Modeling and analysis of new types of electrochemical components : solid oxide fuel cell (SOFC) and vanadium redox flow battery (VRB) for system level application

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Modeling and Analysis of New Types of Electrochemical Components – Solid Oxide Fuel Cell (SOFC) and Vanadium Redox Flow Battery (VRB) for System Level Application

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Abstract

With the prosperous development of distributed power grid and renewable electrical sources, new type of electrochemical components have received the most attention to date for their high efficiency and low pollution. Among all kinds of electrochemical components, vanadium redox flow batteries (VRB) and solid oxide fuel cell (SOFC) are especially suited for large-scale electrical storage and generation correspondingly. However, so far, there are rare models of SOFC and VRB for system-level analysis. This thesis aims to develop the methodologies for SOFC and VRB modeling which are concise and reliable under different operating conditions. Moreover, several novel plant structures are studied based on the proposed models of SOFC and VRB.

At the beginning, two SOFC models, namely, a simplified 1D distributed model and a theoretical lumped model are established for thermal analysis and electrical analysis correspondingly. The form of both models are simplified and verification shows that both SOFC models are accurate. Then, based on the proposed distributed model of SOFC, a novel temperature-maintained SOFC combine gas turbine hybrid plant (SOFC-GT) is built up. Through introducing a heat management subsystem, the average temperature of SOFC can be adjusted by controlling the volume of GT's exhaust and additional fuel. Besides, based on different air and fuel supply patterns, an optimal partial-load strategy of the proposed plant is found out.

On the other hand, based on experimental data, a comprehensive electrical circuit model of VRB is identified by using least square method. The inherent features of flow battery such as shunt current, ion diffusion and pumping energy consumption are considered. The identification model of VRB is suited for power grid analysis due to its straightforward form and favorable accuracy. Finally, a novel DC grid composed of SOFC, VRB and super-capacitor (SC) is proposed to solve the lack of electricity in remote areas. Based on the proposed lumped model of SOFC and identification model of VRB, the novel hybrid DC grid is simulated.

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Table of Contents

Abstract	I
Acknowledgements	II
List of Figures	VII
List of Tables	XI
Nomenclature	XIII
Greek alphabet	XIV
Superscript	XIV
Subscript	XIV
Abbreviations	XV
Chapter 1. Introduction	1
1.1 Motivation and Objective of the Present Work.....	4
1.2 Thesis Structure	6
Chapter 2. Literature Review	8
2.1 Distributed Power Grid	8
2.1.1 Development Status	9
2.2 Solid Oxide Fuel Cell.....	13
2.2.1 Principles and Structure	17
2.2.2 Cell Geometry of SOFC	21
2.2.3 Thermal reliability of SOFC	25
2.2.4 Features of SOFC	26
2.2.5 Fuel Cell System	27
2.3 Vanadium Redox Flow Battery.....	30
2.3.1 Principles and Structure	31

2.3.2 Capacity Fading of VRB	35
2.3.2 Features of VRB	36
2.4 Summary of Literature Review	38
Chapter 3. System Level Modeling of SOFC	40
3.1 Lumped model of hydrogen-driven SOFC	41
3.1.1 Mass Balance	44
3.1.2 Ohmic Polarization	45
3.1.3 Concentration Polarization	46
3.1.4 Activation Polarization	47
3.1.5 Verification	48
3.2 Reduced 1D distributed model of methane-driven SOFC.....	51
3.2.1 Internal Reforming Model	53
3.2.2 Mass Transfer	55
3.2.3 Thermal Model	57
3.2.4 Solution Method and Simulation Results	58
3.3 Conclusion	62
Chapter 4. Temperature-Maintained SOFC-GT System	64
4.1 System Configuration	65
4.1.1 Temperature Regulation Mechanism	67
4.2 Balance of Plant Components	69
4.2.1 Compressor and Turbine	69
4.2.2 Heat Exchanger	73
4.2.3 Combustor	74

4.2.4 Ejector and Bypass Valve	75
4.3 Simulation and Discussion.....	76
4.3.1 Temperature Regulation Mechanism and Safety Issue	76
4.3.2 Optimal Partial-load Strategy	81
4.4 Conclusion	97
Chapter 5. Electrical Modeling of VRB	98
5.1 Structure of VRB System.....	99
5.1.1 External Hydraulic Circle	99
5.1.2 VRB Stack Structure	100
5.2 Comprehensive Equivalent Circuit Model for VRB	102
5.2.1 Nernst Equation and State-of-charge	103
5.2.2 Shunt Current and the Effects of Vanadium Ion Diffusion	105
5.2.3 RC Network Identification	109
5.2.4 Hydraulic Model and Pump Power Consumption	115
5.2.5 Verification	118
5.3 Analysis and Discussion	121
5.3.1 Effect of Shunt Current	121
5.3.2 Effect of Different Current Densities and Electrolyte Flow Rates	123
5.3.3 VRB Dynamic Response to the Step Current Profiles	126
5.4 Conclusion	127
Chapter 6. SOFC/VRB/SC Hybrid Power Supply System	129
6.1 Introduction.....	129
6.2 Structure of the Proposed HPS System	131
6.3 Modeling of the Proposed HPS System	132

6.3.1 VRB System-Level Model	133
6.3.2 SOFC System-Level Model	135
6.3.3 Small-signal Modeling of Boost Converter	137
6.3.4 Regenerative Load Curve	138
6.4 Energy Management System of the Proposed HPS System.....	139
6.4.1 Rate Limiter	140
6.4.2 PI controllers	141
6.5 Configurations of the Proposed HPS System.....	142
6.5.1 SOFC Stack Configurations	142
6.5.2 VRB System Configurations	143
6.5.3 SC Bank Configurations	143
6.6 Simulation and Analysis	144
6.6.1 HPS System's Performance based on Different Load Cycles	144
6.6.2 Sensitivity Studies	149
6.7 Conclusion	157
Chapter 7. Conclusions and Recommendations	158
7.1 Conclusion	158
7.2 Recommendations for Future Work.....	160
Author's Publications	163
References	164

List of Figures

Fig 2- 1 Working Principle of SOFC	17
Fig 2- 2 3D View of tubular SOFC and Planar SOFC	21
Fig 2- 3 Framework of fuel cell system	27
Fig 2- 4 Typical structure of VRB	33
Fig 2- 5 Diffusion coefficients at different temperatures (a) Selemion CMV (b) Selemion AMV (c) Nafion 115 [55].	35
Fig 3- 1 Tubular SOFCs stack of Siemens Westinghouse tubular SOFC	41
Fig 3- 2 H ₂ fueled SOFC model verification	49
Fig 3- 3 Effect of cell pressure on H ₂ fueled SOFC's voltage and power	50
Fig 3- 4 Schematic diagram of a planar DIR-SOFC	52
Fig 3- 5 Effect of different temperatures and pressures on the reforming processing	55
Fig 3- 6 Fuel channel component mole fractions along the cell length.....	60
Fig 3- 7 Temperature variation along the cell length	61
Fig 3- 8 Simplified 1D model compared with detail 1D model [17]	62
Fig 4- 1 Proposed SOFC-GT system layout	66
Fig 4- 2 SOFC Temperature Controlled by Fuel BV and Air BV	68
Fig 4- 3 SOFC Temperature Controlled by Addition Fuel	69
Fig 4- 4 Compressor performance map.....	71
Fig 4- 5 Turbine performance map	72

Fig 4- 6 Icon of heat exchanger	73
Fig 4- 7 Icon of combuster	74
Fig 4- 8 Icons of ejector and bypass	75
Fig 4- 9 Control the SOFC operating temperature by adjusting the shunt ratios of Air BV and Aux CB BV	78
Fig 4- 10 The COMP's operating line of strategy A and B	82
Fig 4- 11 Plant's performance under strategy A ($U_{air}=0.175$, $U_{fuel}=0.8$, $T_{SOFC}=1173K$) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range.....	84
Fig 4- 12 Plant's performance under strategy B ($U_{air}=0.175$, $U_{fuel}=0.8$, Additional fuel=0) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range	89
Fig 4- 13 Plant's performance under strategy C (constant inlet air, $U_{fuel}=0.8$, $T_{SOFC}=1173K$) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range	91
Fig 4- 14 Plant's performance under strategy D (constant inlet air, $U_{fuel}=0.8$, Additional fuel=0) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range	94
Fig 4- 15 Comparison between four different partial-load strategies.....	96
Fig 5- 1 External hydraulic half-circuit of VRB system	100
Fig 5- 2 VRB cell structure [101]	101

Fig 5- 3 Proposed electrical model for VRB.....	103
Fig 5- 4 Electrical circuit analogy of a bipolar stack [108]	106
Fig 5- 5 Prediction of shunt current distribution in the 15 cells stack at 50 mA cm ⁻² and 50% SOC	107
Fig 5- 6 The experimental VI curves from Kim's article [101]	110
Fig 5- 7 Electrical circuit model of VRB (dynamic zone)	111
Fig 5- 8 Electrical circuit model of VRB (stationary zone)	114
Fig 5- 9 Final electrical circuit model of VRB	115
Fig 5- 10 Stack voltage under various flow rates and various current densities [101].....	120
Fig 5- 11 Pump power and pressure drop within VRB [101]	121
Fig 5- 12 SOC fading of tank electrolyte under stack idling condition with pump operation	122
Fig 5- 13 Terminal voltage during charge/discharge cycles at diverse current densities and flow rates	123
Fig 5- 14 Battery's efficiency under different flow rates and current density	126
Fig 5- 15 Battery response under current steps at the flow rate equals of 4 L/min	127
 Fig 6- 1 Topology of the proposed SOFC/VRB/SC HPS system	 132
Fig 6- 2 Simulink model of VRB	133
Fig 6- 3 Look-up table for shunt current prediction	134
Fig 6- 4 SOC prediction by using the proposed VRB model Tank (upper); Cell (lower)	135
Fig 6- 5 Simulink model of SOFC	136
Fig 6- 6 SOFC inlet consumptions: air (upper); fuel (lower)	136

Fig 6- 7 Small-signal equivalent circuit of boost converter in s-domain	137
Fig 6- 8 Final small-signal equivalent circuit of boost converter in s-domain.....	138
Fig 6- 9 Simplified load+RE curve for the proposed SOFC/VRB/SC HPS system	139
Fig 6- 10 Structure of proposed energy management system	140
Fig 6- 11 Schematic diagram for power controlling of VRB	141
Fig 6- 12 Schematic diagram for power controlling of SOFC	141
Fig 6- 13 Schematic diagram for voltage controlling of SC	141
Fig 6- 14 Simulink model of the proposed VRB/SOFC/SC HPS system	145
Fig 6- 15 Decomposition of the load cycle by using rate limiter	146
Fig 6- 16 Simulation results from a simple load cycle test: a) bus voltage; b) SC power; c) VRB power; d) SOFC power	147
Fig 6- 17 Decomposition of another load cycle by using rate limiter	148
Fig 6- 18 System performance prediction based on another load demand: a) bus voltage; b) SC power; c) VRB power; d) SOFC power	148
Fig 6- 19 Two SOFC systems for extension analysis	150
Fig 6- 20 Simulation results of the one module system of SOFC	151
Fig 6- 21 Simulation results of the four modules system of SOFC	151
Fig 6- 22 Two VRB systems for extension analysis	152
Fig 6- 23 Simulation results of the one module system of VRB.....	153
Fig 6- 24 Simulation results of the six modules system of VRB	154
Fig 6- 25 Average model of the proposed SOFC/VRB/SC HPS system	155
Fig 6- 26 Simulation results by using average model: a) bus voltage; b) SC power; c) VRB power; d) SOFC power	156

List of Tables

Table 2- 1 Classification of DG technologies [31]	13
Table 2- 2 Comparison Between Different Types of Fuel Cells[36, 37]	16
Table 2- 3 Requirements of SOFC anode material [40].....	19
Table 2- 4 Comparison between Different Types of Flow Batteries [49, 50]	31
Table 3- 1 Geometry parameters of Siemens Westinghouse tubular SOFC	42
Table 3- 2 Operating conditions	48
Table 3- 3 Physical parameters of Siemens Westinghouse tubular SOFC.....	49
Table 3- 4 Equilibrium composition and partial pressure for each component.....	54
Table 3- 5 Reactant's total quantity and each species' molar fraction.....	54
Table 3- 6 Verification of methane fueled SOFC model [17].....	59
Table 4- 1 Plant configuration [71, 87-89].....	77
Table 4- 2 Plant performance with/without temperature regulation mechanism	80
Table 4- 3 Four partial-load strategies	81
Table 5- 1 Parameters of the VRB system [101]	102
Table 5- 2 Coefficients of minor loss [100]	117

Table 5- 3 Identification parameters under different flow rates and current densities	119
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Table 6- 1 Configurations of SOFC adopted in the HPS system	142
---	-----

Table 6- 2 Configurations of VRB adopted in the HPS system	143
--	-----

Table 6- 3 Configurations of SC adopted in the HPS system	144
---	-----

Table 6- 4 Comparison between two SOFC systems for extension analysis	150
---	-----

Table 6- 5 Comparison between two VRB systems for extension analysis	153
--	-----

Nomenclature

A	Cross area (cm ²)
b	Experimental coefficient
c	Concentration/Heat capacity
D	Diffusion factor
d	Thickness/Diameter(cm)
E	Potential (V)
F	Faraday constant (96487 C/mol)
f	Friction factor
G	Guide channel
g	Gravity
h	Friction/minor loss, Enthalpy
H	Height (cm)
i	Current density (A/m ²)
i_o	Exchange current density (A/m ²)
I	Current
K	Equilibrium coefficient
k	Permeability
L	Length (cm)
$\dot{m}$	Mass flow rate
M	Manifold
n	Cell number
n_e	Transfer electron
$\dot{n}$	Molar flow rate
N	Normalized Shaft speed
P	Pressure (bar)
p	Partial pressure (bar)
Q	Heat loss rate (W)
Q	Flow rate (L/min)
R	Gas constant (8.314 J/(mol.K))
$\tilde{R}$	Hydraulic resistance (Pa.s/m ³)
S	Source term
s	Laplace operator
T	Temperature (K)
U	Utilization factor/ heat transfer coefficient (W/(k.m ²))
V	Voltage(V)/ Volume (L)
W	Width (cm)

Greek alphabet

β	Transfer coefficient,0.5
γ	Activation coefficient
γ_a	Specific heat ratio of air
λ	Conductivity
μ	Viscosity (Kg/(m.s))
π	Pressure ratio
ρ	Material resistivity/Density
σ	Conductivity (1/(Ω .cm))
η	Efficiency/Diffusion ratio

Superscript

in	Inlet
int	Internal
out	Outlet
re	React

Subscript

ac	Anode channel
act	Activation loss
an	Anode
bulk	Bulk flow
ca	Cathode
cc	Cathode channel
cha	Charge
conc	Concentration loss
diff	Diffusion
dis	Discharge
eff	Effective
en	Energy
inter	Interconnection
num	Cell number
o	Standard state
ohm	Ohmic loss

sys	System
s	Isentropic process
Ter	Terminal

Abbreviations

En	Energy
HPS	Hybrid power supply
Man	Manifold
Opv	Open circuit voltage
PEN	Positive Electrolyte Negative structure
Re	Reynolds number
SC	Super capacity
SOC	State of charge
SOFC	Solid Oxide Fuel Cell
SR	Bypass shunt ratio
Sys	System
VRB	Vanadium redox flow batte

Chapter 1. Introduction

With the development of modern industry, energy requirement and fossil depletion become much more severe than ever before. Conventional power stations mainly rely on the combustion of fossil fuels, which will cause environmental issues such as greenhouse gases releasing and noxious emissions. The defects of coal-fired stations have drawn increasing attentions among modern scientific community [1-3].

To solve the environmental problem caused by traditional power stations, the concept of distributed generation has been introduced in recent years. A distributed generation system is combined by a variety of small, grid-connected devices referred to as distributed energy resources (DER). Renewable energy sources such as small hydro, biomass, biogas, solar power, wind power, and geothermal power are regarded as typical DER. A grid-connected device for electricity storage can also be classified as a DER system, and is often called a distributed energy storage system (DESS). Distributed generation and storage system enables collection of energy from many sources and improve reliability of power supply. Moreover, the increasing employment of renewable energy sources can reduce the environmental impacts effectively [4-6].

Among variety of DER technologies, solid oxide fuel cell (SOFC) is regarded as a promising solution for electricity generation. A SOFC is an electrochemical conversion

device with solid ceramic electrolyte that produces electricity directly from oxidizing a fuel. Advantages of SOFC system include design/install flexibility, environmental friendly, quiet and long-term stability. Moreover, the operation temperature of SOFC is very high, typically between 500 to 1,000 °C. The high operating temperature makes SOFC a suitable candidate for combining with gas turbine (GT), which further increases the overall fuel efficiency. All these advantages make SOFC system suitable for distributed generation [7-9].

However, the distributed grid cannot only use fuel cell as its power sources, which will compromise its economy, reliability and safety. For example, if a distributed grid is only powered by fuel cell, the capacity of the fuel cell needs to satisfy the maximal load demand, which is obviously not economic. Besides, power grid needs to guarantee the electricity supply reliability when fuel cells are starting-up or maintaining. Thus, an uninterrupted power supply (UPS) is critical for customer side. Moreover, since the distributed grid is usually integrated with renewable energy sources, storage devices are indispensable to balance the difference between load demand and surplus energy. Therefore, storage devices are necessary for distributed network [10-12].

Among numerous storage devices, all-vanadium redox flow battery (VRB) has drawn more and more attention as a hopeful DESS for distributed grid. The advantages of VRB contain: 1). the power and capacity of VRB are separated and highly flexible according

to the practical requirement 2). since the active species in the electrolyte are only vanadium ions at different oxidation states, any cross contamination would be avoided, allowing the electrolyte lifetime to be extended indefinitely in theory. 3). VRB can be discharged completely without any damage to the electrode or the electrolyte. 4). due to their design flexibility and long service lifetime, the construction and maintenance costs of VRB are low while offering location flexibility. 5). low self-discharge rate and high efficiency. 6). no risk of explosion, security. 7). cheap raw materials and easy to recycle. 8). high starting speed (<2min) and high switching speed during charge/discharge (<0.02s). All these advantages make VRB a promising candidate for DESS application [13-15].

The hybrid system of SOFC and VRB is a novel attempt for distribution generation. Both of these two components have common advantages such as modularization, design/location flexibility, environmental protection, efficiency and reliability. Moreover, it's very convenient to combine these two components together. One major disadvantage of VRB is its low energy density. It can be improved by introducing a fuel cell system. Meanwhile, the battery can supply uninterrupted electricity during the start-up or repair period of fuel cell. Besides, in a distribution network with renewable energy sources, SOFC and VRB combine system is able to supply reliable basic load while reduce the randomness of renewable energy.

The potential applications of SOFC and VRB hybrid system contain: islands and remote area power supply, ship power supply and aerospace power supply. The hybrid system is also reasonable for applications such as building power supply, UPS or auxiliary system for renewable energy sources.

1.1 Motivation and Objective of the Present Work

Despite the fruitful work associated with the recent researches on SOFC and VRB, the challenges of wide commercialization in power grid still exist due to the issues of model simplification, thermal management, auxiliary equipment integration, operation optimization and controller design. On the application levels, the modeling of VRB and SOFC are critical for their integration with distributed grid. The status of components' current, terminal voltage, state of charge (VRB) and stack temperature/temperature gradient (SOFC) need to be predicted and controlled.

The ultimate goal of this thesis is to investigate the performance of SOFC and VRB in a hybrid system. To achieve this goal, four pieces of work have been accomplished consecutively.

To analyze the performance of SOFC, two simplified models have been introduced from Akkaya's [16] and Kang's articles [17]. Akkaya's lumped model is suitable for high speed calculation due to its concise structure. And Kang's 1D model can provide internal

prediction of SOFC in an effective way. The usage of these two simplified models helps to reduce the calculation time in following simulations.

In order to use the high-temperature exhaust from SOFC, a novel SOFC-GT hybrid system has been proposed. Unlike other structures, a heat management subsystem is added to maintain the average temperature of SOFC. Besides, a detailed turbine model and Kang's 1D SOFC model are utilized to evaluate the stability of the whole system. Finally, based on different air/fuel supply patterns, an optimal partial-load strategy is brought up to pursue better efficiency and wider power range.

In the third part, a comprehensive electrical VRB model is proposed for power grid analysis. Inherent features of shunt current, ion diffusion and pump power are considered in this model. Based on experimental results, least square method is used to identify dynamic and stationary characteristics of VRB. Besides, sensitivity analyses have been done to study the relationship between efficiency and electrolyte flow rate.

In the final part, a hybrid system of SOFC and VRB has been built up to analyze the integration between these two components. SOFC is designed to supply the base load without facing sudden fluctuations. VRB helps SOFC to satisfy the variation load and to absorb the surplus power from renewable sources. Besides, a supercapacitor (SC) is adopted to buffer the sudden load variations on SOFC and VRB. Since the simulation

contains power electronic interfaces, Akkaya's SOFC model and electrical VRB model are used here due to their concise structure. The proposed system is able to supply constant voltage based on a simple energy management system.

1.2 Thesis Structure

This thesis includes seven chapters organized in a streamlined manner, whose aim is to concisely express the theoretical findings contributed by the research work. An overview of each chapter is now presented before progressing to the detailed analyses found in each individual chapter.

Chapter 1 introduces the background, motivation and objective. Overall organization of the thesis is also described to give an overview of each individual chapter.

Chapter 2 reviews the background and the development of distributed generation, SOFC and VRB. Recent findings and features of SOFC and VRB are introduced. Efforts have been paid for providing the reader with sufficient knowledge to understand the following works. A summary of the literature review is also provided at the last section of this chapter.

Chapter 3 focuses on the simplified modeling of SOFC for thermal and electrical analysis. Akkaya's lumped model and Kang's reduced 1D model are introduced due to their concise structure. These models are applied in following chapters.

Chapter 4 proposes a novel temperature-maintained SOFC/GT hybrid system. Through simulation, the operating stability of the proposed system is studied. Besides, based on different air/fuel supply patterns, the optimal partial-load strategy is investigated to maximize the conversion efficiency and to extend the output range.

Chapter 5 proposes a comprehensive equivalent circuit model for VRB to predict both state of charge and electrical performance. Both of mathematic modeling and experimental data fitting are utilized in this model. Moreover, a hydraulic model is introduced to calculate the pump losses. Sensitivity study between electrolyte flow rate and VRB's efficiency is investigated at the final section.

Chapter 6 proposes a VRB/SOFC hybrid DC micro-grid to investigate the compatibility of both models of VRB and SOFC. A supercapacitor (SC) bank is introduced to stabilize the DC bus voltage. And a rate limiter is adopted to divide the load demand signal into fast changing part and slow changing part for VRB and SOFC correspondingly. The proposed hybrid system is able to supply stable DC voltage to the load.

Chapter 7 concludes the improvement for the thesis topics and the future research topics suggested.

Chapter 2. Literature Review

2.1 Distributed Power Grid

At present, centralized power system is the most mature structure with features such as large generation units, wide distribution range and high transmission voltage. However, with the developing of power grid, issues like power quality, electrical security and supply reliability have been received more and more attentions. More difficulties occur when running a large power grid. Besides, other disadvantages such as high investment costs and environmental pollution also become more obvious in a large system.

Meanwhile, due to the worldwide crisis of both energy and environment, the development of renewable energy sources becomes an urgent demand. To compensate the deficiencies of traditional power system, small-scale energy conversion units are installed in the grid close to users, namely, distributed generation technology. The combined system of both centralized power system and distributed generation technology are recognized to be able to save investment, reduce energy consumption as well as improve the reliability and flexibility of the whole system. Thus, the distributed generation technology is regarded as the development trends of future electric power industry in the future [18-20].

2.1.1 Development Status

Distributed energy resources (DER) is an important direction in energy industry. This technology has matured and commercialized in many developed countries. According to the 2004 annual report 'World Alliance for Decentralized Energy'[21], the total capacity of distributed energy in USA reached to 67GW, which accounted for 7% of the total capacity of American, same as the world average level. In Europe, the utilization of distributed energy are in the leading position especially in Denmark, Netherlands and Finland, which accounted for 52%, 38% and 36% of total capacity correspondingly in these countries respectively [22].

For the power generation of the whole world, renewable energy (RE) accounted for 19.46% at 3902 TWh in 2009. Hydroelectricity, by far the largest contributor among the renewables, accounted for over 83% of that share. Biomass, wind and PV combined accounted for only 15% of the global RE contribution, or 2.9% of world electricity generation [23]. Thus, while RE as a whole comprises a substantial portion of global electricity generation, the proportion of RE that comes from variable sources such as wind and solar is still relatively limited. Consequently most power system operators to date have had relatively small amounts of variable generation to integrate. However, the situation may change substantially by 2035[24].

The International Energy Agency (IEA) predicts that global electricity production from renewables (including hydroelectricity) will grow to 8108 TWh by 2025, an over 100% increase from 2009. By 2035, that figure rises to 11100 TWh. These estimates are based on IEA's New Policies Scenario, which takes into account recently announced commitments and plans, even if they are yet to be formally adopted and implemented. The New Policies Scenario is the central scenario for IEA's world Energy Outlook 2011, and assumes a global CO₂ price of 30 USD to 45 USD per tonne [23, 24].

There is still no consensus in the literature about the general terminology of distributed energy generation. The terms of 'distributed power', 'distributed generation' and 'DER' are the most common ones. The detailed definitions as: 1) DG, implies the electricity generator which is outside the traditional power grid. Units such as internal combustion engines, gas turbines, fuel cells, solar and small hydropower systems (wind, waste and biomass) and other power generation system belong to DG. 2) DP. DP contains the concept of DG, as well as the electric storage devices. Units such as batteries, flywheel, superconducting magnetic storage devices, and pumped storage station are regarded as DP. 3) DER. Covering a broader concept: to generate electricity or thermal energy close to the user's location, which includes DG [25].

