Study of multi-parameters for the improvement of performance and development of a 1 kW vanadium redox flow battery stack

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**STUDY OF MULTI-PARAMETERS FOR THE
IMPROVEMENT OF PERFORMANCE AND
DEVELOPMENT OF A 1 kW VANADIUM REDOX
FLOW BATTERY STACK**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Arjun Bhattarai

Abstract

The extensive use of intermittent renewable energy supplies from solar and wind in the recent decades resulted in huge demand for large scale energy storage systems. Redox flow batteries (RFB) hold the capacity to meet these demand, of which, the vanadium redox flow battery (VRFB) is the most popular due to its safe chemistry. Compared to other types of secondary batteries, VRFB offers many advantages, such as flexibility to independently design power density and backup time, life-time of decades requiring low maintenance, environmentally-friendly technology, fast response, high efficiency, excellent load levelling and peak shaving capacity, no safety issues with overcharging or deep-discharging and the cheapest leveled cost/cycle/kWh.

Despite commercial availability of VRFB, there have been extensive research interest on improving the performance and reducing the cost of the technology. Research works have mainly focused on the electrode, membrane, electrolyte, and stack design. The VRFB performance is affected by various losses such as activation, Ohmic, mass transport, and other losses such as pump loss, self-discharge, shunt current loss and capacity loss. In conventional designs, electrolyte is forced to flow through the cross section of the porous electrode. Therefore, in a large area cell and stack, optimization of the flow distribution through the porous electrode is important for minimizing the Ohmic and mass transport losses, and protecting the electrode material from degradation. In parallel to improving the flow distribution, the reduction of pump power loss due to the pressure drop across the porous electrode also needs to be considered to maintain a high overall energy efficiency. More importantly, there are no suitable methods available to precisely map the flow behavior through the porous media. Hence, this PhD research aimed to develop suitable methods to study (and improve) the flow distribution in conventional VRFB, minimize the various losses and demonstrate all the improvements by the development of a 1 kW flow battery stack system. The 1 kW stack was aimed to operate at a current density

of 80 mA cm⁻² and deliver a stable energy and voltage efficiency of >80% during long-term testing.

To fulfil the objective of understanding and improving the flow distribution through the porous media, segmented cell and pH tracing approach were developed. A single cell with electrode area of 100 cm² was divided into sixteen segments and was used to study the local voltage and open circuit voltage (OCV) distribution. It was demonstrated for the first time that the in-situ flow behavior can be precisely predicted and quantified using the local OCV or state of charge (SOC) mapping. Similarly, pH tracing test was developed for the easy and fast screening of the flow distribution. This test was found to be useful in comparing the flow frame designs and improving the electrode configurations during the 1 kW stack development. Further, as an approach to improving the flow distribution and reducing parasitic losses, four designs of flow channel on the porous electrode were investigated for the first time. Of the various designs, interdigitated (IDD) channels on the porous electrode was found to be promising due to the improvement of overall energy efficiency up to 2.5% and reduction of pressure drop by ~ 40%, as compared to cell with no flow channels. Next, to fulfil the target of 1 kW stack development, it was necessary to examine and optimize various areas in flow battery that were critical in determining the stack performance. As such, optimization of electrode compression was done by investigating a wide range of compression in order to minimize the Ohmic and mass transport losses. Similarly, a “power drop effect” was reported in operation of flow battery at high current density. This effect was found to be an important performance determining feature, and it is reported for the first time in this dissertation. Further, during flow battery operation, electrolyte species crossover through the membrane causes electrolyte volume imbalance between two tanks and gradual capacity loss. To address this issue, two tanks were made in hydraulic shunt connection with each other and auto rebalancing of electrolyte was made. In addition, the use of a combination of anion exchange membrane (AEM) and cation exchange membrane (CEM) in a stack was investigated to minimize the

capacity loss and experimentally verified for the first time that this concept worked effectively. Similarly, electrode activation is necessary to improve the cell kinetics. Therefore, an investigation was carried out to understand the effects of thermal activation on the electrode performance using surface and electrochemical characterization.

All the improvements made through multi-parameter tests were demonstrated in a 20 cell-1 kW stack. The stack used novel design of flow frames with integrated flow guides in consideration of uniform electrolyte flow distribution, thermally treated porous electrodes machined with IDD flow channels, and thin BPs from SGL Carbon. The test results of 250 cycles at 80 mA cm^{-2} showed a stable energy efficiency and voltage efficiency over 80%, pressure drop reduction by $\sim 40\%$, and a stable capacity achieved through auto rebalancing of electrolyte. Hence, the objective of this PhD research was accomplished.

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List of Publications

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Conferences

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2. **A. Bhattarai**, R. Schweiss, A. Whitehead, G.G. Scherer, N. Wai, P.C. Ghimire, T.D. Nguyen, M. O. Oo, H.H. Hng, Reducing electrolyte imbalance in the all-vanadium flow battery, presented at International Flow Battery Forum (IFBF), Manchester, United Kingdom in June 2017.
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Abbreviations

NTU	Nanyang Technological University
RFB	Redox Flow Battery
kWh	Kilo Watt Hour
ΔP	Pressure Drop
VRFB	Vanadium Redox Flow Battery
BP	Bipolar Plate
SOC	State Of Charge
CFD	Computational Fluid Dynamics
PEM	Polymer Electrolyte Membrane
OCV	Open Circuit Voltage
CC	Current Collector
IDD	Interdigitated
FF	Flow Frame
DC	Direct Current
EE	Energy Efficiency
CE	Coulombic Efficiency
VE	Voltage Efficiency
ASR	Area Specific Resistance
DOE	Department Of Energy
CEM	Cation Exchange Membrane
AEM	Anion Exchange Membrane
G1	Generation 1
PAN	Polyacrylonitrile

PCB	Printed Circuit Board
PVC	Poly Vinyl Chloride
PP	Polypropylene
PTFE	Polytetrafluorethylene
ROC	Rectangular Open Channel
IDD-OC	Interdigitated Open Channel
CPCC	Cross Poked Circular Channel
IDD-CPC	Interdigitated Circular Poked Channel
SCE	Saturated Calomel Electrode
EIS	Electrochemical Impedance Spectroscopy
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
CV	Cyclic Voltammetry

Chapter 1

Introduction

This chapter presents the scientific and technical issues related to the all vanadium redox flow battery (VRFB) and the relevance to conduct this study. Optimizing the flow distribution and minimizing the various losses to improve the long-term performance of the VRFB are among the major research and development focus of the VRFB. This study aims to develop a commercial size flow battery stack with improvement in component design, electrode performance, flow distribution, pump power consumption and capacity decay. This chapter also highlights the major findings and outcomes of the study.

1.1 Problem Statement

Redox flow batteries (RFB) offer the unique advantage of allowing independent scaling of power output (in kW) and energy storage capacity (in kWh). Of the various RFBs, the vanadium redox flow battery (VRFB) is the most widely preferred in commercial systems. Compared to other types of secondary batteries, VRFB offers many advantages, such as flexibility to independently design power density and backup time, life-time of decades requiring low maintenance, environmentally-friendly technology, fast response, high efficiency, excellent load levelling and peak shaving capacity, no safety issues with overcharging or deep-discharging and cheapest levelized cost/cycle/kWh [1, 2]. In a conventional VRFB stack, the cells consist of highly porous ($> 90\%$ porosity) carbon electrodes, separated electrically by ion-exchange membranes on one side, and ionically by non-porous bipolar plates (BP) on the other. Classically, the BPs are in the form of flat sheets without flow fields. This is the so-called ‘flow through’ geometry, which means the electrolytes stored externally in tanks are pumped through the electrodes for energy storage and release.

The viscous resistance to flow, which mainly depends on the permeability of the electrode material and viscosity of the electrolyte results in a differential pressure (Δp) between the inlet and the outlet (over the length of the electrode). The higher is the pressure drop, the more is the pumping loss that reduces the overall energy efficiency (EE) of the battery. Δp increases with compression (which reduces permeability), flow length (L), flow rate (Q) and viscosity of the electrolyte. The energy consumption of the pumps increases linearly with Δp . In a kW size stack, the pump consumes 2-3% of the total energy generated [2]. A simple approach to reducing Δp , and hence reducing the pumping losses, is the use of wide rectangular

electrodes with shorter flow path. However, this type of distorted geometry could cause an uneven flow distribution [3].

In addition to Δp , the flow distribution of electrolyte is an important consideration in VRFB. Ideally, the electrolyte should distribute uniformly through the porous electrode. However, non-uniformity of electrolyte flow may arise from various causes such as improper design of flow frame, non-uniform or excessive compression of the felt electrode, uneven wettability of the bulk electrode or non-uniform thickness of the electrode. A non-uniform flow distribution can result in non-uniform current distribution with the possibility of locally overcharging the electrolyte, which causes gas evolution and degradation of BPs [4]. A non-uniform flow distribution also increases Ohmic and mass transport polarization, which eventually reduces the battery performance. Though the impact of uneven flow distribution is detrimental to battery life, it is difficult to monitor flow distribution inside the porous electrode during the cell operation. So far, none of the literatures has proposed a suitable method for monitoring the flow distribution through the porous electrode. Spatially resolved local current and voltage mapping in a segmented cell is a unique and strong tool to investigate the in-situ behavior of the cell. This approach is well established in polymer electrolyte membrane (PEM) fuel cell research [5-9]. In contrary, segmented cell study on flow battery is scarce. Very few of the available literature on flow battery segmentation focuses on understanding the local behavior on the small size cell of fuel cell design. More importantly, segmented cell study has not been used directly for the flow distribution study.

Capacity loss is also one of the serious problem of flow batteries. Reversible capacity loss happens primarily due to water transfer through the ion exchange membrane, which requires frequent rebalancing of the electrolyte. Whilst, irreversible capacity loss is a function of various operation parameters such as high voltage operation,

high SOC cycling, high temperature operation, surface passivation, leakage, etc. Therefore, eliminating the irreversible losses and reducing the reversible losses are of research interest in VRFB. Finding a suitable method to minimize the reversible capacity loss will help solve the current problem of frequent rebalancing, which results in the loss of usable energy and additional hardware requirement.

There are several areas to be investigated and optimized for improving overall performance of the flow battery. The design of the various mechanical components, electrode activation, optimization of electrode compression, right selection of BPs and membrane, and optimization of operational parameters (current density, flow rate, voltage window, etc.) are equally important for further development of VRFB for commercial application.

1.2 Objectives and scope

The general objective of this study is to develop suitable methods to improve the flow distributions in a conventional VRFB, perform multi-parameter tests to minimize the various losses and to realise all the improvements by developing a 1 kW flow battery stack.

Specific objectives:

- Development of segmented cell approach for the study of in-situ flow behavior in the VRFB.
- Design of advanced porous electrode with flow channels for the performance improvement in flow battery.

- Development of pH tracing test for the study of flow behavior in large area cell and stack.
- Optimization of electrode compression in the conventional VRFB design.
- Explore novel approaches to minimize the reversible capacity loss in the VRFB.
- Optimization of the operational parameters such as flow rate, current density, state of charge (SOC), etc.
- Conduct various tests with different configurations and material combinations to improve the overall performance of the VRFB.
- Demonstration of all the improvements through the development of a 1 kW stack.
- Testing the performance of 1 kW stack.

Project scope:

For the in-situ study of flow distribution of electrolyte through the porous media, a spatially resolved voltage distribution approach using a segmented cell was used. For this, a single cell of 100 cm² active area was divided into sixteen segments and a local study was performed to understand the flow distribution during battery operation. Using this method, it was shown how segmented cell study can be used to improve the design of the flow frame and how severe the non-uniform flow distribution during the operation of the flow battery is. In addition to the segmented cell approach, a flow simulation was also used to optimize the design of the manifolds and flow channels in the flow frame for uniform flow distribution of electrolyte. For the study of flow distribution in a large area cell (of 1 kW class), a simple ex-situ method, named as “pH tracing”, was developed.

For the improvement of the flow distribution and the reduction of the pump power losses, the applicability of flow channels in the porous electrode was studied. The study of flow channel concept was conducted on a 100 cm^2 active area single cell. The promising design of the flow channel on the porous electrode was further tested in a large area cell (active area of 625 cm^2) using pH tracing.

The electrode compression has to be optimized for the best performance. Too high a compression would lead to poor utilization of the electrode and a high pressure drop, whereas, too low a compression would lead to a poor contact resulting in higher Ohmic loss. Therefore, this study optimized the electrode compression in a conventional VRFB design.

Capacity loss primarily due to water transport is considered a big problem in flow battery operation. In this regard, this work attempted to explore some novel approaches to minimize the reversible capacity loss in VRFB. The effects of high current density operation, flow rate, state of charge (SOC), electrode activation, etc. crucial to cell performance were also studied.

A 1 kW stack was developed, which demonstrated all the improvements made during the study of multi-parameters. The development of a 1 kW stack system was realized gradually through three intermediate steps, which consisted of the design, fabrication and testing of; 1) small cells with an active area of 20 and 100 cm^2 ; 2) a two cell stack with an active area of 100 cm^2 ; and 3) a single and a three cell stack with an active area of 625 cm^2 . The stack used 20 cells with an active area of 625 cm^2 per cell, calculated based on the targeted current density of 80 mA cm^{-2} and an average cell voltage of 1.25 V. The stack used the standard graphite felt electrode and expanded graphite BPs (supplied by SGL Carbon, Germany), and membrane and

electrolyte used by commercial VRFB manufacturers. The performance of the stack was tested for 500 continuous cycles.

1.3 Dissertation Overview

The layout of the thesis is structured as follows:

Chapter 1 provides a rationale for the research and outlines the objectives and scope of the thesis. The findings and novelty of the thesis are also highlighted.

Chapter 2 reviews literature related to VRFB, its development and current research interest. Various approaches made to improvement of the flow distribution and to reduce the various losses aiming to improve performance of the cell are also covered.

Chapter 3 discusses the methodology employed to achieve the objectives of developing a 1 kW stack with the improvements on components design, electrode performance, flow distribution, pump consumption, capacity decay, etc. This chapter lists all the experimental set-up, measurement procedures, characterizations and analyses carried out in this dissertation.

Chapter 4 presents results of the flow distribution and pump power losses experiments. This chapter includes three sections. The first section investigates the efficacy of flow channels on the porous electrode for improving the flow distribution of electrolyte and reducing the pumping losses. The second section discusses the flow behavior in VRFB using spatially resolved voltage distribution. For the first time, a segmented cell approach is presented to monitor the in-situ flow behavior and to quantify the flow uniformity. The third section presents a novel method named as “pH tracing” implemented for the first time in VRFB for the quick screening of the

flow distribution. This method is suitable for commercial size cell and stack development.

Chapter 5 provides the results of various approaches to improve the performance of a VRFB. This chapter contains four sections. The first section presents the performance based study on the effects of electrode compression on flow battery performance. The second section discusses an anomalous behavior of the membrane at high current density operation, which has not been reported before in the literature. The third section presents two novel approaches for minimizing the reversible capacity losses in VRFB operation. The last section presents a brief study on the effect of electrode activation on the electrochemical performance.

Chapter 6 summarizes the development work of flow batteries from small laboratory size (20 cm^2) single cell to 1 kW stack. Computational fluid dynamics (CFD) assisted flow simulation was used to optimize the design of the flow frame for the 100 cm^2 cell and the 625 cm^2 cell, which is also discussed briefly in one of the subsection in this chapter. This chapter also discusses all the problems faced during the development phase and ways implemented to solve the problem. This chapter concludes with the testing results of the 1 kW stack.

Chapter 7 presents the conclusion of the thesis. The extent to which the objective is met is adequately addressed. The opportunities and strategies for future work are also highlighted.

1.4 Findings and Outcomes/Originality

On the course of fulfilling objectives of the study, various fundamental research, novel ideas and engineering were involved. During this journey, this PhD research

has delivered several findings and novelties:

- Development of a segmented cell for the study of in-situ flow behavior in VRFB

A completely new method of segmenting a conventional flow cell has been developed, which can be easily scaled up to any size. In order to minimize the issue of lateral flow of current for studying the flow behavior in a flow cell, the use of local mapping of open circuit voltage (OCV) alternative to common charging or discharging voltage or current mapping was proposed. In addition to segmenting the BP and the copper collector (CC), the graphite felt electrode was also segmented in selected cases for the first time to compare the change in resolution of the local voltage distribution. The flow was quantified by converting the OCV to SOC, and a relationship was then established to predict how well the electrode was utilized during the cell operation.

- Advanced porous electrode for performance improvement in flow battery

A new approach of improving the flow distribution of electrolyte through the porous media and reducing the pressure drop significantly was proposed by milling flow channels on the porous electrode. The idea of making flow channels on the porous electrode was proposed in some patent [10-13], however, no study has been made to investigate the usefulness. Of the four new design of channels studied, the best design was implemented in the development of the 1 kW stack. The developed stack is expected to be the first of its kind implementing interdigitated (IDD) channels on the porous electrode.

- Development of pH tracing method for the study of flow distribution in large area cell

A segmented cell study is a complicated study and requires special hardware. For the fast screening of the flow distribution especially for large area cell development, a simple method will be advantageous. To help address this problem, pH tracing method was developed. In order to understand a pH curve with time for qualitative information about the flow, a wide range of experiments were performed at various cell configurations. This test was then used in a kW size cell for finalizing the direction of flow channels on the porous electrode.

- “Power drop Effect” in operation of VRFB

With the continuous development of the VRFB technology, the resistance of the flow cell and stack is reducing, which allows flow cell to operate at high current density. For the first time, an anomalous behavior of membrane at high current density operation was reported based on detail investigation of the effect.

- Optimization of the electrode compression

For the optimal performance of the flow battery/stack, optimization of electrode compression is necessary. Too high a compression will lead to a high pressure drop and an uneven flow distribution. Whilst, too low a compression will increase the contact resistance. Previous studies were unable to report in-depth correlation between the utilization of electrode/electrolyte and contact resistance. Therefore, a performance based study has been conducted to know the optimal compression of electrode in a conventional design of a flow cell.

- Use of hydraulic shunt and alternate membrane to reduce electrolyte imbalance in VRFB

The idea of hydraulic shunt and/or use of combination of anion and cation type membrane for reducing the electrolyte imbalance has been patented [14, 15], but no details as well as experimental investigation have been reported. This study found that the use of hydraulic shunt for automatic rebalancing of electrolyte works efficiently, and this can be implemented in commercial systems. The use of a combination of anion and cation exchange membranes reduced the rate of imbalance, proving the concept for the first time. The use of a hydraulic shunt was later implemented in 1 kW stack testing.

- A novel design of a 1 kW battery stack

Starting from scratch, a 1 kW stack and testing system was developed. The stack used completely new designs of flow frames and other mechanical components, porous electrode with interdigitated flow channels for the first time, 0.6 mm expanded graphite plates as BP and hydraulic shunt for auto-rebalancing (with no capacity loss). The flow frame was designed to achieve superior flow distribution, low shunt current loss and low pressure drop. All the fundamental research performed on the small size cell has been implemented in the development of the 1 kW stack.

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Chapter 2

Literature Review

This chapter reviews the literatures on vanadium redox flow battery (VRFB). This includes the importance of VRBF for energy storage, its working principle, pros and cons, components, various losses and performance measures. In addition, review on the research progress is presented, and relevant research gaps and interests of this PhD thesis are provided. Uniform flow distribution of electrolyte through the porous electrode in VRFB is crucial for obtaining a stable and high performance, and for protecting the electrodes from degradation. However, appropriate methods are not available to precisely monitor the in-situ flow distribution. Capacity loss due to electrolyte crossover through the membrane is another major problem in VRFB operation. In addition, continuously operating pump consumes 1-3% of the overall energy, which should be reduced. For scale up to a commercial size, other areas such as electrode compression, activation condition, design of flow frame and stack configuration, etc. have to be optimized. This PhD study targets to address these gaps.

2.1 Vanadium Redox Flow Battery (VRFB)

2.1.1 Why VRFB?

The movement of the society towards the use of clean and sustainable energy has led to the renewable electricity production from solar, wind, hydro, biomass, etc. However, the electricity production mainly from solar photovoltaics and wind turbines are intermittent and fluctuating, thus an electricity storage system is necessary for storing the energy during the production time and delivering during the demand. Several energy storage systems are developed such as; mechanical storage through pumped hydro, compressed air and flywheel storage, electrical energy storage through capacitors and super capacitors, and electrochemical energy storage through fuel cells and batteries [1, 2]. Figure 2.1 provides a comparison of different energy storage technologies based on power rating, discharge time and application.

Figure 2.1 Positioning of different energy storage technologies in terms of power rating, discharge time and applications [3].

The traditional storage technologies such as pumped hydro and compressed air energy storage (CAES) are good for bulk power management with storage capability of higher than 8 to 10 hours. However, these technologies require favourable geographical locations and sophisticated infrastructure. The flywheel, supercapacitors and family of batteries cluster fall in the lower end of the discharge duration spectrum. Comparing the different types of batteries, lead acid batteries cover the major market segment in energy storage application due to their low cost and popularity. However, these batteries suffer from low cycle life (typically < 2000 cycles), performance degradation and disposal issues. In recent years, Li-ions batteries are aggressively penetrating into the mobility and storage market due to their high energy density, small footprint, good cycle life (~ 3500 cycles) and falling prices. However, there are safety concerns related using Li-ion batteries. Of the different energy storage technologies, redox flow batteries are one of the promising candidates in storing large scale energy. Redox flow batteries hold the capacity to store and deliver large scale stabilized energy for a longer time and serve as the load levelling and peak shaving in load fluctuation. Unlike common batteries available in the market, redox flow batteries are different in a sense that the anodic and cathodic electrolytes are stored externally and circulated to the battery stack by means of a pump. For this, researchers have explored different combination of redox couples such as Iron/Chromium, Zinc/Bromide, Bromide/Polysulphide, all-vanadium, vanadium/air, Vanadium/Bromide and Zinc/Cerium [4-6]. Among these, VRFB has grabbed much attention in recent years for their widespread commercialization.

2.1.2 Working Principle of a VRFB

A VRFB uses a mixture of vanadium salt dissolved in supporting electrolyte (sulfuric acid) as electrolyte for storing the energy. Vanadium is a transition metal and it has four oxidation states, in which, V^{2+} and V^{3+} serve as negative electrolyte species or

anolyte and V^{4+} and V^{5+} serve as positive electrolyte species or catholyte. The electrolyte is normally prepared by dissolving vanadium sulfate or vanadium pentoxide in sulfuric acid. The concentration of sulfuric acid is generally kept below 5 M and vanadium is kept below 2 M due to the solubility limit of vanadium ions in sulfuric acid. In order to avoid the precipitation of the electrolyte, the battery is normally operated between 10° to 40°C.

Two redox couples are separately stored in two electrolyte tanks (Figure 2.2) and physically separated from each other by means of an ion exchange membrane.

Figure 2.2 Schematic diagram of a VRFB.

During the charging and discharging processes, the following reactions take place in both sides of the cell:

At positive side:

At negative side:

During the charging process, VO_2^{+} ions on the positive tank gets oxidized to VO^{2+} and V^{3+} ions on the negative tank gets reduced to V^{2+} . A reverse reaction happens during the discharging process. To maintain the charge balance of the cell reaction, protons (H^{+}) and water (H_2O) are transported from the membrane. The proton transports from the positive electrode to the negative electrode during charging and reverse in discharging. During long-term operation of a flow cell or stack, an imbalance of the electrolyte volume occurs due to the convective transport of electrolyte species. The net electrolyte transfer direction depends on membrane type (anion exchange or cation exchange) used during the assembly of the cell or stack.

2.1.3 Advantages and disadvantages of a VRFB

A VRFB has the following advantages:

- Power density and energy storage capacity are decoupled: As the energy is stored in the electrolyte, increase in the volume of the electrolyte increases the energy capacity with longer charge/discharge cycle. Similarly, increasing the size of the cell or number of cells in a stack ultimately increase the power density of the battery. This makes the VRFB very suitable for large scale energy storage application [2].

- High efficiency and fast response time: Fast response time during operation allows VRFB useful for UPS like application, and can replace diesel generators and lead-acid batteries [4]. Due to a high round trip efficiency, the VRFBs are suitable for load levelling and peak shaving application.
- Deep discharge cycle and no standby loss: Unlike lead acid batteries and Li-ion batteries, the VRFB can be discharged to a very low SOC and easily charged even after keeping fully discharged for a long time. As the electrolyte is stored in two separate tanks, there is no standby losses.
- Use of same electrolyte chemistry in both half-cells: As ion exchange membrane cannot completely block the crossover of electrolyte species between two half-cells over a long run, detrimental effects on stack components are observed in some RFBs [2]. However, the VRFB performance is not affected with the cross mixing of the electrolyte between the two half cells. In addition, the mixed electrolyte can be easily regenerated and the waste vanadium electrolyte after the shelf life can also be reused.
- Longer service life, low maintenance: Theoretically, the electrolyte in VRFB can go for infinite number of charging and discharging cycle and the complete system requires very little maintenance. Therefore, these batteries are also suitable for remote area and standalone applications.

Despite these unique advantages of the VRFB, there are some limitations restricting the wider application of these batteries.

- Low energy density: This is a major drawback of the VRFBs, which restrict their use in vehicular application and installation in confined space. The typical energy density of VRFB is approximately 25 Wh kg^{-1} , which is comparable to lead acid

battery, but quite low compared to other batteries such as, lithium ion battery and nickel metal hydride battery. The low energy density is due to the solubility limit of vanadium sulphate in sulfuric acid.

- **Small temperature window:** The working temperature of VRFB is usually kept between 10 °C to 40 °C. Below 10 °C, the negative side electrolyte (V^{3+} species) gets precipitated irreversibly [7], whereas the positive side electrolyte (V^{5+} species) gets precipitated above 40 °C [8]. This small temperature window limits their application in extreme cold and hot weather regions unless a temperature management system is incorporated [9], which in turn decrease the overall efficiency of the battery system. Further, this narrow temperature window restrict the commercial electrolyte to be prepared at low concentration than the solubility limit in order to avoid precipitation near temperature boundaries. Therefore, increasing the temperature window would allow to use electrolyte at slightly higher concentration, which can improve the energy density.

2.1.4 Components of a VRFB cell/stack

An exploded view of components in a VRFB half-cell is shown in Figure 2.3.

Figure 2.3 Exploded view of different component in a VRFB half cell

The components in VRFB and their functions are discussed below.

- Graphite electrode or Bipolar plate (BP): It is a chemically inert and electrically conductive low density BP made from graphite material. The BPs connect the cells in series in multiple cells stack. In some designs, BPs are milled to provide the flow fields/channels for uniform electrolyte flow.
- Graphite felt electrode: In VRFB, the chemical energy is stored externally on the electrolyte, and therefore, the electrodes with higher surface area are necessary to provide electrode/electrolyte interface for reaction. As the BP has smooth and low surface area, a highly porous felt made from either carbon or graphite are used as the battery electrodes. Graphite felt electrodes are highly conductive to transport the current to BP and are chemically inert to withstand corrosive environment. To improve the reaction kinetics, felts are often treated chemically and thermally [10].
- Membrane: Ion exchange membranes are commonly used in RFBs as a physical separator between two redox zones. It selectively allows the permeation of charge balancing ions such as H^+ , SO_4^{2-} and HSO_4^- [11]. In RFBs, both anion and cation type membranes are used.
- Copper current collector (CC): As copper has excellent electrical conductivity than graphite plates, copper plates are commonly used for the collection of all the current from BP and the stack. In a stack, copper collectors are only used at the two ends for the connection to the load/power source.
- Flow frame (FF): FF is one of the major mechanical component of a VRFB cell/stack. It provides the seating window for graphite felt and manifolds for the

electrolyte to flow in and out. Some design uses flexible materials such as Santoprene (a thermoplastic vulcanizates) or silicones as a FF material. FF made from flexible materials can itself serve as gasket material and no extra gaskets are needed during the assembly. Separate gaskets are only needed if hard materials are used for the FF. The use of hard FF offers precise control over the compression of the electrode and manifolds to be machined for guided flow.

- End plate: The end plate provides uniform compression between the different cell components during the cell/stack assembly. Nut and bolts are used between the two end plates to apply uniform assembly pressure between each component. A wide variety of materials are used as end plate in commercial systems such as stainless steel, alumina, plastics, composites, etc.

A typical VRFB stack consists of number of cells connected electrically in series. The positive and negative electrolytes are stored in separate tanks and circulated to the battery stack by means of two magnetic pumps as shown in Figure 2.4.

Figure 2.4 An in-house developed 1 kW VRFB stack showing different components in a stack.

From the liquid flow perspective, all the cells in the battery stacks are usually connected in parallel. The cells are electrically connected in series. Additionally, a VRFB system also consists of fluidic components (vanadium based electrolyte in storage tanks, pumps for electrolyte circulation to the stack, tubing, valves, collection tray, etc.) and power electronics (battery management system, DC/DC converter, safety switches, sensors, etc.). In some locations, they are also equipped with thermal management system for cooling or heating of the electrolyte.

2.1.5 Performance measure of a VRFB cell/ stack

The cell performance of a VRFB cell/stack is evaluated by cell cycling. Flow cells can be charged and discharged (i.e. cycled) at different current densities using battery tester with electronic loads and power supply. Three efficiencies: coulombic efficiency, energy efficiency and voltage efficiency are calculated for performance evaluation.

Energy efficiency (EE) is a measure of energy harnessed by the battery during discharge in comparison to the energy supplied during the charge.

$$\eta_{energy} = \frac{\int P_{VRFB,discharge}(t)dt}{\int |P_{VRFB,charge}|(t)dt} \quad \text{Eq. (2.1)}$$

Where, $P_{VRFB,discharge}$ is the power delivered by the battery during discharge in Watt, $P_{VRFB,charge}$ is the power consumed during the charge in Watt and t is time in hour.

Coulombic efficiency (CE) is a measure of the charge withdrawn from the battery compared to the charge supplied during the charge.

$$\eta_{coulombic} = \frac{Q_{discharge}}{Q_{charge}} = \frac{\int i_{discharge}(t)dt}{\int |i_{charge}(t)|dt} \quad \text{Eq. (2.2)}$$

Where, $Q_{discharge}$ is charge withdrawn from the VRFB in Amp-hr, Q_{charge} is the charge supplied during the charge, $i_{discharge}$ is the current during discharge in Ampere, i_{charge} is the current during charging and t is the time in hour. Coulombic efficiency is dependent on the membrane properties.

Voltage efficiency (VE) is a measure to compare charge and discharge when the same current is applied for the charge and discharge. It is also a measure of Ohmic losses and polarization losses during the cycling. It is calculated as a ratio of VRFB cell/stack voltage during discharge to the cell/stack voltage during charge.

$$\eta_{Voltage} = \frac{\int U_{VRFB,discharge}(t)dt}{\int U_{VRFB,charge}(t)dt} \quad \text{Eq. (2.3)}$$

Where, $U_{VRFB,discharge}$ is the voltage of the cell/stack during discharge in volt, $U_{VRFB,charge}$ is the voltage of the cell/stack during charge in volt and t is the time in hour.

