

UNIVERSITI TEKNOLOGI MARA

**CHARATERIZATION OF
CORNSTARCH-BASED SOLID
POLYMER ELECTROLYTE WITH
GRAPHENE OXIDE FOR SODIUM
ION BATTERIES**

SYAKIRAH BINTI SHAHRUDIN

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

Faculty of Applied Sciences

June 2019

ABSTRACT

In this work, Corn Starch (CS) was used as the principle host to prepare CS-Sodium salt using solution casting technique. The film of CS-NaI electrolyte with ratio 75:25 yielded highest conductivity which is $(1.43 \pm 0.12) \times 10^{-04} \text{ Scm}^{-1}$. The increase in conductivity is also attributed to the increase in amorphousity in the electrolyte as shown from X-ray Diffactogram (XRD) result. The interaction between the polymer and salt were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) studies where interactions occurred between Na^+ with CS. However, the conductivity value is still not high enough for device application. In order to improve the conductivity of the optimum salted system, Graphene Oxide (GO) was added into the CS-NaI polymer electrolyte system. The system containing 4wt.% of GO exhibited the highest ionic conductivity of $(2.49 \times 10^{-03} \pm 1.53 \times 10^{-05}) \text{ Scm}^{-1}$. The GO seems to enhance conductance due to the fact that it is providing more effective paths for the migration of conducting ions. In temperature-dependent study, the solid polymer electrolytes (SPEs) follow the Arrhenius thermal activated model. In structural study using FTIR and XRD, complexations between polymer, salt and GO were confirmed for all SPEs. Furthermore, Thermal studies using Thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) thermograms demonstrated that decomposition temperature (T_{dc}) and glass transition temperature (T_g) for CS shift upon complexation with iodide salt and GO. The activation energy obtained for CS-NaI is 0.12eV and CS-NaI with GO is 0.08eV. The collected data from Electrical Impedance Spectroscopy (EIS) were analyzed in various complex planes such as impedance, admittance and permittivity for dielectric studies. Ionic transference number were found 0.97 and 0.96 for the optimum composition of salted system and filler system. This implies that the samples are ionic in nature. FESEM revealed that when 4 wt% GO is added, the surface of the electrolyte exhibits increase distribution of porous structure which is the ionic conductivity of an electrolyte is influenced by the porosity since the pore connectivity is important for the transportation of the charge carriers in the electrolyte. Lastly, the optimum solid polymer electrolyte for both systems which are 75:25/CS:NaI and 75:25/CS:NaI-4 wt. % GO respectively were chosen as electrolytes in battery fabrication. Open Circuit Voltage (OCV) shows 1.68 V for 75:25/CS:NaI while the result increases to 2.38 V with addition of 4 wt. % GO in the electrolyte. These two sodium batteries showed better performance with discharge capacity of 114 $\mu\text{Ah/g}$ for CS:NaI system and 218 $\mu\text{Ah/g}$ for addition of GO into the polymer electrolyte system.

ACKNOWLEDGEMENT

In the name of ALLAH The Most Gracious and Most Merciful, I am very grateful to Him for allowing me to complete my Ph.D studies. I would like to take this opportunity to express my thanks and gratitude to all people below for their contributions to my study, which made it better in many ways.

I have been very fortunate to work under the supervision of Prof. Dr. Hjh. Azizah Hanom Ahmad, whose thoughtful advice and captivating spirit contribute to the quality of this study. I greatly appreciate the time she spent on helping me and giving me sound advice and ample assistance, and I extend my most sincere thanks to her. Her contribution in the completion of my project means a lot to me and I am indebted to her.

I am also grateful to all my family and whole family of ICC Lab Universiti Teknologi MARA for their support and guidance. Last but not least, Million thanks to those who involve directly and indirectly for helping me to achieve the success of this project.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xix
LIST OF ABBREVIATIONS	xx
CHAPTER ONE: INTRODUCTION	1
1.1 Background of Research	1
1.2 Problem Statements	3
1.3 Research Objectives	3
1.4 Scope And Limitation Of Research	3
1.5 Significance Of Research	5
1.6 Thesis Organisation	5
CHAPTER TWO: LITERATURE REVIEW	7
2.1 Introduction	7
2.2 Basic Polymer Electrolyte	7
2.3 Classification of Polymer Electrolyte	10
2.3.1 Solid Polymer Electrolytes (SPE)	10

2.3.2	Gel Polymer Electrolyte (GPE)	11
2.3.3	Composite Solid Polymer Electrolyte (CSPE)	13
2.4	Conduction Mechanism of Solid Polymer Electrolyte	14
2.4.1	Cation and Anion Size Effects on Ionic Conduction	16
2.5	Polymer Host	16
2.5.1	Corn Starch (CS) Based Solid Polymer Electrolyte	17
2.6	Doping Salt	20
2.6.1	Sodium Salt as Conducting Ion	21
2.7	Additive or Filler	24
2.7.1	Graphene Oxide (GO) as an Additive in Polymer Electrolyte	25
2.8	Solid State Sodium Batteries	27
CHAPTER THREE: RESEARCH METHODOLOGY		29
3.1	Introduction	29
3.2	Materials	29
3.3	Solution Cast Method	31
3.4	Preparation of CS- Salts Solid Polymer Electrolyte System	31
3.4.1	Different Amount of GO were Incorporated into the Optimum CS-NaI SPE System	32
3.5	Characterization of Polymer Electrolytes	33
3.5.1	Electrochemical Impedance Spectroscopy (EIS)	33
	<i>3.5.1.1 Measurement of electrical conductivity and dielectric properties</i>	34
	<i>3.5.1.2 Transport properties using EIS</i>	38
	<i>3.5.1.3 Measurement of Transference Number</i>	40
3.5.2	X-ray Diffraction (XRD) Technique	42
3.5.3	Fourier Transformed Infrared Spectroscopy (FTIR)	44
3.5.4	Differential Scanning Calorimetry (DSC) Studies	45