Daffodil International University
Dhaka, Bangladesh

Thesis Report
On
An Overview of Future Energy Storage Vanadium Redox Flow Battery (VRFB)

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This thesis has been submitted to the Department of Electrical and Electronic Engineering in partial fulfillment of the requirement for the degree of Bachelor of Science in Electrical and Electronic Engineering.

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APPROVAL LETTER

This thesis report titled **“An Overview of Future Energy Storage Vanadium Redox Flow Battery (VRFB)”,** submitted by Obaidul Haque, ID: 163-33-332

to the Department of Electrical & Electronic Engineering, Daffodil International University has been accepted as satisfactory for the partial fulfillment of the requirements for the degree of Bachelor of Science in Computer Science and Engineering and approved as to its style and contents. The presentation has been held on January, 2021.

Board of Examiners:

DECLARATION

We hereby declare that this thesis is based on the overview found by me. The materials of work that has been by other researchers are mentioned by reference. This thesis is submitted to the Daffodil International University for partial fulfillment of the requirement of the degree of B.Sc. in Electrical and Electronics Engineering. This thesis neither in whole nor in part of this has been previously submitted for any degree.

Supervised by:	Submitted by:
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ABSTRACT

Energy storage analysis is the backbone of power system analysis and design. The Vanadium Redox Flow Battery (VRFB) is one of the foremost promising electrochemical energy storage systems considered to be suitable for an honest range of renewable energy applications, which stores electric energy by changing the oxidation numbers of anolyte and catholyte through redox reaction. This chapter covers the basic principles of vanadium redox flow batteries, component technologies, flow configurations, operation strategies. This thesis reviews several different types of batteries along with its advantages and disadvantages. Further, this thesis focuses on the electrochemistry of Redox Flow Batteries, most recent developments, its applications and a case study. The significance of this study is to figure out a possible comparison between the available energy storage system now a days & adopting the most feasible and efficient energy storage system. From the observation and research, it has been highlighted that vanadium redox flow battery can be the long lasting & recyclable energy storage of future[1]. Besides, there are few limitations & findings of recent researcher pointed that adopting of the VRFB for some particular application are not feasible that have been reviewed.

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ABBREVIATIONS AND NOMENCLATURE

VRFB	- Vanadium Redox Flow Battery
ESS	- Energy Storage System
BESS	- Battery Energy Storage System
PSAT	- Power System Analysis Toolbox
MATLAB	- Matrix Laboratory
P.U	- Per Unit
N-R Technique	- Newton-Raphson Technique
G-S Technique	- Gauss-Seidel Technique
IEEE	- Institute of Electrical and Electronics Engineers

Nomenclature

E_0	-	formal potential (V)
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})
E_{full}	-	the potential difference
R	-	universal gas constant
T	-	absolute temperature
N	-	number of equivalents transferred per mole of reduced or oxidized species
F	-	Faraday's constant.
J_0	-	exchange current density (A cm^{-2})
E_a	-	activation energy (J mol^{-1})
A_m	-	membrane surface area (m^2)
A_e	-	electrode surface area (m^2)
L	-	length
V		electrolyte volume (dm^3)

Chapter 1

1.1 Introduction

Flow batteries can catch up on losses acting as a way of power back-up and may significantly curb the impact of power shortage. Energy storage has the potential to be an integral part of the grid by providing support to more efficient use of assets and seamlessly integrating into the grid with existing power plants and transmission lines[2]. It is also an effective way of using energy arbitrage, wherein individual power producers can store excess energy during off-peak hours and sell this power at a higher price. Intermittent nature of renewable energy resources is also a compelling reason to use battery energy storage. The energy storage system has been created due to the huge electricity load demands and this energy were supply to all electrical appliances especially for large scale energy user. Industrial development and population in the world have been increased dramatically from time to time. The energy storage system from a renewable energy is a solution to solve intermittent energy problem and give a positive environmental view to the world[3]. This renewable energy source will replace the non-renewable energy source which are the most popular global energy resource including in Bangladesh over a last few year. This was the main factor and reason that cause all the researcher to take initiative to develop an energy storage system from a renewable energy because the non- renewable energy source led to the global warming problem from harmful gas released. In the near future, renewable energy is expected to take the role of important to electrical generation. Renewable energy is the energy that can be obtained from natural resources that can be constantly replenished. The renewable energy stated before will suffer from fluctuation and dispersed due to the increasing demand of electricity and the action taken to overcome this deficiency problem related to the electricity and the energy storage technology were introduced and it eventually became the key of motivation for the researchers to enhance the initiative of the energy storage technologies[3]. Energy storage acts as a store to reserve an amount of specific energy for future. Energy storage can be divided into few categories with the respect to certain features i.e., mechanical storage, thermal storage, electrochemical storage.

