

**NUMERICAL STUDY ON ENGINEERING
ASPECT OF THE CELL GEOMETRIES AND
FLOW CHANNEL DESIGN OF VANADIUM
REDOX FLOW BATTERY (V-RFB)**

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GEOMETRIES AND FLOW CHANNEL DESIGN OF VANADIUM REDOX
FLOW BATTERY
(V-RFB)



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Thesis submitted in fulfillment of the requirements
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ABSTRAK

Tesis ini membentangkan ciri-ciri hidrodinamika Vanadium redox battery teralir (V-RFB) dengan menggunakan model dinamik cecair pengkomputeran 3D (CFD) untuk mengkaji daya pam (penggunaan tenaga pam) dan pengagihan aliran elektrolit yang diperlukan dalam sel. Kuasa pengepaman dan aliran elektrolit yang sekata merupakan diantara faktor yang mempengaruhi prestasi sel V-RFB. Antara lainnya, CFD dikenali sebagai salah satu cara untuk mengkaji ciri-ciri hidrodinamika V-RFB. Dalam tesis ini, tiga geometri sel berbeza dari sel V-RFB, iaitu reka bentuk sel persegi, rombus dan bulat dikaji pada tiga kes yang berlainan iaitu tiada saluran (kosong) saluran, saluran selari dan saluran serpentin. Selain itu, kerja telah diperluaskan dengan timbunan modular 100 cm^2 V-RFB. Timbunan sel telah dibangunkan dan diuji untuk memerhatikan kuasa pam dalam timbunan pada tiga reka bentuk yang secara langsung berkait dengan prestasi sel berkenaan dengan pengagihan kuasa dan kehilangan kuasa. Berdasarkan penemuan ini, sel mempamerkan ciri-ciri yang berbeza di bawah V-RFB sel geometri berlainan tanpa penggunaan saluran aliran. Sebaliknya, berdasarkan skala geometri sel, hubungan antara kuasa pam dan geometri sel untuk 100 cm^2 V-RFB telah dibangunkan. Pengagihan aliran optimum dalam sel tanpa saluran aliran bendalir telah direkodkan; penggunaan pam tertinggi dan terendah masing-masing pada 25.6% dan 18.4%. Pengurangan kerugian kuasa sebanyak 53% telah dicatatkan dengan penggunaan saluran aliran selari yang digunakan untuk V-RFB. Hubungan berkala diperhatikan untuk modular V-RFB sebagai hasil penambahan sel dan berpotensi untuk analisa yang akan datang pada lanjutan ke sel-n seterusnya. Kerja-kerja selanjutnya dikemukakan untuk kajian masa depan dalam kajian geometri V-RFB.



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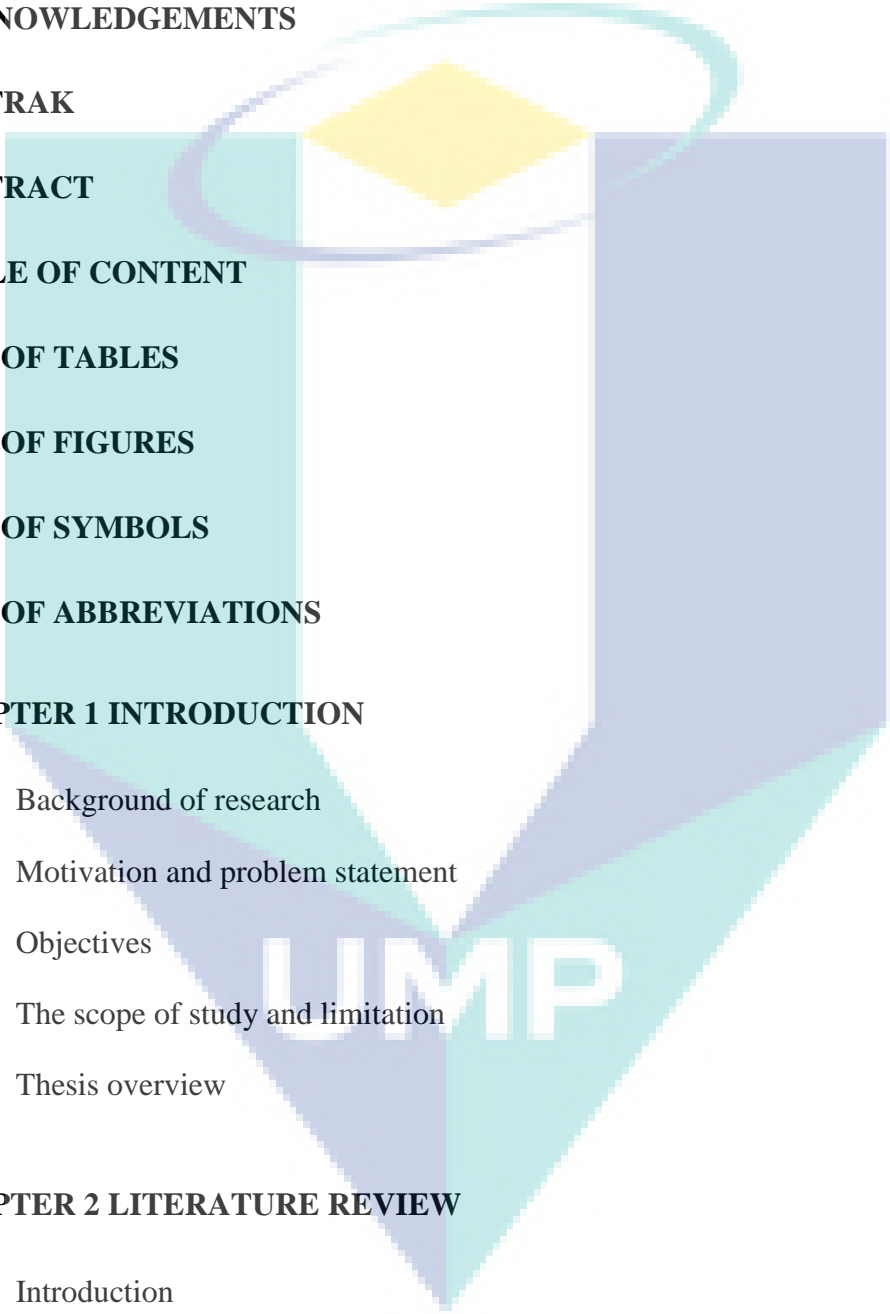
ABSTRACT

This thesis presents the hydrodynamics behavior of the Vanadium redox flow battery (V-RFB) by using 3D computational fluid dynamics (CFD) models to study the pump power (pump energy consumption) and electrolyte flow distribution required within the cell. Pumping power and uniformity electrolyte flow are known as among the factors affecting a V-RFB cell performance. Among others, CFD is recognized as one of methods to study hydrodynamic characteristics of V-RFB. In this thesis, three different cell geometries of V-RFB cell, namely square-, rhombus- and circular cell designs are evaluated at three different cases i.e. no flow (plain) channel, parallel channel and serpentine channel. Furthermore, the work has been extended in modular stack of 100 cm² of V-RFB. The stack has been developed and tested to observe the pump power within the stack in the three designs which directly related to performance of the cell with respect to power distribution and power losses. Based on the findings, the cell exhibits different characteristics under different geometries of V-RFB cell at no flow channel application. Conversely, based on the scaling up of the cell geometry, the relationship between pump power and cell geometry for 100 cm² of V-RFB has been developed. Optimum flow distribution within the cells without fluid flow channels were recorded; highest and lowest pump consumption at 25.6% and 18.4% respectively. Extended reduction of power losses by 53 % were recorded as parallel flow channels was applied to the V-RFB. Proportionate correlations were observed for modular V-RFB as a result of scaling up of the cell and potential for further analysis of extension to the nth-cell. Further works are presented for future research in geometry study of V-RFB.

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LIST OF SYMBOLS

A_{ec}	Area of electrode with distribution channel, mm^2
K_{ck}	Carman kozeny-constant
ρ	Density of electrode, kg/m^3
μ	Dynamic viscosity, kg/ms
E^0	Equilibrium potential
F	Faraday constant
ν	Kinematic viscosity, m^2/s
L_{ec}	Length of flow channel, mm
V_{in}	Mean Velocity, m/s
d_f	Mean fibre diameter, μm
M	Molar mass of reactant, cm/s
ε	Porosity of electrode, ι
ΔP_a	Pressure drop, KPa
K	Permeability of porous media
Re	Reynolds number
A_v	Specific surface area, mm
θ	Thickness of electrode, mm
C	Vanadium concentration, mol/m^3
Q	Volumetric flow rates, cm^3s^{-1}

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LIST OF ABBREVIATIONS



BES	Battery Energy Storage
CAES	Compressed Air Energy Storage
CFB	Circular Flow Battery
CFD	Computational Fluid Dynamics
DC	Direct Current
ECESS	Electrochemical Energy Storage System
EESS	Electrical Energy Storage System
EV	Electric Vehicle
Fe-Cr	Iron Chromium
FESS	Flywheel Energy Storage System
HEV	Hydrogen Evolution Reaction
MESS	Mechanical Energy Storage System
PHES	Pumped Hydro Energy Storage
RES	Renewable Energy
RFB	Redox Flow Battery
SHE	Standard Hydrogen Electrode
SIMPLE	Semi Implicit Method of Pressure-Linked Equation
SMES	Superconducting Magnetic Energy Storage
SOC	State of Charge
UNSW	University of New South Wales
V-RFB	Vanadium Redox Flow Battery
VRLA	Valve Regulated Lead Acid

CHAPTER 1

INTRODUCTION

1.1 Background of research

A large volume of publications have indicated and reported that renewable energy sources are alternative technologies to replace or mark down dependence on fossil fuels, crude oil, natural gas, and coal sources, which currently are the main resources for electric power systems and utility systems in the world (Denholm, Ela, Kirby, & Milligan, 2010; Haralambopoulos & Polatidis, 2003). These renewable energy sources are becoming more prevalent because of the disadvantages of the primary sources of energy, especially on the environment (Duncan, 1988; Pehnt, 2006). So far, implementing renewable energy technologies has successfully minimised greenhouse gas emissions; these technologies are also environmentally friendly (Ipsakis, Voutetakis, Seferlis, Stergiopoulos, & Elmasides, 2009). However, a number of studies have found that these renewable energy sources need a backup storage due to certain limitation factors which are their intermittence and unreliability, which give a huge problem for a smooth utility system, and demand for electricity stabilisation (Beccali, Cellura, & Mistretta, 2003). Because of these reasons, an energy storage technology has been introduced to address the limitations of renewable energy source (Guarnieri, Mattavelli, Petrone, & Spagnuolo, 1932).

Studies have found that energy storage is significant and is a potential solution to stabilise load level and strengthen the power network. There are various types of energy storage that transfer and distribute energy, such as compressed air energy storage (CAES), flywheel energy storage (FES), pumped hydro energy storage (PHES), superconducting magnetic energy storage (SMES), and battery energy storage (BES) (Mahlia, Saktisahdan, Jannifar, Hasan, & Matseelar, 2014). There are many possible

techniques or types of storage in this world, but this work focuses on one of the battery energy storage technologies. Among various battery energy storage technologies, vanadium redox flow battery (V-RFB) offers promising advantages because of its supreme features including effective and simple operation, capability of high power independent of energy and power capacities, fast response and recharging contenders, excellent chemical stability that shows an extremely long-round-trip cycle, operability at room temperature, long discharge times exhibited for highly reversible redox kinetics, suitable for large-scale applications, and reasonable and controlled maintenance cost compared to conventional battery (Miyake & Tokuda, 2001; Park, Jeon, Ryu, & Hwang, 2017). More attention has been given on V-RFB rather than other chemical batteries because V-RFB has unique features which consist of decoupled energy storage and power component. These features give V RFB an independent control of capacity and power and are attractive for optimisation of power and energy in Electric Vehicle (EV) applications (Rusllim Mohammad, Sharkh, & Walsh, 2010). In addition, V-RFB employs the same element in both the positive and negative half-cells, so it does not affect battery capacity as the problem of cross-contamination of ions is avoided.

In the past 20 years, V-RFB has been one of the major projects for commercialisation and industrialisation. This flow battery has been studied since the 1970s, and early development activities continued into the 1980s until now. The V-RFB system was pioneered by Skyllas-Kazacos and her team at University of New South Wales (UNSW) and has been developed by Sumitomo Electric Industries (SEI, OSAKA, JAPAN) with 28 years of V-RFB development experience. Figure 1.1 shows a concept diagram for the V-RFB configuration. The flow battery consists of two electrochemical half-cells (anode and cathode parts) separated by ion exchange membrane. A pump is used to circulate electrolyte through the cell stack. Most of the research and development are focused on the active material (P. Leung et al., 2016), design installation and cell configuration (Blanc, Member, & Rufer, 2008), improving poor kinetic reaction conductivity (A. C. Khor et al., 2016), redox couples (P. K. Leung, Mohamed, Shah, Xu, & Conde-duran, 2015), and battery characterisation (Mohamed, Leung, & Sulaiman, 2015a). Figure 1.2 depicts the time frame of flow battery development which was reviewed extensively by Skyllas-Kazacos and her team (Rychcik & Skyllas-Kazacos, 1988) up to 2000s and later continued by Rahman

(Rahman & Skyllas-Kazacos, 2009) and more detail discussion on 3D V-RFB modelling and engineering aspect reviewed by Yin (Yin, Gao, Guo, & Tang, 2014) and Arenas (Arenas, León, & Walsh, 2017).

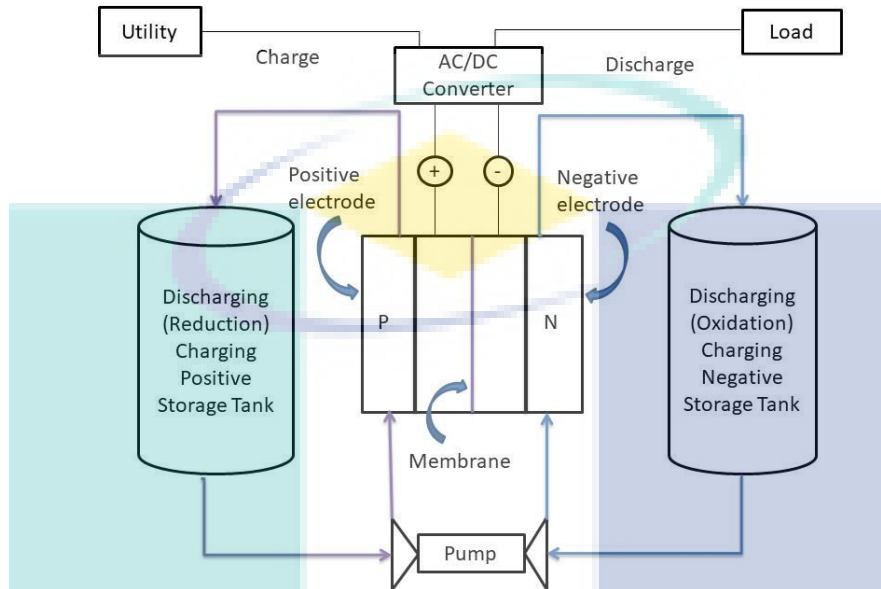


Figure 1.1 V-RFB configuration

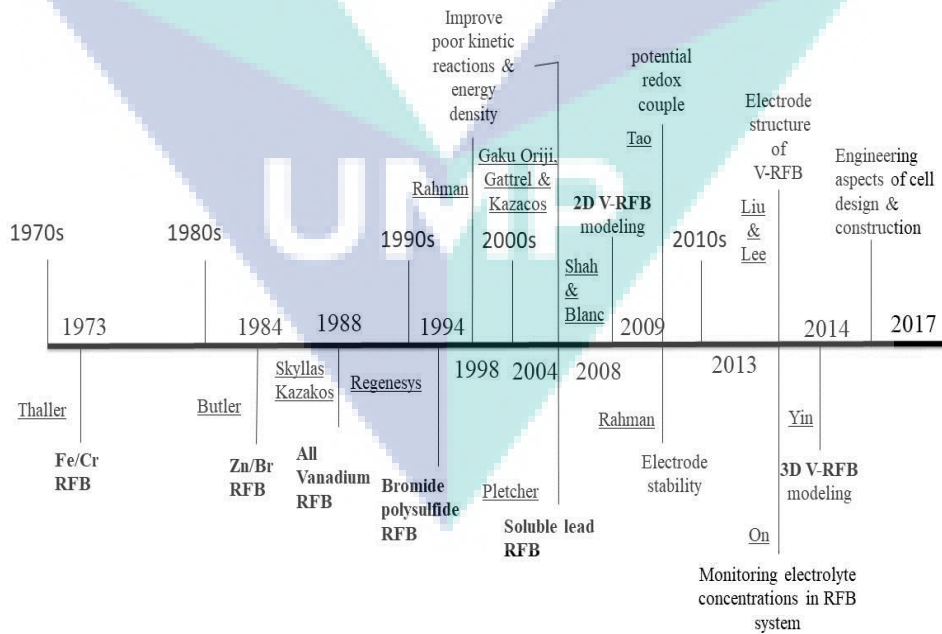


Figure 1.2 Time-line for development RFB (not limited to)

1.2 Motivation and problem statement

Understanding and developing (V-RFB) with high performance are of utmost importance for commercialisation of large-scale installations and efficient power grids. Thus, it is important to find ways for the enhancement and improvement of V-RFB system performances. It should be noted, however, that previous studies that has been carried out since pointed out by Skyllas Kazacos and co. (Rychcik & Skyllas-Kazacos, 1988), the case of information related to cell and system design characterising are limited. Early survey indicated that cell and system design for V-RFB has not been given great attention by the researchers in the past. Therefore, there are issues in the technology that needs to be addressed.

So far, however, there have been research studies and analysis presented in an experimental characterisation of a V-RFB, but all the experimental work has consumed a long hour experiment procedures and consumed high cost with limited work-piece material for testing studies. Therefore, simulation model for V-RFB is carried out to understand the system behaviour with consumed less hour and cost. Modelling is an important tool to reduce the burden of long hour laboratory and cost and represent a true description of a hydrodynamics or natural phenomenon in the system. In addition, modelling is useful for simplifying a complex system and making it easier for further analysis of the system.

Mohamed et al. (Mohamed, Sharkh, Ahmad, Seman, & Walsh, 2012) highlighted that V-RFB has been attracted by many researches; some are under field testing and demonstration stage, but information on cell construction, characterization and overall systems under study, etc. are still limited. Furthermore, the most critical part in V-RFB system is the construction of the cell; hence, deserve the most attention in analysis and manufacturing. Even though much research has been carried on V-RFB system, it should be noted that all previous studies of the use cell geometries for V-RFB with the channel and several patents, especially focusing on different designs, have limited scientific publication.

Due to limited references available from the literature, numerous detailed investigations have been conducted to understand the effect of different types of channel to improve the overall battery performance (Bhattarai et al., 2017).

