

بسم الله الرحمن الرحيم

 $\infty\infty\infty$

تم رفع هذه الرسالة بواسطة / مني مغربي أحمد

بقسم التوثيق الإلكتروني بمركز الشبكات وتكنولوجيا المعلومات دون أدنى مسئولية عن محتوى هذه الرسالة.

AIN SHAMS UNIVERSITY

1992

1992

ملاحظات: لا يوجد



Ain Shams University Faculty of Science Chemistry Department



Preparation of Nanocrystalline Spinel as Interface Layer on Steel Interconnects for Solid Oxide Fuel Cells (SOFCs) Applications

Thesis Submitted
By
Salwa Mohamed Mahmoud
(M. Sc. in Chemistry, 2016)

For the requirement of Doctor of Philosophy
(Ph. D.) Degree of Chemistry
To
Chemistry Department
Faculty of Science -Ain Shams University

Thesis Advisors

Prof. Dr. Mohamed Fathy El-Shahat Prof. Dr. Taha Mohamed Taha Mattar

Prof. of Inorganic & Analytical Chemistry, Faculty of Science, Ain Shams University

Rector of Tabbin Institute for Metallurgical Studies (TIMS) Professor, Central Metallurgical Research & Development Institute (CMRDI)

Dr. Moustafa Mohammed Saad Sanad

Assoc. Prof. at Chemical and Electrochemical Process
Department, Central Metallurgical Research &
Development Institute (CMRDI)



Ain Shams University Faculty of Science Chemistry Department



Preparation of Nanocrystalline spinel as Interface Layer on Steel Interconnects for Solid Oxide Fuel Cells (SOFCs) Applications

By

Salwa Mohamed Mahmoud

Thesis Advisors

Approved

Prof. Dr. Mohamed Fathy El-Shahat

Prof. of Inorganic & Analytical Chemistry, Faculty of Science, Ain Shams University

Prof. Dr. Taha Mohamed Taha Mattar

Rector of Tabbin Institute for Metallurgical Studies (TIMS) Prof., Central Metallurgical Research & Development Institute (CMRDI)

Dr. Moustafa Mohammed Saad Sanad

Assoc. Prof. at Chemical and Electrochemical Processing Department, Central Metallurgical Research & Development Institute (CMRDI)

Head of Chemistry Department

Prof. Dr. Magdi A. M. Ibrahim

Acknowledgement

First and foremost, I would like to thank **Allah** for giving me the opportunity and the strength to accomplish this work.

I would like to express my deep gratitude to my supervisors Prof Dr. M. F. El-Shahat, Prof. of Inorganic & Analytical Chemistry, Faculty of Science, Ain Shams University and Prof Dr. Taha Mattar, Rector of Tabbin Institute for Metallurgical Studies (TIMS) and Professor at Central Metallurgical Research & Development Institute (CMRDI). They are always kind enough to suggest the topics of research and to follow up the progress of the work with keen interest and guidance and valuable criticism. Also, I am deeply indebted to Dr. Moustafa Sanad, Assoc. Prof. at Chemical and Electrochemical-Processing Department, (CMRDI) for his valuable assistance, guidance and continuous help during the progress of the work. I am deeply indebted to, Prof Dr. Said Obbade, Institut polytechnique de Grenoble, Laboratoire d'Electrochimie et de physico-chimie des materiaux et des Interfaces (LEPMI), Grenoble INP - Phelma, Grenoble, France for his guidance and helpful supervision. Great thank to Cecile Rossignol and Laurent Dessemond for their help during experimental work and useful discussion about results. Special thanks to French Embassy at Egypt and Agency Universitaire de la Francophonie (AUF) for the doctoral fellowship that helped me to finish the experimental part efficiently. Great thanks to French Institute at Egypt (IFE) and Campus France at Lyon, France for facilitating my residency in France for more than one year and guiding me patiently.

