ELECTRODEPOSITION OF COPPER ON STAINLESS STEEL FOR SOLID OXIDE FUEL CELL INTERCONNECT APPLICATION

TAN HONG LIANG

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ELECTRODEPOSITION OF COPPER ON STAINLESS STEEL FOR SOLID OXIDE FUEL CELL INTERCONNECT APPLICATION

By

TAN HONG LIANG

Supervisor: Prof. Ir. Dr. Zuhailawati Hussain

Co-Supervisor: Dr. Tuti Katrina Abdullah

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Electrodeposition of Copper on Stainless Steel for Solid Oxide Fuel Cell Interconnect Application’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: Tan Hong Liang Signature: 

Date: 19th August 2022

Witness by

Supervisor: Prof. Ir. Dr. Zuhailawati Hussain Signature:

Date: 19th August 2022

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LIST OF SYMBOLS

s	Seconds
g	Grams
°	Degree
°F	Fahrenheit
°C	Celsius
%	Percentage
K	Kelvin
A	Ampere
V	Voltage
I	Current
R	Resistance
mV	Millivolts
mA	Milliamp
cm	Centimeter
cm^3	Cubic centimeter
mol	Mole
Torr	Unit of pressure

LIST OF ABBREVIATIONS

SOFCs	Solid Oxide Fuel Cells
SS 304	304 Stainless Steel
Cu	Copper
Cu_2O	Cuprous Oxide
CuO	Cupric Oxide
$CuSO_4$	Copper Sulphate
NaOH	Sodium Hydroxide
HCl	Hydrochloric Acid
SiC	Silicon Carbide
H_2O	Water
EDTA	Ethylenediaminetetraacetic Acid
C_3H_6O	Acetone
C_2H_5OH	Ethanol
Cr_2O_3	Chromium oxide
CO_2	Carbon dioxide
O_2	Oxygen
Cu^{2+}	Copper ions
H^+	Hydrogen ions
H_3O^+	Hydronium ions
O^{2-}	Oxygen ions
YSZ	Yttria-stabilized zirconia
ED	Electrodeposition
EPD	Electrophoretic deposition

ELD	Electrolytic deposition
WCA	Water contact angle
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscope
EDX	Energy dispersive x-ray
ASR	Area specific resistance

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Appendix A

ABSTRAK

Keluli tahan karat SS 304 adalah calon berpotensi sebagai penyambung sel bahan api oksida pepejal kerana ia mempunyai kandungan kromium yang sesuai untuk meningkatkan kalis kakisan dan lebih murah. Walau bagaimanapun, pembentukan skala kromium oksida pada suhu tinggi dan kekonduksian elektrik yang rendah perlu diselesaikan untuk meningkatkan prestasi saling sambung. Lapisan salutan Cu telah didepositkan pada keluli tahan karat SS304 menggunakan elektrodeposisi dengan larutan kuprum sulfat beralkali terdiri daripada larutan EDTA. Masa elektrodeposisi salutan Cu (60s, 180s, 300s dan 600s), morfologi salutan dan mekanisme pengoksidaan telah disiasat dengan menggunakan pengimbasan mikroskop elektron dan analisis pembelauan sinar-X. Daripada parameter pembentukan akibat masa elektrodeposisi untuk salutan, didapati masa mendapan memainkan peranan penting dalam tingkah laku salutan. Tembaga dengan 600s menghasilkan saiz butiran yang lebih tebal dan lebih besar dengan salutan seragam. Tambahan pula, keluli tahan karat dengan lapisan salutan dianalisis selepas 30 jam untuk kekasaran permukaan, sudut sentuhan air statik (WCA), pengoksidaan dan ujian empat mata. Ujian pengoksidaan kitaran telah digunakan untuk menilai rintangan pengoksidaan lapisan salutan. Dalam kajian ini, SS 304 bersalut yang menunjukkan ASR yang lebih rendah (7.78 $m\Omega \cdot cm^2$) berbanding SS 304 yang tidak bersalut (38.87 $m\Omega \cdot cm^2$) dan tiada spalasi adalah calon yang paling boleh dipercayai untuk mengurangkan pembentukan lapisan chromia oksida dan meningkatkan kekonduksian elektrik SOFC.

