Developing metallic cathode for low-temperature solid oxide fuel cell applications

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**DEVELOPING METALLIC CATHODE FOR LOW-
TEMPERATURE SOLID OXIDE FUEL CELL
APPLICATIONS**

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2016

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TEMPERATURE SOLID OXIDE FUEL CELL
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**A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of
Doctor of Philosophy**

2016

Statement of Originality

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

5/Aug/2016

Date

Yu Chen-Chiang

Abstract

Solid oxide fuel cell (SOFC) is a high-efficient energy conversion device, which can transform chemical energy into electricity directly. With the effort input by numerous researchers in the past decade, the operating temperature of SOFCs had been successfully decreased to below 500 °C with more than 1 W·cm⁻² of output power density. At low operating temperature, one of the major issues is the sluggish kinetics of oxygen reduction reaction, which causes the major loss. To achieve high performance at a low operating temperature of 300 to 500 °C for SOFC, this dissertation is dedicated to developing metal-based cathodes that can meet the criteria of long-term stability, low area-specific resistance, easy to fabricate, and cost effective.

To study the stability of metallic cathode, an interfacial structure characterization method, double cantilever beam delamination, was developed to determine the triple phase boundary structure for the thin-film electrode. By this delamination technique, the thermal-driven morphological evolution between the electrode top surface and the substrate contact interface were compared. For the nanoporous platinum electrode, the temperature required for significant agglomeration to occur was approximately 100 °C higher at electrolyte contact interface than at the top surface.

In the next stage, inkjet printing technique was employed to fabricate Ag cathode. Comparing to the conventional thin-film electrode that was fabricated by sputtering, the cathode fabricated by inkjet printing showed improved performance and structural stability. In a 45-hour test on fuel cell operation, the cell with an inkjet-printed cathode had a current output degradation of 12.1 % at 400 °C; while the degradation of sputtered Ag cathode was 68.1 % after a 20-hour test. For a high-performance fuel cell, a porous silver cathode is required, and this simple inkjet

printing technique provides an effective way to achieve such desirable porous structure with required thermal morphological stability.

To further enhance the stability of Ag cathode, the surface modification was employed by sputtering a 2 nm-thick of gadolinium-doped ceria (GDC) on the Ag cathode. With the GDC capping layer, the thermal stability of Ag cathode was improved. The GDC-modified cathode could be operated at 400 °C for 24 h with 7.8 % of output degradation. To study the effect of GDC coating on surface O-exchange properties, a “porous and dense” bi-layered Ag cathode and a “porous” Ag cathode were used for surface modification. When GDC capping was applied, the ohmic resistance reduced from 1186.0 to 1052.0 Ωcm^2 while the polarization resistance increased from 767.3 to 2541.4 Ωcm^2 at 400 °C for the bi-layered Ag cathode; for the porous Ag cathode, the ohmic resistance reduced from 1190.0 to 963.5 Ωcm^2 while the polarization resistance increased from 325.8 to 421.2 Ωcm^2 . This GDC capping layer could reduce the ohmic resistance due to the extra ion conduction pathways, while the polarization resistance increased since the GDC capping impeded oxygen surface exchange on Ag. These results provide engineering strategies for applying Ag cathode which operating at a temperature around 400 °C.

Finally, the integration of Ag cathode on a micro-fabricated SOFC (or μ -SOFC) was explored. The Ag cathode penetrated the electrolyte during the operation and caused a short circuit of cathode and anode. Due to the diffusivity of Ag in the electrolyte, the design of μ -SOFC needs to be reconsidered. To employ Ag on a μ -SOFC without the short-circuit failure, further investigation on Ag diffusion-blocking layer and the thickness requirement of the electrolyte is needed. Based on these results, the opportunities and the strategies of future work are discussed.

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“Bear in mind that the wonderful things you learn in your schools are the work of many generations. All this is put in your hands as your inheritance in order that you may receive it, honor it, add to it, and one day faithfully hand it on to your children.”
— Albert Einstein

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Abbreviations

AFC	Alkaline fuel cell
ALD	Atomic layer deposition
ALS	Adler-Lane-Steele
ASR	Area specific resistance
CHP	Combined heat and power
CPE	Constant phase element
CTE	Coefficient of thermal expansion
CVD	Chemical vapor deposition
DCB	Double cantilever beam
DMFC	Direct methanol fuel cell
ECA	Effective Conducting Area
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscope
FRA	Frequency Response Analyzer
GDC	Gadolinium-doped ceria
HER	Hydrogen evolution reaction
HT	High Temperature
LSC	Lanthanum-strontium-cobalt
LSM	Lanthanum strontium manganite
MCFC	Molten carbonate fuel cell
MEMS	Micro Electro Mechanical Systems
MIEC	Mixed ionic and electronic conducting
OCV	Open-circuit voltage
ORR	Oxygen reduction reaction

PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell
PLD	Pulsed laser deposition
PVD	Physical vapor deposition
RF	Radio frequency
SEM	Scanning electron microscope
SOFC	Solid oxide fuel cells
TEM	Transmission electron microscopy
TPB	Triple phase boundary
YSZ	Yttria-stabilized zirconia

Chapter 1

Overview

In this chapter, an overview of this dissertation is presented. Including the problem of developing low-temperature solid oxide fuel cell, objective and scope of this doctoral work, and the findings of this work. This work is dedicated to developing a metal-based cathode for operating at temperatures between 300 and 500 °C. An interfacial structure characterization method, double cantilever beam delamination, was developed to examine the triple phase boundary structure accurately at the electrode|electrolyte interface for the thin-film electrode. In search of a cost-effective cathode, an inkjet-printed Ag cathode was developed with improved thermal stability at 400 °C for 45 hours. The ion-conducting oxides were coated on the Ag cathode to improve the thermal stability further. The electrochemical properties of oxide-modified cathode were studied by electrochemical impedance spectroscopy. The oxide coating could impede oxygen surface exchange on Ag, and these studies provide strategies for metallic cathode engineering.

1.1 Problem Statement

Solid oxide fuel cell (SOFC) is one of the important technologies to convert chemical energy into electricity with high energy conversion efficiency. The typical operating temperature of SOFCs is above 800 °C. This high operating temperature caused some issues such as high operation cost, performance degradations, and long start-up time. To utilize SOFCs in a wide range of applications, especially in portable devices, developing low-temperature SOFCs (LT-SOFCs) that can be operated at 500 °C and below with comparable performance as conventional SOFC became a critical issue. Recent efforts have shown impressive electrochemical performances of SOFCs below 500 °C by using nanoscale thin film electrolytes that minimize the ohmic resistance ¹. Even though the ohmic resistance could be reduced, it is known that the cathode polarization loss is the major loss of SOFC, and the percentage of cathode loss is more pronounced at lower temperature ². The oxygen reduction reaction (ORR) at the cathode became the most rate-limiting step that accounts for the majority of losses due to the sluggish cathode reaction kinetics ^{3,4}.

When operating a SOFC at this low-temperature range, conventional oxide-based ceramic/perovskite cathodes such as lanthanum strontium manganite (LSM), lanthanum-strontium-cobalt oxide (LSC) ^{5,6} or $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) ⁷ are not suitable since the ionic and electronic conductivity of these oxide-based cathode materials decreased with the temperature ⁸, which could result in high power losses.

For LT-SOFCs, metallic cathodes with high catalytic activity such as platinum (Pt) were widely used. To-date, the reported high-performance SOFCs mainly used Pt cathode with nanoporous structure, which could provide more ORR site at triple phase boundary (TPB) ^{1,9}. The major issue of using nanoporous cathode is the degradation at the elevated temperature, which could cause more than 50 % of power

degradation and loss of TPB at 400 °C and above after 12 continuous hours of operation^{10–12}.

For Pt cathode, another major issue is its extremely high cost, which limits the real-world application of LT-SOFC. Therefore, finding substitutes for Pt is a critical issue for LT-SOFCs. In this regard, silver (Ag) can be a possible candidate as the cathode material. Silver has high catalytic activity, excellent oxygen solubility ($\sim 10^{-6}$ mol·cm⁻³¹³), and permeability (oxygen diffusivity $D=4.98 \times 10^{-3} \exp[(0.50 \pm 0.13 \text{ eV})/k_B T]$ ^{13,14}), which are critical properties for effective cathodic ORR. The superior electrical conductivity of Ag over conventional oxide cathode materials for SOFCs also minimizes the ohmic resistance. Studies have shown that the cathode reaction kinetics of Ag on YSZ were comparable to or even better than that of noble metals like Pt due to the increased oxygen incorporation into the electrolyte^{15–17}. Besides, the lower cost of Ag is also attractive when compared to other noble metals. However, the low structural stability of Ag at the elevated temperature could cause severe power degradation or cell failure. To solve the thermal stability issue of Ag cathode is important for utilizing Ag cathode in LT-SOFCs. Therefore, this dissertation is focused on developing the metallic cathodes that can be used at 300 to 500 °C with improved performance, thermal stability, and cost efficient.

1.2 Objective and Scope

This dissertation discusses the development of LT-SOFC with the focus on the cathode design. The purpose of this study is to provide a functional cathode with enhanced stability, cost effective, and higher performance compared to state-of-art nanoporous Pt cathode for low-temperature (300 – 500 °C) operation. Metallic cathodes were chosen to replace the perovskite-based cathode, which has low electrical conductivity issue in the low-temperature range. Currently, metallic cathodes suffer from reaction rate limiting, thermal stability, degradation, and cost

issues. To solve these issues, the alternative fabrication techniques (inkjet printing), cathode structures, and electrochemical properties were studied. Through a thin-film delamination technique, the structure of thin-film electrode could be directly observed. The improved cathode was achieved by optimizing fabrication method and surface modification on the metallic cathode. Finally, an LT-OFC with the optimized cathode was fabricated.

The main contribution of this dissertation are:

- (1) The thermal-driven structure evolution of nanoporous thin film cathode at ORR reaction site is studied to understand the cathode degradation at elevated temperature;
- (2) thermal stability and performance of the cathode were enhanced through surface modification;
- (3) provided a functional silver that could be utilized as an alternative for Pt to make LT-SOFC more cost effective.

1.3 Dissertation Overview

The dissertation is divided into six chapters detailing the development of metallic cathode for LT-SOFC.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 provides the theoretical background of an SOFC and reviews the literature concerning the recent progress of LT-SOFC development, the state-of-art cathode design, and the issues for cathode development.

Chapter 3 introduces the principles underlying the LT-SOFC fabrication, characterization techniques employed and the methods of data analysis.

Chapter 4 discusses the thermal evolution of a Pt nanoporous thin-film electrode. Nanoporous Pt electrode thin films were delaminated from yttria-stabilized zirconia (YSZ) substrates via double cantilever beam delamination. By delaminating the Pt electrode from the electrolyte to reveal the structure located at the interface between electrode and electrolyte. Comparing the structure of Pt thin-film electrode at the surface and at the interface, 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 study provides a method to explore the electrode structure at the ORR site.

Chapter 5 discusses employing inkjet printing technique to fabricate a porous silver thin-film cathode for LT-SOFC applications. The inkjet printing technique was proposed to solve the thermal stability issue of the typical sputtered nanoporous silver cathode at the elevated temperature. A long-term fuel cell operation of 45 h at 400 °C was performed, and the results showed that the cell with an inkjet-printed cathode had a more stable current output.

Chapter 6 discusses the thermal stability and electrochemical properties of the surface-modified Ag cathode for LT-SOFC. By introducing a gadolinium-doped ceria (GDC) coating on silver, the thermal stability of silver was improved, and the structure of silver could retain without significant agglomeration at 400 °C. The results provide engineering strategies for applying Ag cathode which operating at a temperature around 400 °C.

Chapter 7 demonstrates micro-SOFC (μ -SOFC) using Ag as a cathode material to replace the typical Pt cathode. Ag cathode was integrated onto the μ -SOFC by a simple brush painting technique. The electrochemical performance of fuel cells using silver nanoparticle cathode was characterized at temperatures below 400 °C. A satisfactory thermal stability of the silver thin film cathode was achieved with silver nanoparticle cathode, and comparable performance to cells using the costly

platinum cathode was attainable. The issue of silver penetration through the electrolyte is also discussed.

Chapter 8 summarizes the work done in the dissertation and proposes possible future research for low-temperature μ -SOFCs.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

- (1) Establishing a characterization method to reveal real ORR site for metallic thin-film cathode.
- (2) Introducing inkjet printing technique to fabricate Ag thin-film cathode for LT-SOFC. The inkjet-printed showed higher performance and less power degradation than the conventional sputtered Ag cathode.
- (3) Applying a GDC capping layer on the Ag cathode and studying the effect of surface modification. The GDC-capped Ag cathode showed improved thermal stability with lower ohmic resistance but higher polarization resistance.

Chapter 2

Literature Review

In this chapter, an overview of fuel cell technology is presented. The development of SOFCs towards lower operating temperature is reviewed. The reviews include i) the methods of lowering the SOFC operating temperature, ii) state-of-art low-temperature SOFCs, iii) fabrication techniques for the thin-film electrode, iv) electrode materials for LT-SOFC, and v) cathode modification techniques for performance enhancement. In the last, issues arising from the past development and the context of this dissertation are presented.

2.1 Introduction

As the world energy demand is increasing, people start to seek alternative energy sources, which can decrease the dependency on fossil fuel, to achieve a sustainable earth. Fuel cell is one of the potential energy alternatives; it can convert chemical energy into electricity with clean emission. Typical fuel cells used hydrogen as the fuel and the products are electricity, water, and heat. There are numbers of fuel cell applications such as transportation, stationary, portable, and emergency backup power. High efficiency is one of the main advantages of fuel cells. A hydrogen fuel cell can achieve a maximum efficiency of more than 80% at room temperature theoretically; assuming heat rejection at room temperature, the maximum efficiency that a combustion engine can reach is less than 60 % when operating at 500°C.

2.1.1 Type of Fuel Cells

Fuel cells can be classified into categories depending on the type of electrolyte they used. The major types of fuel cells are alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and SOFC. Depending on the characteristics, different types of fuel cells have different operating temperatures, from below 100 °C to 1000 °C, and their characteristics also determine the applications. The types of the fuel cell are summarized in **Table 2.1**. Among the fuel cells, PEMFC and SOFC received lots of research attention currently. These two kinds of fuel cell both use solid phase electrolyte, which is easy to manage in the system. Typical operating temperature range of PEMFC is around 100 °C, and it requires high-cost catalytic material such as platinum. Researchers of PEMFC mainly focus on increasing the operating temperature to improve the efficiency and finding alternative catalytic materials to lower the cost. For the SOFC, high operating temperature (> 800 °C) had limited its application and material selection.

Researchers tried to reduce the operating temperature of SOFC to expand its application field and materials selection. The following sections review the development of lowering the operating temperature of SOFC.

Table 2-1. The summary of different fuel cells characteristics. ¹⁸ Reproduced with permission from Reference 18. Copyright 2001, John Wiley and Sons.

	<i>AFC</i> (Alkaline)	<i>PEMFC</i> (Polymer Electrolyte Membrane)	<i>DMFC</i> (Direct Methanol)	<i>PAFC</i> (Phosphoric Acid)	<i>MCFC</i> (Molten Carbonate)	<i>SOFC</i> (Solid Oxide)
Operating Temp. (°C)	<100	60–120	60–120	160–220	600–800	800–1000 (<500 possible)
Anode Reaction	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
Cathode Reaction	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
Applications	Transportation, space, military, and energy storage system			CHP for decentralized stationary power systems	CHP for stationary decentralized systems and for transportation (trains, boats, etc.)	
Realized Power	Small plants 5–150kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small – medium sized plants 50kW – 11MW	Small power plants 100-kW- 2 MW	Small power plants 100–250kW
Charge Carrier (Electrolyte)	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

2.1.2 Electrochemical Reactions and Thermodynamics

There are three main components of a fuel cell: cathode, electrolyte, and anode. A schematic of fuel cell working principle is shown in **Figure 2-1**. The electrolyte can be proton conductor or oxide-ion conductor, depending on the materials and the structure. Hydrogen is fed to the anode and splits into protons and electrons by oxidation reaction. The electrons pass through the outer circuit to power the load

while the protons (positive ion) pass through the electrolyte. The oxygen is supplied and reduced at the cathode and formed water. The general reaction in a fuel cell is described as following:

The anode and the cathode half-cell reaction can be described as hydrogen oxidation reaction (HOR) (2.1) and ORR (2.2) respectively. The equation (2.3) describes the overall reaction, and the product is water.

The chemical potential difference of the species determines the maximum cell voltage. The theoretical value of the open-circuit voltage (OCV) for a hydrogen fuel cell could be expressed by Nernst equation:

$$E = E^o + \frac{RT}{2F} \ln \frac{f_{H_2} \cdot f_{O_2}^{1/2}}{f_{H_2O}} \quad (2.4)$$

Where E is the ideal potential of the cell, E^o is the reversible fuel cell potential, R is ideal gas constant, T is the absolute temperature in Kelvin, F is Faraday's constant, and f is the fugacity. In generally, fugacity can be approximated by the partial pressure of fuel cell operating pressure.

The major losses of fuel cells are activation loss, Ohmic loss and concentration loss. Activation loss is caused by sluggish electrode kinetic; Ohmic loss comes from the resistance of ions to flow in the electrolyte and the resistance of electrons to flow in the electrode; concentration loss is led by finite mass transportation rate, which limits the reactant supply and the product evacuation. The ideal and actual fuel cell

voltage/current characteristic curve are shown in **Figure 2-2**. As the output current increases (current are drawn from the cell), the output voltage decreases from the reversible cell voltage (ideal voltage). The voltage-drop (or refer as overpotential) represented the irreversible losses in a fuel cell operation.

Figure 2-1 Schematics of fuel cell working principle. (a) Oxygen-ion conducting fuel cell, and (b) proton-conducting fuel cell.

Figure 2-2 Fuel cell voltage-current characteristic curve.

2.2 Solid Oxide Fuel Cells

The development of SOFC has mainly focused on stationary applications because of its high operation temperature. Typical system size of SOFC applications is in the range between 1 kW and 100 kW, with the operating temperature range of 500 to 1000 °C^{19,20}. This high operating temperature can boost the electrolyte conductivity and therefore improve the efficiency. The efficiency is about 60% for typical high-temperature SOFC; in the case of integrated with combined heat and power (CHP) system, the efficiency can be greater than 85%⁴. However, when operating at high temperature, the material selection is limited, and the system cost is high for the interconnecting and the sealing materials.

