CHARACTERIZATION OF POLY (VINYLEDENE FLUORIDE) 
BASED ELECTROLYTES AND BATTERIES

BY

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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. 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.

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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 (vinylidene 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.
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 ($\log \sigma T$ 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.
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