1.2 Methodology

This thesis makes use of qualitative research strategy, where the research approach implemented has been 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. In this paper, also includes the following formulas: concentration over-potential due to the diffusion layer around the fibers of the porous graphite electrodes, shunt currents and diffusion of vanadium ions across the membrane. Furthermore, the Nernst equation also used to obtain the required output. Inverter losses are considered using a detailed model of the topology[4]. The flow rate control strategy has negligible impact on the shunt currents, ohmic losses and inverter losses; however, the interaction of losses due to diffusion, concentration over-potential and pumps is carefully analyzed. Especially, data has been collected from various online sources to analyze and to referred the previous related works on vanadium redox flow battery and energy storage system.

Chapter 2

ENERGY STORAGE

2.1 Brief Review of Energy Storage System

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., plug-in hybrid and full electric vehicles)[5]. The link between this sector and therefore the electric grid integration of the ESS is sort of straightforward. 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

The advancement of modern technology is helpful for distribution networks applications and that all around arrived at a higher specialized status level are the electro-chemical batteries. Such innovations may have internal or external storage. Instances of the last frameworks, dismissing the hydrogen or methane storage that are helpful for long haul administrations, 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 economically accessible with various secluded 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 expense, unequivocally rely upon the particular administrations that they are called to perform. ESS administrations can be: subordinate administrations (i.e., recurrence control, voltage guideline, 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 employments 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 is that one identified with the term and recurrence of intensity supply from the ESS:

1. short-term (seconds to minutes),

2. medium-term (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) are able to provide services of tertiary frequency control, standing reserve, load leveling, islanding, electro-mobility, residential self-consumption increase, UPS. Finally, the long-term ESS (from 50 hours and typically less than 3 weeks) can be exploited for long duration services, during periods when there is no or scarce generation of electricity from wind and solar (“dark- calm periods”). Super-capacitors, superconductive magnetic coils, or flywheels may offer short-term services. Pumped hydropower, compressed air ESS, thermoelectric storages, and electrochemical ESS, 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 the smart distribution networks fall into the medium, or at least short-term services. The pure electrical super-capacitors, superconductive magnetic coil, (since they have some strengths, as high efficiency, high power capability, and long life), are yet affected by the lack in the validation and experimentation for grid purposes and by their very high costs, due to the high innovation degree. The mechanical systems can be subdivided into well-established technologies (i.e., pumped hydropower), the ones that need short time-to-market (i.e., compressed air energy storage), or those that are developed for other applications than the network operation (i.e., flywheels, that are well-established in UPS systems).

Mechanical Energy Storage

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

Electrical Energy Storage

Electrical storage system is basically categorized into two which are double-layer capacitor (DLC) and superconducting magnetic energy storage (SMES). Double-layer capacitor is also known as supercapacitors or Ultracapacitor which contains two conductor electrodes and electrolytes as well as porous membrane separator[12]. The supercapacitors have high power capability and higher energy storage capability when compared with conventional capacitors. However, as highlighted, supercapacitors are more convenient to be used for short-term energy storage applications. Meanwhile, the energy in magnetic field created by the flow of direct current in SMES is stored in a superconducting coil[10]. The features of SMES includes relatively quick response time, high efficiency and high-power production in where it can be supply for a short duration. Unfortunately, it has a weakness, in where 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 to 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 the redox reactions as explained. Electrochemical energy can be specified to different types which are Nickel Cadmium, Lithium Ion, Lead Acid, Fuel Cell and Redox Flow Battery (RFB).

2.3 Battery Energy Storage

Batteries are the most well-known and common, yet advanced energy storage device with a wide range of applications. They are used to power electronics and are versatile, robust, proven and inexpensive. Battery Energy Storage (BES) is a technology used for stationary applications and comes in different types based on the most 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 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.

