

Ain Shams University
Faculty of Science
Chemistry Department



Preparation of new graphite based composite electrodes with some metal oxide nanoparticles and their applications in energy

A Thesis

Submitted to Chemistry Department – Faculty of Science
Ain Shams University in Partial Fulfillment for Requirements of the
Master Degree of Science (M.Sc.) In Chemistry

By

Ahmed Sayed Essa Abd El-Razik

B.Sc. in Chemistry and Physics, Faculty of Science
Ain Shams University
2010

Under Supervision of

Prof.Dr. Hamdy Hassanien Hassan

Professor of Physical Chemistry,
Faculty of Science, Ain Shams University

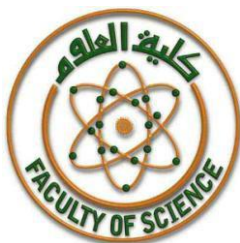
Dr. Mohamed Abd el- Hay Ismail

Assistant Professor of Physical Chemistry,
Faculty of Science, Ain Shams University

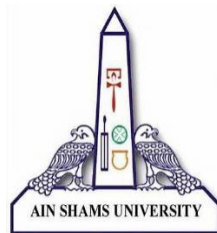
Dr. Hesham Samir Abdel-Samad

Lecturer of Physical Chemistry,
Faculty of Science, Ain Shams University

2018



Ain Shams University
Faculty of Science
Chemistry Department



Approval Sheet

Preparation of new graphite based composite electrodes with some metal oxide nanoparticles and their applications in energy

A Thesis

Submitted to Chemistry Department – Faculty of Science
Ain Shams University in Partial Fulfillment for Requirements of the
Master Degree of Science (M.Sc.) In Chemistry

By

Ahmed Sayed Essa Abd El-Razik

B.Sc. in Chemistry and Physics,
Faculty of Science, Ain Shams University

2010

Under Supervision of

Prof.Dr. Hamdy Hassanien Hassan

Professor of Physical Chemistry,
Faculty of Science, Ain Shams University

Dr. Mohamed Abd el- Hay Ismail

Assistant Professor of Physical Chemistry,
Faculty of Science, Ain Shams University

Dr. Hesham Samir Abdel-Samad

Lecturer of Physical Chemistry,
Faculty of Science, Ain Shams University

Head of Chemistry Department
Prof.Dr. Ibrahim H.A. Badr

2018

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا
إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ
الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

سورة البقرة - الآية (٣٢)

To the soul of my Father

To my Family

To my best teachers and friends

Acknowledgements

At First I'd like to knee praying to ALLAH for helping me to do this work.

I would like to express my deepest gratitude, sincere thanks and appreciation to **Prof. Dr. Hamdy H. Hassan**, Professor of Physical Chemistry, at Chemistry Department, Faculty of Science, Ain Shams University for his suggesting the topic of this thesis, supervision, sponsorship, and deep concern in this work.

Also, I would like to express my deepest gratitude to **Dr. Hesham Samir Abdel-Samad** Lecturer of Physical Chemistry, at Chemistry Department, Faculty of Science, Ain Shams University for planning of the experimental work, continuous encouragement and constructive criticism during the work.

I would like to thank **Dr. Mohamed Abd el- Hay Ismail** Assistant Professor of Physical Chemistry, at Chemistry Department, Faculty of Science, Ain Shams University for his advice and offering technical facilities through out this work.

Thanks are also due to my colleagues of electrochemical lab specially **Mr. Mahmoud A. El Jemni** demonstrator at Chemistry Department, Faculty of Science, Ain Shams University for his sincere cooperation and encouragement.

Abstract

Cobalt/graphite electrodes are prepared by potentiostatic electrodeposition of cobalt from sulphate baths with and without citrate ions on graphite discs. The electrocatalytic activity of the prepared electrodes toward oxygen evolution reaction is investigated by cyclic voltammetry technique, electrochemical impedance spectroscopy and electrochemical quartz microbalance techniques. The electrocatalytic activity increases by increasing the concentration of Co^{+2} ions in the electrodeposition bath up to 0.5 M. The Co/Graphite electrode obtained from electrodeposition bath containing 0.5M Co^{2+} and 0.5M citrate ions, $\text{Co}_{(0.5\text{-Cit})}/\text{G}$ exhibits better catalytic activity toward oxygen evolution reaction than that obtained from citrate free baths. Furthermore, $\text{Co}_{(0.5\text{-Cit})}/\text{G}$ electrode gains extra OER activity when undergoes a successive cycling potentiodynamic polarization in 1M NaOH solution as a result of the formation of cobalt oxyhydroxide phase. Greater stability of $\text{Co}_{(0.5\text{-Cit})}/\text{G}$ electrode is verified by a chronopotentiometric test.

