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Improving the Thermal Stability of Nanoporous Metal Electrode Thin Films for Low Temperature Solid Oxide Fuel Cells

Presented by

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Contents

List of Figures.....	I
List of Tables	V
Abstract.....	VI
Chapter 1	1
1. Introduction.....	1
1.1. Overview	1
1.2. Research Motivation and Objectives.....	2
1.3. Thesis Outline	4
Chapter 2	5
2. Literature Reviews.....	5
2.1 Introduction	5
2.2 Principle of fuel cells.....	8
2.3 Electrochemistry of fuel cells.....	11
2.4 Solid Oxide Fuel Cells	15
2.5 Low-Temperature Solid Oxide Fuel Cells	16
2.5.1 Fabrication	18

2.5.2	Materials	21
2.5.3	System integration	21
2.5.4	Electrode of low-temperature solid oxide fuel cells	23
2.5.5	Thermal stability of metal electrode	26
2.5.6	Oxygen reduction reaction of metal electrode in LTSOFCs	35
Chapter 3		39
3.	Thermal Stability and Performance Enhancement of Nanoporous Platinum Cathode by Nanoscale ZrO₂ Capping	39
3.1	Introduction	39
3.2	Experiment	41
3.2.1	ZrO ₂ capping on nanoporous platinum	41
3.2.2	Thermal stability and cathode performance characterization	41
3.3	Results and Discussion.....	42
3.3.1	Morphological observation	42
3.3.2	Morphological stability under high temperature annealing	45
3.3.3	ORR enhancement of ALD-ZrO ₂ capping.....	46
3.3.4	Performance Stability with Time	52

3.4	Chapter Summary.....	53
Chapter 4		54
4. Thermal Stability Enhancement of Nanoporous Cathode by PtNi Alloying		54
4.1	Introduction	54
4.2	Experimental	59
4.3	Results and Discussion.....	60
4.3.1	Composition and crystallinity of as-deposited nanoporous films.....	60
4.3.2	Morphological stability of nanoporous films at high temperature.....	62
4.3.3	Evolution of crystal structure and grain size in annealed films	64
4.3.4	Fuel cell performance of PtNi thin film cathode	67
4.4	Chapter summary	70
Chapter 5		71
5. Thermal Stability Enhancement of Nanoporous Platinum Cathode by O₂ Plasma Etching		71
5.1	Introduction	71
5.2	Experimental	73
5.3	Results and Discussion.....	75

5.3.1	Effect of improved Pt cathode/electrolyte adhesion	75
5.3.2	Direct morphology observation on Pt/YSZ interface	78
5.3.3	Fuel cell stability and cathode performance by O ₂ plasma etching	80
5.4	Chapter summary	82
Chapter 6		83
6. Nanoporous Metal Thin Film Cathode with Superior Thermal Stability for Low-Temperature Solid Oxide Fuel Cells		83
6.1	Introduction	83
6.2	Experimental	84
6.3	Results and discussion.....	86
6.4	Chapter summary	89
Chapter 7		90
7. Conclusions and Future works		90
7.1	Conclusions and Contributions	90
7.2	Suggested future work.....	93
Appendix A		96
Nanoporous SnO₂ Anode for Direct Ethanol Low- Temperature Solid Oxide Fuel Cells ...		96

A.1	Introduction	96
A.2	Experimental	98
A.2.1	SnO ₂ thin film preparation	98
A.2.2	Material Characterization.....	98
A.2.3	Direct ethanol LTSOFCs testing.....	99
A.3	Results and discussion.....	99
A.3.1	Surface morphology of as-deposited SnO ₂ thin film	99
A.3.2	Composition and Crystal structure of as-sputtered SnO ₂ thin film.....	101
A.3.3	Electrical conductivity of SnO ₂ thin film.....	103
A.3.4	Fuel cell performance by direct ethanol vapor fuel	104
A.4	Chapter Summary.....	106
	Bibliography	107
	Publication list.....	119

List of Figures

Figure 1.1 Proposed strategies to enhance thermal stability of nanoporous Pt	3
Figure 2.1 Schematic of fuel cell basic structure	9
Figure 2.2 Type of fuel cell and the corresponding electrochemical reactions	10
Figure 2.3 A typical polarization curve of fuel cell	12
Figure 2.4 A typical fuel cell output with the dominant losses against current density	14
Figure 2.5 (a) Typical I-V curve of PEMFC; (b) Typical I-V curve of SOFC	14
Figure 2.6 Schematic of SOFC with (a) O ₂ -ion and (b) Proton conducting electrolyte	16
Figure 2.7 FESEM cross section view of (a) conventional SOFCs and (b) micro-SOFCs with a dense electrolyte sandwiched between two porous electrodes	17
Figure 2.8 Schematic of self-limiting process in atomic layer deposition technique	19
Figure 2.9 Sketch of sputtering technique for thin film deposition	20
Figure 2.10 Sketch of the (a) planar -type μ -SOFCs; and (b) cube-type μ -SOFCs	22
Figure 2.11 Investigation of metal electrocatalysts; (a) activity versus binding energy; (b) exchange current density of hydrogen oxidation; (c) exchange current density of oxidation reduction	25
Figure 2.12 Typical nanoporous Pt morphology fabricated by RF sputtering.....	26
Figure 2.13 Nanoporous Pt cathode morphology before and after fuel cell operation at high temperature of 500 and 450 °C	28
Figure 2.14 Schematic of (a) coalescence and (b) Ostwald ripening.....	30
Figure 2.15 The Pt/YSZ/O ₂ : interfaces and factors controlling the electrochemical behavior....	31
Figure 2.16 High-resolution SEM images of as-sputtered Pt electrode at (a) fresh and (b) 450 °C fuel cell operation; and nanostructure Pt at (c) fresh and (d) 500 °C fuel cell operation	32
Figure 2.17 Sketch and top-view images of Pt films (a) without and (b) with a nanoscale YSZ coating before and after an annealing process at 500 °C.....	33
Figure 2.18 Schematic of reaction pathways on solid electrodes:(a) Electrode Surface path;(b) Electrolyte surface path;(c) Bulk path with reaction at the electrode surface; (d) Bulk path with reaction at the electrode/electrolyte interface.....	36

Figure 2.19 Schematic of faradaic pathway of ORR on Pt electrodes:(a) Electrode surface path; (b) Through a foreign phase;(c) Electrolyte surface path.....	36
Figure 2.20 Schematic of the hetero-interfaces incorporated oxygen reduction	37
Figure 2.21 Schematic of the cathode reaction with different material:(a) Electrode; (b) Electro-oxygen ion mixed conductor; (c) Electro-proton mixed conductor; (d) Composites composed with electro-oxygen ion mixed conductor and electro-proton mixed conductor.....	38
Figure 3.1 Sketch of (a) as-deposited Pt and (b) ALD-ZrO ₂ capped Pt electrode.....	41
Figure 3.2 Morphology of as-deposited 10 cycles ALD-ZrO ₂ capped nanoporous Pt in terms of (a) surface top view, (b) and (c) cross-section view and (d) nanoparticles within the film.	43
Figure 3.3 (a) FESEM and (b) HRTEM of as-deposited nanoporous Pt electrode with uncapped, 10-, 15, 30- and 60- cycles ALD-ZrO ₂ capping.	44
Figure 3.4 (a) Sketch and (b) FESEM of as-deposited dense Pt electrode with uncapped, 10-, 15, 30- and 60- cycles ALD-ZrO ₂ capping.....	45
Figure 3.5 FESEM images of uncapped (a~c), 10-cycle (d~f) and 60-cycle (g~i) ZrO ₂ -capped Pt electrodes on YSZ substrate before/after annealing.....	46
Figure 3.6 (a) IV curves the Pt cathodes with 0, 10, 15, 30, 60 cycles ZrO ₂ capping at 450 °C (b) Nyquist plot and; (c) Bode plots of the platinum cathodes with 0, 10, 15, 30, 60 cycles ZrO ₂ capping at 0.9V and 450 °C	49
Figure 3.7 (a) Nyquist plot and; (b) Bode plots of the uncapped cell and 10 cycles ALD-ZrO ₂ capped cell under 4, 20, 50, and 100 % oxygen partial pressure at 450 °C	51
Figure 3.8 Current output with time of fuel cells using uncapped and 10-cycle ALD-ZrO ₂ capped Pt cathodes. The inserts are cathode morphologies after test.	53
Figure 4.1 (a) Average (111) grain size of pure Pt and 10 cycles ALD-ZrO ₂ capped Pt thin film at elevated annealing temperatures, and the XRD patterns were shown in (b) pure Pt and (c) ALD-ZrO ₂ capped Pt.	58
Figure 4.2 Sketch of as-deposited Pt and PtNi alloy electrode	59
Figure 4.3 (a) EDX and (b) XRD patterns of the as-deposited nanoporous Pt, Pt ₈₈ Ni ₁₂ , Pt ₇₅ Ni ₂₅ , and Pt ₆₇ Ni ₃₃ films	61

Figure 4.4 FESEM images of (a) pure Pt, (b) Pt ₈₈ Ni ₁₂ , (c) Pt ₇₅ Ni ₂₅ , and (d) Pt ₆₇ Ni ₃₃ as-deposited and annealed at 450, 600 and 800 °C for 12 hours.....	63
Figure 4.5 (a) XRD pattern of pure Pt, and (b) Average (111) grain size of pure Pt, Pt ₈₈ Ni ₁₂ , Pt ₇₅ Ni ₂₅ and Pt ₆₇ Ni ₃₃ thin films at elevated annealing temperatures; (c) activation energy of grain growth at elevated annealing temperatures.....	66
Figure 4.6 (a) I-V curves of the cell using Pt and Pt ₆₇ Ni ₃₃ cathodes tested at 0 and 48 hours; and microscopy images for Pt and Pt ₆₇ Ni ₃₃ cathode after 48 hours fuel cell test at 450 °C; (b) Nyquist plots; and (c) Bode plots of the cell using Pt and Pt ₆₇ Ni ₃₃ cathode at 0 and 48 hours.....	69
Figure 5.1 FESEM images of ALD-ZrO ₂ capped nanoporous Pt thin films before and after annealing at 600 °C for 12 hours in the view of top surface and cross-section view.....	73
Figure 5.2 Sketch of nanoporous Pt electrode on (a) un-etched and (b) etched YSZ substrate ..	74
Figure 5.3 (a) Microscopy of static contact angle by water droplet on pristine and 1, 3 and 5 minutes O ₂ plasma etched YSZ surface; (b) Selected XPS spectra (C _{1s} and O _{1s}) of the pristine and 1 minute-O ₂ plasma etched YSZ electrolyte	76
Figure 5.4 (a) Curve of AFM Pt probe approaching and withdrawing YSZ electrolyte surface illustrating the approach section (a-d) and withdrawal section (d-h) where jump-to-contact (b-c) and jump-off-contact (f-g) occur. (b) Adhesion force between Pt electrode and YSZ surface	78
Figure 5.5 FESEM of nanoporous Pt viewed from the electrolyte contact interface on the cell with YSZ electrolyte surface un-etched and etched with 1 minute of O ₂ plasma, before and after annealing at 600 °C.	79
Figure 5.6 (a) Current output over time and (b) Nyquist plots of 10 cycles ALD-ZrO ₂ capped nanoporous Pt cathode on the cell with YSZ electrolyte surface un-etched and etched with 1 minute of O ₂ plasma.	81
Figure 6.1 (a) Sketch of sputtered nanoporous Pt cathode; (b) Sketch of metal cathode combine with approaches of O ₂ plasma etching on the YSZ interface, the interior PtNi alloy, and ALD-ZrO ₂ capped surface.	84
Figure 6.2 Flowchart of fuel cell fabrication	85
Figure 6.3 (a) Evaluation of the cell current density and (b) Normalized cell current degradation percentage as a function of time.	88

Figure A.1 Fuel cell test station with customized direct ethanol vapor feeding.....	99
Figure A.2 Surface morphology of as-deposited SnO ₂ by RF sputtering by controlling (a) process pressure and (b) process temperature.	101
Figure A.3 (a) XPS spectra, and (b) XRD pattern of as-sputtered SnO ₂ thin film.	102
Figure A.4 Electrical conductivity of sputtering SnO ₂ thin film at elevated temperatures	104
Figure A.5 Ethanol feeding Fuel cell performance test at 500 °C with SnO ₂ thin film anode via (a) OCV, (b) I-V curves and (c) impedance analysis	105

List of Tables

Table 2.1 Description of major fuel cell types.....	7
Table 2.2 Type of fuel cells by different operating condition and suitable application	7
Table 2.3 Performance degradation of LTSOFCs using nanoporous Pt cathode	28

Abstract

Solid oxide fuel cells (SOFCs) are promising electrochemical devices for the production of electricity due to their high conversion efficiency, environmental friendly and fuel flexibility. Nevertheless, high operating temperature between 750-1000 °C provokes challenges of thermal management and material selection and limits their utility to large and stationary application. Thus lowering the operating temperature of SOFCs to intermediate temperature (500-750 °C) range or even below would greatly expand SOFCs technology to wider applications. Recent studies have shifted their focus to low-temperature solid oxide fuel cells (LTSOFCs) operating at temperatures below 500 °C. Utilizing nanoporous metal electrodes have been widely studied to replace ceramic electrode which is low electrocatalytically-active at such a low operation temperature.

Platinum (Pt) is usually the most common choice as the cathode material for its superior catalytic activity towards oxygen reduction reaction (ORR) at a temperature lower than 500 °C. Typically a nanoporous Pt thin film cathode is often fabricated by sputtering at a high argon gas pressure to generate a high density of nanoscale pores or crack within the film to maximize the electrochemically active reaction sites, or the triple phase boundary (TPBs), where the gaseous fuel, catalytic electrode, and ion conductive electrolyte are in physical contact. The high density of reaction sites allows a high energy conversion rate with low electrode polarization, promising a high power output of the fuel cell. It has been reported that nanoporous Pt cathode can yield a high performance of 1.3 W/cm² at 450 °C, an ultra-low operating temperature of 265 °C achieved 28 mW/cm², and an ultra-low Pt loading of 0.02 mg/cm² for potential applications. One key issue of using nanoporous Pt cathode for LTSOFCs is its poor thermal stability under high

temperature operation. While the high density of nanopores or nanocracks can maximize the electrochemical active sites, the nanoscale feature is easily subjected to thermally-driven agglomeration to low surface free energy as per thermodynamic stability, which inevitably resulted in a rapid loss of the effective surface area and hence lowering fuel cell current output. The thermal agglomeration of a sputtered nanoporous Pt film is reported to initiate at around 300 °C, which is below the typical operating temperature of LTSOFCs between 350 to 500 °C. The irreversible deterioration to fuel cell performance due to thermal agglomeration of pure Pt cathode was reported by approximately 50% at 400 °C for 12 continuous hours of testing, which impedes the development of durable LTSOFCs. The preliminary study in this work also found 86.2% performance loss at 450 °C for 75 continuous hours of operation, and agglomeration occurred at the various site of the nanoporous Pt thin film cathode, including the unbounded surface, the bulk of the thin film, and cathode/electrolyte interface. The present work is dedicated to achieving a thermally stable nanoporous metal cathode with low performance degradation rate for LTSOFCs operating at a temperature of 300-500 °C, and addressing the improved thermal stability in terms of different agglomeration sites of nanoporous Pt cathode.

Firstly, this work applied only few nanometers thin zirconia (ZrO_2) capping on nanoporous Pt surface by atomic layer deposition (ALD) to serve as a geometrical confinement against thermal agglomeration, while an unexpected decrease in cathode polarization resistance was also observed. The thermal stability of the confined nanoporous Pt cathode and the origin of the enhanced cathode ORR were discussed.

Secondly, the effectiveness of Ni alloyed Pt on hindering thermal agglomeration in bulk of nanoporous Pt thin film cathode was examined. The grain growth, which indicates the agglomeration of the Pt nanoparticles in bulk of thin film at elevated temperatures were

compared between PtNi alloy and pure Pt metal to determine the impact of alloying on the thermal stability of the cathode. The performance of fuel cell and the electrochemical behavior using PtNi alloy cathode were also examined.

Thirdly, a high energy O₂ plasma etching technique was applied on the interface of Pt cathode/electrolyte to impede the thermal agglomeration of Pt at electrolyte contact side, where typically shows loss of TPBs from poor adhesion between Pt cathode and YSZ electrolyte. The morphological observation and adhesion measurement at cathode/electrolyte interface were investigated to elucidate the cause of O₂ plasma etching to improved thermal stability. The fuel cell performance and cathode electrochemical performance over time were also examined.

Lastly, three proposed methods were combined and strategized to obtain a highly thermal stable nanoporous metal cathode. Overall current stability of the cell with ALD-ZrO₂ capped PtNi alloy cathode on O₂ plasma etched electrolyte shows an ultra-low current degradation of 9.8% over 100 hours continuous operation at 450 °C. The proposed strategies ensured favorable nanoporous morphology of the film surface, constrained grain growth in bulk of film, and better contact of cathode to electrolyte at high temperature. The origin of improved thermal stability in terms of different agglomeration sites of nanoporous Pt cathode was: 1.) ALD-ZrO₂ capping confines the surface agglomeration of the nanoporous Pt cathode and meanwhile facilitates the surface O₂ adsorption-dissociation process; 2.) Ni alloyed Pt thin films constrains grain growth and maintains the porosity in bulk of cathode film for sufficient oxygen diffusion and adsorption-dissociation process; 3.) O₂ plasma etching technique inhibits thermal agglomeration of Pt at YSZ electrolyte contact side and strengthens adhesion between Pt and YSZ which sufficiently retain the oxygen ion incorporation pathway.

Chapter 1

1. Introduction

1.1. Overview

This thesis mainly discusses the development of low-temperature solid oxide fuel cells (LTSOFCs) with an emphasis on improving the thermal stability of nanoporous metal cathode thin film at an operating temperature less than 500 °C. The LTSOFCs with high fuel cell performance and low degradation rate were achieved by nanoscale thin film engineerings. The causes of the enhanced cathode oxygen reduction reaction and improved thermal stability are elucidated by performance test and impedance analysis.