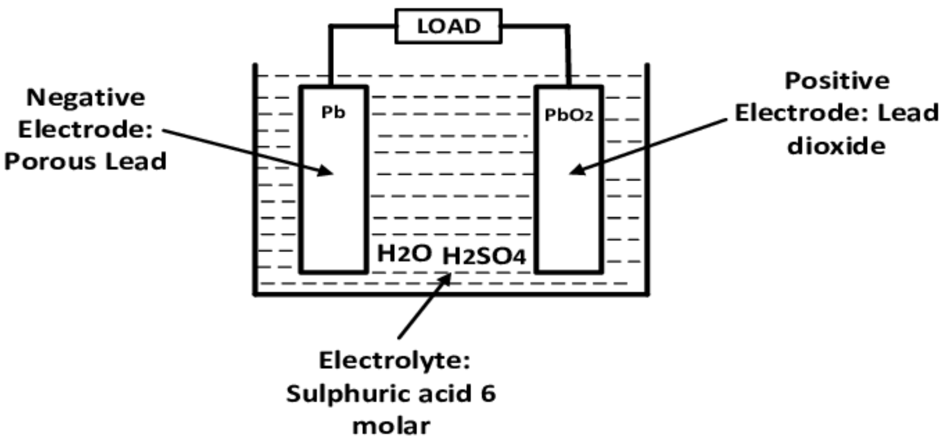

Figure 2.1: Construction of Lead Acid Battery[13]

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 in emergency equipment for power back up. Larger power requirements include home- offices, where the battery is used in its wet-cell formula[9]. It has 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.

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 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 a 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.

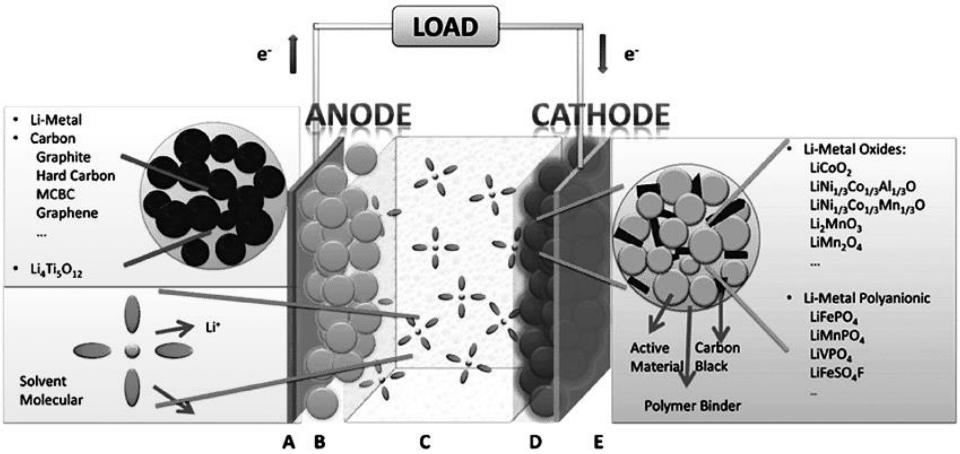

Figure 2.2: The hierarchical structure of lithium-Ion battery[2]

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

$$xLi^+ + xe^- + xC_6 \rightarrow x\ LiC_6$$

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

$$LiCoO_2 \rightarrow Li(1-x)CoO_2 + xLi^+ + xe^-$$

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 in these

Sodium Sulfur Battery

Sodium sulfur batteries are very high-capacity batteries. They work extremely well in large scale applications. They are mainly used in grids due to its very high operating temperature of 300 degrees centigrade. The electrodes are in liquid state at this temperature but the electrolyte remains in the 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. In case if needed it’s possible to discharge its complete charge in 1 ms whenever required. 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].