Key words

Cobalt, Citrate, Chronoamperometry, Chronopotentiometry, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Electrochemical Quartz Crystal Microbalance, Oxygen Evolution Reaction

Abbreviations

symbol	Name
G	bare graphite
SD-Co_(x)/G	electrodeposited cobalt on stationary graphite disk from bath containing x M CoSO₄.
SD-Co_(x,Cit)/G	electrodeposited cobalt on stationary graphite disk from bath containing xM CoSO₄ + xM sodium citrate (Na₃C₆H₅O₇·2H₂O).
RD-Co_(x)/G	electrodeposited cobalt on 1600 rpm rotated graphite disk from bath containing x M CoSO₄.
RD-Co_(x-Cit)/G	electrodeposited cobalt on 1600 rpm rotated graphite disk from bath containing xM CoSO₄ + xM sodium citrate (Na₃C₆H₅O₇·2H₂O).
Co_(0.5)/Au/Q	electrodeposited on Au coated quartz crystal from 0.5 M CoSO₄ bath cobalt
Co_(0.5-Cit)/Au/Q	electrodeposited cobalt on Au coated quartz crystal from 0.5 M CoSO₄ + 0.5M sodium citrate (Na₃C₆H₅O₇·2H₂O) bath.
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction
EIS	Electrochemical Impedance Spectroscopy
CV	Cyclic Voltammetry
eQCM	Electrochemical Quartz Crystal Microbalance
XRD	X-ray Powder Diffraction
FESEM	Field Emission Scanning Electron Microscopy

Contents

<i>Contents</i>	<i>Page No.</i>
Abstract	<i>I</i>
Key words	<i>I</i>
Abbreviations	<i>II</i>
Contents	<i>III</i>
List of figures	<i>V</i>
List of tables	<i>VIII</i>
<i>Chapter 1</i> <i>Introduction and Literature survey</i>	
1. Introduction	<i>1</i>
1.1. Literature Survey	<i>1</i>
1.2. Electrochemical Techniques	<i>5</i>
1.2.1. Chronoamperometry	<i>5</i>
1.2.2. Chronopotentiometry	<i>6</i>
1.2.3. Cyclic Voltammetry	<i>8</i>
1.2.4. Electrochemical impedance spectroscopy	<i>10</i>
1.2.5. Electrochemical quartz crystal microbalance	<i>12</i>
<i>Chapter 2</i> <i>Experimental Work</i>	
2. Experimental Work	<i>15</i>
2.1. Preparation of Co/G electrodes	<i>16</i>

Chapter 3 Results and Discussion	
3. Results and Discussions	18
3.1. G electrodes	18
3.1.2. Graphite CV response in 1M NaOH	18
3.2. Co/G	21
3.2.1. Effect of graphite substrate rotation.(SD, RD)	21
3.2.2. Effect of Cobalt ion concentration	29
3.3. Co_(x-Cit)/G	36
3.4. Successive CV Activation	46
3.5. Electrocatalytic stability	59
3.6. Electrochemical Impedance Spectroscopy (EIS)	61
4. Summary and Conclusions	73
5. References	76

List of figures

<i>Figure No</i>	<i>Figure caption</i>	<i>Page No.</i>
Fig (i)	Current vs. potential plot "duck shape" waveform.	9
Fig (ii)	Comparison of High Q (solid line) and Low Q (dashed line).	14
Fig (1)	Anodic (a) and cathodic (b) potentiodynamic spans for a stationary G1, black dashed line, 1600 rpm rotating G2, red solid line and SD-Co_(0.2)/G , RD-Co_(0.2)/G electrodes 3 blue, 4 pink lines respectively at scan rate 10 mV.s⁻¹ and 1600 rpm rotating in 1M NaOH solution.	20
Fig (2)	XRD patterns of SD-Co_(0.2)/G and RD-Co_(0.2)/G samples.	23
Fig (3)	Anodic (a) and cathodic (b) branches of the cycle potentiodynamic responses for RD-Co_(x)/G-R electrodes at 10 mV.s⁻¹ and 1600 rpm in 1M NaOH solution; x = the concentration of Co²⁺ in the electrodeposition bath.	29
Fig (4)	XRD patterns of the as prepared RD-Co_(0.5)/G (a) and after 30 successive CV cycles activation in 1M NaOH (b).	31
Fig (5)	FESEM image of the as prepared RD-Co_(0.5)/G electrode.	32
Fig (6)	eQCM of the first CV cycle RD-Co_(0.5)/G electrode in 1M NaOH solution. The insert is the zoom in of curve 2 in the potential window -0.5 to 0.9 V.	34
Fig (7)	Proposed OER mechanism.	36

