UNIVERSITI TEKNOLOGI MARA

PROPERTIES OF POLY(VINYLIDENE FLUORIDE)-CO-POLY(VINYLIMIDAZOLE) SOLID POLYMER ELECTROLYTES PREPARED BY RADIATION-INDUCED GRAFTING METHOD FOR PROTON EXCHANGE MEMBRANE FUEL CELL

AJIS BIN LEPIT

Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

November 2016

ABSTRACT

Solid polymer membranes based on graft copolymerization of 1-Vinylimidazole (VIm) onto polyvinylidene fluoride (PVDF) were synthesized. The graft copolymerization process was carried out under nitrogen atmosphere by a radiation-induced grafting (RiG) in aqueous medium. Ferrous ions were used as a redox initiator system. Radiation effects onto PVDF and VIm were investigated with the aim to develope a highly-stable grafted solid polymer membrane for potential use in proton exchange membrane fuel cells. Polymer membranes consist of PVDF as a polymer host and VIm as a monomer were prepared by solution casting technique. Prior to that, PVDF was exposed to γ-rays ranging from 20 to 100 kGy using RiG method to form free radicals that capable to initiate graft copolymerization of VIm onto PVDF backbone as a side chain.Various grafting conditions such as absorbtion dose, effects of different solvents and addition of Iron (II) sulfate heptahydrate were determined. Results showed that the degree of grafting (DG) was strongly influenced by the type of solvent used to dissolve the VIm. The grafted polyvinylimidazole (PVIm) onto PVDF was estimated using gravimetric analysis. DG of the VIm onto PVDF was also found to be dependent on the absorbtion dose exposed to the samples. The best absorbtion dose where the sufficent grafting occured between polymer based and monomer was at 60 kGy. Concentration of ferrous ions was observed to play a major role to initiate grafted VIm onto PVDF samples namely PVDF-co-PVIm membranes during induction of radiation. Samples were then complexed in acid sulfuric to prepare functional solid polymer electrolyte membranes as well as to enhance their ionic conductivity. The PVDF-co-PVIm solid polymer electrolyte membranes were then characterized by degree of swelling, water uptake, ion exchange capacity and degree of protonation. The PVDF, PVDF-co-PVIm, protonated PVDF-co-PVIm, and silicon dioxide composited PVDF-co-PVIm membranes also were: (a) morphology structurally characterized by Field Emission Scanning Electron Microscopy (FESEM) as well as X-ray Diffraction (XRD) (b) thermally characterized by Differential Scanning Calorimetry (DSC)/Thermogrametric Analysis (TGA) studies for phase transition & thermal stability (c) electrically/electrochemically characterized by Electrochemistry impedance spectrocopy (EIS) and transference number (d) optically characterized by Fourier Transform Infrared spectroscopy (FTIR) studies (e) mechanically characterized by Dynamic Mechanical Analysis (DMA). FTIR analysis demonstrated the occurence of scission in the C-H bond of PVDF main chain when exposed to γ-rays. The C-H bonds were observed to reduce in peak intensities and shift in peak position. FESEM reveals that the surface of the pure PVDF becomes rough containing chain grooves, nanopores and the crystal surface was homogenously covered by PVIm after grafted copolymerization. The storage modulus and loss modulus of PVDF-co-PVIm membrane show high mechanical strength at temperature up to 150 ^{o}C. However, the addition of silicon dioxide onto PVDF-co-PVIm reduced the storage modulus and loss modulus of membrane. The protonation of PVDF-co-PVIm membrane enhanced ionic conductivity after complexation in sulfuric acid up to 10^{-4} Scm^{-1} at room temperature and up to 10^{-3} Scm^{-1} at 100^{o}C temperature. The protonated PVDF-co-PVIm could be a good potential candidate as a proton conducting membrane for fuel cells application.

