CHARACTERIZATION OF POLY (VINYLEDENE FLUORIDE) BASED ELECTROLYTES AND BATTERIES

BY

M.MILBURN EBENEZER JACOB

A thesis submitted to

Institute of Postgraduate Studies and Research

University of Malaya

for the degree of

Doctor of Philosophy

INSTITUE OF POSTGRADUATE STUDIES AND RESEARCH ${\bf UNIVERSITY\ OF\ MALAYA}$

KUALA LUMPUR

MALAYSIA 1999

ya III**I**II



DECLARATION

I hereby declare that the work reported in this thesis is my own unless specified and duly acknowledged by quotation.

31 March 1998

M・M' しし M. Milburn Ebenezer Jacob

Acknowledgements

"The Lord will make you the head, not the tail"

(Deu 28:13),

According to the promise, *Lord Jesus* blessed me throughout my life. I dedicate all the glory and honour unto Him. Without His help, I could not complete this impassable task.

I take this opportunity to sincerely thank my supervisor Assoc. Prof. Dr. Abdul Kariem Arof, for his constant source of inspiration, support and bailing me out of difficult and tricky situations during experimental phase. I express my sincere thanks to Prof. Radhakrishna, for his love, support and encouragement throughout my stay. Thanks are due to his friendly love towards me during the initial stages of my research carrier.

Special mention must be made of *Assoc. Prof. Dr. Ambar Yarmo*, UKM, whose help in XPS work is gratefully acknowledged. My sincere appreciation also goes to *Pn. Vijaya*, for her invaluable help in SEM analysis. *Pn. Lim Chor Yoke*, also deserve special mention for the assistance in thermal analytical work. A word of praise must also be made of *Mr. Azmi*, SIRIM, for allowing me to use the facilities.

I wish to thank my colleagues, Mathivanan, Anand, Shameem, Ramesh, Venga, Rajan, Amin, Bouzid and Vicky, who made my stay as a pleasant one. I also wish to thank all my friends from GTPJ.

I acknowledge with gratitude the inspiration and wise counsel received from **Prof. T.**Ohzuku, Osaka City University, Japan and **Prof. J.L. Souquet**, INPG-CNRS, France. I would like to thank the Dean and the Staff of IPSP for the help and IRPA for the financial assistance.

Last, but far from least, I wish to express my heart felt thanks to my father *D. Muthu*, my mother, *C. Chellathai* and my brothers *M. Suresh D. Jacob* and *M. Ramesh T. Jacob* for their moral support, encouragement and love.

M.M.E.J

Preface

An efficient production, storage and distribution of electrical energy are of main

concern to a civilization whose mainstay is electrical energy. An offshoot of

research in these lines is the development of new solid materials for electrode and

electrolyte applications. The present investigation is aimed to develop a poly

(vinyledene fluoride); (PVDF) based polymer electrolytes. Accordingly, the work

embodied in this dissertation is devoted to the development and characterization of

plasticized and unplasticized polymer electrolytes using various physico-chemical

techniques. The dissertation is laid out in seven chapters.

A brief description about the history of solid electrolytes, polymer electrolytes and

batteries are given in the introductory chapter followed by the chapter that reviews

various analytical techniques employed to characterize the polymer electrolyte

sample. Chapter III presents a detailed description about the electrical

characterization of polymer electrolytes. Chapter IV deals with the characterization

of polymer electrolytes by various techniques.

Chapter V gives detailed description about thermal properties of unplasticized and

plasticized polymer electrolytes. The battery characterization was emphasized in

Chapter VI. Chapter VII consolidates the findings of the dissertation and attempts

to foresee the challenges ahead.

PERPUSTAKAAN INSTITUT PENGAJIAN SISWAZAH DAN PENYELIDIKAN MALAYA

UNIVERSITI MALE

V

Abstract

In the present study, poly (vinyledene fluoride) based polymer electrolytes were prepared by the solution cast technique. The polymer salt complex gives very low ionic conductivity of the order of 10⁻⁷ S/cm. The ionic conductivity of the polymer electrolyte is enhanced further by the addition of plasticizers such as dimethyl formamide, methyl formate and ethylene carbonate. The ionic conductivity enhancement is more in the case of DMF plasticizer than the other plasticizers used in the present investigation. The temperature dependent ionic conductivity studies (log σT Vs 1000/T (K-1)) follow Arrhenius type behaviour. This implies the fact that ionic conduction in polymer electrolyte is similar to that of the ionic crystals. X-ray diffraction analysis gives information regarding the semi-amorphous nature of the polymer electrolytes. FTIR and XPS spectroscopic studies show that there is a strong interaction between the plasticizer and the salt and the interaction is mainly with the oxygen atom of the plasticizers. The XPS studies ascertain the fact that there is an interaction between the salt and the polymer and this interaction is with fluorine atom of PVDF and the Li cation of the salt. The SEM analysis provides detailed picture about the plasticizer in altering the surface of the polymer electrolyte sample. The thermal studies on plasticized polymer electrolyte systems suggest that the thermal stability is better and the crystallinity of the polymer electrolyte is reduced considerably. This reduction in crystallinity is prominent in the case of DMF plasticizer than the other plasticizers used in the present study. Polymer batteries were assembled for all the high conducting plasticizer based polymer electrolyte systems. The batteries were analyzed galvanostatically. The battery discharge curve shows poor capacity for all the batteries. This low capacity may be due to the formation of surface layer on the lithium metal, high internal resistance of the battery due to the electrode/electrolyte interface and the low ionic conductivity of the polymer electrolytes. Studies are on to improve the ionic conductivity of the polymer electrolytes further and replacing the lithium metal with lithium transition metal oxides.

