ETFE GRAFTED MEMBRANES USING 1-VINYLIMIDAZOLE, 1-VINYL-2-PYRROLIDONE, TRIALLYL CYANURATE DOPED WITH PHOSPHORIC ACID FOR HIGH TEMPERATURE APPLICATIONS

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This thesis is dedicated to my late father, His Royal Highness Alhaji Shehu Uthman Popoola Aroyehun, Abiolu II, and my late mother Mallama Shikirat Olalohunpe Adelokun Uthman Aroyehun, may their souls rest in perfect peace. Your love, support, hospitality and kindness will forever remain in my fresh memory. To my elder sisters Hajiya R.R. Suleiman and Hajiya Muibat Aibinuola Suleiman. To my late elder brothers, Alhaji Yahya Uthman and Alhaji Abbas Uthman; may their souls rest in perfect peace. Your love, support, hospitality and kindness will forever remain in my fresh memory

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ABSTRACT

Novel phosphoric acid (PA) doped proton exchange membranes were synthesized by radiation induced graft copolymerization of 1-vinylimidazole (1-VIm) and triallyl cyanurate (TAC), and 1-VIm-*co*-1-vinyl-2-pyrrolidone (1-VIm-*co*-1-V-2-P) onto poly (ethylene-*alt*-tetrafluoroethylene) (ETFE) films followed by protonation by PA doping. The ETFE base films were pre-irradiated by an electron beam (EB) accelerator prior to grafting and PA doping. They were denoted as ETFE-*g*-P(1-VIm-*co*-TAC) PA and ETFE-*g*-P(1-VIm-*co*-1-V-2-P) PA doped membranes. The main focus of this work is to synthesize membranes that have desirable properties and to investigate kinetics of 1-VIm and TAC onto ETFE base film and 1-VIm-*co*-1-V-2-P onto ETFE base films. From the optimization study using Box-Behnken design module of the response surface methodology available in the "Minitab®" software, degree of grafting (DG) was found to depend strongly on grafting parameters such as, crosslinker concentration and reaction temperature. Proton conductivity of the membranes was measured using four-probe conductivity cell and conductivity increased with an increase in doping level. ETFE-*g*-P(1-VIm-*co*-TAC) PA doped membranes achieved maximum DG (%) of 53%, proton conductivity of 33 mS cm^{-1} at 120 ^{o}C and 0% relative humidity condition. ETFE-*g*-P(1-VIm-*co*-1-V-2-P) PA doped membranes achieved maximum DG (%) of 76%, of 53 mS cm^{-1} at 120 ^{o}C and 0% relative humidity condition suggesting less water dependent conductivity. Properties of the developed membranes were investigated using different equipment such as, Fourier transform infrared spectrometer, thermal gravimetric analyzer and differential scanning calorimeter. Kinetic modeling of radiation induced graft copolymerization of 1-VIm-*co*-1-V-2-P was also attempted. It can be concluded that the synthesized membranes possessed desirable properties including mechanical and thermal stablility. This makes them appealing for possible application in high temperature proton exchange membrane fuel cell operated above 100 ^{o}C

