

UNIVERSITI TEKNOLOGI MARA

**PHYSICAL AND ELECTRICAL
STUDIES ON METHYLCELLULOSE
BASED ION CONDUCTING
POLYMER ELECTROLYTES**

NURSYAHIDA BINTI SAHLI

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science

Faculty of Applied Science

December 2016

ABSTRACT

In present study, thin film electrolytes were prepared using methylcellulose (MC), lithium triflate (LiCF_3SO_3) and ethylene carbonate (EC) at various weight percentages (wt.%). All samples were prepared by solution cast technique. The impedance spectroscopy (IS) studies shows the highest conductivity of unplasticized system appeared at composition ratio 70:30 wt. % with conductivity value $2.13 \times 10^{-5} \text{ S cm}^{-1}$ and enhanced up $1.24 \times 10^{-4} \text{ S cm}^{-1}$ for plasticized system (49:21:30) wt.%. The temperature dependence conductivity shows the conductivity of for both systems follow the Arrhenius behaviour. The activation energy (E_a) observed to decrease as the temperature increase hence increase the ionic conductivity. Attenuated total reflectance–Fourier transformed infrared (ATR-FTIR) spectroscopy confirmed the complexation between polymer and salt. The Li^+ observed to form a coordination bond with the oxygen atom of the functional group (C-O) to form $\text{Li}^+ \rightarrow \text{OC}$ complexes. ATR-FTIR studies also justified that the plasticizer penetrated into the polymer chains and created more free volume without perturbing the polymer-salt complexes. X-ray diffraction (XRD) analysis proved the formation of polymer-salt complexes through the decreasing of peak intensity at 2θ between 15° to 30° of MC upon the addition of salt content. Further studies on XRD spectra shows that the addition of plasticizer has increased the amorphosity of MC- LiCF_3SO_3 system thus allowed the ion to migrate easily which contribute to the ionic conductivity enhancement. Differential scanning calorimetry (DSC) analysis shows the T_g in MC-salt system increase due to the addition of salt. The addition of EC into polymer electrolyte system has decreases the glass transition temperature (T_g) value signifying that EC has contributed in reducing the degree of crystallinity of the polymer electrolyte system. The surface morphology analysis of plasticized system was fully smooth due to the effect of EC plasticizer. The value of ionic transference numbers found to be 0.95 and 0.96 respectively. The electrochemical window stability for unplasticized was observed around 3.6V and increases to 4.4V for plasticized system

ACKNOWLEDGEMENT

In the name of ALLAH the most gracious and the most merciful. All praise and thanks to ALLAH, for the blessing and the wisdom his bestowed upon me, the strength and the opportunity for me to be able to complete this thesis successfully. I would like to convey my earnest gratitude to all who has contributed in this thesis either directly or indirectly.

I would like to express my special gratitude to my supervisor, Assoc. Prof. Dr. Ab Malik Marwan Ali , my co-supervisor Prof. Dr. Muhd Zu Azhan Yahya and Prof. Dr Ri Hanum Yahaya Subban who imparting their knowledge and the expertise toward the research.

My endless appreciation to my beloved family, my father Sahli Bahrudin, my mother and my siblings Nursyaikhah, Siti Syafiqah, Muhammad Haziq Afif and Muhammad Harith Amsyar who always support and give their trust to me thought out the study.

Thanks to all my Ionic Materials and Devices Research Laboratory (iMADE) members especially Mrs Masni, Zafirah, Sherene, Sahak, Linda, Mashitah, Diana, Hamizah, Khuzaimah, Fadhilah, Syafiqah and Zulaikha who made it possible for me to spend all these precious years in where I could learn so much not only about science but also life in general. Special thanks to my best partner Nordiana Nabilla for her continuously gives me the courage and strength in completing my research.

Thank you to all the staff at Postgraduate Society, UiTM Shah Alam for always guiding and giving me the important information either through emails or call.

Finally, I would like to thank Ministry of Science, (MYBRAIN) scholarship awarded and mostly to UITM MALAYSIA for being a platform for me to finish my MSc study.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF SYMBOLS	xvi
LIST OF ABBREVIATIONS	xvii
CHAPTER ONE: INTRODUCTION	1
1.1 Background	1
1.2 Problem Identification	2
1.3 Objectives of The Research	3
1.4 Scope of The Research	3
1.5 Research Aims and Rationale	4
1.6 Outline Dissertation	4
CHAPTER TWO: LITERATURE REVIEW	5
2.1 Introduction	5
2.2 Polymer Electrolytes	5
2.3 Solid Polymer Electrolyte	6
2.4 Plasticized Polymer Electrolyte	9
2.5 Physical Properties Studies of Polymer Electrolyte	10
2.5.1 Attenuated Total Reflectance-Fourier Transform Infrared Studies	10
2.5.2 X-Ray Diffraction Analysis	11
2.5.3 Thermal Properties of Polymer Electrolyte	13
2.6 Electrical Properties Studies	14
2.6.1 Impedance Spectroscopy	14
2.6.2 Ionic Conduction Mechanism in Polymer Electrolyte	16

2.6.3 Arrhenius Behaviour	20
2.7 Properties For Electrolyte Materials Selection	22
2.7.1 Polymer Host	22
2.7.2 Methylcellulose	22
2.7.3 Lithium Triflate	23
2.7.4 Ethylene Carbonate	24
2.7.5 Solvent	25
CHAPTER THREE: RESEARCH METHODOLOGY	26
3.1 Introduction	26
3.2 Preparation of Samples	26
3.2.1 Preparation of MC-LiCF ₃ SO ₃ System	26
3.2.2 Preparation of Plasticized MC-LiCF ₃ SO ₃ System	28
3.3 Sample Characterizations: Physical Properties	29
3.3.1 Attenuated Total Reflectance Fourier Transform Infrared	29
3.3.2 X-Ray Diffraction Analysis	29
3.3.3 Thermogravimetric Analysis	30
3.3.4 Differential Scanning Calorimetry	30
3.3.5 Environmental Scanning Electron Microscope	31
3.4 Sample Characterization: Electrical Properties	31
3.4.1 Electrochemical Impedance Spectroscopy	31
3.4.2 Transference Number	32
3.4.3 Linear Sweep Voltammetry	32
CHAPTER FOUR: RESULT AND DISCUSSION (PHYSICAL PROPERTIES)	35
4.1 Introduction	35
4.2 ATR-FTIR Spectroscopy Studies on MC Based Polymer Electrolyte	35
4.2.1 ATR-FTIR Spectrum MC	35
4.2.2 ATR-FTIR Spectrum of LiCF ₃ SO ₃	37
4.2.3 ATR-FTIR Spectrum of EC	39
4.2.4 Complexation of MC-LiCF ₃ SO ₃ System	40
4.2.5 Effect of EC Plasticizer on MC-LiCF ₃ SO ₃ System	44
4.2.6 Interaction of MC-EC System	45
4.3 XRD Studies on MC Based Polymer Electrolyte	46
4.3.1 Effect of LiCF ₃ SO ₃ on Structure of MC	46