PROTON CONDUCTING MEMBRANE BY RADIATION-INDUCED GRAFTING OF 1-VINYLIMIDAZOLE ONTO POLY(ETHYLENE-*CO*-TETRAFLUORO ETHYLENE) FILM AND PHOSPHORIC ACID DOPING

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To the Soul of my uncle,

To my beloved mother, father and sister,

To my blessed country: Egypt.

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ABSTRACT

Phosphoric acid doped proton conducting membranes denoted as ETFE-*g*-P(1-VIm) for possible use in high temperature polymer electrolyte membrane fuel cell (PEMFC) were prepared by radiation induced graft polymerization of 1-vinylimidazole (1-VIm) onto poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films followed by doping with phosphoric acid (PA). The ETFE films were irradiated by electron beam (EB) accelerator prior to grafting. The effect of the grafting parameters such as monomer concentration, absorbed dose, reaction time and medium temperature onto the degree of grafting (G%) were studied. The G% was found to be strongly dependent upon the investigated grafting parameters, which were optimized using response surface method (RSM) through the Box-Behnken design expert software. This led to the development of a quadratic model capable of predicting the degree of grafting. The validity of the statistical model was supported by the small deviation between the predicted (G = 61%) and experimental (G = 57%) values. The optimum conditions for achieving maximum G% were determined at: monomer concentration of 55 vol%, absorbed dose of 100 kGy, reaction time in the range of 14-20 h and medium temperature of 61°C. The effect of phosphoric acid doping parameters on the doping behaviour of the grafted ETFE films was also optimized using Taguchi method through implementing a Taguchi L_9 (3^4) orthogonal array. The optimum parameters for achieving a maximum acid doping level (7.45 mmol/repeat polymer unit) were: G of 54%, acid concentration of 65%, temperature of 100^{o}C and time of 5 days. The predicted doping value was deviated by 4.9% from the experimental one suggesting the validity of the model in prediction and optimization of acid doping reaction. The kinetics of phosphoric acid doping reaction was also investigated and two rate constants of 0.46 and 0.16 for PA doping reaction were graphically obtained suggesting a zeroth order reaction. The proton conductivity of the membranes was investigated using 4-probe conductivity cell attached to a direct current source meter in correlation with temperature and relative humidity. The proton conductivity was found to increase with the increase in doping level at constant temperature and relative humidity. Proton conductivity of 143 mS/cm at 20% relative humidity was achieved in the membranes having G of 38 and 54% suggesting a less water dependant conductivity. It can be concluded that the obtained membranes have very good combinations of physico-chemical and material properties suitable for possible application in PEMFC operating above 100 ^{o}C.

