Investigation of operational characteristics of vanadium redox flow batteries

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**INVESTIGATION OF OPERATIONAL
CHARACTERISTICS OF VANADIUM REDOX
FLOW BATTERIES**

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Abstract

Redox flow based batteries are becoming increasingly popular because of the numerous advantages they offer. These systems are modular, highly efficient, and the cost is relatively low, making it easy to scale up. The battery, however, is not commercially widespread as lithium-ion or lead-acid batteries. One of the major reasons for this is not having enough ageing studies for this comparatively recent technology and lack of battery specific unique optimization techniques.

This thesis focuses on the two important issues in batteries, namely capacity decay and charging methodology. The former is essential in the longevity and latter in short term efficiency and the rate of ageing. These are some of the key aspects that are less researched, but important in making the commercial implementation of Vanadium Redox flow Battery (VRB) viable. The capacity loss due to vanadium ion diffusion was simulated for multiple cycles of operation and the effect that flow rate has, on concentration flux in the cell was investigated. The concentration difference between two half cells is one of the major reasons for species crossover. As a consequence of diffusion, the charge transfer current density in the electrode varies. The relationship between charge transfer current density and the concentration of one species of vanadium was analysed at different temperatures. Further, the parameter dependence was analysed during the charging process of VRB for a system-aware building, which has distributed sources of energy production and amenable to flexible load scheduling. Preliminary studies on multi-modal VRB

charging characteristics was done using an equivalent circuit model. The normalized energy and time efficiencies were studied for their operation in buildings. The results obtained show that there is a trade-off between the energy capacity and the charging time, depending on the charging current and flow rate.

The concentration change of different species of vanadium ion was modelled with temperature influence for each of these vanadium ion variants. The concentration change of vanadium electrolyte was simulated for different temperatures. The change in capacity of VRB was calculated for different temperature profiles and the total loss was partially contributed by intrinsic loss and partly due to diffusion. It was also observed that the difference in the loss at different temperatures was higher during the initial 50% of the total life cycle and stabilizes as it proceeds. At the end of 200 cycles, the capacity loss at 40°C was higher (14.23%) than that of 30°C (13.37%) and 20°C (12.67%) of which, a major part was contributed due to diffusion in the first 100 cycles of operation. Further, an extended dynamic model of the vanadium ion transfer was developed, in which, the effect of temperature and transfer of bulk electrolyte across the membrane was included. The model was used to simulate capacity decay for a range of different ion exchange membranes that are being used in the VRB. The model was made more comprehensive by including the effect of bulk electrolyte transfer. A volume change of 19% was observed in each half-cell for Nafion 115 membrane based on the simulation parameters. The effect of this change in volume directly affects concentration, and the characteristics were analysed for each vanadium species as well as the overall concentration in the half-cells.

Following the initial feasibility study on multi-modal charging, a more detailed analysis of charging methodology and a profile based charging optimization for VRB was proposed. Individual over-potentials and the losses due to the pump were separately modelled for accuracy. A fuzzy logic controller was used to uti-

lize the normalized loss values and the state of health of VRB from earlier studies on ageing to provide an optimal value for current and flow rate for the selected profile. The optimization was done in real-time to include flexibility of control due to external factors like temperature, humidity, etc., which can be added as a parameter based on the operator requirement. Three modes were proposed in this study namely, autonomous, time bias and energy bias. These modes, however, are a non-exhaustive fragment of the many control modes that can be achieved.

Graphical Abstract

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Nomenclature

Symbols

$\Delta\Pi_{osmotic}$	Change in osmotic pressure between half cells	Pa
δ_m	Membrane thickness	m
Δp	Pressure drop	N m ⁻¹
Δt	Time taken for one iteration	s
ΔV	Change in volume after each cycle	dm ³
η_{act}	Activation overpotential	V
η_{conc}	Concentration overpotential	V
η_{ele}	Electronic potential	V
η_{ion}	Ionic overpotential	V
η_{ohm}	Ohmic overpotential	V
μ	Dynamic viscosity	kg s ⁻¹ m ⁻¹
ϕ_d	Diffusion flux	mol m ⁻² s ⁻¹
ρ	Electrolyte density	kg m ⁻³
A_e	Electrode surface area	cm ²

A_m	Membrane surface area	dm^2
c_0	Concentration of reactant at electrode surface	mol L^{-1}
c_2	concentration of V^{2+} ions	mol L^{-1}
c_3	Concentration of V^{3+} ions	mol L^{-1}
c_4	Concentration of V^{4+} ions	mol L^{-1}
c_5	Concentration of V^{5+} ions	mol L^{-1}
c_b	Bulk electrolyte concentration	mol L^{-1}
c_f	Fixed acid concentration	mol m^{-3}
c_{H^+}	Concentration of H^+ ions	mol L^{-1}
D_2	Diffusion coefficient of V^{2+} ions	$\text{dm}^2 \text{ s}^{-1}$
D_3	Diffusion coefficient of V^{3+} ions	$\text{dm}^2 \text{ s}^{-1}$
D_4	Diffusion coefficient of V^{4+} ions	$\text{dm}^2 \text{ s}^{-1}$
D_5	Diffusion coefficient of V^{5+} ions	$\text{dm}^2 \text{ s}^{-1}$
D_e	Effective diffusion coefficient	$\text{dm}^2 \text{ s}^{-1}$
d_f	Mean fiber diameter	m
D_{H^+}	Diffusion coefficient of H^+ ions	$\text{dm}^2 \text{ s}^{-1}$
D_i'	Temperature dependent diffusion coefficient	$\text{dm}^2 \text{ s}^{-1}$
E_0	Formal potential	V
E_a	Activation energy	J mol^{-1}

F	Faraday constant	C mol ⁻¹
i_{sh}	Shunt current	A
i_{tot}	Charging/discharging stack current	A
J	Current density	A cm ⁻²
j	Exchange current density	A cm ⁻²
k_{ϕ}	Electrokinetic permeability	m ²
k_p	Hydraulic permeability	m ²
L	Length	m
P_{pump}	Pump power loss	W
Q	Volumetric flow rate	m ³ s ⁻¹
r_c	Hydraulic radius	m
R_m	Membrane resistance	Ω
r_m	Local resistivity of the membrane	Ω m ⁻²
R_{sh}	Shunt resistance	Ω
R	Gas constant	J K ⁻¹ mol ⁻¹
T	Temperature	K
v_m	Electrolyte velocity across the membrane	m s ⁻¹
V_n	Electrolyte volume in negative half-cell	dm ³
V_p	Electrolyte volume in positive half-cell	dm ³

V	Total electrolyte volume	dm^3
w	Width	m
α_a	Anodic charge transfer coefficient	
α_c	Cathodic charge transfer coefficient	
ϵ	Electrode porosity	
λ_x	Empirical coefficient	
f_c	Friction coefficient	
K_{ck}	Carman-Koenzy constant	
K_{fo}	Resistance coefficient of channel form	
k_{mi}	Minor loss coefficient	
k_p	Permeability coefficient	
n_{cell}	Total number of cells	
z	Charge number	

Scripts

+ve	Positive half cell
-ve	Negative half cell
2	V^{2+} ions
3	V^{2+} ions
4	V^{2+} ions

5 V^{2+} ions

e Electrode

ely Electrolyte

H^+ Hydrogen ions

m Membrane

Abbreviations

OCV Open Circuit Voltage

SOC State Of Charge

VRB Vanadium Redox flow Batteries

CC Constant Current

CV Constant Voltage

CCU Current Control Unit

FCU Flow Control Unit

FLC Fuzzy Logic Controller

A Autonomous mode

E Energy bias mode

T Time bias mode

Chapter 1

Introduction

1.1 Background and Motivation

1.1.1 Understanding the Need to Store Electrical Energy

Technological advancement in the electrical power sector has given rise to various improvements in electrical grid infrastructure. The future is about to face great changes by the inclusion of revolutionary technologies such as smart grid, micro grid, etc. Furthermore, the penetration of renewable energy is increasing rapidly. To make all these changes practically feasible, a large scale energy storage system is inevitable. Large scale energy storage also opens up many avenues for enhancement of power quality and reliability of the electric grid [1].

Grid Infrastructure Support

Energy storage systems are a practical solution for enhancing reliability in utility grids. Some of the major areas, where energy storage systems aid the grid infrastructure are, voltage stability, frequency control, upgrading the capabilities of transmission line, and load levelling, thereby increasing the reliability and power

quality [2].

Energy storage systems can support the grid operation in several ways such as:

- Smoothing transient power bursts on the distribution network due to sudden demand from loads like elevators and electrified railways.
- Efficient utilization of capacity of generation unit and deferring generation capacity upgrade.
- Lessen the impact of overload in transmission lines by down streaming the power during low demand and providing the stored power during congestion.
- Consumer level reliability by providing protection against a complete power outage by transferring stored energy during blackouts or providing time for an orderly shut-down
- Energy storage systems also cater to the power quality requirements of the grid architecture by mitigating voltage and frequency variations, power factor improvement, and harmonic reduction.

Renewable Energy Integration

Renewable sources of energy are gaining momentum and the reliance on fossil fuels is reducing as people realize the limitation of fossil fuel resources and their environmental impacts. Wind and solar energy are the most popular choices because of their ease of generation and resource abundance. These sources, however, are intermittent and other conventional utility power plants are needed to support their widespread usage. It is estimated that for a wind power installation, about 2%-4% of balancing power is needed for every 10% of penetration for stable operation. Thus, the system operation becomes more complex with higher penetration [2]. A

high capacity energy storage system with long operating time becomes a necessity in realizing the true potential of renewable energy integration [3, 4].

1.1.2 Batteries for Energy Storage

Battery energy storage systems (BESS) stores electricity in the form of chemical energy. Secondary batteries are those that can support multiple charge/discharge cycles. Secondary batteries have high round-trip efficiency, rapid response times, and very low loss due to self-discharge, when compared to other methods of energy storage [5–7]. Further, the time taken for construction of batteries is lesser with an ability to be produced in bulk quantities. Modularity, and high power and energy densities also make BESS more convenient and compact for most of the applications [8]. That being said, there are still a few challenges in integrating energy storage systems to the power grid. Firstly, there is no widespread standardization of the types of batteries being connected to the grid which gives rise to multiple smaller reliability issues affecting smooth power flow. Secondly, the batteries act as individual nodes satisfying local demand making them poorly optimized for the entire grid. This however will be eliminated with the implementation of smart grid technologies where all the components are optimized for the best efficiency for the overall grid. A comparison on the technical maturity [5] and installed capacity [9] for different batteries are given in Fig. 1.1.

It can be seen from Fig. 1.1 that flow battery is one of the most promising technologies progressing towards technological maturity, having a considerable share on installed projects. With low species crossover issues, vanadium redox flow batteries is considered to be a prominent contender in providing energy storage solutions compared with other flow batteries. In this battery technology, there is no trade-off between the energy rating and the power rating. Hence it can be used in various kinds of applications, where the requirements are different [10–12]. Even though

Figure 1.1: Comparison of different battery technologies
 (a) Technical maturity² (b) Installed capacity³

VRB has significant properties, which make them highly suitable for large scale energy storage, it is still in its nascent stage. It is necessary to bring down the capital cost of the system and improve the energy density to make VRB highly competitive in the energy storage market [13, 14]. Commercialization of this technology will play a very important role in renewable energy penetration. With focused research on specific topics relating to VRB, it could be made more viable thereby creating avenues for enhancement of grid electricity [15–17].

Unique features of VRB

- *Independent Energy and Power Ratings:* Conventional batteries have the need to compromise between their energy and power ratings as they are interdependent. For a flow battery, the size of electrolyte tank decides the energy rating and the power rating depends on the number of cell stacks. This is an important feature as the ratings can be upgraded separately as per the needs.
- *Electrolytes managed at system level:* In flow batteries, as the electrolytes are stored in separate tanks, the regular inspection is less time consuming.

²Image reproduced with permission from [5]

³Image reproduced with permission from [9]

In conventional batteries the electrolytes are managed at cell level, which implies the inspection must be carried out in each cell and that can be time consuming.

- *Relatively long cycle life:* Flow batteries have a relatively long life cycle as the active material in such batteries is the electrolyte that does not degrade. Further, the components can be separately replaced unlike conventional batteries, where the solid electrodes degrade due to mechanical and thermal stress with cycling, rendering the battery useless.
- *Easier Operation in utility environment:* Flow batteries are less prone to conditions such as overcharge, undercharge, and partial state of charge cycling thereby making its operations much easier in utility environment.
- *Negligible Standby Loss:* As the charge carrying electrolytes are stored in separate tanks, there is a very little self-discharge during prolonged gaps in use.
- *Active Thermal Management:* In VRB, the need for an external cooling system is eliminated as the flowing electrolyte itself acts as a coolant. This in turn increases the life of the electrochemical components in the system.

Considering these favourable characteristics of batteries as a means of large scale energy storage, specifically VRB, the motivation of this work is to identify and analyse some key areas of the battery, which have not been previously studied or in its nascent state, thereby enhancing the overall understanding of the technology to provide a comprehensive solution in terms of grid scale energy storage.

1.2 Objectives

With the motivation discussed in the previous section, the objectives of this research study are as follows:

- Conduct a preliminary analysis of capacity decay and multi-modal charging optimization in VRB.
- Investigate the effect of temperature in capacity decay for operation of VRB with different commercial membranes.
- Investigate the role of bulk electrolyte transfer in affecting the capacity loss in VRB.
- Development of a comprehensive capacity decay model for VRB incorporating the effect of temperature and volumetric transfer.
- Development of a real-time charging algorithm for VRB with flexible operator control through profile dependent optimization.

1.3 Major Contributions

Based on the objectives, a research work has been conducted and reported in this thesis. The major contributions of this thesis are as follows:

1. The capacity decay over the lifetime of a flow battery has been investigated through simulations. The relationship between flow velocity and the concentration flux is computed. The variation in concentration flux is analysed for different concentrations and the influence of concentration depletion on the charge transfer current density on the positive electrode of the battery is examined.
-

2. The effect of temperature is introduced into an existing model to depict the influence of temperature on change of concentrations of various species of vanadium ions due to diffusion and the resulting side reactions that occur in the half cells. The effect of temperature on capacity decay is studied for Selemion CMV, Nafion 115, and Selemion AMV membranes. Temperature affected intrinsic losses and diffusive losses are further studied for the commercial Nafion 115 membrane.
 3. Bulk electrolyte transfer phenomena due to ion diffusion is studied for VRB. A comprehensive model is developed for simulation to study the implications of electrolyte transfer in capacity decay due to change in concentrations of vanadium ions. The volumetric change due to the osmotic pressure difference between the half-cells and ionic drag of the water molecules across the membrane is studied. A 19% change in volume is observed due to the bulk electrolyte transfer phenomena with a 0.5% tolerance for the temperature change. An overall capacity decay due to diffusion for Nafion 115 membrane is observed as 13.8% with 2% tolerance for the temperature difference.
 4. Multi-modal charging characteristics of Vanadium Redox Flow battery is investigated for operation in buildings. An equivalent circuit model of the VRB is developed to study the voltage curves at different scenarios. Different modes of operation are analysed from which, the best mode can be chosen by the system based on the requirements. Energetic and temporal characteristics are studied for the proposed modes by analysing their normalized efficiency values. The battery operation with individual over-potentials and the losses due to the pump operation is been modelled to facilitate current and flow rate control. The model accommodates the real-time change in intrinsic losses due to the input parameters. Current state of health of the battery
-

is considered for computing the optimal current and flow rate input. A fuzzy logic control is established to include a real-time control of operator profile based charging. The battery performance is studied for the three proposed modes of operation, namely Energy bias mode, Time bias mode, and Autonomous mode.

1.4 Organization of Thesis

In chapter 1, a brief description of energy storage in current scenario is provided with the motivation and objectives to conduct this research work. The major contributions are introduced along with the organization of this report.

Chapter 2 briefly reviews the research in the field of energy storage, specifically vanadium redox flow batteries to give a background for this work. The review of past and present research related to capacity decay and charging protocols for vanadium redox flow batteries is also discussed.

In chapter 3, an algorithm to study capacity decay is developed and the effect of capacity decay over the lifetime of the flow battery is investigated through preliminary simulations. The variation in concentration flux is analysed for different concentrations of V^{5+} species. Charge transfer current density is identified as a parameter that is affected by the transport of vanadium ions across the membrane. The influence of concentration depletion on the charge transfer current density on the positive electrode of the battery is examined. A feasibility analysis on multi-modal charging in VRB is also explored. A simple equivalent circuit model is developed to study the effects of operation of VRB in different sets of fixed current and flow rate pairs. Normalized energy and time efficiencies are studied for different input parameters within the operable region.

In chapter 4, a dynamic model is developed to depict the influence of temper-

ature on change of concentrations of various species of vanadium ions due to the diffusion and the resulting side reactions that occur in the half cells. The effect of temperature on capacity decay is studied for three different membranes. The change in concentration of species of vanadium ions is investigated for three different membranes. Categorical analysis of loss distribution due to temperature for Nafion 115 membrane is studied.

Bulk electrolyte transfer across the membrane is studied for a flow battery cell with Nafion 115 membrane in chapter 5. A modified ion diffusion model is developed to include the effects of change in volume due to electrolyte transfer. Change of osmotic pressure between the two cells, concentration change of different ions, change of volume in the electrolyte tanks and as a result, change in capacity of the battery is discussed.

In chapter 6, a real-time profile based charging optimization is proposed in order to enable flexible operator control for VRB. An electrochemical model to incorporate the change in real-time current and flow rate is developed. Charging control is achieved with the knowledge of intrinsic losses, pump power loss, and state of health of the battery. Dependence of the losses on input parameters are analysed and fuzzy logic controller is used to set the appropriate optimal values of current and flow rate.