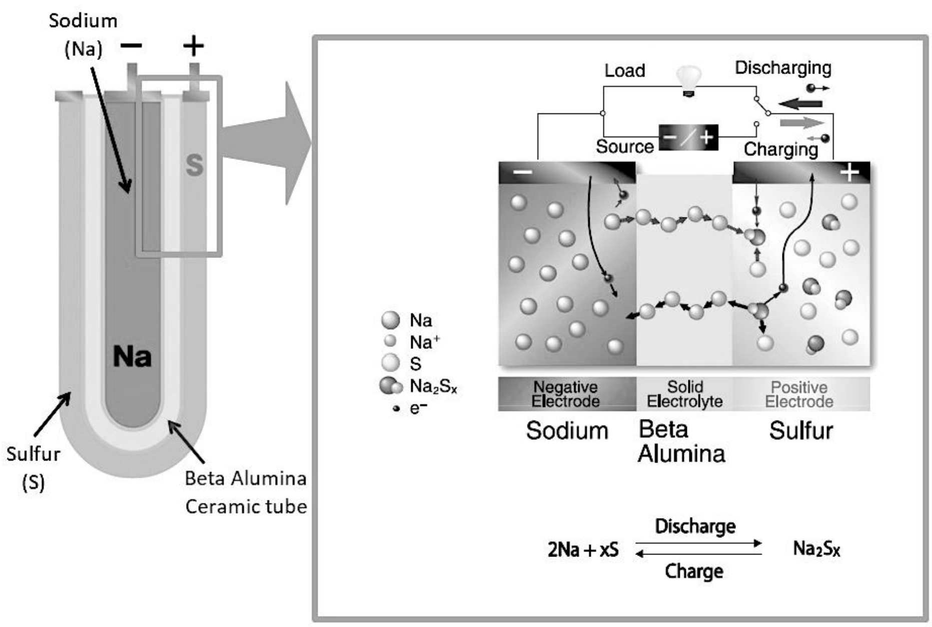

Figure 2.3: Working principle of Sodium Sulfur battery[12]

During the charging cycle, positive Sodium ions are passed, which combine with sodium forming 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:

$$2Na+4S = Na_2S_4$$

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 to energy management by having good load balancing and peak saving abilities.

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 supported 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 is the main driver behind some of the advantages over lead-acid and Ni/Cd systems. Some improvements are needed in the battery 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.

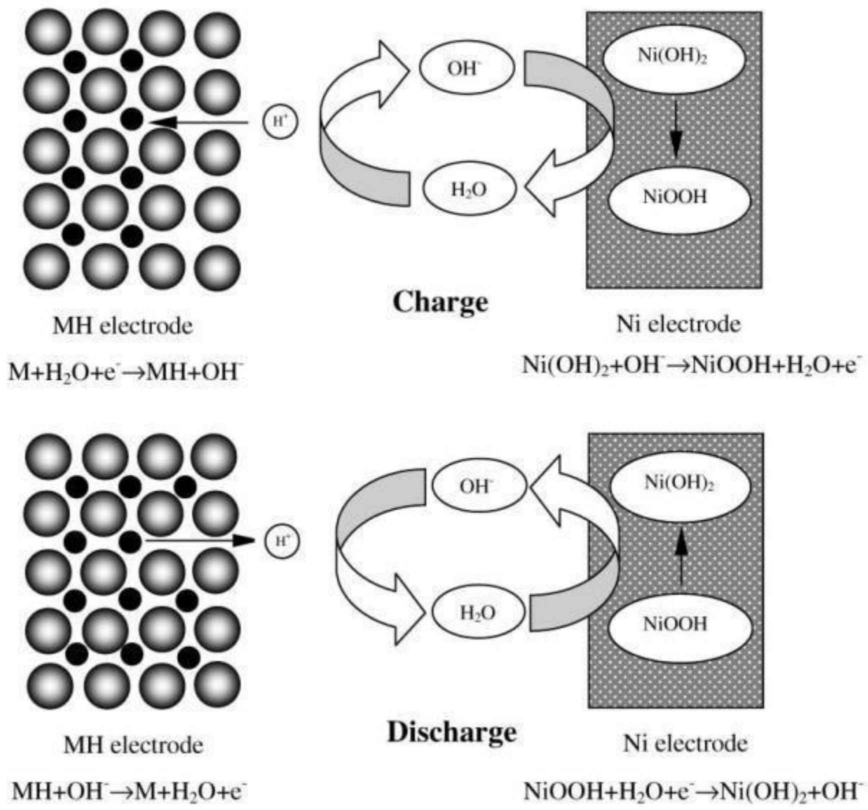

Figure 2.4: For the Charging & Discharging Process of the Nickel metal hydride battery[5]

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

Redox Flow Battery

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. stored in separate tanks 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 electrolyte 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 high energy density. The charge and discharge cycle are long during its life.