ABSTRAK

Membran pengalir proton terdop asid fosforik yang dinamakan sebagai ETFE-GP (1-VIm) mempunyai kemungkinan untuk digunakan dalam suhu tinggi Polimer Elektrolit Bahan Api Sel Membran (PEMFC). Membran telah disediakan menggunakan pencantuman teraruh sinaran 1-vinylimidaszole (1-VIm) ke atas Poli (Etilena bersama Tetrafluoroethylene) (ETFE) filem diikuti dengan proses pendopan dengan asid fosforik. Filem-filem ETFE telah disinarkan dengan pecutan alur elektron sebelum cantuman. Kesan parameter cantuman seperti kepekatan monomer, dos terserap, masa tindak balas dan suhu sederhana ke atas tahap cantuman (G%) telah dikaji. Nilai %G yang didapati amat bergantung kepada parameter cantuman yang disiasat, di mana parameter ini telah dioptimumkan dengan menggunakan kaedah sambutan permukaan (RSM) melalui modul yang terdapat dalam perisian pakar reka bentuk Box-Behnken. Penggunaan kaedah ini telah membawa kepada pembangunan model kuadratik yang mampu meramalkan %G dan mengurangkan penggunaan monomer. Kesahihan model statistik ini disokong oleh nilai sisihan yang kecil di antara yang diramal (G = 61%) dan eksperimen (G = 57%). Keadaan optimum untuk mencapai %G maksimum telah ditentukan pada: kepekatan monomer sebanyak 55 vol%, dos yang diterima sebanyak 100 kGy, masa reaksi dalam julat 14-20 jam dan suhu pada 61 °C. Kesan pendopan asid fosforik ke atas filem ETFE yang dicantumkan juga telah dioptimumkan dengan menggunakan kaedah Taguchi melalui pelaksanaan tatasusunan ortogon L_9 Taguchi (3^4). Parameter optimum untuk mencapai tahap maksimum pendopan asid (7.45 mmol/ulangan polimer unit) adalah: G pada 54%, asid kepekatan ialah 65%, suhu pada 100 ^oC dan masa ialah 5 hari. Nilai ramalan dopan yang diperolehi mencapai sisihan hanya sebanyak 4.9% dari eksperimen di mana ini mencadangkan kesahihan model ramalan dan pengoptimuman tindak balas pendopan asid. Kinetik tindak balas pendopan asid fosforik juga disiasat dan dua pemalar kadar 0.46 dan 0.16 grafik diperolehi menunjukkan tindak balas adalah tertib sifar. Kekonduksian proton membran dikaji dengan menggunakan sel kekonduksian 4-kuar yang dilampirkan pada meter sumber arus terus bersesuaian dengan suhu dan kelembapan relatif. Kekonduksian proton didapati meningkat dengan peningkatan jumlah dopan pada suhu dan kelembapan relatif yang tetap. Keberaliran proton sebanyak 143 mS/cm pada 20% kelembapan relatif telah dicapai pada membran yang mempunyai G sebanyak 38 dan 54%. Ini menunjukkan kekonduksian mempunyai kebergantungan yang rendah terhadap air. Dapat disimpulkan bahawa membran yang diperolehi mempunyai kombinasi yang sangat baik secara fizik-kimianya dan sifat bahannya sesuai untuk aplikasi dalam operasi PEMFC pada suhu melebihi 100 ^oC.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Fuel cell technology is intended to substitute the current internal combustion engine as a green source for power generation. This is due to the various problems associated with the growing use of fossil fuels including air pollution, soaring prices and critical fuel reserves limitations. Fuel cells have the advantages of efficient generation, high power density, zero emission, no moving parts and no noise compared to internal combustion engine. Thus, fuel cells are promising alternative sources for power generation in many sectors including stationary, portable and mobile applications (Ahluwalia and Wang, 2008; Doss et al., 2002).

Historically, the principle of fuel cell technology goes back to more than a decade ago when Sir William Grove had presented the first ever known fuel-cell in 1839. Ever since, various investigation has been carried out onto the fuel cell before it was accepted by the National Aeronautics and Space Administration (NASA) to be used for the purpose of supplying power for the Gemini and Apollo missions in the 1960s. By the beginning of 1980s the fuel cell start to appear in markets, after being mainly utilized for 20 years for serving space programs (Thounthong et al., 2009).

Various types of fuel cells including solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC) and phosphoric acid fuel cell (PAFC) are available. Among all proton exchange membrane fuel cells (PEMFC) are attracting attention

because of its low temperature operation and suitability for transport and stationary applications. Thus, commercialization of PEMFC is currently being pursued.

The basic unit of PEMFC consists of a proton conducting membrane sandwiched between two gas diffusion electrodes forming a membrane electrode assembly (MEA). The MEA then is installed between two flow filed plates and sealing gaskets were used to prevent gas leakage at the MEA - flow field plate interface. Detailed components of PEMFC and their functions are presented in Table 1.1 and Figure1.1 also shows an exploded diagram for fuel cell stack.

