UNIVERSITY OF MALAYA

OPTICAL AND ELECTRICAL PROPERTIES OF POLYMERIC MATERIALS CONTAINING TIN BASED COMPOUNDS

BY
KODUKULA SRINIVAS

A dissertation submitted to
The Institute of Postgraduate Studies and
Research
University of Malaya
for the Degree of
Doctor of Philosophy

INSTITUTE OF POSTGRADUATE STUDIES AND

RESEARCH

UNIVERSITY OF MALAYA

KUALA LUMPUR

MALAYSIA

1999

DECLARATION

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

10 April 1999

K.Srinivas

ACKNOWLEDGEMENTS

I would like to thank my supervisor, ***Professor Suri Radhakrishna*** for his advice, guidance, help, encouragement and motivation towards my well being in academic world. Words alone will not be sufficient to sum up his contribution towards my development.

I would also like to express my sincere gratitude and thanks to ***Prof. V. G. Kumar Das***, my co-supervisor for his advice, guidance and helping me to finish my thesis.

I would like to thank ***Associate Prof. Abdul Kariem Arof*** for his help in discussions regarding my work and all my friends who helped me directly or indirectly for completion of my work.

Finally, I would like to thank my ***parents and brothers*** who always have been with me and also my ***wife*** for making this thesis a success.

K.SRINIVAS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Modified poly(ethylene oxide) (PEO) as a potential solid state electrolyte material for batteries has been investigated through doping with selected organotin compounds. The organotin dopants studied were triphenyltin chloride (Ph_3SnCl), dibutyltin bis {p-[N-(3,4-dinitro phenyl)] amino benzoate and dioctyltin bis {p-[N-(3,4-dinitro phenyl)] amino benzoate; the first mentioned compound was also tested as a dopant for polyvinyl chloride PVC. Tin incorporation in the polymers was established by several physical techniques. UV-Visible spectroscopic analysis of the Ph_3SnCl -doped electrolyte film showed unequivocally the presence of a peak at 268 nm which, is characteristic of the dopant. Likewise in the infrared, the above-mentioned film showed bands at 698 and 735 cm^{-1}, which are also given by pure Ph_3SnCl. DTA analysis showed a distinct broadening of the peak area with increase in the dopant concentration. SEM and EDAX studies performed on all the doped films confirmed the presence of tin.

Different compositions of the tin doped electrolytes (Sn/EO = 0.015, 0.031, 0.063, 0.125) were prepared and conductivity studies on these were performed using impedance spectroscopy, with measurements in the frequency range 40 Hz to 100KHz. From the measurements it was found that the best conductivity of 3.6 $x10^{-7}$ S/cm was obtained for the composition Sn/EO = 0.031. However, it proved possible to increase the conductivity by at least one or two orders of magnitude by the co-addition of plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC), thereby rendering the modified PEO more suitable as an electrolyte material for the solid state batteries. The best conductivity thus attained was of the order of 10^{-5} S/cm for the film of composition Ph_3SnCl – PEO: EC: PC (85: 13: 2). The effect of different molecular weights of PEO was also studied, and it was found that the PEO with a

molecular weight of 900000 gave the best conductivity of 1.1 x 10^{-5} S/cm. X-ray diffraction analysis confirmed the disruption of the crystalline order of PEO upon interaction with the tin dopants, and some correlation between increased amorphous character of the PEO and increased electrical conductivity was noted in the doped films. The temperature dependent studies for the conductivity showed an Arrhenius pattern, with an activation energy of 0.21 eV, which latter is strongly indicative of ionic conductivity rather than electrical conductivity. This implicates either a direct charge mobility on the part of the Ph_3SnCl dopant in the PEO matrix, which may be conceived in terms of an ion-pair formulation for the compound, or an indirect charge mobility via the ion-hopping mechanism involving firm interaction of the tin dopant with the oxygen in the polymer matrix.

A similar pattern of results was also obtained with dibutyltin bis {p- [N-(3,4-dinitro phenyl)] amino benzoate.and dioctyltin bis {p-[N-(3,4-dinitro phenyl)] amino benzoate as dopants. However, the conductivity was not as good as that given by the Ph_3SnCl compound. Another study was done by preparing electrolytes with a different host polymer, namely PVC. The presence of Ph_3SnCl in the PVC matrix was confirmed by XRD and EDAX.

The best conductivity samples from each of the above mentioned systems were used in the fabrication of a primary cell using Sn metal as anode and MnO_2 or Iodine as the cathode material. The above cells showed an open circuit voltage(OCV) of about 0.85 V which is close to the theoretical value. Hence it can be concluded that organotin compounds have the potential for the fabrication of primary cells at ambient temperatures.