MODIFIED ACTIVATED CARBON-BASED CATHODES USING COBALT TETRAMETHOXYPHENYLPORPHYRIN (COTMPP) AND GRAPHENE FOR ZINC-AIR BATTERY

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ABSTRACT

This study proposed on the improvement of the performance of activated carbon (AC)-based electrodes by electrocatalyst doping and modifying the carbon support system for zinc-air battery (ZAB). Electrode or specifically known as air-cathode in ZAB is the key component that contributing to its performance. The catalyst was doped into carbon matrix following by pyrolysis process. Besides catalyst doping, a carbon support material also play the crucial role on the electrocatalytic performance. Combinations of two different carbon materials not only increase the specific surface area but also improve the electric conductivity. At first, different weight percent (wt.%) loading of cobalt tetramethoxyphenylporphyrin (CoTMPP) catalyst (AC-CoTMPP) were prepared using simple ultrasonication technique. The microstructure effects of CoTMPP addition on AC matrix or electrode materials were analysed using X-Ray Diffractometry (XRD), Fourier Transformed Raman spectroscopy (FT-RAMAN) and Field Emission Scanning Electron Microscopy (FESEM). Meanwhile the electrochemical performances of prepared electrodes involved cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) conducted at room temperature (25 ± 1 °C) using three-electrode system. The optimized experimental results from the CoTMPP composition were studied to determine the effect of heat treatment on structural and electrocatalytic activity of the AC-CoTMPP composites and electrodes at elevated temperatures known as pyrolysis process. The reduction peak current value of AC electrode with optimized content of CoTMPP (25 wt.% of CoTMPP loading and heat treatment of 800 °C) is −0.0455 mA. Although catalytic activity of heat-treated AC doped CoTMPP has shown an improvement, the obtained reduction peak current is still lower than that prepared electrode using platinum on carbon (Pt/C) catalyst (−0.0553 mA). Therefore, the proposed carbon-carbon composite through the combination of AC and graphene (Gr) as supports materials has become an effective strategy to enhance the structural morphology and electrochemical activity. This is due to the fact that Gr-AC composite not only enlarges the effective surface area of GrAC composite electrode but also provides a highly conductive graphitized surface thus increasing electrical conductivity. The reduction peak current and effective surface area of GrAC composite electrode has increased by 330 % and 108 % than that pure AC electrode, respectively. Subsequently, the electrode employing GrAC composite as support material doped CoTMPP catalyst has been explored to obtain the optimized structural and electrochemical properties. The heat treated GrAC-CoTMPP-25 wt.% electrode has the highest reduction peak current with −0.0653 mA, which are 36 % and 9 % higher than that heat-treated AC-CoTMPP-25 wt.% and GrAC electrodes, respectively. The Zn-air battery utilizing heat-treated GrAC-CoTMPP as cathode has the highest energy density with value of 122.65 Wh/g. The obtained air-cathode materials (heat treated GrAC-CoTMPP) outperforms commercial Pt/C in oxygen reduction reaction with greater reduction peak current value up to 13 %. When applied in ZAB, a high open- circuit voltage, excellent energy density, and satisfactory stability are achieved, implying that heat treated GrAC-CoTMPP cathode material has potential to replace platinum based catalyst.