When mechanical losses (e.g. pump loss) of the system are neglected, voltage efficiency is equal to the ratio of energy efficiency and coulombic efficiency.

$$\eta_{Voltage} = \frac{\eta_{energy}}{\eta_{coulombic}} \quad \text{Eq. (2.4)}$$

In addition, there are some other parameters used to evaluate the performance of a flow battery.

Area specific resistance (ASR) is a parameter that can be used to compare different cell designs. The average specific resistance during galvanostatic charging and discharging (R_c) can be calculated approximately using the following formula:

$$\rho = \frac{V_0}{j} \cdot \left(\frac{1-VE}{1+VE} \right) \quad \text{Eq. (2.5)}$$

Where j is the current density in A cm^{-2} , V_0 is the average open-circuit voltage during charge and discharge ($\sim 1.38 \text{ V}$ typically), and VE is the voltage efficiency.

This is a simplified equation, which can be derived as follows:

$$\text{The average voltage on charge,} \quad V_{charge} = V_0 + j \cdot \rho \quad \text{Eq. (2.6)}$$

$$\text{The average voltage on discharge,} \quad V_{discharge} = V_0 - j \cdot \rho \quad \text{Eq. (2.7)}$$

$$\text{The voltage efficiency,} \quad VE = V_{discharge} / V_{charge} \quad \text{Eq. (2.8)}$$

$$\text{Or,} \quad VE = (V_0 - j \cdot \rho) / (V_0 + j \cdot \rho) \quad \text{Eq. (2.9)}$$

$$\text{Or,} \quad VE = (V_0 - j \cdot \rho) / (V_0 + j \cdot \rho) \quad \text{Eq. (2.10)}$$

$$\text{Or,} \quad VE \cdot V_0 + VE \cdot j \cdot \rho = V_0 - j \cdot \rho \quad \text{Eq. (2.11)}$$

$$\text{Or,} \quad j \cdot \rho (1 + VE) = V_0 (1 - VE) \quad \text{Eq. (2.12)}$$

$$\text{Or,} \quad \rho = \frac{V_0}{j} \cdot \left(\frac{1-VE}{1+VE} \right) \quad \text{Eq. (2.13)}$$

For comparing the different size of cell and stacks, the best method is ASR. The ASR is sensitive to cell temperature, therefore temperature of the electrolyte has to be reported while comparing the ASR. It is also known as wet resistance.

Self-discharge current density is a parameter to compare the self-discharge in different sizes of cell and stack. It can be calculated using the following formula:

$$j_{sd} = j \frac{(1 - Q_{eff})}{(1 + Q_{eff})} \quad \text{Eq. (2.14)}$$

Where, j is the current density in Acm^{-2} and Q_{eff} is the coulombic efficiency.

State of charge (SOC) is a terminology frequently used in the battery operation. This term does not directly relate to the performance, however, in operation of the battery stacks, lower and upper range of SOC are monitored and controlled accordingly. When a flow cell is fully charged, i.e. 100% V^{5+} on the positive side and 100% V^{2+} on the negative side, SOC is 1. Similarly, when a flow cell is fully discharged, i.e. 100% V^{4+} on the positive side and 100% V^{3+} on the negative side, SOC is 0. Mathematically, the SOC can be represented as:

$$SOC = \frac{C_{V^{2+}}}{C_{V^{2+}} + C_{V^{3+}}} = \frac{C_{VO_2^+}}{C_{VO^{2+}} + C_{VO_2^+}} [\%] \quad \text{Eq.(2.15)}$$

Eq (2.7) can be used to calculate the SOC, if the concentration of the different vanadium ions are known from titration.

In cell operation, SOC can simply be estimated from the open circuit voltage (OCV). The SOC can be calculated using the Nernst equation.

$$OCV = E_{cell} = E_{cell}^o + \frac{RT}{nF} \ln \left(\frac{C_{VO_2^+} \cdot C_{V^{2+}} \cdot C_{H^+}^2}{C_{VO^{2+}} \cdot C_{V^{3+}}} \right) [V] \quad \text{Eq. (2.16)}$$

Where, E_{cell}^o is the standard cell potential, R is the gas law constant, T is the temperature, n is the number of electron transferred in the reaction, F is the Faraday constant, C is the concentration of various ions [12].

In VRFB operation, $C_{VO_2^+} = C_{V^{2+}}$ and $C_{VO^{2+}} = C_{V^{3+}}$. Further, $C_{VO_2^+} \propto SOC$, $C_{VO^{2+}} \propto (1 - SOC)$. Therefore,

$$C_{VO_2^+} = \frac{C_{VO_2^+}}{SOC^*} \text{ and } C_{VO^{2+}} = \frac{C_{VO^{2+}}}{1-SOC^*}$$

Where, SOC^* is the state of charge expressed in fraction.

Now replacing these terms in Eq. (2.16), we get,

$$OCV = E_{cell} = E_{cell}^o + \frac{RT}{nF} \ln C_{H^+}^2 + \frac{RT}{nF} \ln \left(\frac{SOC^{*2}}{(1-SOC^*)^2} \right) [V] \quad \text{Eq. (2.17)}$$

This is a theoretical equation for the estimation of the SOC from OCV. Experimentally, it is found that for a better estimation of the SOC from OCV, the concentration terms in the Nernst equation has to be replaced with activities. In addition to this, membrane junction correction has to be considered. The membrane junction correction is related to Donnan potential, which exists across the membrane due to unequal proton concentration between the two electrolytes. Based on the experimental works, for a cell with electrolyte concentration of 1.6 M $V^{3.5+}$ in 4.5 M H_2SO_4 , the Nernst equation empirically gives:

$$OCV = 1.38 - 0.00193(T - 273) + \frac{RT}{nF} \ln \left[\frac{(1.8 \times SOC' + 3)(1.8 \times SOC' + 4.8).SOC'^2}{(1 - SOC')^2} \right] \quad \text{Eq. (2.18)}$$

Figure 2.5 shows the plot between OCV and SOC using Eq. (2.18).

Figure 2.5 Relation between OCV and SOC according to empirically modified Nernst equation.

In VRFB operation, SOC is monitored not to make the battery operate at the region where exponential rise and fall of OCV (in Figure 2.5) is observed. In practice, a flow battery is usually designed to cycle within SOC range of 10% to 85%.

2.1.6 Losses in VRFB

When an external load is applied to a cell, equilibrium condition terminates as current is drawn from the battery. Hence, the measured voltage of the battery differs from the equilibrium potential. The operating cell voltage (E_c) will always be lower than the open circuit voltage (E_0) as shown in Eq. 2.19 [12].

$$E_c = E_0 - iR_i - \eta_{act} - \eta_{conc} \quad \text{Eq. (2.19)}$$

Where, E_c is the operating cell voltage, E_0 is the open circuit voltage, i is the current density, R_i is the area specific resistance of the cell, η_{act} is the activation polarization and η_{conc} is the concentration polarization.

The difference in voltage between reversible cell potential and cell voltage when current flows is known as overpotential or simply polarization. Polarization curves are often used in fuel cell analysis. In VRFB, they are also becoming popular to estimate the various internal losses quickly. Polarization curve gives different losses occurred in the cell. The polarization curve in Figure 2.6 shows three distinct regions namely, activation polarization, Ohmic polarization and mass transport polarization (also known as concentration polarization). Each of the region is closely related to the concentration of reactants and the electrochemical reaction rate.

Figure 2.6 Polarization curve of VRFB during discharging [13].

In VRFB, the discharging polarization is of more interest as compared to the charging polarization because charging cannot be done at a high current density due to the possibility of side reactions and degradation risk of electrode material at higher cell voltages (typically >1.6 V). Discharging can be conducted up to the limiting current. The various losses are explained as follows:

Activation Loss

The activation loss is a result of slow charge transfer between the electrolyte and the carbon felt electrode dominant at low current density. In other words, it is related to the initiation energy of charge transfer or kinetics of porous electrode used in VRFB. Through thermal and chemical treatment of electrode or through insertion of catalyst into carbon fiber, activation losses can be reduced.

Ohmic Loss

The Ohmic region is the linear part of the polarization curve and the gradient can simply be calculated by the ratio of voltage and current. In this region, the Ohmic loss mainly occurs from the electronic resistance of individual components (felt, BP and copper collector), ionic resistance of membrane and electrolyte, and contact resistance at the contact interface of various components (current collector-BP, BP-porous felt, etc.).

Mass Transport Loss

The mass transport region (concentration polarization) is the convex curvature in the polarization curve, mainly dominant at high current density. This occurs as there is a starvation of fuel (charged species in the electrolyte) where the mass transport of

the reactants limits the current density of the cell [14]. The mass transfer overpotential is affected by the electrolyte flow rate and the electrolyte composition.

Other losses

Shunt current loss:

The shunt current loss is one of the main factors affecting the performance of the VRFB, which will shorten the cycle life and decrease the energy transfer efficiency. In a multi-cell stack, the cells are connected electrically in series by BPs to match the DC voltage requirement. In such configuration, each single cell shares the anode/cathode electrolyte with the anode/cathode manifold. The single cells are connected with the manifold and their channels. Therefore, shunt current will be emitted because of the conductivity of the electrolyte and non-zero electrical field potential gradient. A shunt current flows through the internal (and external) manifolds to discharge the stack. During standby, the discharge induced by the shunt current can generate heat and increase the stack temperature. This could potentially result in thermal precipitation of the charged electrolyte on the positive half-cell. Therefore, shunt current loss results in capacity loss and corrosion of the key materials in the stack, which in turn, shorten the battery cycle life [15].

Therefore, minimizing shunt current loss is a major consideration in designing flow frames. Flow frame design in VRFB is always a compromise between flow resistance and shunt currents. Shunt current loss can be minimized using longer and narrower fluid channel for the electrolyte flow, which on the other hand, could significantly increase the pressure drop and occupy larger area in the flow frame. Therefore, the design of the channel has to be optimized. The shunt current loss can

be minimized by using fewer numbers of cells in series, increasing the resistance of manifolds and channels, and increasing the size of a single cell [16].

Self-discharge

Self-discharge of the stack results in loss of energy capacity. The self-discharge happens mainly due to the crossover of the vanadium ions across the ion exchange membrane. The rate of self-discharge depends on the diffusion coefficients of the vanadium ions, solubility of ion in the membrane and its mobility [15, 17]. Hence, selection of the best membrane with high ion selectivity is important to minimize the self-discharge. In addition, the OCV value always decreases once the electrolytes flow continually through the two surfaces of membrane due to the crossover of vanadium ions. Therefore, draining of the electrolyte from the stack during standby period could reduce the self-discharge to some extent. It was also found that the crossover of vanadium ions intensifies with increasing flow rate, and the self-discharge reactions were accelerated due to the increasing of vanadium crossover amount [17].

Pump loss

In a conventional VRFB stack, the single cells consist of highly porous (> 90% porosity) carbon electrodes, separated electrically by ion-exchange membranes on one side and ionically by non-porous BPs on the other. Classically, the BPs are in the form of flat sheets without flow fields. This is the so-called ‘flow through’ geometry, which means that the electrolytes are pumped through the electrodes. The viscous resistance to flow, which is mainly dependent on the permeability of the electrode material and viscosity of the electrolyte results in a differential pressure (Δp) between inlet and outlet (over the length of the electrode, L). Δp increases with

compression (decrease in permeability), flow rate (Q) and viscosity of the electrolyte (η_e), according to Darcy's law:

$$\Delta p = \frac{\eta_e}{K_e(\varepsilon)} Q \cdot \frac{L}{A} \quad (\text{Eq. 2.20})$$

The permeability (K_e), in turn, is dependent on the porosity (ε) of the electrode. The flow cross sectional area (A) changes with compression.

The energy consumption of the pumps increases linearly with Δp . In a kW size stack, the pump consumed 1-3% of the total energy generated [2, 18] . A simple approach to reducing Δp , and hence reducing the pumping losses, is given by the use of wide rectangular electrodes with shorter flow path. However, at the extreme, this type of distorted geometry could cause an uneven flow distribution [19].

Another possibility to reduce Δp is by using a porous electrode with only a low compression. For instance, conducting plastic BPs, containing a high amount of polymer [19], could be heat bonded with porous electrodes. Cells with these composite bipolar electrodes require very low compression, resulting in low Δp . However, such conducting plastics suffer from poor conductivity, when compared to graphite plates, and low stability of the bonded interface. In the case of the commonly used graphite-polymer composite plates, sufficient compression between the porous electrode and BP is necessary to minimize the contact resistance. In flow batteries, an optimal compression of 20-30% has been reported to keep good contact and maintain a uniform flow rate of electrolyte [20].

Capacity loss

There are several reasons for capacity loss in VRFB. The capacity loss (in Ah) can be categorised into two types: reversible capacity loss and irreversible capacity loss. During the operation of VRFB, proton is migrating through the membrane together with a water molecule. In addition to the water transport, depending upon the type of membrane used, some vanadium, sulphate and bisulphate ions are also transported from the membrane due to having different diffusion rates. Hence, the electrolyte imbalance occurred primarily due to the transfer of water molecule and different diffusion rates of vanadium species across the separator is responsible for the reversible capacity loss. The imbalance of ions and volume between two tanks increase the overpotential during charging and discharging, therefore, electrolyte cannot be charged and discharged to fullest capacity. However, this loss can be prevented by rebalancing of the electrolyte volume and ions. The irreversible capacity loss indicates the permanent loss of capacity. Some common reasons for this loss are overcharging, degradation of the electrode materials, high temperature operation, surface passivation of the current collector, electrolyte leakage, electrolyte contamination from Cu collector, etc.

2.2 Research progress on VRFBs

The VRFB technology is pioneered and developed by Maria Skyllas-Kazacos and her team at University of New South Wales, Australia in 1980's. The technology was further developed and successfully demonstrated in Thailand, Japan and Australia [21, 22] . Today, there are several companies around the globe commercially supplying VRFB system and components. As per the DOE global energy storage database [23], there are a total of 59 large scale VRFBs installations worldwide with total capacity of 75 MW. Looking at the increasing number of

companies in the VRFBs development, it is clear that these batteries have high scope in large scale energy storage applications, remote power supply, load levelling in power plants and emergency backup. The trend of increasing use of renewable energy sources and the widespread installation of solar PV and wind turbines is a proof that the number of companies developing the VRFB stack will continuously grow.

Although VRFB stacks are available commercially in the market, the capital investment for the battery is still quite high to widely use them in stationary applications for large scale energy storage. The price per kWh of VRFB stacks range between US \$ 500 to US \$ 1000 including all the components [24, 25]. The major cost of the technology is contributed from the cost of membrane, electrode, BP and electrolyte. Therefore, enormous research is ongoing to reduce the cost of components, improve the performance, and develop compact stacks to reduce the amount of components and occupy minimal space [26].

2.2.1 Membrane

The research on membrane is mainly focused on finding new materials to replace the expensive Nafion membranes. The ion exchange membrane has to be efficient in proton conductivity (so as to maintain high voltage efficiency) and in ion selectivity (so as to minimize electrolyte imbalance and capacity loss), and low cost [26]. Improving the stability of membrane for several years exposure in corrosive media is also a research focus [26]. Despite the high cost, Nafion membrane (cation exchange membrane, fluorinated) has excellent chemical and mechanical stability, reasonable ion selectivity and high proton conductivity. To reduce the cost of fluorinated Nafion membrane, membranes with partially fluorinated (e.g., anion FAP membrane from Fumatech GmbH) and non-fluorinated (Polyether ether ketone –

PEEK membranes[27], sulphonated PEEK membranes [28], hydrocarbon based CEM , etc.) membrane have been developed [29]. The other research focus on the membrane is minimising the crossover recognized as a serious problem that causes electrolyte imbalance, charge imbalance and loss of usable energy. Anion exchange membrane (AEM) has been found to be more attractive than cation exchange membrane (CEM) due to their fundamental property of restricting the crossover of cationic active species by Donnan effects [30]. In AEM membrane, the positively charged fixed ionic groups repel positively charged vanadium ions, hence reduce the crossover of vanadium ions as compared to CEM membrane. However, AEM membrane usually suffer from poor anion conductivity and high water uptake owing to higher electrolyte imbalance [30]. To minimize the crossover problem, amphoteric membrane [31], bipolar membrane [32] and use of a combination of anion and cation exchange membranes [33, 34] have been proposed. The combination of anion and cation exchange membrane in a single stacks were patented, but no experimental verification is available yet.

2.2.2 Electrolyte

The research on electrolyte is focused towards finding environmentally-friendly additives to widen the working temperature window, and alternative chemistry and/or additives to increase the energy density. Second and third generation VRFB are also being developed by using halide based supporting electrolyte in order to increase the energy density. However, Generation 1 electrolyte is given more focus as they are being used in commercial systems due to the safe operation. The main problem of G1 electrolyte is that the V^{5+} ion has a relatively low solubility in the supporting electrolyte (sulfuric acid) as compared to other three ions (V^{2+} , V^{3+} , V^{4+}), mainly at high temperature operation (typically above 40 °C). Halide based additives (such as HCl) has been proven as an effective additive that can stabilize the V^{5+} ions

from precipitating at relatively high temperature operation or higher concentration, but the risk of releasing toxic chlorine gas under failure conditions hinders its use in commercial system. Therefore, in commercial system, precipitation is avoided by careful control of temperature and SOC of the battery. Implementation of such measures add to the cost and reduce the performance of the battery [35].

Therefore, extensive research has been focused on finding organic and inorganic additives, which are environmentally-friendly, low cost and long-term stable in corrosive environment of V^{5+} . A wide range of organic compounds with carboxyl (oxalic acid, sodium oxalate, potassium oxalate, EDTA disodium salts), alcohol (Resorcinol, Pinacol, Pyrogallol, Xylose, Glucose, PVA), and multi-functional groups (Lactic acid, Cysteine, Ascorbic acid, Citric acid, Ammonium citrate, Tannic acid) have been proposed [36-41]. One of the recent work highlighted that many of the proposed additives in literature are not useful [35]. They were found to be either reducing the V(V) ion to V(IV) or reduce the state of charge of the electrolyte. In this thesis, the scope is limited to G1 electrolyte.

2.2.3 Electrode

The research on electrode material is focused on the modification of the porous carbon electrode using various dry and wet methods to improve the kinetics. In VRFB, polyacrylonitrile (PAN) based carbon felts are commonly used. As the electrode provides the reaction sites for the electrochemical conversion, the search is also on maximizing the electrochemical active surface area, introducing catalysts, improving the electrical conductivity and reducing the price by improving the ease of production [29]. It is believed that thermal and chemical treatments introduce oxygen containing functional groups (C-OH, C=O, etc.) on the carbon fiber, which is responsible for the performance improvement [41, 42]. Therefore, research works

have focused on understanding the electrochemical behavior and surface properties of the modified electrodes [44, 45]. Out of the various activation methods, thermal treatment is usually preferred for industrial production of flow cell stacks due to the ease of handling large volume of felts. In thermal treatment, the activation temperature and time play a significant role [44, 46]. Studies have reported application of a wide range of temperature and treatment time, however, the best method for obtaining a high and stable performance over the life-time is still unclear. A recent study by Schweiss et al. [47] reported that the electrode on the positive side of the flow cell does not require the activation. In the conventional designs, a thick (3-6 mm) porous electrode is used and the flow of electrolyte is maintained through the cross section of the electrode. The electrode is in planar contact with the BP and electrode compression of 20-30% is usually maintained for the fair trade-off between contact resistance and the flow distribution. Despite few studies on electrode compression [20, 48, 49], a more detail investigation is necessary to understand the trade-off between contact resistance and mass transport polarization. The use of thick electrode is one of the reasons for relatively higher resistance of conventional design as compared to zero gap design in fuel cells. Therefore, extensive research on VRFB is focusing on exploring fuel cell design (and optimizing flow fields) containing flow fields for electrolyte distribution on the BP and very thin electrodes for electrochemical conversion [50-55]. This design allows the use of relatively higher compression pressure between thin electrode and BP, which reduces the contact resistance that significantly allow flow cell to achieve very high power density. However, improvements with the use of thin electrodes has been reported only in small size cells. For the scale up to a large area flow cell, thin electrodes have various problems such as, high mass transport polarization, high pressure drop issues, intrusion of porous electrode into the flow channels, etc. This thesis, however, will only focus on conventional design of flow cell employing thick porous electrode.

Considering the high cost of the BP material, the research is also focussing on developing thin plates with improved electrical conductivity, corrosion resistance and sufficient mechanical strength. Unlike fuel cell, the use of thin plates as a BP in VRFB is possible by using separate frames for electrolyte flow. In an n-cell stack, n+1 BPs are used. Therefore, use of thin plates would reduce the weight and cost of the stack significantly. However, too thin plates may suffer from poor mechanical strength and electrolyte permeation from the tiny holes, resulting in capacity loss and self-discharge. Solving of these problems would make expanded graphite BP promising in VRFB due to their light weight, very small thickness, high conductivity and easy to cut into desired size. Alternatively, conducting polymer sheet as a BP are also being developed to reduce the weight and cost of the BP [19, 56].

2.2.4 Stack design

The design of different components of the cell and stack system also plays a significant role in the cost reduction of VRFB technology. As VRFB is bulky in comparison to other batteries, compact design and efficiency improvement are also important for the reduction of weight, space and cost. The cost reduction and efficiency improvement of the stack system can be obtained through optimized cell architecture, development of optimized and low cost cell components, and stack optimization. However, limited literature is available on the design of flow frame and cell configuration. The commercial manufacturer does not disclose the design information, whereas research institutes and universities mainly focus on fundamental research using lab scale cell. Also, most of the previous studies on design related research are simulation and modelling based rather than experimental [54, 57-59].

2.2.5 Flow distribution and pressure drop

A good design of the flow channel and cell configuration is crucial for improving the flow distribution and reducing the pumping power. A uniform flow distribution of electrolyte is necessary to minimize mass transport loss and gas bubbles formation, and also to remove the gas bubbles formed during redox reaction. Ideally, the electrolyte should distribute uniformly through the electrode. However, flow non-uniformity may occur due to various reasons such as improper design of flow frame, non-uniform or excessive compression of the felt electrode, uneven wettability of the bulk electrode or non-uniform thickness of the electrode material. A non-uniform flow distribution can result in non-uniform current distribution, with the possibility of locally overcharging the electrolyte, which, in turn, causes gas evolution and degradation of the BPs. Therefore, numerous studies in VRFBs have been focused on improving the flow distribution through the porous electrode using different approaches, such as operating at above the stoichiometric flow rate [60-62], use of flow channels in the BPs [51, 55, 63, 64], use of optimal electrode compression [20, 48], increasing the flow velocity through the felt [61] and use of thinner electrodes [65-67]. However, each approach is a compromise between flow distribution, pressure drop and contact resistance. Therefore, developers are at pains to design the flow frames to ensure even distribution of the electrolyte through the porous electrode [68, 69].

Stimulated by experiences from proton exchange membrane (PEM) fuel cells, redox flow cells incorporating flow fields in the BPs and the use of thin porous electrodes have been successfully demonstrated [51, 55, 63, 64, 70-73]. For instance, a substantial increase in peak power densities were observed by the UTK/Brane Lab [50] and UTRC [53], using thin carbon paper electrodes and serpentine flow fields. Among the different flow field designs, interdigitated flow fields (IDD) and

serpentine flow fields have shown superior performance, due to improved convection in the through-plane direction as compared to flow fields with channels aligned solely in the flow direction [72, 73]. However, a range of Δp with the use of IDD, serpentine or conventional designs in the VRFB have been reported [51, 55, 63, 71]. Despite the given advantages, flow channels in the BPs for the VRFB have several drawbacks, such as the need for thicker BPs, intrusion of the porous electrode into the channel, increase in stack weight, and increase in material and manufacturing cost of flow fields on BP.

Few patents [74-77] describe the use of two felts stacked together in each half cell, to reduce Δp and to improve electrochemical activity. Examples include a high surface area carbon felt contacting the membrane and lower surface area felt contacting the BP [76, 77]. Alternatively, a high density, thin layer next to the membrane and a low density, thicker layer behind was proposed [75, 78]. Of more interest for this work is the use of a flow channel at the interface between two similar felts [74]. A recent publication [63] studied tapered, interdigitated channels in a 2.5 mm thick, porous felt electrode, stacked together with another 2.5 mm thick felt, in a three cell stack. Their work exhibited a maximum decrease in Δp of up to one third, at a given flow rate. The tapered channel in their stack was facing the BP and was placed perpendicular to the flow direction, but the details of the channel were not provided. Flexible channel designs can be used if two thin felts are stacked together, with one of the felt containing channels. However, this approach could increase the resistance, thickness and cost on electrode for commercial use.

Although very limited scientific publications have been made on the use of electrodes for the VRFB with channels, few patents [74, 79-81] have been published, focusing on different designs. Toyo Boseki [74], proposed parallel flow channels, in the flow direction, with different shapes of groove cross-section, such as square, V-

shaped, semi-circular and convex. 1 to 4 number of channels were cut in every 100 mm of electrode, with a channel width of up to 5 times greater than the depth. The product of the channel width and the number of the channel was preferred not more than 80 % of the width of the liquid flow path. A hot press method was used on the PAN fibers to provide the required pattern. Golden Energy Fuel Cell Co. Ltd. [80] proposed a parallel channel of width 1-5 mm and depth of 1-5 mm for a felt of thickness 2-10 mm. However, the interval between flow channels was only 1-5 mm. Similarly, Sumitomo Electric Ind. Ltd. and Kansai Electric Power Corp. [81] have suggested various felt patterns including parallel channel, half-length parallel channels, non-uniformly spaced parallel channels and non-linear channels (e.g. sinusoidal). The distance between channels was again only 5 mm. Their results showed that parallel cut channels extending from inlet to outlet resulted in the lowest Δp . However, the discharge energy was lower than for half-length channels. The patent literature claim that flow channels can improve the overall battery performance and thus can be attractive approach for developers. Unfortunately, no experimental validation of the patent literature is available.

As per literature, almost all of the studies use polarization curve, current - voltage profiles during the cell cycling, etc. as a tool to show the improvement on flow distribution (or reduction in Ohmic and mass transport). However, these methods are unable to predict locally whether the mass transport inside the porous electrode has been improved. Some ex-situ techniques such as dye, pH or salt tracing [82], thermal dispersion [83] , imaging techniques [84], etc. have been used in various areas of engineering for the study of flow distribution. Since only small temperature gradients are formed during operation and due to the strong optical absorbance of the electrodes, thermal dispersion and imaging techniques or dye tracing are not suitable. Salt or pH tracing, can be used for fast screening of flow profile qualitatively, however, this method is unable to provide the real time localized information of the

cell during operation. So far, pH tracing has not been reported in VRFB. Few attempts have been made in segmenting the flow cell to study the local in-situ behaviour [52, 85], however, few of the available literatures shows that the segmented approach in flow battery research is in very early stage.

2.2.6 Localised in-situ approach

Spatially resolved local current and voltage mapping in a segmented cell is a unique and strong tool to investigate the in-situ behavior of the cell. This approach is well established in PEM fuel cell research [86-91]. By contrast, segmented cell studies of flow batteries are scarce [52, 85, 92, 93].

A segmented cell is similar to a normal cell in terms of cell architecture and flow configuration. A non-segmented cell has two terminals at two end side of a cell, whereas in a segmented cell, the electrode and/or current collector is divided into smaller individual electrode. Therefore, segmented cells have multiple terminals to connect. Each of the divided segments is usually insulated from each other. Hence, charging and discharging of the cell can be independently controlled in each of the segment [88, 91]. The research in fuel cell over the last decade has shown that segmented cell proves to be a good in-situ method to analyse uneven electrochemical response. The commonly used methods for segmentation are printed circuit board technique, shunt resistor network and hall sensor network technique [91]. Segmenting the BP and current collector is common, whereas, the porous electrodes and membranes are rarely segmented.

Hsieh et al. [85] divided the positive half-cell of a 100 cm² size conventional flow cell into 25 segments and used a shunt resistor network to measure the current and voltage of each segment. Two designs were tested, one with a segmented copper

collector, without segmenting the graphite flow field plate (5 mm thick) and secondly with the segmented graphite collector (10 mm thick) plugged directly into the banana plug connector. Due to the variation in the contact resistance among segments, non-uniform compression of the electrode and use of a non-segmented thicker plate in their first design, lateral flow of current largely affected the current distribution. In their second design, the cell suffered from the higher contact resistance resulting in lower voltage efficiency and discharge capacity. Clement et al. [52] segmented a 9 cm² VRFB single cell with a serpentine flow channel architecture using a Printed Circuit Board (PCB) technique, similar to a fuel cell design. The flow field plate was divided into 36 segments. Their study was focused in understanding the effect of electrode (carbon paper) properties and flow rate on local current distribution. The results showed that current distribution changed with varying thickness of the carbon paper and depended on flow rate, electrode wettability, and electrode porosity. Though their findings suggest that the local current distribution reflects the combination of local electrolyte velocity and electrolyte concentration, a more detailed study of flow behavior in a conventional design with a reasonable size of flow cell is necessary. The convection of reactants through the porous carbon paper in fuel cell-type cells is in the through-plane direction to the electrode, whereas, the electrolyte convection through the porous felt in a conventional VRFB is in-plane. Gandomi et al. [92] studied the through-plane potential distribution in multi-layer electrodes, by using the dynamic hydrogen electrode (DHE) concept in the VRFB. In a fuel cell-type cell architecture (zero gap), three layers of carbon paper electrodes were stacked and platinum wire electrodes were inserted between each layer of carbon paper as reference electrodes. The cell used two membranes with two platinum wires inserted as working and counter electrodes. Their experimental and simulation results showed that the mass transport polarization in through-plane concentrated towards the flow field plate. Becker and co-workers [93] introduced six potential probes into the graphite porous electrode of active area 100 cm² in order to

measure the effective resistance of the graphite electrode at different cell compression and flow rates. Their results showed the dependency of the effective resistance of the felt on the flow rate towards electrolyte inlet at low compression.

As discussed above, the segmented cell approach has not yet been used widely in a RFB. Previous studies also have not directly focused on understanding the flow behavior as a function of different operating conditions. Due to the use of thick and highly compressible porous electrodes in a larger area flow cell, the risk of uneven compression as well as unequal contact resistances exist at the electrode-BP interface. In addition, decrease in resistance of the electrode at the flow inlet side was observed with increasing flow rate, mainly at low felt compression [93], which could also result in non-uniform distribution of resistance on a local level. The unequal contact resistances among the segments may cause the segmented cell to suffer from lateral flow of current from one segment to another, giving rise to a misinterpretation of the data gained from the local current-voltage mapping [85]. As a consequence, it becomes unclear whether local current or voltage distribution in a segmented cell can be used for studying flow distribution in a flow cell.