2.2.1 Lowering the Operating Temperature of SOFC

Recent years, studies focused on lowering the SOFC operating temperature^{4,21–25}. Lowering SOFC operating temperature can not only expand the material selection and lowering the system cost but also reducing the start-up-shut-down cycle time and bringing SOFC into mobile applications. The ionic conductivity of electrolyte decrease when lowering the temperature; reducing the electrolyte thickness or finding a material with higher ionic conductivity can be done to compensate the loss.

Conventional SOFCs are less favorable to portable and mobile applications than a PEMFC. While PEMFC also had some issues such as humidification and fuel impurity tolerance²⁶. Researchers had dedicated to development the high-temperature PEMFC to solve current issues, and to easily utilized the waste heat for combined heat and power (COP) or reforming processes²⁶. In past decade, efforts were made by numerous of researchers to drive the operating temperature of PEMFC toward 200 °C and above. To utilize the benefits of SOFCs on mobile applications, the development of SOFC had been toward to a lower operating temperature. With the decreased operating temperature, SOFC became a promising power source for

portable devices; it can provide higher power densities than batteries, quick recharging by swapping fuel cartridge or refueling²⁷. The research trend of PEMFC and SOFC is illustrated in **Figure 2-3**.

When comparing with PEMFC, the fuel of SOFC is not limited by pure hydrogen fuel; hydrocarbon fuel can be used²⁸. Another benefit of SOFC is its high power density, which allows SOFC to offer same power output at the smaller cell size. SOFC can provide a higher power density than other available technologies. A comparison chart of specific power and power density of different technologies was summarized in **Figure 2-4**⁴. This High specific power of SOFC could be the main advantage for portable/mobile applications. Lowering the operating temperature of SOFC shed a light of more applications of SOFC technologies.

Figure 2-3 The research trend of the targeting fuel cell operating temperature.

Figure 2-4 Comparison of SOFC power density with other technologies ⁴. Reproduced with permission from Reference 4. Copyright 2011, American Association for the Advancement of Science.

2.2.2 State-of-Art LT-SOFC

Conventional high-temperature SOFCs were applied in stationary applications at the temperature above 800 °C with the power rating in megawatt range ²⁹. Compare with high-temperature SOFC systems, micro-fabricated SOFCs, also refer as μ -SOFCs, which have reduced electrolyte thickness, could operate at the temperature below 500 °C with comparable high power density ($> 1 \text{ W/cm}^2$) ⁹. These μ -SOFCs are high-potential mobile power sources for devices with power requirement in watt range. The μ -SOFCs were built on silicon ^{9,22,30–34} or Foturan® ^{35,36} substrate with free standing YSZ membranes. Platinum is a commonly used μ -SOFC electrode materials for μ -SOFCs operate at temperatures below 500 °C ^{1,9,12,22,30–33,35} while LSCF cathode was employed at temperatures around 500 °C ^{34,36}. Hydrogen is the most common fuel employed on μ -SOFCs; methane and natural gas can be used as well ³⁷.

To date, μ -SOFC fabricated by micro-electromechanical-system (MEMS) techniques on silicon substrate could provide high power densities of more than a watt per centimeter square at the temperature below 500 °C, which is promising for portable power sources. Another advantage of μ -SOFCs is the flexibility of fuel selection; hydrogen is not the only fuel for SOFCs, they could also operate in methane, ethanol, and natural gas. **Table 2-2** summarized the current development of μ -SOFC which operates at 500 °C and below.

Table 2-2 Overview of μ -SOFC design and performance.

Research Groups	Structure and Materials (cathode / electrolyte / anode)	Fuel	Electrolyte Thickness	Membrane Geometry	Max. Power Density (mW cm ⁻²)
<i>NTU, Singapore</i> <i>Baek et al.</i> ^{38,39} <i>Li et al.</i> ^{40,41}	Freestanding membrane on Si. (Pt/YSZ/Pt, Pt/BYZ/Pt)	H ₂	100nm	3mm Circular	437 (400 °C) 445 (425 °C)
<i>Stanford Univ., USA</i> <i>Huang et al.</i> ²² <i>Shim et al.</i> ³⁰	Freestanding membrane on Si. (Pt/YSZ/Pt)	H ₂	50–60nm	240 μ m ×240 μ m Square	270 (350 °C)
<i>Stanford Univ., USA</i> <i>Su et al.</i> ³¹ <i>Chao et al.</i> ³² <i>An et al.</i> ⁹	Corrugated freestanding membrane on Si. (Pt/YSZ/Pt)	H ₂	60–70nm	100 μ m ×100 μ m Square	1300 (450 °C) 540 (400 °C) 200 (360 °C)
<i>Harvard Univ., USA</i> <i>Johnson et al.</i> ³³ <i>Tsuchiya et al.</i> ³⁴	Freestanding membrane on Si. (LSCF/YSZ/Pt)	H ₂	~100nm	5 mm × 5mm Square	155 (510 °C)
<i>Harvard Univ., USA</i> <i>Kerman et al.</i> ^{12,42}	Freestanding membrane on Si. (Pt/YSZ/Pt)	H ₂ / CH ₄	~100nm	160 μ m ×160 μ m Square	1037 (500 °C)
<i>Harvard Univ., USA</i> <i>Takagi et al.</i> ³⁷	Freestanding membrane on Si. (Pt/YSZ/Ru)	CH ₄ / natural gas	110nm	200 μ m ×200 μ m Square	430 (CH ₄), 410(NG), (500 °C)
<i>ETH Zurich, Switzerland</i> <i>Muecke et al.</i> ³⁵ <i>Tölke et al.</i> ³⁶	Freestanding membrane on Foturan®. (LSCF/YSZ/Pt)	H ₂	550nm	100– 200 μ m circular	209 (550 °C)

2.2.3 Fabrication Techniques of μ -SOFC

The fabrication process of μ -SOFC requires less than 20 steps. This simple fabrication process allows μ -SOFC to be mass produced easily. Since μ -SOFC using a sub-micron scale thin film as the main structure, the quality of the thin film is important for the mechanical strength of a μ -SOFC. To fabricate microscale or even nanoscale thin film SOFC, physical vapor deposition (PVD) such as sputtering and pulsed laser deposition (PLD), chemical vapor deposition (CVD) such as atomic layer deposition (ALD), or liquid-precursor-based thin film deposition techniques had been employed⁴³. With the integration of MEMS fabrication technique, silicon-based μ -SOFCs were developed, and the power density as high as 270 mW/cm² at 350 °C could be reached to date²². For the mechanical stability, Baek *et al.* proposed a circular μ -SOFC membrane, which has a lateral dimension of 3 mm and the thickness be only a hundred nanometer³⁸. The circular membrane design improved the mechanical strength of μ -SOFC, allows the cell to be operated in a harsh environment. To further improve the mechanical strength, a 50- μ m circular membrane array with silicon supporting structure was proposed³⁹. With these enhanced cell structures, μ -SOFC can be operated in portable devices and rapid thermal cycling environment without worrying the mechanical failure. However, there still some issues to be solved for LT-SOFC such as electrolyte conductivity, electrode catalytic activity, and long-term system stability. Researchers are devoted to resolving these issues. Among all issues, ORR at the cathode site is believed to be the bottleneck to achieving high performance because of its sluggish kinetics³. Therefore, this work focused on cathode study to provide an improved cathode for LT-SOFC, the studies are regarding metallic cathode materials and structural modification to realize an applicable and cost-effective metallic cathode for LT-SOFC. The following section introduces the metallic electrode for SOFC.

2.3 SOFC Electrodes

While the physics governing the losses in the oxide electrolyte had been widely studied and understood in the past few decades, the research on the mechanism of fuel and oxygen process in the electrodes still not draw a conclusion yet ³. It was general believed that the cathode is the rate limiting component of SOFC because of the sluggish ORR at the cathode, and the losses introduced by electrodes mostly come from the cathode. The exchange current densities difference between HOR at the anode and ORR at the cathode is by several orders of magnitude; this difference results in higher loss at the cathode. Even the value of the exchange current for the Pt in alkaline medium, which is the case of SOFC, is higher, the exchange current of ORR is still lower than the HOR. The exchange current of ORR and HOR with different electrode materials is listed in **Table 2-3** and **Table 2-4**, respectively. In a view to having better performance on SOFCs, it is important to accelerate the reaction in the cathode.

Table 2-3 Exchange current for oxygen reaction ². Reproduced with permission from Reference 2. Copyright 2009, John Wiley and Sons.

Surface	Electrolyte	$j'_0(\text{A/cm}^2)$
Pt ⁴⁴	Alkaline	10^{-5}
Ag ⁴⁴	Alkaline	10^{-6}
Pt	Acid	10^{-9}
Pd	Acid	10^{-10}
Ir	Acid	10^{-11}
Rh	Acid	10^{-11}
Au	Acid	10^{-11}

Table 2-4 Exchange current for hydrogen reaction ². Reproduced with permission from Reference 2. Copyright 2009, John Wiley and Sons.

Surface	Electrolyte	$j'_0(\text{A/cm}^2)$
Pt	Acid	10^{-3}
Pt	Alkaline	10^{-4}
Pd	Acid	10^{-4}
Rh	Alkaline	10^{-4}
Ir	Acid	10^{-4}
Ni	Alkaline	10^{-4}
Ni	Acid	10^{-5}
Ag	Acid	10^{-5}
W	Acid	10^{-5}
Au	Acid	10^{-6}
Fe	Acid	10^{-6}
Mo	Acid	10^{-7}
Ti	Acid	10^{-7}
Sn	Acid	10^{-8}
Al	Acid	10^{-10}
Cd	Acid	10^{-12}
Hg	Acid	10^{-12}

There are several approaches to increase the exchange current density. The main methods are increasing the reactant concentration, decreasing the activation barrier, increasing the temperature, and increasing the number of reaction sites. Increasing the reactant concentration and lowering the temperature was ruled out in this research since our target is low temperature and mobile application. Material selection is important for decreasing the activation barrier, **Figure 2-5** summarized the ORR catalytic materials, Pt and Pd are the best catalysts for oxygen reduction.

However, the high price of Pt and Pd is an issue when employing these noble metals. Silver is also a high ORR catalytic material, but the low stability at high temperature made it less favorable for SOFC. When the operating temperature of SOFC decreased, the ceramic base cathodes are no longer suitable for their electrical conductivity, ionic conductivity and reaction activity decreased ⁴⁵. Applying Ag cathode becomes beneficial because it has a high electrical conductivity at low temperature, and silver is more thermal stable at low temperature. Silver is one of the promising SOFC cathode candidates not only because of high electrical conductivity and ORR activity but also it has high oxygen diffusivity and solubility ¹³. Another approach of increasing the exchange current density is to increase the reaction site. ORR happened at oxygen, electrode, and electrolyte triple phase boundary (TPB). High porosity cathode structure is widely used for μ -SOFC to increase the amount of TPB. Nevertheless, high porosity structure is less stable at high temperature, and the degradation becomes an issue. To improve the SOFC cathode performance, the design of structure needs further investigation. The following section reviews the SOFC cathodes.

Figure 2-5 Trend of oxygen reduction activity as a function of oxygen binding energy ⁴⁶. Reproduced with permission from Reference 46. Copyright 2004, American Chemical Society.

2.4 Factors Governing SOFC Oxygen Reduction Reaction at Cathode

Although μ -SOFC could achieve more than 1 W cm^{-2} at the temperatures below 500°C , the electrodes for μ -SOFC are still far from optimum. Especially the cathode, which limits the μ -SOFC performance when the operating temperature decreased ¹. The cathode's electrochemical reaction involves ions, electrons, and gas molecules in different phases happened at where the cathode, electrolyte, and gas boundary. This boundary is usually called "TPB". Studies indicated that SOFC performance is improving with the amount of TPB ³. As mentioned by Adler, *"Which step(s) are rate determining, and thus which factors are important for cathode performance, depends strongly on the material(s), microstructure, and processing of the electrode as well as the conditions under which the electrode is tested, including temperature, atmosphere, polarization, time, or other factors, some of which may not be known."* The ORR mechanism at the cathode is not drawn a conclusion yet.

Kim *et al.* ⁴⁷ fabricated well-defined platinum electrodes which contain close-packed arrays of circular openings to study geometric effects at TPBs. They found both electrode impedance and cell performance increased linearly with the TPB length, which indicated that cell performance is governed by the TPB length for the activation polarization. However, Ryll *et al.* ⁴⁸ examined the agglomerated and "dense" Pt thin film electrodes on YSZ and showed that the performance of Pt thin film electrodes was not resulted from microscopic and geometrically measurable TPBs only.

Typical SOFC used porous electronic conducting materials such platinum or lanthanum strontium manganite (LSM). To improve the cathode performance, one strategy is to employ ionic and electronic mixed conductor cathodes such as lanthanum-strontium-cobalt oxide (LSC) ^{5,6} or $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) ⁷. Peng *et al.* ⁴⁹ suggested that mixed proton and electron conducting cathodes are

promising materials for proton conducting SOFC performance improvement. With mixed conducting materials, oxygen could be reduced at the surface of the electrode and oxygen ion could diffuse through the cathode. Therefore, the reaction sites could increase. Similar to the mixed conductor, the materials with oxygen permeability such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF)^{21,50} or silver¹³ are the candidates for cathode performance improvement. The oxygen can diffuse through the cathode for these oxygen permeable materials and reduce at the cathode/electrolyte interface; the reaction sites are not limited to the TPB, and the performance can be improved. Electrical conductivity is another factor which affects cathode performance. Kleitz and Petitbon⁵¹ studied the thin film electrode conductivity and suggested the in-plane electronic conductivity of electrodes should be higher than 1 S cm^{-1} to prevent the significant Ohmic drop. When electronic conductivity is higher than 100 S cm^{-1} , the in-plane Ohmic drop introduced by current collecting is negligible.

Another way to improve the cathode performance is the microstructure engineering. One common approach is depositing nanoporous cathodes by sputtering at low vacuum to increase the TPB. However, this nanoporous structures suffer from Ostwald ripening for thin film μ -SOFCs operated at elevated temperatures and result in performance degradation. Galinski *et al.*⁵² found that the thin-film cathode morphological evolution is dominated by the physical processes and the kinetics of agglomeration at the film-ambient interface and the film-substrate interface. The agglomeration kinetics increased at crystalline/amorphous interface, which suggests the crystallinity of cathode materials affect the stability of the structure. To improve the thermal stability, Ni-Pt metal alloy was employed instead of pure platinum, and the results showed the high thermal stability of the alloy up to 600°C ¹¹; the penalty of using Ni-Pt alloy is decreasing the performance. Kenney and Karan⁵³ did the numerical study and suggested that adding an addition current collector layer enhance cathode performance because of the better oxygen distribution underneath

the interconnect. The porous electrode structure is the most commonly used in SOFC, the contact area between electrode and electrolyte affect the performance. Therefore, Santos *et al.*⁵⁴ proposed the “Effective Conducting Area (ECA)” at the electrode/electrolyte interface. They found that using different electrodes on the same electrolyte affect the measured electrolyte resistance, and therefore we need to take ECA into consideration to get more certain characteristic of the electrochemical electrode polarization.

Employing materials with high catalytic activity is another way to boost the ORR at the cathode site. Han *et al.*⁵⁵ developed a nanoporous $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) catalyst. By coating this SSC onto the surface of a high-porosity $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) cathode, the interfacial resistance decreased to $0.043 \, \Omega \, \text{cm}^2$ and produced a power density of $1.46 \, \text{W} \, \text{cm}^{-2}$ at $600 \, ^\circ\text{C}$. Selecting materials with high catalytic activity could also help to improve ORR kinetics. Nørskov *et al.*⁴⁶ suggested high oxygen reduction activity metals such as platinum, palladium, and silver can provide better cathode performance. A volcano curves of the activity as a function of oxygen and hydroxyl adsorption energies was constructed and the curves give us an indication of metal cathode materials’ selection. Chao *et al.*⁵⁶ fabricated a catalyst structure by combining ALD and sputtering of platinum. A 90% of maximum power densities enhancement was observed.

It is known that factors that affect cathode performance include the fundamental of oxygen diffusion in the solid state ionic system, mechanism of ORR and how oxygen ions incorporating into electrolyte still not clear yet. One of the difficulties is atomic scale observation of oxygen ion transportation. Chroneos *et al.*⁵⁷ tried the simulation approach to understand oxygen diffusion in perovskite-like oxides cathode and electrolyte materials in atomic scale. A “non-traditional conduction paths with structural and transport anisotropy and lattice flexibility/dynamics, unlike the conventional vacancy-driven ionic conduction in traditional SOFC materials.” Flex-

ing cathode structures could help oxygen migration by controlling oxygen-cation bond strengths through lattice strain. Kim *et al.*⁵⁸ developed a technique to direct mapping the oxygen vacancy concentrations by scanning transmission electron microscopy and successfully applied to LSC thin film measurement. The concept was based on chemical expansivity properties. When local stoichiometry varies, it produces local lattice expansion, and the oxygen vacancy distribution could be known by measuring the lattice perimeter. This oxygen vacancy concentration method could help understanding the physics of oxide materials and interfaces for SOFC. Opitz *et al.*^{59,60} investigated oxygen reduction pathways for different electrode materials on YSZ by “voltage-driven ^{18}O tracer experiments in combination with time-of-flight secondary ion mass spectrometry analysis”. The reaction pathways of Pt, LSM, LSC, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) were identified. The ^{18}O tracer experiments method could help determine the electrochemically active zones. Hörlein *et al.*⁶¹ investigated the oxygen exchange kinetics on Pt-YSZ system and found two different processes that changing the electrode kinetics at temperatures between 550 and 900 °C. One is reversible process caused by formation/decomposition of PtO_x phase, and the other is the continuous degradation caused by the impurities accumulation at the TPB. The results showed that the TPB-related polarization resistance was affected by the thermal pre-history of the Pt electrode. Jiménez *et al.*⁶² analyzed electrochemical impedance spectroscopy data of silver droplet on YSZ and found that the oxygen diffusion through the silver is evenly distributed over the whole electrode interface at the high-frequency range; the oxygen diffusion is concentrated along the electrode TPBs under dc conditions. This analysis suggested that the silver electrodes of intimate contact radii varying between 0.2 and 2 mm. The limiting process for the oxygen supply to the electrode interface is oxygen diffusion through the cathode. Researchers were devoted to SOFC ORR studies^{3,6,55,60,63,64}. However, the understanding of electrochemical reaction of SOFC cathode materials at a temperature below 500 °C is lack. To

expand the operating temperature of SOFC into a lower temperature range, further understanding of ORR is needed.

