PROGRESS IN ELECTRON BEAM INDUCED GRAFTING FOR DEVELOPMENT OF ION CONDUCTING MEMBRANES FOR POLYMER ELECTROLYTE FUEL CELLS IN MALAYSIA.

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Abstract

This article briefly reviews the progress taking place in the development of ion conducting membranes (ICMs) using radiation induced graft copolymerization (RIGC) initiated by electron beam (EB) in Malaysia. Three types of ICMs for direct method fuel cell (DMFC) and high temperature proton exchange membrane fuel cell (HT-PEMFC) and alkaline electrolyte membrane fuel cell (AEMFC) were prepared. The ICM for DMFC was prepared by RIGC of 4-vinylpyridine (4-VP) onto EB irradiated *Syn*-polypropylene (*s*-PP) nanofibrous sheet followed by immobilization of phosphotungstenic acid ($H_3PW_{12}O_{40}$, PTA) and subsequent casting of 2 thin layers of Nafion solutions leading to 3-layer (3L) composite membrane with high conductivity and less water dependency beside having superior methanol barrier properties compared to Nafion 115 at both low and high methanol concentrations. The ICM for HT-PEMFC was prepared by grafting a binary mixture of 4-VP/1-vinylimidazole (1-VIm) onto EB-irradiated poly(ethylene-*co*-tetrafluoroethylene) (ETFE) followed by doping with phosphoric acid (PA). The incorporation of two basic monomers was highly effective in enhancing PA doping level, proton conductivity and overall performance of the membrane in fuel cell operated at 120°C. The ICM for AEMFC was prepared by incorporating imidazolium head groups to EB irradiated nanofibrous *s*-PP grafted with vinylbenzyl chloride (VBC), crosslinked by 1,8-octanediamine and functionalized with -OH group. The membranes displayed not only high ion exchange capacity (1.9 mmol/g) but also high ionic conductivity (130 mS/cm at 80°C) and reasonable alkaline stability. The membrane showed a high-power density reaching 440 mW/cm^2 at a current density of 910 mA/cm^2 when combined with electrodes using diamine crosslinked quaternised polysulfone binder at 80°C making it a promising candidate for application in AEMFC. It can be concluded that EB is highly effective in facilitating the development of ICMs precursors for various polymer electrolyte fuel cells.

1. INTRODUCTION

There is a strong demand for migration from the reliance on fossil fuels to renewable energy. This is to reduce greenhouse gas emissions to mitigate climate change and global warming. Electrochemical Energy systems such as fuel cells (FCs) are promising sustainable energy candidates suitable for supporting the shift to renewable energy [1]. FC, which is a system converting the free energy of fuel at the anode (e.g., H_2) into electricity in presence of an oxidant at the cathode (e.g., O_2) without combustion and releasing water as waste, uses ion conducting membrane (ICM) to transfer ions between electrodes and prevent bulk mixing reactants. The ions that can be transferred between electrodes are H^+ in both high temperature-proton exchange membrane fuel cell (HT-PEMFC) and direct methanol fuel cell (DMFC). The former is known as H_2/O_2 FC and is operated at a temperature range of 100-200ºC to enhance the performance (increase tolerance to CO gas, speed up electrode kinetics and increase fuel use efficiency) and reduce the complexity of the system, whereas the latter uses liquid fuel such as methanol giving it simplicity and suitability for portal uses. On the other hand, OH^- is transferred in ICM (anion exchange membrane in this case) from cathode to anode in the alkaline electrolyte membrane fuel cell (AEMFC), which has the advantage of using less-precious metals to make the electrodes. Commercial ICMs for FCs are challenged by a few issues including high cost, high methanol crossover (in DMFC) [2] and loss of fuel barrier properties in HT-PEMFC in addition to low ion exchange capacity and conductivity in AEMFC [3]. This situation raised the demand for development of alternative ICMs with enhanced properties and cheaper costs.