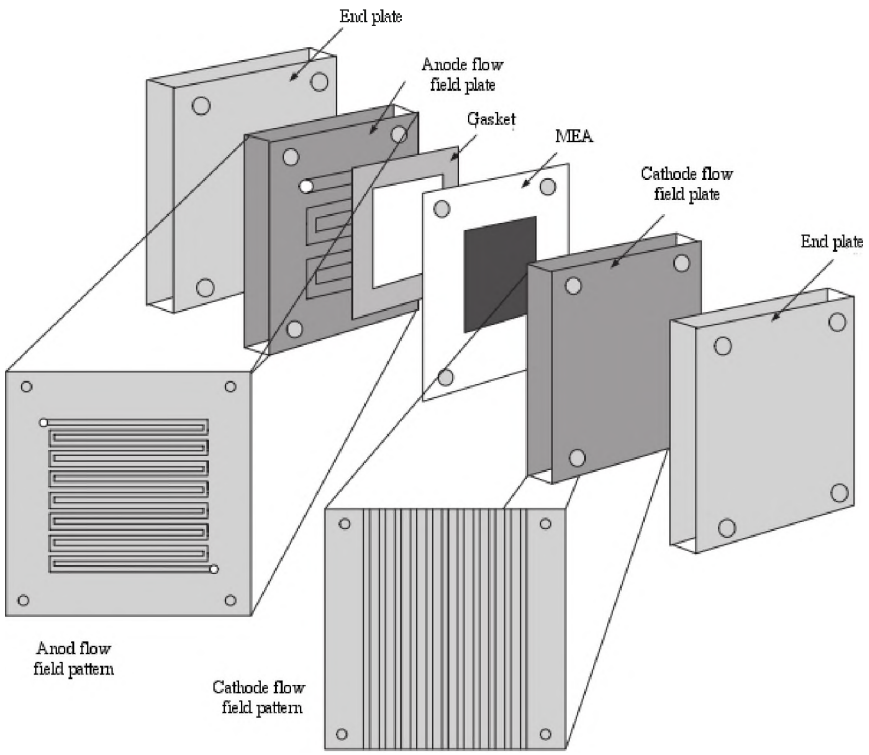

Figure1.1 Exploded diagram for fuel cell Stack

Table1.1 Fuel cell components

Component	Function	Common materials
Proton exchange membrane	Enables protons to travel from the anode to the cathode.	Perflurosulfonic acid membrane (Nafion 112, 115, 117)
Catalyst layers	Breaks the fuel into protons and electrons. The protons combine with the oxidant to form water at the fuel cell cathode. The electrons travel to the load.	Platinum/load on carbon
Gas diffusion layers	Allows fuel/oxidant to travel through the porous layer, while collecting electrons	Carbon cloth or carbon paper
Flow field plates	Distributes the fuel and oxidant to the gas diffusion layer	Graphite, stainless steel
Gaskets	Prevent fuel leakage, and helps to distribute pressure evenly	Silicon and Teflon
End plates	Holds stack layers in place	Stainless steel, graphite, polyethylene, PVC

At present the average cost for generating 1kW using fuel cells is around 50-750 USD for transport and stationary applications, respectively. This is quite expensive when compared to combustion engine but still lying within the allowable limits of the market. Thus, one of the greatest difficulties facing researchers regarding this issue is to develop a cost effective and efficient fuel cell systems based on the fuel cell concept. It was reported that reduction of materials (electrodes and membranes) cost can efficiently reduces the cost of the overall system reduction (Frank et al., 2009).

Proton exchange membrane (PEM) is an extremely critical component of PEMFC; it acts as a barrier between the supplied H_2 and O_2, thus prevents their undesired mixing. It also allows the protons (H^+) resulting from the oxidation of H_2 to migrate through it from the anode to the cathode (Hinaje *et al.*, 2009). The state of the art in PEMs includes Nafion$^{(TM)}$ (DuPont), and its analogous materials such as Dow (Dow Chemicals), Aciplex® (Asahi Chemicals Co.), Aciplex-S® (Asahi Kasei) based on a weak functional acid –COOH, Flemion® (Asahi Glass Co.), Gore-Tex (Gore and Associate), BAM 3G (Ballard), CRA and CRS (Solvay), and Dais membranes (Dais Co.) (Tian and Savadogo, 2005; Ennari, 2008). Such perflourinated PEMs like Nafion combine hydrophobic (perfluorocarbon backbone) and hydrophilic (sulfonic acid groups) domains together, thus the hydrophilic domain act as a conductive domain that allows the coupled proton and water migration, while the hydrophobic domain act as a robust support, and hence the membrane combines superior mechanical and electrochemical properties. Among all membranes, Nafion is the most used material as it indicated by wide range of investigation. Despite showing adequate proton conductivity when sufficiently humidified, Nafion and its analogous membranes considered to be expensive (500-700 USD/m^2) adding to high cost of PEMFC system. A barely, less expensive (370 USD/m^2) family of membranes such as sulfonated poly(ether ether ketone) membranes (sPEEK) were developed to overcome the cost problem. However an economic membrane that conduct proton efficiently is yet required. Finally, all these membranes are relying on water as main charge transporters and it was reported that the ionic conductivity of it is strongly water dependant. (Kerres et al., 2009).

1.2 Problem Statement

High temperature polymer electrolyte membrane fuel cell (HT-PEMC) has been proposed for replacing its counterpart operating at 60-80°C. This is to bring about benefits associated with high temperature operation such as: better electrode kinetics, elimination of humidification, high tolerance to fuel impurities, higher efficiency and higher values of excess heat by cogeneration (Li *et al.*, 2003).