2.5 Cathode Materials for LT-SOFC

General requirements for LT-SOFC cathode materials are high electronic conductivity for current collecting (typically $>100 \text{ S cm}^{-1}$ ⁶⁵), high catalytic for ORR, and high thermal stability. Further requirements such as good alignment on thermal expansion with electrolyte materials (typically in the range of $10\text{--}12.5 \cdot 10^{-6} \text{ K}^{-1}$), easily to fabricate, and low cost are also important factors for improvement of the μ -SOFC system. Oxide-based ceramic/perovskite cathodes such as LSM or LSCF are widely used for high-temperature SOFC. However, the ionic and electronic conductivity of these oxide-based cathode materials decreased with the temperature⁸ and made them less suitable for low-temperature operation. For example, Jung *et al.* investigated cathode performances of Pt, Ni, and LSC at 350–450 °C. They found that when the operating temperature reduced to 350 °C, metallic cathode outperformed LSM cathode⁶⁶. Using perovskite oxide at lower temperature results in high polarization resistance and introduces significant loss. In the case of low-temperature operation, metallic cathodes can be suitable candidates. Platinum has the highest ORR catalytic activity and therefore it is the most commonly used electrode material⁴⁶. Recent efforts have shown impressive electrochemical performances of LT-SOFCs with peak power densities up to $1.3 \text{ W} \cdot \text{cm}^{-2}$ at 450 °C using Pt cathode^{9,32}. However, the high cost of platinum made it less favorable for wide application. Therefore, finding substitutes for Pt is one of the most critical issues for LT-SOFCs to be used in real-world applications. In this regard, Ag can be a possible candidate as the cathode for μ -SOFCs. Ag has high catalytic activity, excellent oxygen solubility ($\sim 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$)¹³, and diffusivity (oxygen $D = 4.98 \times 10^{-3} \exp[(0.50 \pm 0.13 \text{ eV})/k_B T]$)^{13,14}, which are critical properties for effective cathodic ORR. The superior electrical conductivity of Ag over conventional oxide

cathode materials for SOFCs also minimizes the ohmic resistance. Studies have shown that the cathode reaction kinetics of Ag on YSZ were comparable to or even better than those of noble metals such as Pt due to the increased oxygen incorporation into the electrolyte ^{15–17}. Besides, the lower cost of Ag is also attractive when compared to that of other noble metals.

2.5.1 Silver as the SOFC Cathode Materials

On the contrast of platinum, the cost of silver much lower and it has relatively high catalytic activity on ORR, excellent electronic conductivity. Another benefit of silver is the oxygen permeability ¹³ which extends the reaction sites to the whole electrode, not necessarily limits the ORR at the TPBs. The volatility at high temperature, 50 nm per year of silver would be lost at 700 °C and 0.3 μm at 750 °C ⁶⁷. This thermal stability issue made silver less favorable for conventional HT-SOFC. Nevertheless, the volatility of silver at low temperature can be neglected. Morse *et al.* ⁶⁸ showed the feasibility of using silver as the cathode at the temperature below 400 °C. However, the Ag/YSZ/Ni thin film SOFC could only reach ~0.8V of OCV and 3.8 mW cm^{-2} of maximum power density at 316 °C, further improvement is needed to employ silver cathode. For thin film electrodes, thermal stability is one of the issues need to be solved. Simrick *et al.* ⁶⁹ examined the thermal stability of silver thin film on YSZ substrate at the temperatures of 250–550 °C and found a de-wetting process occurred in which grain boundaries ruptured. The results suggest the silver on YSZ should be more than 300 nm thick to remain electronic conductivity through the electrode plane. A patterned nano-mesh could help to ease the thermal degradation of thin film cathodes ^{17,47}. Instead of using only mixed conductors or pure metals as cathode materials, applying oxide-metal composites is another strategy for improving cathode performance. Camaratta *et al.* ⁷⁰ developed a pure silver and $\text{Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$ (ESB20) composite cathode which could reduce 25% of initial area specific resistance (ASR) and 95% of ASR degradation rate at 650 °C. Akimune *et*

*al.*⁷¹ employed silver nanoparticles as electrode materials with yttria-doped BaCeO₃ (BCY) electrolyte and found the SOFC with the platinum anode and silver cathode had higher performance at the temperatures of 300–500 °C. SOFC configuration of Ag/BCY/Pt had the highest performance, followed by Pt/BCY/Pt, and Ag/BCY/Ag had the poorest performance. However, the detail mechanisms of Ag/BCY oxygen incorporation still not clear to date. Further investigation on the ORR in this temperature range is needed to make an improvement on the cathode of LT-SOFC.

2.5.1.1 Silver Oxides

The Ag–O system includes several compounds such as AgO, Ag₂O, Ag₂O₃, Ag₃O₄, and Ag₄O₃⁷². Ag₂O·(Ag⁺) and Ag₂O₃ (Ag³⁺) are the stable species. For the AgO, it is not composed of Ag²⁺ and O²⁻, studies showed that it contains Ag₂O and Ag₂O₃⁷³.

The presence of silver oxides could affect the electrical conductivity^{74,75} and the stability of Ag cathode. These silver oxides tend to decompose at the elevated temperature due to the lower affinities of silver for oxygen, which could result in instability of the structure. AgO and Ag₂O are the two most thermodynamically stable oxides of silver, and their thermal decomposition properties had been widely studied^{72,76–84}. There are several chemical states of oxygen can be found on the surface of Ag, including oxide, atomically adsorbed oxygen, carbonates, and dissolved atomic oxygen and hydroxyl groups. Studies showed that most of these species could be decomposed at 100 °C except silver oxides (AgO and Ag₂O) and carbonate species^{80,81}. The AgO decomposed to Ag₂O at around 200 °C. As the temperature increased to 300 °C, the concentration of dissolved oxygen in the near-surface region tend to increase since the bulk dissolved oxygen formed during the decomposition migrates to surface^{81,84}. Serval reports showed that silver oxides were fully decomposed to silver at 400 °C^{77,80,81,83,84}. For the chemisorbed O atoms, Pettinger et al. found that these O atoms recombine and desorb at around 327 °C,

which reflected their relatively low thermal stability. Since the LT-SOFC is targeting to be operated at the temperature around 400 °C, the presence of silver oxide could affect its thermal stability. The formation of silver oxides during the fabrication process need to be carefully controlled.

2.5.2 Surface Modification of Metallic Electrode

The main issue of using metallic cathodes for SOFCs is their poor thermal stability, which may cause electronic connection network breakage or the decrease of porosity. In the case of Ag cathode, it is highly mobile at the elevated temperatures due to its relatively low melting point (961 °C) and high volatility ⁶⁷; applying a thermally stable protective layer on Ag could improve the thermal stability of Ag under elevated temperatures. The oxygen permeability of Ag allowing the ORR site expand to two-phase-boundary, where cathode and electrolyte in contact, instead of at TPB only, as a typical metallic cathode. In this case, surface oxygen adsorption and dissociation become important when designing an Ag cathode. Ion-conducting materials such as zirconia and ceria are potential candidates as a protective coating layer because of their high thermal stability. With an ion-conducting metal coating on Ag surface, the cathode can be considered as a mixed ionic and electronic conducting (MIEC) material. For MIEC, the surface oxygen exchange and oxygen diffusion are believed to be the rate-limiting steps for ORR ^{65,85–88}. The oxygen surface exchange coefficients k and oxygen bulk diffusion coefficients D_δ are the dominant factors for cathode performance ⁶⁵. The cathode characteristic resistance (R_G) can be illustrated by Adler-Lane-Steele (ALS) model ^{89,90} as shown in (2.5):

$$R_G = \frac{RT}{4F^2} \frac{1}{\sqrt{4a \frac{1-\varepsilon}{\tau_{solid}} \Re_o c_o x_v^0 D_v}} \quad (2.5)$$

where R is the gas constant, T is the absolute temperature, F is Faraday's constant, a is the surface area to volume ratio, τ_{solid} is and tortuosity of the solid-state transport path, ε is the porosity, $\mathfrak{R}_o$ is the equilibrium molar exchange rate of O_2 between gas and the cathode surface, c_o the mobile oxygen concentration, x_v^0 is the mole fraction of oxygen vacancies at equilibrium state, and D_v is the effective oxygen vacancy diffusion coefficient.

Earlier studies had shown that a few nanometers of ion-conducting materials such as zirconia or ceria coating on thin film metallic electrode could help to maintain Ag's microstructure under elevated temperatures. Besides, the cathode impedance could be reduced with the oxide coating due to the extra ion-conducting pathways provided by the coating ^{10,63,91,92}.

2.6 Chapter Summary

LT-SOFCs, which operate at a temperature below 500 °C, had achieved high performance in the past decade by the efforts of researchers. However, the development of cathode materials is limited. Most of the high-performance cells reported rely on using rare elements in the earth crust such as Pt as the cathode. For the real world applications of LT-SOFCs, developing cost-effective alternatives for Pt is essential, and therefore, cathode study became one of the critical issues for LT-SOFC development. In this regards, this dissertation is focused on the cathode study, which includes structural characterization, fabrication techniques, performance and thermal stability, and integration of thin-film cathode on μ -SOFCs.

Chapter 3

Experimental Methodology

This chapter introduces the experimental methodology including material selection, SOFC fabrication methods, and characterization techniques. In materials selection part, the rationale for material selection, including electrode and electrolyte, is elaborated. Next, the fabrication techniques, including ALD, sputtering, and inkjet printing, for the cathode are introduced. The last part of this section introduces the sample characterization techniques and SOFC test method.

3.1 Selection of Materials and Methods

3.1.1 Materials

3.1.1.1 Electrode

Cathode polarization loss dominates the overall losses for an LT-SOFC. General requirements for LT-SOFC cathode materials are high electronic conductivity for current collecting (typically $>100 \text{ S cm}^{-1}$ ⁶⁵), high catalytic for ORR, and high thermal stability. Further requirements such as good alignment on thermal expansion with electrolyte materials (typically in the range of $10\text{--}12.5 \cdot 10^{-6} \text{ K}^{-1}$), easily to fabricate, the matching of coefficient of thermal expansion (CTE) with electrolyte, chemical and mechanical stability, and low cost are also important factors for improvement of the μ -SOFC system. Conventional oxide-based ceramic/perovskite cathodes such as LSM or LSCF are widely used for high-temperature SOFC. However, the ionic and electronic conductivity of these oxide-based cathode materials decreased with the temperature ⁸ and made them less suitable for low-temperature operation. For LT-SOFCs, metallic cathodes are suitable candidates. Platinum is one of the most popular cathode materials for LT-SOFC because of its high catalytic activity, which could provide LT-SOFC a higher performance. To compromise the performance and the cost, silver is a potential cathode material at the lower temperature. Therefore, platinum and silver are selected as the based cathode materials in this work. For the anode selection, low-cost materials such as nickel can be used without sacrificing much of the cell performance since the reaction kinetics is higher than the cathode reaction. However, we still used platinum as the anode material for all the experiment since it is widely used in μ -SOFC and the anodic loss can be minimized. This configuration allows us to make a comparison with other works easily.

3.1.1.2 Electrolyte

YSZ is a well-studied electrolyte material. Even though it has a low ionic conductivity at low temperature, YSZ is selected due to that it is stable and easily to acquire. In this dissertation, two types of YSZ were used. One is the commercially available single crystalline YSZ <100> (8YSZ, Latech Scientific Supply Pte. Ltd., Singapore); another is thin-film YSZ deposited by ALD or sputtering in our laboratory.

3.1.2 Fabrication Methods

3.1.2.1 ALD

ALD is a surface self-limiting chemical vapor deposition process, which can achieve atomic layer control and conformity⁹³. The atomic layer by atomic layer deposition could provide a high-quality and crack-free nanoscale thin-film. An ALD cycle includes four basic steps: i) exposure of precursor, ii) reaction chamber purge, iii) exposure of oxidant, and iv) reaction chamber purge. By repeating the deposition cycle, the desired thickness can be obtained. An example of zirconia ALD cycle is illustrated in **Figure 3-1**. The first step is the chemical absorption of the metal amide. In this step, the metal-oxygen bond formed on the substrate surface. The excess precursors are purged from the reaction chamber in the second step. Then the oxidant reacts with the surface- bound metal amides, flowing by a chamber purge step to finish one layer of zirconia deposition.

An in-house ALD system was used for YSZ thin film deposition. The detailed design of the ALD system, deposition parameters, and film characterization can be found in the Appendix. The tetrakis(dimethylamino)zirconium(IV) (99.99%) (Strem Chemicals Inc.) and tris(methylcyclopentadienyl)yttrium(III) (Strem Chem.) was used as the precursors for ZrO_2 and Y_2O_3 deposition. ALD-YSZ was deposited by

cycling ZrO_2 and Y_2O_3 deposition. A deposition cycle includes four steps: i) precursor evaporation pulse for 0.1s; ii) precursor purging by inert gas (Ar or N_2) for 20s; iii) oxidant pulse (H_2O or O_2) for 0.02s, and iv) oxidant purging by an inert gas for 30s. The cycle ratio of ZrO_2 and Y_2O_3 was 4:1. The tetrakis(dimethylamino)zirconium(IV) and tris(methylcyclopentadienyl)yttrium(III) was heated to 65 °C and 170 °C to evaporate. The purging gas was maintained at a flow rate of 3 sccm during the deposition. The process chamber was maintained at the base pressure of 150 mTorr. A YSZ deposition cycle, which contains four ZrO_2 cycles and one Y_2O_3 cycle, has the thickness of 5.5 Å. By control the cycle number, the desired thickness of YSZ can be deposited.

Figure 3-1 Schematics of ZrO_2 ALD cycle steps. Reproduced with permission from Reference ⁹⁴. Copyright 2012, American Chemical Society.

3.1.2.2 Sputtering

Sputtering is a widely used PVD technique for thin-film growth. The coating material is transfer into the vapor phase by ion bombardment on a target material. By controlling the deposition parameters such as power, deposition atmosphere, and substrate temperature, the structure of deposited film can be controlled. The metal film structure is mainly affected by the process gas pressure and the ratio of substrate temperature (T) to the metal's melting point (T_m). The structural zone model proposed by Thornton describes the sputtered metal film growth under different

conditions ⁹⁵. As illustrated in **Figure 3-2**, the sputtered film structure can be classified into three zones. Zone I ($T/T_m < 0.3$) consists of tapered crystals with separate tops. Zone 2 ($0.3 < T/T_m < 0.5$) consists of columnar grains separated by grain boundaries. Zone 3 ($0.5 < T/T_m < 1$) consists of larger and compact grains with a smooth surface. Based on the structural model, sputtering was carried out at a lower substrate temperature and higher process gas pressure to obtain a porous metal electrode.

Figure 3-2 Structural zone model for sputtered metal growth. Reproduced from Reference ⁹⁵. Copyright 1977, Annual Reviews.

A custom designed RF sputtering system and a DC sputtering system were utilized in this work. For the electrode delamination test (Chapter 4), DC sputter was used with three-inch circular platinum (99.99%, Latech Ltd., Singapore) target to fabricate the porous Pt films. The process was carried out at a high Ar pressure of 80 mTorr and 250 W of DC power at 22 °C with the deposition rate of 75 nm min⁻¹. For the rest of electrode fabrication, two-inch circular platinum (99.99%, Latech Ltd., Singapore), silver (99.99%, Latech Ltd., Singapore), YSZ (8 mol% Y₂O₃, Latech Ltd., Singapore), and GDC (Ce_{0.9}Gd_{0.1}O_{1.95-δ}, Latech Ltd., Singapore) target were used. The deposition parameters and the deposition rate of the RF sputter are listed in **Table 3-1**. As shown in **Figure 3-2**, the morphology of sputtered materials is

mainly affected by the process pressure and the deposition temperature. Therefore, for the porous electrode, the deposition was carried out at room temperature with higher process pressure; for the dense electrolyte, the deposition was carried out at the highest temperature (800 °C) we could achieve by our apparatus and lower process pressure. For the dense Ag, since the melting temperature (T_m) is relatively low, it could achieve dense structure by lowering the process pressure without substrate heating. To determine the suitable process pressure, the deposition was first carried out at different Ar pressure, ranging from 10 to 80 mTorr. **Figure 3-3** shows an example of the morphology difference of Pt when deposited under different Ar pressure. Since the porous electrode with highest triple phase boundary is required, the process pressure of 30 mTorr was selected. The deposition rate is proportional to the power in general. Moreover, higher deposition power introduces more intense ion bombardment and increases substrate temperature, which could result in denser structure. Therefore, for the electrolyte materials, higher power (200W) was selected.

Figure 3-3 Surface morphology of Pt deposited under the Ar pressure of 10 to 80 mTorr.

Table 3-1 Sputtering parameters and deposition rate.

Material	Deposition Parameters			
	Process Pressure (mTorr Ar)	Power (W)	Substrate Temperature (°C)	Deposition Rate (min ⁻¹)
Porous Pt	30	100	22	11
Porous Ag	30	100	22	28
Dense Ag	1	100	22	33
YSZ	1	200	800	1.25
GDC	1	200	800	0.8

3.1.2.3 Inkjet printing

Inkjet printing is a solution-based deposition technique, which requires simple equipment⁹⁶. The material that contained in the solution, or ink, can be deposited on the substrate directly through a piezoelectric drop-on-demand print head. A typical print head is illustrated in **Figure 3-4**. To eject the ink, a voltage signal is applied to the piezoelectric actuator to generate a sudden volume change. This volume changes results in a positive wave pressure and squeezes the ink out of the nozzle. When the kinetic energy transferred is larger than the surface energy of the droplet, a droplet is ejected. The print-on-demand property allows the material to be patterned without masking, and it minimized the material loss during the process when compared with a conventional lithography process.

In this work, the Ag ink for deposition was prepared by adding 10 wt.% Ag nanoparticles with 200 nm in diameter into a humectant solution (30 % ethylene glycol and 70 % water). A MicroFab JetLab4 inkjet printing system (MicroFab Technologies Inc., USA) was used for all printing process. During the printing, the ink droplets with 56 μm in mean diameter were ejected at the frequency of 250 Hz. The spacing between each ejected droplet was 80 μm and the distance between two printed lines was 20 μm . With this configuration, the droplets were overlapped and formed a continuous film with Ag nanoparticles. The morphology of as-printed Ag

film is shown in **Figure 3-5**. The thickness of one printed layer was ~ 400 nm. After the printing had been done, the as-printed Ag films were baked at $200\text{ }^{\circ}\text{C}$ for 30 min to remove the solvent in the ink.

Figure 3-4 Illustration of a piezoelectric inkjet print head.

Figure 3-5 Morphology of as-printed Ag nanoparticles.

