.; VFlowTech, n.d.)

Product	Power cube (Vflow-tech)			Cell cube	
<b>Max power</b>	8KW	15KW	130KW	399KW	798KW
<b>Voltage</b>	230VAC	400VAC	400VAC	400VAC	400VAC
<b>Energy capacity</b>	30KWh	100KWh	500KWh	1064KWh	2128KWh
<b>Size(L*W*H)</b>	1.5*1.7*1.2 m	3*2.44*2.66 (Std 10-foot container)	12.2*2.44*2.59 (Std ISO 40-foot container)	12.2*4.9*5.9 m	12.2*4.9*7.5 m
<b>Weight</b>	1000 Kg	2500 Kg	-	20 tons	40 tons
<b>Weight (with electrolyte)</b>	3000 Kg	9000 Kg	-	115 tons	225 tons

The following are some of the most important characteristics of flow batteries (de Boer and Raadschelders 2007):

- The cell's potential is determined by the chemical reaction taking place, and the cell stack determines the power rating, which means it may generate a lot of power if everything is implemented right.
- The amount of electrolyte consumed, and the associated capacity of the holding tanks determine the energy rating.
- Highly flexible: since the power and energy rating are decoupled.
- The flow batteries can charge and discharge rapidly because most chemical processes have extremely fast reaction kinetics.
- Flow batteries cannot self-discharge since the electrolyte is kept in two distinct tanks and cannot come into touch with each other to cause a reaction.

### 3.1 Concept of Flow Battery

A flow battery as seen in Figure 3, is an electrochemical cell that uses two separate tanks to hold the required electrolytes. In each tank, an active chemical component (metallic salt) is added to the solvent to form the electrolyte. Electrolytes are catalysts that aid in the free movement of ions between the cathode and the anode. Whereas as a hybrid flow battery are battery systems in which one of the electrolytes is in different state compared to the other half. Half of the cell is in liquid form, consisting mostly of chemical salts dissolved in solvents, and the other half is in solid form, consisting primarily of active chemical species that deposit on the solid electrode throughout the electrochemical process by the process of electroplating.

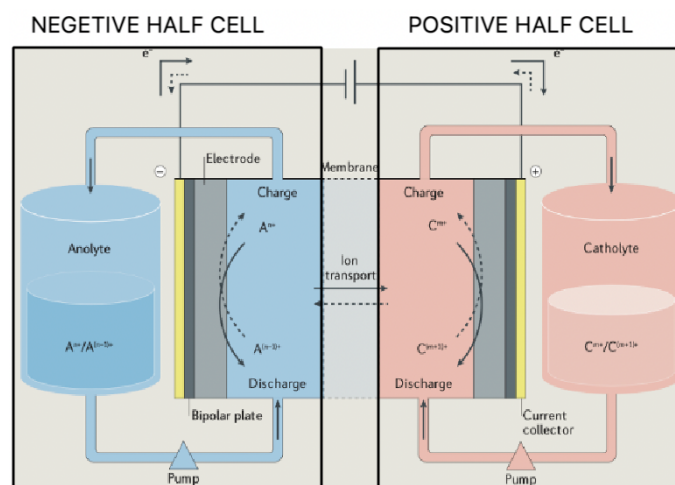
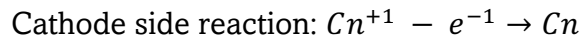
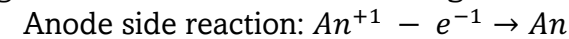


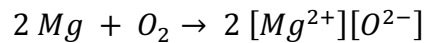
Figure 3 Schematic representation of a full flow battery (liquid system) adapted with permission (Park et al. 2017)

The electrolytes from the separate tanks known as catholyte and anolyte are forced into the cell stack holding the cathode and anode in a flow battery by means of a pump. Separating the anode and cathode is an ion-exchange membrane. The ion exchange between the anode and the cathode causes a potential difference in this region, which causes electricity to be generated. The benefit is that the electrolyte lost during charging and discharging can be replenished by pumping fresh electrolyte into the tank storage.

The type of reaction occurring at the anode and cathode during the discharge cycle is:



Flow batteries are referred to as redox flow batteries because the electrochemical processes occurring inside the cell stack include reduction (red) and oxidation (ox). Electrochemical processes occur when electrons are lost, while reduction reactions occur when electrons are gained, as illustrated by the equation below:



From the above chemical reaction, we can see that the magnesium compound undergoes an oxidation reaction as it loses 2 ions which is accepted by the oxygen through a reduction process. With flow batteries, an electron is produced on the anodic side of the cell during the discharge process through an oxidation reaction. After passing via an external circuit, the electron is reduced and received at the cathode side of the battery. A higher chemical potential state is facilitated to a lower chemical potential state during the discharge process. Both the current and chemical processes are reversed by the charging mechanism. To maintain charge neutrality in redox flow cells, hydrogen ions ( $H^+$ ) are transferred between the two half-cells. The cell is divided into two half-cells by the ion-membrane present. With the help of a pump, the electrolyte is pumped into the respective tank whenever required. The positive side of the cell is known as the cathode and negative side is the anode.

A Schematic representation of the components used in constructing a flow battery can be seen in Figure 4.

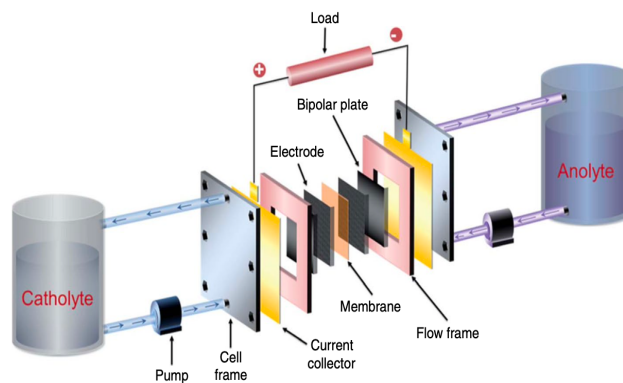


Figure 4 Schematic representation of a RFB copied with permission (Chen et al. 2022)

The cell frame as seen above provides the equipment with the necessary physical stability, the bipolar plates help in keeping the cells electrically connected but hydraulically separated, the electrodes are carbon-based polymer materials which provide reaction sites for redox reactions, the electrolytes in each half cell is separated by an ion-exchange membrane (Noack et al. 2015). Several other critical components and their definition are listed below:

**Half-cells** - A half-cell is formed when a single electrode is submerged in an electrolyte, a potential difference is created. The flow battery, as seen in Figure 3, consists of two half-cells, one on the anolyte side and one on the catholyte side. The anolyte side undergoes oxidation, whereas the catholyte side undergoes reduction. Each half-cell contains a tank containing the respective electrolyte, normally electrolyte is filled over the entire volume of the tank. During

operation, the pump pumps electrolyte into the cell stack through the tubes, forming an empty volume and decreasing the electrolyte levels. This vacant area is referred to as head space.

**Membranes** - As one of the most critical components of a flowing battery, membranes are situated between the two half-cells. When the two electrolytes of each half-cell are separated, it prevents them from combining with each other. When a current is supplied, the membrane functions as a selective membrane, allowing only certain ions to flow through. There are generally two types of membranes - anion exchange membrane (which only permits anions to pass through, anions are negatively charged ions) and cation exchange membrane (which only permits cations to pass through, cations are positively charged ions) (Xu 2005). Another way to classify membranes is by the substance they are made of, such as perfluorinated ionomers, partly fluorinated polymers, or non-fluorinated hydrocarbons, among which perfluorinated is regarded the best owing to its excellent chemical stability, conductivity, and mechanical strength (Prifti et al. 2012b). Nafion (sulfonated tetrafluoroethylene based) membranes developed by Dupont is one of the most used membranes for vanadium redox flow battery (Chalamala et al. 2014).

**Electrodes** - Positive and negative electrodes of flow batteries, particularly those used in VRFBs (Vanadium redox flow battery), are often made of carbon-based materials such as carbon or graphite felts, graphite or carbon fabric, or carbon powder. These materials shows a high degree of stability, operability, and reversibility. A typical electrode should exhibit the qualities of a good conductor, such as low resistance and a large surface area (more reaction sites); improving these features of the electrode would also boost the battery system's efficiency. Coating graphite and carbon felts with metal improves the electrode's conductivity (Kim 2011).

**Bipolar plates** – The bipolar plates provide a connection point to the adjacent cell connected in series helping to form a cell stack. Generally, a single cell of a flow battery cannot give enough output power to fulfill the demand; consequently, a series connection of many single cell batteries is used to get the necessary output, which is accomplished using bipolar plates. Bipolar plates are constructed of graphite or carbon because they must be very conductive and able to endure the pressure generated by the surrounding electrolyte.

**Pumps** – The cell stack is the site of all electrochemical processes that occur during charging/discharging in a flow battery. Depending on the scenario, two pumps are often utilized to push electrolyte from the electrolyte reservoirs of both half-cells into the cell stack. This electrolyte movement facilitated by pumps also assists in eliminating heat (after chemical reactions start) and in minimizing precipitation (Tang, Bao, and Skyllas-Kazacos 2014).

**Balance of plant (BOP)** - This is defined as all supporting components and ancillary equipment that are linked to the system and aid in the delivery of the energy generated within. For flow batteries, this comprises the tanks, pumps, pipelines, and control systems, all of which operate as a unified unit.

Various kinds and forms of electrolytes are available, including soluble salts, acids in liquid, gel, or solid form, different types of electrolytes used in flow batteries can be seen in Table 5.

Table 5 Typical electrolyte used for flow batteries (M. Skyllas-Kazacos et al. 2011)

Type of System	Electrolyte	Electrolyte composition
<b>REDOX</b>	<b>Anolyte/Catholyte</b>	
<b>All vanadium</b>	$H_2SO_4/H_2SO_4$	1.6-2M (Molar) vanadium ions in sulphuric acid in both catholyte and anolyte
<b>Vanadium-polyhalide</b>	$VCl_3 - HCl/NaBr - HCl$	Catholyte-1M NaBr in 1.5M HCl and Anolyte-1M $VCl_3$ in 1.5M HCl
<b>Bromine-polysulfide</b>	$Na_2S/NaBr$	5M NaBr saturated with $Br_2$ and 1.2M $Na_2S$ in both catholyte and anolyte
<b>Iron-Chromium</b>	HCl/HCl	1M $CrCl_3$ and $FeCl_2$ in 2M HCl in both anolyte and catholyte
<b>HYBRID</b>	<b>Anolyte/Catholyte</b>	<b>Electrolyte composition</b>
<b>Zinc-Bromine</b>	$ZnBr_2/ZnBr_2$	1-7.7 mol $dm^{-3}$ $ZnBr_2$ with excess of $Br_2$ in both catholyte and anolyte
<b>Zinc-cerium</b>	$CH_3SO_3H$	Catholyte-0.3M $Ce_2(CO_3)_3$ and 0.9M ZnO in methane sulfonic acid, Anolyte-0.3M $Ce_2(CO_3)_3$ and 1.3M ZnO in methane sulfonic acid

## 3.2 Types of Flow Batteries

There are many characteristics that may be used to classify redox flow batteries (RFB), depending on the active species, the solvent type (aqueous or non-aqueous), and the condition in which the active species is (solid, liquid, or gaseous).

One of the earliest flow batteries to be developed is the Iron/Chromium (Fe/Cr) battery which has an aqueous phase of ferric-ferrous ( $Fe^{2+}/Fe^{3+}$ ) as the catholyte and aqueous solution of chromous-chromic ( $Cr^{2+}, Cr^{3+}$ ) as the anolyte with hydrochloric acid being the supporting electrolyte. Unlike the vanadium flow battery, this system utilizes two different types of active species which can lead to cross-contamination issues. Also, ( $Cr^{2+}, Cr^{3+}$ ) has slow reaction kinetics (M. Skyllas-Kazacos et al. 2011) and low redox potential which (Pan and Wang 2015) might lead to hydrogen evolution. Both of which reduces the efficiency of the battery.

