STUDY OF FUTURE ENERGY STORAGE VANADIUM REDOX FLOW BATTERY(VRFB)

A PROJECT AND THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN ELECTRICAL AND ELECTRONIC ENGINEERING

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Certification

This is to certify that this project and thesis entitled**“An Overview of Future Energy Storage Vanadium Redox Flow Battery (VRFB)”** is done by the following students under my direct supervision and this work has been carried out by them in the laboratories of the Department of Electrical and Electronic Engineering under the Faculty of Engineering of Daffodil International University in partial fulfillment of the requirements for the degree of Bachelor of Science in Electrical and Electronic Engineering. The presentation of the work was held on 31 May 2021.

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Dedicated to

My Parents With Love & Respect

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List of Abbreviations

VRFB - Vanadium Redox Flow Battery

ESS - Energy Storage System

BESS - Battery Energy Storage System

DSA - Dimensionally Stable Anodes

PHS - Pumped Hydro Storage

CAES - Compressed Air Energy Storage

DLC - Double Layer Capacitor

EMF - Electromotive Force

PSAT - Power System Analysis Toolbox

P.U - Per-Unit

SMES - Superconducting Magnetic Energy Storage

OCV - Open Circuit Voltage

SOC - State of Charge

MATLAB - Matrix Laboratory

G-S Technique - Gauss-Seidel Technique

N-R Technique - Newton-Raphson Technique

IEEE - Institute of Electrical & Electronics Engineers

VLA - Vented Lead- Acid

VRLA - Valve – regulated Lead – Acid

PCS - Power conversion system

BOP - Balance of plant

RTE -Round – trip efficiency

O&M - Operations and Maintenance

BNEF - Bloomberg New Energy Finance New Energy Outlook

Li - Lithium

NaS - Sodium-Sulfur

DoD - Depth of discharge and Department of Defense

PSH - Pumped Storage Hydropower

ORNL - Oak Ridge National Laboratory

KW - Kilowatt

KWh - Kilowatt –hour

MW - Megawatt

MWh - Megawatt – hour

GW - Gigawatt(s)

$ - Doller

€ - Euro

CAES - Compressed Air Energy Storage

EPRI - Electric Power Research Institute

NOMENCLATURE

Nomenclature

E_{full} - The potential difference

E_0 -The standard reduction potential (v)

R - The Universal Gas Constant

T - Is the absolute temperature

N - Number of Equivalents Transferred Per mole of Reduced or Oxidized Species

F - Faraday,s Constant

C_x - Concentration of V^{x+} ions (mol L^{-1})

c_0 - Concentration of the reactant at electrode surface (mol L^{-1}) C_b bulk Concentration (mol L^{-1})

η_{OP} -Total cell overpotentials (V)

η_{act} - Activation overpotential (v)

η_{conc} - Concentration overpotential (V) η_{ohm} ohmic overpotential (V)

D_x - Maximum diffusion coefficient of V^{x+} ions ($dm^2\ s^{-1}$) J current density (A cm^2)

J_0 - Exchange current density (A cm^2)

E_a - activation energy (J mol^{-1})

L - Length

V - electrolyte volume (dm^3)

A_e - electrode surface area (m^2)

A_m - membrane surface area (m^2)

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First of all, we give thanks to Allah. Then we would like to take this opportunity to express our appreciation and gratitude to our project and thesis supervisor **ENGR. Mr.Md. Ashraful Haque, Assistant professor** of Department of EEE for being dedicated in supporting, motivating and guiding us through this project. This project can't be done without his useful advice and helps. Also thank you very much for giving us opportunity to choose this project.

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ABSTRACT

Interest in the advancement of energy storage methods has risen as energy production trends toward renewable energy sources. Vanadium redox flow batteries (VRFB) are one of the emerging energy storage techniques being developed for the purpose of effectively storing renewable energy. The limitations of each component and what has been/is being done to address said limitations. This review briefly discusses the current needs and state of renewable energy production, the fundamental principles behind the VRFB, how it works and the technology restraints. The working principles of each component are highlighted and what design aspects/cues are to be considered when building a VRFB. To address these limitations, the limiting determinants of some components are being investigated alongside previous/current research.Finally, critical research areas are highlighted along with future development recommendations.

CHAPTER 1

INTRODUCTION

1.1 Introduction

A redox flow type battery has active materials in electrolytic solution form and charging and discharging are carried out by the redox reaction, by circulating the active materials on positive and negative electrodes in a circulating type electrolytic cell and an intermittent circulating type solution having a membrane, and employing a solution permeable porous electrode.[27] Today, for various reasons, such as rising energy prices or environmental laws, people try to use renewable energy when possible. Bangladesh is a developing country with a huge energy demand. Electricity is a must for the recent development of Bangladesh. It is predicted that some parts of Bangladesh will not get a taste of electricity from the national grid within the next 30 years. Control of the control has grown significantly in Bangladesh as a result of rapid industrialization and more than two decades of development.

The vanadium-redox-flow-system has received significant attention in recent years [1–4] as a promising candidate for photovoltaic energy storage due to its numerous advantages, the most important of which is the presence of only vanadium species at both electrodes.Hence, battery failure is prevented in the case of cross flow of the electrolyte, e.g. due to separator damage, causing only an increase in self-discharge and enabling the use of microporous separators. Moreover, independence of performance (power output) and capacity of the battery are achieved by adapting the stack size (number of cells) and the electrolyte volume (amount of active material) to the requirements to be met.One of the most popular types is the all –vanadium redox battery (VRB), which has been developed by many institutes and companies.

The rapid commercialization of VRB poses a number of challenges for the technology's developers, primarily in terms of lowering production costs and optimizing the system.Until now, most VRB research has concentrated on key materials such as electrodes, current collectors, and ion exchange membranes.There are only a few documents related to the modeling of the all-vanadium cell or the cell system.Enomoto [23] proposed an equivalent circuit model of VRB based on both the electrochemical reaction and the electric circuit response to study the relationship between the equivalent series resistance and the state of charge. based on conservation laws of charge, mass and momentum to study the effects of variation in concentration, electrolyte flow rate and electrode porosity on cell performance.

The present study completes some aspects that are not discussed, and puts forward different views on the effects of electrode porosity.

1.2 Problem Statement

As we see, unlike Vanadium redox battery has an essentially infinite lifetime. The source of this advantage is the inherent nature of battery chemistry. The lifetime of a vanadium redox battery is bulk components, such as plastic tanks that can last more than twenty years. In the case of a different battery, the capacity can drop by 50% within only 1500 cycles, requiring full replacement. For grid –based battery energy storage, vanadium redox batteries are far more useful than others. The vanadium content of a vanadium redox battery is easily recycled at the end of its life and used in new flow battery systems. Vanadium also has the advantage of being recovered from industrial waste products such as fly ash or mine tailings. The process of vanadium recovery from these sources actually cleans up the environment. The vanadium redox flow battery (VRFB) is one of the most mature and commercially available electrochemical technologies for large-scale energy storage applications. The VRFB has several distinct advantages, including power and energy capacity separation, a long lifetime (> 20 years), stable performance under deep discharge cycling, few safety issues, and easy recyclability.

1.3 Objectives:

The objectives of this project and thesis are

- To investigate utilizing different electrolytes to achieve higher power and energy densities.
- To study extending the operating temperature range.
- To improve the stack and overall structure to increase power production and decrease costs.
- To design membranes with lower resistance and lower cost.
- Comparison between batteries and cost analysis of battery technologies.

1.4 Methodology

This thesis makes use of a qualitative research strategy, where the research approach implemented is that of interpretivism. It has an approach which is implemented by the researcher in order to synthesize facts which are derived mainly from secondary sources, and which are qualitative in nature. The following formulas are also included in this paper: concentration over-potential due to the diffusion layer around the fibers of the porous graphite electrodes, shunt currents, and vanadium ion diffusion across the membrane.In addition, the Nernst equation is used to obtain the required output.Inverter losses are considered using a detailed model of the topology. The flow rate control strategy has a negligible impact on shunt currents, electrical losses and inverter losses. However, the interaction of losses due to diffusion, concentration over-potential and pumps is carefully analyzed. Data was gathered from a variety of online sources.To examine and refer to previous research on vanadium redox flow batteries and energy storage systems.

1.5 Thesis Outline

This project/thesis is organized as follows:

1.Introduction

2.Energy Storage

3.Flow Battery Technology

4.Discussion and Result

5.Conclusion

6.Recommendation

CHAPTER 2

ENERGY STORAGE

2.1 Brief Review of Energy Storage Systems

The two fields more involved within the development of ESS are the facility system and therefore the transport sector. Now a days the demand for especially lithium-ion battery systems increases rapidly because of the electro-mobility promotion (i.e., plugin hybrid and full electric vehicles)[5]. The link between this sector and therefore the electric grid integration of the ESS is sort of straight forward. Electro mobility requires more efficient batteries and large-scale production is predicted to offer impetus to the usage of ESS in distribution systems because of cost reduction. Furthermore, of the V2G option that permits using the vehicle batteries as grid storage during times when the vehicles are plugged-in for charging; secondly because the utility companies necessarily start getting involved within the upgrading of their infrastructures to integrate the EV charging stations[5]. However, the improvement of batteries dedicated to grid applications goes rapidly on and a number of other technologies are often considered quite mature for these purposes. Energy storage systems (ESSs) are demonstrated to be useful assets to utilities and to others that generate, supply, or utilize electricity. Utilities, as an example, have historically relied upon spinning reserve, occasionally provided by a neighboring utility, as a quickly available source of electrical power to deal with a number of power-line anomalies. For example, a battery energy storage system (BESS), functioning as a rapid reserve resource, is an excellent substitute for spinning reserve in that its stored energy can be available to power utility loads in less time than power from a spinning reserve resource[6]. The Energy Storage section gives a key description of the different technologies available. Different types of battery technologies along with their respective advantages and disadvantages are discussed. Battery Energy Storage (BES) is currently being used in several different applications, as stand-alone devices powering individual units such as telecom towers and also as synchronized units integrated into a smart grid electricity network[7]. This section explores different types of batteries. Battery energy storage systems also are utilized as uninterruptible power supply to support relatively isolated utility lines also as dedicated loads. Other applications include storing energy from renewable, intermittent resources like photovoltaics wind-driven generators, and little hydro facilities. In these points of view, the BESS gives an advantageous disconnect between resource availability & exploitation of the renewable energy.

2.2 Technological Overview

Modern technology advancement is beneficial for distribution network applications, and all that have reached a higher specialized status level are electro-chemical batteries.Such innovations may have internal or external storage. Instances of the last frameworks, dismissing the hydrogen or methane storage that is helpful for long haul administration, are the redox-flow batteries, which have the preferred position that energy and force are freely versatile (energy limit relies upon the tank while the cell stack decides the flow) [8]. Vanadium redox-flow batteries are inexpensive and come in a variety of secluded and versatile sizes.However, the still significant expenses of the electrolyte arrangement and the upkeep deterrent their enormous scope dissemination [9]. The ESS advancements, and thus their cost, are unquestionably dependent on the specific administration that they are called to perform.ESS administrations can be: subordinate administrations (i.e., recurrence control, voltage guidelines, turning and stand holds, dark beginning assistance, and so on), top shaving, load leveling, islanding support, or other help, for the most part, identified with private employment of the ESS (e.g., private use for expanded self-utilization of DG generation, modern applications, uninterruptable force supply and so forth). Various orders can be applied to the ESS [10]. Yet, quite possibly the best thing is that one is identified with the term and recurrence of intensity supply from the ESS:

1. Short-term ESS (seconds to minutes),

2. Medium-term ESS (daily storage), and

3. Long-term ESS (weekly to monthly).

The short-term ESS (<0.25 hours) can be used for primary and secondary frequency control, spinning reserve, black start, peak shaving, islanding, electro-mobility, and uninterruptable power supply (UPS). The medium-term ESS (1–10 hours) is able to provide the services of tertiary frequency control, standing reserve, load leveling, islanding, electro-mobility, residential self-consumption increase, and UPS. Finally, the long-term ESS (from 50 hours and typically less than 3 weeks) can be exploited for long-term services, during periods when there is no or scarce generation of electricity from wind and solar ("dark-periods"). Super-capacitors, superconductive magnetic coils, or flywheels may offer short-term services. Pumped hydropower, compressed air ESS, thermoelectric storage, and electrochemical ESS, such as lithium-ion, lead-acid, high temperature and flow batteries, are able to perform medium-term services. Long-term services can be offered by hydrogen or natural gas storage systems [7]. The main applications that can be suitably exploited by smart distribution networks fall into medium, or at least short-term services. Pure electrical supercapacitors and superconductive magnetic coils (which have some advantages such as high efficiency, high power capability, and long life) are still hampered by a lack of validation and experimentation for grid purposes, as well as their extremely high costs due to their high degree of innovation.Mechanical systems can be classified as well-established technologies (e.g., pumped hydropower), those with a short time-to-market (e.g., compressed air energy storage), or those developed for purposes other than network operation (e.g., flywheels, which are widely used in UPS systems).