The main contributions of this thesis are: (1) demonstrates a high fuel cell performance and ultra-low degradation LTSOFCs using nanoporous metal cathode; (2) substantiate the effectiveness of proposed strategies toward improved thermal stability and enhanced cathode oxygen reduction reaction at different agglomeration site of nanoporous Pt cathode; (3) provide an instruction of designing a thermally stable nanoporous metal cathode for potential applications; (4) elaborates the mechanism of few nanometers ZrO₂ capped Pt facilitates oxygen adsorption/desorption process; (5) quantified the effect of alloying Ni toward the thermally-driven grain growth in bulk of Pt thin film; (6) explains the mechanism of O₂ plasma etching enhances the thermal stability of Pt/YSZ interface.

1.2. Research Motivation and Objectives

Nanoporous Pt cathode for LTSOFCs has demonstrated its great potential for portable power sources owing to advantages of high power density, low operation temperature, low catalyst loading, scalability, etc. However, the irreversible deterioration to fuel cell performance due to thermal agglomeration of nanoporous Pt cathode occurs at a temperature above 300 °C which restricts the development of durable LTSOFCs. The thermal agglomeration behaviors of nanoporous Pt had been reported, but the effective methods for improving its thermal stability have not been studied yet. The United States Department of Energy set up the durability targets for fuel cell as portable power sources in their Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRD&D) Plan that 20 % performance loss within 1,500 hours in 2015 and 20 % performance loss within 5,000 hours as the ultimate target. The present work is dedicated to achieving a thermally stable nanoporous metal cathode with low performance degradation rate less than 0.013% per hour for LTSOFCs operating at a temperature of 300-500 °C. The fabrication strategies towards improved thermal stability in terms of different agglomeration sites of nanoporous Pt cathode were proposed accordingly. This thesis addresses the improved thermal stability in terms of different agglomeration sites of nanoporous Pt cathode. The sketches of different agglomeration sites of the nanoporous Pt electrode, and the corresponding strategies to improve thermal stability were shown in Figure 1.1.

Figure 1.1 Proposed strategies to enhance thermal stability of nanoporous Pt at different agglomeration sites.

1.3. Thesis Outline

The outline of this thesis contains seven chapters:

Chapter 2 provides the theoretical background of fuel cells, including basic operation principles, types of fuel cells, and typical thermal agglomeration mechanisms. The current status of low-temperature SOFCs researchers and techniques were discussed as well.

Chapter 3 demonstrates a nanoscale zirconia layer coated by atomic layer deposition (ALD) with only a few coating cycles on a nanoporous Pt cathode surface to prevent the electrode surface agglomeration and meanwhile to enhance cathode ORR.

Chapter 4 demonstrates a nickel alloyed Pt cathode by RF sputtering to inhibit the agglomeration in bulk of cathode film. The PtNi alloy was found to constrain the grain growth of the electrode and maintain the sufficient gas diffusion pathway for cathode ORR.

Chapter 5 demonstrates an improved interfacial adhesion between Pt cathode and YSZ electrolyte by O₂ plasma etching technique to inhibit Pt agglomeration at YSZ contact interface, strengthen adhesion force at Pt/YSZ interface, and enhance cathode ORR activity.

Chapter 6 combines three methods to apply as a comprehensive fabrication process to obtain a highly thermal stable nanoporous metal cathode with low performance degradation rate for LTSOFCs operating at temperatures lower than 500 °C.

Chapter 7 concludes the research work and contribution of this thesis and provides possible future research direction related to LTSOFCs.

The feasibility of direct utilization of ethanol fuel LTSOFCs using a tin oxide anode for ethanol oxidation reaction at temperatures of 300~500 °C was included in Appendix A.

Chapter 2

2. Literature Reviews

2.1 Introduction

Humans used fossil fuel since the ancient times, and wide-scale extraction occurred since the Industrial Revolution. Humans have consumed an incredible amount of them and caused severely impact on the global climate. As time goes by, humans relied on more and more energy to obtain the requirement for modern life. The limited fossil fuel on earth is running out and will be all gone soon. For the past decades, human always looks for alternative energy sources with a sustainable property, such as sunlight, wind power, hydropower, geothermal heat, and hydrogen energy.

Fuel cells are electrochemical conversion devices which directly convert chemical energy into electricity via the hydrogen oxidation reaction and oxygen reduction reaction, and the by-products of the electricity generation from the fuel cell are water and heat. Fuel cells can continuously convert electricity as long as the fuels are supplied. Fuel cells are much more environmental friendly than other energy devices due to the advantages of no-burning, quiet electricity generation process, and pollution-free, which is considered the most potential alternative clean energy. A zero-emission source of electricity can be realized by fuel cell system while the supplied fuel is produced from the non-polluting process. Fuel cells come in different types which majorly based on material of electrolyte and supplied fuel, and can generally be

classified into three categories: (1) Polymer based electrolyte (e.g. proton exchange membrane); (2) liquid based electrolyte (e.g. alkaline and phosphoric acid) and (3) ceramic based electrolyte (e.g. solid oxide). Table 2.1 showed the major fuel cell types.¹

The high efficiency of energy conversion is also one of the most significant advantages. The efficiency of a fuel cell is generally between 40-60% or up to 85-90%² if waste heat is captured as a combined heat and power system. Compare with other power sources, the efficiency of the internal combustion engine of a car is about 25%,³ solar cell is about 44.7%,⁴ and the wind turbine is about 59%.⁵ Besides, fuel cells can be applied to a wide range of application, including portable devices, stationary power, transportation, and power plant. Different types of fuel cells have corresponding limitation and potential application which was shown in Table 2.2.

Table 2.1 Description of major fuel cell types¹

	PEMFC (Proton Exchange Membrane)	AFC (Alkaline)	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
Electrolyte	Polymeric Ion Exchange Membrane	Potassium Hydroxide Solution	Phosphoric Acid	Molten Mixture of Alkali Metal Carbonates	Perovskites
Electrode	Carbon	Transition Metals	Carbon	Nickel and Nickel Oxide	Perovskite and Perovskite /Metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or Metal	Metal	Graphite	Stainless Steel or Nickel	Nickel, Ceramic, or Steel
Operating Temperature	40-80 °C	65-220 °C	160-220 °C	600-650 °C	600-1000 °C
Charge carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻
Fuel Compatibility	H ₂ , CH ₃ OH	H ₂	H ₂	H ₂ , CH ₄	H ₂ , CH ₄ , CO
Cell component	Carbon-based	Carbon-based	Carbon-based	Stainless- based	Ceramic- based
Water management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product

Table 2.2 Type of fuel cells by different operating condition and suitable application⁶

Fuel cell type	Mobile ion	Operating Temperature	Application and Notes
PEMFC	H ⁺	30-100 °C	Vehicles and mobile applications, and for lower power CHP systems
AFC	OH ⁻	50-200 °C	Space vehicle, e.g. Apollo, Shuttle
DMFC	H ⁺	20-90 °C	Portable electronic system of low power, running for long time
PAFC	H ⁺	~220 °C	Large numbers of 200-kW CHP system
MCFC	CO ₃ ²⁻	~650 °C	Suitable for medium- to large scale CHP systems, up to MW capacity
SOFC	O ²⁻	500-1000 °C	Suitable for all size of CHP systems, 2kW to multi-MW

Among various types of fuel cell, solid oxide fuel cells (SOFCs) provide the possibility of high energy conversion efficiency, a high volumetric and gravimetric energy density as well as the usability of alternative hydrocarbon fuel. Dry hydrocarbon fuels were used to generate electrical power and prevent carbon formation via direct electrochemical oxidation.⁷ Liquid fuels were investigated for the selection of alternative anode.⁸ The main issue of SOFCs lies in its high operating temperature from 750 to 1000 °C which resulting in the limited choice of materials, high operation cost, and difficulties of thermal management. These disadvantages constrain its application to stationary power sources which were studied mostly.⁹ Recently, the demand for portable power sources is constantly growing because of the rapid rise of consumable electronic devices, resulting in the requirement of lower operation temperature for easier system design. Therefore, intermediate temperature SOFCs (ITSOFCs) operating in 500-750 °C and low-temperature SOFCs (LTSOFCs) operating in 300-500 °C (LTSOFCs) have been researched actively with an aim to develop a highly efficient alternative portable power.¹⁰ Less facility and infrastructure requirement make LTSOFCs more approachable than conventional SOFCs for the development of portable power sources.

2.2 Principle of fuel cells

A fuel cell is an electrochemical conversion device which can directly convert the chemical energy of fuel into electricity without combustion. The by-products of the energy conversion are heat and pure water only. In addition, a fuel cell can provide stable power output as long as fuels are supplied continuously. The basic structure of fuel cells comprises one anode, one cathode, and sandwiches with an ionic or proton conductive electrolyte. The anode and cathode electrochemically catalyze the gaseous fuel such as H₂ and hydrocarbons and oxidants such as air and oxygen respectively. The created ions or protons from the electrode reactions pass through

the sandwiched electrolyte, and the electricity can be extracted out for the application. Electrolytes can be proton conductor, or oxide-ion conductor depends on the selection of the material and structure. Figure 2.1 illustrated the basic sandwiched structure of oxygen ion conductor based fuel cell.

Figure 2.1 Schematic of fuel cell basic structure¹¹

The overall reaction of oxygen ion conductor based fuel cells is

The electrochemical reactions of

A summary of the different type of fuel cells is listed in Figure 2.2 regarding operation temperature,¹ reducing/oxidizing agents, conductive ions and the corresponding electrochemical

reactions. Among them, polymer exchange membrane fuel cell (PEMFCs) and solid oxide fuel cells (SOFCs) attract more attention because solid state type of electrolyte is easier for further fuel cell system integration. PEMFCs can only be applied at a temperature less than 200 °C due to the thermal nature of the polymer based electrolyte. Conversely, the operating temperature of SOFCs is typically higher than 750 °C as the oxide based electrolyte can initiate the ions conduction at such a high temperature. At the same time, the material cost and limitation of the system go up as temperature increases. Hence, there is an increasing interest in exploring the lower temperature applicability of SOFCs to reduce the material cost, improve the system durability and reliability.

Figure 2.2 Type of fuel cell and the corresponding electrochemical reactions¹

2.3 Electrochemistry of fuel cells

The fuel cell open circuit voltage (OCV) is determined by the potential difference between anode and cathode. Nernst equation is related to the reduction potential of a half-cell. It can be given by:

$$\Delta_R G = -nF\Delta U \quad (2.1)$$

Where ΔG is Gibbs free energy, F is Faraday constant; n is the participated electron number

For a half cell reaction, it can be converted into:

$$U_{eq} = U^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \quad (2.2)$$

U_{eq} : Equilibrium potential; U^0 : Standard potential;

R : Ideal gas constant, 8.314 J/(mol K); F : Faraday constant, 96485 C/mol,

n : Number of transferred electrons; a_i : Activity of the species i

For the theoretical OCV value of the ideal H_2/O_2 fuel cells, $2H_2 + O_2 \rightarrow 2H_2O$,

$$\text{Nernst equation is presented as } U = U^0 + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \quad (2.3)$$

Where U is the potential of the full cell; U^0 is the ideal potential; R is ideal gas constant, T is the absolute temperature in Kelvin, F is Faraday's constant, and a is the activity. Referred to the equation, the equilibrium potential is related to the parameters, such as partial pressure, and temperature. The ideal cell potential can be increased by operating at a higher reactant pressures or a lower temperature. When reducing the partial pressure of the products and increase the

partial pressure of the reactants, the overall cell potential will increase. For instance, as the reactant pressures increase, the ideal cell voltage can also increase at a given temperature for the hydrogen reaction.

The electrical property of a fuel cell is usually evaluated by a polarization curve, representing the current density against the applied voltage (I-V curves). A typical polarization curve of fuel cells was shown in Figure 2.3, showing the output voltage of a fuel cell at a given current density.

Figure 2.3 A typical polarization curve of fuel cell

At the lower current density region, activation loss is the major dominator which comes from the intrinsic activity of the electrocatalyst. At the middle region of the current density, ohmic loss dominates mostly, including the kinetic drop and ohmic drop. Ohmic drop can be further divided into electrolyte resistance, electrode resistance, and contact resistance. At the

higher current density region, concentration loss dominated mostly which comes from the mass transport or diffusion of the species. More detail description about three losses in I-V curve was listed below:

Activation losses: reduced electrochemical potential because energy is needed to drive the electrochemical reactions in the desired forward direction, i.e. reduction of oxygen at the cathode and oxidation of fuel gasses (*e.g.*, hydrogen) at the anode.

Ohmic resistance losses: which occur in the solid electrolyte phases due to ions flow and in the electrode phases and metal interconnects due to electrons flow. It is caused by the electrical resistances of the electrodes and resistance of ion transport in the electrolyte. Three general methods of reducing this polarization are the use of high conductivity electrodes, the use of appropriate interconnect materials and design, and the use of thin electrolyte.

Concentration losses: reduced Nernst potential at the electrochemically active reaction zone due to depletion of charge carrying reactants caused by slow diffusion from the bulk of the gas channels through the porous electrodes.

The net fuel cell output is the result of reversible voltage deducts activation loss, ohmic loss and concentration loss. Figure 2.4 showed the corresponding dominant losses against the current density of a typical PEMFC I-V curve, and Figure 2.5 showed the typical I-V curves of PEMFCs and SOFCs.

Figure 2.4 A typical fuel cell output with the dominant losses against current density¹

Figure 2.5 (a) Typical I-V curve of PEMFC; (b) Typical I-V curve of SOFC⁶

2.4 Solid Oxide Fuel Cells

Solid oxide fuel cell is a type of fuel cell in which the electrolyte is a dense layer of ceramic that conducts oxygen ions and limits electronic conductivity. The high operating temperatures of conventional SOFCs, usually 750-1000 °C allow the kinetics of oxygen ion transport to be sufficient for high fuel cell performance. The electrolyte layer should be fully dense and pin-hole free structures to obtain high ion conductivity and avoid electric-shortening. Large ionic transport resistances occurred which affected the fuel cell performance as the operating temperature approaches the lower limit of SOFCs at around 600 °C. There are few popular electrolyte materials widely studied because of the advantages of high oxygen conductivity, high chemical stability, and high operation stability, including Yttria-stabilized Zirconia (YSZ) (often the 8 % form 8YSZ),¹² Scandia stabilized Zirconia (ScSZ) (often 9 % form 9ScSZ), and Gadolinium doped Ceria (GDC). Both cathode and anode require the porous structure to allow fuel of oxidant to flow towards the electrolyte and unobstructed gas feedings. Figure 2.6 illustrate the working principles of SOFCs with different types of conducting electrolytes as (a) an oxygen ion (O^{2-}) conductor and (b) a proton (H^+) conductor. For an oxygen ions-conducting SOFC, oxygen reduction occurs at the cathode to oxygen ions which can transfer through the electrolyte for the fuel oxidation reaction, and water was formed at the anode. Oppositely, in a proton conducting SOFC, protons migrate through the electrolyte from anode to cathode for the reaction of oxygen reduction, and water was formed at the cathode. A fully dense and solid-oxide electrolyte layer is spatially sandwiched between the porous cathode and anode, and electrons are directly released to the external circuit by the electrochemical reaction from fuels.

The electrodes usually have requirements of high electronic conductivity and high electrocatalyst activity as hydrogen oxidation reaction for anode and oxygen reduction reaction

for the cathode. The material used for an electrode of SOFCs is perovskite or perovskite/metal cermet. For example, nickel oxide-YSZ is an anode material for the cell with YSZ electrolyte, and lanthanum strontium manganite is a cathode material for the cell with YSZ because of its compatibility with doped zirconia electrolytes.

Figure 2.6 Schematic of SOFC with (a) Oxygen-ion conducting and (b) Proton conducting electrolyte

2.5 Low-Temperature Solid Oxide Fuel Cells

Large ionic transport resistances occurred and affected the performance as the operating temperature approaches the lower limit of SOFCs at around 600 °C. The resistance of the ceramic based electrolyte increases dramatically as the operating temperature decrease,¹³ which are simply governed by Ohm's law:

$$V = I * R = I * \left(\frac{L}{A\sigma}\right)$$

Where A is the reaction area; L is the length of the ions conductive path, which is the same as electrolyte thickness; σ is the conductivity of the material. V is the voltage, which must be applied to transport a charge at a given current I. The voltage V can represent Ohmic loss.

According to Ohm's law, the electrolyte ionic conductivity is reversely proportional to the electrolyte thickness and positively proportional to the intrinsic material conductivity. Therefore, there are two ways to compensate the low ionic conductivity of the ceramic electrolyte when operating at a low temperature between 300-500 °C, including (1) reduction of the electrolyte thickness from micrometers to nanometers; (2) Introduce of the novel electrolyte with high ionic conductivity. The high fuel cell performance can be obtained using nano engineering technology to fabricate a thin film electrolyte thickness of tens nanometer. This kind of thin LTSOFCs is often referred as micro-SOFCs (μ -SOFCs) or thin film solid oxide fuel cells (TF-SOFCs) because of their miniature size upon conventional SOFCs development. Figure 2.7 showed the thickness image comparison between (a) conventional SOFCs, and (b) micro-SOFCs, which exhibited higher ion conductivity with reduced electrolyte thickness to tens of nanometers. The morphology difference between the dense electrolyte and the porous electrode was also shown in both cases.

Figure 2.7 FESEM cross section view of (a) conventional SOFCs¹⁴ and (b) micro-SOFCs with a dense electrolyte sandwiched between two porous electrodes

2.5.1 Fabrication

Conventional SOFCs usually adopts powder-based fabrication such as spin coating, spray pyrolysis, tape casting, and sol-gel process for the micrometer-thick electrolyte and electrode. Powder-based fabrication has the difficulties to achieve a pinhole-free or defect-free thin film with nanoscale thickness. Fabrication of micro-SOFCs requires the vacuum-based thin film deposition of electrolyte and electrode to obtain controllable morphology and thickness in nanoscale. Ceramic-based electrolyte thin films must be continuous and crack-free to prevent gas leakage and must be sandwiched between two electrodes. The electrode thin film must be a nanoporous through which gaseous fuels and oxidants can pass freely to or away from the active sites for electrochemical reactions near the electrode-electrolyte interface.