2.2.7 Capacity loss

In addition to addressing activation, Ohmic and mass transport losses in VRFB, a wide range of research on VRFB also focuses on minimizing the capacity loss. During the operation of VRFB, proton is transported through the membrane with a water molecule. In addition to water transport, depending upon the type of membrane used, some vanadium, sulphate and bisulphate ions are also transported from the membrane. This creates the imbalance of electrolyte volume as well as imbalance of the charged species on the two tanks, resulting capacity loss over the time. This is a reversible loss, however, frequently requiring rebalancing of the electrolyte in

operation of VRFB causes loss of usable energy and requirement of extra hardware. To minimize this loss, different types of membrane have been proposed, such as, bipolar ion-exchange membrane, membrane containing combination of anion and cation exchange species, amphoteric membranes, etc. In some patent, use of anion and cation exchange membrane alternately in a multi-cell has been proposed, however, no experimental work has been reported. Mechanically, use of a tube connecting positive and negative tank has also been proposed, in which, excess electrolyte after imbalance can flow back to the low volume tank. In some patents, idea of using hydraulic shunt from the bottom of the electrolyte tank have been proposed, however, no experimental proof is available.

2.3 PhD in context of literature

From the literature review, it is revealed that research works on VRFB primarily focussed on four major areas: electrode, electrolyte, membrane, and optimization of stack design and operation. This PhD research aimed to work on the stack design and performance improvement. The scope of this PhD research was designed in collaboration with electrode manufacturer (SGL Carbon) and flow battery developer (Gildemesiter Energy Storage GmbH). It was decided that electrode material developed by SGL Carbon would be used. Similarly, standard electrolyte concentration ($1.6 \text{ M V}^{+3.5}$ in total 4 M sulfate from GFE, Germany) and AEM (FAP 450, Fumatech GmbH, Germany) that are being used by commercial manufacturers to be primarily studied for this work.

As discussed earlier, understanding flow distribution through the porous media is a major problem in flow battery operation. However, a suitable method for this has not been developed. Hence, a major focus of this PhD research was given in developing

suitable methods for the study of flow distribution. Therefore, segmented cell approach and pH tracing test were developed.

For minimising the different losses discussed in section 2.1.5, various novel ideas were tested and those found useful were implemented in the 1 kW stack development. Some of the approach that were explored are:

- New designs of flow channels on the porous electrode for improving the flow distribution and minimising the pump power loss.
- Study on hydraulic shunt of electrolyte tanks and use of a combination of anion and cation exchange membrane for minimizing the capacity loss.
- Optimization of electrode compression for minimising the Ohmic and mass transport losses.
- Study of “Power Drop Effect” at high current density operation.
- Novel design of flow frame and battery components.

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Chapter 3

Experimental Methodology

This chapter describes the experiment design and testing procedures in detail. The significance of all the tests performed are discussed, and the sections are structured in accordance to the results and discussion in the subsequent chapters. VRFB single cells and stacks of various sizes were developed for scale up and performance evaluation. For improving the flow distribution and reducing the pump power consumption, the porous electrodes were structured with various types of flow channels. A segmented cell components consisting of sixteen segments together with a completely new hardware system was developed for in-situ flow visualization. A pH tracing test method was developed for studying flow distribution in large area cell and stack. For investigating power drop effect, half-cell potential measurement set-up with reference electrode was developed. Electrolyte tanks were modified with a hydraulic shunt and stack was assembled with a combination of anion and cation exchange membrane for reducing the capacity loss. Various surface and electrochemical characterization methods were implemented to optimize the activation condition for the electrode. The design of stack components was performed using CAD software, and flow simulations were run to improve the flow.

3.1 Test cell/stack and test set-up

To fulfil the objective of conducting multi-parameter tests and thereafter developing a 1 kW VRFB stack, small test cells/stacks were developed. The developed cell and stack were tested for improving the design, and understanding and optimizing of various operational parameters. Finally, a 1 kW stack was developed to demonstrate all the improvements. Therefore, all the testing were performed in the flow cells and stacks of different sizes given below:

- 20 cm² single cell (active area: 5 cm x 4 cm)
- 100 cm² single cell (active area: 10 cm x 10 cm)
- 100 cm² size two cell stack (active area per cell: 10 cm x 10 cm)
- 625 cm² size three cell stack (active area per cell: 25 cm x 25 cm)
- 625 cm² size twenty cell (1 kW) stack (active area per cell: 25 cm x 25 cm)

Figure 3.1 and Figure 3.2 show the components used in a half cell and n-cell stack, respectively.

Figure 3.1 A half-cell arrangement showing various components in a single cell.

The arrangement of the components during assembly was similar for all the cells and stacks. The details on the design and development of individual components are discussed in Chapter 6.

A single cell consists of two half cells, separated by an ion exchange membrane. The flow frame (FF) and insulator plate were made of PVC. The FF had an integrated flow guides for improving the flow distribution and a recess at the back side for placing the BP. Copper plate was used as current collector due to its high electrical conductivity and reasonable cost.

Figure 3.2 shows the assembly order of the different components in an n -cell stack. A stack consists of multiple number of cells connected electrically in series. The electrolyte flow was made parallel to each individual cells.

Figure 3.2 Components in a two cell stack of VRFB.

In an n -cell stack, $n-1$ number of middle cell components were used and other components (copper collector, insulator plate and end plate) remained at the two ends. All the components were tightened between two steel end plates (1) using nut and bolts.

Table 3.1 lists the materials commonly used for testing the performance of the flow cells and stacks. For some specific tests, different materials other than those listed in Table 3.1 are described in the respective sections.

Table 3.1 Material used in the cell/stack assembly

Flow frame	Made of PVC with integrated flow guides
Gasket	Silicone gasket of thickness 0.5 mm
Porous electrode	PAN based carbon felt SIGRACELL GFD 4.6 EA from SGL Carbon (Meitingen, Germany), thermally activated at 600 °C for 5 hours, uncompressed thickness = 4.6 mm
Bipolar plate (BP)	TF6 or PV15 (SGL Carbon) , thickness = 0.6 mm
Membrane	Anion exchange membrane FAP 450 (Fumatech GmbH, Bietigheim, Germany), assembled as supplied
Vanadium Electrolyte	1.6 M $V^{+3.5}$ in 4.5 M total sulphate (from GFE, Nuremberg, Germany) (Note: hereafter, this concentration will be abbreviated as standard electrolyte)

Three types of test set-ups were used for testing the cells and stacks, as shown in Figure 3.3. For testing the cells of 20 cm² and 100 cm² sizes, small set-up (Figure 3.3-a) with two small electrolyte tanks and peristaltic pumps was used. Sometimes, pressure sensor and temperature sensor were also used to monitor the pressure drop and electrolyte temperature, respectively.

(a) Set-up developed for testing 20 cm², and 100 cm² single cell and stack

(b) Set-up developed for testing large area single cell and three cell stack

(c) Set-up developed for testing 1 kW-20 cell stack

Figure 3.3 Test set-ups developed for performance testing of the various sizes of cell and stacks

In larger set-ups (Figure 3.3-b & c), magnetic pumps (Iwaki, Japan) were used. The electrolyte tanks were made of polypropylene (PP). Pressure, flow and temperature sensors were always connected on both sides for continuous measurement of pressure drop, flow rate and temperature, respectively. The test set-up shown in Figure 3.3-c was developed for testing a 1 kW stack, in which, electrolyte tanks are located below the stacks to reduce the self-discharge during standby period as well as to ease the electrolyte drainage, similar to commercial systems.

Electrolyte volume of 150 mL, 1.5 L and 10 L per tank were used for testing 100 cm² single cell (and 2- cell stack), 625 cm²-3 cell stack and 20 cell- 1 kW stack, respectively. For testing small cells, either nitrogen ($\sim 10 \text{ mL min}^{-1}$) or paraffin oil (1 cm thick layer above the electrolyte) was used on both tanks for protecting the aerial oxidation of V²⁺. In larger area set-up, sealed tanks with hydrogen atmosphere and a gas bubbler system were developed to create the inert gas environment above the electrolyte on both half cells. The detail description of the developed gas bubbler system is given in Chapter 6. For testing a 1 kW stack, two tanks were connected with a short and a narrow tube (hydraulic shunt) to minimize the reversible capacity loss.

3.2 Preparation of flow channels on the porous electrode

With the objective of improving the flow distribution through the porous electrode and reducing the pressure drop, efficacy of various novel designs of flow channels on the porous electrodes were investigated.

A single cell with active area of 100 cm² (10 cm x 10 cm) was used. The materials used for the assembly of the cell were the same as those given in Table 3.1. The electrolyte volume in each tank was 150 mL and the flow through both half-cells

was kept constant at 100 mL min^{-1} using peristaltic pumps. Nitrogen at a flow rate of 10 mL min^{-1} was continuously passed through the headspace of both electrolyte tanks to hinder aerial oxidation of V^{2+} . The compression of the felt was kept constant at 20% (equivalent to 80% of initial thickness) for all types.

A similar set-up as shown in Figure 3.3-a was used. Pressure sensors (Georg Fischer) were used to continuously measure Δp in each half cell. The viscosity of the electrolytes was measured at different temperatures and state of charge (SOC), using a Hydramotion digital viscometer. The temperature of the electrolyte in both tanks was continuously monitored using PT100 type temperature sensors. During experiments the electrolyte temperature was kept at $24 \pm 1^\circ\text{C}$. A battery tester from Neware, China (10 V, 10 A) was used for charging and discharging.

Four different channel designs as shown in Figure 3.4 (a - d) were tested and compared with the standard blank electrode.

The shape of the interdigitated open channel (IDD-OC) was made according to interdigitated channels used in PEM fuel cells [1]. The cross-section of the channel was $2 \text{ mm} \times 2 \text{ mm}$ and the product of the channel width and number of channel was 12% of the width of the liquid flow path, within the range suggested by Toyo Boseki [2] for their parallel channels. The length of each of the IDD channels was 80% of L . For rectangular open channels (ROC), open cut channels were made with a cross section of $2 \text{ mm} \times 2 \text{ mm}$, similar to the IDD-OC. A total of six channels were obtained by manual cutting, in order to keep the active area similar to the IDD-OC. For poked channels in interdigitated circular poked channel (IDD-CPC) and cross poked circular channel (CPCC), a long needle with diameter of 1.5 mm was inserted at roughly half the thickness of the felt, with the help of guide plates. Channel formation, in this manner, did not visibly remove any material, but broke and pushed

the fibers, to make a hole for easy passage of electrolyte. The objective of the poked channel was not to reduce the active surface area, but to improve the active area utilization.

Figure 3.4 Different designs of channels on 4.6 mm porous graphite felt electrode.

Cells were assembled with the open cut channels facing the BP in order to have a similar configuration to fuel cell designs, in which the BP contains the flow channels. Channels in opposing half cells were lined-up parallel and aligned to each other.

The electrical resistance of a dry cell, assembled without using the membrane, was also measured in order to compare the effect of channels on electrical conductivity.

The dry resistance measurements were conducted on two cells for each channel type. A four probe method was used for the measurement of resistance.

Cell cycling was performed for testing various types of channel designs. Five charge-discharge cycles at current densities of 40, 50, 60, 70 and 80 mA cm⁻² were performed, followed by a long-term cycling test at 40 mA cm⁻² for 45 cycles. The cycling was performed in galvanostatic mode with voltages limits of 1.65 V and 0.9 V.

IDD-OC was also demonstrated by CNC machining on a stack size porous electrodes of dimension 25 cm x 25 cm x 4.6 mm. The size of the channels was 2 mm x 2 mm in cross section and length of the channel was 80% of the total flow length. Due to the spongy nature of the felt, the machining was performed by first pressing the felt between two metal plates and then the channels were cut through the metal plate. Figure 3.5 shows the picture of the felt with IDD channels.

Figure 3.5 A CNC milled interdigitated channel on a 1 kW stack size square electrode (25 cm x 25 cm x 4.6 mm). Size of channels, LxWxH = 200 mm x 2 mm x 2 mm.

The size and depth of the channel after milling was uniform, suggesting that any shape of channel could be easily cut into the surface. The heat treatment of the felt was done after channels were milled. This structured felt was later used and tested on a 3 cell stack and on a 1 kW stack (with active area of 625 cm²/cell).

3.3 Segmented cell set-up and testing procedure

Segmented cell study was performed for in-situ investigation of the cell performance and flow behavior in a conventional VRFB.

3.3.1 Test cell and experimental set-up

The BP and current collector (CC) of a positive half-cell in a 100 cm² (10 cm x 10 cm) active area size VRFB single cell were divided into sixteen segments. An exploded view of half-cell components at the segmented side is shown in Figure 3.6.

Figure 3.6 Exploded view of half-cell components at the segmented side.

The segmentation was done by modifying the insulator plate of the conventional flow cell design. Sixteen cavities were milled in the PVC insulator plate to accommodate the segmented CC and segmented BPs. Holes were drilled in the end plate to allow banana plugs to insert into the CCs. The BPs were first inserted into the Teflon frame and the frame was pushed into the slot milled on the insulator plate. During assembly, the Teflon frame was pressed by the flow frame's back window. The other components were similar to those of a single cell. The flow frame was made of PVC material milled with integrated flow guides. The back side of the flow frame consisted of a cavity for the BP to be attached for the non-segmented side. Using the silicone gaskets, the cell was protected from internal and external leakage of electrolyte.

The materials used for the assembly of the cell are listed in Table 3.2.

Table 3.2 Materials used in the cell assembly.

Porous electrode	PAN-based carbon felt SIGRACELL GFD 4.6 EA from SGL Carbon (Meitingen, Germany), thermally activated in air at 600 °C for 5 hours, uncompressed thickness = 4.6 mm
Bipolar plate (BP)	Customised 2 mm thick F100 graphite plate segments embedded in a PTFE frame from SGL Carbon (Meitingen, Germany)
Membrane	Anion exchange membrane FAP 450 (Fumatech GmbH, Bietigheim, Germany), used as received
Vanadium Electrolyte	0.8 M $V^{+3.5}$ in 4.5 M total sulfate (GFE, Nuremberg, Germany)

The schematic of the experimental set-up and picture of the segmented side are shown in Figure 3.7-a and 3.7-b, respectively.

The positions of the different segments are shown in Figure 3.7-c. The four segments 1, 2, 3 and 4 are inlet segments and 13, 14, 15 and 16 are outlet segments. The flow of electrolyte through the porous felt is expected to be parallel and uniform.

Figure 3.7 Schematic of the experimental set up (a), sixteen cables on the positive side along with electrolyte inlet and outlet tubes (b), position of sixteen segments and showing direction of electrolyte flow (c) and seating arrangement of segmented felt (dark black) and insulating frame (light black) on the flow frame window (d).

In some experiments, the porous electrode in the positive half-cell was segmented in the same way as the BP and the CC for comparing the change in resolution of the local voltage distribution. The majority of experiments were performed with segmentation by means of divided BPs and CCs only. Designing a segmented cell

with divided porous electrode is difficult, and such studies are scarce. This study for the first time segmented the thick porous electrode. Segmentation of the porous graphite electrode was accomplished by using a non-conductive, compressible and highly porous frame made from polyurethane, which is a commonly used material for packaging purposes. The polyurethane frame was made hydrophilic by soaking in vanadium electrolyte for one day. All the segments were confirmed to be electrically insulated from one another after the assembly. The flow distribution, when using an insulating frame, was assumed to be the same as in a non-segmented felt. The segmented felt and polyurethane plastic frame arrangement in a flow frame is shown in Figure 3.7-d.

The low vanadium concentration in the electrolyte solution of 0.8 M was chosen deliberately in order to reach the mass transport polarization zone at relatively low current densities during polarization measurement. The electrolyte volume in each tank was 300 mL and the flow through both half-cells was maintained at a fixed rate by using a peristaltic pump attached with two synchronized heads (Masterflex). Paraffin oil was used on both tanks to prevent aerial oxidation of V^{2+} . The compression of the felt was kept constant at 20% (equivalent to 80% of initial thickness) for all cell assemblies studied. The flow was parallel in both half-cells, unless indicated separately.

A battery tester (Neware, China) with integrated loads/power supplies consisting of sixteen channels was used to charge and discharge each segment. The battery software BTS7.5.4, provided with the battery tester, was able to control each channel together as well as individually. For segmenting the positive half-cell, each positive terminals from the battery tester were connected to individual segments of the positive half cells and sixteen negative terminals from the tester were shunt together

and then connected to a single copper terminal of the non-segmented negative half-cell.

3.3.2 Measurement procedure

Cell cycling and polarization measurement were carried out at varying current densities and flow rates. The polarization was measured at 50% state of charge with one minute of consecutive charging and discharging including 1-3 minute of hold at open circuit voltage (OCV) in between. The OCV hold time was chosen such that the electrolyte could redistribute uniformly throughout the complete active area before starting the next charging or discharging routine. At a high flow rate of 60 mL min^{-1} , 1 minute hold at OCV was sufficient, whereas, it required up to 3 minute at a flow rate of 20 mL min^{-1} . The polarization was measured from 1 mA cm^{-2} up to 200 mA cm^{-2} , depending upon the stoichiometry of the flow. A typical polarization measurement routine of segment 1 at a flow rate of 60 mL min^{-1} is shown in Figure 3.8.

Figure 3.8 A typical polarization measurement routine of segment 1 at a flow rate of 60 mL min^{-1} .

In order to protect the cell from reaching high cell voltages, which would cause side reactions and excessive gas evolution, the cell was charged at low current density for longer times to keep the SOC constant at 50% following discharge, as shown in Figure 3.8. All the experiments were carried out in galvanostatic mode with the same current density passing through each segment while recording the potential of each segment. Experiments in potentiostatic mode with monitoring the current distribution could not be performed due to the limitation of the battery tester. The voltage data obtained from the sixteen segments during the polarization measurement were plotted into contour diagrams.

3.4 The pH tracing test for flow distribution study

Alternative to segmented cell approach, a simple test method was developed for qualitative investigation of the flow distribution in a flow cell. The test, named as pH tracing, consists of tracing of pH change during the flow through the cell, thereby obtaining flow related information. The pH tracing is an ex-situ method, which can only provide qualitative information on the flow distribution.

The pH tracing was performed on both 100 cm² and 625 cm² cell. The test was performed on 100 cm² size cell to understand the pH curve at various conditions, such as flow rate, electrode compression and design of flow frame. The study on 625 cm² size cell was mainly focused on comparing the flow distribution using the porous electrode with and without IDD channel, and orientation of the channel. To avoid the effect of pressure difference between two half-cells, only one half cell was assembled and used.

The experimental set-up for testing 625 cm² size cell is shown in Figure 3.9. A similar set-up was also used for testing 100 cm² size cell. At a defined flow rate,

water from the tap was circulated through the cell and pH electrode was placed at the outlet tube using a “T-joint”. The pH meter was able to record the pH values in a SD card in every 1 second. After the pH recording started, acid was injected at 30 second from the inlet nozzle, using a syringe. 1 mL of electrolyte ($1.6 \text{ M V}^{+3.5}$ in 4.5 M total sulphate) was injected in one shot. The liquid coming out of the outlet tube was discarded. The recorded pH was plotted against time and various information on the flow distribution were obtained. In testing the large area cell of 625 cm^2 active area, pressure sensor was connected at the inlet for continuous recording of the pressure drop at different flow rates and at various configurations of IDD channels.

Figure 3.9 Test set-up for the pH tracing test

In order to understand the nature of the pH curve, flow rate, compression of the electrode, inlet cross-section and orientation of the channels on the electrode were varied.

3.5 Testing of effect of electrode compression

An in-house developed single cell with active area of 100 cm^2 ($10 \text{ cm} \times 10 \text{ cm}$) was used to study the effect of electrode compression on the battery performance, and hence to optimize it for the future development. A set-up, similar to that shown in Figure 3.3-a (section 3.1), was used for the study.

A combination of two 3 mm thick (total thickness = 6 mm) Poly-acryl nitrile (PAN) based porous graphite felt (SGL carbon, Germany) was used. The electrode was thermally activated in air at 600°C for 5 hours. The information on the BP, membrane and electrolyte concentration are provided in Table 3.1. The volume of the electrolyte in each tank was 150 mL. The flow rate of electrolyte on both half-cell was kept constant at 100 mL min^{-1} using a peristaltic pumps. Nitrogen at a flow rate of 10 mLmin^{-1} was supplied continuously on both electrolyte tanks to prevent the aerial oxidation.

Five different compressions of the porous electrode; 15%, 20%, 25%, 30%, 35% and 40% were investigated. The electrode compression was varied by using the combination of silicone and Teflon gaskets of different thicknesses. A torque wrench was used to ensure the uniform compression of the electrode.

The pressure drop and temperature of the electrolyte was continuously recorded. The electrolyte temperature was kept at $24 \pm 1^\circ\text{C}$ during the operation of the cell. The dry cell resistance was measured using four probe method.

Cell cycling was performed for monitoring the performance of the cell at various compressions. Short five cycles were run at varying current densities between 40 to 80 mA cm^{-2} , followed by 50 long-term cycles at 40 mA cm^{-2} . Charge discharge

cycles were conducted between cut-off voltages of 0.9 V and 1.65 V, under the galvanostatic condition.

3.6 Investigation of the ‘power drop effect’

An anomalous behavior of the membrane that appeared mainly at the activation cycle as well as at high current density operation was investigated. For this test, various sizes of cells and stacks were used, and discharged at high current densities. This effect was investigated for AEM (FAP450) membrane. For the monitoring of this effect, voltage data over time were plotted during the cell cycling operation. The BP, electrode, electrolyte and cell configuration were similar to that given in Table 3.1. In addition to the cell cycling, half-cell potential measurement were performed in a 20 cm² cell to ascertain the specific half-cell responsible for the power drop effect. As shown in Figure 3.10, reference electrodes (Hg/Hg₂SO₄, K₂SO₄ (saturated)) were inserted near the flow outlet of each half cell. For inserting the reference electrodes, three way opening was machined on a transparent Polypropylene cube. The tip of the inserted reference electrode was just in contact with outflow electrolyte. The cell was cycled (charged at 80 mAcm⁻² and discharged at 120 mAcm⁻²) using the battery tester terminals connected to the two copper terminals of the cell. At the same time, using two channels from a multi-channel potentiostat (VMP3- BioLogic, France), the half-cell potential across each half cell terminal and reference electrode was measured (OCV vs SCE). From this measurement, cell voltages of individual half cells and full cell during cycling were separately recorded. By measuring the half-cell voltage separately, the effect of membrane on the cell voltage was excluded.

Figure 3.10 Set-up developed for half-cell voltage measurement.

It was hypothesized that the power drop effect was observed due to the increase in resistance of the membrane. Therefore, to further validate this, the resistance of the membrane in the electrolyte solution was measured ex-situ. The resistance of both AEM and CEM membranes in presence of H_2SO_4 , V^{2+} , V^{3+} , V^{4+} and V^{5+} was measured using electrochemical impedance spectroscopy (EIS) in a glassy carbon electrode ($\Phi=0.5\text{cm}$) set-up (Figure 3.11).

Figure 3.11 EIS set-up for measuring the impedance of membrane.

The set-up used a glassy carbon electrode into a Teflon bar, which vertically pressed the base plate. The alignment of the glassy carbon rod was made using a special holder and tripod stand as shown in Figure 3.11. The glassy carbon electrode was connected to the working electrode and the base plate (graphite plate -TF6) was connected to the counter electrode (two electrodes set-up) of a potentiostat. The resistance of the set-up without the membrane was first measured using EIS. The intercept of the Nyquist diagram at the real part impedance axis was used to obtain the Ohmic resistance value. Afterwards, membrane was pressed between the glassy carbon electrode and the base plate. From these, the membrane resistance was calculated by subtracting the Ohmic resistance value measured without membrane from the value obtained with membrane. The membranes were initially dipped into the respective electrolyte ion solution for 24 hours before the EIS measurement. During the measurement, few drops of corresponding vanadium solution were also spread around the glassy carbon electrode in order to eliminate the measurement area exposure from air.

3.7 Tests for minimising the capacity loss

The VRFB operation suffers from electrolyte imbalance primarily due to the transfer of ions and water across the membrane. Depending upon the type of membrane used, permeation of some vanadium and sulphate / bisulphate ions also occurs at different rates. This imbalance creates gradual capacity loss, which requires frequent rebalancing of the electrolyte. To solve this problem, two methods for reducing the reversible capacity loss were explored. For testing these methods, different sizes of cell and stack were used.

3.7.1 Hydraulic shunt of electrolyte tanks

A 2-cell stack of 100 cm² size was assembled for the testing. The stack used anion type membranes (FAP450), thermally treated electrodes (GFD 4.6 EA, 600°C-5 hr) and BPs (PV 15). The electrolyte volume was 300 mL per tank and concentration was 1.6 M V^{+3.5} in 4.5 M total sulphate. The flow rate was maintained constant at 100 mL min⁻¹ per cell using two diaphragm type DC pumps (KNF Neuberger Inc., Germany). Paraffin oil (1 cm thick) was used on both tanks to prevent the aerial oxidation of V²⁺. The test set-up is shown in Figure 3.12. The glass tanks were modified with nozzle at the bottom of the tanks with needle valve to open or close the auto-rebalancing. The internal diameter of the nozzle is 2 mm. Two tanks were hydraulically shunted using a flexible tube (Teflon) of internal diameter of 2 mm and length of 0.5 m to balance the level of the electrolyte automatically.

Figure 3.12 Test set-up developed for hydraulic shunt measurement in a 100 cm² size two cell stack.

A schematic of the set-up during opening and closing of the auto-rebalancing is shown in Figure 3.13.

Figure 3.13 Schematic of the set-up showing opening and closing of the auto-rebalancing.

This test was also performed on a 3 cell stack and on a 20 cell stack of 1 kW class. For testing 3 cell stack and 20 cell stack, electrolyte volume of 1.5 L/tank and 10 L/tank were used, respectively. A same test set-up shown in Figure 3.3-b and 3.3-c, in section 3.1, was used.

An electrolyte sample of 1 mL was also taken periodically from both half cells for potentiometric titration in order to observe how well the concentration of ions and state of charge in two half-cell electrolyte was balanced with the auto-rebalancing. The titration was done using a titrator from Mettler Toledo (DMi144-SC metal sensor). A solution of 0.02 M potassium permanganate (KMnO_4) was used for oxidising the vanadium ions. Cell cycling at different current density was performed for screening the performance.

3.7.2 Stack set up with a combination of AEM and CEM

An anion (partially-fluorinated, FAP450) and a cation (fluorinated, Nafion 117) exchange membrane combination was used in a two cell stack set-up, as shown in Figure 3.12. The auto-rebalancing was switched off, i.e. valve was closed. A schematic of the set-up is shown in Figure 3.14.

Figure 3.14 A schematic of the test set-up for testing alternate membrane combination for reducing capacity loss.

An equal flow rate of the electrolyte was maintained at each half cells. Cell cycling at various current densities was performed for screening the performance. An electrolyte sample of 1 mL was also taken periodically for potentiometric titration.

3.8 Characterization of electrode materials

A wide range of treatment temperature and treatment time have been reported in literature. Generally, a too low temperature ($<400\text{ }^{\circ}\text{C}$) is not suitable as it is unable

to introduce sufficient oxygen containing functional group as well as nearly no mass loss to increase the surface area. In contrast, activation at too high temperature ($> 700\text{ }^{\circ}\text{C}$) could burn-off the fibers faster, i.e. higher mass loss, which could reduce the surface area (as well as thickness) significantly.

In order to know the degradation temperature of the carbon felt, thermogravimetric (TGA) measurement was done. The temperature was increased from room temperature to $900\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The weight of the felt (GFD 4.6 EA) sample was recorded. The measurement was performed in air at a flow rate of 60 mL min^{-1} .

It has been reported that the activation time at $400\text{--}500\text{ }^{\circ}\text{C}$ requires longer duration up to 30 hours [3]. As the target was also to shorten the activation time, the same sample was investigated at three different treatment temperatures (500 , 550 and $600\text{ }^{\circ}\text{C}$) for 5 hour duration. As the burn off is higher in 5 hours, treatment above $600\text{ }^{\circ}\text{C}$ was not done. The activated felts were compared with the as-received felts to compare the improvements in the performance. Hence, four samples: three with heat treated and one untreated felt were investigated.

In order to investigate the surface morphology changes by the thermal oxidation, scanning electron microscopy (SEM) image was taken. The measurement was done using JEOL FESEM 6340F equipment.

The electrochemical investigation on the performance of four samples were performed using cyclic voltametry (CV) and electrochemical impedance spectroscopy (EIS). A BioLogic (VMP3, France) potentiostat was used for the measurement. The CV and EIS measurements were performed using three electrode set-up in a customised electrochemical cell, as shown in Figure 3.15.

Figure 3.15 Electrochemical cell set-up for measuring CV and EIS.

Graphite felt (1 cm x 1 cm) attached to the expanded graphite plate and compressed in a plastic holder as the working electrode (WE), platinum mesh as counter electrode and mercury sulphate as the reference electrode were used. CV and EIS were measured in both positive (V(IV)/V(V)) and negative redox couples (V(II)/V(III)), separately. The vanadium concentration was diluted to 0.1 M in 4 M H_2SO_4 in order to reduce the peak current since working electrode had a large surface area and potentiostat could only handle the current of ± 400 mA. The electrolytes from both half cells were prepared after charging to 90% SOC. For the positive and negative redox couples, the CV was performed from 0.5 to 1.3 and -0.85 to -0.25 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$, $\text{K}_2\text{SO}_{4\text{sat'd}}$ at a scan rate of 2 mVs^{-1} , respectively. Using the same set-up, each sample was also investigated using EIS measurement with an AC signal of 10 mV and frequency swept from 100 kHz to 100 mHz. The Ohmic and charge transfer resistance were obtained by fitting the Nyquist plots using Zfit software.

Further, Raman spectra were obtained for four samples using Confocal Raman Spectroscopy (WITec alpha300 SR). During the measurement, the laser wavelength was 488 nm and spot size was 318.5 nm. The spot size is the radius of the beam itself. The objective of performing Raman spectrum was to gather information on the change in disorder or defects with the thermal treatment. Furthermore, single cell of 100 cm² active area was assembled and tested for all four samples. For this measurement, the test set-up for small cell as discussed in section 3.1 was used. The cycling results at different current densities were compared among the differently treated felts.

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Chapter 4

Improving the flow distribution and reducing the pump losses

This chapter discusses three core set of results related to the flow distribution and pump power reduction. The use of flow channels on the porous electrode to improve the flow distribution and reducing the pumping losses are given in the first section. The second and third sections present two suitable methods for studying the flow distribution in flow battery: segmented cell approach and pH tracing test. For the first time, the flow distribution was quantified using local OCV distribution. The pH tracing test was useful in configuring the electrode orientation during 1 kW stack assembly. The design of the flow frame and cell architecture were modified based on the findings.