Currently, commercial perfluorosulfonated polymers such as Nafion and its analogous membranes are subjected to deterioration in their proton conductivity when operated at temperature above 80°C due to dryness and variation in their viscoelastic properties (Ennari, 2008). Therefore, a strong need for proton conducting membranes that meet high temperature operation in PEM fuel cell has been aroused.

Basic membranes doped with inorganic proton donors have recently attracted much attention as polymer electrolytes of HT-PEMC due to their high proton conductivity, chemical and electrochemical stability at high temperature, in addition to, facile processing procedure (Pisani, 2009). Particularly, phosphoric acid (PA) is one of the most attractive inorganic proton donors that have been found to maintain high conductivity and stability at elevated temperature. A typical example of membranes for high temperature PEM is phosphoric doped polybenzimadazole membranes which have been subjected to frequent investigations and showed reasonable performance in PEM fuel cell at temperatures up to 190 °C without humidification (Che *et al.*, 2010). However, such membranes suffer from a degradation partially caused by the loss of electrolyte (Li et al., 2003).

Alternatively, PA membranes prepared by doping of precursor films obtained by radiation induced grafting of heterocyclic monomers such as 4-vinylpyridine (4-VP) and 1-vinylimidazole (1-VIm) onto poly(ethylene-co-tetraflouroethene) (ETFE) were reported in literature and found to be an attractive materials for high temperature PEM fuel cell (Schmidt and Schmidt-Naake, 2007; Şanlı and Gürsel, 2010). The use of radiation induced grafting simplifies the preparation procedure, allows composition and properties of the membranes to be controlled and provides solution for film formation as reaction starts from pre-existing sheets (Nasef and Saidi, 2002). The selection of heterocyclic monomers was to provide a basic center ($-N^{+}-$) resembling that of PBI to conduct protons at temperatures above 100 °C when protonated by doping with phosphoric acid (PA) (Matar *et al.*, 2010).On the other hand, the selection of ETFE film as a base polymer is owing to its outstanding properties including chemical inertness, thermal stability and mechanical integrity, in addition to, high radiation resistance.

Despite being recently reported in literature; the preparation of PEMs for high temperature PEMFC using radiation induced grafting of 1-VIm onto ETFE films and subsequent doping with phosphoric acid was not comprehensively covered. The modelling of the effect of the interaction of the reaction parameters on the degree of grafting and the acid doping level for both grafting and acid doping processes was not reported in literature. Also, there no optimization studies for both grafting and acid doping reactions. A kinetic study on the phosphoric acid doping of the grafted ETFE precursors was also not reported. Thus, present work is intended to provide a comprehensive investigation for the preparation of proton conducting membranes by radiation induced grafting of VIm onto ETFE film and subsequent acid doping covering the details of modelling, prediction, and optimization of the grafting and doping parameters together with kinetic investigation for acid doping. Such investigation would lead to reduction in; the number of experiments and monomer consumption and improve the economy of the preparation method. It would also results in a better understanding for the role of reaction parameters in two preparation stages (i.e. grafting and PA doping) in controlling the structure and the properties of these membranes.

1.3 Objectives of the Study

The objective of the present study is to prepare and characterize composite, less water dependent proton conducting membranes containing PA by radiation induced graft copolymeriztion (grafting) of 1-VIm onto ETFE film and subsequent acid doping with PA for possible use in a high temperature PEMFC (above 100°C). The objective can be divided into the following sub-objectives:

1. To study the effect of grafting conditions on the degree of grafting of 1-VIm monomer onto ETFE films.
2. To optimize the grafting parameters and develop a statistical model to predict the degree of grafting using response surface method (RSM).

3. To optimize the reaction conditions for phosphoric acid doping required for converting the obtained grafted membrane precursors into proton conducting membrane.
4. To determine the various chemical and physical properties of the obtained membranes using analytical and materials research aspects.
5. To evaluate proton conductivity of the obtained membranes under various levels of relative humidity and temperatures.