ELECTRODEPOSITION OF COPPER ON STAINLESS STEEL FOR SOLID OXIDE FUEL CELL INTERCONNECT APPLICATION

ABSTRACT

SS 304 stainless steel is potential candidate as solid oxide fuel cell interconnector since it has appropriate chromium content to increase corrosion resistant and is less expensive. However, formation of chromium oxide scale at elevated temperature and low electrical conductivity needed to be solved to improve interconnect performances. Cu coating layer was electrodeposited on SS304 stainless steel using electrodeposition with alkaline copper sulphate solution consisted of EDTA solution. Electrodeposition time of Cu coating (60s, 180s, 300s and 600s), the morphology of the coating and oxidation mechanisms were investigated by using scanning electron microscopy and X-ray diffraction analysis. From the formation parameter due to electrodeposition time for the coating, it was found that deposition time plays significant roles in coating behavior. The copper with 600s results in thicker and larger grain size with uniform coating. Furthermore, the stainless steel with coating layer was analysed after 30 hours for surface roughness, static water contact angle (WCA), oxidation and four-point test. Cyclic oxidation test was applied to evaluate the oxidation resistance of the coating layer. In this study, the coated SS 304 which showed lower ASR (7.78 $m\Omega \cdot cm^2$) compared to uncoated SS 304 (38.87 $m\Omega \cdot cm^2$) and no spallation is the most reliable candidate to reduce formation of chromia oxide layer and improve electrical conductivity of SOFC interconnects.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Solid oxide fuel cells (SOFCs) are solid-state devices that produce electricity by electrochemically combining fuel and air across an ionically conducting electrolyte. During the operation of SOFC, the anode is fed of hydrogen and the cathode is supplied with O_2 or air. At the operating temperature, hydrogen is oxidized at the anode to H^+ ions. The freed electrons are conducted to the external circuit to the cathode, enabling the reduction of the oxygen ions O^{2-} which are transported from the cathode to the anode through the electrolyte (ionic conductor). At the interface, anode/ electrolyte anions O^{2-} react with H^+ to form H_2O (Garcia et al. 2013).

The current trend toward lowering the operating temperatures of SOFCs aims to reduce the degradation of elements and replace the noble metals used in high-temperature devices with cheaper materials such as stainless steel. However, a decrease in operating temperature leads to a decrease in the thermoactivated electrical properties of the cell components – anode, cathode and electrolyte. In addition, the low temperature cells have also experienced significant coking, further reducing productivity. Hence, new technologies are needed to reduce the cost of SOFCs without sacrificing productivity. Electrodeposition is a technique based on the application of an electric field that does not require expensive equipment and allows precise control over the coating thickness. It is suitable for deposition on the substrates of complex shapes and covering the surface of interconnect to create a barrier and act as protective coatings.

1.2 Problem Statement

Several research papers and review papers are being published regarding the metallic interconnect of solar oxide fuel cells. However, it is still immature and insufficient to apply the technology of the electrodeposition of copper on stainless steel interconnect. Therefore, more research and investigation into the surface coating of copper on stainless steel are needed to make the technology more mature. Three main challenges exist in the metallic interconnect of solar oxide fuel cells: high temperature oxidation, chromium poisoning and intermediate cell operating temperature.

High temperature oxidation is one of the crucial problems in stainless steels due to the formation of an oxide scale of chromia (Cr_2O_3). The oxide scale increases the system's resistance, which deteriorates the performance and long-term stability of SOFC stacks. Besides, chromium poisoning occurs by the chromium diffusion from the oxide scale into the yttria-stabilized zirconia (YSZ) electrolyte on the cathode side decreases the system's power density. Next, interconnects must remain stable in a dual atmosphere of air and hydrogen-based fuel on opposing sides by separating these gases and ensuring the gases flow to their respective electrodes for proper cell function and the entire cell lifespan to maintain cell efficiency. However, at the intermediate cell operating temperature (600-800°C), interconnects undergo aggressive corrosion via iron oxidation. The phenomenon occurs due to hydrogen permeation in the metal and its movement through the metal and oxide scales, where it contributes to nodule iron oxide growth and ultimately platelet-like outward growth. It also appears to occur more severely at lower operating temperatures.

The main challenges in the metallic surface coating of copper on stainless steel are the passive coating of stainless steel, acid copper plating solutions and alkaline with cyanide-based copper plating solutions. Firstly, the passive coating of stainless steel is mainly due to the chromium content of the stainless steel, which gives it its resistance to oxidative degradation. Hence, we need to take several steps to ensure good adherence of copper plating. Next, acid copper plating on stainless steel directly is difficult and has bad adhesion because of its high sulphuric acid content and produces immersion deposits with poor adhesion. It cannot be directly applied to stainless steel. Next, alkaline copper solutions have better throwing power than acid copper solutions but cannot be used at a high current density and are more difficult to control. Besides, cyanide must be handled carefully because it involves special handling and treatment procedures because of its acute health hazards and waste disposal requirements. Therefore, the investigation of alkaline with non-cyanide based is important due to the environmental issues.