4.1 Flow channels on the porous electrode for improving the flow distribution and reducing the pressure drop

A part of the findings in this section was published as an original research paper: A. Bhattarai, N. Wai, R. Schweiss, A. Whitehead, T. M. Lim, H. H. Hng, Advanced porous electrodes with flow channels for vanadium redox flow battery, Journal of Power Sources, 341 (2017) 83-90.

The objective of this study is to correlate the electrode channel design with the overall cell performance. As material was removed for OC (open cut) type channels, there should be a trade-off between conductivity, reaction area and pump power losses. Therefore, a comparison was made through studying the cycling efficiencies, cell resistivity, pressure drop (Δp), polarization, etc. The detail experimental set-up and conditions are discussed in Section 3.2. In short, four types of flow channels (IDD-OC: Interdigitated Open Channel, ROC: Rectangular Open Channel, IDD-CPC: Interdigitated circular poked channel and CPCC: Cross poked circular channel) on the porous electrodes were investigated against conventional electrode without flow channels. Among the four channel designs, two designs were cut channel type (removal of material) and the remaining two were pierced (poked) channels type (without removal of material).

4.1.1 Cell performance

4.1.1.1 Cell performance at different current densities

The voltage efficiency (VE), energy efficiency (EE), coulombic efficiency (CE) and discharge energy at current densities of 40, 50, 60, 70 and 80 mA cm⁻² are shown in Figure 4.1.1-a, -b, -c and -d, respectively.

Figure 4.1.1 Comparison of (a) VE, (b) EE, (c) CE and (d) discharge energy of four channel designs with respect to 'No channel'.

The EE and VE of the ROC design were significantly lower than the standard electrode and the other channel designs. The poor performance of the ROC channel could be due to rapid flow through the open channels with little spreading into the felt and the small reduction in conduction, because of active area removal. The electrical resistance of all channels measured in dry condition without membrane was slightly higher as compared to that of standard electrode, and the results are listed in Table 4.1.1.

Table 4.1.1 Electrical resistance of the cell without membrane at dry condition.

Channel type	No channel	Interdigitated open channel (IDD-OC)	Rectangular open channel (ROC)	Interdigitated circular poked channel (IDD-CPC)	Cross poked circular channel (CPCC)
Electronic resistance ($\Omega \cdot \text{cm}^2$)	0.37	0.63	0.53	0.57	0.58

The poor performance of ROC design compared to interdigitated channel and standard flow through type design is in agreement with the results obtained using parallel flow fields on BPs (BPs) [1, 2].

Comparing all types of channel with standard electrode, higher EE and VE were observed for IDD-CPC and IDD-OC. At the low current density of 40 mA cm^{-2} , the EE and VE for IDD-CPC, IDD-OC, no channel and CPCC were very similar. Differences arose at higher current densities due to the resistive losses and starvation of electrolyte. At 80 mA cm^{-2} , an average (of 5 cycles) EE of 81.0% was obtained for IDD-CPC followed by 80.7% for IDD-OC, 80.0% for CPCC, 78.8% for no channel and 72.5% for ROC.

The poked channels in IDD-CPC and cut channels in IDD-OC extended to 80% of the electrode length (L). Unlike ROC, IDD channel restricts the bypass of electrolyte from channel inlet to outlet and thus allows the electrolyte to spread more uniformly. As can be seen, the VE and EE were slightly higher in IDD-CPC and IDD-OC, when compared to the standard electrode. From Figure 4.1.1-c, IDD-CPC and IDD-OC also exhibited stable and high CE.

The reduction in contact area at the BP and felt interface due to flow channels in IDD-OC and ROC are 14.4% and 12.0%, respectively. Surprisingly, with the loss of 14.4% contact area in IDD-OC, the voltage efficiency did not decrease, but slightly improved as compared to the standard electrode. This indicates that the improvement in flow distribution outweighed the loss of electronic conductivity. In ROC, the VE dropped sharply, which shows the dominant effect of flow distribution on the cell performance. Further, in IDD-CPC and CPCC, poking caused the fibers near the holes to be denser in order to create a hole of 1.5 mm in diameter. The ratio of the volume of the circular channels to the total volume of the felt for IDD-CPC and CPCC was 2.8% and 5%, respectively. Though electronic conduction reduced slightly by poking, the EE and VE were increased for both poked channels as compared to standard electrode. This again suggests that the effect of improvement in the active area utilization is more important than the slight reduction in electronic conductivity. Our study did not focus on optimizing a specific channel design, so the extent to which the felt can be safely removed, without decreasing the efficiency, has not been determined. However, comparing the channel designs suggested by the patent literature [3], contact surface area reduction up to 36% of the total surface area could be envisaged.

Discharge energy is a critical design parameter for energy storage systems and can vary for several reasons such as energy efficiency, utilisation of the electrolyte, etc. A comparison of the discharge energies has been made and shown in Figure 4.1.1-d. As can be seen, the discharge energies improved by flow channels, except for ROC. The discharge energy for ROC was slightly decreased in comparison to the standard electrode. However, the discharge energies for IDD-CPC, IDD-OC and CPCC were higher than the standard electrode. At 80 mA cm^{-2} , as compared to the standard electrode, the specific discharge energy for IDD-CPC, IDD-OC and CPCC was higher by about 65%, 38% and 25%, respectively. The improvement in

discharge energy by the use of flow channels is attributed to improvement in the electrolyte utilisation, which is attributable to the elimination of dead zones in the electrodes. Consequently, this reduces the internal resistance which in turn the cell can utilize more capacity before reaching limiting voltage. The higher discharge energy in IDD-OC compared to ROC is in agreement with the patent literature [3]. A small continuous fall in discharge energy in each cycle is expected due to the net mass transfer from the positive to negative tank, whereas a more significant fall in capacity can be seen to result from the stepwise increase in current density.

4.1.1.2 Cell performance in long-term cycling at 40 mA cm^{-2}

The flow cell was further tested at 40 mA cm^{-2} for 45 cycles, in order to study the long-term performance of differently structured electrodes. The EE and VE for various channel designs are compared in Figure 4.1.2–a and 4.1.2-b, respectively.

Figure 4.1.2 Long-term performance testing at 40 mA cm^{-2} , (a) voltage efficiency, and (b) energy efficiency.

The efficiencies all decline by less than 2.3%, with IDD-OC and IDD-CPC showing the higher efficiencies. A slight reduction in the efficiencies with cycling is most

likely due to the mass transfer from positive to negative electrolyte tanks. An average net mass transfer of 7 g/day was recorded at 40 mA cm⁻².

4.1.2 Area specific resistance (ASR) of the flow cell

The ASR of the cell for different channel design at various current densities calculated using Eq. (2.5) is given in Table 4.1.2.

Table 4.1.2 Average area specific resistance during cycling of the cell.

Area specific resistance ($\Omega \cdot \text{cm}^2$) at	Channel type				
	No channel	IDD-OC	ROC	IDD-CPC	CPCC
$j = 40 \text{ mAcm}^{-2}$	1.84	1.79	2.59	1.79	1.82
$j = 50 \text{ mAcm}^{-2}$	1.83	1.74	2.56	1.74	1.83
$j = 60 \text{ mAcm}^{-2}$	1.86	1.75	2.62	1.75	1.87
$j = 70 \text{ mAcm}^{-2}$	1.91	1.76	2.68	1.76	1.86
$j = 80 \text{ mAcm}^{-2}$	1.91	1.75	2.68	1.74	1.86

The ASR was highest for ROC, whereas, it was lowest for IDD-CPC and IDD-OC. This reflects the trend observed previously in the discharge energies, and likely arises from the same cause, namely improved flow distribution in the IDD-CPC and IDD-OC electrodes.

The combined membrane and charge transfer resistances as well as concentration change in the cell can be estimated by taking the difference between the wet and dry resistance. For example, by comparing the resistance data from Table 4.1.1 and Table 4.1.2, the calculated resistance are 1.54, 1.12, 2.15, 1.17 and 1.28 $\Omega \cdot \text{cm}^2$ at 80 mA cm⁻² for No channel, IDD-OC, ROC, IDD-CPC and CPCC, respectively. Interestingly, cells with higher flow uniformity use the electrode and membrane area

more effectively and therefore have a lower difference in resistivity, as can be seen for IDD-OC and IDD-CPC. The membrane (FAP 450) alone has a specific resistance of about 0.7 Ohm.cm^2 as stated in the manufacturer's data sheet [4].

4.1.3 Pressure drop

The pressure drop (Δp) was continuously recorded for all experiments. Pressure variation in the first five cycles, for both positive and negative half cells of different cells are shown in Figure 4.1.3-a and Figure 4.1.3-b, respectively.

Figure 4.1.3 Pressure drop (Δp) at the (a) positive half-cell and (b) negative half-cell of the different cell assemblies.

As both tanks were initially filled with the same electrolyte, with vanadium at an average oxidation state of 3.5, the initial Δp in both half-cells was similar. Upon charging, the viscosities changed due to the formation of different vanadium species in both half cells. For comparison, viscosities were measured (Figure 4.1.4) which turned out to be maximum on the negative half-cell at full discharge conditions and lowest at full charge condition in both half-cells. The trend of viscosity change was in agreement with available literatures [5, 6].

Figure 4.1.4 Viscosity measured for (a) positive electrolyte and (b) negative electrolyte at different temperature and SOC. The initial electrolyte concentration was 1.6 M $V^{+3.5}$ in total 4.5 M sulphate.

Accordingly, Δp in the negative half-cell is highest at full discharge condition and lowest at fully charged condition. In the positive half-cell, the difference in Δp during charging and discharging was not as significant as in the negative half-cell because the variation in viscosity during charging and discharging was small.

It can be seen that a significant reduction in Δp occurred for both IDD-OC and ROC by an average of 36% and 39%, respectively. For IDD-CPC and CPCC, the reduction in Δp , as compared to standard electrode, was only 2.4% and 6.3%, respectively. As pump energy consumption is directly proportional to Δp , reduction in Δp lowers the energy lost in pumping. Moreover, the difference in pressure between the two half cells (i.e. across the membrane) was reduced in open channel (OC) type cells. The full extent of Δp change during a complete charging and discharging cycle in a negative half-cell of non-OC type electrodes was about 65 mbar while the reduction of 40 mbar was obtained by the OC type electrodes. Similarly, for the positive half-cell, the range of Δp was also slightly reduced in OC types.

The maximum difference in pressure between two half cells occurred in the full discharge condition (low SOC).

4.1.4 Overall energy efficiency including pump losses

Figure 4.1.5 shows a plot of Δp and pump power consumption for cells with different channels. The pump power (P_p) in Watt was calculated assuming a pump efficiency of 70% by:

$$P_p = 2 \cdot \frac{\Delta p \cdot Q}{0.7} \quad \text{Eq. (4.1.1)}$$

Where, Δp is the pressure drop in Pascal and Q is the flow rate in $\text{m}^3 \text{s}^{-1}$. The calculation was performed for considering two pumps each for positive and negative electrolyte.

The frictional loss in pipes, bends and manifolds was deemed to be negligible in comparison to pressure loss through the electrodes. An average of Δp from two half cells was used for simplification.

Figure 4.1.5 Pressure drop (Δp , in mbar) and average pump power consumption (in mW) calculation for different channels.

As per Eq. (4.1.1), the pump loss depends on the felt height (or flow length) and flow rate of the electrolyte. The calculated pump power in Figure 4.1.5 was done for a single cell having a felt height of 10 cm and flow rate of 100 mL min⁻¹. In a multiple cell stack of larger size, the felt height and flow rate will change and hence the pump loss may slightly vary. As per literature, pump consumption of 1%-3% of the overall EE can be expected [7].

The overall energy efficiency including the pump loss for various channels are given in Figure 4.1.6-a, together with those without pump loss in Figure 4.1.6-b.

Figure 4.1.6 Energy efficiency at different current density, (a) including pump power consumption and (b) excluding pump power consumption.

Taking the total energy consumption into consideration (Figure 4.1.6-a), the best results were achieved by the use of IDD-OC followed by IDD-CPC, CPCC, no channel and ROC. Comparing IDD-OC to standard electrode, a maximum improvement in EE of 2.7% at 80 mA cm⁻² and minimum of 1.4% at 40 mA cm⁻² was achieved. Similarly for IDD-CPC, a maximum of 2.5% at 80 mA cm⁻² and a

minimum of 0.7% at 40 mA cm⁻² in EE were achieved. The contribution of the pump power reduction on EE increment in IDD-OC was calculated to be 1% at 40 mA cm⁻² and 0.4% at 80 mA cm⁻².

Hence, from the study of four different designs of channel, the IDD-OC and IDD-CPC are the most promising.

4.1.5 Polarization at various flow rates

The IDD-OC electrode was further compared with the standard electrode, by polarization measurements at 50% SOC with one minute of consecutive charging and discharging, including one minute at open circuit voltage (OCV) in between. The polarization was measured at current densities from 1 to 100 mA cm⁻².

A typical discharge voltage curve was plotted from the average voltage during 1 minute discharge at each current density, during the polarization measurement, as shown in Figure 4.1.7.

Figure 4.1.7 Polarization plot of the cell with (a) No channel and (b) IDD-OC, during discharging at various flow rates. The lines with close symbol represents the discharge voltage and the open symbol represents the stoichiometry at various current density and flow rates.

The polarization plot for the cell with standard electrode (Figure 4.1.7-a) shows that the ohmic polarization is dominant at flow rates of 50 and 100 mL min⁻¹. However, at low flow rates of 40, 30 and 20 mL min⁻¹, mass transport is limiting for current densities of more than 40 mA cm⁻². A sharp drop in discharge voltage was observed below a stoichiometry of 5. The stoichiometry (λ) is the ratio of the applied flow rate (Q) to the stoichiometric flow rate for specific current density (Q_{st}). The latter describes the minimum flow rate required to sustain the current if full conversion occurs during a single pass. Using Faraday's law, we obtain:

$$\lambda = \frac{Q}{Q_{st}} = Q \cdot \left(\frac{SOC \cdot n \cdot c_V \cdot F}{I} \right) \quad \text{Eq. (4.1.2)}$$

Where I is total current, SOC the state-of-charge (0.5), n the number of electrons per mole of V ion involved (1), C_V is concentration of V ion in mol l⁻¹ (1.6), F is the Faraday constant (96485 C mol⁻¹).

In the case of IDD-OC (Figure 4.1.7-b), linear ohmic polarization was observed even at stoichiometry close to 1. The results indicates that the cell with IDD channels can be operated at much lower flow rates compared to the standard electrode due to the improvement in the flow distribution. Operating the cell at low flow rate further decreases the pump power and also provides an opportunity to use higher electrode compression, which would lower the electronic resistivity.

Hence, it can be concluded that IDD-OC performed the best among the design of channels studied, in terms of improving the flow distribution and reducing the pressure drop. Hence, it was decided that the IDD-OC channel would be further investigated for application in 1 kW stack development. Therefore, on electrode size of 25 cm x 25 cm, IDD channels were milled at a local workshop in Singapore. The

details of the channel and method to make the channel on the spongy electrode is discussed in Section 3.2. In a 3 cell stack of 625 cm² active area per cell, IDD-OC (both horizontally and vertically aligned) and no channel were tested for evaluating flow distribution and pressure drop using pH tracing test. These results are discussed in Section 4.3. A 1 kW stack consisting of 20 cell was also developed using IDD channels on the felt. The results of the stack testing are discussed in Chapter 6.

4.2 Segmented cell study for in-situ visualization of flow distribution of electrolyte in the porous electrode

A part of the findings in this section was published as an original research paper: A. Bhattarai, N. Wai, R. Schweiss, A. Whitehead, G.G. Scherer, P.C. Ghimire, T.D. Nguyen, H.H. Hng, Study of flow behavior in all-vanadium redox flow battery using spatially resolved voltage distribution, Journal of Power Sources, 360 (2017) 443-452.

The objective of the segmented cell study was to establish a method to investigate and improve the flow distribution in RFB using local voltage/current distribution. The developed approach in this study is completely new in segmented cell as well as in flow battery literature. In this study, porous felt electrode was also segmented for some cases in order to investigate the change on the spatial resolution. This is the first time such study is conducted. The first subsection (4.2.1) focuses on understanding local voltage distribution, and effect of felt segmentation for different flow rates and current densities. The second subsection (4.2.2) focuses on understanding and quantifying the flow distribution.

The details of the cell design, segmentation method and measurement procedures are given in Section 3.3. However, to make it easier to follow the next subsections, the position of the sixteen segments are given again in Figure 4.2.1.

Figure 4.2.1 Position of sixteen segments in the porous electrode (inlet segments: 1,2,3,4 and outlet segments: 13,14,15,16, the flow was in upward direction and expected to be parallel and uniform along the cross section).

4.2.1 Local voltage distribution and effect of felt segmentation

The bipolar plate (BP) and current collector (CC) on the positive half-cell were segmented in all experiments presented in this study. For selected case, additional segmentation of the felt was done (corresponding data indicated when applicable).

Figure 4.2.2-a shows a typical polarization measurement routine of segment 1 as an example measured at flow rate of 60 mL min^{-1} . The remaining fifteen segments also followed the same routine during the measurement. A plot of discharge voltage vs current density was obtained by averaging the data recorded during the last 10 s during a 1 minute discharge period at different current densities. Figure 4.2.2-b and 4.2.2-c show the polarization curves at flow rates of 60 and 20 mL min^{-1} ,

respectively. Figure 4.2.2-d shows the polarization behavior of a cell with felt being segmented together with the BP and CC (flow rate = 60 mL min⁻¹).

Figure 4.2.2 A typical polarization measurement routine of segment 1 at a flow rate of 60 mL min⁻¹ (a), and polarization plot of sixteen segments during discharging calculated by taking the average of last 10 sec data during discharging at each current densities for: flow rate of 60 mL min⁻¹ (b), flow rate of 20 mL min⁻¹ (c) and segmented felt at flow rate of 60 mL min⁻¹ (d).

Due to the relatively high flow rate of 60 mL min⁻¹ (Figure 4.2.2-b) as compared to 20 mL min⁻¹ (Figure 4.2.2-c), the polarization curve showed a linear drop even at the elevated current density of 200 mA cm⁻², indicating that the voltage is dominated by the Ohmic drop. However, with a decrease in the flow rate (Figure 4.2.2-c), the effect

of concentration polarization was dominant mainly at a current density above 120 mA cm^{-2} . With the use of a segmented felt (Figure 4.2.2-d), the separation of the discharge voltage among segments became larger and clearer as compared to the same flow rate with non-segmented felt (Figure 4.2.2-b). To illustrate this, contour diagrams of the discharge voltage at 160 mA cm^{-2} during a polarization measurement are compared in Figure 4.2.3-a, 4.2.3-b and 4.2.3-c, for the three cases described in Figure 4.2.2-b, 4.2.2-c and 4.2.2-d, respectively. The width of the each color bands in the contour diagram is created by the contour profile function of Origin Pro software. It actually shows the voltage profile/gradient rather than single segment color in order to best visualize the flow profile.

Figure 4.2.3 Contour diagram of discharge voltage at (a) flow rate = 60 mL min^{-1} , $j=160 \text{ mA cm}^{-2}$, (b) flow rate = 20 mL min^{-1} , $j=160 \text{ mA cm}^{-2}$ and (c) segmented felt, flow rate = 60 mL min^{-1} , $j=160 \text{ mA cm}^{-2}$, and (d) segmented felt, flow rate = 60 mL min^{-1} , $j=10 \text{ mA cm}^{-2}$.

The flow of electrolyte was in the upward direction. For galvanostatic measurements, a dispersion of local voltages during charging and discharging from the electrolyte entrances to the electrode exit was expected due to the continuous change in concentration of charged species in the electrolyte. During discharging, higher voltages were seen at the 1st row segments (segments 1-4) i.e. towards the flow entrance and lower voltages were seen at the 4th row segments (segments 13-16) i.e. towards the flow exit.

A clear and distinct separation of the discharge voltage was monitored along the flow direction in a segmented cell with divided felt (Figure 4.2.3-c) as compared to a segmented cell with non-segmented felt (Figure 4.2.3-a). In the case of a segmented cell assembled using an undivided porous felt, higher voltages appeared on the 1st row segments, which was expected. The voltage distribution, however, became unclear towards the middle and outlet sides of the electrode. A clear separation of voltage from flow inlet to the outlet was observed in a cell with segmented felt, which gave evidence that the voltage distribution in the cell with non-segmented felt was affected from the lateral flow of current. This is not surprising, since the specific conductivity of the felts in the lateral direction (in-plane) is around twice as high as the conductivity in the through-plane direction.

A slightly better performance was observed in the polarization curve of the segmented felt (Figure 4.2.3-d) as compared to that of the non-segmented felt (Figure 4.2.3-b). This is because the segmented felt plot in Figure 4.2.2-d was made by normalising the current density as per geometric area felt. When the absolute current density was considered, the performance for both plots were similar, and an even higher separation for the segmented felt was observed.

For the four contour diagrams shown in Figure 4.2.3, the electrolyte stoichiometry was 2.4, 0.9, 2.4 and 38, respectively. The stoichiometry (λ) was calculated using Eq. (4.1.2). It should be noted that the electrolyte stoichiometry of 0.9 in Figure 4.2.3-b was maintained for a short time such that some of the segments could no longer supply the required current. Therefore, this stoichiometry might be thought of as ≤ 1 or about 1.

In a cell with non-segmented felt, a clear and distinct dispersion of discharge voltage between flow inlet to outlet was only observed at a low stoichiometry of around 1 (Figure 4.2.3-b), when the mass-transport polarization was dominant in the cell. The local voltage distribution at mass-transport limiting conditions reflects the combination of transport and concentration gradient due to the depletion of charged species [9]. For a segmented porous electrode, a gradient of discharge voltages between flow inlet to outlet was observed even at a very high stoichiometry of 38 (Figure 4.2.3-d) and despite a voltage deviation of only 10 mV between the inlet to the outlet. This confirms that the information about electrolyte transport can be obtained through the study of local voltage distribution even at high stoichiometry. However, the information could be misleading, especially if the lateral flow of current exists, as seen with non-segmented felt at high stoichiometry. In a segmented VRB study conducted in a 9 cm² cell with serpentine flow fields and carbon paper as an electrode [9], separation of discharge voltage was observed only at the mass transport loss dominant regions and the voltage distribution at high stoichiometry was unclear.

A voltage gradient (dV) indicated in each contour diagram in Figure 4.2.3 was calculated by subtracting the maximum and minimum voltage measured. As expected, dV was a function of flow rate and current density. It is interesting to note that dV was higher for the cell with the segmented felt (156 mV in Figure 4.2.3-c vs

121 mV in Figure 4.2.3-a), measured at the same current density and flow rate. This trend was valid for all current densities and flow rates. Hence, not only the clear separation, but also a higher resolution of the local voltage distribution was obtained with the segmented felt.

As anticipated, dV increased with a decrease in flow rate (121 mV in Figure 4.2.3-a vs 196 mV in Figure 4.2.3-b) and with an increase in current density (10 mV in Figure 4.2.3-d vs 156 mV in Figure 4.2.3-c). Moreover, the pattern of the voltage distribution was flipped in charging or with flow reversal, compared to the discharge contours measured with upward flow. A similar observation was also made by Clement et al. [9].

4.2.2 Flow behavior

The operation of a flow cell or stack having a minimum dV or small deviation from the average is desirable to protect the cell from operating in a range where mass transport losses dominate. This parameter can also be used to improve the design for better flow distribution. In Clement's work [9], in which the convection of electrolyte was in the through-plane direction of the carbon paper electrode, the percentage of deviation of discharge voltage from the average was about $\pm 5\%$ at high stoichiometry ($\lambda > 9$, calculated using Eq. (4.1.2)) and $\pm 20\%$ at low stoichiometry ($\lambda < 6$). With the use of a 3 mm porous felt (GFD 3) as well as multi-layer of carbon papers, the deviation from the average increased to $\pm 50\%$ at $\lambda = 6$. In all our experiments and for all types of cell examined at various flow stoichiometry, deviation of $< \pm 1\%$ was obtained at high stoichiometry ($\lambda > 9$) and maximum deviation of $\pm 21\%$ obtained at stoichiometry close to 1. This indicates a better flow distribution of electrolyte in our conventional design.

From Figure 4.2.3 (b-d), it is also observed that the discharge voltage is slightly higher at the right side, possibly due to non-uniform flow distribution. To further investigate, contour diagrams of the OCV measured 10 s after terminating charging and discharging (of Figure 4.2.3-b) were plotted as shown in Figure 4.2.4-c and Figure 4.2.4-d, respectively. For the sake of comparison, the SOC corresponding to each OCV was calculated and indicated in the contour's legend together with the OCV.

Figure 4.2.4 OCV vs time curve after (a) terminating charge at 60 mA cm⁻² and (b) after terminating discharge at 160 mA cm⁻². The corresponding contour diagrams at 10 s in OCV after termination are represented in c and d. The flow rate was 20 mL min⁻¹ and felt was not segmented.

Although the voltage gradient was reduced in OCV contour compared to discharge contour, an equipotential distribution pattern appeared at OCV (Figure 4.2.4-d) similar to that observed during discharging (Figure 4.2.3-b). The OCV contour after terminating charge at 60 mA cm^{-2} (Figure 4.2.4-c) showed the opposite pattern as compared to discharge, as expected. dV decreased with time and as a function of the flow rate. As the voltage distribution at OCV reflects the status of charged species in the electrode, the distribution of the voltage at OCV can be used to gain insight into the flow distribution. By comparing the discharge and OCV contours, it can be qualitatively deduced that the flow was slightly higher at the right side of the test cell. It is advantageous to use the OCV for this study, because it is unaffected by the difference in contact resistances among the segments. In addition, OCV can be converted to SOC, which is an added benefit for easier understanding. As the flow non-uniformity happened from the 1st row i.e. entrance to the felt cross section, the problem was from the flow frame channel design.

It is important to note that an OCV gradient in the flow direction existed in a non-segmented felt only if the CCs and BPs were both segmented. That is because the use of un-divided BPs can immediately redistribute the potential gradient formed at the wet porous felt which even makes it difficult to see a clear separation during discharging at low stoichiometry. Similar observations were also made by Hsieh et al.[10].

The flow frame was re-designed (with the help of CFD assisted flow simulation using ANSYS Fluent 14.0) in order to ensure a uniform distribution of electrolyte at the felt entrance. The details of the simulation is given in Annex A. In the new design, it was ensured that the electrolyte velocity from the individual flow guides is equal for the wide range of flow rates. The modification was done on the shape of the flow guides, gap between them and having one extra channel connecting the main

manifold to left part (at the top) and right part (at the bottom), as shown in Figure 4.2.5.

Figure 4.2.5 Flow frame design before (left) and after (right) the modification.

Subsequently, an approach was made to predict the flow behavior by studying the OCV contour at various flow configurations. Figure 4.2.6-a shows the OCV contour of normal flow and Figure 4.2.6-b to 4.2.6-d represent OCV contours at blocked flow configurations. The corresponding SOC is indicated in each contour's legend. The blockage was done on both half cells by inserting a thin silicone sheet (thickness 0.5mm) at the interface between flow frame entrance and felt entrance as well as flow frame exit and felt exit, as indicated schematically in each diagram. The flow rate was 60 mL min^{-1} , λ was 2.4 and the felt was not segmented.

(Figure Cont'd)

Figure 4.2.6 Different types of flow configurations (left diagrams) and corresponding OCV contours at 5 s after terminating discharge at 160 mA cm^{-2} (right diagrams).

After terminating charge or discharge, and depending upon the flow rate and current density, the time for the equalization of the OCV was different. However, the pattern of the OCV between inlet to outlet segments, from which the flow could be reconstructed, remained after a short time. Therefore, for qualitative investigation of the flow uniformity, monitoring the OCV from a few seconds to approaching equilibrium after terminating the discharge could be used. The OCV contour, immediately after terminating the discharge, gave an accurate approximation to the SOC distribution during discharge. However, as the temporal resolution of the battery tester was $\sim 1 \text{ s}$, it was decided that 5 s after the end of discharge offered a fair compromise between measurement noise and flattening of the SOC profile.

In order to know how closely the SOC distribution during discharging could be replicated by monitoring the OCV at $t = 5 \text{ s}$ or 10 s , the change in SOC was estimated using Faraday law.

$$\Delta SOC = I / (Q \cdot C_v \cdot F) \quad \text{Eq. (4.2.1)}$$

Where ΔSOC is the change in state-of-charge between inlet to outlet in a single pass, I is total current in A, Q is the flow rate in $L s^{-1}$, C_V is concentration of V ion in $mol l^{-1}$ (0.8) and F is the Faraday constant ($96485 As mol^{-1}$).

For normal flow case as represented in Figure 4.2.6-a, and using Eq. (4.2.1), the expected ΔSOC was calculated to be $\sim 20\%$. Close to the end of discharge, the SOC of the electrolyte at the inlet was $\sim 36\%$. Therefore, the ΔSOC at 5 s and 10 s after terminating discharge was $\sim 18\%$ and $\sim 14\%$, respectively, which are close to the theoretical value. This indicates that monitoring the OCV immediately after terminating charging or discharging provides the real time SOC distribution during current flow.

By monitoring the OCV contour diagram for the four different flow configurations, it can be confirmed that OCV distribution precisely reflects the flow pattern in a VRFB. As can be seen in Figure 4.2.6-a, a uniform flow distribution of electrolyte at the felt entrance resulted in uniform bands of voltage along the flow cross section. This confirms the superior flow distribution after modifying the design of the flow frame. A similar uniform voltage band appeared at all flow rates and current densities. This type of information can only be obtained through the study of a segmented cell. As OCV is unaffected from the variation in contact resistance, this approach can be implemented in designing commercial size cell and stacks as well.

By blocking the flow at the inlet as well as the outlet on both half cells, the OCV distribution reproduces the electrolyte flow streamlines. When flow was only allowed from one quarter of the cross section (Column 1) as shown in Figure 4.2.6-b, a higher voltage appeared on the same cross section compared to the remaining segments at the three-quarter area on the right side. As the felt was hydrophilic, some electrolyte also flowed to the right section, and therefore, a lower voltage appeared

on segments at columns 2, 3 and 4. The change in SOC between inlet segments to outlet segments was nearly three times (23.5%) higher than that of normal flow (8%), which indicates that the relative flow was reduced three times than the normal flow when three-quarter section was blocked. With diagonal flow in Figure 4.2.6-c, the voltage band between inlet to outlet also appeared diagonally. The change in SOC between inlet to outlet (15.5%) also became double than that of normal flow condition (8%), suggesting relative flow was reduced to 50% with blockage of the half section as compared to normal flow. With middle flow (Figure 4.2.6-d), a slightly higher OCV at the middle section was observed. The change in SOC from inlet to outlet (13%) was also higher than that of normal flow (8%), indicating that the relative flow was reduced to about 60% of the normal flow.