Another type of flow battery researched was the PSB (polysulphide bromide) battery which consisted of sodium bromide (NaBr) as the catholyte and sodium sulphide ( $Na_2S$ ) as the anolyte (Pan and Wang 2015). The main advantage of this system was the high solubility of the participating active species which means high energy density. However, even though  $Na_2S$  is highly soluble, it does not eliminate the problem of solid precipitation caused by insoluble short

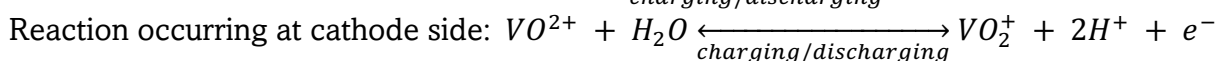
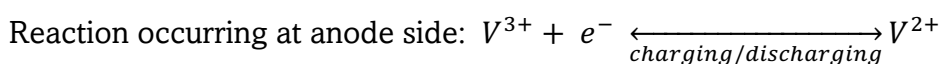
chain polysulfides developing during lengthy battery cycle runs (Lowe, Gao, and Abruña 2014), meaning the deposition of sulfur on the ion exchange membrane surface reduces the transfer of ions and battery performance (M. Skyllas-Kazacos et al. 2011). Other drawbacks with this type of system are (Ponce de León et al. 2006) cross contamination due to different types of active species being used, formation of bromide gas (toxic) and hydrogen sulfide gas (toxic, corrosive, and flammable).

Since its inception, the Zinc Bromine Battery has shown to be one of the most reliable and efficient ways to generate higher power compared to VRFB's. These types of batteries are also known as hybrid flow batteries as one electrode is in a solid state whereas the other electrode can be in liquid/gas state. The electrolyte  $ZnBr_2$  is kept in both half cells; the only variation between the solutions in the half cells is the concentration of elemental bromine; hence, throughout the charge/discharge cycles, the concentrations of zinc and bromide ions must stay constant. The membrane, which regulates the ion-exchange only allows zinc and bromide ions to flow through while not allowing bromine or polybromide to get through at all, is a crucial factor during the battery's design (Steven Eckroad 2003). Some difficulties associated with the Zinc-bromine battery include the creation of dendrites, the fact that bromine is very corrosive, and thus the battery's cycle life is reduced (Weber et al. 2011).

Single flow batteries were created to better understand the impacts of lead acid batteries as flow batteries. There is no need for an ion-exchange membrane in these "single flow" batteries since just one liquid electrolyte and one pair of solid electrodes come into contact with each other. To move electrolyte around, a pump is employed. Flow batteries were shown to be more readily scaled up to large energy storage systems than standard stationary lead acid batteries in studies comparing the two technologies (C.-P. Zhang et al. 2011).

### 3.2.1 Vanadium Flow Battery

All-vanadium redox flow battery system (VRFB) is a type of flow cell that incorporates only one type of metal ions (Vanadium), by taking advantage of the four different oxidation states that it is available in  $V^{2+}$ ,  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$ , in which  $V^{2+}/V^{3+}$  are located at the anode side of the half cell and  $V^{4+}/V^{5+}$  at the cathode side of the half-cell, respectively. There is a significant advantage to employing this metal in four distinct oxidation states since it reduces the possibility of cross-contamination between the half-cells. An electron is produced during the process of charging and discharging because a proton is released through the ion-membrane, which helps to balance the changes in the vanadium oxidation states, which in turn helps to produce electrons that are transported through the flow battery's external circuit. Full flow systems, such as the one seen below, where the redox couples are in liquid/gas state and are circulated throughout the system by means of a pump. The chemical redox reactions that are taking place are depicted below:



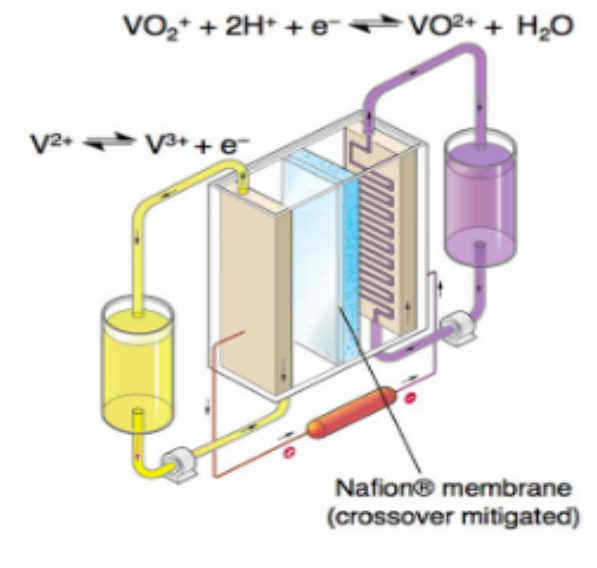
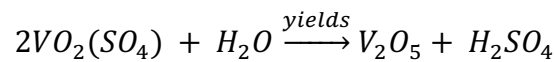


Figure 5 Example of a redox flow battery with full flow vanadium system, copied with permission, (Chalamala et al. 2014) , Sandia National Laboratories

In the all-vanadium flow battery system, the commonly used electrolyte is sulfuric acid. The amount of vanadium-metal salt introduced into electrolyte can be manipulated by altering the concentration of the sulfuric acid. There are two crucial factors which effect the solubility of the vanadium salt (Chalamala et al. 2014):

- At lower temperatures, solubility of the vanadium salts reduces also can cause precipitation and electrolyte freezing.
- At higher temperatures, endothermic reactions as seen below might occur with the  $V^{5+}$  species :



The resulting product has low solubility and hence leading to precipitation. Another type of full flow battery system is the iron-chromium battery (FeCr), but very little progress is made with this type of system due to low chemical reversibility of chromium, chances of cross-contamination between the half cells, hydrogen production and requirement of electrocatalyst to increase overall efficiency (Giner, Swette, and Cahill 1976). Vanadium flow battery is the most researched redox flow battery, as it has already been commercialized. The two different types of vanadium redox flow batteries are seen below.

### 3.2.2 Vanadium – Bromide Redox Flow Battery

Several studies have shown that the vanadium-bromide flow battery, like other vanadium-flow batteries, is advantageous in terms of enhanced performance. In this configuration, the vanadium-bromide solution is held in both half cells at the same time. Cross-contamination is minimized in vanadium systems by maintaining equivalent electrolyte solutions in both tanks, as is the case with all vanadium systems. When comparing the potentials of  $V^{5+}/V^{4+}$  solutions, the potential of bromide/polyamide solutions is lower, suggesting that the majority of bromide ion oxidation occurs at the anode during the charging process (Parasuraman et al. 2013). Another benefit of this setup is that we can get a larger concentration of  $V^{2+}/V^{3+}$  ions in the HCL electrolyte, resulting in a higher energy density of the system when compared to previous



vanadium-flow batteries (Maria Skyllas-Kazacos 2003). Due to the increased solubility of bromide, this system allows the battery to operate at a significantly lower temperature ( $0^{\circ}\text{C}$  –  $50^{\circ}\text{C}$ ) than all vanadium systems ( $5^{\circ}\text{C}$  –  $40^{\circ}\text{C}$ ) (Prifti et al. 2012a), (Maria Skyllas-Kazacos et al. 2010).

One significant downside of this sort of battery system is the development of bromine vapors, which are very corrosive and deadly in nature, necessitating the use of catalysts to neutralize the generation of vapors, which increases the cost of the system.

### 3.2.3 Vanadium Air Redox Flow Battery

Studying the effects of using oxygen as a reduction/oxidation resource, which is readily accessible in the environment, was done in order to improve cost efficiency even more. Because of this, metal-air flow batteries were developed. Metal plate is used as the Anodic/negative site of the half-cell in this system, while the cathodic/positive site uses oxygen. The oxygen in this system offers oxygen reduction reactions (ORR) as well as oxygen evolution reactions (OER). Since the electrolyte in the anodic part of the cell remained stationary during the charging and discharging process, by products were formed, which accumulated on the metal electrode, reducing reaction sites. The efficiency of this system was dependent on the size of the metal anode used in conventional designs (reaction site area) (Rahman, Wang, and Wen 2013). In order to resolve this issue, two methods were used, as shown in the following Figure 6, left-The technique involved using a pump to push in fresh anolyte that contained metals and ions, and right-The technique involved supplying fresh electrolyte to increase reaction efficiency with the metal anode.

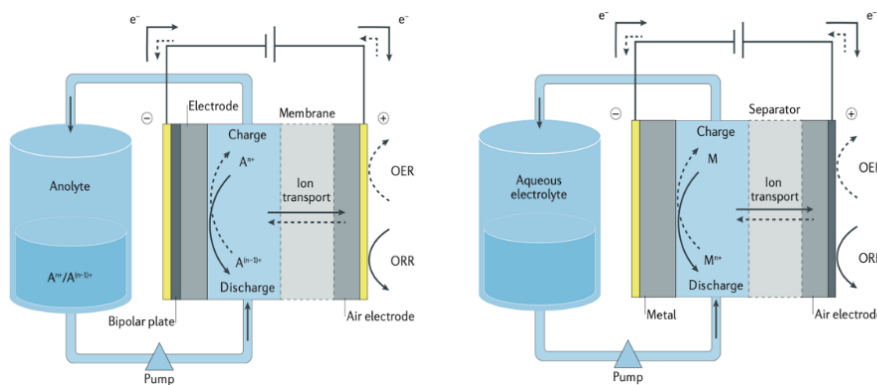


Figure 6 Schematic representation of Metal air flow batteries – left and right copied with permission (Park et al. 2017)

But this system has some drawback such as vanadium ions being very susceptible to oxygen attack, which reduces efficiency of the cell (Wen et al. 2008), and it is difficult to change the valence of the vanadium ions  $V^{3+}$  back to  $V^{2+}$  making it hard to perform as a rechargeable battery system (Menictas and Skyllas-Kazacos 2011).

### 3.2.4 Hybrid Flow Battery

Hybrid flow batteries are battery systems in which one of the electrolytes is different from the other electrolytes. Half of the cell is in liquid form, consisting mostly of chemical salts dissolved in solvents, and the other half is in solid form, consisting primarily of active chemical species that

deposit on the solid electrode throughout the electrochemical process. When a hybrid flow battery is used, a metal is often used as the charge-negative reactant, and this reactant is electrodeposited on the surface of the anodic electrode during the charge process (Chalamala et al. 2014). The  $Zn/Br_2$  and  $Zn/Cl_2$  systems in hybrid flow batteries are found to be especially promising in terms of long-term performance due to their high energy density and cost efficiency. It is expected that during the charging phase, zinc is deposited on the anodic side of the battery, and this process will reverse itself during the discharge cycle. Figure 7 shows the process occurring in the Zn-Br battery.

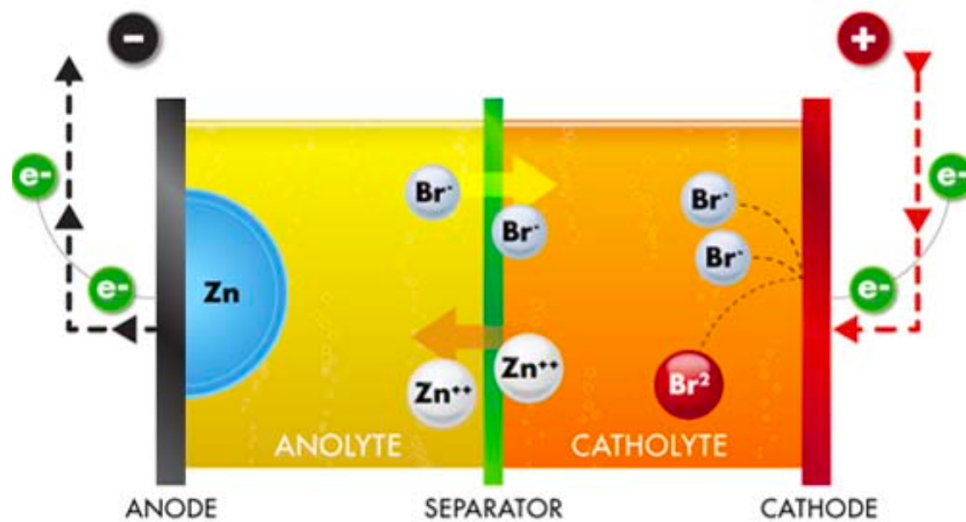


Figure 7 Schematic representation of Zinc-bromide RFB copied with permission. (Chalamala et al. 2014), ZBB energy storage

In the  $Zn/Cl_2$  systems while charging, zinc is deposited on the anodic side of the half-cell and chlorine gas is released from the cathodic side of the half-cell, which is kept in a separate compartment, as with Zinc-Bromide Flow Batteries (ZBFs). The zinc oxidizes back to its original condition during the discharge phase, while the chlorine gas is heated and recovered as chloride ions. Because of this, it is possible that even if the  $Zn/Cl_2$  system shows encouraging results, there is a high likelihood of leakage that would result in the discharge of chlorine gas, which would have a negative impact on humans and nearby materials due to its toxic and corrosive nature.