Chapter 8 concludes this thesis with a comprehensive summary and recommendations for future research in this area.

Chapter 2

Literature Review

In this chapter, various battery energy storage systems are introduced and a literature review on the operations, capacity decay, and charging protocols for vanadium redox flow batteries are presented.

2.1 Battery Energy Storage

The use of battery based energy storage for electricity, dates back to the time before AC power system was demonstrated by Nikola Tesla. Many battery technologies were invented since then and efficient ways to use the combination of DC and AC power are being continuously proposed. With a growing interest in renewables, electric vehicles, and the need for energy independence for consumers from large blackouts, energy storage is more relevant now, than ever. Some of the most prominent battery technologies for large scale energy storage are listed below.

- *Lead-acid batteries* are one of the oldest and most mature rechargeable batteries. It consists of a lead anode sponge and a lead acid cathode with sulphuric acid solution as the electrolyte. It has several advantages such as simple manufacturing process with low cost and an acceptable cycle life.

However, the battery uses heavy metal and the cost per unit rises in proportion to scale making [18, 19].

- *Lithium-ion batteries* are the most popular and widespread owing to their high energy density, good cycling efficiency, and low self-discharge. They are predominantly phosphate or cobalt based. Some of the disadvantages are, limited lithium resource, high cost, and concerns with safety, requiring a sophisticated BMS [20, 21].
 - *Metal-air batteries* are compact and cheap alternatives for small scale usage. Zinc-air and Lithium-air are the two main variations with Zn-air being preferred due to their low material cost and environmental safety [22, 23]. The restrictions on scaling and low efficiency are the major drawbacks [24].
 - *Sodium-Sulfur battery* is the most successful high temperature battery. It has high efficiency, an excellent energy density, long cycle life, and low material cost. Some of the restrictions stalling the applicability of this battery are, the need to maintain high temperature, operator safety, and the need to isolate the system from atmosphere, as pure sodium causes instant explosion on contact with air [25, 26].
 - *Flow batteries* are similar to conventional batteries in terms of reaction methodology. The electrolytes are, however, stored separately in tanks and are made to flow through the stack during operation and hence the name. There are several types of flow cells being researched. All vanadium, Iron-Chromium, Zinc-Bromine, Zinc-Cerium, and Bromine-Polysulphide are a few of the popular options. There are several advantages of flow batteries such as decoupled power and energy capacity, negligible maintenance cost, ability to be deployed in massive scales, and negligible self-discharge [27, 28]. Some of the
-

disadvantages are, the complexity of system with requirement of pumps and low energy density. The technology is still evolving with improved methodologies in tackling the disadvantages making it one of the most promising technologies for large scale energy storage [27–29].

2.2 All Vanadium Redox Flow Batteries

The all-vanadium redox flow battery (VRB) is the most researched and successful among other flow batteries. It was initiated by Maria Skyllas-Kazacos and co-workers at the University of New South Wales (UNSW) in the year 1984. A historical overview of the developments in flow batteries is shown in Fig. 2.1.

Figure 2.1: Historical overview of the developments in Redox flow batteries

An all-vanadium redox flow battery system consists of one stack, two electrolyte tanks, pumps, and hydraulic pipes as shown in Fig. 2.2. The stack is assembled by a series of paralleled single cells that are constructed by electrodes, membranes, and current collectors. The electrolytes are stored in separate tanks and they are pumped into the cell stack when the battery becomes operational. The ion exchange membrane should ideally allow only H^+ ions to pass through, however,

due to concentration difference in the two half-cells, some vanadium ions tend to crossover causing self-discharge.

Figure 2.2: (a) Typical VRB Schematic, (b) VRB stack components⁴

The VRB stack consists of many cells with solid electrodes in contact with electrolytes. The two half-cell electrolyte tanks are separated by an ion exchange membrane. Electrolytes are stored in two separate electrolyte tanks, and are pumped into the cell with two external pumps. The total amount of energy stored in the system is determined by the concentration of the vanadium species in each electrolyte and by the volume of the reservoirs. The charge and discharge reactions occur on the surface of the solid electrodes and the total power discharge capacity is decided by the number of cells in a stack. Fig. 2.2 shows the schematic of a stack structure in VRB.

The capability of vanadium to exist in 4 oxidation states namely V^{2+} , V^{3+} , V^{4+} , V^{5+} , is exploited in the design of VRB. During the process of charging, V^{3+} is reduced to V^{2+} by gaining an electron and V^{4+} is oxidized to V^{5+} by losing an electron. This reaction is reversed during the discharging process [31]. The vanadium electrolytes, in addition to the vanadium ions, contains sulphate ions

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and protons playing a key role in satisfying the law of conservation of mass. The complete ionic equations that happens in the cell is represented in Fig. 2.3

Figure 2.3: Ionic equations in VRB during charging⁴

As it can be observed from earlier schematics, pumps are crucial in any flow battery system, to circulate the electrolytes between the storage tanks and the active cells. This pump flow gives rise to pump power losses. Multiple cells are typically lumped to form a stack and to constitute a kW/MW scale module, these stacks are connected in parallel and series combinations. For the total pressure drop to be reduced, all the inlet and outlet pipes are generally connected in parallel. This path creates an electrical pathway through the electrolytes in the pipe for shunt current to flow due to the voltage imbalance between the cells.

There is a trade-off between pump power loss and shunt current loss due to their contradicting nature. Shunt current can be minimized by using longer and thinner pipes, thereby increasing the electrical resistance. This, however, would give rise to increased pressure drop and hence the pump power losses associated with it. Active research is being carried out in this area to find an optimal sizing of hydraulic circuit [32].

Figure 2.4: Typical hydraulic circuit in a 3x4 VRB setup⁵

Considering the complexity in flow arrangement and the pump setup unique to flow batteries, it is important to understand the interconnection of VRB with external sources/loads. A typical VRB/grid interconnection is shown in Fig. 2.5.

Figure 2.5: Power flow in VRB⁴

In this example, it can be seen that the stack is connected to the external circuit by means of a bi-directional AC/DC converter. The DC voltage is stepped down by a DC/DC converter to support the pump. In some cases, there can be a secondary DC/DC converter between the stack and the primary bidirectional AC/DC converter in case of voltage mismatch between the stack and the primary

⁵Image reproduced with permission from [32]

converter.

2.3 Ageing and Capacity Decay

Battery ageing is a major problem that the electrochemical energy storage industry is facing. In this section, ageing studies for lithium-ion and lead-acid batteries are reviewed, followed by the progress in this area for vanadium flow batteries.

Ample research on the ageing of lead-acid batteries have been carried out owing to its technological maturity. Ageing mechanisms, failure prognostics, and service life of lead-acid batteries are studied in detail in the 90's [33, 34]. In the year 2004, Ruetschi published a paper on lead-acid batteries' ageing mechanism and service life. Major processes in lead-acid battery that causes ageing are formation of lead-sulphate in the active mass, active mass degradation on the positive side, water loss, short circuits, and anodic corrosion [35]. Many of these processes are irreversible and hence causes permanent damage to the battery.

Lithium ion batteries have a complex ageing mechanism as there are multiple origins to be attributed for the capacity and power fading. These batteries suffer in two major areas due to ageing, namely, reduction in storage capacity and performance degradation due to cycling. In 2004, Sarre *et al.* published their work on the ageing of lithium-ion batteries [36]. Storage and use according to the application specific charge/discharge profile were considered as the two cases in Sarre's paper. It was studied that the ageing phenomena arises from active material reactions at the electrolyte-electrode interface, active materials' self degradation due to cycling, and degradation of non-active components due to ageing.

The rate of ageing depends on the reaction kinetics of different systems depending on their material reactivity, operational temperature, impurities, operating profile, design considerations, and the manufacturing process. In a paper from Broussely

et al., it was described that ageing is a result of reversible material degradation coming from phase transformation that occur during lithium insertion. Hence, a highly reversible positive material is used for the battery in their studies.

Figure 2.6: Capacity decay in Li-ion battery⁶

Further, the sudden rate change (inflexion) in capacity decay is discussed. A typical capacity decay curve for two different electrolytes are shown in Fig. 2.6(a) and a rapid decline of capacity in lithium ion pouch cells is shown in Fig. 2.6(b). The key to overall cell stability was described as the stability of the passivating layer and the link to high reactivity of lithiated carbon.

Vetter *et al.* studied the ageing mechanism of anodes and cathodes separately, in detail. In this work, methods to improve the retention of capacity were described along with the reasoning for the same. In comparatively recent works by Dubarry *et al.*, electrochemical techniques for identifying cell degradation were studied [38, 39]. Two large format lithium ion cells were analysed to investigate the origins of capacity loss along with the study on degradations at higher temperature [40]. There is continuous progress in studying the ageing process in Li-ion batteries [41].

⁶Image reproduced with permission from [37]

Capacity Decay in VRB

Capacity decay investigation for flow batteries began recently in comparison to other batteries. Several device level studies on ageing [42] as well as models have been developed to study the performance of VRB [43–48]. A dynamic model to study the capacity fade, however, was developed only in the year 2011 by Tang *et al.* [49]. In this work, capacity decay was modelled and studied for two cases, 1) with side reactions and 2) without side reactions. This work extends the simple charging and discharging mechanism in VRB to an ageing model by the inclusion of the ion kinetics across the membrane. This model however, is developed for a battery operating at a standard constant temperature of 25°C which limits the applicability in practical scenarios. In the year 2011, a transient flow battery model incorporating water transport and vanadium crossover across the membrane was reported by Knehr *et al.*. The transport mechanism was studied for charged species due to convection, diffusion, and migration. It was reported that the capacity loss has minimal effect on the efficiency of the cell from a 45 cycle simulation [50].

This work was further extended by Ertan *et al.* from the same research group as Knehr *et al.*, to study the species transport mechanism in s-Radel and Nafion 117 membranes leading to capacity loss [51]. The results of this study indicates the importance of hydraulic and electro-kinetic permeability in evaluating membranes for VRB. It was also observed that, minimizing concentration imbalances in the half-cells will minimize the extent of capacity decay. It is necessary to have membranes with high ion selectivity. Various studies have been conducted in this field to facilitate the membrane to allow more protons and block vanadium ion crossover [52–55]. Operation of VRB under asymmetric current and its effect on capacity decay was studied by Agar *et al.* in a later research [56]. In this study, different charging and discharging currents were applied and their influence

on vanadium ion crossover was examined. It was shown that, the magnitude of electro-osmotic convection is increased by higher charging currents. Reduction of capacity decay was reported by operating the VRB with asymmetric current at the expense of increased ohmic losses and reduced voltage efficiency. These models however do not study the effect of ion diffusion due to the bulk electrolyte transfer at various temperatures and the osmotic pressure on the membrane due to this electrolyte imbalance and concentration change between the two half-cells.

2.4 Charging Protocols

Considering the number of different batteries and the multitude of applications that come along with them, having specific charging protocols are key to their efficient usage. Several charging methodologies for conventional batteries have already been proposed. The most commonly used protocol is charging the battery with constant current followed by constant voltage, to prevent over-charge. Charging protocols are important in improving the battery life, enhancing the operational efficiency and optimization to provide fast charging in batteries.

Figure 2.7: Typical charging voltage (a) and time (b) curves for different charging profiles⁷

⁷Image reproduced with permission from [61]

Numerous model based approaches have been reported in literature for lithium ion battery charging [57–59]. A typical charging curve with different charging profiles is shown in Fig. 2.7. Current is the primary control parameter in all these charging control techniques. Considering the maturity of lithium ion batteries in the market, it is interesting to see several papers still being published on the charging protocols of this battery [60]. A recent paper by Guo *et al.*, uses genetic algorithm for an optimal charging method for Li-ion batteries accommodating ageing consideration [61]. These papers have been incrementally advantageous to the optimization of charging process for lithium ion batteries. This techniques can serve as a case study and reference, but can not be directly implemented in other battery chemistries. Thus, it calls for unique charging algorithms for different types of batteries and VRB is both chemically and physically different from other mainstream battery technologies.

VRB Charging

Unlike conventional batteries, VRB has two primary parameters that affect the charging characteristics, namely charging current and flow rate. Comprehensive optimization of charging in VRB is an important area, which is yet to be explored. In this section, literature on individual optimization of current and flow rate for different requirements will be analysed.

Charging Current

It is evident that charging current affects the battery performance in terms of operational efficiency and time. From literature it can be observed that the coulombic efficiency is high, when VRB is charged with low current density [56]. The charging time and the long-term effect on the capacity decay is, however, low for charging with higher current. In [56], researchers studied the characteristics of capacity de-

cay at different charging currents and found out that there is an inverse relationship between capacity decay and charging current. This is due to the decreased rate of convective crossover of electrolyte at higher currents. Fig. 2.8 shows the effect of capacity decay at different currents and the typical charge/discharge curve for VRB at different current densities.

Figure 2.8: (a) Capacity loss at different currents⁸

(b) Typical voltage curve at different currents⁹

Figure 2.9: Current density vs. Fixed capital cost¹⁰

A recent finding reported by Moore *et al.* shows the relationship of operating

⁸Image reproduced with permission from [56]

⁹Image reproduced with permission from [62]

¹⁰Open access content from [63]

current density versus the fixed capital costs [63]. The rate of increase in costs is seen to be linear till 2000 mA cm^{-2} and there is a near-exponential increase of the costs beyond 2000 mA cm^{-2} (Fig. 2.9). The cost calculations are connected to the cost of individual components of the VRB stack and their deterioration with respect to current density. Different current densities in charging VRB can thus affect the cycling efficiency, time taken to charge, energy loss due to species crossover induced capacity decay and capital costs due to material degradation.

Electrolyte Flow Rate

Electrolyte flow rate in VRB has a great impact on the operation of the battery. Higher flow rates typically improve the performance of the battery in terms of efficiency as well as stored capacity. The drawback, however, is that it will result in higher power consumption of the pump reducing the overall efficiency. The need for determining an optimal flow rate is hence crucial for VRB. Ma *et al.* published their work on devising an optimal flow rate for VRB in the year 2011 [64]. Ma *et al.* fabricated a kW class stack and analysed the charge/discharge operation under different currents and flow rates leading to the development of an optimal strategy of electrolyte flow rate.

¹¹Image reproduced with permission from [66]

Figure 2.10: (a) Optimal flow rate for different scenarios¹¹(b) Efficiencies at different flow rates⁸

The hydraulic behaviour along with thermal constraints was analysed by Xiong *et al.*, where a comprehensive thermal/hydraulic model was developed and the effect of flow rates on the stack level energy efficiency and overall system efficiency were studied. In this work, they reported an increased energy and battery efficiency of approximately 1.23% for the proposed system. The efficiencies at different flow rates is shown in Fig. 2.10b and the optimal flow rate at different state of charges and current densities are reported, as shown in Fig. 2.10a.

Concentration over-potential as a function of flow rate was modelled and analysed for a 40 cell stack by Tang *et al.* [65]. It was reported that, premature voltage cut-off occurs due to an increase in concentration over-potential. High flow rate shows a reduction in concentration over-potential, but affects the efficiency by increased pump power loss. Further, for the proposed stack, variable flow rates are found to deliver better results than constant flow rate. This work gives a detailed overview through modelling and simulation on the effect of flow rate in VRB. The paper however does not discuss about the implementation of a real-time control of flow rate and current, so that optimal values can be calculated and applied to the battery at different time points during the operation. Pulsating electrolyte flow

is another recent development in this area, slated to reduce more than 50% of pumping energy while maintaining more than 80% energy efficiency.

2.5 Summary

VRB is expected to be a viable solution for widespread, large scale energy storage. The suitability of its application in a grid infrastructure can be realized from the various unique operational features explained in this chapter. Even though there are multiple deployments around the globe, it is evident that the battery is not mature when compared to lithium-ion and lead-acid batteries. The background on two focus areas namely, capacity decay and charging optimization have been discussed for other batteries along with the review of progress in that direction for VRB.

Chapter 3

Capacity Decay and Multi-modal Charging

3.1 Introduction

Two of the major research areas in batteries are, investigation of the state of health and the state of charge. In this thesis, a fragment of the bigger picture is taken from these areas to investigate the effect of temperature and electrolyte transfer in affecting the state of health of the VRB, followed by a proposal of a charging methodology to suit its unique features. This chapter serves as the preliminary study to investigate the feasibility to conduct further research in the above mentioned topics.

For VRB, The electrolyte is considered to have a theoretically indefinite life since both half-cells contains vanadium ions and thus, it reduces contamination due to diffusion. However, diffusion/crossover of vanadium ions from one half-cell to the other causes degradation of capacity of the battery. This capacity decay due to ion-diffusion can be overcome by timely re-balancing of electrolyte [67,68].

In cell reaction, the V^{4+} ions are oxidized to V^{5+} during charging and release an electron. During discharge, V^{5+} ions accept an electron and are reduced to V^{4+} . The proton (H^+) is passed through the semi-permeable membrane. Similar redox reactions take place, where V^{3+} is reduced to V^{2+} while charging, and V^{2+} is oxidized to V^{3+} during discharge [45]. The electrolytes are stored in separate tanks and they are pumped into the cell stack, when the battery becomes operational. The ion exchange membrane ideally allows only H^+ ions to pass through, however, due to concentration difference in the two half-cells, some vanadium ions crossover and this causes self-discharge.