1.4 Scope of the Study

To achieve the objective of this study, the work was performed in three phases; i) irradiation of ETFE films, ii) preparation of the membranes which involves preparation of membranes precursors and functionalized by PA doping, iii) characterization of the obtained membranes Figure 1.3 presents a flow chart summarizing the scope of this study. The details of the scope of the present study cover the following stages:

1. Irradiation of ETFE film with electron beam (EB) accelerator under controlled conditions.
2. Radiation induced grafting of 1-VIm monomer onto ETFE films under various grafting conditions to obtain membrane precursors.
3. Establishing the effects of grafting conditions on the degree of grafting.
4. Optimization of the grafting parameters using RSM.
5. Introducing the functional groups to the prepared precursors by PA doping under controlled conditions.
6. Determination of various physical and chemical properties of the prepared membranes using techniques such as Fourier transform infrared (FTIR) spectral analysis, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), gravimetric analysis, back titration and DC impedance spectroscopy.
7. Testing the proton conductivity of the membrane under various relative humidifies and temperatures above 100^{o}C.

1.5 Thesis Outline

The thesis contains five chapters. The first chapter provides a general brief background about the fuel cells and the role of PEMs in fuel cells. It also includes the problems statement, the objectives of and the scope of work. The second chapter presents a review of literature including an introduction about the fuel cell technology and types of fuel cell systems. The state of the art of PEMs is also reviewed including its preparation methods and preparation conditions. The progress in developing PEMs for high temperature PEMFC is also discussed. The use of radiation induced graft copolymerization for preparation of PEMs is thoroughly reviewed. The third chapter covers the methodology and includes a list of all the materials and equipments and techniques used in this work to prepare and characterize the membranes. In the fourth chapter, the results of experimental work, statistical modelling and characterization analysis are presented and discussed. The overall conclusions obtained from the presented work together with some recommendation for future works are presented in chapter 5.