3.1.3 Sample Characterization

3.1.3.1 Morphological Characterization

The sample morphology was analyzed by a field emission scanning electron microscope (FESEM, JOEL JSM 7100F) and a transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). FESEM was operating at an acceleration of 5 to 20 kV and a current of 7 mA; TEM was operating at an acceleration of 200 kV. For the metallic materials, the samples were analyzed in FESEM directly without conductive coating; for the ceramic materials such as YSZ and GDC, a conductive coating was applied on the sample before FESEM characterization. FESEM-integrated energy dispersive X-ray spectroscopy (EDS) (Oxford Instruments, UK) was used for elemental and chemical analysis.

3.1.3.2 Fuel Cell Test

For the cathode performance test, the cathodes to be tested were deposited on 100- μm thick single crystalline YSZ by either inkjet-printing or RF sputtering technique. The YSZ substrates were cleaned by acetone, IPA, and distil water with the aid of ultrasonic for 10 minutes, respectively. After cleaning, the surface condition of YSZ substrate was checked by contact angle measurement. The contact angle of a water droplet on the YSZ surface was 80° . A nanoporous Pt thin film with the thickness of 100 nm was sputtered on the other side of the YSZ substrate as the anode for all cells tested. The cell structure is illustrated in **Figure 3-6**. The diameter of all the cathodes deposited on the YSZ was 6 mm, and the lateral dimension of the cathode is the active area of all cells.

Figure 3-6 Schematics of SOFCs with a 6 mm circular cathode on the YSZ electrolyte substrate. The 100 nm-thick of porous Pt anode was deposited on the other side of the YSZ substrate.

Fuel cell test was carried out in a custom-made test station. The sample was fixed on the fuel chamber and supplied with pure hydrogen at the anode side; the cathode side was open to air. The fuel chamber is located inside a tube furnace to ensure the uniform operating temperature. The cell was connected to a potentiostat (Solartron 1470E, Solartron Analytical, USA) and frequency analyzer (Solartron 1255B, Solartron Analytical, USA) to test the cell performance and acquire electrochemical impedance spectroscopy data for the cell. For the measurement, two probes configuration was used, in which working and working sense are connected to a working electrode and reference and counter are connected to a second electrode. The schematic of test station and the photo of test station used for all measurement are shown in **Figure 3-7**.

Figure 3-7 (a) Schematic of SOFC test station and (b) photo of the SOFC test station.

To reach the test temperature, the furnace was heated up at a $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate. A gold-coated tungsten probe was placed on the cathode for current collection. The anode was in contact with the fuel chamber, which was also used as a current collector, and connected to the potentiostat and frequency analyzer. During the cell test, pure hydrogen (99.99%) was supplied as a fuel at a flow rate of 20 sccm and ambient air as an oxidant. The electrochemical impedance spectroscopy (EIS) measurement was conducted at the frequency range from 1 MHz to 0.1 Hz with the oscillation amplitude of 50 mV. The impedance data was fitted by Z-Plot software

(Scribner Associates Inc., USA) based on complex nonlinear least-squares fitting method, using the model of one resistor with one or two parallel resistors/constant phase elements (CPE) in series. **Figure 3-8** shows the fitting model used and an example of a typical Nyquist plot. The model in can be described as:

$$Z(f) = R_1 + \frac{R_2}{R_2 Q_2 (i2\pi f)^{\alpha_2} + 1} \quad (3.1)$$

Where $Z(f)$ is the impedance, R_1 is the ohmic resistance, R_2 is the polarization resistance, Q_2 is the CPE, α_2 is the coefficient of CPE, and f is the frequency. If α_2 equals 0.5, a 45-degree line is produced on the Nyquist plot; if α_2 equals 1, a semi-circle is produced on the Nyquist plot. The polarization impedance calculated was normalized by the cell active area to get the ASR of the fuel cells.

Figure 3-8 (a) Equivalent circuit model of one resistor with one parallel resistors/constant phase elements (CPE) in series; and (b) the example of Nyquist plot for the model.

Chapter 4

Direct Observation of Nanoscale Pt Electrode Agglomeration at the Triple Phase Boundary*

Nanoporous platinum electrode thin films were delaminated from YSZ substrates via double cantilever beam delamination to reveal the structure located at the interface between electrode and electrolyte. The thermal-driven morphological evolution between the electrode top surface and the substrate contact interface of agglomerated nanoporous platinum thin films were compared. We found the temperature required for significant agglomeration to occur was approximately 100 °C higher at electrolyte contact interface side than at the top surface side. Judging the reaction active site from the electrode top surface could be inaccurate since the higher resistance of thermal agglomeration at the interface could retain the reaction active site during fuel cell operation.

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4.1 Introduction

Nanoporous platinum thin films deposited on YSZ substrates as cathodes for oxygen reduction reactions have important applications in miniature solid-state electrochemical devices such as oxygen sensors and μ -SOFCs^{1,9,97,98}. μ -SOFCs use a combination of nanoscale thin film components including a freestanding YSZ electrolyte membrane and two porous metal thin film electrodes that sandwich the YSZ electrolyte, and all thin films are in the thickness range of tens to hundreds of nanometers. Because the thickness of the electrolyte is significantly minimized, the ohmic resistance is also significantly reduced; therefore, a high device performance even at very low temperatures is possible^{9,22,31}.

For μ -SOFCs operated at temperatures below 500 °C, because the electrode kinetics is reduced exponentially with a decreasing temperature, the sluggish ORR at the cathode becomes the most rate-limiting process. Among the cathode ORR steps, the oxygen incorporation from the Pt electrode surface into the YSZ electrolyte at the vicinity of the Pt/YSZ/O₂ junctions (or the triple phase boundaries, TPBs) is believed to be the slowest step³. 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. Therefore, a high density of TPB sites at the Pt/YSZ contact interface is critical to obtain high device performance.

The thin-film platinum electrodes for μ -SOFC are usually deposited on YSZ via sputtering at high Ar pressure and low DC power to generate a high density of nanopores within the electrode⁹⁹. The pore sizes produced by this method are in the range of a few to tens of nanometers^{11,12}. These nanoscale pores are poor in maintaining thermal stability and are vulnerable to agglomeration by heat, which inevitably results in decreased TPB densities. Therefore, knowing the

microstructural morphology of porous Pt electrodes at the Pt/YSZ contact interface precisely and how the morphology evolves with increasing operating temperatures can provide an important indication of the appropriate operating temperature range for low temperature μ -SOFC without suffering from performance degradations.

The observation of the pore evolution of Pt on YSZ with increasing temperatures is not new, but the observation of nanoscale pores is rare. Studies have been dedicated to exploring the effects of temperature on the TPB density and their impact on the electrode performances^{11,12,48,69,100}. However, the pore dimensions were mostly at micrometer scales with relatively lower TPB densities of only a few micrometers per unit area (μm^{-1})^{48,100}. In these studies, Pt thin films with micrometer pores were prepared via initially depositing a “dense” Pt film, followed by thermal annealing at very high temperatures (650-800 °C) to generate pores in the films through the dewetting of Pt from YSZ substrate or Pt agglomeration (a). Then, the TPB densities were estimated through counting the line density of the pore perimeters in a FESEM image of the electrode “top view”⁵². However, such estimations of TPB have been undertaken with the assumption that the top morphology of the porous Pt is identical to the morphology at the Pt/YSZ contact interface. This assumption might be only valid when the pores in the Pt thin film are all through-holes across the electrode thickness. In such cases, the pore peripherals are considered to be the only effective TPB sites, and the dense part of the Pt film between the pores is assumed to have little or no contribution to the effective TPB sites because the oxygen bulk diffusion through Pt is insignificant compared with the oxygen surface diffusion.

In contrast, the Pt electrodes for the application of μ -SOFCs are typically deposited directly as “porous” films using DC magnetron sputtering at a high Ar pressure and low DC power. The resulting pore sizes are in the range of only a few nanometers to tens of nanometers (b), which enables TPB densities in the range of tens of micrometers per unit area (μm^{-1}). That is, there is a very high density of nanoscale

features, such as nano-cracks, nanopores, and grain boundaries within the thin film Pt electrodes. These nanoscale features can be non-perforating through the electrode film and are therefore not visible from electrode top view, but still function as effective TPB sites. In this case, the surface morphology of the porous Pt thin film no longer represents the microstructural contacts at the Pt/YSZ interface that contribute to the effective TPBs. Recently, Ryll *et al.* reported a significant contribution of the effective TPB within a dense electrode with thicknesses of 15 to 360 nm⁴⁸. They compared the impedance data between two dense electrodes and proposed the existence of “nanoscopic” TPBs (e.g. grain boundaries, invisible cracks, or combinations thereof) that are not visible from the electrode’s top surface but are oxygen-permeable and can function as effective ORR sites. The density of the nanoscale features at the Pt/YSZ contact interface is expected to have a significant influence on the electrode performance, but the direct observation of the Pt morphology at the Pt/YSZ interface remains lacking.

Under the effect of high operating temperature, the thermal behavior of nanoscale pore agglomeration becomes of vital interest as it is directly affecting the effective TPB density at the Pt/YSZ interface contact. It is intuitive to expect the electrode agglomeration behavior with temperature to be different between at the electrode surface and the Pt/YSZ contact interface since the surface Pt is unlimited and free to migrate under heat treatment, while the interfacial Pt is bonded to the YSZ substrate. Therefore, the capability to obtain information about the Pt pore morphology at the Pt/YSZ interface and hence the effective TPB density is necessary if the cathode performance is to be precisely correlated with the TPB density evolution with temperatures. Also, for μ -SOFCs using porous Pt as electrodes, it is important to identify accurately the critical temperature at which the nanoscopic TPB density significantly decreases to determine the highest suitable operating temperature for such a device using porous metal electrodes.

Figure 4-1 Different ways of porous Pt thin film preparation result in the various scale of pore-size and different film structure during TPB study: (a) The Pt electrode is first deposited as a dense film followed by high-temperature annealing to generate pores in the thin-film. The pore formed is in micrometer-scale and perforated. (b) Porous Pt thin film is deposited directly with nanometer-scale pores and treated at the lower temperatures to study morphological evolution. Non-perforating pores are hiding beneath the surface.

In this work, the necessity of the direct electrode morphology observations of the nanoscale pores for these two-dimensional TPB systems at the Pt/YSZ interface is addressed. A method based on a double cantilever beam (DCB) delamination technique is demonstrated to reveal the hidden interfacial morphology at the Pt/YSZ interface. DCB is a testing method based on fracture mechanics theory that enables the investigation of the adhesion properties of thin films. It allows accurate measurement of fracture energies and precise control of delamination up to atomic-thin monolayer along the targeted interface^{101,102}. Because the load applied during the delamination is in the normal direction to the crack plane (Mode I loading), the porous Pt thin film is only delaminated by out-of-plane movements, and it does not

experience shear forces. This characteristic is an important feature of DCB because it allows the original interfacial morphology at the Pt/YSZ interface to be preserved without distortion. From this, the temperature-driven thermal agglomeration behaviors of the nanoscale pores between the Pt top view and Pt/YSZ contact interface are compared. The corresponding electrode and fuel cell performance are also characterized to correlate and identify the critical temperatures for μ -SOFC operation.

4.2 Experimental Methods

4.2.1 Deposition of Nanoscale Porous Pt Thin Film.

First, 150 nm-thick porous Pt films were deposited on a YSZ substrate via DC magnetron sputtering at a high Ar pressure of 80 mTorr and 250 W of DC power at 22 °C. The Ar pressure during Pt sputtering was set to be high intentionally to create a high density of nanoscale pores. The YSZ substrate is a 150 nm-thick 8 mol% YSZ film deposited on a <100> silicon substrate via ALD with the same process as reported in reference ³¹. The <100> silicon substrate was passivated with a 200 nm silicon nitride layer to prevent inter-diffusion between YSZ and silicon. The as-deposited porous Pt thin films were purposefully agglomerated via thermal annealing at 300, 400, 450, 500, and 600 °C in a tube furnace for 8 hours at a heating and cooling rate of 15 °C/min.

4.2.2 Delamination

Porous Pt thin films annealed at various temperatures were prepared for DCB delamination to reveal the electrode morphology at the Pt/YSZ interface. The annealed porous Pt/YSZ substrates were cleaved into 10 mm × 40 mm strips for the DCB sample preparation. A dummy silicon strip with the same dimension as the Pt/YSZ substrate was diced and coated with a thick layer of epoxy adhesive (Epo-Tek 353ND; Epoxy Technology, USA) (**Figure 4-2a**). The epoxy on the dummy

silicon was bonded to the porous Pt on the YSZ substrate and cured at 120 °C for 2 hours (**Figure 4-2b**) to create adhesion between the epoxy and Pt. The bonded DCB specimen was mounted on a high precision micromechanical test system (Delaminator Adhesion Test System, DTS Company, USA) to delaminate the porous Pt thin film from the YSZ substrate (**Figure 4-2c** and **Figure 4-2d**). The delamination is expected to occur at the Pt/YSZ interface rather than at YSZ/SiN or SiN/Si interfaces due to the relatively weaker van der Waal bonding between Pt and YSZ. Furthermore, because the depositions of YSZ and SiN on the silicon substrate were undertaken using chemical vapor deposition, the bonding was expected to be significantly stronger than the PVD utilized for the Pt on YSZ. During the DCB delamination, the adhesion energy between the porous Pt and YSZ was measured to be 1.2 J/m², which was slightly higher than the range of typical adhesion energy values between noble metals and various oxide substrates (0.9~1.0 J/m²). The adhesion energy is mostly dominated by van der Waals interactions¹⁰³. This phenomenon results from the mechanical interlocking between Pt and YSZ introduced by the physical bombardment of the sputtering process¹⁰⁴. The delaminated surfaces (surfaces A and B in **Figure 4-2d**) were also examined, and neither Pt residue on the YSZ surface nor YSZ residue on the Pt surface was found. This result indicates that fractures and distortions did not occur within the porous Pt films during the delamination and that the original Pt porosity was successfully preserved.

Figure 4-2 The DCB delaminating process of nanoporous Pt from a YSZ substrate. (a) Porous Pt was deposited on YSZ; (b) A dummy silicon strip with epoxy adhesive was bonded on Pt top surface; (c) Delamination of porous Pt film from YSZ; (d) Delaminated porous Pt film for interfacial observation.

4.2.3 TPB Calculation.

The morphologies of the porous Pt at the electrode surface and Pt/YSZ contact interface were examined by field emission scanning electron microscopy (FESEM, JOEL JSM-7600F). The TPB density between the top and contact interfaces for the Pt annealed at temperatures above 400 °C was estimated using image processing software (ImageJ, NIH, USA). The images were binary converted and then the pixels

of the pore peripheral, where the TPBs were located, were counted to calculate the line density¹¹. The smaller cracks for the as-deposited and 300 °C-annealed Pt were too small to be correctly identified using the software; therefore, the TPB densities were not estimated here (see **Figure 4-3** for the TPB profile using the image pixel counting process).

Figure 4-3 TPD profile by image pixel counting process, the red outlines are the counting TPBs.

4.2.4 Fuel Cell Characterization.

To determine the influence of the cathode TPB densities on the fuel cell performance, fuel cells with porous Pt cathodes deposited on 100 μm -thick <100> single crystal YSZ substrates (MTI Corporation, USA) were prepared. The cathodes were annealed at 400, 450, 500, and 600 °C before the cell performance characterization. The anodes were deposited after the cathode annealing via DC sputtered Pt thin film with a thickness of 150 nm using the same deposition parameters as used for the

cathode deposition. All fuel cells were tested at 400 °C to avoid further agglomeration of the annealed cathode. The polarization curves were tested using a potentiostat (Solartron 1470E, Solartron Analytical, USA) with pure hydrogen supplied at a flow rate of 5 sccm on the anode side and ambient air as an oxidant at the cathode. The AC impedance spectra of the cells were obtained using a frequency analyzer (Solartron 1255B, Solartron Analytical, USA) operated between 1 MHz and 0.1 Hz with an oscillation amplitude of 100 mV. The impedance data was fitted by ZView (Scibner Associates) using one resistor, two parallel resistors, and one CPE in series to estimate the ASR of the electrodes (see **Figure 4-4** for the test setup, fitting model, and fitting results). Since the identical Pt anode was applied on all samples. The main differences of electrode ASR were originated from cathodes with different microstructures.

Figure 4-4 (a) Fuel cell test configuration. (b) Equivalent circuit for impedance data fitting. (c) Electrochemical impedance spectroscopy and fitting results. All samples are measured at 400 °C

4.3 Results and Discussion

The evolution of porous Pt morphologies and densities with increasing annealing temperatures is illustrated in the FESEM images in **Figure 4-5**. In the as-deposited Pt thin film, a very high density of short and narrow nanometer-scale cracks exist between the larger, wider, and tens to hundreds of nanometers cracks (**Figure 4-5a**). At annealing temperatures below 400 °C, no apparent agglomeration was observed at both the top and interface because the temperature remained too low to activate the Pt migration (**Figure 4-5b**). At 400 °C, the agglomeration became noticeable, and the cracks at both the top and interface merged and grew larger. As expected, the pore density evolution with the increasing temperature differed significantly between the top and interface, particularly in the temperature range between 400 to 500 °C (**Figure 4-5c** to **Figure 4-5e**). The smaller cracks on the top surface appeared to have completely merged at 400 °C, while those on the Pt/YSZ interface predominantly remained and not until the temperature increased to 500 °C did the merging become completed. That is, the smaller cracks at the Pt/YSZ contact interface merged at 100 °C higher (500°C) than those at the Pt top surface (400°C). As the annealing temperature further increased to 600 °C (**Figure 4-5f**), the medium to large cracks merged further and became wider both at the top and at the interface. The morphology changes between the top and interface from 500 to 600 °C appeared to be similar without an apparent TPB density difference.

Figure 4-5 SEM images of the nanoporous Pt morphologies viewed from the top and interfacial perspectives for (a) as-deposited electrode and (b-f) electrodes annealed at 300 to 600 °C.

From the TPB density estimation results obtained from the image processing, as shown in **Figure 4-6**, the Pt/YSZ contact interface had higher TPB densities at temperatures below 500 °C, as observed in the SEM images in **Figure 4-5a** to **Figure 4-5c**. The results from the bonding force between the Pt and YSZ substrate that limits the mobility of the Pt particles, which caused the interfacial nano-cracks to become more resistant to thermally driven migrations. When the annealing temperature reached 500 °C, the smaller nanometer cracks have been fully merged both on the top and interfacial surfaces, and these cracks further merged into larger pores at this temperature; they also have similar TPB densities on the top and interface. At 600 °C, the TPB densities for the top and interface appeared to have similar counts, although the top surface TPB density was slightly higher than that at the interface, which likely resulted from the rough surface of the Pt top image that led to higher counts of TPB by the software. The difference of the TPB density trend between Pt-top and Pt-interface can be explained as follows. As illustrated in **Figure 4-7**, since the Pt-top surface was not constrained, the majority of the smaller cracks on the top surface merged at a lower temperature of 450 °C, which led to a significant drop in its TPB density. The TPB Pt-interface density remains high at 450 °C since the bonding confined the cracks to the substrate. As temperature increased from 450°C to 500°C, the majority of the smaller cracks at the Pt-interface merged significantly, and the TPB continued to drop, while the TPB density decrease at Pt-top was less significant since the majority of the smaller cracks have already merged at lower temperatures. The cross-sectional SEM images of nanoporous Pt electrode are shown in **Figure 4-8**. It clearly shows the columnar Pt merged into larger clusters at 600 °C.