The end of life for VRB have not been clearly defined in literature, considering its ability to recover from capacity fade. However in practical scenario, the capacity at which the VRB becomes unusable economically or for a smooth operation is considered as its end of life. Currently, most of the studies on capacity decay in flow batteries concentrate on the chemical and materials' aspect of the battery. Several improvements are regularly suggested, one of which, is employing a membrane with high selectivity and proton permeability [52–55]. Also a few studies discuss the impact of charging/discharging current on capacity degradation [56]. This problem can be overcome by designing a battery control system to perform regular remixing of electrolytes. However, such a system will only be able to reclaim the capacity loss due to ion diffusion. It will not be able to regain the capacity lost due to gas evolution and side reactions [56].

The second section of this chapter focuses on the charging methodology for VRB. The most commonly used battery algorithms are Constant Current - Constant Voltage (CC-CV), pulse charging, and multi-stage current charging. The efficiency of the battery is highly dependent on the charging technique adopted [88, 89]. Unlike other batteries, VRB has control over flow rate of the electrolyte in addition to current control. A typical VRB consists of two electrolyte tanks on either side,

two half-cells separated by an ion exchange membrane and pumps to circulate the electrolyte from the tank to the cell, and vice versa. The reduction and oxidation (redox) reactions take place inside the cell. An all-vanadium battery is considered, where all the active species are vanadium ions at different oxidation states. The flow rate is controlled by the electrolyte pump. A small amount of power is lost in the pump operation in spite of which, the performance is still comparable if not better than other large scale electrochemical energy storage technologies. Thus considering the inherent complexity of the battery, it is important to model and analyse the effect of current and flow rate control during the charging process.

3.2 Capacity Decay

The average life of flow batteries is around 20 years, considering a regular and uniform charge/discharge pattern. Several commercial establishments have started developing state of the art batteries for specific applications, one of which is, developing large scale batteries with long life for grid scale implementation. Being a large scale and static energy storage option, VRB completely fits this requirement. Capacity fading is one of the important issues that have to be considered when installing a large scale battery system. The importance is because of the significant difference it makes to the operation and the cost of the system for a long term operation. Being a considerably new technology, it is necessary to perform life cycle simulation analysis to predict the behaviour of redox flow batteries on a long run.

This issue of capacity decay was not considered in flow batteries for a long time. Even though flow batteries are considered to have a very low self-discharge, it is necessary to study its effect and impact. Capacity decay occurs due to various reasons such as ion diffusion, side reactions, and gas evolution. During long term

operation of VRB, disequilibrium of concentration in the vanadium species was observed. Due to the electric field between the two half cells of VRB, the vanadium ions are transported across the proton exchange membrane. In a Vanadium flow battery, the vanadium ions exist in four different states of oxidation namely V^{2+} , V^{3+} , V^{4+} (VO^{2+}), and V^{5+} (VO_2^+) [69, 70]. In this chapter, the effect of ion diffusion, which leads to depletion in the concentration of the electrolyte is discussed in detail.

To analyse the effects of capacity decay, it is necessary to study the operation of VRB and incorporate the capacity decay effect in it. The following parameters were assumed for the purpose of simulation:

- Overall concentration of the vanadium species was taken as 1.5 mol/dm^3 .
- A constant charging and discharging current density of 60 mA/cm^2 and a formal potential of 17 V .
- The charging and discharging resistances (assumed as constant) are taken as 0.015Ω and 0.02Ω respectively.

Figure 3.1: Block diagram for capacity decay estimation

Figure 3.2: Charge/Discharge cycle with capacity decay

Figure 3.2 is obtained based on the capacity decay estimation as shown in Fig. 3.1 to study the capacity decay in Vanadium Redox flow Batteries. From Fig. 3.2, it can be inferred that there is a significant drop in the time taken for charging or discharging after a number of cycles. This difference can be directly attributed to the reduction in the capacity of the battery. The comparison of capacity loss due to different rates of concentration depletion was studied and the results are shown in Table A.1 and Fig. 3.3.

The algorithm based on Fig. 3.1 was used for a simulation of a number of charge/discharge cycles to examine capacity decay in VRB, where charging and discharging are shown in different colours. Initial values are provided such that the cycle begins with a charging curve. The simulation was performed for 10000 cycles with a maximum voltage of 20.25 V and a minimum voltage of 16.75 V. The charge/discharge cycle shown in Fig. 3.2 shows the Voltage vs. Time characteristics with a concentration depletion assumed at 0.000015% per cycle.

From Fig. 3.3, it can be observed that there is a considerable percentage of capacity decline at the end of 10000 cycles. Moreover, it can also be seen that the rate of capacity decay increases along the time scale, which is crucial to determine the time for electrolyte balancing.

Figure 3.3: Capacity decay for different rates of diffusion

3.2.1 Concentration Flux and Capacity loss

Being one of the many factors contributing to the diffusion of vanadium ions across the membrane, the concentration gradient between the vanadium species plays a significant role. Due to the concentration difference and the velocity of electrolyte, concentration flux is present near the membrane. The amount of vanadium ions will be dependent on the amount of concentration flux present near the membrane, and hence, it is important to study its characteristics. A modified Nernst-Planck equation was used to understand the relationship between the flow velocity of the electrolyte and the concentration flux [44, 66]. For the purpose of simplicity, only the V^{5+} species of vanadium was considered for the analysis.

The total concentration flux is given by:

$$Flux = -D_{eff} \nabla c - \frac{zcD_e}{RT} F \nabla \eta_{ion} + vc \quad (3.1)$$

where D_e is the effective diffusion coefficient, which can be calculated from $D_e = \epsilon^{3/2} D_i$. ϵ is the porosity of the electrode, c is the concentration of the vanadium

species, z is the charge of species, η_{ion} is the ionic potential, v_m is the electrolyte velocity, and T is the temperature of the system. F and R are Faraday constant, and gas constant, respectively. The relationship of concentration flux with respect to the flow rate of the electrolyte was studied for different species concentration. The results are shown in Table A.2 and Fig. 3.4.

The relationship of concentration flux and flow rate is linear for a specific concentration, however, for higher flow rates the difference in the value of concentration flux for different concentrations is more significant, which is understandable, considering the mobility of ions in the electrolyte due to increased kinetic energy from the greater flow rate.

Figure 3.4: Flow rate vs. Concentration flux

3.2.2 Effect of Species Crossover

In a redox flow battery, the proton exchange membrane is responsible for separating the positive and negative half-cell electrolytes during the operation. The membrane should ideally let the hydrogen ions to pass through for balancing the reaction. However, this is not completely achievable and the vanadium ions crossover

from one half cell to the other. This leads to some self-discharge reactions, which reduces the available species vanadium in electrolyte for constructive cell reactions. The following are the prominent self-discharge reactions that are observed in VRB.

Positive half cell:

Negative half cell:

As shown in the reactions above, the vanadium ions react and thereby cause imbalance in both the half-cells since the rate of diffusion on each species of ion is different from others. This eventually causes a specific species of ion to get accumulated in one of the half-cell. The total capacity of the battery is defined by the minimum capacity of either of the half-cells, and hence the overall capacity of the battery is reduced during a period of time.

3.2.3 Charge Transfer Current Density

The diffusion of vanadium ions may also lead to a difference in the charge transfer current density of the battery. The value of charge transfer current density at the electrode of the half-cell is proportional to the concentration of the individual species of vanadium.

The over-potential η is given as the difference between the electronic and ionic over-potential along with the electrode potential.

$$\eta = \eta_{ele} - \eta_{ion} - E_{+ve/-ve} \quad (3.2)$$

The electrode potentials for the positive and negative electrodes can be deter-

mined by Nernst equation.

Positive electrode:

$$E_{+ve} = E_0 + \frac{RT}{F} (\ln c_5 - \ln c_4) \quad (3.3)$$

Negative Electrode:

$$E_{-ve} = E_0 + \frac{RT}{F} (\ln c_3 - \ln c_2) \quad (3.4)$$

Based on the above equations and an operational model of VRB proposed by Watt-Smith *et al.* [71], the charge transfer current density at positive electrode is given by:

$$j = A_e \epsilon F k_i \sqrt{(c_{4/2})(c_{5/3})} \sinh \left(\pm \frac{F\eta}{2RT} \right) \quad (3.5)$$

From Eqn. 3.5, the influence of the concentration of each species of vanadium in determining the value of j can be inferred. a is the volumetric surface area of electrodes, k_i is the rate constant of the reaction in the positive half-cell and c_i is the concentration of different species of vanadium ions and for this analysis we have considered the concentration of V^{4+} constant. The behaviour of the charge transfer current density for positive electrode with respect to the change in vanadium concentration at different temperatures was analysed and the results are shown in Table A.3 and Fig. 3.5.

The charge transfer current density varies linearly with the concentration and reduces with the decrease in concentration. The response for different temperatures is also comparable. The effect of temperature is not very prominent in affecting the charge transfer current density, but it plays a major role in capacity decay due to ion diffusion. A detailed study on this relationship will play an important role

Figure 3.5: Concentration vs. Charge transfer current density

for optimizing the battery control system for VRB.

3.3 Feasibility of Multi-modal Charging

The charging process of a Vanadium Redox Flow Battery (VRB) is studied for a system-aware unit, which has distributed sources of energy production and flexible load scheduling. One major advantage of flow batteries is that the energy and power components of the battery can be decoupled due to their modular nature. This gives VRB the benefit of easy scaling according to application demand.

The model used in this chapter is an extension of the simple equivalent circuit model proposed by Zhang Yu *et al.* [90]. The model consists of an open circuit potential, which acts as the Nernst potential dependent on the *SOC* of the battery. RC (Resistor-Capacitor) network is used to account for the static and dynamic losses, while the ion diffusion across membrane and shunt current are represented by controlled current sources in the equivalent circuit model. Pump power is predicted by a hydraulic model, which gives the real-time pump power losses affected by the required flow rate of the electrolyte.

Figure 3.6: Block diagram of the kW scale electrical model for VRB

3.3.1 Equivalent Electrical Circuit

An equivalent circuit model used for this study is shown in Fig. 3.7. The Nernst equation can be given as a function of the standard electrode potential, temperature and *SOC* of the cell.

$$E_{ocv} = E_0 + \frac{2RT}{F} \ln \left(\frac{SOC}{1 - SOC} \right) \quad (3.6)$$

where E_c is the open circuit potential of the cell, E_0 denotes the standard electrode potential of 1.39V. The terms R , T and F corresponds to gas constant, temperature, and Faraday constant respectively. The *SOC* of the battery indicates the energy level of battery at any point of time depending on the active species of vanadium ions available for discharge reaction. Thus, the cell *SOC* can be formulated as a function of the initial *SOC* based on the electrolyte in tank, bulk electrolyte concentration, flow rate and stack current as shown in Eqn. 6.2.

$$SOC(t) = SOC_{\text{tank}}(t) + \frac{i_{\text{tot}}}{2FQc_b} \quad (3.7)$$

As it can be seen from the block diagram in Fig. 3.6, *SOC* acts as variable input to the open circuit voltage calculation and to the hydraulic model. The flow rate and charging current are the controlled inputs supplied by the user. These input values are used for parameter estimation based on the characteristic relationship

between both to obtain parameter values, which are then used in the equations. The constants are introduced into the model by the initialization block along with the conditions under which, the model is expected to operate.

Figure 3.7: Equivalent electrical circuit model for VRB

The internal resistance is a function of cell SOC and the theoretically computed *SOC* may differ from actual *SOC*. A fitting coefficient a is added to correct this inaccuracy. The RC parameters R_1 , C_1 , R_{int} and coefficient a can be identified least square method and by making the equivalent circuit operate in dynamic and stationary zone as elaborated in [90]. The model is assumed to work in an operating temperature of 42.5 °C. The terminal voltage is thus given by:

$$E_{ter} = n_{cell} \times \left(E_0 + a \frac{2RT}{F} \ln \left(\frac{SOC}{1 - SOC} \right) \right) + I_{ter} R_{int} \quad (3.8)$$

The model has two branches, the electrical model characterizes the cell stack and the factors associated with it. The Nernst potential is modelled as a controlled voltage source with current sources representing diffusion losses and shunt current losses connected in parallel to it. Other fixed and resistive losses are modelled as *RC* networks.

3.3.2 Hydraulic Circuit

The hydraulic model accounts for the pump power losses as well as the losses due to the hydraulic architecture. The net energy is finally calculated after taking all these elements into consideration. The mechanical power required by the pump is given by,

$$P_{pump} = (\Delta p_e + \Delta p_c) Q / \eta_{pump} \quad (3.9)$$

where the total loss is the function of pressure difference in the stack, pressure difference due to the hydraulic connections to the stack, flow rate, and the efficiency of the pump. The individual pressure losses can be given by Eqn. 6.5 and Eqn. 6.6.

$$\Delta p_e = Q \frac{\mu L n_{cell}}{2.86 \times K_p r_c w} \quad (3.10)$$

where μ is the electrolyte viscosity, L is the length, K_p is the permeability coefficient, and r_c is the channel radius.

$$\Delta p_c = \rho g \left(h_{work} - \frac{V}{2g} \left(\frac{f_c L}{2r_c} + k_{mi} \right) \right) \quad (3.11)$$

where ρ is the electrolyte density, g is the acceleration due to gravity, V is the electrolyte volume, h_{work} is the work done by the system and k_{mi} is the minor loss coefficient. Table 3.1 gives the list of parameters used for this VRB system simulations.

Table 3.1: Parameters for sensitivity analysis of charging process²

Parameter	Value
Number of cells, n_{cell}	15
Dimension of half-cell (cm)	30 x 26 x 0.3
Permeability of porous electrode, k	$1.685 \times 10^{-10} \text{ m}^2$
Diameter of Manifold, D_{man}	2.54 cm
Height of Manifold for each cell, H_{man}	1.65 cm
Dimension of guide channel (cm)	32 x 0.1 x 0.3
Electrolyte density, ρ	1400 kg m^{-3}
Electrolyte viscosity, μ	$0.006 \text{ kg m}^{-1} \text{ s}^{-1}$
Electrolyte conductivity, σ	$0.2 \Omega^{-1} \text{ cm}^{-1}$
Internal cell resistance, r_{int}	$1.0 \Omega \text{ cm}^2$
Tank volume, V_{tank}	30 L

A typical battery consists of many cells stacked together and in practical cases there exists a potential gradient across this stack. The potential gradient gives rise to shunt current, which affects the coulombic efficiency of battery. One way to minimize the shunt current losses is by making the electrolyte guide channels narrow and having common manifolds thereby increasing the resistance of the electrolyte path [92]. Another important contributor to the cell level losses in a VRB is the vanadium ion diffusion across the membrane. Ideally, the ion exchange membrane should restrict the passage of active vanadium ion species across. This does not reflect in practical applications, where there is a considerable amount of vanadium ions that crossover to the other half-cell along with change in temperature [93]. This also serves as a major reason for all-vanadium redox flow batteries becoming widespread compared to other flow battery technologies. The model considered in this chapter, however, does not take the differential transfer of electrolyte across membrane resulting in volume change, which in turn leads to a reduction in battery

²Parameters were selected in accordance with [91]

efficiency and capacity loss over an extended time period [56,94].

3.3.3 Analysis of Results

In this section, the results obtained by simulation are showcased and analysed for its effect on the battery performance for buildings. Their electrical loads are well suited to be flexibly scheduled to optimize energy performance of its energy storage systems.

Figure 3.8: Charging curve at flow rate 2 L min^{-1}

Figure 3.9: Charging curve at flow rate 4 L min^{-1}

Figure 3.10: Charging curve at flow rate 6 L min^{-1}

The voltage curves during charging at different current densities and flow rates can be seen in Fig. 3.8, Fig. 3.9 and Fig. 3.10. The characteristics are analysed for current densities ranging from 80 mA cm^{-1} to 160 mA cm^{-1} at equal 20 mA cm^{-1} intervals. It can be noticed that the time taken for charging the battery with the same current, increases with the increase in flow rate.

Relationship between the current density and time is straightforward following an inverse proportionality. The result with respect to the current density is very obvious and follows the expected proportionality feature. A quick comparison can be made between the voltage curve with a current density of 80 mA cm^{-1} and that with a current density of 160 mA cm^{-1} . The charging time is reduced to nearly half in the latter. The effect of flow rate is, however, small but will have a significant contribution to the long term efficiency of the system. Considering huge energy consumers such as large data centres, it is important to optimize the working of its battery to suit its needs. The right flow rate and charging current should be chosen to have the optimum balance between energy efficiencies or charging times, which is then facilitated by appropriate computational load scheduling.

Figure 3.11: Normalized efficiency at 2 L min⁻¹ flow rate Figure 3.12: Normalized efficiency at 4 L min⁻¹ flow rate Figure 3.13: Normalized efficiency at 6 L min⁻¹ flow rate

The efficiency in terms of time as well as energy for each mode of operation is shown in Fig. 3.11, Fig. 3.12, and Fig. 3.13. The values are normalized

Figure 3.14: Dependence of Capacity on flow rate and current density

with the maximum value under each category. A decreasing trend for both the efficiencies can be observed as the flow rate increases. This can be attributed to the insufficiency of free ions for optimal electrochemical reactions to happen.

For a generic large system, where the battery is being operated on a daily basis, it is preferred to have maximum charging current density and lower flow rate. It can, however, be seen that the energy efficiency becomes lower as the current density increases. Hence, if there is no restriction on the charging time, the overall efficiency is better if a smaller charging current is used to charge the battery. Further, this comparison can serve as an indicator for choosing the right mode of operation, when there is a limited control on the system level. Where a mode is essentially a combination of a specific current and flow rate value.

The dependence of capacity on the flow rate and current density is shown in Fig. 3.14. This plot gives an inclusive perspective on how the parameters are interconnected. The capacity has minimum value when the flow rate and current density are maximum, which can be observed from the blue region. Considering the scale of large buildings, it is implied that energy efficiency would be of prime importance, which tends towards the dark orange patch of the plot.