Contents	Page/s
Abbreviations	I
Abstract	II-III
A. List of Figures	IV-V
B. List of Tables	VI-VII
Chapter I: Literature Survey	1-38
1.1. Introduction	1
1.1.1. Proposed solutions for metallic interconnects	5
1.1.2. Structure and properties of (Mn,Co,M) ₃ O ₄ (M=Fe, Cu, Ni) spinels	10
1.1.3. Transition metals in coating layer	15
1.1.4. Protective coating deposition techniques	27
1.1.4.1. Screen printing process	28
1.1.5. Coating evaluation	29
1.1.5.1. Area specific resistance (ASR)	29
1.1.5.2. Coefficient of thermal expansion (CTE)	33
1.1.5.3. Oxidation behavior and calcination	34
1.2. Aim of the work	36
Chapter II: Materials and Experimental Techniques	
2.1. Materials	39
2.2. Procedure	39
2.2.1. Powder synthesis	39
2.2.2. Powder processing	41
2.2.3. Preparation of spinel pellets for different	44
measurements at high temperature	7-7
2.3. Powder characterization	44
2.3.1. X-ray diffraction analysis (XRD)	44
2.3.2. Raman spectroscopy analysis	45
2.3.3. X-ray photoelectron spectroscopy analysis (XPS)	46
2.3.4. Thermal gravimetrical analysis (TGA)	46
2.3.5. Dilatometery measurements for spinel pellets	47
2.3.6. Electrical conductivity measurements	48
2.4. Coating layer design and characterization	49
2.4.1. Substrate preparation for screen printing coating	49

2.4.2. Slurry preparation	50
2.4.3. Coating layer treatment and application	50
2.5. Coating layer characterization	51
2.5.1. Area specific resistance measurements	51
2.5.2. Microstructure analysis	53
Chapter III: Results and Discussion	54-112
3.1. Phase evolution	55
3.1.1. Effect of calcination time on phase purity	59
3.1.2. Effect of temperature on phase purity	65
3.1.3. Effect of stoichiometric concentration on phase	69
purity	09
3.2. Microstructure	72
3.3. Spectroscopic analysis	75
3.3.1. Raman spectroscopy analysis	75
3.3.2. X-ray photoelectron spectroscopy analysis (XPS)	79
3.4. Thermal analysis	88
3.4.1. Thermal gravimetrical analysis (TGA)	88
3.4.2. Dilatometry measurements	94
3.5. Electrochemical performance	98
3.5.1. Electrical conductivity measurements for pellets	98
3.5.2. Area specific resistance (ASR) for the coating	105
layer	103
3.5.3. Coating layer microstructure investigation	109
Chapter IV: Summary and Conclusions	113-121
References	122-145
Summary	i
Arabic Summary	ii-x

ABBREVIATIONS

Symbol	Description
AC	Auto-combustion
AISI 430	American iron & steel institute standard 430
APS	Air plasma spray
ASR	Area specific resistance
CroFer 22 APU	Chromium ferrite 22 auxiliary power unit
CTE	Coefficient of thermal expansion
DGPA	Double glow plasma alloying technique
DTGA	Differential thermo gravimetric analysis
Ea	Activation energy
EDS	Energy dispersive spectroscopy
FE-SEM	Field emission scanning electron microscope
FSS	Ferritic stainless steel
FWHM	Full width at half maximum
ISO	International standardization organization
IT-SOFCs	Intermediate temperature solid oxide fuel cells
LSCF	Lanthanum Strontium cobalt ferrite
LSM	Lanthanum Strontium Manganite
MCO	$Mn_{1.5}Co_{1.5}O_4$
NTC	Negative temperature coefficient
PVDF	Polyvinyledene diflouride
SOFCs	Solid oxide fuel cells
SP	Screen printing
SSRx	Solid state reaction
TGA	Thermo gravimetric analysis
USS 316L	Austenitic stainless steel 316L
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
YSZ	Yttria stabilized zirconia

Abstract

Protective coatings are used on ferritic stainless-steel interconnects to prevent the transport of the harmful CrO₃(g) and CrO₂(OH)₂(g) compounds in solid oxide fuel cells. As these compounds pass along the triple-phase boundary of the cathode, they electrically reduce back to Cr₂O₃, causing degradation of the cell. The most cells promising material for protecting the is (Mn,Co)₃O₄. Nevertheless, to provide good protection over a long period of time (5 years or more), these coatings should possess a dense microstructure, excellent adhesive properties, excellent electrical conductivity, and good thermal and chemical stability when exposed to an oxidizing atmosphere at high temperatures. Wet ceramic processes and thin film processes have both been studied as deposition techniques. It has been demonstrated, however, that the coatings produced by these methods do not have sufficient density, making their long-term protection questionable. The main objective of this study is to develop, protective spinel