From the first row in each OCV contour of the blocked flow cases as shown in Figure 4.2.6 (b-d), it can be seen that the SOC at the blocked segments was lower than that at the open segment. This is expected, because electrolyte can only enter these cells after passing through the open segment, and will hence already be slightly discharged. Recalling the diagonal flow case shown in Figure 4.2.6-c, a higher voltage at the two blocked corners appeared as compared to the voltage at the outlet segments. This means that the electrolyte, which entered perpendicularly to the cross section of the porous electrode from segment 1 and 2, reached the bottom right corner slightly faster than the top left corner due to the wettability of the felt and small effect from gravity. The electrolyte finally left the electrode from the top right segments. At 10 cm height of the felt, the static pressure due to gravity would be 13.5 mbar, which will have negligible effect on the flow.

The equilibration time for the SOC to become uniform between inlet and outlet segments also increased with blocked flow. With increase in flow rate of electrolyte, the equilibration time also reduced.

In an ideal flow cell, ΔSOC between flow inlet and outlet is expected to be close to the theoretical ΔSOC . ΔSOC increases as flow non-uniformity increases, which is an indication of the local overcharging and local over-discharging of electrolyte during charging and discharging, respectively. Local overcharging leads to reduced battery performance (e.g., lower electrolyte utilization) and accelerated corrosion of the BPs, shortening the life cycle. In some cases, when the stoichiometry was close to 1 (e.g. Figure 4.2.4-d), all the segment could not draw the set current for prolong period. In such situation, the experimental ΔSOC was much lower than the theoretical ΔSOC estimated using Faraday's law. The contour diagram showed that the outlet segments no longer provided the set current due to the complete depletion of charged species at the downstream segments.

Concluding from several experiments for different cases, it was found that the difference between theoretical and experimental ΔSOC creates three possibilities:

- (i) Experimental $\Delta SOC \approx$ Theoretical ΔSOC , optimal utilization of electrolyte, excellent flow distribution
- (ii) Experimental $\Delta SOC >$ Theoretical ΔSOC , poor utilisation (higher overpotential either due to mass transport loss or Ohmic loss).
- (iii) Experimental $\Delta SOC <$ Theoretical ΔSOC , very low stoichiometry i.e. not enough charged species available for complete discharge or all segments could not supply the set current.

This relation can be used to design a flow cell with maximum utilization of electrolyte through the porous electrode.

4.2.3 Non-uniform flow and its effect on cell performance

In a non-segmented flow cell, cell cycling was performed at normal flow and flow blocked configuration similar to the experiments described in Figure 4.2.6-a and 4.2.6-d, respectively. The coulombic, energy and voltage efficiencies between the normal and blocked flow are compared in Figure 4.2.7.

Figure 4.2.7 Cell performance showing coulombic, energy and voltage efficiency at different current densities for cell operating at “Normal flow” configuration i.e. no blockage as described in Figure 4.2.6-a (closed symbol) and “Blocked flow” configuration similar to Figure 4.2.6-d (open symbol).

The experimental conditions for the measurement were: flow rate = 100 mL min^{-1} , electrolyte volume = 150 mL per tank and electrolyte concentration = $1.6 \text{ M V}^{+3.5}$ in total 4.5 M sulfate.

A direct correlation of dV or ΔSOC to cell efficiency is difficult, since cell cycling was performed at varying SOC (between 90% to 10%) in a non-segmented cell and at much higher stoichiometry ($\lambda > 29$) to that used in segmented cell. However, the study of cell cycling helps to visualize the impact of non-uniform flow in cell operation.

As can be seen, the EE and VE significantly dropped with flow being allowed to enter and exit only through the half of the cross section (i.e. from middle). A minimum of about 25% drop in VE and EE observed at 40 mAcm^{-2} and maximum of about 40 % drop in VE and EE observed at 80 mAcm^{-2} . The drop in efficiency was due to the increased overpotential caused by greater magnitude of ΔSOC locally, during charging and discharging, from the stagnated electrolyte.

4.3 Improving the flow distribution by pH tracing test for the development of large area flow cell

As reviewed in Chapter 2, there are limited methods to predict the flow distribution in a flow battery cell or stack. Segmented cell approach is useful, but for large size cell development, it requires multi-channel battery tester capable of handling high current and voltage, and a new hardware. This section therefore introduces a new method, which has not been reported to be used so far in VRFB.

This method is known as pH tracing test. The idea of this method includes introducing a small amount of acid solution (1 mL) to a continuously flowing water streamline through a flow cell inlet and obtaining the flow related information by plotting the pH of the dispersed acid solution at the outlet with time. This method can only provide a qualitative information. The details of the experimental set-up are given in Section 3.4.

The content of this section is divided into two subsections. The first subsection focuses on understanding the nature of the pH curve. For this, a half cell of 100 cm² was examined at various operational conditions. The second subsection focuses on examining the performance of IDD channel on large area flow cell of 1 kW size. Based on the information gained from this test, it was decided whether the flow channels on the porous electrode would be used for the development of a 1 kW stack.

4.3.1 Understanding the pH curve

The pH value recorded each second was plotted against time. A typical pH curve, as an example, is shown in Figure 4.3.1.

Figure 4.3.1 A typical pH-time curve from pH tracing.

The pH was above 7 before the acid was injected. As tap water was used, the initial pH of the water varied between 7 and 9. However, this variation did not affect the qualitative information gained from this study. After 30 s of recording, the acid was

injected and as a result, a sharp drop in pH was observed after a few seconds after injection. The pH diluted with the water and after reaching a low value, slowly recovered back to the initial pH of above 7.

At the low pH zone, a sharp narrow dip shows that electrolyte once entered, quickly left the cell. If the electrolyte is flowing non-uniformly along the cross section or if the flow streamline is split along the cross section or if the flow rate is very low, a wider dip is expected.

During the recovery of pH back to the initial value, qualitative information about the nature of the flow can be obtained. The plateau of the recovery curve shows how fast it took for the felt to be completely cleaned from the injected acid. A quick steady recovery shows absence of dead zones or retarded flow within the felt. In the presence of dead zones or blocked flow or uneven flow, the steady recovery might be interrupted due to the slow dilution of acid within the stagnant zone. Hence, a prolonged recovery is expected.

To further understand the changes on the nature of the curve, the flow rate of the electrolyte, electrode compression, etc. were varied.

4.3.1.1 Effect of flow rate

A half-cell was assembled with felt compression of 20%. The pH test was performed for various flow rates. The test was repeated three times at each flow to ensure the reproducibility of the results. The pH curve for different flow rates are compared in Figure 4.3.2.

Figure 4.3.2 pH-time graph at different flow rates.

At the low pH zone, the width of the dip was increased with decrease in flow rate, which indicates that the injected acid was dispersed over large volume of water in the porous electrode and therefore, a minimum pH was recorded for longer period of time. During the recovery phase, the time taken for the acid to completely flush out from the cell was increased with a decrease in flow rate of water. During the recovery, the pH curve showed steady increment, hence it can be inferred that flow was nearly uniform along the cross section.

For the size of the cell tested, it can be seen that 50 mL min^{-1} flow rate was too low. Leaving the active area faster is beneficial for a cell as there is less chance of overcharging of the electrolyte near high SOC caused by the slow movement of the charged species. However, too high a flow rate would significantly increase the pressure drop through the porous felt, thereby increasing the pump power consumption and risk of leakage. From the graph, flow rate of $100\text{--}150 \text{ mL min}^{-1}$ appeared to be reasonable for the size of the cell tested.

4.3.1.2 Effect of blocked flow

In order to examine the effect of stagnant flow in the porous electrode, 75% of the cross section of the porous electrode both at the inlet and outlet side was blocked by inserting a thin silicone sheet at the entrance and exit of flow frame. The method of blockage was exactly the same as was performed in segmented cell study (Figure 4.2.6-b). A schematic of the normal flow and blocked flow is shown in Figure 4.3.3.

Figure 4.3.3 Schematic of the normal flow (left) and blocked flow (right).

For the two configurations, pH tracing was carried out for three flow rates. The pH vs time curves are shown in Figure 4.3.4.

Figure 4.3.4 pH vs time curves for normal flow and blocked flow for flow rate of 50 mL min⁻¹ (a), 100 mL min⁻¹ (b) and 150 mL min⁻¹ (c).

The pH value reached minimum in the cell with normal flow as compared to the cell with the blocked flow. This trend was observed for all flow rates. As the flow was only allowed to pass through one quarter of the area of the porous electrode at the left side, stagnant zone was created at the right section of the electrode, similar to the effect discussed in segmented cell study. Therefore, some of the diluted acid went straight from inlet to outlet at the left corner, but a significant portion of acid solution remained trapped at the right corner leading to slow dilution and higher pH dip.

At low flow rate, the difference between normal flow and blocked flow is larger than at high flow rates. Surprisingly at high flow rates, most of the part of the felts except

the corners, were being used as the curve at inlet and outlet looked very similar for the two types of flow configurations. An increase in pressure difference at higher flow might be the reason for the improved utilization of electrode area at high flow rate of 150 mL min^{-1} . Certainly the peak occurred in roughly the same place, which would not be true if the flow just followed a narrow strip from inlet to outlet (then the peak would be sooner, due to the higher flow velocity).

At all flow rates, the time taken for the acid to completely flush out from the cell was much higher for the blocked flow. Hence, it is clear that flow distribution in no blockage configuration was better than that in blocked flow configuration. During the recovery period, the curve showed fluctuation (noise) on the curve at all flow rates for blocked case as compared to steady increase in the normal flow case. This could be due to the discontinuous dispersion of acid solution from the stagnant zones within the felt. The pH of diluted acid, which was trapped within the blocked zones, would slowly dilute as neutral water was constantly pumped through the cell.

4.3.1.3 Effect of electrode compression

A detail investigation of the effect of electrode compression on the cell performance is included in Chapter 5. Too low a compression of the electrode would lead to high contact resistance, whereas, too high a compression would result in poor flow distribution because of the porosity reduction. In addition, the presence of dead zone or stagnant flow due to poor flow distribution of electrolyte limit a flow cell from using 100% of its active areas and reduce the electrode life. To understand the nature of the pH curve with changes in electrode compression, two cells at electrode compressions of 25% and 40% were assembled and tested using pH tracing.

Figure 4.3.5 pH vs time curve for comparing the effect of change in electrode compression at flow rate of 100 mL min⁻¹ (left) and 150 mL min⁻¹ (right).

The nature of the curve at 40% compression is similar to the blocked flow case. It is clear that the flow distribution was poor at 40% compared to 25% compression. At low pH zone, two peaks were observed for 40% compression, which is attributed to the dividing of the streamline that reached the outlet at two different times. During the recovery zone, noise on the curve was observed for 40% compression, which is also an indication of stagnant flow, as was observed in the blocked flow configuration.

At a fixed flow rate, it was expected that the acid would go through a more compressed felt (i.e. thinner) faster than the less compressed felt. However, the graph shows that the acid go slightly faster through low compressed felt and also the peak is smaller at high electrode compression. This indicates that some bending around the corner (with bulging at the center) of the cell occurred at high compression of 40% so that flow is first through the center and then through the edge regions before leaving the cell.

4.3.1.4 Old flow frame vs modified flow frame

It was found from the in-situ investigation using segmented cell approach that the flow distribution was slightly poorer in the old design of flow frame (FF). After modifying the design of the FF (Figure 4.2.5), the flow distribution was improved. Therefore, both FFs were tested using pH tracing test to examine the changes. The pH vs time curves from the pH tracing tests for old and new FF are compared in Figure 4.3.6.

Figure 4.3.6 pH vs time curve for cell with old FF (top) and new FF (bottom).

As can be seen, the recovery time was reduced after the FF was modified. This proves that the flow distribution slightly improved after the modification, justifying the observation made through segmented cell study.

4.3.2 Effect of IDD channel on large area cell

The main purpose of developing pH test was to implement this simple technique to large scale flow cell and stack development.

From the study of flow channels on the porous electrode, as reported in Section 4.1, significant improvement in performance and about a 40% reduction in pressure drop was observed by using IDD channels on the porous felt aligned in parallel to the flow direction. In a recent publication by other group [13], they tested tapered channels on a 1 kW size-3 cell stack and reported an improvement in flow distribution and significant reduction in pressure drop by using channels directed in perpendicular to flow direction. Therefore, for the development of a 1 kW stack, it is necessary to test both configurations (i.e. channels aligned both perpendicular and parallel to flow direction) in a 625 cm² cell and compare the results with a cell without flow channels. As such, three cells were assembled using IDD channel parallel to flow direction, IDD channel perpendicular to flow direction and no channel.

The results of the pH tests performed for each cell at three flow rates: 300, 450 and 600 mL min⁻¹ are shown in Figure 4.3.7, 4.3.8 and 4.3.9, respectively.

Monitoring the low pH region at all flow rates, it can be seen that uniform flow distribution appears for cell with IDD channel aligned parallel to the flow direction. It is evident by monitoring the peak observed at low pH region before it recovered back to initial pH of water. For cell with no channel, two peaks were observed at all flow rates. The reason for the appearance of two peaks was possibly due to divided streamlines, one exited the cell faster and other exited slower. In the case of dividing of the streamlines, multiple peaks are expected.

Figure 4.3.7 pH vs time curve for three configurations at flow rate of 300 mL min⁻¹.

Figure 4.3.8 pH vs time curve for three configurations at flow rate of 450 mL min⁻¹.

Figure 4.3.9 pH vs time curve for three configurations at flow rate of 600 mL min⁻¹.

For IDD channel aligned perpendicular to the flow direction, multiple peaks were observed, indicating that flow streamlines were divided at several locations. In other words, the liquid was trapped locally at several location and exited at different time period, indicating poor flow distribution amongst other two configurations. In addition, the time taken for the pH to recover back to normal value (~7) was longest for the IDD channel aligned in perpendicular to the flow direction. The recovery time for the electrode without flow channel was minimum. This is expected because the felt with IDD channel had several rectangular open channels leading to increase in cavity area. Therefore, the injected acid after dilution took longer time to completely flush out from the cell. Further, the recovery of the pH after reaching the minimum value was faster in the cell with no channels on the felt. This is an indication that some bypass flow around the felt occurred, which is very fast compared to main flow. This shows the complexity of scaling up even with just a single cell. With the use of IDD channel (directed along the flow), no sign of by-pass flow was observed

and it can be confirmed that all the electrolyte went through the porous electrode, which was desired.

Monitoring the three configurations, IDD channel aligned in parallel to the flow direction showed the best flow distribution at all flow rates. For the three flow configurations, pressure drop was also measured to be minimal for cell with IDD channel aligned parallel to the flow direction, as shown in Figure 4.3.10.

Figure 4.3.10 Pressure drop for three flow configuration.

Hence, for the 1 kW stack assembly, porous electrode with IDD channels was used with channel faced BP and aligned parallel to the flow direction. The detail discussion on the 1 kW stack development will be given in Chapter 6.

4.3.3 pH test on a large area 3-cell stack

A 3-cell stack was assembled for the performance evaluation. The stack used IDD channels aligned in parallel to the flow direction. After the cell cycling, the stack

was rinsed with water and pH tracing test was carried out to examine the nature of the curve in a stack.

Figure 4.3.11 pH vs time curve of pH test on a 3 cell stack. The active area of each cell was 625 cm². The IDD channels on the porous electrode directed along the flow direction were used.

As can be seen from Figure 4.3.11, a similar nature of pH curve as compared to testing a single cell was obtained when a 3-cell stack of 1 kW size was tested. The recovery time increased with decrease in flow rate.

Comparing single cell and three cell stack (Figure 4.3.7 vs Figure 4.3.11) for the same flow rate of 300 mL min⁻¹ per cell (green line in both diagram), it can be seen that the recovery time reduced in a 3-cell stack, which is expected because the acid was diluted in the main manifold and exited equally from three cells. Comparing the different flows, flow rate of 300 mL min⁻¹ per cell seems to be optimum for this cell size.

4.4 Conclusion

The flow distribution of electrolyte through the porous electrode in VRFB was studied and improved using three novel approaches namely, structured electrodes, segmented cell study and pH tracing.

Four different electrode designs with flow channels were tested in a VRFB single cell with an active area of 100 cm^2 and compared to standard electrode (No channel). The results showed that the energy and voltage efficiencies are superior with interdigitated circular poked channel (IDD-CPC) and interdigitated open channels (IDD-OC) for all current densities tested. This was interpreted as resulting from a more uniform flow distribution that gave improved utilization of the reactive surface. The discharge energy was also improved by the use of flow channels, as suggested by the patent literature, again as a consequence of better flow distribution through the electrode. Taking pump losses into account, up to 2.7% and 2.5% improvement in overall EE could be demonstrated with the use of IDD-OC and IDD-CPC types, respectively. Especially, for the electrodes with IDD-OC design, the contribution of the pump saving, on the improvement in overall EE, was up to 1%, which is a significant improvement considering a pump loss of 1-3% of EE reported in flow batteries. The study on flow channels on the porous electrode concludes that IDD-OC mainly reduced Δp and the IDD-CPC mainly improved flow distribution, and both gave a similar overall improvement in EE. IDD-OC was also easier to fabricate uniformly than IDD-CPC. Hence, it was decided that IDD-OC would be fabricated on an electrode size of $25 \text{ cm} \times 25 \text{ cm}$ for 1 kW stack development. The efficacy of the IDD-OC channel as compared to standard electrode without flow channel was further examined using pH tracing test. In commercial application, despite several advantages, additional cost would incur in designing these flow channels, which should also be taken into account.

A segmented cell was developed to study local voltage distribution and hence to extract the flow distribution related information. With the understanding of in-situ flow distribution, it was aimed that the design of the flow frame and configuration of the electrode can be optimized. In this regard, a new approach of segmenting a flow cell for local potential mapping was introduced. In addition to dividing the BP and CC, segmentation of a thick porous electrode was demonstrated for the first time. This concept resulted in higher resolution as compared to the common method of using a segmented collector only - even at a very high stoichiometry. Monitoring the voltage contours during charging, discharging and OCV for various cell operational conditions, a voltage gradient was formed between flow inlet and outlet. This was due to the continuous change of charged species during charging and discharging. Of greatest interest, the OCV, directly after cessation of current, replicated the status of charged species in the electrode. In addition, OCV was unaffected by the variation in contact and electrode resistance among segments. Therefore, OCV distribution was used to predict the in-situ flow behavior at various flow configurations. This study exhibits that the OCV contour can exactly image the flow pattern in the porous electrode. A relation between theoretical change in SOC and experimental change in SOC was established in order to predict how well the electrolyte conversion through the porous electrode occurred. Using the information gained from the segmented cell study, the design of the integrated flow guides on the flow frame was improved for the better flow distribution of electrolyte through the porous electrode. Segmented cell study also provided the information that inlet guides on the flow frame should be designed properly to secure the uniform entrance of electrolyte to the porous electrode. All the above information were used in the 1 kW stack development.

The pH tracing test was developed to examine the flow distribution with various cell configurations during the large area cell and stack development. This test was found to be a quick and easy method to evaluate the flow distribution for different sizes of

cell. The pH curve changed accordingly with change in flow rate, electrode compression, flow blockage, design of flow frame, etc. Using this test, it was concluded that the IDD channel on the porous electrode aligned in parallel to the flow direction would be used in the 1 kW stack development. Accordingly, a 1 kW stack consisting of 20-cell was developed using IDD channels on the porous felt. The results of the stack testing will be given in Chapter 6.

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Chapter 5

Multi parameter tests for improving the flow battery performance

This chapter discusses four important areas to improve the performance of the flow battery, which are crucial for development and scale up. The first section deals with finding an optimal compression of the porous electrode for the best performance. The results showed that 25% compression is the optimal trade-off between cell efficiencies, contact resistance and pump power losses. The second section investigates a unique feature observed during the operation of the flow battery at high current density. This effect caused by the membrane was found to be critical when operating a flow battery. During the operation of a flow battery, capacity loss occurred due to electrolyte crossover from one tank to other through membrane, which resulted in requirement of frequent rebalancing and loss of usable energy. The third section investigates two novel approaches to minimize the capacity loss. Of these, the best approach was implemented in the 1 kW stack system. The last section briefly investigates the effect of thermal activation on the battery performance using surface and electrochemical characterization. For the stack development, one of the best performing activation method was implemented.

5.1 Optimization of the electrode compression for improving the cell performance

This is a performance based study, which examines the effect of variation of electrode compression on cell efficiencies, area specific resistance (ASR), pump power and overall EE. A single cell of 100 cm² was used to perform this study.

5.1.1 Cell performance at different current densities

The CE, EE, VE and specific capacity for six different electrode compressions are compared in Figure 5.1.1-a, 5.1.1-b, 5.1.1-c and 5.1.1-d, respectively.

Figure 5.1.1 Comparison of: CE (a), EE (b), VE (c) and specific capacity (d) for different electrode compressions.

CE remained unchanged and were nearly 100% for all the electrode compressions. This is expected since CE is dependent on the membrane properties. The VE and EE at 15% electrode compression were significantly lower as compared to other compressions. The poor performance at 15% compression was due to the high contact resistance. Table 1 compares the electrical resistance of a dry cell at various electrode compressions.

Table 5.1.1 Electrical resistance of a dry cell (without membrane) at various electrode compressions.

Compression (%)	15	20	25	30	35	40
Electronic resistance ($\Omega \text{ cm}^2$)	1.1	0.78	0.75	0.72	0.61	0.58

As can be seen, the Ohmic resistance decreased as electrode compression was increased. Comparing the six different compressions, electrical resistance was significantly reduced between the compression of 15% and 20%. Afterwards, a small reduction in contact resistance was observed with further increase in the felt compression. The trend observed are in good agreement with the reported study [1]. The poor EE and VE at 15% electrode compression was predominantly because of poor contact at the interface between the porous felt and BP.

Comparing electrode compressions between 20% and 40%, small variation on the EE and VE was observed. At low current densities of 40 and 50 mA cm^{-2} , a very small difference on the effect of electrode compression was observed. However, at higher current density of 80 mA cm^{-2} , the separation was slightly pronounced due to the increased iR drop. As can be seen, the highest EE and VE appeared for cell with compression of 25% and 30%, whereas minimum EE and VE was appeared for compression of 20%, 35% and 40%. Interestingly, the EE and VE at 40% compression was better than 15% compression, but poorer than all other

compressions. This is an indication that the cell performance cannot be improved by reduction in contact resistance only. At higher current densities, mass transport losses also need to be addressed. A similar effect was also observed during the study of flow channels on the porous electrode (Section 4.1).

Figure 5.1.1-d shows the cell voltage versus specific capacity plot during charging and discharging at current density of 80 mA cm^{-2} for different electrode compressions. The cell voltage vs specific capacity plot is commonly used in the literature for comparing the overpotential during charge/discharge cycle. The overpotential was highest for 15% compression, which appeared as high charging voltage plateau and low discharging voltage plateau. At low compression, a high overpotential was solely due to high electrical contact resistance. As compression increased, the overpotential in corresponding charge and discharge cycle was reduced. The overpotential was minimum at 20% and 25% electrode compression. Further increase in compression to 35% and 40% resulted in increase in overpotential. This brings another factor into consideration, namely electrolyte utilization. The specific capacity at 20% and 30% electrode compression was higher than 15% and 40% electrode compression by ~28% and ~23%, respectively. This signifies the improved electrolyte utilization at compression of 25% and 30%. Improvement in electrolyte flow distribution in porous felt electrode reduces chances of forming dead zone, increases reactive zone and hence facilitates better electrolyte utilization.

5.1.2 Cell performance at 40 mA cm^{-2} in long-term cycling

Fifty cycles at 40 mA cm^{-2} were performed to monitor the long-term performance. The EE and discharge energy at various electrode compressions are compared in Figure 5.1.2-a and 5.1.2-b, respectively.

Figure 5.1.2 (a) EE and (b) discharge energy, during long-term performance testing at 40 mA cm^{-2} for different electrode compressions.

The CE was close to 100% and was similar to short term cycling, and therefore it is not shown. The VE showed exactly the same trend as the EE, and therefore, only the EE plot is shown.

A nearly stable EE with small reduction was observed at all compressions during the long-term testing. The small reduction in the EE over the cycling was likely due to the electrolyte imbalance. The highest fall in EE ($\sim 4\%$) over 50 cycles was observed for cell with electrode compression of 15%, which was due to the highest capacity drop at 15% compression.

During short term cycling, electrode compression varied from 20% to 30% showed the highest efficiency for all current density tested. At 80 mA cm^{-2} , 25% compression exhibited the best performance. As the cell completed 25 short-term cycling before testing the long-term performance at 40 mA cm^{-2} for 50 cycles, a slight changes on the trend of EE was observed, which was due to the electrolyte crossover at different rates for different compression. During long-term cycling, the highest performance was observed for 25%-35% compression. The EE for 20% compression slightly

reduced as compared to during short term cycling, which was solely due to higher crossover from the membrane.

In previous studies, attention has not been given to the discharge energy (DE) or capacity while monitoring the electrode compression. However, DE is an important parameter that provides information on the amount of energy being delivered from the energy storage device. DE depends upon several factors such as, EE, electrolyte utilization, cell resistance, etc. When the electrolyte was fully utilised with improved flow distribution, a higher discharge energy was observed as mentioned in Section 4.1 on electrodes with flow channels [2]. Therefore, it is also important to compare the discharge energy with varying electrode compression, as flow distribution is affected by the variation in electrode compression. A discharge energy plot during the long-term testing for various electrode compression is shown in Figure 5.1.2-b. The flow cell was operated at constant voltage cut-off mode, and therefore the discharge capacity (Ah) and discharge energy (WhL^{-1}) showed the same pattern. Interestingly, the rate of discharge energy (WhL^{-1}) and discharge capacity (Ah) decay were dependent on the electrode compression. For example, the discharge capacity loss in 50 cycles for the different electrode compression are summarized in Table 5.1.2. Note that the charging capacity also showed the same trend as the discharge capacity, and therefore only the discharge capacity will be discussed.

Table 5.1.2 Discharge capacity (mAh) decay (%) for different compressions.

Compression (%)	15	20	25	30	35	40
Discharge capacity loss in 50 cycles (%)	55	44	36	35	29	23

The initial DE as well as DE over 50 cycles remained highest for the electrode compressed at 25%, as shown in Figure 5.1.2-b. As cycling was done at constant cut-off voltage for all electrode compressions, this can be attributed to the reduced

overpotential during charging and discharging cycle due to optimal trade-off between contact resistance and electrolyte utilisation.

In VRFB, reversible capacity loss occurs mainly due to the electrolyte imbalance between the two tanks, whereas, irreversible loss might occur from various reasons such as, high voltage cycling, mass loss or precipitation of V^{5+} due to high temperature operation, degradation of electrodes and membrane, aerial oxidation of V^{2+} ions, etc. However, the capacity fade in Figure 5.1.2-b was reversible. The fall in capacity (also EE) was recovered when rebalancing of the electrolyte was made. In Table 5.1.2, the discharge capacity reduced when the electrode compression was increased. A similar trend was earlier reported [1], however, this effect was not discussed. The discharge capacity loss is primarily dependent on the imbalance between the electrolytes, and so is a membrane property. This study shows that compression of the felt can influence the imbalance. Two possible reasons could be responsible for this effect. A possible reason behind this effect could be increased dead zone on the electrode, thereby on the membrane, which increased with the electrode compression. The lesser the membrane area is utilized, the lesser would be the electrolyte crossover. Another possible reason for reduced capacity loss with compression could be due to the variation in differential pressure between the two half cells. At a given flow rate the pressure will be a function of the compression, and the differential pressure will be higher for higher electrode compression. The pressure drop is higher on the negative side (as shown in Figure 5.1.4). With an AEM membrane, the net electrolyte transfer direction is from the positive side to the negative side. Hence, convective transport due to difference in pressure drop may act in opposite direction to the natural transfer direction. This could be another possible reason for the decrease in capacity decay with increase in electrode compression.

As the flow through the porous electrode was laminar ($Re = 0.09$), only viscous resistance dominated the flow through the porous electrode. Using the data sheet provided by the manufacturer [3], the permeability at various electrode compressions are summarized in Table 5.1.3. For simplification, average values of the permeability for each compression were taken. The viscous resistance, which is an indication of resistance to flow, are calculated by reciprocating the permeability.

Table 5.1.3 Permeability, viscous resistance and porosity change at various electrode compression.

Electrode compression (%)	0	15	20	25	30	35	40
Average permeability (m^2) ($\times 10^{-11}$)	11	7	6.25	6	5.5	5	4.9
Viscous resistance (m^{-2}) ($\times 10^{10}$)	0.91	1.43	1.6	1.67	1.82	2.00	2.04
% increase in viscous resistance	0	57	75	84	100	120	124
Porosity (%)	92	90.6	90	89.3	88.5	87.6	86.6

The change in porosity with increase in electrode compression was estimated using the following formula:

$$\varepsilon = 1 - \frac{h_0}{h} \cdot (1 - \varepsilon_0) \quad \text{Eq. (5.1.1)}$$

Where, h_0 is the initial thickness, h is the thickness after compression, ε_0 is porosity before compression and ε is porosity after compression.

Summarizing Tables 5.1.1 and 5.1.3, it is evident that at lower compressions (< 20%), the contact resistance was higher and flow distribution could be assumed to be superior due to higher permeability. With increase in compression, the contact resistance reduced, but viscous resistance increased significantly and affected the

flow distribution. At 40% electrode compression, the minimum value of discharge energy and capacity were an indication that the electrolyte was not fully utilised due to poor flow distribution through the electrode. An increase in dead zone on the electrode with the increase in compression was expected.

Comparing the efficiencies and discharging energy at the various electrode compressions, it is concluded that the cell with 25% compression gave the best performance. Therefore, electrode compression of 25% is recommended in conventional VRFB design. To support this conclusion, ASR and pump losses are also compared in the next subsection.

5.1.3 Change in area specific resistance (ASR) of cell

Table 5.1.4 summarizes the ASR at different current densities for cell assembled with different compressions. The ASR was calculated using Eq. (2.5)

Table 5.1.4 ASR at different current density during cell cycling

Area specific resistance ($\Omega \text{ cm}^2$)	Electrode compression					
	15%	20%	25%	30%	35%	40%
$j = 40 \text{ mAcm}^{-2}$	2.59	1.96	2.1	2.01	2.11	2.40
$j = 50 \text{ mAcm}^{-2}$	2.58	1.98	1.97	1.95	2	2.19
$j = 60 \text{ mAcm}^{-2}$	2.6	2.06	1.96	1.91	1.98	2.20
$j = 70 \text{ mAcm}^{-2}$	2.61	2.05	1.93	1.96	2	2.15
$j = 80 \text{ mAcm}^{-2}$	2.64	2.05	1.89	1.98	2	2.15

ASR is the highest at 15% compression, whereas, the lowest at 25% and 30% compression, at all current density tested. A similar trend was also observed during long-term cycling at 40 mA cm^{-2} , as shown in Figure 5.1.3. A small increment in

ASR with cycling was due to the decrease in EE in Figure 5.1.2-a as a result of electrolyte crossover.