ACKNOWLEDGEMENTS

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

Alhamdulillah! Praise is to Allah SWT the creator of the whole universe that has inspired and motivated me to discover and investigate a very broad knowledge that is spread between the sky and the earth. Indeed, the blessings You have given are innumerable. Hopefully, this study will not only increase my knowledge in the field of science alone but simultaneously increased my knowledge of tawheed to Him. Hopefully we are among the most ungrateful people. Indeed, too many blessings that You have given to mankind. Thank you Allah.

First of all, I wish to express my great appreciation to my supervisors Professor Dr. Muhd Zu Azhan Yahya (UPNM) and Associate Professor Dr. Ab Malik Marwan Ali as well as Associate Professor Dr.-Ing. Oskar Hasdinor Hassan for their advice, concern, guidance and motivation to me until this thesis is completed. Thanks for being so understanding and supportive.

I am very grateful to all my family, Zuraida, Akmal, Akram & Fatin for their prayers and support throughout PhD journey. Thank you to my mother and father and my families who patiently waiting and give full support to end this study. Also, I would like to wish my deepest thank to all my labmates in *i*-MADE for your cooperation, teamwork and friendships. May Allah blessings and fill your life with happiness, sakinah, mawaddah, wa rahmah.

To Cik Masni Soberi (assistant science officer), Muhamad Faisal Abd Halim (TGA & DSC), Hj Hayub Taha (FESEM), Irmaizatussyedany (FTIR), Juliana Kasim (XRD) and Mohd Azlan Jaafar (DMA) are all from Institute of Science, Faculty of Applied Sciences and NanoTech for your kindness and cooperation for helping me towards completing my experiments.

Special thanks to Dr Mohd Zuli Bin Jaafar, UiTM Negeri Sembilan who provides a course of MS word for thesis formatting that helps me a lot in preparing theses for submission to the university.

We also gratefully acknowledge to the Ministry of Higher Education Malaysia for the scholarship, and Fundamental Research Grant Scheme [600-RMI/ST/FRGS5/3/Fst(33/2009)] and Research Excellence Fund [600-RMI/ST/DANA 5/3/Dst (299/2009)] for the grants awarded.

TABLE OF CONTENT

CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

Energy is one of the most important needs in human life. Energy should be managed efficiently in a way of reducing waste, cost and time savings. However, the phenomenon of environmental pollution such as carbon dioxide emissions and global warming is rising and it has catalyzed and aggressively facilitated the development of study on green technology such as fuel cells. In line with the requirements of the development of human civilization, therefore research in green technology motivates scientists to continuously study in the field of the membrane for energy conversion as well as electrochemical energy storage.

Energy is an everlasting need of mankind and the absolute necessity for its existence. Energy supply with good efficiency is one of the main objectives of new era in modern society. Despite, the environmental considerations concerning fossil fuels such as carbon dioxide accumulation, air pollution and global warming, in addition to their limited reserves, have recently led to the active development of electrochemical energy devices such electrochemical energy storage and conversion (EESC) technologies (Sik et al., 2013; Stoševski et al., 2015; Wang et al., 2015). EESC devices such as batteries, fuel cells, and supercapacitor have stimulated intense research owing to the increasing demands for portable digital communication devices and electric vehicles (Kalyani & Anitha, 2013; Xinping et al., 2013). However, the use of liquid electrolytes in these EES devices is facing with many safety issues such as flammable electrolyte leakage, the production of gas during cycling (overcharge or over discharge), risky thermal explosion at high operating temperature and the hazardous materials (Xia et al., 2012; Li et al., 2013).

As an alternative to address the above issues such as leakage, a free standing polymer electrolyte (PE) film has been used. The free standing PE may have many advantages such as light weight, easily shaped and processed as well as excellent mechanical strength. It also acts as an ion conductive electrolyte and separator (Shi et al., 2015; Li et al., 2014). Moreover, solid polymer ionic electrolytes membranes (SPIEM) have been received attention as electrolyte materials for electrochemical devices such as