Due to the energy shortage and environmental pollution, distributed energy systems have been drawn increasingly attention in recent years and many researches have been done

this area. In 'DER benefits analysis studies: final report'[26], 31 reports of the distributed energy systems have been commented. The report summarizes the characteristics and evaluation standards of distributed energy system, as shown below [27-29]:

(1) Improve energy utilization efficiency by comprehensive energy cascade use. Conventional centralized system mainly supplies electricity. It is difficult to implement the cascade utilization when customers require other forms of energy, such as heat or cooling. With the characteristics of small-scale and flexibility, distributed energy system is able to provide electric, heating and cooling energy to nearby users and thus, improve the conversion efficiency. The energy conversion efficiency of large power plants is around 35% -55%. After taking into the consideration of the effects of auxiliary power and transmission loss, the terminal conversion efficiency reduces to 30-47%. But the conversion efficiency of distributed energy system can be higher than 80% since there is no transmission losses.

(2) Improve the reliability and stability of conventional power grid. In recent years, several major blackouts in world reflect the vulnerability of centralized power grid. For example, the blackouts of eastern California cost a loss of 30 billion USD per day. Meanwhile, after '9.11', reliability of energy supply has risen to the national security level. However, the rapid expansion of power grid has brought a great threaten to the supply reliability. A distributed energy system close to the user can greatly improve the

supply reliability when grid crashing or unexpected disasters happening. The power supply of prioritized customer can be guaranteed.

(3) Small-scale and low initial investment. The distributed energy system can reduce the long-distance transmission losses and save the capital cost of transmission grid. Due to the flexibility, distributed energy systems can be installed according to user's requirements. Compared with centralized energy system, distributed energy system is more economical. Besides, it can provide customers a flexible and energy-saving service. The distributed energy system is especially suited for the users in remote areas where it is not suitable for laying the transmission grid.

(4) Environmental friendly and fuel diversity. Distributed energy system generally consumes clean fuels, while its high efficiency also benefits environment. According to the report of CCHP2020 [30], the CO₂ emission of US will reduce 19% when part of the new buildings applies CCHP technology. Compared with fossil fuel, renewable energy such as solar, geothermal and wind are distributed and have low energy density. It is difficult to be used as a centralized plant. In contrast, the nature of renewable energy makes it suitable to be combined with distributed energy system.

There are numerous classification methods for distributed generation. For instance, depending on fuels, distributed generation can be divided into fossil fuels powered,

renewable energy powered, secondary energy powered and waste energy powered. Or, depending on applications, distributed generation can be divided into electric generator, Combined Heat and Power (CHP) and Combined Cooling Heating and Power (CCHP). Usually, distributed generation can be classified according to technologies, primary fuels or interface technologies [18-20].

Table 2- 1 Classification of DG technologies [31]

Type of technology	primary fuel	output	interface	Small-scale <1MW	Middle-scale ~1MW	Large-scale >1MW
Turbine	fossil fuels/ renewable energy	AC	Direct connect			√
Geothermal generator	renewable energy	AC	Direct connect		√	√
hydroelectricity	renewable energy	AC	Direct connect		√	√
Wind farms	renewable energy	DC	inverter	√	√	√
PV	renewable energy	DC	inverter	√	√	
Fuel cell	fossil fuels/ renewable energy	DC	inverter	√	√	√
Battery	Power grid/DG	DC	inverter	√	√	√
Super Capacity	Power grid/DG	DC	inverter	√	√	
Fly wheel	Power grid/DG	DC	inverter		√	√
SMES	Power grid/DG	DC	inverter		√	√
Micro turbine	fossil fuels/ renewable energy	AC	inverter	√	√	

2.2 Solid Oxide Fuel Cell

Fuel cell is an energy conversion device, in which the chemical energy converts into electricity directly. It does not store energy but only provides the venue for

electrochemical reaction. Thus, fuel cell is able to produce electricity uninterruptedly as long as both fuel and air are supplied continuously. Besides, since there is no combustion within fuel cell, the conversion efficiency of fuel cell is higher than heat engine [32, 33]. Compared with other generators, fuel cells have advantages such as:

- (1) High conversion efficiency: Free from the restriction of Carnot efficiency, the electrical conversion efficiency of fuel cell is between 45–60%. If the tail gas from high temperature fuel cells were utilized, the CHP system's conversion efficiency can reach to 80%. The mass-energy density of fuel cell is ideal, where only nuclear is comparable [34].
- (2) Low noise: There are no moving components within fuel cell. It can work quietly. Experiments show that the 40kw phosphoric acid fuel cells only create 60dB noise in a 4.6m distance [12].
- (3) Low pollution: Hydrogen, as the most common fuel for fuel cells, only produce water during reaction. Compared with burning fossil fuels directly, producing hydrogen from fossil fuels can reduce 40% of CO₂ emission. Besides, the hydrogen must be desulphurized before they were used by fuel cells, the emission of SO₂ can be reduced significantly [35].

(4) Fuel diversity: Various fuels such as natural gas, methane, ethanol and so on can be utilized by some types of fuel cells. The depletion of major fossil fuels can be slowed down by using fuel cells [32].

(5) Multi-functions: due to the design flexibility, the power capacity of fuel cell ranges from kW to MW. Besides, the scale of fuel cell has little impact on its efficiency. These make fuel cells be applied in many areas, such as portable power source, electric vehicle, CHP, distribution generation, etc [33].

In addition, fuel cells have other advantages such as high energy density, no requirements for recharging and long lifetime.

Usually, fuel cells are classified by the materials of electrolyte. Up to now, various types of fuel cell have been invented and studied. There are 5 kinds of fuel cell that have been drawn most attentions, namely, alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cells (SOFC). The comparison among these five kinds of fuel cells are shown in Table 2-2. In this thesis, we mainly focus on the SOFC [36, 37].

Table 2- 2 Comparison Between Different Types of Fuel Cells[36, 37]

Types	AFC	PEMFC	PAFC	MCFC	SOFC
Electrolyte	KOH	PEM	H ₃ PO ₄	Li ₂ CO ₃ -K ₂ CO ₃	Y ₂ O ₃ -ZrO ₂
Conductive ions	OH ⁻	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Anode reaction	H ₂ +2OH ⁻ →2H ₂ O+2e ⁻	H ₂ →2H ⁺ +2e ⁻	H ₂ →2H ⁺ +2e ⁻	H ₂ + CO ₃ ²⁻ →H ₂ O+ CO ₂ +2e ⁻	H ₂ + O ²⁻ →H ₂ O +2e ⁻
Cathode reaction	0.5O ₂ + H ₂ O+2e ⁻ →2 OH ⁻	0.5O ₂ + 2H ⁺ +2e ⁻ →2 H ₂ O	0.5O ₂ + 2H ⁺ +2e ⁻ →2 H ₂ O	0.5O ₂ + CO ₂ +2e ⁻ →CO ₃ ²⁻	0.5O ₂ +2e ⁻ →O ²⁻
Anode catalyst	Ni or Pt/C	Pt/C	Pt/C	Ni(with Cr,Al)	Ni,Zr
Cathode catalyst	Ag or Pt/C	Pt/C	Pt/C	NiO	Sr doped LaMnO ₄
Temperature	65~220 °C	25~80 °C	180~200 °C	~650 °C	500~1000 °C
Pressure	<0.5 MPa	<0.5 MPa	<0.8 MPa	<1 MPa	1 atm
Fuels	Pure H ₂	H ₂ , Methanol	H ₂	H ₂ , CH ₄ , Gas, methane	H ₂ , CH ₄ , Gas, methane
Efficiency	50%~60%	40%	40%	50%	50%
Features	Require high purity H ₂ as fuel Low corrosivity Low temperature.	High power density, small size, light weight; Low corrosivity low temperature.	CO can cause catalyst poisoning; Exhaust can be further used.	immune from CO; Reaction require CO ₂ ; Exhaust can be further used.	immune from CO; High operating temperature; Exhaust can be further used.
Advantages	1.Rapid start ability; 2.Work under NPT.	1.Air can be used as oxidant; 2.Solid electrolyte; 3.Work under NPT; 4.Rapid start ability;	1.Insensitive to CO ₂ ; 2.Relatively low capital cost.	1.Air can be used as oxidant; 2.CH ₄ can be used as fuel.	1.Air can be used as oxidant; 2.CH ₄ can be used as fuel.
Disadvantages	1.Only pure O ₂ can be used as oxidant; 2.High capital cost.	1.Sensitive to CO; 2. humidification is required	1.Sensitive to CO; 2.Slow start 3.High capital cost.	1.high operating temperature	1.high operating temperature
Applications	Spacecraft; AIP system for submarine	Distributed generation; Vehicle Power; Portable power	CHP plant; Distributed generation.	CHP plant; Distributed generation.	CHP plant Distributed generation; Vehicle Power; Portable power

2.2.1 Principles and Structure

Fig 2- 1 Working Principle of SOFC

Fig 2-1 exhibits the principle of SOFC. Air is pumped into cathode channels of SOFC. After penetrating through the porous cathode and receiving the electrons from extend circuit, an oxygen molecule splits into two oxygen ions. The oxygen ions are transported through the YSZ layer, and arrive to the anode layer. Meanwhile, the hydrogen gas penetrates to the connect part of anode and electrolyte. The oxygen ions and the hydrogen combine into water while large amount of heat is released. The remaining electrons go through external circuit loop and flow back into the cathode [38].

The basic electrochemical reaction of SOFC can be represented as follows:

From Fig 2-1, it is clear that a SOFC cell is made by four components as electrolyte, cathode, anode and interconnect.

Electrolyte: as the electrolyte of SOFC, it has to be stable in both reducing and oxidizing environments and must have sufficiently high ionic conductivity with low electronic conductivity at cell operating temperature. In addition, it must be possible to form the material into a thin, strong gas-tight layer. Stabilized zirconia (ZrO), especially yttria-stabilized zirconia (YSZ), is the most common electrolyte in SOFCs because the material possesses an adequate level of oxygen-ion conductivity and exhibits desirable stability in both oxidizing and reducing atmospheres [39, 40]. The conductivity of YSZ is around 0.1S/cm under 1000 °C [41].

Anode: the basic requirement of anode in SOFC is to form a good triple phase boundary (TPB) for fuel oxidation. Besides, the anode materials need to withstand high temperature and varying O₂ partial pressures without performance loss, microstructure change or reactions with other components of SOFC. A general set of requirements for SOFC anode is listed in Table 3 [39, 40].

Table 2- 3 Requirements of SOFC anode material [40]

Requirements	Guide parameter
Electronic conductivity	$>100 \text{ S cm}^{-1}$
Ionic conductivity	$>10 \text{ mS cm}^{-1}$
Catalyst for fuel reduction	$<0.1 \text{ } \Omega\text{cm}^{-2}$ for electrode
Electrode resistance	Total $<0.15 \text{ } \Omega\text{cm}^{-2}$
Thermal stability	At operating temperature, for long time
Chemical stability	At operating temperature in contact with other materials (electrolyte, interconnect)
Thermal expansion match	Cell experiences large temperature changes
Reduction stability	Highly hold porosity at operating temperature, for long time
Structural stability	Must hold porosity at operating temperature, for long time

At high operating temperature of YSZ-based SOFCs, suitable anode metals are limited mainly to nickel, cobalt, and noble metals. Nickel is most commonly used because of its low cost. To maintain the porous structure of nickel over long periods at high temperature and to provide other desired properties for the anode, nickel metal is often dispersed on the surface of a YSZ support. The functions of the YSZ support in the anode are to support the nickel-metal particles, inhibit coarsening of the metallic particles at high temperature, and provide an anode thermal expansion coefficient acceptably close to those of the other cell components. Other material such as ZrO₂-cermet is also used for manufacturing anode [39, 40].

Cathode: In fuel cells, oxygen dissociation reaction generally requires a large overpotential and causes the major loss in efficiency. High temperature operation of

SOFC helps the electrode reaction to proceed without precious metal catalysis, which, however, does not mean any material can be used as the cathode. Properties required for cathode materials are [40]:

- (1) High catalytic activity
- (2) High electronic conductivity (preferably, electronic-ionic mixed conductivity)
- (3) Chemical stability and compatibility with other cell components
- (4) Morphological stability
- (5) Mechanical stability and compatibility

They must be achieved in a cost-effective manner.

At present, doped lanthanum manganite (LaMnO_3) is most commonly used for SOFC cathode, which are less reactive to YSZ and have closer thermal expansion coefficient. When the ratio of Sr to La is around 0.2, the thermal expansion coefficient of cathode is close to YSZ. Lanthanum manganite-based cathodes show sufficiently high electrochemical performance at high temperature and good conductivity. It was widely utilized in tubular and planar cells fabrication. Other material such as SrMnO_3 is also used for manufacturing SOFC cathode [39, 40].

Interconnect: Two adjacent SOFC cells are connected by interconnects for electricity conducting. In planar SOFC, interconnects also used as gas channel. To SOFC, the most important properties required for the interconnect material are high electronic conductivity, thermal stability and similar thermal expansion coefficient to other

components. Ceramic, perovskite-type materials on the basis of Lanthanum chromite (LaCrO_3) have been shown to possess the property combination required for interconnect materials. Main drawbacks of the ceramic materials are their brittleness, high price and troublesome shaping technology [39, 40].

Metallic construction materials offer a number of advantages over ceramics: they are easier and cheaper to fabricate, less brittle, easier to machine and can be joined with a number of standard welding or brazing techniques. Additionally, they possess higher electrical and thermal conductivities than most ceramics [39, 40].

2.2.2 Cell Geometry of SOFC

There are two major geometry designs for SOFC, which are tubular SOFC and planar SOFC. The perspective view of these two SOFCs are shown in Fig 2-2 [42].

Fig 2- 2 3D View of tubular SOFC and Planar SOFC

Tubular SOFC

The original Westinghouse tubular design was ingenious because 1.5m long cells could be manufactured and handled as a result of the inherent strength of the tube structure. In 1997, a 100 kW SOFC system has been built by using 1152 tubular cells. Individual cells are bundled in series and parallel electrical connection by using Nickel felt to protect the stack against complete failure if an individual cell fails. The felt is also able to minimize stress placed on the cells during operation [39, 40].

One distinct feature of this design is that it has no seals; the sealing problem was eliminated by inserting an air feeder tube down the cell tube. In addition, this design has the advantage that each single cell is built as a unit structure. This allows some freedom of thermal expansion and minimizes the problem of cracking caused by undue thermally induced stresses [39, 40].

On the other hand, tubular cell has a relatively long current path, which increase the resistive loss. Besides, the support tube is a limitation on cell performance. The thick support tube restricts the amount of oxygen which can be transported to the cathode/electrolyte interface. Thus, gas diffusion through the tube can become the rate-limiting step and sets the limiting current for the cell. Even below the limiting current, gas transport represents a loss in cell performance. Moreover, the electrochemical vapor

deposition (EVD) process used in the fabrication limits the selection of suitable dopant materials for the electrolyte and interconnect to a small number [39, 40].

The power density of Westinghouse tubular pack depends on the diameter D of cells and the gap g between them according to $\pi D\rho/(D + g)^2$ which gives 0.6 kW/L for Westinghouse tubes 2 cm in diameter with a 0.2 cm gap. [39, 40].

Although the Westinghouse tubular design was large and expensive, it did demonstrate several important features of SOFC technology [40]:

- (1) The cells ran for long periods without much deterioration
- (2) The efficiency was impressive, around 60%
- (3) Methane was used as fuel after desulphurising and pre-reforming
- (4) The SOFC exhaust could drive a gas turbine
- (5) Emissions were low

The advantages of tubular SOFC contains: a) due to the specific geometry, the structure of tubular SOFC is strong; b) less issues with thermally induced stresses; c) easy for building; d) single cell damage has little effect on whole stack; e) simpler sealing. Its disadvantages contains: a) relatively long current path; b) relatively low power density; c) hard to establish; d) high manufacture cost [39, 43, 44].

Planner SOFC

Compared with tubular SOFC, the performance and power density of planner SOFC have been significantly improved. The planar design can provide short current pathways

through interconnects. Cell components can be made very thin to minimize the electrical resistance. If p is the power in watts per square centimeter and g is the gap in centimeter between planar electrolyte layers, then stack volumetric power density is p/g kW/L, typically 1kW/L for a Hexis planar stack where p is 0.5 Wcm⁻² [39, 40].

The planar design also offers simpler fabrication. The planar SOFCs can be readily electroded by screen printing and both electrolyte and interconnect can be fabricated independently. This avoids the difficulties in co-sintering interconnect and provides multiple processing options. Furthermore, the fabrication of planar SOFC allows cell components to be assessed individually, thus ensuring better quality control [39, 40].

The advantages of planar SOFC contains: a). flexibility in gas channel design; b). compact structure, high energy density; c). easy for production, low manufacture cost; d) Each components can be built separately, the manufacture quality can be guaranteed.

Its disadvantages contains: a). potential scale-up limit to large sizes for self-supporting cells; b). sealing requirements and potential contact issues (between cells and interconnects) [39, 40].

2.2.3 Thermal reliability of SOFC

Any large YSZ structure will suffer the problem as thermal gradients are set up through the ceramic. It is a consequence of the high thermal expansion coefficient and brittleness of YSZ. If the SOFC stack is heated to high temperature (800-1000°C) too rapidly, then it may crack, causing catastrophic failure. Thus it is important to use smaller plates or tubes to resist thermal shock. The downside of this is the greater assembly problem for large numbers of small cells [39, 40].

Compared with planar SOFCs, tubular SOFCs are able to withstand larger temperature gradients, it is because:

- 1). Compared with plate, the cylinder has a better mechanical strength.
- 2). Efficient sealing of the edges is vital in the case of planar SOFCs, and glass ceramics are used for sealing. The brittle nature of the glass seals will cause gas leakage under high temperature gradients. This is a non-issue in the case of tubular SOFCs.
- 3). In tubular SOFCs stack, the gap between each individual cell are relatively large. The stress caused by thermal expansion is not easy to accumulate. However, in planar SOFCs stack, cells are integrated tightly. The accumulated stress caused by thermal expansion is more likely cause crack.

2.2.4 Features of SOFC

SOFC is currently being developed vigorously. In addition to the general advantages of fuel cell such as high efficiency and low pollution, SOFCs have the following advantages [45-47]:

- 1) The operating temperature of SOFC can reach to 1000 °C, which is the hottest type among all kinds of fuel cells. By combining with the heat engine, more electricity can be produced. The tail gas from SOFC is also able used for heating. The overall CHP efficiency of SOFC can reach to 80%.
- 2) Since the electrolyte of SOFC is solid, there is no evaporation or leakage problems for SOFC's electrolyte. The geometric shape of SOFC is also flexible. Besides, the electrodes of SOFC are chemical stable, which benefits for extending the lifetime.
- 3) Due to the high operating temperature, SOFC doesn't require precious catalysts. Besides, high temperature makes the internal reforming possible. Natural gas, coal gas, or other hydrocarbons can be directly utilized by SOFC.

The disadvantages of SOFC includes: a) Strict requirements for battery materials; b) Low open circuit voltage; c) All components within SOFC (anode, electrolyte, cathode and bipolar) must be compatible with each other in both physical and chemical sides; d) The thermal expansion coefficients of each components should be similar [45-47].

2.2.5 Fuel Cell System

Fig 2-3 shows the framework of fuel cell system. The working method of fuel cell system is similar with those of combustion engine; both systems require continuous supply of air and fuel. Moreover, fuel cell needs to expel the produced vapor and heat [32, 33, 48].

Fig 2- 3 Framework of fuel cell system

Low-temperature fuel cell such as PEMFC and PAFC requires pure hydrogen as fuel. When alcohols or hydrocarbon was used as fuel, it needs to pass the reformer firstly. The reformer helps to convert the alcohols and hydrocarbons into hydrogen-rich gas and removing the catalyst toxic substances before entering the fuel cell stack. High-temperature fuel cell such as SOFC and MCFC has internal reforming ability. It could directly use methane or nature gas without reformer [32, 33, 48].

Same as battery, fuel cell is a DC source. Its voltage varies with load requirement. Therefore, DC/DC converter must be installed if the user requires stable DC voltage. For the AC customer or synchronization, DC/AC inverters are necessary.

Currently, the conversion efficiency of the fuel cell is between 40 to 60%. Thus, nearly half of chemical energy converts into heat. In order to maintain the operating temperature of fuel cell, the produced heat need to be cooled down or recycled. In general, the produced heat from low-temperature fuel cell usually used for generating steam. And the tail gas from high-temperature fuel cell can be used by turbine for generating electricity. The combined system helps to improve the conversion efficiency as well as the fuel utilization [32, 33, 48].

Except the components such as supply system, reformer, stack, power electronics as well as heat manage system; the central control unit is the most critical component for fuel cell system. Thereby, fuel, air, water, heat and electricity can be controlled and managed. The whole system is able to operate automatically [32, 33, 48].

SOFC-GT System

The SOFC can be combined with another power generating equipment such as a heat engine to form a hybrid power system. Hybridization of the SOFC with a gas turbine is the most common hybrid cycle [40].

The tail gas from the SOFC is combusted and then fed to the turbine section of the GT to generate additional electricity. In a generic SOFC/GT hybrid design, the SOFC produces about 65-80% of the power and about 20-35% is from the GT. Hybridization of the SOFC with a GT significantly improves system efficiency and can be beneficial for use in large ($\geq$ hundreds of kW) power plants. As shown in the Table 2-4, the estimated efficiencies of three SOFC power systems are compared: simple cycle, SOFC/GT hybrid and the SOFC/GT hybrid with anode and cathode gas recycle. It can be seen from the table that the hybrid cycle arrangement shows much higher efficiencies. The estimated efficiency of the SOFC/GT hybrid with gas recycle is 71.0%, about 26% higher than that of the simple SOFC [40].

Table 2 Efficiency comparison among three SOFC power systems [40]

	Simple cycle	SOFC/GT hybrid	SOFC/GT hybrid with gas recycle
Efficiency (%)	44.8	61.1	71.0
SOFC power (kW)	3709	3709	4099
GT power (kW)	0	976	1447
Parasitic power (kW)	(389)	(100)	(288)
Net plant power (kW)	3320	4585	5258
SOFC pressure (atm)	1.3	4.6	4.6

2.3 Vanadium Redox Flow Battery

In distributed power grid, solar, wind and other renewable energy have characteristics of unpredictable and intermittent. Energy storage technologies are regarded as the solution of these problems [20]. In generation side, energy storage technologies enable renewable energy to connect with power grid safely and efficiently; in distribution side, energy storage technologies reduce the requirements of transmission network and cut down the expenses; and in consumption side, energy storage technologies provide more flexibility for power supplying. Thus, energy storage technologies are critical for future power industry [20].

Compared with other storage technologies, chemical batteries show some advantages in scale flexibility, portability and develop potential. Flow battery is a type of chemical batteries where rechargeability is provided by two chemical components dissolved in liquids contained within the system and separated by a membrane. It has the advantages of a). power and capacity of flow batteries are separated and highly flexible according to the practical requirement; b). long cycle life; c). quick response times; d). easy to determinate the state-of-charge; e) low maintenance; f) and tolerance to overcharge or overdischarge. Although the energy density of flow battery needs to be further improved, this technology has attracted more and more attentions.

So far, 4 types of flow batteries have attracted most attentions, which are vanadium redox flow battery (VRB), zinc-bromine flow batteries (Zn-Br₂), iron-chromium flow battery (Fe-Cr) and bromine flow battery (PSB). Due to the environmental considerations, only first three batteries have been commercialized. The following table compares these three batteries. In this thesis, we mainly focus on the VRB [49, 50].

Table 2- 4 Comparison between Different Types of Flow Batteries [49, 50]

Types	Fe-Cr	Zn-Br ₂	VRB
Electrolyte	HCl solution	ZnBr ₂ solution	HCl.H ₂ SO ₄ solution
Electrochemical reaction	$\text{Fe}^{3+} + \text{Cr}^{2+} \leftrightarrow \text{Fe}^{2+} + \text{Cr}^{3+}$	$\text{Zn} + \text{Br}_2 \leftrightarrow \text{ZnBr}_2$	$\text{V}^{2+} + \text{V}^{5+} \leftrightarrow \text{V}^{4+} + \text{V}^{3+}$
Theoretical energy density (Wh.kg ⁻¹)	103	430	342
Open-circuit voltage (V)	1.0	1.82	1.3
Operating temperature (°C)	20~65	20~50	-5~60
Disadvantages	Low energy density	Storage of Br ₂ , self-discharge	High capital investment

2.3.1 Principles and Structure

In 1980s, Skllas-Kazacos and her research group developed the first all-vanadium redox flow battery (VRB) successfully at the University of New South Wales, Australia. So far, VRB is the only one MW-level chemical storage technology, which was utilized for amplitude adjustment and frequency modulation for wind farm. VRBs have been successfully demonstrated and commercialized for many years. The working principle of VRB can be described as: When the VRB is charged, the V⁴⁺ ions in the positive half-cell are converted to V⁵⁺ ions when electrons are removed from the positive terminal of

the battery. Similarly in the negative half-cell, electrons are introduced converting the V^{3+} ions into V^{2+} . During discharge, this process is reversed and results in a typical open-circuit voltage of 1.41 V at 25 °C [15].

The basic electrochemical reaction equations in the operation period of the VRB can be represented as follows:

In VRB, vanadium ions with different valence exhibit different colors, V^{2+} solution is purple; V^{3+} solution is green, V^{4+} solution is blue and V^{5+} solution is yellow. Therefore, the status of VRB can be roughly estimated by observing the color of solution. Besides, since the active substances of both anode and cathode are vanadium ions with different valence, the contamination can be avoided. This feature improves the theoretical lifetime of VRB and reduces the operating cost as well [51].