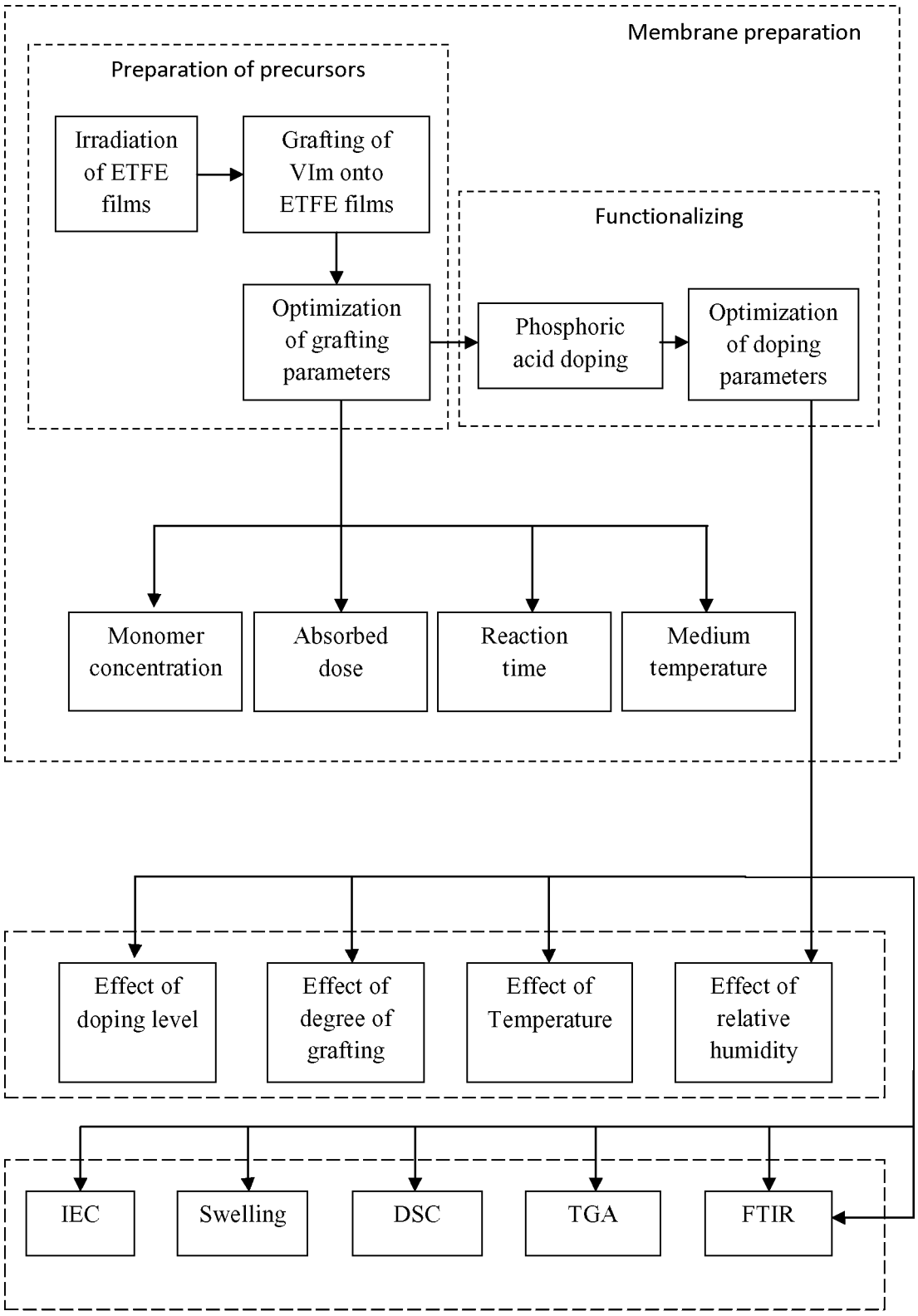

Figure 1.2 Flow chart summarizing the scope of work

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LIST OF ABBREVIATIONS

1-VIm	1-Vinylimidazole
2-VP	2-Vinyl pyridine
4-VP	4-Vinylpyridine
AFC	Alkaline fuel cell
AMS	α-Methylstyrene
ANOVA	Analysis of variance
ATR	Attenuated total reflectance
DMFC	Direct methanol fuel cell
DOG	Degree of grafting
DSC	Differential scanning calorimetry
DVB	Divinyl benzene
EB	Electron beam
ETFE	Poly(ethylene-*co*-tetraflouroethene)
ETFE-*g*-p(1-VIm)	ETFE films grafted with poly(1-vinylimidazole)
FEP	Poly(tetrafluoroethylene-*co*-hexafluoropropylene)
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
HT-PEMFC	High temperature polymer electrolyte fuel cells
IEC	Ion exchange capacity
LT-PEMFC	Low temperature polymer electrolyte fuel cells
MCFC	Molten carbon fuel cell
NASA	National Aeronautics and Space Administration
NVF	N-vinylformamide

NVP	N-vinyl-2-pyrrolidone
PA	Phosphoric acid
PBI/H_3PO_4	Phosphoric acid-doped polybenzimidazole
PE	Polyethylene
PEM	Proton exchange membrane
PFA	Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether)
PSSA-*co*-MA	Poly(styrene sulfonic acid-*co*-maleic acid)
PTFE	Polytetrafluoroethylene
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVDF-*co*-HFP	Poly(vinylidenefluoride-*co*-hexafluoropropylene)
PVF	Poly(vinyl fluoride)
RH	Relative humidity
RSM	Response surface method
SPBI	Sulfonated polybenzimidzole
SPEEK	Sulfonated poly(ether ether ketone)
SPEEK/PEI	Sulfonated poly(etheretherketone) and polyetherimide
SPES	Sulfonated polyether sulfones
SPPO	Sulfonated poly (2,6-dimethyl-1,4-phenylene oxide)
TFS	α,α,β-trifluorostyrene
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis
T_m	Melting temperature
VA	Vinylamine
VBC	Vinylbenzyl chloride

LIST OF SYMBOLS

A	Surface are of the sample (cm^2)
b	Regression coefficient (-)
e	Experimental error (-)
G%	Degree of grafting (wt%)
L	Thickness of the membrane sample (cm)
mg	Weight of the grafted film (g)
mo	Weight of the original film (g)
M_p	Molar mass of repeat unit (g/mol)
M_{pa}	Molar mass of phosphoric acid (g/mol)
V_{NaOH}	Volume of NaOH (ml)
W_{dry}	Weight of the dry membrane (g)
W_{dry}	Weight of dry membrane (g)
Wg	Weight of grafted film (g)
W_o	Weight of original film (g)
W_p	Weight of phosphorylated membrane (g)
W_{uptake}	Water uptake of the membrane from the vapour phase (wt%)
W_{wet}	Weight of the swelled membrane (g)
x	Independent parameter (-)
X_d	Acid doping level per repeated unit of grafted polymer (mmol/repeating unit)
y	Response (-)
σ	Proton conductivity (Scm^{-1})