Furthermore, in-depth information related to cell design system is limited (Cervantes-Alcala & Miranda-Hernandez, 2018) and more focus is given on flow field design and position of inlet/outlet while maintaining one-cell geometry design. Thus, this limitation was the motivation behind the present study to focus and study the flow channel design with different cell geometries of V-RFB.

V-RFB is an interesting choice as one of the energy storage systems for automotive applications due to its supreme features that offer a green, safe, and flexible operation that can be scaled independently of power and energy, which makes it suitable for electric vehicles (Weber et al., 2011). Shah et al. (Shah, Al-Fetlawi, & Walsh, 2010) pointed out that several challenges remain in optimising and improving of current V-RFB design, particularly with respect to scale-up. Studies found that scale-up progress may lead to an efficient and cheaper device commercialisation; also, scale-up work is important for flow cell engineering technologies (Arenas et al., 2017). Scale-up may be performed by parametric studies (current density, electrolyte flow rate, linear velocity, and electrode size), modelling, etc., and this scale-up effort enables researchers to better understand the complex work and relationship between performances. There are a number of studies that estimated the size and performance of a series of scaled-up electric vehicles that use V-RFB (Rusllim Mohammad et al., 2010). However, these case studies did not provide enough numerical investigation or experimental work to support the scaled-up size result. Therefore, another motivation for this study is to study the scaling-up for V-RFB system in terms of parametric studies.

This study focuses on V-RFB system particularly on the design, construction, and cell features through modelling of the V-RFB systems. The analysis of the results obtained through modelling and simulation could lead toward a better understanding of the hydrodynamics aspect that may influence and affect the performance of the V-RFB system. Information gathered through modelling could provide a relationship between cell features or design of V-RFB with parametric studies (flow distribution in cell and energy pumping consumption) and cell performance which would be useful to improve the design of the battery and provide data for experimental analysis.

1.3 Objectives

The aim of the present work is to numerically investigate an important factor in determining battery performance. Therefore, the main objectives of this project are given as follows:

- I. To design battery cell geometries and flow channel for V-RFB on different shaped.
- II. To design a modular stack of V-RFB based on different cell geometries.

1.4 The scope of study and limitation

The scope of study and limitations of the research are as follows:

- I. This study investigates the three-dimensional model of a cell unit in V-RFB system, focusing on the relationship between the constructions of the cell and different modes of operation. This study is based on 100 cm² unit of V-RFB for modelling. The same size of battery is available at the lab. Therefore, that battery can be used for experimental work in the future project to validate the result. The design and development of a modular stack of V-RFB cell are also considered in this study. Modular stack model that connected in series were developed for scaled-up studies for better understanding of the complex works and relationship between performances.
- II. The simulation and modelling of V-RFB are evaluated with different V-RFB geometries under three cases which is plain (no flow channel), parallel, and serpentine, at flow rates of 5 - 30 cm³s⁻¹. The controlled flow rates parameter is use in the range as stated above. 5 cm³s⁻¹ is shown as laminar flow, whereas 10, 15, 20, 25 and 30 cm³s⁻¹ present as turbulent flow. These studies are operating in laminar and turbulence flow at the cell geometries that in practise for non-ideal condition. Other parameters such as temperature, current densities and performance of cell laboratory unit of V-RFB at voltage, coulombic, and energy efficiency are not calculated and considered because these studies are focusing in analysing the hydrodynamic behaviour and natural phenomenon inside the V-RFB cells.

- III. The electrical circuit modelling and electrical characteristics development are out of scope for this study. The primary aim for V-RFB modelling analysis is to capture the hydrodynamics trends within the V-RFB cell geometries by representing in terms of pump power and electrolyte flow distribution on single unit and modular stack system.
- IV. Analysis of results and performance of V-RFB is based on pressure drop in the cell, pumping power, and flow distribution of the entire surface of the electrode.

1.5 Thesis overview

Chapter 1 is about background of the research and study objectives. This chapter describes an overview of energy storage technologies and V-RFB. The first chapter explains the background of the research project to meet the objectives. The problem statement and scope of the project are discussed in detail.

Chapter 2 provides a literature review; this study is based on a literature review of previous research that provides information on related studies. The literature review includes the electrochemical process, novel electrode material, the characterisation, and the engineering aspect of battery design and construction.

Chapter 3 presents brief methodologies. The methodology section describes 3-D Computational Fluid Dynamics (CFD) simulation works performed by using a commercial software package, ANSYS WORKBENCH 16.2. Numerical and theoretical works are stated in this chapter.

Chapter 4 This chapter presents the numerical and calculation results and detailed discussion to answer the objectives of the present study. The unit cell performances with respect to pump power and flow distribution within the cell under different operating parameters.

Chapter 5 This final chapter concludes the entire work for the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The primary sources of energy like crude oil, natural gas, coal, nuclear, and hydroelectric are the main supplies for energy demand of all the population in the world. Fossil fuels are one of the energy sources that are used to generate electricity. However, the burning of fossil fuels leads to global warming due to the emission of CO₂ (Duncan, 1988), which has a damaging impact on the climate and the environment. Previous researches proved that the burning of fossil fuel has a major impact on global warming. Due of this, renewable energy sources have been introduced to meet the power demand and supply energy for future development; these sources have less environmental effects and reduce the dependency on fossil fuels (Denholm et al., 2010; Wei, Zhao, Zeng, Zhou, & Zeng, 2016).

The primary goal of renewable energy sources (RES) is to develop an alternative power supply. Generally, RES is from natural resources, such as wind and solar energy that have the potential to generate electricity for various industrial and domestic applications. However, RES is still unable to meet the electrical demands as the energy is meant for short-term storage and relies on the weather to work efficiently. Thus, there would always be on intermittent output because sources like the wind and the sun are unpredictable. To control the supply-demand imbalance, the energy storage system is needed to store the energy and give back the power at certain times during high power demands. Findings of energy storage technologies have provided insights for the development of large scale storage which is more efficient and has a longer lifespan (Haralambopoulos & Polatidis, 2003; Ipsakis et al., 2009; Painuly, 2001).

In the mid-1970s, redox flow batteries were developed with promising features that are suitable for stationary and automotive applications. Among various redox flow battery technologies, V-RFB has shown to be promising because of its unique features such as effective and simple operation (Kear, Shah, & Walsh, 2011), capability of decoupling high power and energy (Rusllim Mohammad et al., 2010), operationally at room temperature (Alotto, Guarnieri, & Moro, 2014), fast response, and recharging contenders (Verma, Gambhir, & Goyal, 2013). Furthermore, it comprises excellent chemical stability that shows an extremely long-round-trip cycle (Weber et al., 2011), has long discharge times, good modular design (Fisher, Ieee, Anstey, Viswanathan, & Perry, 2014) and exhibits for highly reversible redox kinetics (Rychcik & Skyllas-Kazacos, 1988). These features enable the technology for large-scale applications with theoretically reasonable and controlled maintenance cost compared to the conventional battery (Jyothi Latha & Jayanti, 2014a). Afterwards, the V-RFB was successfully developed by the company Sumitomo Electric Industries from Osaka, Japan (Miyake & Tokuda, 2001).

As the name implies, flow battery is an electrochemical cell that produces an electrical output through electrochemical reactions of two electrolytes that flow within the cell. Past studies have focused on improving poor kinetic reaction conductivity (Mohammadi, 1995), redox couples (Mohamed, Leung, & Sulaiman, 2015b), electrodes (P. Leung et al., 2016), and battery characterisation (Mohamed, Ahmad, Seman, Razali, & Najib, 2013). More recent works focused on improving mass transport issues in a redox flow battery. Mass flow plays an important role in the battery to perform well (Parasuraman, Lim, Menictas, & Skyllas-Kazacos, 2013; Zhang, Zhao, Gao, & Zhao, 2012). Thus far, (a C. Khor, Mohamed, Sulaiman, & Daud, 2014; P. Leung et al., 2016) have brought up and systematically discussed the electrode porosity (electroactive sites) that acts as a key in V-RFB systems where the electrochemical reaction and mass transportation reaction take place. Numerous investigations have been conducted, but very few of them focused on RFB transport phenomena such as hydrodynamics factor (pressure drop and flow distribution) in the battery cell. So, it is necessary to do in-depth research on electrochemical cell geometry that influences the flow and mass distribution, which would bring significant improvements to RFB performances.

A previous study on the experimental investigation on a unit cell of V-RFB estimated the size and performances of a V-RFB system for a series of electric vehicles and compared them to other conventional batteries (Rusllim Mohammad et al., 2010). Battery data is available, but there is no evident based on the numerical investigation to support the scaled-up size result. Hence, it is essential to perform a battery modelling and numerical investigation for scaled-up work in terms of parametric studies to get an accurate and fast result with less cost and laboratory work period.

The next section overviews the technology of energy storage while bringing V-RFB into perspective. Subsequently, the section focuses on the RFB system, particularly V-RFB as the focus of the study.

2.2 Various energy storage technologies

Energy storage is required to store electrical energy during times of low demand at low energy cost and for the surplus energy generated from intermittent energy sources of RES (Alamri & Alamri, 2009). The demand for electricity varies emergently; there may be days or seasons where there is maximum demand of supply which may last for a few hours each year. This leads to the inefficient power supply, over-designed power storage and supply, and expensive costs (D. You, Zhang, & Chen, 2009). So far, energy storage plays an important role in power system operation, control, and management. Efficient energy storage can add the following benefits to power utilities by reducing energy consumption, cost and overcome energy shortages problem (Fisher et al., 2014). Generally, energy storage technologies are categorised into three main types, which are electrical, mechanical, and electrochemical energy storage systems. The comparison among these three types of energy storage in terms of applications, capital cost, life time and impact on environment is presented. Generally, energy storage technologies are categorised into three main types, which are Electrical Energy Storage System (EESS), Mechanical Energy Storage System (MESS), and Electrochemical Energy Storage Systems (ECESS).

EESS functions as backup energy to supply load demands from new energy sources as another way to replace conventional and harmful energy production. Electrical storage is important and has been introduced to match the output and requirement power demands (Hadjipaschalis, Poullikkas, & Efthimiou, 2009). EESS

balances between the load demand and power supply, thus, it is beneficial to produce a stable power network operation. There are several categories of EESS which can be classified to super-capacitor and superconducting magnetic energy storage (SMES) based on their storage durations and their operational system configurations (Luo, Wang, Dooner, & Clarke, 2015).

Super-capacitor, also known as an ultra-capacitor, has a dielectric to separate charge by using a molecule-thin layer of the electrolyte with a high surface area of the activated capacitor. Meanwhile, SMES contains three main parts, which are superconducting coil unit, power conditioning subsystem and vacuum systems. SMES system offers standard electrical energy form by generating from direct current (DC) in the superconducting coil, through the magnetic field (Conway, 1991). However, both of this system is suitable as an energy storage backup for a short time application with required high capital cost in construction and material, high daily self-discharge, lead to loss much of energy and give negative environmental impact (Dekka et al., 2015). Thus, It was found that this EESS technologies system is not intended to replace, but rather to compliment the other energy storage system (Blanc et al., 2008) .

Electricity can also be stored in mechanical energy form to be converted back to electricity when needed. MESS can be categorised as potential energy storage, compressed air energy storage (CAES), pumped hydroelectric energy storage (PHES) for large-scale batteries, and kinetic energy storage (flywheels). CAES is one of the available technologies that provide large energy storage up to 100 MW (H. Chen, Ngoc, Yang, Tan, & Li, 2009). CAES system works on the basis of gas turbine technology that consists of generator/motor. Even tough CAES system capable deliver large scale energy storage, there has been discussion about major barrier and challenges with this storage. This system is not an independent system, cannot be associated with other types of power plants and the system is limited to the location and it is used more at rock mines and depleted gas fields (Dekka et al., 2015). Conversely, PHES is one very important technology in the generation of electricity and has been installed over 300 plants worldwide (Deane, Ó Gallachóir, & McKeogh, 2010), but PHES exhibits disadvantages , the system faces difficulties in terms of bad environmental impact on water quality and aquatic habitats, scarcity of available sites and high capital cost (C. J. Yang & Jackson, 2011).

Meanwhile, flywheels have been designed for storing and retrieving energy by stores the kinetic energy in a rotating mass. In principle, flywheels devices consist of a vacuum enclosure, flywheel, generator, and shaft (Alamri & Alamri, 2009). However, the weaknesses of this system come from the friction with the surrounding air that leads to loss of energy stored and the lifetime depending on the bearing used (Mahlia et al., 2014).

The principle of the ECESS is storing electrical energy in the form of chemical energy. It is one of the oldest energy storage technologies that are able to meet user's demands (Prifti, Parasuraman, Winardi, Lim, & Skyllas-Kazacos, 2012). Its main advantages are modular in design, independent from fossil fuel, may store energy on the medium to large scale, flexibility and safety advantages over others energy sources (P. Leung et al., 2012; Nair & Garimella, 2010), making it very attractive for various application. ECESS can be categorised as conventional lead acid, nickel-cadmium, lithium ion, fuel cells and flow batteries (Manders, Lam, & Peters, 1996; Verma et al., 2013).

Lead-acid battery is the earliest battery and has been long established in battery technologies world. It has been used for electrical energy storage and delivery for a long time (Mahlia et al., 2014). Lead-acid battery was invented in 1859 and became the solution to the large-scale energy storage problem. The advantages of lead-acid batteries are that the system is operated at a low cost, high reliability and efficiencies and has fast electrochemical reaction kinetics (D. Chen, Hickner, Agar, & Kumbur, 2013). Although lead-acid batteries exhibit many advantages, the battery system still needs review and improvement because the manufacture of the battery uses heavy metal components which are highly toxic and hazardous and may cause damaging environmental impacts (Mahlia et al., 2014). Other reasons why lead-acid battery is not favourable in large-scale applications are its limited lifespan, practical difficulties in construction, poor performance at low and high ambient temperature, and low battery operational lifetime (Hadjipaschalis et al., 2009; Nair & Garimella, 2010). The lead-acid battery system still requires more improvement to be a better system for large-scale applications.

One of the most significant advances in the electronic market such as mobile electronics and computer applications that addressed the power and energy demand from consumer application is the lithium-ion battery system. Li-ion batteries can

potentially be used for large-scale energy storage like electric vehicles in the near future (Väyrynen & Salminen, 2012). Lithium-ion batteries offer some of the greatest advantages and which make them one of the promising storage technologies. Lithium-ion batteries have a storage efficiency of almost 100%, making Li-ion batteries an appealing technology for future development and optimisation. However, it should be noted that Li-ion battery technologies have some major issues which are safety, cost (Ritchie & Howard, 2006), wide operational temperature range, and material availability (Scrosati & Garche, 2010). The top issues about safety concerns are regarding the elimination of metallic lithium plating that may lead to overcharging by proposing internal protection circuit or special circuitry to protect the battery system. This may cause high cost, making it one of the major disadvantages of the battery system (Divya & Østergaard, 2009).

With design amenability, high density, robust reliability, fast response time, and low maintenance requirements and were used for many purposes and appliances such as emergency lighting, portable devices, and mobile telephones (H. Chen et al., 2009), Nickel-based batteries are one of the batteries that are suitable for power utility applications and as backup energy for intermittent renewable energy. Rechargeable nickel batteries are ranked as secondary batteries and inclusive of active material and the most developed and focused on by many researchers because they offer tremendous advantages to meet the needs and demands, especially in electric vehicles (Shukla, Venugopalan, & Hariprakash, 2001). Although Nickel batteries have been widely used in the past, unfortunately, the materials used in these batteries pose hazardous effects because it's consumed a heavy metal and is extremely toxic. It causes an environmental hazard and can harm the surroundings (Zhu, Zhang, Li, & Cai, 2003). In addition, the manufacture of Nickel batteries requires a high cost, making it challenging for stationary markets. As a result, a feasible alternative from other battery technologies are being studied to meet the energy demand (Xie et al., 2013).

The storage of hydrogen as chemical fuel that feed in the fuel cell has converted the chemical energy into electrical energy. The reactants of fuel cell is stored externally to the cell are consumed in producing an electricity. Fuel cell energy systems are popular as energy production systems due to the fact as a clean, environmentally friendly and comprise of high power (Nair & Garimella, 2010). In addition, these fuel

cells, using hydrogen as fuel, became a possibility to replace conventional lead batteries. Fuel cell operates by using a platinum electrode immersed in acid and performs much like engine-generator sets (P. Leung et al., 2012; Verma et al., 2013). Fuel cells has high energy density, has independent system charge rate and storage capacity and ability to implement systems over a wide range of scales. Nevertheless, fuel cells suffers from critical safety issues, this hydrogen preferred to store it in any useful form by mechanically changes its pressure and temperature by compressing it, otherwise by store it chemically bonding the hydrogen with different atom molecules, but all this method consumes expensive cost at the present time and relatively suffer with low round-trip efficiency (Schaber, Mazza, & Hammerschlag, 2004).

Meanwhile, RFB provide a promising technology to store the energy, to stabilise and counterbalance power generation and power consumption and this flow battery application is supplementary to transportation system (electric vehicles) (Ponce de León, Frías-Ferrer, González-García, Szánto, & Walsh, 2006). Redox flow battery has many superior, unique, and good features compared to other battery storage systems. Many studies have indicated the potential of redox flow battery for wide and gigantic amounts of electrical energy reserve and this energy storage has been considered for intermittent high power backup on megawatt-scale (Weber et al., 2011). A large and growing body of literature has shown successful RFB implementation due to the capability of this system to partition the power and energy parts to meet particular requirements (Mohamed, Ahmad, & Seman, 2009). This is much safer compared to other conventional battery systems because RFB stores active reactants in separate tanks. Others features of RFB are that it is easier to handle, simple to operate, and requires less maintenance. It also has high rates of output performances, high overall energy efficiency, reduced environmental impact, no cycle life limitation, high dynamic response, modularity and transportability, and high power density (Alotto, Guarnieri, Moro, & Stella, 2012; Ponce de León et al., 2006). Thus, RFB systems have potential to be the main technology for large-scale energy applications that support system balance and steadiness, regulation of power quality, and may also be marketable for electric vehicles (transportation system) (Parasuraman et al., 2013). In the next section, brief overview of operation of RFB system and different types of RFBs system are presented.

2.3 Overview of RFBs

In previous section, various energy storage technologies are presented. In electrical energy storage system, while it is able to operate at very high efficiency and has quick response for immediate backup power during interruptions but it has lower energy density and consumes high capital cost and it is actually suitable to use to complement other types of energy storage technologies. While, in mechanical energy storage safety is a major obstacle. Electrochemical energy storage technology is well suited for much large scale application as it's provides flexible operation, high dynamics response, and high efficiency. Because of these unique features, electrochemical energy storage technology is really suitable emergency backup power and electric utility (Fujimoto et al., 2014).

Due to system power and capacity can be largely decoupled, RFB seem to be especially attractive system in electrochemical energy (Rusllim Mohammad et al., 2010). An RFB electrolyte is typically composed of three species: a solvent, supporting electrolyte, and the active species, or redox couple. Redox reactions are reduction and oxidation reactions in which the oxidation states of molecules change. RFB configuration; the characteristics and components are similar to those of fuel cell in the way that electrochemical energy is reserved in the tank that is occupied with active species.