Mechanical energy Storage

Nowadays, all bulk power storage concepts exceeding 50MW come from the conversion of mechanical energy to electrical energy [11]. The most common ones are pumped hydro storage (PHS) and compressed air energy storage (CAES). PHS has the largest storage capacity compared to other energy storage systems. During off-peak electricity demand hours, a typical PHS plant will pump the water from the lower to the higher level of the reservoir. Later, where electricity is in peak demand, it lets the water flow down through the turbines with a generator to produce electricity. underlined that, with high efficiency and very high reliability, PHS has served for more than a century and further plants will be built in the future, even in places with less suitable geological conditions. CAES compresses the air to a high pressure before storing it in a structure underground or in tanks above the ground [1]. On demand, compressed air is mixed with natural gas, burned, and expanded through the turbine, which is linked to the generator.Then, the electricity will be stored. Conventional CAES plants reach an efficiency of less than 55%. For better performance, the compressed air needs to be increased. The increment of compressed air might bring fewer safety issues.

Electrical Energy Storage

Electrical storage systems are broadly classified into two types: double-layer capacitor (DLC) and superconducting magnetic energy storage (SMES).A layer capacitor is also known as a supercapacitor or an Ultracapacitor, which contains two conductor electrodes and electrolytes as well as a porous membrane separator [12]. Supercapacitors have a high power capability and a higher energy storage capability when compared with conventional capacitors. However, as highlighted, supercapacitors are more convenient when used for short-term energy storage applications. Meanwhile, the energy in the magnetic field created by the flow of direct current in SMES is stored in a superconducting coil [10]. The features of SMES include a relatively quick response time, high efficiency and high-power production where it can be supplied for a short duration. Unfortunately, it has a weakness. SMES is only appropriate for short-term energy storage.

Electrochemical Energy Storage

Electrochemical energy storage comprises the usage of various appliances which transform chemical energy into electricity. Rechargeable or storage batteries are the oldest form of electricity storage [7]. It is stored in the form of chemical energy and the process of converting the energy is based on redox reactions, as explained above. There are several types of electrochemical energy, including Nickel Cadmium, Lithium Ion, Lead Acid, Fuel Cell, and Redox Flow Battery (RFB).

2.3 Battery Energy Storage

The most well-known and widely used, but sophisticated energy storage technology with a wide variety of applications is the battery. They're used to powering devices, and they're adaptable, durable, reliable, and cheap. Battery Energy Storage (BES) is a stationary energy storage technology that comes in a variety of forms depending on the application.

Lead Acid Battery

Lead-Acid batteries are used in Uninterrupted Power Supply systems and as batteries in vehicles. They can be connected in parallel and provide power to homes as a standby during power outages. Lead Acid batteries contain dilute Sulfuric acid (H_2SO_4) as the electrolyte [2]. Both the negative and positive electrodes are made from lead sulfate ($PbSO_4$). During the charging state, the positive electrode takes up the form of lead oxide (PbO_2) and the negative electrode takes up the form of lead in its elemental form (Pb). The electrolyte used is 33.5% w/w sulfuric acid. Lead acid batteries are typically used in automobiles.

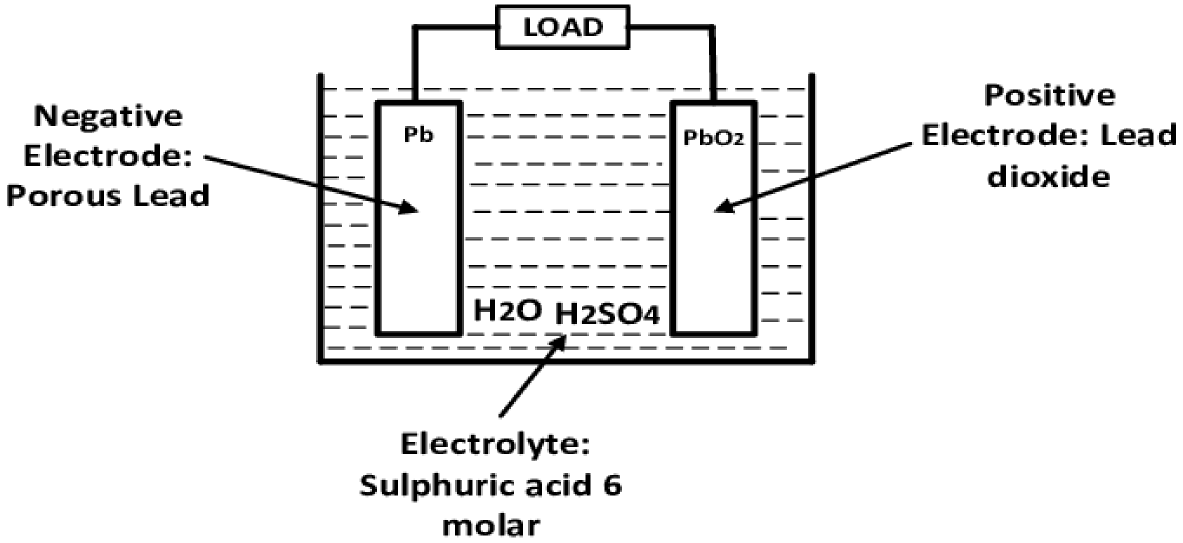


Figure 2.1: Contraction of a Lead Acid Battery [13].

The complete reaction taking place in this battery is described as:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O\ (l)$

The negative plate reaction is given by:

$$Pb(s) + HSO^{-}(aq) \rightarrow PbSO\ (s) + H^{+}(aq) + 2e^{-}$$

The positive plate reaction is given by:

$$PbO_2(s) + HSO^{-}(aq) + 3H^{+}(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O(l)$$

The valve-regulated lead acid battery is largely ‘maintenance free’ and comes sealed. It can be fitted into small enclosures, and also has a wide operating temperature. It has the ability to absorb vibrations. At the time of the life cycle of any battery, interrupted or incomplete charging can cause sulfuric acid to travel through the water-acid mixture and collect at the base of the unit.[14] Due to the lack of acid on the top of the battery, i.e. closer to the electrode plates, the performance of the battery decreases over time. This also leads to corrosion and a reduction in battery capacity. Complete charging solves this problem, which mixes the electrolyte completely and leaves an even distribution of the chemicals in the battery. Lead acid batteries are most commonly used in automobiles to start the engine. They are also used as backup power sources in the event of a power outage.Larger power requirements include home- offices, where the battery is used in its wet-cell formula [9]. It has a large power discharge capacity for long hours during power shut-down situations. It is used as an Uninterrupted Power Supply (UPS) source. It is also flexible across small electric vehicles such as golf carts, wheelchairs and e-scooters [5]. Military applications include the use of these batteries in nuclear submarines for power back up.

Advantages & Disadvantages of Lead acid Batteries

Table2.1: Advantages & Disadvantages of Lead acid Batteries

Advantages	Disadvantages
i) Low cost and simple manufacture low cost per watt-hour.	i) Low specific energy; poor weight-to-energy ratio
ii) High specific power ,capable of high discharge currents. Good performance at low and high temperatures.	ii) Slow charging ;Fully saturated charge takes 14-16 hours Need for storage in charged condition to prevent sulfation Limited cycle life;repeated deep cycling reduces battery life Watering requirement for flooded type
iii) high cycle life in a partial SOC cycling regime at various rates	iii) Electrolyte can evaporate
iv) good charge acceptance leading to faster recharge	iv)Flammable Gases while charging
v) Low installation cost	v) Low Energy density

Lithium-Ion Battery

A Lithium Ion (Li-Ion) battery is extremely popular due to its ability to not only be recharged, but also due to its extreme portability in hand-held devices. They can be designed in various shapes, such as cylindrical, flat-bodied, and in long sandwich forms to be used in electric vehicles [5]. These batteries have high-energy storage capabilities in a small space and discharge slowly when not in use. Lithium-Ion batteries are much lighter than lead-acid batteries, are able to provide the same amount of voltage and can be replaced in electric vehicles without much modification. The negative electrode is made from carbon. And the positive electrode is made of metal oxide [5]. Popular materials for the negative electrode are graphite, hard carbon and silicon. These are paired with Lithium Manganese Oxide or Lithium Iron Phosphate. The electrolyte used is an organic solvent with lithium salt.

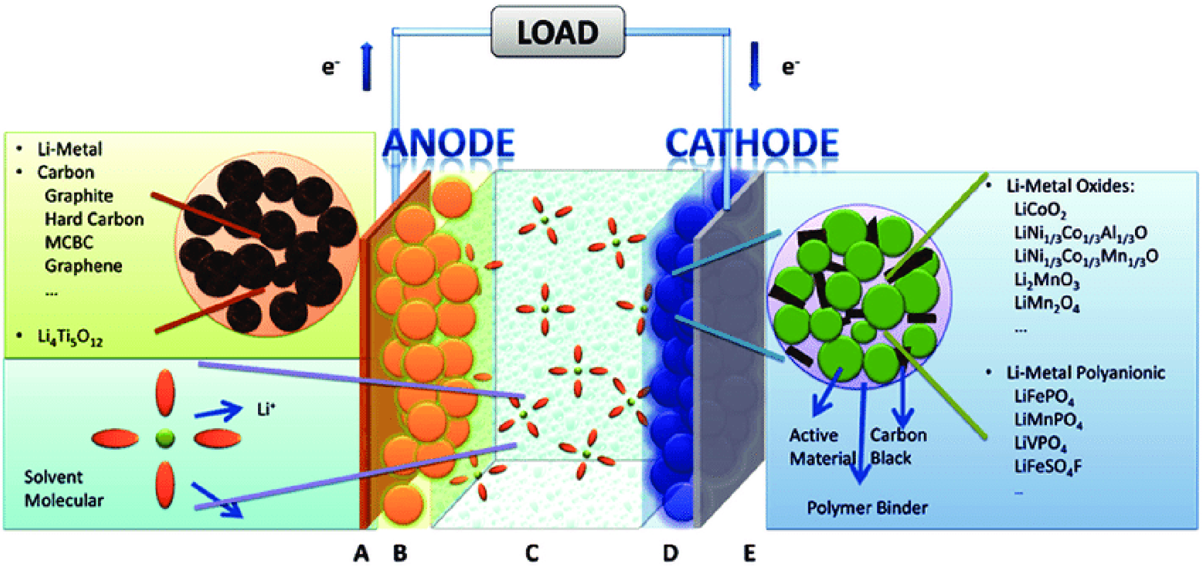


Figure 2.2: The lithium-ion battery's hierarchical structure [2].

The negative electrode half reaction is written in its general form as:

$xLi+ + xe- + xC6 \rightarrow x\ LiC6$

The positive electrode half reaction is written in its general form as:

$LiCoO2 \rightarrow Li\ (1-x)\ CoO2 + xLi+ + xe\ -$

Current flows from the negative electrode to the positive electrode during the discharge cycle. Charging causes the ions to move in the reverse direction by applying a high voltage [11]. The ions are thus stored in the negative electrode at full charge. Li-Ion batteries have a tendency to become electroplated at the negative electrode if the battery is charged in conditions below 0 degrees centigrade irreversibly. Other applications for Li-Ion batteries include common household indoor and outdoor power tools. These batteries also have the ability to be connected in parallel and be used in high-powered electric vehicles. Special circuitry must be designed for these.

Advantages & Disadvantages of Lithium-Ion Batteries

Table 2.2: Advantages & Disadvantages of Lithium-Ion Batteries[30]

Advantages	Disadvantages
i) High capacity, low internal resistance, good coulombic efficiency	i) Impossibility of rapid charge at freezing temperatures (<32°F)
ii) High specific energy and high load capabilities with power cells	ii) Need for protection circuit to prevent thermal runaway if stressed
iii) Simple charge algorithm and reasonably short charge times	iii) Need for transportation regulations when shipping in larger quantities
iv) Long cycle and extended shelf-life; maintenance-free	iv) Need for protection circuit to prevent thermal runaway if stressed
v) High energy density compared to other technologies.	v) Sensitivity to high Temperature

Sodium Sulfur Battery

Sodium sulfur batteries are very high-capacity batteries. They work extremely well in large-scale applications. They are mainly used on grids due to their very high operating temperature of 300 degrees centigrade. The electrodes are in a liquid state at this temperature, but the electrolyte remains in a solid state. These batteries last approximately 2500 cycles. That can be translated into a time period of 15 years when charged and discharged completely. If charged and discharged to only 65% of capacity, they can last for nearly 6000 cycles [11]. Some of the characteristics of this battery include a rapid response time. If necessary, it is possible to discharge its entire charge in 1 ms.The energy density of this battery can be up to five times that of a lead acid battery. It requires minimal maintenance and can work remotely. Additionally, it can function in any environment and causes zero emissions or vibrations. Another feature of this battery is that 98% of the components can be recycled [15].