3.4 Summary

In this chapter, preliminary studies on the effect of capacity decay and multi-modal charging are done. For different rates of vanadium ion diffusion, the decrease in the percentage of energy capacity was computed. The concentration flux has a direct impact on the magnitude of the rate of species crossover. Using modified Nernst-Planck equation, the relationship between flow velocity and the concentration flux was computed and plotted. The variation in concentration flux was analysed for different concentrations of V^{5+} species. Charge transfer current density was identified as another parameter that is affected by the transport of vanadium ions across the membrane. The influence of concentration depletion on the charge transfer current density on the positive electrode of the battery was examined. A linear association was observed and the charge transfer current density decreased with the decrease in the concentration. For different temperatures, the curve was plotted. It was found that, the effect of temperature has a greater impact on the overall capacity decay effect of the battery and it has to be studied in greater detail. In the next two chapters, an elaborate model of the VRB operation is developed and the effect of temperature and bulk electrolyte transfer on capacity decay due to ion diffusion is studied.

Further, multi-modal charging characteristics of Vanadium Redox Flow battery has been investigated for operation in buildings. Charging current and flow rate are the two key input parameters considered as they have the most significant effect on the performance. An equivalent circuit model of the VRB was developed to study the voltage curves at different scenarios. Energy efficiency and charging time serve as the indicators to determine the feasibility of operating in any given mode. From the results, it is observed that the energy efficiency decreases with the increase in charging current and with the increase in flow rate. The charging

time, however, decreases with the increase in charging current. Different modes of operation are analysed from which, the best mode can be chosen by the system based on the requirements. Control strategies specific to VRB charging are also being studied by which, the optimization can be further fine-tuned and modified based on application requirements. Later part of the thesis deals with a detailed model and implementation of profile based charging for VRB considering current, flow rate, and previous knowledge on capacity decay.

Chapter 4

Effect of Temperature in Capacity Decay due to Ion Diffusion

4.1 Introduction

One of main reasons that the vanadium redox battery is popular among the redox flow batteries is due to the fact that both the half cells of the battery employ different species of vanadium in the electrolyte. As a result, the problem of cross contamination during long term usage is eliminated and the lifetime of the electrolyte is extended by a significant amount [49]. Also, it was found that the environmental impact caused by the vanadium redox batteries is lower in comparison to other conventional ones like the lead acid battery [72].

A VRB has vanadium ions reacting in both half cells of the battery. The two half cells are separated by an ionic membrane, which lets H^+ ions to pass through to maintain charge balance. An ideal ion exchange membrane should limit the flow of vanadium ions through it and should possess good conductivity and chemical stability [73]. A lot of research has gone into improving this very important part of

the battery, which is very vital for maintaining the capacity of the battery during long term cycling [74–76]. Further research is carried out in capacity loss reduction by altering the current for charging and discharging [56]. The tanks beside the cell stack store the positive and negative electrolytes from which they are pumped to circulate in the stack that in turn improves the battery performance and efficiency.

One of the major concerns with redox flow batteries is that of self-discharge, which happens when the battery is in idle mode. Apart from this, the side reactions involved such as air oxidation of V^{2+} and the evolution of hydrogen in the negative electrolyte and the electrode respectively also result in capacity loss [45, 77]. Ion diffusion is one of the major causes for capacity loss, where the vanadium ions crossover the membrane to the other half cell and reacts with the active species. This phenomenon paves way for accumulation of a specific species of vanadium in one half-cell and decrease in the other causing imbalance, which leads to capacity loss. Depending on the type of the membrane used, the amount of vanadium ions diffusing across the membrane differs which in turn affects the coulombic efficiency. Extensive research has been carried out for improvement of the membrane to minimize the water and electrolyte transfer, which in turn leads to reduced operational problems and capacity loss in the battery [73, 78]. As a result, a control system is very important in maintaining the State of Charge *SOC* levels so as to prevent capacity decay in the battery. Before trying to develop a control system, the process of capacity decay needs to be understood in detail.

Over the years, many models have been developed for VRB by researchers all over the world to study the performance of VRB [79, 80]. A model based on the principles of conservation linked to the kinetics of the reaction is used to simulate the performance of VRB with response to variation of battery parameters was developed by A. Shah and co-workers [44]. Models focusing particular on vanadium ion diffusion across the membrane have also been simulated like the one by Maria

Skyllas Kazacos along with Lessan Goh [69]. However, very few models have been developed focusing on capacity decay aspect of vanadium Redox battery. An accurate model for depicting the capacity loss in the battery would be very useful in developing a control system, which would systematically re-balance by changing the electrolytes thereby maintaining the efficiency of the battery at acceptable levels.

Tang *et al.* have already come up with a dynamic model to study the effects of ion diffusion and side reaction for capacity loss in a membrane. They have concentrated on simulating capacity loss for different membranes with different rates of evolutions of hydrogen and air oxidation during long term charge-discharge cycling operation. However, all the previous models were developed by assuming a constant temperature. The electrolyte temperatures will vary during operation conditions. More importantly, the ion diffusion rate is strongly dependent on temperatures and the temperature stability is different for different species of vanadium ions [81]. Therefore, it is necessary to develop a temperature depended model to evaluate the capacity decay caused by ion diffusion. This chapter aims at introducing the effect of temperature on diffusion causing change in concentrations of vanadium ions and reduction in capacity of the battery.

4.2 Model Development

The temperature of the battery is an important factor in defining its capacity decay during long term operation. It is influenced by many factors such as atmospheric temperature, flow rate of the electrolyte, heat generated from stack resistance losses, and self-discharge reactions. The electrolyte temperature in particular is affected by the flow rate, heat transfer through the pipes and stack, and then more importantly by the self-discharge reactions especially in idle mode or

conditions with slow discharge of energy [82].

One way by which the operational temperature affects the capacity of the battery is by the phenomenon of precipitation. The vanadium ions used in the battery precipitate at different temperatures. For example, the precipitation of V^{2+}/V^{3+} ions happens in the negative electrode when temperatures drop, typically below 5 °C. Similarly V^{5+} ions in the positive electrode tend to precipitate with temperature rise. This leads to blocking of electrolyte channels and results in deterioration in the capacity of the battery [66, 82]. Moreover, the membrane separating the half cells is also affected by high temperatures leading to water loss [43].

The use of mathematical modeling along with chemistry to model a Redox Flow battery to study the changes that happen in a battery due to change in external factors has proved to be very useful in monitoring the (*SOC*) and capacity of the battery making it easier to determine the battery charging/discharging processes to ensure maximum efficiency. A dynamic model is better suited to this particular need in comparison to a steady state model as it can monitor and act upon the transient changes in the characteristics of the battery in response to the changes in the operating conditions. The battery needs to be monitored as the diffusion of various species of vanadium ions across the membrane and the side reactions lead to an imbalance in ratio between vanadium ions in the two half cells. This imbalance can be remedied by remixing of the electrolyte in the battery. As a result, a dynamic model is necessary to determine the appropriate time for remixing of electrolyte to attain optimal efficiency over long periods of operation. Dynamic models are being developed on the basis of conservation of mass and energy to observe the changes in concentrations. A model dealing with the ion diffusion and side reactions for different membranes was developed by Ao Tang [49]. This chapter aims to improve the model by incorporating the effect of temperature. The diffusion coefficients of various species of vanadium ions, which are an integral

part of the model are influenced by the temperature and therefore, provide a more accurate assessment of the state of the battery, when the effect of temperature is included. To achieve simplicity and to focus more on the pertinent issue, the following assumptions are made.

4.2.1 Assumptions

- Volume is considered to be constant at 1L for the entire operation.
- The charging/discharging current and the flow rate of the electrolyte are considered constant.
- The electrolytes are uniformly mixed and the chemical reactions due to diffusion are considered instantaneous.
- Proton concentration was considered constant for the entire operation.
- Rates of charge/discharge reactions of the cell are described by Faraday's law of electrolysis.

4.2.2 Temperature Dependence

To develop a temperature dependent model, it is necessary to understand the effect of temperature in determining the diffusion coefficients of the vanadium ions.

$$D_i' = D_i \times e^{-E_a/RT} \quad (4.1)$$

The effect of temperature on the diffusion coefficients can be denoted by the relationship to the Arrhenius model. Further, Nernst equation that gives us the potential of the cell is also affected by temperature variations and this accounts to the intrinsic capacity loss. The Arrhenius model denoting the temperature dependence of diffusion coefficient is given by Eqn. 4.1.

Figure 4.1: Diffusion coefficients at different temperatures
 (a) Selemon CMV (b) Selemon AMV (c) Nafion 115

where D_i' is the diffusion coefficient, D_i is the maximum diffusion coefficient (when temperature tends to infinite), i denote the vanadium ion species, E_a is the activation energy, T is the temperature in kelvins and R is the gas constant. The activation energy is taken as 17341 J mol^{-1} assuming that the activation energy is same for each of the vanadium ion species [70, 82]. The relationship between the diffusion coefficient and temperature at different temperatures for Selemon CMV, Selemon AMV, and Nafion 115 membranes is shown in Table A.4, Table A.5, and Table A.6 respectively along with Fig. 4.1.

4.2.3 Ion Diffusion

The capacity of the battery is also affected by the side reactions of air oxidation of the negative electrolyte and the evolution of hydrogen at the negative electrode. These are effects which cannot be eliminated just by mere readjustment of electrolyte. These reactions can be overcome by employing an inert blanket or limiting the surface area to volume ratio thereby decreasing the reaction area in the case of air oxidation and by operating the battery in the range of 10-90% *SOC* to mitigate the problem of hydrogen evolution sacrificing some usable capacity. In this study, these side reactions are ignored to focus on effects of diffusion process on capacity decay.

The model that is used in this chapter is developed by using the conservation of molar mass coupled together with the Arrhenius model for mass diffusivity. The diffusion of vanadium ions across the membrane can be derived from Fick's law defined as follows:

$$\phi_d = -D'_i \left(\frac{dc_i}{dx} \right) \quad (4.2)$$

where ϕ_d is the diffusion flux, D'_i is the diffusion coefficient, c_i is the concentration, and x is the length. According to Fick's law, the flux of diffusion is from a high concentration region to a low concentration region for which, the magnitude is proportional to the concentration gradient. On combining the above equation with Eqn. 4.1, we get the flux with modified diffusion coefficients according to the temperature variance.

$$\phi_d = -D_i e^{-E_a/RT} \left(\frac{dc_i}{dx} \right) \quad (4.3)$$

The diffusion of various species of vanadium ions across the membrane and the

resulting chemical reactions mentioned above are taken into account. The diffusion coefficients employed for the model are calculated taking into account, the operational temperature of battery. The dynamic concentrations thus calculated are then keyed into Nernst equation to calculate the dynamic voltage of the cell during operation. This helps us establish the range of operating conditions and to determine the periods of charging and discharging to ensure optimal usage of the battery. The values chosen for model are such that the battery life is around 200 charging cycles for practical considerations of the parameters used. The dynamic equations thus developed are as follows:

Charging:

$$\begin{aligned}
 V \frac{dc_2}{dt} &= +\frac{iA_e}{zF} - D_2c_2 \frac{A_m}{d} e^{-E_a/RT} - 2D_5c_5 \frac{A_m}{d} e^{-E_a/RT} - D_4c_4 \frac{A_m}{d} e^{-E_a/RT} \\
 V \frac{dc_3}{dt} &= -\frac{iA_e}{zF} - D_3c_3 \frac{A_m}{d} e^{-E_a/RT} + 3D_5c_5 \frac{A_m}{d} e^{-E_a/RT} + 2D_4c_4 \frac{A_m}{d} e^{-E_a/RT} \\
 V \frac{dc_4}{dt} &= -\frac{iA_e}{zF} - D_4c_4 \frac{A_m}{d} e^{-E_a/RT} + 3D_2c_2 \frac{A_m}{d} e^{-E_a/RT} + 2D_3c_3 \frac{A_m}{d} e^{-E_a/RT} \\
 V \frac{dc_5}{dt} &= +\frac{iA_e}{zF} - D_5c_5 \frac{A_m}{d} e^{-E_a/RT} - 2D_2c_2 \frac{A_m}{d} e^{-E_a/RT} - D_3c_3 \frac{A_m}{d} e^{-E_a/RT}
 \end{aligned} \tag{4.4}$$

Discharging:

$$\begin{aligned}
V \frac{dc_2}{dt} &= -\frac{iA_e}{zF} - D_2 c_2 \frac{A_m}{d} e^{-E_a/RT} - 2D_5 c_5 \frac{A_m}{d} e^{-E_a/RT} - D_4 c_4 \frac{A_m}{d} e^{-E_a/RT} \\
V \frac{dc_3}{dt} &= +\frac{iA_e}{zF} - D_3 c_3 \frac{A_m}{d} e^{-E_a/RT} + 3D_5 c_5 \frac{A_m}{d} e^{-E_a/RT} + 2D_4 c_4 \frac{A_m}{d} e^{-E_a/RT} \\
V \frac{dc_4}{dt} &= +\frac{iA_e}{zF} - D_4 c_4 \frac{A_m}{d} e^{-E_a/RT} + 3D_2 c_2 \frac{A_m}{d} e^{-E_a/RT} + 2D_3 c_3 \frac{A_m}{d} e^{-E_a/RT} \\
V \frac{dc_5}{dt} &= -\frac{iA_e}{zF} - D_5 c_5 \frac{A_m}{d} e^{-E_a/RT} - 2D_2 c_2 \frac{A_m}{d} e^{-E_a/RT} - D_3 c_3 \frac{A_m}{d} e^{-E_a/RT}
\end{aligned} \tag{4.5}$$

where c_2 , c_3 , c_4 and c_5 are the concentrations (mol L^{-1}) of V^{2+} , V^{3+} , V^{4+} , and V^{5+} ions respectively. D_2 , D_3 , D_4 , and D_5 are diffusion coefficients for V^{2+} , V^{3+} , V^{4+} , and V^{5+} respectively, whose values are calculated based on data in [46, 82]. The signs of the dynamic equations are determined by whether the battery is being charged or discharged. During the charging process, the equations concerning c_2 and c_5 have a positive sign and that of c_3 and c_4 have a negative sign. They are opposite for the discharging process with c_3 and c_4 having a positive sign, and c_2 and c_5 having a negative sign.

The modified cell voltage balance derived from Nernst equation is given by (3.4). The proton concentration term is combined with the standard potential term E_0 to produce formal potential E_0' , which can be determined experimentally.

$$E(t) = E_0' + \frac{RT}{zF} \ln \left[\frac{c_2(t) \times c_5(t)}{c_3(t) \times c_4(t)} \right] \tag{4.6}$$

Where E_0' is the formal cell potential measured at 50% state of charge. The formal cell potential for 2M vanadium in 5M sulphate electrolyte is measured at 1.4 V [49].

4.3 Simulation Results

Before moving on to discuss the results obtained during simulation, it is important to define the parameters and conditions under which, the simulation was performed. In the previous chapter, a VRB stack is considered for preliminary investigation, in this chapter smaller details affecting the battery performance is being modelled and it is logical to study the effect in a single cell. For this study, three different membranes (Selemion CMV, Selemion AMV, and Nafion 115) were considered and the voltage limits for the battery were assumed to be 1.7 V as the upper limit and 1.1 V as the lower limit. The diffusion coefficients for each membrane was calculated separately by making use of the Arrhenius equation to calculate the respective activation energy and then reconstituting it to get the diffusion coefficient at a particular temperature. A current density value of 60 mA cm⁻² was taken for uniformity purposes so that it is easier to observe the capacity decay across three membranes. The total amount of moles of vanadium ions used in simulation was taken to be 2M with initial concentration of V²⁺ and V⁵⁺ set as 0.01 M and that of V³⁺ and V⁴⁺ set as 1.99 M to ensure that the situation of logarithmic zero is prevented in Nernst equation.

The physical parameters for the simulation were set as follows:

- The volume of electrolyte is considered constant at 1L for each half-cell.
- The surface area of membrane (A_m) and that of electrode (A_e) have the same value 30 dm².
- The end of charge and discharge cycles were taken at voltage limits 1.7 V and 1.1 V, respectively.
- The total amount of vanadium ions used for simulation was assumed to be 2 mol L⁻¹. However, to avoid logarithmic zero term in Nernst equation, the

initial values are taken as 1.99 mol L^{-1} for V^{5+} and V^{2+} , and 0.01 mol L^{-1} for V^{3+} and V^{4+} .

- The current density is 60 mA cm^{-2} , which is equivalent to 180 A charging/dis-charging current.

The next section will discuss the results for each membrane separately and comparison studies between membranes will also be done along the way.

4.3.1 Selemion CMV

Vanadium ion diffusion coefficients were calculated according to the method described. Concentration profiles for V^{2+} , V^{3+} , V^{4+} , and V^{5+} at 1.1 V and 1.7 V were plotted over 200 cycles for different temperatures as shown in figures below. Concentration profile for V^{5+} at 1.1 V and V^{3+} at 1.7 V is not drawn as it reaches zero quickly once the simulation is started. It was seen that the effect of temperature was felt at most between 25-100 cycles in all of the concentration profiles and that the concentration profiles for different temperatures equalize after a while, close to 200 cycles.