Figure 4-6 TPB density as a function of annealing temperature by binary converted images method.

Figure 4-7 Illustration of Pt agglomeration at 400 to 500 °C.

Figure 4-8 Cross-sectional view of the nanoporous Pt electrode annealed at (a) 300 °C and (b) 600 °C.

Previously, Wang *et al.* also conducted similar experiments that observed the nanoporous electrode agglomeration with different temperatures, but only through looking at the electrode “top view”¹¹. They concluded that the significant porosity reduction from the merger of the nanometer pores began to occur at 400 °C, which agrees with the current observations at the top surface. However, the interfacial morphology image clearly demonstrated that the high density of smaller cracks remained at 400 °C, and even at 450 °C, the pore densities at the interface were higher than at the electrode top. The porous Pt morphology and TPB densities between the top and interface became similar when the annealing temperature reached 500 °C and above. Therefore, it would be more accurate to assume very similar top and interface morphologies for Pt films annealed at temperatures above 500 °C, at which the smaller nanoscale features were already eliminated through the thermal annealing. However, assuming that the top and interface have the same morphology may underestimate the TPB density for electrodes with nanoporous structures at temperatures below 500 °C. Also, the high surface roughness of the porous Pt thin films increased the difficulty of correctly recognizing the pores on the electrode top view with SEM images.

Figure 4-9a presents the ASR of the annealed electrodes measured from the AC impedance of the fuel cells using annealed Pt cathodes. As expected, the ASR increased as the annealing temperature increased and this apparently results from the pore consolidation with increasing temperatures. Furthermore, a significant increase in the ASR was observed when the temperature was increased from 500 to 600 °C. Also, the fuel cell polarization curves (**Figure 4-9b**) also exhibited a significant drop in performance from the cathode annealed at 500 °C to 600 °C. From the TPB density estimation in **Figure 4-6**, a higher drop appeared in the cathode performance between the as-deposited cathode and cathode annealed at 500 °C, and a smaller drop from 500 to 600°C would be expected. Although the corresponding TPB

density drop from 500 to 600 °C was not as significant as the fall from 400 to 500 °C, the cell performance degradation was more significant as seen in the j-V curve of the cell with the 600 °C-annealed Pt cathode. The additional performance degradation might have been caused by the elimination of “nanoscopic” TPBs, as reported by Ryll *et al.*, being completed at this stage and leading to a higher ASR of the electrode with the TPB density decrease⁴⁸. As proposed by Ryll *et al.*, these nanoscopic TPBs can be grain boundaries, triple lines, grooves, or voids, which are not geometrically measurable. By employing delamination technique in this study, the geometrically measurable cracks and pores were identified to provide a more accurate estimation of the TPB density with changes in the annealing temperature. Further identification of the geometrically non-measurable nanoscopic TPBs might be observed using more advanced imaging techniques.

Figure 4-9 (a) Area-specific resistance of the as-deposited electrode and annealed electrodes. The results were measured at 375 and 400 °C. (b) Fuel cell performance of Pt cathode/YSZ/Pt anode single cell with cathode as-deposited, 400, 500, and 600°C annealed. The test was conducted at 400 °C, with pure H₂ as fuel and the cathode was open to ambient air.

From the perspective of the nano-cracks dimensions, it is proposed that the degradation of fuel cell performance resulting from Pt cathode agglomeration occurs in two stages. In the first stage, at temperatures below 500 °C, the decrease in the TPB density results from the merging of the nanometer-sized smaller cracks. In the second stage, as temperatures reached 500 °C and above, the geometrically measurable nanometer-sized cracks have merged completely, and the electrode agglomeration proceeded further through the merging of existing large pores, which are in the size range of tens of nanometers. In addition to the additional merging, the geometrically invisible nano-features might have also been eliminated at this temperature, which caused a significant cathode performance drop. Therefore, to retain high performance in nanoporous electrodes without significant thermally driven degradation, it is proposed that the suitable device operating temperature is below 500 °C, where a high density of nanoscale TPBs exist at the electrode/electrolyte contact.

4.4 Conclusion

In summary, the direct observations of the nanostructures at the Pt/YSZ contact interface were revealed by using the DCB method to delaminate the nanoporous Pt thin film from the YSZ substrate. Significant morphological differences between the Pt/YSZ interfaces were observed at annealing temperatures between 400 and 500 °C, and the nanoscale pores at the Pt/YSZ interface merged at 100 °C higher temperature than at the top surface, showing the better thermal stability of nanoscale TPB pores at the interface.

From the perspective of the crack dimensions, we propose the pore agglomeration occurs in two stages. The first stage occurs at temperatures at or below 500 °C, where the decrease in the TPB density results from the merging of the nanometer-sized smaller cracks. The second stage occurs as the temperature is higher than 500 °C,

where nanometer-sized cracks have merged completely, and the electrode agglomeration proceeded further through the merging of existing pores into tens to hundreds of nanometers size. To retain the thermal stability of μ -SOFCs using a nanoporous electrode without significant degradation of cell performance, the operating temperatures can be higher than 400 °C but below 500 °C.

Chapter 5

Inkjet-printed Porous Silver Thin Film as a Cathode for Low-Temperature Solid Oxide Fuel Cell [†]

This work reports the porous silver thin film cathode that was fabricated by a simple inkjet printing process for low-temperature solid oxide fuel cell applications. The electrochemical performance of inkjet-printed silver cathode was studied at 300 – 450 °C and was compared with silver cathodes that were fabricated by the typical sputtering method. Inkjet-printed silver cathodes showed lower electrochemical impedance due to its porous structure that facilitated the oxygen gaseous diffusion and oxygen surface adsorption-dissociation reactions. Typical sputtered nanoporous silver cathode became essentially dense after the operation and showed high impedance due to lack of oxygen supply. The results of long-term fuel cell operation show that the cell with an inkjet-printed cathode had a more stable current output for more than 45 hours at 400 °C. A porous silver cathode is required for high fuel cell performance, and the simple inkjet printing technique offers an alternative way of fabrication for such desirable porous structure with required thermal morphological stability.

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5.1 Introduction

The broad application of SOFCs has been limited by the requirement of high operating temperatures, typically above 800 °C. Therefore, to lower the operating temperature without sacrificing the device's performance is one of the major trends to pursue. Recent efforts have shown impressive electrochemical performances of SOFCs below 500 °C by using nanoscale thin film electrolytes (often referred as μ -SOFCs) that minimize the ohmic resistance¹, and the obtained peak power densities were up to 1.3 W·cm⁻² at 450 °C^{9,56}. At such low temperatures, the ORR at the cathode becomes the most rate-limiting step that accounts for the majority of losses due to the sluggish cathode reaction kinetics^{3,4}. The impressive cell performances reported to date were mostly achieved by utilizing platinum (Pt), which is catalytically the most active material, as the cathode material. However, Pt, as one of the rare elements in the earth crust, is prohibitively expensive to be used for wide application. Therefore, finding substitutes for Pt is one of the most critical issues for SOFCs to be used in real-world applications at temperatures below 500 °C. In this regard, silver (Ag) can be a possible candidate as the cathode for μ -SOFCs. It has high catalytic activity, excellent oxygen solubility ($\sim 10^{-6}$ mol·cm⁻³¹³), and permeability (oxygen diffusivity $D = 4.98 \times 10^{-3} \exp[(0.50 \pm 0.13 \text{ eV}) k_B^{-1} T^{-1}]$ ^{13,14}), which are critical properties for effective cathodic ORR. The superior electrical conductivity of Ag over conventional oxide cathode materials for SOFCs also minimizes the ohmic resistance. Some studies have shown that the cathode reaction kinetics of Ag on YSZ were comparable to or even better than that of noble metals like Pt due to the increased oxygen incorporation into the electrolyte¹⁵⁻¹⁷. Besides, the lower cost of Ag is also attractive when compared to other noble metals.

The main issue of using pure Ag as the cathode material for SOFCs is its poor thermal-morphological stability. Ag is highly mobile at the elevated temperatures due to its relatively low melting point (961 °C) and high volatility (2 μ m thick Ag

will be lost per year at 800 °C)⁶⁷. Therefore, Ag was seldom used in pure metallic form at the temperature above 500 °C, and rather it was presented as a constitute of the composite with perovskites or ion-conducting electrolytes^{91,92,105–112}. However, with the low operating temperature of μ -SOFCs, the technical feasibility of using Ag as a cathode is reconsidered.

For the ORR on Ag cathode, two possible pathways of oxygen diffusion were proposed^{13,62,113}. The first is through the bulk path as shown in **Figure 5-1** (the path I), where the adsorbed oxygen molecules are dissociated into atomic oxygen and diffuse through the bulk Ag, and finally reduced at the two-phase boundary (2PB), which is the two-dimensional interface between the Ag cathode and the electrolyte. The second route is through the surface path (the path II in **Figure 5-1**), where the adsorbed and dissociated oxygen molecules on Ag surface diffuse along the Ag surface and reduce at the TPB, which is the one-dimensional line interface where gaseous oxygen, Ag cathode, and electrolyte are in physical contact. The bulk path is expected to be the rate-limiting step at temperatures from 400 °C to 900 °C according to previous experimental results^{13,62,114,115}. Therefore, it is intuitive that the porous Ag cathode can facilitate ORR and results in a better fuel cell performance. Typical porous Ag electrode can be fabricated by applying the commercial Ag paste followed by a high-temperature (~800 °C) firing to build adhesion with the substrate. However, such high-temperature firing may cause mechanical failures of μ -SOFCs on the electrolyte layer. Also, the thickness and the pore size of the film made by Ag paste is typically tens of micrometers, which may not be suitable for the μ -SOFCs application.

Figure 5-1. Schematic of possible oxygen diffusion pathways of Ag on YSZ electrolyte.

Currently, sputtering is one of the most widely used methods for fabricating porous metal thin film electrodes such as Pt, Ag, Au, Ru, etc.^{1,9,31,32,34,98,116}, and by controlling the supplied gas pressure during the sputtering process, electrodes with nanoscale pores can be fabricated¹¹⁷. However, it is difficult to fabricate a porous Ag electrode, which is stable at the elevated temperature, by sputtering due to the relatively low melting point of Ag (961 °C) compare to Pt (1768 °C). According to the microstructure zone model of evaporation and sputtering^{95,117}, the resulting microstructure of thin films by sputtering will be affected by the ratio between the sputtering temperature (T) and the melting point of the material (T_m), T/T_m (in Kelvin). The higher ratio of T/T_m of silver will easily result in a denser structure during sputtering.

To utilize the advantages of Ag in the application as an SOFC cathode material, it is imperative to improve the thermal stability of Ag thin film cathodes. Shim *et al.* applied the nanosphere lithography technique to fabricate an Ag thin film nano-mesh having perforated pores inside the film with diameters around 500 - 600 nm¹⁷. The Ag nano-mesh remained stable for 2 hours without significant cell performance degradation, but the test was done at a very low operating temperature of 277 °C,

which may not be sufficient to provide a satisfactory SOFC performance. Another recent work has demonstrated a temporarily improved thermal stability of sputtered porous Ag thin film cathode at 450 °C by introducing a 5 nm-thick of conformal capping layer of YSZ by the ALD ^{91,92}.

In addition to fabricating Ag thin film with a porous structure and maintaining the porosity at elevated temperatures, the electrical connectivity of the Ag cathode is also an important parameter to consider for the current collection. If the Ag thin film deposited on the electrolyte is not sufficiently thick, the thermally driven agglomeration may cause breakage in the thin film network that resulted in electrical disconnection⁶⁹. Simrick *et al.* reported that at least 1 µm of thickness is required for thin film Ag cathode on a zirconia substrate to prevent the network breakage at temperatures below 500 °C ⁶⁹.

In this work, the inkjet-printed silver thin film that fulfilled the requirement of the porous structure and thermal-morphological stability was demonstrated to overcome the difficulty of fabricating a porous silver cathode by conventional sputtering techniques. Inkjet printing technique could fabricate dense Ag films on ceramic oxide substrates ¹¹⁸ as well as mesoporous Ag films ¹¹⁹. A porous Ag cathode with connected pores throughout the film with the thickness larger than 1 µm was demonstrated for the application in low-temperature SOFCs. The EIS and polarization (I-V) curves of inkjet-printed Ag cathodes were compared with those of sputtered Ag and sputtered Pt cathodes.

5.2 Experimental Methods

5.2.1 Fabrication of Silver Thin Film Cathodes

The porous Ag cathodes were fabricated by MicroFab JetLab4 printing system (MicroFab Technologies Inc., USA). The outlet diameter of the printing piezoelectric nozzle is 50 µm. The ink for Ag deposition was prepared by adding 10

wt. % Ag nanoparticles with 200 nm in diameter into a humectant solution (30 % ethylene glycol and 70 % water). Details of Ag nanoparticle synthesis can be found in the reference ¹²⁰. 100 μm -thick single crystalline YSZ <100> wafers (8YSZ, Latech Scientific Supply Pte. Ltd., Singapore) were used as the electrolyte substrate for Ag cathode printing, and the YSZ substrate was heated to 50 °C during the deposition. Droplets with 56 μm in mean diameter were ejected at a speed of 1.65 $\text{m}\cdot\text{s}^{-1}$ at 250 Hz. The spacing between each ejected droplet was 80 μm and the distance between two printed lines was 20 μm . The cathode was printed in a circular shape with the diameter of 6 mm. A total of 6 printed layers was required to complete a fully connected Ag film with a thickness of approximately 2.5 μm . The as-printed Ag films were baked at 200 °C for 30 min to remove the solvent in the ink and to establish connectivity between the Ag nanoparticles for required electrical conductivity. Finally, the Ag thin films were annealed at 300 °C for 1 hour to create the interconnected pores. For comparison, the conventional sputtered Ag cathode thin films were also prepared with the thickness of 1 and 2.5 μm . The deposition was carried out by a custom-built radio-frequency (RF) sputtering apparatus at 6 mTorr of Ar pressure and 100 W of RF power at room temperature (23 °C), with a resulting deposition rate of 35 $\text{nm}\cdot\text{min}^{-1}$. Both the inkjet-printed and RF sputtered Ag thin films were annealed at 250 °C, 300 °C, 350 °C, and 400 °C for 1 hour in a tube furnace to examine the morphological evolution at our targeted operating temperature range. The surface and cross-sectional morphology of the Ag cathodes were examined before and after cell test using a field emission secondary electron microscope (FESEM, JEOL JSM-7600F, USA).

5.2.2 Fuel Cell Fabrication

Fuel cells with either inkjet-printed or RF sputtered Ag cathodes were fabricated to characterize the cathode impedance and the fuel cell performance. A nanoporous Pt thin film with the thickness of 100 nm was sputtered on the other side of the YSZ

substrate as the anode for all cells tested, and the deposition parameters can be found in the previous reports ^{10,116}. A fuel cell with a typical nanoporous Pt cathode was also fabricated as a reference to compare the cathode performance with Ag cathodes, and it was deposited with the same parameters as the porous Pt anode. The diameter of all the cathodes deposited on the YSZ was 6 mm, and the lateral dimension of the cathode is the active area of all cells. The schematics and image of the fabricated SOFCs are illustrated in **Figure 5-2**.

Figure 5-2. Schematics of SOFCs with (a) inkjet-printed porous Ag cathode with thickness of 2.5 μm; (b) sputtered nanoporous Ag cathode with two thicknesses of 1 μm or 2.5 μm; (c) sputtered nanoporous Pt cathode; and (d) image of the SOFC with a 6 mm circular inkjet-printed Ag cathode on the transparent YSZ electrolyte substrate. The 100 nm-thick of porous Pt anode (the dark gray square) on the other side of the YSZ substrate.

5.2.3 Electrochemical Characterization

The polarization resistance and the current density-voltage curves of the SOFCs using the 300 °C-annealed thin film cathodes were measured at 300 °C to 400 °C using a potentiostat (Solartron 1470E, Solartron Analytical, USA) with a frequency analyzer (Solartron 1255B, Solartron Analytical, USA). The characterization was

done using pure hydrogen (99.99%) as a fuel at a flow rate of 20 sccm and ambient air as an oxidant. The EIS measurement was conducted at the frequency range from 1 MHz to 0.1 Hz with the oscillation amplitude of 50 mV. The impedance data was fitted by Z-Plot software (Scribner Associates Inc., USA) based on complex nonlinear least-squares fitting method, using the model of one resistor with two parallel resistors/CPE in series. The polarization impedance was normalized by the cell active area to get the ASR of the fuel cells.

5.3 Results and Discussion

5.3.1 Microstructures of Silver Cathode Thin Films

Figure 5-3 shows the comparison of cross-sectional microstructures of Ag thin films prepared by inkjet printing and by RF sputtering. After the low-temperature baking at 200 °C to remove the solvent, the inkjet-printed Ag nanoparticles were sintered to form a continuous film (**Figure 5-3 a**). More obvious agglomeration of Ag particles on the surface of the film was observed after it was annealed at 250 °C (**Figure 5-3 b**) due to the inhomogeneous nucleation that made it energetically more favorable for agglomeration¹²¹. The surface agglomeration continued up to the annealing temperature of 300 °C, where an obvious change in pore size inside the film was observed (**Figure 5-3 c**). As the annealing temperature increased to 350 °C and 400 °C, the pore sizes did not show any noticeable change (**Figure 5-3 d and e**). Therefore, before the fuel cell test, the inkjet-printed Ag cathode was pre-annealed at 300 °C to drive its microstructure change to a porous structure with interconnected pores, this would also help to prevent severe morphological change during the test and affect the measurement. Note that the difference in the thickness of the inkjet-printed films was due to non-uniform ink distribution during the printing process. On the other hand, the sputtered Ag films appeared to be mostly dense with little pores exist over all annealing temperatures (**Figure 5-3 g –j**).

Figure 5-3. Cross-sectional views of the microstructure evolution of Ag thin films annealed at 250 °C to 400 °C on YSZ substrate for (a) – (e): inkjet-printed Ag, and (f) – (j): RF sputtered Ag. The inkjet-printed Ag thin film annealed at 300 °C and the as-sputtered Ag thin film was used as the cathode for subsequent tests.