ABSTRAK

Membran baharu pertukaran proton didopkan asid fosforik (PA) yang disintesis secara cantuman pengkopolimeran aruhan radiasi 1-vinilimidazol (1-VIm) dan triallil sianurat (TAC), dan 1-VIm-*co*-1-vinil-2-pirrolidon (1-VIm-*co*-1-V-2-P) ke atas filem poli (etilena- *alt*-tetrafloroetilena) (ETFE) diikuti dengan pemprotonan oleh pendopan PA. Filem asas ETFE diprasinarkan oleh pemecut alur elektron (EB) sebelum cantuman dan pendopan PA. Filem-filem ini ditandakan sebagai membran ETFE-*g*-P(1-VIm-*co*-TAC) PA dan membran ETFE-*g*-P(1-VIm-*co*-1-V-2-P) didopkan PA. Fokus utama kajian ini adalah untuk mensintesis membran yang mempunyai ciri-ciri diingini dan untuk mengkaji kinetik 1-VIm dan TAC ke atas filem asas ETFE dan 1-VIm-*co*-1-V-2-P ke atas filem asas ETFE. Daripada kajian pengoptimuman menggunakan modul reka bentuk Box-Behnken bagi kaedah tindak balas permukaan yang terdapat dalam perisian "Minitab®", darjah cantuman (DG) didapati bergantung kuat kepada parameter cantuman seperti kepekatan perangkai silang dan suhu tindak balas. Kekonduksian proton membran diukur dengan menggunakan sel kekonduksian empat prob dan kekonduksian meningkat dengan peningkatan dalam tahap pendopan. Membran ETFE-*g*-P(1-VIm-*co*-TAC) didopkan PA mencapai DG maksimum (%) sebanyak 53%, kekonduksian proton 33 mS cm^{-1} pada suhu 120 °C dan keadaan kelembapan relatif 0%. Membran ETFE-*g*-P(1-VIm-*co*-1-V-2-P) didopkan PA mencapai DG (%) maksimum sebanyak 76%, kekonduksian proton 53 mS cm^{-1} pada suhu 120 °C dan keadaan kelembapan relatif 0%. Sifat-sifat membran yang dibangunkan dikaji dengan menggunakan peralatan yang berbeza seperti spektrometer inframerah transformasi Fourier, penganalisis gravimetrik terma dan kalorimetri pengimbasan pembezaan. Pemodelan kintetik pengkopolimeran cantuman aruhan sinaran 1-VIm-*co*-1-V-2-P telah dicuba. Dapat disimpulkan bahawa membran yang disintesis mempunyai sifat-sifat yang dikehendaki termasuk kestabilan mekanikal dan terma. Keadaan ini menjadikan membran-membran ini menarik bagi kemungkinan penggunaan sel bahan api membran pertukaran proton pada suhu yang tinggi yang dikendalikan melebihi suhu 100 °C.

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LIST OF ABBREVIATIONS

1-VIm	-	1-Vinylimidazole
1-V-2-P	-	1-Vinyl-2-pyrrolidone
N-VIm	-	N-Vinylimidazole
NVF	-	N-vinylformamide
NVP	-	N-vinyl-pyrrolidone
2-V-P	-	2-Vinyl pyridine
4-V-P	-	4-Vinyl pyridine
A	-	Pre-exponential factor or frequency factor
ABPBI	-	Poly (2,5-bibenzimidazole)
ADL	-	Acid doping level
AFC	-	Alkaline fuel cell
AHOR	-	Anodic hydrogen oxidation reaction
AMS	-	α-Methyl styrene
ATR	-	Attenuated total reflectance
BVPE	-	*p*,*p*-bis (vinyl phenyl) ethane
co	-	Copolymerization
CO	-	Carbon (ii) oxide
CORR	-	Cathodic oxygen reduction reaction
CsPMA	-	Caesium silico-tungstic acid
CsSiMA	-	Caesium phosphotungstic acid
CsSiTA	-	Caesium silico-tungstic acid
D	-	Absorbed dose
DG (%)	-	Degree of grafting
DL	-	Doping level
DIPB	-	1,3-diisopropenylbenzene
DMFC	-	Direct methanol fuel cell

DSC	-	Differential scanning calorimetry
DT	-	Doping temperature
Dt	-	Doping time
DTG	-	Differential/first derivative thermogravimetric
DVB	-	Divinyl benzene
EB	-	Electron beam
EDX	-	Energy Dispersive X-ray spectroscopy
EIS	-	Electrochemical impedance spectroscopy
ETFE	-	Poly(ethylene-*alt*-tetrafluoroethylene)
ETFE-*g*-P(1-VIm)	-	ETFE films grafted with poly(1-vinylimidazole)
ETFE-*g*-P(1-V-2-P)	-	ETFE films grafted with poly(1-vinyl-2-pyrrolidone)
ET-PCFC	-	Elevated temperature proton conducting fuel cell
FEP	-	Poly(tetrafluoroethylene-*co*-hexafluoropropylene)
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
g	-	Grafted
GT	-	Grafting temperature
Gt	-	Grafting time
HBr	-	Hydrogen bromide
HCl	-	Hydrochloric acid
HT-PEMFC	-	High temperature proton exchange membrane fuel cell
HPA	-	Heteropolyacid
IEC	-	Ion exchange capacity
IL	-	Ionic liquid
LT-PEMFC	-	Low temperature proton exchange membrane fuel cell
Im	-	Imidazole
LDPE	-	Low density polyethylene
M	-	Monomer concentration
MBAA	-	N,N-methylene-bis-acrylamide
MCFC	-	Molten carbonate fuel cell
NASA	-	National Aeronautics and Space Administration
MEA	-	Membrane electrode assembly
NVF	-	N-vinylformamide