Figure 5.1.3 Areas specific resistance for different compression during long-term cycling at 40 mAcm⁻².

The combination of membrane resistance, charge transfer resistance and concentration change can be estimated by subtracting dry cell resistance from the wet cell resistance. The membrane resistance is around 0.7 Ohm.cm² as stated in the manufacturer's data sheet [4]. The resistance value, at 80 mA cm⁻², obtained for 15%, 20%, 25%, 20%, 35% and 40% of electrode compression are 1.54, 1.27, 1.14, 1.25, 1.39, 1.56 Ohm cm², respectively. This signifies that cell with uniform flow distribution and reasonable contact resistance utilizes the electrode and membrane area effectively and results in lower difference in resistance, as observed for electrode compressed at 25% and 30%.

5.1.4 Effect on Pressure drop (Δp) and pump power

Δp for both positive and negative half-cell for the first five cycles are compared as shown in Figure 5.1.4. The positive and negative electrolyte containers were filled initially with the electrolyte of the same vanadium species ($V^{+3.5}$). A sinusoidal variation in pressure drop in both half-cells occurred during cell cycling because of the continuous change in viscosity of the electrolyte species at different rates. The viscosity was the highest at the negative side during discharging and minimum at the positive side during charging. The variation in viscosity of both half-cell with change in SOC was discussed in Chapter 4 (Figure 4.1.4).

Figure 5.1.4 Pressure drop in the positive half- cell (left) and in negative half cell (right) for different electrode compression.

A significant increase in Δp was recorded as electrode compression was increased. As electrolyte pumping energy is directly proportional to Δp , the increase in pressure drop increases the energy lost in pumping. Similarly, pressure difference between the two half-cell was lower for the electrode with low compression. During complete charging and discharging, the full change in Δp in the negative half-cell was 187 mbar for 40% electrode compression, whereas it was only 73 mbar for 25%

compression. The difference in pressure between the two half-cells at 40% electrode compression was about 107 mbar, while it reduced to 43 mbar at 25% of compression. The reduction of differential pressure between the two half-cells could reduce the convective drag resulting in less amount of vanadium crossover.

5.1.5 Effect of pumping loss on the overall EE

A similar approach was also performed in the study of flow channel (Section 4.1.4) to estimate the overall EE considering the pumping loss. It is important because the pumps are continuously operating during the operation of the flow battery and consumes a certain portion of the stored energy.

Figure 5.1.5 shows the pressure drop (in mbar) and consumed pump power (in mW) for the different electrode compressions.

Figure 5.1.5 Pump power consumption and pressure drop at different electrode compressions.

Figures 5.1.6-a and 5.1.6-b show the EE with and without considering the pump losses, respectively.

Figure 5.1.6 EE at different current density, including power consumed by pump (a) and excluding power consumed by pump (b).

The overall EE reduced after deducting the pump energy from the measured EE. The trend of EE after considering pump losses indicates that the compression of 20%-35% showed the good results and compression of 40% and 15% showed poor performance. The poor performance of 40% is attributed to the increased overpotential due to poor flow distribution or possibility of dead zones, despite the contact resistance was reduced as compared to low compressions. One possibility of reducing overpotential at high compression of 40% can be achieved by operating the flow cell at higher flow rate, however, this will increase the pump power loss as well. Therefore, it is also important to know whether the improvement on contact resistance plus flow distribution (mass transport) or reduction on pump losses has higher impact on the overall EE.

Comparing 25% compression to 15% compression (Figure 5.1.6-a), a maximum improvement in EE of 6.4% at 80 mA cm⁻² and minimum of 2.2 % at 40 mA cm⁻² was achieved at the compression of 25%. Similarly, comparing 25% to 40%

compression, a maximum improvement of 3.1% at 40 mA cm⁻² and a minimum of 2.3% at 80 mA cm⁻² in EE were achieved at the compression of 25%. At 40% compression, the pump consumed 2.3% of EE at 80 mA cm⁻² and 5% of EE at 40 mA cm⁻². This is significantly higher, as compared to improvement on the EE by contact resistance decrement. At 25%, which is found to be optimal, the pump consumed 1.6% of EE at 80 mA cm⁻² and 3.4% of EE at 40 mA cm⁻². Hence, by reducing the electrode compression from 40% to 25%, an increase in overall EE up to 1.6 % can be achieved due to pump power reduction.

5.2 Investigation of the “Power drop effect” in operation of flow cell

With the improved kinetics of electrode materials, the use of thin electrodes and improved architecture of the cell components, area specific resistance (ASR) of commercial VRFB stacks decreases. This enables VRFB to operate at much higher current densities due to the reduced Ohmic polarization. Increasing the operating current is a major focus for developer of flow battery to increase the power density, and reduce the footprint and weight of the stack. The charging at very high current density near high state of charge (SOC) is still restricted due to the possibility of side reactions at higher voltages (typically above 1.6 V per cell), but discharging can be done at much higher current density compared to charging. The most promising achievement was demonstrated by Showa Denko group at international flow battery forum in 2017 by operating VRFB stack up to a current density 1200 mA cm⁻² [5]. They used a thin electrode stacked together with multiwall carbon nanotube sheet.

This section investigates an interesting feature observed during the operation of flow cells and stack at high current density. During galvanostatic operation of a flow battery, an unusual sudden drop in discharge voltage occurred for a few minutes followed by recovery to normal was observed near high SOC region, which was

attributed to the membrane effect. The feature was also observed during activation cycle (initial few cycles when a new cell was first tested). This effect was named as “Power Drop Effect”, and has not been reported before. This effect was observed for various operating conditions in different sizes of cell and stack. The two conditions for the occurrence of this feature and possible reasons are discussed. The investigation was mainly performed on anion type membrane (FAP450) as this is a commonly used membrane in commercial VRFB stacks, and it is available at a lower cost as compared to Nafion membranes.

The details of the experimental set-up and measurement procedures are given in Chapter 3 (Section 3.6). Figure 5.2.1 shows a typical charge discharge curve without and with appearance of power drop effect. As indicated in the right diagram, an unusual drop in discharge voltage was observed and it was observed at various measurement conditions. This drop of discharge voltage at a set current would result in drop of power. As the charging and discharging of commercial flow batteries are regulated in terms of power, this effect was named as power drop effect.

Figure 5.2.1 A normal charge-discharge voltage curve (left) and a charge-discharge voltage curve with “Power drop effect” (right).

5.2.1 Appearance during the activation cycle

In a newly assembled cell/stack, this feature was usually observed at the first cycle. When the current density was high, it also appeared in the second cycle, but less pronounced than in the first cycle. Figure 5.2.2 shows some of the cases where this feature was recorded during the activation cycles.

Figure 5.2.2 Appearance of power drop effect at the activation cycles for different cell and stack assemblies.

Cell 1 and Cell 2 in Figure 5.2.2 had an active area of 100 cm^2 . The electrolyte volume and current density during cycling was different in the two cells, which is

indicated in each diagram. Stack 1 represents the testing in a 3-cell stack of 1 kW class.

The sharp voltage drop in Cell 1 was observed on the first cycle at a current density of 40 mA cm^{-2} . When the current density was increased to 80 mA cm^{-2} (Cell 2), this feature also appeared in the second cycle. The time of recovery from sharp drop to reaching the normal was reduced in the second cycle as compared to first cycle. However, in both cycles, it took more than 10 minutes for the recovery. The feature was also shortly observed during the first cycle in a 625 cm^2 size 3-cell stack (Stack 1) for about 80 s.

The felt was thermally activated and electrolyte was circulated each time for few hours through the cell before cycling, the felts and membranes were supposed to be fully wetted. Therefore, it is unlikely that the electrode activation caused this feature.

A possible reason behind the occurrence of this feature in both single cell and stack could be due to the pores of the membrane not being fully activated. For the FAP-type membrane, SO_4^{2-} or HSO_4^- ions go into the membranes and are held in place by the positively charged quaternary nitrogen. This might take some time for charges at the pores to fully activate as membranes were assembled in dry condition, as instructed in the manufacturer's datasheet.

If this effect only apparent in first few cycles during the activation, this would not be a serious problem in a flow battery operation. However, it was also observed after the activation cycles at different testing conditions.

5.2.2 Appearance at various conditions other than activation cycles

The power drop effect was also observed at different conditions after the activation cycles. The effect was reproducible. The feature was observed during the discharging from a high SOC at high current densities and in some special cases.

A single cell of 100 cm^2 size was run several cycles at 80 mA cm^{-2} . After two cycles, the voltage drop feature disappeared as the membrane was fully activated. Afterwards, the cell was cycled by increasing the discharge current, while keeping the charging current density constant at 40 mA cm^{-2} . The discharge current density was increased from 80 mA cm^{-2} to 130 mA cm^{-2} , as shown in Figure 5.2.3. As can be seen, with increase in current density during discharging, this feature started to appear from the current density of 100 mA cm^{-2} and become more pronounced with further increase in discharge current. The drop was always appeared sooner after a discharge from a high SOC. After a sharp drop of the voltage, the time taken for the discharge voltage to recover to normal was about 4 minutes and 5 minutes at a discharge current density of 120 mA cm^{-2} and 130 mA cm^{-2} , respectively.

Figure 5.2.3 The power drop effect with increase in discharge current density.

After several cycles of charging and discharging, Cell 2 was exposed to a high SOC for few days by continuously pumping the charged electrolyte through the cell. After continuous exposure for six days at SOC of 85%, the cell was discharged at 80 mA cm^{-2} . The same feature appeared for a long period of time as shown in Figure 5.2.4.

Figure 5.2.4 Power drop effect observed after long exposure to a high SOC. The cell was previously completed 100 cycles at 80 mA cm^{-2} before exposure.

Figure 5.2.5 Power drop effect observed between 70th and 80th cycle in a 100 cm^2 single cell measured at 40 mA cm^{-2} .

During the long-term cycling test of a 100 cm^2 single cell at a current density of 40 mA cm^{-2} , the feature appeared after 70 cycles (Figure 5.2.5).

As the cell was run continuously without rebalancing, a significant imbalance of the electrolyte with higher volume on the negative tank and lower volume on the positive tank was observed. The FAP 450 membrane has a high selectivity for vanadium ions, and therefore the major transfer through the membrane is water. The concentration of V^{+4} and V^{+5} ions on the positive side becomes higher after the imbalance.

To monitor the effect of temperature on the PDE, the electrolyte temperature was increased from $25\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$ at intervals of $5\text{ }^{\circ}\text{C}$, and the cell cycling was performed. The PDE was less pronounced with increase in electrolyte temperature, as shown in Figure 5.2.6.

Figure 5.2.6 Effect of temperature on the PDE. The charging and discharging current density were 70 and 130 mA cm^{-2} , respectively. The test was performed on a 20 cm^2 size flow cell.

5.2.3 Investigation of the effect

The first attempt was made to separate the voltage drop through the membrane from the voltage drop through a full cell (i.e. between two terminals). This was accomplished by half-cell potential measurements, as shown in Figure 5.2.6 (a).

The reference electrodes ($\text{Hg/Hg}_2\text{SO}_4$, K_2SO_4 (saturated)) were inserted near the flow outlet of each half cells. The cell was cycled (charged at 80 mA cm^{-2} and discharged at 120 mA cm^{-2}) using the battery tester. At the same time, using the two channels from a multi-channel potentiostat, the half-cell potential (OCV vs SCE) across each half cell terminal and reference electrode was measured. From this measurement, the half-cell voltages and full cell voltage during cycling were recorded separately. The half-cell potential as well as full cell potential over time are plotted as shown in Figure 5.2.6 (b). The black line shows the voltage measured by the battery terminals, which shows the power drop effect. The voltage across the negative half-cell (negative terminal vs reference electrode) and across the positive half-cell (positive terminal vs reference electrode) did not show the sharp voltage drop due to power drop effect. As the voltage drop across the membrane was not included in the half-cell potential measurements, this proves that the membrane was responsible for the effect.

Figure 5.2.6 Set-up for half-cell voltage measurement (a) and cell voltages over time (b).

A segmented cell study was used to find out whether the power drop effect was a localized phenomenon or observed throughout the membrane surface.

The design of a segmented cell, measurement procedures and analysis methods are given in Section 3.3 and 4.2. A segmented cell assembled using FAP 450 membrane was charged to a SOC of 90 % at a current density of 40 mA cm⁻² and discharged to a SOC of 5% at a current density of 80 mA cm⁻². The cell was initially run one complete charging and discharging cycle at 40 mA cm⁻² for activation. The flow rate was maintained at 100 mL min⁻¹. The left diagram in Figure 5.2.7 shows the initial OCV, discharge voltage and final OCV of all sixteen segments. The right diagram in Figure 5.2.7 shows the applied current in all sixteen segments.

Figure 5.2.7 “Power drop effect” observed in a segmented cell study.

The stoichiometry of the electrolyte was much higher (~14), however, the power drop effect was observed equally on all sixteen segments. This concludes that the power drop effect is neither related to mass transport polarization nor a localized effect, but appears across the whole surface area of the membrane.

To further investigate, the resistance of the membrane was measured ex-situ. Table 5.2.1 shows the resistance of the two membranes (FAP 450 and Nafion 117) in the presence of electrolyte solution containing vanadium at different oxidation states. The resistance of Nafion 117 membrane, which is also used in VRFB application, was also measured to compare the resistance values of FAP 450 membrane.

Table 5.2.1 Membrane resistance measured by EIS.

Area specific resistance (Ohm cm ²) in	FAP 450	Nafion 117
H ₂ SO ₄	0.37	0.32
V ²⁺	0.75	0.68
V ³⁺	0.68	0.61
V ⁴⁺	0.81	0.52
V ⁵⁺	5.41	0.44

The membrane resistance in presence of H_2SO_4 , V^{2+} , V^{3+} and V^{4+} ions was less than 1 Ohm cm^2 for both membranes. However, the resistance of FAP 450 membrane increased by about six times in the presence of V^{5+} ions. The resistance increment of FAP 450 membrane in V^{5+} solution can be correlated to a fully charged (high SOC) positive half-cell in a flow cell.

Hence, combining all the findings, we hypothesize that the PDE is caused by a thin, outermost, resistive layer of the membrane, in contact with the positive half-cell, where V_2O_5 has precipitated within the pores of the membrane. The precipitate acts to increase the membrane resistivity and limit the maximum current density that can be supported (reduced number of active channels). This precipitate can be re-dissolved by action of V(II) and V(III) ions diffusing through the membrane from the negative half-cell. Therefore, PDE was most apparent when; (i) the positive electrolyte is highly charged (Figure 5.2.5, Figure 5.2.6), (ii) the current density is high so that the membrane resistivity becomes the dominant resistive term (Figure 5.2.1, Figure 5.2.3), (iii) the temperature is lower so that the rate of diffusion of the V(II) and V(III) ions are lower (Figure 5.2.6), and (iv) the membrane is in contact with the highly charged positive electrolyte for extended period of time allowing time for the V_2O_5 nuclei to grow (Figure 5.2.4).

5.3 Approaches for minimising the capacity loss in flow battery operation

A part of the finding in this section was presented and published at a conference. A. Bhattarai, R. Schweiss, A. Whitehead, G.G. Scherer, N. Wai, P.C. Ghimire, T.D. Nguyen, M. O. Oo, H.H. Hng, Reducing electrolyte imbalance in the all-vanadium flow battery, presented at International Flow Battery Forum (IFBF), Manchester, United Kingdom in June 2017. A full length manuscript is submitted to Journal of Power Sources.

Capacity loss in VRFB is an important factor that affects the performance in long-term operation. The irreversible capacity loss during VRFB operation might occur from various reasons such as, charging to a high voltage (>1.6 V), mass loss or precipitation of V^{5+} due to high temperature operation, degradation of electrodes and membrane, aerial oxidation of V^{2+} ions, etc. The reversible capacity loss is a function of membrane properties, which happens primarily due to the transfer of ions and water through the membrane to complete the redox reaction. Capacity loss due to electrolyte imbalance between the two tanks can simply be recovered by back circulating the excess volume of electrolyte from the tank to the other tank containing low volume of electrolyte. However, frequent rebalancing results in loss of usable energy and requires extra hardware such as SOC monitoring equipment, rebalance cell, level monitoring sensors, etc. Therefore, two novel methods were investigated to minimize the reversible capacity loss. Out of the two methods, the best method was implemented in 1 kW stack testing.

5.3.1 Minimising capacity loss by the hydraulic shunt of the electrolyte tanks

The idea of hydraulic shunt of two electrolyte tanks for the auto-rebalancing of the electrolyte level was claimed in a patent [6], but no experimental verification is available yet. Therefore, this study investigates the applicability of this method. The experimental set-up is given in Section 3.7.1.

Keeping the nozzle closed (no auto-rebalancing), a 2-cell stack of 100 cm^2 active area per cell assembled with FAP 450 membrane was cycled at a current density of 80 mA cm^{-2} for 50 cycles. The cycling was continued for another 100 cycles by opening the nozzle from 51st cycle for auto-rebalancing of electrolyte. The

efficiencies and capacity are compared before and after the rebalancing as shown in Figure 5.3.1-a and 5.3.1-b, respectively.

The CE, EE and VE remained similar before and after the nozzle was opened. The capacity dropped sharply at a rate of ~ 10 mAh/cycle before rebalancing of electrolyte that stabilised when the auto-rebalancing was started. This proves that the concept of auto-rebalancing works.

Figure 5.3.1 Comparison of efficiencies (left) and capacity (right) of a two-cell stack with and without auto-rebalancing. The current density was 80 mA cm^{-2} .

The stack was further cycled at current densities of 40, 50, 60, 70 and 80 mA cm^{-2} , with 6 cycles at each current density. The test was performed for both cases. The efficiencies and capacities are compared in Figure 5.3.2.

Figure 5.3.2 Comparison of efficiencies (left) and capacity (right) of a two-cell stack with and without auto-rebalancing, at different current densities.

The CE, EE and VE remained unchanged with auto-rebalancing and without rebalancing during the short-term cycling test at different current densities, as shown in Figure 5.3.2-a. However, a sharp drop in capacity (Figure 5.3.2-b) was observed before rebalancing at each current density. With auto-rebalancing, a nearly constant capacity was observed at each current density. A drop of capacity with change in current density was because of iR drop at a constant cut-off voltage cycling. This proves that the auto-rebalancing is a very useful method to eliminate the frequent requirement to rebalance in VRFB operation.

The test was also carried out on a 3-cell stack of 625 cm² active area per cell. The stack used 1.5 L of electrolyte on each tank and a current density of 80 mA cm⁻² was used for the cycling. Therefore, the electrolyte imbalance occurred at much faster rate as compared to that observed in 100 cm² stack. In addition, the tube length was varied to examine the effect of tube length on the capacity rebalancing.

Figure 5.3.3 shows the discharge capacity for different tube length, which is plotted against discharge capacity without rebalancing of the electrolyte. As charge and

discharge capacity followed the same trend, only discharge capacity is shown. The right diagram shows the potentiometric titration measurement results (vanadium concentration $c(V)$ and SOC of each half cell electrolyte) measured after a full imbalance and after the end of rebalance.

Figure 5.3.3 Effect of tube length on the capacity rebalancing.

Without rebalancing of the electrolyte, a sharp drop in capacity was observed. As seen in the image in Figure 5.3.3, the electrolyte volume on the negative tank is nearly double than the volume in the positive tank. Initially, the vanadium concentration $c(V)$ was 1.6 M and oxidation state of V was 3.5. At the end of 25 cycles without rebalancing, the concentration of vanadium and oxidation state imbalanced largely due to the transfer of electrolyte species from positive tank to negative tank. With electrolyte imbalance, a higher vanadium concentration was observed on the positive tank and lower concentration on the negative tank. This means the major transfer through the FAP membrane is water. This observation is also in agreement with previous studies that report high ion selectivity of AEM. As the concentration was varied between the two tanks, the SOC was also imbalanced. When a cell was charged to a set OCV (or SOC) using imbalanced electrolyte, the

side with higher vanadium concentration (i.e. positive tank) reached above the set SOC and the diluted side (i.e. negative tank) was unable to reach the set SOC.

The capacity loss rate was largely reduced after the auto-rebalancing and with increase in the tube length. The titration results of the samples taken after 30 cycles with auto-rebalancing also indicated that the concentration of vanadium and oxidation state (or SOC) largely balanced compared to fully imbalanced case. As the electrolyte volume was small (cycling time ~ 15 minutes) as compared to cell size, the effect of imbalance on capacity decay was large. This indicates that, in a large volume electrolyte system with few hours of cycling time, the auto-rebalancing approach would work more effectively. In a 100 cm² size stack, after completion of 100 cycles with auto-rebalancing (Figure 5.3.1), the vanadium concentration and SOC of a charged electrolyte (OCV = 1.52 V) was measured. The concentration of vanadium c(v) was 1.6 M and 1.8 M on positive and negative tank, respectively. Similarly, the SOC was 97% and 93% on positive and negative tank, respectively. This indicates that the auto-rebalancing approach is very effective for maintaining a nearly constant capacity. A slightly higher concentration of vanadium ion on the negative side (i.e. 1.8 M) is attributed to the water loss by evaporation from the tank as electrolyte temperature was above the ambient temperature. The tank consisted of holes near the headspace for inserting the sensor. A small measurement error is also expected from the titration. Nevertheless, auto-rebalancing through hydraulic shunt of electrolyte tanks was found to be a suitable approach to largely reduce the capacity loss due to electrolyte imbalance. The length and diameter of the tube, however should be optimized for more effective results.

5.3.2 Minimising the capacity loss by the use of a combination of anion and cation exchange membrane in a stack

Another alternative approach by using a combination of AEM and CEM to reduce the electrolyte imbalance was tested. In a cell/stack assembled with a CEM membrane, the net transfer of electrolyte occurs from the negative to the positive tank, whereas in a cell/stack assembled with an AEM membrane, the net transfer of electrolyte occurs from the negative to positive tank. Therefore, if a combination of two type of membranes is used alternately in a multi-cell stack, the electrolyte imbalance and hence the capacity loss could be reduced. However, no experimental proof of this concept is available in literature. Therefore, the use of a combination of AEM (FAP 450) and CEM (Nafion 117) in a 2-cell stack of 100 cm^2 active area per cell was tested using cell cycling.

The cell cycling results at different current densities and long-term performance at 80 mA cm^{-2} are shown in Figure 5.3.4-a and b, respectively.

Figure 5.3.4 CE, VE and VE during short term cycling (a) and long-term cycling at 80 mA cm^{-2} (b), of a 2-cell stack assembled with a combination of AEM and CEM membrane.

A stable performance was observed at all current densities, as shown in Figure 5.3.4-a. A slight increment in the VE at 40 mA cm^{-2} was due to the activation of the

membrane. A stable performance over 160 cycles was observed during long-term cycling at 80 mA cm^{-2} as shown in Figure 5.3.4-b.

Figure 5.3.5 compares the performance of a 2-cells stack with identical membranes (with only AEM or only CEM) and a combination of membranes (AEM+CEM).

Figure 5.3.6 compares the capacity loss for the three configurations.

Figure 5.3.5 CE, EE and VE of a two cell stack with, AEM+AEM membrane combination (a), CEM+CEM membrane combination (b) and AEM+CEM membrane combination.

Figure 5.3.6 Discharge capacity loss for three combinations of membrane.

The CE of the stack with Nafion membrane (Figure 5.3.5-b) was slightly lower than CE of stack with FAP 450 membrane (Figure 5.3.5-a). This is due to a relatively high vanadium transport in Nafion membranes. AEM offers a high vanadium selectivity. On the other hand, the VE was higher in the stack assembled with CEM (Figure 5.3.5-b) because Nafion membranes has an excellent ionic conductivity compared to AEM membranes. The performance of the stack assembled with a combination of AEM and CEM was also similar to that of stack assembled with identical membranes.

Of more interest, the capacity loss reduced in a stack assembled with a combination of AEM and CEM membrane is shown in Figure 5.3.6. The capacity loss is higher for the stack assembled with only AEM (FAP450) than only CEM (Nafion 117). The capacity loss trend for AEM and CEM is in agreement with the literature [7].

An attempt was also made to use the auto-rebalancing approach on the stack assembled with a combination of AEM and CEM. The capacity with auto-rebalancing for 125 cycles are shown in Figure 5.3.7.

Figure 5.3.7 Charging and discharging capacity over 125 cycles after auto-rebalancing of an alternate membrane stack.

With continuous rebalancing of electrolyte through hydraulic shunt, the capacity remained stable over 125 cycles. This indicates that auto-rebalancing works efficiently with both types of membranes. The use of a combination of AEM and CEM without hydraulic shunt also minimized the capacity loss, however, in a multi-cell stack, the number of AEM and CEM has to be optimized for the stable capacity over prolonged operation. Hence, this study verified the concept of using AEM and CEM for the first time. For the use in the 1 kW stack development, further study was necessary in a larger area stack and in a stack with more than two cells. Due to the limitation of the time, these tests were not performed.

5.4 Effect of electrode activation in VRFB performance

A brief study was conducted to investigate the effect of thermal activation on the porous electrode. The optimal treatment method with the best performance was implemented in the development of 1 kW stack.

The porous electrodes are usually treated thermally in air to improve the hydrophilicity and reaction kinetics. It is believed that the introduction of oxygen containing functional groups and the increase in electrochemical active surface area (by the increase in surface roughness) by thermal activation are responsible for the improvements in the electrode kinetics. This study did not focus on wet (chemical) treatment methods as the target was to find a suitable, fast and easy method.

A wide range of treatment temperature and treatment time are found in literatures. It can be roughly said that, too low a temperature ($<400\text{ }^{\circ}\text{C}$) is not suitable as it is unable to introduce sufficient oxygen containing functional group as well as no mass loss to contribute in surface area increment. In addition, the felt would not be completely hydrophilic at low temperature treatment. On the other side, activation at too high temperature ($>700\text{ }^{\circ}\text{C}$) could burn-off the fibers faster i.e. higher mass loss, which could reduce the surface area (as well as thickness) significantly.

5.4.1 Thermogravimetric Analysis

Figure 5.4.1 shows the TGA diagram of GFD 4.6 EA porous electrode. It can be seen from the figure that the weight loss of the electrode becomes significant as the temperature increases mainly after $600\text{ }^{\circ}\text{C}$.

Figure 5.4.1 Thermogravimetric curve for virgin felt.

In literature, for activation at 400-500 °C, the activation time required are usually up to 30 hours [8]. As the target was to shorten the activation time, treatment time of 5 hour was chosen as a standard time of activation. The performance was investigated for samples treated at three temperatures: 500, 550 and 600 °C . As the burn off was higher, treatment for 5 hours at temperature above 600 °C was not taken into consideration. The activated felts were compared with the as received felts in order to compare the improvement on the performance.

5.4.2 Burn-off

The burn off (mass loss) after the thermal treatment are compared in Table 5.4.1.

Table 5.4.1 Burn-off amount after the thermal activation.

Sample	Burn off (%)
500°C_5hr	2.5
550°C_5hr	5.1
600°C_5hr	7.9

5.4.3 Scanning Electorn Microscopy

Figure 5.4.2 shows the scanning electron microscopy (SEM) image of the as-received felt (left) and sample treated at 600°C (highest temperature among three samples), in order to compare if any change in surface morphology is observed.

Figure 5.4.2 SEM image of carbon felt before (left) and after thermal oxidation (600°C_5hr, right).

As can be seen, no effect of the thermal treatment on the morphology of the carbon fiber was observed. The surface of the graphite felt is smooth and no visible changes are observed with the thermal oxidation.

5.4.4 Electrochemical characterization

The electrochemical characterization of the samples was performed in a CV set-up. CV and EIS measurement were performed. The details of the experimental set-up are given in Chapter 3 (Section 3.8).

Figure 5.4.3 presents the CV curves obtained for four different samples of carbon felt (i.e. as received, 500°C_5hr, 550°C_5hr and 600°C_5hr). The electrochemical parameters obtained are listed in the Table 5.4.2. The samples exhibited an anodic peak associated with the oxidation and a cathodic peak associated with the reverse reduction reaction.

As can be seen from the CV curve, it is clear, that the improvement of the thermal oxidation is higher on the negative redox couple. The reduction peak (V^{2+}) has become more pronounced after the heat treatment. Similarly, the peak current has increased after the treatment, which could possibly be due to the increase in electrochemical active surface area. The peak potential separation has also reduced after the treatment.

Figure 5.4.3 Cyclic voltammetry for the carbon felts treated at different temperature at a scan rate of 2 mV/s in (a) positive electrolyte V(IV)/V(V) and (b) negative electrolyte V(II)/V(III).

The electrolyte was 0.1 M V in total 4 M H₂SO₄ at 90% SOC.

Table 5.4.2 Electrochemical parameters obtained from CV: positive (left) and negative (right) electrolyte.

Sample	Positive electrolyte		Sample	Negative electrolyte	
	$\Delta E_p(V)$	I_{pa}/I_{pc}		$\Delta E_p(V)$	I_{pa}/I_{pc}
As received	0.35	1.32	As received	0.6	0.98
500°C-5hr	0.35	1.01	500°C-5hr	0.55	0.99
550°C-5hr	0.31	0.99	550°C-5hr	0.49	0.95
600°C-5hr	0.27	1.03	600°C-5hr	0.47	0.95

Comparing only the heat-treated samples, sample treated at 500°C exhibited poor performance than the other two, which is evident from the relatively higher peak separation potential. The felt was wetted (tested with droplet of water), however, the activation time was probably not sufficient for the best performance. Comparing samples treated at 550 °C and 600 °C, both showed similar performance with slightly better performance of sample treated at 600 °C.

To further investigate, EIS measurements were performed on all samples. The Nyquist diagrams for each sample in positive and negative electrolyte is compared in Figure 5.5.4-a and 5.4.4-b, respectively. The EIS was measured in a CV set-up containing 0.1 M V in total 4 M H₂SO₄ at 90% SOC. The EIS measurement was carried out with AC perturbation of 10 mV and frequency sweep from 100 kHz to 100 mHz. The left diagram shows measurement in positive electrolyte V(IV)/V(V) and right diagram shows measurement in the negative electrolyte V(II)/V(III).

Figure 5.4.4 Nyquist diagram for the carbon felt treated at different temperature.

For obtaining the value of charge transfer resistance from the Nyquist diagram, Randle circuit with constant phase element (double layer capacitance of electrode/solution interface) and Bisquert diffusion (valid for porous electrodes) was used, as shown in Figure 5.4.5. Since the electrode is a porous material, the EIS data cannot be modeled simply with standard circuit components. Hence transmission lines are required due to the distributed nature of the interfacial impedance throughout the pore. The dotted line in Figure 5.4.4 represents the fitting from the software (Zfit).

Figure 5.4.5 Equivalent circuit model for the estimation of charge transfer resistance.

The Nyquist diagram in Figure 5.4.4 shows a semicircle at high frequency zone and a linear part at low frequency zone. This indicates that the redox reaction is controlled by charge transfer and diffusion. The semicircle part at high frequency

gives the information about the charge transfer process and the linear part at low frequency provides the information on the diffusion process.