ABSTRAK

Kajian ini mencadangkan penambahbaikan prestasi elektrod yang berasaskan karbon aktif (AC) dengan pendopan elektrokatalis dan mengubahsuai sistem sokongan karbon untuk bateri zink-udara (ZAB). Selain dari pemilihan logam zink sebagai bahan anod, elektrod atau dikenali sebagai katod udara di ZAB juga merupakan komponen penting yang menyumbang kepada prestasi ZAB. Prestasi elektrokatalitik katod udara ditingkatkan dengan memperkenalkan pemangkin logam peralihan ke dalam matriks karbon diikuti oleh proses pirolisis. Selain daripada pemilihan pendopan yang baik, bahan sokongan karbon yang stabil dengan luas permukaan spesifik yang tinggi dan kekonduksian elektrik yang baik juga memainkan peranan penting dalam meningkatkan prestasi elektrokatalitik bahan katod udara. Pada peringkat awal, pemangkin kobalt tetramethoxyphenylporphyrin (CoTMPP) dengan peratusan berat yang berbeza (wt.%) (AC-CoTMPP) disediakan menggunakan teknik ultrasonication yang ringkas. Selanjutnya, hasil eksperimen daripada dari komposisi CoTMPP yang dioptimumkan dikaji untuk meneliti kesan rawatan haba terhadap ciri-ciri struktur bahan komposit dan aktiviti elektrokatalitik elektrod (AC-CoTMPP) pada suhu-suhu yang berbeza yang dikenali sebagai proses pirolisis. Kesan pada mikrostruktur bahan elektrod dianalisis menggunakan Pembelauan Sinar-X (XRD), Spectroskopi Raman Fourier Transformed (FT-RAMAN) dan Mikroskopi Pengimbasan Pelepasan Pelepasan Medan (FESEM). Sementara itu, prestasi elektrokimia elektrod melibatkan voltammetri kitaran (CV) dan spektroskopi impedans elektrokimia (EIS) yang dijalankan pada suhu bilik (25 ± 1 °C) menggunakan sistem tiga elektrod. Nilai arus puncak pengurangan elektrod AC dengan kandungan CoTMPP yang dioptimumkan (25 wt.% berat CoTMPP dan rawatan haba 800 °C) adalah −0.0455 mA. Struktur morfologi dan aktiviti elektrokimia komposit AC-CoTMPP yang dioptimumkan ditingkatkan dengan mengubahsuai sistem bahan sokongan karbon. Gabungan AC dan graphene (Gr) bukan sahaja meningkatkan luas permukaan spesifik elektrod komposit GrAC tetapi juga memberikan permukaan grafit yang sangat konduktif sehingga meningkatkan kekonduksian elektrik. Nilai pengurangan puncak arus dan luas permukaan elektrod komposit GrAC telah meningkat masing-masing sebanyak 330 % dan 108 % daripada elektrod AC tulen itu. Oleh itu, elektrod yang menggunakan komposit GrAC sebagai bahan sokongan dan pemangkin CoTMPP sebagai elektrokatalis pendopan telah dieksplorasi untuk mendapatkan sifat struktur dan elektrokimia yang optimum. Elektrod GrAC-CoTMPP-25 wt.% yang telah dirawat mempunyai arus puncak pengurangan tertinggi iaitu −0.0653 mA, berbanding dengan elektrod AC-CoTMPP-25 wt.% dan GrAC yang telah dirawat, dengan peningkatan sebanyak 36 % dan 9 %. ZAB menggunakan GrAC-CoTMPP yang telah dirawat sebagai katod mempunyai nilai ketumpatan tenaga tertinggi dengan iaitu 122.65 Wh/g. Bahan katod udara yang diperoleh (GrAC-CoTMPP yang dirawat) mengatasi Pt/C komersial dalam tindak balas pengurangan oksigen dengan penurunan nilai arus puncak yang lebih tinggi iaitu sehingga 13 %. Apabila digunakan dalam ZAB, voltan litar terbuka tinggi, ketumpatan tenaga yang sangat baik, dan kestabilan yang memuaskan dicapai, menunjukkan bahawa bahan katod GrAC-CoTMPP yang dirawat berpotensi untuk menggantikan pemangkin berasaskan platinum.

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“This thesis is dedicated to those who always been there to share the laughter, happiness, tears, disappointment and frustration”