NVP	-	*N*-vinyl-2-pyrrolidone
PA	-	Phosphoric acid
PAFC	-	Phosphoric acid fuel cell
PEEK	-	Poly (ether ether ketone)
PEI	-	Poly (ethylene imine)
PEO	-	Poly (ether oxide)
PET	-	Poly (ethylene terephthalate)
PFSA	-	Perfluorosulphonic acid
PBI	-	Poly (benzimidazole)
PBI/H_3PO_4	-	Phosphoric acid-doped Poly(benzimidazole)
PBI-imi	-	Poly (2,2′-imidazole-5,5′-bibenzimidazole)
PBI-ph	-	Poly (2,2′-*m*-phenylene)-5,5′-bibenzimidazole
PCMs	-	Proton conducting membranes
PE	-	Polyethylene
PEMs	-	Proton exchange membrane
PEMFC	-	Proton exchange membrane fuel cell
PCM	-	Proton conducting membrane
PFA	-	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether
PFSA	-	Perfluorosulfonic acid
PEI	-	Poly(ether imide)
PES	-	Poly (ether sulfone)
PO	-	Propylene oxide
PP	-	Polypropylene
PPA	-	Polyphosphazene
PPO	-	Polyphenylene oxide
PS	-	Polystyrene
PSA	-	Perfluorocarbon sulphonic acid ionomer
PSEPVE	-	Perfluoro-sulfonylfluoride ethyl-propyl-vinyl-ether
PTFE	-	Polytetrafluoroethylene
PVA	-	Poly (vinyl alcohol)
PVDF	-	Poly (vinylidene fluoride)
PVDF-*co*-HFP	-	Poly(vinylidene fluoride-*co*-hexafluoropropylene)
PVF	-	Poly (vinyl fluoride)

PVP	-	Poly (vinyl pyrrolidone)
P-1VIm	-	Poly (1-vinylimidazole)
P4-VIm	-	Poly (4-vinylimidazole)
P2VP	-	Poly (2-vinylpyridine
P4VP	-	Poly (4-vinyl pyridine)
R_g	-	Grafting rate
RH	-	Relative humidity
RIG	-	Radiation induced grafting
RIGC	-	Radiation induced graft copolymerization
RIGCTech	-	Radiation induced graft copolymerization technique
RSM	-	Response surface methodology
RT	-	Reaction temperature
R*t*	-	Reaction time
SPBI	-	Sulphonated polybenzimidazole
SPEEK	-	Sulphonated poly (ether ether ketone)
SPES	-	Sulphonated polyether sulfones
SPPO	-	Sulphonated poly (2, 6-dimethyl-1, 4-phenylene oxide)
S_{ty}	-	Solvent type
TAC	-	Triallyl cyanurate
TFE	-	Tetrafluoroethylene
TFS	-	α,α,β-trifluorostyrene
THF	-	Tetrahydrofuran
T_g	-	Glass transition temperature
TGA	-	Thermogravimetric analysis
T_m	-	Crystalline melting temperature
UHMWP	-	Ultra-high molecular weight polyethylene
VA	-	Vinylamine
VBC	-	Vinylbenzyl chloride
VP	-	Vinyl pyrrolidone
XPS	-	X-ray photoelectron spectroscopy
ZrP	-	Zirconium phosphate

LIST OF SYMBOLS

A	-	Area (m^2)
A	-	Surface area of the sample (cm^2)
DG (%)	-	Degree of grafting (wt%)
E_a	-	Activation energy
ΔH_m	-	Heat of melting of ETFE film (J g^{-1})
$\Delta H_{m\,100}$	-	Heat of melting of 100% crystalline ETFE polymer (J g^{-1})
k-	-	Rate constant
k_p	-	Polymerization rate constant (L mol^{-1} s^{-1})
k_t	-	Rate constant of bimolecular termination (L mol^{-1} s^{-1})
L	-	Distance between probes (cm)
L	-	Thickness of membrane sample (cm)
w_g	-	Weight of the grafted film (g)
w_o	-	Weight of the original ETFE film (g)
$[\mathbf{M}]_0$	-	Monomer concentration (vol%)
M_d	-	Molar mass of phosphoric acid (g mol^{-1})
Mp	-	Molar mass of polymer repeat unit (g mol–1)
[P.]0	-	Initial radical concentration
rp0	-	Initial polymerization rate
R	-	Gas constant = 8.314 (J K^{-1} mol^{-1})
R	-	Resistance (Ω)
t_0	-	Delay time
T	-	Thickness of the membrane sample (cm)
T	-	Temperature (°C)
T	-	Absolute temperature (K)
T^{-1}	-	Reciprocal of absolute temperature (K^{-1})
T_g	-	Glass transition temperature (°C)

