Ain Shams University
Faculty of Science
Chemistry Department

Nano metallic particles and their applications for development of direct alkaline fuel cell electrode

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

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B.Sc. in Chemistry, Faculty of Science
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Approval Sheet

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بِسْمِ اللّهِ الرَّحْمنِ الرَّحِيمِ

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

صدق اللَّهُ العظيم

سورة البقرة – الآية (32)

To my Family

To my best friends

To the soul of uncle Samir Osman

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Aim of the study

Alternative energy resources are considered to be the focus of the current research efforts. Investigations of new sources for clean and renewable energy conversion methods become the hope to decrease the dependency on fossil fuels. Although the existing sources of energy and conversion methods may have the ability to meet energy needs for now, yet it will not be able to face the massive increase in the rate of world-wide energy demand. It is also well-known that many of energy conversion methods are associated with great danger to environment and human health. It is also noticed that one of the most important issues in energy is its storage.

Direct Alkaline Fuel Cell (DAFC) is one of the most desirable forms of alternative energy conversion techniques for both high efficiency in energy conversion and for being an eco-friendly technique. Using ethanol rather than hydrogen as a fuel has many advantages such as; ease of production from bio-mass making it to be considered as renewable source of energy, ease of storage and transportation…etc.

The proper electro-catalyst design is the major technical problem facing both alternative energy conversion and energy storage. Since the catalyst must maintain both high efficiency and durability.

Hence in this thesis we aim to develop a new level of understanding for the changes occur to the graphitic support surface. Through this level one can develop a low cost high efficient electrocatalyst acts as effective anode material for DAEFC.

ENGLISH SUMMARY

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Part (I)

Graphite is a typical electrocatalyst support in alkaline energy conversion and storage devices such as fuel cells, supercapacitors and lithium ion batteries. The electrochemical behaviour of graphite electrode in 0.5M NaOH was studied to elucidate its surface structure/electrochemical activity relationship. Graphite cyclic voltammograms were characterized by an anodic shoulder AI and a cathodic peak CI in addition to the oxygen reduction reaction plateaus, PI and PII. AI and CI were attributed to oxidation and reduction of some graphite surface function groups, respectively. Rotating ring disk electrode (RRDE) study revealed two different oxygen types assigned as inner and outer oxygen. The inner oxygen was reduced via the more efficient 4-electron pathway while the outer oxygen proceeded with a lower efficient 2-electron pathway. The calculated percentages of the 4-electron pathway were ranged from 70% to 90%. A full mechanism over

the studied potential window was suggested through the combination between the voltammetric and FT-IR results.

Part (II)

Nano nickel modified graphite (Ni/G) electrode was prepared through the electrodeposition of Ni on graphite support as a typical anode material for Direct Alcohol Fuel Cells. The deposited nano nickel was found to undergo the instantaneous nucleation at the initial stages and converted to the progressive nucleation at the later stages of electrodeposition. The morphology of the electrodeposited nano nickel was characterized and found to be a nano spherulite like structure. The electrochemical behaviour of Ni/G electrode was studied in 0.5M NaOH without and with 1M EtOH. However, the behaviour of the Ni/G electrode was found to be a complex combination between the electrochemical behaviour of bare graphite (BG) and pure bulk Ni electrodes. The cyclic voltammetry feature of Ni/G electrode involved three anodic peaks in the forward span A1, A2 and A3 similar to bulk Ni electrode. On the reverse span

reactivation peak RA3 was also appeared. Moreover, a single step plateau (PIII) was observed in the oxygen reduction reaction potential range. In addition, one cathodic peak $C_{Ni/G}$ was observed and attributed to overlapping between C1 of the BG and C2-C3 of bulk Ni electrode. The $C_{Ni/G}$ cathodic peak is maintained almost constant while PIII enhanced on repetitive cycling with increasing vertex potential. However, it was lowered by repetitive cycling with fixing the potential window limits. The effect of the electrodeposition bath parameters was examined towards the electro-catalytic activity of the modified electrode for ethanol electrooxidation. Where the maximum obtained stable response value was 162mA/cm ^{2}. Very interesting discrepancies in the cyclovoltammetric behaviours of the Ni/G electrode appeared when we its surface was laterally faced with the electrolyte since it give a higher and more stable response than that produced by downward faced electrode surface. Although XRD was unable to detect the deposited nano Ni on the graphite surface, EQCM combined CV was used as an effective tool to detect the nature

and phases of Ni on the surface of Ni/G electrode. The mass profile of the electrodeposited layer revealed the formation of mixed type of α,β and γ $Ni(OH)_2$/NiOOH layer. The % of the β components increase during the EtOH oxidation and also increase as the number of successive cycles increase.