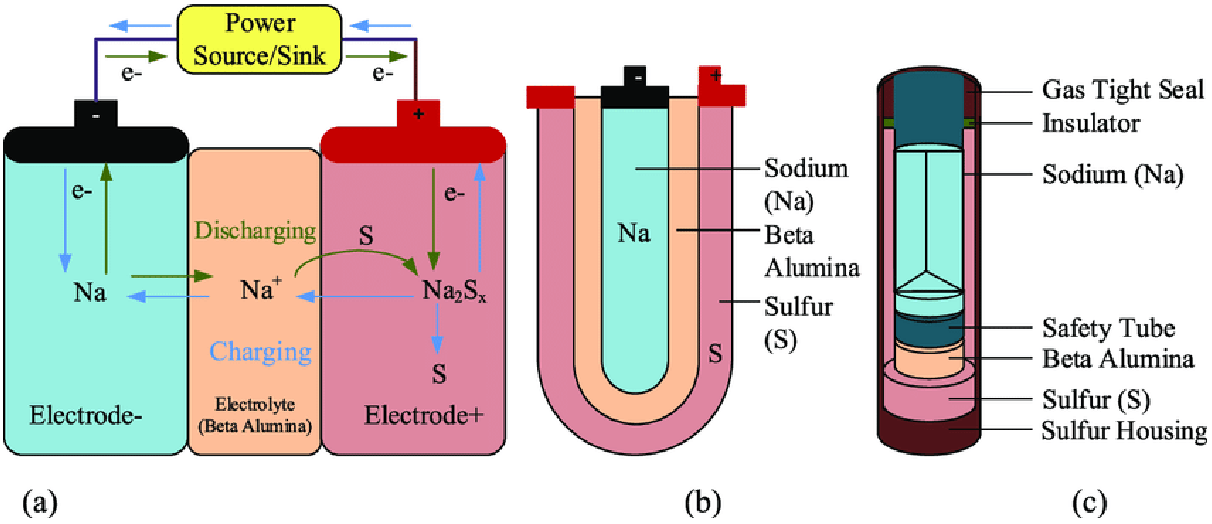


Figure 2.3: Sodium -Sulfur Battery Chemistry: During charging & discharging [12]

During the charging cycle, positive sodium ions pass through, combining with sodium to form sodium polysulfide.During the discharge cycle, the electrode allows positive sodium ions to flow through and, at the same time, electrons flow through the circuit of the device. The total chemical reaction is given by:

$2Na+4S = Na2S4$ Small scale distributed power generation systems like photovoltaic systems usually require only a few MW of energy storage. For these applications, NaS batteries are well suited. The batteries are able to effectively serve as a robust solution for energy management by having good load balancing and peak saving abilities.

Advantages & Disadvantages of Sodium Sulfur Batteries

Table2.3: Advantages & Disadvantages of Sodium- Sulfur Batteries [31]

Advantages	. Disadvantages
i) High cycle life; liquid electrodes.	**i)** High temperature must be managed.
ii) Low-cost potential: Inexpensive raw materials and sealed, no-maintenance configuration.	**ii)** Need to be operated above 300°C.
iii) Flexible operation: Cells functional over a wide range of conditions (rate, depth of discharge, temperature).	**iii)** Stringent operation and maintenance requirements.
iv) High energy efficiency: 100% coulombic-efficient, reasonable resistance	**iv)** Limited self-life-2 to 5 years.
v) Good energy and power density: Low-density active materials, high cell voltage.	**v)** Extra cost of constructing the enclosing structure to prevent leakage.
vi) Insensitivity to ambient conditions: Sealed, high temperature systems.	**vi)** Requires bulky insulation.
vii) State-of-charge identification: Voltage rise and top-of-charge and end-of-discharge.	**vii)** Useful applications in solar and wind farm energy storage. Poses accidental hazards brought on by violent reaction b/w sodium and sulfur.

Nickel Metal Hydride Battery

Nickel Metal Hydride batteries or Ni/MH batteries have several advantages over lead acid and older Nickel Cadmium (Ni/Cd) batteries. The severe toxicity to the environment caused by cadmium disposal has led to faster development of the Ni/MH device [7]. Thus, Ni/MH batteries are directly replaceable in electronic devices that support Ni/Cd batteries. Ni/MH batteries are based on the concept of an alkaline storage device. It has a 1.2V rating. These batteries are connected in series and offer more energy per unit weight and volume than lead acid batteries or older Ni/Cd batteries. These batteries have excellent energy density and high-power density. The negative electrodes consisting of the Metal Hydrides compound are the main driver behind some of the advantages over the lead-acid and Ni/Cd systems. The battery requires some enhancements due to a moderate to high rate of self-discharge [6].Additionally, a longer cycle life is needed for it to be adopted in applications such as electric vehicles and in other bipolar designs.

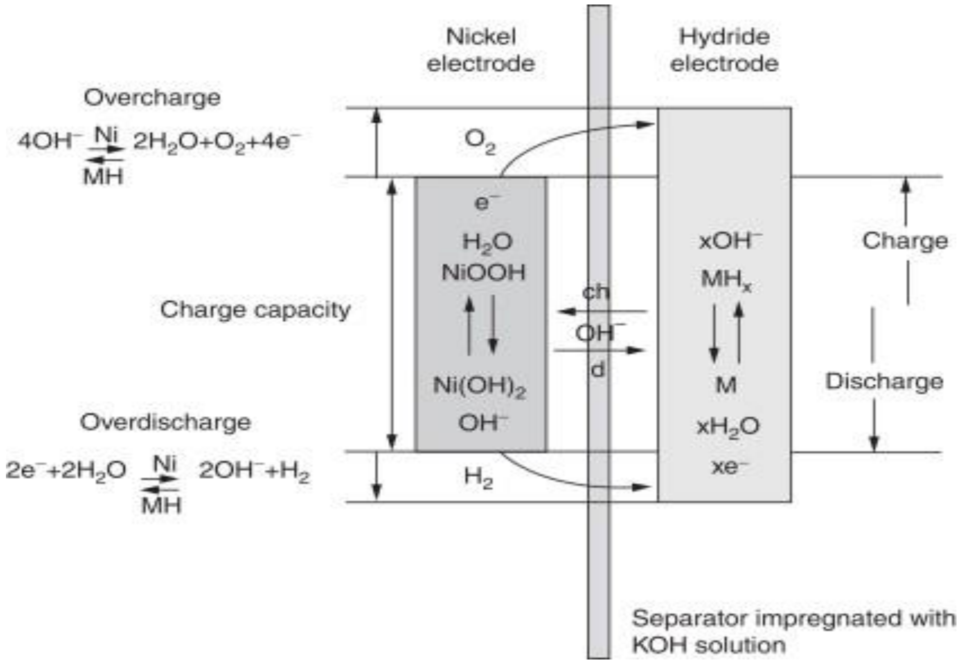


Figure 2.4: For the Charging & Discharging Process of the Nickel metal hydride battery[5]

The hydride forming alloy, which is the active anode material, determines the durability, capacity and kinetics. Most of the research is being done on proposing the design and modeling of metal hydride materials for electrodes.

Advantages & Disadvantages of Nickel Metal Hydride Batteries

Table 2.4: Advantages & Disadvantages of Nickel- Metal Hydride Batteries[32]

Advantages	Disadvantages
i) Greater service advantage over other primary battery types at extreme low-temperature operation (–20°C)	**i)** High self-discharge: The Ni–MH has about 50% higher self-discharge compared with the Ni–Cd. New chemical additives improve the self-discharge, but at the expense of lower energy density.
ii) Energy density, which can be translated into either long run times or reduction in the space needed for the battery	**ii)** Limited services life: If repeatedly deep-cycled, especially at high load currents, performance starts to deteriorate after 200–300 cycles. Shallow, rather than deep, discharge cycles are preferred.
iii) Energy density, which can be translated into either long run times or reduction in the space needed for the battery	**iii)** Limited services life: If repeatedly deep-cycled, especially at high load currents, performance starts to deteriorate after 200–300 cycles. Shallow, rather than deep, discharge cycles are preferred.
iv) Simplified incorporation into products currently using nickel–cadmium batteries because of the many design similarities between the two chemistries	**iv)** Need for a more complex charge algorithm: The Ni-MH generates more heat during charge and requires a longer charge time than the Ni–Cd. The trickle charge is critical and must be controlled carefully.

Redox Flow Battery

Redox flow batteries offer a very different type of system than the other battery systems described in this report. The flow battery consists of two tanks of electrolyte solution, a cathode and two other anodes. The electrolyte is passed through a membrane to store and produce energy. The technology is still in the early stages of commercialization compared to more mature battery systems such as Li-ions and lead-acids. However, redox flow batteries offer advantages over competitive systems such as lead long life cycle, low temperature range for operation and easy scalability. Vancomycin Redox Flow Batteries are primarily commercialized by several companies: United States-based Uni University Technology (UET) and Vionex Energy, German-based Guildmister and Sumitomo Electronic from Japan. To compete with the Li-ion, these manufacturers have begun to move towards off-seashell systems as opposed to custom ones. UET also offers up to 25 years of warranty with rates increasing by 21 years (Aquino et al. 2017a). [33]

A redox flow battery works on the principle of oxidation and reduction between two active chemicals. Two external tanks hold the electrolytes and these are passed through the cell, which also holds the electrodes [16]. In this cell, positive and negative parts have their own respective electrolytes. Separate tanks are used to prevent self-discharge.The active chemical contains metal ions that are restrictively soluble in a solution. The ability to respond to any changes in frequent short-cycle grid fluctuations is nearly instantaneous, with a response time of only a few milliseconds. This is particularly useful in applications regarding renewable energy generation where energy generation is not constant. The electrolytes need not be changed at all. It is only recycled within the battery. The only change happening within the cell system is the change in ion balance. External power is connected to circulate the electrolyte through the cells. This is done by pumps [2]. Flow batteries are fairly large in size because they do not have a high energy density. The charge and discharge cycle is long during its life.

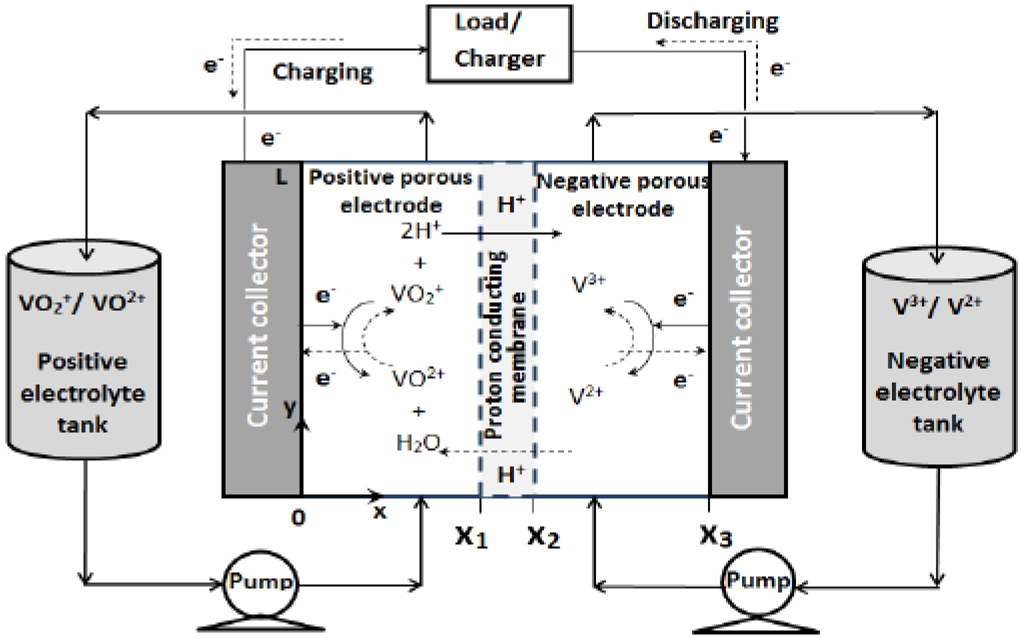


Figure 2.5: A-Schematic diagram of an all vanadium redox flow battery [10]

The Vanadium-Vanadium system or V-V system uses the same metal ions in both negative and positive electrodes. If the material is mixed through the membrane, the battery capacity remains the same.The below mentioned reactions show the concept of functioning in a V-V system:

2.4 Positive Electrode

VO2+ (tetravalent) + H20 ↔ VO2+ + 2H+ + e--

The direction from left to right represents the charging cycle. Tetravalent Vanadium ions get oxidized to Pentavalent Vanadium ions at this juncture. The hydrogen ions that are produced by the positive electrode are transferred to the negative electrode through the membrane. This assures that the electrolyte remains electrically neutral.

2.5 Negative Electrode

V3+ (Trivalent) + e- ↔ V2+ (bivalent)

Trivalent Vanadium ions get reduced to bivalent Vanadium ions.

During the discharge cycle, the energy stored in the system is given out by the reverse process. The electromotive force (EMF) achieved in this configuration is 1.26V. Different configurations are able to produce more EMF. These cells are connected in series as cell stacks to produce high voltages for real world applications.

Table 2.5: Types of Vanadium Redox Batteries [29]

Types	Description
Vanadium redox battery (VRB)	VRBs use two vanadium electrolytes (V2+/V3+ and V4+/V5+), which exchange hydrogen ions (H+) through a membrane.
Zinc–bromine (Zn–Br) battery	Solutions of zinc and a complex bromine compound are used as electrodes.
Polysulfide–bromine battery (PSB)	Sodium sulfide (Na_2S_2) and sodium tribromide ($NaBr_3$) are used as electrolytes. The sodium ions (Na+) pass through the membrane during the charging or discharging process.