Practically, the RFB mechanism consists of three segments including the cell stack, energy reserve tank, and flow circulation system. The cell stack consists of individual cells where every single cell contains a part where the electrochemical charge transfer reaction happens to store or release energy under redox reaction. Redox reaction is a reduction and oxidation process where the reduction involved the release of electron, and the oxidation involved the gain or recombination of the ions (Kear, Shah, & Walsh, 2012).

The reactants in the tank are recirculated through the redox flow cell. Pumps are used in flow batteries to help flow circulation by circulating the electrolyte for redox reaction which occurs through the cell stack and a porous electrode to generate electrons, which flow through the external circuit (Ponce de León et al., 2006).

On the negative side, flow batteries are rather complicated in comparison with other standard batteries as it is required much component which were pumps, sensors, control unit, reservoir tanks and electrolyte tube. The energy densities are relatively small compared to Lithium ion batteries.

2.4 Categories of RFB

RFB is one of the high potential batteries from electrochemical energy storage system that has been used in many applications because of its excellent characteristics such as good scalability, independent sizing of power and energy, and fast response. Multifarious types of redox flow battery like zinc–bromine (Zn-Br RFB), iron–chromium (Fe-Cr RFB), vanadium–vanadium (V-RFB) have great performance and outstanding role for stabilisation of both generation and grid load. They also offer a good system for electrical applications (Winsberg, Hagemann, Janoschka, Hager, & Schubert, 2016). These redox flow batteries are advantageous and one of the newer technologies that are capable of reserving production surplus to act as emergency backup power during unexpected conditions and times (Miyake & Tokuda, 2001). The following section provides brief categories of RFBs.

2.4.1 Zinc-bromine battery

The intermittence of energy generation from renewable energy sources has caused more attention to be focused on large-scale energy storage devices. Zinc–bromine battery is one of the redox flow batteries that have been designed and studied for large-scale applications. However, more studies need to focus on the up growth and reinforcement of Zinc-bromine RFB (Byrne & Macartain, 1999)

Zinc-bromine battery has been strongly established because of its superior high energy density, unlike other redox flow batteries. The electrochemical reaction shows that the Zn ion turns into zinc metal in the reduction process, while at the same time the bromide ion undergoes oxidation process and become bromine gas at the cathode during charging time (H. S. Yang, Park, Ra, Jin, & Yang, 2016). Unfortunately, electrochemical reaction of the zinc-bromine also causes the formation of poly-bromide at the negative electrode and deposition of zinc at the positive electrode during charging time, causing complication that may lead to decrease of energy efficiency, disrupted stability and durability of zinc-bromine electrolyte, crossover, lowering of coulombic

efficiencies, and reduction of battery life (J. D. Jeon, Yang, Shim, Kim, & Yang, 2014; Kim & Jeon, 2015).

Studies have found that some additives may improve and recover zinc-bromine electrolyte conductivity as they enhance and boost the stability and durability of the electrolyte. Quaternary ammonium salts and dendrite inhibitors are some examples of additive which couple with energised bromine and directly inhibit the general formation of zinc dendrite. However, more studies about flow characteristic and behaviour are needed to increase stability, flexibility, and performance of the zinc-bromine RFB (H. S. Yang et al., 2016).

2.4.2 Iron-chromium battery

The first serious discussions and analyses of redox flow battery emerged during issues of unstable power distribution and iron-chromium RFB as the first RFB system appeared, employing Fe(II)/Fe(III) and Cr(II)/Cr(III) soluble redox couples as the anode and cathode active materials respectively, which are set apart by an ion exchange membrane as a separator and use carbon felts as the electrode material (Zeng, Zhou, An, Wei, & Zhao, 2016).

Iron–chromium redox flow batteries studies by (Fedkiw & Watts, 1984) have revealed these batteries as an auspicious energy storage system. However, a drawback of this flow battery is that it requires a catalyst to improve the electrochemical kinetics of the Cr(II)/Cr(III) redox reaction at the negative side. The chosen catalyst must have a high over potential towards the hydrogen evolution reaction; because these reactions may reduce coulombic efficiency and cause an imbalanced state of charge (SOC) that leads to capacity decay. Some catalysts like Au-Ti and Bi are deposited on the electrode surface and lighten the process. Yet, there is a problem that needs to be tackled; this flow battery is different from other flow batteries because the membrane of iron–chromium battery is permeable both to charge carrier ion(H^+/Cl^-) and active species (Fe/Cr) (Zeng, Zhao, An, Zhou, & Wei, 2015). This phenomenon will form a large concentration difference through the membrane and cause a high crossover rate effect.

2.4.3 Bromide- polysulphide

Bromine–polysulphide battery is a flow battery that comprises sodium bromide at the positive electrolyte and sodium polysulphide on the negative side. Bromine–polysulphide battery was patented by Remick and further studied by Regenesys technologies since 1993s (Weber et al., 2011). This flow battery has been favoured for commercialisation for redox flow technologies since 1993s until 2003s due to its good characteristics and significance by having a moderate cost and being highly soluble in aqueous solution without implementing any catalyst to speed up the reaction.

Studies on bromine–polysulphide batteries have shown the unique features of this energy storage system which are the abundance of the two electrolytes, reasonably inexpensive cost, and high solubility in aqueous solution. However, the disadvantages of this flow battery are complex electrode reaction, the risk of cross-contamination and need to be fully monitored (Denholm et al., 2010). This flow cell also releases heat and toxic gases which are not environmentally friendly, thus calling for new action and plan for future implementations of bromine–polysulphide flow battery.

2.4.4 Vanadium RFB (V-RFB)

Works on Vanadium Redox Flow Battery (V-RFB) technology was spearheaded by Maria Skyllas-Kazacos and her colleagues at the University of New South Wales (UNSW), Australia in the 1980s (Parasuraman et al., 2013). The Kazacos research team has revealed and shown that this battery has many unique features and characteristics compared to other conventional batteries. V-RFB is already commercialised in Japan by Sumitomo Electric Industries (SEI) and has already been tested and practised in Tottori Sanyo Electric (Fisher et al., 2014). However, the research and development of V-RFB are continuing until today to suit the demands of technologies and for more practicalities in various applications. There is a large volume of published studies describing the fundamentals and proposition of V-RFB system. A standard structure of V-RFB reserves energy in two separate liquids involving the same redox couples and the same metal ions in both half-cells. Here, vanadium ions are used at the coupled positive and negative electrodes through the membrane V(II)/V(III) redox couple is active at the anode side while the cathode side uses the V(IV)/V(V) redox couple

(Huang, Li, Liu, Tan, & Chen, 2008). The system also consists of two pumps, electrodes, flow frames, bipolar plate, and ion exchange membrane (Blanc et al., 2008).

During the charging stage, hydrogen ions (H^+) are initially at the positive side and move to the other side through the exchange membrane and vice versa during the discharging moment. The balance in the electric charge is obtained by the transfer of hydrogen ions beyond a membrane that functions to separate the electrolytes (Ponce de León et al., 2006). Among various energy storage technologies, V-RFB appears promising because of its supreme features such as effective and simple operation, capability of high power, operationally at room temperature, fast speed response and recharging contenders, excellent chemical stability that shows an extremely long-round-trip cycle, long discharge times, and good modular design (Alotto et al., 2012). V-RFB also exhibits for highly reversible redox kinetics, has been developed for large-scale applications and has reasonable and controlled maintenance cost compared to conventional batteries (Hopkins, Smith, Slocum, & Chiang, 2015). The unique feature of V-RFB is that it has decoupled energy storage and power component that give independent control of capacity and power (Rusllim Mohammad et al., 2010). V-RFB has become the most attractive battery for EV applications on target for vehicle configuration especially for optimisation of power and energy.

V-RFB cells may be constructed in a series or parallel arrangement (Zhao et al., 2006). In the past 20 years, V-RFB has been one of the major projects for commercialisation and industrialisation (Parasuraman et al., 2013). Furthermore, V-RFB performance has been extended and prolonged by focusing more on the invention on new novel electrode materials, catalyst on different substrates, enhancement on electrolytes to increase energy density, ion exchange membranes and additives, and optimisation of the system that included a battery cell/stack on the structure and operating conditions (Jyothi Latha & Jayanti, 2014b). In addition, there is no risk of hydrogen explosion hazard due to technically good charging and discharging processes without harming the battery (Skylas-Kazacos, Chakrabarti, Hajimolana, Mjalli, & Saleem, 2011). Despite many interesting studies indicating the potential of V-RFB have been reported before, the V-RFB development system remains to be further explored. The many potential benefits of V-RFB makes this battery is chosen rather than other batteries for this study.

2.5 Key components of V- RFB

Figure 2.1 represent the components of V-RFB cell to become one complete cell stack. The main parts of a unit cell of V-RFB, which consist of cell membrane, flow frame electrode (cell geometry) and pumping system. V-RFB basically comprises of positive and negative parts containing an anolyte and catholyte with an interposed membrane or ionic separator. So, one-unit cell stack consist of two half-cell is separated by a membrane. V-RFB store energy in two electrolytic solutions containing redox couples. The solutions are circulated through their external tanks by means of two pumps. Similarly, to fuel cell this architecture decouples power rating, which depends on the stack size, from stored-energy rating, which depends on the tanks volume. The overall stack structure is shown in Figure 2.2. Next, a multiple cell can be stacked together in series to produce a modular stack as illustrated in Figure 2.3.

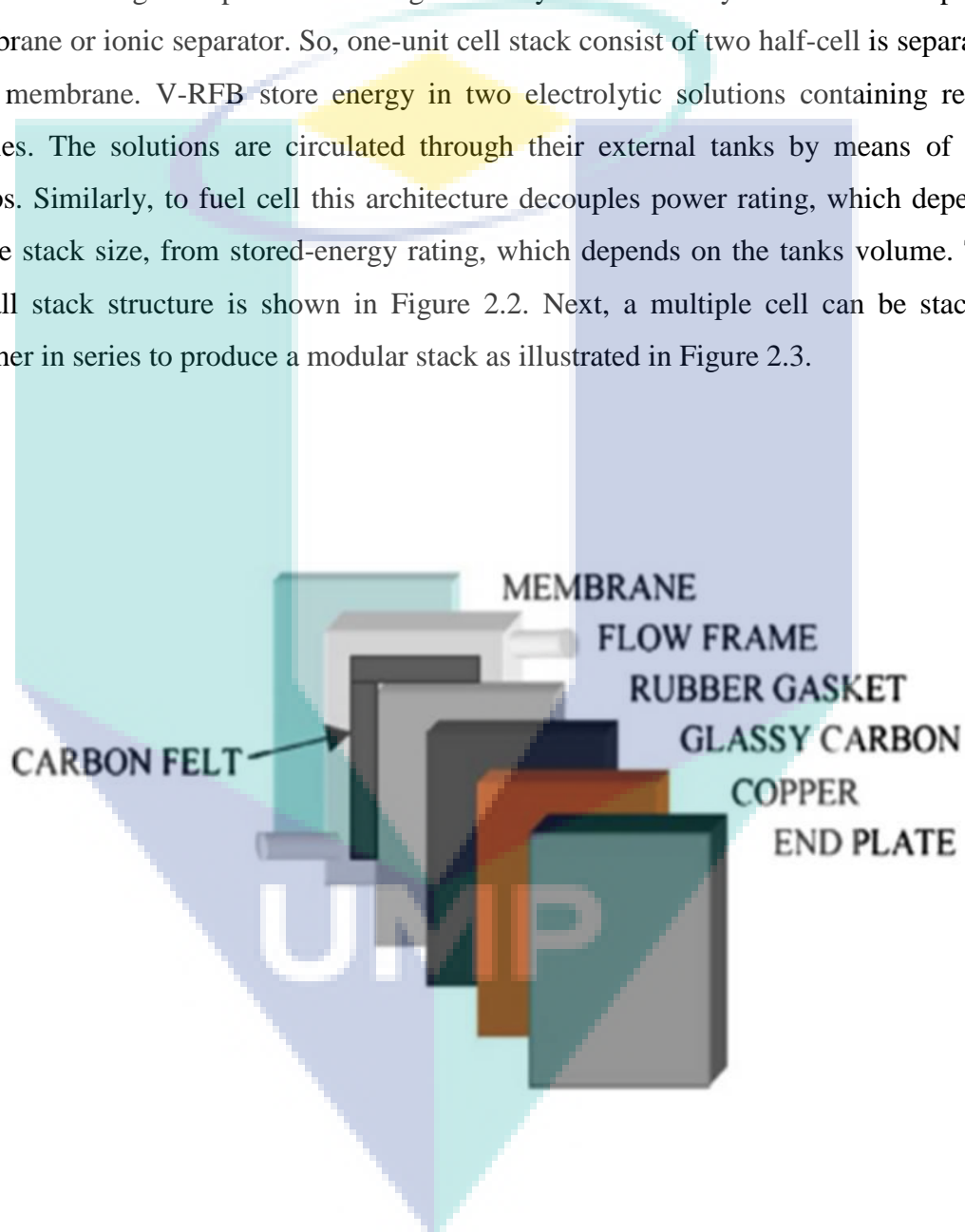


Figure 2.1 Components of V-RFB cell stack

Source: (Parasuraman et al., 2013)

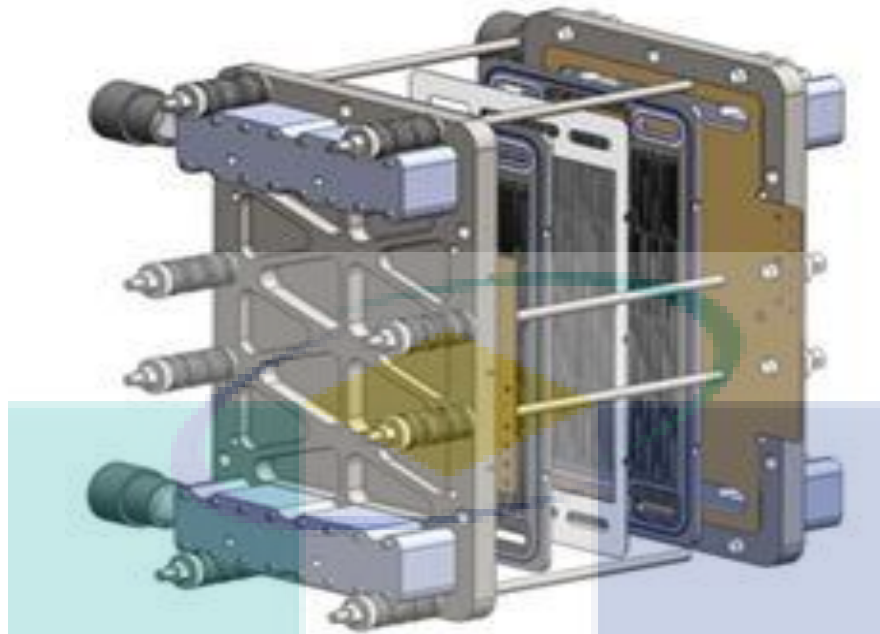


Figure 2.2 Complete single unit of V-RFB cell
 Source: (Fisher et al., 2014)

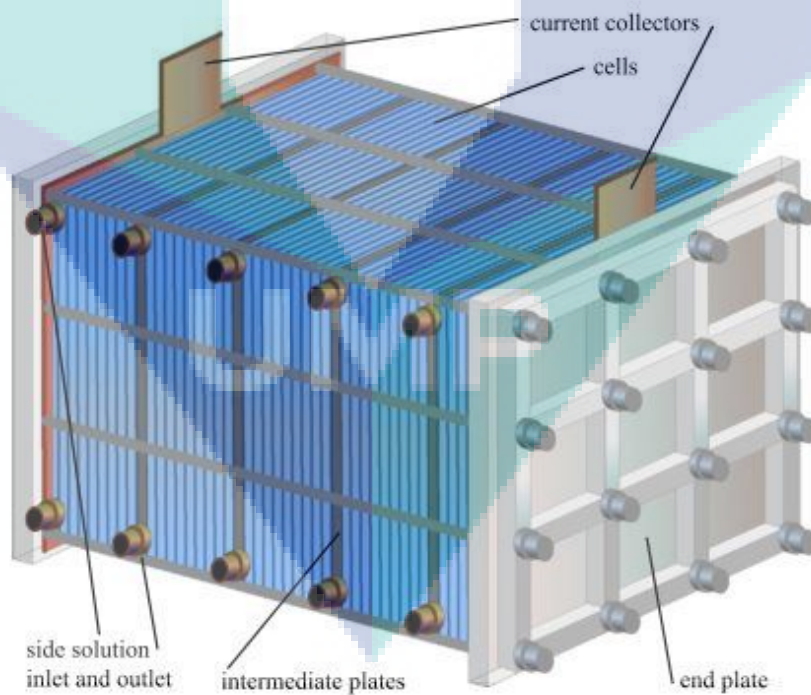


Figure 2.3 Modular stack
 Source: (Alotto et al., 2014)

2.5.1 Electrode material (cell geometry)

The electrode material contributes a significant impact on the redox reaction in the electrochemistry of V-RFB. The electrode is porous and made from a carbon-based material, such as carbon felt, and graphite felt. The electrode material is easily corroded due to CO₂ evolution. CO₂ evolution leads to battery failure and directly lowers its energy efficiency (Liu, Xu, Yan, & Qiao, 2011). Carbon-based material is an excellent V-RFB electrode material because of its three-dimensional network structures and has wide operating potential range, good electrical and chemical conductivity and stability, relative inertness, acid resistance, and long cycle life in an acidic environment (Chakrabarti et al., 2014). Unsuitable design of electrode material (cell geometry) could make the flow of the electrolyte non uniform. Uneven flow distribution may result in non-uniform current distribution, with the possibility of locally overcharging causing gas evolution and degradation of the bipolar plates (Bhattarai et al., 2017). Therefore, more developers and researchers are at pains to design the cell geometry to ensure even distribution of the electrolyte through the porous electrode. Hence, most suitable electrode material in anode and cathode half-cells design in vanadium flow battery is selected to enhance the electrochemistry activities and maintain mechanical integrity (Parasuraman et al., 2013).

2.5.2 Membrane (ionic separator)

There are three main components for the V-RFB storage system. One of the main components is an ion exchange membrane or called separator. The separator's role is to passage the ion between the positive (catholyte) and negative (anolyte) sites while prohibiting the crossover of the electrolytes during the transfer of current (D. Chen et al., 2013). The membrane normally used in the flow battery is from perfluorosulfonic acid polymer like DuPont's Nafion membrane (Wu et al., 2014). To improve the performance and energy efficiencies of the V-RFB, a high-quality membrane has been the focus for development in V-RFB system. The criteria for selecting a good and ideal membrane are listed as follows (Fujimoto et al., 2014; Parasuraman et al., 2013):

- I. Good membrane durability to enhance oxidation resistance and good ionic exchange capacity.

- II. High ionic conductivity and good chemical stability under strong acidic environment.
- III. High permeability to the charge-carrying ions & excellent thermal stability.

