OBAFEMI AWOLOWO UNIVERSITY

SYNTHESIS AND CHARACTERIZATION OF SOME PORPHYRIN MOLECULES AS POTENTIAL ELECTROCATALYST FOR FUEL CELL

BY

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CERTIFICATION

We certified that this research work was carried out by Mrs OLAJIDE Afusat Ajoke in the partial fulfillment of the requirements for the award of Master of Science (M. Sc.) Degree in Chemistry, Obafemi Awolowo University, Ile – Ife, Osun State, Nigeria.

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DEDICATION

This work is dedicated to my wonderful family for their endurance, understanding and encouragement.

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ABSTRACT

This study synthesized and characterized two negatively charged porphyrin molecules and four positively charged metalloporphyrins, fabricated porphyrin nanostructures using various combination of the negatively charged molecules and the studied the electronic properties of the nanostructures formed. This was with a view to fabricating of nanostructures that could be used as electrocatalyst for fuel cells.

Porphyrin nanostructure were fabricated using two oppositely charged porphyrin molecules. The negatively charged molecules were meso-tetra (4-sulphonatophenyl) porphyrin ($TPPS_4^{4-}$) and meso-tetra (4-carbonxyphenyl) porphyrin ($TCPP^{4-}$) and the positively charged molecules were protonated to generate the positively charged species [zinc, nickel, cobalt and manganese meso- tetra (4-pyridyl) porphyrin ($ZnTPyP^{4+}$, $NiTPyP^{4+}$, $CoTPyP^{4+}$ and $MnTPyP^{4+}$]. They were synthesized following standard synthetic methods and characterized using ultraviolet-visible spectrophotometry, infrared spectrophotometry, ^{1}H and ^{13}C nuclear magnetic resonance and mass spectrometry. The porphyrin nanostructure were fabricated by ordinary electrostatic self -assembly and phase transfer self–assembly and characterized using ultraviolet-visible spectrophotometry only.

All the spectroscopy data confirmed the structure of the synthesized compounds. The electronic spectra of TPPS-MTPyP (M=Zn, Ni, Co and Mn) using ordinary electrostatic self-assembly technique showed the typical J-aggregation influenced by TPPS with bands around 492 nm and 708 nm. These bands were absent in the case of TCPP-MTPyP instead,

there was a shift of the absorption bands to shorter wavelength, indicating H-aggregation. For the phase-transfer electrostatic self-assembly technique, the electronic spectra were quite complex and bands were narrower than expected for aggregation.

This study concluded that ordinary electrostatic self-assembly was more effective method for the fabrication of nanostructure than the phase transfer method in producing a robust and well-defined porphyrin nanostructures.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

The rise in public awareness on the need for environmental protection from the pollution from fossil fuels has raised great effort on research so as to generate alternative/renewable energy sources. Small-scale generation systems, such as wind turbines, photovoltaic cells, micro-turbines, fuel cells etc., could play a significant part in meeting the rising in consumer demand by using the concepts of distributed generation (i.e. small-scale generation that is located near the consumers rather than the central or remote locations) (Ramakumar and Chiradeja, 2004). Fuel cell is the greatest among the different distributed generation systems due to the fact that they have the potential capability of providing both power and heat.

A fuel cell is a device that directly converts chemical energy to electrical energy without using a combustion reaction thereby producing water as its byproduct (Telila *et al*., 2009). Conventional heat engines produce electricity from chemical energy with the use of intermediate mechanical energy conversion resulting in reduced efficiency compared to fuel cells. Fuel cells are more efficient than combustion engines as they are not limited by the Carnot efficiency. The fuel cells combine the best features of engines and batteries; like an engine they can operate for long as fuel is available without any intermediate mechanical energy conversion and the characteristics of fuel cells are similar to a battery under load conditions (Brian, 2002). Also discussed in the literature are some of the advantages of distributed power generation; these include the interface of fuel cells with grid connection and their ability to control the grid voltage and frequency thereby improving the quality of supplied current. Fuel cells are classified according to the choice of presently six major different types of fuel cells are available.

i. Proton exchange membrane fuel cell (PEMFC):

(a) Direct formic acid fuel cell (DFAFC);

(b) Direct Ethanol Fuel Cell (DEFC).

ii. Alkaline fuel cell (AFC):

(a) Proton ceramic fuel cell (PCFC);

(b) Direct borohydride fuel cell (DBFC).

iii. Phosphoric acid fuel cell (PAFC)

iv. Molten carbonate fuel cell (MCFC)

v. Solid oxide fuel cell (SOFC) and

vi. Direct methanol fuel cell (DMFC)

They are further classified on the basis of operating temperature. The low operating temperature is in the range of 50–250 °C for PEMFC, AFC and PAFC, and high operating temperature in the range of 650–1000 °C like MCFC and SOFC.

Since oxygen is essential components of fuel cell and as a result there is a widespread of interest in the electrocatalytic reduction of oxygen (ORR) using cheaper electrodes. The standard reduction potential of oxygen in acidic aqueous media is -1.23 V vs standard hydrogen electrode (SHE) (Yeager, 1986) and the peak potential for the electrocatalyst ORR would be less negative than this value. Lots of investigations are being carried out in a search for cheaper electrode that would function at more favorable temperatures. One of the ways of overcoming the challenges of unfavorable reactions, lower rates of reaction, resistance to motion of the ion and mass transport losses is that these electrodes have to be modified (Brett and Brett, 1994; Zanello, 2003). The electrodes supplies the electronic and ionic conductivities and it is also interface for charge transfer for the mediator bound to the electrode surface. Therefore, electrocatalysis on a modified electrode surface is usually an electron transfer reaction between the electrode and some solution substrate which, when mediated by an immobilized redox couple (i.e. mediator) proceed at a lower over-potential than would otherwise occur at a bare electrode surface (Durst, 1997). Porphyrin serves as a good modifiers of electrodes surfaces and this is due to the fact that they possess high electron density in their ring structure, producing good electrical conductivity. Porphyrins are also thermally stable and inexpensive to manufacture in large quantities (Shi *et al*., 1990; Golubchikov and Berezin, 1986).

1.2 THE PORPHYRINS

Porphyrins and related tetrapyrrolic compounds, which have been the subject of intense interest since the early 19th century, have attracted scientists from many areas due to their immense biological importance and their fascinating physical, chemical, and spectroscopic properties (Kadish and Van Caemelbecke, 2003). The word *porphyrin* has its origin from the Greek word "*porphura*" meaning purple as a result of their intense purple colour (Milgrom, 1997). The main historical events that led to the discovery of porphyrins have been the subject of many discussions and review. The correct structure of porphyrin was first proposed in 1912 by Küster; but unaccepted until Fischer and Klarer (1926) who confirmed the structure proposed by Küster almost twenty years earlier which later won Nobel Prize in 1930. The simplest form of porphyrin, called porphine, (Figure 1.1a), is made of four pyrrolic units connected by four methine (*meso*) bridges. The pyrrole units bridging ensures extended conjugation of the unsaturated atomic centers resulting in a large, planar macrocycle with 22π electrons with only eighteen of them take part in any one of the several delocalization pathways(Desiraju, 1995). Based on Hückel's (4n+2) rule, porphyrins are consideredhighly aromatic. These aromatic properties contribute many of their useful applications.