Advantages and Disadvantages of Redox Flow Batteries

Table 2.6: Advantages and Disadvantages of Redox Flow Batteries [29]

Advantages	Disadvantages
i) Long service life: RFBs have a system endurance period of 20 years, with an unlimited number of charge and discharge cycles available without degradation. In addition, the electrolytes can be used semi-permanently.	**i)** Complexity: RFB systems require pumps, sensors, flow and power management, and secondary containment vessels.
ii) Relatively high energy efficiency	**ii)** Extra maintenance due to the special battery design
iii) Versatility: With the output and the capacity of a battery capable of being designed independently of each other, RFBs allow flexible design. In addition, the batteries allow a single system to address	**iii)** Low energy density: The energy densities of RFBs are usually low compared with those of other types of batteries.

both short and long periods of output variation, enabling cost effective power generation.	
iv) High safety: RFBs are capable of operating under normal temperatures and are composed of noncombustible or flame-retardant materials. The possibility of a fire with the batteries is extremely low.	**iv)** Electrolytes used have a low self-discharge rate
v) Electrolytes used have a low self-discharge rate	**v)** Manufacturing is expensive as it is a complex system to build

CHAPTER 3

FLOW BATTERY TECHNOLOGY

3.1 Technical Review of vanadium redox flow battery(VRFB)

The all-vanadium redox flow cell contains redox couples of Vanadium (II)/Vanadium (III) and Vanadium (V)/Vanadium (IV) in the negative and positive half cells respectively. Sulfuric acid is used as the supporting electrolyte. The dual electrolyte system achieves the separation of the redox couple using a cation exchange membrane (H+). The transfer of a proton takes place through this membrane [17]. Simultaneously, an electron is transferred through the external circuit of a connected load. During the discharge cycle, the reactions occur in the forward direction. During the charge cycle, the reactions occur in the reverse direction. The reactions occurring on the positive electrode are:

$$VO2+ (aq) + H+ (m) + e- + H3O+ (aq) \rightarrow VO2+ (aq) + 2\ H2O (l)\ -$$

The reactions occurring on the negative electrode are:

$$V2+ (aq) + H3O+ (aq) \rightarrow V+3 (aq) + H+ (m) + H2O (l) + e-$$

Positive Electrode

Electrode

Normally, carbon electrodes seem to be successful adoption in the V-V system. Mono fiber electrodes made from bundles of 3000 carbon cloth fibers of 7-10 micrometers have been found to be excellent. These are well defined with electrode reaction rates similar to graphite. More recent research has continued the trend of testing materials which are graphite based [8]. Carbon nanotubes, which have good electrical conductivity, have not shown the desired reversibility features. The chemical stability of the electrodes with the solution is also taken into consideration. Carbon felt electrodes are being used most commonly for commercial applications. Carbon felt can be used in pure form or in doped form. It is able to provide stability for the electrolytes and materials. Polypropylene is a carbon polymer design that has also been successfully tested for this purpose.

Solution

New techniques for preparing $VOSO_4$for use in a positive electrolyte solution are currently being researched. A few companies have recently set up a procedure to prepare this using vanadium bearing slag [18].The positive electrolyte solution contains vanadium with redox numbers of 5 and 4 and has VO + and VO+2 ions. Few defined key components like KCl, which is a precipitation inhibitor been used to minimize precipitation of solid vanadium in the positive electrolyte solution.

Negative Electrode

Electrode

The negative electrode is commonly manufactured with carbon felt or carbon-based electrodes. This material is regarded as a good fit for maintaining the required chemical stability and kinetics for optimum performance of the all-vanadium redox flow cell. A 23 mol/l solution of H2SO4 and 1 mol/l Vanadium species ensures that the reactions take place as expected. The positive electrode solution contains VO + and VO+2 electrolyte. The active ions associated with these, V2+ and V3+, are not present in the negative electrolyte solution.Negative electrodes have received less attention due to the greater importance of positive electrolytes in influencing various factors.

Alternate Negative Electrode

Recently, researchers have developed an alternate negative half-cell that contains the redox couple given by V2+/V3+. The electrolyte is designed using VCl2 or VCl3 dissolved with HCl (aq). To prevent or minimize any cross-contamination problems, it has been recommended that the VCl2/VCl3 couple be used rather than the Br-/Br3-couple.

The half reaction for this electrode can be represented by the equation below.

$$V3+ (aq) + e- \rightleftarrows V2+ (aq)$$

The reaction occurs from left to right during the charging phase. The reaction occurring from right to left is during the discharge phase. The VCl2/VCl3 redox couple also has good reversibility.

3.2 The Nernst Equation :

Current voltage prediction models have inaccuracies of 131 mV, to 140 mV or approximately 10% of the total voltage. This difference is typically added to the data for account for discrepancies that might result from using experimental data to the calculated open circuit voltage (OCV). Furthermore, these errors are caused by the model taking into account only a few parameters [4]. The Nernst equation addresses this issue by including the electrochemical mechanisms and accurately describes the potential difference between the electrolyte and electrode at no net reaction inside the cell.

The Nernst Equation is described as follows:

$$E_{full} = E^{0}\mathrm{o} - \frac{RT}{nF} \ln \left[\frac{C_{ox}\delta_{ox}}{C_{red}\cdot\delta_{red}} \right]$$

where E_{full} is the potential difference, E°0 is the standard reduction potential, R is the universal gas constant, T is the absolute temperature, n is the number of equivalents transferred per mole of reduced or oxidized species and F is Faraday’s constant [15].The term c describes the ionic concentration and delta represents the activity coefficient of the species. Additionally, red and ox describes reduced and oxidized species, respectively. The activity coefficient (δ) is typically 1 for redox flow batteries due to negligible interactions among ions.

This is due to the usage of liquid electrolytes and good circulation. The two half reactions that are used to calculate the cell potential are:

Positive electrode: (1/2) Br2 (aq) + e- ⇄ Br- (aq)

Negative electrode: V3+ (aq) + e- ⇄ V2+ (aq)

Membranes

Ion Exchange membranes are defined as the most critical part of the redox flow battery. It defines its economic value to a large extent and even the battery's performance. The membrane prevents the oxidation and reduction reactants from mixing and undergoing a direct chemical reaction. It is a separator that provides a path for ionic conduction between the two electrolytes [14]. Membranes are engineered to be highly selective in their ability to conduct charge-carrying ions.The Hydrogen Ion is the main charge carrying cell in the Vanadium Bromide cell. Additionally, the flow of vanadium and polybromide ions is restricted. Nafion 112 and Nafion 117 are commonly used cation exchange membranes [15]. The thickness of a membrane can range from 0.03 to 0.62 mm.

3.3 Complete Cell System Characteristics of VRFB

The chemical reaction of the Vanadium Bromide Redox Flow Battery is mentioned in the equation below. The reaction occurring from left to right is during the charging cycle, whereas the reaction occurring from right to left is during the discharge cycle.

$$\mathrm{VO2+\ (aq) + V2+\ (aq) + 2\ H3O+\ (aq) \leftrightarrow VO2+\ (aq) + V+3\ (aq) + 3\ H2O\ (l)}$$

The power output or the performance and the capacity of the redox flow battery is determined by the stack size of the number of cells and the volume of the active material (electrolyte). Carbon and plastics have low costs and are usable components in designing the cell. Vanadium concentrations of 1.5 to 5.4 M are used along with 3.6 to 4.3 M of H_2SO_4.

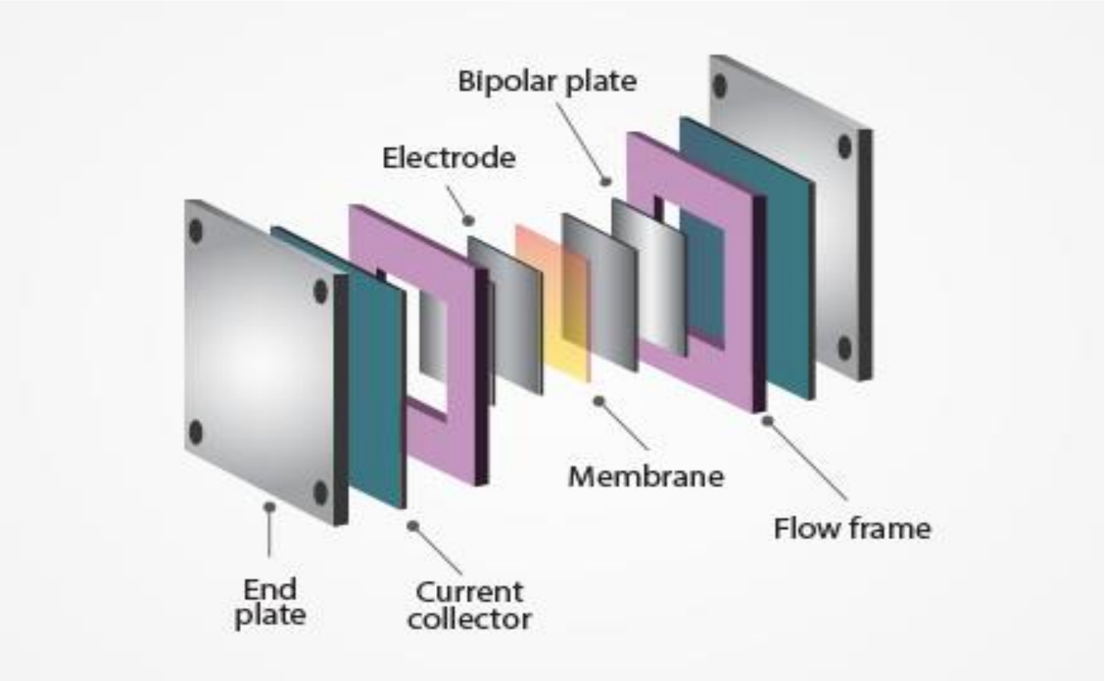


Figure 3.1 : Cell stack design of VRFB[19]

This is determined by using different electrode materials, like carbon or platinum. The values for VO2+/VO+ 2and V2+ / V3+ are reversible. They are designed with ratings from 1kW to 10 MW. They are able to discharge power for up to 16 hours and are able to carry out load leveling and can balance out other factors such as intermittent renewable energy production. The life span of the battery lasts for approximately 10,000 cycles and can be operated at a discharge efficiency of approximately 70%. Some of the biggest challenges to overcome in the performance of vanadium batteries are thermal stability related to the membrane, precipitation of vanadium and viscosity [20]. This limits the working temperature to between -5 and 40 degrees centigrade. All Vanadium batteries can be used to support emergency equipment in hospitals, industrial trucks, railroad signaling, telecom towers, renewable energy load leveling and applications involving peak shaving. Batteries can last for up to 15 years and are available in configurations from 1 kW to 10 MW.

Membrane

When a membrane allows the transfer of a proton, it is best suited for these applications.It must, however, resist the crossover of vanadium and water. Furthermore, it must be highly resistant to the chemical degradation of VO2+ and V5+.Some early tests have revealed that, other than defluorinated membranes, most other membranes, like Sulaimon CMV, showed poor stability in vanadium solutions. A modification of the Dioramic Company manufactured microporous separator, Dioramic Membrane, was used in the Vanadium Redox Batteries due to their high stability. These membranes can not be used without modification because of high permeability, leading to low coulombic efficiency [3]. The Nafion solution is used to produce the Dioramic Composite membrane. In tests, the Dioramic/Nafion2 membrane with a back web thickness of 0.25 mm had a low water uptake of 31.2%/wet membrane. When the separator was used with vertical ribs, the lowest water uptake of 28.8%/wet membrane was noticed. Nafion contributes to low water uptake [15]. The Dioramic/Nafion composite membrane limits self-discharge and gives high current efficiency.

3.4 Technical Properties of vanadium redox flow battery

Conductivity

The conductivity of the membranes is measured using the method of impedance spectroscopy. The frequency range is from 1 to 106 Hz with an AC amplitude of 0.2V. Additionally, the resistance of the conductivity cell is measured with and without the membrane.

Diffusion of Vanadium Ions

A static diffusion test determines the rate of diffusion of vanadium ions across the membrane. In addition, the rate of decline in solubility is larger when the concentration of H2SO4 is in the range of 0–7M but smaller at 8 or 9M H2SO4 solution [19]. The influence of temperature is also more significant in the lower sulphuric acid concentration range (0–7M) and less in the highly concentrated sulphuric acid (8 or 9 M).

Water Content

To calculate the water content of a membrane, it is immersed in distilled water for 24 hours. It is then removed, patted dry and placed on filter paper. The weight is measured until the surface of the membrane is dry. It is then further dried at 60 degrees centigrade in a vacuum. The water content of the membrane is measured by taking the percent weight change before and after vacuum drying.

Dimensional Stability

Samples were immersed in a solution of distilled water, a solution containing 1 M V3+ and 1 M V4+ in 6.4 M HBr, 2 M HCl and in 6.4 M HBr, 2 M HCl for 15 days to determine the dimensional stability [15]. Physical changes in length, width and thickness were determined using a digital caliper.

Energy Density

A redox flow battery's energy density is proportional to the concentration of redox ions in solution, the cell voltage, and the number of electrons transferred during discharge per mole of active redox ions.