Different technologies like chemical vapor deposition (CVD), atomic layer deposition (ALD), electrochemical vapor deposition, various sputtering or physical vapor deposition (PVD) processes using ion beam, magnetron, electron beam and so forth, ink jet printing, and sol-gel processing can be used to achieve thin film deposition.^{15–21} The choice of an appropriate thin film deposition technique is strongly influenced by the material to be deposited and the desired film quality.^{10,22} Among the various methods available for thin film deposition, CVD (atomic layer deposition) and PVD (sputtering) techniques are the two most commonly employed techniques for thin film electrolyte and electrode deposition.

The self-limiting process of ALD dominates the formation of dense electrolyte thin films at moderate temperatures and meanwhile maintains the uniformity and purity of the films. In each of these pulses, the precursor molecules react with the surface in a self-limiting way, so that the reaction terminates once all the active sites on the surface complete the oxidation reaction. Consequently, the maximum amount of material deposited on the surface after a single exposure

to all of the precursors is determined by the nature of the precursor-surface interaction.²³ Figure 2.8 shows a sketch of ALD cycle with the self-limiting process, and the deposition rate can be controlled around few angstroms per ALD cycle. By increasing the number of ALD cycles, deposition with precise thickness and composition control can be achieved. For example, YSZ is still one of the most commonly used electrolytes in SOFCs. ALD deposited YSZ thin films can be obtained by alternating Zr/Y pulse of the desired ratio. More specifically, YSZ films containing around 8 mol % yttria can be fabricated by sequentially depositing seven layers of zirconia from zirconium precursor and one layer of yttria from yttrium precursor using distilled water or oxygen as oxidants.^{15–18,20}

Figure 2.8 Schematic of self-limiting process in atomic layer deposition technique

Sputtering is another one of the widely used thin film deposition technique. Sputtering is a term used to describe the mechanism in which particles are ejected from the surface of a target material when the surface is bombarded by energetic particles, mostly from the inert gas ionization. Argon gas is supplied into the process chamber, and the applied high voltage induces

ionization. The ionized positive ions moved towards the negatively charged target, and the ejected target material is sputtered on the substrate. Sputtering sources often employ magnetrons that utilize strong electric and magnetic fields to confine charged plasma particles close to the surface of the sputter target. The electrical conductive targets were usually sputtered using direct current (DC) magnetron sputtering while the charge build-up on insulating targets can be avoided with the use of radio frequency (RF) sputtering where the sign of the anode-cathode bias is varied at a high rate (commonly 13.56 MHz). Different morphologies like dense and porous films can be obtained by adjusting sputtering parameters, including gas pressure, bombardment power and rate, substrate temperature, sputtering time, etc. Various materials can be deposited by sputtering, including metal (e.g. Pt, Ag, Sn, Ni) and ceramic (e.g. YSZ,) in terms of DC magnetron sputtering and RF sputtering.¹⁵⁻²¹

Figure 2.9 Sketch of sputtering technique for thin film deposition

2.5.2 Materials

The materials used for the anode, electrolyte, and cathode of micro-SOFCs should have proper electrical, ionic or electrical/ionic conductivity accordingly. Dense and good ionic conductivity are required for electrolyte while porous, good electrical conductivity and catalytic properties are required for electrodes. The state-of-the-art electrolyte material of micro-SOFCs is YSZ, and according to the research, 8 mol % Yttria (Y_2O_3) in 92 mol % Zirconia (ZrO_2) have the best ionic conductivity.^{15–17,19,20} As for electrode material, precious metal, platinum (Pt), has good catalyst property on both anode and cathode. Some other research also works on various anode material, like Ru,^{18,21} Ni,²⁰ and Sn, and the cathode material, like LaSrCo-based materials.^{19,21,24,25}

2.5.3 System integration

The system integration of the μ -SOFCs which included planar^{16,26} and tubular type^{27,28} were shown in Figure 2.10. The work of planar μ -SOFCs utilized microfabrication and micromachining technique while the tubular μ -SOFCs relied on powder ceramics fabrication. The design of the planar μ -SOFCs comprises one ion conducting electrolyte and two electron conductive porous electrodes. Electrolyte required a dense property to provide a gas barrier between anode and cathode while electrode required a highly porous property to provide both high gas contact area and electron conducting path. Three layers structure Positive electrode-Electrolyte-Negative electrode was shortened into PEN element. In fact, nanoscale thin film PEN fabrication requires a micro-scale intermediate for supporting the PEN as a result of interconnected conjunction including Free-standing PEN^{16,17} on the substrate and supported PEN on a porous substrate.²⁹ Different substrates have its own advantage/disadvantage which can be discussed furthermore by material, membrane size, fabrication method, etc. In order to get higher

power output, enlarge PEN size (the same as membrane size) would be directly related to the help. However, nanometer membrane is easily encountered rupture phenomenon due to poor mechanical stability. It's very critical to design the fabrication process and structure which enhance the strength of the larger membrane. The researcher studied on membrane geometry to enlarge the electrochemical reaction area.^{16,17,19,20} From the studies, most researchers have the membrane area less than 1 mm². Baek et al³⁰ demonstrated that a tapered silicon membrane support with the thickest end of 30 mm was introduced as an effective membrane stress absorber. The new architecture effectively suppressed membrane buckling and decreased the maximum principal stress by 30-40%, and the largest lateral dimension of the stable membranes was 3 mm in diameter. Rey-mermet et al²⁹ demonstrated the 1μm thickness membrane in biggest diameter 5mm with the supported by nickel grid anode. The membrane geometry was taken into concern as well, such as square shape^{16,17,20} and circular shape.^{19,29}

Figure 2.10 Sketch of the (a) planar -type μ-SOFCs¹⁶; and (b) cube-type μ-SOFCs²⁸

2.5.4 Electrode of low-temperature solid oxide fuel cells

Among the entity of charge transport and transfer processes in an operating SOFC, the activation loss η_{act} associated with the oxygen reduction reaction (ORR) at the cathode is the main contribution to the overall voltage drop (compare with session 2.3). A relation between the current density j and activation loss (overpotential) η_{act} has been elucidated for the mechanism of the ORR and the origin of η_{act} . Butler-Volmer equation (equation 2.4),¹ where α is the charge transfer coefficient and j_0 is the exchange current density, which corresponds to the exchange rate in equilibrium is a measure for the performance of a cathode.

$$j(\eta_{act}^c) = j_0^c (e^{\frac{\alpha n_e F}{RT} \eta_{act}^c} - e^{\frac{-(1-\alpha)n_e}{RT} \eta_{act}^c}) \quad (2.4)$$

Referring to the Butler-Volmer equation, a decrease of the cathodic activation loss, or overpotential, η_{act} at a given current density requires an increase of $j_0^c = n_e F e^{-\frac{\Delta G}{RT}}$. n_e : the number of exchanged electrons, F : Faraday constant 96485 Cmol^{-1} . To accomplish the electrochemical reaction, the activation barrier between the reactant and its activated states, ΔG has to be overcome. Based on the above relation and given a constant temperature and concentration of reactants, the strategies towards more active cathode categorize into following choices:

- (1) The decrease of the activation barrier ΔG by the development of more catalytically active cathode material. For examples, reported highly active cathode material BSCF,³¹ LSCF^{32,33} or the enhancement of the catalytic activity of Pt by alloying with nickel.^{34,35}

- (2) Increase the possible reaction sites by optimization of the cathode microstructure. This approach requires a maximization of the TPBs, which solely have an interface between reactant gas, electrically conducting electrode and the ionic conduction electrolyte.

The choice of cathode materials is confined to noble metal or cermet due to the operating temperature and oxidizing conditions in LTSOFCs. Noble metal electrodes are widely studied in the field of fuel cells, particularly in the type of operating temperature less than 200 °C. The function of the electrode is to increase the rate of an electrochemical reaction by lowering the energy barrier for the catalytic reaction at a given temperature or reactant concentration.

Pt is considering the best catalyst for oxygen reduction reactions due to highest exchange current density among the noble metals. Meanwhile, the intrinsic activity of platinum is the highest compared with other metal based catalyst. Pt is a transition metal with a face-centered cubic lattice structure with a lattice parameter of 3.91 Å and an electrical resistivity of 105 nΩ·m (at 20 °C). The later value decreased with increasing temperature due to increasing scattering of the electron waves and lattice vibration, which is a nature of metal. Researchers discussed the optimum parameter on fabricating Pt electrode, including geometry, composition, thickness, porosity, etc., to have higher catalytic property.^{24,36,37} The high catalyst activity of Pt surface towards ORR results from the well-balanced binding energy for oxygen dissociative adsorption which also facilitates a high surface coverage as well as an efficient removal of product species.³⁸ The binding energies of adsorbed species on catalytic metal surfaces correlate with the average energy were shown in Figure 2.11a. The corresponding exchange current density of catalytic metals for hydrogen oxidation reaction and oxygen reduction reaction were shown in Figure 2.11b and c. Above investigation firmly inform the potential using Pt for cathode ORR, which has been studied for decades.

However, one chronic issue of using Pt cathode for LTSOFCs is its poor thermal stability under high temperature operation. Despite the high density of nanopores and cracks that can maximize the electrochemically active sites or the TPBs, the nanoscale features are subjected to thermally-driven agglomeration to lower its high surface free energy to a thermodynamic balance, which inevitably resulted in a rapid loss of the effective surface area and hence the lower cell current output. The thermal agglomeration of a sputtered nanoporous Pt film is reported to initiate at around 300 °C,³⁹ which is way below the typical operating temperature of LTSOFCs between 350 to 500 °C. The irreversible deterioration to fuel cell performance caused by the cathode agglomeration severely impedes the development of LTSOFCs and we have detail discussion in a later session.

Figure 2.11 Investigation of metal catalysts; (a) activity versus binding energy,³⁸ (b) exchange current density of hydrogen oxidation;¹ (c) exchange current density of oxidation reduction¹

2.5.5 Thermal stability of metal electrode

Pt-based electrocatalyst is considered as one of the best catalyst for oxygen reduction reaction (ORR) for a fuel cell operating at a temperature less than 500 °C. Advantages of Pt include excellent catalyst activity of hydrogen splitting and oxygen reduction, minimization of the activation loss, and good electrical conductivity. However, lowering the operating temperature regime adversely affects the cathode oxygen reduction reaction which is known to be the rate determining step for SOFCs reaction. Typically a nanoporous Pt thin film cathode is often fabricated by direct current (DC) magnetron sputtering, or radio frequency (RF) sputtering at high gas pressures to generate a high density of nanoscale pores or crack within the film to maximize the electrochemically active reaction sites, or the TPBs and the resulting pore size are in the range of tens to a few nanometers. Figure 2.12 shows a typical nanoporous Pt morphology fabricated by RF sputtering under high argon pressure.

Figure 2.12 Typical nanoporous Pt morphology fabricated by RF sputtering

It has been reported that nanoporous Pt cathode can yield a high performance of 1.3 W/cm^2 at 450°C ,⁴⁰ an ultra-low operating temperature of 265°C achieving 28 mW/cm^2 ,¹⁷ and an ultra-low Pt loading of 0.02 mg/cm^2 ⁴¹ for potential applications. Despite these advantages, poor thermal stability is the major issue using sputtered Pt thin film at a temperature higher than 300°C . The severe agglomeration of Pt is typically understood in view of thermodynamic instability, and the high free energy of nanoscale Pt thin film tends to agglomerate to lower the surface energy, which inevitably results in decreased TPBs density.

Few researchers had found this drawback of using nanoporous Pt as LTSOFCs cathode, but still very few studies work on improving its thermal stability so far. Table 2.3 summarizes the reported performance degradation at the operation temperatures of LTSOFCs. The irreversible deterioration to fuel cell performance due to thermal agglomeration of pure Pt cathode were reported by approximately 50% at 400°C for 12 continuous hours of testing,⁴² 30% at 450°C for 4 continuous hours of testing,⁴³ and 20% at 500°C for 2 hour continuous testing,⁴⁴ which are very far from the target of United States Department of Energy 2015 with 20% performance loss within 1,500 hours operation for the requirement of portable power sources.⁴⁵ These studies inform a critical drawback of using nanoporous Pt electrode for LTSOFCs. Figure 2.13 showed the nanoporous Pt cathode morphology before and after fuel cell operation at a high temperature of 500°C ⁴⁴ and 450°C ⁴⁶ which clearly reveals the significant agglomeration of Pt cathode and the loss of TPBs.

Table 2.3 Performance degradation of LTSOFCs using nanoporous Pt cathode

	Kerman ⁴²	Ji ⁴³	Takagi ⁴⁷	Jeong ⁴⁸	Wang ⁴⁹	Chang ⁴⁴	This work
Cathode	Pt	Pt	Pt	Pt	Pt	Pt	Pt
Operation Temperature (°C)	400	450	500	450	400	500	450
Cathode thickness (nm)	80	200	30-40	150	80	~100	100
Operation voltage (V)	Peak Power	Peak Power	0.6~0.75	Peak Power	0.45	0.6	0.5
Duration (hr)	12	4	3	3	1	2	75
Degradation (%)	50	30	62	>99	20	20	86
Oxidant	Air	Air	Air	Air	Air	Air	Air
Electrolyte	YSZ	GDC/YSZ	YSZ	YSZ	YSZ	YSZ	YSZ
Anode	Pt	Pt	Ru-CGO	PtRu	Pt	Pt	Pt
Fuel	5% wet H ₂	H ₂	Methane	Methanol	H ₂	H ₂	H ₂

Figure 2.13 Nanoporous Pt cathode morphology before and after fuel cell operation at high temperature of 500 °C⁴⁴ (a and b) and 450 °C⁴⁶ (c and d)

In general, any first-order phase transformation process results in a two phase mixture composed of a dispersed second phase in a matrix. However, as a result of the large surface area present, the mixture is not initially in thermodynamic equilibrium. The total energy of the two-phase system can be decreased via an increase in the size scale of the second phase and thus a decrease in total interfacial area. Such a process is termed Ostwald Ripening or Coarsening.⁵⁰ Since the excess energy associated with the total surface area is usually small, such surface energy driven morphological changes typically manifest themselves as the last stage of a first-order phase transformation process. The driving force for the ripening process is the well-known curvature dependence of the chemical potential which, assuming isotropic surface energy is $\mu = \mu_0 + V_m \gamma k$, where k is the mean interfacial curvature and μ_0 is the chemical potential of an atom at a flat interface. V_m is the molar volume and γ is the surface energy. The equation shows that atoms will flow from regions of high to low curvature. This results in the disappearance of surface possessing high curvature and an increase in the size scale of dispersed second phase, which is consistent with the necessary decrease in total energy of the two-phase system.

The difference between Coarsening and Ostwald Ripening towards thermally-driven agglomeration are discussed by Michael Bowker et al.⁵¹ Coalescence occurs when the two clusters are close enough to touch or collide and merge to form one cluster with the bigger size. Ostwald ripening⁵¹ occurs by evaporation of the surface atom from one cluster and then transfer or re-deposit to another cluster. It's a dynamics process which the rate of the evaporating surface atom from the smaller cluster is higher. Thus cluster becomes bigger as a result of exhausting the small cluster. Figure 2.14 shows the sketch of the difference between coalescence and Ostwald ripening. Coalescence and Ostwald ripening are observed phenomenon on morphology changed over time. The diffusion process and mass transfer process are involved in the region transition

from high interfacial curvature site to low interfacial curvature site. Thermal-, electrical-, mechanical- forces are the possible driving forces.

Figure 2.14 Schematic of (a) coalescence and (b) Ostwald ripening⁵¹

Additionally, Mutoro et al⁵² demonstrated a detail picture of the Pt/YSZ system dominating the electrochemical behavior, including structure and orientation of the materials, grain boundaries, defect chemistry, interface phases, interdiffusion, morphologies of the surfaces and the interface, pores, impurities, which may also be a factor of thermal instability (see Figure 2.15). Various factors located at different part of the thin film electrode can influence the electrochemistry behaviors, which are believed that the factors at various part of the thin film will also have difference behavior to resist thermal agglomeration. It is reported the thermally-driven morphological evolution between the top surface and the substrate contact interface of agglomerated nanoporous Pt electrode using double cantilever beam technique and found that the temperature required for significant agglomeration to occur was approximately 100 °C higher at the electrolyte contact interface side than at the top surface side.³⁹ This is because the unbounded surface of Pt is free to migrate under the thermally driven effect whereas the bonded interfacial

Pt to the electrolyte experienced a constraint to migrate.³⁹ This reported work further clearly informed us that the thermal agglomeration behaviors are different from various part of the thin film electrode

Figure 2.15 The Pt/YSZ/O₂: interfaces and factors controlling the electrochemical behavior⁵²

Following sessions will discuss the work has been done for improving the thermal stability of nanoporous Pt electrode at high temperatures. The discussed segments are categories as:

- Fabricate a well-spaced substrate for the deposition of the metal electrode.
- Electrode surface decoration to inhibit the thermal agglomeration effect
- Nanocomposites or alloy to increase the integrity of the metal electrode.
- Adhesion modification on the interface between the substrate and metal electrode.

Kim et al⁵³ proposed that separated space between Pt clusters can build a preventing-migration barrier, like a forming gap to inhibit the thermally-driven agglomeration. Nanopore patterned Pt array electrode was fabricated by silica template for the purpose of preventing

agglomeration. The separated space, 400 nm pore in diameter, provided a controlling geometry of the Pt electrode. Anodized Aluminum Oxide (AAO) membrane template was investigated as an electrode support and improve the thermal stability of the microstructure.⁵⁴ The separated space within the AAO is around 100 nm. The deposited Pt clusters were separated by 100 nm in space, and the consistent morphology of Pt was observed after high temperature annealing as shown in Figure 2.16. Multi-scale architecture⁵⁵ are also proposed for enhancing the thermo-mechanical stability of the electrodes. A NiO-YSZ anode support is employed as the substrate, and the microstructure scale was changed from micrometer to nanometer. Bi-layer electrolyte 150 nm thick YSZ and 450nm-thick was fabricated for the thermal-cycling test at 700 °C.