### 3.2.5 Membraneless Flow Battery

In order to have a sustainable energy storage system, safety and performance which falls under the dimension of social sustainability are not the only necessary factors. The cost of the system is also crucial. 20-40% of the cost of a flow battery is attributable to the ion-exchange membranes, therefore, to minimize costs, a flow battery without an ion-exchange membrane was developed (Kear, Shah, and Walsh 2012). The idea behind not using a membrane was to keep the chances of reactants crossing over to a bare minimum while still allowing for selective ions crossing over. Because the problem is no longer centered on the type of material used, it is now more concerned with fluid mechanics and species transport. The system is constructed in accordance with one of the following concepts as described in sections 3.2.5.1-3.2.5.5 (Bamgbopa, Almheiri, and Sun 2017).

### 3.2.5.1 Single-phase Co-laminar Flow (SLF)

When the membrane is removed from the system as seen in figure 8, the electrolytes of the catholyte and anolyte flow laminarly side by side in a single phase co-laminar flow. This is one of the most widely researched membraneless designs. The electrochemical reaction products are flushed out of the system by the stream flow. There are two sorts of zones in a flow-based system, namely the diffusion zone and the depletion zone. The diffusion zone serves as the ion conducting medium, in which diffusive mixing occurs at the surface of the catholyte and anolyte, and the depletion zone guarantees that the concentration gradient in the flow is maintained until it reaches the electrode, respectively.

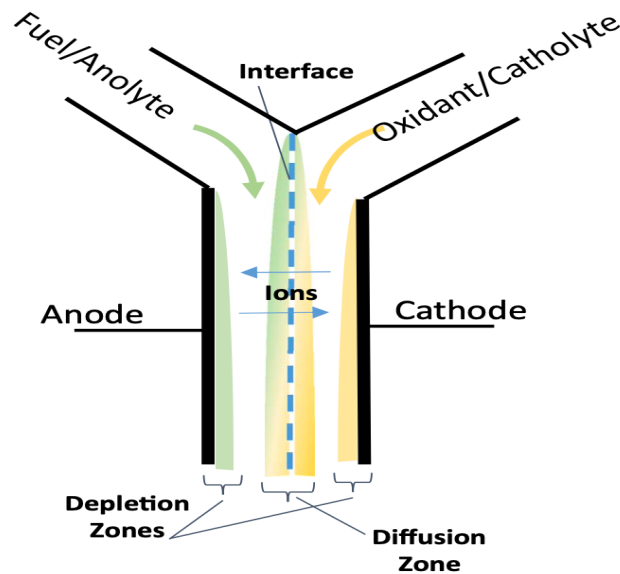


Figure 8 Schematic of the most common membranelles design (SLF) Copied with permission (Bazylak, Sinton, and Djilali 2005)

### 3.2.5.2 Flowing electrolytes separated by a flowing stream of supporting electrolyte (FSE)

Flowing electrolytes separated by a flowing stream of supporting electrolyte is a conceptual idea in which, as previously stated the catholyte and anolyte flow as separate streams and a third medium is made to flow in the middle that acts as an ion conducting medium, this is known as the flowing separating electrolyte. By introducing a stream of electrolyte, this sort of design may decrease cross-over of reactants.

### 3.2.5.3 Multiphase co-laminar flow (MLF)

As an extension of the FSE architecture, multiphase co-laminar flow (MLF) membrane less cells are developed. For the separation of reactants from a multiphase system, there are two options: (1) utilize gaseous fuels and an FSE to produce a gas-liquid interface on one or both sides of the cell or (2) employ a combination of all-liquid fuel/anolyte/oxidant/catholyte and FSE streams to generate a gas-liquid interface.

### **3.2.5.4 Membraneless hybrid flow batteries (MHFB)**

When using this type of flow battery system, there is no reactant crossover because there is only one electrolyte system contained in one half-cell. Whereas the other half-cell reaction involves the deposition of active solid particles, which is the electrode, takes part in the chemical reaction with the deposition or dissolution of metal ions from the electrolyte (M. Skyllas-Kazacos et al. 2011). The main disadvantage of this system is that it has the potential for overpotential owing to deposition or dissolution, as well as the potential for electrode deterioration, both of which may result in power loss as a result.

### **3.2.5.5 Ionically inert solid separators (IIS)**

One alternative to using an ion exchange membrane is to use ionically inert solid separators, whose function is to maintain a separation between the reactants and the flowing supporting electrolyte (FSE) or between the catholyte and anolyte flowing in a co-laminar type design, thereby decreasing the area of contact between both liquids and, as a result, decreasing reactant crossover. Among the technologies discussed before, ionically inert solid separators have the potential of being scalable with a standard RFB design, since they do not suffer from difficulties like as reactant cross-over or decreased electrolyte reusability associated with the other designs.

## **4. Application of Flow Battery**

Renewable power sources were developed to help the world lessen its reliance on nuclear energy and fossil fuels and transition to a more sustainable future by increasing our reliance on renewable energy sources. However, renewable energy sources such as wind and solar are weather-dependent, rendering them unstable, and directly connecting them to power grids results in concerns such as overvoltage, frequency variations, and uncontrolled electricity. Thus, in order to address these concerns, we want a flexible energy storage system that is environmentally friendly, provides reliable and continuous power, and is safe to operate. Consider solar energy, which is collected by photovoltaic cells (PV), are reliant on the quantity of sunshine available and may decrease production on overcast days. This is where flow batteries come into play, as they can balance the output when there is an increased demand for energy but no supply and can be quickly supplied when there is no demand but sufficient supply.

Figure 9 (left) illustrates the output fluctuations of a photovoltaic cell throughout the day, which are absorbed by the flow battery (indicating that it did not need to provide energy because sufficient energy is available) and used to generate output power when the energy from the photovoltaic cell suddenly decreased, assisting in stabilizing the output.

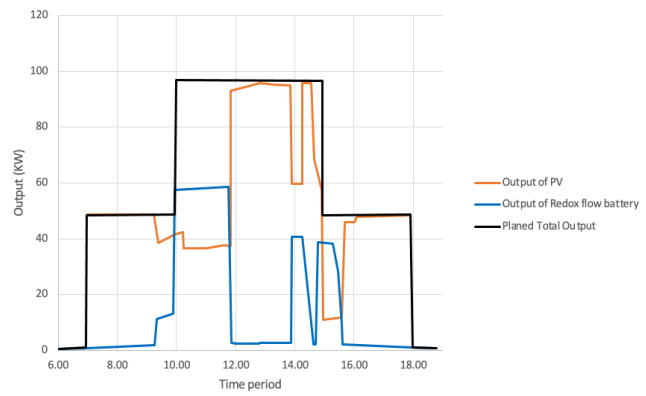
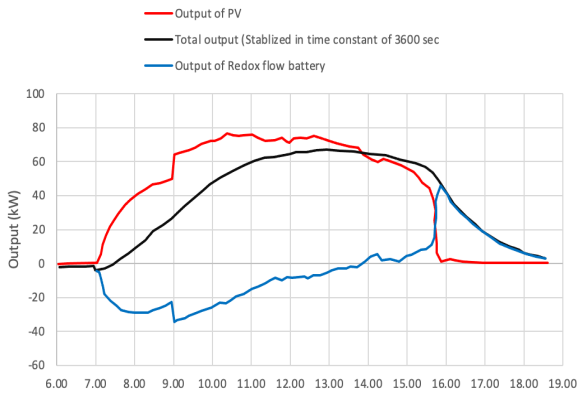


Figure 9 Representation of output being stabilized (left) and peak shaving (right) by RFB, adapted from (Shibata et al. 2013)

Thus, during operation, we can observe from Figure 9 (left) that the redox flow battery provided the required power with each charge and discharge. The charge and discharge of redox flow batteries help to balance and even out the fluctuated output from renewable power source. To perform successfully during these types of jobs, energy storage components must be able to charge and discharge rapidly and completely. Additionally, it is critical to precisely regulate the state of charge (SOC) to prevent running out of charged electrolyte.

Another important application of redox flow batteries would be during peak shaving events as seen in figure 9 (right) where during peak demands, instead of increasing the output of nonrenewable sources like coal/gas industries, RFB's can help in compensation and providing the required energy as per demand.

## 4.1 Charging & Discharging of Flow Battery

Flow batteries work similar to other batteries when it comes to charging and discharging. A potential difference arises between the two electrodes of the battery system when a load (discharge process) is attached to it. When a load induces a change in potential at the negative electrode, a flow of electrons occurs from the negative to the positive electrode. Figure 10 depicts a vanadium redox flow battery in which oxidation occurs at the negative electrode, causing vanadium ions at the positive electrode to shift their valence from  $V^{2+}$  to  $V^{3+}$ . While this is going on, there is a drop in the potential at the positive electrode, causing reduction to take place, which results in the vanadium ions' valence being changed from  $V^{5+}$  to  $V^{4+}$ . During this time, current is created inside the system. During these electrochemical processes, hydrogen ions permeate over the ion-exchange membrane, allowing the system's charge to be maintained. When the system reaches an equilibrium state, that is, when both half-cells attain a balanced state of charge, the redox processes halt, the system ceases to generate current and stops producing current.

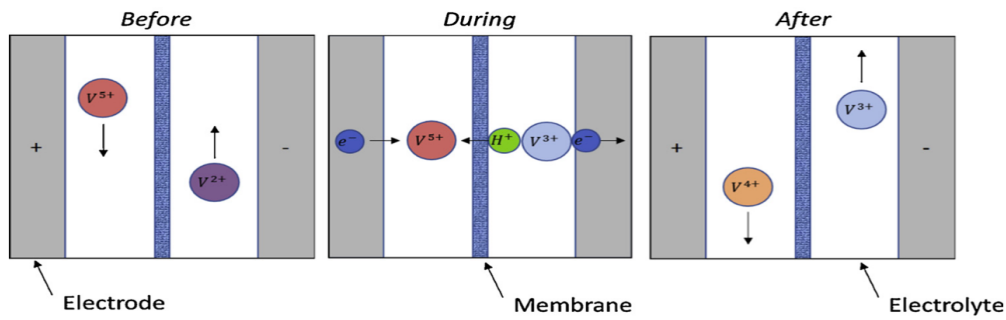


Figure 10 Discharge process in a VRFB system, copied with permission (Lourenssen et al. 2019)

When a charging source is attached to the system, the process is reversed as seen in Figure 11, resulting in a change in the system's potential during charging. The potential at the positive electrode rises, causing the valence of vanadium ions to change from  $V^{4+}$  to  $V^{5+}$  through the process of oxidation; when this occurs, the negative electrode, which is experiencing a decreased potential, accepts electrons through the process of reduction, causing the valence of vanadium ions to change from  $V^{3+}$  to  $V^{2+}$ . During both cycles there is no changes occurring physically/no electrolyte is spent/added, which is main advantage of the flow battery as it has long cycle life and charging-discharging process can keep occurring multiples times.

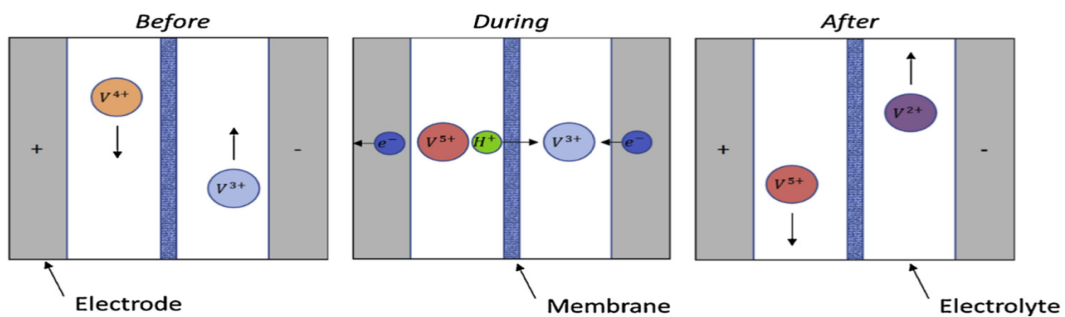


Figure 11 Charging process in VRFB system, copied with permission (Lourenssen et al. 2019)

During both cycles charging/Discharging the power control system (PCS)/ Battery management system (BMS) provides the necessary input signals to turn on/off the pumps. The pumps generally used in flow batteries are bi-directional flow, which helps in reversing the flow of electrolytes based on the operation.