Figure 4.2: V^{2+} concentration change for 200 cycles (CMV)

(a) at 1.1 V (b) at 1.7 V

It can be seen from Fig. 4.2 that the concentration of V^{2+} at 1.1 V increases with the increase in number of charging/discharging cycles. The rate of increase in the concentration increases proportionally with the increase in temperature. The effects of temperature seems to fade away with the increase in charging/discharging cycles as it is seen that the concentration levels seem to be moving towards a common finishing point. It was seen that the concentration of V^{2+} at 1.7 V decrease with the increase in the number of cycles. The rate of decrease of concentration of vanadium ions at different temperatures increases with increasing temperatures and the effect of temperature decreases as the number of cycles increase as the characteristic curves move towards to a comparable end concentration level.

Fig. 4.3 shows the concentration profile of V^{3+} at 1.1 V plotted over 200 cycles and it can be seen that it decreases with increasing concentration. The extent of decrease in the concentration of V^{3+} seems to be dependent on the temperature as it can be seen that concentration at 40 °C decreases at a faster rate than that of 10 °C.

Figure 4.3: V^{3+} concentration change for 200 cycles (CMV)

The effect of temperature was again felt the most at around 50 cycles as it can be seen in the figure that the difference between the concentration profiles at 40 °C and 10 °C happens to be around that point.

Figure 4.5: V^{5+} concentration change for 200 cycles at 1.7 V (CMV) Figure 4.4: V^{4+} concentration change for 200 cycles (CMV)

(a) at 1.1 V (b) at 1.7 V

The concentration profile of V^{4+} over 200 charging/discharging cycles at the voltages of 1.1 V and 1.7 V is shown in Fig. 4.4. It was seen that, in both the cases, concentration of V^{4+} increases with the number of cycles and the rate of increase of vanadium ions at different temperature seems to increase with increasing temperature. As mentioned before for other vanadium ion associated with Selemion CMV membrane, the concentration of vanadium ions at different temperatures tends to stabilize as the number of cycles increases and attains the point of maximum difference at around 50 cycles. Fig. 4.5 shows the concentration variation of V^{5+} at 1.7 V plotted over 200 cycles at temperatures ranging from 10 °C to 40 °C. It

was seen that the concentration decreases with the increase in the number of cycles. Furthermore, the rate of decrease of vanadium ion concentration at different temperatures increases with increasing temperatures and the effect of temperature decreases as the number of cycles increase. To clearly illustrate the effect of temperature on the concentration of the vanadium ions, the concentration profiles for all the four ions was plotted by calculating the difference in diffusion between 10 °C and 40 °C at both ends of the charging/discharging cycles (1.1 V & 1.7 V).

From Fig. 4.6, it can be observed that the concentration of ions at 1.1 V and 1.7 V behave differently with respect to temperature. For example, the concentration of V^{2+} at 40 °C relative to 10 °C increases with temperature at 1.1 V and decreases at 1.7 V. This is in accordance with the chemical reactions that occur at the two ends of charging/discharging cycle.

Figure 4.6: Difference in diffusion due to temperature (CMV)

(a) at 1.1 V (b) at 1.7 V

The relative concentrations at different temperatures of V^{5+} at 1.1 V and V^{3+} at 1.7 V reach zero value after a few cycles. This concurs with the earlier analysis that these particular concentrations reach zero after a few cycles irrespective of the temperature of the experiment. It can be observed that the maximum difference occurs approximately around 50 cycles and that the difference reduces as the number of cycles increase.

4.3.2 Selemion AMV

The diffusion characteristic of the vanadium ions is different in different membranes. The concentration profiles for vanadium ions were plotted at both ends of the charging/discharging cycle at different temperatures. V^{5+} and V^{3+} quickly reach zero for 1.1 V and 1.7 V respectively, when the simulation was started. It can be seen that the concentration profiles for other vanadium ions at both 1.1 V and 1.7 V vary almost linearly with the number of cycles and that the gradient increases with increase in temperature. However, unlike Selemion CMV, the concentration profiles do not tend to equalize as the number of cycles increase and the difference keeps on increasing with the increase in cycle number.

Figure 4.7: V^{2+} concentration change for 200 cycles (AMV)

(a) at 1.1 V (b) at 1.7 V

Figure 4.8: V^{3+} concentration change for 200 cycles at 1.1 V (AMV)

Fig. 4.7 shows the concentration change of V^{2+} at 1.1 V and 1.7 V at different temperatures across 200 cycles. The concentration of V^{2+} increases as the number of charging/discharging cycles increase. The rates of increase of V^{2+} concentration increase with increasing temperature, for example, the rate of increase of concentration at 20 °C is higher than that of 10 °C.

At 1.7 V, it was seen that the concentration of V^{2+} decrease with increasing number of cycles. This can be attributed to the chemical reactions that happen at 1.7 V. The rate of decrease is determined by the operational temperature of the battery. It was observed that the rate of decrease in the concentration increases with increasing temperature. Moreover, similar to the vanadium ion concentrations at 1.1 V, the difference between the concentrations of ions at different temperatures keeps increasing and does not settle down at a common point. On plotting the concentration of V^{3+} at 1.1 V for different temperatures over 200 battery charging/discharging cycles, it is observed from Fig. 4.8 that the concentration of V^{3+} decreases as the number of cycles increase and that the rate of decrease is determined by the operational temperature. The rate of decrease increases with the increase in operational temperature.

The concentration profile of V^{4+} for different operational temperatures at 1.1

V and 1.7 V plotted over 200 cycles is shown in Fig. 4.9. It was seen that the concentration of V^{4+} at all temperatures increase with increasing number of cycles. The rate of increase of concentration of V^{4+} was seen to be dependent on the operational temperature of the battery.

Figure 4.9: V^{4+} concentration change for 200 cycles (AMV)

(a) at 1.1 V (b) at 1.7 V

It was observed that the rate increased with increasing temperature. The difference between the concentration of vanadium ions at different temperatures was observed to increase linearly with the increase of number of cycles similar to the behaviour of other vanadium ions in Selemion AMV.

Figure 4.10: V^{5+} concentration change for 200 cycles at 1.7 V (AMV)

Figure 4.11: Difference in diffusion due to temperature (AMV)
(a) at 1.1 V (b) at 1.7 V

The concentration variation of V^{5+} ions for 200 cycles at 1.7 V is very similar to the characteristics of V^{2+} ions at 1.7 V. It can be observed from Fig. 4.10 that the concentration decreases with increase in time, however, the rate of diffusion of V^{5+} is higher than V^{2+} , which reaches a final concentration of 1.4 mol L^{-1} compared to 1.7 mol L^{-1} . The concentration profiles for all the four ions at 40°C with respect to 10°C over 200 cycles at both ends of the charging/discharging cycle (1.1 V & 1.7 V) was plotted and it is as shown in Fig. 4.11. It was observed that the relative difference also varies linearly with the number of cycles and does not equalize as the difference keeps on increasing as the number of battery charging/discharging cycles increase. This is in contrast to the behaviour of vanadium ions in Selemion CMV. As mentioned before, the vanadium ions behave differently at the two ends

of the charging/discharging cycle (1.1 V and 1.7 V). This can be attributed to the side reactions, which happen at the two ends of the charging/discharging cycle.

4.3.3 Nafion 115

Nafion 115 is one of the most commonly studied membranes in the purview of redox flow batteries. The concentration profiles were plotted and were observed to be very similar to that of Selemion CMV membrane although individual ions behave differently and mirror the behaviour of other ions in Selemion, for example V^{2+} in Nafion 115 mirrors the behaviour of V^{5+} Selemion CMV at 1.1 V. The characteristic curves for the variation in the concentrations of vanadium ions are plotted below for different species at 1.1 V and 1.7 V for different operating temperatures.

Figure 4.12: V^{2+} concentration change for 200 cycles at 1.7 V (N115)

Figure 4.13: V^{3+} concentration change for 200 cycles (N115)

(a) at 1.1 V (b) at 1.7 V

Figure 4.14: V^{4+} concentration change for 200 cycles at 1.1 V (N115)

Figure 4.15: V^{5+} concentration change for 200 cycles (N115)

(a) at 1.1 V (b) at 1.7 V

Similar to the other membrane studies, to clearly illustrate the effect of temperature on the concentration of the vanadium ions, the concentration profiles for all the four ions at 40 °C was plotted at both ends of the charging/discharging cycles (1.1 V & 1.7 V) relative to the ones at 10 °C as shown in Fig. 4.16(a) and Fig. 4.16(b).

Figure 4.16: Difference in diffusion due to temperature (N115)

(a) at 1.1 V (b) at 1.7 V

It was seen that, the effect of temperature on concentrations of the vanadium ions with Nafion 115 membrane is very similar to that of Selemion CMV membrane. The effect of temperature of the battery on the capacity of the battery was plotted over 200 cycles as shown in Fig. 4.16 and it can be seen that capacity decay with Nafion 115 membrane is also very similar to that of Selemion CMV membrane. However, the effect is more pronounced in Nafion 115 membrane in comparison to Selemion CMV membrane.

4.4 Effect on Capacity Decay

The capacity of the battery follows the trend set by the concentration of vanadium ions in the battery and decreases with the increase in the number of cycles and the gradient of the capacity decay increases with increasing temperature. Unlike the Selemion CMV membranes and Nafion 115, capacity decay in Selemion AMV membranes does not equalize as the number of cycles increase nor do they experience a maximum at around 50 cycles.

Figure 4.17: Capacity decay with respect to temperature

(a) Selemion CMV (b) Selemion AMV (c) Nafion 115

Figure 4.18: Voltage vs. Cycle number (Nafion 115 at 40°C)

The time taken for the end of 100th discharge cycle is shown in Fig. 4.19. From the voltage and current waveforms shown, it can be clearly inferred that there is a considerable difference between the times taken for discharge at different temperatures. The capacity change of the battery over 200 cycles is plotted over different temperatures in Fig. 4.17. A typical voltage curve is shown in Fig. 4.18, which is obtained for operating temperature of 40 °C for Nafion 115 membrane.

Figure 4.19: Time vs. voltage and current for 100th cycle

Figure 4.20: Capacity loss analysis at different temperatures

Apart from the loss due to diffusion, there is an intrinsic capacity loss due to temperature, which explains the difference at the start of the cycling. This difference can be attributed to the effect of temperature in the Nernst equation. The total capacity loss at different temperatures and the contribution of each process is shown in Fig. 4.20. The capacity at 20°C is taken as the reference to show the relative change in capacity for the other temperatures. It can be observed that the intrinsic loss increases with increase in temperature. The maximum loss in capacity occurs within 100 cycles of operation and the diffusion rate is lower for the last 100 cycles as there are comparatively less ions available for diffusion. The total capacity loss is 12.67%, 13.37%, and 14.23% for 20°C, 30°C, and 40°C, respectively.

4.5 Summary

One of the main reasons for capacity decay in VRB is due to interaction of vanadium ions amongst themselves when some of them diffuse from one half-cell

to another half-cell. The diffusion of ions across the ion exchange membrane is influenced by many factors ranging from charging current to temperature. The temperature effect on diffusion and hence the capacity decay was analysed in this chapter. In this study, the temperature is considered to remain constant for the whole period of operation. However, in reality the temperature of the stack increases with the cycle number. This variation is not taken into account for this model as it would complicate the dynamic equations and has a very little effect in the overall capacity loss.

The effect of temperature on capacity decay was studied for three different membranes namely, Selemion CMV, Nafion 115, and Selemion AMV. It was observed that the effects of temperature for the Selemion CMV and Nafion 115 membranes was confined to the initial 25-100 battery discharging/charging cycles and that the characteristics equalize as the number of cycles increase. Also, the maximum difference for concentration of vanadium ions is seen to be between the effects at 10 °C and 40 °C is seen to be around 50 cycles for both Selemion CMV and Nafion 115. As for the capacity, it follows a trend similar to that of the concentration and as the maximum difference at around 50 cycles and tends to equalize as the number of cycles increase. However, the intrinsic loss due to the temperature difference results is a loss of overall capacity in the batteries. The results for Selemion AMV are very different from that of Selemion CMV and Nafion 115. The change in concentration seems to be linear with respect to the number of charging/discharging cycles and the gradient for change in concentration for both positive and negative gradients increase with the increase in temperature. As a result, the difference in concentration of vanadium ions between that of 40 °C and 10 °C increase as the number of cycles increase and do not equalize at the end.

A dynamic model was developed to depict the influence of temperature on change of concentrations of various species of vanadium ions due to the diffusion and the

resulting side reactions that occur in the half cells. The model was then used to predict the capacity of the battery with the concentration obtained from before, which was then used to identify the capacity loss due to the cross-contamination process over long periods of operation at different temperatures. The change in concentration of species of vanadium ions was investigated for three different membranes. It was seen that the loss in capacity of the battery increases with increase in temperature. Moreover the membranes exhibited different behaviour, Selemion CMV, and Nafion 115 experienced the maximum amount of capacity loss during the first 100 operating cycles and seemed to stabilize as the number of cycles increased. However, for Selemion AMV membrane, the capacity loss seemed to increase linearly as the number of cycles increased and showed no sign of stabilizing. The dominant part of the capacity loss (change in capacity) due to the temperature change stems from the different values for diffusion coefficients of each species of vanadium ions, which are also temperature dependent as shown in the earlier part of this chapter.

Chapter 5

Bulk Electrolyte Transfer due to Ion Diffusion

5.1 Introduction

A Vanadium Redox Battery has vanadium ions reacting in both half cells of the battery, each being separated by an ion exchange membrane, which allows H^+ ions pass through to maintain charge balance. As it was already discussed, an ideal ion exchange membrane should limit the flow of vanadium ions through it and should possess good conductivity and chemical stability [83]. A lot of research has gone into improving this very important part of the battery, which is very vital for maintaining the capacity of the battery during long term cycling [74, 75]. However, no membrane is 100% selective, thus, vanadium ions are still able to diffuse through the membrane from one half-cell to the other. The differential rate of vanadium ion diffusion across the membrane is one of the major causes of capacity loss, when there is an accumulation of vanadium ions in one half-cell and a decrease in the other. Although the self-discharge reactions between the

vanadium ions across the membrane lead to capacity fade, this can be readily restored by simply remixing the two half-cell solutions periodically [67]. On the other hand, other side reactions such as air oxidation of V^{2+} and the evolution of hydrogen in the negative electrolyte and the electrode, respectively, also result in capacity loss, but this cannot be restored by simple remixing of the electrolytes and requires a chemical or electrochemical re balance [49, 67]. Several approaches have been proposed to reduce capacity fade by varying the operating conditions of the battery [56, 77].

The type of the membrane used determines the rates of water transfer and vanadium ion diffusion across the membrane, which in turn affects both capacity fade and coulombic efficiency [78]. Extensive research has been carried out for improvement of the membrane to minimize the water and electrolyte transfer, which in turn reduces operational problems and capacity loss in the battery [56, 77, 78, 83]. Furthermore, a sophisticated *SOC* monitoring and control system is very important in managing the electrolytes and maintaining balanced half-cells electrolytes [45, 67, 84] so as to prevent capacity decay in the battery. Before trying to develop a control system, the process of capacity decay needs to be understood in detail.

5.2 Model Development

Over the years, many models have been developed for VRB by researchers all over the world to study the performance of VRB [49, 79, 80]. A model based on the principles of conservation linked to the kinetics of the reaction is used to simulate the performance of VRB with response to variation of battery parameters was developed by Shah and co-workers [44]. Models focusing particularly on vanadium ion diffusion across the membrane have been reported by Skyllas Kazacos and

Goh [69]. In this chapter, the dynamic model developed in the previous chapter is further extended to include the effect of bulk electrolyte transfer across the membrane, which occurs during battery operation and results in a change of volume in each half cell. Even though the overall volume of the battery remains constant; the difference in volume in each half cell has considerable effect on the battery capacity and performance. This study aims at investigating capacity decay due to bulk electrolyte transfer phenomenon along with the temperature variations in causing volume and concentration imbalance by developing a comprehensive model. As the electrolyte moves from one half-cell to the other, the loss of electrolyte volume on one side is approximately equal to the increase in electrolyte volume of the other half cell. Slight variations will arise due to non-ideal mixing and variations in electrolyte density [78]. For the computational simplicity of the model, however, the electrolyte is considered to be evenly mixed with uniform electrolyte density. The change in electrolyte volume for this model is taken at a resolution of 500 milliseconds, which incorporates even the minor changes providing improved accuracy.

Small change in electrolyte volume is given by:

$$\Delta V = \vec{v}^m A_m \Delta t \quad (5.1)$$

where $\vec{v}^m$ is the velocity of electrolyte across the membrane, A_m is the membrane surface area in dm^2 and Δt is the time taken for one cycle of operation. The velocity of electrolyte transfer across membrane for any cycle can be given by the alternate form of Schlogl's equation, which describes the convective transport of bulk electrolyte [51].

$$\vec{v}^m = -\frac{k_p}{\mu_w} |\Delta \Pi_{osmotic}| - \frac{k_\phi}{\mu_w} c_f F \left(\eta_m - \frac{RT}{F} C_{norm} - \frac{RT}{F} \left(\frac{D_{H^+}^m \Delta c_{H^+}}{c_{H^+}} \right) \right) \quad (5.2)$$

This equation accounts for the bulk electrolyte movement due to osmosis, the transfer due to the interactions between the vanadium ions and the fluid, and also the water transfer due to the movement of H^+ ions across the membrane. The pressure difference across the half-cells ($\Delta\Pi_{osmotic}$) can be approximated from the Van't Hoff equation, given by:

$$\Delta\Pi_{osmotic} = [((c_2 + c_3) - (c_4 + c_5)) + (c_{H^{+}neg} - c_{H^{+}pos})] * R * T \quad (5.3)$$

The equation for osmotic pressure accounts for the pressure difference due to the concentration of vanadium ions at different oxidation states as well as the proton concentration. The proton concentration, however, does not build up for an ideal proton exchange membrane as there is free movement of proton across the membrane. The issue of proton concentration gradient, however, might become an issue in the case of prolonged operation of the VRB causing active sites of the membrane being blocked by the larger vanadium ions and also due to rapid charge/discharge causing imbalance in proton concentration.