Figure 2.16 High-resolution SEM images of as-sputtered Pt electrode (a) fresh and (b) 450 °C fuel cell operation; and nanostructure Pt (c) fresh and (d) 500 °C fuel cell operation⁵³

Electrode surface decoration was demonstrated as an effective method to inhibit the thermal agglomeration of the metal electrode at high temperatures. Nanoscale zirconia film (ZrO_2) was demonstrated on the LaSrCoOx cathode for an intermediate-temperature solid oxide fuel cell for the operation temperature of 700 °C. The geometrical confinement which is provided by the conformal zirconia overcoats showed a benefit factor of 19 reduction in the area-specific resistance of the LaSrCoOx cathode.⁵⁶ Chang et al⁴⁴ proposed an ultrathin YSZ coated on the porous Pt cathode by the atomic layer deposition to be confinement agent of avoiding thermal

agglomeration of metal electrodes. A 5 nm-thin YSZ coating is found to maintain the morphology of its underlying nanoporous Pt at a high temperature operation of 500 °C, which was shown in Figure 2.17. The demonstrated highly stable powering operation with 250 mW/cm² at 500 °C for more than 8 hours. Chang et al⁵⁷ also proposed ultra-thin tin oxide (SnO₂) coats platinum by atomic layer deposition. They observed the ultra-thin tin oxide-coated Pt samples heated at 300 °C and found a suppressed metal agglomeration and in-situ sheet resistance variations is more stable over Pt for 20 hours.

Figure 2.17 Sketch and top-view images of Pt films (a) without and (b) with a nanoscale YSZ coating before (left) and after an annealing process (right) at 500 °C.⁴⁴

Platinum-Nickel (PtNi) alloy was used to prove the anti-Ostwald ripening effect of the as-deposited platinum morphology at an elevated operating temperature of 350-500 °C based on quantum simulation results by *ab initio* calculation.⁴⁹ It was reported that both the surface energy of a Pt_{0.7}Ni_{0.3} cluster and the energy change of the PtNi alloy cluster upon ripening on YSZ solid

electrolyte were lower than pure Pt. SEM images show dramatic porosity reduction from the top surface morphology for pure Pt after annealing at temperatures of 400-600 °C but insignificant microstructure change for PtNi nanoporous thin films. Schmid et al⁵⁸ reported the impact of thermal annealing by titanium/platinum thin film on resisting the Pt agglomeration. The impact of the titanium thickness on the electrical performance is comprehensively evaluated, and results showed the influence of Ti migration into Pt electrode for a lower electrical resistivity and better thermal stability, which depends on the control of deposition thickness of Ti. Richter et al⁵⁹ reported a high-temperature stability of platinum, platinum-rhodium, iridium as well as lanthanum strontium manganite (LSM) regarding the electrical measurement, and the morphology was also observed. Among the metal based films, Pt/Rh (10 %) exhibits the best high-temperature stability for a given film thickness. A stability of the film is demonstrated up to temperatures of 900 °C for the application of wireless surface acoustic wave device.

It was reported the active area of the platinum electrodes decreased gradually by increasing thermal-annealing duration, and the power density was reduced by 50 % at 400 °C after 12 testing hours,⁴² and the preliminary study in this work also found 86.2% performance loss at 450 °C for 75 continuous hours of testing. Platinum clusters begin to agglomerate from 300 °C annealing and much severe at higher temperatures.³⁹ Clusters and grains of platinum electrode grow exponentially after annealing beyond 400 °C,⁴⁹ which result in forming a larger gap between platinum clusters. The microstructure and morphology of platinum electrodes suffer agglomeration which may arise from Ostwald ripening.⁵⁰ Hörlein et al⁶⁰ proposed the long-term changing behavior of the polarization resistance of Pt on YSZ can be studied into two independent processes. The growth of non-stoichiometric PtOx leads to degradation behaviors which were supported by the vanished effect when applying measurement into reducing oxygen

atmosphere. Accumulation and diffusion of the impurity at the three-phase-boundary leads to the continuous degradation of the performance.

2.5.6 Oxygen reduction reaction of metal electrode in LTSOFCs

Solid oxide fuel cells comprise an anode, cathode, and electrolyte which are all in solid states. Therefore, the electrode reaction in solid state electrochemistry is significantly different from the one in liquid electrochemistry. In the case of liquid electrochemistry, gas, solid and liquid will be mixed to form an electron conductor, ion conductor and gas transport path respectively. However, in the case of a solid state fuel cell at high temperature, the electrochemical reaction occurs on gas-solid electrode-solid electrolyte interface. Opitz et.al⁶¹ investigated four possible mechanisms for the solid state oxygen reduction reaction shown in Figure 2.18. The adsorbed oxygen diffuses along the surface of electrode or electrolyte, and then catalyzed reaction occurs at the interface between the electrode, electrolyte, and gas. The adsorbed oxygen diffuses through the bulks is another kind of mechanism. The reaction occurs at the surface of the electrode or the interface of electrode/electrolyte.

Figure 2.18 Schematic of reaction pathways on solid electrodes:(a) Electrode Surface path;(b) Electrolyte surface path;(c) Bulk path with reaction at the electrode surface;(d) Bulk path with reaction at the electrode/electrolyte interface.⁶¹

Opitz et.al⁶¹ also reported a pathway which was identified on Pt-YSZ. Results showed that the faradaic reaction pathway depends not only on the temperature but also the electron concentration. Oxide ions may go through the bulk electrode, diffuse through a foreign phase and electrolyte surface path. The schematic was shown in Figure 2.19.

Figure 2.19 Schematic of faradaic pathway of ORR on Pt electrodes:(a) Electrode surface path;(b) Through a foreign phase;(c) Electrolyte surface path⁶¹

The same group, Optiz et al⁶² investigated that the resistance of the rate determining step depends on three-phase-boundary length with an electrode conductivity of $6.6 \pm 0.9 \cdot 10^{-7} \Omega \cdot \text{cm}^2$. The Pt(O₂)/YSZ composite represents a surface path system which assumes that TPB is related to the active region for oxygen incorporation and the rate-limiting step located close to the TPB-zone. Hayd et al⁶³ also demonstrated that hetero-interfaces at nanoscale thin film cathode could enhance incorporation of oxygen. The oxygen surface-exchange coefficient of hetero-interfaces was determined up to 47 times than the pure perovskite phase. The hetero-material is SrCoO while the perovskite material is LaSrCoO. Figure 2.20 showed the sketch of the hetero-interfaces incorporated oxygen reduction.

Figure 2.20 Schematic of the hetero-interfaces incorporated oxygen reduction⁶³

Peng et al⁶⁴ reviewed the low frequency polarization resistance which was changed accordingly with parameters of the component, microstructure, conducting species and material. The material factor is the most particular one with suggesting mixed electron and oxygen ion (proton) conducting cathode. The experimental and theoretical analyses suggest the ion-electron mixed cathode present smaller polarization resistance. Schlupp et al⁶⁵ demonstrated oxygen ion

conductivity of yttria-stabilized zirconia thin film, and the microstructure and crystallinity are the most impact factor while there is no size-effect of the grain and fabrication method effect on the oxygen ion conductivity. It was reported the oxygen ion conductivity of the randomly oriented nanocrystalline YSZ is determined by grain boundary, which shows lower transport properties than grain interior. But for columnar microstructure with preferred (111) orientation, the conductivity of oxygen ionic transport through the grain interior is determined. Agglomerated Pt thin film on YSZ has been proposed that the improved electrochemical properties result from the increased “nanoscopic” triple-phase boundary where Pt, YSZ, and air are in contact.⁶⁶ The oxygen permeable grain boundary which comes from the nanoscopic TPB may provide reactive site and the transport path of oxygen ions.

Figure 2.21 Schematic of the cathode reaction mechanism with different material:(a) Electrode; (b) Electro-oxygen ion mixed conductor; (c) Electro-proton mixed conductor; (d) Composites composed with electro-oxygen ion mixed conductor and electro-proton mixed conductor⁶⁴

Chapter 3

3. Thermal Stability and Performance Enhancement of Nanoporous Platinum Cathode by Nanoscale ZrO₂ Capping

3.1 Introduction

Recent advances in ultra-low temperature solid oxide fuel cells (SOFCs), also referred as micro-SOFCs in some literature, operating at a temperature below 500 °C with superior performance have been demonstrated using nanoscale thin film electrolytes.^{15–17,67,68} The highest power density reported to date was 1.3W/cm² at 450 °C,⁴⁰ and the lowest temperature demonstrated was at 265 °C with a power density of 28mW/cm²,¹⁷ both of which have shown great potential for the extension of SOFC applications from conventional stationary to portable power sources. Since the operating temperature is much lower than conventional SOFCs, the cathode oxygen reduction process becomes the most rate-limiting among all polarization processes. Currently, noble metal cathodes with high activities such as platinum^{15,22} or its

alloys^{29,49} with a high density of nanoscale pores are still common choices for a demonstration of such high performance.

One major issue of using nanoporous metal as the electrode is the poor thermal stability which often causes irreversible deterioration to cell performance. Among the reported observation of thermally-driven agglomeration in nanoporous platinum⁴² and its alloy with nickel,⁴⁹ severe losses in effective triple phase boundary (TPB) densities with increasing temperature were consistently observed. Using oxide materials as cathodes can have superior thermal stability over metal, but the cell performance is still far from satisfactory at a temperature below 500 °C.^{25,69} Therefore, maintaining the thermal stability of the nanoporous electrode is critical for practical application of micro-SOFCs.

Earlier literature have proposed the capping of electrodes using atomic layer deposition (ALD) with zirconia (ZrO_2) films on oxide or metal electrodes of electrochemical devices, with the purpose either to maintain the electrode chemical stability or to introduce additional reaction sites between the backbone electrode and the ZrO_2 .^{33,56,70} In this chapter, we applied only a few cycles of ALD- ZrO_2 capping on nanoporous metal to serve as a geometrical confinement against thermal agglomeration, while an unexpected decrease in cathode polarization resistance was also observed. The thermal stability of the confined nanoporous platinum cathode, the origin of the cathode enhancement, and the cell durability testing up to 120 hours were presented and discussed.

3.2 Experiment

3.2.1 ZrO₂ capping on nanoporous platinum

Nanoporous platinum cathodes (100 nm-thick) were deposited on yttria-stabilized zirconia (YSZ) substrates using radio frequency sputtering.³⁹ ZrO₂ capping layer was then deposited by ALD (CN1 Co., Ltd. South Korea) onto the platinum cathode for 0, 10, 15, 30, and 60 cycles, with tetrakis(dimethylamino)zirconium(IV) (99.99%) (Strem Chemicals Inc.) as ZrO₂ precursor, oxygen (99.999%) as oxidant at the substrate temperature of 250 °C. Here one ALD cycle refers to the combination of one pulse of a precursor followed by one pulse of oxygen oxidant, and both pulse time for ZrO₂ precursor and oxygen are 0.5 second/pulse. The sketch of as-deposited Pt and ALD-ZrO₂ capped Pt electrode were shown in Figure 3.1.

Figure 3.1 Sketch of (a) as-deposited Pt and (b) ALD-ZrO₂ capped Pt electrode

3.2.2 Thermal stability and cathode performance characterization

The uncapped and ZrO₂-capped Pt were annealed at 450 and 600 °C for 12 hours to test the effectiveness of capping on the thermal stability of cathode, and their microstructures were observed by field emission scanning electron microscopy (FESEM).

Fuel cells with uncapped and ZrO₂-capped cathodes were fabricated on (100) single crystalline YSZ substrates, and uncapped Pt was used as the anodes. The polarization and

electrochemical impedance spectroscopy (EIS) curves were retrieved at 450 °C using an electrochemical potentiostat (Solartron Analytical, 1470E) and a frequency response analyzer (Solartron Analytical, 1255B) with 99.99% hydrogen as fuel and air as the oxidant.

3.3 Results and Discussion

3.3.1 Morphological observation

The SEM images of the morphological observation of 10 cycles ALD-ZrO₂ capped Pt by sputtering was shown in Figure 3.2a and b. Top surface view of the ALD-ZrO₂ capped Pt electrode shows a very high density of short, narrow, and nanometer scale cracks exist between the larger, wider, and tens to hundreds of nanometers cracks, which are the effective TPBs for cathode reactions, and the same to traditional nanoporous morphologies by sputtering. Moreover, nanoscopic features, like invisible pores, cracks, and grain boundary within the bulk of the Pt electrodes also presented some TPB regions. The cross-section view of the electrode showed a columnar structure which was created at a high argon gas pressure during the sputtering process. The Pt nanoparticles created from Pt target by high energy argon plasma bombardment to form a columnar structure with a length of around 100 nm on the substrate, which also represents the thickness of the sputtered Pt. The clear HRTEM images (Figure 3.2c) presented a single columnar Pt structure with a corresponding thickness of 100nm. The conformal and ultra-thin ALD-ZrO₂ coating was observed on whole columnar structure from the electrode top surface to the bottom. The further high magnitude in Figure 3.2d showed the structure in the bulk of the Pt film. The size of Pt nanoparticles was visible with clear domains. The average size of Pt nanoparticles is around 10 nm, and the space between Pt nanoparticles may represent the formed nanopore/nanocracks in bulk of Pt film. The morphology observation of ALD-ZrO₂ capped Pt

electrode in terms of top surface view, and cross-section view confirmed that RF sputtering at high argon gas pressure had formed nanoporous and columnar Pt structure resulting from nanoparticles stacking.

Figure 3.2 Morphology of as-deposited 10 cycles ALD-ZrO₂ capping on nanoporous Pt electrode in terms of (a) surface top view, (b) and (c) cross-section view and (d) nanoparticles within the film.

The morphological observation of as-deposited nanoporous Pt electrode with uncapped and 10-, 15-, 30- and 60- cycles ALD capping were examined by FESEM surface top view shown in Figure 3.3a. All the as-deposited films showed the typical nanoporous patterns, where a high density of cracks and grooves presented and were the effective TPBs for cathode reactions, and the insignificant difference was observed. The ultra-thin ALD cappings on top of such nanoporous electrodes were invisible from top view observation due to the interference of nanopore structure. Figure 3.3b further showed the HRTEM image of controllable growth thickness of ZrO₂ on porous platinum film by ALD with uncapped, 10-, 15, 30- and 60- cycles from the cross-section view. The ALD-ZrO₂ capped nanoporous Pt electrode have a conformal coating on the top surface of Pt electrode with a uniform thickness. The HRTEM image can clearly distinguish the difference of Pt and ZrO₂ for the precise determination of thickness. The deposition rate of ALD is approximately 0.9 Å/cycle for the corresponding thickness of 10- cycles for 0.9 nm, 15- cycles for 1.3 nm, 30- cycles for 2.5 nm and 60- cycles for 5.0 nm.

Figure 3.3 (a) FESEM and (b) HRTEM of as-deposited nanoporous Pt electrode with uncapped, 10-, 15, 30- and 60- cycles ALD-ZrO₂ capping.

Since the growth of ALD films will undergo the nucleation and crystalline growth process, depending on the substrate material and deposition temperature,⁷¹ surface morphologies were examined approximately when the film became continuous over Pt surface. Figure 3.4a shows the experiment to grow ALD-ZrO₂ on “dense” platinum film instead of a nanoporous film to avoid geometrical confusion when identifying the ALD-ZrO₂ by FESEM imaging. A bare Pt surface or Pt capped with non-continuous ZrO₂ film will give minimized electron charging during FESEM imaging, while the charging will appear with continuous ZrO₂ film. The platinum surface without capping showed a high density of grain boundaries (Figure 3.4b), and similar morphologies after 10- and 15-cycle of ALD-ZrO₂ capping were observed with insignificant charging effect. However, the 30-cycle ZrO₂ capping appeared to block the platinum surface since the surface grain boundaries and grooves became invisible, while the electron charging was severe. Same observation became more obvious with 60-cycle capping. Therefore, we expect the

ALD-ZrO₂ capping on nanoporous platinum to show similar behavior, forming a discontinuous film at 10- and 15-cycle and a continuous blocking film over 30-cycle.

Figure 3.4 (a) Sketch and (b) FESEM of as-deposited dense Pt electrode with uncapped, 10-, 15, 30- and 60- cycles ALD-ZrO₂ capping

3.3.2 Morphological stability under high temperature annealing

Figure 3.5 showed the surface morphologies of cathodes with/without ZrO₂ capping and before/after thermal annealing. The uncapped platinum electrode (Figure 3.5a) showed the expected nanoporous structure with columnar grains and high TPB density and agglomerated significantly after annealed at 450 and 600°C (Figure 3.5b and c), which is consistent with literature.⁴² With only 10-cycle ZrO₂ capping (Figure 3.5d-f), the agglomeration was effectively hindered. With 60-cycle capping (Figure 3.5g-i), the cracks between platinum clusters were narrower by thicker ZrO₂ deposition, but stable nanoporous morphologies after annealing was still maintained.

Figure 3.5 FESEM images of uncapped (a~c), 10-cycle (d~f) and 60-cycle (g~i) ZrO_2 -capped Pt electrodes on YSZ substrate before/after annealing.

3.3.3 ORR enhancement of ALD- ZrO_2 capping

The I-V curves (Figure 3.6a) showed that the cell with 10-cycle capped cathode had the highest performance, followed by cell with 15-cycle capping. With thicker capping of 30- and 60-cycle, the performance dropped below the cell of the uncapped cathode.

The EIS curves (Figure 3.6b) were retrieved at 0.9V of cell voltage and showed a parallel trend with I-V curves. The Ohmic contribution due to the variation of thickness among YSZ substrates was subtracted and re-drawn in the insert to compare only the polarization resistance values (R_p) among cells. We ascribe R_p to mainly the resistance of cathode reactions due to the sluggish ORR over anode reactions at 450 °C. The R_p was $50.3 \Omega\text{cm}^2$ for the uncapped cathode

and dropped to $5.3 \Omega\text{cm}^2$ at 10-cycle capping. But after 15-cycle, R_p increased and became higher than the uncapped cathode at 30-cycle. At 60-cycle, huge polarization resistance of up to $640 \Omega\text{cm}^2$ was observed. In other words, the improved ORR activity was only observed in cathodes with low capping cycles (10- and 15-cycle).