5.3.2 EIS Analysis on Silver Cathodes

Oxygen reduction reaction at the cathode is known to be the rate-limiting step for the entire fuel cell reactions during low-temperature operation. To investigate how the different cathode structures affect the ORR process, the cathode impedance measurements were performed. **Figure 5-4** shows the Nyquist plots measured on the cells using inkjet-printed Ag (300 °C annealed), sputtered Ag (1 μm or 2.5 μm), and sputtered porous Pt cathode at 400 °C. Two distinct arcs in the plots for the cells with Ag cathode were observed (**Figure 5-4a – c**). The high-frequency arcs were ascribed to the ohmic resistance with a capacitance value less than 10^{-9} F, which was mainly associated with the series ionic resistance of electrolyte and electric resistance in the electrode as well as the contact resistance¹²¹, and they were independent of the voltage. The low-frequency arcs were attributed to the electrochemical reaction processes on the electrode. In this case, it can be attributed mainly to the cathode ORR polarization process^{121,122}. For the Pt cathode, only one

lower frequency arc was observed in the Nyquist plot (**Figure 5-4d**), and it was mainly attributed to cathode ORR process. The ASR of the cathode can be calculated from the EIS results, the equivalent circuit model, which consists of one resistor and two parallel resistor-constant phase elements (R-CPE) in series, was used in the EIS fitting as shown in **Figure 5-5**. The fitting was done by Z-plot software based on complex nonlinear least-squares fitting method.

For the electrode ASR analysis, we assumed that anodic impedance is negligible since ORR processes at the cathode are more sluggish than hydrogen oxidation process⁴⁶. Also, identical Pt anode was applied on all samples. Therefore, the main differences of electrode ASR were originated from cathodes with different microstructures. **Figure 5-6** shows the calculated electrode ASR by EIS fitting. It clearly shows that the dense Ag cathode had higher ASR, and the ASR increased with the cathode thickness. To be noted, the dense Ag cathodes had highest polarization resistance at 0.5 V. The change of polarization resistance is possibly due to the balance of oxygen supply. Silver oxides were formed under the applied voltage¹²³, which led to the insufficient supply of oxygen through bulk Ag when the current density increased, and resulted in high polarization resistance. When the voltage became lower (0.3V), the silver oxides decomposed and provided more oxygen for the ORR. The same trend of the change of polarization resistance was reported in the earlier studies on Ag cathode^{17,124}. For the porous Ag, since gaseous oxygen could directly supply to TPB, there was no increase of polarization resistance observed when the current density increased. The Pt cathode had lowest ASR among all samples due to its nanoporous structure, which effectively increases the reaction site for ORR. However, such nanoporous Pt structure is not stable at the elevated temperature since it may suffer from severe degradation in few hours of operation as the earlier studies reported^{10,116}.

Figure 5-4 Electrochemical impedance spectrum of (a) inkjet-printed porous Ag cathode, (b) 1 μm -thick sputtered Ag cathode, (c) 2.5 μm -thick sputtered Ag cathode, and (d) 100 nm-thick sputtered Pt cathode with equivalent circuit fitting results. All results were measured at 400 $^{\circ}\text{C}$ and 0.3 V.

Figure 5-5 Equivalent circuits used for ASR calculation

The values of polarization ASR observed are generally in the sequence of Pt < inkjet-printed Ag < sputtered Ag (1 μm) < sputtered Ag (2.5 μm), as shown in **Figure 5-6**. These results indicate that the bulk oxygen diffusion is the rate-determining step for

dense Ag cathode, and the fuel cell performance aggravates as the Ag thickness increases. The use of porous Ag facilitates ORR process by reducing the ASR. Interestingly, higher electrode ASR of dense Ag cathode was observed at 0.5 V and 0.3 V (**Figure 5-6 b** and **Figure 5-6 c**). This phenomenon is not often observed in SOFCs. However, it is a common occurrence, which is thought to be increased in mass transfer limitation ¹²⁵, in PEMFCs.

From the cathode ASR extracted from EIS results measured at 300 to 450 °C, the activation energy of Ag and Pt cathodes were calculated. **Table 5-1** summarized the activation energy (E_a) of Ag and Pt cathodes under different voltages. The activation energy of 1 μm -thick sputtered Ag cathode was ~ 1.2 eV within the measured voltage range while the activation energy of inkjet-printed Ag cathode was lower than 1.1 eV and decreased with increasing voltages. These results indicate that the change of electrochemical reaction process under different voltages. The activation energy of inkjet-printed Ag was close to the activation energy of oxygen adsorption and dissociation process, 1 eV, experimentally reported by Van Herle *et al.* ¹³ and 0.6 – 1.3 eV from the calculation of density functional theory by Wang *et al.* ¹²⁶. Therefore, the oxygen adsorption and dissociation could be the dominant processes for porous Ag cathode at the reduced temperature. For the Pt cathode, since Pt has a higher oxygen reduction activity and a lower oxygen binding energy compared to Ag ⁴⁶, its activation energies for cathode reactions were lower than that of Ag in general.

Table 5-1 Activation energies of Ag cathodes calculated from polarization ASR fitting results.

	$E_a(\text{eV})$		
	OCV	0.5 V	0.3 V
Sputtered 1μm	1.22 $\pm$ 0.03	1.20 $\pm$ 0.02	1.22 $\pm$ 0.03
Sputtered 2.5μm	1.20 $\pm$ 0.14	0.45 $\pm$ 0.08	0.50 $\pm$ 0.08
Inkjet-printed 1μm	1.10 $\pm$ 0.06	0.96 $\pm$ 0.06	0.82 $\pm$ 0.09
Pt	0.50 $\pm$ 0.07	0.73 $\pm$ 0.04	0.80 $\pm$ 0.02

Figure 5-6. Polarization ASR plots derived from EIS fitting at 300 – 450 $^\circ\text{C}$ and at the voltage of (a) OCV, (b) 0.5 V, and (c) 0.3 V.

5.3.3 Fuel Cell Performance

Figure 5-7 (a) – (c) shows the polarization (I - V) curves of SOFCs with inkjet-printed Ag, sputtered Ag, and sputtered Pt cathodes. The cell with inkjet-printed porous Ag cathode had higher peak power density than those of cells with sputtered dense Ag cathodes. At 400 $^\circ\text{C}$, the peak power density of the cell with inkjet-printed Ag, sputtered Ag (1 μm), sputtered Ag (2.5 μm), and Pt cathode was 0.58, 0.37, 0.12,

and $0.75 \text{ mW}\cdot\text{cm}^{-2}$, respectively. These results were in line with EIS results; the lower ASR resulted in higher cell output. The nanoporous Pt structure provided a high density of reaction site (i.e. TPB), which is essential to improve the cell performance. While the sputtered Ag could not retain its nanoporous structure and became essentially dense at the operating temperature, a significant mass transport loss on the cell with $2.5 \text{ }\mu\text{m}$ -thick sputtered Ag was observed at all temperatures. It is because of insufficient supply of oxygen at the Ag|YSZ interface and such loss was reduced when the thickness of cathode decreased to $1 \text{ }\mu\text{m}$. Unlike sputtered Ag cathodes, the inkjet-printed Ag cathode could retain porous structure at the operating temperature and resulted in higher power density. However, the inkjet-printed Ag could not provide such a high TPB density as sputtered Pt, the power density is therefore slightly lower for the cells with the inkjet-printed Ag cathode.

Considering the long-term operating stability of Ag cathodes, **Figure 5-7** (d) shows the current output test of the fuel cell with inkjet-printed porous Ag at $400 \text{ }^{\circ}\text{C}$ for over 45 hours. The fluctuation of output current was observed during the test, and this phenomenon may come from the slight change of Ag cathode morphology during the test that caused the change of effective ORR site. After the test, the current density was about 12 % lower than the initial current density. The current density of sputtered nanoporous Ag cathode ($2.5 \text{ }\mu\text{m}$) decreased more than 68% after 20 hours of operation. An earlier study also showed that when nanoporous Pt cathode was used, the current output decreased more than 86 % after operating at $450 \text{ }^{\circ}\text{C}$ for 40 hours^{10,116}. The results suggest that nanoporous pure metal cathode may not be suitable for long-term operation.

Figure 5-7. Polarization (I-V) curves of SOFCs measured at (a) 300 °C, (b) 350 °C, and (c) 400 °C. (d) Current density over 45 hours at 400 °C for the SOFC with inkjet-printed Ag and sputtered Ag cathode. The output current decreased 12.1 % and 68.1 % on average at 0.7 V after the test for inkjet-printed Ag and sputtered Ag, respectively.

The comparison of Ag thin film morphology before and after fuel cell test is shown in **Figure 5-8**. The inkjet-printed Ag film remained a porous structure with larger pore size after cell test, while the sputtered Ag films (1 μm and 2.5 μm) became denser with larger grain size. These results were similar to the samples which were annealed at 400 °C as shown in **Figure 5-3**.

To facilitate oxygen gas diffusion on the cathode, a porous structure is necessary. Therefore, from **Figure 5-3** and **Figure 5-8**, sputtering technique, which is typically used to create a porous thin film electrode structure, may not be suitable as a deposition method for porous Ag thin film, compared to the inkjet-printed technique.

Figure 5-8. (a) – (c) Morphology of as-prepared Ag thin films before fuel cell test. (d) – (f) Morphologies of Ag thin film after fuel cell test at 400 °C.

5.4 Conclusions

The Ag cathodes fabricated by two methods, inkjet-printing and sputtering, were examined at 300 °C to 450 °C using EIS technique. The inkjet-printed Ag film maintained a porous structure at the elevated temperature and stable current output test at 400 °C for 45 hours. By introducing a porous structure within Ag thin film cathode, the polarization resistance was significantly reduced at temperatures below 400 °C. For cathode thin film fabrication, inkjet printing technique using Ag nanoparticles can be an excellent method to create morphologically stable and porous Ag electrodes, which is difficult to be obtained by conventional vacuum-based deposition methods.

Chapter 6

Stability and Performance of Silver Cathode with Surface Modification for Low-Temperature Solid Oxide Fuel Cells

Thermal stability and electrochemical properties of the surface-modified silver cathode for low-temperature solid oxide fuel cells (LT-SOFCs) were studied in this work. The thermal stability of silver thin film could be improved by depositing a 2nm-thick of gadolinium-doped ceria (GDC). The effect of GDC capping on surface O-exchange properties was studied by the electrochemical impedance spectroscopy (EIS) measurement. The GDC capping could reduce the ohmic resistance while increase the polarization resistance since GDC capping impedes oxygen surface exchange on silver, resulting in a significant reduction of the fuel cell performance. The GDC-modified cathode could be operated at 400 °C for 24 h with 7.8 % of output degradation. These results provide engineering strategies for applying silver as a cathode for LT-SOFCs.

6.1 Introduction

Silver is one of the potential cathode candidates for solid oxide fuel cells (SOFCs) because of its high catalytic activity ¹²⁷, excellent oxygen solubility ($\sim 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$) ¹³, and permeability (oxygen diffusivity $D = 4.98 \times 10^{-3} \exp[(0.50 \pm 0.13 \text{ eV}) / k_B T]$) ^{13,14}. These properties are crucial for efficient oxygen reduction reaction (ORR) at the cathode. Moreover, the excellent electrical conductivity and lower cost as compared to other noble metals, such as platinum (Pt) and palladium (Pd), also make Ag a promising cathode material for SOFCs. However, due to its poor thermal stability, pure Ag is not employed as the main cathode material for conventional high-temperature or intermediate-temperature SOFCs, which operates at temperatures above 500 °C. At elevated temperatures, the thermally unstable Ag cathode may suffer from breakage of electrical connection network or a decrease in porosity ⁶⁹, resulting in performance degradation and SOFC failure.

In the past few years, researchers had successfully lowered the operating temperature of SOFCs from 800 °C to below 500 °C without sacrificing its high performance ^{1,9,31,38}. Lowering the operating temperature of SOFC makes it possible to apply Ag as the main cathode material. These low-temperature SOFCs (LT-SOFCs) utilized thin-film electrolyte structure to minimize the ohmic resistance for oxygen ion transport and applied nanoporous metallic cathode to maximize triple phase boundary (TPB), where the ORR takes place. However, these nanoporous cathodes are vulnerable at elevated temperature and resulting in significant fuel cell performance degradation after few hours of operation ¹⁰. Therefore, developing a stable metallic thin-film cathode is one of the major issues for the development of LT-SOFC. To enhance the thermal stability when applying Ag cathode on SOFC, Shim *et al.* designed an Ag thin-film nanomesh, which had perforated pores with around 500–600 nm in diameter ¹⁷. The Ag nanomesh remained stable for two hours without significant cell performance degradation at 277 °C. However, this low

operating temperature may not be sufficient to provide a satisfactory SOFC performance to date. To employ Ag cathode at higher temperature, a pure Ag cathode with connected pores throughout the film, which was fabricated by inkjet printing technique, was used¹²⁸. This inkjet-printed Ag cathode could operate at 400 °C for 40 hours with a total power output degradation of ~12 %. Apart from using pure Ag as a SOFC cathode, surface modification is a feasible method to enhance the thermal stability of metallic electrodes. Electrolyte materials such as zirconia, YSZ, or ceria are often used for surface modification on metallic cathodes because of their high thermal stability and ion conductivity. By introducing these thermally stable protective layers on a metallic cathode, the thermal stability of thin-film electrode can be improved at operating temperature below 500 °C^{10,63,91,92}. The ion-conducting material capping on the surface can also serve as an extension of the electrolyte and provides ion-conducting pathways, resulting in higher TPB density. It has been reported that the surface exchange processes, such as O-adsorption, dissociation, and charge transfer, are the limiting factors in ORR^{88,89,129,130}. However, the effect of such ion-conducting materials layer on surface O-exchange kinetics is still unclear to date.

Among the electrolyte materials, doped ceria is one of the promising materials since it has high ionic conductivity at low temperature (< 650 °C)¹³¹; it is also a catalytically superior material for ORR^{9,22,41}, which can help improve ORR kinetics^{131,132}. Comparing the ceria-based oxides with zirconia-based oxides, studies from quantum mechanical simulations and experiments showed that yttria-doped ceria (YDC) had much lower activation energy, of 0.07 eV, compared to 0.38 eV of YSZ for oxygen incorporation¹³³. For the surface modification on the metallic cathode, gadolinium-doped ceria (GDC) could be a better choice since Ga doping provides higher oxygen diffusion coefficient than Y, Sm, or La -doped ceria¹³⁴. Therefore, GDC was selected as the surface modification material in this work.

In this study, GDC was applied on the surface of Ag by radio frequency (RF) sputtering to improve the thermal stability of Ag. The thermal stability of surface-modified Ag cathodes was evaluated by morphological characterization, and their performance was also evaluated by electrochemical impedance spectroscopy (EIS).

6.2 Experimental Methods

Two Ag cathode structures, a porous Ag cathode and a combined porous and dense Ag cathode, were used in this work as shown in **Figure 6-1**. For the porous Ag cathode, with a GDC layer deposited on the surface (refer as porous Ag/GDC cathode hereafter), the oxygen ion can be conducted from cathode surface to the electrolyte. In this case, the GDC capping functions as an extended TPB^{63,91,92}. For the combined porous and dense Ag structure (refer to as Ag cathode hereafter), a defined TPB is provided. This dense Ag layer has two main functions. First, to minimize TPB variation caused by cathode agglomeration during testing. Second, when applying GDC surface modification on Ag cathode (refer as Ag/GDC cathode hereafter), the dense Ag layer could also minimize the conduction of the surface reduced oxygen ion. This design allows us to observe the variation in surface O-exchange properties on an Ag cathode with surface modification.

6.2.1 Preparation of Ag Thin Film Cathodes

A 1.5 μm -thick dense Ag layer was used to prevent significant structural change at the interface during the test. Dense Ag layer was deposited on a 200 μm -thick single crystal $\langle 100 \rangle$ YSZ (8YSZ, Latech Scientific Supply Pte. Ltd., Singapore) by RF sputtering. The Ag was sputtered at 3 mTorr of Ar atmosphere and 100 W of power using pure Ag target (99.99%, Latech Scientific Supply Pte. Ltd., Singapore); the deposition rate was 26 nm min⁻¹.

The porous Ag layer was deposited by brush-painting technique. The painted-Ag ink contains 10 wt.% of 200-nm Ag particles in a humectant solution (30% ethylene

glycol and 70% water). After deposition, the painted-Ag ink was annealed at 200 °C for 1-hour to burn out the solvent and sinter the particles together to form a porous film.

For the surface modification on Ag cathode, 2 nm-thick GDC was capped on the Ag surface by RF sputtering using $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$ (Latech Scientific Supply Pte. Ltd., Singapore) target. The deposition was carried out at 3 mTorr of Ar atmosphere with a power of 200W, and the deposition rate is 1 nm min^{-1} .

Figure 6-1 Illustration and the SEM images of the cathode structures used for the test. (a) The porous Ag cathode with a GDC capping layer, the oxygen ion can be conducted from cathode surface to the electrolyte; (b) the combined porous and dense Ag structure which provides a defined TPB to minimize variation during the test, the dense Ag layer also minimized the conduction of the surface reduced oxygen ion.

6.2.2 Morphological Characterization.

The porous Ag film was annealed at 300, 350, and 400 °C for 1 hour before the examination of the morphology. Surface and cross-sectional microstructure of the

porous Ag film was characterized by field-emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan).

6.2.3 EIS and Fuel Cell Measurement

For the EIS and fuel cell measurement, a 150-nm-thick porous Pt was sputtered as the anode at 30 mTorr of Ar atmosphere and 100 W of power. To minimize the morphological difference of Ag cathodes, which may affect the performance during the measurement, all Ag cathodes for EIS and fuel cell measurement were pretreated at 400 °C before GDC capping. EIS of Ag cathodes was measured at 300 to 400 °C and the frequency range between 1 MHz and 0.05 Hz with an oscillation amplitude of 50 mV by Solartron 1470E potentiostats system and a 1255B Frequency Response Analyzer (FRA). The characterization was done using hydrogen (99.99%) as a fuel at a flow rate of 20 sccm and ambient air as an oxidant. The obtained EIS curves were fitted by Z-Plot software (Scribner Associates Inc., USA) based on a complex nonlinear least-square fitting method with equivalent circuit model of the model of one resistor with two parallel resistors/constant phase elements (R-CPEs) in series.