Temperature Influence

Voltage efficiency falls as temperature and current increase owing to reduced response rates and electrical losses. Current efficiency, on the other hand, rises with increased current but decreases with rising temperature because of greater diffusion rates of vanadium and poly bromide ions through the membranes at higher temperatures.

3.5 Recent Developments

Most membranes being tested are unsuitable for use in vanadium bromine flow batteries due to low chemical stability or very high resistance. One of the membranes, to be exact, the ABT3 seems to have shown pretty good adaptability towards use in a Vanadium Bromide flow cell [3]. The highly oxidizing nature of Br3-ions causes rapid deterioration of most polymeric membranes and, thus, only limited types of membranes can be used for a long life. Another problem that could occur with the vanadium bromine flow cell is the possible emission of bromine gas during cell charging. This mainly occurs due to multiple ionic equilibria of bromide ions in aqueous solutions. Various bromine complex agents have been added to address this issue.The complex agents bind with bromine, producing an orange layer, which settles down at the bottom and can be easily separated. Another important issue with energy storage technologies is the cost of raw materials. In 2008, there were large variations in the prices of vanadium pentoxide [15]. This led to fluctuations in vanadium redox flow battery pricing and thereby caused investor hesitation. The largest reserves of vanadium are in China and are usually sourced from fly-ash, spent catalysts and waste slags from steel production.

Table 3.1: Main exiting installed storage of VRFB(Collected from wikipedia)

Name	Place	Year	Energy	Power
Kashima-Kita Electric Power	Japan	1996	800KWh	200KW
Kansai Electric	Japan	2000	1.6MWh	200KW
Sumitumu Electric Group	Japan	2005	6 MWh	4MW
Pullman Washington	USA	2015	4 MWh	1MW
Hokkaido Electric Power	Japan	2016	60 MWh	15KW
SnoPUD MESA2 project	USA	2017	8 MWh	2 MW
San Miguel Substation	USA	2017	8 MWh	2 MW
Frauhofer Project	Germany	2019	20 MWh	2MW

Vanadium Pentoxide prices have stabilized in recent years. A mechanism to lower battery prices is to use vanadium pentoxide with high impurities. However, extensive research is required to identify the appropriate impurity level for specific materials that

can be used successfully in commercially produced batteries to minimize fouling and precipitation. A few companies have recently been able to produce flow batteries from recycled vanadium from mining slag, oil field sludge, fly ash and other environmental waste, thereby lowering its cost from $500 per kWh to under $300 per kWh for its flow batteries. Additionally, this has led to the doubling of the energy density.

3.6 Commercial Products

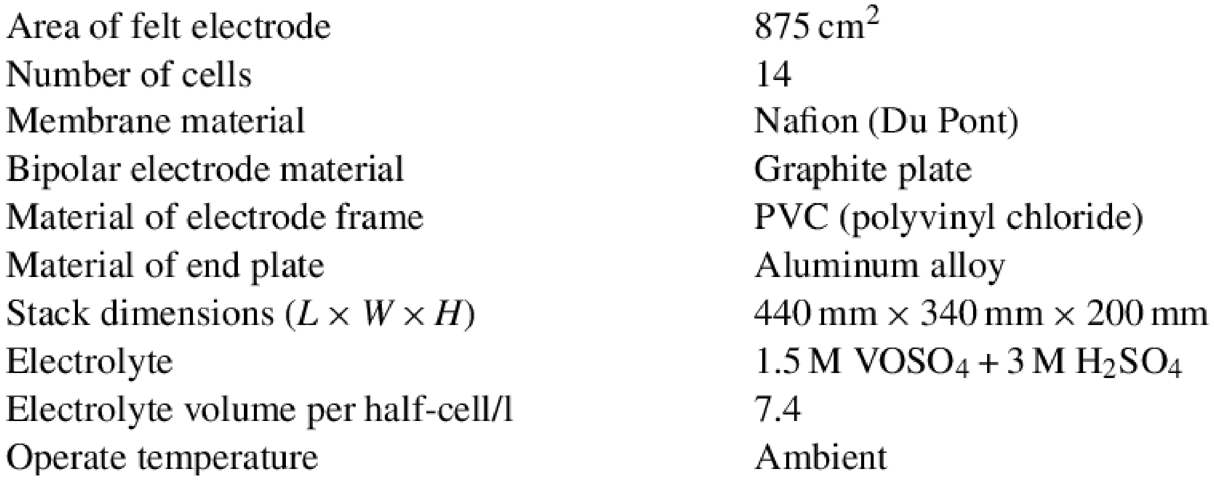
V-Fuel Pty Ltd was founded by the inventor of the Vanadium Redox Batteries, Professor Maria. V-Fuel was founded by the University of New South Wales in Australia and has an exclusive worldwide license for Vanadium Bromine Technology.Conventional batteries are normally available with power outputs ranging from 5 to 50 kW. A few more Japanese and Chinese companies have already installed large capacity storage based on the Vanadium redox flow battery mentioned in table 3.1.

3.7 Design Cell & Stack

It is desirable to find costs for building and installing a battery with a power capacity of 10 kW. The energy density of the battery is 40 kWh. The battery is capable of delivering power of 10 kW for a period of 4 hours. A VRB cell stack was designed and fabricated that produced an average power output of 1.1 kW at a current of 60 mA. The current density during discharge was 60 mA cm-2. The energy efficiency of this battery was 77.7% (Skyllas-Kazacos, Kasherman et al. 1991). When the charge is applied to the battery cell stack, the electrolyte species in the two middle compartments undergo a reaction called redox [19]. The changes in the concentration of the electrochemical species affect the thermodynamic conditions and they will result in equilibrium differences in potentials due to the Nernst equation. It is crucial to balance both vanadium and supporting electrolyte concentration in order to achieve better performance for the V-RFB. Excessive usage of vanadium concentration will result in a lower discharge cell voltage. To avoid mass transport limitation and excessive side reactions such as gaseous evolutions, a typical V-RFB is charge–discharge cycled within 10% – 90% SOC, with current densities lower than 12 mA. Using the previously discussed formula, the voltage efficiency and thermal efficiency are 66% and 95%, respectively, resulting in a 63% energy efficiency.Based on analysis, increasing the current density could be one of the factors that can improve the performance of V-RFB. Research on this effect is still on-going and the finding is expected to be discussed in a forthcoming research activity.

Table 3.2: Detailed Specifications for VRB Stack [22]

Specifications for 1 KW Class VRB Stack



Area of felt electrode	875 cm^2
Number of cells	14
Membrane material	Nafion (Du Pont)
Bipolar electrode material	Graphite plate
Material of electrode frame	PVC (polyvinyl chloride)
Material of end plate	Aluminum alloy
Stack dimensions ($L \times W \times H$)	440 mm × 340 mm × 200 mm
Electrolyte	1.5 M $VOSO_4$ + 3 M H_2SO_4
Electrolyte volume per half-cell/l	7.4
Operate temperature	Ambient

To produce the required power, it was determined that a total of 112 cells would be required. To optimize stacking, 8 stacks of 14 cells each are used. Cells are stacked on 2 top and bottom shelves, alongside 4 on each shelf. The connection between series and parallel can be done either way as it can affect the power only negligibly. All vanadium batteries operate mostly on carbon-felt electrodes or carbon-based electrodes. Sodium polysulfide/bromine redox flow batteries also use similar carbon felt electrodes or active carbon electrodes. However, direct comparison studies between the two show superior characteristics of carbon felt electrodes for use in redox flow batteries.

3.8 Design Development of Cell Components

In recent years, researcher has shown an increasing attention to the issue of energy security worldwide. With today’s modern economics development, demands on the stability in energy security has multiplies for future accessibility. First and foremost, energy security is primarily associated with the availability of natural resources for energy consumption [12]. New threats to energy security have arisen when the world competes for energy resources due to the increase in the industrialization process in every country. This leads to the possibility of the volatility in the crude oil price. Hence, this encourages researchers, industries and governments to embark on new research into energy storage technologies. Some approaches to new energy storage technologies have been introduced in order to improve and manage the amount of power required to create and supply energy for infrastructure as well as bring profits in terms of cost savings for both utilities and consumers. Energy storage can be classified into several types, which are mechanical, electrical energy storage and electrochemical energy storage. Among those, electrochemical energy storage system is still widely used storage and have the strongest advantages such as quick load demand response, high efficiency, eco-friendly and provide dependable solution for applications that is mobile or stationary. Lead Acid (LA), Lithium Ion (Li-ion), Nickel Cadmium (Ni-Cd), Fuel Cell (FC) and Redox Flow Battery (RFB) are some of the energy storage pointed before under the category of electrochemical. Among all, the vanadium redox flow battery (VRFB) is the most developed and the closest to commercialization compared to other types of RFB [10]. Historically, V-RFB was patented by Maria Skyllas-kazacos and by late 1980's, it is demonstrated successfully at University of New South Wales. V-RFB has a characteristic of a rechargeable flow battery which can produce energy by utilizing vanadium redox solution where it stores chemical potential energy by redox reaction. So far, V-RFB is one of the most promising technology and it is satisfactorily to be used for a wide range of renewable energy applications due to its safeness, long lasting and capable of being scaled. Moreover, Toshio also reported that V- RFB storage is especially favorable because it uses the same redox couple at both electrodes and the capacity of the battery does not lessen even when both side of couple are mixed via the membrane[20]. Recent research focuses more on the V-RFB characteristics but there is a limited research on the characterization of the cell stack of V-RFB. This paper will be the extended research to achieve the potential performance characterization of V- RFB. Different methods and approaches to solve this problem are presented and discussed. The performance characterization of V-RFB is analyzed based on the state of charge and discharge of the battery. From the core theory of vanadium redox flow battery, performance of the battery could be influenced of the V-RFB's efficiency & stability. The better the performance of the battery, the higher the efficiency of V-RFB can be achieved.

3.9 Summery of Flow Battery

This thesis addresses the issues underlying the feasible adoption of redox flow batteries as a model state for future cross-deployment. In fact, energy and power rating of flow batteries are independent because the rating of the energy dependent on the electrolyte tanks size, where as the rating of the power dependent on the cell stack size. Vanadium redox flow battery(VRFB) with the attractive features of independently tunable power and capacity, long cycle life ,high safety, high efficiency and environmental friendliness has become one of the most reliable technologies for vast quantity of energy storage applications. In contrast to the conventional energy storage technologies ,VFB can independently scale the power and energy components of the system by storing the redox-active species outside the battery container itself. In a VFB, the power is generated in a device resembling a fuel cell, which contains electrodes separated by an ion conductive membrane. Liquid electrolytes of redox-active species are pumped into the cell ,where they can be charged and discharged, before being returned to storage in an external tank.This unique trait has therefore made VFBs hold great promise for use in large scale energy storage applications. while VFBs offer a number of advantages, challenges with the relatively low energy density and low power density far have prevented their large-scale commercialization. Although low energy density is a significant problem for electric vehicle applications, it is not necessarily a parimary issue for stationary use with a VFB system, where the mass and volume constraints are much less important. However, larger-size cells must be employed to satisfy the power demand for the low power density VFBs,which correspondingly introduces a significant increase in the system cost. Therefore, any appreciable improvements in power density can yield significant cost-savings, making VFBs more competitive for grid-scale applications.

CHAPTER 4

COMPARISON AND COST ANALYSIS OF ENERGY STORAGE TECHNOLOGIES

4.1 Lead-Acid Batteries :

Lead-acid batteries are utilized in a wide range of applications, although they are rarely seen in compact, portable devices. There are two types of lead-acid batteries: flooded (vented lead-acid [VLA]) and valve-regulated lead-acid (VRLA) (VRLA). The technology generally has a power range of a few megawatts and a 10 megawatt-hour energy range.In comparison to the VLA competitors, the VRLA technology choice has fewer maintenance requirements. Overall, technology provides efficient performance at a reasonable cost, and its use is projected to grow in popularity in future years (EASE 2016).

4.1.1 Capital Cost:

A grid plate for the positive electrodes and either copper or lead grids for the negative electrodes are found in both types of lead-acid batteries. The lead-acid system, like the Li-ion battery, requires a PCS as one of the components for functioning.

Table 4.1. The capital cost of lead-acid battery installations. [33]

Capital Cost ($/kWh)	Notes	Source
$200 - $500	$150-$350/kW for PCS	Aquino et al. (2017b)
$183	100 kWh installed, 50 kWh usable	Power Tech Systems (2015)
$400 - $700		Kamath (2015)
$240	12 V, >150 Ah module	Quote received from a vendor
$160 - $240	$400-$600/kWh installed. Remove PCS, BOP, and C&C costs.	May et al. (2018)

4.1.2 Fixed and Variable Operations and Maintenance Costs

The absence of maintenance needs is an advantage of VRLA technology. Nonetheless, Aquino et al. (2017a) estimate the fixed O & M cost for an advanced lead-acid battery paired with an asymmetric supercapacitor to be in the range of $7–$15/kW-yr, with a variable cost of $0.0003/kWh. The constant and variable O & M for all battery technologies were maintained the same, as mentioned in the Li-ion O & M section.

4.1.3 Cycles, Lifespan, and Efficiency

As a result, while lead-acid systems have a lower initial capital cost than the other battery technologies studied in this paper, their complete life-cycle costs are equivalent to those of Li-ion battery systems.