Bode plots were further analyzed to identify the rate-limiting processes affected by the ALD-ZrO₂ capping (Figure 3.6c). Two overlapped peaks of phase angles were observed, where a higher and obvious peak dominates at low frequency and a suppressed peak at high frequency. The phase angle at a high frequency range (10^5 - 10^3 Hz) is ascribed to the charge transfer process, while the phase angles at a low frequency range (10^2 -0.1Hz) relate to the non-charge transfer processes, including gas diffusion and dissociative adsorption.^{72,73} The high frequency peak had no significant change with capping, while the low frequency peak remarkably decreased with only 10-cycle ZrO₂ capping, indicating the promotion of oxygen gas adsorption and dissociation process. With 15-cycle capping, the low frequency phase angle increased back, but still smaller than that of uncapped platinum. At 30- and 60-cycle capping, the continuous coverage of ALD-ZrO₂ had fully blocked the platinum surface, and both increased magnitude of phase angle and its shift to lower frequencies were observed, meaning the oxygen gas adsorption and dissociation process was blocked by thicker ZrO₂. Especially, the 60-cycle capped cathode showed a clear gas diffusion resistance as evidenced by a large phase angle at the characteristic relaxation frequency of 0.1-1 Hz.⁷³

The origin of the observed enhancement in oxygen gas adsorption and dissociation can be explained as follows. At low ALD-capping cycles, the ZrO₂ film was not continuous and may be only scattered nanoparticles or connected particle networks, where a majority of platinum surface remained exposed to an oxygen atmosphere. Thus, the surface diffusion pathways for

adsorbed oxygen are still available. The existence of ALD-ZrO₂ on platinum surface may either provide a facile oxygen diffusion pathway⁷⁴⁻⁷⁶ or assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface, thus facilitated the ORR process. When the surface of platinum is completely covered by ZrO₂ with higher ALD cycles, both the diffusion of gaseous oxygen onto platinum surface and the transfer of adsorbed oxygen along platinum active surface become difficult, resulting in a slower ORR. A recent study by Chang et al⁴⁴ also observed the cathode enhancement with thicker ALD-YSZ capping, but only when the initially dense YSZ broke into interconnected networks after heating. No enhancement was shown with the initially dense capping film. The ALD-YSZ on Pt may behave like cermet which mixed ionic/electronic conducting effect can be expected by YSZ capping. The oxygen dissociation mechanism is totally different near catalyst/electrolyte interface due to the high ion conductivity from yttria doping effect. However, unlike what Chang claimed, where the origin of enhancement was from an enhanced triple phase boundary area at the vicinity of the Pt/electrolyte interface, our results showed the enhancement is more likely from the non-charge transfer process of surface adsorption/dissociation, as evidenced by the suppressed low frequency phase angles with 10- and 15-cycle capping.

Figure 3.6 (a) IV curves the Pt cathodes with 0, 10, 15, 30, 60 cycles ZrO₂ capping at 450 °C (b) Nyquist plot (from 0.1 to 20,000Hz) and; (c) Bode plots of the platinum cathodes with 0, 10, 15, 30, 60 cycles ZrO₂ capping at 0.9V and 450 °C

To further confirm the enhancement of the existence of ALD-ZrO₂ on Pt surface by either provide a facile oxygen diffusion pathway or assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface, the cell with uncapped and 10 cycles ALD-ZrO₂ capping were analyzed with the oxygen partial pressure controlled at 4, 20, 50 and 100 %. The Nyquist plots (Figure 3.7a) showed the polarization resistance of uncapped cell increased as the decrease of the oxygen partial pressure significantly, meaning the cathode ORR of the uncapped cell depends on sufficient oxygen supply, which also meet the principle of the electrochemical kinetics. The huge cathode ORR resistance was observed at oxygen partial pressure of 4%, which is an extremely low oxygen supply. Differently, the polarization resistance of the cell with 10 cycles ZrO₂-capping remained similar at oxygen partial pressure of 50, 20 and 4%, indicating the lower amount oxygen supply did not deteriorate the cathode ORR in the ALD-ZrO₂ capped cell. The polarization resistance of the cell with 10 cycles ZrO₂-capping only increased when oxygen partial pressure decrease from 100 to 50%. This result again confirmed the ALD-ZrO₂ capping can assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface. Furthermore, the uncapped cell had a higher resistance of cathode reactions than the cell of 10 cycles ZrO₂-capping at same oxygen partial pressure, meaning ALD-ZrO₂ facilitate the adsorption-dissociation process to a depressed cathode ORR. At oxygen partial pressure of 100%, obviously depressed polarization resistance was observed at the ALD-ZrO₂ capped cell than the uncapped cell. The Bode plots (Figure 3.7b) showed a significant increase of phase angle on non-charge transfer behavior in the uncapped cell than ALD-ZrO₂ capped cell at an elevated oxygen partial pressures. This also gives the evidence of ALD-ZrO₂ facilitates the adsorption-dissociation process.

Figure 3.7 (a) Nyquist plot (from 0.1 to 20,000Hz) and; (b) Bode plots of the uncapped cell and 10 cycles ALD-ZrO₂ capped cell under 4, 20, 50, and 100 % oxygen partial pressure at 450 °C

3.3.4 Performance Stability with Time

The stability of output current between cells with 10-cycle ZrO₂-capped and uncapped Pt cathode were compared at 450 °C for 120 hours (Figure 3.8), which is the longest test duration among literature for metal electrode based micro-SOFCs. The current was drained at 0.5V around the voltage of the peak power density to accelerate the agglomeration. Both cells went through a continuous current drop and then stabilized. The cell with capped cathode dropped 29.5% upon stabilization, and the cell with uncapped cathode dropped 86.2%. After the test, the capped cathode remained similar to its initial morphology (FESEM insert in Figure 3.8). The low 10-cycle capping had effectively hindered the agglomeration of the nanoporous Pt cathode during fuel cell operation by more than 50%. The remaining 29.5% degradation could come from the agglomeration of uncapped nanoscopic features^{39,66} that resided within the platinum clusters which were unreachable by ZrO₂ precursors with our deposition parameters. Since we purposefully chose pure Pt as the backbone cathode, which is more vulnerable to agglomeration, to demonstrate the effectiveness of ALD-ZrO₂ capping, less degradation of output current over time can be expected if Pt alloys such as PtNi were used as the backbone electrode.

Figure 3.8 Current output with time of fuel cells using uncapped and 10-cycle ALD-ZrO₂ capped Pt cathodes. The inserts are cathode morphologies after test.

3.4 Chapter Summary

Few nanometers-thin of ALD-ZrO₂ capping on nanoporous Pt cathode have effectively hindered the surface thermally-driven agglomeration of the cathode, and the fuel cell with low 10-cycle capped (1.3nm thin) Pt cathode, had retained the fuel cell performance by more than 50% after 120 hour continuous operation at 450 °C. An improved cathode ORR was also observed, which originate from the non-continuous ALD-ZrO₂ film attached on Pt surface that can assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface, and promote oxygen adsorption and dissociation for cathode ORR. The benefit brought by ALD-ZrO₂ capping on cathode ORR can be optimized by carefully control the ZrO₂ coverage on Pt to maximize the oxygen adsorption/desorption without sacrificing the gas diffusion and oxygen surface migration.

Chapter 4

4. Thermal Stability Enhancement of Nanoporous Cathode by PtNi Alloying

4.1 Introduction

Nanoporous Pt thin film is one common choice of cathode for low-temperature solid oxide fuel cells (LTSOFCs) operating at a temperature below 500 °C.^{16,30,77,78} The superior catalytic activity of Pt is necessary to compensate for the sluggish cathode oxygen reduction reaction (ORR) kinetics when operating at such low temperatures.^{66,79} The nanoporous Pt cathode films are often fabricated by direct current (DC) magnetron sputtering or radio frequency (RF) sputtering at a high argon gas pressure to generate a high density of nanoscale pores or cracks within the film, and the resulting pore size is in the range of tens to a few nanometers. The high density of reaction sites allows a high energy conversion rate with low electrode polarization so that a high power output of the fuel cell is promised.^{15,17,40}

One chronic issue of using nanoporous Pt cathode is its poor thermal stability under high temperature operation. Despite the high density of nanopores and cracks that can maximize the electrochemically active sites, or the triple phase boundaries (TPBs), the nanoscale features are

subjected to thermally-driven agglomeration to lower its high surface free energy to a thermodynamic balance, which inevitably resulted in a rapid loss of the effective surface area and hence the lower cell current output. The thermal agglomeration of a sputtered nanoporous Pt film was reported to initiate at around 300 °C,^{39,66} which is below the typical operating temperature of LTOSFCs between 350 to 500 °C. The irreversible deterioration to fuel cell performance caused by the cathode agglomeration was reported to be about 50% after 12 hours of operation at 400 °C,⁴² and our earlier report also showed an 86.2% of performance loss at 450 °C after 75 hours.⁴⁶ Although replacing Pt with conventional oxide cathodes materials for SOFCs, such as LSCF, was reported, it requires the operating temperature to be higher than 500 °C to obtain satisfactory performance.^{32,33} Therefore, it is worthwhile to search for solutions to improve the thermal stability of nanoporous Pt cathodes.

Reported methods to maintain the high density of nanoporous features of pure Pt electrode include electrode surface-capping by a thin layer of oxide,^{44,46,57} employing the core-shell structure of the nanoparticles,⁸⁰ or alloying with another catalytically active element such as nickel⁴⁹ or ruthenium.⁴⁸ Wang et al reported that alloying Ni with Pt to form Pt_{0.7}Ni_{0.3} decreased the electrode impedance, based on quantum simulation results by *ab initio* calculation. Jeong et al⁴⁸ demonstrated heterogeneous Pt-Ru and Ni-Ru catalysts are synthesized by atomic layer deposition (ALD) of Ru onto a porous Pt mesh and employed as the anode in direct methanol solid oxide fuel cells. In particular, alloying Pt with Ni can be a simple solution to effectively hinder thermal agglomeration since the melting temperature of PtNi nanoalloys is higher than Pt.⁸¹ Our reported work,⁴⁶ which was also discussed in chapter 3 in this thesis that few nanometers-thin ALD-ZrO₂ capping on Pt surface can sufficient retain 70.5% performance upon current stabilization, and we were also interested in whether does the remaining loss come from.

The remaining 29.5% degradation could come from the agglomeration of uncapped nanoscopic features that resided within the Pt clusters which were unreachable by ZrO₂ precursors with the deposition parameters. The grain growth, which indicates the agglomeration of the Pt nanoparticles and surface morphology at elevated temperatures between pure Pt and 10 cycles ALD-ZrO₂ capped Pt electrode was shown in Figure 4.1. The significant grain growth of ALD-ZrO₂ capped Pt was observed (Figure 4.1a) even if the nanoporous Pt surface was confined (Figure 4.1a inserts) by few nanometers ALD-ZrO₂, meaning ALD-ZrO₂ can not confine the extremely tiny nanoscale features in bulk of Pt thin film. Figure 4.1a showed the grain size of pure Pt and ALD-ZrO₂ capped Pt films as-deposited and annealed at 300, 450, 600, and 800 °C for 12 hours. The grain size was calculated using Scherrer equation⁸² on (111) peak which has the highest intensity. Significant grain growth occurred from 300 to 450 °C on pure Pt film, and similar trend of grain growth was also observed on ALD-ZrO₂ capped Pt thin film. Meanwhile, the corresponding surface morphologies at elevated temperatures in inserts showed the confined nanoporous morphology was obtained in ALD-ZrO₂ capped Pt thin film. The result of confined nanoporous Pt surface but significant grain growth in bulk of film further informed the insufficiency of ALD-ZrO₂ to the thermal agglomeration in bulk of Pt thin film. The corresponding XRD pattern of pure Pt and ALD-ZrO₂ capped Pt was shown in Figure 4.1b and c. The grain sizes of the ZrO₂ capped Pt are consistently larger than uncapped Pt, which is counter-intuitive, and the author has a few speculations: 1. The residual stress in Pt thin film caused by the fabrication process of ALD-ZrO₂ capping may be an extra energy source for the grain growth. The 10 cycles of ALD-ZrO₂ capped Pt cell was in the process temperature of 250 °C, and the rapid cooling to room temperature after deposition can be considered as a quenching process which could produce residual stress in the thin film.^{83,84} It is reported that the grain growth is one

kind of the stress relief mechanism.⁸⁵ Therefore, the ALD-ZrO₂ capped Pt electrode would have extra driving force for thin film grain growth compared with the uncapped Pt electrode. Thus, bigger grain sizes of Pt were observed in ALD-ZrO₂ capped Pt electrode. 2. The shape factor of crystallites, a term in the Scherrer equation used in X-ray diffraction may also mislead the interpretation of XRD result to grain size calculation. It is reported the shape factor for a crystal of cubes, tetrahedral and octahedra, sphere, rectangular and crystallite-size distribution should be considered different for the determination of crystallite size.⁸⁶ A constant shape factor of 0.94 was usually used for spherical nanoparticles,⁸⁷ and we applied it to both the cells, which may induce arguable grain size interpretation from ZrO₂ nanoparticles capped nanoporous Pt and uncapped Pt.

In this chapter, the effectiveness of Ni alloyed Pt on hindering thermal agglomeration of nanoporous thin film cathode was examined and compared with nanoporous pure Pt cathode. The thermally-driven morphological observation on the film surface and the grain growth in bulk of film were compared between PtNi and pure Pt. The fuel cell performance and cathode electrochemical performance over time were examined. The nanostructure observation, crystallinity, and grain growth were also investigated to confirm the origin of the improved thermal stability in nanoporous PtNi cathode.

Figure 4.1 (a) Average (111) grain size of pure Pt and 10 cycles ALD-ZrO₂ capped Pt thin film at elevated annealing temperatures, and the XRD patterns were shown in (b) pure Pt and (c) ALD-ZrO₂ capped Pt.

4.2 Experimental

Pt and PtNi thin films were deposited on silicon substrates using radio frequency (RF) sputtering at 100 W and 30 mTorr of argon pressure at room temperature. The thickness of all films was 100 nm. Figure 4.2 showed sketch of as-deposited Pt and PtNi alloy electrodes. Three different compositions of PtNi were deposited, with the Ni content being varied by placing 2, 4, and 6 of Ni rods (6 mm tall and 6 mm in diameter) on Pt target. The compositions of the as-deposited Pt and PtNi films were examined by energy-dispersive X-ray spectroscopy (EDX, OXFORD).

Figure 4.2 Sketch of as-deposited Pt and PtNi alloy electrode

The as-deposited pure Pt and PtNi films were annealed at 450, 600, and 800 °C for 12 hours to verify the effectiveness of Pt alloying with Ni on improving the thermal stability. The surface morphologies of the as-deposited and annealed films were observed by field emission scanning electron microscopy (FESEM, JOEL-7600F), and crystal structure and lattice parameters were determined by X-ray diffractometer (XRD, PANalytical Empyrean).

Fuel cells using Pt and PtNi cathode were fabricated to test the performance of the cathode over time. The electrolyte substrate is a 200 μm -thick (100) single crystal yttria-stabilized zirconia (YSZ) substrate (Latech Scientific Supply Pte. Ltd.). Nanoporous Pt anode film with

100 nm in thickness was first deposited by RF sputtering on one side of the YSZ electrolyte, followed by annealing at 450 °C for 12 hours in a tube furnace. The annealing is to purposefully drive the coagulation of the nanoporous anode so as to avoid interfering the interpretation of cathode performance data. Pt or PtNi cathode film with a thickness of 100 nm was then sputtered on the other side of the annealed substrate to complete the fuel cell fabrication.

The fabricated cells were tested at 450 °C using pure hydrogen (99.99%) as fuel at a flow rate of 20 sccm and ambient air as the oxidant. Current was drained for more than 48 hours at a reference cell voltage of 0.5 V, which is around the voltage of peak power density. The current-voltage curves (I-V curves) and electrochemical impedance spectroscopy (EIS) of the cells were captured at 0 and 48 hour using an electrochemical potentiostat (Solartron Analytical, 1470E) and a frequency response analyzer (Solartron Analytical, 1255B).

4.3 Results and Discussion

4.3.1 Composition and crystallinity of as-deposited nanoporous films

Figure 4.3a showed the EDX results of pure Pt film and three different compositions of PtNi films deposited on silicon substrates. As expected, the characteristic peaks of Pt M and Pt K α at 2.048 and 9.441 keV appeared in both pure Pt and PtNi films, and peaks of Ni L α and Ni K α at 0.851 and 7.471 keV appeared only in PtNi films. The composition of the PtNi thin films with 2, 4, and 6 of Ni rods placed on the Pt disk target was determined to be Pt₈₈Ni₁₂, Pt₇₅Ni₂₅, and Pt₆₇Ni₃₃ in atomic ratio, respectively.

The XRD patterns (Figure 4.3b) showed that all sputtered films were crystalline. A typical FCC structure with main diffraction peaks of (111), (200), and (220) were observed in pure Pt at

39.54°, 45.99° and 67.07°, respectively (indexed to PDF #01-087-0636). No diffraction peak of pure Ni (indexed to PDF#01-089-7129) was observed in all PtNi films, meaning that single phase PtNi alloy was the preferential formation in the co-sputtered PtNi, which is preferred for better thermally stability. The diffraction peaks of PtNi shifted to the higher angle from pure Pt angle, which was caused by the smaller radius of Ni atom that resulted in the shorter bond length of Pt-Ni than that of Pt-Pt, leading to lattice contraction, shorter d-spacing distance, and shift of diffraction peaks to higher angles.⁸⁷ The diffraction pattern of Pt₆₇Ni₃₃ was well-matched with the major characteristic peaks of PtNi alloy at 41.28°, 48.04°, 70.29° (indexed by PDF#03-065-9445), meaning that the nanoparticles within the Pt₆₇Ni₃₃ film were already in the form of an alloy.