2.5.3 The unit cell and modular stack

This unit cell of V-RFB cell comprises a bipolar electrode which is electrically conductive carbon-composite material, an ion-exchange membrane which acts as a separator between two electrode layers in anion and cation electrodes, and a non-conductive plastic as the frame as shown in Figure 2.4. This complete single unit of the battery cell is connected together with positive and negative tanks that store the active material, pump, and piping for the circulation of electrolyte from the tanks to the battery cell (Shigematsu, 2011). V-RFB stacks are built from individual or single unit cells which are stacked in series or parallel. This single unit are assembled to form a V-RFB stack. A multi-layer structure of cells in which the electrochemical reaction occurs is called a cell stack (Shibata, Kumamoto, Nagaoka, & Kawase, 2009). Figure 2.4 present the configuration of a single unit, cell stack, and V-RFB system.

This cell stack is constructed with flow frame's cavity flow for pathways of electrolyte for absorbent activities in carbon felts that are inserted into the flow frames. Every single cell contains a location or marks the spot where the chemical charge transfer reaction occurs (Weber et al., 2011). The performance of a RFB system is highly dependent on cell materials, cell design, stack design, and electrolytes (Fisher et al., 2014). A single unit can be arranged in two manners: unit cell fed by electrolyte in parallel or arranged in series, where all the modules operate with the same inlet with a stack arranged in parallel or the modules are connected hydraulically in a series, and the electrolytes flow successively through each of them (Arenas et al., 2017).

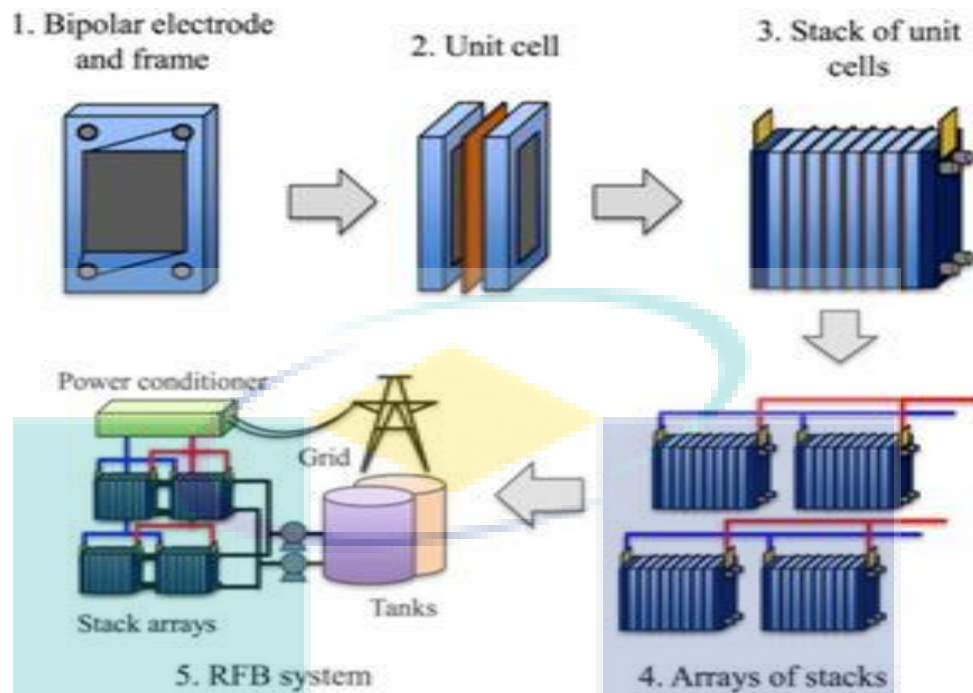


Figure 2.4 Configuration of single unit, modular stack and complete battery system of V-RFB

2.6 V-RFB cell features and design

V-RFB cell design, first patented by Skyllas-Kazacos and team in 1988s (Rychcik & Skyllas-Kazacos, 1988). An historical overlook of early RFBs pattern is followed and inspired by a report of (Thaller, 1976). Ever since, various publications emerge for redox couples (P. K. Leung et al., 2015), material properties (Seyed Schwan Hosseiny, 2011) and cell design (Aaron et al., 2012). However, the studies on the cell design for V-RFB remain limited. Hence, the key issue associated with the flow geometry design is improvising to get an optimal design and operating conditions for V-RFB system.

2.6.1 Cell geometries design (electrode compartment)

One of the most significant current discussions in the optimisation of V-RFB is on cell design and architecture of flow stack battery system. The cell geometry is one of the crucial parts for determining flow distribution of liquid and mass transport within the cell. Good cell geometry designs exhibit uniform electrolyte distribution to the entire surface of the electrode and leading to minimize pump power consumption of the cell, which is one of the key requirements for energy storage technologies. Cell

geometry aspect correlation is also important (Houser, Pezeshki, Clement, Aaron, & Mench, 2017). It is interesting to note that currently, new and flexible cell geometries are being studied and redesigned by previous researchers as an alternative to replace the conventional one for optimisation. (A. C. Khor et al., 2016) proposed rhombus cell geometry as an alternative design for use in V-RFB system instead of the conventional square design. The study found that rhombus cell geometry exhibited the best uniformity of electrolyte in the cell and showed the lowest pressure drop compared to conventional square design. Nevertheless, the studies implemented only on one flow pattern and are concluded in general terms and no specific data result on the overall pump power required of V-RFB with a proposed cell design.

(Xu, Zhao, & Leung, 2013) proposed no flow, parallel and serpentine flow channel pattern while maintaining a traditional square shaped. (Jyothi Latha & Jayanti, 2014b) present comparative studies with various flow channel pattern which were plain, parallel, serpentine and an interdigitated design, exhibits a new flow channel pattern but same as previous work by maintaining a traditional square cell shaped. All this work claimed that by adding a flow channel pattern is much better and successfully minimizing pump power consumption needed by V-RFB system. However, studies mostly focused on flow channel design, thickness of electrode, and different positions of inlet/outlet channel while maintaining square cell geometry because the focus is more on the characterisation of V-RFB, and not cell and architecture design development (Alotto et al., 2014; Mohamed et al., 2015a). It should be noted that electrochemical cell geometry has not been well studied and deeply discussed.

Therefore, this calls into question whether this flow cell design is optimum to be applied or if other geometries may lead to a more efficient flow battery cell, because different cell configurations may have different electrolyte distributions (Bortolin, Toninelli, Maggiolo, Guarnieri, & Del Col, 2015). An exhaustive review of these studies has suggested a direction for future development and lead to the motivation to study alternative cell geometries with a various flow channel to enhance flow distribution, minimise the pump power within the cell, and improve the performance of the flow battery.

2.6.2 Flow channel pattern

The cell geometries are designed with precise flow channels that will direct the electrolyte to flow through the entire area of electrode evenly and completely. Studies on flow channel development aim to develop better electrolytes on the electroactive site compartment and strengthen the structure for electrode material (Xu et al., 2013). Figure 2.5 shows the complete schematic of a battery system with/without flow channel to study the flow behaviour in the cell. By applying a good flow channel, the pump loss would be lessened and may improve and stabilise the uniformity of concentration distribution, and enhance mass transport due to good convection and diffusion of electrolytes (Bortolin et al., 2015; X. You, Ye, & Cheng, 2016).

(Xu, Zhao, & Zhang, 2014a) have reported their experimental and numerical investigations concerning RFB. They studied the performance of V-RFB with and without a flow field (flow channel) by carrying out the experiment while at the same time numerically designing a three-dimensional model to study the flow field design for the flow battery. Results from experimental work showed that energy efficiency of V-RFB is much higher (around 5%) when electroactive sites of the flow field are applied compared to energy efficiency without the flow field. Therefore, the conclusion here is that a flow field channel in V-RFB improves system efficiency of the battery. The numerical work result showed that there is a uniform distribution of electrolytes over the entire active area of the electrode surface when a flow field channel is applied. A cell with a flow field has a more significant reduction in the pressure drop, especially with the parallel design.

(Tüber, Oedegaard, Hermann, & Hebling, 2004), proved that pressure drop is not the only criterion that needs to be investigated; the reactant transportation through the reaction sites also needs to be included. They also claimed that the design of flow channel for V-RFBs is an important area that needs more investigation and as there is not much literature on the subject. (Bhattarai et al., 2017) proposed four types of electroactive flow channels: rectangular open channel, interdigitated open cut channel, interdigitated circular poked channel, and cross poked circular channels. All four types were compared to the conventional channel. In the study, using a flow channel improved the overall battery performance. However, there is limited information about the effect of different types of channel from the literature.

Numerical and experimental studies of flow channel and flow distribution effects in V-RFB have also shown that a flow channel design would be advantageous for large-scale systems and suitable flow channel configuration designs may give significant differences on the performance and uniformity of flow batteries (D. H. Jeon, Greenway, Shimpalee, & Zee, 2008).

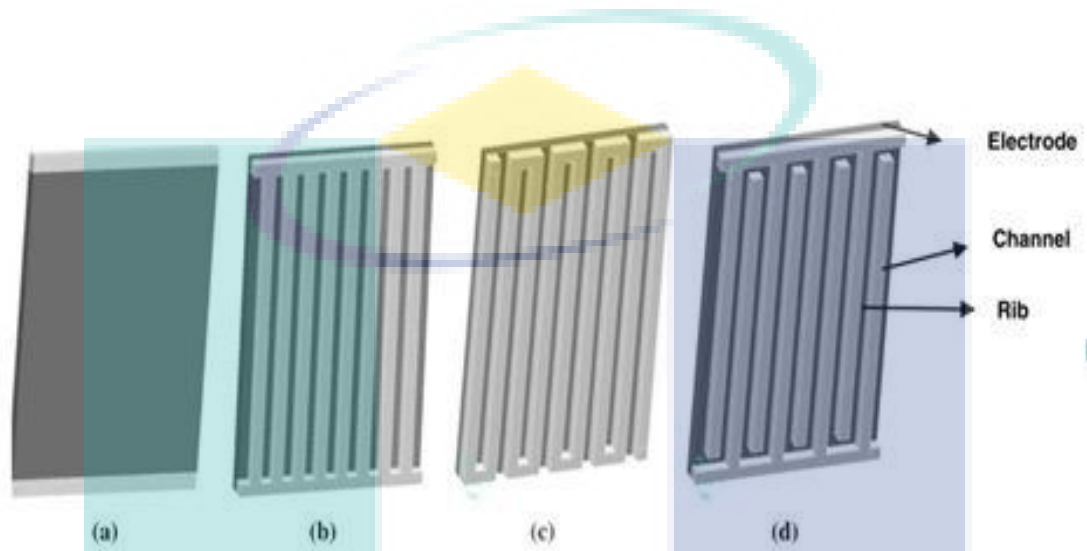


Figure 2.5 Schematic of a battery system with/without flow channel a without flow channel, b parallel, c serpentine, d interdigitated

2.6.3 Pressure drop and pump power effect within the cell geometries design

The pressure drop in V-RFB cell geometries is the most important indicator to ensure the suitability of the cell geometries, as indicated by the lesser pressure drop required with optimum flow rates within the cells. More pressure drop losses are in between the stack, manifolds, and channel, so there is a significant relationship of pressure drop losses with the battery system which needs to be focused on for continuous circulation of the electrolytes through the cell, based on the suitable flow rates applied (Jyothi Latha & Jayanti, 2014a). Then, pump energy consumptions (pump power) is dependent on the pressure drop; the higher the pressure drop within the cell, the higher the pump energy consumption in V-RFB system (Brown et al., 2016). Researchers have revealed that high pressure drop consumes excessive pumping energy that may lead to lower system efficiency (Xu et al., 2013).

This high pressure drop factor is related with improper flow frame cell geometries, which tend to give lack of good control in a real behaviour system and may restrain battery performance (Yin et al., 2014).

2.7 Scale-up system

There are few researches that focus on the engineering aspect of design, cell construction, and scale-up progress. Several studies have revealed that one of the limitations of this green energy storage system is unsuccessful scale-up, poor maintenance, the high cost of development, and low efficiency (Perry & Weber, 2016). So, the consideration of the effect of cell design, electrode structure, and operational conditions need to be focused on to overcome these problems. This is supported by a study which highlighted on the design of energy storage system and scaling up work for a better adoption for these battery technologies (Arenas et al., 2017).

Scaling up lead to an efficient system and less cost consumed for device commercialisation. Scale-up may be performed through parametric studies (current density, electrolyte flow rate, linear velocity and electrode size, mass transport, and dimensionless group), modelling, and simulation, and these studies enable researchers to better understand the complex work and relationship between performances (Cervantes-Alcala & Miranda-Hernandez, 2018). Dimensional analysis that includes electrode geometry, reaction kinetic and fluid flow is also included in the process and stages on the development of scale-up works. Thus, the design and scale-up of these devices have to take such relationships into account. The V-RFB flow cell battery is tested in a laboratory or simulated as a single unit cell and then scaled-up to a pilot stack, which are designed by taking into account the effects of the electrolyte flow regime. This pilot stack should be easy to modify and test to control another operating parameter such as shunt current, electrode potentials, and pressure drop (Arenas et al., 2017).

There is a research by (Rusllim Mohammad et al., 2010) that estimated the size of scaled-up and performance of a series of electric vehicles that use V-RFB. However, the case study did not provide enough numerical investigation or any experimental work evident to support the scaled-up size result. Therefore, this became a motivation for this work to study the scale-up progress for V-RFB system in terms of parametric studies.

2.8 Chapter summary

In this chapter, an extensive review on V-RFB cell geometries and flow channel pattern design is discussed. This chapter also discussed the studies on pressure drop, pumping power, and flow distribution effect. In addition, this chapter highlighted a scale-up work of a modular stack of V-RFB system connected in series.

V-RFB system beats the advantages and performance of other reliable energy storage technologies such as flywheel, PHES, CAES, and other conventional batteries due to its flexible battery design which offers independent power and energy capabilities and a long life cycle. V-RFB system also uses the same element for the positive and negative active materials, thus reducing the risk of cross contamination that may otherwise lead to poor performance.

This chapter provides a relevant and clear understanding on how the different cell geometries and flow channel designs influence the pump energy consumption (pump power) and electrolyte distribution. Based on the brief review, optimisation of V-RFB needs continuous efforts, especially on the development of cell design, which is a key component of V-RFB.

Hence, the present work aims to develop a three-dimensional V-RFB battery model with simple yet effective cell geometries and flow channel design to extend the knowledge on the flow distribution and pump power in each design for improvement of V-RFB performance, as the information in the literature is limited and the best architecture design of cell geometry in V-RFB for an ideal battery condition to be implemented is still unknown.

CHAPTER 3

METHODOLOGY

3.1 Introduction

As an effort to enhance the performance of the battery by further improving mass transport and flow distribution of electroactive electrolytes within the cell, three-dimensional models of V-RFB cell, namely square-, rhombus- and circular-cell designs were developed. By using Computational Fluid Dynamics (CFD), the investigations were carried out by evaluating pressure drop, pumping power and flow distribution of the electroactive electrolytes in these three different electrode configurations. A three-dimensional model based on the operation principle of V-RFB with the implementation of flow distribution channel with various flow rates applied, was developed.

One unit of cell battery and modular stack consist fifth cell was constructed based on a 100 cm² electroactive site area of the electrode with a geometric parameter of 3 mm deep flow distribution channel. The key component in a V-RFB is the ion exchange membrane that acts as a separator, sandwiched by two electrodes. This V-RFB is closed by two plates consisting of a flow distribution channel. The electrolyte flow in the electrode compartment interacts with the membrane and plays an important role for the general performance of V-RFB cell. Figure 3.1 shows the flowchart for this research projects.

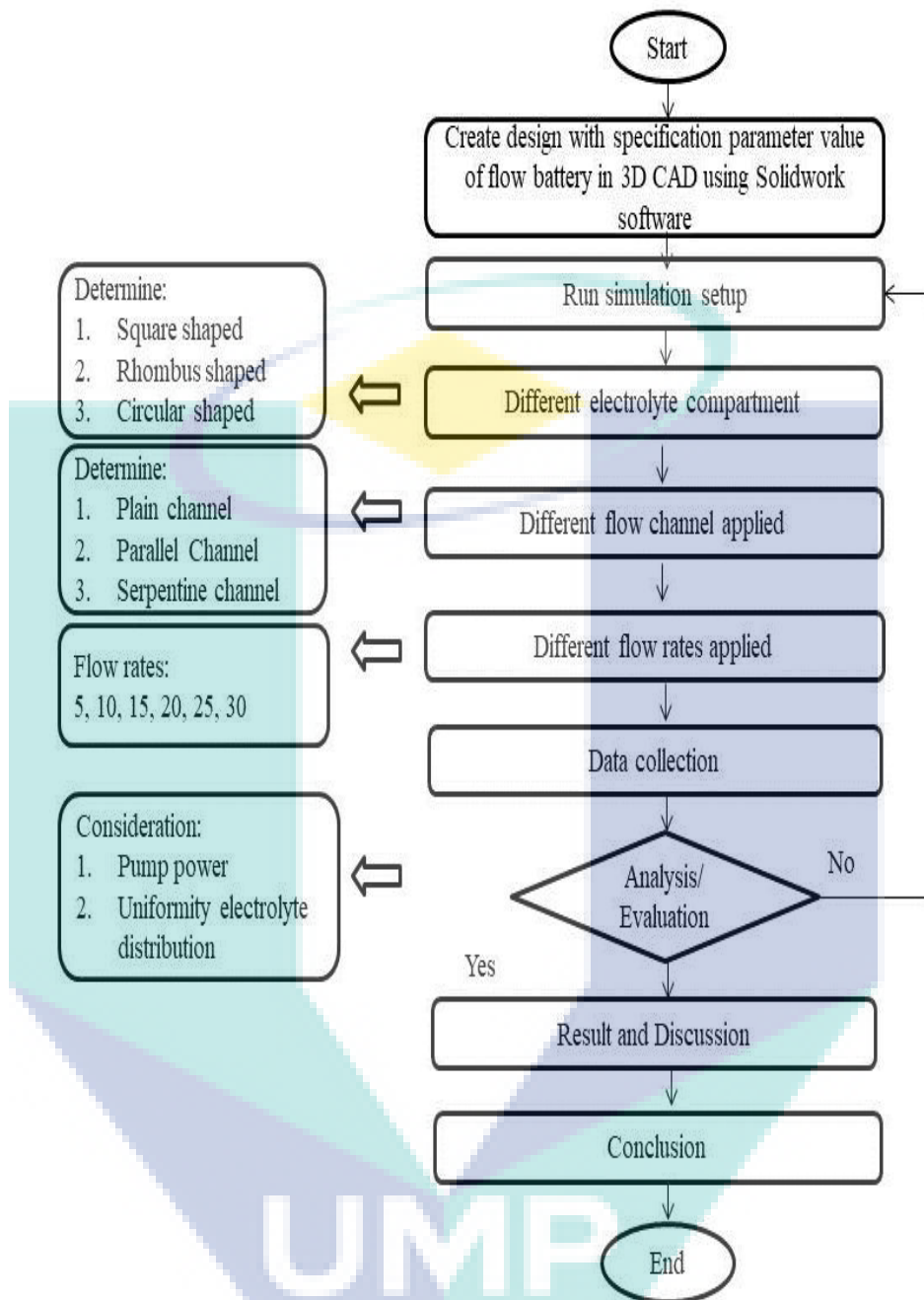


Figure 3.1 Flowchart of simulation process

3.2 V-RFB geometries model

This mass transport model and fluid flow is design with a flow channel pattern. The key component in a V-RFB is the ion exchange membrane that acts as a separator, sandwiched by two electrodes. This V-RFB is closed by two plates consisting of a flow model distribution channel. In the present work, focuses on three possible geometrical configurations V-RFB cell, namely square-, rhombus- and circular-cell designs were evaluated under three different cases which were plain, parallel and serpentine flow channel pattern on active sites of V-RFB cell where the electrochemical process happen. 100 cm² active sites of electrode with a thickness of 3 mm with 0.00424 m cross section area of the channel were design. The geometric design with different cases applied is shown in Figure 3.2 & Figure 3.3. Figure 3.4 depicts the details out the overall component for a complete unit cell battery.

