بسم الله الرحمن الرحيم

∞∞∞

تم رفع هذه الرسالة بواسطة / مني مغربي أحمد

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

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

Prof. Dr. Taha Mohamed Taha Mattar
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 Proces
Department, Central Metallurgical Research &
Development Institute (CMRDI)

2022

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.

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
E_a	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 CrO_3(g) and $CrO_2(OH)_2$(g) compounds in solid oxide fuel cells. As these compounds pass along the triple-phase boundary of the cathode, they electrically reduce back to Cr_2O_3, causing degradation of the cell. The most promising material for protecting the cells is $(Mn,Co)_3O_4$. 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 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 $(Mn,Co)_3O_4$ and doped $(Mn,Co,M)_3O_4$ (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, $Mn_{1.5}Co_{1.5}O_4$ 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