## 4.2 Infrastructure & Maintenance

Flow batteries have the benefit of being readily scaled due to their high degree of flexibility; as power and capacity are different entities, and power production happens at the cell stack chemically, they are more long-lasting than other types of batteries. Vanadium ions exist in four chemical states, making them an excellent candidate for use in a full flow battery. Each chemical state of vanadium is represented by a distinct color, as seen in the illustration in Figure 12. The positive electrolyte circuit contains +4 vanadium ions. Anode oxidizes to +5 vanadium ions once energy is given. On full charging, the electrolyte is vanadium +5 is oxidized to vanadium +3 ions in the negative electrolyte. Its oxidation state drops to +2 as seen in Figure 12 when energy is given. When fully charged, the electrolyte will be vanadium +2. In this context, energy is defined as current delivered by the grid or any other source (renewable sources such as solar and wind). So, initially, the electrolytes are charged, altering their valence state, but no physical changes occur. So, flow batteries last longer. When it comes time to discharge or provide current to a

load, the electrolytes are pumped into the cell stack where the reversible chemical process happens regaining their original valence state, therefore no electrolyte or material is lost.

Thus, electricity serves as the principal input to commence the electrochemical reactions and is reproduced as the principle out during the discharge phase. A 1 MWh flow battery system may need at least 10,000 liters of electrolyte in each half cell (Lourenssen et al. 2019). One of the biggest installations of vanadium flow battery systems (17MW/51MWh) is in Japan's Hokkaido, which was completed in 2016 and has an area of around 5000 square meters, or 83.3 square meters/MWh.

Redflow, an Australian based flow battery company has designed the world's smallest Zinc-bromine flow battery, is already available for commercial deployment. The ZBM claims to be the world's most sophisticated flow battery technology, and the smallest, with a capacity of 10 kWh. The nominal voltage is 48 Vdc, which makes it appropriate for a broad variety of applications. The module is about the size of a "small bar refrigerator", weighing around 250 kilograms (500 lb) and carrying 100 liters (26 gal) of aqueous electrolyte ("Redflow ZBM Fire Safety" 2022). One of their projects involve a children center in Australia where 36 ZBM2 batteries were installed storing up to 360 KWh of energy (seen in the below Figure 13).



Figure 12 Representation of ZBM (Gen 3 Redflow, Redox flow battery) and representation of a scaled-up installation for a larger site, copied with permission ("Redflow ZBM Fire Safety" 2022)

When current is applied to the system, electrochemical reactions in zinc bromide cause zinc ions to migrate across the ion exchange and become electroplated on the anode side, while bromide is left behind to form complex bromine. When the system is discharged, this process is reversed, resulting in the formation of zinc bromide solution and the generation of electricity. One of the test methods suggested by UL 9540A to identify thermal runaway threats is by ASTM D93 closed cup flash point test (flash point- It is the lowest temperature at which when an ignition source is brought close to the test sample, an ignition occurs due to vapor formed above the sample). From the report analysis of ZBM batteries, ignition didn't occur even up till 80°C ("Redflow ZBM Fire Safety" 2022). Also, a short circuit test was conducted as per the standard UL 1973, where a temperature rise was noted only after 87 minutes showing warm orange as shown in Figure 13 (right), during which time the induced heating triggers the control system which turns off the power of pumps preventing electrolyte from being pumped into the cell stack limiting the release of energy as seen in Figure 13 (left). As per information obtained from suppliers only annual

checkups are done – to monitor pH of the electrolyte and check for electrolyte leakage in the system (Hickey 2022).

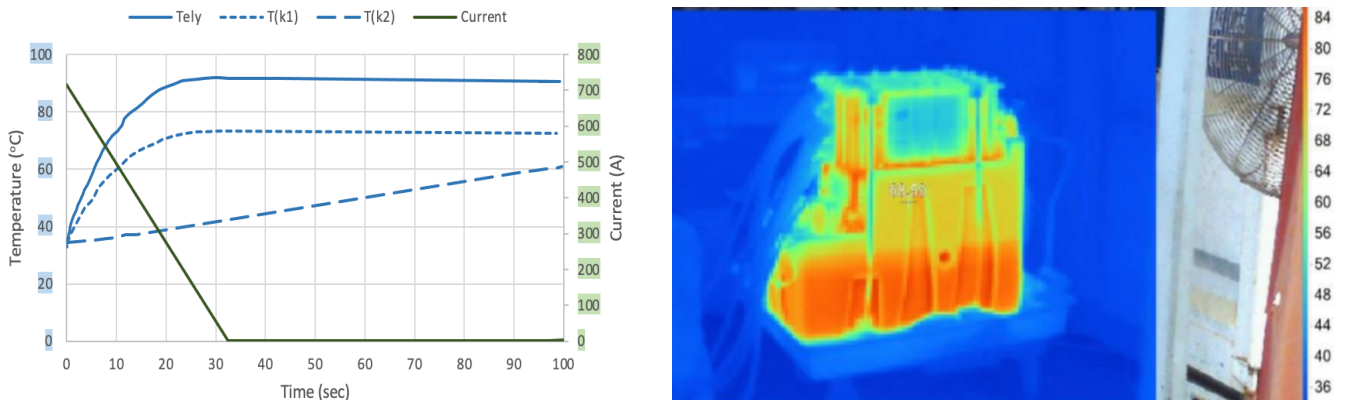


Figure 13 Thermal image (right) after the short circuiting of the ZMB flow battery and graph showing the drop in current once pump shutdown (left), copied with permission ("Redflow ZBM Fire Safety" 2022)

**Leakages** – One of the drawbacks of flow batteries is that the electrolyte is in liquid form, which means that leakage is always a possibility, reducing efficiency and posing a safety threat owing to the electrolyte's poisonous and corrosive nature. Mechanical abuse may distort the battery, resulting in fractures that can leak electrolyte. The electrolyte in a vanadium flow battery is sulfuric acid, which is very corrosive; use of alkaline electrolytes may result in generation of carbonates if the electrolyte leaks and reacts with carbon dioxide present in the atmosphere (Bopp et al. 2016). Due to the fact that vanadium flow batteries are extremely acidic, it is necessary to use non-corrosive materials and sealants during construction, such as stainless bolts to secure the cell stack and prevent leakage, additionally, the contact pressure between the electrodes and bi-polar plates must be considered (Lourenssen et al. 2019). Electrolytes containing hydrochloric acid produce chlorine gas, which can mix exothermically with hydrogen, resulting in containment failure (Chen et al. 2022).

Because the pumping system is the only moving portion in a flow battery, its maintenance is critical to system function. Following many years of installation, some maintenance needs for VRFB are as follows, (S Eckroad 2007): (1) visual check of pipelines and tanks on a monthly basis, followed by a detailed inspection every six months ;(2) Pumps must be inspected every six months; (3) After five years, pump bearings and seals may require replacement ;(4) The cell stack has a life expectancy of almost ten years and requires external cleaning and visual examination every six months.

## 4.3 Future of Flow Batteries

Due to their mechanical complexity and associated costs, flow batteries are shown to be more appropriate to grid-scale energy storage systems with capacities ranging from 100KW to 10MW, where there is no space constraint, which is one of the flow battery's downsides. However, since the energy and power generation components may be separated, the battery system can simply be expanded up, saving further expenditure. Because Zn-Br flow batteries offer a greater energy density than conventional vanadium flow batteries, they are being made commercially accessible



for household use in garages and other areas with enough storage space. At present, 5 kW units are available for backup power applications, most notably in telecom, substation, and UPS applications.

Even though several redox flow batteries, such as VRFB and ZFB, are now commercially available, research is continuously being performed to improve design efficiency while lowering costs. To maximize the influence of solar energy, the potential of directly incorporating photovoltaic cells into the RFB is being investigated. This kind of battery is referred to as a solar redox flow battery. This is accomplished in two ways (Sánchez-Díez et al. 2021) by stacking the photovoltaic and electrochemical cells together, with the solar cell producing the appropriate voltage independently of the RFB cell. The second technique involves the use of photoelectrochemical cells and dye-sensitized solar cells. Drawbacks which are still being researched are the low output voltage and material instability.

Another form of flow battery is the air breathing sulfur flow battery, which is constructed of cheap materials and is capable of operating with both alkaline and acidic electrolytes. The negative electrolyte in this battery idea is composed of an aqueous solution of polysulfide containing lithium/sodium ions, whereas the positive electrolyte is composed of an acidic/alkaline solution containing ions  $Li_2SO_4 / Na_2SO_4$  (Li et al. 2017). Some of the disadvantages involve the production of  $H_2S$  and membrane resistance.

To develop toward a more sustainable future, researchers investigated the problem of  $CO_2$  recycling, which resulted in the Metal- $CO_2$  flow battery, which combines the concepts of  $CO_2$  reduction and power generation. This is the same idea as the Zn- $CO_2$  flow battery concept, which incorporates nanofibers as the anode through which  $CO_2$  gas flows, a zinc wire as the cathode, and an ionic liquid as the electrolyte. Zinc is oxidized to zinc hydroxide during operation, giving electrons for the conversion of  $CO_2$  to  $CH_4$ .

## 5. Safety Hazards in Flow Batteries

Flow batteries are generally safer than standard Lithium-ion batteries as seen in Table 3, because all the flow batteries contain water-based electrolytes which are not flammable by nature (Chalamala et al. 2021). For example, VRFB systems contain– 15% Vanadium, 25% Sulfuric acid and 60% water. In unsafe or uncontrolled situations, it is possible to effectively decrease or halt the creation of hydrogen gas by shutting off the pumps, which in turn stops the flow of electrolyte into the cell stack. This is a crucial safety feature of flow batteries. Voltage is created only when the system is in use; with RFBs, while the system is in standby or shutdown mode, the electrolyte is drained from the system, resulting in insignificant or zero voltage at the cell stack terminals; this is one of the safety features of vanadium flow batteries. In hybrid batteries, such as zinc-bromide, the zinc plate that develops owing to electro deposition of zinc particles from the electrolyte may retain a charge, posing a shock danger. Another critical feature of VRFBs in terms of short circuit potential is that the energy released is limited to the amount of fluid in the cell stack at any given time "*typically less than 1% of total stored energy and they have been tested under dead-short conditions resulting in normal operation posing no danger to personnel or equipment*" (A.H. Whitehead et al. 2017).

**Toxicity** -In the aqueous electrolyte or in the off-gassing products produced during normal operation or by a raise in temperature due to external/internal factors, there may be corrosion or toxicity due to these by products. In addition, the burning of materials comprising hydrocarbons, polymers, or acidic electrolytes which make up a flow battery during a fire, may result in the production of toxic fumes. “*While vanadium is poisonous in its powder form, it is deemed non-toxic when used as an electrolyte in flow batteries owing to its low concentration*” (Energy Response Solutions 2017).

Occasionally, a mixed electrolyte composed of sulfuric acid and hydrochloric acid is employed to enhance thermal stability and boost the diffusion concentration of vanadium-ions in the electrolyte. As a result, there is a chance of producing very poisonous  $Cl_2$  gas.

In zinc-bromine flow battery, off-gassing production of bromine is dangerous which might occur during a fire, (Hill and Davion M 2016) bromine is a skin irritant and toxic to marine life and humans. Whereas in PBS and vanadium/bromine flow battery, bromine gas evolves even during normal operation.

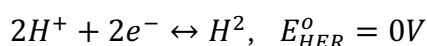
To determine the contribution of flow battery components to fires, cone calorimeter tests were conducted which revealed that (Chen et al. 2022): (1) burning membranes produces HF and  $SO_2$ , which are irritants and toxic in nature; and (2) electrodes are typically composed of carbon and nitrogen compounds, which contribute to the production of CO, NO, and  $NO_2$  which are toxic and harmful to humans.

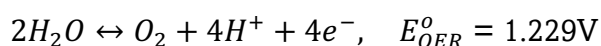
Table 6 Typical hazard based on ESS (Energy Response Solutions 2017)

Risk	Lithium-ion	VRB Flow battery
Voltage	X	
Arc-Flash	X	
Toxicity	X	X
Deflagration	X	
Stranded energy	X	

To cause an arc flash, the output voltage must be at least 100V (Energy Response Solutions 2017), which is typically the operating voltage of lithium-ion, not flow batteries. The most common safety concerns with flow batteries are gas evolution and the possibility of a thermal runaway. Gas evolution happens in aqueous-based flow batteries, depending on the chemical composition of the active species utilized.