Fig (8)	XRD patterns of the as prepared RD-Co_(0.5-Cit)/G (a) and after 30 successive CV cycles activation in 1M NaOH (b).	38
Fig (9)	FESEM image of the as prepared RD-Co_(0.5-Cit)/G.	39
Fig (10)	eQCM study during Co deposition from the two baths on upward faced gold coated quartz crystal. Curves 1,3 are the current-time transient, while curves 2,4 are their simultaneous mass change - time relations. (b) and (d) are a comparison between the fitted experimental current transient (black lines) with both Scharifker and Hills instantaneous model (red line) and progressive model (green line).	42
Fig (11)	The 1st and the 30th cycles of the potentiodynamic responses for RD-Co_(0.5)/G -R (black), and RD-Co_(0.5-Cit)/G -R (red) electrodes while 1600 rpm rotation in 1M NaOH solution at 10mV.s⁻¹.	43
Fig (12)	eQCM of the first CV cycle RD-Co_(0.5-Cit)/G electrode in 1M NaOH solution, the insert is the zoom in of curve 2 in the potential window -0.4 to 0.9 V.	46
Fig (13)	FESEM image of the RD-Co_(0.5-Cit)/G after 30 successive CV cycles activation in 1M NaOH.	47
Fig (14)	(a) 1st CV and their simultaneous mass change eQCM results of Co-deposited on gold coated quartz crystal from CoSO₄ bath for 100 s (b and c) are the three successive CVs and their simultaneous mass change eQCM results respectively.	49
Fig (15)	(a) 1st CV and their simultaneous mass change eQCM results of Co-deposited on gold coated quartz crystal from CoSO₄-citrate bath for 100 s. (b and c) are the	50

	three successive CVs and their simultaneous mass change eQCM results respectively.	
Fig (16)	Selected cycles of 30 successive CV (a) forward and (b) backward scan of RD-Co_(0.5-Cit)/G electrode in 1M NaOH at scan rate of 10 mV.s⁻¹.	52
Fig (17)	$\eta_{t=0}$ values for some selected successive potentiodynamic cycles at scan rate of 10 mV.s⁻¹ in 1M NaOH solution.	53
Fig (18)	Tafel lines of potential region 0.5-0.7 V for selected cycles of CV activation of RD-Co_(0.5)/G (a) and RD-Co_(0.5-Cit)/G electrodes (b) in 1M NaOH solution.	55
Fig (19)	Two hours stability test for fresh electrode (1, 2 black solid curves) and after 30 CV response cycles in 1M NaOH (3, 4 red dashed curves).	60
Fig (20)	Electrochemical impedance spectra of the prepared electrodes at OCP.	62
Fig (21)	Electrochemical impedance spectra of the prepared electrodes at OER.	69

List of tables

Table No.	Figure caption	Page No.
Table (I)	Symbols for the prepared electrodes and their preparation conditions.	17
Table (II)	$\eta_{t=0}$ and OERonset of the cyclic voltammetric responses at scan rate 10 mV.s⁻¹ in 1M NaOH solution for different electrodes in a stationary (S) and 1600 rpm rotating conditions.	28
Table (III)	$\eta_{t=0}$ values for some selected successive potentiodynamic cycles at scan rate of 10 mV.s⁻¹ in 1M NaOH solution.	54
Table (IV)	Tafel line parameters in potential region 0.5-0.7V for RD- Co_(0.5)/G.	56
Table (V)	Tafel line parameters in potential region 0.5-0.7V for RD- Co_(0.5-cit)/G.	58
Table (VI)	Electrochemical impedance parameters for the prepared electrodes obtained from the fitting of the electrodes configuration measurements at OCP, Fig 20, with the equivalent circuit presented in the insert of Fig 20. ($R_s = 12 \pm 1 \Omega$).	67
Table (VII)	Electrochemical impedance parameters for the prepared electrodes obtained from the fitting of the electrodes configuration measurements at OER, Fig 21, with the equivalent circuit presented in the insert of Fig 21. ($R_s = 7.5 \pm 1 \Omega$).	72

Chapter 1

Introduction

and

Literature survey

Introduction

1.1. Literature Survey

The global challenge for discovering sustainable and renewable energy sources as alternative to the irrecoverable fossil fuels has been grown up in the last few decades and might extend for the next two decades [1, 2]. Electrochemical science and technology can play a vital role for the indirect storing of extra renewable energy through converting the electricity into chemical energy [3]. For instance, water splitting into hydrogen and oxygen by electrolysis is considered as a hopeful substitute to electricity storage systems using batteries [4].

Recently, many intensive studies focused on constructing high efficient and low cost electrocatalysts mostly for water splitting reactions: oxygen evolution reaction (OER), and hydrogen evolution reaction (HER). Owing to, hydrogen creation from water splitting reactions is highly obstructed by the sluggish kinetics of the multistep 4-electron OER. Consequently, there is a great necessity for fabricating high efficient electrocatalysts of low overpotential to overcome this energy barrier. Basically, iridium dioxide, and ruthenium dioxide are inordinate examples for high performance electrocatalysts with low overpotential and Tafel