The main objective of this study is to develop, protective spinel coatings by convenient and economical screen printing (SP) technique. The target is to obtain a dense microstructure, high conductive and low resistance coating. For fulfillment of ideal coating, investigation of the coating layer composition and evaluation of pure (Mn,Co)₃O₄ and doped (Mn,Co,M)₃O₄ (M=Cu, Fe, Ni, Na and Mg). Since (SP) process has no enough study for preparing such kind of spinel material coating, substitution by

transition and alkali metal effect was deeply studied parallel to optimization of screen-printing process to build-up mechanism for a well-designed coating. The synthesized spinel powder materials before and after coating process were investigated in order to obtain more detailed information about microstructure, thermal stability, electrochemical properties. Consequently, spinel powders and coatings sinter at high temperatures due to their metastable phase structure and small particle and crystallite sizes. The coatings had an excellent Cr barrier and electrical properties, despite being exposed to a harsh environment, due to their dense microstructure and fully recovered spinel phases. As protective coatings for metallic interconnects, Mn_{1.5}Co_{1.5}O₄ doped spinel coatings are ideal candidates for screen printing.

Keywords

Solid oxide fuel cells, Interface layer, screen printing coating, Area specific resistance (ASR), Coefficient of thermal expansion

Figure	Figure captions	Page
number	Schamatic diagram of SOECo	number
1	Schematic diagram of SOFCs	2
2	Schematic diagram of SOFC operation concept	3
3	Unit cell of spinel structure of cubic MnCo ₂ O ₄ and tetragonal Mn ₂ CoO ₄ illustration made using VESTA software	11
4	Empirical site preference energies for selected ions in the spinel structure	13
5	Phase diagram for the Mn ₃ O ₄ -Co ₃ O ₄ system	15
6	Synthesis of spinel powders by sol-gel auto-combustion method	42
7	Flow chart represents the spinel powders synthesis by (a) sol-gel auto-combustion and (b) solid state reaction processes	43
8	Experimental set-up for electrical conductivity measurement	49
9	Illustration of screen printing.	51
10	Schematic diagram of the sample ASR measurement	53
11	XRD patterns of pure and modified MCO, synthesized by AC and sintered at 850 °C for 40 h	58
12	XRD patterns of (a) MCO, (b) Cu _{0.25} Ni _{0.5} @MFCO, (c) Cu _{0.5} Ni _{0.2} Na _{0.05} @MFCO, (d) Cu _{0.5} Ni _{0.2} S@MFCO, (e) Cu _{0.5} Ni _{0.2} Mg _{0.05} @MFCO compositions, synthesized by AC, before and after calcination at 850 °C for 40, 80, and 120 h	61
13	XRD patterns of (a) MCO, (b) Cu _{0.25} Ni _{0.5} @MFCO, (c) Cu _{0.5} Ni _{0.2} Na _{0.05} @MFCO, (d) Cu _{0.5} Ni _{0.25} @MFCO, (e) Cu _{0.5} Ni _{0.2} Mg _{0.05} @MFCO composition synthesized by SSRx, after calcinations at 850 °C for 80 and 120 h	63
14	XRD patterns of (a) MCO, (b) Cu _{0.25} Ni _{0.5} @MFCO, (c) Cu _{0.5} Ni _{0.2} Na _{0.05} @MFCO, (d) Cu _{0.5} Ni _{0.25} @MFCO, (e) Cu _{0.5} Ni _{0.2} Mg _{0.05} @MFCO compositions synthesized by AC, before and after calcinations at 850, 900, and 1100 °C/40 h	67
15	XRD patterns of (a) MCO, (b) Cu _{0.25} Ni _{0.5} @MFCO, (c) Cu _{0.5} Ni _{0.2} Na _{0.05} @MFCO, (d) Cu _{0.5} Ni _{0.25} @MFCO, (e) Cu _{0.5} Ni _{0.2} Mg _{0.05} @MFCO synthesized by SSRx after	68