The evolution of gases is mostly caused by charge imbalance and self-discharge. It is possible, for example, that during the long-term operation of flow batteries, there is an imbalance on the quantity of active species in the anolyte and catholyte due a number of different reactions. Examples of such reactions include those at the electrode surface that function as a parasite, devouring the electrical input/output for charging/discharging if the potential of the electrode is lesser than the SHE (standard hydrogen evolution process) or OER (oxygen evolution reaction) reactions are seen below:





**Hydrogen evolution** – hydrogen is produced when the operating potential of the cell is more negative than the hydrogen evolution potential, these side reactions reduce the cell efficiency by consuming the current density (Suárez et al. 2014). Because the electrodes are made of porous materials, it is possible that oxygen and hydrogen molecules may stick to the surface, limiting the surface area available for electro-chemical reactions to occur and also these molecules might block ions from passing through the porous electrode (Shah, Al-Fetlawi, and Walsh 2010). Additionally, the rate of hydrogen production is temperature dependent, meaning that the higher the system's operating temperature, the more hydrogen is produced (Jirabovornwisut and Arpornwichanop 2019). This temperature increase could be caused by internal chemical reactions or by external factors (Radiation from another fire source etc). When the volume proportion of  $H^2$  in air is between 4% and 75%, the gas combination is considered flammable and explosive (cameochemicals.noaa.gov, n.d.).

When the electrode of the negative half-cell encounters air, there is a risk that vanadium ions may undergo oxidation, which may result in the occurrence of undesirable side reactions (Jirabovornwisut and Arpornwichanop 2019). Side reactions can also lead to production of hydrogen gas. The presence of an imbalance in the volume of electrolytes in the half-cell can also be caused by a failure of the membrane to effectively prevent uncharged ions from crossing over due to osmosis pressure, resulting in a shift in the vanadium concentration and electrolyte concentrations in the respective cells (Jirabovornwisut and Arpornwichanop 2019). If excess up buildup of the gas occurs this might even cause the system to fail mechanically leading to possible gas leak which can lead to explosions/fire risk.

**Gas evolution** - Due to the fact that flow batteries may include a range of electrolytes/active species based on their redox potential, there is always a danger of the production of various toxic gases. In zinc-bromide flow battery systems, bromine in its liquid condition is not flammable, but its vapor state poses a considerable risk, (10,000 Pascal Pa and boiling point of 58 °C) making it hazardous especially if there is a secondary fire (Hill and Davion M 2016).

Since the electrodes are carbon-based materials and are kept in acidic electrolytes, there are possibilities of intergranular corrosion occurring on the surface of the electrode leading to carbon dioxide generation (Jirabovornwisut and Arpornwichanop 2019).

To increase the efficiency of VRFB's (increasing energy density, by adding HCl which allows for higher concentration of vanadium ions to be soluble in the electrolyte) addition of HCL to the primary electrolyte sulfuric acid was done leading to the possibility of production of  $Cl_2$  gas which is toxic in nature. The main issue here would be that  $Cl_2$  can easily react with  $H_2$  in the presence of catalysts such as UV light, sparks leading to exothermic reactions which might affect the structural integrity of the battery housing as seen in below Figure 14, and this can possibly lead to catastrophic dangers (Alagia et al. 1996).

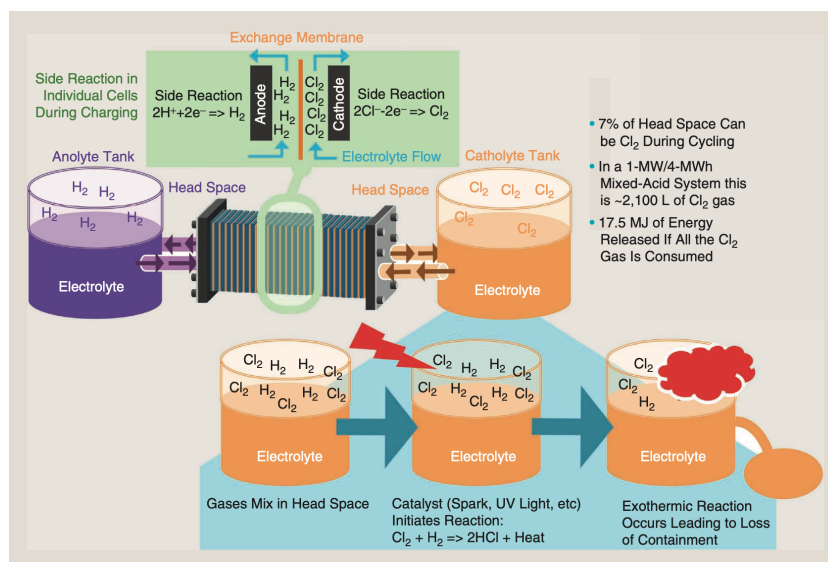


Figure 14 Schematic representation of Gas evolution in RFB's © 2021 IEEE, copied as per IEEE reuse license agreement (Chalamala et al. 2021)

**Thermal Runaway** - Flow batteries have a lower chance of experiencing thermal runaway than standard lithium-ion batteries since the energy released at the cell stack is typically very low. However, there is always a chance of thermal runaway occurring if an uncontrolled self-inducing loop between the chemical reaction and heat produced occurs. Hydrogen gas development causes electrolyte depletion in lead acid batteries (lithium-ion battery thermal runaway is mentioned in the later sections), which exposes the electrode. As oxygen travels from the cathode to the anode, it generates heat and reacts with the exposed electrode; as the temperature rises, oxygen generation increases, creating a feedback loop (Chalamala et al. 2021). The affected battery cell may cause the surrounding battery cells to overheat, potentially resulting in thermal runaway. This chain reaction might spread from module to rack, ending in a massive fire if the gases produced not correctly ventilated.

## 5.1 Mitigation Strategy for Hydrogen Release

Researchers are working to find a solution to the problem of hydrogen evolution, which occurs due to impurities in the electrolyte, by utilizing hydrogen reabsorption cells, (Hagedorn 1984) these cells are called rebalance cells which are individual cells stored separately from the RFB's setup. They consist of a cathode similar to the flow battery and a hydrogen anode. Their role is to restore the state of charge (SOC) of both half-cells after imbalance has occurred. However, these cells also suffer from catalytic poisoning due to the presence of chloride species, which is solved by a novel in-tank capillary-action galvanic reactor that mitigates this issue (Selverston et al. 2019).

Charge imbalance problems can be solved with a dual circuit RFB, in which the catholyte and anolyte are circulated to a separate catalytic reactor where hydrogen and oxygen gas are evolved (Selverston et al. 2019). This system incorporates a supplementary energy platform for the conversion of electrochemical energy to hydrogen through mediated water electrolysis. The negatively and positively charged active redox species can be circulated out of the containment through catalytic bed reactors where they act as electron mediators oxidizing water and reducing protons across electrically floating electrocatalysts, these types of gas recombination systems

are commonly used in sealed type batteries such as lead-acid to prevent overpressure. Table 7 also shows different forms and possible outcomes of degradation.

Table 7 Possible methods of degradation in aqueous batteries (Wittman et al. 2020)

Type of degradation	Degradation process	Possible outcome	Focus of research	Measurement studies
<b>Membrane (chemical)</b>	Decomposition -By impurities -By electrolyte	-Decreased conductivity -Gas evolution (species cross over) -Increased charging voltage -Internal short circuit	-To study long term chemical stability of membranes in supporting electrolytes -Crossover rate over various electrolyte composition	-Rate of crossover -Ionic conductivity -Strength of membrane
<b>Electrode</b>	-Passivation -Impurities poisoning	-Internal short circuit -Raises cell voltage -Increases side reactions	-Stability in electrolyte -Passivation mechanism	-Surface changes -Gas evolution
<b>Electrolyte</b>	-Precipitation of active species -Spontaneous reactions	-Loss of capacity -Self discharge -Increase cell voltage	-Pourbiax diagram for all electrolyte reaction -Experimental rate of side reactions	-Changes to chemical composition -Rate of side reactions effects capacity
<b>Electrode</b>	-Shape changes (Physical/thermal)	-Gas evolution -Increase resistance -dendrite growth	-Thermal stability -Gas evolution due to shape changes -Side reactions due to shape changes	-Electrode voltage -Temperature where degradation occurs -Surface structure changes
<b>Electrochemical membrane</b>	-Electrochemical degradation	-Active species crossover -Increased charging voltage	-Conductivity in electrolyte during cycling -Selectivity in electrolyte during cycling	-Rate of crossover -Ionic conductivity -Mechanical strength

## 5.2 Types of Degradation

Charge imbalance and side reactions are the primary causes of flow battery deterioration, which introduces a new set of dangers and risks as seen in section 5. In electrochemical cells, there are primarily four forms of degradation: electrochemical, chemical, mechanical, and abuse (Wittman et al. 2020).

### 5.2.1 Electrochemical

This term refers to the processes that occur when current flows through a battery cell, resulting in a capacity imbalance between the positive and negative half-cells. The imbalance occurs for a variety of reasons, including fluctuating species concentrations in the electrolyte because of

species cross-over, precipitation, dendritic formation, and electrode deformity (Choi et al. 2017). Depending on the state of charge of either half-cell, whether high or low can drive the cell to imbalance causing the mass transport of species to the electrode to become rate limiting in current generation (Adam H. Whitehead and Harrer 2013). This forces side reactions which lead to gas evolution such as hydrogen to occur to compensate the electric charge at the electrode location. These side reactions frequently throw the cell out of equilibrium, resulting in further side reactions and deterioration.

## 5.2.2 Chemical

This form of deterioration happens even when no current is flowing through the battery system, with one of the primary reasons being the breakdown of the ion-exchange membrane due to the electrolyte's excessively acidic/basic character. Degradation of membrane may result in decreased conductivity (increasing cell resistance which leads to gas evolution) and increased species cross-over across half-cells (Alotto, Guarnieri, and Moro 2014). One strategy to mitigate this is to monitor the membrane's performance over time in various test electrolytes and to measure the volume of electrolyte containing active species in the half-cell volume.

## 5.2.3. Mechanical Deterioration

Any type of deterioration in the physical form would be involved in this category like change in shape of the electrode or the membrane which is quite common in flow batteries. Flow battery systems like ZRB's involve one of the active compounds being deposited on the surface of the electrode during charging process. This deposition of metal causes loss in the cell capacity promoting gas evolution and dendrite growth which might even lead to short circuits (irregular deposit of metal ions on the electrode also leads to reaction area reduction).

## 5.3 Fire Risk in Flow Battery Components

Because flow battery systems use a non-flammable water-based electrolyte, they pose no immediate danger. However, they can cause significant damage to life and property if a secondary fire occurs. This is because flow battery components contain combustible materials that can ignite and produce toxic fumes such as HF,  $Cl_2$ ,  $SO_2$ ,  $NO_2$ ,  $NO$ , and others. For example, in flow batteries such as zinc-bromide systems (Hybrid), the byproducts of which contain bromine, a fire retardant perceived to be safe but, because bromine gas has a high vapor pressure, temperature increases can result in containment failure due to uncontrolled expansion of the gas and lead to explosion. Because the acidic electrolyte in flow batteries is very poisonous and corrosive, any leaks caused by fire or confinement results in skin and eye irritation, and they should be handled with caution.

Auxiliary systems such as PCS (power control system) and BMS (battery management system) are included in flow battery systems. These systems can shut off pumps in the event of a temperature increase or electrolyte leakage, which leads to shutting down the power production. Since all the electrochemical reactions occur at the stack, it is important to understand the components which make up the stack. Flow battery cell stack consists of electrode, electrode

frame, bipolar plates, and ion-exchange membrane. Generally, the flow battery cells are connected in series or in parallel depending on the requirement.

Thus, if a fire were to develop, it would include a large number of materials. While this is very unlikely to occur inside the system (cannot be neglected completely), there is always the risk of a secondary fire spreading to the flow battery portion. For instance, an RFB system utilized as a backup to a diesel generator inside a structure may get unintentionally involved in a fire if the diesel stored next to it catches fire. Thus, it is critical to recognize the fire hazards associated with these components.