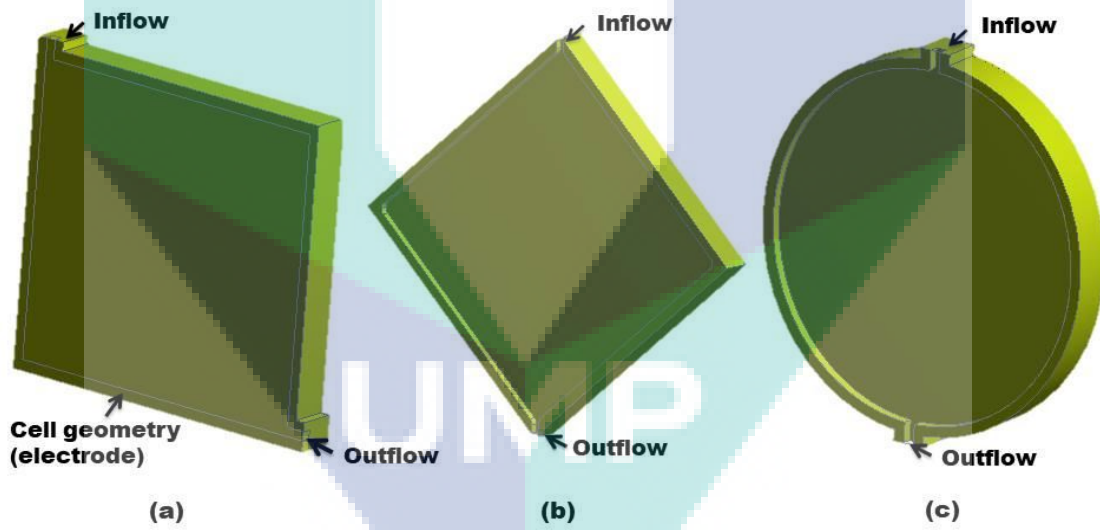


Figure 3.2 Schematic of the V-RFB cell geometries: (a) Square cell (b) Rhombus cell (c) Circular cell

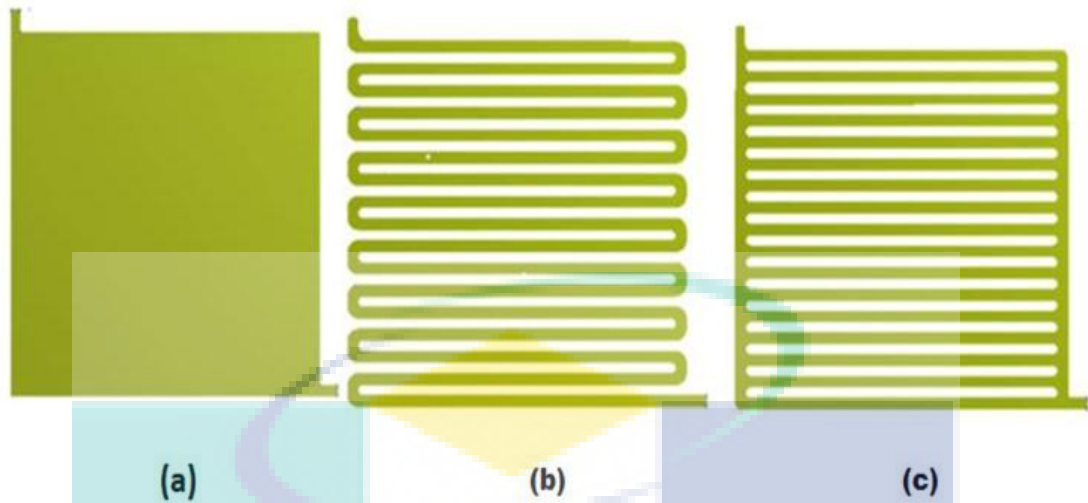


Figure 3.3 Schematic of the three types of flow channels applied in V-RFB geometries

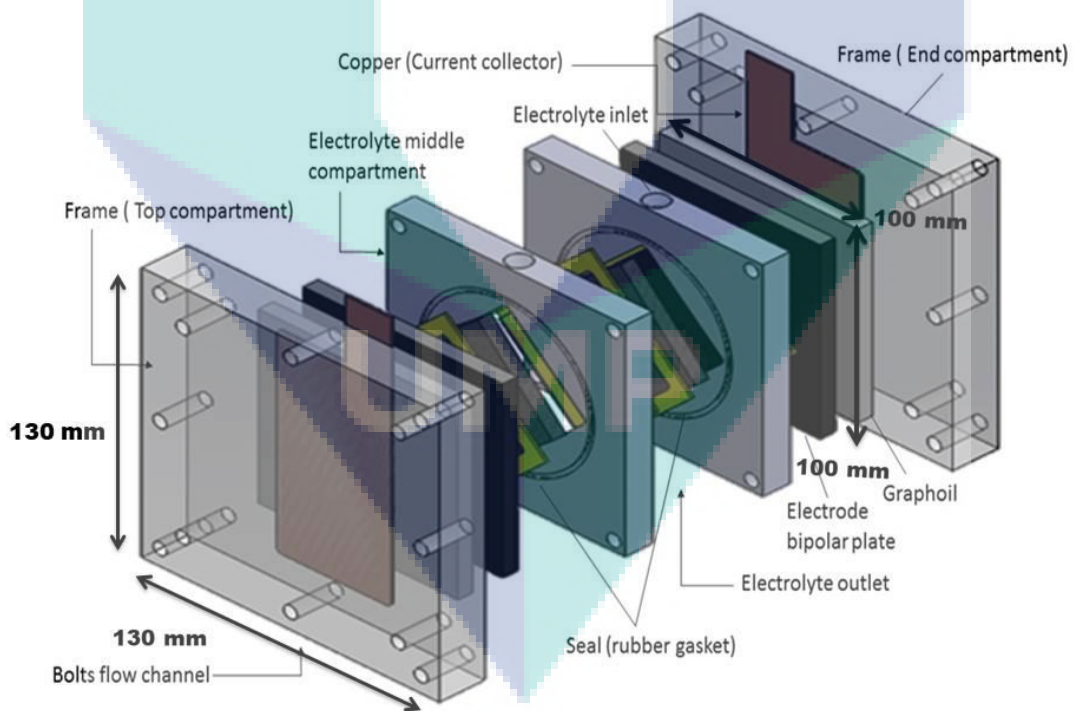


Figure 3.4 Schematic drawing complete unit cell of V-RFB

This study, the extension of the initial work, focuses on build up to create a modular stack by summation of the individual cells. Numerical simulations were carried out using CFD to design and scale-up of V-RFB cells to study an interrelated factors that determine the performance of V-RFB system by investigating a flow features and pump power required in a half-cell modular stack geometries. Figures 3.5 shows a number of fifth single half-cells developed to create modular stacks. The V-RFB work here has been scaled-up the cells connected hydraulically with a series configuration to evaluate the pressure drop & pump power in order to look behaviour and trends in the fifth cell stack is similar to that obtained for the single stack system.

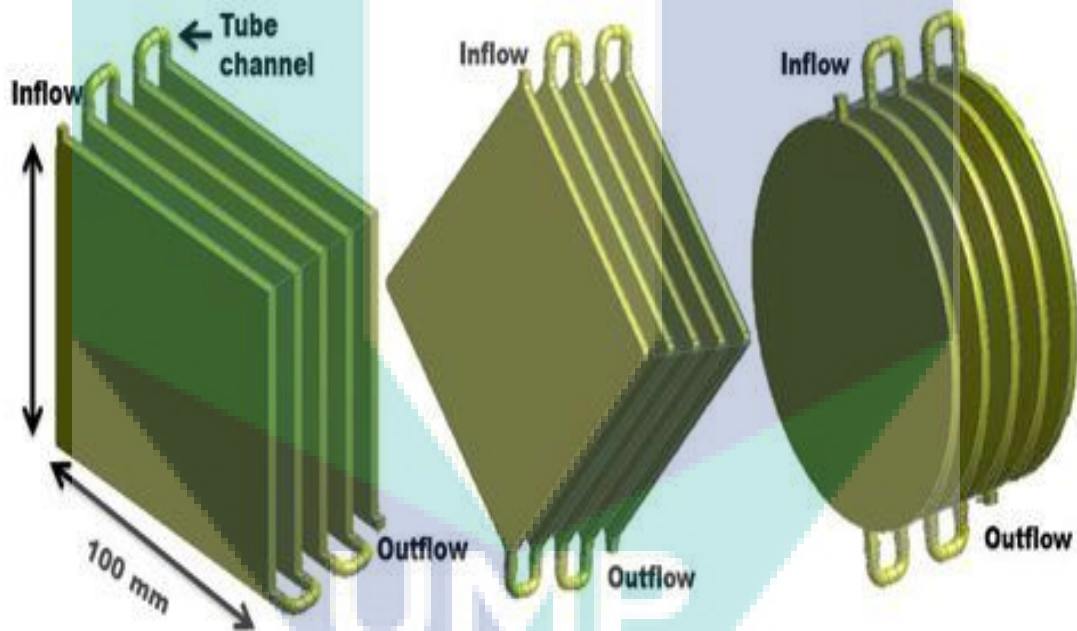


Figure 3.5 Modular stack with 100 cm² different V-RFB geometries

3.3 Fluid flow (assumptions and model scope)

The numerical analysis of the free fluid flow in three dimensional models between the channel walls and the manifolds was performed at steady state. Several implications and assumptions were made in the present work to simplify the model as described below:

- I. As indicated that volume change was small, so incompressible fluid was assumed for the electrolyte used.
- II. An isothermal condition was assumed in the active sites of the electrolyte compartment.
- III. Any side reaction is coming from inter-reaction that occurs in the electrodes, such as oxygen and hydrogen evolution, is neglected here.
- IV. According to calculated Reynolds number (Re) for the given channel area and range of flow rates setting, it was reasonable to consider flow rates at 5 - 30 cm^3s^{-1} .

To summarise, the flow is assumed to be incompressible, isothermal, in steady state, and considered as laminar and turbulent flow models.

3.4 Setup and configuration

CFD is a tool for analysing and modelling software. Systematic studies on cell features and parameter may be conducted with this simulation, which is more beneficial compared to experimental work by consuming less time and cost and may undergo various explorations. By utilising CFD simulations, this study numerically examined specific features of a unit cell of V-RFB system to obtain performance enhancement of the cell. This investigation was conducted in a three-dimensional model and the result showed the real behaviour for actual flow domain in the studied model. The investigation was furthered by testing different geometries on single and modular stack to enhance flow distribution in V-RFB cell and demonstrate the influence of flow channel on cell geometries to get more uniform electrolyte distribution and less pump power consumption within the cell. Figure 3.6 presents flowchart describing detail the simulation process.

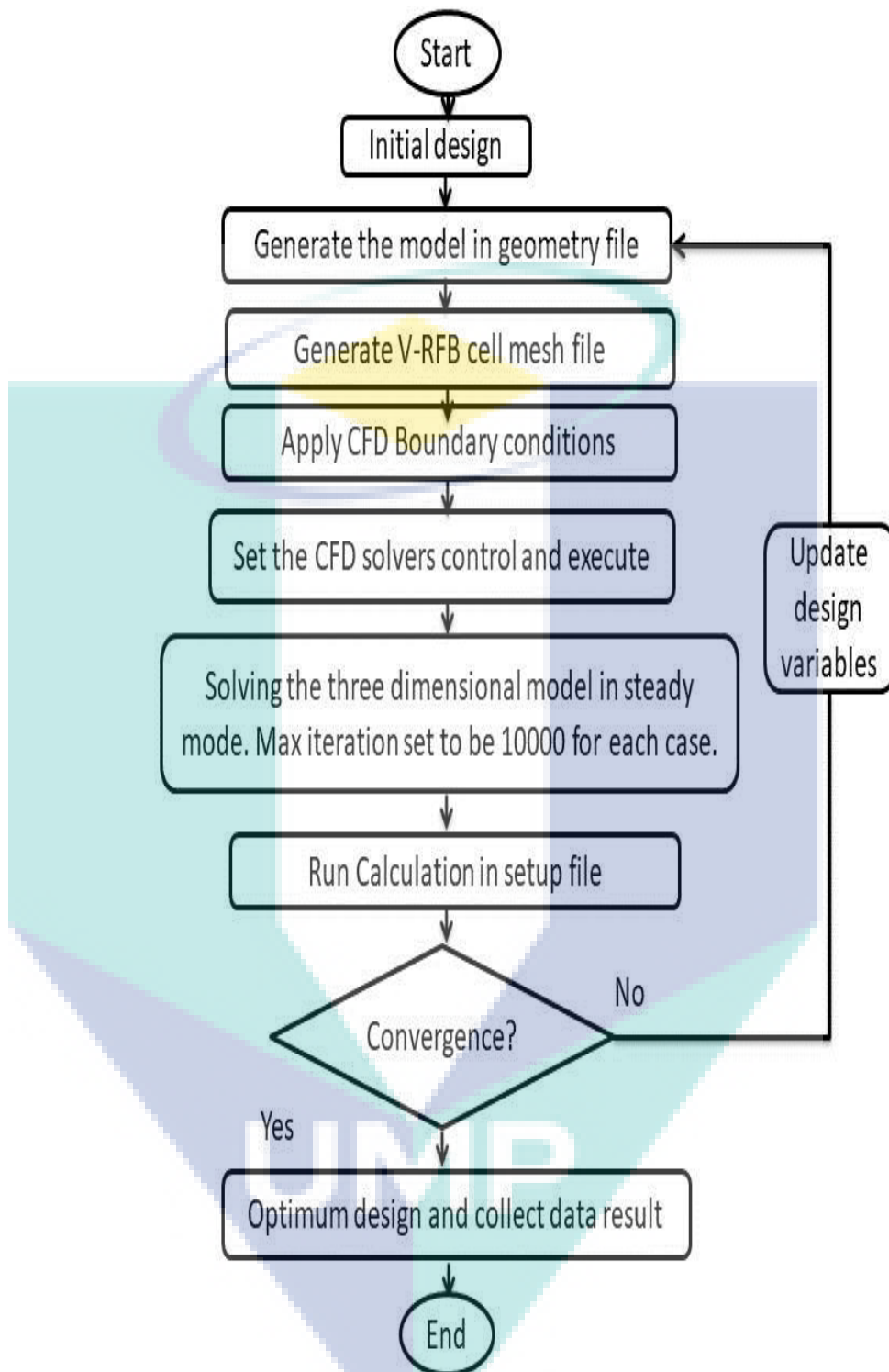


Figure 3.6 Flowchart of simulation process

Numerical simulations were carried out and solved using the ANSYS Workbench 19.2 package with an ANSYS FLUENT communication in console zone. Three-dimensional models were built in Fluid Flow (Fluent) under analysis systems for handling the flow in the porous carbon electrode. The fluid model used was sulfuric acid solution diluted with vanadium oxides. The fluid was examined to be compact and isothermal, its density and dynamic viscosity were 1334.9 kgm^{-3} and 0.0024 Pa.s respectively. Active sites of electrode with an area of 100 cm^2 , a thickness of 3 mm , and a cross-section area of 0.00424 m of the channel were designed. The details of the operating parameter in the cell are shown in Table 3.1.

This dynamic model was simulated with different velocity inlet conditions that has been calculated analytically and stated at inlet channel as flow velocity and no applied pressure at the outlet channel was set in the boundary condition. Slip and flux condition on the walls were not applied to the domain surfaces except for the inlet and outlet flow channels. In all simulations, the fluent was set with double precision and pressure-based solver. The porous media model was evaluated with a pressure–velocity coupling algorithm SIMPLE (Semi Implicit Method for Pressure-Linked Equation) in solution methods. To choose the best configuration or design model of V-RFB, numerical investigations by using CFD simulation were conducted with different flow cell geometries and flow channel at various flow rates as an operating parameter for improving the performance of V-RFB.

To complete the modelling process, the set of all electrochemistry and flow channel in different cell geometries and transport properties values is set up as shown in Table 3.1.

Table 3.1 Transport properties

Parameters	Symbols	Value	Unit	Ref
Electrode thickness	δ_e	3	mm	
Electrode height	h	100	mm	
Electrode width	w	100	mm	
Polymer electrolyte membrane	δ_{mem}	3	mm	
Operating temperature	T	288	K	
Electrode porosity	ϵ_0	0.7	τ	(Xu et al., 2013)
Electrode fiber diameter	df	17.6	μm	
Electrolyte volumetric flowrate	Q	5, 10, 15, 20, 25, 30	$\text{cm}^3\cdot\text{s}^{-1}$	
Electrolyte density	ρ	1334.9	$\text{kg}\cdot\text{m}^{-3}$	
Electrolyte kinematic viscosity	ν	3.2×10^{-6}	$\text{m}^2\cdot\text{s}^{-1}$	
Carman-Kozeny constant	KCK	5.55		(Xu et al., 2013)
Carbon density	ρ	2240	$\text{kg}\cdot\text{m}^{-3}$	
Specific heat of carbon	c_p	710	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$	
Thermal conductivity of carbon		0.2	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	
Vanadium concentration	c	1.6	$\text{mol}\cdot\text{m}^{-3}$	
Electrolyte dynamic viscosity	μ	0.0024	$\text{Kg}\cdot\text{m}^{-\text{s}}$	
Thermal conductivity of electrolyte		0.67	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	
Reservoir volume	VC	200	mL	
Rib width		3	mm	

The FLUENT CFD solver is used to solve the governing equations for the conservation of mass, momentum and energy for a Newtonian incompressible fluid. This study only considers the steady state condition, and the relevant equations are summarized as:

$$\nabla \cdot \vec{v} = 0 \quad 3.1$$

$$\rho (\vec{v} \cdot \nabla) \vec{v} = -\nabla \rho + \nabla \cdot \tilde{\mu} (\nabla \vec{v}) - \mu K^{-1} \vec{v} \quad 3.2$$

where ρ is electrolyte density, \vec{v} is fluid velocity, K is permeability tensor, $\tilde{\mu}$ is effective viscosity, and μ is physical viscosity of electrolyte.