The obtained value of solution resistance (R_s) and charge transfer resistance (R_{ct}) from the fitting software are given in Table 5.4.3.

Table 5.4.3 Ohmic resistance and charge transfer resistance obtained from curve fitting of the impedance plot.

Sample	Positive electrolyte V(IV/V)				Negative electrolyte V(II/III)			
	R_s (ohm)	R_{ct} (ohm)	CPE	a	R_s (ohm)	R_{ct} (ohm)	CPE	a
As received	1.44	0.31	0.042	0.768	1.39	1.4	0.11e-3	0.981
500°C_5hr	1.41	0.26	0.067	0.719	1.45	1.15	0.15e-3	0.931
550°C_5hr	1.44	0.15	0.074	0.835	1.42	0.42	3.22e-3	0.936
600°C_5hr	1.42	0.14	0.097	0.805	1.38	0.35	3.86e-3	0.770

It is observed from Table 5.4.3 that the charge transfer resistance decreased with the increase in heat treatment temperature of the electrode. The decrease in charge transfer resistance for the felt treated at 600°C for 5 hours is almost half than that of as-received felt in positive electrolyte and four times less in negative electrolyte, signifying the reduced activation barrier for vanadium redox reaction. The improved performance of thermally oxidized carbon felt is attributed to the increased activity and wettability with higher improvement on the negative side. Electrodes has higher charge transfer resistance for V (II)/V (III) compared to V (IV)/(V), which is in agreement with the results obtained from the cyclic voltammetry. This indicates that the negative side in VRB is the performance limiting factor. The constant phase

element (CPE), obtained from the EIS fitting, increased with increase in activation temperature on both positive and negative side.

5.4.5 Confocal RAMAN

The oxygen containing functional group can be estimated through X-ray photoelectron microscopy (XPS). However, this was not carried out as the measurement was not available in-house and therefore out of scope of this thesis. As an alternative, con-focal RAMAN measurements were carried out and spectra are compared in Figure 5.4.6.

Figure 5.4.6 Confocal RAMAN spectra for different electrode samples.

In the RAMAN spectra, the D band ($\sim 1350 \text{ cm}^{-1}$) represents the disordered graphitic lattice (edges) or defect intervened zone-edge phonons, whereas, the G band ($\sim 1590 \text{ cm}^{-1}$) represents the ideal graphitic lattice or in-plane vibration of sp^2 atoms present in carbon fiber. The ratio between D to G band provides the information about the

increase or decrease in defects and disordered structures. The D to G band ratio for four different samples are listed in Table 5.4.4.

Table 5.4.4 D-band and G-band intensity ratio for four electrode samples.

Sample	I_D/I_G
As received	0.53
500°C_5hr	0.60
550°C_5hr	0.96
600°C_5hr	1.02

The D band has been increased with the temperature. The ratio of D to G band increased from 0.53 (in as-received electrode) up to 1.02 (in 600 °C_5 hr treated sample). This indicates that the as-received electrode was highly graphitic whereas after thermal treatment in air, graphitic domains decrease. This is accompanied by an increase in surface area.

5.4.6 Cell cycling performance

Of more interest, cell cycling of four different electrodes were tested on a 100 cm² active area flow cell. The CE, EE and VE are compared in Figure 5.4.7. The current density was varied from 40 mA cm⁻² to 80 mA cm⁻².

From the cell cycling, it can be observed that the as received felt shows a very poor performance as compared to activated felts. Among the three samples, the felt treated at 500 °C-5 hr resulted in slightly poor performance as compared to other two activated electrodes. Two electrode samples treated at 550 °C-5 hr and 600 °C- 5 hr had almost similar performance.

Figure 5.4.7 CE, EE and VE comparison of cell with differently treated electrodes.

Hence, combining the information gained from electrochemical characterization, surface characterization and cell cycling, it was found that the electrode treated at 600 °C for 5 hour showed the best performance among the other samples. Hence, for the stack development, the electrode would be treated thermally in air at 600 °C for 5 hours.

5.5 Conclusion

In this chapter, multi-parameters in VRFB operation were tested in order to improve the performance. The specific problems related to electrode compression, high current density operation, capacity loss due to electrolyte imbalance and electrode activation were addressed. The major findings are briefly summarized below.

The effect of electrode compression on the cell efficiency, contact resistance, ASR, discharge capacity, pressure drop, flow distribution and electrolyte utilization was investigated in a 100 cm² cell. The compression of the electrode was varied from 15% to 40% in an interval of 5%. The cell with electrode at low compression suffered from high electronic contact resistance, whereas high compression suffered from poor mass transport, mainly at high current densities. Considering both limitations, electrode compressed at 25% showed the highest EE, VE and specific capacity among others. ASR value for 25% compression, being the lowest, provides the further evidence for its superior performance. A significant increase in ΔP was recorded with the increase in electrode compression. A maximum contribution on overall EE at 25% compression was calculated to be 6.4% and 3.1% higher as compared to 15% and 40% compression, respectively. This is attributed to the optimal trade-off between flow distribution, contact resistance and pumping losses. At 40% compression, the pump consumed up to 5% of EE. By reducing the compression from 40% to 25%, an increase in overall EE up to 1.6% can be achieved due to reduction in pump power consumption. Hence, based on the outcome of this study, electrode compression of 25% was implemented in the prototype VRFB stack development.

Due to advancement in the electrode material and improvements in cell architecture, flow batteries can be operated at much higher current densities ($>100 \text{ mA cm}^{-2}$). Considering this development, the behavior of FAP450 membrane at a high current density was investigated. FAP450 membrane is an AEM, which is widely used in commercial VRFB. In this study, a strange behavior of this membrane was observed during the discharging of a cell at high current density (typically $> 100 \text{ mA cm}^{-2}$), showing a sudden drop in voltage near high SOC followed by a recovery to normal after few minutes. This feature was named as power drop effect. This effect was reproducible and was not reported before. This sudden drop near high SOC was due

to the increase in membrane resistance caused by the accumulation of V^{5+} ions at the membrane surface. This fall was recovered back to normal in few minutes as the discharging continued. Such sudden drop in voltage or power during the operation of a flow battery should be avoided, especially at high current surge, in real operation requiring delivery of constant power.

The capacity loss due to the electrolyte imbalance in VRFB is also a major problem and therefore, a huge effort is given in developing membranes that could reduce the electrolyte crossover. In this study, two novel approaches were investigated for minimising the reversible capacity loss. The auto-rebalancing through hydraulic shunt of two electrolyte tanks showed an excellent performance. This approach is simple and can be implemented in a commercial system. Due to the simplicity of the technique and promising results, it was implemented in the development of a 1 kW stack system. The usage of a combination of AEM and CEM in a stack was also tested, which resulted in stable performance with minimal capacity loss as compared to a stack with identical membranes.

The optimal condition for the electrode activation is necessary for improving the kinetics (to increase the EE) and securing a long-term stable performance of VRFB. Considering the objective of development of a 1 kW stack, thermal activation in air was chosen due to the ease of handling large amounts of samples within a short time. It was decided that the activation time will be kept constant at 5 hours. Therefore, four samples (as received vs sample treated at 500°C, 550°C and 600°C) were investigated using surface and electrochemical characterization, and cell cycling. From the study, it was found that thermal activation is must needed for improving the performance. Among activated samples, sample activated at 600 °C for 5 hours showed the best results. Hence, this activation condition was used for the prototype development.

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Chapter 6

Flow cell and stack development

This chapter summarizes the development work of flow batteries from small laboratory size (20 cm^2) single cell to 1 kW-20 cell stack. Computational fluid dynamics (CFD) assisted flow simulation was used to optimize the design of the flow frame for 100 cm^2 and 625 cm^2 cells. This chapter also discusses the problems faced during the development phase and approaches implemented to solve the problems. Finally, the objective of this research was accomplished with the successful development and testing of a 1 kW-20 cell stack.

6.1 Development of a 20 cm² cell

In order to perform the initial performance test of a flow cell and to understand the areas of improvement on the design, a single cell with active area of 20 cm² (5 cm x 4 cm) was designed and fabricated. Each components was designed using AUTOCAD software and fabricated at a local workshop in Singapore. As the active area of the cell was small, no flow simulation was done to design the flow frame. Figure 6.1.1 shows all the components used in the assembly of a single cell.

Figure 6.1.1 Components used in assembly of a single cell.

Among the various mechanical components, flow frame (FF) is one of the crucial component as it guides the flow through the porous electrode. The design of the integrated flow guides on the FF is given in Figure 6.1.2-a and b. An image taken during assembly process showing the porous felt on the FF window and gaskets on the front face of the FF is shown in Figure 6.1.2-c.

Figure 6.1.2 Flow frame (FF): front view (a) and back view (b), and an image taken during assembly showing porous felt sitting on the FF window and gaskets on the front face of the FF (c).

The flow guides were milled on the FF to uniformly distribute the electrolyte before entering the porous felt. Identical flow guides were located at both inlet and outlet side to allow switching the inlet and outlet side whenever necessary. The thickness of the FF, depth of channels on the FF and window depth for BP were designed by taking into consideration the availability of electrode and BP size from the manufacturer. A 0.6 mm thick BP (TF 6, expanded graphite, SGL

Carbon) was glued at the cavity on the back side of the FF, as shown in Figure 6.1.2-b. The size of the BP was 6 cm x 5 cm, which was 1 cm bigger than the felt size. In some conventional designs, the BP with size of outer dimension of FF is used, but an attempt was made in this study to use the size of the BP close to the active area size. In a large area stack, this approach would help to reduce the weight of the stack and cost on the BP. A silicone sheet (0.5 mm thick) for each FF was used to protect the cell from leaking. Use of silicone sheet allowed the uniform seal over the surface area of the flow frame and protected the cell from both internal and external leakage. The membrane was cut into a size that was slightly bigger than the active area window, and was sandwiched between the two porous electrodes.

During the design, a major problem was encountered in covering the flow channels on the FF. If silicone is laid directly on the front side of the FF, it could flow into the flow channels and block the flow. Therefore, few options were tested to solve this problem. Hard gaskets (PTFE, 25% glass filled PTFE, etc.) were tested as they had both gasket properties and hardness. After testing several times, it was found that the hard gasket are not a good solution because leaks were sometimes observed. Therefore, soft silicone or neoprene gasket was necessary. To prevent the protruding of the soft gasket into the flow channels in the FF, hard covers (Polypropylene of 0.2 mm thickness) were used. For this, a groove was milled on the front side of the flow frame as shown in Figure 6.1.2-a. The PP sheet was glued on the groove using transparent silicone glue. The use of hard plastic to cover the flow channels worked effectively for this cell size. Figure 6.1.2-c shows the image taken together with hard cover and silicone gasket.

Considering the goal of large area development and given the fact that high assembly force would be used, the use of 0.2 mm cover was not a good solution.

The tearing of the PP sheet near the open channel was expected. Therefore, some other method for covering the channel was further explored.

A new flow frame with inlay concept was designed and fabricated, as shown in Figure 6.1.3.

Figure 6.1.3. Modified flow frame design with inlay

In this modification, a separate PVC cover (so called “inlay”) was fabricated. The flow guides were machined on the inlay, instead of machining on the FF. The inlay can be glued permanently using PVC cement glue or silicone glue. As silicone gasket was used, it was also not necessary to use any glue for this cell size. A slot near nozzle was made on both inlay and FF to hold the inlay tightly on the FF. This design was tested and the cell worked perfectly. However, the fabrication cost of the inlay was very high. Therefore, it was necessary again to find a way to reduce the cost or to find other ways to cover the channel for the 1 kW stack development.

The cell cycling result of a 20 cm² cell assembled with heat treated felt (600 °C, 5 hr in air) is given in Table 6.1.

Table 6.1 Performance of a 20 cm² cell with heat treated felt in air at 600 °C-5 hr.

Current density (mA cm⁻²)	CE (%)	EE (%)	VE (%)	ASR (Ω cm²)
40	98.9	89.4	90.4	1.74
50	98.4	86.8	88.2	1.75
60	98.7	84.8	85.9	1.74
70	99.3	83.2	83.8	1.74
80	99.4	80.9	81.4	1.78

These data were taken as a reference to compare for the development of larger area cell and stack.

6.2 Development of a 100 cm² cell

The size of 20 cm² cell was very small as compared to the target of 1 kW stack with active area of 625 cm² per cell. Before the development of a large area cell of 625 cm², it was aimed that all the multi-parameter testing for improving the performance will be carried out on a small area cell. Therefore, it was decided that a 100 cm² cell would be a fair size for performing multi-parameter studies (segmented study, flow channels, electrode compression, etc.). The active area of 100 cm² cell is four times larger than 25 cm² cell and about six times smaller than 625 cm² cell, suggesting that 100 cm² size cell would be a suitable intermediate size to develop before the development of a large area cell of 1 kW class. In addition, most of the available literatures on flow cell used 100 cm² cell for studying various areas, therefore, developing a similar size cell would also be helpful in comparing the results. It was decided that the improvement made on this 100 cm² cell will be directly implemented for the large area cell development. The multi-parameter testing on a large area cell (625 cm²) for the performance improvement was not possible as assembly of large area cell multiple times is not within the scope of this PhD study.

Three types of geometries for the flow frame development, as shown in Figure 6.2.1, were investigated using flow simulation. For the study, ANSYS Fluent 14 commercial software was used. The purpose of flow simulation was to choose a suitable geometry of FF that can secure a uniform flow distribution of electrolyte. Based on the geometry of the flow frame, other components were designed accordingly.

In geometry A, electrolyte enters and exits the manifolds from the corner, the felt has a square shape and there is a gap of 1 mm for electrolyte redistribution between flow distributing islands and felt entrance/exit. All dimensions are given in mm.

In geometry B, the electrolyte enters and exits the manifold from the center of the cross section, the felt has a square shape and there is a gap of 1 mm between flow distributing islands and felt entrance/exit.

In geometry C, electrolyte enters and exits the manifold from the corner, the felt has a rectangular shape and there is a gap of 1 mm between manifold and felt entrance/exit.

Figure 6.2.1 Front view of three geometries of FF proposed for 100 cm² cell development

As it was important to have a uniform flow distribution of electrolyte across the porous felt and it was also necessary to estimate the pressure drop, flow simulation was performed using ANSYS Fluent. Different parameters such as porosity of the felt, permeability, viscous resistance, electrolyte properties (viscosity and density), etc. were estimated and input into the software. The details on the simulation parameters are provided in Annex A.

The velocity and pressure profile for three geometries are given in Figure 6.2.2 and Figure 6.2.3, respectively. The simulation was run at the electrolyte flow rate of 120 mL min⁻¹. As gravity was not considered in the simulation, flow from top or from the bottom had no difference. Figure 6.2.5 shows the velocity line diagram at the cross section of electrode entrance, middle of the electrode and electrode exit.

(a): Geometry A

(b): Geometry B

(c): Geometry C

Figure 6.2.2 Velocity contour for geometries A, B and C.

Figure 6.2.3 Pressure contour for geometries A, B and C.

Figure 6.2.4 Velocity streamlines for geometries A, B and C. The distribution of spheres in 3 zones along the Y-axis (flow length) shows the particles flow at 5 sec, 10 sec and 15 sec.

(a) Geometry A

(b) Geometry B

(c) Geometry C

Figure 6.2.5 Velocity line diagrams for three geometries at electrode inflow, middle of the electrode and electrode outflow.

The velocity contour diagrams in Figure 6.2.2 show uniform velocity distribution on the porous electrode for all three geometries. The pressure contour shows that the pressure drop will be reduced if rectangular cross section with shorter flow length is chosen. However, velocity profile (Figure 6.2.2-c) shows that the electrolyte may not redistribute uniformly through the flow guides before entering the porous electrode. A gap of 1 mm between guiding lands and electrode cross section might help to redistribute the electrolyte over the cross section. However, as the felt is hydrophilic and soak the electrolyte, possibility of non-uniform flow of electrolyte from the porous electrode may exist. The velocity streamline in Figure 6.2.4 shows that with the flow entrance and exit from middle of the cross section (Geometry B), a faster flow is observed at the middle and slower flow at the corners.

The velocity line diagram along the cross section of the felt at three different zones is shown in Figure 6.2.5. The velocity line diagram was found to be more useful in obtaining information regarding the velocity distribution and possibility of presence of dead zones compared to other diagrams. A uniform velocity along the cross section at different position in the flow direction is always desired. In geometry A, the velocity is fluctuating at the electrode inflow, and uniform at the middle and outflow. The velocity at the electrode inflow and outflow is fluctuating whereas nearly uniform at the middle of the felt in geometry B. A slightly higher velocity at the middle of the cross section at the electrode entrance can be seen in geometry B, which is expected. In geometry C, the velocity is fluctuating at electrode outflow, whereas uniform at the electrode inflow and middle. The zero velocities obtained at the edge in all three diagrams are due to the no slip boundary condition used in the simulation. Neglecting the zero velocity at two edge points close to the wall, it is also important to monitor the velocity gradient from the edge towards the centre. In Figure 6.2.5-b, it is observed that up to 5 mm away from the wall, the velocity is smaller than the velocity at the centre. This could lead to the presence of dead zone or stagnant flow during electrolyte circulation. This behavior was not observed in geometries A and C.

Comparing the three geometries using velocity contours, pressure contours, streamlines and velocity line diagrams, it was decided that geometry B will not be fabricated as higher flow velocity at the centre and possibility of stagnant flow at the two corners were observed. Comparing geometry A and C, both have pros and cons. Having a shorter flow length (Geometry C) will reduce the pressure drop, however, having longer cross section in Geometry C could lead to increased non-uniformity in the electrolyte flow. In larger area cell, this effect will be more intensified. Therefore, to secure uniform distribution of electrolyte, it was decided that geometry A (i.e. square geometry) will be developed. In order to

reduce the pressure drop, other methods (e.g. flow channels on the electrode, low compression of the electrode, etc.) were planned to be explored.

Figure 6.2.6 100 cm² size flow frame after fabrication.

The components of a 100 cm² single cell was fabricated. Figure 6.2.6 shows the picture of the flow frame after fabrication. A collar was glued (using PVC cement) on the inlet and outlet. The collar internally had metric thread, on which the nozzle (with male threads) for the electrolyte flow was connected. In the first version, it was decided that the earlier concept of using thin 0.2 mm PP sheet to cover the channel will be used. The other components were similar to the components fabricated for 20 cm² cell, only the size of the components was bigger.

After testing for several months, two problems were identified. As the FF thickness was only 3.5 mm, the collar glued on the flow frame was weak. When the nozzle was connected to collar for electrolyte flow, the collar broke for few times. Therefore, modification was done by detaching the collar from the nozzle using an O-ring set-up. In addition, as the cell size was about 5 times bigger than 20 cm² cell, the 0.2 mm plastic used for covering the channel was cracked at the

open channel area of the flow frame. It was also observed that some electrolyte could internally short circuit through this plastic cover. Therefore, the design of the flow frame was modified. In the modification, the groove for PP sheet was removed and on the front side of the FF, a 1 mm PVC cover extending over the complete surface area of the FF was permanently glued using PVC cement. The PVC cement was diluted with acetone for increasing the curing time. The FF after the modification together with the remaining components in a half cell is shown in Figure 6.2.7.

Figure 6.2.7 Fabricated components for the half-cell showing modified flow frame and insulator plate design.

As can be seen in Figure 6.2.7, the collar (which was glued on the flow frame) used O-ring. The collar was inserted into the hole made on the insulator plate. The O-ring provided on the collar helped to tightly fit into the hole of insulator plate. The copper plate was inserted in a 2 mm groove made on the insulator plate. This method also reduced the size of the copper plate compared to conventional designs. The PVC nozzle, which was directly connected to the collar in the previous design, now is connected on the back side of the insulator

plate. The insulator plate has a female thread and the nozzle has a male thread. This modification on the design eliminated the chance of stress on the collar and therefore, projected the collar from breaking.

A single cell was assembled and tested. Table 6.2 shows the performance of the single cell at different current densities.

Table 6.2 Performance of a 100 cm² cell assembled with heat treated felt in air at 600 °C-5 hr.

Current Density (mA/cm ²)	CE (%)	EE (%)	VE (%)	ASR (Ohm. cm ²)	Self-discharge current density (mA/cm ²)
40	98.2	88.3	89.8	1.85	0.35
50	97.4	85.3	87.6	1.83	0.65
60	97.3	82.8	85.1	1.85	0.82
70	97.9	80.6	82.4	1.91	0.74
80	98.3	78.7	80.1	1.91	0.69

The multi-parameters tests, such as study of flow channel, electrode compression, segmented study, pH tracing, etc. were performed on this developed cell. From the segmented cell and pH tracing test, it was found that the flow distribution in the porous electrode was slightly non-uniform (details in Chapter 4). Later it was also observed visually, that the velocity of electrolyte did not exit from the flow guides at the same velocity. Though there was a clearance of 1 mm between felt entrance and FF islands for distribution of the electrolyte along the cross section, it did not work as expected. It was also observed that having a single long channel (or passage) from the inlet/outlet nozzle to flow guides is not a good design because in the event of any particles (such as glue, precipitate from electrolyte, etc.) trapped into the channel could completely block the flow and increase the pressure drop. Therefore, FF design was again modified, as shown in Figure 6.2.8 (b). In the new design, it was ensured that the electrolyte velocity from the individual flow guides is equal for wide range of flow rates. A flow simulation

was run to optimize the size of each islands and gap between them. The modification was mainly performed on the shape of the flow guides, gap between them and one extra channel connecting main manifold to left part (at the top) and right part (at the bottom).

Figure 6.2.8 Flow frame design before (left) and after (right) the modification.

The flow distribution was slightly improved after the modification, which was confirmed from the locally resolved study using segmented cell and from pH tracing test, which was discussed in Chapter 3. As the electrolyte stoichiometry at 100 mL min^{-1} was sufficiently high for a 100 cm^2 cell, noticeable difference on the cycling performance within few cycles was not observed. However, improving the flow distribution would definitely protect the electrode materials from degradation in long-term operation.

6.3 Development of a 100 cm^2 - 2 cell stack

Before a 100 cm^2 size cell was scaled up to a 1 kW stack size, a 2-cell stack of 100 cm^2 size was developed to test the design, leakage issues and performance in a stack. A 2-cell stack consists of two end cells (same as in a single cell) and one middle cell. The middle cell was prepared by combining two flow frames together. The design of the middle flow frame is given in Figure 6.3.1.

Figure 6.3.1 Middle flow frame: front view (left) and back view (right).

During assembly of the middle cell, a BP is shared between two FFs. Both FF has a recess of 0.3 mm at the back side for accommodating a 0.6 mm BP. A 2-cell stack of 100 cm² size was assembled and cycled for monitoring the efficiencies. The stack was cycled between cut-off voltage of 1.8 V and 3.3 V, which is double than the voltage set during single cell testing. The performance of the stack is summarized in Table 6.3.

Table 6.3 Performance of a two cell stack of 100 cm² active area per cell.

Current Density (mA/cm ²)	CE (%)	EE (%)	VE (%)	ASR (Ohm. cm ²)	Self-discharge current density (mA/cm ²)
40	98.6	89.0	90.3	1.76	0.29
50	98.8	87.0	88.1	1.75	0.30
60	99.0	85.2	86.0	1.73	0.29
70	99.2	83.3	83.9	1.72	0.29
80	99.3	81.4	82.0	1.71	0.30

The stack performance slightly improved than the single cell performance. It is expected because the contact resistance between copper plate and BP is shared between two cells.

For combining two middle FFs together with a BP, silicone glue was used. In a 100 cm² size stack, no collar was used for combining two FFs. However, it was

realised that for the large size stack development, collar should be used between two holes of the FF to protect any internal leak from the interface of two FFs.

During testing of the stack for several months, sometimes small permeation of electrolyte from a thin (0.6 mm) BP was observed. As very thin expanded graphite plates (TF6) were used, minor permeation of acid electrolyte from the end BP reacted with the copper collector. Therefore, new BPs (PV 15 from SGL Carbon) of same thickness manufactured with slightly higher polymer content were proposed for further development. PV 15 plates were found to be excellent with respect to permeation of electrolyte. There was no change observed on the performance, as both TF6 and PV15 plate had similar resistance.

6.4 Development of 625 cm² – 3 cell stack

A part of finding in this section has been filed as a technology disclosure (TD) at NTU: A. Bhattarai, N. Wai, R. Schweiss, Design of flow frame channel and channel cover, and methodology on making modules for the assembly of redox flow batteries, Ref. no. TD/171/17.

The design of the FF for a large area cell (of active area 625 cm²) was optimized from the flow simulation. Figure 6.4.1 shows the design of the flow frame.

The FF has a central cavity (d) to hold the porous electrode. The FF has flow channels (of variable cross section) and distribution islands (a, b) of varying sizes present at both the electrolyte entrance (bottom) and exit (top) side. From the lesson learned from the development of a 100 cm² cell, multiple entrances from the main inlet channel to the flow guides were provided.

Figure 6.4.1 Design of flow frame: front view (left) and back view (right).

The channels and islands were fabricated using the CNC machining. The channels connecting the main manifold (f, g) to 1st layer of distribution island (a) was tapered in order to secure a uniform velocity of the electrolyte along the cross section. The electrolyte, after entering uniformly from the 1st layer distributor, will enter the 2nd layer distributing islands (b). The shape and size of each islands were varying as well as the gap between the two islands were also varying for ensuring same velocity of electrolyte along the cross section before entering the porous electrode situated at the cavity (d). In order to further ensure that the electrolyte enters the felt at a same velocity for a wide range of flow rates, a 5 mm of clearance was provided between 2nd layer distributor and felt entrance. The use of two layer of distributor and varying size of guiding islands would help increase the flow resistance at the channel and flow guides, hence reduce the shunt current loss. Despite the flow resistance was increased, the pressure drop at the channel and flow guiding islands was negligible (~10 mbar) as compared to pressure drop at the porous electrode. The use of double layer distributor also eliminated the necessity of using long narrow channels in FF from shunt current consideration. The present design is scalable to any size of the flow frame.

For improving the EE and achieving stable performance, it is important that all the electrolyte flows to the greatest possible extent through the porous electrode and no internal short-circuiting or leakage of the electrolyte around the electrode is present. During the development of a small cell of 100 cm² size, it was sometimes observed that gluing of the PVC sheet on the complete surface area of the FF created micro-channels due to the non-uniform spread of glue, resulting in short circuiting of the electrolyte from the micro-channels. In a large area cell, it was also difficult to glue the PVC cover on a large area FF using a fast curing glue (e.g. PVC cement). On the other side, it was learned during the development of inlay for a 20 cm² cell that machining of inlay was complicated, which incurred a large cost for fabrication. Therefore, it was necessary to design a simple inlay to solve all these problem.

As such, a simple inlay was designed to cover the open channel on the flow frame (Figure 6.4.2).

Figure 6.4.2 Inlay for covering the channel.

The channel cover was designed according to the channel designed on the FF. The channel cover was inserted (tight fit) into the groove machined on the FF (c in Figure 6.4.1). The depth of the groove and cover's thickness (=1 mm) was same. The rigid channel cover would help guiding all the electrolyte to flow through the flow frame channels and protect from any unwanted external path of electrolyte. As silicone sheet was used over the full surface of the FF for sealing purpose, it was optional to use glue for fixing the inlay on the flow frame.

For the assembly of a 3-cell stack, modules were developed. Figure 6.4.3 shows the components used in a 3-cell stack.

Figure 6.4.3 Schematics of the components used in an n-cell stack.

In an n-cell stack, $n-1$ numbers of middle cell components are used and rest of the components (as shown in Figure 6.4.3) are remained at the two ends. In a 3-cell stack, two middle cells were used. All the components were tightened between two end plates (1) using nut and bolts.

The FF (e on Figure 6.4.1) has a central recess on the back side, wherein, BPs are seated. The BP on the recess was glued. For the FF at the two end sides, BP was in direct contact with the current collector (3). For the middle cells, modules were prepared for easier assembly of the stack. Modules were prepared by combining various components (8-7-6-10-4-10-6-7-8). In other words, channel covers (6) were fixed on the grooves above the channels present on each FFs. Two middle FFs (10), which also had central recess at the back side shared a common BP. The two middle FFs (10) were fixed together with BP using glue. Afterwards, two gaskets (8) at two front side of the FF were glued to make a single module (M). The felts were inserted into the cavity of the FF during the assembly. The triangular spikes (h in Figure 6.4.1) facing towards the cavity of the FFs protected the porous felts from falling during the assembly process. In addition to this, these spikes would protect from the chances of short circuiting of electrolyte along the edges. Each components had two guide pin holes (in Figure 6.4.1), which provided the access to guide pin in order to align each components during the assembly. When the modules were prepared, the stack was assembled simply by

stacking $n-1$ number of modules (M) for an n -cell stack. An ion exchange membrane was sandwiched between two modules. The benefit of this design is that the sizes of the membrane and BP do not need to be same as the outer dimension of the FF. This would significantly reduce the amount of material used, thereby reduce weight of the stack and the cost on BPs and membrane.

The performance of a 1 kW class- 3 cell stack was tested, which is shown in Figure 6.4.4.

Figure 6.4.4 CE, EE and VE of a 3 cell stack (625 cm^2 size) at different current density (a), performance during long-term cycling at 80 mA cm^{-2} (b) and flow rate and pressure drop over 25 hours operation during cycling (c).

For all current densities, VE was measured more than 80%. The area specific resistance (ASR) of the stack at 80 mA cm^{-2} was $1.74 \Omega \text{ cm}^2$ at an electrolyte temperature of $38^\circ\text{C} \pm 1^\circ\text{C}$. The long-term performance testing also showed a stable performance over 100 cycles. The average flow rate of electrolyte was

1200 mL min⁻¹ and average pressure drop in two half-cell was ~ 640 mbar. The performance results of the stack are in good agreement with the results obtained from small size cell and stack testing, however, there were still some areas for improvement before fabricating the components for a 20 cell-1 kW stack.

The stack was designed for an average flow rate of 300-500 mL min⁻¹ per cell. The pressure drop of 640 mbar could be reduced significantly by using the flow channels, as suggested by the study in Section 4.1. Therefore, pH testing was performed on a large area cell for three configurations: no channel, IDD channel aligned in parallel to flow direction and IDD channel in perpendicular to flow direction. From the pH testing, it was found that IDD channel aligned in parallel to flow direction could improve the flow distribution significantly and reduce the pressure drop by about 50% (detail in section 4.3). Therefore, on a 20 cell stack, it was decided that IDD channels will be used.

6.5 Development of a 20 cell - 1 kW stack

Development of a leak proof and efficient 1 kW stack was the major deliverable of this PhD research. Similar to a 3-cell stack of 625 cm² size, a 20-cell stack of 1 kW size was assembled and tested. The detail design of the stack components are provided in the Annex B. The stack and testing system used various innovative approaches developed during the study on small size cells and stacks. The findings from segmented cell study, pH tracing, flow channel study, electrode compression and approaches for reducing electrolyte imbalances, etc., discussed in earlier sections were used to develop and test the 20 cell stack of 1 kW size.