6.3 Results and Discussion

6.3.1 Thermal Stability of GDC-Capped Ag

The cross-sectional view of Ag cathodes is shown in **Figure 6-1**. The painted Ag nanoparticles formed a connected porous film after annealed at 350 °C for 1 hour. **Figure 6-1b** shows a porous and dense “bi-layer” structure of Ag cathode. This dense Ag at the interface ensured that the interfacial structure remains stable without affecting TPB density during the test. The stable cathode structure can minimize the impedance variation caused by the interfacial structural change during EIS

measurement. On the other hand, the porous Ag layer provided a higher surface area for oxygen adsorption and dissociation.

The surface morphologies of Ag cathode were examined to verify the thermal stability at the target operating temperature of 400 °C. **Figure 6-2** shows the surface morphologies of porous Ag films under different temperature. The as-deposited film was composed of Ag nanoparticles in close contact (**Figure 6-2a**). For the Ag thin-film with GDC capping, it showed less morphological change on the surface at 300 to 400 °C (**Figure 6-2b - 2d**). For the Ag thin-film without GDC capping, it agglomerated and formed micron-scale pores at 300 °C, and the thin-film kept merging into larger Ag clusters/grains at 350 and 400 °C.

Figure 6-2 Microstructure evolution of porous Ag thin film at 300 °C to 400 °C for (a) – (d) porous Ag with GDC surface capping, and (e) – (h) bare porous Ag. All images are at the same magnification.

The cross-sectional morphology of GDC-capped Ag thin film was also examined. As shown in **Figure 6-3**, the inner structure, which was composed of Ag nanoparticle, was agglomerated and formed micron-scale pores and Ag cluster after annealed at 400 °C. Since the GDC layer covered the very top surface of Ag thin film only, the

improvement of thermal stability was only effective up to ~ 250 nm below the surface of Ag thin film. To fully cover the interior pore surface of the Ag thin film, alternative surface modification technique such as atomic layer deposition, which can form a conformal deposit on irregular substrates⁹³, is needed.

Figure 6-3 Cross-sectional images of (a) as-prepared and (b) 400 °C annealed GDC-capped Ag thin film. The GDC layer enhanced thermal stability on the surface of Ag thin film, while the inner structure agglomerated after annealed at 400 °C.

Figure 6-4 shows the TEM images of GDC capping on Ag thin-film surface. As shown in the subset of **Figure 6-4a**, the fringe distance of GDC was $3.1 \text{ \AA}$, which matches with the reported lattice constant of ceria (111)¹³⁵. The sputtered GDC capping was ~ 2 nm in thickness on the surface of Ag cathode. As shown in **Figure 6-4b**, this thin GDC layer was thermally stable after annealed at 400 °C. The GDC capping layer remained similar structure without breakage, and it could prevent Ag being agglomerated into larger cluster/grain-agglomeration at 400 °C. Also, the continuous GDC layer could provide ion conduction pathways for ORR.

Figure 6-4 TEM image of GDC capping on the surface of Ag thin-film for (a) as-deposited GDC capping on Ag surface; and (b) GDC capping on Ag surface after annealed at 400 °C. The morphology of GDC capping on Ag remained similar without significant change.

6.3.2 EIS Analysis of Ag Cathodes

EIS of the cells with and without surface modified cathodes are shown in **Figure 6-5**. In the Nyquist plot (**Figure 6-5a** and **Figure 6-5b**), the first intercept on the real axis (Z') represents the Ohmic resistance R_Ω of the cell; the horizontal span of the curve represents the polarization resistance, R_p , of the cell. There are two arcs can be identified in the EIS curves. One arc has the characteristic frequency at the medium-frequency range (MF, $\sim 10^3$ Hz) and the other at low-frequency range (LF, ~ 1 Hz) as shown in the Bode plot (**Figure 6-5c**). The EIS curves were fitted using the equivalent circuit model of one resistor and two parallel R-CPEs connected in series, as shown in the inset of **Figure 6-5a**. By fitting the data to the R-CPE model, the effective resistances and capacitances for the EIS curves may be extracted¹²¹. The values derived from the curve fitting are summarized in Table 1.

As compared to the cells with different cathode structures, the polarization resistances R_p of the cell with Ag cathode were 1171.4, 948.5, and 767.3 Ωcm^2 at 350, 375, and 400 °C, respectively; the cell with porous Ag cathode were 1694.1, 574.5, and 352.8 Ωcm^2 at 350, 375, and 400 °C, respectively. Since the electrolyte and anode were identical for all cells measurement, the variation of R_p came from

different cathode structure. The dense Ag layer impeded oxygen diffusion and removal of this dense Ag layer could reduce polarization resistance. This result also reflected in the suppression of LF phase angle, which relates to the oxygen diffusion and dissociative adsorption process^{10,121,136}, when employing porous Ag cathode (**Figure 6-5c**).

The polarization resistances R_p of the cell with Ag/GDC cathode were 8746.0, 4965.8, and 2541.4 Ωcm^2 at 350, 375, and 400 °C, respectively; the cell with porous Ag/GDC cathode were 3338.4, 1242.9, and 421.2 Ωcm^2 at 350, 375, and 400 °C, respectively. Applying GDC surface capping resulted in an increase of polarization resistance for both of the Ag/GDC and porous Ag/GDC cathodes. Since Ag had higher oxygen exchange kinetics¹³⁷, the GDC capping could form a “blocking” layer for oxygen surface exchange and result in higher polarization resistance. This phenomenon reflected on the increase of LF phase angle in Bode plots (**Figure 6-5c**). To recover the surface O-exchange properties on GDC-capped Ag cathode, an extra Ag layer can be deposited on the GDC capping to promote the surface O-exchange kinetics.

Comparing the effect of GDC capping on two different Ag structure, the increase of phase angle is more pronounced in Ag cathode than porous Ag cathode. Since the gaseous oxygen could not reach the TPB directly, the oxygen supply to the electrolyte interface was mainly from the surface adsorption. The insufficient oxygen supply resulted in high impedance in the LF region. While on the porous Ag cathode, the gaseous oxygen could still reach TPB; therefore, the increase of LF impedance was less significant.

Figure 6-5 Nyquist plots of EIS measurements for (a) Ag/GDC cathodes, (b) porous Ag/GDC cathodes, and (c) Bode plots for all cathodes. The EIS was measured at 400 °C and 0.7 V of applied voltage.

Another effect of GDC capping on Ag cathode is that the Ohmic resistance R_Ω was reduced as shown in **Table 6-1**. This phenomenon is likely resulting from the increase of TPB length with the GDC capping, as reported in earlier works^{91,92}. With more TPB, the resistance for ion-conduction was reduced, which reflected on the decrease of Ohmic resistance. Since the increase of polarization resistance was less than the decrease of Ohmic resistance, the total impedance ($R_\Omega + R_p$) reduced with GDC capping for the porous Ag; while the total impedance increased for the Ag cathode with GDC capping because of the significant increase of polarization resistance.

Table 6-1 Summary of the equivalent circuit fitting of the EIS at 350, 375, and 400 °C.

Fuel Cell Cathode	Temp (°C)	R_{Ω} (Ωcm^2)	R_p (R_1+R_2) (Ωcm^2)	MF Arc			LF Arc		
				R_1 (Ωcm^2)	$\text{CPE}_1\text{-T}$ (F)	$\text{CPE}_1\text{-P}$	R_2 (Ωcm^2)	$\text{CPE}_2\text{-T}$ (F)	$\text{CPE}_2\text{-P}$
Ag	400	1186.0	767.3	575.3	3.33E-04	0.50	192.0	1.50E-03	0.90
	375	2612.0	948.5	456.2	1.35E-04	0.69	492.3	1.07E-03	0.99
	350	6109.0	1771.4	1166.0	9.76E-05	0.68	605.4	1.50E-03	0.98
Ag/GDC	400	1052.0	2541.4	600.4	1.15E-04	0.71	1941.0	3.07E-04	0.96
	375	2260.0	4965.8	556.8	4.16E-05	0.90	4409.0	2.23E-04	0.83
	350	5048.0	8746.0	2580.0	1.57E-04	0.66	6166.0	2.57E-04	0.99
Porous Ag	400	1190.0	325.8	74.6	9.43E-05	0.90	251.2	3.63E-04	0.43
	375	2850.0	574.5	339.3	1.02E-05	0.99	235.2	1.54E-04	0.99
	350	6753.0	1694.1	375.1	1.18E-06	0.94	1319.0	7.50E-05	0.68
Porous Ag/GDC	400	963.5	421.2	148.5	4.84E-05	0.77	272.7	8.69E-04	0.76
	375	1952.0	1242.9	681.6	3.02E-04	0.38	561.3	7.78E-04	0.85
	350	4491.0	3338.4	256.4	2.69E-06	0.98	3082.0	2.92E-04	0.55

6.3.3 Fuel Cell Performance

Figure 6-6 shows the polarization (I–V) curves of SOFCs with Ag, Ag/GDC, porous Ag, and porous Ag/GDC cathodes at 400 °C and the peak power density at 300 to 400 °C. The cell with nanoporous Pt cathode is included as a reference. At 400 °C, the peak power densities are 185.1, 131.0, 196.5, 225.2, and 216.2 μWcm^{-2} for the cells with Ag, Ag/GDC, porous Ag, porous Ag/GDC, Pt cathodes, respectively. These results are in line with the EIS measurement; the cell with lower total impedance had higher maximum power density. Employing porous Ag/GDC cathode could reach similar performance as the Pt cathode at 300 to 400 °C as shown in **Figure 6-6b**.

Figure 6-6 (a) Polarization (I-V) curves of SOFCs measured at 400 °C and the maximum power density of the SOFCs at 300 to 400 °C.

Considering the long-term stability of GDC-capped Ag cathode, **Figure 6-7** shows the current output test of the fuel cell with porous Ag/GDC cathode by applying 0.7 V at 400 °C for 24 h. Since the GDC capping was deposited by sputtering, it could not cover the interior pore surface of Ag cathode entirely. Therefore, the morphology of porous Ag cathode may change, which resulted in a change of the effective ORR site, during the test and led to the fluctuation of the output current. After the test for 24 h, the current density was about 7.8 % lower than the initial current density.

Figure 6-7 Current density curves for the SOFC with porous Ag/GDC cathode at 400 °C and 0.7 V over 24 h. The output current decreased 7.8% after the test.

6.4 Conclusion

The electrochemical properties of GDC-capped Ag cathode were investigated in this work. Surface modification by GDC capping could enhance the thermal stability of Ag cathode at 400 °C. However, employing GDC on Ag cathode impeded the oxygen surface exchange kinetics and led to a higher polarization resistance. These results showed that when using ion-conducting materials for surface modification on Ag cathode, the electrochemical performance of the cathode could be worse. On the other hand, the GDC capping could extend the TPB length and provided ion-conducting pathways to lower the Ohmic resistance. These results could be used to provide engineering strategies when applying Ag cathode for LT-SOFCs.

Chapter 7

Silver as a Cathode for Silicon-Based Micro Solid Oxide Fuel Cells[‡]

In this chapter, μ -SOFCs using pure silver thin film as a lower cost cathode material to replace the typical porous platinum cathode is presented. The drastically reduced operating temperature of μ -SOFCs below 400 °C has enabled the application of silver as a cathode that was considered impractical for conventional SOFCs operating at temperatures higher than 800 °C. The fabrication of the μ -SOFCs with a robust nanoscale electrolyte membrane that could integrate silver nanoparticle cathode on to the fragile membrane is presented. The electrochemical performance of fuel cells using silver nanoparticle cathode was characterized at temperatures below 400 °C and was compared with the silver cathode deposited by typical sputtering method. A satisfactory thermal stability of the silver thin film cathode was achieved by using silver nanoparticle cathode, and comparable performance to cells using costly platinum cathode was attainable.

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7.1 Introduction

With the help of silicon micromachining and thin film deposition technologies, silicon-based nano-thin film electrolyte solid oxide fuel cell, or usually referred as a μ -SOFC which utilizes silicon as a supporting substrate for the nanoscale electrolyte shows great potential as a portable power source. The success in fabricating free-standing electrolyte membranes with only tens of nanometer thickness drastically decreases the ohmic resistance from ion transport across the electrolyte, thus allows lower operating temperature of SOFCs from conventionally more than 800 °C to below 500 °C^{9,31,38}.

Figure 7-1 (a) shows a typical μ -SOFC schematic with the anode, the electrolyte, and the cathode, altogether supported by a micro-machined silicon substrate as a free-standing membrane. As shown in **Figure 7-1** (b) and **Figure 7-1** (c), the main features of a silicon-based μ -SOFC are the nano-thin film porous metallic cathode and anode that are usually deposited by sputtering, and a nano-thin film oxide electrolyte that is dense and pinhole-free to allow only ion conduction without electric leakage between the two electrodes.

One major obstacle to the advance of μ -SOFCs is the high cost of the noble metal catalytic cathode, which is platinum in most reported high-performance μ -SOFCs^{9,31,38}. Due to the drastically reduced operating temperature of SOFCs that causes sluggish cathode reaction kinetics, the catalytically most active platinum cathode is so far the best and the most common choice for μ -SOFCs.

In search of a suitable cathode material for μ -SOFCs, silver is a potential alternative to platinum since it has a comparable catalytic activity to platinum¹²⁷. Silver also has excellent oxygen solubility ($\sim 10^{-6}$ mol $\cdot$ cm $^{-3}$ ¹³) and permeability (oxygen diffusivity $D = 4.98 \times 10^{-3} \exp[(0.50 \pm 0.13 \text{ eV}) / k_B T]$ ^{13,14}), which does not exist in platinum, and therefore can likely further enhance the cathodic reaction kinetics.

Studies have shown that the ORR of silver on YSZ was comparable to or even better than that of noble metals like platinum due to the increased oxygen incorporation into the electrolyte ^{16,17}. Also, the superior electrical conductivity of silver also minimizes the sheet resistance of the electrode. The much lower cost of silver is another attractive advantage for such application.

The main issue of using silver as a cathode for SOFCs is its poor thermal-morphological stability. Silver particles are very mobile at the elevated temperatures ⁶⁷, and therefore is seldom employed in a pure metallic form for SOFCs at temperatures above 500 °C, but more often as a constituent of the composite with perovskite oxides or ion-conducting electrolytes ^{108,111}. For applications of the pure silver cathode at temperatures below 500 °C, also only a few reports are available ^{17,91,138}. The lack of reports at this temperature regime may be due to the limited access to fabricate reliable nano-thin film μ -SOFCs for such purpose. Another challenge to utilize pure silver is the difficulty in fabricating nanoporous silver by conventional sputtering technique as what has been done for nanoporous platinum, as well as the difficulty in maintaining the high density of the porosity during the fuel cell operation, both because of the poor morphological stability.

In this work, a pure silver thin film cathode with nanoscale pores and thermal-morphological stability under fuel cell operating conditions was integrated as a cathode for μ -SOFCs. The electrochemical properties of silver cathodes were studied to characterize the performance of the cathode at temperatures between 300 and 400 °C. Long term current stability test was also done to verify the thermal-morphological stability of silver cathode.

Figure 7-1 (a) Schematic of a typical silicon-based μ -SOFC, with the free-standing membrane supported by a (100) single crystalline silicon. The electrolyte membrane is sandwiched by nano-thin film cathode and anode; (b) Cross-sectional SEM image of fuel cell membrane (Pt/YSZ/Pt), with a total thickness of ~ 300 nm only; (c) SEM image of the top view of a typical nano-porous platinum cathode deposited by RF sputtering.

7.2 Experimental Methods

7.2.1 Fabrication of μ -SOFCs

Figure 7-2 shows the fabrication process for the circular membrane μ -SOFC recently developed in our laboratory. The μ -SOFC is a free-standing membrane fabricated on a (100) single crystalline silicon substrate by a series of micromachining process, and the membrane is composed of a thin film silver cathode deposited by sputtering or brush-painting, a YSZ electrolyte, and a sputtered platinum anode. Compared to most of the reported μ -SOFCs which usually have the membrane shape to be square, this circular membrane has effectively enhanced the mechanical stability of the membrane. This design allows the free-standing

membrane to have a diameter of up to 2 mm to be utilized as a reliable platform for the study of the silver cathode. For the electrolyte thin film, 100 nm-thick YSZ was deposited by ALD at 250 °C of substrate temperatures. For the anode, 150-nm-thick porous Pt was sputtered at 30 mTorr of Ar atmosphere and 100 W of power. A detailed description of the cell fabrication process can be found in reference ³⁸.

Figure 7-2 Fabrication process for the circular thin film μ -SOFC with tapered edge support.

7.2.2 Fabrication of Nanoporous Thin Film Silver Cathode

The bare nanoporous thin film silver cathode was fabricated by two different methods, namely sputtering and brush-painting. The sputtered silver thin film cathode (sputtered-Ag hereafter) was deposited with a high density of nanoscale porosity using a custom-made RF (radio frequency) sputtering apparatus at the power of 100 W under 30 mTorr of Ar atmosphere at room temperature. The thickness of sputtered-Ag was 200 nm. The brush-painted silver thin film cathode (painted-Ag hereafter) was painted by utilizing a silver ink, which was prepared by adding 10 wt. % of silver nanoparticles 200 nm in diameter into a humectant solution (30% ethylene glycol and 70% water). The painted-Ag was post-annealed at 350 °C

for 1 hour after painting to sinter the particles together as an integrated thin film and at the same time to establish the porosity. Both the bare sputtered-Ag and painted-Ag were then coated with a 2 nm-thick YSZ layer conformally by ALD to prevent the porosity of silver from severe thermal agglomeration, and at the same time to improve the cathode surface adsorption^{91,139}.

7.2.3 Fuel Cell Test and Electrochemical Characterizations of Silver Cathode

The fuel cells with silver cathodes were measured at temperatures between 300 °C to 400 °C using an electrochemical potentiostat (Solartron 1470E, Solartron Analytical, USA). The characterization was done using hydrogen (99.99%) as a fuel at a flow rate of 20 sccm and ambient air as an oxidant.

The electrochemical impedance spectroscopy (EIS) measurement of cathodes was performed on a commercial single crystalline YSZ substrate (8YSZ, 100 μ m-thick, Latech Scientific Supply Pte. Ltd., Singapore) to minimize the error introduced by the electrolyte. The measurement was conducted at the frequency range between 1 MHz and 0.1 Hz with an oscillation amplitude of 50 mV. The impedance data was fitted by Z-Plot software (Scribner Associates Inc., USA) based on complex nonlinear least-squares fitting method, using the model of one resistor with two parallel resistors/CPE in series. The polarization impedance was normalized by the active planar surface area (0.04 cm²) of the cell to obtain the ASR of the electrodes.

7.2.4 Morphological Characterization of Silver Cathode

The surface morphology of the silver cathodes was studied using a field emission secondary electron microscope (FESEM, JEOL JSM-7600F, USA). The operating voltage of FESEM was 15kV.