A typical structure of VRB system is shown in Fig 2-4. One unit cell of VRB contains:

a) Anode/cathode electrodes; b) Proton exchange membrane; c) Electrolyte containers; d) pumps and piping system. Adjacent cells are connected in series by using interconnects. An integrated stack consists of numerous cells and control system [50].

Fig 2- 4 Typical structure of VRB

The oxidizing and reducing electrolyte of VRB are stored in different containers. During operation, the active electrolyte flows into the stack by circulating pumps. Within the stack, chemical energy and electric energy can be interconverted [49, 50]. The function of each components are: (1) Electrolyte: electrolyte contains the active material and used as energy storage media. (2) Stack: stack consists of an assembly of cells, which contain membranes, electrodes, interconnects as well as electrolyte circulation system. Membranes are used to separate oxidant and reductant to avoid the self-discharging. Electrolyte circulation system achieves the exchange of active substances between battery and containers. (3) Electrolyte containers, pumps and piping system: There are two different containers for storing anode and cathode electrolyte separately. Through piping system, the hydraulic circuit between containers and stack are formed. Pumps

help the electrolyte to cycle within the whole system. (4) Control system: Control system is indispensable for the management of electrolyte temperature, pressure as well as flow rate [49, 50].

The materials of electrodes have features like high conductivity, corrosion resistance, impermeable, not easily deformation and high electrochemically active. Normally, the electrodes are carbon-based, such as carbon fiber or carbon felt [52].

Membrane is adopted to separate the positive and negative electrolytes, avoid the cross-contamination of ions with different valence as well as provide the path for protons. The requirements contain: 1. Low permeability for vanadium ions, avoiding the cross-contamination, reducing battery self-discharge and increasing energy efficiency. 2. High permeability for H^+ . 3. Considerable mechanical strength and inoxidizability, long life-time. 4. Low permeability for water, able to maintain the aqueous balance during operation. Nafion is the most common membrane for VRB [53].

As the active substances of VRB, electrolyte is the key component. Concentration of the electrolyte is critical for batteries' performance. The energy density of VRB increases with concentration. However, high concentration will cause the hydrolysis or precipitation. At present, H_2SO_4 is the most commonly used electrolyte for VRB [54].

2.3.2 Capacity Fading of VRB

Materials that used to fabricate vanadium flow battery could influence the performance of the battery. One key component of the battery is the ion-exchange membrane. An ideal ion-exchange membrane should only allow H^+ ions to pass through for maintaining charge balance and limiting the ion diffusion. The membrane should have good conductivity and chemical stability. Three types of membranes, the Nafion 115 membrane, Selemion cation exchange membrane, and Selemion anion exchange membrane are the most commonly used ones. The diffusion coefficients of these three membrane are studied in Fig 2-5 under different temperatures by Badrinarayanan [55].

Fig 2- 5 Diffusion coefficients at different temperatures (a) Selemion CMV (b) Selemion AMV (c) Nafion 115 [55].

The type of the membrane used determines the rates of water transfer and vanadium ion diffusion across the membrane, which in turn affects both capacity fade and coulombic efficiency [56]. Extensive research has been carried out for improvement of the membrane to minimize the water and electrolyte transfer, which in turn reduces operational problems and capacity loss in the battery. In 2011, Tang [57] developed a dynamic model based on mass balance equations and Fick's law for diffusion and used it to study the capacity loss caused by ion diffusion and gassing side reactions as function of time. The different diffusion rates of vanadium ions will cause the self-discharge, resulting an imbalance between the two half-cell electrolytes and thus the capacity loss.

2.3.2 Features of VRB

Among the multitude of large-capacity rechargeable batteries, the VRB has been viewed as the most promising technique for the unique advantages as follows. Firstly, VRB stores the chemical energy in the form of two vanadium electrolytes contained in two independent reservoirs. Therefore, the battery capacity can be easily enlarged by simply adding more electrolytes, which is quite cost efficient compared with the scale up of other battery systems like the lithium-ion battery. Otherwise, the output power of VRB is determined totally by the electrode area and the number of single cells connected in series or parallel, indicating that the power and capacity of VRB is separated and highly flexible according to the practical requirement. Secondly, the VRB applies vanadium

solutions in both half-cells. The use of a single-metal system makes it free from the problem of cross-contamination caused by the transfer of ions across the membrane as well as any problems associated with the use of pre-mixed solutions [58]. Thirdly, the VRB can be over-charged and over-discharged within the limits of the capacity and current density. It can also be cycled from any state of charge without permanent damage to the cells or electrolytes [59]. Finally, the electrolytes are circulated with the outer loops, so that the thermal management system can be easily designed with either natural cooling or forced cooling technique.

Currently, VRBs have already been industrialized and applied. However, there are still some technical challenges for VRBs: 1. the oxidation activity of V^{5+} is strong. Chemical stable electrodes need to be invented. 2. Positive electrolyte is sensitive to high temperature and negative electrolyte is sensitive to low temperature. Temperature control of VRB is necessary. 3. Operation will cause aqueous migration, which leads to the variation of concentration and solution volume. 4. Mass production technology needs to be improved [60].

The major applications of VRB contain: load shifting for power grid; used as storage system for wind farm or PV array; utilized as UPS for important customers such as hospital or military; integrated with renewable energy for remote electrical supplying.

2.4 Summary of Literature Review

Based on the previous reviews, SOFC and VRB have many common features such as high-efficiency, environmental-friendly, quiet and suited for large-scale system. There are many structures of distributed network that have been studied. However, previous researchers rarely mention the hybrid system of SOFC and VRB. For this structure, SOFC can provide electricity and heat efficiently, and VRB can smooth the load and absorb the redundant power generated by SOFC. The hybrid system can be used as clean power sources for remote customers.

Before investigating on this hybrid system, the performances of both VRB and SOFC need to be analyzed. Mathematic model is an effective tool in issues such as cell/stack design, transient and stationary performance prediction and control purpose. In the past decades, diverse sophisticated SOFC and VRB mathematic models have been established. However, in this thesis, simplified and concise model are required for increasing the calculation speed. The corresponding work is shown in chapter 3 and 5.

The high operating temperature of SOFC makes it possible to combine a gas turbine for generating additional power or supplying heat. Besides, operation temperature is important for the SOFC's performance. The operation temperature helps to improve cell's performance as well as eliminate the negative effect of the overpotentials during

transient process. However, exceeding high temperature may cause thermal cracking of materials or even permanent damage. Currently, it is difficult to control the operating temperature of SOFC within such complex SOFC-GT system. A simple temperature control strategy will be given in chapter 4.

It is a new attempt to combine VRB and SOFC together. Based on previous models, a SOFC/VRB DC network is proposed in chapter 6. The models of inverters are also considered in this section. Through a simple control method, the hybrid system is able to provide stable DC voltage to its user.

Chapter 3. System Level Modeling of SOFC

Predicting the performance of SOFC cogeneration systems before they are actually manufactured and installed is an important issue for optimal design and the resultant energy saving. Due to a variety of physical and chemical mechanisms occurring within SOFCs and the relevant parameters involved, computational modeling is chosen for the prediction of the SOFC stack performance because of its capability to model those complicated processes. However, major existing SOFC models are stack-level model. Compared with the system-level model, the focus of stack-level model are the physical design and optimization of the components itself, which is too complex and inefficient for system-level analysis. Besides, major existing system-level SOFC models do not fully integrate the heat and mass transfer with the electrochemistry. Moreover, currently most proposed system-level SOFC models are still tedious for component safety judgment and controller design.

The objectives of this chapter are to establish the simplified SOFC models for system-level analysis. Two dynamic computer-based models of SOFC are introduced for different applications. Starting from an existing tubular SOFC system driven by hydrogen, Akkaya's [16] lumped SOFC model is introduced. Besides, Kang's [17] simplified model are developed for a methane-driven planar SOFC stack. Compared with traditional SOFC system-level model, these two dynamic models are simple,

suitable for cogeneration analysis, and able to provide thermal safety information. Theoretical method for model development herein allows easy modification of the models on multiple levels for simulation of various SOFC structure. The pertinent physical phenomena are captured, including temperature, pressure, chemical, and electrochemical dynamics.

3.1 Lumped model of hydrogen-driven SOFC

This section describes the electrochemical model of the SOFC. Specifications for activation polarization, ohmic polarization and concentration polarization are investigated. A lumped dynamic model is proposed to predict the performance of Siemens Westinghouse tubular SOFC, which is shown in Fig 3-1.

Fig 3- 1 Tubular SOFCs stack of Siemens Westinghouse tubular SOFC

In the most common tubular design, pioneered by Siemens Westinghouse Power Corporation, the cell components are deposited in the form of thin layers on a cylindrical tube. Compared with planar SOFC, this type of SOFC eliminates the seal problems between adjacent cells. In the latest design of commercial prototype air electrode supported cell, the active length and diameter of the cells are 150 and 2.2 cm, respectively [61, 62]. Fig 3-1 illustrates the structure of SOFCs stack [38]. From the above figure, it is clear that fuel flows pass the anode on the exterior of cell and air is channeled to the inner tube and flow through the cathode. The schematic cross-section of the Siemens Westinghouse cell is also shown in Fig 3-1.

Table 3- 1 Geometry parameters of Siemens Westinghouse tubular SOFC

Geometry parameters	Nomenclature	Value
Cell length (m)	l_{SOFC}	1.5
Cell outer diameter (m)	d_{SOFC}	2.2×10^{-2}
Anode thickness (m)	d_{an}	1×10^{-4}
Cathode thickness (m)	d_{ca}	2.2×10^{-3}
Electrolyte thickness (m)	$d_{electrolyte}$	4×10^{-5}
Interconnection thickness (m)	d_{inter}	8.5×10^{-5}

The lanthanum manganite-based air electrode is a tube with a 2.2mm thickness wall and about 30-35% porosity. Ytria-stabilized zirconia (YSZ) electrolyte is deposited in form of about 40 μm thick layer. The Ni/YSZ anode is 100–150 μm thick. Doped lanthanum chromite interconnection is deposited in the form of about 85 μm thick along the air electrode tube. Base on literature [63], table of the geometry parameters of this cell is shown Table 3-1.

The ideal performance of a fuel cell is defined by its Nernst potential, represented as open-circuit voltage. The corresponding Nernst equation for the above reaction is:

$$E_{Nernst} = E_0 + \frac{RT_{cell}}{2F} \ln \frac{p_{H_2}^{bulk} (p_{O_2}^{bulk})^{0.5}}{p_{H_2O}^{bulk} (p_0)^{0.5}} \quad (3-1)$$

$$E_0 = 1.2723 - 2.7645 \times 10^{-4} \times T_{cell} \quad (3-2)$$

where p_0 is the standard atmospheric pressure (1.013 bar), R is the gas constant (8.31 J/mol.K), T_{cell} is the SOFC operating temperature, F is the Faraday constant (96487 C/mol). E_0 is the standard potential at 1atm and 25°C. Usually, it is represented as a function of T_{cell} , which is shown below [64, 65].

p_i^{bulk} is the effective partial pressure of species i (bar). In hydrogen fueled SOFC, the effective gas partial pressure approximately equals to the arithmetic average value of channel inlet value and channel outlet value [66].

$$p_{H_2}^{bulk} = \frac{p_{H_2}^{in} + p_{H_2}^{out}}{2} \quad (3-3)$$

$$p_{O_2}^{bulk} = \frac{p_{O_2}^{in} + p_{O_2}^{out}}{2} \quad (3-4)$$

$$p_{H_2O}^{bulk} = \frac{p_{H_2O}^{in} + p_{H_2O}^{out}}{2} \quad (3-5)$$

As the external load connects with SOFC, the terminal voltage of SOFC will be less than the open-circuit voltage. This is caused by the polarization effects of three irreversible processes, which are known as activation polarization (V_{act}), ohmic polarization (V_{ohm}) and concentration polarization (V_{conc}). The cell overall performance is given by:

$$V_{cell} = E_{Nernst} - (V_{act} + V_{ohm} + V_{conc}) \quad (3-6)$$

For simplification, a first-order delay element is added in front of the activation polarization as well as the concentration polarization, the delay time constant τ_{delay} is set to 10s based on NedStack PS6 data sheet.

3.1.1 Mass Balance

The equations based on mass balance between inlet and outlet of SOFC cell are given as follows [16]:

$$n_{H_2}^{out} = n_{H_2}^{in} - n_{H_2}^{re} \quad (3-7)$$

$$n_{H_2O}^{out} = n_{H_2O}^{in} + n_{H_2O}^{re} \quad (3-8)$$

$$n_{O_2}^{out} = n_{O_2}^{in} + n_{O_2}^{re} \quad (3-9)$$

$$n_{N_2}^{out} = n_{N_2}^{in} \quad (3-10)$$

$$n_{H_2}^{re} = -n_{H_2O}^{re} = 2n_{O_2}^{re} = \frac{i_{cell}A_{cell}}{2F} \quad (3-11)$$

where n_i denotes the mole flow rate of species i (mol/s), r_e denotes the quantity involved in reactions, i_{cell} denotes SOFC current density (A/m²), A_{cell} denotes the effective reaction area of SOFC. The mole flow rates of inlet gas is obtained by SOFC current density if the fuel utilization and the oxygen utilization are known,

$$n_{O_2}^{in} = \frac{n_{O_2}^{re}}{U_{O_2}} \quad (3-12)$$

$$n_{H_2}^{in} = \frac{n_{H_2}^{re}}{U_{H_2}} \quad (3-13)$$

In this study, the anode inlet gas contains both hydrogen and vapor. Their proportion denotes as X_{H_2} and X_{H_2O} , respectively.

3.1.2 Ohmic Polarization

Ohmic polarization is caused by the transmission of electron and ion through anode, cathode, electrolyte and interconnection. The cell's ohmic resistance is determined as,

$$V_{ohm} = i_{cell} \sum_k r_k \quad (3-14)$$

$$r_k = \rho_k d_k \quad (3-15)$$

$$\rho_k = a_k \exp\left(\frac{b_k}{T_{cell}}\right) \quad (3-16)$$

where r_k is the respective ohmic resistance; d_k is the thickness of each layers and ρ_k is the corresponding material resistivity. Resistivity of each layers are a series exponential functions which dependent on temperature. The coefficients of a_k and b_k are related to component materials [16, 63].

3.1.3 Concentration Polarization

The difference in partial pressures between the electrode-electrolyte interface and bulk flow of gas channel leads to concentration polarization. During the reaction process, the effective partial pressures of hydrogen and oxygen at the reaction layer are less than those in the gas channels since the electrochemical reactions take place at the interface of electrode-electrolyte. Oxygen and hydrogen cannot be replenished readily because porous electrode will resist diffusion process. On the contrary, the effective partial pressure of water vapor at the reaction site is higher than that in the anode channel since water is produced at the reaction sites. Concentration gradient is formed within electrodes. The concentration polarization can be expressed as follow [67, 68].

$$V_{conc}^{an} = -\frac{RT_{cell}}{2F} \ln \frac{p_{H_2}^{int} p_{H_2O}^{bulk}}{p_{H_2}^{bulk} p_{H_2O}^{int}} \quad (3-17)$$

$$V_{conc}^{ca} = -\frac{RT_{cell}}{4F} \ln \frac{p_{O_2}^{int}}{p_{O_2}^{bulk}} \quad (3-18)$$

$$V_{conc} = V_{conc}^{ca} + V_{conc}^{an} \quad (3-19)$$

In above equations, p_i^{int} is the partial pressure of species i at the electrode-electrolyte interface (bar). According to the research of Chan et al [69], the partial pressures of hydrogen, vapor and oxygen at the actual reaction site are given by:

$$p_{H_2}^{int} = \int_0^{d_{an}} \frac{dp_{H_2}}{dx} + p_{H_2}^{bulk} = p_{H_2}^{bulk} - \frac{RT_{cell} d_{an} i_{cell}}{2FD_{an}(eff)} \quad (3-20)$$

$$p_{H_2O}^{int} = \int_0^{d_{an}} \frac{dp_{H_2O}}{dx} + p_{H_2O}^{bulk} = p_{H_2O}^{bulk} + \frac{RT_{cell} d_{an} i_{cell}}{2FD_{an}(eff)} \quad (3-21)$$

$$p_{O_2}^{int} = \int_0^{d_{ca}} \frac{dp_{O_2}}{dx} + p_{O_2}^{bulk} = p_{O_2}^{bulk} - \frac{RT_{cell} d_{ca} i_{cell}}{4FD_{ca}(eff)} \quad (3-22)$$

where $D_{k(eff)}$ denotes the effective gas diffusion factor. The detail derivation of $D_{k(eff)}$ was presented in literature [69]. The calculation of gas diffusion factor $D_{k(eff)}$ gets involved with the micro-structure of SOFC. Parameters such as porosity (ε), tortuosity (τ) and average pore radius (r_{por}) of porous electrodes were needed in diffusion factor calculation. Both Knudsen diffusion and binary diffusion were considered in this study.

3.1.4 Activation Polarization

Chemical reactions involve energy barriers that must be overcome by reacting species. This energy barrier is called the activation energy and results in activation polarizations, which is due to the transfer of charges between the electronic and ionic conductors. Comparing with Tafel equation and linear current-potential equation, Butler–Volmer equation gives more accurate results to estimate activation polarization. It is expressed as follows [70]:

$$i_{cell} = i_0 \left[\exp\left(\frac{\beta n_e F V_{act}}{RT_{cell}}\right) - \exp\left(-\frac{(1-\beta) n_e F V_{act}}{RT_{cell}}\right) \right] \quad (3-23)$$

$$V_{act} = \frac{2RT_{cell}}{n_e F} \times \sinh^{-1}\left(\frac{i_{cell}}{2i_0}\right) = \frac{2RT_{cell}}{n_e F} \ln \left[\frac{i_{cell}}{2i_0} + \sqrt{\left(\frac{i_{cell}}{2i_0}\right)^2 + 1} \right] \quad (3-24)$$

In above equation, β is the transfer coefficient, its value is generally 0.5 for SOFC, and i_0 is the exchange current density. The exchange current density relates to the forward and reverse electrode reaction rate at equilibrium potential. Its calculation is complex and difficult, the following semi-empirical equations for tubular SOFC are generally accepted [63] shown below

$$i_0^{an} = \gamma^{an} \left(\frac{p_{H_2}^{int}}{p_{cell}} \right) \left(\frac{p_{H_2O}^{int}}{p_{cell}} \right) \exp\left(-\frac{E^{an}}{RT_{cell}}\right) \quad (3-25)$$

$$i_0^{ca} = \gamma^{ca} \left(\frac{p_{O_2}^{int}}{p_{cell}} \right)^{0.25} \exp\left(-\frac{E^{ca}}{RT_{cell}}\right) \quad (3-26)$$

Where γ^k is the pre-exponential coefficient, p_{cell} is SOFC operating pressure, E^k is the activation energy.

3.1.5 Verification

Base on the previous sections, the lumped SOFC model was established. Operating conditions and Physical parameters of Siemens Westinghouse tubular SOFC of experimental tests are given in Table 3-2 and Table 3-3 respectively [16].

Table 3- 2 Operating conditions

Operating parameters	Value	Operating parameters	Value
P_{cell} (bar)	1,3,5,10,15	X_{H_2}	0.89
T_{cell} (K)	1273.13	X_{H_2O}	0.11
U_{O_2}	0.167	X_{O_2}	0.21
U_{H_2}	0.89	X_{N_2}	0.79

Table 3- 3 Physical parameters of Siemens Westinghouse tubular SOFC

Ohmic polarization			Activation polarization			
Component	$a_k(\Omega \cdot m)$	$b_k(K)$	Component	$E^k(J/mol)$	$\gamma^k(A/m^2)$	
Cathode	8.11×10^{-5}	600	Anode	1.1×10^5	7×10^9	
Anode	2.98×10^{-5}	-1392	Cathode	1.55×10^5	7×10^9	
Electrolyte	2.94×10^{-5}	10350	Concentration polarization			
Interconnection	1.2×10^{-3}	4690	Component	$r_{por}(m)$	ε	τ
			Anode	1×10^{-6}	0.5	3
			Cathode	1×10^{-6}	0.5	3

Simulated voltage-current density curves are compared with published experimental data [71], as shown in Fig 3-2.

Fig 3- 2 H₂ fueled SOFC model verification

Comparisons show good agreement between the experimental data [72] and the simulation results at the current density range of 1500-6500 A/m^2 and pressure range of 1-15 atm. The maximal error of this model is less than 3.5%. The model has been proved accurate in predicting the SOFC performance under different pressures

Fig 3- 3 Effect of cell pressure on H2 fueled SOFC's voltage and power

The effect of pressure was shown in Fig 3-3. It's obvious to find out that the power reaches a maximum value when the cell voltage is around 0.49V in each pressure. Results show that increase of operation pressure could improve the maximum output power. The value of maximum power density are 2590, 3070, 3240, 3430 and 3530 W/m^2 for 1, 3, 5, 10 and 15 atm. Maximum output power increases around 25% by increasing cell pressure from 1 to 5 atm. Further pressure enhancing (from 5 to 15 atm)

leads to a 9% gain of SOFC maximum output power. The SOFC power density can be strongly enhance through pressurization. The effect is more obvious, especially in the low-pressurization zone.

The general conclusion is that, Akkaya's model is able to predict the performance of the hydrogen fueled SOFC accurately under different condition. The advantages of lumped model are their simple forms and high computational efficiency. However, due to the neglect of the internal transport processes and the spatially distributed nature of SOFC, the accuracy of the lumped model can be impaired and the spatially information such as temperature gradient cannot be obtained.

3.2 Reduced 1D distributed model of methane-driven SOFC

In order to consider the complex processes and to predict the thermal performance inside the SOFCs, a comprehensive distributed model is required. Aguiar et al proposed both steady-state and dynamic 1D distributed models for anode-supported SOFC [73, 74]. However, these kind of distributed model has two major disadvantages in system-level studies. They are difficult to build, and are usually time-consuming for calculation. The target of this section is to establish a simple and accurate distributed SOFC model. Besides, compared with hydrogen, naturel gas-SOFCs are more suitable for commercial

application. An internal reforming model with the necessary theoretical depth to predict the compositions of SOFC anode gases is required [75, 76].

Fig 3- 4 Schematic diagram of a planar DIR-SOFC

Based on Kang's work [17], a simplified 1D model for direct internal reforming planar SOFC (DIR-SOFC) has been established. The schematic diagram of this SOFC is shown in Fig 3-4. The cell unit is divided into several nodes along with z direction. Therefore, the spatially distributed nature can be considered. For simplifying model and improving calculation speed, Kang proposes two assumptions, (a) there are only one temperature layer within each node. The complex heat transfer and gas diffusion between solid phase and gas phase are neglected, which greatly simplify the model form; (b) current density is assumed to be uniform within the whole SOFC, and the cell voltage is directly

calculated by the average cell temperature and gas mole fraction. Therefore, the tedious iterative computation for current density distribution can be avoided.

3.2.1 Internal Reforming Model

The fuel used in commercial SOFC applications is typically natural gas whose composition varies quite significantly with geographic location and time. The high temperature of SOFC allows to sustain the reforming process within the SOFC anode channel, which converts most of the inlet methane into hydrogen. The reaction mechanisms for the internal reforming of SOFC stack are shown below [75, 76],

where x y and z indicate the reaction rate of each formula. x is calculated as follow [17],

$$x = 4273 \times p_{CH_4} \exp\left(\frac{-82 \times 10^3}{RT}\right) \quad (3-30)$$

where p_k is the partial pressure of species k, i is the current density. The shifting reactions is assumed to be always at equilibrium [63].

$$K_y = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = 1.767 \times 10^{-2} \exp\left(\frac{4400}{T}\right) \quad (3-31)$$

And the electrochemical reaction rate is calculated from the current density.

$$z = \frac{i_{SOFC} A_{SOFC}}{2F} \quad (3-32)$$

It is assumed that the initial components of each species were already known, the components of production is represented in Table 3-4 [71, 72, 77].

Table 3- 4 Equilibrium composition and partial pressure for each component

Component	Initial status	Final status	Partial pressures
CH ₄	$n_{CH_4,in}$	$n_{CH_4,in} - x$	$p_{CH_4} = \frac{n_{CH_4,in} - x}{n_{tot,in} + 2x} p_{cell}$
H ₂ O	$n_{H_2O,in}$	$n_{H_2O,in} - x - y + z$	$p_{H_2O} = \frac{n_{H_2O,in} - x - y + z}{n_{tot,in} + 2x} p_{cell}$
CO	$n_{CO,in}$	$n_{CO,in} + x - y$	$p_{CO} = \frac{n_{CO,in} + x - y}{n_{tot,in} + 2x} p_{cell}$
H ₂	$n_{H_2,in}$	$n_{H_2,in} + 3x + y - z$	$p_{H_2} = \frac{n_{H_2,in} + 3x + y - z}{n_{tot,in} + 2x} p_{cell}$
CO ₂	$n_{CO_2,in}$	$n_{CO_2,in} + y$	$p_{CO_2} = \frac{n_{CO_2,in} + y}{n_{tot,in} + 2x} p_{cell}$
Total	$n_{tot,in}$	$n_{tot,in} + 2x$	

The equilibrium constants for reforming and shifting reaction are represented by following equation [71] ,

$$K_x = \frac{p_{CO} p_{H_2}^3}{p_{CH_4} p_{H_2O}} \quad (3-33)$$

$$K_y = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} \quad (3-34)$$

The final products' component could be obtained through solving Eq. (3-33) and Eq. (3-34) simultaneous equations. The internal reforming model has been simulated. For simplification, assume there are no electrochemical reaction occurs. The reactant's total quantity and each species' molar fraction were shown in Table 3-5.

