



UNIVERSITI
TEKNOLOGI
MARA

THE DOCTORAL RESEARCH ABSTRACTS

Volume: 11, Issue 11

April 2017

ELEVENTH ISSUE

INSTITUTE of GRADUATE STUDIES

IGS Biannual Publication

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Title : PROPERTIES OF POLY(VINYLDENE FLUORIDE)-CO-POLY(VINYLMIDAZOLE) SOLID POLYMER ELECTROLYTES PREPARED BY RADIATION-INDUCED GRAFTING METHOD FOR PROTON EXCHANGE MEMBRANE FUEL CELL

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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 develop 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 absorption 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 absorption dose exposed to the samples. The best absorption dose where the sufficient grafting occurred 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)/Thermogravimetric Analysis (TGA) studies for phase transition & thermal stability (c) electrically/electrochemically characterized by Electrochemistry impedance spectroscopy (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 occurrence 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 homogeneously 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 oC. 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 100oC temperature. The protonated PVDF-co-PVIm could be a good potential candidate as a proton conducting membrane for fuel cells application.