The volume in the negative half-cell is denoted by V_n and the volume in the positive half-cell is denoted by V_p . The second term of the velocity equation attributes to the drag of fluid molecules along with the vanadium ions during diffusion process and the term C_{norm} represents the normalized value of contribution of each of the vanadium ion species to the bulk transfer.

$$C_{norm} = \frac{z_2 D_2^m \Delta c_2^m + z_3 D_3^m \Delta c_3^m + z_4 D_4^m \Delta c_4^m + z_5 D_5^m \Delta c_5^m}{z_2^2 D_2^m c_2^m + z_3^2 D_3^m c_3^m + z_4^2 D_4^m c_4^m + z_5^2 D_5^m c_5^m} \quad (5.4)$$

Further, it is necessary to compute the ionic potential across the membrane. The ionic potential can be calculated by determining the voltage drop across the membrane. By using Ohm's law the membrane ionic potential can then be computed.

$$\eta_m = i_{tot} * R_m \quad (5.5)$$

where i_{tot} is the total current across the membrane, which is the product of current density and the area of the membrane. R_m is the resistance of the membrane, which causes the potential difference. The total membrane resistance can be obtained by integrating the resistivity along the thickness of the membrane δ_m in decimeters.

$$R_m = \frac{1}{A_m} \int_0^{\delta_m} r_m(f) df \quad (5.6)$$

where $r_m(f)$ is the resistivity of the membrane along the axis of diffusion f . According to the reference [85], the local resistivity model for a Nafion type membrane is given by:

$$r_m(f) = \frac{181.6 \left[1 + 0.03J + \left(0.062 \left(\frac{T_m}{303} \right)^2 J^{2.5} \right) \right]}{e^{\left(4.18 \left(\frac{T_m - 303}{T_m} \right) \right)} \cdot [\lambda(f) - 0.634 - 3J]} \quad (5.7)$$

where J is the current density with cell current i_{tot} (A) and A_m is the membrane area.

$$J = \frac{i_{tot}}{10^4(A_m)} \quad (5.8)$$

The description for all the variables mentioned in the above modelling equations is given in the nomenclature with the simulation parameters denoted in Table 5.1. The use of mathematical modelling along with chemistry to model a redox flow battery, to study the changes that happen due to the change in external factors has proved to be very useful. Especially, in monitoring the state of charge (*SOC*) and capacity of the battery, to determine the battery charging/discharging processes ensuring maximum efficiency. A dynamic model is better suited to this particular

need compared to a steady state model as it can monitor and act upon the transient changes in the characteristics of the battery in response to changes in operating conditions.

Dynamic models are developed on the basis of conservation of mass and energy to observe the changes in concentrations. A model dealing with the ion diffusion and side reactions for different membranes was developed by Tang *et al.* [49, 70] who investigated the effect of temperature on the diffusion coefficients of the various species of vanadium ions for self-discharge reactions. A similar approach is used in the present model, which has been extended to include the effect of bulk electrolyte transfer so as to provide a more accurate assessment of the state of the battery. Other assumptions made are:

- The charging/discharging current and the flow rate of the electrolyte are considered constant.
- The electrolytes are uniformly mixed and the chemical reactions due to diffusion are considered instantaneous.
- The ionic potential across the membrane is constant.
- Rates of charge/discharge reactions of the cell are described by Faraday's law of electrolysis.

The reactions between vanadium ions which occur in both the half cells influence the concentrations and need to be analysed in the development of the model according to Tang *et al.* [70]:

Table 5.1: Parameters used in simulation¹

Parameters	Value
Membrane surface area (A_m)	30 dm ²
Electrode surface area (A_e)	30 dm ²
Membrane thickness (δ_m)	125x10 ⁻⁶ m
Upper voltage limit	1.7 V
Lower voltage limit	1.1 V
Upper concentration limit	1.99 mol L ⁻¹
Lower concentration limit	0.01 mol L ⁻¹
Current density (J)	60 mA cm ⁻²
Charging/Discharging current	180 A
Universal Gas constant (R)	8.314 JK ⁻¹ mol ⁻¹
Activation energy (E_a)	17341 J mol ⁻¹
Formal potential (E_0)	1.4 V
Hydraulic permeability (k)	1.58x10 ⁻¹⁸
Electro-kinetic permeability (k_ϕ)	1.13x10 ²⁰
Viscosity of bulk electrolyte (μ_w)	8.684x10 ⁻⁴ Pa s
Fixed acid concentration (c_f)	1990 mol m ⁻³
Initial volume (V)	Positive half-cell: 1 dm ³
	Negative half-cell: 1 dm ³
Ionic potential of the membrane (η_m)	660 mV

The capacity of the battery is also affected by the side reactions of air oxidation of V(II) in the negative electrolyte and the evolution of hydrogen at the negative electrode during charging. These reactions can be overcome by employing an inert blanket or limiting the surface area to volume ratio thereby decreasing the reaction

¹Parameters were selected in accordance with [49, 56, 67]

area in the case of air oxidation and by operating the battery in the range of 10-90% *SOC* to mitigate the problem of hydrogen evolution sacrificing some usable capacity [49,70]. In this chapter, these side reactions are therefore ignored so as to focus on the effects of the diffusion processes on capacity decay.

The model used in this thesis is developed by using the conservation of molar mass coupled together with the Arrhenius model for mass diffusivity. The diffusion of various species of vanadium ions across the membrane and the resulting chemical reactions mentioned above are taken into account. The diffusion coefficients employed for the model are calculated by taking into account the operational temperature of the battery. The dynamic concentrations thus calculated are then keyed into the Nernst equation to calculate the dynamic voltage of the cell during operation. This helps to establish the range of operating conditions and to determine the periods of charging and discharging to ensure optimal usage of the battery.

The values chosen for the model are such that 200 charging cycles could be simulated for practical considerations of the parameters used. The dynamic equations based on the extended model for the process of charging and discharging is given by Eqn. 4.4 and 4.5 respectively, as discussed in the previous chapter.

State-space model for ion diffusion can be represented by:

$$\begin{aligned} \dot{x} &= A'x + B'u \\ y &= C'x + D'u \end{aligned} \tag{5.9}$$

where the input vector is the current density J applied to the battery system and the state vector x is the concentration of different vanadium ion species. The coefficients are chosen from the dynamic equations where A' represents the state matrix inherent to the battery. B' is the input matrix which is the change induced by the input, C' is the output matrix which is an identity matrix here as we are

determining the concentrations of different vanadium ions. D' is zero as there is no feed forward in this system.

$$x = \begin{bmatrix} c_2 & c_3 & c_4 & c_5 \end{bmatrix}^T$$

$$A' = \begin{bmatrix} \frac{-D_2 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} & 0 & \frac{-D_4 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} & \frac{-2D_5 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} \\ 0 & \frac{-D_3 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} & \frac{2D_4 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} & \frac{3D_5 A_m e^{-E_a/RT}}{\delta_m(V - \Delta V)} \\ \frac{3D_2 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} & \frac{2D_3 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} & \frac{-D_4 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} & 0 \\ \frac{-2D_2 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} & \frac{-D_3 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} & 0 & \frac{-D_5 A_m e^{-E_a/RT}}{\delta_m(V + \Delta V)} \end{bmatrix}$$

Parameter B' changes for charging and discharging processes as the reaction change leads to sign change for the different ion species in the equation.

$$B'_{(Charging)} = \begin{bmatrix} \frac{A_e}{zF(V - \Delta V)} & 0 & 0 & 0 \\ \frac{-A_e}{zF(V - \Delta V)} & 0 & 0 & 0 \\ \frac{-A_e}{zF(V + \Delta V)} & 0 & 0 & 0 \\ \frac{A_e}{zF(V + \Delta V)} & 0 & 0 & 0 \end{bmatrix} \quad B'_{(Discharging)} = \begin{bmatrix} \frac{-A_e}{zF(V - \Delta V)} & 0 & 0 & 0 \\ \frac{A_e}{zF(V - \Delta V)} & 0 & 0 & 0 \\ \frac{A_e}{zF(V + \Delta V)} & 0 & 0 & 0 \\ \frac{-A_e}{zF(V + \Delta V)} & 0 & 0 & 0 \end{bmatrix}$$

$$C' = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad D' = 0$$

The modified cell voltage balance is derived from the Nernst equation and the cell resistance as given by Tang *et al.*. The cell voltage is calculated based on the open circuit voltage equation along with the cell resistance during charging and discharging processes. The proton concentration term in the Nernst equation is combined with the experimentally determined standard potential term E_0 to produce Nernst potential E_0' (ref. Eqn. 4.6).

5.3 Simulation Results

Before moving on to discuss the results obtained during the simulation, it is important to define the parameters and the conditions under which the simulation is performed. The voltage limits for the battery are assumed to be at 1.7 V as the upper limit and 1.1 V as the lower limit. The diffusion coefficients for each of the membrane is calculated separately by making use of the Arrhenius equation to calculate the respective activation energy and then reconstituting it to get the diffusion coefficient at a particular temperature. For the simulation of bulk electrolyte transfer across the membrane, the interval for iteration is taken as 1 cycle. Also the ionic potential across the membrane is calculated by using the voltage drop across the membrane from the electrical resistance of the Nafion 115 membrane obtained from [86] and from Eqn. (5.5-5.8).

The physical parameters for the simulation are set as given in Table 5.1. To avoid logarithmic zero term in Nernst equation, the initial values are taken as 1.99 mol L⁻¹

for V^{5+} and V^{2+} , and 0.01 mol L^{-1} for V^{3+} and V^{4+} . The initial simulation results are validated by comparing with the results from the Skyllas-Kazacos and Goh [69] and Tang *et al.* [49] models at 25°C with the same parameters. The bulk electrolyte transfer across the membrane is caused mainly by: 1) the osmosis phenomena, 2) the drag of water molecules induced by the diffusion of the vanadium ion species across the membrane, and 3) the transfer of water with the protons as they move through the membrane to balance the charge. The number of water molecules transferred by the protons will vary for different membranes. Considering the practical applicability, the analysis for the bulk electrolyte transfer phenomena is done for Nafion 115 membrane including all the factors influencing volume change, as discussed above.

5.3.1 Volumetric Change

Figure 5.1: (a) Change in osmotic pressure as a function of ionic concentration
(b) Region 1: (0-50 cycles), (c) Region 2: (50-100 cycles)

Figure 5.2: Change in volume due to bulk electrolyte transfer for 200 cycles.

The osmotic pressure change between the two half cells for 200 cycles for 4 different temperatures with the pressure value in Pascal on the Y axis and number of cycles in the X axis is shown in Fig. 5.1. The osmotic pressure change is given as a function of the ionic concentration of the vanadium ion species in the half-cells. From the figure, it can be observed that the increase in pressure is significantly steep for the first 50 cycles and tends to stabilize around the 50-100 cycles range with a maxima at 75th cycle.

The change of volume in each of the two half cells for 200 cycles with the volume change in liters given on the Y axis and number of cycles in the X axis is shown in Fig. 5.2. From the figure it can be observed that there is about 19 percent change in volume in each of the half-cell, where the electrolyte from the negative half-cell is transferred to the positive half-cell, which is in conformity with the work by Sukkar *et al.* [87] for a cation type ion exchange membrane. The total volume of the battery, however, remains constant following the law of conservation of mass. This change in volume has immediate effect on the diffusion behaviour of the vanadium ions and the overall concentration change in the cell.

Figure 5.3: (a) Change in half-cell concentration at different temperatures (b) Region 1: Negative half-cell (50-200 cycles), (c) Region 2: Positive half-cell (50-200 cycles)

5.3.2 Change in Concentration

The total concentration change in each of the half-cell is plotted in Fig. 5.3, where the positive half-cell concentration constitutes of the concentration if V^{4+} and V^{5+} ions. The negative half-cell concentration constitute of the concentrations of V^{2+} and V^{3+} ions, which is plotted in the same figure. As it can be observed, the concentration in the negative half-cell increases initially and stabilizes after decreasing with maxima at the 75th cycle. The concentration is plotted for 4 different temperatures with the region of 50-200 cycles emphasized in the figure for better understanding.

The change in volume has a direct effect in the diffusion characteristics of each

Figure 5.4: Concentration change of V^{2+} ions for 200 cycles at 1.7 V

species of vanadium ions present in the battery. The change in the concentration of V^{2+} ions at different temperatures is shown in Fig. 5.4. The characteristics of V^{2+} at 1.7 V are shown with ion concentration on the Y axis and the number of cycles on the X axis. At 1.1 V, the concentration decreases to zero mol L^{-1} soon after the cycling starts and hence it is not shown in the figure. At 1.7 V, the concentration remains in the initial state until the volume change dominates causing it to increase and stabilize with a change of 5% to the initial concentration, which is shown in Fig. 5.4.

Figure 5.5: Concentration change for V^{3+} ions for 200 cycles

(a) At 1.1 V, (b) At 1.7 V

The concentration change for V^{3+} ion at 1.1 V and 1.7 V for temperatures ranging from 10°C to 40°C is shown in Fig. 5.5. The concentration profile of V^{3+} at the end of charge suffers a slight bulge during the initial cycling, however, the effect of volume change makes the concentration stabilize at the end of 200 cycles.

At the end of discharging, the concentration increases and reaches steady state. There is a decrease in the concentration after 75th cycle with a very small slope before reaching the steady state. The concentrations of V^{3+} and V^{2+} ions complement each other and contribute to the overall balance in the negative half-cell.

Figure 5.6: Concentration change for V^{4+} ions for 200 cycles

(a) At 1.1 V, (b) At 1.7 V

The concentration change of V^{4+} ions at the end of discharge and charge cycles respectively is shown in Fig. 5.6. The change that is observed is only about 20% in the case of 1.1 V shown in Fig. 5.6(a), where there is a steep decrease of V^{4+} concentration to 1.575 mol L⁻¹ at the end of cycling. The change at 1.7 V is observed only latter half of operation and the trend takes a positive slope to reach 0.18 mol L⁻¹. It can also be inferred that, when the cycling proceeds towards the end, the effect of temperature on the ion diffusion decreases and is almost nil at the end of the respective charge and discharge cycles.

Similar to the complementary relationship between V^{2+} and V^{3+} , V^{5+} ions complement for V^{4+} ions thereby contributing to the overall concentration in the pos-

itive half-cell.

Figure 5.7: Concentration change for V^{5+} ions for 200 cycles

(a) At 1.1 V, (b) At 1.7 V

The concentration of V^{5+} ions at 1.1 V increases with a steady positive slope and deviates to 15.7% from the initial value. The concentration at the end of charge cycle decreases from the initial value to about 9.5% at the end of 200 cycles. The rate of decrease is not constant throughout the period as the slope increases post first 100 cycles as shown in Fig. 5.7(b).

5.3.3 Change in Capacity

The capacity of the battery is plotted in Fig. 5.8 for different temperatures, including the phenomenon of bulk electrolyte transfer. The capacity in ampere hours is given on the Y axis, against the number of cycles in the X axis. Considering the change in the volume of the half-cells during the cycling process and the effect it has on the concentration of the vanadium ions, the capacity curve also follows a trend in accordance. Initially, the capacity decreases and as expected, it tends to reach a steady state around 100 cycles.

Figure 5.8: Capacity decay in Nafion 115 membrane with electrolyte transfer

The capacity decay slope is high in the last 100 cycles of operation as it follows the concentration trend of the vanadium ions in the half-cells. The effect of temperature on the overall capacity change is very small as the cycling progresses and becomes negligible at the end of 200th cycle with not a very significant effect during the process of cycling as that of the bulk electrolyte transfer.

On comparing the effect of bulk electrolyte transfer on capacity decay due to ion diffusion, it can be observed from Fig. 5.9 that there is no big difference at the end values of both simulations. There is a very significant difference, however, in the trend followed to reach the final value. With the consideration of bulk

Figure 5.9: Comparison of capacity change with and without bulk electrolyte transfer at 30 °C

electrolyte transfer phenomena, there are 2 stages of decay trend with different slopes as shown. On computing the maximum difference between both the trends, it is observed at the 100th cycle with a difference of 2.675 Ah. Further, to observe the decay in the capacity due to the effect of temperature is done by comparing the width of the voltage curves at different temperatures.

The voltage curves of the battery at different temperatures around the 50th cycle of operation is shown in Fig. 5.10. It can be observed that the plot corresponding to 40°C is lagging the 10°C plot due to the cumulative decrease in the capacity due to temperature causing decrease in the width of the voltage curve.

Figure 5.10: Voltage plot at different temperatures

5.4 Summary

One of the main reasons for capacity decay in VRB is due to interaction of Vanadium ions that diffuse from one half-cell to another half-cell. The diffusion of ions across the ion exchange membrane varies significantly from one membrane to another and is influenced by many factors ranging from charging current to temperature.

The extended model developed for simulation includes the effect of temperature and the bulk electrolyte transfer phenomena to study the characteristics of ion diffusion. For reducing computational complexity, the ionic potential across membrane is assumed as constant throughout the whole period while calculating the velocity across the membrane. It is observed that bulk electrolyte transfer across the membrane has a significant effect on the concentration change over 200 cycles and eventually the battery capacity. This is modelled for the Nafion 115 membrane that has been widely studied for the VRB. The change in volume between the half-cells may not be linear in practical case, considering all the other environmental parameters affecting the bulk electrolyte movement across the membrane, including hydraulic pressure differences from pump operation. On comparing the

results with the models neglecting the effect of bulk electrolyte transfer, a substantial difference in the ion diffusion behaviour of the different vanadium ions can be observed making the proposed model more comprehensive.