Table 3- 5 Reactant's total quantity and each species' molar fraction

Initial quantity	H ₂	H ₂ O	CH ₄	CO	CO ₂
1 mol	15%	25%	25%	15%	20%

The effect of temperature and pressure on the reforming processing was shown in Fig 3-5. The equilibrium molar fraction of each species (H_2 , H_2O , CH_4 , CO , CO_2) are shown in first 5 plots. The final plot reveals the variation of total quantity. It is clear that, the temperature and pressure has big effect on the final status of reforming process.

Fig 3- 5 Effect of different temperatures and pressures on the reforming processing

3.2.2 Mass Transfer

Since the humidifying methane is used as fuel, five components of gases exist in the anode channel, namely, H_2 , H_2O , CH_4 , CO , CO_2 . The mass transfer equation are as following [17]:

$$\frac{\delta C_{i,an}}{\delta t} + \frac{1}{A_{ac}} \frac{\delta \dot{n}_{i,an}}{\delta z} = S_{m,i,an} \quad i \in (H_2, H_2O, CH_4, CO, CO_2) \quad (3-35)$$

where i represents for different species, C stands for molar concentration, $\dot{n}$ is the molar flow rate of the anode gases, A_{ac} is the section area of anode channel, and $S_{m,i,an}$ is the molar source term on the anode side. Comparing with the differential of molar flow rate and the molar source term, the molar concentration transient can be neglected. Then, Eq. (3-35) is simplified as:

$$\frac{1}{A_{ac}} \frac{\delta \dot{n}_{i,an}}{\delta z} = S_{m,i,an} \quad (3-36)$$

Similarly, on the cathode side we have [17]:

$$\frac{1}{A_{cc}} \frac{\delta \dot{n}_{i,ca}}{\delta z} = S_{m,i,ca} \quad i \in (N_2, O_2) \quad (3-37)$$

The molar source term $S_{m,i,an}$ and $S_{m,i,ca}$ are related to the reaction rate of x , y and z , which can be expressed as:

$$S_{m,an} = \begin{matrix} H_2 \\ H_2O \\ CH_4 \\ CO \\ CO_2 \end{matrix} \begin{bmatrix} 3 & 1 & -1 \\ -1 & -1 & 1 \\ -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \div d_{ac} \quad (3-38)$$

$$S_{m,ca} = \begin{matrix} N_2 \\ O_2 \end{matrix} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -0.5 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \div d_{cc} \quad (3-39)$$

where d_{ac} and d_{cc} are the height of the anode channel and the cathode channel, respectively.

3.2.3 Thermal Model

According to Kang's assumption (a), there is only one temperature layer in each node, the energy balance equation can be written as [17],

$$\begin{aligned} \frac{A_{PEN}\rho_{PEN}c_{p,PEN}+A_{int}\rho_{int}c_{p,int}}{A}\frac{\partial T}{\partial t} + \frac{A_{ac}}{A}\frac{\partial(C_{an}h_{an})}{\partial t} + \frac{A_{cc}}{A}\frac{\partial(C_{ca}h_{ca})}{\partial t} + \frac{1}{A}\frac{\partial(\dot{n}_{an}h_{an})}{\partial z} + \\ \frac{1}{A}\frac{\partial(\dot{n}_{ca}h_{ca})}{\partial z} = \frac{A_{PEN}\lambda_{PEN}+A_{int}\lambda_{int}}{A}\frac{\partial^2 T}{\partial z^2} + S_h \end{aligned} \quad (3-40)$$

The first term on the left-hand side of Eq. (3-40) represents the heat energy used for enhancing the temperature of solid material. The second and third terms represent those for anode and cathode gases. Compared with solid material, the heat capacity of the gas phases is much smaller, therefore the second and third terms can be ignored. The fourth and fifth terms represent the enthalpy change of anode and cathode gases across each node. The first term on the right-hand side of Eq. (3-40) represents the heat conduction between adjacent nodes. Last term represents the heat source term, and is expressed as,

$$S_h = \frac{(-x\Delta H_x - y\Delta H_y - z\Delta H_z - V_{SOFC}i_{SOFC})}{d_{SOFC}} \quad (3-41)$$

where ΔH_j is the enthalpy change of reaction j at standard condition [17] and V_{SOFC} represents the cell terminal voltage.

The electrochemical model of the distributed model is similar with the one of the lumped model. As shown in Eq. (3-6), the terminal voltage of SOFC consists of two parts, i.e.

the Nernst voltage and overpotentials. The three overpotentials known as activation polarization (V_{act}), ohmic polarization (V_{ohm}) and concentration polarization (V_{conc}) are introduced in previous sections.

3.2.4 Solution Method and Simulation Results

The SOFC unit is divided into n uniform nodes along the z direction. The two ends of the SOFC are both assumed to be insulated. Conditions such as temperature, molar fraction and flow rate of the first and last node are same with those of SOFC inlet and outlet gases. In each time step, based on the average current density and the cell temperature, Eq. (3-6) is firstly applied for obtaining the cell voltage. After that, internal reform model is used for estimating the reaction rate of x y and z . The source terms of Eq. (3-38,39,41) are calculated. Next, the molar flow rates $\dot{n}_{i,an}$ and $\dot{n}_{i,ca}$ are established from Eq. (3-36) and Eq. (3-37). Finally, each node's temperature are updated from Eq. (3-40). A co-flow operating pattern is adopted here. The specifications of the planner SOFC are listed in Table 3-6.

Table 3- 6 Verification of methane fueled SOFC model [17]

Dimensions of the cell	
Cell length	0.1 (m)
Cell width	0.1 (m)
Anode thickness	500×10^{-6} (m)
Cathode thickness	50×10^{-6} (m)
Electrolyte thickness	20×10^{-6} (m)
Interconnect thickness	500×10^{-6} (m)
Anode channel height	1×10^{-3} (m)
Cathode channel height	1×10^{-3} (m)
Material properties of the cell	
Anode electrical conductivity	8.0×10^4 ($\Omega^{-1}\text{m}^{-1}$)
Cathode electrical conductivity	8.0×10^3 ($\Omega^{-1}\text{m}^{-1}$)
Electrolyte ionic conductivity	$3.34 \times 10^4 \times \exp(-10,300/T)$ ($\Omega^{-1}\text{m}^{-1}$)
PEN density	5900 (kg m^{-3})
PEN heat capacity	500 ($\text{J kg}^{-1}\text{K}^{-1}$)
PEN thermal conductivity	2 ($\text{W m}^{-1}\text{K}^{-1}$)
Interconnect density	8000 (kg m^{-3})
Interconnect heat capacity	500 ($\text{J kg}^{-1}\text{K}^{-1}$)
Interconnect thermal conductivity	25 ($\text{W m}^{-1}\text{K}^{-1}$)
Activation and concentration overpotential data	
Activation energy of anode	140 (kJ mol^{-1})
Activation energy of cathode	137 (kJ mol^{-1})
Pre-exponential coefficient for anode	8×10^{10} (A m^{-2})
Pre-exponential coefficient for cathode	1.5×10^{10} (A m^{-2})
Limiting current density	12,000 (A m^{-2})
Operating conditions	
Average current density	5000 (A m^{-2})
Fuel flow rate	2.9443×10^{-4} (mol/s)
Air flow rate	55.5219×10^{-4} (mol/s)
Operating pressure	1 (bar)
Inlet gas temperature	1023 (K)
Inlet gas composition	Fuel: CH_4 0.33, H_2O 0.67; air: O_2 0.21, N_2 0.79

The established model is able to predict the gas composition in fuel/air channels and the temperature variation along the z direction. Fig 3-6 presents the molar fraction profiles along the cell length inside the fuel channel. At the beginning of the cell unit, due to the high reforming reaction rate, methane is consumed rapidly and lots of hydrogen and carbon monoxide are produced. After the methane is exhausted, electrochemical reaction dominates inside the cell, hydrogen is oxidized into steam. At the exit of the fuel channel, all the methane has been fully consumed and the stream content is 68% in H₂O, 4% in CO, 12% in H₂, and 16% in CO₂.

Fig 3- 6 Fuel channel component mole fractions along the cell length

Fig 3-7 presents the temperature profiles along the cell length. Due to the heat generated by electrochemical reaction, the cell temperature increases along with the fuel and air

flow directions. The maximum and minimum temperatures within the SOFC are 1168 and 1007 K, respectively, leading to a maximum temperature difference of 161K. Temperature gradients can be obtained by this model as well.

Fig 3- 7 Temperature variation along the cell length

Compared with the results of a detail 1D model shown in [17], the simplified 1D model matches well as shown in Fig 3-8. It is clear that the steady-state error of the simplified 1D model is close to zero. Although during the dynamic process, the overshooting of simplified 1D model is larger than detail model's prediction, and the trends of both curve are similar. The simulation time of the simplified 1D model takes several seconds, which is much shorter than CFD model. It makes the simplified model more suitable for system level analysis. Furthermore, the temperature profile along the cell length as well as the

maximum temperature gradient is able to be obtained by this 1D model. The safety of the stack can be estimated.

Fig 3- 8 Simplified 1D model compared with detail 1D model [17]

3.3 Conclusion

In this chapter, both SOFC models proposed by Akkaya and Kang were introduced.

Chapter 4 and Chapter 6 are based on the contents of this Chapter.

Based on Akkaya's work, a simplified tubular SOFC model was built. In order to pursue more accurate simulation results, some parameters have been changed, as shown in

Table 3-3. The major advantage of this lumped model is concise. In chapter 6, this lumped model was encapsulated into a M-file for power electronics simulation. Since the calculation times are decided by the on-off frequency of power electronics, a concise SOFC model can save a lot of calculation time.

For the same reason, Kang's simplified 1D model is chosen due to its concise structure. Moreover, since excessive temperature-gradient will cause SOFC crack, the prediction of temperature-gradient is also critical. Kang's 1D model is able to estimate the temperature-gradient in a simple way. In system-level simulation, calculation efficiency is important. Overly complicated models may require more calculation time or even cannot get the results.

Chapter 4. Temperature-Maintained SOFC-GT System

High operating temperature of 600-1000 °C allows SOFC integrate with gas turbine (GT) to make use of high temperature exhaust and produce more power, and thus improve the overall efficiency. Therefore, the research of SOFC- GT hybrid system has been drawn much attention. Theoretical studies [78-80] show that the potential efficiencies of the SOFC-GT hybrid plants are higher than 70%. Besides, a prototype 220 kW SOFC-GT hybrid plant has been established by Siemens with a conversion efficiency up to 53% [81]. Furthermore, since the reforming process of hydrocarbon fuel is promoted by high temperature, various fuels such as natural gas, syngas from coal and biofuels can be directly applied by SOFC.

In this chapter, based on the reduced 1D SOFC model proposed in section 3.2, characteristics of a novel SOFC-GT hybrid plant are investigated. Three adjustable bypass valves are installed in this system for stack average temperature regulation. A plant's model is established at first and then the temperature regulation mechanism is tested. The operation safety is also discussed to make sure all components operate within their own constraints. In addition, according to different stack inlet air/fuel supply patterns and the usage of additional fuel, four partial-load strategies are compared. The optimized strategy is found out finally.

4.1 System Configuration

The SOFC-GT structure proposed in this thesis is mainly inspired by Calise's work [11] and Kaneko's work [12].

Calise[11] proposed a SOFC-GT structure. In this structure, gas turbine was used for air supplying and electricity generating. The tail gas from GT is directly sent into heat exchangers for inlet gas pre-heating. Based on different air/fuel supply patterns, three partial-load strategies were discussed in Calise's article [11]. It was concluded that the pattern of constant stack inlet air/fuel ratio enhances plants' efficiency and the pattern of constant stack inlet air flow rate widens the plants' output range. However, due to the use of lumped SOFC model, the temperature gradient within SOFC cannot be predicted, for which the knowledge is critical for SOFC reliability. The system also lacks of an effective method for SOFC temperature maintaining.

In order to control SOFC's temperature, Kaneko[12] proposed a simple and reliable regulation mechanism. Coupled with the heat exchanger for preheating inlet air, a bypass valve was introduced. It was possible to control of the flow rate of turbine exhaust bypassing the heat exchanger and thus adjust the stack temperature. Simulation results showed that this mechanism possess a good dynamic characteristic. However, Kaneko did not consider the scenario that the hot exhaust is not enough for stack preheating.

The operating principles can be summarized as follows: surrounding air is compressed by the COMP to a specific pressure and is sent into the Air Hx. Meanwhile, methane is delivered into two branches, one branch is sent into ejector and the other branch is sent into the Aux CB. Before entering the SOFC subsystem, both air and methane are preheated within the heat management subsystem. Since low steam to methane ratio (S/C) leads to carbon deposition [82], before entering into stack, methane mixes with anode exhaust firstly in ejector. The anode exhaust is rich of steam. Usually, the S/C of the anode inlet gas is higher than 2 for preventing carbon deposition.

After electrochemical reacting, the stack's exhaust is completely burned within CB. AUX CB is used for further improving the thermal energy of stack's exhaust. The high temperature, high pressure AUX CB exhaust is used to drive GT and PT. G1 and G2 are connected with GT and PT for generating additional electricity. The exhaust of PT is used as the heat source for the heat management subsystem. Normally, the temperature of the plant's final exhaust can reach to 600 K, an organic Rankine cycle [83] can be used for collecting the waste heat.

4.1.1 Temperature Regulation Mechanism

According to previous studies [84, 85], increasing the stack temperature improves its performance remarkably. Nevertheless, over-heating may cause permanent damage to

the stack's internal structure. How to maintain stack's average temperature and maximal temperature gradient within the safe level becomes very critical.

One effective way to adjust the stack temperature is to control the temperature of its inlet gases, which is directly heated within fuel Hx and air Hx. As shown in Fig 4-2, both heat exchanger's hot stream are controlled by the opening of fuel BV and air BV. Therefore, the exchanged thermal energy within fuel Hx and air Hx can be adjusted. Thereby, the stack temperature can be controlled by the configuration of fuel BV and air BV.

Fig 4- 2 SOFC Temperature Controlled by Fuel BV and Air BV

However, this method has one problem. Under some scenarios, even all PT's exhausts are used for preheating, the stack temperature cannot able to reach the desire value. To solve this problem, as shown in Fig 4-3, additional fuel is burned to increase the heat energy of PT's exhaust. Aux CB BV is applied to control the additional fuel. In general,

stack temperature can be controlled by adjusting these three bypass valves: Fuel BV, Air BV and Aux CB BV.

Fig 4- 3 SOFC Temperature Controlled by Addition Fuel

4.2 Balance of Plant Components

This section describes the specific details and algorithms for the balance-of-plant (BOP) components. These components include compressor, gas turbine, heat exchanger, combustor, ejector and bypass valve.

4.2.1 Compressor and Turbine

Model of the compressor is based on the ideal gas equations and polytropic transformations. The mechanical power consumed by the compressor is represented as,

$$\frac{T_{out,s}}{T_{in}} = \left(\frac{p_{out}}{p_{in}}\right)^{\frac{\gamma_a-1}{\gamma_a}} \quad (4-1)$$

$$\eta_{comp} = \frac{h_{out,s}-h_{in}}{h_{out}-h_{in}} = \frac{T_{out,s}-T_{in}}{T_{out}-T_{in}} \quad (4-2)$$

$$\Delta T_{comp} = \frac{T_{in}}{\eta_{comp}} \left[\left(\frac{p_{out}}{p_{in}}\right)^{\frac{\gamma_a-1}{\gamma_a}} - 1 \right] \quad (4-3)$$

$$W_{comp} = \dot{m}_{comp} C_p \Delta T_{comp} \quad (4-4)$$

where γ_a is the specific heat ratio of air, which equals to 1.4; ΔT_{comp} is the work fluid temperature rise within the compressor. η_{comp} is the isentropic efficiency of compressor.

The mechanical work required by compressor can be finally obtained by Eq. (4-4).

Since the compressor isentropic efficiency varies at different operation points, the performance map is applied to determine the isentropic efficiency at given conditions. Experimental data from off-design operation are plotted in a performance map, in which the number of free variables is reduced by means of non-dimensional parameters. Based on data from Bao's work [86], a 3D compressor map combining pressure ratio, corrected mass flow rate, rotating speed and isentropic efficiency is plotted in Fig. 4-4. Unlike the traditional performance map, the figure uses different colors to describe different isentropic efficiency.

Fig 4- 4 Compressor performance map

The solid line in Fig. 4-4 stands for the shaft rotating speed and the dash line stands for the beta line. The ‘pressure ratio’ of compressor equals to p_{out}/p_{in} , it is an important index to describe the performance of compressor. The corrected mass flow rate related with original mass flow rate is expressed as,

$$\dot{m}_{comp,cor} = \dot{m}_{comp} \frac{\sqrt{T_{in}/288.13}}{p_{in}/1.013} \quad (4-5)$$

The turbine model is similar with the compressor model. The mechanical power generated by the turbine can be represented by following equations, where γ_{mix} is the specific heat ratio of turbine work fluid.

$$\frac{T_{in}}{T_{out,s}} = \left(\frac{p_{in}}{p_{out,s}} \right)^{\frac{\gamma_{mix}-1}{\gamma_{mix}}} \quad (4-6)$$

$$\eta_{turb} = \frac{h_{in}-h_{out}}{h_{in}-h_{out,s}} = \frac{T_{in}-T_{out}}{T_{in}-T_{out,s}} \quad (4-7)$$

$$\Delta T_{turb} = T_{in} \eta_{turb} \left[1 - \left(\frac{p_{out}}{p_{in}} \right)^{\frac{\gamma_{mix}-1}{\gamma_{mix}}} \right] \quad (4-8)$$

$$W_{turb} = \dot{m}_{turb} C_p \Delta T_{turb} \quad (4-9)$$

A properly scaled turbine map is used in this work. The original turbine map can be found in Bao's paper [86]. The proposed turbine map is plotted in Fig 4-5,

Fig 4- 5 Turbine performance map

Similar with previous map, the solid lines stand for the shaft rotating speed and the dash lines stand for beta lines. The 'pressure ratio' of turbine equals to p_{in}/p_{out} . The original inlet mass flow rate needs to be transformed to the corrected mass flow rate by using Eq. (4-5).

When the turbine is coupled with compressor, the rotating speed of both turbine and compressor are same. According to the mass balance, the following equation is obtained,

$$\dot{m}_{turb} = \dot{m}_{comp} + \dot{m}_{fuel} \quad (4-10)$$

The output power of the compressor-turbine combined system can be expressed as,

$$W_{G1} = (W_{turb}\eta_{shaft} - W_{comp})\eta_{G1} \quad (4-11)$$

where η_{shaft} is the mechanical efficiency of shaft, η_{G1} is the electrical efficiency of G1.

4.2.2 Heat Exchanger

Fig 4- 6 Icon of heat exchanger

Heat exchangers transfer the heat between two work fluids with different temperatures. There are two operating mode of heat exchanger, i.e. parallel-flow and counter-flow. In this paper, counter-flow mode is chosen. The temperature difference at the both ends of heat exchanger is represented as:

$$\Delta T_1 = T_{hot,out} - T_{cold,in} \quad (4-12)$$

$$\Delta T_2 = T_{hot,in} - T_{cold,out} \quad (4-13)$$

where ΔT_1 and ΔT_2 are the temperature differences at the both ends of the heat exchanger. By using the log mean temperature difference method (LMTD), the total transfer heat can be expressed as:

$$Q_{Hx} = UA \frac{(\Delta T_1 - \Delta T_2)}{\ln(\Delta T_1 / \Delta T_2)} \quad (4-14)$$

where, U is the overall heat transfer coefficient, A is the total heat transfer area.

According to the energy balance equation, Q_{Hx} can be expressed as:

$$Q_{Hx} = \dot{n}_{cold} C_{p,cold} (T_{cold,out} - T_{cold,in}) \quad (4-15)$$

$$Q_{Hx} = \dot{n}_{hot} C_{p,hot} (T_{hot,in} - T_{hot,out}) \quad (4-16)$$

given UA , $\dot{n}_{hot}$, $\dot{n}_{cold}$, $T_{hot,in}$, $T_{cold,in}$, the value of $T_{hot,out}$ and $T_{cold,out}$ can be obtained by solving Eq. (4-15,16).

4.2.3 Combustor

Fig 4- 7 Icon of combustor

For simplification, all residual fuels are burned completely in combustor. The temperature of the outlet gasses can be calculated as,

$$\dot{n}_{CB,in} h_{CB,in} = \dot{n}_{CB,out} h_{CB,out} + Q_{loss} \quad (4-17)$$

$$Q_{loss} = (1 - \eta_{CB}) \times \sum_i \dot{n}_i \bar{h}_{rxn,i} \quad (4-18)$$

where, Q_{loss} is the heat loss of combustor, its value depends on the combustor isentropic efficiency (η_{CB}). Assuming the pressure loss within the combustor is Δp_{CB} , the outlet pressure of combustor can be expressed as ,

$$P_{CB,out} = (1 - \Delta p_{CB}) \times P_{CB,in} \quad (4-19)$$

4.2.4 Ejector and Bypass Valve

Fig 4- 8 Icons of ejector and bypass

For simplification, it is assumed that no chemical reaction occurs within the Ejector.

Energy and mass conservation are considered in this model:

$$\dot{n}_{ejc,in1} + \dot{n}_{ejc,in2} = \dot{n}_{ejc,out} \quad (4-20)$$

$$\dot{n}_{ejc,in1} h_{ejc,in1} + \dot{n}_{ejc,in2} h_{ejc,in2} = \dot{n}_{ejc,out} h_{ejc,out} \quad (4-21)$$

The function of the bypass valve is to divide fluid into two branches. Only the mass conservation needs to be considered.

$$\dot{n}_{bp,in} = \dot{n}_{bp,out1} + \dot{n}_{bp,out2} \quad (4-22)$$

The shunt ratio of branch 1 can be expressed as,

$$SR_{bp,out1} = \frac{\dot{n}_{bp,out1}}{\dot{n}_{bp,in}} + \dot{n}_{bp,out2} \quad (4-23)$$

4.3 Simulation and Discussion

This section is divided into two parts. Firstly, the effectiveness of temperature regulation mechanism improves the plant safety is investigated. For better understanding, a specific operating point is analyzed. Secondly, the partial-load performance of the plant is discussed. Based on different air supply patterns and additional fuel supply patterns, four partial-load strategies are given. An optimal partial-load strategy is explored for achieving wider output range and higher conversion efficiency.

4.3.1 Temperature Regulation Mechanism and Safety Issue

After the plant model has been established, the feasibility of the proposed temperature regulation mechanism is investigated. The relationship between the configurations of heat management subsystem and the average temperature of SOFC is plotted in Fig 4-9. Table 4-1 displays the plant's initial configurations. Some configurations are recommended by other researchers [71, 87-89].

Table 4- 1 Plant configuration [71, 87-89]

Parameter	Value	Parameter	Value	Parameter	Value
Air flow rate (kgs ⁻¹) (79% N ₂ ,21% O ₂)	2.359	SOFC Num.	15000	Power turbine efficiency	0.75
COMP pressure ratio (bar/bar)	3.75	i _{SOFC} (Am ⁻²)	8840.9	Shaft mechanical efficiency	0.98
Air utilization	0.2	UA _{HxSOFC} (kW.K ⁻¹)	0.75	Power converter efficiency	0.95
Fuel utilization	0.80	UA _{HxAir} (kW.K ⁻¹)	10	Pressure loss during combustion	0.025
Steam to methane ratio	2.5	UA _{HxFuel} (kW.K ⁻¹)	0.165	Combustion efficiency	1

As shown in Fig 4-9, once the expected stack temperature is set, the shunt ratios of both Aux CB BV and Air BV can be estimated. It is clear that, Air BV shunt ratio ($\dot{n}_{16}/\dot{n}_{10}$) is lower than its maximal value (98%) and Aux CB BV shunt ratio ($\dot{n}_{15}/\dot{n}_1$) equals 100% when the desired stack temperature is lower than 826°C. It implies the stack can be heated to the desired temperature only by using PT's outlet gas, no additional fuel is required. Conversely, when the desired stack temperature is higher than 826°C, Air BV shunt ratio ($\dot{n}_{16}/\dot{n}_{10}$) equals to its maximal value (98%) and Aux CB BV shunt ratio ($\dot{n}_{15}/\dot{n}_1$) is less than 100%. It means the PT's outlet gas is insufficient for heating the inlet gases of SOFC, additional fuel is required to enhance the stack temperature.

In fact, Fuel BV shunt ratio ($\dot{n}_{17}/\dot{n}_{14}$) also effects the stack average temperature, however, it is ignored in Fig 4-9. Since the mass flow of stack inlet fuel is very small comparing with stack inlet air, the fuel temperature has little impact on the stack

temperature. For the same reason, only 2% of PT exhaust is sufficient for pre-heating the stack inlet fuel. Majority of PT's exhaust (98%) is utilized for pre-heating the stack inlet air.

Fig 4- 9 Control the SOFC operating temperature by adjusting the shunt ratios of Air BV and Aux CB BV

Components such as heat exchanger, stack, combustor and gas turbine have their own constraints for temperature, pressure and so on. To select an appropriate BOP component, the design limitations need to be considered firstly. Although cost is often the primary criterion, several other selection criteria are also important such as operating temperature, pressure drops limits, materials and so on. For example, high operating temperature requires high-quality components made by titanium alloys or ceramic, which price are 4

to 11 times higher than the similar components made by carbon steel [90]. The capital investment will increase accordingly. On the other hand, pressurization also requires high-quality components. However, the pressurization of this work is relatively small (under 10 bar). It has no obviously effect on the capital investment [90].