The Bipolar plate is a crucial component of a cell stack, it provides a connection point to the adjacent cell connected in series, also separates the catholyte and anolyte and should provide necessary structural support to the cell. Since the electrolytes used are basically acidic in nature graphite is a suitable choice for such systems and due to its good conductivity, but because of its brittle nature carbon polymer composite is used as an alternative, thermal hazards related to this component can be understood by studying parameters such as flammability, fire growth and total heat release (THR) (Zhong 2006). Figure 15 shows the combustion behavior of the bipolar plate tested under a C80 cone calorimeter.

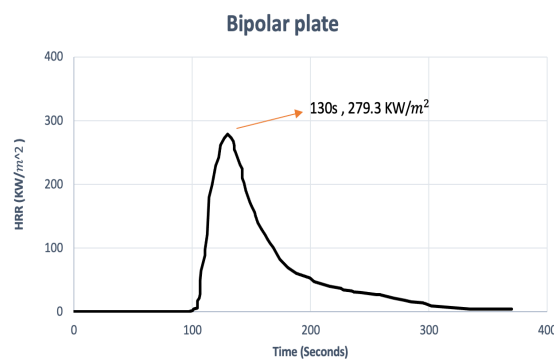


Figure 15 Figure illustrating the heat release rate of a bipolar plate, adapted with permission (Chen et al. 2022)

Because the bipolar plates are composed of polymers, they degrade when the external heat flux exceeds around  $25 \text{ KW}/\text{m}^2$ , resulting in the formation of a volatile mixture that, when mixed with air, reaches the flammability stage, and ignite ensues.

The electrode frame is another key component of the cell stack; it has an entrance that allows for optimum electrolyte transport through the porous electrode. It ensures full sealing of the electrode, and the frame is constructed of electrically insulating materials such as polyethylene and polypropylene to avoid shunt currents (Cunha et al. 2015). The electrode frame exhibits comparable combustion behavior to the bipolar plate, since polymers comprise the majority of materials and degrade into volatile mixtures when subjected to the same heat flux as above, reaching the flammability area. However, the HRR found is double that of the bipolar plate as seen in Figure 16, suggesting a quicker rate of fire propagation and spread.

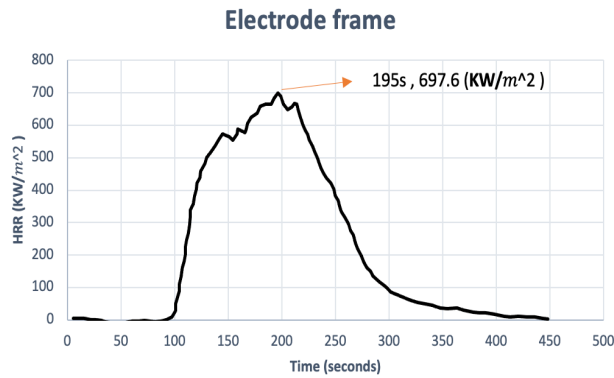


Figure 16 Figure illustrating the heat release rate of electrode frame, adapted with permission (Chen et al. 2022)

Positive and negative electrodes are another critical component that are composed of carbon-based materials. They must be corrosion resistant and stable during chemical reactions since they are submerged in acidic electrolyte. The electrodes are carbon based porous materials that operate as reaction sites for redox processes without actively participating in them. The sample was placed in the cone calorimeter under constant heat fluxes  $25\text{KW/m}^2$ ,  $45\text{KW/m}^2$  and  $65\text{KW/m}^2$ . From Figure 17, we can see that the electrode poses low threat in a fire scenario, till 600 seconds no fire was observed, slight increase in the heat release rate was noticed at 1200 seconds due to smoldering. No ignition was observed even when a spark igniter was introduced into thick black smoke at 1800 seconds. There is possibility of toxic smokes such as CO being produced.

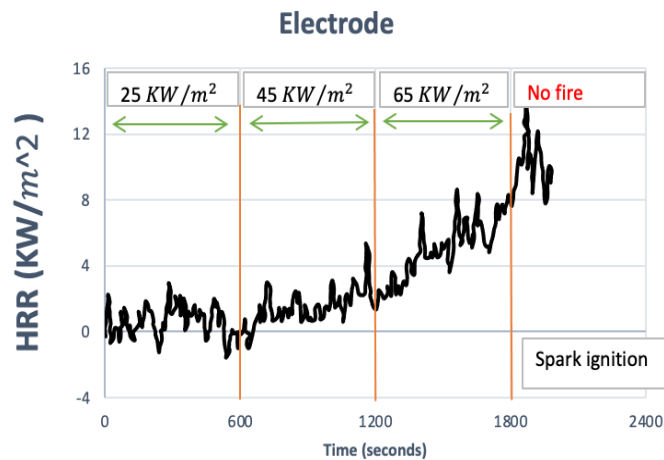


Figure 17 Figure illustrating the heat release rate of electrode, adapted with permission (Chen et al. 2022)

As a result, we can observe that in terms of combustion behavior, the electrode frame and bipolar plater provide a greater danger than the other components. Excessive heating of membranes such as Naflon results in the emission of hazardous gases such as HF and  $\text{SO}_2$  (Chen et al. 2022). If we assume a scenario with more than 30 cell stacks and 50 RFB batteries, the overall energy released during a fire might be enormous.



## 6. Other Energy Storage Systems (ESS)

Figure 1 in the introductory section of this thesis compares several small-scale energy storage technologies based on their power and energy density capabilities. Batteries and flow batteries have become more viable alternatives to capacitors as a source of energy storage owing to their longer discharge duration. Over the past decade, a variety of electricity or energy storage systems were developed, tested, and commercialized, as well as researched and experimented further. Battery technology has been demonstrated to be advantageous due to its scalability and mobility. This technology has the potential to be applied to a wide range of sectors, ranging from small electronics to massive energy systems. Furthermore, it has been demonstrated to be a superior storage system to other systems on the market due to its qualities of longevity, low maintenance, and low environmental impact. Some of the earlier and still widely used energy storage systems are mentioned below.

**Lead-Acid** - They are one of the first created battery systems and are still in use today, mostly in automobiles, since they are relatively inexpensive in comparison to the newer battery technology being developed presently. The battery is composed of lead oxides and an electrolyte of sulphuric acid. Lead and sulfuric acid are both very hazardous. The primary disadvantage of lead-acid batteries is the production of hydrogen and oxygen during overcharging.

**Pump Hydroelectric storage (PHES)** – This is one of the most widely utilized energy storage technologies to date and is now the most prevalent type of energy storage system in the world. This mechanism utilizes gravitational and kinetic energy. When energy demand is low, a system is utilized to move huge amounts of water from a lower to a higher level; when electricity demand is high, the water is allowed to flow through turbines from the higher level, spinning the turbines and producing power.

**Compressed air energy storage (CAES)** – When energy demand is low, power is used to drive compressors to create compressed air, which is then held in highly pressured containers until demand grows, at which point the compressed air is forced to flow through air turbines, which generate electricity.

**Flywheel** – Another effective technique of storing electricity is to utilize a motor to spin a flywheel during periods of low demand. When demand grows, the flywheel converts the stored energy to kinetic energy and generates electricity by activating a generator.

**Supercapacitors** – Unlike a standard capacitor, which stores energy in a magnetic field while current travels across it, this ESS device utilizes two electrodes, an ion exchange membrane, and an electrolyte. During charging, ions cross across, generating a layer of opposing polarity at each electrode. These systems have a very short discharge rate, so applications are limited.

**NaS (Sodium-sulfur)** – The NaS battery uses sulfur as the anode and sodium as the cathode, both of which are molten. Due to the high energy density and power density of this battery, it is a typical energy storage strategy for power plants.

**Li-ion** – Lithium-ion batteries are the most sophisticated and portable rechargeable batteries presently available. Because of their small size and portability, they are the most common power

source for computers and mobile phones. More research is being done to improve the performance of lithium-ion batteries because customers want their phones, tablets, and laptops to last longer, charge faster, and need to be charged less often. To help usher in a more sustainable future, an increasing number of individuals are opting for electric vehicles, which necessitate lithium-ion batteries with a high-power density, rapid charging rate, and prolonged cell life that are also secure and dependable.

Similar to redox flow batteries, lithium-ion battery generates electric current by undergoing redox reactions at active material sites. During the first stages, electrons are transferred from the positive electrode to the negative electrode by oxidation and accepted into the negative electrode via reduction. Electrons move through a secondary circuit way instead of the electrolyte. To maintain charge neutrality inside the cell, lithium ions travel from the positive electrode to the negative electrode through the electrolyte, where they integrate with the mesh-like graphite sheet (unstable condition for lithium-ion). For lithium-ion batteries, this is referred to as the charged state. When a load is attached to the battery during the discharge state, the lithium-ion in an unstable condition returns to the positive electrode through the electrolyte, while the electrons go via the external circuit linked to the load producing current. To prevent moving electrons from contacting the electrolyte, which might result in a possible disaster during the early charging stage as the lithium-ions flow through the electrolyte, they are engulfed by solvents contained in the electrolyte. Together with the solvent, the lithium ions react with the graphite to form an interface known as the SEI (Solid electrolyte interface) layer.

## 7. Hazards of Lithium-ion Battery

Flow batteries are electrochemical cells that convert chemical energy into electrical energy, they generate current in the same way as lithium-ion batteries do. Because of its great power/energy density and mobility, lithium-ion batteries are the most extensively used batteries, making them one of the most popular energy storage alternatives on the market and a formidable competitor to flow batteries. Lithium-ion batteries account for 90% of all battery storage systems in the world. One of the primary reasons why flow batteries may be a better alternative for large-scale grid-level energy storage than lithium-ion is due to some of its inherent safety properties and capacity to discharge energy over a longer period. Because of the commercialization and widespread use of lithium-ion batteries, there is an abundance of research and knowledge on the fire hazards connected with lithium-ion batteries. As a result, these available data can be used as a reference to compare with flow batteries.

*“Lithium-ion batteries are always a safer alternative than lithium-metal batteries since they do not need lithium metal to be redeposited on the electrode surface during the charging process”* (Balakrishnan, Ramesh, and Prem Kumar 2006). As with flow batteries, lithium-ion batteries are sensitive to side reactions, which may result in a variety of risks.

When the cell temperature hits 70-100°C, the solid electrolyte interface layer (SEI) that keeps the electrolyte from coming into touch with the electrode becomes unstable and starts to decompose exothermically (Lisbona and Snee 2011). Typically, lithium-ion batteries remain inert until an external load is applied, at which point energy is released in the form of current. When a battery fails due to internal or external sources, an uncontrolled discharge of energy occurs, generating a great deal of heat. This growing heat might result in thermal feedback, which further raises the

cell's temperature and also increasing reaction rate, resulting in a thermal runaway. Thermal runaway can be described in three stages in a lithium-ion battery (Abraham et al. 2006).

1. When the cell temperature hits around 120°C, the solid electrolyte interface (SEI) degrades, exposing the electrolyte at the lithiated graphite negative electrode.
2. With a further rise in temperature to around 140 degrees Celsius, exothermic processes at the positive electrode begin to occur, resulting in the fast generation of oxygen.
3. Decomposition of the positive electrode and oxidization of the electrolyte occur at temperatures around 180°C, this highly exothermic process which leads to temperature rise of 100°C/minute.

Thermal runaway is dependent on the level of charge of the battery cell; a cell with very little charge requires a higher temperature to induce adverse consequences, while cells with a high charge or full charge need a lower temperature.

Mechanical abuse – Each lithium-ion cell comprises an exterior shell composed of plastic, aluminum, or steel. This layer serves as the first line of protection against heat or mechanical dangers by enclosing the cathode, anode, and separator in a jelly roll configuration (Choi et al. 2017). When an external force ruptures or deforms the battery, a significant quantity of heat is generated, which might result in thermal runaway. This is a critical safety feature in an electric car since crashes may seriously damage the battery and result in a fire. A possibility of short circuit might also arise even if a slight deformation results in the internal components coming in contact with each other (C. Zhang et al. 2017). This short circuit can cause a temperature rise, which in turn induces additional short circuits within the area, resulting in thermal runaway (Finegan et al. 2015). Studies have shown that when a lithium-ion cell is penetrated by a nail, the air surrounding the nail initiates vigorous exothermic oxidation reactions causing increasing in temperature of nearby areas (Choi et al. 2017).