An extended dynamic model was developed to predict the capacity of the battery with the concentration obtained from initial simulations. The predicted capacity is then used to identify the capacity loss due to the cross-contamination process over long periods of operation at different temperatures. Nafion 115 membrane is considered for studying the combined effect of bulk electrolyte transfer and temperature in capacity fade. There was a 19% change in volume due to the bulk electrolyte transfer phenomena with a 0.5% tolerance for the temperature change. This translates to a considerable change in the concentration trend across 200 cycles from the initial concentration. The overall concentration in each half-cell tends to stabilize after 75 cycles of operation. The capacity characteristics can be analysed in two regions, region 1 from 1-100 cycles and region 2 from 100 to 200 cycles. The average slope showing the rate of capacity decay in region 1 is 5.2% and the average slope for capacity decay in region 2 is 8.9%. The overall capacity decay due to diffusion for Nafion 115 membrane is 13.8% with 2% tolerance for the temperature difference.

Chapter 6

Profile Based Charging

Optimization of VRB

6.1 Introduction

Flow battery is still evolving with active research being carried out on different materials, and various methods are being employed to study the battery characteristics in detail. Developing an adaptable real-time charging algorithm is important in realizing the potential of the battery in different scenarios. Several studies have been conducted to show the importance of charging algorithms for standard batteries. In these cases, the magnitude of current is controlled to vary the rate of charging of the battery, which in turn, affects the charging time and efficiency. It is shown that the battery performance and battery life in longer term is affected not only by the rate of charge, but also by the charging protocol used in accordance to the battery chemistry [95–97]. In the case of flow batteries, flow rate of the electrolytes act as a controllable input parameter in addition to the current. These input parameters have a direct correlation to the battery performance. Analysis on

losses arising due to the effect of change in flow rate and the ways to mitigate this issue have been studied [64, 65, 91, 98, 99]. Intrinsic losses in the battery occur due to activation overpotential, concentration overpotential, and ohmic overpotential. Pump power losses and shunt current losses are also of concern in flow batteries. Shunt current losses arise due to the low resistance path created by the hydraulic circuit connecting the flow channels to the individual cells [100, 101]. Some earlier works on the area of charging current shows that the losses are lower, when the current is lower, however, the effect of capacity decay has an inverse proportionality [56, 93, 94, 102]. Determining the optimal charging current is hence necessary for short term and long term benefits.

All of these studies on the effect of input parameters are done in a measure to identify an optimal flow rate or current for a specific scenario. Considering multiple input sources and dynamic operational conditions, it is important to have a real-time optimization of the battery charging where the variables control of the variables are online with continuous feedback. The realization of real time optimization is possible with the availability of state of the art sensors and new methodologies to estimate the batteries' state of charge during operation [84, 103]. Investigation of different charging methodologies for standard batteries also shows change in performance for different operating conditions [95, 96]. A control input is therefore included to facilitate profile based charging to optimize the parameters depending on the operating scenario. A fuzzy logic controller is used to handle the multi-variable system as it performs well in a dynamic scenario. Inclusion of additional parameters is easier with the linguistic approach and it can provide definite values based upon discrete or unpredictable variables [104–106].

6.2 Model Development

Model formulation takes into account, the internal losses, pump losses, and also the state of health of the battery that are then fed into the controller to provide operator based charging optimization. Voltage curve is a common indicator of the current state of operation of any battery and different components of the characteristic equation for cell voltage is used to represent various intrinsic losses. Difference between the measured voltage and thermodynamically calculated reduction potential is defined as over-potential and it directly affects the cell efficiency.

The charging voltage curve depends on the *SOC* of the battery, which in turn, is affected by the concentration of the individual vanadium species. The concentration at any given time t is defined by the dynamic equations as discussed in the earlier chapter (Eqn. 4.4). Cell voltage for charging is given by $E(t)$ as defined by the Nernst equation (Eqn. 4.6) for the given concentration values.

6.2.1 Intrinsic Losses

The cell level intrinsic losses and pump power losses are modelled separately. The intrinsic cell level over-potentials include activation over-potential, concentration over-potential, and ohmic over-potential [65].

$$\eta_{op} = |\eta_{act}^{+ve}| + |\eta_{act}^{-ve}| + |\eta_{conc}^{+ve}| + |\eta_{conc}^{-ve}| + \eta_{ohm} \quad (6.1)$$

Activation over-potential defines the energy required for an electron to get transferred from electrode to electrolyte. The electrochemical kinetics associated with the activation over-potential can be given by Butler-Volmer equation.

$$J = j \left\{ \exp \left[\frac{\alpha_a z F \eta_{act}}{RT} \right] - \exp \left[-\frac{\alpha_c z F \eta_{act}}{RT} \right] \right\} \quad (6.2)$$

where j is the exchange current density, α_a , and α_c are the dimensionless anodic and cathodic charge transfer coefficients, respectively. In case of flow batteries with porous electrodes, the electrode surface area is maximized and the magnitude of activation potential is considerably minimized.

Concentration over-potential is caused by the difference between reactant concentration near the surface of electrode and bulk electrolyte concentration. The effect becomes prominent as the concentration of active species of vanadium ions decreases to an extent, where electron transfer becomes dependent on the mass-transfer. Concentration over-potential can be mathematically defined by Nernst equation as shown in Eqn. 7.3.

$$\eta_{conc} = \frac{RT}{zF} \ln \frac{c_0}{c_b} \quad (6.3)$$

where c_0 is the concentration of reactant at electrode surface and c_b is the bulk concentration. Fick's law is applied to determine the rate of diffusion and the final equation for determining concentration is derived.

$$\eta_{conc} = \frac{RT}{zF} \ln \left(1 - \frac{J}{(1.6 \times 10^{-4}) zF (Q/A_e) c_b} \right) \quad (6.4)$$

where Q is the volumetric flow rate and A_e is the area of the porous electrode. Ohmic loss occurs in a flow cell as the resistances of various components such as membrane, electrode, and electrolyte restricts the current flow along the electric path. The total ohmic drop is the summation of individual potential drops across these cell components.

$$\eta_{ohm} = \eta_m + \eta_e + \eta_{ely} \quad (6.5)$$

$$\eta_{ohm} = i \times \left\{ \frac{\delta_m}{\sigma_m} + \frac{\delta_e}{\sigma_e} + \frac{\delta_{ely}}{\sigma_{ely}} \right\} \quad (6.6)$$

Table 6.1: Parameters for determining electrolyte conductivity³

Parameters	+ve half-cell electrolyte	-ve half-cell electrolyte
λ_A	1.8	0.7
λ_B	93.5	55.04
λ_C	4.67	2.62
λ_D	172.07	122.37

where i is the current flowing across the cell components, δ is the thickness, and σ is the conductivity of different components. Subscripts m , e , and ely denotes membrane, electrode, and electrolyte, respectively. In the case of membrane and electrode, dimensions as well as conductivity can be directly measured. In case of electrolyte conductivity calculation, we use a state of charge dependent empirical model [67].

$$\sigma_{ely} = (\lambda_A \times T + \lambda_B) \times SOC + (\lambda_C \times T + \lambda_D) \quad (6.7)$$

where λ_A , λ_B , λ_C , and λ_D are the empirical coefficients determined by experimental data fitting. The design of flow batteries including pipes and smaller channels for the flow of electrolytes gives rise to shunt current losses. Small imbalances in cell voltage causes a potential difference between the cells. The hydraulic circuit formed by electrolyte flow to different cells causes a shunt current to flow from a higher potential to lower potential. Shunt current is not favourable as it affects the overall operational potential created by the battery. A simple equation to show the shunt current flow is given as follows:

$$i_{sh}(t) = \sum_{k=1}^n \frac{E_{k+1}(t) - E_k(t)}{R_{sh}} \quad (6.8)$$

where i_{sh} is the shunt current, n is the total number of cells and R_{sh} is the shunt resistance created by the electrolyte path. Potential for individual cells can be

³Parameters were selected in accordance with [67]

calculated by the following equation (Eqn. 7.9).

$$E_k(t) = \left\{ E_0^k + \frac{RT}{zF} \ln \left[\frac{c_2^k(t) \times c_5^k(t)}{c_3^k(t) \times c_4^k(t)} \right] + \left| \eta_{k_{conc}}^{+ve/-ve}(t) \right| \right. \\ \left. + \eta_m + \eta_e + \eta_{k_{ely}}^{+ve/-ve}(t) \right\} \quad (6.9)$$

6.2.2 Pump Power Loss

Pump power loss is a unique and a significant contributor to the battery efficiency in case of flow batteries. The pump power loss can be calculated by finding the product of flow rate and pressure drop in the cell [107].

$$P_{pump} = \Delta p \times Q \quad (6.10)$$

when there is a direct electrolyte flow through the porous electrode, Darcy's law is used to determine the pressure drop as shown in Eqn. 7.11.

$$\Delta p_e = \frac{\mu L_e Q_e}{K_p A_e} \quad (6.11)$$

where μ is the dynamic viscosity of the electrolyte, K_p is the permeability coefficient, Q_e is the volumetric flow rate across the electrode, and L_e and A_e are the electrode length and area, respectively. Permeability coefficient can be computed by Kozeny-Carman equation.

$$K_p = \frac{d_f^2 \epsilon^3}{K_{ck} (1 - \epsilon)^2} \quad (6.12)$$

where K_{ck} is the Kozeny-Carman constant, ϵ is the electrode porosity and d_f is the mean fibre diameter. Two sources contribute to the pressure drop across

the distribution channel. First is caused by friction of fluid with the wall of the channels and drop within the fluid due to the influence of viscosity. Second is the pressure drop is caused by the change of velocity and direction of the fluid in the channels. The overall pressure drop in the channels can be determined by Eqn. 7.13.

$$\Delta p_c = \left(f_c \frac{L_c}{2r_c} + K_{fo} \right) \times \frac{\rho}{2A_c^2} Q_c^2 \quad (6.13)$$

where f_c is the friction coefficient, L_c and A_c are the length and cross-section area of the channels, respectively. r_c is the hydraulic radius, K_{fo} is the resistance coefficient due to the channel form, ρ is the electrolyte density, and Q_c is the flow rate across the channels.

$$f_c = 64 \frac{\mu A_c}{\rho (2r_c) Q_c} \quad (6.14)$$

The fluid flow is considered to be at laminar conditions, so the friction coefficient is expressed using the Darcy-Weisbach equation.

$$\begin{aligned} P_{bat} = & \left\{ i(t) \times \sum_{k=1}^n \left(E_0^k + \frac{RT}{zF} \ln \left[\frac{c_2^k(t) \times c_5^k(t)}{c_3^k(t) \times c_4^k(t)} \right] \right. \right. \\ & \left. \left. + \left| \eta_{kconc}^{+ve/-ve}(t) \right| + \eta_m + \eta_e + \eta_{kely}^{+ve/-ve}(t) \right) \right\} \\ & + \left\{ \left[\frac{\mu L_e Q_e(t)}{K_p A_e} + \left(\left(f_c \frac{L_c}{2r_c} + K_{fo} \right) \times \frac{\rho}{2A_c^2} Q_c^2(t) \right) \right] \times 2Q(t) \right\} \\ & + \left\{ \frac{[E_n(t) - E_1(t)]^2}{R_{sh}} \right\} \end{aligned} \quad (6.15)$$

By combining all the over-potentials, pump power and the shunt current losses, the effective battery power (P_{bat}) at any time is given by the above equation.

where $i(t)$ is the current supplied by the source at time t , and $Q(t)$ is the vol-

Figure 6.1: Block diagram showing battery with fuzzy logic controller

umetric flow rate at time t . In practical situations, there will be variances in the concentration of the ions in different cells.

6.2.3 Fuzzy Logic Control for Charging Optimization

The fuzzy logic controller uses a set of fuzzy rules to determine the optimal value of current and flow rate for a specific mode of operation. The output from the fuzzy logic controller is basically the set-point value for the Current Control Unit (CCU) and Flow Control Unit (FCU), which in turn controls the physical quantities.

There are several examples in literature using fuzzy logic controller (FLC) for fuel cells, which is operationally similar to flow batteries. FLCs offer a very good dynamic performance with minimal overshoot and a fast response. It follows a linguistic approach, where the rules are defined by an antecedent (IF statement) and a consequent (THEN statement). The rule can have more than one ‘if’ condition affecting more than one variable. FLC is especially useful, when there are several variables and in cases where some of the variables are unpredictable and/or discontinuous. For the purpose of this simulation, intrinsic losses (measured, calculated and normalized individually), pump power loss, battery life, and operator mode selection are given as the FLC input variables. The lower and upper limits

for the current and flow rate values are 39.325-65.625 A and 0.2-0.71 m³ h⁻¹ respectively. The model is initially swept through the extremes of current and flow rate to determine the maximum values of the losses in the battery and the membership functions of the fuzzy logic controller are set based on these values.

The capacity decay of the battery is added as one of the input variables to the FLC. On studying how charging current affects the decay of capacity, it is shown that higher current causes lower decay in long term cycling [56]. One of the major indicators of capacity loss is the change in vanadium ion concentrations. The trend in variation of concentration and the way it affects the battery capacity is studied in chapter 6 and data from the model is used. In this simulation, the decay trends of V³⁺ and V⁴⁺ ions at fully discharged state are used to estimate the current state of life of the battery.

Operators are seldom given control to define the charging protocol of batteries because of the strict parameter constraints. However, in this case, by using a system aware model and fuzzy control, different modes of operation can be provided to the operator. The limits are set in the controller and there is a continuous real-time monitoring of the constraints to establish a safe operating region. Three simple operational modes namely time biased mode (*T*), energy biased mode (*E*) and autonomous mode (*A*) are proposed. In the time biased mode, there is a preferential bias in the controller for higher current and lower flow rate to make the battery reach full SOC faster by sacrificing the energy efficiency and capacity. In energy biased mode, there is a preferential bias in the controller for lower current and higher flow rate to achieve higher energy efficiency. The autonomous mode is a middle ground, where the flow rate and current are determined by the controller such that a satisfactory performance of both energy efficiency and time efficiency are achieved. The following fuzzy rules are devised to implement the control strategy:

- IF *intrinsic losses* are *high* and *pump loss* is *not high* – THEN *current* is set *low* and *flow rate* is set *high*
- IF the controller is set in *power bias* mode and *none of the losses* are *high* – THEN *current* is set *low* and *flow rate* is set *high*
- IF the controller is set in *time bias* mode and *none of the losses* are *high* – THEN *current* is set *high* and *flow rate* is set *low*
- IF *pump loss* is *not low* - THEN *flow rate* is *not set high*
- IF *decay* is *not less* – THEN *current* is *not set low*

6.3 Simulation Results

For this study, a kilo-watt scale 15 cell flow battery system is modelled. Dimensions of the cells are considered such that the interacting surface area of the electrode is $8.75 \times 10^{-2} \text{ m}^2$. A typical flow battery setup with Nafion 115 membrane, bipolar plates, gaskets, electrolyte tanks, and two pumps are considered.

The following assumptions are made for the simulation, i) concentration overpotential due to formation of bubbles at the electrode is neglected, ii) volume is assumed to be constant and parameters such as pressure, concentration, and potential are considered to be isotropic in the cell, iii) operational voltage boundaries are set as 1.1 V at the end of discharge and 1.7 V at the end of charge, iv) concentration boundaries are set 0.001 & 1.999 mol L⁻¹ to maintain logarithmic stability, v) electrolyte flow is incompressible, vi) hydrogen and oxygen evolution or any other side reaction is neglected. The parameters used for simulations are mentioned in Table 6.2. A simple block diagram of battery along with the fuzzy control system used for this study is shown in Fig. 6.1. Data from the sensors are continuously

collected and fed into the processing unit, where the losses are calculated. The absolute values are then input to the normalizing unit to get the respective relative magnitudes. The output from the normalizer is sent to the fuzzy logic controller.

Table 6.2: Specifications of the flow battery simulation parameters

Parameters	Values
Kozeny-Carman constant (K_{ck})	5.0
Cell voltage boundary	1.1 V - 1.7 V
Channel length (L_c)	12 cm
Diffusion coefficient of V^{2+} ion (D_2)	$6.9 \times 10^{-7} \text{ dm s}^{-1}$
Diffusion coefficient of V^{3+} ion (D_3)	$2.54 \times 10^{-7} \text{ dm s}^{-1}$
Diffusion coefficient of V^{4+} ion (D_4)	$5.37 \times 10^{-7} \text{ dm s}^{-1}$
Diffusion coefficient of V^{5+} ion (D_5)	$4.64 \times 10^{-7} \text{ dm s}^{-1}$
Dynamic viscosity (μ)	4.928×10^{-3}
Electrode conductivity (σ_{eld})	500 S m^{-1}
Electrode length (L_e)	35 cm
Electrode porosity (ϵ)	0.68
Electrode surface area (A_e)	875 cm^2
Electrode thickness (δ_{eld})	$4 \times 10^{-3} \text{ m}$
Electrolyte concentration	2 mol L^{-1}
Electrolyte density (ρ)	1400 kg m^{-3}
Faraday constant (F)	$96485 \text{ s A mol}^{-1}$
Formal cell potential (E_0)	1.4 V
Gas constant (R)	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Hydraulic radius (r_c)	0.003 m
Mean fibre diameter (d_f)	$3 \times 10^{-15} \text{ m}$
Membrane surface area (A_m)	875 cm^2
Membrane thickness (δ_m)	$125 \times 10^{-6} \text{ m}$
Number of cells (n)	15
Temperature (T)	303.2 K

The impact of the fuzzy input parameters on current control and flow rate control is shown in Fig. 6.2, 6.3, 6.4, and Fig. 6.5, 6.6, 6.7, respectively. The parameters are defined by three membership functions each, namely low, medium, and high. The visualizations also provide an idea on how seemingly disconnected variables interact, when introduced in a system of multiple constraints.