T_m	-	Melting temperature (°C)
T_p	-	Peak temperature (°C)
T_{onset}	-	Onset temperature of degradation (°C)
V_{NaOH}	-	Volume of NaOH (ml)
W	-	Width of the membrane (cm)
w_d	-	Mass fraction of dopant (g)
w_i	-	Percentage of weight increase of the grafted ETFE film
W_{dry}	-	Weight of dry membrane (g)
w_g	-	Weight of the grafted ETFE film (g)
w_o	-	Weight of the original ETFE film (g)
W_{wet}	-	Weight of the swelled membrane (g)
X_c	-	Degree of crystallinity
X_{PA}	-	Acid doping level per repeated unit of polymer (mmol repeat unit^{-1})
γ	-	Characteristic radical recombination rate
σ	-	Proton conductivity (S cm^{-1})

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CHAPTER 1

INTRODUCTION

1.1 Proton Exchange Membrane Fuel Cells (PEMFCs)

PEMFCs cells are simple, silent, single step, low noise, reliable, environmental friendly and potentially high electrochemical energy converter (devices for electricity generation) which provides a suitable primary power source for stationary and transportation applications (Abdulkareem, 2009, Ahmad, 2005, Barbir, 2005). They have the ability to electro-catalytically converts directly and continuously the gaseous fuel's free chemical energy in the presence of oxidant through electrochemical redox reaction into electrical energy. Water and heat are usually the by-products (Sopian and Wan Daud, 2006, Zhang and Shen, 2012a, Zhang and Shen, 2012b). As there is no occurrence of thermal combustion of fuel with air, production of pollutants such as nitric oxides are avoided (Zhang, 2008, Zhang et al., 2006). General Electric initially developed the first practical fuel cell application where it was used as a power source for the Gemini Earth-orbiting programme in the early 1960s. A potentially great future sources of clean energy for various uses is fuel cells (Ergün, 2009, Scott et al., 2014, Xu, 2013).

Up to now, however, fuel cells production in large scale is limited to governmentally subsidized programmes, niche markets and premium power sector. Consumer electronics, power backup, cogeneration and forklift traction power were the early markets (Gubler, 2014). Cost and durability are the main barriers to commercialization of fuel cells. Furthermore, in aging processes, the conditions of operation perform an important function. Consequently, to drive forward the technology of fuel cell development and to ensure its early commercialization. Continuous research into components and material's fundamental in needed. In addition, introduction of novel materials is necessary or improving the ones in existence. Furthermore, it is essential to identify limitations of existing materials. From application view-point, it is important to know the requirements for the synthesis of PEMs having desirable properties suitable for application in HT-PEMFC and structure–property–performance relationships should be established (Gubler, 2014).

In PEMFCs, typically, the oxidant is oxygen and the fuel is hydrogen. However, for practical reasons the hydrogen may be derived from reformed organics such as natural gas, gasified coal, methanol or other hydrocarbons and the oxygen is replaced with air. As long as the oxygen is supplied to the cathode and hydrogen to the anode, PEMFCs continue to generate electricity, dissimilar to batteries possessing an output dependent on the chemical energy being stored. Furthermore, compared to other conventional power sources, they possess high current densities, high energy per volume as well as per weight. In addition, it has significant emission reduction, neatness, easy refueling, quite operation, high current density, high energy per weight as well as per volume and etcetera (Nasef et al., 2013a). PEMFC fundamental operation unit consists of an electrolyte otherwise called proton conducting membrane (PCM) which separate two porous gas diffusion electrodes (GDEs), similar to other electrochemical cells. The two electrodes are often loaded with a small amount of a noble metal (catalyst) such as platinum and are conventionally made of polymer-bonded carbon-cloth/-paper having porous structure (Hickner, 2003, Zhang, 2006).

Despite being a challenging research work the interest in the development of desirable, highly conductive and stable PEMs for HT-PEMFC application is fast growing. New alternative low cost membranes with appropriate structure that can withstand the operation in HT-PEMFC application in the temperature range of 100-200^{o}C are being designed and developed continuously. This is done using various approaches and applying different preparation routes to overcome the high cost and other problems associated with PFSA membranes (Nasef et al., 2013b).