Improving an electrolyte distribution may reduce pumping power required; an alternative approach was proposed by designing different cell geometries with several flow channel designs on electrode porous media. Different flow channel designs in the cell electrode (active area) may give a different flow distribution and pressure drop.

In the present work, at a low flow rate, the flow was considered as laminar flow and the high flow rate was considered as turbulent flow. This flow consideration was supported by the calculation by referring to the Reynolds number formulae. Varied flow rates of fluid were applied with the inlet tube modelled at 3 mm diameter. Here, flow through with no flow pattern, parallel, and serpentine flow field were tested. The flow of the electrolyte, the pressure drop in V-RFB cells, mean velocity, and Reynolds number (Re) were determined using the following equations:

$$\text{Mean Velocity of fluid flow, } V_f = \frac{Q}{A} \quad 3.3$$

where V_f is the mean velocity of fluid flow (electrolyte) in ms^{-1} , Q is volumetric flow rates of electrolytes in $\text{m}^3 \cdot \text{s}^{-1}$, and A is the total area of electrode domains in m^2 .

$$Re_{efb} = \frac{\rho_{efb}VD}{\mu_{efb}} \quad 3.4$$

where Re_{efb} is Reynolds number of electrode flow battery, ρ_{efb} is the density of electrode flow battery in kgm^{-3} , V is average velocity in ms^{-1} , D is a diameter in m, and μ_{efb} is dynamic viscosity of electrode flow battery in Pa.s.

3.5 Mathematical model for pump power consumption with/without flow channel

Pressure drop influences a pumping energy required in RFB cell. As the pressure drop of the cell battery decreases, lower pumping energy is needed. Different flow pattern designs in the cell electrode (active area) may give a different flow distribution and pressure drop. Differential pressure (Δp) is the pressure between the inlet and the outlet (over the length of the electrode, L), and this result comes from the relationship of the viscous resistance flow, permeability of the electrode material, and viscosity of the electrolyte. A pressure drop through this electrode can be resolved according to Darcy's Law by including a flow rate (Q) and viscosity of the electrolyte (η_e). For determining performance of battery cell, the pump power consumption is one of the factors that need to be calculated to get maximum efficiency and performance of the cell battery. P_{pump} is the pumping power and this power depends on the flow rate, Q ; pump efficiency, ψ_{pump} and pressure drop across the cell.

Configuration 1: V-RFB cell without flow channels

In this plain channel of V-RFB cell geometry, given a direct flow of electrolytes through the active sites, the pressure drop through these cell geometries can be resolved according to Darcy's Law as below:

$$\Delta P = \frac{\eta_e}{K_e(\varepsilon)} Q \cdot \frac{L}{A} \quad 3.5$$

ΔP is the pressure difference between the inlet and the outlet, L is the length of the electrode over an entire domain, Q is the flow rate, η_e is viscosity of the electrolyte, K_e is permeability coefficient value, which is dependent on the porosity (ε) of the electrode. The permeability of porous electrode is calculated using Carman–Kozeny equation and the C_2 is an inertial loss coefficient that shows a geometrical aspect of the porous medium from the Blake-Kozeny formula:

$$K_e = \frac{d_f^2 \varepsilon^3}{K_{ck} (1 - \varepsilon)^2} \quad 3.6$$

The elements contained in the formula above are functions of the d_f as mean fibre diameter of the electrode and ε as medium porosity of felt electrode. K_{ck} is the Carman–Kozeny constant.

$$C_2 = \frac{3.5 (1 - \varepsilon)}{d_f \varepsilon^3} \quad 3.7$$

Configuration 2: V-RFB cell with flow channels

In the flow through the stack flow pattern of porous medium model that corresponds to parallel and serpentine flow channels, pressure drop can be measured and calculated by:

$$\nabla P_{ec} = \frac{\eta_{ec}}{K_{ec}(\varepsilon)} Q \frac{L_{ec}}{A_{ec}} \quad 3.8$$

where L_{ec} is the total length channel of electrode, Q is the volumetric flow rate of electrode, and A_{ec} is the area of electrode with channel, which is indicated as:

$$A_{ec} = (W_r + W_c)\theta_e \quad 3.9$$

where W_r and W_c are rib width and distribution channel and θ_e is the thickness of the porous medium. The pressure drop will directly change when a different direction of fluid flow or velocity is applied.

For determining performance of battery cell, the pump power consumption is one of the factors that need to be calculated to get maximum efficiency and performance of the cell battery P_{pump} is the pumping power and this power depends on the flow rate, Q ; pump efficiency, ψ_{pump} and pressure drop across the cell. The pumping power equation is represented as:

$$P_{pump} = Q \cdot \Delta P / \psi_{pump} \quad 3.10$$

3.6 Chapter summary

In this chapter, the methodologies used in the study are outlined. As the thesis is written, all the methodologies on simulation and calculation work were defined in each sub-chapter accordingly.

UMP

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter provides the results from the simulation and calculation works and discussion for the several important factors that affect V-RFB performances. The chapter also discusses flow distribution of the electrolyte on the cell geometries and flow channel applied and pumping power for each design proposed. In addition, for verification, results from the simulation were compared with the theoretical calculation results. The proven true relationship of modular stack data is also presented here.

4.2 Effect of cell geometry on flow distribution

From observation throughout this simulation result, a main reason which influences the performances of V-RFB system is due to the poor cell design that affects the flow distribution of electrolyte inside the cell. A comparison of flow electrolyte distributions and pressure drop has been performed to highlight the hydraulic performance of different cell geometries tested. This method aims at evaluating the best configuration in terms of flow distribution and pump energy consumption (pump power) within the cells.

Figure 4.1 depicts an electrolyte flow distribution for 100 cm² conventional square geometry at 30 cm³s⁻¹ flow rate applied. Result from the Figure 4.1 indicates a region A and B at square cell designed. Region A clearly shows dry zones whereas region B presents a recirculation zones inside the cell. A problem appears where there were seen a dry zone (region A) inside the cell geometry in the opposite corner to the outlet and recirculation zones (region B) can be seen in the left upper corner. This

indicated that the end result was undesirable and can lead to decrease battery performances.

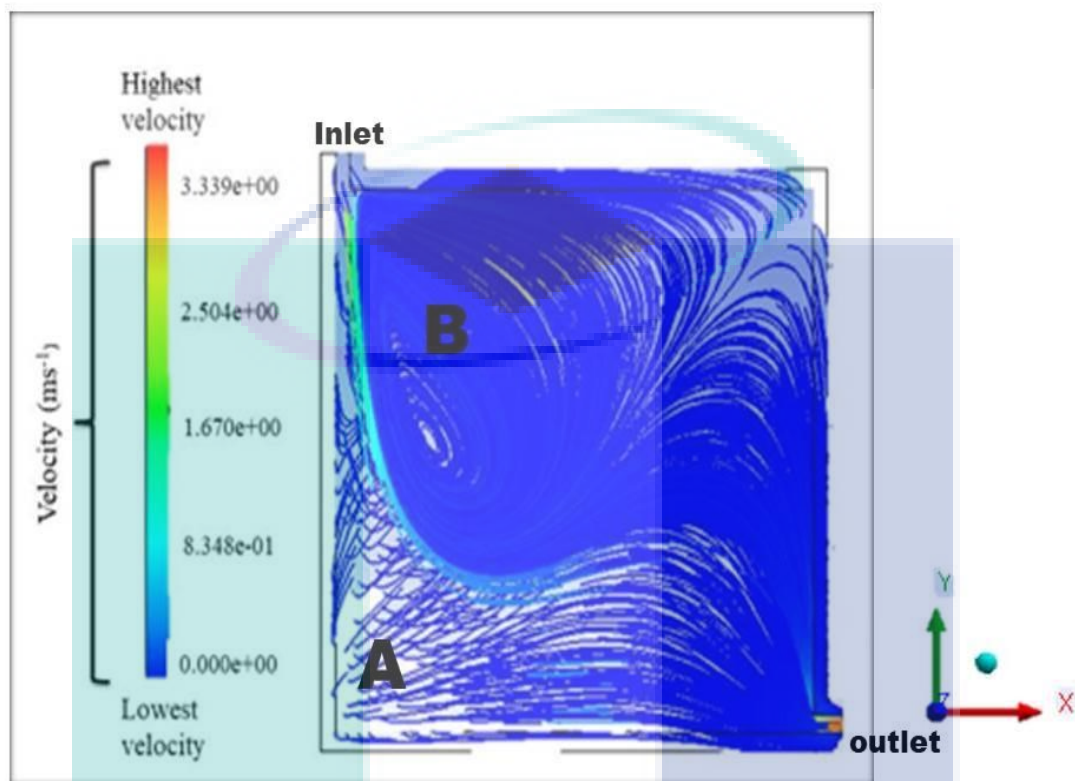


Figure 4.1 Flow electrolyte distribution obtained for a flow rate of $30 \text{ cm}^3\text{s}^{-1}$ in square cell geometry design

The fluid goes slower into certain parts of the cell geometry, thus creating dry zones. A dry zone indicates poor electrolyte flow distribution inside the cell, even though highest flow rate were applied due to inefficient cell design. Studies highlighted a uniform and good distribution of the electrolytes in the cell were achieved by avoiding stagnant zones, dry zones and having no recirculation zones, low pressure drop and pumping consumption (Bortolin et al., 2015; Cervantes-Alcala & Miranda-Hernandez, 2018).

The same study was conducted with rhombus cell geometry. Figure 4.2 illustrates flow electrolytes distribution in 100 cm^2 rhombus cell design. From Figure 4.2, it is observed that inhomogeneous electrolyte flow was seen inside the cell.

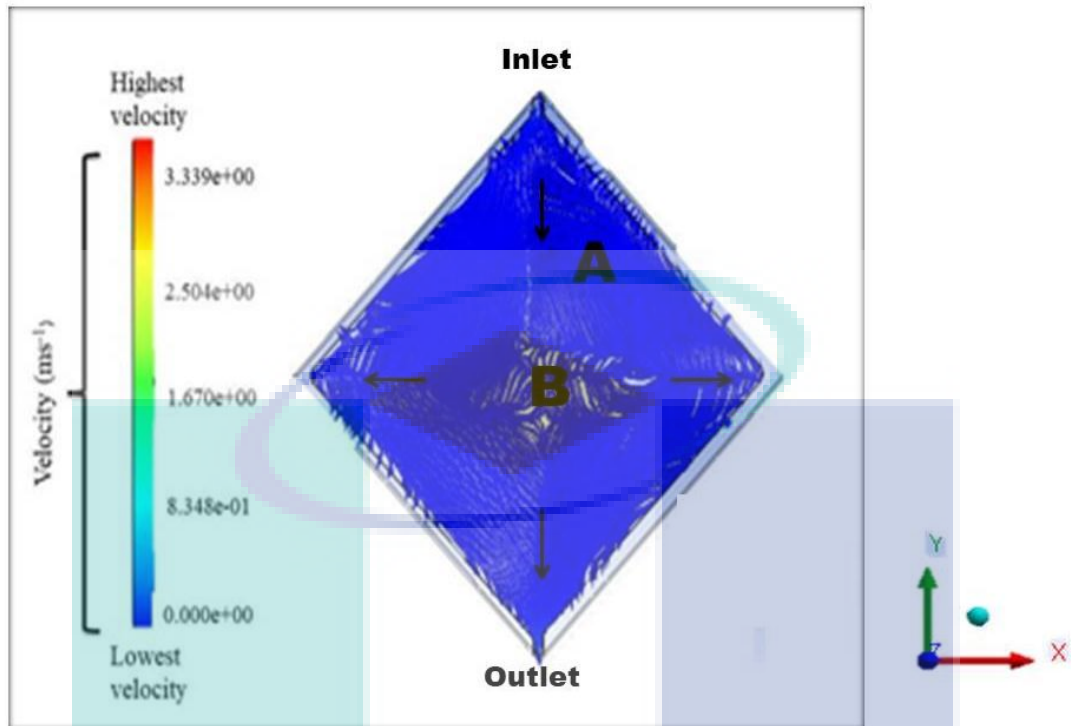


Figure 4.2 Flow electrolyte distribution obtained for a flow rate of $30 \text{ cm}^3\text{s}^{-1}$ in rhombus cell geometry design

Inhomogeneous and maldistribution happens as shown in region A with an arrow direction indicated that present of stagnant zones located at each lateral sides caused by inefficiently design that provides undesired route, which is theoretically not good for the system to achieve the hydrostatic equilibrium due to imbalance flow of electrolytes. Due to this problem appears, creating a little dry zone at the centre of the cell as shown in region B. This hydrodynamics behaviour is quite similar to square cell geometry due to the dryness of the zones, but the rhombus cell geometry indicates less dry zones compared to square cell geometry. Also note that, rhombus cell present of hindered fluid access due to low velocity of each side, which can cause stagnant and dry zone in which secondary reactions can occur, thereby hindering V-RFB performances.

Similar flow simulation test can be observed for 100 cm^2 circular cell geometry design. Figure 4.3 demonstrates flow electrolytes distribution in 100 cm^2 circular cell design. It appears from Figure 4.3 that, a calm zone was seen in the entire area of circular cell geometry design as shown in region B.

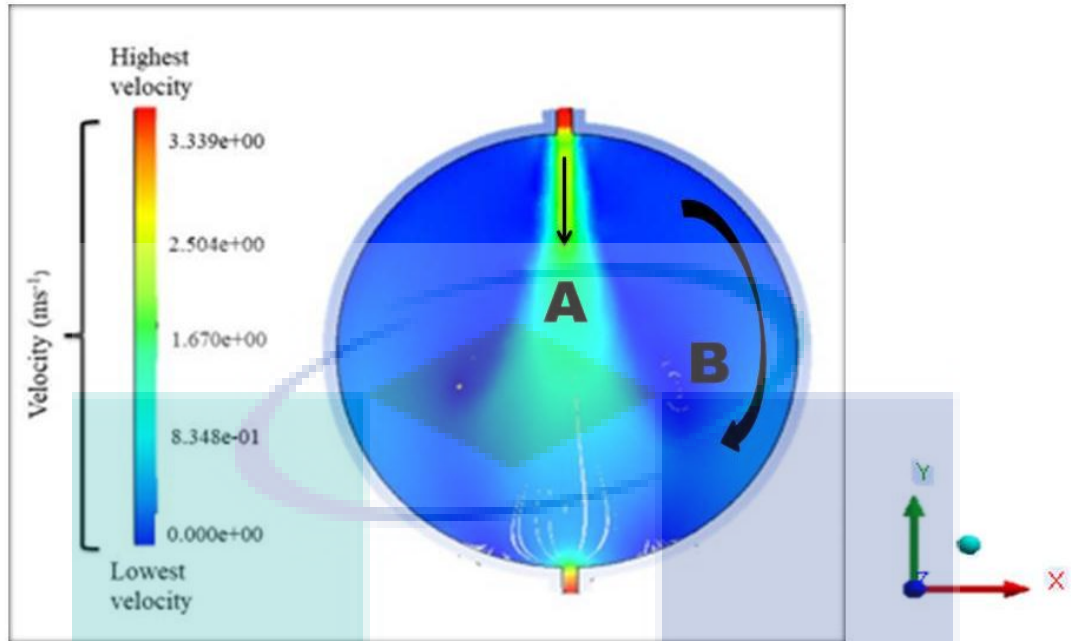


Figure 4.3 Flow electrolyte distribution obtained for a flow rate of $30 \text{ cm}^3\text{s}^{-1}$ in circular cell geometry design

In addition, region A indicates that high velocity from inlet of the circular cell caused more uniform electrolyte distribution inside the cell as shown in red to yellowish-green and intense blue colour. In this case, an improved flow distribution resulted, in which no recirculation or stagnant zones were present. Calm zones facilitate a more homogeneous flow distribution within the cell electrodes. Thus, a uniform electrolyte should be ensured so that the reactant supply and mass transport are high enough and maintain good performances of the V-RFB system (Xu & Zhao, 2015). The findings reveal that, an alternative cell designs were presented and the weaknesses of the proposed design were discussed. The newly developed 100 cm^2 circular cell design of V-RFB has been presented and performing better electrolyte flow distribution compared to previous designs which are conventional square and rhombus cell shaped, yet suitable for expanding the studies on V-RFB.

4.3 Effect of cell geometry on pump energy consumption (Pump power)

The effect of pump energy consumption on 100 cm² unit cell V-RFB was examined under various flow rates in the range of 5 - 30 cm³s⁻¹. Here, the pump power consumption has been calculated in order to evaluate the performance of the RFB cell in terms of pressure drop. For the estimation of pressure drop, the area-weighted average of static pressure has been calculated at the inlet and outlet of channels for each configuration. Figure 4.4 representing the effect of pressure drop in 100 cm² for different unit cell geometries design (square, rhombus, circular) with plain (no flow channel) applied at controlled flow rates (5 – 30 cm³s⁻¹) with setting operating parameter.