Contents

Decla	aration		ii	
Ackn	owledg	ements	iii	
Prefa	ice		v	
Abst	ract		vi	
Chap	oter 1.	Introduction		
1.1	Electr	ochemical Power Sources or Batteries	1	
1.2	Theor	etical Cell Voltage and Capacity	3	
	1.2.1	Free Energy	3	
	1.2.2	Theoretical Voltage	4	
	1.2.3	Theoretical Capacity	4	
	1.2.4	Voltage Definitions	5	
		1.2.4.1 Some Definitions About Different Voltages	7	
1.3	Why I	Lithium Batteries?	7	
1.4	Why l	Polymer Electrolytes?	10	
1.5	Types	Types of Ion Conducting Polymers		
1.6	Essen	Essential Requirements of Good Polymer Electrolytes		
1.7	Mech	anisms of Ion Conduction	13	
	1.7.1	Solid State Theory (Arrhenius Equation)	17	
		1.7.1.1 Schottky and Frenkel Mechanism	18	
	1.7.2	Free Volume Theory (Vogel-Tamman-Fulcher Equation)	19	
	1.7.3	WLF Equation	21	
	1.7.4	Bruce's Theory on Ion Conduction Mechanism	23	

	1.7.5	The Microscopic Approach of Ion Transport in Glasses	24
	1.7.6	Ion Conduction Mechanism in Plasticized Polymer Electrolytes	24
1.8	Solid State Batteries		
	1.8.1	Disadvantages	28
		1.8.1.1 Volume Change	28
		1.8.1.2 Electrolyte Impedance	28
		1.8.1.3 Discharge Product Impedance	28
		1.8.1.4 Materials Compatibility	29
		1.8.1.5 Manufacturability	29
1.9	Lithiu	m Primary Batteries with Non-aqueous Electrolytes	29
1.10	Lithium Metal Secondary Batteries 3		
1.11	Disadvantages of Secondary Lithium Batteries 3		
1.12	Lithium Ion Batteries or Rocking-Chair Batteries		
1.13	What is Meant by Intercalation		
	1.13.1	Criteria for Selecting Insertion Electrodes	33
1.14	Advar	ntages of Graphite Anodes	34
1.15	Intercalation in Graphite 3		
1.16	New A	Anode Materials for Lithium Secondary Batteries	37
1.17	Objec	tives of the Present Work	38
Chap	ter 2.	Experimental	
2.1	Metho	d of Sample Preparation	40
2.2	ac-Im	pedance Spectroscopy	42

42

2.2

2.3	X-ray Diffraction 4		
2.4	Thermal Analysis		
	2.4.1	Differential Scanning Calorimetry	48
	2.4.2	Thermogravimetric Analysis	51
2.5	Infrared Spectroscopy 5		
2.6	X-ray Photoelectron Spectroscopy (XPS) 55		
2.7	Scanning Electron Microscopy 57		
2.8	Battery Charge Discharge		
Chapt	ter 3.	Electrical Characterisation Studies	
3.1	ac-Im	pedance Analysis	63
	3.1.1	Unplasticized Systems	63
	3.1.2	Plasticized Systems	65
3.2	Choice of the Better Plasticizer for Conductivity Enhancement 66		
3.3	Dielectric Relaxation Studies 72		
3.4	Ion Conduction Mechanism 79		
3.5	Summary		82
Chapter 4.		Characterisation of Polymer Electrolytes	
4.1	X-ray Analysis		
	4.1.1	Unplasticized Systems	83
	4.1.2	Plasticized Systems	86

4.2	Fourie	r Transform Infrared Spectroscopy (FTIR)	90
	4.2.1	DMF Spectra	90
		4.2.1.1 DMF + LiBF ₄ Spectra	92
		4.2.1.2 BF ₄ * Spectra	95
		4.2.1.3 DMF + PVDF Spectra	95
	4.2.2	MF Spectra	101
		4.2.2.1 MF + LiBF ₄ Spectra	101
		4.2.2.2 MF + PVDF Spectra	104
	4.2.3	EC Spectra	108
		4.2.3.1 EC + LiBF ₄ Spectra	108
		4.2.3.2 EC + PVDF Spectra	111
4.3 X-ray Photoelectron Spectroscopy (XPS)		Photoelectron Spectroscopy (XPS)	114
	4.3.1	1 Unplasticized Systems	
	4.3.2	Plasticized Systems	117
		4.3.2.1 DMF Based Polymer Electrolyte System	117
		4.3.2.2 MF Based Polymer Electrolyte System	119
		4.3.2.3 EC Based Polymer Electrolyte System	119
4.4	Scann	ing Electron Microscopy	123
4.5	Summary		129
Chapter 5. Thermal Studies			
5.1.	Differ	rential Scanning Calorimetry (DSC)	131
		5.1.1 Unplasticized Systems	137

		5.1.2	Plasticized Systems	138
			5.1.2.1 DMF Based Polymer Electrolyte System	138
			5.1.2.2 MF Based Polymer Electrolyte System	138
			5.1.2.3 EC Based Polymer Electrolyte System	139
5.2	Thermogravimetric Analysis		141	
		5.2.1	Unplasticized Systems	141
		5.2.2	Plasticized Systems	142
5.3	Summ	ary		153
Chap	ter 6. B	attery	Characteristics	
6.1	Battery Studies		15	
	6.1.1	DMF	Based Polymer Electrolyte System	157
	6.1.2	MF B	ased Polymer Electrolyte System	161
	6.1.3	EC B	ased Polymer Electrolyte System	162
6.2	Summ	ary		163
Chapter 7. Conclusions and Suggestions for Further Work				164
References			xii	

Publications

xxvi