To evaluate the effectiveness of heat management subsystem for enhancing the safety of SOFC-GT plant, the performances of a plant with or without the heat management subsystem are compared in Table 4-2. Some indexes related with safety are selected for analyzing. For simplifying, a specific operating point is selected as shown in Table 4-2. Other configurations same as Table 4-1.

From Table 4-2 it is clear that, when the heat management system is adopted, only 91.6% of PT's exhaust is used for heating. Comparing with the plant without heat management subsystem, the stack average temperature decreases 80 K, and the temperature of other downstream components also decreases. The cooling effect helps each components running safely. However, the maximal temperature gradient of SOFC increases 6.8 Kcm^{-1} when the heat management subsystem is adopted. It may cause thermal cracking of SOFC. Based on Kulikovsky's work [89], 28.0 Kcm^{-1} is still in the reasonable level. In general, the plant's safety can be improved by applying the heat management subsystem.

Table 4- 2 Plant performance with/without temperature regulation mechanism

Inputs of the specific case		
Compressor pressure ratio, π_{COMP}	2.75	
Air flow rate, $\dot{m}_{12}$	1.7696 (kgs ⁻¹)	
Current density, i_{SOFC}	6630.7 (Am ⁻²)	
Air utilization, U_{air}	0.2	
Fuel utilization, U_{fuel}	0.8	
Fuel flow rate, $\dot{m}_1$ (98% CH ₄ , 2% N ₂)	0.02636 (kgs ⁻¹)	
Simulation results	Plant performance without temperature regulation mechanism	Plant performance with temperature regulation mechanism
Shunt ratio of Air BV, $\dot{n}_{16}/\dot{n}_{10}$	98%	91.6%
Additional fuel to Aux CB	no	no
Air Hx outlet temperature, T_{22}	1066.4(K)	996.9(K)
SOFC average temperature, T_{SOFC}	1253.1(K)	1173.1(K)
SOFC Hx inlet temperature, T_9	1476.6(K)	1402.9(K)
GT inlet temperature, T_{21}	1376.4(K)	1303.3(K)
PT outlet temperature, T_{10}	1142.7(K)	1080.9 (K)
SOFC max temperature gradient, $\dot{T}_{\text{SOFC}}$	21.2(Kcm ⁻¹)	28.0 (Kcm ⁻¹)

4.3.2 Optimal Partial-load Strategy

When the proposed plant is used as an independent power source, the plant's output power needs to satisfy different load-demand. Thus, the partial-load performance of the plant becomes a critical index. The main target of this section is to investigate the partial-load performance of the proposed plant.

Table 4- 3 Four partial-load strategies

Additional fuel Stack inlet air	Additional fuel is used for maintaining the stack average temperature	No additional fuel is used
Constant air utilization, air flow rate is varied with the change of current density	Strategy A	Strategy B
Constant air flow rate, air utilization is varied with the change of current density	Strategy C	Strategy D

According to Calise's research [87], the partial-load operating can be achieved by varying: 1). air flow rate; 2). fuel flow rate; 3). stack current density; 4). stack operating temperature; 5). plant operating pressure, etc. al. Since the hybrid plant is a strong coupled system, these variables cannot be tuned independently without affecting other variables. The partial-load strategies need to be implemented firstly. According to

different air supply patterns and additional fuel usage patterns, four partial-load strategies are proposed as shown in Table 4-3.

In strategy A and B, the air utilization and the fuel utilization are set as 0.175 and 0.8 respectively. Constant air utilization implies the air flow rate is proportional with the stack current density. Fig 4-10 shows the COMP's operating line of strategy A and B. The plant inlet air varies from 1.65kg/s to 2.85kg/s, the corresponding pressure ratio ranges from 2.5 to 4.5. The operating line does not exceed the constraints of COMP's map, which guarantees the safety of COMP. Moreover, for pursuing better performance, the COMP's operating line stays in the high-efficiency region.

Fig 4- 10 The COMP's operating line of strategy A and B

In previous strategies, plant inlet air is proportional with the overall output power. However, plant inlet air cannot be changed arbitrarily due to the constraints of COMP's map. To extend the plant output range, constant air flow rate with variable air utilization is implemented in strategy C and D.

When the load-demand is lower than the minimal output of strategy A and B, COMP operates at the minimum point of previous strategies (1.65kg/s, 2.5). The current density decreases with the load-demand, thus, less air participates into the electrochemical reaction and the air utilization decreases simultaneously. In this way, a lower output power can be achieved.

In theory, if COMP operates at the maximal point of previous strategies (2.85kg/s, 4.5), a higher output power can be obtained. However, this situation is not considered in this paper because the increase of air utilization will lead to a higher temperature gradient of SOFC, which has negative impact on the stack safety.

Strategy A

Based on Calise's research [87], maintaining the high stack temperature helps to improve the efficiency of whole plant. To prove this, Calise adopted a constant fuel to air rate to stabilize the stack temperature. However, since Calise's plant lacks of a heat

management system, the stack temperature decreases when the load is heavy, which impacts the plant's performance.

Fig 4- 11 Plant's performance under strategy A ($U_{air}=0.175$, $U_{fuel}=0.8$, $T_{SOFC}=1173K$) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range

In strategy A, the air utilization and fuel utilization are set as 0.175 and 0.8 respectively. Besides, the stack average temperature is maintained at 1173 K in this strategy. As a result, both of safety and performance are considered.

The configuration of heat management system is shown in Fig 4-11b. When the plant output power is lower than 819.6 kW, air is relative less and the stack temperature can be maintained at 1173 K only by using PT's exhaust. The shunt ratio of Aux CB BV equals to 1 (no additional fuel are required) and the shunt ratio of Air BV is less than 0.98 (partial exhaust is able to heat up the stack to 1173K).

Conversely, when the plant output power is higher than 819.6 kW, the inlet air is relative more and PT's exhaust is not enough for preheating. Additional fuel is required to heat up the PT's exhaust. The shunt ratio of Aux CB BV is less than 1 (additional fuel are necessary) and the shunt ratio of Air BV equals to 0.98 (all PT's exhaust are used to heat up the stack). The variation can be found in Fig 4-11b. Moreover, the corresponding flow rate of plant inlet air, stack inlet fuel and additional fuel are illustrated in Fig 4-11a. Besides, in order to keep the text concise, similar analysis method will be used in strategy B, C and D.

Fig 4-11c shows the temperature variation of SOFC, CB outlet gases and GT inlet gases. The stack average temperature is maintained at 1173 K. The CB outlet temperature is

stabilized around 1400 K because: 1). since the air utilization and fuel utilization keep in constant, the components of CB inlet gases are stable; 2). since the SOFC average temperature keeps at 1173 K, the CB inlet temperature is stable. GT inlet temperature increases as $W/W_{\max}$ increases due to the burning of additional fuel.

GT's performance is also related to its efficiency. Fig 4-11d illustrates GT's operating line on its performance map. It's clear that GT is working within the high-efficiency region. It helps to enhance the GT output power.

Besides GT, SOFC is the main electrical source of the proposed plant. For the SOFC safety, the maximal and minimum SOFC local temperature are both shown in Fig 4-11e. The maximal temperature difference within the SOFC is stabilized around 190 K in this strategy. Moreover, the maximal temperature gradient of SOFC is also shown in this figure, which equals to 40 Kcm^{-1} . The maximal temperature gradient is mainly caused by the cooling effect of the reforming reaction at the beginning part of SOFC. According to Kulikovskya's work [89], the obtained temperature gradient is reasonable.

Since the stack average temperature keeps constant, stack's performance is mainly affected by its current density (Operating pressure also affects SOFC's performance. But the impact is not obvious). Overpotentials of SOFC increases as the current density

increases, which leads to the decrease of stack's terminal voltage. This phenomenon is presented in Fig 4-11f.

The output power generated by SOFC, GT subsystem and the overall plant are shown in Fig. 10g. The output power of GT subsystem presents a high slope curve due to: 1). both of the GT mass flow rate and the GT inlet temperature increase obviously as the $W/W_{\max}$ increases; 2). GT always stays on its high-efficiency region. The output power of SOFC also increases due to the increase of current density.

The plant's efficiency is ranging from 70.8% at minimal load (734.0 kW) to a maximum of 72.5% at intermediate load (819.6 kW), and back to 61.0% at maximal load (1540.7 kW). When the load demand is increased, more power is generated by GT subsystem and lower stack terminal voltage is detected. Both of them will impact the whole plant's efficiency. The turn down ratio of this strategy is about 47.0% ($W_{\min}/W_{\max}$). The operating range under this strategy is considerable.

Strategy B

As a control group, strategy B has a similar air supply pattern as previous strategy, but differs in the usage of additional fuel. There is no additional fuel burnt in this strategy.

The mole flow rate of plant inlet air and stack inlet fuel is presented in Fig 4-12a. It is clear that changing the air flow rate has little effect on the plant's output power. The turn

down ratio of this strategy is about 96.7% ($W_{\min}/W_{\max}$), which means the operating range is very narrow. The plant can be treated as a constant output source under this strategy.

The configurations of the heat management subsystem are shown in Fig 4-12b. Both bypass valves are opened to their maximum value. It implies all PT's exhaust is utilized for heating the stack. Even through, the stack temperature decreases sharply as the air flow rate increases. The temperature variation of CB outlet gas and GT inlet gas also present the similar trend, as shown in Fig 4-12c. It is because excess air carries away lots of heat from the stack.

Besides of the low inlet temperature, GT operates at its poor-efficiency region as shown in Fig 4-12d. Low inlet temperature and poor efficiency both impair the performance of GT, which can be found in Fig 4-12g.

Fig 4-12e is plotted for estimating the safety of SOFC. The maximal temperature difference is stabilized around 195 K under this situation. Moreover, the highest temperature gradient of SOFC equals to 34.4 Kcm^{-1} , which is lower than the previous strategy. Stack's V-I curve is presented in Fig 4-12f. Since the decrease of stack temperature also enhances the overpotential, the stack's terminal voltage of this strategy is lower than the one of strategy A.

Fig 4- 12 Plant's performance under strategy B ($U_{air}=0.175$, $U_{fuel}=0.8$, Additional fuel=0) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range

The power generated by stack and GT subsystem is presented in Fig 4-12g. The overall plant's efficiency is shown in Fig 4-12h. The efficiency ranges from 46.0% at minimal

output power (822.3 kW) to 69.4% at maximal output power (850.4 kW). Comparing with Fig 4-12h, strategy A shows a better performance on both output range and conversion efficiency. It is concluded that, when stack's air to fuel rate is constant, maintaining the stack average temperature at a proper value will benefit the plant's performance.

Strategy C

To extend the plant's output range, the air flow rate in this strategy is set to 56.2 mol/s, which is the minimal mole flow rate of previous strategies. Since the reactive air is proportional to the stack current density, the air utilization is varied from 0.11 to 0.19 in this strategy. The stack average temperature is maintained at 1173K by burning addition fuel as well. The mole flow rate of plant inlet air, stack inlet fuel and additional fuel are illustrated in Fig 4-13a.

The corresponding configuration of the heat management subsystem is shown in Fig 4-13b. It is clear that, when the plant output power is lower than 666.1 kW, PT's exhaust is not enough for preheating the stack to the desired temperature. Additional fuel is burnt. On the other hand, when the plant output power is higher than 666.1 kW, air is relative less and the stack temperature could be maintained at 1173 K only by using PT's exhaust.

Fig 4- 13 Plant's performance under strategy C (constant inlet air, $U_{fuel}=0.8$, $T_{SOFC}=1173K$) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range

Fig 4-13c shows the temperature variation of SOFC, GT inlet gas and CB outlet gas.

Due to the increases of air utilization, CB outlet temperature increases as the $W/W_{\max}$ increases. GT inlet temperature is directly affected by the usage of additional fuel.

GT's operating line is illustrated in Fig 4-13d. The variation of the operating line is quite narrow in this strategy, which implies the change of GT's output power is not obvious, as presented in Fig 4-13g. Stack's output power is also shown in this figure.

Since high air utilization is bad for the cooling of stack, both of the maximal temperature difference and the maximal temperature gradients increase as the air utilization increases (Fig 4-13e). Therefore, the air utilization cannot be increased arbitrarily, stack's safety should be considered as well.

Stack's V-I curve is presented in Fig 4-13f. Stack's terminal voltage decreases as the current density increases. The increase of air utilization also impacts SOFC's terminal voltage, but the effect is not obvious.

The plant's efficiency is ranging from 69.9% at minimal load (572.4 kW) to a maximum of 74.9% at intermediate load (666.1 kW), and drop to 68.6% at maximal load (771.9 kW), which is shown in Fig 4-13h. The turn down ratio of this strategy is about 74.0% ($W_{\min}/W_{\max}$). The plant's output range is narrow in this strategy.

Strategy D

As a control group, strategy D has the similar air supply pattern as strategy C, but differs in the usage of additional fuel. There is no additional fuel burnt in this strategy, all fuel is delivered into the stack shown in Fig 4-14a. The configuration of the heat management subsystem is plotted in Fig 4-14b. When the plant output power is lower than 666.1 kW, air is relatively more due to low utilization. Stack average temperature cannot be heated to the desired value. For pursuing a higher stack temperature, the shunt ratio of Air BV is set to the maximal value. On the other hand, when the plant output power is higher than 666.1 kW, PT's exhaust is enough to heat the stack to 1173 K. For guaranteeing the stack's safety, the shunt ratio of Air BV is reduced. The corresponding stack temperature is shown in Fig 4-14c. The figure also includes the temperatures variations of CB outlet gas and GT inlet gas, which have similar trend with stack temperature.

Fig 4-14d exhibits the GT's operating line. It is clear that GT operates at its high-efficiency region in this strategy, which enhances its performance.

To estimate the stack safety, Fig 4-14e is plotted. In this strategy, the maximal temperature difference is around 193 K, and the highest temperature gradient equals to 30.4 Kcm^{-1} . The stack safety can be guaranteed.

Fig 4- 14 Plant's performance under strategy D (constant inlet air, $U_{fuel}=0.8$, Additional fuel=0) (a) mole flow rate (b) bypass shunt ratio (c) temperature (d) turbine characteristic map (e) SOFC thermal status (f) stack electrical output (g) output power (h) efficiency and power range

Stack's performance is presented in Fig 4-14f. When the stack temperature is lower than 1173 K, SOFC's terminal voltage increases as current density increases. This

phenomenon can be explained as, although increase of current density will impair the stack's terminal voltage, the increase of stack temperature has the opposite effect. Here, the effect of temperature increase plays a dominant role. On the other hand, when the stack temperature equals to 1173K, SOFC's terminal voltage decreases as current density increases.

The power generated by SOFC and GT subsystem is shown in Fig 4-14g. The plant's performance is shown in Fig 4-14h. The plant's efficiency is ranging from 56.8% at minimal load (370.1 kW) to a maximum of 75.0% at intermediate load (666.1 kW), and back to 68.6% at maximal load (771.9 kW). The turn down ratio of this strategy is about 47.9% ($W_{\min}/W_{\max}$). The output range of this strategy is considerable. From strategy C and D, it can conclude that, when the air flow rate maintains constant, changing the stack temperature is an effective way to extend the plant's output range. This is valuable when the load-demand is low.

Optimal strategy

From previous analysis, it's clear that, when the air utilization is unchanged, maintaining the stack temperature by using the heat management subsystem benefits the plant's efficiency; when the air flow rate is constant, changing the stack temperature benefits the plant's output range.

For pursuing an optimal strategy, Fig 4-11h, 12h, 13h and 14h are plotted together in Fig. 4-15. The power of 1550 kW is chosen as the based power for normalization. A feasible partial-load operating strategy is proposed by combining strategy A and strategy D together: (1) when the load demand is low, the air flow rate maintains constant and no additional fuel is delivered into the Aux CB. (2) when the load demand is high, the air utilization maintains constant and additional fuel is burnt for maintaining the stack average temperature at 1173 K.

Fig 4- 15 Comparison between four different partial-load strategies

Under this combined strategy, the plant's efficiency is ranging from 56.8% at a minimal load of 370.0 kW to a maximum of 75.0% at intermediate load of 666.1 kW, and back

to 61.0% at a maximal load of 1540.7 kW. The turn down ratio of this combined strategy is 24.0% ($W_{\min}/W_{\max}$).

4.4 Conclusion

In this chapter, a novel SOFC-GT hybrid plant has been proposed. The stack average temperature can be controlled by using the heat management subsystem. The plant's model has been described and established. Moreover, based on the plant's model, the partial-load performance of the proposed plant can be analyzed.

Simulation of specific point proves that applying the heat management system can effectively enhance the plant's safety. Partial-load analysis shows that, when the air utilization keeps constant, maintaining the stack average temperature at proper value (1173 K) benefits for improving the plant's performance; besides, when the air flow rate keeps constant, changing the stack average temperature benefits for extending the plant's output range. An optimal strategy is achieved by combining two strategies together. The proposed SOFC-GT plant shows a wide output range (370.0-1540.7 kW) with remarkable efficiency (56.8%-75.0%).

Chapter 5. Electrical Modeling of VRB

With the increasing development of renewable energy such as solar and wind, large scale energy storage systems have become especially critical for the stability of micro-grids due to the stochastic behavior and intermittency of the renewable sources [91]. The all-vanadium redox flow battery (VRB) initialized by Skyllas-Kazacos and co-workers [58, 92] has been widely investigated and commercialized due to its outstanding advantages such as capacity and output power design independency, cross contamination elimination, infinite life cycle and high energy efficiency [93-95].

As a kind of electrochemical technology, the modeling of VRB is similar with the one of SOFC. The electrochemical models of the VRB [96, 97] are based on the conservation law of mass, species concentration and energy. These models give insights on membrane investigation, electrodes design, electrolyte selection and flow frame optimization. Since the electrochemical model is complex and time consuming however, it is necessary to develop a practical model for control purposes in power grid analysis [98, 99].

Electric equivalent circuit models demonstrate excellent adaptability and simplicity in predicting the electrical dynamic response of the VRB system and are proper candidates for system level control. In this chapter, a comprehensive equivalent circuit model of VRB with the effects of shunt current and pump power is proposed. In the first part, the

shunt current model is set up. The hydraulic model of pump is also established by empirical equations. Then, the charging and discharging curves are applied to identify the RC network in the model by using the least square method. After model establishment, the self-discharge caused by ion diffusion across the membrane, the parasitic losses associated with shunt currents, as well as the battery performance under different terminal currents and electrolyte flow rates are analyzed. Lastly, the simulated dynamic responses to step currents are shown.

5.1 Structure of VRB System

A typical VRB system includes at least one stack, two electrolyte tanks, two circulating pumps and other components. The VRB structure is divided into two parts, namely, the external hydraulic circuit and the VRB stack [100]. The proposed model in this chapter is based on a practical 1 kW/ 1 kWh VRB system established by Kim et al.[101].

5.1.1 External Hydraulic Circle

Since the VRB system is symmetrical, one half-side of the whole system is shown in Fig 5-1. The mixed acid ($2\text{M VOSO}_4 \cdot x\text{H}_2\text{O} + 2\text{M H}_2\text{SO}_4 + 5\text{M HCl}$) was used as electrolyte, which can avoid electrolyte precipitation of temperature above 40 °C. Each of anolyte and catholyte with volume of 30 L were contained in two electrolyte tanks. Through 1” PVC pipe, electrolyte flows from tank outlet to pump inlet. 1/2” PVC pipe was used in

other places. The diameters and lengths of each pipe, bends, sudden contraction and expansion are all marked in the figure. All of these geometric parameters are required for the hydraulic circuit model.

Fig 5- 1 External hydraulic half-circuit of VRB system

5.1.2 VRB Stack Structure

Normally, the geometry of VRB stack is complex and is composed of multiple cells, each comprising bipolar or end plate – graphite felt – membrane – graphite felt – bipolar or end plate, which are piled to form a stack. The 1 kW VRB stack proposed by Kim consists of 15 unit cells. Between each cell, 1” (1.27cm) manifolds are used to connect the electrolyte channel together. Fig 5-2 illustrates the flow frame plate of the 1 kW VRB stack that includes five electrolyte guide channels (32 cm effective length with 1 mm

width and 3 mm depth). Each flow frame plate is connected to a common buffer layer and diffusers prior to the porous electrodes (26 cm length, 30 cm wide and 3 mm depth). Based on these geometric parameters, shunt current and the pressure drop within the VRB stack can be estimated.

Fig 5- 2 VRB cell structure [101]

In addition to the geometric parameters illustrated in Fig 5-1 and Fig 5-2, other parameters such as electrolyte density, viscosity or conductivity can be found in Ref. [101], which are summarized in Table 5-1.

Table 5- 1 Parameters of the VRB system [101]

Number of cells, n_{cell}	15
Dimension of half-cell	30×26×0.3 (cm)
Permeability of porous electrode, k	$1.685 \times 10^{-10} \text{ m}^2$
Diameter of Manifold, D_{Man}	2.54 cm
Height of Manifold for each cell, H_{Man}	1.65 cm
Dimension of guide channel (effective value)	32×0.1×0.3 (cm)
Electrolyte density, ρ	1400 kg m ⁻³
Electrolyte viscosity, μ	0.006 kg m ⁻¹ s ⁻¹
Electrolyte conductivity, σ	0.2 $\Omega^{-1}\text{cm}^{-1}$
Internal cell resistance, r_{int}	1.0 $\Omega \text{ cm}^2$
Tank volume, V_{tank}	30 L
Concentration of V ion, c_v	2 M
Operating temperature of VRB, T	42.5 °C
Diffusion ratio of the membrane, η_{diff}	0.95

5.2 Comprehensive Equivalent Circuit Model for VRB

An equivalent electrical model consists of a SOC dependent voltage source in series with resistor-capacitor (RC) networks, resembling the model used for Li-ion and NiMH batteries [102]. However, the inherent features of VRB, shunt current, vanadium ion diffusion across the membrane, as well as the pump consumption cannot be ignored. The comprehensive model proposed in this paper takes into account of all these features, as shown in Fig 5-3. The model consists of an open circuit potential, E_{opv} , two controlled current sources, I_{diff} and I_{shunt} , that correspond to the effect of membrane diffusion, shunt current, RC network circuit that stands for the stationary and the dynamic characteristics

of electrical response, and a hydraulic circle model that is used to predict the power consumption of pumps. In the following sections, all these four units will be explained in detail.

Fig 5- 3 Proposed electrical model for VRB

5.2.1 Nernst Equation and State-of-charge

The open circuit voltage represents the battery electromotive force at the ideal state, which depends on the vanadium species concentration and on the operation temperature.

This potential can be obtained by the Nernst equation [51],

$$E_{ocv} = E^{\theta} + \frac{RT}{zF} \ln \left[\left(\frac{(c_{V^{2+}})(c_{VO_2^+})(c_{H^+}^2)}{(c_{VO^{2+}})(c_{V^{3+}})} \right) \left(\frac{(\gamma_{V^{2+}})(\gamma_{VO_2^+})(\gamma_{H^+}^2)}{(\gamma_{VO^{2+}})(\gamma_{V^{3+}})} \right) \right] \quad (5-1)$$

where E^{θ} is the standard electrode potential, c_i denotes the concentrations of species I and γ is the activity coefficients.

The concentration of protons in the catholyte is difficult to estimate due to ion pairing equilibria in the solution and it is usually considered as 1M. Alternatively, it is assumed to remain constant and is incorporated into the formal electrode potential that is experimentally measured at 50% SOC [103]. The second term of activity coefficient product in brackets is approximated to be 1 unit reflecting the cancellation of each species, but can also be incorporated into the experimentally determined standard electrode potential [51].

The Nernst equation is simplified as,

$$E_{ocv} = E_0 + \frac{2RT}{F} \ln\left(\frac{SOC_{cell}}{1-SOC_{cell}}\right) \quad (5-2)$$

By fitting the experimental data [104], the value of E_0 was set to 1.39V according to previous articles [51, 104]. The SOC of battery is an indication of energy level of the battery, which is related to the concentrations of the different vanadium species.

$$SOC = \frac{c_{V^{2+}}}{(c_{V^{2+}})+(c_{V^{3+}})} = \frac{c_{VO_2^+}}{(c_{VO_2^+})+(c_{VO^{2+}})} \quad (5-3)$$

The electrolyte SOC reflects the overall vanadium ion concentration level of the battery and indeed the value is proportional to the quantity of electrons that have been transferred into the stack. Therefore, SOC_{tank} is related to the initial SOC of electrolyte

in the tank, the size of the tank, V_{tank} , and the current, I_{cell} , that flows through the cell stack.

$$SOC_{\text{tank}}(t) = SOC_{\text{tank}}(0) + \frac{n_{\text{cell}}}{FV_{\text{tank}}c_v} \int_0^t I_{\text{cell}} d\tau \quad (5-4)$$

The cell SOC is needed to solve the Nernst potential as shown in Eq. (5-2). Since the SOC inside the cell is not uniformly distributed, the mean value of $SOC_{\text{cell,in}}$ and $SOC_{\text{cell,out}}$ is used to replace the distributed value [100].

$$SOC_{\text{cell}} = \frac{SOC_{\text{cell,in}} + SOC_{\text{cell,out}}}{2} \quad (5-5)$$

For simplicity, SOC_{cell} is related to the cell current I_{cell} , the electrolyte flow rate Q_{vrb} , the inlet SOC and the cell number n_{cell} . The average SOC of cell can be obtained as,

$$SOC_{\text{cell}}(t) = SOC_{\text{tank}}(t) + \frac{n_{\text{cell}} I_{\text{cell}}}{2FQ_{\text{vrb}}c_v} \quad (5-6)$$

5.2.2 Shunt Current and the Effects of Vanadium Ion Diffusion

Shunt currents are caused by the potential gradient across the cell stack that drives the ions moving through the conducting manifold and guide channels. For higher coulombic efficiency, minimization of shunt current is important and this is achieved by increasing the electrolyte path resistance with long narrow electrolyte guide channels and common manifolds [105].