A. LIST OF FIGURES

	calcinations at 850, 900, and 1100 °C for 40 h	
16	Observed and calculated XRD profiles of cubic spinel phase of Cu _{0.25} Ni _{0.5} @MFCO and Cu _{0.5} Ni _{0.25} @MFCO sintered at 850 °C for 40 h	70
17	FE-SEM of (a) pure MCO, (b) Cu _{0.25} Ni _{0.5} @MFCO, (c) Cu _{0.5} Ni _{0.2} Na _{0.05} @MFCO, (d)Cu _{0.5} Ni _{0.2} S@MFCO, and (f) Cu _{0.5} Ni _{0.2} Mg _{0.05} @MFCO synthesized by AC, after calcinations at 850 °C for 4 h	74
18	Raman spectra of pure and modified MCO compositions synthesized by AC, after calcinations at 850 °C for 4 h	78
19	Raman spectra of (a) Cu _{0.25} Ni _{0.5} @MFCOand (b) Cu _{0.5} Ni _{0.25} @MFCOpowders (calcined at 850 °C in air)	79
20	Room temperature XPS spectra of Cu _{0.25} Ni _{0.5} @MFCO and Cu _{0.5} Ni _{0.25} @MFCO powders (calcined at 850 °C in air)	85
21	TGA for pure and modified MCO compositions after calcinations at (a) 850 °C and (b) 400 °C for 4 h	91
22	TGA analysis of modified MCO precursors followed by XRD analysis	93
23	Sintering behavior of pure and doped MCO compositions synthesized by AC method	97
24	Arrhenius plots of electrical conductivity of pure and modified MCO compositions between 250-750 °C in air	100
25	Dependence of ASR of pure and modified MCO coated USS 316L alloy as a function of measurement temperature in air at (150-750 °C) during ascending and descending cyclic oxidation	108
26	SEM surface microstructures of (a,b&c) MCO, (d,e&f) Cu _{0.25} Ni _{0.5} @MFCO and (g,h&i) Cu _{0.5} Ni _{0.25} @MFCO films: (a,d&g) without calcination, (b,e&h) calcination at 1000 °C for 4 h and (c,f&i) after ASR measurments at air	111
27	SEM surface microstructures (larger magnification) of (j,k&l) MCO, (m,n&o) Cu _{0.25} Ni _{0.5} @MFCO and (p,q&r) Cu _{0.5} Ni _{0.25} @MFCO films: (j,m&p) without calcination, (k,n&q) calcination at 1000 °C for 4 h and (l,o&r) after ASR measurments at air	112

Table number	Table caption	Page number
1	Performance of various spinel oxide coatings on metallic interconnects	32
2	CTE of various spinel oxide coatings	34
3	Spinel powder compositions synthesized by AC &SSRx	42
4	Standard austenitic stainless steel (USS) 316L stainless steel composition in wt.%	50
5	Lattice parameters and different of density of pure and modified MCO spinel oxides	58
6	Crystal size at 850 °C after 120 h of heat treatment for synthesized powder by AC and SSRx	64
7	Cubic spinel phase % at 850 °C after 120 h of heat treatment for synthesized powder by AC and SSRx	64
8	Lattice parameters of Cu _{0.25} Ni _{0.5} @MFCO and Cu _{0.5} Ni _{0.25} @MFCOpowders calcined at 850 and 1100 °C in air	69
9	XPS area of different Co2p peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO	86
10	XPS area of different Mn2p peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO	86
11	XPS area of different Cu2p peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO	86
12	XPS area of different Ni2p peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO	87
13	XPS area of different Fe2p peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and	87

	Cu _{0.25} Ni _{0.5} @MFCO	
14	XPS area of different O1s peaks at room temperature of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO	87
15	Thermal properties of spinel pellets sintered in air at 1050 °C for 3 h then annealed in air at 850 °C for 2 h synthesized by AC method	96
16	Activation energy (E _a) and electrical conductivity (σ) values of spinel pellets tested in air at (200-750 °C)	104
17	Comparison of the electrical properties of Cu _{0.5} Ni _{0.25} @MFCO, and Cu _{0.25} Ni _{0.5} @MFCO compounds with some spinel oxides	104
18	ASR values of coated layer tested in air at (250-750 °C)	108