Figure 6.2: Current — Mode and Pump power loss

Figure 6.3: Current — Mode and Intrinsic losses

Figure 6.4: Current — Pump power loss and Capacity decay

The effect of operational mode and pump power losses on current is shown in Fig. 6.2. It can be seen that the current is varying only in energy biased mode and is maximum in modes T and A . The current value is low at low and medium values of pump loss and is high, when the pump loss increases in energy bias mode. In Fig. 6.3, the change in current control value based on the mode and intrinsic losses can be seen. There is a steady depression of current in the energy biased operation for improved efficiency with the lowest point for both E and A modes at high loss. Fig. 6.4 shows that the current value is increased as the capacity decay increases to elongate battery life. In this case, the current is highest, when the pump power is high near the end of a battery's lifetime.

Figure 6.5: Flow rate — Mode and Pump power loss

Figure 6.6: Flow rate — Mode and Intrinsic losses

Figure 6.7: Flow rate — Capacity decay and Pump power loss

In Fig. 3, the flow rate variation with respect to different input parameters is shown. The change in flow rate control value based on the mode and pump power losses can be seen in Fig. 6.5. There is a steady bulge of current in the energy biased operation for improved efficiency with the highest point for both E and A modes at high loss. The flow rate is set lowest at the high power loss, when the controller is set in time bias mode. In Fig. 6.6, the controlled change in flow rate with respect to operational mode and intrinsic losses is shown. The flow rate is higher in energy bias mode and it is set at a lower value in modes A and T . Further, the flow rate is reduced, when the intrinsic losses are high even in energy bias mode. There is no change in flow rate with respect to capacity decay in this

model and it is shown in Fig. 6.7. In the same plot (Fig. 6.7), the pump power loss and flow rate relationship can be seen. Flow rate is lowered, if the pump power loss is high as there is an exponential rise in pump power loss in relation to flow rate increase.

6.3.1 Results

The performance of the battery in different operational scenarios regulated by the controller is discussed below. The capacity at the end of charge cycle for extreme values of current and flow rate have been plotted and compared with the experimental results based on the work published by Ma *et al.* [64]. It can be seen from Fig. 6.8 that the simulation values follow the experimental values reported in the literature closely [64]. Where in L is the lower limit, H is upper limit, and the first position corresponds to current and the second position corresponds to flow rate. The graph also shows the drastic variation in the energy capacity at 100% SOC measured by OCV based on battery voltage characteristics.

Figure 6.8: Comparison of experimental and simulation results of capacity for different test cases

The voltage profiles of the battery at different operating conditions are shown

in Fig. 6.9, where AS , ES , and TS are the operator defined Autonomous, energy biased, and time biased modes for a new battery with no capacity decay, respectively. The maximum voltage is capped at 23.5 V as analysed from the literature for a safe battery operation.

Figure 6.9: Comparison of voltage curves for different operation modes

The typical voltage characteristics for charging is seen in Fig. 6.9, where there is a rapid increase in voltage initially due to the offset created by the nominal voltage and the over-potentials. The battery, when operated in time bias mode, the voltage reaches the maximum value at a lower capacity value, whereas in the case of energy bias mode, the ascent is slower. In autonomous mode, there is no bias and the capacity-voltage relationship is seen to have a middle point. The three operation modes can further be compared to the relevant boundary values of the respective operational variables.

In Fig. 6.10, the different operation modes are compared with the modes LL , where both current and the flow rate are set to the lowest limit, and LH , where current is set to the lowest limit and flow rate is set at maximum. Energy capacity at the end of charge, pump power, and the respective current values are presented.

Figure 6.10: Comparison of Capacity, Pump loss and Current density in different operation modes

In *LL* mode, the energy loss due to the pump operation is the lowest at 3 Wh as the flow rate is minimum. The energy capacity is at 32 Ah in this mode. The capacity is reduced to 23 Ah in time biased mode (*TS*) as the current is increased to 71 A and there is a small increase in pump loss at 8.5 Wh as compared to the *LL* mode. The trends for the *AS* and *ES* modes are predictable with decreasing current values, increasing pump loss due to increasing flow rate. The capacity is

Figure 6.11: Comparison of Electrolyte utilization, Current density and flow rate in different operation modes

also highest in *ES* mode among the operator defined modes. It can be observed that the capacity is high at 41 Ah, when the current is at the lowest limit and the flow rate is at the highest. The pump loss, however is high at 110 Wh owing to the exponential rise in power with respect to flow rate.

One of the important indicators of energy efficient operation of battery is the utilization of electrolyte. In Fig. 6.11, the modes are compared with *HH* (75 mA cm^{-2} current and $0.71 \text{ m}^3 \text{ h}^{-1}$ flow rate) and *LH* (45 mA cm^{-2} current and 0.71

$\text{m}^3 \text{ h}^{-1}$ flow rate). Lowest electrolyte utilization at 42% is observed in time bias mode, where the flow rate is low at $0.41 \text{ m}^3 \text{ h}^{-1}$ and 71 mA cm^{-2} . There is a strong correlation between charging current density and electrolyte utilization with inverse proportional relationship. By comparing the correlation, it can be observed that there is a 23% increase in electrolyte utilization as the current density is reduced by 28% in the operator defined mode between energy bias, and time bias mode. Percentage increase in flow rate is just about 6% for the same region as the flow rate is greatly restricted by the controller to reduce the pump power loss. Thus, the electrolyte utilization is determined more by the current density, than the flow rate in the battery.

In Fig. 6.12, the intrinsic losses are compared for the different operation modes as the capacity of the battery decays. The losses are compared at the start of operation, after 50% battery life, and the state near end at 95% of the battery life. In energy bias mode the loss is at 8.7% at start, 10.04% in autonomous mode, and 11.23% in time bias mode. The losses are very similar for both scenarios at 50% and 95% of the battery life. Comparison of E , A and T modes, is about 10%, 10.34%, and 10.38%, respectively. There is a steady trend showing the increase in intrinsic losses moving from energy bias mode to time bias mode and the difference is about 2.53% at the start. The difference, however, reduces with time showing only 0.38% between T and E modes with a major difference around 0.34% between A and T mode. The losses are about constant in autonomous mode as the time progresses, the energy bias operation shows an increase with increasing time and a decreasing trend of loss is observed in time bias mode as time progresses.

Figure 6.12: Comparison of Intrinsic losses at start, mid and end of life

6.4 Summary

The battery operation with individual over-potentials and the losses due to the pump operation have been modelled to facilitate current and flow rate control. A 15 cell, kW scale battery is used as the reference for this model, which can be scaled up based on the application needs. The model is used to include a real-time control of operator profile based charging by means of fuzzy logic controller. The battery sensor data, pump power, and battery life along with different modes of operation defined by the operator is used to control the charging current and the flow rate

value. The charging process of the battery is defined by concentration change of the vanadium ions determined by state space equation. Activation over-potential, concentration over-potential, ohmic over-potential, shunt losses, and pump power losses are individually modelled and appended to the basic model.

Capacity degeneration due to ion diffusion is considered based on the loss characterization profile from literature to include the decay properties in the control mechanism. Three operator defined modes namely autonomous, time bias, and energy bias are considered. However, these modes are not exhaustive but a fragment of the many forms of control that can be achieved by using fuzzy logic control for flow battery. It is important to include source and load profile to achieve a more efficient battery operation. The charge controller with an effective energy management system will improve the battery life and reduce the time to get return on investment. Fuzzy logic charging control is the first step towards adaptive, system aware battery control. The work can be extended to have different sources such as solar PV or wind energy, where the operation is adaptively enhanced by learning the source characteristics.

Such optimization have a role to play in other state of the art systems such as micro-grids. These self reliant small grids are highly flexible systems with several energy sources and sinks. Considering the unpredictability of power delivery by renewable sources and varying demand, an adaptive buffer is the key for their smooth interconnection. Flow batteries are a popular choice when it comes to adaptive energy storage solutions. Adding to that, profile based optimization can have different user profiles based on the micro-grid design and need, thereby the system becomes more robust without adversely affecting the performance or life of the battery. Different profiles can be added or remapped to give room for future changes in the micro-grids.

Chapter 7

Conclusions and Recommendations

7.1 Conclusions

Grid scale energy storage will undoubtedly play a major role in the near future with the advancements in grid infrastructure and the need for making renewable energy penetration more reliable and robust. Several energy storage technologies have been developed over the years and some are more promising than the others with batteries being one of the most practical and widespread choices. The popularity and applicability of any battery depends on factors such as, availability of resources, cost of production and finding its right place in the variety of applications.

Considering the unique features and the growth of VRB in the past few years, it is an outstanding choice for large scale energy storage. A significant effort is taken up by researchers and companies to increase the energy density, reduce the operational cost, and make it more commercially viable. In this thesis, a modest effort is made to contribute towards the advancement of this technology by investigating its

operational characteristics on reducing the capacity decay and introducing operator based control to enhance the applicability to different scenarios.

The effect of capacity decay over the lifetime of flow battery was investigated through simulations (Chapter 3). For different rates of vanadium ion diffusion, the decrease in the percentage of energy capacity was computed. The concentration flux has a direct impact on the magnitude of the rate of species crossover and the relationship between flow velocity and the concentration flux was computed. The variation in concentration flux was analysed for different concentrations of V^{5+} species. The influence of concentration depletion on the charge transfer current density on the positive electrode of the battery was examined and a linear association was observed.

The magnitude of capacity decay depends on various factors and ion-diffusion is the most dominant of them all. The effect of temperature on capacity decay due to ion-diffusion was studied for three different membranes. This was done by developing a dynamic model to depict the influence of temperature on change of concentrations of various species of vanadium ions due to the diffusion and the resulting side reactions that occur in the half cells. The analysis was extended to study the temperature affected intrinsic losses and diffusive losses in Nafion 115 membrane (Chapter 4).

In practical scenarios, as the ions diffuse through the membrane, they drag the electrolyte along with them to the other half-cell. There are several different processes leading to this transfer of bulk electrolyte such as 1) water transport across the membrane due to concentration gradient 2) water carried by the charge balancing species in the battery, and 3) electrolyte transfer due to the pressure difference between the two half-cell solutions, which is a result of volume imbalance between them. The amount of transfer is dependent on the type of membrane and the SOC of the vanadium electrolytes giving a different rate of transfer for each membrane.

This preferential transfer might lead to issues such as precipitation of vanadium salts due to increase in concentration of one half-cell electrolyte and dilution of the other. This transfer of electrolyte causes change in concentration between the half-cells thereby reducing the energy capacity of the battery. A comprehensive model including the volumetric change in the battery is developed. Concentration change of the individual vanadium species is studied along with the transfer of volume and loss of capacity due to this phenomena (Chapter 5).

Preliminary studies on multi-modal charging characteristics of vanadium redox flow battery is done for their operation in buildings using an equivalent circuit model of the VRB. Energetic and temporal characteristics were studied for fixed values of flow rate and current (Chapter 3). Following this, an electrochemical model incorporating individual over-potentials of the battery along with the losses due to the hydraulic circuit is developed. An operator profile based charging by enabling real-time control of input parameters was introduced. A fuzzy logic controller is used to implement the profile based control by considering the normalized values of the various intrinsic losses, loss due to pump power operation, and state of life of the battery (Chapter 6). Three operator defined modes namely autonomous, time bias, and energy bias are considered, however, these modes are not exhaustive but a fragment of the many forms of control that can be achieved. It is important to include source and load profile to achieve a more efficient battery operation. The charge controller with an effective energy management system will improve the battery life and reduce the time to achieve return on investment.

7.2 Recommendations for Future Research

- The proposed ageing model focuses only on the first generation of vanadium flow batteries. Several new technologies are being proposed with different electro-chemistries and improved energy density. Many new membranes have also been proposed since the start of this work, of which, some are even commercially available. The process of capacity decay due to ion-diffusion can be studied for these newer technologies and a comparison can be made on how these batteries perform in the longer run. Comparison of capacity decay between different flow battery technologies is a critical area of research and the work in this thesis can be used to study these differences.
 - The charging optimization work proposes only three generic modes of operation with the loss values and state of health of the battery consideration. Flow battery based energy storage, however, can be applied in a plethora of applications in a grid infrastructure ranging from power quality improvement, providing ancillary services, to EV charging, and so on. Each application has its own requirements for efficient operation and there might be a need to consider additional parameters due to limitations based on geographical constraints. This opens up a new area of adaptive control based on input data or algorithms based on machine learning to be devised to target a wider field of application.
 - Optimizing the discharge characteristics based on the operator needs, considering the safe operation of the battery is important. Research on this area has been carried out for other mainstream batteries, but it is important to investigate the operation of VRB for different load profiles. An effective chemistry based optimization of complete charging and discharging cycles for
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VRB in buildings for various source and load profiles is yet to be studied.

- A comprehensive optimization methodology comprising of device level optimization and power electronics control for different scenarios should be investigated. These studies are usually time consuming and mathematically complex. However, with the technological improvements of sensors, and state of the art SOC estimation techniques, an accurate comprehensive optimization of batteries is becoming a reality. Research on fast converters, innovative control methodologies and battery materials are important to realize the true potential of large scale flow battery based energy storage systems.

Appendix A

Additional Content

A.1 Capacity Decay and Multi-modal Charging

Table A.1: Capacity decay for 10000 cycles

Cycles	15 ⁻⁶ %	20 ⁻⁶ %	25 ⁻⁶ %
	Depletion/cycle		
0	100.00%	100.00%	100.00%
1000	98.58%	97.87%	97.16%
2000	97.16%	95.74%	95.03%
3000	95.74%	93.61%	91.49%
4000	93.61%	90.78%	87.94%
5000	91.49%	87.94%	84.39%
6000	89.36%	85.10%	79.43%
7000	87.23%	81.56%	74.47%
8000	85.10%	77.30%	68.79%
9000	82.27%	73.05%	61.70%
10000	79.43%	68.79%	55.32%

Table A.2: Concentration flux for various concentrations

Velocity	Concentration Flux ($\text{mol m}^{-2} \text{s}^{-1}$)			
	0.5	0.6	0.7	0.8
m/s	mol/dm ³			
0.01	0.0050	0.0060	0.0070	0.0080
0.012	0.0060	0.0072	0.0084	0.0096
0.014	0.0070	0.0084	0.0098	0.0112
0.016	0.0080	0.0096	0.0112	0.0128
0.018	0.0090	0.0108	0.0126	0.0144
0.02	0.0100	0.0120	0.0140	0.0160
0.022	0.0110	0.0132	0.0154	0.0176
0.024	0.0120	0.0144	0.0168	0.0192
0.026	0.0130	0.0156	0.0182	0.0208
0.028	0.0140	0.0168	0.0196	0.0224
0.03	0.0150	0.0180	0.0210	0.0240

Table A.3: Charge transfer current density at different temperatures

Conc.	Charge transfer current density (A dm^{-3})			
	at 20 °C	at 25 °C	at 30 °C	at 35 °C
1.5	21.15834	20.80341	20.46019	20.12812
1.45	20.80271	20.45375	20.1163	19.78981
1.4	20.4409	20.098	19.76643	19.44561
1.35	20.07256	19.73585	19.41024	19.09521
1.3	19.69734	19.36692	19.0474	18.73826
1.25	19.31483	18.99083	18.67752	18.37438
1.2	18.92459	18.60714	18.30015	18.00314
1.15	18.52614	18.21536	17.91484	17.62408
1.1	18.11892	17.81498	17.52106	17.23669
1.05	17.70234	17.40538	17.11823	16.84039
1	17.27571	16.98591	16.70568	16.43454

A.2 Diffusion Coefficient values

Table A.4: Diffusion coefficient values for Selemion CMV

Temperature	D_2' (dm s ⁻¹)	D_3' (dm s ⁻¹)	D_4' (dm s ⁻¹)	D_5' (dm s ⁻¹)
10 °C	2.19E-07	4.95E-08	1.38E-07	8.64E-08
20 °C	2.82E-07	6.36E-08	1.78E-07	1.11E-07
30 °C	3.56E-07	8.04E-08	2.25E-07	1.4E-07
40 °C	4.44E-07	1E-07	2.8E-07	1.75E-07

Table A.5: Diffusion coefficient values for Selemion AMV

Temperature	D_2' (dm s ⁻¹)	D_3' (dm s ⁻¹)	D_4' (dm s ⁻¹)	D_5' (dm s ⁻¹)
10 °C	2.44E-08	1.51E-08	6.29E-09	1.78E-08
20 °C	3.14E-08	1.94E-08	8.09E-09	2.28E-08
30 °C	3.97E-08	2.45E-08	1.02E-08	2.89E-08
40 °C	4.94E-08	3.05E-08	1.27E-08	3.6E-08

Table A.6: Diffusion coefficient values for Nafion 115

Temperature	D_2' (dm s ⁻¹)	D_3' (dm s ⁻¹)	D_4' (dm s ⁻¹)	D_5' (dm s ⁻¹)
10 °C	4.77E-07	1.75E-07	3.71E-07	3.21E-07
20 °C	6.13E-07	2.25E-07	4.77E-07	4.13E-07
30 °C	7.75E-07	2.85E-07	6.03E-07	5.22E-07
40 °C	9.65E-07	3.55E-07	7.51E-07	6.5E-07

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