A typical electrical circuit of shunt current in a flow battery is shown in Fig 5-4 [106], where the current source I_{ter} is the terminal current and R_{cell} is the cell resistance. The subscripts ‘M’, ‘G’, ‘A’, ‘C’ represent the manifold, guide channel, anode and cathode respectively, while the superscripts of ‘in’ and ‘out’ stand for inlet and outlet of the flow battery[107].

The ionic resistance of the channel and manifold are calculated on the basis of specific flow-frame design and electrolyte conductivity determined according to Eq. (5-7),

$$R = \frac{l}{\sigma A} \quad (5-7)$$

where l is the effect length, A is the cross sectional area and σ is the electrolyte conductivity. All these values are listed in Fig 5-2 and Table 5-1.

Fig 5- 4 Electrical circuit analogy of a bipolar stack [108]

The shunt loss predicted for 1 kW VRB stack is shown in Fig 5-5. During the charge process, the shunt current reduces the actual cell current available for electrochemical reactions, while during discharge process, the actual cell current is increased due to the shunt current. The coulombic efficiency will be reduced due to the shunt current losses. In this work, the effect of the shunt current is not obvious (less than 0.15A). However, it will increase with increasing series number of cells, which makes the effect of shunt current an important factor in large-scale VRB system.

Fig 5- 5 Prediction of shunt current distribution in the 15 cells stack at 50 mA cm^{-2} and 50% SOC

The shunt current model in Fig 5-4 is lumped as a controlled current source in the overall VRB model in Fig 5-3. The total shunt current of VRB stack is the average value of all

single cells, as shown in Fig 5-5. If the terminal current ' I_{ter} ' and the open circuit voltage of single cell ' E_{cell} ' are known, the total shunt current of VRB stack ' I_{shunt} ' can be obtained.

In addition to the shunt current, the diffusion of vanadium ions also has a significant impact on the coulombic efficiency [108]. When there is a vanadium ion concentration difference across the membrane, self-discharge and side reactions will occur and reduce the capacity of battery in long-term cycling [109, 110]. Based on the conservation of mass, Tang's work [57] provides a dynamic model to predict the capacity loss caused by the diffusion effect and battery side reactions. However, Tang's model is complex and time-consuming for power grid analysis. A simplified equation is used to estimate the effect of diffusion effect [111],

$$I_{diff} = \left(\frac{\eta_{diff}}{2 - \eta_{diff}} \right) |I_{ter}| \quad (5-8)$$

where η_{diff} , is the complementary part of coulomb efficiency, η_{CE} , representing the self-discharge loss due to the ion diffusion in each cycle of charge/discharge. The diffusion ratio is defined as $\eta_{diff} = 1 - \eta_{CE}$. According to the literature of Kim's report [101], the coulomb efficiency equals to 95%, thus the diffusion ratio η_{diff} is set as 5%. The item ' I_{diff} ' is used to estimate the self-discharge current by ion diffusion.

It should be mentioned however, that this assumption does not account for the differential transfer of the different vanadium ions across the membrane that leads to a build-up in one half-cell and a depletion in the other. While the Eq. (5-8) used here accounts for coulombic efficiency losses therefore, it cannot estimate the capacity loss from the differential vanadium ion transfer across the membrane. Nor does it account for capacity loss associated with side reactions such as hydrogen evolution during charging and air oxidation of V^{2+} in the negative half-cell. For simplicity however, these effects have been ignored in the present model.

5.2.3 RC Network Identification

Compared with the electrochemical model, an equivalent circuit model is suited for describing the electrical behavior of the VRB, which makes it adaptable in electrical and control analysis owing to its simplicity. Usually, the model consists of an open-circuit potential, an internal resistance, and ‘n’ order RC pairs [102].

The experimental VI curves from Kim’s article [101] have been divided into two parts, namely, the dynamic zone and the stationary zone, as shown in Fig 5-6. Based on the beginning part of Kim’s experimental data, a 1st order RC pair is adopted to identify the dynamic characteristic of VRB stack. After several seconds, the capacitor of the 1st order RC pair has been fully charged. The VRB’s terminal voltage enters into steady-state. In

order to identify the stationary characteristic of VRB stack, a resistor network is used in this work. Based on the latter half of Kim's experimental data, the unknown parameters of the resistor network can be obtained. Finally, the 1st order RC pair of dynamic model and the resistor of stationary model are considered together to form a final electrical circuit model. Therefore, the proposed model can reflect both of the dynamic and stationary characteristics of VRB stack.

Fig 5- 6 The experimental VI curves from Kim's article [101]

As shown in Fig 5-7, a 1st order RC pair is adopted to identify the dynamic characteristic of VRB stack. In order to identify the dynamic characteristic of VRB system, the beginning part of Kim's experimental data has been used [101], as shown in Fig.6. Moreover, it can be reasonable assumed that before the VRB stack has been

charged/discharged, the terminal current equals to zero. And the initial open circuit voltage can be estimated by using Nernst equation (initial SOC are 0.15 and 0.85 for charge and discharge respectively [101]). If the step input current and its corresponding voltage response are known, all components shown in Fig 5-7 can be identified by using least square method. Based on KVL theory it has:

Fig 5- 7 Electrical circuit model of VRB (dynamic zone)

$$\begin{cases} \frac{E_{opv}}{s} - V_{ter} - I_1 R_0 - (I_1 + I_2) R_1 = 0 \\ \frac{U_{c1}(0^-)}{s} - \frac{I_2}{C_1 s} - (I_1 + I_2) R_1 = 0 \end{cases} \quad (5-9)$$

where I_1 equals to I_{ter} , after rearranging, the transfer function between the terminal voltage and the terminal current can be obtained as,

$$V_{ter} = \frac{E_{opv}}{s} - \frac{U_{c1}(0^-) C_1 R_1}{1 + C_1 R_1 s} + I_1 \left(-R_0 - R_1 + \frac{R_1^2 C_1 s}{1 + C_1 R_1 s} \right) \quad (5-10)$$

$$tf(s) = \frac{\partial \Delta V_{ter}}{\partial I_{ter}} = \frac{b_1 s + b_2}{a_1 s + 1} \quad (5-11)$$

where

$$\begin{cases} a_1 = C_1 R_1 \\ b_1 = -R_0 C_1 R_1 \\ b_2 = -R_0 - R_1 \end{cases} \quad (5-12)$$

Eq. (5-11) can be further rewritten in time domain,

$$a_1 \Delta V_{ter}'(t) + \Delta V_{ter}(t) = b_1 I_{load}'(t) + b_2 I_{load}(t) \quad (5-13)$$

or,

$$\Delta V_{ter}(t) = -\frac{1}{a_1} \int_0^t \Delta V_{ter}(\tau) d\tau + \frac{b_1}{a_1} I_{load}(t) + \frac{b_2}{a_1} \int_0^t I_{load}(\tau) d\tau \quad (5-14)$$

To calculate the integration from a set of sample data, the numerical integrator can be used to transform the integration into discrete data,

Combined with experimental data, Eq. (5-14) can be rewritten into a simple form,

$$\gamma(t) = \phi(t)\theta + e \quad (5-15)$$

where 'e' is measurement noise and 'θ' is the matrix of unknown parameter,

$$\begin{cases} \gamma(t) = \Delta V_{ter}(t) \\ \theta = [\frac{1}{a_1} \quad \frac{b_1}{a_1} \quad \frac{b_2}{a_1}]^T \\ \phi(t) = [-\int_0^t \Delta V_{ter}(\tau) d\tau \quad I_{load}(t) \quad \int_0^t I_{load}(\tau) d\tau] \end{cases} \quad (5-16)$$

Since there are many measure point distributed in different time, all the data is combined to get,

$$\Gamma = \Psi\theta + \Delta \quad (5-17)$$

where Δ is measurement noise array and $\Psi = \begin{bmatrix} \phi(t_1) \\ \phi(t_2) \\ \vdots \\ \phi(t_N) \end{bmatrix}$, $\Gamma = \begin{bmatrix} \gamma(t_1) \\ \gamma(t_2) \\ \vdots \\ \gamma(t_N) \end{bmatrix}$

As the rows in Ψ are independent to each other, $\Psi^T \Psi$ is nonsingular. Thus the ordinary least squares method can be used to find out the unknown parameters

$$\hat{\theta} = (\Psi^T \Psi)^{-1} \Psi^T \Gamma \quad (5-18)$$

The unknown parameters can be recovered from

$$\begin{bmatrix} a_1 \\ b_1 \\ b_2 \end{bmatrix} = \begin{bmatrix} 1/\theta(1) \\ \theta(2)/\theta(1) \\ \theta(3)/\theta(1) \end{bmatrix} \quad (5-19)$$

And the value of R_0 , R_1 and C_1 can be obtained as,

$$\begin{cases} R_0 = -b_1/a_1 \\ R_1 = \frac{b_1}{a_1} - b_2 \\ C_1 = \frac{a_1^2}{b_1 - a_1 b_2} \end{cases} \quad (5-20)$$

Except the 1st order RC pair model for VRB's dynamic performance, a steady-state resistor circuit is shown in Fig 5-8, which is used for identifying VRB's stationary performance. The stationary model includes an internal resistor network, $R_{\text{int_cha}}$ and $R_{\text{int_Dis}}$ for charging and discharging respectively.

Fig 5- 8 Electrical circuit model of VRB (stationary zone)

To reduce the complexity of including a thermal model, the operating temperature of VRB stack is set to a constant value of 42.5 °C based on experimental data [101]. Meanwhile, according to Baccino's analysis [112], the 'derived' SOC by theoretical calculation may differ from the 'true' SOC inside the stack; and the internal resistance of VRB is a function of cell SOC. In order to correct the effect of varying SOC, a fitting coefficient 'a' is added in front of the natural logarithm term of the original Nernst equation, as described in Eq. (5-21),

$$V_{ter} = n_{cell} \times \left(E_0 + a \frac{2RT}{F} \ln \left(\frac{Soc_{cell}}{1-Soc_{cell}} \right) \right) + I_{ter} R_{int} \quad (5-21)$$

Similar with the dynamic zone identification, the value of 'a' and 'R_{int}' can be easily obtained by using the least square method.

Finally, based on both identifications of dynamic zone and stationary zone, 5 unknown parameters can be figured out. They are 'R₀', 'R₁', 'C₁', 'R_{int}' and 'a'. However, these 5 parameters are belonged by two different models. The VRB's dynamic characteristic is

primarily decided by the R_1C_1 pair of dynamic model and its stationary characteristic is mainly decided by ' R_{int} ' and ' a ' of the stationary model. Therefore, in order to build an accurate model in both dynamic and stationary zone. The ' R_1C_1 ' pair as well as ' R_{int} ' and ' a ' are selected to represent the electrical characteristics of the VRB system. The final electrical circuit model of the VRB system is shown in Fig 5-9.

Fig 5- 9 Final electrical circuit model of VRB

5.2.4 Hydraulic Model and Pump Power Consumption

Mechanical power drives the electrolyte flowing through the hydraulic circuit of the VRB. In order to determine the power consumption of the pumps, it is necessary to model the hydraulic circuits first and the pump consumption can be estimated under any operating conditions.

As introduced in the previous section, the hydraulic circuit consists of an external electrolyte circuit and a VRB stack. The stack is comprised of several cells aligned

hydraulically in parallel as shown in Fig 5-2. Most of the pressure drop occurs within the VRB stack of which about 70% is due to the pressure drop in the felt electrodes [101]. The felt electrode is similar to a porous sponge structure and its hydraulic resistance can be estimated by using Darcy equation,

$$\tilde{R}_{cell} = \frac{\mu L_{cell}}{kW_{cell}D_{cell}} \quad (5-22)$$

where ‘k’ is the permeability of the porous electrode and ‘μ’ is the electrolyte viscosity.

The total pressure drop of VRB stack can be obtained as,

$$\Delta p_{stack} = Q_{vrb} \frac{\tilde{R}_{cell}}{0.7n_{cell}} \quad (5-23)$$

From the external circuit as shown in Fig 5-1, two kinds of losses namely form loss and friction loss need to be considered. Form loss happens when the electrolyte changes its direction and velocity and the roughness of pipe and the fluid viscosity lead to friction loss [113].

To calculate the pressure drop within the external circuit, the Reynolds number ‘Re’ needs to be calculated to determine whether the flow is laminar or turbulent.

$$Re = \frac{\rho V_s D}{\mu} \quad (5-24)$$

where ‘V_s’ is the flow velocity of electrolyte and ‘D’ is the hydraulic diameter.

With the value of Reynolds number ‘ Re ’, the friction factor ‘ f_i ’ is determined by Eq. (5-25) for a laminar flow and Eq. (5-26) for a turbulent flow.

$$f_i = \frac{64}{Re} \quad (Re < 2000) \quad (5-25)$$

$$f_i = 0.316Re^{-0.25} \quad (4000 < Re < 10000) \quad (5-26)$$

The friction loss ‘ $h_{f,i}$ ’ can be calculated with Darcy-Weisbach equation,

$$h_{f,i} = f_i \frac{L_i}{D_i} \frac{V_{s,i}^2}{2g} \quad (5-27)$$

where ‘ L ’ is the length of the pipe and ‘ g ’ is the acceleration due to gravity. The minor loss ‘ $h_{m,i}$ ’ is determined by Eq. (5-28), where the minor loss coefficients ‘ $k_{L,i}$ ’ is given in Table 5-2 [100].

$$h_{m,i} = k_{L,i} \frac{V_{s,i}^2}{2g} \quad (5-28)$$

Table 5- 2 Coefficients of minor loss [100]

Components	loss coefficients $k_{L,i}$
Flanged 90° elbow	0.2
From tank into pipe	0.4
From pipe into tank	1
From 1” pipe into 0.5” pipe	0.33
From 0.5” pipe into 1” pipe	0.5625

Finally, combined the effects of fraction loss and minor loss, the pressure drop of the external hydraulic circle can be determined by the Bernoulli equation,

$$\Delta p_{hydr} = \rho g \left(h_{work} - \frac{\Delta V_{s,i}^2}{2g} - \Delta z - h_{f,i} - h_{m,i} \right) \quad (5-29)$$

where the first term ' h_{work} ' stands for the work done to the system, the second term stands for the change of potential energy and the third term stands for the change of the kinetic energy. For computational simplicity, all these three terms are assumed to be zero.

The corresponding mechanical power ' P_{pump} ' is calculated as,

$$P_{pump} = (\Delta p_{stack} + \Delta p_{hydr}) Q_{vrb} / \eta_{pump} \quad (5-30)$$

' η_{pump} ' is the transfer efficiency of pump with a value is set to 0.5 [101].

5.2.5 Verification

In this section, the proposed VRB equivalent electrical circuit model is validated in two aspects, namely electrical response and the pumps' power consumption. The corresponding experimental data are obtained from earlier work in the same area [101].

Terminal voltage validation

The experimental values of charge/discharge at different flow rates and different current densities are obtained from Ref. [101] as shown in Fig 5-10. The three different flow rates of 2, 4 and 6 L/min and the four different current densities of -160, -80, 80, 160 mA cm⁻² are tested. Based on these results and the least square method introduced before, the parameter identification results are shown in Table 5-3.

Table 5- 3 Identification parameters under different flow rates and current**densities**

$i_{\text{ter}}(\text{mAcm}^{-2})$	$Q_{\text{vrb}}(\text{L min}^{-1})$	a	$R_{\text{int}}(\Omega)$	$R_0(\Omega)$	$R_1(\Omega)$	$C_1(\text{F})$
160	2	1.6999	0.0294	0.0209	0.0085	1.16E+03
160	4	1.4537	0.0248	0.0217	0.0031	1.90E+03
160	6	1.3364	0.0231	0.0218	0.0013	4.48E+03
80	2	1.3203	0.0320	0.0222	0.0098	1.34E+03
80	4	1.2534	0.0291	0.0247	0.0044	3.77E+03
80	6	1.2176	0.0271	0.0252	0.0019	6.57E+03
-80	2	1.3461	0.0222	0.007	0.0152	1.77E+03
-80	4	1.2738	0.0191	0.0102	0.0089	2.84E+03
-80	6	1.2471	0.0168	0.0103	0.0065	4.42E+03
-160	2	1.5531	0.0244	0.0107	0.0137	1.61E+03
-160	4	1.3921	0.0201	0.0104	0.0097	1.11E+03
-160	6	1.3491	0.0186	0.0102	0.0084	1.65E+03

In Fig 5-10, the identification results are compared with the practical experimental data, where the simulation results are plotted as a black line and the experimental data are marked as circles. It is clear that the simulation results demonstrates a good degree of accuracy in both the dynamic region as well as the stationary region. The mean error of all these twelve curves equals 0.09V confirming that the simulation results fit the practical data. However, due to the lack of other experimental data, when the operating conditions are changed, all unknown parameters can be obtained by interpolation. To ensure the correctness and reasonableness of the fitting results, more experimental

measurements are required to obtain accurate fitting results under different operational conditions using the methodology described in this work.

Fig 5- 10 Stack voltage under various flow rates and various current densities [101]

Pump power consumption validation

Fig 5-11 shows the pump power consumption and the pressure drop within the VRB system. The hydraulic model introduced in this paper shows good agreement with the results provided by Kim [101]. It is clear that the pressure drop increases linearly with the flow rate with an overall mean error of 0.674 psi. The pump power shows a quadratic growth with the flow rate with a mean error of 0.49 W. Normally high electrolyte flow rate reduces the concentration overvoltage losses of VRB battery which benefits the stack voltage efficiency and performance, but high flow rate consumes more power for

circulating the electrolyte. Thus, there is a tradeoff between the performance of the stack and the pumps' power consumption.

Fig 5- 11 Pump power and pressure drop within VRB [101]

5.3 Analysis and Discussion

Based on the proposed VRB model, the effects of the shunt current, terminal current density and electrolyte flow rate are analyzed in this section. The dynamic response of the proposed model is exhibited in the final part of this section.

5.3.1 Effect of Shunt Current

The variation of electrolyte tank SOC during the stack idling period is shown in Fig 5-12. Here it has been assumed that the pumps continue to operate even if no charging or discharging is taking place. Due to the effect of shunt current, power loss exists even

when the terminal current equals to zero when the pumps are operating. Under these conditions, the SOC of the electrolyte in the tanks decreases by 0.45% in 5 hours. From Eq. (5-7), it is clear that the shunt current amplitude is directly influenced by the design of cell flow frame. The SOC fading or self- discharge caused by the shunt current is not obvious due to the appropriate design of cell flow frame. However, the impact of shunt current will become more severe if the series number of cells is increased. Moreover, in practical conditions, the operating time of storage equipment may last for several weeks and hence the SOC fading caused by the shunt current should not be ignored in the power system analysis. On the other hand, if the pumps are turned off during battery idling, the SOC of the electrolyte in the tanks will be unaffected, despite the fact that the stack electrolyte might become fully discharged as a result of the shunt current and ion diffusion processes across the membrane.

Fig 5- 12 SOC fading of tank electrolyte under stack idling condition with pump operation

5.3.2 Effect of Different Current Densities and Electrolyte Flow Rates

To further demonstrate the feasibility of the proposed model in estimating VRB performance, the full cycle charge/discharge curves have been obtained as shown in Fig 5-13.

Fig 5- 13 Terminal voltage during charge/discharge cycles at diverse current densities and flow rates

For avoid serious deviation, current density and electrolyte flow rate are chosen as 100/150 mAcm⁻² and 3/5 Lmin⁻¹ correspondingly. Both I and Q are within the known practical operating range. (The practical current density changes from 80 to 160 mAcm⁻², and the experimental electrolyte flow rate changes from 2 to 6 Lmin⁻¹) In all four

curves, the initial SOC of tank is set to 0.15. The cells are charged to an SOC of 0.85 by a constant current and finally discharged to the initial state. From Fig 5-13, it is clear that the charge/discharge curve is mainly affected by the current density and the flow rate.

As a known fact, higher current reduces charge/discharge time and increases the internal voltage loss. Hence the cycling time for 150 mA cm^{-2} is shorter than the cycling time for 100 mA cm^{-2} . And also, the voltage difference between charge and discharge for 150 mA cm^{-2} is higher than that for 100 mA cm^{-2} . On the other hand, as the concentration overpotential is reduced by increasing the electrolyte flow rate, while the terminal voltage is decreased during charge and the opposite happens during discharge. In a practical battery management system, the stack terminal voltage is usually used as the threshold value for the charging/discharging process. A lower internal overpotential benefits the VRB system for deep charge/discharge cycles. The cycling time of the higher electrolyte flow rate is relatively long.

The proposed model can also assess the stack efficiencies during a series of charge/discharge cycles. The definition equations of energy efficiency and system efficiency are shown as follows [114],

$$\eta_{en} = \frac{\left| \int_0^{t_d} U_{dis}(t) i_{dis} dt \right|}{\int_0^{t_c} U_{cha}(t) i_{cha} dt} \quad (5-31)$$

$$\eta_{sys} = \frac{\left| \int_0^{t_d} (p_{dis} - p_{pump}) dt \right|}{\int_0^{t_c} (p_{cha} + p_{pump}) dt} \quad (5-32)$$

Fig 5-14 (a) shows the effect of electrolyte flow rate on battery efficiency and Fig 5-14 (b) shows the effect of terminal current on battery efficiency. As represented in Fig 5-14 (a), the energy efficiency improves with the increase of electrolyte flow rate. Since high electrolyte flow rate leads to lower concentration overpotential and a higher SOC range during the charge/discharge processes, the energy efficiency of the VRB eventually increases. Nevertheless, the high flow rate leads to the high consumption of pump. Taking into account the fact that high flow rate increases the power consumption of the pumps, the system efficiency is a more appropriate term to evaluate the performance of VRB system. As shown in Fig 5-14 (a), the system efficiency increases quickly at the low flow rate stage due to the low pump consumption, while increasing gradually slow due to the high pump power consumption. An optimal flow rate must be attained which can balance the increase of energy efficiency as well as the power consumption of the pumps [115]. A more detail analysis has been demonstrated by Tang et al, considerable savings in pumping energy consumption can be achieved by using a variable flow-rate that is continuously adjusted to suit the operating current and SOC condition of the battery [116]. On the other hand, since a high terminal current aggravates the internal loss of battery, both energy efficiency and system efficiency decreases as the terminal current increased as shown in Fig 5-14 (b).

Fig 5- 14 Battery's efficiency under different flow rates and current density

5.3.3 VRB Dynamic Response to the Step Current Profiles

As this model is proposed for the application of power system analysis, it needs to predict the dynamic response under changing currents. From Fig 5-15, it is clear that the terminal current densities change every 5 minutes and the initial tank SOC is set to 0.5. Based on the proposed VRB model, the variations of the stack terminal voltage and the tank SOC can be simulated at any time. For each current step, the unknown parameters of VRB model are estimated firstly based on the current density and the electrolyte flow rate. Combined with the effects of shunt current and ion diffusion, the SOC in the tank is obtained in the last plot of Fig 5-15. By using the final electrical circuit model, the stack terminal voltage is estimated as represented in the middle plot of Fig 5-15. It is worth noting that, the dynamic response caused by the R_1C_1 chain is also predictable by using

this model. When we design the power electronics for the VRB stack, the dynamic characteristics of VRB is important for the control loop design. By knowing the R_1C_1 chain, the frequency-domain's characteristic of VRB can be simply estimated.

Fig 5- 15 Battery response under current steps at the flow rate equals of 4 L/min

5.4 Conclusion

In this chapter, the modeling method of VRB system has been investigated. Based on the practical VRB system proposed by Kim [101], a complete equivalent circuit model has been proposed for power system analysis. The model consisting of an open-circuit voltage (OCV) source, two parallel current sources, a 1st order resistor-capacitor network and a hydraulic model. The OCV source is described by the modified Nernst potential based on state-of-charge (SOC). Two parallel current sources represent the effects of shunt current and ion diffusion. The 1st order resistor-capacitor network depicts both

dynamic and stationary characteristics of the VRB stack. The hydraulic model gives an empirical method to analyze pump power. Based on the time scale of battery operation, the dynamic and stationary characteristics of VRB are identified by using least square method. Moreover, by considering the effects of shunt current and hydraulic losses, the proposed model can also predict the SOC fading during idling as well as the pump power consumption. All of these parameters are crucial for battery management and converter design. Validated with experimental data, the model demonstrates a good degree of accuracy. The mean-error of stack terminal voltage and pump consumption equal to 0.09V and 0.49 W correspondingly.

Based on the proposed model, several sensitivity studies have been done to further understand the VRB system. It is found that the battery performance is significantly influenced by the electrolyte flow rate. As the pump power consumption exhibits a quadratic growth with the flow rate, the system efficiency does not improve monotonically with the increase of electrolyte flow rate. These factors necessitate the requirement for an optimal flow rate strategy to maximize the system efficiency, which is similar with the conclusion of Tang [116].

Furthermore, the proposed model can predict the dynamic response of VRB under changing terminal currents where both SOC and the stack terminal voltage can be obtained.

Chapter 6. SOFC/VRB/SC Hybrid Power Supply System

Both system-level models of VRB and SOFC have been introduced in previous chapters. However, the proposed models need to be tested in an electrical system. A SOFC/VRB/supercapacitor(SC) hybrid power supply(HPS) system is established in this chapter. The integration among these three components as well as its corresponding energy management system are studied. Traditional boost converters are utilized as the interfaces between SOFC, VRB or SC to the DC-link bus. Moreover, a simple energy management system based on rate limiter is used to stabilize the voltage of DC-link bus and to coordinate the power flows among each components. Simulation results prove that the proposed distribution HPS system is able to supply stable 50V DC voltage to a renewable source-penetrated load demand.

