Faculty of Science
Chemistry Department

Development of Metal/Metal Oxide Nanostructures-Based Anodes for the Electro-Oxidation of Ethylene Glycol for Fuel Cell Applications

Thesis

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By

Ghada Hassanien Abd El-Hameed El-Nowihy

(B.Sc. Microbiology/Chemistry, 2010)

Supervisors

Dr. Mostafa M. H. Khalil

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

Dr. Mohamed S. El-Deab

Professor of Chemistry, Chemistry Department,
Faculty of Science, Cairo University

Dr. Ahmad M. Mohammad

Professor of Chemistry, Chemistry Department,
Faculty of Science, Cairo University

Dr. Mohamed A. Sadek

Professor of Chemical Engineering, Chemical Engineering Department,
Faculty of Engineering, the British University in Egypt

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Chemistry Department

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Thesis submitted by

Ghada Hassanien Abd El-Hameed El-Nowihy

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To

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Chemistry Department

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Name of candidate:
Ghada Hassanien Abd El-Hameed El-Nowihy

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This thesis has been approved by:

1- Prof. Mostafa Mohamed Hassan Khalil
2- Prof. Mohamed Saada El-Deab
3- Prof. Ahmad Mahmoud Mohammad
4- Prof. Mohamed Amin Elshahir Sadek

Approval

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

DEDICATION

" قَالُواْ سُبْحَانَكَ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَّمْتَنَا إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ "

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Promising ethylene glycol electro-oxidation at tailor-designed NiOx/Pt nanocatalyst

Ghada H. El-Nowihy [a], Ahmad M. Mohammad [b,*], Mostafa M.H. Khalil [c], Mohamed A. Sadek [a], Mohamed S. El-Deab [b,**]

[a] Department of Chemical Engineering, Faculty of Engineering, The British University in Egypt, Cairo, Egypt
[b] Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt
[c] Department of Chemistry, Faculty of Science, Ain Shams University, Cairo 11566, Egypt

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ABSTRACT

The significant hydrogen content and energy density in addition to the liquid nature and the high boiling point of ethylene glycol (EG) have recommended it as a potential replacement for hydrogen in proton exchange membrane fuel cells (PEMFCs). We herein report an enhanced electrocatalytic activity of EG electro-oxidation (EGO) in alkaline medium on a binary catalyst composed of platinum nanoparticles (nano-Pt) and nickel oxide nanoparticles (nano-NiOx) and assembled electrochemically on a glassy carbon (GC) electrode. The electrocatalytic activity of this catalyst towards EGO depended significantly on the loading level of the constituting ingredients of the catalyst, electrolyte acidity (pH) and the operating temperature. Several tools of electrochemical and materials characterization including the cyclic voltammetry (CV), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were all employed to confirm the successful deposition, to probe the relative ratio of the catalysts ingredients and to evaluate the surface topography, bulk composition and structure of the proposed catalyst. The results indicated a volcano-shaped dependence of the catalytic activity towards EGO on the loading level of nano-pt and nano-NiOx in the recommended catalyst. The investigation succeeded to optimize the synthetic procedure to reduce the amount of the precious Pt in the catalyst while maintaining a better catalytic activity than that obtained at the bare Pt surfaces. Interestingly, adding nano-NiOx to the catalysts ingredients (NiOx/Pt/GC) ended up with a significant lowering (13.90 kJ mol^{-1}) in the activation energy (E_a) of EGO in comparison to that (E_a = 18.83 kJ mol^{-1}) obtained at the Pt/GC electrode.

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Investigating a sequentially assembled MnOx/Pt nanocatalyst as a potential anode for ethylene glycol fuel cells

Ghada H. El-Nowihy[1,*], *Ahmad M. Mohammad*[2], *Mostafa M. H. Khalil*[3], *M. A. Sadek*[1], *Mohamed S. El-Deab*[2,*]

[1] Department of Chemical Engineering, Faculty of Engineering, The British University in Egypt, Cairo, Egypt
[2] Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt
[3] Department of Chemistry, Faculty of Science, Ain Shams University, Cairo 11566, Egypt
[*]E-mail: Ghada.Nowihy@bue.edu.eg, msaada68@yahoo.com