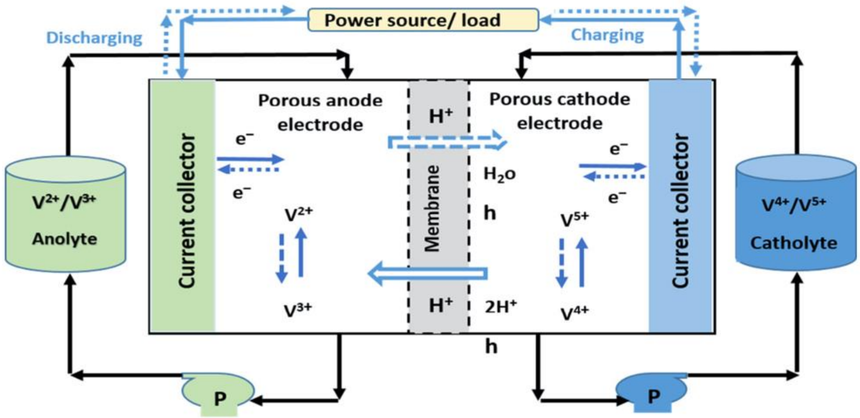

Figure 2.5: Schematic diagram of VRFBs[10]

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. Below mentioned reactions show the concept of functioning in a V-V system:

2.3 Positive Electrode:

$$VO^{2+}\text{(tetravalent)} + H_20 \leftrightarrow VO^{2+} + 2H^{+} + e^{-}$$

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 at the positive electrode are transferred to the negative electrode through the membrane. This assures that the electrolyte remains electrically neutral.

2.4 Negative Electrode

V^{3+} (Trivalent) + e^{-} ↔ V^{2+} (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.

2.5 Summery of Advantage & Disadvantage

Lead-Acid Batteries

- Battery technology is well developed and reliable
- Capable of producing high voltages
- Low internal impedance thereby leading to the lowest discharge rate among rechargeable systems
- Robust; low maintenance requirements; long shelf life if stored without electrolyte.
- Construction is simple; low manufacturing costs. Energy density is relatively low leading to degraded performance over time
- It has a limitation that it's mandatory to be stored in a charged state once the electrolyte has been introduced to prevent deterioration of the active chemicals.
- Electrolytes and lead used are toxic to environment
- Danger of overheating during charging and not suitable for fast charging.

Sodium Sulfur (NaS)

- Up to four times as efficient as lead acid battery owing to high energy density.
- Production costs are low as sodium and sulfur are cheap.
- Useful applications in solar and wind farm energy storage. Poses accidental hazards brought on by violent reaction b/w sodium and sulfur.
- Only one known application till date-load leveling by electrical utilities in Japan.

- Limited self-life-2 to 5 years.
- Requires bulky insulation.

Lithium-ion Batteries

- High energy density compared to other technologies.
- Low self-discharge rate
- Low maintenance-no periodic discharge required
- Battery shape and size can be customized according to requirements and space constraints.
- High energy density compared to other technologies
- Low self-discharge rate
- Low maintenance-no periodic discharge required
- Battery shape and size can be customized according to requirements and space constraints

Nickel-Metal –Hydride (NiMH)

- Voltages similar to standard alkaline batteries
- Multiple recharges possible thereby making frequent battery replacements obsolete
- Easy storage and transportation
- Inexpensive
- Absence of cadmium makes it relatively environmentally friendly; contains mild toxins. Voltages similar to standard alkaline batteries
- Multiple recharges possible thereby making frequent battery replacements obsolete.
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- Absence of cadmium makes it relatively environmentally friendly; contains mild toxins.

Flow Batteries

- For the flow battery cell, electrolyte and electroactive materials are normally stored separately, so the uncharged solution can be replaced like refueling a vehicle.

- Long lifetime
- Electrolytes used have a low self-discharge rate
- Installation time period is short (8 mo for multi-MW systems and 3 mo for smaller systems)
- No toxic or polluting gas emissions; silent operation. Low energy density
- Manufacturing is expensive as it is a complex system to build
- Toxic electrolyte leaks possible.

