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.