6.1 Introduction

Based on the reports of U.S. Energy Information Administration, about 40% of total energy requirement was consumed by residential and commercial building. Power sources for building proposes have received increasing attentions during the last several years due to its high efficiency and low pollution. Due to the advantages of reliability and sustainability, a system consisted of fuel cell, battery and renewable energy is suitable for building proposes. If heat cogeneration was also considered, the overall

efficiency of the HPS system is more than 70% [117]. However, the research about building power suppliers are still in the early stages [118].

Compared with another promising fuel cell -- PEM, SOFC is more suitable for building proposes. Due to the scale flexibility, SOFC can be widely used from single-family to one community. Besides, the hot exhaust from SOFC can be used for heating or producing domestic water. PEM doesn't include this feature. Moreover, compared with PEM, SOFC has longer lifetime and lower price.

However, disadvantages such as high capital investment, long start-up time (15-30 minutes) and lousy dynamic characteristic make SOFC cannot be used as the unique source for a distribution grid. For example, if the grid is only powered by SOFC, the capacity of SOFC needs to satisfy the maximal load demand, which is obviously not economic. Besides, uninterrupted electricity needs to be guaranteed during the start-up or maintaining period of SOFC. The lousy response speed also limits the application of SOFC. Moreover, in a renewable energy- penetrated system, absorbing of surplus power needs to be considered as well. Thus, a storage device with fast response speed is a great complement for SOFC.

Among various storage devices, VRB has advantages such as capacity flexibility, low capital investment, high efficiency, high reliability and long lifetime. Both of power and

capacity of VRB can be designed separately during the manufacture phase. The design flexibility makes VRB able to satisfy different applications (from single-family to one community). Besides, VRB are quiet and safety, which make it suitable to be installed in densely populated areas. The low price and long lifetime of VRB help to reduce the operating/maintaining fees. The chargeable feature makes VRB a great complement for renewable energy. Although the energy density of VRB is lousy, the application of residential power source commonly doesn't require mobility.

Thereby, the HPS system consisted of SOFC and VRB is suitable for residential power supplying.

6.2 Structure of the Proposed HPS System

In this chapter, three renewable energy sources, i.e. SOFC, VRB, and SC, are utilized to construct a HPS system, respectively through three DC-DC boost converters, which is shown in Fig 6-1. The outputs of the three converters are parallel connected to a bus terminal for powering the load demand. The SC has the fastest response time among the three sources for the sudden disturbances in lines or load demand, which is thus used to regulate the output voltage of the bus terminal. The SOFC is recommended to operate at the relatively stable mode, so it is designed to powering the slow variation part of the load demand, while the VRB is responsible for the fast part. An energy management

system is established to coordinate each individual components and to stabilize the DC bus voltage.

Fig 6- 1 Topology of the proposed SOFC/VRB/SC HPS system

6.3 Modeling of the Proposed HPS System

In this section, the models of VRB, SOFC, boost convertor and regenerative load will be introduced.

6.3.1 VRB System-Level Model

Based on Chapter 5, a VRB system-level model has been established in Simulink as shown in Fig 6-2.

Fig 6- 2 Simulink model of VRB

The open circuit voltage of VRB is based on Nernst equation,

$$E_{ocv} = E_0 + \frac{2RT}{F} \ln\left(\frac{SOC_{cell}}{1-SOC_{cell}}\right) \quad (6-1)$$

where, SOC_{cell} is a function of the cell current I_{cell} , the flow rate of electrolyte Q_{vrb} , the tank SOC, the cell number nc_{ell} and the concentration of the vanadium ion c_v .

$$SOC_{cell}(t) = SOC_{tank}(t) + \frac{n_{cell}I_{cell}}{2FQ_{vrb}c_v} \quad (6-2)$$

In order to estimate the effect of ion diffusion, a simplified equation is used here,

$$I_{diff} = \left(\frac{1-\eta_{CE}}{1+\eta_{CE}}\right)|I_{ter}| \quad (6-3)$$

where η_{CE} is the coulomb efficiency of VRB, it was set to 0.95 in this work.

Besides, the effects of shunt current are modeled by using a look-up table (Fig 6-3). The corresponding data in the look-up table are calculated from the equivalent electrical model of shunt current as shown in Fig 5-4.

Fig 6- 3 Look-up table for shunt current prediction

Moreover, the pumps' consumption can be obtained by

$$P_{pump} = 2 \times \hat{R}_{hydr} Q_{vrb}^2 / \eta_{pump} \quad (6-4)$$

where ' η_{pump} ' is the transfer efficiency of pump with a value is set to 0.5 and ' $\hat{R}_{hydr}$ ' is the hydraulic resistance of VRB. By using hydraulic model, the value of ' $\hat{R}_{hydr}$ ' can be obtained as $2.514 \times 10^8 \text{ Pa.s.m}^{-3}$.

Based on the proposed VRB model, the SOC of tank and cell can be estimated as shown in Fig 6-4. Besides, the pump's consumption can be obtained as well. The value of SOC is a critical parameter for battery management system and the consumption of pumps will affect the overall efficiency of VRB. Corresponding optimization and control method can be implemented based on the proposed VRB model.

Fig 6- 4 SOC prediction by using the proposed VRB model Tank (upper); Cell (lower)

6.3.2 SOFC System-Level Model

According to the article published by Akkaya [16], a SOFC model has been established in Simulink as shown in Fig 6-5. The architecture of the SOFC model is referring to the original model of a proton membrane exchange fuel cell provided in the library of the MATLAB/Simulink.

In this model, Nernst equation and three internal overpotentials of SOFC have been considered for calculating the terminal voltage of SOFC, The corresponding equations are shown below

$$V_{cell} = E_{Nernst} - (V_{act} + V_{ohm} + V_{conc}) \quad (6-5)$$

$$E_{Nernst} = E_0 + \frac{RT_{cell}}{2F} \ln \frac{p_{H_2}^{bulk} (p_{O_2}^{bulk})^{0.5}}{p_{H_2O}^{bulk} (p_0)^{0.5}} \quad (6-6)$$

$$V_{ohm} = i_{cell} \sum_k r_k \quad (6-7)$$

$$V_{act} = \frac{2RT_{cell}}{n_e F} \ln \left[\frac{i_{cell}}{2i_0} + \sqrt{\left(\frac{i_{cell}}{2i_0} \right)^2 + 1} \right] \quad (6-8)$$

$$V_{conc} = \frac{RT_{cell}}{2F} \ln \left(1 - \frac{i_{cell}}{i_{limit}} \right) \quad (6-9)$$

Fig 6- 5 Simulink model of SOFC

By using the proposed SOFC model, the inlet mole flow of both fuel and air can be obtained, as shown in Fig 6-6.

Fig 6- 6 SOFC inlet consumptions: air (upper); fuel (lower)

The mole flow rates of inlet gases are critical for the design of fuel/air supply system.

The effects caused by stack consumptions can be predicted, and corresponding system optimization can be studied.

6.3.3 Small-signal Modeling of Boost Converter

All converters used in this work are boost converters, and its small-signal equivalent circuit in s-domain is shown in Fig 6-7 [119]:

Fig 6- 7 Small-signal equivalent circuit of boost converter in s-domain

At a certain equilibrium point (EP), the following formula can be established

$$\begin{cases} L \frac{dI_L}{dt} = -r_L I_L + (D - 1)U_c + V_s = 0 \\ C \frac{dU_c}{dt} = (1 - D)I_L - \frac{U_c}{R} = 0 \end{cases} \quad (6-10)$$

where D' equals to $1 - D$

The steady-state value at the EP can be obtained:

$$U_c = \frac{V_s - r_L I_L}{D'} \quad (6-11)$$

$$I_L = \frac{U_c}{R D'} \quad (6-12)$$

Replace U_c and I_L in Fig 6-7 and ignore the effect of r_L , we have

Fig 6- 8 Final small-signal equivalent circuit of boost converter in s-domain

The transfer function $G_{ui}(s)$ between inductor current $\hat{i}_L$ and output voltage $\hat{u}_c$ are

$$Z = \frac{R}{RCs+1} \quad (6-13)$$

$$G_{ui}(s) = \left. \frac{\hat{u}_c(s)}{\hat{i}_L(s)} \right|_{\hat{v}_s=0} = \frac{(D'^2 R - sL)Z}{D'(R+Z)} \quad (6-14)$$

The transfer function $G_{id}(s)$ between inductor current $\hat{i}_L$ and duty cycle $\hat{u}_c$ are

$$G_{id}(s) = \left. \frac{\hat{i}_L(s)}{\hat{d}(s)} \right|_{\hat{v}_s=0} = \frac{U_c}{D'^2 R} \times \frac{RCs+2}{\frac{LC}{D'^2} s^2 + \frac{L}{D'^2 R} s + 1} \quad (6-15)$$

6.3.4 Regenerative Load Curve

In this work, a square wave shown in Fig 6-9 stands for the combining effect of load demand and renewable energy. We are considering the bidirectional power flow at the load side and the square wave has a negative part from 0.5s to 0.625s as shown in the red dotted box to represent the reverse power flow from the load side to the input side due to the existing of renewable energy or regenerative energy. By introducing the

negative value, the charging process from the load side to VRB and SC can be analyzed.

Practical load curve, detail model of renewable energy and the corresponding converters will be discussed in future work.

Fig 6- 9 Simplified load+RE curve for the proposed SOFC/VRB/SC HPS system

6.4 Energy Management System of the Proposed HPS System

Energy management system likes the central nervous system of distributed network, it helps to control each components for achieving a certain goal. The energy management system proposed in this work is shown in Fig 6-10. It includes three PI controllers for each boost converters and a rate limiter to coordinate the power flow between SOFC and VRB. The main objectives include: a) reference signals modulation for each components and b) bus terminal voltage stabilization.

Fig 6- 10 Structure of proposed energy management system

6.4.1 Rate Limiter

In this case, the current of both SOFC and VRB are controlled by their convertors. Thus, the two components behave like current sources. A rate limiter is adopted here to decompose the original load signal into two parts, which are the fast variation part (derivative $> \pm 300\text{W/s}$) and the slow variation part (derivative $\leq \pm 300\text{W/s}$). Since the dynamic characteristic of VRB is superior to SOFC, the fast variation part is supplied by VRB and the slow variation part is supplied by SOFC. Besides, SC is responsible for stabilizing the bus voltage at 50V. SC is also an ideal complement to follow the sudden load variation.

6.4.2 PI controllers

PI controller for regulating the output power of VRB is shown in Fig 6-11

Fig 6- 11 Schematic diagram for power controlling of VRB

The parameters of VRB PI controller are: $K_P=3$, $K_I=1$;

PI controller for regulating the output power of SOFC is shown in Fig 6-12

Fig 6- 12 Schematic diagram for power controlling of SOFC

The parameters of SOFC PI controller are: $K_P=1$, $K_I=25$;

PI controllers for regulation the output voltage of the bus terminal through SC is shown in Fig. 5.

Fig 6- 13 Schematic diagram for voltage controlling of SC

The parameters of the SC PI controllers are: $K_{P1}=20$, $K_{I1}=100$; $K_{P2}=0.01$, $K_{I2}=0.2$;

In this system, the switching frequency for all the involved converters equals to 20kHz.

6.5 Configurations of the Proposed HPS System

In this section, the configurations of each components will be introduced.

6.5.1 SOFC Stack Configurations

As the primary power source, SOFC supplies base load demand. The lumped SOFC introduced in section 3.1 is adopted here. Other configuration parameters of the SOFC are shown in Table 6-1:

Table 6- 1 Configurations of SOFC adopted in the HPS system

Configuration parameters	Nomenclature	Value	Configuration parameters	Nomenclature	Value
Rated power (kW)	$Power_{SOFC}$	1	Rated voltage (V)	V_{SOFC}	19
Pressure (bar)	p_{SOFC}	3	Cell Num.	n_{SOFC}	16
Temperature (K)	T_{SOFC}	1273	Cell length (m)	l_{SOFC}	0.1875
Dynamic time constant (s)	τ_{SOFC}	15	Cell outer diameter (m)	d_{SOFC}	0.022
Air utilization	U_{air}	0.167	Fuel utilization	U_{fuel}	0.85
H ₂ mole fraction	X_{H2}	0.85	H ₂ O mole fraction	X_{H2O}	0.15

Compared with the 1D distributed model, the lumped model is more suited for power grid analysis due to its concise form and high computational efficiency. Although 1D distributed model is able to provide more detail spatial information, more computational resources are required. Beside, in this case, sufficient air has been injected into the SOFC to ensure its thermal safety. Thus, the 1D distributed model is unnecessary [120].

6.5.2 VRB System Configurations

The VRB is used to absorb surplus regenerative energy and to supply the fast variation load. The model proposed in chapter 5 is used here to predict the performance of VRB.

Unknown configurations of VRB are shown in Table 6-2:

Table 6- 2 Configurations of VRB adopted in the HPS system

Configuration parameters	Nomenclature	Value	Configuration parameters	Nomenclature	Value
Rated power (kW)	$Power_{VRB}$	1	Rated voltage (V)	V_{VRB}	18
Capacity (kWh)	Cap_{VRB}	4	Cell Num.	n_{VRB}	15
Flow rate (L/min)	Q_{VRB}	4	Initial SOC	SOC_{VRB}	0.5
Fitting parameter	a_{VRB}	1.3035	Equivalent resistor of R_0 (Ω)	R_0	0.0211
Equivalent resistor of R_1 (Ω)	R_1	0.0069	Equivalent capacitor of C_1 (F)	C_1	1957.5

The equivalent circuit of VRB consists of a series resistor R_0 and one R_1C_1 networks. R_0 is responsible for the instantaneous variation for terminal voltage. R_1C_1 are used to describe the transient characteristic of VRB. The values of R_0, R_1 and C_1 can be identified by using least square method as shown in section 5.2.3 [120].

6.5.3 SC Bank Configurations

Usually, SC is appropriate to satisfy the transient and instantaneous load variations. In this work, the instantaneous load variation which cannot be followed by VRB are

supplied by SC. The SC model is taken from the library of Simulink, the corresponding configurations is shown in Table 6-3,

Table 6- 3 Configurations of SC adopted in the HPS system

Configuration parameters	Nomenclature	Value	Configuration parameters	Nomenclature	Value
Rated capacitance (F)	C_{SC}	10	Num. of capacitors	n_{SC}	12
Rated voltage (V)	V_{SC}	32	Initial voltage (V)	V_{SC0}	16
DC resistance (m Ω)	R_{SC}	2.1			

SC has advantages such as no memory effect, wide operation range and high conversion efficiency. The average current of SC should equal to zero during long period. In this work, a SC bank is adopted to stabilize the voltage of DC-link bus and to supply the sudden load change [121].

6.6 Simulation and Analysis

In this section, the performance of the proposed SOFC/VRB/SC HPS system has been tested by using two different load cycles. Besides, sensitivity studies of using average converter model and connection extension are both analyzed.

6.6.1 HPS System's Performance based on Different Load Cycles

Based on the models introduced in previous sections, the whole HPS system's Simulink model is proposed as shown in Fig 6-14:

Fig 6- 14 Simulink model of the proposed VRB/SOFC/SC HPS system

The load curve is shown in Fig 6-15(a). It includes negative value due to the existing of renewable energy. For simplification, a step wave is adopted here to stand for the load demand. The maximum load equals to 340W and the maximum surplus power equals to -180W. Rate limiter decomposes the slow variation load from the original curve. Fig 6-15(b) shows the slow variation part and it is used as the reference power for SOFC. The highest derivative of SOFC's reference power equals to 300W/s. Meanwhile, the remaining part of load curve is sent to VRB as shown in Fig 6-15(c).

Fig 6- 15 Decomposition of the load cycle by using rate limiter

Fig 6-16 illustrates the performance of the SOFC/VRB/SC HPS system. Fig 6-16(a) shows the bus voltage varies around 50V. The SC bank is properly controlled by the reference signal V_{SC}^* . Fig 6-16(b) exhibits the power flow of SC bank. It alternates

around zero in high frequency and supply the sudden load fluctuations successfully. The output power of VRB is shown in Fig 6-16(c). Except the sudden variation part, the output power of VRB is able to follow its reference signal I_{VRB}^* closely. Similar phenomenon can be found on the performance of SOFC as shown in Fig 6-16(d). Therefore, the proposed HPS system can successfully satisfy the renewable energy-penetrated load and provide a wonderful response speed to sudden load change

Fig 6- 16 Simulation results from a simple load cycle test: a) bus voltage; b) SC power; c) VRB power; d) SOFC power

The load cycle is not unique. Any load cycle consists of both positive and negative parts and able to be divided into two sub-loads with different derivatives (the slower and the faster ones) can be tested by the proposed HPS system. Another load cycle and its corresponding sub-loads for VRB and SOFC are shown in Fig 6-17,

Fig 6- 17 Decomposition of another load cycle by using rate limiter

As shown in Fig 6-18(a), the bus voltage is stabilized around 50V due to the utilization of SC bank. Its corresponding power is shown in Fig 6-18(b). Fig 6-18(c,d) proves that both SOFC and VRB are able to follow their reference load signal closely. It is clear that the proposed SOFC/VRB system is able to supply different load cycle.

Fig 6- 18 System performance prediction based on another load demand: a) bus voltage; b) SC power; c) VRB power; d) SOFC power

6.6.2 Sensitivity Studies

In this section, sensitivity studies of model extension as well as the effects of changing average converter models will be discussed.

Series and parallel extension of SOFC model

In order to study the limitation of model extension, series and parallel connections of proposed models have been studied. At the beginning, the nomenclature needs to be claimed for accurate description. One VRB or SOFC system only contains one stack. Within the stack, modules can be connected in series or parallel ways. And one module is only combined by several cells in series. All models proposed in this section is for modules [122].

As shown in Fig 6-19, a SOFC system consisted by one 16-cell module ('one module system' for short) has been compared with another SOFC system consisted by four 8-cell modules ('four modules system' for short). The four modules system has 2 parallel branches and each branches contains two 8-cell modules in series. Both of two SOFC systems use the same boost converter, PI controller and resistive load. In order to make the two systems comparable, the parameters of these two SOFC systems are deliberately set as Table 6-4.

Fig 6- 19 Two SOFC systems for extension analysis

Table 6- 4 Comparison between two SOFC systems for extension analysis

	One module system	Four modules system
Series Num.	1	2
Parallel Num.	1	2
PI controllers gains	$K_p=1$, $K_I=25$;	$K_p=1$, $K_I=25$;
Resistive load	$10\ \Omega$	$10\ \Omega$
Series cells	16	8

Fig 6-20 shows the performances of the one module system, the output power follows with the load demand, the voltage variation is relatively smaller due to the inherent feature of SOFC. The current variation is similar to the trend of power variation. The values of voltage, current, and power are observable as shown in Fig 6-20.

Fig 6- 20 Simulation results of the one module system of SOFC

Fig 6- 21 Simulation results of the four modules system of SOFC

As the control group, the performances of the four modules system are shown in Fig 6-21. The four modules system and one single module from this system are both plotted in Fig 6-21. The four modules system's performances are similar to the one module system due to the same load demand, the control method and the load characteristics. Within the four modules system, it is clear that each module's voltage and current equal to the half

of those of the entire system and the power equals to one quarter of the power of the entire system. It can conclude that no matter in which connection method, the simulation results of SOFC model are not affected by model extension.

Series and parallel extension of VRB model

Similar analysis has been conducted based on proposed VRB model. As shown in Fig 6-22, a VRB system consisted by one 15-cell module ('one module system' for short) has been compared with another VRB system consisted by six 5-cell modules ('six modules system' for short). The six modules system has 2 parallel branches and each branches contains three 5-cell modules in series. Both of two VRB systems use the same boost converter, PI controller and resistive load. In order to make the two systems comparable, the parameters of these two VRB systems are deliberately set as Table 6-5.

Fig 6- 22 Two VRB systems for extension analysis

Table 6- 5 Comparison between two VRB systems for extension analysis

	one module system	six modules system
Series Num.	1	3
Parallel Num.	1	2
PI controllers gains	$K_P=3, K_I=1$;	$K_P=3, K_I=1$;
Resistive load	$10\ \Omega$	$10\ \Omega$
Series cells	15	5

Fig 6-23 shows the performances of the one module system, the output power follows with the load demand, the voltage variation is relatively smaller due to the inherent feature of VRB. The current variation is similar to the trend of power variation. The values of voltage, current, and power are observable as shown in Fig 6-23.

Fig 6- 23 Simulation results of the one module system of VRB

As the control group, the performance of the six modules system are shown in Fig 6-24.

The six modules system and one single module from this system are both plotted in Fig 6-24. The six modules system's performances are similar to the one module system due

to the same load demand, the control method as well as the load characteristics. Within the six modules system, it is clear that each module's voltage, current and power equal to $1/3$, $1/2$, $1/6$ of those of the entire system correspondingly. It can conclude that no matter in which connection method, the simulation results of the proposed VRB model are not affected by model extension.

Fig 6- 24 Simulation results of the six modules system of VRB

The effects of using average converter model

Replacing the original switched model by average converter model, the new HPS system model is shown in Fig 6-25. The replaced average converter models are emphasized in the blue boxes. Compared with the original switched model, the carrier wave generator can be omitted. The input signal of the average converter models is only the duty ratio from PI controllers. The average model is taken from the library of the

MATLAB/Simulink, which using a switching-function model and providing the fastest simulations.

Fig 6- 25 Average model of the proposed SOFC/VRB/SC HPS system

The simulation results by running the average model are shown in Fig 6-26 where the steady-state values of the DC-link bus voltage, the SC bank power, the SOFC power as well as the VRB power are the same as those by using the original switched model as shown in Fig 6-16. Compared Fig 6-26 and Fig 6-16, it is clear that the average model is saving a lot of simulation time (i.e. 30s for average; 50s for switched) at the expense of losing some dynamic details in the circuit waveforms that the switched model can exhibit. It is a trade-off between the simulation speed and the accuracy of the result.

Fig 6- 26 Simulation results by using average model: a) bus voltage; b) SC power; c) VRB power; d) SOFC power

6.7 Conclusion

This chapter introduces the integration among SOFC, VRB and SC. SOFC is designed to supply the base load without facing sudden fluctuations, which benefits for extending its lifetime. VRB helps SOFC to satisfy the fast variation load and to absorb the surplus energy from renewable source. The existing of SC effectively buffer the sudden load variations on both SOFC and VRB. And the proposed simple energy management system is able to stabilize the bus terminal voltage around a set value. Simulation results show that both system-level models of SOFC and VRB can be utilized in the electrical analysis. Sensitivity studies about model extension as well as the effects of using average converter models are discussed in this chapter.

However, the rate limiter used in this work only able to decompose the load demand by different derivatives, optimization control strategy cannot be achieved by using this method. Moreover, practical load model, detail models for renewable energy and the corresponding converters are not considered in this work. More efforts need to be paid in future.

Chapter 7. Conclusions and Recommendations

7.1 Conclusion

Among all electrochemical components, SOFC and VRB are considered as the promising candidates for large-scale electrical generation and storage correspondingly. Research orientations like system-level modeling, thermal reliability, integrations between SOFC and GT, SOFC and VRB are required to be deeply investigated before the practical commercialization of SOFC and VRB. The thesis mainly focuses on the mentioned orientations.

In Chapter 3, lumped model and 1D distributed model of SOFC are established. Both models include the electrochemical sub-model, thermal sub-model and mass transfer sub-model. Simulation results are verified with the experimental data from Akayya's and Kang's papers [16, 17]. Then, by using the lumped model, the effects of pressurization and heating on SOFC performance are analyzed. The advantages of lumped model are its concise form and high computational efficiency. However, the internal information within the SOFC cannot be obtained by using lumped model. This problem can be solved by using 1D distributed model. The temperature profile along the cell length and the maximum temperature gradient can be obtained by using the 1D distributed model.

In Chapter 4, a novel temperature-maintained SOFC-GT system is proposed. The SOFC's average temperature can be controlled by using the proposed thermal management subsystem. Temperature gradient within SOFC can be estimated for thermal reliability estimation. Besides, a detail GT model has been built for better understanding the integration between SOFC and GT. Finally, the optimization of the partial load strategy has been obtained based on the proposed SOFC-GT system. The proposed SOFC-GT system shows a wide power range (370.0-1540.7 kW) with remarkable conversion efficiency (56.8%-75.0%).

In Chapter 5, a comprehensive equivalent circuit model for VRB is investigated based on the experimental data proposed by Kim [101]. By using the least square method, both of the dynamic and stationary characteristics of VRB are identified into a 1st order resistor-capacitor network. The effects of shunt current on SOC fading is predicted in this work. Besides, the pump consumption for electrolyte cycling is also estimated by using hydraulic model. The proposed VRB model demonstrates a considerable degree of accuracy compared with the practical data. Based on the proposed model, the trade-off between the electrolyte flow rate and the system efficiency are studied. The proposed model is also able to predict the dynamic response of VRB under different conditions.

In Chapter 6, the integration of a SOFC/VRB/SC HPS system is studied. In this topology, both of the SOFC and VRB are used to satisfy the major load demand while VRB and

SC are jointly adopted to store the surplus energy from renewable energy source. The models of VRB and SOFC proposed in previous chapters are utilized in this section. Besides, a rate limiter is applied here to decompose the load signal into a slow variation part and a fast variation part. Depend on different dynamic features, the slow reference signal and the fast reference signal are sent to SOFC and VRB correspondingly. SC is adopted to maintain the DC link-bus voltage and to supply the sudden load demand due to its ideal dynamic feature. The structure of the proposed hybrid system is rare in previous literatures.

7.2 Recommendations for Future Work

Notwithstanding the progress made so far in the thesis, there are still several potential orientations worthy of pursuing. In Chapter 3, both the lumped and distributed model are built based on theoretical equations, which requires lots of parameters about the micro-structure of SOFC. A model by using identification method can further simplify the existing model of SOFC. In Chapter 4, only the stationary state of the proposed SOFC-GT system has been analyzed. More efforts need to be paid to establish the dynamic model of SOFC-GT system. During transient process, the SOFC's thermal reliability is important for practical operation. Moreover, how to operate the SOFC-GT system properly under partial-load condition is also a potential topic to study.