Chapter 3

FLOW BATTERY TECHNOLOGY

3.1 Technical Review of 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 at the positive electrode are:

$$VO_{2+}\ (aq) + H^{+}(m) + e^{-} + H_3O^{+}(aq) \rightarrow VO^{2+}\ (aq) + 2\ H_2O(l)^{-}$$

The reactions occurring at the negative electrode are:

$$V^{2+}\ (aq) + H_3O^{+}(aq) \rightarrow V^{+3}\ (aq) + H^{+}(m) + H_2O(l) + e^{-}$$

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 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 to the electrolytes and materials. Polypropylene is a carbon polymer design that has also been successfully tested for this purpose.

Solution:

New techniques of preparing $VOSO_4$ for use in the positive electrolyte solution are being researched. Recently, few Corporation 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 has 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. 23 mol/l solution of H_2SO_4 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 negative electrolyte solution does not have the active ion associated with these, V2+ and V3+. The negative electrodes are less studied due to the greater significance of positive electrolyte in affecting different factors.

Alternate Negative Electrode

Recent researcher 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.

$$V^{3+}(aq) + e^{-} \rightleftarrows V^{2+}(aq)$$

The reaction occurs from left to right during the charging phase. The reaction occurring from right to left is during the discharge phase. The VCl_2/VCl_3 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 to account for discrepancies that might result from using experimental data to the calculated open circuit voltage (OCV). Additionally, these errors are caused due to only few parameters considered in the model[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:

$$E_{full} = E°_0 - \frac{RT}{nF}\ln\left[\frac{c_{ox}\cdot\delta_{ox}}{c_{red}\cdot\delta_{red}}\right]$$

where E_{full} is the potential difference, □$°_0$ 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 activity coefficient of species. Additionally, red and ox describes the reduced and oxidized species respectively. The activity coefficient (□) 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 potentials are:

Positive electrode: (1/2) Br_2 (aq) + e−⇄Br−(aq)

Negative electrode: V_3+(aq) + e−⇄V_2+(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 designed to be extremely selective towards conducting the charge-carrying ion. 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, Nafion 117 is a commonly used cation exchange membrane[15]. The thickness of a membrane can ranges 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 by 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.

$$VO_2+(aq) + V_2+(aq) + 2\ H_3O+(aq) \leftrightarrow VO_2+(aq) + V+3(aq) + 3\ H_2O(l)$$

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 cost 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

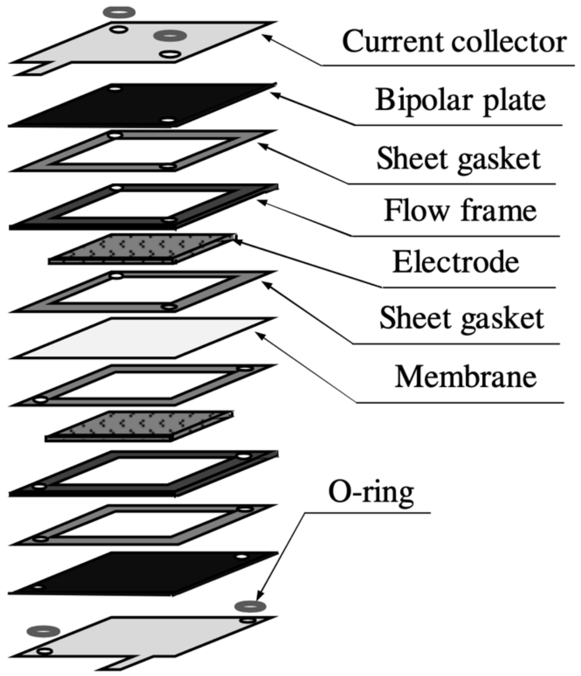

Figure 3.1: Cell stack design of VRFB[19]

H_2SO_4.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 battery lasts for approximately 10,000 cycles and can be operated at a discharge efficiency of approximately 78%. 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 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 10 years and are available in configurations from 1 kW to 10 MW.