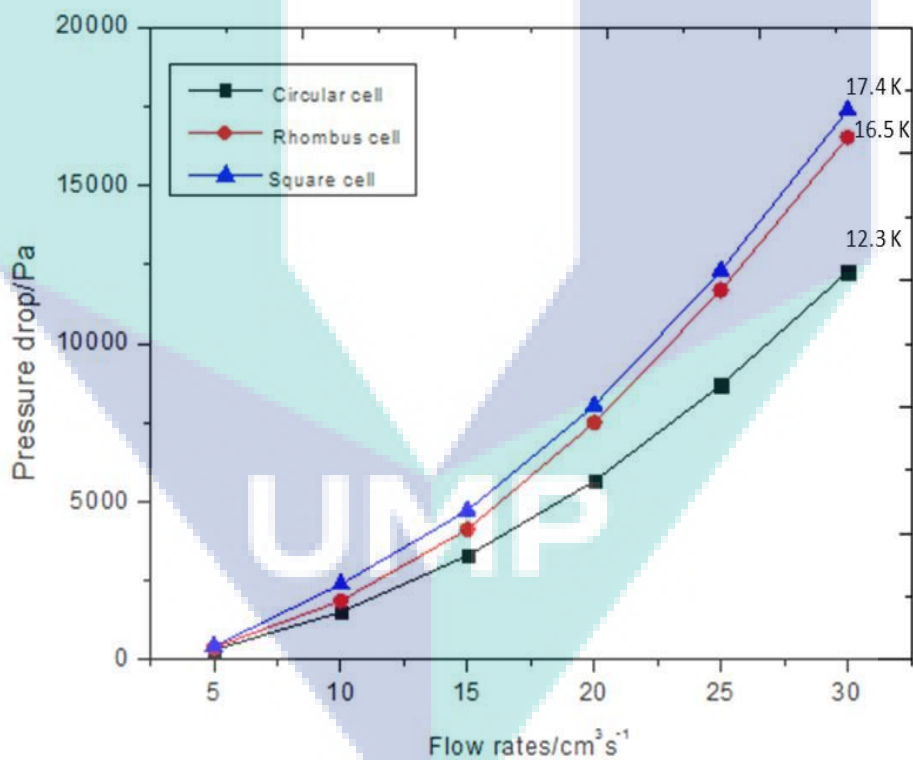


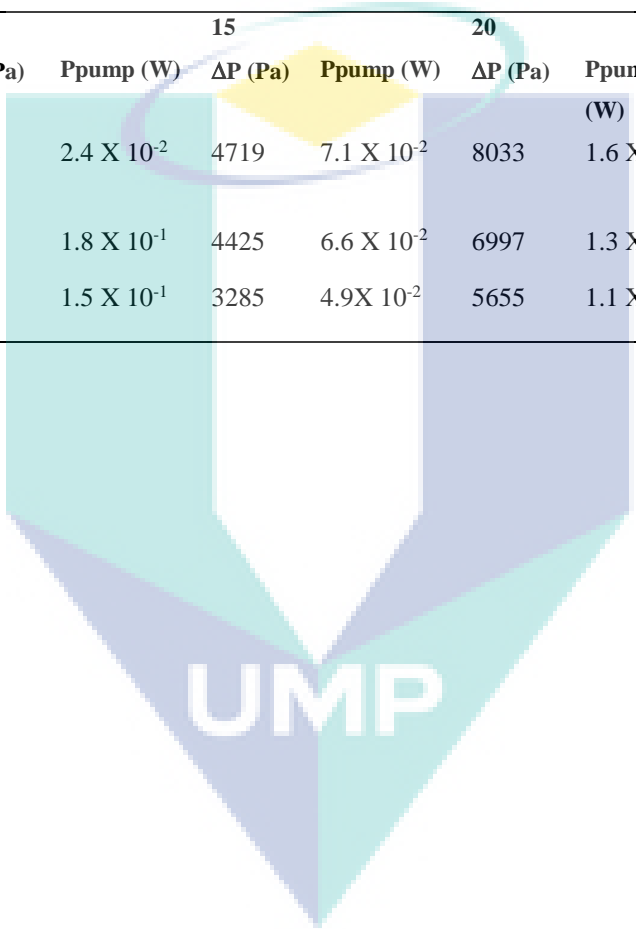
Figure 4.4 Representing the effect of pressure drop in 100 cm² for different unit cell geometries design (square, rhombus, circular) with plain channel applied at controlled flow rates (5 - 30 cm³s⁻¹)

As clearly seen in Figure 4.4, it is noted and was observed that the increase in volumetric flow rate also cause the total pressure in the cell to increase. The result showed a conventional square cell geometry had a pressure drop of 422 Pa, followed by rhombus cell at 385 Pa and circular cell design at 314 Pa at lowest flow rates applied which are $5 \text{ cm}^3\text{s}^{-1}$. Furthermore, as observed in Figure 4.4, the findings showed that the square flow cell geometry had the highest pressure drop (17.3 kPa), followed by rhombus cell (16.5 kPa) and circular cell (12.2 kPa) at highest flow rates applied which are $30 \text{ cm}^3\text{s}^{-1}$. This finding highlights, a conventional square cell design exhibits the highest pressure drop among others design, followed by rhombus cell and the present findings indicates a circular cell design maintain the lowest pressure drop in all control flow rates applied.

In general, the pressure losses associated with flow electrolyte distribution in a V-RFB system and have more predominant impact on pumping energy system. Pumping power is one of the key requirements that determine battery performances (Park et al., 2017). It can be seen in Table 4.1, a different pressure drop and pumping power consumption results exhibited by different flow cell geometries showed that cell geometry is one of the factors that influence battery performances. Conventional square required large pump power and shows the highest pressure drop compared to others design due to severe flow non-uniformity inside the cell which are $2.1 \times 10^{-3} \text{ W}$ (422 Pa) at lowest and 5.2×10^{-1} (17.4k) at highest flow rates. Pressure drop result is directly proportional to pump power. Interestingly, this correlation is related when higher the pressure drop, the larger pump power required within the cell. It can be seen in Figure 4.4 that the overall result of pressure drop from all types of cell geometries tested is clearly shown upwards trends as the pressure drop increases, which is a significant indication that more pumping power required. The result of the present study also revealed that, when more pump power required within the cell, the higher pumping losses happen that could affect the V-RFB performances.

Table 4.1 Pump power consumption (in W) for different flow cell geometries in various flow rate applied in range (5 - 30 cm³s⁻¹)

Cell geometries	Flow rates (cm ³ s ⁻¹)											
	5		10		15		20		25		30	
	ΔP (Pa)	P_{pump} (W)	ΔP (Pa)	P_{pump} (W)	ΔP (Pa)	P_{pump} (W)	ΔP (Pa)	P_{pump} (W)	ΔP (Pa)	P_{pump} (W)	ΔP (Pa)	P_{pump} (W)
Square cell	422	2.1×10^{-3}	2382	2.4×10^{-2}	4719	7.1×10^{-2}	8033	1.6×10^{-1}	12.3k	3.1×10^{-1}	17.4k	5.2×10^{-1}
Rhombus cell	385	1.9×10^{-3}	1807	1.8×10^{-1}	4425	6.6×10^{-2}	6997	1.3×10^{-1}	11.2 k	2.9×10^{-1}	16.5k	4.9×10^{-1}
Circular cell	314	1.5×10^{-3}	1511	1.5×10^{-1}	3285	4.9×10^{-2}	5655	1.1×10^{-1}	8.6k	2.1×10^{-1}	12.3k	3.7×10^{-1}



As illustrated in Table 4.1, rhombus cell follows the same pattern of pressure drop in square cell and the result indicates that a slight different pressure drop in rhombus cell, whereas higher pressure drop different is observed in a circular cell design compared to conventional square and still kept low pressure drop than rhombus designs. From Table 4.1 presents pressure drop and pump power inside the rhombus which were 385 Pa (1.9×10^{-3} W) at $5 \text{ cm}^3\text{s}^{-1}$ and 16.5 kPa (4.9×10^{-1} W) at $30 \text{ cm}^3\text{s}^{-1}$, whereas circular cell required 314 Pa (1.5×10^{-3}) at $5 \text{ cm}^3\text{s}^{-1}$ and 12.3 kPa (3.7×10^{-1} W) at $30 \text{ cm}^3\text{s}^{-1}$ controlled flow rates. Rhombus cell presents high pressure drop result and required more pumping power due to non-uniform electrolyte flow and has stagnation zones. Table 4.1, however, shows that circular cell design exhibits lesser pressure drop and pumping energy consumption. Uniform distributions of electrolyte on the circular cell geometry required minimize pressure drop and lower pump power. Lower consumption of pumping power energy due to a smaller pressure drop within the cell may lead to best performances of the battery system (Xu et al., 2013).

For simplicity of this part, Table 4.2 summarised the data of pump power difference with all geometries tested at lowest and highest flow rate applied are shown. Table 4.1 shows the highest pump energy consumption presents by conventional square cell. Thus, conventional square was decided as unlike design to be chosen for further analysis. Its apparent from Table 4.2, other cell geometries as rhombus and circular cell has been compared with square cell, which were required a lesser pump power reduction. It can be seen that a reduction in pump power occurred for rhombus and circular cell presenting decrements of 8.5% and 25.6% at lowest flow rate, whereas 5.17% and 18.4% at highest flow rate applied in pumping power respectively. Consuming excessive pump power will lower the system performances (Yin et al., 2014). Thus, pressure drop has to be kept minimum so as to minimize pumping power.

Based on the result shows in Table 4.2, a slight decrease of pump power reduction in rhombus cell is observed due to quite similar characteristic of flow regime inside the cell compared to square shaped. Whereas, better result is observed in circular cell design at controlled flow rates applied with pump power reduction recorded a large difference compared to rhombus cell result. Circular cell design shows highest decrement percentage of pump power reduction indicating a better flow regime with low pressure drop and pump energy consumption.

Analysis of the computed result shows that circular cell geometry design gives the best uniformity electrolyte distribution, lesser pressure drop and pumping power; it is clear that this design outperforms the conventional and rhombus cell shaped. (Arenas et al., 2017) reported that, critically considers design, construction and cell features together with a benefits and problems, leading to good practice through improved battery performance. Next, this circular cell design study set out to determine the effectiveness for flow channel applied to provide a better pathway for electrolyte distribution within the cell.

Table 4.2 Pump power difference within the cell geometries

Cell geometries	Pump power reduction (%)	
	At lowest flow rate applied (5 cm ³ s ⁻¹)	At highest flow rate applied (30 cm ³ s ⁻¹)
Rhombus cell vs Square cell	- 8.5	- 5.17
Circular cell vs Square cell	- 25.6	- 18.4

4.4 Effect of flow channel applied on selected flow geometry

Circular cell geometry design showed the best result for both pressure drop and pump energy consumption at various flow rates applied. So, the study was extended to determine which flow channel design would be the best to be applied on 100 cm² circular cell design to circulate and transport electrolyte to the reaction site which has an impact also on pressure drop, pump power and cell performances. Table 4.3 shows the pressure drops for plain cell and two types of flow channel at the flow rates in the range 5 to 30 cm³s⁻¹. When the flow rate becomes higher, e.g. 30 cm³s⁻¹, the pressure drop for plain cells and two types of flow channel increase, as illustrated in Figure 4.5. For the first two flow channel, the pressure drops for parallel and serpentine increase from 130 to 8978 Pa and from 650 to 18.9 kPa respectively, while for the plain one, from 314 to 12.3 kPa as the flow rate increases from 5 to 30 cm³s⁻¹. These patterns are shown in Figure 4.5 indicate that the pressure drop increases linearly with the flow rates. It can be seen that parallel flow channel is required lower pressure drop compared to the plain cells. However, as Figure 4.5 shows serpentine flow channel indicates the highest pressure drop.

Table 4.3 The pressure drops under different flow channel (plain, parallel, serpentine) with controlled flow rates as an operating parameter

Pressure drop (Pa)		Flow rates (cm ³ s ⁻¹)						Pump Power (Watt)	
		5	10	15	20	25	30	Lowest flow rate (5 cm ³ s ⁻¹)	Highest flow rate (30 cm ³ s ⁻¹)
Flow stack channel	Plain	314	1511	3285	5655	8863	12.3k	1.57 x 10 ⁻³	6.13 x 10 ⁻²
	Parallel	130	880	2563	3780	6434	8978	6.50 x 10 ⁻⁴	4.48 x 10 ⁻²
	Serpentine	650	2870	4716	8503	1209	18.9k	3.25 x 10 ⁻³	9.49 x 10 ⁻²

From the result in Table 4.3, also shows the corresponding pumping powers for the plain cells and with two types of flow channel. As stated in Table 4.3, serpentine flow channel shows the highest pump power which is 3.25 x 10⁻³ W at 5 cm³s⁻¹ and 9.49 x 10⁻² W at 30 cm³s⁻¹, followed by plain cell 1.57 x 10⁻³ W and 6.13 x 10⁻² W, whereas the parallel flow channel shows the lesser pump power which is 6.50 x 10⁻⁴ W and 4.48 x 10⁻² W. Excessive pump energy consumption may lead the cell performance to decline (Xu, Zhao, & Zhang, 2014b). This flow channel differs in terms of their ability to transport electrolyte to the reaction site.

Plain cell is a cell geometry without any flow channel pattern, it is required much pump power within the cell compared to the parallel design. This is because on the plain channel of an electrolyte is start to flow directly into the cell geometry at one corner of the cell and it allowed to distribute itself throughout to the entire of the cell and this is lead to high pump power that required to flow an electrolyte through the entire of cell geometry. Whereas, serpentine shows the highest pump power due to severe flow non-uniformity can be expected among the channel. Then, Table 4.3 indicates parallel flow channel could enhance the cell performance without increasing the pressure drop and significantly consumed lesser pump energy consumption. In addition, circular geometry with parallel flow channel design show the rate of percentage on pump energy reduction is decreasing 53% when compared to conventional square cell design.

(Jyothi Latha & Jayanti, 2014b) reported a suitable flow channel design through the cell geometries can significantly reduce a pressure drop and pump energy consumption of the V-RFB system.

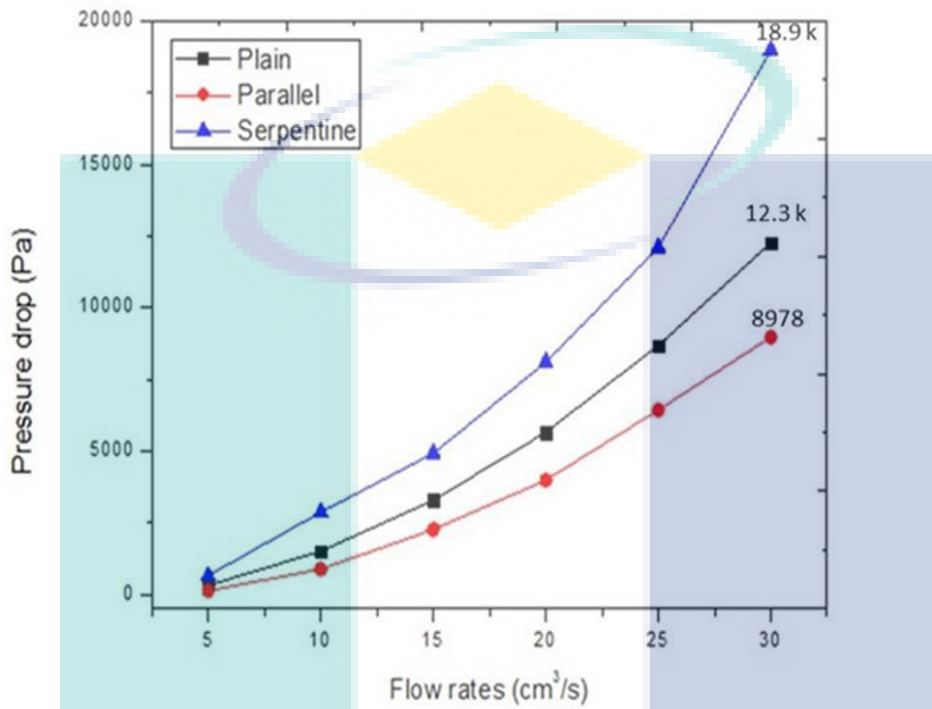


Figure 4.5 Representing the effect of pressure drop in 100 cm² of circular cell geometry with plain and two types of flow channel (parallel, serpentine) applied at controlled flow rates (5 - 30 cm³s⁻¹)

4.5 Effect of 100 cm² modular stack in different cell geometries on pump power

V-RFB is known as one of the energy storage technologies that provide simplicity of design and principle operation. This study indicates a scale up work of V-RFB system. This scaling up studies is for increasing output and storage capacity. But the main focus on this work is for analysing an increasing output result. Due to simplicity of V-RFB design the output and capacity specification is designed independently of each other. The output specification result is depending on the number of cell stacks whereas for storage capacity is depending on the amount of electrolyte which are not considered in this studies. Figure 4.6 shows a pressure drop for conventional square compartment of a V-RFB 5 cell stack. Flow rate applied: 5 - 30 cm³s⁻¹. It was observed that the pressure drop is increase by adding a number of cell, which is clearly indicates the pump power is also increased.

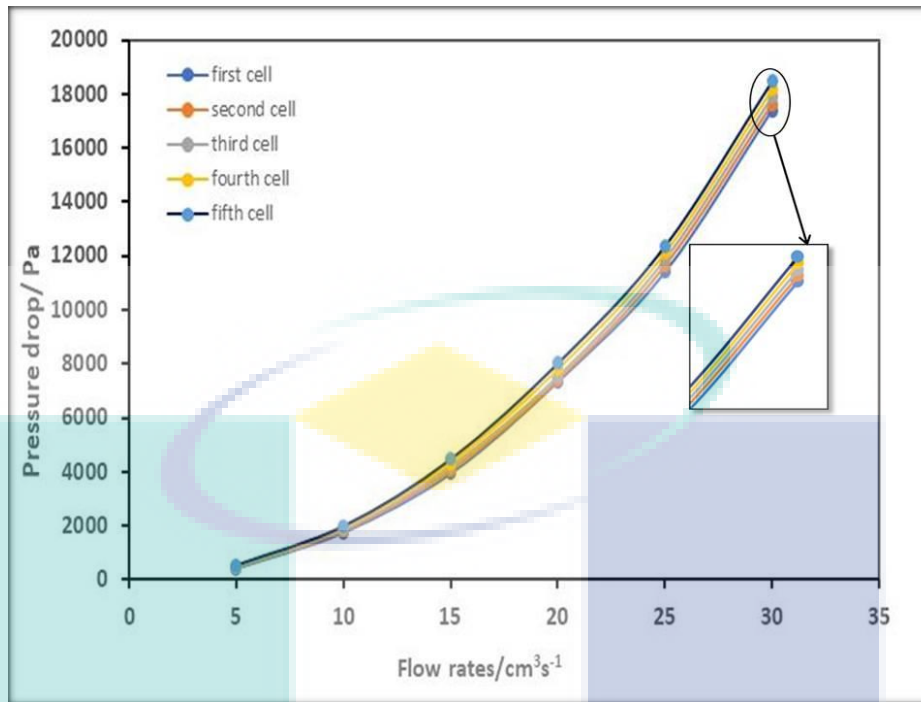


Figure 4.6 Pressure drop for conventional square compartment of a V-RFB 5 cell stack. Flow rate applied: 5 - 30 cm^3s^{-1}

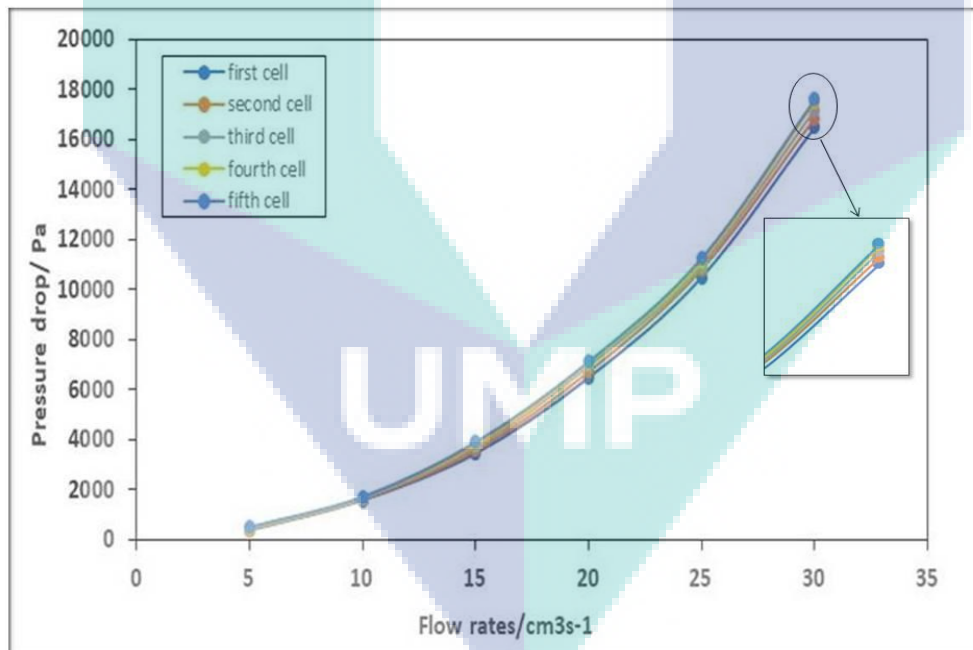


Figure 4.7 Pressure drop for the rhombus compartment of a V-RFB 5 cell stack. Flow rate applied: 5 - 30 cm^3s^{-1}