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Aiming at a better electrocatalytic enhancement of ethylene glycol (EG) electro–oxidation (EGO) in an alkaline medium for EG fuel cells (EGFCs), a MnOx/Pt anode was developed. A sequential layer-by-layer electrodeposition technique was employed to assemble first platinum nanoparticles (nano-Pt) directly onto the surface of a glassy carbon (GC) electrode then manganese oxide nanoparticles (nano-MnOx) were next immobilized. Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) were employed to evaluate the surface morphology and the bulk composition of the proposed catalyst in addition to the relative ratio of the catalyst's ingredients. On the other hand, the catalyst was characterized electrochemically using cyclic voltammetry (CV) technique. The results manifested the superiority of the developed MnOx/Pt/GC catalyst for enhancing EGO while the degree of enhancement depended on the loading level of the catalyst components and the acidity (pH) of the EG-containing electrolyte. The best electrocatalytic enhancement towards EGO was achieved at MnOx/Pt/GC electrode with nano-Pt = 3.8 μg and nano-MnOx, θ = 52 %, in 0.5 M NaOH solution (pH= 11.5) containing 0.5 M EG. Under these conditions, an increase in the oxidation peak current, I_p (1.7 times) along with a negative shift in the onset potential, E_{onset} (ca. 120 mV) of EGO was obtained in reference to the Pt/GC electrode. The developed catalyst exhibited a reasonable catalytic stability upon subjecting for a continuous potential cycling.

Keywords: Direct ethylene glycol fuel cells; Electrocatalysis; Platinum nanoparticles; Manganese oxide nanoparticles.

CONFERENCE PAPERS

No.	Title	Conference	Location	Date
1	Enhanced electro-oxidation of ethylene glycol at nanostructured modified Pt anodes for fuel cell applications	Egyptian- Italian Workshop on Energy & Related Materials	Pyramisa Hotel, Dokki, Egypt	October 17-19, 2016
2	Development of efficient nanoparticle-based catalysts for the direct ethylene glycol fuel cell	BUEACE1	Fairmont Heliopolis and BUE Campus, Cairo, Egypt	November 7-9, 2016
3	Platinum nanoparticles-cobalt oxide nanostructures as efficient binary catalyst for ethylene glycol electro-oxidation	5th MacroTrend Conference on Energy Issues	Espace vocation Haussmann, Saint-Lazare, Paris, France	December 28-29, 2017

TABLE OF ABBREVIATIONS AND SYMBOLS

C	Capacitance (μF cm^{-2})
C_{im}	Imaginary capacitance (μF cm^{-2})
C_{max}	Maximum capacitance (μF cm^{-2})
C_{min}	Manimum capacitance (μF cm^{-2})
C_{re}	Real capacitance (μF cm^{-2})
CO_{ads}	Adsorbed carbon monoxide
CPE_{dl}	Constant phase element of the double layer
CV	Cyclic Voltammetry
DEGFC	Direct ethylene glycol fuel cell
DFAFC	Direct formic acid fuel cell
DMFC	Direct MeOH fuel cell
E_a	Activation energy (kJ mol^{-1})
E_f	Material's Fermi level
$E_{v,\infty}$	Material's local vacuum level
EDS	Energy dispersive X-ray spectroscopy
EGO	Ethylene glycol electro-oxidation reaction
EIS	Electrochemical impedance spectroscopy
FAO	Formic acid electro-oxidation reraction
FE-SEM	Field emission scanning electron microscope
GC electrode	Glassy carbon electrode
HFC	Hydrogen fuel cell
HPLC	High performace liquid chromatography
I_p	Peak current
I-t	Chronoamperometry
LSV	Linear sweep votammetry
MOR	MeOH electro-oxidation reaction

MOx	Metal oxides
Nano-CoOx	Cobalt oxide nanoparticles
Nano-MnOx	Manganese oxide nanoparticles
Nano-NiOx	Nickel oxide nanoparticles
Nano-Pt	Platinum nanoparticles
NPs	Nanoparticles
OCP	Open circuit potential (volt)
Poly-Pt	Polycrystalline platinum electrode
Q	Electronic charge consumed (Coulomb)
R_{ct}	Charge transfer resistance (Ohm)
R_p	Polarization resistance (Ohm)
R_s	Solution resistance (Ohm)
t_d	Deposition time
XRD	X-ray diffraction spectroscopy
Z'	Real resistance (Ohm)
Z''	Imaginary resistance (Ohm)
ε	Activity index
θ, %	Surface coverage
$\theta_{oxide,}$%	Surface coverage of the oxide
ϕ	Work function of material
ϕ_0	Work function of the bare metal surface
s	The surface concentration of the adsorbate
μ	The dipole moment of the adsorbate that is directed perpendicularly to the metal surface

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