Table 4.2. Lead-acid battery cycle life, longevity, and round-trip efficiency. [33]

cycles	Life Years	Round Trip Efficiency (RTE)	Source
2,000	15	79-84%	May et al.(2018)
500	5.2		Power Tech Systems (2015)
1200	20	95%	C&D Technologies, Inc. (2015)
600-1250		80%	DiOrio et al. (2015)

4.2 Lithium-Ion Batteries:

By 2015, more than 500 MW of stationary Li-ion batteries had been installed worldwide, with that figure rising to 1,629 MW by 2018. According to Bloomberg New Energy Finance's New Energy Outlook (BNEF 2018), over 1,200 GW of new Li-ion battery capacity is expected to be installed by 2050.Investments are likely to be made throughout Asia and Europe during the next few years, predominantly at a combined total cost of $544 billion (BNEF 2018).

4.2.1 Capital Cost:

A Li-ion battery's major components are modules made up of an assembly of cells that contain electrodes, electrolytes, and separators. Between 2010 and 2017, battery prices fell by 80%, hitting around $200/kWh, and it is expected that the price will fall to around $96/kWh during the following 8 years (EASE 2016).

Table 4.3. The capital cost of Li-Ion battery installations. [33]

Capital Cost ($/kWh)	Notes	Source
$300	The whole system balance was $570/kW or $143/kWh.	DiOrio et al. (2015)
$325 - $450	NMC system	DNV GL (2016)
$350 - $525	LFP system	DNV GL (2016)
$325 - $700	Includes DC-Side Modules and BMS	Lahiri (2017)
$340 - $450	NMC system	Aquino et al. (2017a)
$340 - $590	LFP system	Aquino et al. (2017a)
$209 - $343	Calculated by removing PCS from installation costs of $335–$530/kWh.	Damato(2017)

4.2.2 Fixed and Variable Operations and Maintenance Costs

Li-ion systems have a 10-year average useful life and require considerable battery system maintenance every 5 to 8 years to be functional (Balducci et al. 2017).

Table 4.4 Li-ion battery systems have fixed and variable O & M costs. [33]

Fixed O & M Cost ($/kW)	Variable O & M Cost ($/kWh)	Notes	Source
$6 - $12	$0.0003	Excludes major maintenance cost	Lahiri (2017)
$6 - $14	$0.0003	Excludes major maintenance cost	Aquino et al. (2017)
$10			Manuel (2014)
$20			DiOrio et al. (2015)

4.2.3 Cycles, Lifespan, and Efficiency

While Li-ion technology is the most advanced of the battery storage technologies, advancements will continue to be made in order to enhance the calendar life, energy density, and number of cycles that Li-ion technology systems can provide.

Table 4.5 Lithium-Ion battery cycle life, longevity, and round-trip efficiency. [33]

Cycle	Life Years	Round Trip Efficiency (RTE)	Source
3,500	10	77-85%	Aquino et al. (2017)
2,500	15		May et al. (2018)
400-1200		80-90%	Greenspoon (2017)
5,475		70% DoD	DiOrio et al. (2015)
2,000-1,0000	15-20	90-98%	EASE (2016)
	9	89%	Newbery(2016)

4.3 Sodium-Sulfur Batteries:

Sodium-sulfur batteries are very efficient electrochemical energy storage systems which have deployed 450 MW of the technology throughout the world to date. For one battery, an NGK battery generally comprises of twenty 50 kW and 100 kWh modules, allowing for systems of several megawatts.It's a well-proven technology, with the largest system yet being a 34 MW/245 MWh plant in Aomari, Japan. The system is normally kept at temperatures between 300°C and 350°C to keep the battery in a molten condition. Because the system requires additional heating, applications with long idle times are not recommended (IRENA, 2017).

4.3.1 Capital Cost:

A sodium-sulfur battery unit's fundamental components are a system made up of a large number of modules, a control system, and a PCS. To calculate the current capital cost, a number of sources were used. When the findings of the gathered literature were averaged, the anticipated cost for this system appeared to be around $750/kWh.

Table 4.6 The capital cost of sodium-sulfur battery installations. [33]

Capital Costs ($/kWh)	Notes	Source
$500		Crowe (2011)
$500 - $1,000	4MW/16 MWh	Aquino et al. (2017a)
$400 - $1,000		Kamath (2016)
$800 - $1,000		DNV GL (2016)

4.3.2 Fixed and Variable Operations and Maintenance Costs

A small number of sources estimated the operating and maintenance costs for a sodium-sulfur battery system.Aquino et al. (2017a) supplied a fixed O & M estimate of $7–15/kW-year, but no variable O & M estimate was offered. According to DNV GL (2016), the fixed cost range was narrowed to $7–$12/kW-year.

4.3.3 Cycles, Lifespan, and Efficiency

Table 4.7 Sodium-sulfur battery cycle life, longevity, and round-trip efficiency. [33]

Cycles	Life Years	Efficiency	Source
4,500	15	77-83%	Aquino et al. (2017a)
4,000	10	77%	May et al. (2018)
2,000-5,000	15	75-85%	EASE (2016)
	15	77%	DNV GL (2016)

4.4 Redox Flow Batteries :

The flow battery is made up of two electrolyte solution tanks, one for the cathode and one for the anode. After that, an electrolyte is transported across a membrane to store and create energy.In comparison to more established battery systems such as Li-ion and lead-acid, the technology is still in its early stages of commercialization. Nonetheless, redox flow batteries have benefits over competing systems, such as extended lifecycles, low operating temperature ranges, and simple scaling.

However, the ZnBrFB has troubles with high self-discharge rates, low energy efficiency and high cost (IRENA, 2017). VRFB use the redox couples V2+/V3+ and V5+/V4+ dissolved in sulphuric acid. The two redox couples are held separate by a membrane and upon operation one of the couples is oxidized while the other is reduced.

4.4.1Capital Cost :

Table 4.8 The capital cost of redox flow battery installations. [33]

Capital Costs ($/kWh)	Notes	Source
$676	The cost of a Volterion stack, including control devices, was 800 Euros per kW. Conversion to US dollars, with stack expenses accounting for 35% of DC system expenses.	Seipp (2018)
$490	5 kW, 20 kWh	RedT Energy Storage (2018)
$488	Mid-term stack expenses for Volterion — the mid-term period was not mentioned, but it is likely to be in 2021.	Seipp (2018)
$730 - $1,200	Includes PCS cost and $131/kWh performance	Aquino et al. (2017a)

	guarantee	
\$542 - \$952	After removing PCS and performance guarantee costs	Aquino et al. (2017b)
\$444	400 Euros	Uhrig et al. (2016)
\$357- \$552	Installed costs range from \$570 to \$910. PCS, grid integration, and equipment tax, fees, and G&A costs were all eliminated.	Damato(2017)

4.4.2 Fixed and Variable Operations and Maintenance Costs

According to Aquino et al. (2017a), the fixed O & M cost for a vanadium redox flow battery system is between \$7 and \$16 per kW-year, while the variable O & M cost is the same as other systems at \$0.0003/kWh. Because of a lack of understanding and dependability regarding O & M & M costs, the same O & M & M prices were applied to all battery technologies.The operating and maintenance costs are at least as high as previous battery technologies due to the "growing pains" associated with a new technology.

4.4.3 Cycles, Lifespan, and Efficiency

Vanadium redox flow batteries have a cycle life of more than 10,000 cycles and a life expectancy of more than 15 years (May et al. 2018; Greenspon 2017). Redox flow batteries, according to EASE (2016), should be able to provide > 12,000 cycles at an unknown depth of drain.For vanadium and zinc-bromide, Aquino et al. (2017a) report significantly more cautious estimates of 5,000 and 3,000 cycles, respectively. The stack may need to be replaced over time, even though the electrolyte is non-degradable when used appropriately.For this study, a cycle life of 10,000 cycles at 80% DoD, a calendar life of 15 years, and a system RTE of 67.5 percent were estimated for 2018, with the RTE predicted to rise to 70% by 2025.

Table 4.9 Redox Flow battery cycle life, longevity, and round-trip efficiency. [33]

Cycles	Life Years	Efficiency	Source
10,000	15	70%	May et al. (2018)
>12,000	10-20	70-75%	EASE (2016)
>10,000	20-30	75-80%	Greenspon (2017)
		70.5%	Uhrig et al. (2016)
5,000	14	65-78%	Aquino et al. (2017)

4.5 Pumped Storage Hydropower:

PSH units are sought after for their capacity to offer bulk electricity and associated services to the grid at a cheap cost per kilowatt hour. PSH is a well-known technology that has been around for over a century.[33] Moving water between low and high altitude is a way of storing energy, specifically: potential energy. This is done in pumped hydro storages (PHS) where electricity is being used to pump water from a low reservoir, often a river, to a high reservoir, often a dam or lake. This leads to huge upfront investment costs. The major advantages are although that you can store your water for as long as you need without losing much of your energy (around 0.01% energy loss/day), as well as a large amount of cycles and long life-time (IRENA, 2017) (Akhil, et al., 2013). PSH is extremely effective at ensuring that renewable energy supply is smoothed out during moments of high demand. To provide a constant supply of solar and wind energy, certain meteorological conditions must be present.

4.5.1Capital Cost:

Two water reservoirs, a canal to connect them, and a power station with a pump and turbine are the major components of a traditional PSH plant. Because PSH can provide grid-scale quantities of electricity, the average project costs more than other ESSs because of the building, commissioning, and necessary environmental evaluations.

Table 4.10 The capital cost of pumped storage hydropower battery installations. [33]

Capital Cost ($/kW)	Notes	Source
$1,300	Projected cost for Eagle Mountain PSH in Southern California	Manwaring (2018a)
$1,500 - $4,700		Aquino et al. (2017b)
$3,000	For 50 MW system	Manwaring (2018a)
$70 - $230/kWh		Kamath (2016)
$2,020	$762/kW in 1985 converted to 2018 dollars using 3% escalation rate	United States Bureau of Reclamation (2018)
$1,800 - $3,200	Adjustable-speed PSH	Shan & O’Connor (2018)
$1,500 - $5,100		EPRI 2017

4.5.2 Fixed & Variable Operations and Maintenance Costs

Aquino et al. (2017a) projected fixed O & M expenses to be between \$6.20 to \$43.30 per kW-year. During the 2014–2016 period, ORNL averaged the O & M costs for 11 PSH plants, finding that O & M costs varied from \$20/kW-yr at 200 MW to \$5/kW-yr at 2,800 MW (Shan and O'Connor 2018). According to Black & Veatch (2012) research, the annual O & M cost is \$30.8/kW-year. Table 4.25's statistics are averaged (excluding the highest value of 43.3) to arrive at a \$15.9/kW-yr O & M expenditure. Labor, insurance, and taxes are among the fixed expenses.

The number of starts and stops determines the variable expenses. Rehabilitation or repairs of welding joints, circuit breakers, and runners are among the variable expenses. ORNL anticipated that the initial cost of a unit would be in the \$300–\$1,000 range.If the plant is 100 MWh and cycles 20 times a year, the cost per kWh is in the range of 0.000094 to 0.0003 cents/kWh. PSH variable costs have been adjusted to 0 in this report due to the extremely low value.

4.5.3 Cycles, Lifespan, and Efficiency

According to May et al. (2018), a PSH unit with an RTE of 80 percent and 20,000 cycles can live for up to 50 years. ORNL estimates the useable life to be closer to 20 years, with an RTE range of 82 percent and 70–87 percent, respectively (Shan and O'Connor 2018 and Aquino et al. 2017b). This report was written with an RTE of 80%.The life expectancy is predicted to be greater than 25 years, with 15,000 cycles.

Table 4.11 Pumped Storage Hydropower battery cycle life, longevity, and round-trip efficiency. [33]

Cycles	Life Years	Efficiency	Source
20,000	20	82%	Aquino et al. (2017b)
20,000	50	80%	May et al. (2018)
20,000	>20	70-87%	Shan and O’Connor (2018)

4.6 Flywheels:

Flywheels are a type of electromechanical energy storage device with a limited lifespan of only a few minutes.Storing electrical energy as kinetic energy is possible through flywheels. A technique where a large wheel is accelerated by electrical energy and to regain it the wheel is braked. Flywheels are particularly useful when the time-period between charging and discharging is short due to great self-discharge (around 60% energy loss/day) (IRENA, 2017) (Akhil, et al., 2013). Long lifecycles and quick reaction times are two major advantages that flywheels may provide as a technology. These are usually accompanied by a high RTE value. They require little maintenance over the course of their lives and may run for a long period without the negative side effects associated with electrochemical storage.

4.6.1 Capital Cost:

Flywheels, as previously said, are made up of a revolving cylinder coupled to a kinetic energy-based engine. The footprint for bulk quantities of the resource can be considerable, rivaling that of PSH, which has a far longer lifespan. Flywheels used as a source of uninterruptible power supply have a substantially lower footprint than equivalent flywheels.

