

**UNIVERSITI TEKNOLOGI MARA**

**ELECTRODEPOSITION AND  
CHARACTERIZATION OF Pt AND  
PtCu COATINGS FOR METHANOL  
OXIDATION IN ALKALINE  
MEDIUM**

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## ABSTRACT

In this research, Pt based coatings (i.e.: pure Pt and PtCu alloys) were successfully electrodeposited on the Ti substrate using chronoamperometry to investigate the methanol oxidation reaction (MOR) in alkaline medium. The main problems dealing with the Pt bulk electrode surface during methanol oxidation are: i) low surface area of the pure Pt bulk leading to low current density for methanol oxidation reaction and ii) the formation of intermediate adsorbed CO species during methanol oxidation reaction which inhibits the catalytic function of Pt. Therefore, the aim of this research is to prepare high surface area Pt based coatings with good catalytic performance and high stability which can offer an alternative pathway for methanol oxidation reaction. Deposition parameters such as deposition potential, time and molar ratio of electrolytes were optimized in order to produce the best Pt based coatings. FESEM analysis showed that different applied potential used during deposition process has produced different morphologies of Pt coatings such as cauliflower-like, durian-like, needle-like and worm-like Pt structures which are due to different nucleation rate and growth rate during deposition process. The findings revealed that the best pure Pt coating with durian-like structure was prepared via chronoamperometry by applying a constant potential of -0.20 V for 60 min from 0.3 M H<sub>2</sub>SO<sub>4</sub> containing 0.01 M H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O. The coating labelled as Pt(-0.20 V, 60 min) produced the highest ECSA (i.e.: 8.08 m<sup>2</sup> g<sup>-1</sup>), current density peak (i.e.: 170.38 mA cm<sup>-2</sup>), If/Ib ratio (i.e.: 2.63) and the lowest onset potential (i.e.: -0.50 V) for methanol oxidation reaction in alkaline medium as compared to other pure Pt coatings. Subsequently, the addition of second metal (Cu) to pure Pt was found to give positive impact by minimizing the CO poisoning effect and reducing the Pt loadings on Ti substrate with excellent catalytic activity for methanol oxidation reaction. The best PtCu alloy coating with 81% Pt and 19% Cu (labelled as Pt<sub>81</sub>Cu<sub>19</sub>(-0.30 V, 30min)) was prepared by chronoamperometry at -0.30 V for 30 min showing the most significant enhancement of catalytic performance of Pt for MOR (ECSA: 12.07 m<sup>2</sup> g<sup>-1</sup>, current density peak: 196.32 mA cm<sup>-2</sup>, If/Ib ratio: 3.60 and onset potential: -0.54 V) as compared to other PtCu alloys composition. EDX and ICP-OES analysis showed that the content in PtCu alloy increased with increasing Cu concentration present in the Pt:Cu electrolyte solution. XRD confirmed that Cu was inserted into a face-centered cubic Pt structure forming PtCu alloys. Meanwhile, XPS analysis showed that the Pt peak for PtCu alloy shifted to lower binding energy than that of pure Pt, indicating the electron transfer occurred from Cu to Pt due to its electronegativity differences. The shift in electron transfer from Cu to Pt would increase the valence electron (5d) vacancy of Pt, thus contributing to the modification in the electronic properties of Pt at Pt<sub>81</sub>Cu<sub>19</sub> alloy, hence weakening the Pt-CO bonding energy. EIS analysis revealed lower electron transfer resistance of the Pt<sub>81</sub>Cu<sub>19</sub> alloy surface coating/electrolyte interface indicating faster electron transfer kinetics on its surface as compared to pure Pt, thus, enhancing MOR. In addition, the Pt<sub>81</sub>Cu<sub>19</sub> alloy coating showed slower current degradation corresponding to better stability with higher resistance to CO poisoning effect during MOR than pure Pt. These findings contribute to the basis and further understanding about the relationship between the deposition parameters towards surface properties and electrocatalytic behaviour of the prepared Pt based coatings for methanol oxidation reaction in alkaline medium.

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# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	ii
<b>AUTHOR'S DECLARATION</b>	iii
<b>ABSTRACT</b>	iv
<b>ACKNOWLEDGEMENT</b>	v
<b>TABLE OF CONTENTS</b>	vi
<b>LIST OF TABLES</b>	x
<b>LIST OF FIGURES</b>	xii
<b>LIST OF ABBREVIATIONS</b>	xix
<b>CHAPTER ONE: INTRODUCTION</b>	1
1.1 Background of Study	1
1.2 Problem Statements	4
1.3 Objectives of Study	6
1.4 Significance of Study	6
1.5 Scope and Limitation of Study	7
1.6 Thesis Organization	8
1.7 Conceptual Framework	9
<b>CHAPTER TWO: LITERATURE REVIEW</b>	10
2.1 Effects of Substrate	10
2.2 Various Methods of Pt Catalysts Preparation	12
2.3 Electrodeposition Methods	12
2.4 Electrochemical Deposition Theories	14
2.4.1 Cyclic Voltammetry	14
2.4.2 Chronoamperometry	16
2.4.3 Nucleation and Growth	17
2.4.4 Electrodeposition of Alloys	18
2.4.5 Properties of Electrodeposited Materials	19

# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Fuel cell is a 19<sup>th</sup> century invention (1839) of William Grove. Nonetheless, a fuel cell that could produce substantial energy was developed by Bacon (1959). Fuel cell is a device that enables to transform chemical energy of a fuel into electrical energy through a chemical reaction of positively charged hydrogen ions ( $H^+$ ) with oxygen ( $O_2$ ) or another oxidizing agent. There are many types of fuel cells such as Proton Exchange Membrane Fuel Cell (PEMFC), Direct Alcohol Fuel Cell (DAFC), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). These fuel cells are classified by the types of electrolytes used. This classification determines the types of electrochemical reaction take place in the cell, the temperature range to cell operates, the kind of fuel and catalyst etc.

Fuel cells are different from batteries, due to fuel cells require a continuous source of fuel and oxygen in order to sustain the chemical reaction for producing the electricity. Meanwhile, the chemicals present in the battery react with each other to generate an electrical energy. Accordingly, the fuel cell can generate electricity as long as the fuels are supplied. The fuels that normally used in fuel cells are hydrogen, methanol, ethanol and hydrocarbon.

Meanwhile, Direct Methanol Fuel cell (DMFC) is a category of DAFC in which methanol is used as the fuel. Generally, the DMFC is widely used in portable applications such as in mobile phones, laptops, digital cameras etc. The main advantage of using methanol as fuel is its stable liquid at all environmental conditions due to liquid form of fuel, thereby, it is easy to be handled, transported and stored. Additionally, the methanol is considered as a promising fuel in DAFC due to an abundant availability at low cost and relatively environmentally friendly. Other alcohols such as ethanol, propanol, etc. have also been considered as fuels in DAFC.

Figure 1.1 illustrates the basic operational diagram of the DMFC. The DMFC consists of anode, which oxidizes fuel ( $CH_3OH$ ) to produce carbon dioxide ( $CO_2$ ) and