Membrane:

A membrane is best suited to be used for these applications when it allows the transfer of a proton. It must however resist the crossover of vanadium and water. Additionally, it must be maximally resistant towards the chemical degradation fromVO2+and V5+. Some early tests had 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 Vanadium Redox Batteries due to their high stability. These membranes cannot be used without modification because of high permeability leading to low coulombic efficiency[3]. 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 the low water uptake[15]. The Dioramic/Nafion composite membrane limits self-discharge and gives high current efficiency.

3.4 Technical Properties of VRFB

Conductivity

The conductivity of the membranes is measured using the method of impedance spectroscopy. The frequency range is from 1 to 10^6 Hz with AC amplitude of 0.2V. Additionally, the resistance of the conductivity cell is measured with and without the membrane.

Vanadium Ion Diffusion

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 by 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 V^{3+} and 1 M V^{4+} 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 of length, width and thickness were determined using a digital caliper.

Energy Density

The energy density of a redox flow battery is proportional to the concentration of the redox ions in solution, to the cell potential and to the number of electrons transferred during discharge per mole of active redox ions.

Temperature Effect

Voltage efficiency decreases with decreasing temperature and increasing current due to lower reaction rates and ohmic losses. On the other hand, current efficiency increases with increasing current and decreases with increasing temperature due to faster diffusion rates of vanadium and poly bromide ions across 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 the pretty good adaptability towards use in a Vanadium Bromide flow cell[3]. he highly oxidizing nature of Br3-ions causes rapid deterioration of most polymeric membranes and thus only limited types of membranes can be used for 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. To overcome this issue, various bromine complexing agents are added. The complexing 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.

Name	Place	Year	Energy	Power
Kashima-Kita Electric Power	Japan	1996	800 KWh	200 kW
Kansai Electric	Japan	2000	1.6 MWh	200 kW
Sumitumu Electric Group	Japan	2005	6 MWh	4 MW
Hokkaido Electric Power	Japan	2016	60 MWh	15 kW
Frauhofer Project	Germany	2019	20 MWh	2 kW

Table 3.1: Main exiting installed storage of VRFB (Extracted from Wikipedia)

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 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 has an exclusive world-wide license for the Vanadium bromine Technology and was founded in the University of New South Wales, Australia. Conventional batteries are normally available with power outputs ranging from 5 to 50 kW. Few more companies from Japan and China already been installed vast capacity's storage based on Vanadium redox flow battery that has been mentioned on table 3.1.

3.7 Design Cell & Stack

It is desired to find costs of building and installing a battery of power capacity 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 electrolytes 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 it will result in the equilibrium different in potentials due to the Nernst equation. It is crucial to balance both of vanadium and supporting electrolyte concentration in order to achieve better performance of V-RFB. Excessive usage of vanadium concentration will result on 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 cm-2.

By using the formula discussed earlier, the voltage efficiency and columbic efficiency are 66% and 95% respectively in which producing a 63% of 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.

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

Table 3.2: Detailed specification for VRB stack[22]

To produce the required power, it was determined that a total of 112 cells will be required. To optimize stacking, 8 stacks of 14 cells each are used. Cells are stacked in 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 shows 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 was primarily associated with the availability of natural resources for energy consumption[12]. New threats for energy security have arisen when the world competes for energy resources due to the increase in industrialization process by every country. This leads to the possibility of the volatility in the crude oil price. Hence, this encourages researchers, industries and government to embark into a new research for energy storage technologies. Some approaches for the 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 saving 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, vanadium redox flow battery (V-RFB) is the most developed and the closest to commercialization compared to other types of RFB[10]. Historically, V-RFB has been 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, whereas 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[6]. 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 primary 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

4.1 Discussion & Conclusion

Vanadium Flow batteries do not let out any carbon emissions. They burn clean and only require electricity 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 by 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. For example, some companies employ dimensionally stable anodes (DSA) in the electrolysis cells used to produce the 50/50 V^{3+}/V^{4+} solution used as the initial electrolyte for the VRFB. DSAs have very short life must needed frequent & maintenance because the noble metal coating can gradually dissolve in 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 5

5.1 Recommendation

A small flow battery with a small generator could be installed, for emergency backup purposes. After the electricity market matures into time of use pricing and opportunities for energy arbitrage are available, it would make economic sense if proper sized equipment is installed at that point to lower expenditure on electricity. This is an opportunity for public and private sector banks, 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 manage electricity demand over the longer term by assisting in the deployment of renewable energy systems.

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