Electric abuse – Overcharging or over discharging is one of the most prevalent kinds of electric abuse; generally, a battery is charged to a specified state of charge (SOC), but if it has a greater state of charge, any further energy input results in an overcharge. This phenomenon results in electrolyte decomposition at the cathode (Patel et al. 2020) which causes the lithium-ions at the cathode to deintercalate and become unstable, resulting in the release of oxygen; additionally, excess lithium-ions from the cathode may deposit on the anode, forming lithium (Arai et al. 2015). All of these processes result in heat and gas evolution, which may result in cell rupture or explosion (Lisbona and Snee 2011).

Thermal abuse – When a lithium-ion battery becomes heated leading to a thermal runaway the thermal shock can affect adjacent batteries which are present in the proximity resulting in a major thermal runaway hazard. Both mechanical and electric abuse causes an increase in the battery's interior temperature. Because the amount of heat created is theoretically equal to the amount of heat lost by the battery to the environment, reactions at the anode and cathode do not result in a considerable temperature increase during normal operation. If heat dissipation is inefficient, however, thermal stress may cause the battery to go through reactions that produce more heat, eventually exploding (Bandhauer, Garimella, and Fuller 2011).

Table 8 Example of some lithium-ion battery fires

Date	Description of the Accident	Cause
07/01/13	Fire accident of Boeing 787, USA	Short circuit
23/03/18	Tesla Model X causes fire in California	Crash
07/03/17	ESS of a thermal power plant causes fire, China	High temperature

Table 8 details some fire events using lithium-ion batteries and the contributing variables. Unlike flow batteries, Li-ion batteries have been used commercially for a long time, resulting in many cases of battery fires. In the Boeing 787 incident, a short-circuit caused the main battery to experience thermal runaway, which then extended to the secondary batteries, resulting in the emission of hazardous gases and electrolyte ejection (Patterson 2014). Tesla vehicles involved in a collision repeated the nail-piercing test of lithium-ion batteries, in which oxygen comes into touch with the electrode or the impact of the collision causes the internal components of the battery to come into contact, resulting in a short circuit (Shepherd and Siddiqui 2021). The mishap in China using Li-ion batteries that culminated in an explosion was reportedly caused by thermal failure of the battery after exposure to unfavorable circumstances such as dust and sand buildup (International Association of Fire and Rescue Services 2021).

## 8. Flow vs. Lithium-ion Battery Comparison

When compared to other battery storage systems on the market, lithium-ion batteries have dominated the market since they began commercial production on a large scale in the 1990s. Their high energy density, high efficiency, long shelf life, and low environmental impact distinguish them from other battery storage systems. LIBs (lithium-ion batteries) come in a variety of chemical compositions, including lithium-manganese-oxide, lithium-cobalt-oxide, lithium-titanate-oxide (LTO), lithium-nickel-manganese-cobalt-oxide (NMC), and others. LIB's raw materials have increased greatly in value over the years as a result of its widespread use, and as a result, there is a pressing need to identify alternate energy storage technologies that may reduce the burden associated with obtaining raw materials (da Silva Lima et al. 2021).

An alternative energy storage system could be redox flow batteries (RFB) The essential properties of both LIB and RFB, as well as their pros and disadvantages, are listed in the following table (da Silva Lima et al. 2021).

Table 9 Basic characteristics of LIB & RFB (da Silva Lima et al. 2021)

Type of Storage Technology	Power Capacity/Density	Lifetime	Cycle Efficiency	Advantages	Disadvantages
<b>Lithium-ion Battery (LIB)</b>	200 Wh/kg	10-15 years or 3000 cycles	65-95%	High energy density; High efficiency; Long lifetime	Short lifetime and elevated costs during large scale applications
<b>Redox Flow Battery (RFB)</b>	16-33 kWh/m <sup>3</sup>	5-20 years or 1500 - 15000 cycles	70-80%	High efficiency; Long lifetime	High cost; Low energy density; Risk of cross-contamination of electrolyte

While both lithium-ion and flow batteries offer significant advantages as energy storage systems, each kind of battery system has distinct advantages over the other and vice versa. “While lithium-ion batteries have a higher power and energy density than flow batteries, their low impedance feature makes them desirable for frequency and voltage control (Vassallo 2015) while flow batteries have a lower power density but a longer discharge period”. Additionally, flow batteries have the following characteristics: the energy (electrolyte) and power (cell stack) components of the system are separated, allowing for easy scaling; no physical changes occur within the electrodes during cell operation; and the battery system's components can be easily replaced, extending the battery's life cycle. Some characteristic differences between RFB's and LiB can be seen in Table 10.

Table 10 Characteristics of RFB Vs lithium-ion battery (Daggett n.d.)

Characteristics	Redox flow batteries (RFB)	Lithium-ion battery (LiB)
<b>Cycle life</b>	Greater than LiB	Lesser than VRFB
<b>Self-discharge</b>	Almost zero	Low
<b>Decoupled power and energy</b>	Mostly possible	Not possible
<b>Risk of fire/thermal runaway</b>	Very low/Zero	Flammable electrolyte
<b>Safe servicing</b>	Possible	Cannot discharge and service
<b>Simple monitoring</b>	Cell-balancing not required	Cell balancing required
<b>Complexity of balance of plant</b>	Relatively complex	Liquid cooled complex
<b>Gravimetric energy density</b>	Low	High
<b>Volumetric energy density</b>	Low	High
<b>Diversity of applications</b>	Fewer compared to LiB	Higher compared to VRFB
<b>Cost/KWh</b>	Lower to LiB	Higher

When cycle life is considered, self-discharge and depth of discharge are the most desirable characteristics of flow batteries. Self-discharge scenarios are almost non-existent in flow batteries because they occur only at the battery's cell stack, where the electrochemical reaction

occurs. Since no physical changes occurs in electrolyte during charging/discharging the life cycle efficiency of the electrolyte is very high (Doetsch and Pohlig 2020). Unlike lithium-ion batteries, the depth of discharge (DoD) has no effect on the performance of RFBs. RFBs may be drained to 100%, while lithium-ion and lead-acid batteries have a maximum discharge capacity of 80% and 50%, respectively, to prevent cell damage (Doetsch and Pohlig 2020).

Due to the high-power density and small size of lithium-ion batteries, they are ideally suited for mobile operations rather than permanent applications where location and size of storage are not critical, such as grid-based applications. To get a better understanding of the use of RFBs in hybrid electric cars, tests were undertaken by Mohamed, Sharkh, and Walsh in 2009; the comparison of the findings is presented in Table 11 (Mohamed, Sharkh, and Walsh 2009).

*Table 11 Results comparing VRFB's, Lead-acid and lithium-ion, (Mohamed, Sharkh, and Walsh 2009)*

<b>Requirement for the EV vehicle- 72 V,110 Ah,300 A</b>	<b>Lithium-ion</b>	<b>Lead acid</b>	<b>Redox flow battery</b>
	60 Kg,96 L	250 Kg,300 L	400 Kg, 424 L

**Temperature Analysis** – Lithium-ion batteries are highly temperature dependent, necessitating thermal controls to maintain the operating temperature within the recommended range of 15-35°C (Ma et al. 2018), and vanadium flow batteries, operate at temperatures ranging from -40 to 75°C avoiding the need for any auxiliary equipment such as HVAC for cooling (Gibbard and Cipriano n.d.). This results in increased efficiency and ensures that HVAC unit breakdowns have no harmful impact (Marshall et al. 2020).

**Environmental Impact** – When comparing lithium-ion and vanadium flow batteries, lithium-ion batteries have a much greater environmental impact due to the lack of effective recycling plants for their toxic waste components such as cobalt, nickel, copper, and zinc (Mejame et al. 2020), whereas vanadium flow batteries have a major toxic issue with the sulfuric acid used as an electrolyte (toxicity is significantly less than that of lead-acid batteries), and the vanadium dissolved in the electrolytes is less toxic. Following operation of the vanadium battery, the salt may be reprocessed and utilized for a new battery system, resulting in zero waste (Sloop et al. 2018).

## 9. Discussion

Both flow batteries and lithium-ion batteries have their own set of disadvantages in terms of fire and safety issues, with RFBs having a greater probability of failure owing to their complicated system design. The system is composed of several mechanical components, such as pumps, tanks, tubing, and valves, which increases the likelihood of failure as seen in Figure 18.

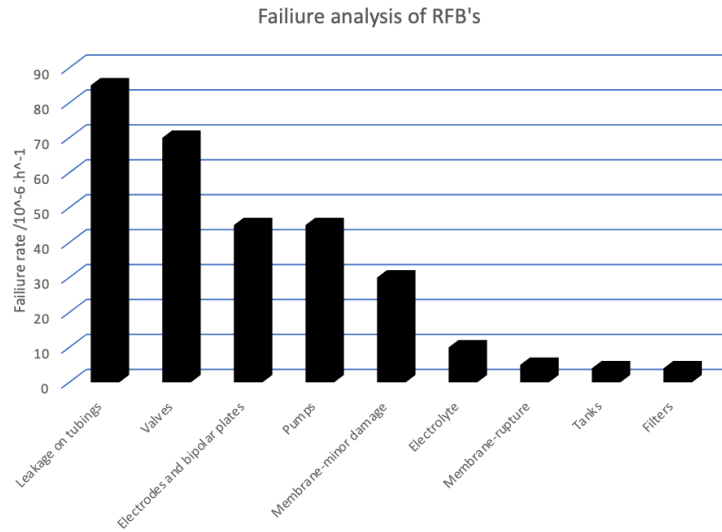


Figure 18 Possibility of equipment failures in RFB's, adapted with permission (Reichelt and Müller 2020)

Electrolyte leaks, valve failures, and pump failures are all probable causes of failure. Corrosion may result in both electrolyte loss and pump failure. Corrosion may occur as a result of the electrolyte's acidic composition or as a result of vanadium ion oxidation. Corrosion may result in electrolyte leakage from tanks, pipelines, and other components if it is severe enough. Corrosion byproducts may have an adverse effect on the pump's performance.

When it comes to hybrid flow batteries, such as zinc-bromine, the primary concern is bromine evolution, which may occur even if a secondary fire elevates the electrolyte temperature over 50 degrees Celsius (Hill and Davion M 2016). Bromine is also very corrosive and toxic, which creates further complications. The hazards and severity of a zinc-bromine flow battery are shown in Figure 19.

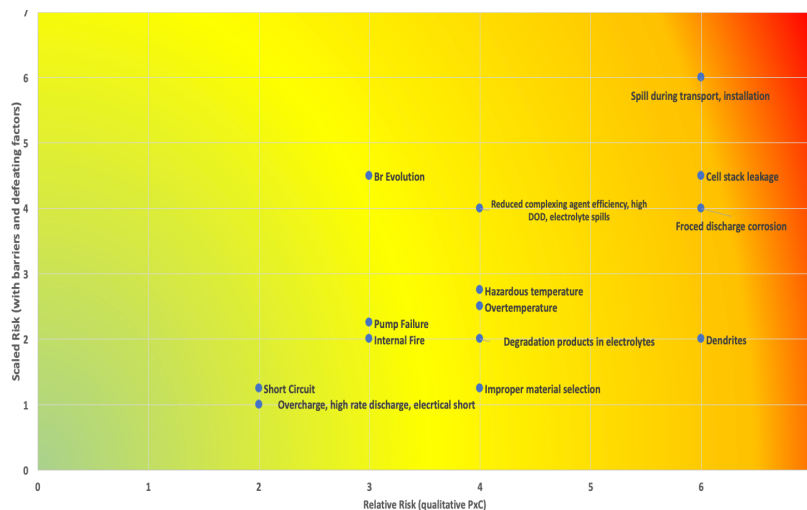


Figure 19 Risk and severity of hazards in Zn-Br flow battery adapted and redrawn from (Hill and Davion M 2016)

Even though Zn-Br system is not a direct fire hazard, there is a chance of fire occurring in secondary auxiliary equipment's connected to the system such as resistors, inverters etc (Rose, Schenkman, and Borneo 2013) .

Table 12 illustrates some of the risks associated with flow batteries and lithium-ion batteries.