Figure 4.3 (a) EDX and (b) XRD patterns of the as-deposited nanoporous Pt, Pt₈₈Ni₁₂, Pt₇₅Ni₂₅, and Pt₆₇Ni₃₃ films

4.3.2 Morphological stability of nanoporous films at high temperature

The FESEM images in Figure 4.4 showed the surface morphologies of pure Pt (Figure 4.4a), Pt₈₈Ni₁₂ (Figure 4.4b), Pt₇₅Ni₂₅ (Figure 4.4c), and Pt₆₇Ni₃₃ (Figure 4.4d) films as-deposited and after annealed at 450, 600, and 800 °C for 12 hours. All the as-deposited films showed the typical nanoporous patterns, where a high density of cracks and grooves presented and were the effective TPBs for cathode reactions. After annealing, as expected, pure Pt agglomerated significantly at a higher temperature, while all PtNi films were apparently more resistive to agglomeration. At 450 °C, PtNi films remained similar morphologies with as-deposited films, while in Pt the nanoscale pores and cracks had obviously merged. At 600 °C, the nanocracks between the clusters in Pt merged further, but only merged slightly in PtNi films. At a very high annealing temperature of 800 °C, the agglomeration of all three compositions of PtNi films became more visible, but still relatively insignificant as compared to pure Pt film. No noticeable difference in surface morphologies among the three PtNi compositions was observed at all temperatures. Our observation showed that PtNi alloy cathode indeed has effectively suppressed the surface agglomeration, which is consistent with previous reports on pure Pt thin films^{46,88,89} and Pt alloy thin films.^{19,24}

Figure 4.4 FESEM images of (a) pure Pt, (b) $\text{Pt}_{88}\text{Ni}_{12}$, (c) $\text{Pt}_{75}\text{Ni}_{25}$, and (d) $\text{Pt}_{67}\text{Ni}_{33}$ as-deposited and annealed at 450, 600 and 800 °C for 12 hours

4.3.3 Evolution of crystal structure and grain size in annealed films

The effectiveness of alloying on hindering thermal agglomeration was further verified by examining the grain growth within the annealed films. Figure 4.5a showed the XRD patterns of nanoporous Pt films as-deposited and annealed at 300, 450, 600, and 800 °C for 12 hours. The typical FCC crystal structure was still observed. The as-deposited Pt film showed broader peaks, which is typical for materials with nanoscale grains. As the annealing temperature increased, the full width at half maximum of three corresponding crystalline faces became narrower, showing the grain growth within the films.

The grain size of the as-deposited and annealed Pt and PtNi films was calculated using Scherrer equation⁸² on (111) peak which has the highest intensity. Note that PtNi films retained their single phase structure after annealing at 800 °C, and the narrower full width at half maximum of three corresponding crystalline faces is the major difference before and after annealing. Figure 4.5b showed the average grain sizes against the annealing temperature. All the grain sizes in the nanoporous films increased with temperature as expected. For pure Pt, a significant grain growth occurred from 300 to 450 °C, which is not shown for all PtNi films. At annealing temperature above 450 °C, the significant grain growth for pure Pt has almost completed, while for all three PtNi compositions, the growth became obvious. This again confirms that the grain growth of Pt nanoparticles was effectively delayed by alloying Ni with Pt. It is noteworthy that Pt₆₇Ni₃₃ showed less obvious grain growth than Pt₈₈Ni₁₂, Pt₇₅Ni₂₅ from 600 to 800 °C, likely due to the sufficient Ni content that allows the formation of a more stable structure.

The definition of activation energy can be described as the minimum energy required for a potential reactant to start a chemical reaction. Activation energy can also be thought of as the height of the energy barriers, separating the reactants and products of a reaction. The activation energy for grain growth is the minimum energy barrier that the grains need to overcome for boundaries diffusion or grain growth. The higher activation energy for grain growth indicated the more difficult for the grain growth to occur.

Figure 4.5c is the plot of activation energy for Pt and PtNi alloy grain growth, the author followed the reported work⁹⁰⁻⁹³ to calculate the activation energy (Q , kJ/mol): $D_t = D_0 \exp(\frac{-Q}{RT})$, where D_0 and D_t are the initial and final grain sizes, R is the gas constant (kJ/degree · mol), T is the calcination temperature (K). The grain size of D_0 and D_t were calculated from the (111) diffraction peak (in Figure 4.5a and b) using Scherrer equation.⁸² The activation energy, Q can be obtained from the linear fitted slopes ($-Q/R$) in the plots of $\ln D_t - \ln D_0$ (Y-axis), v.s. $1/T$ (X-axis). Following the cited works about the calculation, the results were recalculated and shown below. In the plots, the $\text{Pt}_{67}\text{Ni}_{33}$ showed the highest activation energy of 46.5 kJ/mol compared to pure Pt and other two PtNi alloys, meaning the energy barrier for grain boundary diffusion in $\text{Pt}_{67}\text{Ni}_{33}$ electrode is higher, and the grain growth is more difficult to occur. This is attributed to the formed intermetallic crystal in $\text{Pt}_{67}\text{Ni}_{33}$ alloy. Lower activation energies were observed in the cells with less Ni amounts. This is because $\text{Pt}_{88}\text{Ni}_{12}$ and $\text{Pt}_{75}\text{Ni}_{25}$ are in the form of solid solutions, and the Ni atoms are still free to diffuse and migrate. The diffraction angle shift in XRD results (in Figure 4.3b) and Pt-Ni phase diagram⁹⁴ also supported the evidence that $\text{Pt}_{67}\text{Ni}_{33}$ has formed an intermetallic crystal while $\text{Pt}_{88}\text{Ni}_{12}$ and $\text{Pt}_{75}\text{Ni}_{25}$ are still in the form of solid solutions.

Figure 4.5 (a) XRD pattern of pure Pt, and (b) Average (111) grain size of pure Pt, Pt₈₈Ni₁₂, Pt₇₅Ni₂₅ and Pt₆₇Ni₃₃ thin films at elevated annealing temperatures; (c) activation energy of grain growth at elevated annealing temperatures.

4.3.4 Fuel cell performance of PtNi thin film cathode

The electrochemical performance of cells using pure Pt and Pt₆₇Ni₃₃ cathodes was compared at the beginning of the fuel cell operation and after 48 hours of operation. As seen in the I-V curves (Figure 4.6a), at the beginning of operation (at 0 hour), the cell using Pt cathode (Pt-0h) exhibited a peak power density of 1.23 mW/cm², and dropped to 0.6 mW/cm² at 48 hour (Pt-48h), which corresponds to a large power density loss of 51%. For the cell using Pt₆₇Ni₃₃ cathode, the peak power density was 1.15 mW/cm² at 0 hr (PtNi-0h) and dropped only 25% to 0.86 mW/cm² after 48 hours (PtNi-48h), showing the effectiveness of the electrode alloying for better thermal stability. Note that the low cell performance was majorly due to the high Ohmic resistance (~200 Ω cm², shown in Figure 4.6b) from the 200 μm-thick YSZ electrolyte substrate, and the cell performance can usually be amplified with a hundreds nanometer-thin electrolyte. The resistance of the electrolyte reduces dramatically as the electrolyte thickness reduces which are simply governed by Ohm's law: $V = I * R = I * (\frac{L}{A\sigma})$. Huang et al¹⁶ reported that I-V curves at 350 °C of micro-SOFCs consisting of 50, 100, and 150 nm YSZ electrolyte with both cathode and anode are 80 nm nanoporous Pt performed around 130, 80, 55 mW/cm² accordingly, and the significant small Ohmic resistance, less than 1 Ω cm², was observed in the cell of 50 nm-thin YSZ electrolyte.

The morphologies of Pt and Pt₆₇Ni₃₃ cathodes after 48 hours at 450 °C of the test were examined and shown in Figure 4.6a inserts. In the FESEM images, the Pt cathode showed serious surface agglomeration, while Pt₆₇Ni₃₃ remained a high density of nanoporous surface. In the HRTEM images, the grain domains on both Pt₆₇Ni₃₃ and pure Pt were clearly visible. The

average grain size of Pt is around 100 nm, much larger than that of Pt₆₇N₃₃ of around 9.45 nm, which reconfirmed the effective suppressing of grain growth by alloying Pt cathode with Ni.

Whether the improved retention of power density came from the alloyed cathode was further confirmed by EIS characterization. The polarization resistance (R_p) of all cells can be extracted from the Nyquist plot (Figure 4.6b), which is the difference between the two intersects at Z'_{real} . Both the R_p values of Pt and Pt₆₇N₃₃ cathodes increased after 48 hours of operation. The increase of resistance R_p from Pt-0h to Pt-48h is 366 $\Omega\text{ cm}^2$, which is much higher than 162 $\Omega\text{ cm}^2$ from PtNi-0h to PtNi-48h. The less R_p increase in the Pt₆₇N₃₃ cathode can be a direct evidence on the improved thermal stability of the alloyed cathode. In addition, replacing Pt with Ni in the cathode did not deteriorate the cathode kinetics. The R_p values are 361.4 $\Omega\text{ cm}^2$ for Pt-0h and 237.8 $\Omega\text{ cm}^2$ for PtNi-0h, showing improved cathode performance by Ni alloying. Wang et al⁴⁹ also reported that alloying Ni with Pt to form Pt_{0.7}Ni_{0.3} decreased the electrode impedance, based on quantum simulation results by *ab initio* calculation. Note that the extracted R_p value here was taken to mainly account for the cathode polarization resistance because of the rather smaller polarization resistance of hydrogen oxidation on Pt anode.

The corresponding Bode plot (Figure 4.6c) further gives the characteristic frequencies of the cathode processes affected by the cathode agglomeration. The increase in phase angles at low-frequency region (10^{-1} - 10^2 Hz) was observed for both Pt and Pt₆₇N₃₃ after 48 hours of operation and is more pronounced for the cell using Pt cathode. Usually, the phase angles in this frequency range for a Pt/YSZ system are related to the non-charge transfer processes on the cathode surface including gas diffusion and oxygen dissociative adsorption.^{72,73} The observed increase in phase angle delay at the low-frequency region is attributed to the less surface area for the difficulty of gas diffusion due to loss of electrode porosity.

Figure 4.6 (a) I-V curves of the cell using Pt and Pt₆₇Ni₃₃ cathodes tested at 0 and 48 hours; and microscopy images of FESEM and HRTEM for Pt and Pt₆₇Ni₃₃ cathode after 48 hours fuel cell test at 450 °C; (b) Nyquist plots; and (c) Bode plots of the cell using Pt and Pt₆₇Ni₃₃ cathode at 0 and 48 hours.

4.4 Chapter summary

The alloying of Ni with Pt nanoporous thin film cathode has effectively improved the performance stability of low-temperature solid oxide fuel cells operating at 450 °C by impeding the thermally-driven agglomeration of the cathode nanoparticles. The grain growth, which indicates the agglomeration of the nanoparticles, were constrained, as observed by comparing the grain sizes in bulk of film between pure Pt and PtNi alloy cathodes. The temperature required to drive significant grain growth in nanoporous PtNi thin film was about 150 °C higher than in pure Pt, showing PtNi alloyed cathodes are more resistive to thermal agglomeration. The fuel cell using Pt₆₇Ni₃₃ as the thin film cathode showed only 25% of performance degradation after 48 hours of operation as compared to 50% and 86% of reported loss in cells using pure Pt cathodes, and the increase in polarization resistance was less than half of that for the cell using Pt cathode. The constrained grain growth by alloying with Ni maintained the porosity in bulk of cathode film for sufficient oxygen diffusion and adsorption/dissociation processes in cathode reactions. The *in-situ* characterization of fuel cell test can clearly disclose a relation of thermally-stable alloy structure towards better cathode ORR for a potential construction of durable LTSOFCs electrode.

Chapter 5

5. Thermal Stability Enhancement of Nanoporous Platinum Cathode by O₂ Plasma Etching

5.1 Introduction

Nanoporous platinum (Pt) thin films deposited on yttria-stabilized-zirconia (YSZ) substrate are one of the traditional electrode-electrolyte systems in miniature solid state electrochemical devices, such as micro-solid oxide fuel cells (μ -SOFCs) operating at a temperature of 300-500 °C, which is also named as low-temperature solid oxide fuel cells (LTSOFCs) due to the low operating temperature. Pt shows the highest catalytic activities among all pure metals for the rate-limiting cathode oxygen reduction reaction. The surface area of porous Pt electrode enables a high energy conversion efficiency at low electrode polarization and provides a high power output of the fuel cell. For LTSOFCs operated at temperatures below 500 °C, the sluggish cathode ORR becomes the most rate-limiting process. The oxygen incorporation from the Pt electrode into the YSZ electrolyte at the vicinity of the Pt/YSZ/O₂ junctions (or the triple phase boundaries, TPBs where effective reactions occurred) is believed to be one of the slowest ORR steps. Because the interface between the Pt thin-film electrode and YSZ electrolyte is two-

dimensional, the effective TPBs for ORRs are only located at the Pt pore boundaries on the surface of the YSZ substrate (i.e., TPBs). Therefore, a high density of TPB sites at the Pt/YSZ contact interface is critical to obtain high device performance. However, the severe thermally-driven agglomeration of nanoporous Pt at the Pt/YSZ interface was reported in literature³⁹ and was also found in our observation. It is reported the thermally-driven morphological evolution between the top surface and the substrate contact interface of agglomerated nanoporous Pt electrode using double cantilever beam technique. The agglomeration behavior of Pt is different from the top surface and the substrate contact interface. It is found that the temperature required for significant agglomeration to occur was approximately 100 °C higher at the electrolyte contact interface side than at the top surface side. This is because the unbounded surface of Pt is free to migrate under the thermally driven effect whereas the bonded interfacial Pt to the electrolyte experienced a constraint to migrate. In our observation shown in Figure 5.1, the annealed ALD-ZrO₂ capped nanoporous Pt had severe agglomeration occurred at the Pt/YSZ interface and formed an obvious gap after annealing at 600 °C while the top surface showed slight agglomeration. The Pt/YSZ interfacial agglomeration was considered to impede the oxygen ions incorporation for cathode ORR and reduce the fuel cell performance. In this chapter, we proposed an approach of O₂ plasma etching technique to create hydroxyl groups on the electrolyte surface for better adhesion between Pt electrode and YSZ electrolyte at the operation temperature for LT-SOFCs. The modification was found to inhibit Pt agglomeration at YSZ contact interface, strengthen adhesion force, and enhance cathode ORR activity.

Figure 5.1 FESEM images of ALD-ZrO₂ capped nanoporous Pt thin films before and after annealing at 600 °C for 12 hours in the view of top surface (a and b) and cross-section view (c and d)

5.2 Experimental

The surface of a 200 μm -thick (100) single crystal YSZ electrolyte was etched with oxygen plasma to improve the adhesion between the sputtered Pt/PtNi cathodes and YSZ. The O₂ plasma etching was performed for 1, 3 and 5 minutes at a high power of 600 watts and 300 mTorr of oxygen pressure. Nanoporous platinum cathodes (100 nm-thick) were then deposited on etched YSZ substrates using radio frequency sputtering. The sketch of nanoporous Pt electrode on (a) un-etched and (b) etched YSZ substrate was shown in Figure 5.2.

Figure 5.2 Sketch of nanoporous Pt electrode on (a) un-etched and (b) etched YSZ substrate

The change of surface property of YSZ after oxygen plasma etching was initially verified by measuring the static contact angle between water and YSZ. A 1 μL de-ionized water droplet was placed on the etched YSZ surfaces, and the contract angle was measured from the captured images. X-ray photoelectron spectroscopy (XPS) was used to verify the chemical state of O_{1s} after etching.

The difference of adhesion force between Pt and YSZ before and after plasma etching on YSZ was measured by using a Pt-coated atomic-force microscopy (AFM) tip to contact on the etched and unetched YSZ electrolyte directly. The forces of the AFM tip leaving the YSZ surfaces were recorded.

A customized chamber equipped with a temperature controller, a fuel supply controller and a probe testing station was used to obtain the fuel cell operation condition. The test cells were set at 450 $^{\circ}\text{C}$, using pure hydrogen (99.99%) as fuel at a flow rate of 20 sccm and ambient air as the oxidant. The current was drained at a reference cell voltage of 0.5 V, at which is the voltage of the peak power density. The current-voltage curves (I-V curves) and electrochemical impedance spectroscopy (EIS) of the cell with un-etched and O_2 plasma etched electrolyte were captured at operation time of 0 and 12 hours using an electrochemical potentiostat (Solartron Analytical, UK). The dynamic behavior was applied using a sinusoidal AC voltage with the amplitude of 20 mV on top of a 0.5 V of DC bias for a range of frequency (0.1 $\sim 10^5$ Hz).

5.3 Results and Discussion

5.3.1 Effect of improved Pt cathode/electrolyte adhesion

We first verified that the adhesion between Pt and YSZ were indeed improved after the O₂ plasma treatment on YSZ surface. Figure 5.3a showed the change of contact angle between water and YSZ with O₂ plasma etching time. The contact angle of pristine YSZ was 80.9°, and it was 28.1°, 18.9° and 16.1° after 1, 3 and 5 minutes of etching, showing the more hydrophilic nature as etching time increases. The more hydrophilic surface usually indicates higher electronegative surface and are more readily to attach to other partial charged species or polar molecule (*e.g.* water).

Figure 5.3b showed the selected XPS spectra (C_{1s} and O_{1s}) of the pristine and 1 minute-O₂ plasma etched YSZ electrolyte. Both the pristine and O₂ plasma etching electrolytes showed a similar C_{1s} and O_{1s} spectrum with the bonding of C-C, O-C=O, and O-C, which comes from the atmosphere carbon species.⁹⁵ The additional peaks appeared at a binding energy of 532.4 eV is the characteristic of the hydroxyl group (OH⁻) which was functionalized by high energy O₂ plasma etching under moisture-less atmosphere. The free radical from the OH⁻ group and the electrostatic interaction of OH⁻ group to Pt surface activated the inert nature of YSZ surface and provided an attractive medium to sputtering Pt electrode.⁹⁶⁻⁹⁸

Figure 5.3 (a) Microscopy of static contact angle by water droplet on pristine and 1, 3 and 5 minutes O_2 plasma etched YSZ surface; (b) Selected XPS spectra (C_{1s} and O_{1s}) of the pristine and 1 minute- O_2 plasma etched YSZ electrolyte

Nevertheless, the water droplet wetting test did not give direct evidence of improved adhesion. Therefore, we used AFM to directly measure the actual adhesion force between Pt and YSZ. Force curves are plots of the deflection of the cantilever (force) versus the extension of the piezoelectric scanner (sample displacement); the cantilever spring constant is 0.4 N/m, then the force can be calculated based on the Hookes' law.⁹⁹

The sputtered Pt coated AFM Tip was probed on the YSZ substrate for the adhesion measurement, which can simulate the adhesion behavior between sputtering Pt cathode and YSZ electrolyte. Figure 5.4a showed typical curves of attraction/adhesion force versus sample displacement.⁹⁹ Section a-d represents the curve of the probe approaching to substrate while section d-h represented the curve of the probe withdrawing from the substrate. The zero line of force is obtained when the probe is far from the YSZ substrate, and the cantilever deflection is close to zero. The most interesting regions of the force curve are the regions of the jump-to-contact (JTC) and the jump-off-contact (JOC), which can refer to attraction force and adhesion force respectively. The non-contact region in the approaching curve provides information about attractive force before contact, and this discontinuity (b-c) occurs when the Pt-YSZ force exceeds the spring constant of the cantilever. The maximum forward deflection of the cantilever multiplied by the effective spring constant of the cantilever is the Pull-on Force. The non-contact region in the withdrawal curve provides information about adhesion force after contact, and this discontinuity (f-g) that occurs when the cantilever's spring constant is greater than the Pt-YSZ adhesion forces. The maximum backward deflection of the cantilever multiplied by the effective spring constant of the cantilever is the Pull-off Force. The adhesion force measurement by AFM technique was calculated and shown in the Figure 5.4b, the etched YSZ surface showed higher adhesion force to Pt than un-etched YSZ, although no significant trend was observed among 1, 3,

and 5 minutes of etching. Therefore, 1 minutes of etching was selected for the simplicity of process.