7.3 Results & Discussion

7.3.1 Thermal Stability of Silver Thin Film Cathodes

Figure 7-3 (a) shows the fabricated circular freestanding membrane μ -SOFC with the silver thin film cathode on top of the electrolyte. The freestanding part of the YSZ membrane (the inner circle) has a lateral dimension of 2 mm, which is also the effective reaction area of the μ -SOFC. The silver cathode thin film was deposited to be larger than the freestanding membrane to allow ease of current collection by a micromanipulator.

The surface morphologies of sputtered-Ag and painted-Ag with and without the 2 nm ALD-YSZ capping are shown in **Figure 7-3**. The sputtered-Ag has an initial smaller pore size but with poorer thermal stability, and it was agglomerated severely after fuel cell tests at 400 °C for 24 hours (**Figure 7-3c**). The 2 nm ALD-YSZ capping was not effective for the sputtered-Ag to maintain its morphology, and also showed agglomeration with the majority of the pores closed after 24 hours. The agglomeration pattern of ALD-YSZ-capped sputtered-Ag (**Figure 7-3d**) was different from the uncapped sputtered-Ag (**Figure 7-3c**) due to the thin YSZ capping that prevented the dewetting of Ag from the underneath YSZ electrolyte but did not prevent the pores from closing. For the painted-Ag, the fuel cell test at 400 °C caused only a minor morphological change (**Figure 7-3f**) since the film was post-annealed at 350 °C when it was fabricated. The 2 nm ALD-YSZ capping on painted-Ag seemed to be effective since the morphology after testing (**Figure 7-3g**) was similar to the as-prepared film (**Figure 7-3e**).

Figure 7-3 (a) Circular free-standing membrane μ -SOFC with the silver cathode. (b) Morphologies of sputtered-Ag: (b) as-deposited sputtered-Ag, (c) sputtered-Ag after tested at 400 °C, and (d) sputtered-Ag with 2 nm ALD-YSZ capping after tested at 400 °C. Morphology of painted-Ag: (e) as-prepared painted-Ag, (f) painted-Ag after tested at 400 °C, and (g) painted-Ag with 2 nm ALD-YSZ capping after tested at 400 °C.

7.3.2 Current Stability of SOFCs with Sputtered and Painted Silver Cathodes

Figure 7-4 shows the fuel cell current density obtained at 0.7 V of the voltage at 400 °C for more than 20 hours. The current stability is directly related to the thermal stability of the silver cathode since the cathode ORR is the most critical in determining the cell performance. The cell using painted-Ag showed higher output current density with thermal stability. With the ALD-YSZ capping on sputtered-Ag, the current density was further improved. For the cell using sputtered-Ag cathode, the current density dropped at the first few hours due to the unstable silver cathode morphology, as observed in **Figure 7-3** (c). For the painted-Ag, the output current

was not only higher than sputtered-Ag, but it also showed much less current degradation at 400 °C over 24 hours. The current output dropped only 6.5 %, 13.8 % from the initial value for cells using YSZ-capped and uncapped painted-Ag, respectively, but dropped 68.1 % after over 20 hours of operation for sputtered-Ag. These results showed that the painted-Ag had a better thermal stability than the silver cathode prepared by sputtering for the longer term operating of μ -SOFCs.

Figure 7-4 Long term current density test for painted-Ag, ALD-YSZ-capped painted-Ag, and sputtered-Ag cathodes for over 20 hours at 0.7 V and 400 °C. The painted-Ag showed stable current output, and with the YSZ-capping on painted-Ag, the current stability was further improved. The sputtered-Ag showed severe degradation in cell current density.

7.3.3 Electrochemical Impedance Analysis

Figure 7-5 (a) shows the equivalent circuit for fitting and the representative Nyquist plots of the μ -SOFC with the uncapped sputtered-Ag cathode at OCV and under different applied DC biases of 0.7 V and 0.3 V at 400 °C. There are two distinct semi-arcs. The high-frequency arc on the left is mainly associated with the series ionic resistance of electrolyte and electronic resistance in the electrode ¹²¹ and was independent of the magnitude of the applied DC bias. The low-frequency arc on the right is attributed to anode and cathode reaction processes, where in this case should

mainly come from the contribution of cathode reactions due to the much more sluggish ORR kinetics on the cathode ¹²⁷.

Figure 7-5 (a) EIS plots of sputtered-Ag under different applied DC bias (bottom), with the fitting model used (top); (b) EIS plots of sputtered-Ag, sputtered-Pt, and painted-Ag measured at 400 °C measured at OCV with the high-frequency electrolyte resistance subtracted. All cathodes were not capped with YSZ.

To compare and to verify the electrochemical performance of silver cathodes, the low-frequency arcs of a fuel cell with sputtered-Ag, painted-Ag, and the typical sputtered-Pt cathodes (all without capping of YSZ) were extracted from the curve fitting, as shown in **Figure 7-5** (b). The cell with sputtered-Ag showed the highest ASR than the other cells with painted-Ag and sputtered porous Pt, where the high resistance value came from the very limited porosities that hindered the gaseous oxygen diffusion through the Ag cathode for cathode reaction. The high ASR is also from the limited porosities after the agglomeration that resulted in insufficient triple phase boundaries (TPBs) for ORR at the cathode|electrolyte interface. On the other hand, the low ASR for painted-Ag was attributed to the well-maintained porosity during testing that rendered minimum morphological changes to facilitate the

gaseous oxygen diffusion and maintained high TPBs for low impedance ORR. The interconnected pore network also provided a larger surface area which may have enhanced oxygen adsorption and dissociation, which is one of the rate-limiting steps among ORRs¹³⁹. Compared to the typical high-performance sputtered-Pt cathode among the reported μ -SOFCs, the painted-Ag showed a similarly low ASR value, indicating that silver can be a promising substitute for the costly Pt with a well-designed porous structure.

7.3.4 μ -SOFC with Silver Cathode

The EIS results showed painted-Ag has higher performance than commonly used sputtered-Ag, and it also showed comparable performance as the sputtered-Pt cathode. Therefore, we adopt painted-Ag electrode in μ -SOFC and compared with μ -SOFC with SP-Pt cathode. The result is shown in **Figure 7-6**. The OCV of μ -SOFC with sputtered-Pt cathode was around 0.7 V at 400 °C; this low OCV was due to the electron leakage through the electrolyte. While applying silver cathode on the μ -SOFC, the OCV was down to ~0 V as shown in **Figure 7-6b**. Since silver is mobile under elevating temperature, silver may diffuse into the pinholes in the electrolyte and caused electron leakage. To overcome the challenge of using silver cathode, thicker electrolyte or a blocking layer is needed. A recent report demonstrated a high-performance SOFC with 11.8 μm -thick $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) electrolyte, which could achieve a peak power density of 1116 mW cm^{-2} with the ohmic resistance of $9.05 \Omega \text{ cm}^2$ at 500 °C¹⁴⁰. The electrolyte thickness was only 100 nm in this study, and since the ohmic resistance is proportional to the electrolyte thickness, it is possible to utilize the electrolyte with the micrometer-scale thickness without scarifying much of the performance.

Figure 7-6 (a) Polarization (I-V) curves of μ -SOFCs; (b) OCV of μ -SOFC with the painted-Ag cathode, OCV was close to zero volt due to silver penetrated through YSZ membrane and caused a short circuit.

7.4 Conclusion

We demonstrated a silicon-based μ -SOFC using pure silver as a cathode alternative to the typically utilized platinum. Comparable electrode performance from the silver electrode fabricated by paint-brushing with nanoparticles was obtained, with much better thermal morphological stability than the cell using silver cathode prepared by the commonly used sputtering technique. A 2 nm of ALD-YSZ capping layer improved the thermal stability of brush-painted silver cathode as well as the current density. This work shows the feasibility of using pure silver as a cathode material for μ -SOFCs operating at a temperature below 400 °C that can potentially be further advance the practical commercialization of such device.

Chapter 8

Conclusion and Future Work

The threads of this doctoral work are drawn together in this chapter. A characterization method to reveal real ORR site for LT-SOFC development was established in this work. This DCB method can be utilized in thin-film cathode design, providing precise TPB structural information. An Ag cathode with enhanced thermal stability and performance was developed. By cathode surface modification, the Ag cathode is possible to be operated at 400 °C without significant output degradation. This Ag cathode could be utilized as an alternative for Pt with comparable performance. Based on the current outcome, opportunities and strategies for future work such as optimizing Ag cathode structure, integrating Ag cathode into μ -SOFC, and developing oxide/metal hetero cathode structure are proposed.

8.1 Summary and Contributions

The objective of this doctoral project is to develop a metallic cathode that could be operated at 500 °C and below with comparable high performance and long-term stability. Also, the cathode developed needs to be integrated into μ -SOFC. Therefore, the thin-film metallic cathode was chosen and studied. The major contributions of this dissertation are addressed as follow:

- **A precise structural characterization technique was established.** To understand the effect of thermal driven structural evolution on cathode/cell performance, a DCB delamination method for cathode|electrolyte interfacial characterization was developed. This method enabled direct observation of the electrode morphology at the Pt/YSZ interface, where the effective TPB was located. The DCB method was applied to nanostructure observations of the at the cathode|electrolyte interface. Through this approach, we found a different thermal-driven morphology evolution pattern on the cathode free surface and at the electrolyte interface for the nano-thin-film electrode. By this method, we could estimate the suitable operating temperature for the cathode precisely.
- **Developed a non-vacuum based thin-film cathode fabrication method.** An Ag cathode fabricated by inkjet printing were examined at 300 °C to 450 °C using EIS technique. The inkjet-printed Ag film maintained a porous structure at the elevated temperature and stable current output test at 400 °C for 45 hours. By introducing a porous structure within Ag thin film cathode, the polarization resistance was significantly reduced at temperatures below 400 °C. For cathode thin film fabrication, inkjet printing technique using Ag nanoparticles can be an excellent method to create morphologically stable

and porous Ag electrodes, which is difficult to be obtained by conventional vacuum-based deposition methods.

- **Enhancing thermal stability of the metallic cathode.** A GDC-coated Ag cathode was introduced to provide a better thermal stability. By investigating the electrochemical properties of GDC-coated Ag, we found that the GDC coating might impede the oxygen surface exchange kinetics and led to a higher polarization resistance. An extra decoration of Ag on the GDC-coated Ag cathode could be employed to recover the oxygen surface exchange kinetics. However, the resulting polarization resistance with Ag decoration was still higher than the bare Ag cathode. These results imply that when using ion-conducting materials for surface modification, the electrochemical performance of the cathode could be worse without efficient ion-conducting pathways. The results could be used to provide engineering strategies when applying Ag cathode for low-temperature SOFCs.

8.2 Suggested Future Work

8.2.1 Optimization of Ag structure

This dissertation had successfully demonstrated an Ag cathode fabricated by a non-vacuum based technique. To further enhance the cathode performance, durability, and reduce the precious metal loading, optimization of Ag cathode structure is needed. For the performance improvement, porosity (TPB) optimization can be done since the systemic study on cathode pore structure is lack. For the durability enhancement, further study on oxide/metal composite cathode is needed. There are two main factors to be considered when using composite cathode. Firstly, the content of oxide needs to be optimized to reach a balance between electronic conductivity and thermal stability. Secondly, the structure of a composite cathode, e.g. surface-coated oxide or layer by layer oxide insert or randomly distributed oxide in the Ag

cathode. These questions remain unsolved at the current stage. The other issue to be solved is to reduce the precious metal loading. Even the price of Ag is much lower than Pt. However, the thickness of Ag cathode is much thicker to maintain its structure under elevated temperature. It is addressed in this dissertation that applying oxide coating can enhance the thermal stability of Ag. Therefore, reduce the thickness is possible with suitable modification on the Ag cathode such as oxide coating. With further optimization, it is expected that Ag cathode could reach similar or even higher performance than Pt for LT-SOFC.

8.2.2 Integration of Ag cathode into μ -SOFC

The Ag cathode developed in this work showed a comparable performance to Pt cathode. However, when applying Ag cathode in μ -SOFC, the Ag could penetrate electrolyte and cause a short circuit between cathode and anode. This phenomenon was caused by thermo-electro migration and diffusion of Ag through YSZ^{141,142}. The possible solutions for this issue are introducing an Ag diffusion blocking layer or simply increase the electrolyte thickness. However, searching an effective blocking layer in nanometer scale is not an easy task; and increasing the electrolyte thickness of μ -SOFC may introduce higher stress on the electrolyte thin-film, the ohmic resistance increases as well. Therefore, extra work is needed to apply Ag-based cathode in μ -SOFC.

8.2.3 Develop oxide/metal hetero cathode structure

High-performance oxide materials had been developed for operating at a lower temperature (~ 600 °C)^{21,143–146}. However, these oxide materials still suffer from chemical stability, compatibility, or CO₂ poisoning issues¹⁴⁰. To solve these issues and enable the cathode to operate at a lower temperature (< 500 °C). The composite cathode was proposed to fulfill the requirement of LT-SOFC. This hetero cathode structure could promote ORR and therefore enhance the SOFC performance^{137,140,147}.

A recent work had successfully demonstrated a high-performance SOFC ($\sim 1 \text{ W cm}^{-2}$ at 500°C) with stable current output for 140 hours by using $\text{Sr}_{0.95}\text{Ag}_{0.05}\text{Nb}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}/\text{Ag}$ hetero cathode structure¹⁴⁰. These kinds of hetero cathodes were synthesis by in-situ growth phenomena of metal nanoparticles exsolved directly from the perovskite oxides (ABO_3) with thermal stability, and therefore, they could be a promising cathode material for LT-SOFC. Integration of such cathode on μ -SOFC would be one of the directions for LT-SOFC development.

Appendix

Tubular Atomic Layer Deposition System – Design and Deposition Parameter

Figure A-1 ALD Layout. 2 precursors (Y and Z) and 1 oxidant line (H_2O or O_2), purging by N_2 gas.

Figure A-2 ALD process chamber design. Stainless steel with replaceable quartz tube ($\phi 23\text{mm} \times 300\text{mm}$) inside.

Table A-1 Deposition parameters for ZrO₂

Zirconia	
Precursor	Tetrakis(dimethylamino)zirconium(IV), 99% TDMAZ (STREM)
Precursor temperature	65 °C
Line temperature	195 °C
Deposition temperature	245 °C
Chamber base pressure	150 mTorr
Oxidant	Water (room temperature, 25 °C)

*Deposition rate: 1.1 Å/cycle

Table A-2 ALD cycle for ZrO₂

Deposition cycle	
Precursor pulse	0.1 s
N₂ purging	20 s
Oxidant pulse	0.02 s (pulse pressure ~150 mTorr)
N₂ purging	30 s

Table A-3 Deposition parameters for Y₂O₃

Yttria	
Precursor	Tris(methylcyclopentadienyl)yttrium (99.9%-Y) (REO) (STREM)
Precursor temperature	170 °C
Line temperature	195 °C
Deposition temperature	245 °C
Chamber base pressure	150 mTorr
Oxidant	Water (room temperature, 25 °C)

*Deposition rate: 0.7~0.8 Å/cycle

Table A-4 ALD cycle for Y_2O_3

Deposition cycle	
Precursor pulse	0.1
N_2 purging	20 s
Oxidant pulse	0.02 s
N_2 purging	30 s

Figure A-3 Deposition rate versus temperature plot of ALD yttria and zirconia.

Table A-5 Deposition parameters for YSZ

YSZ	
Precursor temperature (Z)	65 °C
Precursor temperature (Y)	170 °C
Line temperature	195 °C
Deposition temperature	245 °C
Chamber base pressure	150 mTorr
Oxidant	Water (room temperature, 25 °C)

*Deposition rate: 6.3 Å/YSZ cycle

Table A-6 Yttria content in ALD YSZ**Deposition cycle (Z:Y = 4:1)**

Sample	Y ₂ O ₃ %
#1	9.54%
#2	7.14%
#3	6.99%
Average	7.89%
STDEV	1.17%

Figure A-4 Morphology of ALD YSZ

Publication List

- **Yu, C.-C.**; Baek, J. D.; Su, C.-H.; Fan, L.; Wei, J.; Liao, Y.-C.; Su, P.-C. Inkjet-Printed Porous Silver Thin Film as a Cathode for a Low-Temperature Solid Oxide Fuel Cell. *ACS Appl. Mater. Interfaces* **2016**.
- **Yu, C. C.**; Baek, J. D.; Su, P. C. Silver as a Cathode for Silicon-Based Micro Solid Oxide Fuel Cells. In *2016 IEEE 29th International Conference on Micro Electro Mechanical Systems (MEMS)*; **2016**; pp. 1260–1263.
- Baek, J. D.; **Yu, C.-C.**; Su, P.-C. A Silicon-Based Nanothin Film Solid Oxide Fuel Cell Array with Edge Reinforced Support for Enhanced Thermal Mechanical Stability. *Nano Lett.* **2016**, *16*, 2413–2417.
- Liu, K.-Y.; Fan, L.; **Yu, C.-C.**; Su, P.-C. Thermal Stability and Performance Enhancement of Nano-Porous Platinum Cathode in Solid Oxide Fuel Cells by Nanoscale ZrO₂ Capping. *Electrochemistry Communications* **2015**, *56*, 65–69.
- **Yu, C.-C.**; Kim, S.; Baek, J. D.; Li, Y.; Su, P.-C.; Kim, T.-S. Direct Observation of Nanoscale Pt Electrode Agglomeration at the Triple Phase Boundary. *ACS Appl. Mater. Interfaces* **2015**, *7*, 6036–6040.

Conference Presentations

- **International Conference on Technological Advances of Thin Films & Surface Coatings 2016**, Singapore
“Stability and Performance of Silver Cathode with Surface Modification for Low-Temperature Solid Oxide Fuel Cells”
- **29th IEEE Conference on Micro Electro Mechanical Systems (MEMS 2016)**, Shanghai, China
“Pure Silver as a Cathode for Silicon Micro Solid Oxide Fuel Cells”
- **International Conference on Materials for Advanced Technologies (ICMAT) 2015**, Singapore
“Enhancement of Thermal Stability and Performance on Inkjet-Printed Silver Cathode for Solid Oxide Fuel Cells”
- **International Conference on Technological Advances of Thin Films & Surface Coatings 2014**, Chongqing, China
“Reinforced Silicon-Supporting Electrolyte Membranes for a Large-scale and Nano-Thin-Film Solid Oxide Fuel Cell Array”
- **International Conference on Materials for Advanced Technologies (ICMAT) 2013**, Singapore
“Inkjet-Printed Porous Silver Thin Films as Cathodes for Low Temperature Solid Oxide Fuel Cells”

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