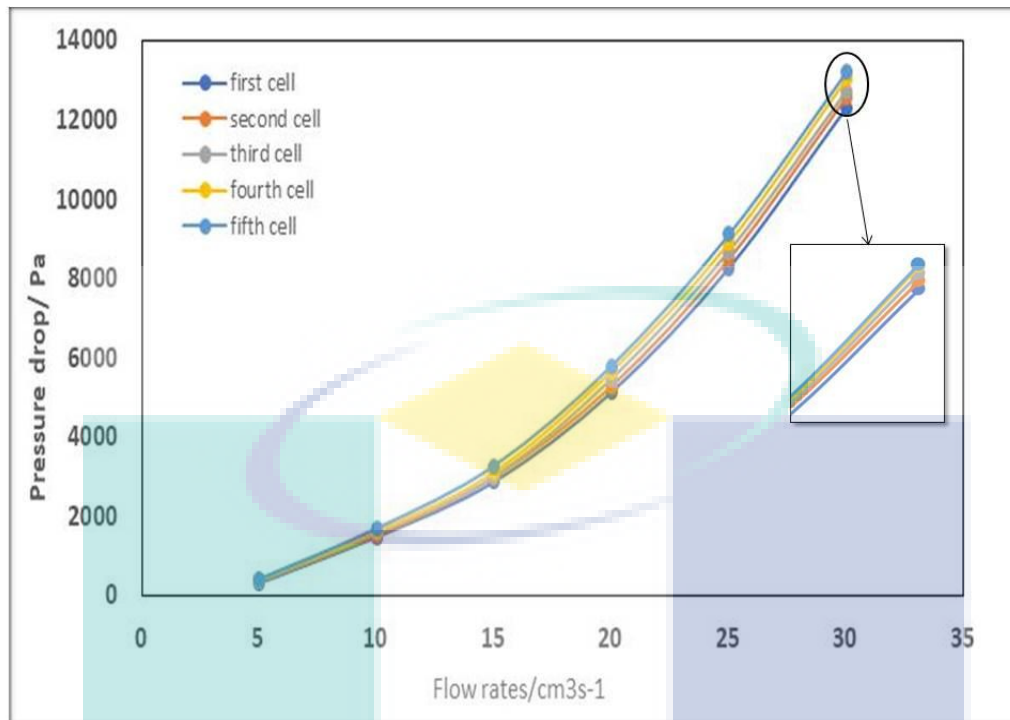


Figure 4.8 Pressure drop for the circular compartment of a V-RFB 5 cell stack. Flow rate applied: 5 - 30 cm³s⁻¹

Figure 4.7 and Figure 4.8 represents pressure drop for the rhombus and circular compartment of a V-RFB 5 cell stack at highest flow rates applied. The pattern of the data for these two compartments is same as shown in Figure 4.6. From these result, can be concluded that each cell has maintaining a same difference pressure drop and pump energy consumption value, the proportion is same with increasing a number of each cell. Detail information of pressure drop, pumping power, average mean for conventional square, rhombus and circular cell geometries of V-RFB is present in Table 4.4, Table 4.5 and Table 4.6. Square compartment shows scale-up result for pressure drop and the pump power average difference is 274 Pa (0.537 W) for each number of the cell added, whereas rhombus and circular cell shown 332 Pa (0.514 W) and 224 Pa (0.383 W). Furthermore, the individual batteries cell is connected each other in series configuration, so it can be equalized easily the pump power of modular stack. The capture trends data is useful for optimizing other parameter like charge condition and current distribution because the simplicity of V-RFB design allow predicting and calculate other performances and behavioural in V-RFB systems. Scale up studies enable to better understanding of the complex work and relationship between performances (Arenas et al., 2017).

Table 4.4 Pressure drop, pumping power, average mean for the square V-RFB in range 1 - 5 cell stack. Flow rates applied : $30 \text{ cm}^3\text{s}^{-1}$

Number of cell	Pressure drop (Pa)	Pump Power (Watt)	Average Mean (Pa)/(W)
1	17390	0.522	
2	17634	0.529	274Pa/
3	17892	0.537	0.537W
4	18178	0.545	
5	18465	0.554	

This scale-up work start with involving modelling the reaction environment, studies the design of flow distributor, evaluation of fluid flow and pressure drop before go to monitoring the electrical parameter like scale up studies of current distribution or shunt current in the V-RFB system.

Table 4.5 Pressure drop, pumping power, average mean for the rhombus V-RFB in range 1 - 5 cell stack. Flow rates applied: $30 \text{ cm}^3\text{s}^{-1}$

Number of cell	Pressure drop (Pa)	Pump Power (Watt)	Average Mean (Pa)/(W)
1	16500	0.495	
2	16859	0.506	332 Pa/
3	17198	0.516	0.514 W
4	17498	0.525	
5	17601	0.528	

Table 4.6 Pressure drop, pumping power, average mean for the circular V-RFB in range 1 - 5 cell stack. Flow rates applied: $30 \text{ cm}^3\text{s}^{-1}$

Number of cell	Pressure drop (Pa)	Pump Power (Watt)	Average Mean (Pa)/(W)
1	12300	0.369	
2	12567	0.377	224 Pa/
3	12725	0.382	0.383 W
4	13025	0.391	
5	13197	0.396	

The findings reveal as shown in Table 4.4, Table 4.5 and Table 4.6 that an average different expressing the equality average difference result of pressure drop and pumps power for all types of cell geometries in modular stack. This proportion is shown near to linear result. From these results shown above, it can be concluded that working with stack formed by 100 cm² cell, the pressure drop and pump power may be calculated and expected. The designed cell stack could be incremented to 100th cell, 10,000th cell and above while maintaining the mean average and apply the general formulae that have been developed as below:

$$\text{Formulae} = (\text{Mean different, } \mu \times \text{no of cell, } N) + (\text{1st Cell result, Pa/W}) \quad 4.1$$

This useful scale-up studies by simulation and modelling approaches, reducing the financial burden on physical experimentation and accelerating process development for testing work and providing confidence for commercialization.

4.6 Model verification

Consistency is an important criterion in evaluating the performance of V-RFB cells towards a pressure drops required within the cells. Figure 4.9 shows a pressure drop of the circular cell geometry at simulation and calculation studies at various flow rates applied in the range 5 to 30 cm³s⁻¹. From Figure 4.9, it is interesting to note that circular simulation proved to be consistent in estimating the circular calculation result with mean-error recorded at 169 Pa. Furthermore, the mean-error is found to be in the range of pressure drop, Pa throughout all the flow rates applied. It is also found that the pressure drop required in circular cell throughout the simulation is increase by increasing the flow rates. A clear indication shown that the pressure drop calculated inside the circular cell is also increase.

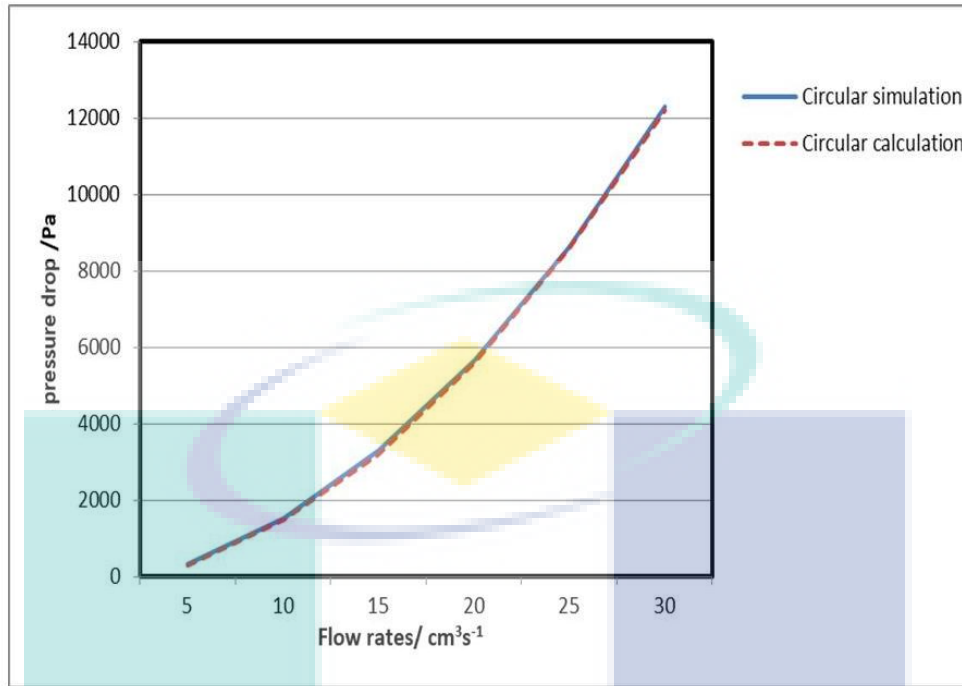


Figure 4.9 Pressure drop vs. flow rate of the circular cell geometry for simulation and calculation result

4.7 Chapter summary

This chapter focuses on simulation and calculation work of a 100 cm² cell geometries V-RFB under controlled flow rates applied as an operating parameter. The effect of pump energy consumption on 100 cm² unit cell V-RFB was examined under various flow rates in the range of 5 - 30 cm³s⁻¹. This method aims at evaluating the best configuration in terms of flow distribution and pump energy consumption (pump power) within the cells. Circular cell exhibits uniformly electrolyte distribution inside the cell, in which shows no recirculation, stagnant zones and dry zones presents. At pump energy consumption result, conventional square cell showed a highest pump power which are 422 Pa at lowest and 17.3 kPa at highest flow rates applied. Follow by rhombus cell design and circular. It can be seen that a reduction in pump power occurred for rhombus and circular cell presenting decrements of 8.5% and 25.6% at lowest flow rate, whereas 5.17% and 18.4% at highest flow rate applied in pumping power respectively when compared to the conventional square shaped. Circular cell geometry design presented the best result for electrolyte flow distribution and required lesser pump power inside the cell at various flow rates applied.

The study was extended to determine which flow channel design would be the best to be applied on 100 cm² circular cell design to circulate and transport electrolyte to the reaction site which has an impact also on pressure drop, pump power and cell performances. The best application of flow channel result present a parallel flow channel is a suitable channel to be applied on circular cell geometry. Parallel flow channel shows lowest pump power consumed which is 6.50×10^{-4} W and 4.48×10^{-2} W at the lowest and highest flow rate applied. The percentage on pump energy reduction different improved to a 53% compared to the conventional square cell geometry without any flow channel.

Furthermore, an extension of the initial work is focuses on build up a modular stack by summation of the individual cells. This is for scale up studies. This scaling up studies is for increasing output and storage capacity. But the main focus on this work is for analysing an increasing output result. The V-RFB single cell is scale-up to 5 cells stacked. A pressure drop, pumping power and average different between each cell is analysed. The result shows that square compartment shows scale-up result for pressure drop and the pump power average difference is 274 Pa (0.537 W) for each number of the cell added, whereas rhombus and circular cell shown 332 Pa (0.514 W) and 224 Pa (0.383 W). From this result, can be concluded that each cell has maintaining a same difference pressure drop and pump energy consumption value, the proportion is same with increasing a number of each cell. This proportion is shown near to linear result. Thus, a general formula has been developed for working with stack formed by 100 cm² cell, the pressure drop and pump power may be calculated and expected. The designed cell stack could be incremented to 100th cell, 10,000th cell and above while maintaining the mean average.

The accuracy of the model was verified the pressure drop inside the cell at various flow rates applied and the model is proved to be consistence throughout the calculation model result. Ultimately, the model was validated to a calculation pressure drop of V-RFB system and the result indicated that the proposed simulation work result has demonstrated a good degree of accuracy in predicting the trends observed in calculation work with minimum mean-error of 169 Pa.

CHAPTER 5

CONCLUSION

5.1 Statement contributions and conclusion

Based on the study, it is worth to mention that:

1. This thesis presented a simulation work for analysing a single cell and modular stack of V-RFB system to study the factor that gives an impact to the battery performances. A review of previous work mostly developed an experimental work to study the characterisation and behavioural of V-RFB cells. This work consumed long hour and high cost. Thus, an alternative way was presented through simulation model by using CFD software. This simulation works able to represent a true description and natural phenomenon in V-RFB system by consuming less hour and cost.
2. This thesis summarises for critically considers design, construction and cell features together with their benefits and problems, leading to good practice through improved cell performance. This work presented a new design and development of single cell and modular stack of V-RFB. The newly developed 100 cm² conventional square, rhombus and circular cell geometries with flow channel added have been presented in details; in which the cell geometries and flow channel were suitable for expanding the studies on V-RFB. Notably, the optimum results of the V-RFB cell indicate that the circular geometric cells design without fluid flow channels record evenly electrolyte distribution within the cells and shows the lowest pump power consumption reduction is 25.6% at the lowest and 18.4% at the highest flow rate. In addition, circular geometry cells show the rate of percentage is decreasing 53% with parallel flow channels applied.
3. The V-RFB work here has been scaled-up to a fifth-cell stack assembly and connected hydraulically with a series configuration to evaluate the pressure drop &

pump power in order to look behaviour and trends in the fifth cell stack is similar to that obtained for the single stack system. From this result, it can be concluded that working with stack formed by 100 cm² fifth cell, the pump power can be calculated. The cell stack designed could be incremented to 100th cell, 10,000th cell and above while maintaining the mean average and apply the general formulae that have been developed. Throughout these studies, a new general formula for 100 cm² modular stacks has been created. Useful scale-up work by simulation and modelling approaches, reducing the financial burden on physical experimentation and accelerating process development for testing work and providing confidence for commercialization.

5.2 Recommendation of future works

1. In this study, only the different cell geometries and flow channel patterns were investigated. Another important factor that needs to be further researched is the vanadium concentration of V-RFB electrolytes that would help to establish a greater degree of accuracy on these battery performances due to interplays between the electrolyte and the electrode, which may influence the solubility and stability and become one of the factors for improvement on energy density of V-RFB.
2. It is recommended that further research is undertaken in the following areas: size of channel, pore diameter, and effect of an applied catalyst on graphite felt. All these areas of research would be a great help to fully study the behaviour of V-RFB system. Further investigation on the thermal response on different V-RFB cell designs is strongly recommended.

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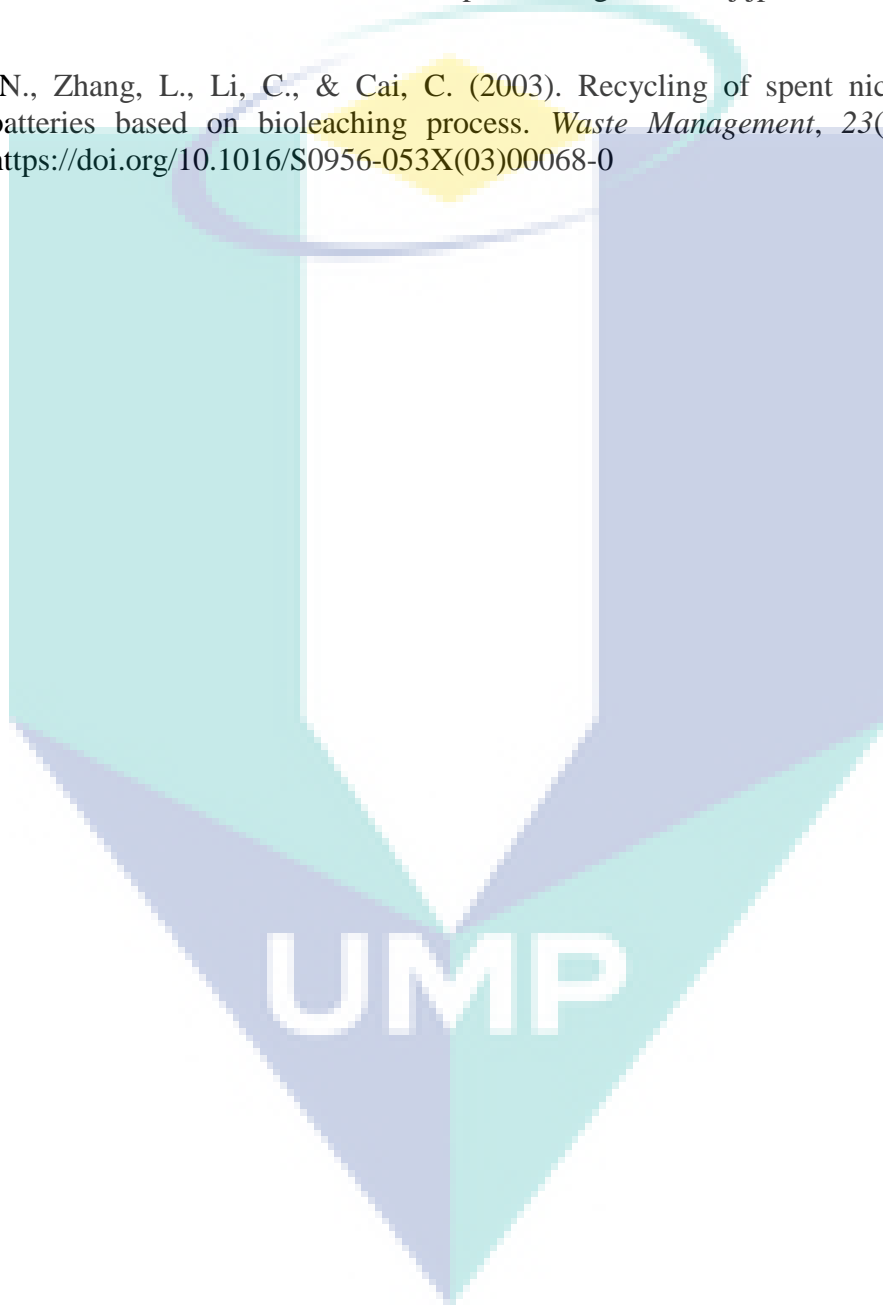
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APPENDIX LIST OF PUBLICATION

The list of publications during my master study is stated as below:

Published paper:

1. S. Sujali, M. R. Mohamed, S. A. Mad Don, N. Yusoff, ' Method approaches to prevent leakage cell stack of vanadium redox flow battery (VRFB), 4th IET International Conference on Clean Energy and Technology.
2. Suhailah, Sujali and Mohd Ruslim, Mohamed and Oumer, A.N. AND Azizan, Ahmad and Leung, P. (2018) Study on architecture design of electroactive sites on Vanadium Redox Flow Battery (V-RFB) In: International Conference on renewable Energy and Environment Engineering (REEE 2018), 29-31 October 2018, Paris, france, pp 1-5.



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