Table 12 Risk comparison of few hazards in RFB and Li-ion cells

Hazards/Risks	Lithium-ion battery	Redox flow battery
<b>Electrolyte leakage</b>	<ul style="list-style-type: none"> <li>Does not occur during normal operation but possible due to external factors such as nail piercing, explosion, cell rupture etc ejecting toxic and flammable gas</li> </ul>	<ul style="list-style-type: none"> <li>Can occur during normal operation due to electrolyte being in liquid form</li> <li>Toxicity/Corrosive issues</li> </ul>
<b>Secondary fire (fire in the building / Arson)</b>	<ul style="list-style-type: none"> <li>Chemical degradation, possibility of thermal runaway, flammable electrolyte</li> </ul>	<ul style="list-style-type: none"> <li>Components can partake in combustion, gas evaporation leading to high pressure in containment</li> </ul>
<b>Hydrogen evolution</b>	<ul style="list-style-type: none"> <li>Occurs due to different reaction mechanism- between lithium metal &amp; water, sulfuric acid &amp; metals, hydroxide ions &amp; metals etc</li> <li>Can lead to explosion if released gases meet the flammability criteria</li> </ul>	<ul style="list-style-type: none"> <li>Occurs due to Side reactions or due to chemical imbalance</li> <li>Can lead to explosion if released gas meets flammability criteria</li> </ul>
<b>Short circuit/ Over discharge</b>	<ul style="list-style-type: none"> <li>Possible of occurrence due to dendrite formation or an external path of lesser resistance which permits flow of current</li> <li>Thermal runaway possibilities</li> </ul>	<ul style="list-style-type: none"> <li>Can also occur due to dendrite formation (commonly in hybrid flow battery) or also due to a secondary circuit</li> </ul>
<b>Thermal runaway</b>	<ul style="list-style-type: none"> <li>Mechanical/Electrical/abuse which might cause the battery temperature to rise resulting to thermal failure</li> </ul>	<ul style="list-style-type: none"> <li>Mechanical/Electrical/Chemical/Electrochemical abuses can cause a thermal runaway, but detailed processes are still unclear due to lack of information</li> </ul>

One of the most significant distinctions between the two systems is the likelihood of electrolyte leakage in flow batteries, which may occur even during normal operation owing to leaks in pipes, valves, or containment failure. As an electrolyte, flow batteries such as VRFBs use sulfuric acid. Being a carcinogenic material, sulfuric acid may cause irreversible harm to the lungs, teeth, and stomach, and its corrosive nature can cause serious irritation to the skin and eyes if it comes into contact with them. As a fire hazard, sulfuric acid is a highly powerful oxidant that promotes the burning of other substances; during a fire, sulfuric acid may create sulfur oxides, which are a



hazardous gas. The acid aggressively interacts with alcohol, water, and organic substances (wood, paper, etc.) to generate heat. Since it combines with the majority of metals and produces hydrogen gas as a byproduct, it poses a risky situation, since hydrogen gas within its flammability limitations is very explosive. The best technique to neutralize sulfuric acid spills is by using crushed limestone or soda ash, and suitable safety gear is essential when dealing with sulfuric acid leaks.

While in ZFB's systems even though bromine is not a flammable substance, it poses flammability risks in the form of fumes during processes in which bromide is converted to bromine. During these reactions, if the substance comes into touch with sawdust, cotton, or metal particles, etc., it poses a danger of spontaneous combustion. Bromine is very toxic and has a major negative effect on skin, eyes and if inhaled. As a safety hazard, bromine is very corrosive to aluminum, steel, bronze, and copper, and as a fire hazard, it interacts severely with rubber, phosphorous (ignites and generates deadly explosions), methyl alcohol, acetylene, ammonia, etc. Like sulfuric acid, bromine is also a strong oxidizing agent promoting combustion of other materials and when heated it produces toxic and corrosive fumes. Spills which contain bromine should be handled using inert materials such as dry sand, soda ash. Electrolyte leak from flow batteries should be handled swiftly with the help of a containment area preventing the electrolyte spill from reaching drains, or areas where ignition source is available.

Compared to flow battery, lithium-ion cells need to go through some sort of degradation process such as mechanical crush, nail piercing, short-circuiting due to dendrite formation causing the battery to explode/vent or an abuse for the electrolyte to leak out. Electrolyte (organic solvents and lithium salts) would seep out due to the perforation. These electrolytes being flammable are also toxic if they come into contact with the skin, and since standard Li-ion cells are stacked, they may short out other batteries. Experiments on the puncturing of lithium-ions revealed that in addition to electrolyte leak, gases such as  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$  were also emitted. Flammability of such released gases are as (Mikolajczak et al. 2011).

Table 13 Flammability of released compounds

<b>Compound</b>	<b>LFL (lower flammability limit)</b> %	<b>UFL (upper flammability limit)</b> %
<b>Hydrogen</b>	4.0	75.0
<b>Carbon monoxide</b>	12.5	74.0
<b>Methane</b>	5.3	15
<b>Ethylene</b>	3.1	32.0
<b>Ethane</b>	3.0	12.5

One of the biggest threats to battery energy storage systems is the presence of a fire, whether triggered due to internal hazards of the battery system or by a secondary source such as arson, heat radiating from nearby fire. Secondary fires may have a significant effect on flow battery systems. Even though the electrolyte is a water-based aqueous electrolyte that is not flammable whereas li-ion contains flammable electrolyte, additional dangers remain, such as flow battery components that may contribute to a fire owing to their combustibility characteristics. Components such as bipolar plate and electrode frames are made of polymers and polyethylene material respectively which means they can burn and melt producing volatile mixtures. The combustion of these components produces poisonous gases, mostly  $CO$ ,  $NO_2$ ,  $SO_2$ ,  $HF$  which are

fatal to humans. Also, polymers in a condition of melting may drop and fall off, igniting nearby flammable materials and posing a difficult problem of flame spread. Due to the presence of bromine, secondary fire-generated heat creates extra issues in the ZFB system. Bromine evaporates at elevated temperatures, and since its vapor pressure at ambient temperature is 10,000Pa, the heat might induce expanding gas to cause the container to explode. The water content in flow batteries would most probably help in absorbing the heat imposed on it. But, in worst case toxic fumes are the most dangerous outcomes from this scenario. Possibility of explosion leading to building collapse, toxic fumes and short-circuit are reasons due to which fire fighter chose a defensive approach to fighting battery fires, also care is given to ensure to toxic run off of water does not occur.

In scenarios where external heat impinges on the lithium-ion cell, the rise in temperature can cause cell overpressurisation (Lisbona and Snee 2011), which might lead to explosion or evolution of toxic gases such as  $CO$ ,  $CO_2$ ,  $CH_4$ , ethane  $C_2H_4$ ,  $HF$ ,  $HCN$  and ethylene  $C_2H_6$  occurs, but the temperature rise also causes the degradation of the SEI layer causing electrolyte to come in contact with the electrode, finally resulting to thermal runaway issues.  $HF$  gases are very toxic to humans and requires proper protective wear while fighting these toxic fumes, fluoride can easily mix with the runaway water so special care must be given to where the water leads to.

Flow batteries may produce hydrogen during the charging/discharging cycle if parasitic processes absorb cell voltage and cause an imbalance between the two cells. When a cell is unable to provide the required output voltage, side reactions occur. These side reactions in flow batteries often yield a small amount of hydrogen as a byproduct. When several cell stacks are layered, greater amounts of hydrogen may be produced. Hydrogen has a highly sensitive flammability limit and improper venting may result in explosions; this is one of the perilous situations encountered by firefighters battling battery fires. On the cathode side, chlorine may be produced if the flow battery includes chlorine-based electrolytes. In the presence of simple catalysts such as UV light, chlorine and hydrogen may mix exothermically and violently to make hydrochloric acid. This might cause a breach in the containment vessel.

In Li-ion cells, hydrogen is created by a variety of processes (Amon et al. 2012), including the reduction of hydrogen ions at electrodes, the interaction between sulfuric acid and metals, the reaction between lithium metal and water, the reaction between hydroxide solutions and water, and any kind of misuse.

Unlike Li-ion batteries, internal and external short circuits in flow batteries do not provide a substantial safety risk (A.H. Whitehead et al. 2017). Generally, a short circuit develops when a secondary channel with lower resistance exists between both terminals. In ZFBs, dendritic development on the zinc anode may potentially cause short circuits. However, this only impacts cell performance since the voltage created in the cell stack is far too low. When current flows through this secondary channel in a li-ion battery, the temperature rises as a result of the production of heat. If this heat is not immediately released, a self-heating loop may form, resulting in severe chemical breakdown and the production of poisonous and combustible gases.

## 10. Conclusion

The objective of this study is to provide an overview of flow batteries and their possible risks. Earlier portions of the research were devoted to elucidating the operation of flow batteries, the many types of electrolytes, and their applications. Focusing on vanadium and zinc bromine flow batteries, the fire hazard and safety risks during normal operation and hazardous situations were studied. A broad comparison of the fire and safety issues of flow batteries with lithium-ion batteries was performed. Due to a lack of information, it was not possible to conduct research on electrolyte storage, handling, and refilling risks, as well as thermal runaway concerns. Each form of energy storage system has its own distinct benefits and drawbacks, so selecting a feasible choice often comes down to cost savings, safety, and scalability. Flow batteries are well suited for integration with renewable energy sources such as solar, wind, etc. where space is not a concern and high output voltage over a short time is not required.

The primary emphasis of this study is the influence of flow batteries on fire safety, even though the battery's nonflammable electrolyte and low operating voltage does not necessarily imply it is much safer than Li-ion. Redox flow batteries pose significant dangers, such as hydrogen evolution caused by electrolyte imbalance/side reactions. Due to its flammability and explosiveness, the evolution of hydrogen gas has always been a crucial safety factor in battery storage systems. The pace and likelihood of hydrogen generation is greater in lithium batteries only during hazardous conditions/battery abuse state and not during normal operations as seen in flow batteries. Since the electrochemical reactions for flow batteries occur exclusively at the cell stack, which contains relatively less electrolyte at the time, the quantity of hydrogen gas created is of low volume. But if multiple cell stacks are placed together then the quantity of hydrogen gas produced would be much higher. In grid energy storage, dozens of flow batteries are stacked together to provide the required output. The size of cell stack containing the electrolyte is also why short-circuit/over-discharge in flow batteries does not have such a high safety hazard as the energy stored at the cell stack during the time is not enough to create a major shock hazard but there is always a possibility.

During a fire, both Li-ion and flow batteries emit toxic fumes. Even during normal operation, the Vanadium Redox flow battery containing HCL and the Hybrid flow battery containing zinc-bromide can create chlorine and bromine gas, respectively. Both gases are poisonous, corrosive, and hazardous to people and property. If substances such as metal dust, cotton, etc. come into contact during the process in which bromide is converted to bromine, spontaneous ignition might occur. Similarly, with simple catalysts such as UV radiation, hydrogen may combine exothermically with chlorine. Like the possibility of explosion in li-ion batteries when internal components, electrolyte (flammable), etc. are forcibly released, the same may occur when a temperature increase leads bromine vapors to expand or when the production of HCL exothermically causes the containment to fail or burst.

A fire occurring within the vicinity of flow batteries or on it due to secondary sources also leads to chances of toxic fumes such as HF,  $SO_2$ , CO and  $CO_2$  etc. being produced, these toxic fumes are more less like fumes produced when a li-ion cell is involved in a fire.

Most important difference between both systems is the possibility of electrolyte leakage during normal operation which can only occur in flow due to all the mechanical components involved in running the system efficiently.

As with other BESS, flow batteries have their own benefits and drawbacks when compared to Li-ion. However, as flow batteries are still a small industry, most of the current research is focused on improving the efficiency and performance of the battery. When it comes to high density and portability, lithium-ion remains superior.

Some key inherent safety aspects which are only linked to flow batteries can be summarized as:

- Possibility of turning off the pump which feeds the electrolyte into the cell stack where the electrochemical reactions occur, thus preventing or reducing the chances of hazards.
- Nonflammable electrolytes with high composition of water.
- Low energy output in a single cell stack.
- Draining out the electrolytes leaves negligible charge at the terminals reducing shock hazards.

Consequently, in terms of future research or queries requiring more answers, the following points are yet to receive more importance:

- More detail analysis of battery abuse testing of flow batteries, Electrical, mechanical, and chemical degradation impacts.
- Safety features of flow batteries that can prevent/resolve hydrogen gas release similar to VRLA (Valve regulated lead acid batteries).
- Effect of temperature on the electrolyte (focused on safety/hazards and not reaction kinetics) used in flow batteries.
- Detailed study on the fire behavior of flow batteries which include lab full-scale fire experiments – details study on the heat release rate, gas production etc.
- Analysis and effect of thermal runaway possibilities in flow battery.
- Risk and hazard analysis of electrolyte leakage/ storage and refilling processes.
- Long term operational hazards/ safety risks of flow batteries.

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