APPROVAL

The Examination Committee has met on 30th September 2020 to conduct the final examination of Ruslinda binti Md Ali on her degree thesis entitled 'Modified Activated Carbon-based Cathodes using Cobalt Tetramethoxyphenylporphyrin (CoTMPP) and Graphene for Zinc-Air Battery'.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
Ag	Silver
Al	Aluminium
Ca	Calcium
CB	Carbon Black
CC	Current Collector
Cd	Cadmium
C_{DL}	Interfacial Capacitance
Cl	Chloride
CE	Counter Electrode
CL	Catalyst Layer
CNT	Carbon Nanotube
CoTMPP	Cobalt Tetramethoxyphenylporphyrin
CPE	Constant Phase Element
Cu	Copper
CV	Cyclic Voltammetry
DL	Diffusion Layer
EDX	Energy-Dispersive X-Ray
EES	Electrochemical Energy Storage
EIS	Electrochemical Impedance Spectroscopy
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy
FeTMPP	Iron Tetramethoxyphenylporphyrin
FT-RAMAN	Fourier Transformed Raman Spectroscopy
FWHM	Full Width at Half Maximum
GC	Glass Carbon
GDL	Gas Diffusion Layer
GO	Graphene Oxide
Gr	Graphene
GrAC	Graphene-Activated Carbon
HOMO	Highest Occupied Molecular Orbital
HT	Heat Treatment
ITO	Indium Tin Oxide
K	Potassium
Li	Lithium
LUMO	Lowest Unoccupied Molecular Orbital
LSV	Linear Sweep Voltammetry
Mg	Magnesium
Na	Sodium
Ni	Nickel
OCV	Open Circuit Voltage
OH	Hydroxide
ORR	Oxygen Reduction Reaction
Pt	Platinum
Pt/C	Platinum on Carbon
PTFE	Polytetrafluoroethylene

R_{CT}	Electron-Transfer Resistance
RE	Reference Electrode
R_S	Solution Resistance
R_W	Warburg Diffusion Element
r^2	Linear Regression
SSA	Specific Surface Area
SWCNT	Single Wall Carbon Nanotube
XRD	X-Ray Diffraction
WE	Working Electrode
Wt.%	Weight Percentage
ZAB	Zinc-Air Battery
Zn	Zinc
Z_W	Warburg Impedance

LIST OF SYMBOLS

°C	Degree Celsius
µl	Microliter
Ω	Ohm
λ	Wavelength
θ	Half-Width Peak
A	Area
A	Amphere
C	Molar Concentration
cm	Centimeter
d	Interlayer Spacing
D	Diffusion Coefficient
E	Potential
$\mathrm{E_A}$	Activation Energy
E_{pa}	Anodic Peak Potential
E_{pc}	Cathodic Peak Potential
i	Current
I_{pa}	Anodic Peak Height
I_{pc}	Cathodic Peak Height
h	Hour
k	Slope
kg	Kilogram
min	Minute
mg	Milligram
ml	Milliliter
nm	Nanometer
Q	Charge
t	Time
v	Scan Rate
V	Volt

CHAPTER ONE

INTRODUCTION

1.1 Research Background: Electrochemical Energy Storage

Developing clean and renewable energy technologies are one of the major challenges that researchers face worldwide. The increasing market size and advancement in microelectronic devices demand for higher energy density, safe, low cost and reliable power sources. Among of the alternatives to address the above issues is with the development of electrochemical energy storage such as batteries and supercapacitors. Solid state metal-air battery technologies have been reported to possess excellent theoretical specific energy density [1], [2] and longer cycle life and have been used as a key component in portable microelectronic devices for the mass market such as watches and hearing aids. Zn-air batteries have been considered to be one of most promising energy storage and conversion technologies. Bifunctional oxygen catalysts with outstanding electrocatalytic activities are critical to the efficiency of Zn-air batteries. In the recent years, extensive researches have been devoted to exploring, designing, and preparing cost-effective and high-performance bifunctional electrocatalysts in alkaline media, such as transition-metal oxides and carbon-based materials.

Electrode materials have a vital role in energy production, conversion and storage. As the cost and performance of metal-air battery greatly influenced by the electrode, the exploration of new electrode materials and designation of efficient electrode architectures is inevitable. Although well-known platinum catalyst and Nafion binder provide desired electrochemical energy storage device performance, the high cost and scarcity materials hindered its application in industrial scale. For the past decade, there are many efforts by researchers worldwide to design electrode without using platinum-based catalyst and Nafion binder by replacing platinum with cheaper metal catalysts while Nafion binder was replaced with polytetrafluoroethylene (PTFE) binder which is less expensive. Although catalyst metals such as metal oxides [3]–[5], silver [6], [7], perovskites [8], [9] and transition metal N_4-macrocyclic compounds [10]–[13] have been extensively developed as cathode material, the performance of these materials are still cannot surpass the performance of noble-metal materials. In order to encounter this matter, combination of two or more different carbon materials have been previously reviewed and analysed as carbon-carbon composite or modified carbon support materials [14]–[16] for these metal catalysts. These carbon-carbon composites have demonstrated an improvement in the electrochemical performances of cathode due to high specific surface area and excellent electrical conductivity [17]–[19].