The FF design and assembly process was exactly same as used for a 3-cell stack assembly. Figure 6.5.1 shows the image of the stack taken after the assembly.

Figure 6.5.1 1 kW stack after assembly.

The following are the specifications of the stack:

- No of cells = 20
- Active area of each cell = 25 cm x 25 cm = 625 cm²
- Electrodes: Thermally treated (in air) Sigracell GFD 4.6 EA, SGL Carbon
- BPs : Sigracell PV 15, SGL Carbon
- Membrane: Fumasep FAP 450, anion type membrane
- Felt compression: ~25 %
- Flow frame : CNC milled PVC frames with integrated flow guides and a PVC inlay for covering the channels
- Unique features:
 - IDD channels milled on the felt (Figure 6.5.2) – to reduce ΔP and improve the flow distribution. The channels faced towards the BP and aligned in parallel to the flow direction.

- Membrane and BP sizes close to felt area (reduced the use of membrane and BPs area by $\sim 45\%$, comparing to the outer area of the FF).
- Dry weight : ~ 60 kg (major weight from steel plates ~ 30 kg)

Figure 6.5.2 A CNC milled interdigitated channel on a 1 kW stack size square electrode (25 cm x 25 cm). The size of channels were $L \times W \times H = 200 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$.

Figure 6.5.3 shows the schematics of the components used in a stack.

Figure 6.5.3 Schematics of the components used in an n-cell stack.

The stack used 20 cells connected in series. The flow of the electrolyte was made parallel to each individual cell. In a 20-cell stack, $n-1 = 19$ number of middle cell components were used (8-7-6-10-4-10-6-7-8) and rest of the components were remained at the two ends. All the components were tightened between two end plates (1) using nut and bolts.

For testing the stack, a completely new test set-up was developed, as shown in Figure 6.5.4. The details on the experimental set-up is also given in Chapter 3.

Figure 6.5.4 Test set-up for testing 20 cell stack.

The electrolyte tanks are located below the stack. This allowed easy drainage of electrolyte from the stack and collection in the tank, whenever necessary. It also reduces self-discharge during the standby time. The electrolyte volume was 10 L per tank. The concentration of the electrolyte was $1.6 \text{ M V}^{+3.5}$ in total 4.5 M sulphate. The flow rate was maintained between $7\text{--}9 \text{ L min}^{-1}$. Pressure sensors (George Fischer), temperature sensors (PT100 type), flow sensors (Omega) and a H_2 sensor (Hydrosen 1000 P, Germany) were used on both sides in order to measure the pressure drop, electrolyte temperature, electrolyte flow rate and hydrogen gas generated, respectively. Two magnetic pumps (Iwaki MD-55 RM)

were used. Needle valves were used to control the flow. As the volume of electrolyte was relatively small as compared to stack size, frequent imbalance of the electrolyte is expected. Therefore, auto-rebalancing approach was implemented through hydraulic shunt of two electrolyte tanks at the bottom using a long narrow tube ($\Phi=2$ mm, $L = 2$ m), as shown in Figure 6.5.4. The efficacy of this novel approach is discussed in Section 5.3.1. To eliminate aerial oxidation of V^{2+} , a unique gas bubbler approach was developed. For this, the electrolyte tanks were made seal tight and initially purged sufficiently with nitrogen gas. As negative tank generates hydrogen gas during the charging-discharging cycle, this gas was circulated to both tanks to create an inert atmosphere above the electrolyte on both tanks. The schematic of the gas bubbler system is shown in Figure 6.5.5.

Figure 6.5.5 Schematic of the gas bubbler system to protect the aerial oxidation of V^{2+} .

The stack was first cycled at current densities of 40, 50, 60, 70 and 80 mA cm⁻² (5 cycle each). Afterwards, it was cycled continuously at 80 mA cm⁻² (or 50 A) for 250 cycles. The stack was cycled in a constant current mode with cut-off voltage limit of 1.1 V-1.65 V per cell (or 22 V – 33 V). During operation at 50 A, the nominal power of the stack was 1.3 kW and rated power was 1.5 kW. The cycling test results are shown in Figure 6.5.6 and Figure 6.5.7.

Figure 6.5.6 Short term cycling results at different current densities.

Figure 6.5.7 (a) Coulombic, energy and voltage efficiency, (b) charge/discharge capacity (in Ah) and (c) charge/discharge energy (in Wh).

An EE of $> 80\%$ and VE of $\sim 84\%$ was obtained at a current density of 80 mA cm^{-2} during both short-term and long-term testing. This was one of the target of this PhD research, which is achieved. The CE was slightly below 95% at 40 and 50 mA cm^{-2} , which was increased above 96% and stabilized from 70 and 80 mA cm^{-2} . This fluctuation is attributed to the combine effect of membrane activation and temperature fluctuation during initial cycles. In order to monitor the long-term performance, more than 250 cycles were continuously run at 50 A (i.e. 80 mA cm^{-2}), as can be seen in Figure 6.5.7-a. The results show a stable CE, EE and VE throughout the cycling. Figure 6.5.7-b and 6.5.7-c shows the charge/discharge capacity (in Ah) and charge/discharge energy (in Wh). A stable capacity can be observed, which indicates that the auto-rebalancing approach worked effectively. Without the auto-rebalancing, previous studies on a 3-cell stack showed a sharp capacity decay within few cycles (Chapter 5).

Figure 6.5.8 shows the flow rate and pressure drop plot for first sixteen hours of operation during long-term cycling.

Figure 6.5.8 Pressure drop and flow rate.

The benefit of using IDD channel on the porous electrode was observed on pressure drop. An average pressure of 380 mbar was recorded at an average flow rate of 415 mL min^{-1} per cell. Without IDD channels, in a 3-cell stack of similar

size, an average pressure drop of 640 mbar at an average flow rate of 400 mL min⁻¹ per cell was recorded. This means the pressure drop was reduced by about 40%, which would contribute to a pump power saving of ~9 Watt.

Figure 6.5.9 shows the temperature profile during long-term cycling plotted together with cell voltage.

Figure 6.5.9 Temperature and voltage plot.

The temperature of the electrolyte reached close to 40°C. It was mainly because of continuous cycling at a high current (50 A) and use of relatively low volume of electrolyte. There was no cooling device used in the set-up. The electrolyte temperature reached maximum when the cell was discharged. At full charge, the electrolyte temperature was minimum. It is because of the slightly higher IR drop during discharging as compared to IR drop during charging. The energy loss is dissipated as heat to the electrolyte.

Figure 6.5.10 shows the plot of hydrogen generated during cycling for 10 hours. The stack voltage is also plotted together.

Figure 6.5.10 Hydrogen production during stack cycling.

During continuous cycling at 80 mA cm^{-2} , 30-60 ppm of hydrogen was recorded by the hydrogen sensor. The sensor worked according to the solid oxide fuel cell principle. As per literature, a maximum hydrogen is generated during full charge condition and becomes minimum during discharging. However, the results showed an opposite trend. As the hydrogen generated on the negative tank was transported to the positive tank through a PVC tube and the sensor was mounted at the exit of the gas bubbler connected on the positive tank, a measurement delay is expected. Therefore, the hydrogen trend is slightly lagging behind the stack voltage profile. The excess gas was released through the gas bubbler. The hydrogen at the head space of the tank was maintained at maximum around 60 ppm in long-run cycling tests.

The long-term testing was performed at a high flow rate ($\sim 8 \text{ L/min}$ or 400 mL min^{-1} per cell) because the stack was continuously operated at a high current of 50 A . After long-term testing, an attempt was made to test the performance at different flow rates. To do so, polarization measurements were performed at varied flow rates from 3 L min^{-1} (i.e. 150 mL min^{-1} per cell) up to 8 L min^{-1} (i.e. 400 mL min^{-1} per cell). The polarization routine included: 1 min OCV, 1 min charge, 1 min OCV and 1 min discharge. This routine was repeated with increase in current density from 10 mA cm^{-2} up to 95 mA cm^{-2} . The battery tester was

unable to supply beyond 95 mA cm^{-2} . The polarization curve was plotted by taking the average of last 10 s data. The polarization plot during both charging and discharging is shown in Figure 6.5.11.

Figure 6.5.11 Polarization curve at different flow rates during charging (a) and discharging (b).

A very small improvement on the performance by increasing the flow rate was observed. The maximum voltage difference between lowest flow and highest flow during the polarization measurement at 95 mA cm^{-2} was 160 mV during charging and 207 mV during discharging. In a 20 cell stack, this separation is very small. Therefore, it can be roughly said that even a lowest flow of 3 L min^{-1} was sufficient to run the stack at low current densities.

Organic additives were later added on the electrolyte to operate the stack at higher temperature. The additive was developed by other researchers in the group. The testing of additive on a 1 kW stack was part of the target of this collaboration project, which has also been completed.

Figure 6.5.12 shows the long-term cycling results at 80 mA cm^{-2} after the addition of the additive. In both electrolyte tanks, additive mixture of 0.025% wt PVP + 0.25% wt $\text{NH}_4\text{H}_2\text{PO}_4$ was used. This mixture was stirred for long time in the electrolyte solution before circulating to the stack. With additive, the stack was cycled at an average temperature of $45 \pm 1^\circ \text{C}$.

Figure 6.5.12 Long-term performance at 80 mA cm^{-2} after addition of additives.

Comparing the performance after the addition of additive (Figure 6.5.12) and performance before addition (Figure 6.5.7-a), a drop in EE by $\sim 2\%$ and drop in VE by $\sim 1\%$ was observed, which is expected as addition of PVP could slightly increase the resistance. The efficiencies remained stable during cycling.

6.6 Conclusion

A 20 cell-1 kW stack of VRFB was developed as a part of fulfilling the objective of this PhD research. The stack used all the learnings and improvements made during the multi-parameter tests. The development was made through progressive scale up from a small cell of 20 cm^2 to a 100 cm^2 and finally to a 625 cm^2 size cell and stack. The design of the cells and stacks was improved several times. To reduce the pressure drop and improve the flow distribution, the stack used electrodes with interdigitated flow channels. The stack was tested for more than 500 cycles without any leakage. The performance results showed a stable EE and VE above 80% at a current density of 80 mA cm^{-2} . The capacity remained stable due to the use of auto-rebalancing.

The stack was later delivered to SGL Carbon, Meitingen, Germany for further investigation, as a part of project agreement.

Chapter 7

Conclusion and Future work

This chapter presents the conclusion of this PhD research. The extent to which the targeted objectives are met is addressed. Recommendations for the future work have also been provided. This PhD research developed segmented cell approach and pH tracing test for the study and improvement of flow distribution of electrolyte through the porous media. The local OCV distribution predicted the in-situ flow behavior precisely. The use of interdigitated channels on the porous electrode improved the flow distribution and reduced the pump power consumption significantly. An electrode compression of 25% was found to be optimal for the best performance. The power drop effect was found to be an important problem, which was resulted from the membrane. All the learnings from multi-parameter testing were implemented in the development and testing of a 20 cell- 1 kW stack of VRFB. The various approaches developed in this thesis opened up new research areas such as implication of segmented approach in electrode modification, investigation of power drop effect in different types of membranes, development of a multi-cell stack with a combination of AEM and CEM, etc. These works will help to further improve the performance of existing VRFB technology.

7.1 Conclusion

This PhD research targeted in developing methods and their implementation for improving the flow distribution and reducing various losses to achieve a high and stable performance of VRFB. The ideas and methods developed through the multi-parameters testing were implemented in the developed 1 kW stack. The objectives of the project have been accomplished. The major findings and outcomes of this PhD research are summarized below.

7.1.1 Segmented cell

A new approach of segmenting a flow cell for local potential mapping was introduced. In addition to dividing the BP and current collector, segmentation of a thick porous electrode was demonstrated for the first time. This concept resulted in a higher resolution as compared to the common method of using a segmented collector only - even at a very high stoichiometry of electrolyte. Monitoring the voltage contours during charging, discharging and OCV for various cell operational conditions, a voltage gradient appeared between flow inlet and outlet. This was due to the continuous change of charged species during charging and discharging. Of the greatest interest, the OCV, directly after cessation of current, replicated the status of charged species in the electrode. In addition, the OCV was unaffected by the variation in contact and electrode resistance among segments. Therefore, the OCV distribution was used to predict the in-situ flow behavior at various flow configurations. The finding exhibits that the OCV contour can exactly image the flow pattern in the porous electrode.

An attempt was also made to quantify the flow by converting the local OCV to local SOC. The change in SOC between inlet to outlet of the cell provided an important information on the utilization of the electrolyte through the electrode.

Consequently, a relationship between ΔSOC and flow distribution was established.

7.1.2 pH tracing

As an alternative method to the segmentation of the cell, a simple ex-situ method to perform a qualitative investigation on the flow distribution was developed. This research, for the first time, employed the pH tracing method in the VRFB. Using a 100 cm² half-cell, the pH vs time curve was examined and attempts were made to predict the flow behavior. Later, this study was extended to large area cell of 1 kW size in order to investigate the efficacy of the cell with interdigitated (IDD) channels vs cell without channels.

7.1.3 Flow channels on the porous electrode

Four different electrode designs with flow channels were tested in a VRFB single cell with an active area of 100 cm² and compared to standard electrode (No channel). The results showed that the energy and voltage efficiencies are superior with interdigitated circular poked channel (IDD-CPC) and interdigitated open channels (IDD-OC) for all current densities tested. This was interpreted as resulting from a more uniform flow distribution that gave improved utilization of the reactive surface. The performance results were in good agreement with the results obtained in similar studies [1, 2] made by the use of flow fields on the BPs. The discharge energy was also improved by the use of flow channels, as suggested by the patent literature, again as a consequence of better flow distribution through the electrode. The cell resistivity was measured to be lowest for IDD-CPC and IDD-OC designs. Taking pump losses into account, up to 2.7% and 2.5% improvement in overall energy efficiency could be demonstrated with the use of IDD-OC and IDD-CPC types, respectively. Especially, for the

electrodes with IDD-OC design, the contribution of the pump saving on the improvement in overall energy efficiency was up to 1%.

Polarization measurements at varying flow rates showed that securing the uniform flow distribution of electrolyte, by the use of interdigitated open channels allowed the flow cell to operate at comparatively low flow rates, without significant loss of performance. This provides an opportunity to lower the pumping power further and gives more flexibility to system designers.

The outcome of this study was used in the 1 kW stack development. The IDD-OC channel design was selected, which were milled on the 25 cm x 25 cm felt using CNC milling. The improvement of the IDD-OC channel was further verified using pH tracing test and pressure drop measurement. Finally, all forty felts were structured with IDD-OC channels in a 20 cell stack of 1 kW class. So far known, the developed 1 kW stack is the first stack of its kind assembled with IDD-OC channels on the porous electrode.

7.1.4 Minimizing electrolyte imbalance to reduce the capacity loss

Two novel approaches were tested in order to minimize the electrolyte imbalance, reducing the reversible capacity loss in a VRFB. The two approaches were: i) hydraulic shunt at the bottom of the electrolyte tanks to have continuous rebalancing, and ii) use a combination of AEM and CEM alternately in a stack. Both tests were initially performed in a 2-cell stack of 100 cm² active area per cell. It was found that the auto-rebalancing approach works efficiently, to possess equal level of the electrolyte on both tanks, without loss of capacity and efficiency. It was found that the length and diameter of the shunt tube have to be optimized for each system in order to obtain a best performance. The second approach of using a combination of AEM and CEM also worked effectively. However, it was found that the use of AEM and CEM need to be optimized by

considering the ionic conductivity and water transfer rate of each type of membrane. Therefore, a detail study is necessary before implementation of this approach on the multi cell stack. Nevertheless, the idea of using two types of membrane was experimentally verified in a VRFB for the first time.

The outcome of this study was implemented in the testing of a 1 kW stack. The electrolyte tank was hydraulically shunt to have a constant rebalancing of the electrolyte level. Both energy (in Wh) and capacity (in Ah) could be maintained constant, which exhibited that this method can be implemented in a commercial system to solve the problem of frequently requiring rebalancing.

7.1.5 “Power drop effect” at high current density operation

The research on VRFB is also focused on reducing the resistivity of the stack to operate the stack at high current density in order to obtain high power density. The charging at very high current density near high state of charge (SOC) is still restricted due to the possibility of side reactions at higher voltages (typically above 1.6 V per cell), whilst discharging can be done at much higher current density compared to charging. Therefore, in characterizing the flow cells developed in-house, high current density ($> 100 \text{ mA cm}^{-2}$) operation was tested. A unique feature was recorded during the testing of AEM membrane, which included a sharp fall in discharge voltage near high SOC range that disappeared after few minutes. As such drop in discharge voltage could have a detrimental effect on the battery application, an in-depth analysis of the feature was performed. It was found that the sharp fall in discharge voltage was a result of short time accumulation of V^{5+} at the membrane surface and pores at high SOC. This feature was also recorded for CEM membrane, but less pronounced compared to AEM membrane.

7.1.6 Optimization of electrode compression

The electrode compression plays an important role in determining the Ohmic drop as well as mass transport losses under flow battery operation. Using a 100 cm² single cell, compression of the electrode was varied from 10% to 40%. The results showed that the higher the electrode compression, the better is the electronic contact. However, the electrode utilization might be poor due to the non-uniform electrolyte flow distribution. A high electrode compression also reduces the porosity of the felt, which significantly increases the pressure drop, resulting in increased pump losses. In contrast, a too low compression resulted in poor contact resistance leading to poor voltage and energy efficiencies. Hence, an optimal compression of about 25% was found to be a fair trade-off between contact resistance, and flow distribution and pressure drop.

The outcome of this study was implemented in developing the 1 kW stack. An electrode compression of 25% was maintained.

7.1.7 Development of 1 kW stack

This PhD research was completed with the development of 1 kW VRFB stack as one of the major achievements. The stack was tested for 500 cycles and stable performance was obtained. A target of achieving more than 80% voltage and energy efficiency was accomplished. The configuration of the various components in the stack was optimized through the implementation of improvements made during multi-parameter tests performed on small size cells and stacks.

The final stack was developed through several modifications. Firstly, a 20 cm² and a 100 cm² single cell were developed for finalising the design of the various components. After optimization of the design, a large area (with active area of

625 cm²) single cell and three cell stack were developed. After optimization of the design and performance, finally a 1 kW stack with 20 cells was developed. The design of the flow channels and manifolds on the flow frame were optimized using flow simulation in order to have uniform distribution of electrolyte before entering the porous felt. The design of flow guiding islands were designed such that there will be higher flow resistance to minimize shunt current loss with minimal pressure drop to reduce parasitic losses. As a square geometry of the active area was chosen, porous felts were milled with interdigitated channels to minimize the pressure drop and improve the flow distribution inside the porous electrode further. The compression of the electrode was maintained at 25% and electrodes were treated at 600 °C for 5 hours in air, as concluded from multi-parameters test. For the ease of assembly, modules were built joining the middle flow frames, BP, collars, gaskets, etc. For testing of the stack, a test set-up was also developed. For achieving the stable performance, two novel approaches were used: i) two tanks were hydraulically shunt with a tube in order to automatically rebalance the electrolyte, and ii) a gas bubbler system was developed, employing H₂ produced on the negative tank transferred to the positive side to create an inert environment. Due to the use of a hydraulic shunt, a constant capacity over 250 cycles was obtained. The stack was further tested at 45 °C for 250 cycles with addition of organic additives and showed a stable performance.

7.2 Future work

This PhD research was focused on improving several problem areas in VRFB technology in order to achieve the broader objective of developing commercial size 1 kW stack with novel design of components, optimized cell architecture, and a high (>80% EE @ 80 mA cm⁻²) and stable performance for few hundred cycles. Various new approaches, such as segmented cell, pH tracing, auto-rebalancing, flow channels on the electrode, etc. were explored to improve the

performance. Based on the findings, several aspects are recommended for further studies.

The segmented cell study was found to be a most suitable method for the quantification of the flow distribution during operation of the flow battery. Due to the time limitation, the study was only focused on using a 100 cm² single cell. As the method of segmentation is simple as well as easily scalable to commercial size cells, this study is useful for improving flow channel designs, optimizing electrode compression and flow rate, study of electrode modification, degradation study, etc. in commercial size cells. This study can also be extended for performing local analysis in a commercial size cell and stack.

Out of various types of flow channels, IDD channel performed the best in terms of improving the flow distribution and pressure drop reduction. This study opened up opportunities to further explore different types of channels and optimize the design. Implementing the channel concept on porous electrode is simple and easy on the conventional design than machining the flow fields on the BP.

The pH tracing test was found to be a quick and easy method to screen the flow distribution qualitatively. During this PhD research, the study mainly focussed to compare the cells with and without channels. This method can be further implemented in investigating flow distribution on the stack. Due to time constraint, simulation of pH distribution was not carried out, which could have otherwise contributed to quantifying the flow.

In operation of flow battery, the 'Power drop effect' is a serious problem. In this PhD research, the cause behind the effect was explored using an FAP 450 membrane. This effect should be also investigated in other types of commercial membrane.

The hydraulic shunt for minimizing the capacity loss was found to be a suitable approach. The applicability of this method was tested for 500 cycles. This test can be extended for a few thousand cycles to verify the use in commercial systems. In addition, this test has to be performed at the larger size stack and larger storage tank system, and for optimizing length and diameter of the shunt tube. Similarly, the use of a combination of AEM and CEM was also found to be an effective approach in minimising capacity loss. However, the number and type of AEM and CEM has to be optimized in the future.

References

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ANNEX A: Parameters for flow simulation

Different parameters necessary for the simulation were calculated as follows:

1. Porosity of the felt:

Using the data sheet from SGL Carbon, following values were obtained:

Bulk density= 0.09 g/cc and

Fiber density=1.8 g/cc

Therefore, **Porosity= $1 - (\text{bulk density} / \text{particle density}) = 1 - (0.09 / 1.8) = 0.95$**

2. Permeability at 25% felt compression:

An average value of the permeability was chosen from manufacturer's data sheet for different compression rates.

Figure A.1: Change in permeability with compression rate

Permeability at 0% compression= $1.1 \times 10^{-10} \text{ m}^2$

Permeability at 25% compression= $6.0 \times 10^{-11} \text{ m}^2$

3. Electrolyte Properties:

The density and viscosity of the electrolyte in VRFB cells vary with the concentration of V ions dissolved in H_2SO_4 , concentration of H_2SO_4 , temperature and state of charge. These values are also different between two half-cells in a VRFB cell due to the presence of different charge species and water movement during charging and discharging. For the simulation, an average viscosity value of **0.00498 Pa. s** and density of **1.35 g/cc** was used. The density of the fresh electrolyte was measured experimentally through weighing method of defined volume and viscosity value was measured using viscometer.

Figure A.2 shows the flow frame and porous body.

Figure A.2: Flow frame and porous body showing flow inlet and outlet

4. Inlet velocity:

The stoichiometric flow rate for a single cell is given by Faraday's law as:

$$Q = S * I / (soc * n * M * F)$$

Where,

I = Total current in Ampere
 n = number of electrons per mole of V ion involved =1 (one electron from V^{4+} to V^{5+} , V^{3+} to V^{2+});
 F = Faradays constant = 96485 coulombs;
 soc = state of charge = 1 (from 0% to 100 %, no control of flow rate with respect to SOC);
 M = Molarity of V ion (moles per liter) = 1.6;
 Current density= 80 mA cm⁻²;
 Active area = 100 cm²;
 Therefore, Total current I = 80 mA/cm² * 100 cm² = 8 A
 S = stoichiometric coefficient = around 2-8, depends on the cell design

Therefore, stoichiometric flow rate, Q = 24.894 mL min⁻¹, for maximum value of S =8.

The stoichiometric flow rate is too low compared to the flow rate that is being used in practice for a 100 cm² cell. Therefore, for the comparison of different geometries of the flow frame, a constant flow rate of 120 mL min⁻¹ was used as a default value in the simulation.

Now, calculating the inlet velocity at the flow frame channel,

Inlet cross section of the channel =3.5 mm* 8 mm (channel height * channel width)

Therefore, Inlet velocity = flow rate/cross section area = 0.07143 m s⁻¹

For flow rate comparison, the velocity at different flow rate was calculated similarly.

5. Reynolds number at the flow frame (FF) channel inlet and at the porous felt:

To choose a suitable viscous model, Reynolds number at solid channel and porous felt was calculated as follows:

a. Reynolds number in porous media is,

$$Re = (\rho * v * \delta) / \mu$$

Where,

ρ = density of the fluid = 1350 kg/m³,

v = specific discharge velocity at the porous media = 0.00816 m/s
calculated assuming a porosity of 70 % after compression of felt by 25%. The cross section of the felt is 3.5 mm x 100 mm.

δ = characteristics pore size = 63 microns (obtained by mercury intrusion porosimetry)

μ = viscosity of the fluid = 0.00498 Pa. s

Therefore, Reynolds number in porous felt is, $Re = 0.132 < 1$, flow is laminar.

b. Reynolds number in channel flow is calculated by,

$$Re = (Q * D_h) / (v * A)$$

Where,

Q = volumetric flow rate = 2×10^{-6} m³/s,

A = pipe cross sectional area = 3.5 mm*8 mm = 2.8×10^{-5} m²

v = kinematic viscosity = 3.69×10^{-6} m²/s

D_h = hydraulic diameter of the pipe = $4 * A / P$

Where,

P = wetted perimeter = $2 * (3.5 + 8)$ mm = 0.0239 m

D_h = $4 * A / P = 0.004869565$ m

Therefore, Reynolds number in the channel is, **Re= 94.29** <2300 and the flow is expected to be laminar.

As the flow in both FF channel and porous felt is laminar, a Viscous-Laminar model was used in the simulation set-up.

6. Resistant coefficients in porous flow:

As the flow through the porous electrode is laminar, viscous resistance is dominant. Therefore, the inertial resistance is neglected.

$$\text{Viscous resistance} = 1 / \text{Permeability} = 1.67 \times 10^{10} \text{ m}^{-2}$$

7. Face permeability:

Face permeability is necessary for defining the porous jump in boundary condition for porous body. Face permeability is calculated by:

$$\text{Face permeability} = \text{permeability} / \text{cross section of the porous media}$$

$$\text{Cross section of the porous media} = 3.5 \text{ mm} \times 100 \text{ mm}$$

$$\text{Therefore, Face permeability} = 1.714 \times 10^{-07} \text{ m}^2$$

8. Pressure drop through the porous electrode:

The solver in Ansys fluent calculates the pressure distribution; however, pressure drop between inlet and outlet can be manually calculated by using Darcy's law assuming laminar flow in the porous media. This was helpful to compare the pressure drop calculated by commercial software.

From Darcy's Law,

$$\frac{dP}{L} = (Q * \mu) / (k * A)$$

Where,

$$Q = \text{total discharge} = 2 \times 10^{-6} \text{ m}^3/\text{s},$$

$$K = \text{intrinsic permeability} = 6 \times 10^{-11} \text{ m}^2,$$

$$\mu = \text{viscosity} = 0.00498 \text{ Pa. s},$$

$$A = \text{cross sectional area to flow} = 0.00035 \text{ m}^2,$$

$$\text{Therefore, } dP/L = 7.8925 \text{ bar/m}$$

$$\text{Distance between electrode inflow and outflow} = 100 \text{ mm}$$

Therefore, **Pressure drop (dP) = 0.46959 bar = 469.59 mbar**

Now, the information regarding geometry, mesh, boundary conditions and convergence of the result are also discussed briefly.

Geometry: The geometry of the flow frame and porous body was created using Design Modeler in Ansys Workbench. Three surfaces were generated separately for inlet body, porous body and outlet body.

Mesh: Triangular type meshes were created with maximum face size of $8.8 \times 10^{-4} \text{ m}^2$, minimum face size of $5.94 \times 10^{-5} \text{ m}^2$ and total number of mesh element used were 36612.

Boundary conditions: Three boundary conditions for inlet, outlet, wall and porous zone were used.

Inlet zone	:	velocity inlet	-	velocity magnitude in m/s
Porous zone	:	porous-jump	-	Face permeability in m^2
			-	Porous medium thickness in mm = 3.5 mm
			-	Pressure-jump coefficient in $\text{m}^{-1} = 0$ in viscous flow
Outlet zone	:	pressure outlet	-	Gauge Pressure in Pa = 0 Pa
Wall	:	No slip condition, stationary wall		

Convergence: To confirm the convergence of the solution after each simulation, residuals and mass flow at the outlet from the flow frame were monitored. Monitoring the mass flow at outlet, sufficient number of iterations was provided to confirm the convergence at all the time.

Grid independency: To confirm the results to be independent from the selection of the grids; the size and type of the grids were changed for one case and the results were compared. The change in grid size and type did not affect the results.

ANNEX B: List of all components used in the stack and drawing of components used in 1 kW stack

Table 1 summarizes the list of components used in the stack.

Table 1. List of components used in the 1 kW stack

SN	Name of component	No of units required	Material	Supplier	Remarks
1	End plate	2	Stainless steel	Local workshop (LW), Singapore	
2	Insulator plate	2	PVC	LW, Singapore	
3	Copper collector	2	Copper	LW, Singapore	
4	End flow frame	2	PVC	LW, Singpaore	
5	Middle flow frame	38	PVC	LW, Singapore	
6	Inlay	80	PVC	LW, Singapore	
7	Collar for end flow frame	4	PVC	LW, Singpaore	
8	Collar for middle flow frame	76	PVC	LW, Singapore	
9	Nozzle	4	PVC	LW, Singapore	
10	Guide pin	2	PVC	LW, Singpaore	
11	Electrode	40	GFD 4.6 EA, thermally treated in air at 600 °C for 5 hours	SGL Carbon, Germany	-Size : (25 cm x 25 cm x 4.6 mm) -IDD channels

					milled on the felt
12	Bipolar plate	21	PV 15	SGL Carbon, USA	Size: (30 cm x 30 cm x 0.6 mm)
13	Membrane	20	FAP 450	Fumatech GmbH, Germany	Size: (35 cm x 35 cm)
14	Nut and bolts, spring wasser	16	-	Local hardware, Singapore	M10 SS bolts, both side open, full thread, 30 cm long
15	Gasket for end flow frame	2	Silicone sheet	Local hardware, Singapore	Self cut using cutting die
16	Gasket for middle flow frame	38	Silicone sheet	Local hardware, Singapore	Self cut using cutting die
16	O- ring for collar (end frame)	4	Rubber	Local hardware, Singpaore	21 mm ID, $\Phi = 3$ mm
17	O-ring for nozzle	4	Rubber	Local hardware, Singapore	20 mm ID, $\Phi = 2$ mm
18	Silicone glue + pvc cement	1	-	Local shop, Singpaore	PVC cement diluted with acetone to increase the curing time

Technical drawing of all the components used in the stack are given. All dimensions are in mm.