

**UNIVERSITI TEKNOLOGI MARA**

**SUPERCAPACITOR AND DYE-  
SENSITIZED SOLAR CELL BASED  
ON QUASI-SOLID STATE POLYMER  
ELECTROLYTE AND IRON  
COBALTITE ELECTRODE**

**FARISH IRFAL BIN SAAID**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Doctor of Philosophy**  
**(Science)**

**Faculty of Applied Sciences**

**June 2022**

## ABSTRACT

Electrochemical devices based on liquid electrolytes are known to have high performance. However, problems associated with liquid electrolytes are electrolyte leakage, volatilization and corrosion of the electrode. The quasi-solid state polymer electrolytes (QSSPEs) are used in these devices to overcome the shortcomings of liquid electrolytes. In this work, the QSSPEs were used in both supercapacitor and dye-sensitized solar cells (DSSCs). For supercapacitor, a typical QSSPE was prepared by incorporating 0.4 g polyvinyl alcohol (PVA) in a 2 M potassium hydroxide (KOH) dissolved in distilled water. Whereas for DSSC, an optimized QSSPE was prepared by incorporating poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) in a propylene carbonate (PC) / 1,2-dimethoxyethane (DME) / 1-methyl-3-propylimidazolium iodide (MPII) liquid electrolyte. The semi-crystalline PVdF-HFP was used as a gelling agent because crystalline VdF provides mechanical strength to the electrolyte, whereas the amorphous HFP entraps the liquid electrolyte. Conductivity decreases gradually with increasing PVdF-HFP from  $1.3 \times 10^{-2}$  to  $2.0 \times 10^{-3}$  S cm<sup>-1</sup> due to decreased ion mobility. No-flow “jelly-like” electrolyte samples were obtained for PVdF-HFP  $\geq 0.2$  g. The fabricated DSSC without PVdF-HFP shows higher efficiency than DSSCs with PVdF-HFP. The presence of PVdF-HFP deteriorates the performance of DSSCs, but problems associated with liquid electrolytes are eliminated. Presence of sodium iodide (NaI), 4-tert-butylpyridine (TBP) and guanidine thiocyanate (GuSCN) further increases the efficiency of DSSCs. Apart from electrolytes, electrodes also play a significant role in electrochemical devices. Platinum (Pt) is an expensive material commonly used as a counter electrode in DSSC. Commercial supercapacitors are commonly made from carbonaceous materials and they generally exhibit low specific capacitance ( $C_{sp}$ ). Therefore, in this work, iron cobaltite (FeCo<sub>2</sub>O<sub>4</sub>) has been explored as an alternative material for the counter electrode in DSSC and cathode in supercapacitor. FeCo<sub>2</sub>O<sub>4</sub>, iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) were synthesized by a simple hydrothermal process. Field-emission scanning electron microscope (FESEM) images show that Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> exhibit different morphology even though they were synthesized via a similar method. The electrochemical properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and FeCo<sub>2</sub>O<sub>4</sub> electrodes were obtained in a 6 M KOH electrolyte solution. The FeCo<sub>2</sub>O<sub>4</sub> electrode has the highest  $C_{sp}$ , followed by Co<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The highest  $C_{sp}$  of FeCo<sub>2</sub>O<sub>4</sub> is because of its large nanosheets morphology, better transportation of ions through its expanded crystal structure, and weak crystallinity, which facilitates the intercalation of ions. By varying the duration of hydrothermal reaction, four different FeCo<sub>2</sub>O<sub>4</sub> structures, namely nanoneedles, nanorods, nanosheets and microcubes, have been obtained. The morphological evolution of FeCo<sub>2</sub>O<sub>4</sub> is well-explained based on FESEM and high-resolution transmission electron microscopy (HRTEM) analysis. The FeCo<sub>2</sub>O<sub>4</sub> nanosheets have the highest  $C_{sp}$ , followed by nanorods, nanoneedles and microcubes. The highest  $C_{sp}$  of FeCo<sub>2</sub>O<sub>4</sub> nanosheets is attributed to its highest specific surface area and porosity. A solid-state asymmetric FeCo<sub>2</sub>O<sub>4</sub> nanosheets / PVA-KOH / reduced graphene oxide (rGO) supercapacitor was fabricated. The supercapacitor exhibits a maximum power density of 3202 W kg<sup>-1</sup> and a maximum energy density of 24.5 Wh kg<sup>-1</sup>. It demonstrates 70% capacitance retention after 3000 cycles. The optimized PVdF-HFP QSSPEs were assembled into DSSCs with FeCo<sub>2</sub>O<sub>4</sub> nanosheets as the counter electrodes. It shows an efficiency of 6.04 %.