In this thesis, the doping of cobalt tetramethoxyphenylporphyrin (CoTMPP) as catalyst and carbon-carbon composite as support material (graphene-activated carbon) were leveraged to achieve better electrochemical activity for zinc-air battery (ZAB) application. The framework in this work is constructed based on current problems encountered in development of cathode which are high cost material and inadequate energy density with respect to cathode material selection, structural analyses and electrochemical performances, as discussed in the following Section 1.2.

1.2 Problem Statement

The main purpose of this study is to enhance the performance of Zn-air battery (ZAB) by improving the electrochemical activity of air-cathode. ZAB becomes the center of attention as alternatives to Li-ion battery (LIB) as it possesses comparable specific energy density to LIB and at the same time easier in handling process, fully recyclable and lesser in cost [20] compared to LIB. The crucial component contributing to high energy density for metal-air battery is air-cathode. Although noble metal-based electrode such as platinum, ruthenium and iridium possess excellent energy density but their high cost, poor durability and slow electron-transfer kinetic [21] restricted their application in large-scale commercialization [22]. Therefore, this research project will explore the potential of graphene-activated carbon (GrAC) composite doped with transition metal catalyst as an active cathode material for ZAB.

Carbon-carbon composite materials have drawn much attention as support material as well as metal-free catalysts for ORR due to their superior electrocatalytic activities along with low cost, good durability and environmental benignity. The studies of carbon materials (e.g., carbon black, activated carbon, graphite, carbon nanotube and graphene) doped with transition metal porphyrin (e.g., CoTMPP and FeTMPP) have shown to possess pronounced catalytic activity for ORR [23] motivated the exploration in developing novel carbon-carbon composite materials doped with transition metal porphyrin catalyst. The development of carbon-carbon composite (GrAC) doped with transition metal porphyrin (CoTMPP) catalyst as active cathode material is expected to greatly improve the electrocatalytic performance of oxygen reduction reaction (ORR) of air-cathode and increases the energy density of Zn-air battery. CoTMPP catalyst is considered as promising material to replace platinum-based catalyst considering the cost and reliability.

There are three approaches used in this research to enhance the cathode materials properties, the first approach is to determine the best composition of CoTMPP catalyst in AC-CoTMPP composite by varying the CoTMPP composition (5, 10, 15, 20, 25 and 30 wt. %). The second approach is to find out the optimum temperature for electrochemical activities. The untreated sample was compared to heat treated samples at 200, 450, 650, 750, 800 and 950 °C to study the effect of heat treatment on AC-CoTMPP composites. The last approach is modifying the carbons supported using carbon-carbon composite (AC and Gr) and doped with CoTMPP catalysts. To the best of our knowledge, there is only a little report on graphene-activated carbon (Gr-AC) composite as supports material for CoTMPP-based catalyst. Examining the effect of GrAC composite on the structural properties and its electrochemical performances may help in discovering better cathode material for application in Zn-air battery.

1.3 Research Objectives

This study aims to achieve following objectives:

i. **To determine** the effect of CoTMPP composition on AC-based electrode on the structural properties (FESEM-EDX and XRD) and its electrochemical performances (CV and EIS) as cathodes.

ii. **To determine** the effect of heat treatment (200, 450, 650, 750, 800, 950 °C) on the optimized AC-CoTMPP composite on the structural properties (FT-RAMAN) and its electrochemical performances (CV and EIS) as cathodes.

iii. **To appraise** the effect GrAC composite on the structural properties (FESEM-EDX, XRD and FT-RAMAN) and its electrochemical performances (CV and EIS) as cathodes.

iv. **To evaluate** the electrochemical performances (OCV, discharge profile and EIS) of prepared cathodes in fabricated Zn-air battery system.

1.4 Scope and Limitation of Research

This study focuses on developing AC-based cathodes using CoTMPP catalyst and Gr. The scope and limitations of the research are as follows:

i. AC-CoTMPP composites were limited to 30 wt.% with 5 wt.% increments of CoTMPP composition relative to AC.

ii. The optimized AC-CoTMPP composition is subjected to heat treatment with temperature ranging from 200 to 950 °C.

iii. GrAC composite was prepared in weight ratio of 9:1.