Table 4.12 The capital cost of flywheel battery installations. [33]

Capital Cost ($/kW)	Notes	Source
$2,400	Beacon Power's 20 MW/5 MWh flywheel plant	Aquino et al.(2017a)
$1,050	Installation of a 1 MW, 0.0074 MWh system	Helix Power(2018)
$600	333 kW, 1.5 kWh system excluding installation	Goodwin(2018)

4.6.2 Fixed and Variable Operations and Maintenance Costs

Only a few publications supply information on operations and maintenance for this technology category. Aquino et al. (2017) and Manuel (2014), for example, calculated fixed O & M to cost $5.56 per kW-year and $5.80 per kW-year, respectively. Manuel (2014) also included a variable O & M estimate of $0.30/MWh in his report. Maintenance expenses are estimated to be modest by Helix Power and $5 per kW-year ($1500 per year for a 333-kW system) by Kinetic Traction (Lazarewicz 2018).

4.6.3 Cycles, Lifespan, and Efficiency

Because of their lengthy lifecycles and high RTE levels, flywheels are in considerable demand as an energy storage device. These systems last anywhere from 1 to 30 minutes. When it comes to useful life,The useful life of a flywheel system was estimated to be around 20 years in all of the materials reviewed for this research.

Table 4.13 Flywheels battery cycle life, longevity, and round-trip efficiency. [33]

Cycles	Life Years	Round Trip Efficiency (RTE)	Source
Unlimited	20	70-80%	Aquino et al.(2017a)
100,000	20	81%	Manuel(2014)
<4million	20	85-90%	Helix Power (2018)
	20	98%	Active Power(2017)
	20	85%	Stometic (2018)
175,000-200,000			Aquino et al.(2017b)

4.7 Compressed Air Energy Storage:

A compressed air energy storage (CAES) system uses power to pump air into an underground cavern. The compressed air is sent via turbines to reclaim the power. CAES, like PHS, essentially necessitates the creation of the "right nature." As a result, CAES' application is limited to certain locations (IRENA, 2017).CAES entails filling a cavern with compressed air during off-peak hours, then releasing the air during peak hours and sending it to combustion turbines that generate electricity using natural gas. (Hydrodynamics 2018)

4.7.1 Capital Cost:

Equipment, building, installation, engineering, and other expenditures associated with the grid-level storage system are included in the capital cost of CAES facilities. Using all available data, a 16-hour plant's capital cost was projected to be $1,669/kW.

Table 4.14 The capital cost of compressed air energy storage battery installations. [33]

Capital Cost ($/kW)	Notes	Source
$1,105	$590/kW in 1991 U.S. dollars	Siemens (2017)
$1,600 - $2,300	Includes 12 to 48 hours of solution-mined storage capacity	Aquino et al.(2017a)
$1,481		Aquino et al.(2017b)
$1,047	900$/kW in 2010 U.S. dollars	Black & Veatch(2012)
$1,050 - $1,400		Bailie(2018b); Siemens (2018a)

4.7.2 Fixed & Variable Operations and Maintenance Costs

Fixed O & M expenditures for a 100 MW CAES plant, according to Aquino et al. (2017a), will be around $19/kW-yr for either a diabatic or adiabatic system. They estimate variable O & M expenses for a plant of the same scale, excluding fuel-related expenses, to be roughly $2.3/MWh-yr in 2017 USD. The fixed O & M cost for the Iowa Stored Energy Park was projected to be in the range of $18.7/kW-yr, close to the Aquino et al. (2017a) number, while the variable O & M cost was projected to be $2.28/MWh-yr. Based on 2010 USD, Black & Veatch (2012) calculated a fixed O & M cost of $11.6/kW-year and a variable O & M cost of $0.00155/kWh. This equates to $14.7kW per year and $0.00196 per kWh, respectively.For this project, the average of these numbers was used: $16.7/kW-year for fixed O & M and $0.00212/kWh for variable O&M. [33]

4.7.3 Cycles, Lifespan, and Efficiency

Table 4.15 Compressed Air Energy Storage battery cycle life, longevity, and round-trip efficiency. [33]

Cycles	Life Years	Efficiency	Source
10,000	25	65%	May et al. (2018)
10,000		73%	Dresser Rand (2018)
10,000	>30	>70%	EASE (2016)
10,000		67.12%	Li et al. (2016)
10,000	>30	>70%	Aquino et al. (2017a)

COMPARISON

Table 4.16 Comparative Analysis of Batteries

	Lead-Acid Batteries	**Li-Ion Batteries**	**Sodium-Sulfur Batteries**	**Redox Flow Batteries**	**Pumped Storage Hydropower**	**Flywheel**	**Compressed Air Energy Storage**
Capital cost ($/kWh)	$160 - $240	$340 - $590	$500 - $1000	$676	$1300 - $2020	$600 - $1050	$1600 - $2300
Operation & Maintenance Cost($/kW-yr)	$7 - $15/kW year	$6 - $14/kW year	$7 - $12/kW year	$7 - $16/kW year	$6.20 - $43.30/kW year	$5.56 - $5.80/kW year	$19/kW year
Cycles	2,000	3,500	4,000	10,000	20,000	<4	10,000

						million	
Life Years	15	10	10	20	>20	20	25
Efficiency	79-84%	77-85%	77%	70%	70-87%	85-90%	65%
Response Time	1sec	1sec	1sec	1sec	5-70sec	0.25sec	0.016sec

4.8 Finding & Analysis of Storage Technology

Now taking the latest & highest data in table 4.17 and latest & lowest data in table 4.18 of capital cost and operation & maintenance cost from all of the table of chapter 4 to analysis costs. So, taking data from the 8 storages technology which are discussed already in our thesis paper.

Analysis:01

Table: 4.17: Annualized cost value by technology ($/kW) [33]

Batteries Name	**Capital Cost ($ / kW)**	**Operations and Maintenance Costs ($ / kW)**	**Total Cost ($ / kW)**
Lead-Acid Batteries	240	15	255
Li-Ion Batteries	590	14	604
Sodium-Sulfur Batteries	1,000	12	1,012
Redox Flow Batteries	676	16	692
Pumped storage Hydropower	2,020	43.30	2,063.3
Flywheel	1,050	5.80	1,055.8
Compressed Air Energy	1,400+890(Break down cost)	19	2,309
Zinc-Hybrid Cathode Batteries	250	2	252

In this digital world, we can see the available use of li-ion battery in smart devices. Also, there are many electric cars which are powered by li-ion battery. Now showing the data table of highest total cost then the lead-acid batteries are bear low cost than the li-ion batteries. And the difference is too much to see.

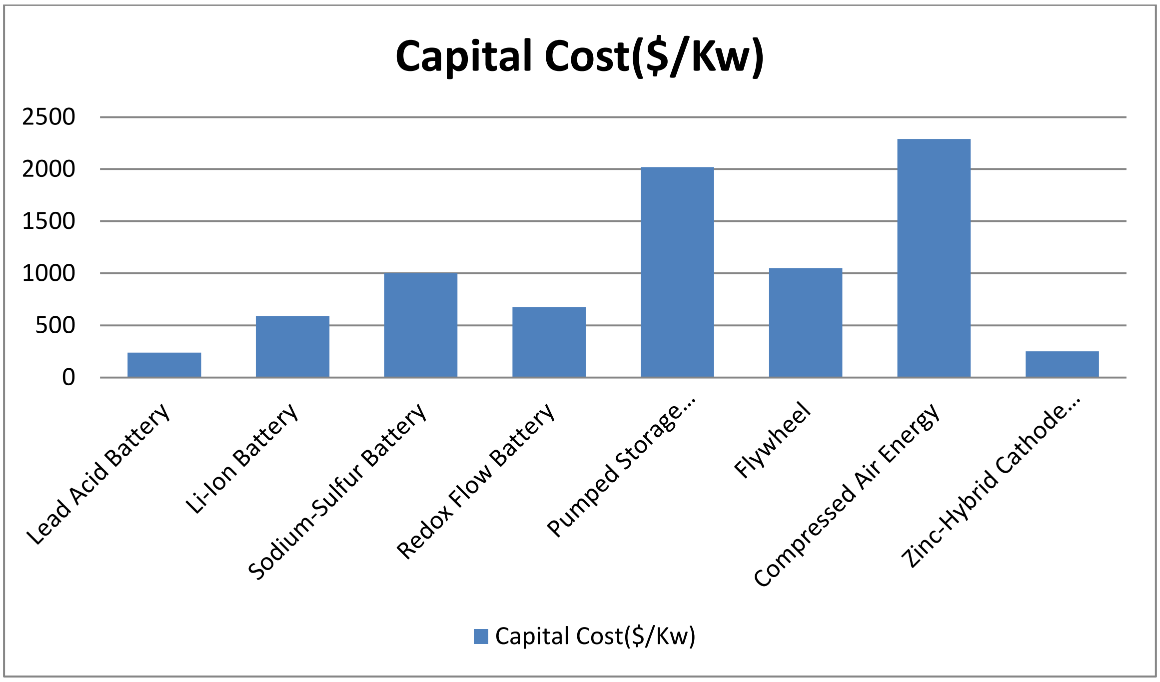


Figure 4.1: Analyzed capital cost value by technology ($/kW)

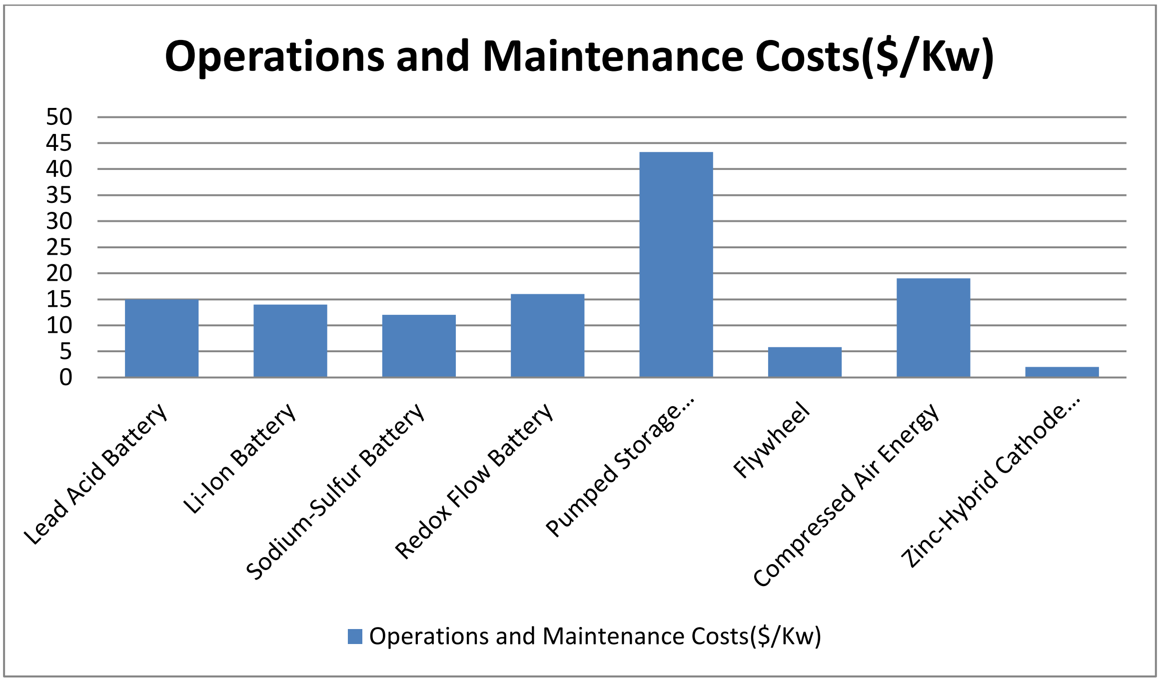


Figure 4.2: Analyzed operations and maintenance cost value by technology ($/kW)

Analysis: 02

Table: 4.18: Analyzed cost value by technology ($/kW) [33]

Batteries Name	Capital Cost ($/kW)	Operations and Maintenance Costs ($/kW)	Total Cost ($/kW)
Lead Acid Batteries	160	7	167
Li-Ion Batteries	340	6	346
Sodium-Sulfur Batteries	500	7	507
Redox Flow Batteries	676	7	683
Pumped storage Hydropower	1,300	6.20	1,306.2
Flywheel	600	5.56	605.56
Compressed Air Energy	1,600	11.6	1,611.6
Zinc-Hybrid Cathode Batteries	200	2	202

Here also, showing the data table of lowest total cost then the lead-acid batteries are bear low cost than the li-ion batteries. And the difference is too much to see.