## ACKNOWLEDGEMENT

Firstly, Alhamdulillah, I wish to thank God for giving me the opportunity to embark on my PhD and for completing this long and challenging journey successfully.

My deepest appreciation and sincere thanks, goes to my supervisor, Prof. Ts. Dr. Tan Winie on her advice, encouragement, help and care in executing this research. Guidance and insight provided by my supervisor helped to the success of this thesis. A million thanks to my co-supervisor Prof. Dr. Tseung-Yuen Tseng for teaching and helping me in my research attachment in National Chiao Tung University, Taiwan.

My appreciation goes to the Institute of Sciences (IOS) and Faculty of Applied Sciences (FSG) staff members who provided the facilities and assistance during sampling. Special thanks to my colleagues and friends for helping me with this project.

Finally, I wish to express gratitude sustainable utmost appreciation to my beloved family members, especially my parents and wife above all sacrifices, encouragement and enthusiasm that was given to me during the period of study.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	<b>ii</b>
<b>AUTHOR'S DECLARATION</b>	<b>iii</b>
<b>ABSTRACT</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>TABLE OF CONTENTS</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>x</b>
<b>LIST OF FIGURES</b>	<b>xii</b>
<b>LIST OF SYMBOLS</b>	<b>xix</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xxii</b>
<b>CHAPTER ONE INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	2
1.3 Significance of Research	4
1.4 Objectives	4
1.5 Scope of Research	5
1.6 Thesis Outline	6
<b>CHAPTER TWO LITERATURE REVIEW</b>	<b>7</b>
2.1 Introduction	7
2.2 Structure and Mechanism of Supercapacitors	9
2.3 Structure and Mechanism of Dye-Sensitized Solar Cells (DSSCs)	13
2.4 Transition Metal Oxides as Electrode Materials	15
2.4.1 Single vs Mixed Transition Metal oxides	16
2.4.2 Synthesis of Transition Metal Oxides	18
2.4.3 Transition Metal Oxides with Various Nanostructures, Synthesised via Hydro/Solvothermal Method	28
2.5 Application of Transition Metal Oxides in Supercapacitor and DSSC	37
2.6 Electrolytes	41

2.6.1	Electrolytes for Supercapacitors	41
2.6.2	Electrolytes for DSSCs	47

**CHAPTER THREE PREPARATION AND CHARACTERIZATION OF PVDF-HFP/PC/DME/MPII QUASI-SOLID-STATE ELECTROLYTE FOR APPLICATION IN DSSC 49**

3.1	Introduction	49
3.2	Experimental	50
3.2.1	Materials	50
3.2.2	Sample Preparation for ATR-FTIR Studies	50
3.2.3	Preparation and Characterization of Liquid Electrolyte	51
3.2.4	Preparation and Characterization of QSSPEs	52
3.2.5	DSSC Fabrication and Characterization	54
3.3	Results and Discussion	55
3.3.1	FTIR studies	55
3.3.2	Conductivity Studies of Liquid Electrolyte	74
3.3.3	Quasi-solid-state polymer electrolyte (QSSPE)	78
3.4	Conclusion	95

**CHAPTER FOUR PREPARATION AND CHARACTERIZATION OF COBALT IRON-BASED SINGLE OXIDE AND MIXED OXIDE ELECTRODE MATERIALS 96**

4.1	Introduction	96
4.2	Experimental	97
4.2.1	Chemicals and Materials	97
4.2.2	Synthesis of Fe <sub>2</sub> O <sub>3</sub>	97
4.2.3	Synthesis of Co <sub>3</sub> O <sub>4</sub>	98
4.2.4	Synthesis of FeCo <sub>2</sub> O <sub>4</sub>	99
4.2.5	Synthesis of Graphene Oxide (GO)	99
4.2.6	Preparation of FeCo <sub>2</sub> O <sub>4</sub> and GO Electrodes	100
4.2.7	Materials Characterization	100
4.2.8	Fabrication of Asymmetric FeCo <sub>2</sub> O <sub>4</sub> /KOH/GO Supercapacitor	101
4.2.9	Electrochemical Measurements	101