Figure 5.4 (a) Curve of AFM probe approaching and withdrawing YSZ surface illustrating the approach section (a-d) and withdrawal section (d-h) where jump-to-contact (b-c) and jump-off-contact (f-g) occur. (b) Adhesion force between Pt electrode and YSZ surface

5.3.2 Direct morphology observation on Pt/YSZ interface

The morphology of nanoporous Pt at electrolyte contact side was directly observed by using double cantilever beam technique¹⁰⁰ to delaminate Pt electrode from YSZ electrolyte, and the observed Pt morphology can refer to effective TPBs density^{39,49} where oxygen ions incorporation from the Pt cathode into the YSZ electrolyte at the vicinity of the Pt/YSZ/ O_2 junctions. Figure 5.5 sketch showed the Pt morphologies viewed from the electrolyte contact interface on the cell with YSZ electrolyte surface un-etched (Figure 5.5a and c) and etched with 1 minute of O_2 plasma (Figure 5.5b and d), before and after annealing at 600 °C. Nanoporous morphologies were shown on both the cells with O_2 plasma etching and un-etched cell before annealing, indicating a good contact between Pt and YSZ which can provide sufficient ion incorporation pathways. After an annealing temperature of 600 °C for 12 hours, a severe thermally-driven Pt agglomeration occurred on the electrolyte contact surface of the un-etched cell (Figure 5.5c). The

thermal agglomeration had decreased the TPBs length and impeded the ion incorporation, resulting in the loss of fuel cell performance. As expected, O₂ plasma etching treatment maintained the nanoporous Pt features on electrolyte contact interface after 600 °C annealing (Figure 5.5d). This is because the OH⁻-rich YSZ surface can form a strong chemical adsorption bonding of Pt-OH which can restrict the thermally-driven Pt migration. Therefore, retained nanoporous Pt features on the electrolyte contact interface and enhanced interfacial adhesion forces were found in the cells of the O₂ plasma etched YSZ as a comparison to un-etched YSZ. O₂ plasma etching treatment have certainly hindered the thermally-driven Pt agglomeration on YSZ electrolyte contact interface.

Figure 5.5 FESEM of nanoporous Pt viewed from the electrolyte contact interface on the cell with YSZ electrolyte surface un-etched (a and c) and etched with 1 minute of O₂ plasma (b and d), before and after annealing at 600 °C.

5.3.3 Fuel cell stability and cathode performance by O₂ plasma etching

Figure 5.6a showed the curves of the current output with time of cells with YSZ electrolyte surface un-etched and etched with 1 minute of O₂ plasma. Both cells went through a significant current drop at the first hour and then current stabilization. The cell with 1 minutes-O₂ plasma etched YSZ have dropped the current of 11.8% upon stabilization, while the cell with un-etched YSZ has dropped the current of 19.1%. The major difference between two cells is possibly due to the preservation of the nanoporous Pt features on the electrolyte contract interface by O₂ plasma etching, which can retain TPBs and the ion incorporation pathways. Figure 5.6b showed the Nyquist plots retrieved at 0 and 10 hour of the continuous fuel cell testing with cells of YSZ surface un-etched and etched with 1 minute of O₂ plasma. We ascribed R_{ohm} (the value of Z'_{real} on $-Z''_{image} = 0$ at high frequency region) to the resistance of ion conduction through the electrolyte and ion incorporation from electrode to electrolyte. The increase of R_{ohm} is solely from the behavior of ion incorporation because both cells were deposited on the same piece of YSZ substrate to eliminate the variation of the ion conductive resistance. The R_{ohm} of the Nyquist plots on both cells at 0 hours are nearly the same, and the increased of R_{ohm} is approximately 20 % lower in the cell of O₂ plasma etched YSZ than the un-etched cell, meaning a 20% reduction of ion incorporation resistance. Additionally, the polarization resistances (R_p) of the cells can be extracted from the Nyquist plot, which is the difference between the two intersects at Z'_{real} . Both the R_p values of cell un-etched and etched with 1 minute of O₂ plasma increased after 10 hours of operation. The R_p of the etched cell showed a suppressed increase after 10 hours continuous operation.

Figure 5.6 (a) Current output over time and (b) Nyquist plots of 10 cycles ALD-ZrO₂ capped nanoporous Pt cathode on the cell with YSZ electrolyte surface un-etched and etched with 1 minute of O₂ plasma.

5.4 Chapter summary

The better Pt/YSZ interfacial adhesion obtained by O₂ plasma etching showed improvement in the thermal stability of low-temperature solid oxide fuel cells at the operating temperature below 500 °C. The actual adhesion force measured by AFM showed higher adhesion force in Pt/YSZ with 1, 3, and 5 minutes of O₂ plasma etching. The adhesion force is approximately 25% higher in the cell of 1 minute etching than un-etched cell by 9 nano Newton. The nanoporous morphology at the electrolyte contact interface was directly observed, and results showed a retained TPBs density after high temperature annealing is higher at the cell with O₂ etched than the un-etched cell. The hydroxyl group on the YSZ which was functionalized by high energy O₂ plasma etching dominated the improved adhesion between Pt and YSZ. The performance stability of cells using O₂ plasma etched YSZ at 450 °C were improved, showing better power retention by 8 %. The improved adhesion of Pt/YSZ interface has suppressed the increase of the contact resistance and lead to sufficient oxygen ion incorporation during the fuel cell operation.

Chapter 6

6. Nanoporous Metal Thin Film Cathode with Superior Thermal Stability for Low-Temperature Solid Oxide Fuel Cells

6.1 Introduction

The agglomeration of the sputtered Pt film occurred at three sections: (1) the unbounded surface, (2) the film interior, and (3) the Pt/YSZ interface, and the proposed methods including ALD-ZrO₂ capping on top surface of Pt, alloying Ni with Pt, and O₂ plasma etching have confirmed the enhancement of thermal stability accordingly in chapter 3, 4 and 5 of this thesis. This chapter applied a comprehensive fabrication process, which combined three above-discussed three methods to obtain a thermal stable nanoporous metal cathode with low performance degradation rate for LTSOFCs operating at temperatures lower than 500 °C. The targeted rate of 0.013% per hour was set up, following the U.S. Department of Energy's durability targets for fuel cell as a portable power sources with 20% loss within 1,500 hours.

Figure 6.1 illustrated the three strategies for different agglomeration sites of nanoporous metal cathode, and the detail fabrication flow was described in the experimental session 6.2.

Figure 6.1 (a) Sketch of sputtered nanoporous Pt cathode; (b) Sketch of metal cathode combine with approaches of O_2 plasma etching on the YSZ interface, the interior PtNi alloy, and ALD- ZrO_2 capped surface.

6.2 Experimental

The fuel cell fabrication started from sputtering a nanoporous Pt as a catalytic anode on the bottom side of a 200 μm -thick (100) SC-YSZ electrolyte. The YSZ and the nanoporous Pt anodes were annealed at 450 $^{\circ}\text{C}$ for 12 hours to intentionally drive the anode agglomeration to prevent it from affecting the overall current stability over time.

The cathode was then fabricated onto the Pt-annealed anode/YSZ with the following sequence: (1) O_2 plasma etching on the front side of YSZ; (2) sputtering of nanoporous PtNi onto the O_2 plasma-etched YSZ; (3) surface capping of sputtered PtNi with ALD- ZrO_2 . The flow of cell fabrication is illustrated in Figure 6.2.

The current stability of the fuel cell over time was recorded to verify the effectiveness of the methods in preventing agglomeration in nanoporous cathode. The current was drained at a reference cell voltage of 0.5 V, at which is the voltage of the peak power density to monitor the change of cell performance and impedance over time.

Figure 6.2 Flowchart of fuel cell fabrication

6.3 Results and discussion

The current stability of the proposed cells was monitored at a temperature of 450 °C for continuous fuel cell operation with a drain voltage of 0.5V. Figure 6.3a showed the evaluation of the cell current density over time. At the beginning of the testing, the cell with ALD-ZrO₂ capped PtNi cathode on O₂ plasma etched YSZ showed the highest current output among all cells, which is around 70% improvement compared with the cell with pure Pt cathode. The performance improvement is a combinational effect of the facilitated oxygen adsorption-dissociation on the cathode surface, and the enhanced ion incorporation process at the cathode/YSZ interface. The current density between the cell with pure Pt cathode and the cell with ALD-ZrO₂ capped PtNi cathode on O₂ plasma etched YSZ have 5.3 times difference as testing time increase to 60 hours, which means a better power retention was obtained by the cathode with comprehensive fabrication process. The cell current degradation over time was normalized and shown in Figure 6.3b. The overall current degradation of the cell with pure Pt cathode is 72.3 % over 60 hour operation as the degradation rate is around 1.2%/hour. The cell with ALD-ZrO₂ capped Pt cathode, and ALD-ZrO₂ capped Pt₆₇Ni₃₃ cathode, has degraded for 27.8% and 17.3% respectively upon current stabilization. Meanwhile, the cell with ALD-ZrO₂ capped PtNi cathode on O₂ plasma etched YSZ exhibited an ultra-low performance loss of 9.8% after 120 hours continuous fuel cell operation, referring to a low performance degradation rate of 0.081%/hour. The low degradation rate is a combinational effect of surface confinement, limited grain growth in bulk of film and enhanced cathode/electrolyte adhesion at high operation temperature. Additionally, the effectiveness of three respective methods can be ranked as ALD-ZrO₂ capping > PtNi alloy > O₂ plasma etching. The present work is dedicated to achieving a thermally stable nanoporous metal cathode with low performance degradation rate less than

0.013% per hour for LTSOFCs operating at a temperature of 300-500 °C, following the United States Department of Energy target that 20 % loss within 1,500 hours. Performance loss of 20% can be set as the lifetime of the testing cell. As shown in Figure 6.3b, the lifetime of pure Pt cell is 3 hour, and the lifetime of cell with ALD-ZrO₂ capped PtNi cathode on O₂ plasma etched YSZ is much higher than 120 hour. The durability of the cell with developed metal cathode has increased more than 40 times, compared to the cell with pure Pt cathode. Furthermore, the 120 hour continuous operation is not the limited of the cell. The current degradation rate of 9.8% @ 120 hours estimates that over 500 hour lifetime can be easily achieved until 20% performance loss since the current stabilized until 10 hours with around 8% performance loss. Regarding the practical and cost issue in implementing three developed methods for a single cell fabrication, the developed methods in this study for fabricating thermally stable metal electrode are easily to attach onto the current fabrication process since the ALD-ZrO₂, PtNi sputtering, and oxygen plasma etching are all easily-accessible equipment in both mass-production line of lab-scale batch production. The cost of the developed cell in lab-scale batch production is estimated to be around 15% higher than pure Pt cell. This was calculated by the fabrication per batch based on the equipment charge fee of NTU-cleanroom. Only two times of sputtering are required for the cell of pure Pt, while the developed cell need to add on one ALD process and one O₂ plasma etching.

Figure 6.3 (a) Evaluation of the cell current density and (b) Normalized cell current degradation percentage as a function of time.

6.4 Chapter summary

We have successfully demonstrated a new platinum-based cathode for LTSOFCs with superior thermal stability by three fabrication methods to constrain the thermal agglomeration of the vulnerable nanoporous cathode. The fuel cell performance of the proposed cathode can sustain both high current output and low degradation rate of 9.8 % over 100 hours continuous operation. The corresponding enhancement from three fabrication methods in this study was summarized briefly: 1.) O₂-plasma etching has retained the nanoporous Pt features on the electrolyte contact interface after annealing at 600 °C. The suppressed cathode ORR can originate from the enhanced adhesion between Pt electrode and YSZ electrolyte to secure the oxygen ion incorporation pathway; 2.) Ni alloyed Pt cathode has constrained the grain growth in the bulk of film at elevated temperatures. The temperature required for significant grain growth to occur is approximately 150 °C higher on PtNi alloys than on pure Pt, and the grain size of Pt-Ni alloys can retain nearly the same at the operating temperature of 450 °C. The benefit of alloying Ni to Pt can majorly be ascribed to a consistent microstructure which maintained sufficient gas diffusion pathways for cathode ORR; 3.) Nanoscale ALD-ZrO₂ capping has provided a physical confinement on the nanoporous Pt surface and inhibits the thermal agglomeration under long duration. Few nanometers thin ALD-ZrO₂ film attached on Pt surface can assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface which facilitates the oxygen dissociative-adsorption process; 4.) Overall current stability of the cell with ALD-ZrO₂ capped Pt-Ni cathode on O₂ plasma etched YSZ electrolyte shows an ultra-low current degradation of 9.8% over 100 hour continuous operation. Moreover, an improved cathode ORR was found to be 70% higher at the beginning of the continuous testing and 4.3 times greater upon current stabilization as compared to the pure Pt cathode.

Chapter 7

7. Conclusions and Future works

7.1 Conclusions and Contributions

This work is dedicated to achieving a highly thermal stable metal cathode for LTSOFCs operating at a temperature lower than 500 °C, with a target set up by United States Department of Energy's for fuel cell as a portable power sources with 20% loss within 1500 hours, referring to performance degradation rate of 0.013%/hour. This work also demonstrated the continuous fuel cell mode operation up to 120 hours, showing both improved performance output and low performance degradation. Three fabrication methods have been proposed to refrain nanoporous Pt cathode from thermal agglomeration: (1) on the unbounded surface, (2) the film interior, and (3) at the Pt/YSZ interface, and the effectiveness of the methods were substantiated. The origin of the cathode ORR enhancement and performance retainess during long operation were presented and elaborated.

Firstly, few nanometers-thin of ALD-ZrO₂ capping on nanoporous Pt cathode have effectively hindered the thermally-driven agglomeration on the cathode surface, and the fuel cell with low 10-cycle capped (1.3nm thin) Pt cathode, had retained the fuel cell performance by more than 50% after 120 hours continuous operation at 450 °C, compared to uncapped Pt cathode. 10 and 15-cycle ALD-ZrO₂ attached on Pt surface can assist the oxygen adsorption onto the oxygen-adsorbing favorable ZrO₂ surface, and promote oxygen adsorption and dissociation

for cathode ORR. The benefit brought by ALD-ZrO₂ capping on cathode ORR can be optimized by carefully controlling the ZrO₂ coverage on Pt to maximize the oxygen adsorption/desorption without sacrificing the gas diffusion and oxygen surface migration.

Secondly, the alloying of Ni with Pt nanoporous thin film cathode has effectively impeded the thermally-driven agglomeration of the nanoparticles in bulk of cathode film. The grain growth, which indicates agglomeration of the nanoparticles, were constrained, as observed by comparing the grain sizes between pure Pt and PtNi alloy cathodes. The temperature required to drive significant grain growth in nanoporous PtNi thin film was about 150 °C higher than in pure Pt, showing PtNi alloyed cathodes are more resistive to thermal agglomeration. The fuel cell using Pt₆₇Ni₃₃ as the thin film cathode showed only 25% of performance degradation after 48 hours of operation, and the increase in polarization resistance was less than half of that for the cell using Pt cathode. The constrained grain growth by alloying Ni with Pt maintained the porosity in bulk of cathode film for sufficient oxygen diffusion and adsorption/dissociation processes in cathode ORR.

Thirdly, the better Pt/YSZ interfacial adhesion obtained by O₂ plasma etching showed thermally stable Pt cathode at the operating temperature below 500 °C. The hydroxyl groups which were functionalized by high energy O₂ plasma etching on the YSZ have improved Pt/YSZ adhesion force by 25%, and have effectively retained the nanoporous Pt morphology at the electrolyte contact interface. The fuel cells using O₂ plasma etched YSZ exhibited better power retention by 8 % than the cell with un-etched YSZ at an operation temperature of 450 °C. The improved Pt/YSZ interfacial adhesion had suppressed the increase of the contact resistance and meanwhile led to sufficient oxygen ion incorporation between Pt and YSZ.

Overall current stability of the cell with ALD-ZrO₂ capped PtNi alloy cathode on O₂ plasma etched YSZ electrolyte showed an ultra-low current degradation of 9.8% over 100 hour continuous operation (0.098%/hour), which is the lowest value in the reported work so far. Moreover, an improved cathode ORR was found to be 70% higher at the beginning of the continuous testing and 4.3 times greater upon current stabilization as compared to the pure Pt cathode. The three proposed strategies, including ALD-ZrO₂ surface capping, PtNi alloy film, and O₂ plasma etching on Pt/YSZ interface in this thesis effectively inhibits thermal-driven agglomeration of nanoporous Pt, which provides a potential construction of durable LTSOFCs cathode.

The main contributions of this thesis are: (1) demonstrates a high fuel cell performance and ultra-low degradation LTSOFCs using nanoporous metal cathode; (2) substantiates the effectiveness of proposed strategies toward improved thermal stability and enhanced cathode oxygen reduction reaction at different agglomeration site of nanoporous Pt cathode; (3) provides a instruction of designing a thermally stable nanoporous metal cathode for potential applications; (4) elaborates the mechanism of few nanometers ZrO₂ capped Pt facilitates oxygen adsorption/desorption process; (5) discussed the effect of alloying Ni toward the thermally-driven grain growth in bulk of Pt thin film; (6) explains the mechanism of O₂ plasma etching enhances the thermal stability of Pt/YSZ interface.