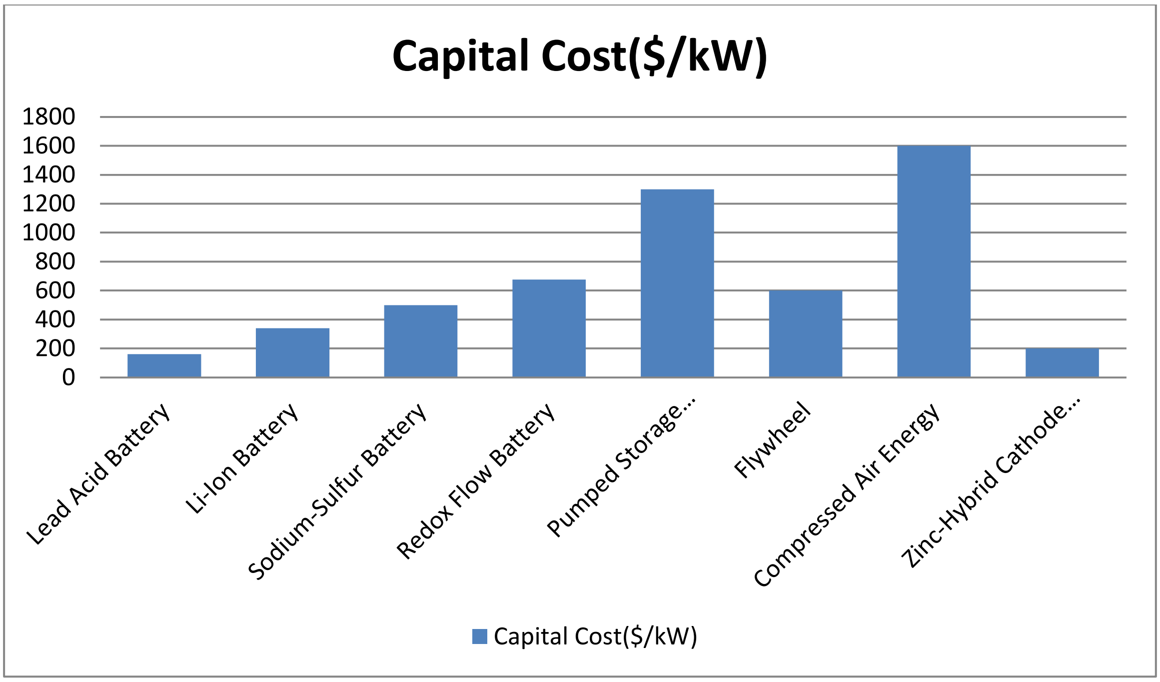


Figure 4.3: Analyzed capital cost value by technology ($/kW)

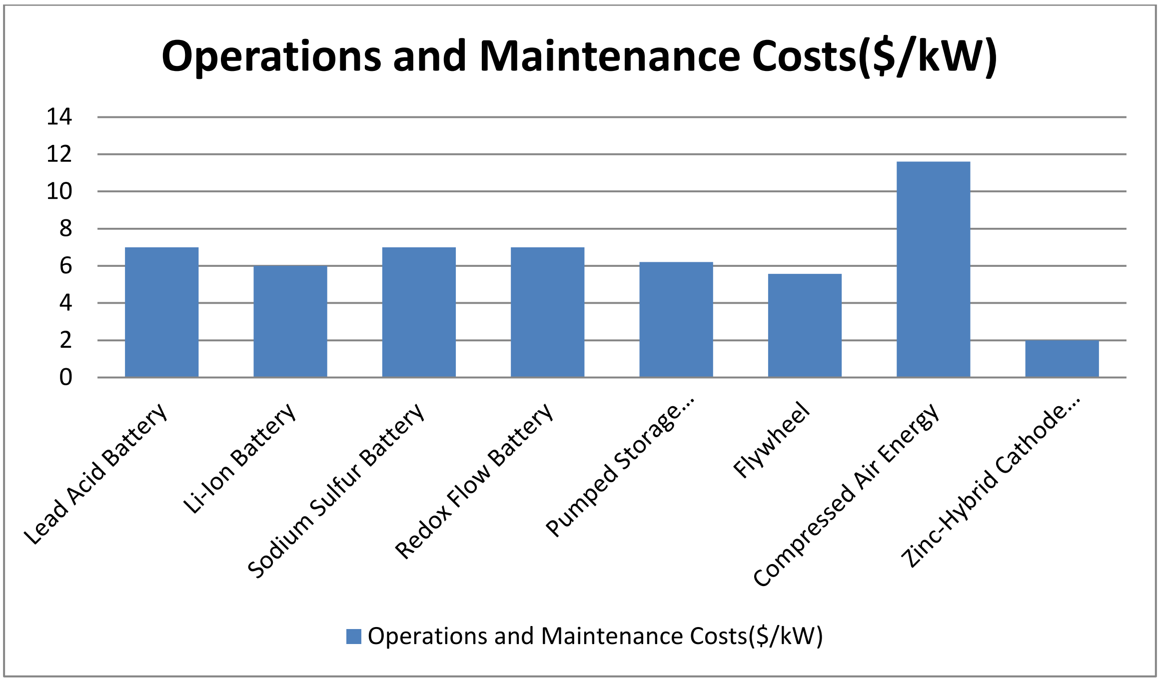


Figure 4.4: Analyzed operations and maintenance cost value by technology ($/kW)

4.9 Analysis

From the data table 4.17 and 4.18, seeing that the summation of capital cost and operation & maintenance cost are available there. The total lower cost available in lead acid batteries and zinc-hybrid cathode batteries. On the other hand, li-ion batteries storages are more than costly of them.

Here are the reasons that, though li-ion batteries total cost is more than lead-acid batteries. Uses of the li-ion batteries in most of the devices which are very much needed in daily life. Now comparing these two batteries on the basis of the following parameters.

- **Capacity:** A battery's capacity is the amount of charge that can be stored in it. While capacity can change between the models and manufacturer's lithium batteries have always had a higher capacity per unit volume than their lead acid counterparts.

- **Weight:** For the same capacity li-ion batteries are known to be much lighter than their lead acid counterpart. A good example is the SLI batteries used in automobiles. SLI batteries have a capacity of 35amp-h. Lead acid batteries of the same capacity would weigh at least 10 kgs more than its li-ion counterpart.
- **Efficiency:** The efficiency of a battery also plays an important role in its usage. In a battery, efficiency is a ratio of the amount of charge entering the battery during the charging phase to the amount of charge leaving the battery during the discharge phase. But this value is actually dependent on the rate of discharge. If the battery is discharged at a much faster rate the efficiency of the battery reduces. Lithium-ion batteries tend to have very high efficiency of 92% against 60% efficiency of lead acid batteries for similar capacity and discharge condition.
- **Cycle life:** Battery life is specified in terms of charge-discharge cycle. One cycle consists of charging the battery to its full level and then discharging it to the minimum permissible lower limit. Lead acid batteries tend to have a life of around 300 cycles with a depth of discharge of 50%. This way by the time the battery undergoes 300 charge cycles the capacity of the battery would be reduced to 50% of its original value. Lithium-ion batteries have a much higher life cycle. The batteries that we normally use in our smartphones have a life of thousand two hundred cycles with the depth of discharge being 80%. Lithium-ion battery chemistry is like lithium titanate developed by Toshiba tends to have life cycles higher than 40,000 at 80% depth of discharge.
- **Reusability:** Battery reusability or recycling is the activity in which a non-functional battery or its materials are repurposed to be used again. Lead acid batteries have the highest value of reusability almost 90% of the battery materials is recycled and reused. The recycling infrastructures for these batteries is also well established. Majority of the lead acid batteries that are used in automobiles and home backup systems use recycled lead from old battles. On the other hand, lithium-ion batteries have very low reusability the recycling infrastructure for lithium-ion batteries is growing gradually with newer methods being developed every day.
- **Safety:** Safety of a battery is normally considered by its thermal runaway property. Thermal runaway is a process in which an increase in temperature leads to a rapid release of energy that further adds temperature and in worst case

scenario leads to an explosion. The thermal runaway of lithium-ion batteries is the highest as it is very dependent on the charging condition. Sometimes overcharging can lead to dendrite formation on the electrodes over time these dendrites grow in size puncturing the separator and can cause a short-circuit. Thermal runaway can occur in lead acid batteries also it occurs most often when the rate of internal heat generation exceeds the rate at which they eat can be expect. If this condition continues for an extended period the battery temperatures tend to rise until the cells dry out and the container, softens, breaks and melts. Since lithium-ion batteries contains more energy per unit volume than lead acid batteries the thermal runaway can be more violent. This can be awarded with an intelligent battery management system which monitors its voltage current and temperature. [35]

Again,

Also, zinc-ion batteries have some disadvantages. That’s why li-ion is better than zinc-ion batteries.

The migration of zinc-ion batteries from alkaline electrolyte to neutral or mild acidic electrolyte promotes research into their flexible applications. However, discharge voltage of many reported zinc-ion batteries is far from satisfactory. On one hand, the battery voltage is substantially restricted by the narrow voltage window of aqueous electrolytes. On the other hand, many batteries yield a low-voltage discharge plateau or show no plateau but capacitor-like sloping discharge profiles. This impacts the battery's practicability for flexible electronics where stable and consistent high energy is needed. Herein, an aqueous zinc hybrid battery based on a highly concentrated dual-ion electrolyte and a hierarchically structured lithium-ion-intercalative $LiVPO_4F$ cathode is developed. This hybrid battery delivers a flat and high-voltage discharge plateau of nearly 1.9V, ranking among the highest reported values for all aqueous zinc-based batteries. The resultant high energy density of 235.6 Wh kg^{-1} at a power density of 320.8W kg^{-1} also outperforms most reported zinc-based batteries. A designed solid-state and long-lasting hydrogel electrolyte is subsequently applied in the fabrication of a flexible battery, which can be integrated into various flexible devices as powerful energy supply. The idea of designing such a hybrid battery offers a new strategy for developing high-voltage and high-energy aqueous energy storage systems. [36]

For the reasons, li-ion batteries are available in mobiles and smart devices though it is costly more than lead acid batteries. The storages are used in different electronics devices.

On the other hand, pumped storage hydropower, flywheel, compressed air energy storages are used in largely power produce. The compressed air energy storage and pumped storage hydropower are used as power plant backup. These are costly more than flywheel. Flywheel storages are used to make a medium power supply from low power as input. So, it could not be possible to make a power plant backup storage as flywheel, though it is lower in cost from pumped storage hydropower and compressed air energy storage.

Vanadium Redox Flow Battery is they Compare to Lithium-Ion Battery

Table 4.19 Vanadium Redox Flow Battery Vs Lithium-Ion Battery.[34]

Categories	**VRFBs**	**Li-Ion Batteries**
1.Technical Performance	Excellent for energy applications (4+hrs), Lower roundtrip efficiency but longer life and no degradation.	Excellent for power applications, Degradation accelerates with frequent use, temperature and deep discharges.
2. Cost	Have yet to experience scale economics, High contribution of vanadium is both a risk and an opportunity.	Cost reductions expected to slow, Significant cost decreases in recent years due to R&D and capacity growth.
3. Safety	No risk of thermal runaway, Electrolyte spillage is main risk.	Thermal runaway creates risk of fire and smoke that must be managed.
4. Market acceptance	Challenge from fragmented supply market dominated by start up companies, More nascent technology.	Credibility of large, consolidated cell manufacturers helps, Growing acceptance from deployment in frequency control markets.

In this summery, there is no clear superiority, with use cases and site requirements often determining the optimal solution.

CHAPTER 5

5.1 Results & Discussion

Vanadium flow batteries don’t let in any carbon emissions. They burn cleanly and only require power from the plant to charge.These can replace current generators that are both noisy and carbon-emitting. Imergy power systems recently designed vanadium flow batteries from recycled vanadium of 98.5% purity. A single percentage brings the cost down to a great degree. Slag from steel plants can be used to recover vanadium. It’s a clean source of fuel. The possible build-up of oxidation intermediates in the electrolyte during long-term use is not understood, however, and needs further investigation. Similarly, impurities introduced during electrolyte production, either from the use of chemical reductants or from electrode materials used during suspended powder electrolysis, need detailed investigation. Some companies, for example, use dimensionally stable anodes (DSA) in the electrolysis cells used to generate the 50/50/ as the initial electrolyte for the VRFB.DSAs have a very short life and must need frequent maintenance because the noble metal coating can gradually dissolve into the anolyte during electrolysis. This could lead to the introduction of noble metal impurities into the electrolyte that could not only increase hydrogen evolution during charging, but more significantly, could catalyze the oxidation of V (II) by hydrogen ions in the negative half-cell, leading to hydrogen evolution even during stand by. These are all potential issues that need to be further investigated to ensure the stable operation and long cycle life of the VRFB.

CHAPTER 6

6.1 Conclusions and Outlook

1. At activated carbon/plastic composite electrodes, the V2+/V3+ and VO2+/VO2+ redox couples demonstrate sufficient reaction rates.

2. Side reactions, migration, and diffusion phenomena (water drag) generated by the nature of the separator material and aberrations in the hydrodynamic conditions in the circulation loops generate capacity losses, charge imbalances, and asymmetric electrolyte distribution in the system.

3. Self discharge is mainly due to poor separator efficiency (electrolyte cross flow). It is usually negligible even in unlimited stand by (rest) periods of the battery.

Necessary future R&D efforts concern the optimization of electrode and separator materials as well as the composition and properties of the electrolyte to ensure technical and economic success.

6.2 Recommendation

A small flow battery with a small generator could be installed for emergency backup purposes. When the electricity market matures to time of use pricing and opportunities for energy arbitrage become available, it would make economic sense to install appropriately sized equipment at that point to reduce electricity expenditure.This is an opportunity for public and private sector banks and government departments to set up programs to incentivize businesses, residences and industries to adopt flow batteries to not just solve the power situation in the short term, but also to manage electricity demand over the longer term by assisting in the deployment of renewable energy systems.

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