1.3 Objectives

The objectives of this research project are:

i. To study the deposition time to obtain a good copper coating by alkaline non-cyanide based copper plating with EDTA solution
ii. To evaluate chromium formed at oxide scale layer of the surface on stainless steel interconnect with and without copper coating.
iii. To investigate the electrical properties of stainless steel interconnect of protective copper coating by electrodeposition.

1.4 Scope of Research

In this work, copper coating was deposited on SS 304 using the electrodeposition technique. The properties of the as-deposited copper layer on the surface of SS 304 was studied using X-ray Diffraction (XRD), SEM with EDX, Atomic Force Microscopy (AFM) and Contact Angle (CA) goniometer. The effect of electrodeposition was investigated. After optimizing the best electrodeposition time in this work, the oxidation resistance and electrical conductivity properties of the protective copper layer under isothermal and cyclic oxidation were evaluated.

1.5 Dissertation Outline

Chapter 1 contains the background of the research project, problem statement, research objectives and scope of the study. Chapter 2 highlights the literature review which is related to the research. Chapter 3 explains the research methodology which includes the sample fabrication, the design of experiments, and the theory for analysis. Chapter 4 discusses the results of various characterization techniques on the product and will support the arguments with the theoretical body of knowledge. Chapter 5 concludes all key findings of this project and recommends potential research works for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) have elicited huge interest in the present research, which focuses on cleaner and more efficient energy sources to reduce CO_2 emissions and the projected shortages of fossil fuels. SOFCs are one of the fuel cells that use natural gas to produce electric current at operating temperatures that reach up to 1000ºC (about 1800ºF). SOFCs achieve extremely high electrical efficiency reaching up to 60%. Its high power efficiency and low operating cost delivers financial benefits and minimize the environmental footprint.

Solid oxide fuel cells (SOFCs) are a good alternative for electric power generation systems. SOFCs show high energy conversion efficiency, clean power generation, reliability, modularity, fuel adaptability, noise-free, excellent long-term stability, and versatility for direct conversion of chemical energy to electrical energy.

Methodological aspects of the life-cycle sustainability of SOFCs were considered by Mehmeti et al. (2016). The authors compared SOFCs with other technologies competing for electricity production and substantiated their advantages from the environmental perspective. They also revealed that, due to their superior energy efficiency, SOFCs are economically competitive even when their production costs are higher than those of traditional systems.

Modern research in the field of SOFCs is focused on solving the following problems: reducing the operating temperature, increasing the specific power, optimizing the technology and the successful commercialization and industrial implementation of SOFCs (Kalinina and Pikalova 2021).

2.2 Interconnects

Interconnect is the element which electrically connects two fuel cell elements to form a “stack”, which conducts electricity between the cell and separates the fuel and oxide gas from mixing to obtain high voltage and power density. The interconnects are in contact with both electrodes (cathode and anode) and must meet several requirements (Garcia et al. 2013). For example, low area specific resistance (ASR) which is 0.10 Ohm cm^{-2} (an acceptable value after 40,000 working hours), chemical stability in both atmospheres (reducing and oxidant) at high temperatures between 600 °C and 1000 °C, impermeability to O_2 and H_2 and linear thermal expansion coefficient that compatible with the other components of the cell (value close to $12.5 \times 10^{-6} K^{-1}$).

2.2.1 Ceramic Interconnect Materials

Ceramic is traditionally used as an interconnect material due to its high heat resistance(Isyraf Aznam et al. 2018). However, ceramic materials are difficult to fabricate, limiting the geometrical design of interconnect. Besides, the development of thinner electrolytes has reduced the operating temperature of SOFCs to the range of 600ºC to 800ºC. Hence, researchers have pursued opportunities to lower fabrication costs using materials such as metal alloys. In comparison with ceramics, metal alloys have higher oxidation resistance, better heat and electrical conductivity, and better manufacturability and mechanical strength.

2.2.2 Metallic Interconnect Materials

Metal interconnect issues such as chromium poisoning and the use of a protective coating to overcome it which further discussed in the subsequent sections. Research has focused on suitable coating development to overcome the issue and prolong the cell lifetime. As Yang et al. (2007) reported that high concentrations of Cr- (>23%) can reduce contact resistance and oxide scale growth whereas low Cr- content

(<5%) leads to low oxidation resistance and increased electrical resistance. Therefore, austenitic stainless steel is the best candidate compared to the others due to its optimum Cr- content of around 18-20%. Furthermore, the face-centered cubic structure of the steel provides CTE compatibility with other SOFC components, which is important to avoid spallation or cracks because of mechanical stress produced by thermal cycling (Isyraf Aznam et al. 2018).