7.2 Suggested future work

This thesis demonstrated three effective strategies to enhance thermal stability on different agglomeration sites of nanoporous Pt cathode for LTSOFCs operating at a temperature lower than 500 °C. The effectiveness of the methods including ALD-ZrO₂ capping confined the nanoporous Pt surface, PtNi alloy constrained the grain growth in bulk of film, and O₂ plasma etching enhanced the interfacial Pt/YSZ adhesion have been discussed. The conclusions from this thesis suggested the potential future research directions:

- **Develop durable micro-SOFCs with nanoscale thin film electrolyte**

In this thesis, the knowledge of superior thermal stability of nanoporous Pt cathode was established based on the 200 μm-thick bulk YSZ electrolyte substrate. Although an ultra-low power degradation rate was obtained, the power output is still relative low due to thick electrolyte substrate. The concluded methods in this thesis are potential to be used in a nanometer-thin YSZ electrolyte to demonstrate an ultra-high performance with ultra-low power degradation micro-SOFCs. The ultra-thin YSZ substrates can be obtained via semiconductor manufacturing technique. Fig. 7.1 showed the fabrication steps, and the step of atomic layer deposited-YSZ is the most critical part to control the thickness of YSZ electrolyte. Besides, micro-SOFCs have been demonstrated the potential as a portable power source because of miniature size, light weight, scalability, and low cost for mass production. Micro-SOFCs will be a more approachable portable power by applying the developed thermally-stable metal cathode on a tens of nanometer thin YSZ.

- **Develop thermally-stable nanoporous anode for LTSOFCs**

In this thesis, the knowledge of superior thermal stability of nanoporous Pt cathode was studied firstly for durable LTSOFCs. The Pt anode was purposely annealed to eliminate the interference from anode and to interpret the phenomenon from cathode precisely. However, the thermal stability of LTSOFCs anode is also important since the anode can oxidize alternative fuel (*e.g.* hydrocarbon), and the corresponding exothermic reaction is considered to trigger worst thermal stability than cathode. Therefore, the ALD-capping and alloying methods provide a strategy for selecting alternative anode material for the corresponding fuel oxidation reaction. For example, Pt/SnO₂ nanocomposites anode was demonstrated for direct ethanol oxidation at an operating temperature less than 200 °C, and it is worth to have ALD-SnO₂ capping on Pt anode

to achieve a thermally-stable anode for ethanol oxidation. The co-sputtering anode material like Pt-Ru, Pt-Sn, Pt-Pd, etc. are also considered a potential anode material to further obtain a thermally-stable electrocatalyst.

- **Develop non-noble metal electrode material for LTSOFCs**

Currently, noble metal cathodes with high activities such as platinum or its alloys with a high density of nanoscale pores are still common choices for a demonstration to high fuel cell performance. But the high cost using platinum always impedances the application. This study has demonstrated the potential of using Ni as an alloy material to increase thermal stability and effectively reduce the usage amount of Pt. The effect of cost reduction will be more significant as operation time increased. The outcome of this study may recommend adding one more active cathode nanoparticles, like LSCF, LSC. The nanosize cathode dopants may potentially exhibit improve ORR at such a low operation temperature for LTSOFCs.

Appendix A

Nanoporous SnO₂ Anode for Direct Ethanol Low- Temperature Solid Oxide Fuel Cells

A.1 Introduction

Direct ethanol fuel cells (DEFCs) are a new source of energy which can convert the energy through electro-oxidation of ethanol, into electrical energy. DEFCs allow the usage of easy handling and storage of high energy density liquid ethanol; therefore provide a promising alternative to gaseous hydrogen fuel cells in portable applications.^{101,102} The DEFCs rely upon the oxidation of ethanol on an electrocatalyst layer and water is consumed at the anode to form carbon dioxide, while oxygen reduction reaction occurs at the cathode. The generated electrons are transported through an external circuit from anode to cathode, providing power to connected devices. The advantages of DEFCs are the fact that a supply chain is already available and that ethanol can be generated from some sources, particularly biomass like sugar cane, wheat, and corn. The benefit of using biological sources to produce ethanol is that it can reduce the overall amount of carbon dioxide released by a fuel given that plants absorb carbon dioxide.

Ethanol has several advantages when compared with other alcohol, namely the low toxicity, higher theoretical energy density (8.0 kWh kg^{-1}) and, mainly the fact that it can be produced from renewable biomass energy. The complete ethanol oxidation to CO_2 involves 12 electrons per molecule, but at low temperature the kinetics of ethanol electro-oxidation is slow and produces different intermediates such as acetaldehyde, acetic acid, and adsorbed carbon monoxide, reducing considerably the fuel cell efficiency in practical applications.

Increasing the operating temperature of DEFC is advantageous to the ethanol oxidation reactions. The need for highly active catalysts for the ethanol oxidation reaction (EOR) that takes place at anode at a temperature range of $200\text{--}400^\circ\text{C}$ is the main challenge in the development of DEFCs. Pt-based catalysts are commonly used in low temperature polymer electrolyte DEFCs due to its high catalytic activity towards ethanol. However, the poisoning of Pt catalysts, e.g. carbon monoxide arouses performance degradation, leading to lower fuel utilization and cell performance. Also, it requires for the excess of Pt loading for efficient fuel oxidation.^{103,104} Recently, Pt alloy electrocatalysts, like Sn, Ru, Rh, Ir, Cu, Mn, Cr^{104–110} and Pt cermet, like SnO_x ^{111–114} were studied widely for on both purposes of the reduction of noble metal usage and a sustainable ethanol oxidation electrocatalysts property at a temperature below 200°C . SnO_2 was considered a good candidate for ethanol oxidation at a temperature higher than 200°C among the electrocatalysts because of its low price, high thermal stability, poison resistive and potential to EOR. SnO_2 has high surface area, which can help to reduce the amount of Pt required for ethanol oxidation. SnO_2 has high thermal and chemical stability which is not prone to catalyst poisoning, which happens severely in the presence of Pt. SnO_2 can also enhance the efficiency of the conversion of ethanol to CO_2 due to intermediates adsorption at low potentials. It is also cost effective and more viable than other electrocatalyst.

In this study, preparation and characterization of SnO₂ were evaluated as ethanol oxidation electrocatalysts for solid oxide fuel cells operating at a temperature range of 300-500 °C. The vacuum technique base deposited SnO₂ thin film were prepared by RF sputtering. The characterization of SnO₂ thin films were investigated, including surface morphology, crystallinity, porosity and electric conductivity. At the same time, ethanol oxidation reaction of SnO₂ anode was compared with pure Pt under direct ethanol-fed fuel cell operation at high temperature.

A.2 Experimental

A.2.1 SnO₂ thin film preparation

Nanoscale SnO₂ thin film was sputtered on silicon substrates using radio frequency sputtering at a fixed power of 100 W, 30 and 1 mTorr of argon pressure and post-annealing temperature of 400 and 600 °C to control the surface morphology of dense or porous.

A.2.2 Material Characterization

The compositions of the as-deposited SnO₂ thin films were examined by energy-dispersive spectroscopy (EDS, OXFORD). The surface morphologies of the as-deposited SnO₂ thin films were observed by field emission scanning electron microscopy (FESEM, JOEL-7600F). The crystal structure and lattice parameters of the as-deposited and annealed PtNi thin films were determined by X-ray diffractometer (XRD, PANalytical Empyrean). The composition and chemical states of as-deposited SnO₂ films were determined using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with a monochromatic AlK α (1486.71 eV) X-ray radiation (15 kV/10 mA). The sheet resistance of the as-deposited thin films was measured by four-probe type multimeter.

A.2.3 Direct ethanol LTSOFCs testing

The fuel cell fabrication started from sputtering a nanoporous Pt as a catalytic cathode on the bottom side of a 200 μm -thick (100) single crystal yttria-stabilized-zirconia electrolyte. The substrates of nanoporous Pt cathode on YSZ were annealed at 500 $^{\circ}\text{C}$ for 12 hours to intentionally drive the anode agglomeration to prevent it from affecting the overall current output. The as-deposited SnO_2 thin films was then sputtered as an anode on the top side the substrate of YSZ/annealed Pt cathode, and the complete cell with SnO_2 anode/YSZ/Pt cathode was ready for testing. Figure A.1 sketched the fuel cell test station with customized direct ethanol vapor feeding.

Figure A.1 Fuel cell test station with customized direct ethanol vapor feeding.

A.3 Results and discussion

A.3.1 Surface morphology of as-deposited SnO_2 thin film

The FESEM images in Figure A.1 showed the surface morphological evaluation of RF sputtering SnO_2 with process pressure of 1 and 30 mTorr, and process temperatures of room

temperature, 400 and 600 °C. The as-deposited films showed two different surface morphologies based on the different process pressures. The process temperature was employed on the sputtering substrate to provide an in-situ sintering influence. Figure A.2a showed FESEM image of the SnO₂ sputtering with a process pressure of 30 mTorr at different process temperature showed nearly dense morphology by close stacking of sputtered nanoparticles. There is not obvious difference between different process temperatures at 30 mTorr. Figure A.2b showed FESEM image of the SnO₂ sputtering with a process pressure of 1 mTorr at different process temperature showed nanoporous patterns with a high density of cracks and grooves, which means higher surface area and more effective reactions sites obtained. Slightly cluster size difference was observed between different process temperatures. With increasing the process temperature of sputtering at 1 mTorr, the cluster size of SnO₂ showed slightly decrease with similar nanoporous features. It may because of the in-situ thermally-driven sintering when sputtering at higher temperatures. The deposition rate of sputtering SnO₂ is around 9nm/minutes and the insert in Figure A.2b showed the cross-section view with a corresponding thickness of 260 nm for 30 minutes sputtering. In a summary, the surface morphology can be controlled by process gas pressure with low pressure of 1 mTorr for nanoporous features and high pressure of 30 mTorr for dense features. The in-situ sintering with process temperature less than 600 °C did not have an obvious influence on morphology. The SnO₂ thin film sputtered at 1mTorr, 600 °C has the smallest cluster size, which may have higher effective surface reaction sites.

Figure A.1 surface morphology of as-deposited SnO₂ by RF sputtering by controlling (a) process pressure and (b) process temperature.

A.3.2 Composition and Crystal structure of as-sputtered SnO₂ thin film

Figure A.2a showed the selected XPS spectra (Sn_{3d} and O_{1s}) of the as-sputtered SnO₂ thin film. The Sn_{3d} spectrum has two individual peaks located at a binding energy of 494.7 and 486.6 eV, and the O_{1s} spectrum has one peak located a binding energy of 530.3 eV, referring to a typical chemical state of SnO₂.¹¹⁵ The as-deposited SnO₂ thin films in terms of different process pressures and temperature showed the same position of Sn_{3d} and O_{1s} spectrum, and slightly different intensity. The element composition ratios of O_{1s} to Sn_{3d} of the as-sputtered SnO₂ was

shown similar O_{1s}/Sn_{3d} ratio at around 2.215 with standard deviation of 0.068. Note the XPS spectrum was referenced to adventitious C_{1s} peak at 284.8eV. The crystalline structure of the as-deposited SnO_2 thin film was confirmed by XRD as shown in Figure A.2b. The diffraction peaks of three 1 mTorr as-sputtered film can be indexed to the rutile phase SnO_2 (JCPDS No. 41-1445), and no impurity is observed. The crystallinity was known to depend on the sintering temperature and the crystallinity in this case increased as the in-situ sintering temperature increased to 600 °C. Interestingly, the diffraction peaks of three 30 mTorr as-sputtered film showed nearly much less crystallinity than the 1 mTorr as-sputtered film. An amorphous structure was even observed at parameters of 30 mTorr and room temperature. It implied that the process pressure of RF sputtering may influence the formation of crystal structure, which is interested in figuring out.

Figure A.2 (a) XPS spectra (Sn_{3d} and O_{1s}), and (b) XRD pattern of as-sputtered SnO_2 thin film.

A.3.3 Electrical conductivity of SnO₂ thin film

Figure A.3 showed the electrical conductivity of SnO₂ thin film at elevated temperatures. The thickness of all tested thin films include pure Pt and SnO₂ were controlled to be around 250 nm on a silicon substrate. The conductivity of the bare silicon substrate showed a typical semiconductor property. The conductivity of base silicon increase as the testing temperature increased. Bare silicon exhibited a conductive property at a temperature higher than 300 °C. The sputtered pure Pt exhibited an electrical conductor at all testing temperatures. The slight conductivity decrease as temperature increase is due to the thermally-driven lattice vibration which impedes the electric conduction, which is the typical conductor behavior of metal. The consistent conductivities were obtained at elevated temperatures in all SnO₂ thin film except the sputtered film on R.T. 30 mTorr. Three SnO₂ thin films which were sputtered under 1 mTorr of process pressure showed higher electrical conductivity than the film sputtered under 30 mTorr. In a summary of sputtering parameter for SnO₂ electrode, a process temperature of 600 °C and a process pressure of 30 mTorr were selected because of the obtained nanoporous features with smaller cluster size, strongest crystallinity, and highest electrical conductivity. We further investigated the potential of the SnO₂ thin film anode for ethanol oxidation reaction for LTSOFCs.

Figure A.3 Electrical conductivity of sputtering SnO₂ thin film at elevated temperatures

A.3.4 Fuel cell performance by direct ethanol vapor fuel

Fuel cell performance evaluations at 500 °C were investigated by monitoring open-circuit-voltage (OCV), polarization curves, impedance characterizations between cells using pure SnO₂ (600°C and 30 mTorr) and pure Pt anode, shown in Figure A.4a. The OCV of the cells were monitored under 20 sccm hydrogen feeding and ethanol vapor feeding with 20 sccm carrier nitrogen accordingly. At the initial state of pure Pt anode with hydrogen fuel, the OCV increased gradually and stabilized at a voltage of 1.05 V, which is around the OCV of typical hydrogen feeding-Pt based fuel cell. The OCV showed a sudden drop to 0.83V when switching to ethanol vapor feed testing, and the OCV showed gradually decrease over time, indicating the different catalytic capability of Pt to hydrogen and ethanol vapor. At the initial state of SnO₂ anode with hydrogen fuel, a stabilized OCV of 0.82 V was observed. The OCV of 0.82V was kept when switching the fuel feed of hydrogen to ethanol, indicating the similar catalytic capability of SnO₂

to hydrogen and ethanol. The OCV of SnO₂ with ethanol feeding is more stable compared with pure Pt anode.

The I-V curves (Figure A.4b) of the cell using pure Pt and SnO₂ anode were obtained using ethanol feeding and operated at 500 °C. Both cells using pure Pt and SnO₂ anode have similar OCV around 0.8 V, and the cell of pure Pt anode has higher power output than the cell of SnO₂. The corresponding EIS analysis (Figure A.4c) showed the cell of pure Pt anode has smaller polarization resistance than the cell of SnO₂ anode. Although the fuel cell performance of the cell of SnO₂ anode is poor than the cell of Pt anode, the I-V curves of the cell using SnO₂ anode showed obvious current output, which is interested. This result indicated the potential of using sputtering SnO₂ thin film for ethanol oxidation reaction in LT-SOFCs at an operation temperature of 500 °C.

Figure A.4 Ethanol feeding Fuel cell performance test at 500 °C with SnO₂ thin film anode via (a) OCV, (b) I-V curves and (c) impedance analysis

A.4 Chapter Summary

Direct ethanol SOFCs using nanoporous SnO₂ thin film anode has been fabricated and demonstrated. The crystalline SnO₂ thin film with nanoporous features can be obtained at an operation temperature of 600 °C and a low deposition pressure of 1 mTorr. The electrical conductivity of the as-deposited SnO₂ is about 1 order less than pure Pt thin film. Although the I-V curves of SnO₂ cell was still much worse than Pt cell, the OCV of SnO₂ showed the same 0.8 OCV at both hydrogen and ethanol vapor fuel. Moreover, SnO₂ thin film anode showed a better OCV stability on ethanol feeding compared to a slow OCV degradation on pure Pt thin film. These preliminary results in this work presented the potential of SnO₂ as a LTSOFCs anode.

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Publication list

- **K.Y. Liu**, L.D. Fan, C.C. Yu and P.C. Su, “Thermal stability and performance enhancement of nano-porous platinum cathode in solid oxide fuel cells by nanoscale ZrO₂ capping”, **Electrochemistry Communication** 56 (2015) 65-69
- **K.Y. Liu**, Y.J. Yoon, S.H. Lee, and P.C. Su, ”Sputtered Nanoporous PtNi Thin Film Cathodes with Improved Thermal Stability for Low Temperature Solid Oxide Fuel Cells, **Electrochimica Acta** 247 (2017) 558–563
- **K.Y. Liu**, J.D. Baek, C.S. Ng and P.C. Su, ” Thermal Stability of Nanoporous Pt Cathode in Low Temperature Solid Oxide Fuel Cells by Improved Pt/YSZ Interfacial Adhesion, under preparation.
- **K.Y. Liu**, L.D. Fan, C.C. Yu, T.H. Lee and P.C. Su, **20th International Conference on Solid State Ionics**, “Microstructural Effect to Thermal Stability and Cathode Performance by Nanoscale ZrO₂ Capping in Platinum Based-Solid Oxide Fuel Cells”, A2.29, Keystone, USA June 2015
- K.Y. Liu and P.C. Su, **THINFILMS2016**: The 8th International Conference on Technological Advances of Thin Films & Surface Coatings, Co-sputtered Nanoporous PtNi Alloy for Improved Thermal Stability of Cathode in Low-Temperature Solid Oxide Fuel Cells, ICF-8373, Singapore, July 2016
- **K.Y. Liu** and P.C. Su, **ECS230th meeting**, Pacific Rim Meeting on Electrochemical and Solid-State Science, “Nanoporous Pt Thin Film Cathodes with Superior Thermal Stability for Low Temperature Solid Oxide Fuel Cells”, I02-2894, Honolulu, USA, Oct 2016