In Chapter 5, the main circuit of VRB is obtained by using least square method. The values of R_1C_1 are always changing with operation conditions. One solution is to use artificial neuron network (ANN) or support vector machine (SVM) methods to identify the performance of VRB. The performance under different operation conditions can be summed up as one unit model. In Chapter 6, a simple energy management system based on rate limiter is adopted. This study ignores the extreme SOC controlling of VRB or SC. An advanced energy management system is expected to ensure the suitable operation of VRB and SC.

Besides the improvements mentioned above, other relevant topics can be further studied. One relevant topic is the energy management system of SOFC and VRB. A comprehensive energy management system is including battery status monitoring, interface design, online parameters identification, cooling system, input/output power control, capacity estimation, etc. Among them, online parameters identification and interface design are considerable topics for future study.

For the application level of SOFC/VRB/SC HPS system, renewable energy sources such as wind and PV are suitable for penetrating into this structure. How does the HPS system smooth the intermittent renewable energy and how to stabilize the bus voltage are critical issues for power quality. In addition to that, GT integration and heat cogeneration are not involved in this thesis. How to integrate the GT system and how to supply both

electricity and heat in a proper ratio are also promising fields to study. Moreover, suitable capacity sizing of SOFC and VRB in the HPS system is important for cost-effectiveness consideration.

Author's Publications

1. Zhang Y, Zhao J, Wang P, Xiong B, Xian L, Badrinarayanan R. *Partial-Load Analysis of a Temperature-Controlled Solid-Oxide Fuel Cell–Gas Turbine (SOFC–GT) Hybrid Power Plant*. Energy Technology. 2015;3:601-17.
2. Zhang Y, Zhao J, Wang P, Skyllas-Kazacos M, Xiong B, Badrinarayanan R. *A comprehensive equivalent circuit model of all-vanadium redox flow battery for power system analysis*. Journal of Power Sources. 2015;290:14-24.
3. Wu J, Chan CK, Zhang Y, Xiong BY, Zhang QH. *Prediction of solar radiation with genetic approach combining multi-model framework*. Renewable Energy. 2014;66:132-9.
4. Xiong B, Zhao J, Tseng KJ, Skyllas-Kazacos M, Lim TM, Zhang Y. *Thermal hydraulic behavior and efficiency analysis of an all-vanadium redox flow battery*. Journal of Power Sources. 2013;242:314-24.
5. Zhang Y, Jiyun Z, Liang X. *Studies on operation parameters of SOFC-compressor combine system*. Power and Energy Society General Meeting (PES), 2013 IEEE: IEEE; 2013. p. 1-5.
6. Badrinarayanan R, Zhang Y, Tseng KJ. *Performance Study of a Vanadium Redox Flow Battery (VRB) for Use in Green Data Centers*. International Telecommunications Energy Conference (INTELEC), 2015 IEEE

References

- [1] Kaldellis JK. Stand-alone and hybrid wind energy systems: technology, energy storage and applications: Elsevier; 2010.
- [2] Yang Z, Zhang J, Kintner-Meyer MC, Lu X, Choi D, Lemmon JP, et al. Electrochemical energy storage for green grid. *Chemical reviews*. 2011;111:3577-613.
- [3] Suberu MY, Mustafa MW, Bashir N. Energy storage systems for renewable energy power sector integration and mitigation of intermittency. *Renewable and Sustainable Energy Reviews*. 2014;35:499-514.
- [4] Jiayi H, Chuanwen J, Rong X. A review on distributed energy resources and MicroGrid. *Renewable and Sustainable Energy Reviews*. 2008;12:2472-83.
- [5] Dunn B, Kamath H, Tarascon J-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science*. 2011;334:928-35.
- [6] Chen H, Cong TN, Yang W, Tan C, Li Y, Ding Y. Progress in electrical energy storage system: A critical review. *Progress in Natural Science*. 2009;19:291-312.
- [7] Stambouli AB, Traversa E. Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renewable and Sustainable Energy Reviews*. 2002;6:433-55.
- [8] Kakaç S, Pramuanjaroenkij A, Zhou XY. A review of numerical modeling of solid oxide fuel cells. *International Journal of Hydrogen Energy*. 2007;32:761-86.
- [9] Kirubakaran A, Jain S, Nema RK. A review on fuel cell technologies and power electronic interface. *Renewable and Sustainable Energy Reviews*. 2009;13:2430-40.
- [10] Sedghisigarchi K, Feliachi A. Dynamic and transient analysis of power distribution systems with fuel Cells-part I: fuel-cell dynamic model. *IEEE Transactions on Energy Conversion*. 2004;19:423-8.
- [11] George RA. Status of tubular SOFC field unit demonstrations. *Journal of Power Sources*. 2000;86:134-9.
- [12] Nehrir H, Caisheng W, Shaw SR. Fuel cells: promising devices for distributed generation. *IEEE Power and Energy Magazine*. 2006;4:47-53.

-
- [13] Joerissen L, Garche J, Fabjan C, Tomazic G. Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems. *Journal of Power Sources*. 2004;127:98-104.
- [14] Li L, Kim S, Wang W, Vijayakumar M, Nie Z, Chen B, et al. A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. *Advanced Energy Materials*. 2011;1:394-400.
- [15] Kear G, Shah AA, Walsh FC. Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects. *International Journal of Energy Research*. 2012;36:1105-20.
- [16] Akkaya AV. Electrochemical model for performance analysis of a tubular SOFC. *International Journal of Energy Research*. 2007;31:79-98.
- [17] Kang Y-W, Li J, Cao G-Y, Tu H-Y, Li J, Yang J. A reduced 1D dynamic model of a planar direct internal reforming solid oxide fuel cell for system research. *Journal of Power Sources*. 2009;188:170-6.
- [18] Ackermann T, Andersson G, Söder L. Distributed generation: a definition1. *Electric Power Systems Research*. 2001;57:195-204.
- [19] Pepermans G, Driesen J, Haeseldonckx D, Belmans R, D'haeseleer W. Distributed generation: definition, benefits and issues. *Energy Policy*. 2005;33:787-98.
- [20] El-Khattam W, Salama MMA. Distributed generation technologies, definitions and benefits. *Electric Power Systems Research*. 2004;71:119-28.
- [21] WADE. World Survey of Decentralized Energy.
http://www.localpower.org/nar_publications: World Alliance for Decentralized Energy; 2004.
- [22] Toledo OM, Oliveira Filho D, Diniz ASAC. Distributed photovoltaic generation and energy storage systems: A review. *Renewable and Sustainable Energy Reviews*. 2010;14:506-11.
- [23] IEA. World Energy Outlook 2011. <http://www.worldenergyoutlook.org/>: International Energy Agency; 2011.

-
- [24] Commission IE. Grid Integration of Large-capacity Renewable Energy Sources and Use of Large-capacity Electrical Energy Storage: White Paper; October 2012: International Electrotechnical Commission; 2012.
- [25] Alanne K, Saari A. Distributed energy generation and sustainable development. *Renewable and Sustainable Energy Reviews*. 2006;10:539-58.
- [26] Iannucci JJ, Cibulka L, Eyer J, Pupp R. DER Benefits Analysis Studies: Final Report: National Renewable Energy Laboratory; 2003.
- [27] Xu J, Sui J, Li B, Yang M. Research, development and the prospect of combined cooling, heating, and power systems. *Energy*. 2010;35:4361-7.
- [28] Chicco G, Mancarella P. Distributed multi-generation: A comprehensive view. *Renewable and Sustainable Energy Reviews*. 2009;13:535-51.
- [29] Yu Z, Han J, Cao X, Chen W, Zhang B. Analysis of total energy system based on solid oxide fuel cell for combined cooling and power applications. *International Journal of Hydrogen Energy*. 2010;35:2703-7.
- [30] Wu DW, Wang RZ. Combined cooling, heating and power: A review. *Progress in Energy and Combustion Science*. 2006;32:459-95.
- [31] Giraud F, Salameh ZM. Steady-state performance of a grid-connected rooftop hybrid wind-photovoltaic power system with battery storage. *IEEE Transactions on Energy Conversion*. 2001;16:1-7.
- [32] Williams MC. Fuel cell handbook. US Department of Energy, Morgantown. 2000.
- [33] O'Hayre RP, Cha S-W, Colella W, Prinz FB. Fuel cell fundamentals: John Wiley & Sons New York; 2006.
- [34] Hoogers G. Fuel cell technology handbook: CRC press; 2002.
- [35] Larminie J, Dicks A, McDonald MS. Fuel cell systems explained: Wiley New York; 2003.
- [36] Steele BC, Heinzl A. Materials for fuel-cell technologies. *Nature*. 2001;414:345-52.
- [37] Hoogers G. Fuel cell technology handbook. Boca Raton, Fla.: CRC Press; 2003.

-
- [38] Chinda P, Wechsato W, Chanchaona S, Brault P. Microscale Modeling of an Anode - Supported Planar Solid Oxide Fuel Cell. *Fuel Cells*. 2011;11:184-99.
- [39] Minh NQ. Ceramic fuel cells. *J Am Ceram Soc*. 1993;76:563-88.
- [40] Kendall K, Kendall M. High-temperature solid oxide fuel cells for the 21st century : fundamentals, design and applications. London: Academic Press is an imprint of Elsevier,; 2016. p. 1 online resource (xii, 508 pages).
- [41] Brandon NP, Skinner S, Steele BCH. Recent advances in materials for fuel cells. *Annu Rev Mater Res*. 2003;33:183-213.
- [42] Steele* BCH. Materials for IT-SOFC stacks: 35 years R&D: the inevitability of gradualness? *Solid State Ionics*. 2000;134:3-20.
- [43] Veyo SE, Shockling LA, Dederer JT, Gillett JE, Lundberg WL. Tubular solid oxide fuel cell/gas turbine hybrid cycle power systems: Status. *J Eng Gas Turb Power*. 2002;124:845-9.
- [44] Larminie J, Dicks A. Fuel cell systems explained. 2nd ed. Chichester, West Sussex: J. Wiley; 2003.
- [45] Huang K, Goodenough JB. Solid oxide fuel cell technology: principles, performance and operations: Elsevier; 2009.
- [46] American Ceramic Society. Progress in solid oxide fuel cells. Hoboken, N.J.: Wiley-Interscience; 2006.
- [47] Singhal SC, Kendall K. High temperature solid oxide fuel cells : fundamentals, design, and applications. Oxford ; New York: Elsevier; 2003.
- [48] Vielstich W, Lamm A, Gasteiger HA. Handbook of fuel cells : fundamentals, technology, and applications. Chichester, England ; New York: Wiley; 2003.
- [49] Skyllas-Kazacos M, Chakrabarti MH, Hajimolana SA, Mjalli FS, Saleem M. Progress in Flow Battery Research and Development. *Journal of the Electrochemical Society*. 2011;158:R55-R79.
- [50] Wang W, Luo QT, Li B, Wei XL, Li LY, Yang ZG. Recent Progress in Redox Flow Battery Research and Development. *Advanced Functional Materials*. 2013;23:970-86.

-
- [51] Skyllas-Kazacos M, Kazacos M. State of charge monitoring methods for vanadium redox flow battery control. *Journal of Power Sources*. 2011;196:8822-7.
- [52] Li W, Liu J, Yan C. Multi-walled carbon nanotubes used as an electrode reaction catalyst for VO_2^+ for a vanadium redox flow battery. *Carbon*. 2011;49:3463-70.
- [53] Xi J, Wu Z, Qiu X, Chen L. Nafion/SiO₂ hybrid membrane for vanadium redox flow battery. *Journal of Power Sources*. 2007;166:531-6.
- [54] Li S, Huang K, Liu S, Fang D, Wu X, Lu D, et al. Effect of organic additives on positive electrolyte for vanadium redox battery. *Electrochimica Acta*. 2011;56:5483-7.
- [55] Badrinarayanan R, Zhao J, Tseng KJ, Skyllas-Kazacos M. Extended dynamic model for ion diffusion in all-vanadium redox flow battery including the effects of temperature and bulk electrolyte transfer. *J Power Sources*. 2014;270:576-86.
- [56] Mohammadi T, Kazacos MS. Modification of anion-exchange membranes for vanadium redox flow battery applications. *Journal of Power Sources*. 1996;63:179-86.
- [57] Tang A, Bao J, Skyllas-Kazacos M. Dynamic modelling of the effects of ion diffusion and side reactions on the capacity loss for vanadium redox flow battery. *Journal of Power Sources*. 2011;196:10737-47.
- [58] Sum E, Rychcik M, Skyllas-Kazacos M. Investigation of the V (V)/V (IV) system for use in the positive half-cell of a redox battery. *Journal of Power sources*. 1985;16:85-95.
- [59] De Leon CP, Frias-Ferrer A, González-García J, Szánto D, Walsh FC. Redox flow cells for energy conversion. *Journal of Power Sources*. 2006;160:716-32.
- [60] Li XF, Zhang HM, Mai ZS, Zhang HZ, Vankelecom I. Ion exchange membranes for vanadium redox flow battery (VRB) applications. *Energy & Environmental Science*. 2011;4:1147-60.
- [61] Calise F, d'Accadia MD, Palombo A, Vanoli L. Simulation and exergy analysis of a hybrid solid oxide fuel cell (SOFC)–gas turbine system. *Energy*. 2006;31:3278-99.
- [62] Bharadwaj A, Archer D, Rubin E. Modeling the performance of flattened tubular solid oxide fuel cell. *Journal of Fuel Cell Science and Technology*. 2005;2:52-9.

-
- [63] Campanari S, Iora P. Definition and sensitivity analysis of a finite volume SOFC model for a tubular cell geometry. *Journal of Power Sources*. 2004;132:113-26.
- [64] Cheddie DF, Munroe ND. A dynamic 1D model of a solid oxide fuel cell for real time simulation. *Journal of Power Sources*. 2007;171:634-43.
- [65] Ni M, Leung MK, Leung DY. Parametric study of solid oxide fuel cell performance. *Energy Conversion and Management*. 2007;48:1525-35.
- [66] Nehrir MH, Wang C. Modeling and control of fuel cells: distributed generation applications: John Wiley & Sons; 2009.
- [67] Suwanwarangkul R, Croiset E, Fowler M, Douglas P, Entchev E, Douglas M. Performance comparison of Fick's, dusty-gas and Stefan–Maxwell models to predict the concentration overpotential of a SOFC anode. *Journal of Power Sources*. 2003;122:9-18.
- [68] Li P, Kotwal A, Sepulveda J, Loutfy R, Chang S. An easy-to-approach and comprehensive model for planar type SOFCs. *International Journal of hydrogen energy*. 2009;34:6393-406.
- [69] Chan S, Khor K, Xia Z. A complete polarization model of a solid oxide fuel cell and its sensitivity to the change of cell component thickness. *Journal of Power Sources*. 2001;93:130-40.
- [70] Noren D, Hoffman M. Clarifying the Butler–Volmer equation and related approximations for calculating activation losses in solid oxide fuel cell models. *Journal of Power Sources*. 2005;152:175-81.
- [71] Chan S, Ho H, Tian Y. Modelling of simple hybrid solid oxide fuel cell and gas turbine power plant. *Journal of Power Sources*. 2002;109:111-20.
- [72] Chan S, Low C, Ding O. Energy and exergy analysis of simple solid-oxide fuel-cell power systems. *Journal of Power Sources*. 2002;103:188-200.
- [73] Aguiar P, Adjiman CS, Brandon NP. Anode-supported intermediate temperature direct internal reforming solid oxide fuel cell. I: model-based steady-state performance. *Journal of Power Sources*. 2004;138:120-36.
- [74] Aguiar P, Adjiman CS, Brandon NP. Anode-supported intermediate-temperature direct internal reforming solid oxide fuel cell - II. Model-based dynamic performance and control. *Journal of Power Sources*. 2005;147:136-47.

-
- [75] Aguiar P, Adjiman CS, Brandon NP. Anode-supported intermediate-temperature direct internal reforming solid oxide fuel cell: II. Model-based dynamic performance and control. *Journal of Power Sources*. 2005;147:136-47.
- [76] Aguiar P, Adjiman CS, Brandon NP. Anode-supported intermediate temperature direct internal reforming solid oxide fuel cell. I: model-based steady-state performance. *Journal of Power Sources*. 2004;138:120-36.
- [77] Chan S, Ho H, Tian Y. Modelling for part-load operation of solid oxide fuel cell–gas turbine hybrid power plant. *Journal of Power Sources*. 2003;114:213-27.
- [78] Zhang X, Chan S, Li G, Ho H, Li J, Feng Z. A review of integration strategies for solid oxide fuel cells. *Journal of Power Sources*. 2010;195:685-702.
- [79] Facchinetti E, Favrat D, Marechal F. Design and Optimization of an Innovative Solid Oxide Fuel Cell–Gas Turbine Hybrid Cycle for Small Scale Distributed Generation. *Fuel Cells*. 2014;14:595-606.
- [80] Mehrpooya M, Akbarpour S, Vatani A, Rosen MA. Modeling and optimum design of hybrid solid oxide fuel cell-gas turbine power plants. *International Journal of Hydrogen Energy*. 2014;39:21196-214.
- [81] Eveloy V. Numerical analysis of an internal methane reforming solid oxide fuel cell with fuel recycling. *Applied Energy*. 2012;93:107-15.
- [82] Yan M, Zeng M, Chen Q, Wang Q. Numerical study on carbon deposition of SOFC with unsteady state variation of porosity. *Applied Energy*. 2012;97:754-62.
- [83] Tuo H. Energy and exergy - based working fluid selection for organic Rankine cycle recovering waste heat from high temperature solid oxide fuel cell and gas turbine hybrid systems. *International Journal of Energy Research*. 2013;37:1831-41.
- [84] Komatsu Y, Brus G, Kimijima S, Szmyd J. The effect of overpotentials on the transient response of the 300W SOFC cell stack voltage. *Applied Energy*. 2014;115:352-9.
- [85] Razbani O, Wærnhus I, Assadi M. Experimental investigation of temperature distribution over a planar solid oxide fuel cell. *Applied Energy*. 2013;105:155-60.
- [86] Bao C, Cai N, Croiset E. A multi-level simulation platform of natural gas internal reforming solid oxide fuel cell–gas turbine hybrid generation system–Part II. Balancing

units model library and system simulation. *Journal of Power Sources*. 2011;196:8424-34.

[87] Calise F, Palombo A, Vanoli L. Design and partial load exergy analysis of hybrid SOFC–GT power plant. *Journal of Power Sources*. 2006;158:225-44.

[88] Costamagna P, Magistri L, Massardo A. Design and part-load performance of a hybrid system based on a solid oxide fuel cell reactor and a micro gas turbine. *Journal of Power Sources*. 2001;96:352-68.

[89] Kulikovskiy A. A simple equation for temperature gradient in a planar SOFC stack. *International journal of hydrogen energy*. 2010;35:308-12.

[90] Hanson FV. Heat exchangers selection, design and construction: by EAD Saunders, Longman Scientific and Technical, Essex, England, 1988, ISBN 0-47020870-8, pp. 568, price: US \$99.95 (co-published in the United States with John Wiley & Sons, Inc., New York). Elsevier; 1989.

[91] Shigematsu T. Redox flow battery for energy storage. SEI technical review. 2011;73:5-13.

[92] Skyllas-Kazacos M, Rychcik M, Robins RG, Fane A, Green M. New all-vanadium redox flow cell. *J Electrochem Soc*;(United States). 1986;133.

[93] Skyllas-Kazacos M, Chakrabarti M, Hajimolana S, Mjalli F, Saleem M. Progress in flow battery research and development. *Journal of the Electrochemical Society*. 2011;158:R55-R79.

[94] Wang W, Luo Q, Li B, Wei X, Li L, Yang Z. Recent progress in redox flow battery research and development. *Advanced Functional Materials*. 2013;23:970-86.

[95] Schwenzer B, Zhang J, Kim S, Li L, Liu J, Yang Z. Membrane development for vanadium redox flow batteries. *ChemSusChem*. 2011;4:1388-406.

[96] Al-Fetlawi H, Shah A, Walsh F. Non-isothermal modelling of the all-vanadium redox flow battery. *Electrochimica Acta*. 2009;55:78-89.

[97] Shah A, Watt-Smith M, Walsh F. A dynamic performance model for redox-flow batteries involving soluble species. *Electrochimica Acta*. 2008;53:8087-100.

-
- [98] Chidambaram I, Paramasivam B. Control performance standards based load-frequency controller considering redox flow batteries coordinate with interline power flow controller. *Journal of Power Sources*. 2012;219:292-304.
- [99] Shibata A, Sato K. Development of vanadium redox flow battery for electricity storage. *Power Engineering Journal*. 1999;13:130-5.
- [100] Blanc C, Rufer A. Multiphysics and energetic modeling of a vanadium redox flow battery. *Sustainable Energy Technologies, 2008 ICSET 2008 IEEE International Conference on: IEEE; 2008*. p. 696-701.
- [101] Kim S, Thomsen E, Xia G, Nie Z, Bao J, Recknagle K, et al. 1 kW/1 kWh advanced vanadium redox flow battery utilizing mixed acid electrolytes. *Journal of Power Sources*. 2013;237:300-9.
- [102] Mohamed M, Ahmad H, Seman MA, Razali S, Najib M. Electrical circuit model of a vanadium redox flow battery using extended Kalman filter. *Journal of Power Sources*. 2013;239:284-93.
- [103] Xiong B, Zhao J, Wei Z, Skyllas-Kazacos M. Extended Kalman filter method for state of charge estimation of vanadium redox flow battery using thermal-dependent electrical model. *Journal of Power Sources*. 2014;262:50-61.
- [104] Corcuera S, Skyllas-Kazacos M. State-of-charge monitoring and electrolyte rebalancing methods for the vanadium redox flow battery. *European Chemical Bulletin*. 2012;1:511-9.
- [105] Schaeffer JA, Chen L-D, Seaba JP. Shunt current calculation of fuel cell stack using Simulink®. *Journal of Power Sources*. 2008;182:599-602.
- [106] White RE, Walton C, Burney H, Beaver R. Predicting shunt currents in stacks of bipolar plate cells. *Journal of the Electrochemical Society*. 1986;133:485-92.
- [107] Tang A, McCann J, Bao J, Skyllas-Kazacos M. Investigation of the effect of shunt current on battery efficiency and stack temperature in vanadium redox flow battery. *Journal of Power Sources*. 2013;242:349-56.
- [108] Kim S, Yan J, Schwenzer B, Zhang J, Li L, Liu J, et al. Cycling performance and efficiency of sulfonated poly (sulfone) membranes in vanadium redox flow batteries. *Electrochemistry Communications*. 2010;12:1650-3.

-
- [109] Badrinarayanan R, Zhao J, Tseng K, Skyllas-Kazacos M. Extended dynamic model for ion diffusion in all-vanadium redox flow battery including the effects of temperature and bulk electrolyte transfer. *Journal of Power Sources*. 2014;270:576-86.
- [110] Li X, Zhang H, Mai Z, Zhang H, Vankelecom I. Ion exchange membranes for vanadium redox flow battery (VRB) applications. *Energy & Environmental Science*. 2011;4:1147-60.
- [111] Ontiveros LJ, Mercado PE. Modeling of a Vanadium Redox Flow Battery for power system dynamic studies. *International Journal of Hydrogen Energy*. 2014;39:8720-7.
- [112] Baccino F, Marinelli M, Nørgård P, Silvestro F. Experimental testing procedures and dynamic model validation for vanadium redox flow battery storage system. *Journal of Power Sources*. 2014;254:277-86.
- [113] Xiong B, Zhao J, Tseng KJ, Skyllas-Kazacos M, Lim TM, Zhang Y. Thermal hydraulic behavior and efficiency analysis of an all-vanadium redox flow battery. *Journal of Power Sources*. 2013;242:314-24.
- [114] Li L, Kim S, Wang W, Vijayakumar M, Nie Z, Chen B, et al. A Stable Vanadium Redox - Flow Battery with High Energy Density for Large - Scale Energy Storage. *Advanced Energy Materials*. 2011;1:394-400.
- [115] Ma X, Zhang H, Sun C, Zou Y, Zhang T. An optimal strategy of electrolyte flow rate for vanadium redox flow battery. *Journal of power sources*. 2012;203:153-8.
- [116] Tang A, Bao J, Skyllas-Kazacos M. Studies on pressure losses and flow rate optimization in vanadium redox flow battery. *Journal of power sources*. 2014;248:154-62.
- [117] IE A. *Energy Technology at the cutting edge*. France: international energy technology collaboration IEA implementing agreements. 2005.
- [118] Onovwiona H, Ugursal V. Residential cogeneration systems: review of the current technology. *Renewable and sustainable energy reviews*. 2006;10:389-431.
- [119] Rogers E. *Understanding boost power stages in switchmode power supplies*. Texas Instrument Application Reports. 1999.

-
- [120] Erdinc O, Vural B, Uzunoglu M. A wavelet-fuzzy logic based energy management strategy for a fuel cell/battery/ultra-capacitor hybrid vehicular power system. *Journal of Power sources*. 2009;194:369-80.
- [121] Ferreira A, Pomilio JA, Spiazzi G, de Araujo Silva L. Energy management fuzzy logic supervisory for electric vehicle power supplies system. *Power Electronics, IEEE Transactions on*. 2008;23:107-15.
- [122] Zhao P, Zhang H, Zhou H, Chen J, Gao S, Yi B. Characteristics and performance of 10kW class all-vanadium redox-flow battery stack. *Journal of Power Sources*. 2006;162:1416-20.