Metallic interconnects have attracted great attention due to their high electric and thermal conductivity, low cost and good manufacturability compared to traditional ceramic interconnects. In recent years, many works have been focused on austenitic stainless steel due to its low cost and adequate linear thermal expansion coefficient.

Three major degradations of metallic interconnect are corrosion, chromium evaporation and increasing electrical resistance. The coating systems add costs to the already expensive raw materials and production methods. Costs can be reduced in several ways, either by using thinner coatings, using pre-coated materials to simplify the interconnect production or one trying to use cheaper materials. Additionally, environmental and health aspects must be considered when it comes to the use of copper. Investigating such a material as a potential interconnect coating is worthwhile by considering factors such as material costs and availability.

Hence, a coating of stainless steel has been proposed to improve surface electrical properties and reduces the amount of chromium in the oxide film. The stainless steel without a coating of copper subjected to a strongly oxidizing condition of cathode forms an oxide film very irregular. In contrast, coated copper shows up very regular and without chromium oxide on its surface. The stainless steel with electrodeposited copper tends to improve in high temperature and reduce chromium evaporation, coating maintains electrical contact and offers oxidation protection in stainless steel at lower chromium content and is capable of significantly retarding chromium evaporation which reduces chromium poisoning of the fuel cell. Hence, electrodeposition is an excellent alternative for achieving highly conductive films at high temperatures.

2.3 Stainless Steels

Stainless steel is an alloy of iron which includes a substantial amount of chromium. The addition of chromium gives stainless steel desirable properties, including its resistance to corrosion and brilliant appearance. Stainless steel comes in many different types that vary by composition. Carbon content, chromium content and the content of other metals like nickel and molybdenum set the different types of stainless steel apart and make them suitable for different functions.

The steel that does not corrode is also known as inox or corrosion-resistant steel. It is an alloy steel with at least 10.5% chromium, making it highly resistant to oxidation. The chromium in stainless steel reacts with the oxygen to create a chromium oxide film, which becomes a protective layer that blocks further oxygen penetration into the seal and its subsequent corrosion.

Stainless Steel 304 is a member of the austenitic family of stainless steels and contains nickel in addition to chromium. Its inclusion of at least 18% chromium and 8% nickel, also known as 18/8 steel (Otsuka et al. 2011).

Table 2.1: Material Composition of Stainless Steel 304 (Maruthi et al. 2018)

Grade		C	Mn	Si	P	S	Cr	Ni	N
304	Min	-	-	-	-	-	18.0	8.0	-
	Max	0.08	2.0	0.75	0.045	0.030	20.0	10.5	0.10
304L	Min	-	-	-	-	-	18.0	8.0	-
	Max	0.030	2.0	0.75	0.045	0.030	20.0	12.0	0.10
304H	Min	0.04	-	-	-	-	18.0	8.0	-
	Max	0.10	2.0	0.75	0.045	0.030	20.0	10.5	-

2.4 Protective Surface Coating of Metallic Interconnects

Effective and low-cost protective coating on interconnect has been developed to reduce the challenges which drastically deteriorate cell performance. The coating helps to reduce gaseous Cr species migration from the Cr_2O_3-rich scales to the oxide surface, reduce electrical resistance due to rapid Cr_2O_3-scale growth at elevated temperatures and improve rust resistance. However, aside from the types of coating materials, other factors such as deposition technique also significantly affect the final performance of the coating.

2.5 Electrodeposition (ED)

Electrodeposition is a promising process which enables to deposition of coatings on a large variety of substrates comprised of metals, ceramics and polymers. The electrodeposition process provides many other advantages as well, which broadly include good economy, less porosity, good phase purity, mass productivity, ease of shapes handling, ability to process different materials, good compositional control and ability to produce unique compositions that cannot be achieved by other methods (Shakoor et al. 2017)

Electrodeposition is primarily an oxidation-reduction electrochemical reaction. It uses electrical current to reduce cations of a desired material from a solution and achieve a thin coating layer over the other object as shown in Figure 2.1. The deposits' properties depend on their microstructure, which in turn is influenced by the parameters, such as electrolyte composition, pH, electrodeposition temperature and current density.

The electrodeposition process consists of a power source to supply current to flow in one direction when a potential difference is imposed across the system. The cathode is where the metal or alloy is deposited while the anode is present primarily to