To solve problems associated with PFSA membranes such as, Nafion® used in PEMFC. High temperature operation (above 100°C) is highly desirable due to these advantages: improve efficiency and overcoming of some of the inherent problem associated with the use of hydrogen obtained from the reformed hydrocarbon fuels and water management system. Particularly, better electrode kinetics, elimination of humidification, high tolerance to fuel impurities for example, carbon monoxide (CO). Furthermore, higher efficiency and higher values of excess heat by cogeneration can be achieved. Development of membranes that are less-water dependent, low relative-humidity dependent and operational above 100^{o}C is another excellent solution to myriad problems facing Nafion® membrane (Nasef et al., 2013b).

The main focus of this dissertation is the proposed acid-base polymers and their composite membranes such as, PEM having PA and its derivatives loaded onto base films were recently proposed as alternative PEM. For example, excellent alternative acid-base composite membranes such as, PA doped poly (benzimidazole) (PBI) membrane (Nasef et al, 2013a, Schmidt and Schmidt-Naake, 2007b).

1.2 Problem Statement

Nafion® membrane is considered to be the most effective PCM for PEMFC application and they have been employed extensively due to striking characteristics which include: higher oxidative stability, higher mechanical strength, hydrolytically stable and higher conductivity. Presently, comparing PEMFC to conventional technology, one of the main barrier that must be surmounted to guarantee its commercialization is the cost of production. Using expensive materials such as, solid polymer electrolyte (Nafion®) and noble metal (catalyst) leads to this high cost. Some of the problems associated with the use of Nafion® include: it is costly (~700 \$/m^2), PEM cost 27-30% of the overall estimate PEMFC. In addition, it dehydrates at temperature > 80ºC and operating it at relative humidity less than 100% reduces its efficiency and ability to conduct protons.

Furthermore, the requirement of full hydration to maintain higher conductivity pegs its temperature of operation to 90ºC and high dependence of its operations on full humidification for conductivity of proton which makes it very highly problematic to use it at elevated temperatures. Moreover, it swells excessively in solvents and it is highly permeable to fuel and other species. CO intolerance leads to higher dependence on pure H_2 in place of reformed H_2 obtained from gasified coal, natural gas, biomass, ethanol and etcetera. It degrades easily at temperatures 110-130ºC owing to low glass transition temperature (T_g) which leads to reduction in its durability. ETFE-*g*-P(1-VIm-*co*-TAC)/PA and ETFE-*g*-P(1-VIm-*co*-1-V-2-P)/PA doped membranes were synthesized in this research work, in order to reduce cost, to improve desirable properties such as proton conductivity, improve stability and durability. Synthesized membranes have the capacity to simplify water and heat management. Thus, eliminating the risk of cell flooding.

a. What are the effects of using RIGC method to prepare membrane from 1-VIm, 1-V-2-P, TAC, ETFE films followed by PA doping and the effects of RIGC on the DG (%) and level of doping?
b. Is it necessary to optimize membranes' synthesis conditions using Box-Behnken module of response surface methodology (RSM) available in "Minitab®" Software?
c. In PA doped PBI membranes, what are the limiting factors that could be overcome possibly in this research?
d. Do PA doped PBI PEMs qualify for applications in HT-PCMFCs? Is there any room for improvement?
e. Do the present synthesized HT-PCMs possess some merits over PA doped PBI membranes?

1.3 Objectives

a. To establish optimal synthesis conditions for the membranes using Box-Behnken module of response surface methodology (RSM) available in "Minitab®" Software.
b. To synthesize membranes that have desirable properties such as high proton conductivity, high thermal and mechanical stability applicable in HT-PEMFC.
c. To study grafting kinetics of 1-VIm and TAC onto ETFE base film and 1-VIm-*co*-1-V-2-P onto ETFE base films.
d. To characterize the synthesized membranes' properties namely: proton conductivity, thermal and mechanical stability.
e. To attempt model free kinetic modeling of Radiation induced graft copolymerization of 1-VIm-*co*-1-V-2-P using Flynn Wall Ozawa (FWO) model and Kissinger Akahira Sunose (KAS) model.

1.4 Scope

a. Optimization of the synthesis parameters using RSM available in "Minitab®" Software.
b. Radiation induced co-grafting of 1-VIm and TAC onto the EB-preirradiated ETFE films under selected conditions.
c. Radiation induced copolymerization of 1-VIm-*co*-1-V-2-P onto the EB-preirradiated ETFE films under selected conditions.
d. Acid doping of the grafted ETFE films with PA under controlled conditions.
e. Characterization of the synthesized membranes to determine desirable properties that are applicable to HT-PEMFC employing equipment such as: FTIR-ATR, DSC, TGA, FESEM-EDX, XRD and XPS.

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