Radiation-induced graft copolymerization (RIGC) is a highly effective method for development of ICMs with the advantage of being more environmentally friendly compared to chemical grafting providing efficient means to control the degree of grafting (DG) and the level of the covalently bonded ionic moiety imparted to the

polymer substrate present in a film form and thus allow facile preparation of defect free membranes with desired properties [4]. The ICM preparation starts with irradiation from high energy sources such as γ-rays or EB triggering the formation of radicals that provides sites for reaction with desired monomers under controlled conditions allowing incorporation of desired functional groups. Interestingly, the use of EB provides significant advantages including not only speedy processing, controlled penetration depth and ease of operation but also it is radiation hazardless and more suitable for industrial application [5]. This made EB more appealing for irradiation of various polymer films to initiate grafting for the preparation of ICMs for FC applications in our work.

2. RADIATION GRAFTED ICM FOR DMFC

The membrane preparation was carried out by RIGC of 4-VP onto EB-irradiated electrospun *s*-PP with a dose of 20 kGy and a monomer concentration of 50 vol% in THF, temperature of 60°C and reaction time of 6 h. The obtained poly(4-VP) grafted nanofibrous s-PP sheets were loaded with PWA and subsequently coated with 2 layers of Nafion solution leading to 3-L composite membrane. The physicochemical properties of the obtained ICM are summarized in Table 1. Both 3-L membranes with PWA loading of 51 and 45% showed superior proton conductivity and selectivity in addition to having better methanol barrier properties and less-water dependency.

TABLE 1. Properties of 3-L composite membranes for DMFC [6]

Membrane	PWA loading (%)	Thickness	Water uptake (%) at 30°C	Proton conductivity (mS /cm)	CH_3OH permeability × 10^8 (cm^2/s)	Selectivity ×10^8 ($mS.s/cm^3$)
3-L1	51	95	5.2	58.6	3.60	16.3
3-L2	46	95	5.0	40.0	3.00	13.2
Nafion 115	N/A	127	13.1	23.2	104	0.50

The performance in DEMFC depicted in Fig. 1 showed that both 3-L membranes demonstrated a higher open circuit voltage (OCV) of 6.3% and power density of 49.6% compared to Nafion 115 membrane when 2M methanol was used as a fuel at 60°C. Higher performance was also obtained with 5 M methanol fuel [6]. Such higher performance could be attributed to the lower methanol crossover and higher membrane selectivity coupled with high proton conductivity.

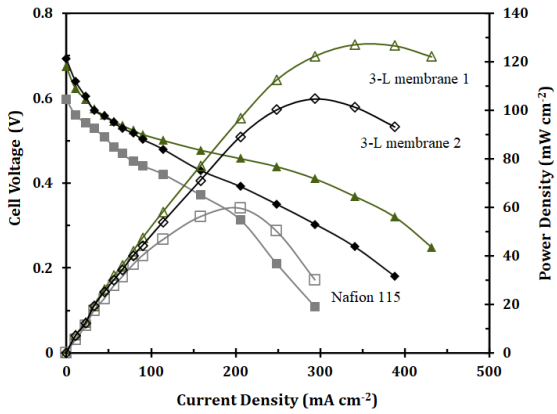

FIG. 1: Polarization curves of DMFC single cell with two 3-L membranes and Nafion 115 membrane. Operating conditions of anode are: 2 M methanol, 4 mL/min and 60°C.

3. RADIATION GRAFTED ICM FOR HT-PEMFC

Phosphoric acid (PA) doped membranes based on polybenzimidazole (PBI) have low proton conductivity and acid leaching problems. ICMs based on alkaline film grafted with 4-VP or 1-VIm monomer were proposed to enhance PA doping levels, yet their performance was unsatisfactory. Thus, grafting a mixture of 4-VP and 1-VIm onto ETFE film is likely to yield more alkaline intermediate films allowing more PA doping that led to higher conductivity than counterparts grafted with either single monomer. The membrane was prepared by RIGC mixture of 4-VP and 1-VIm (60/40, v:v) in 40 vol% deionized water at 60°C onto EB irradiated ETFE films followed by treatment with 85% PA and the plausible structure of the obtained membrane is illustrated in Fig. 2.

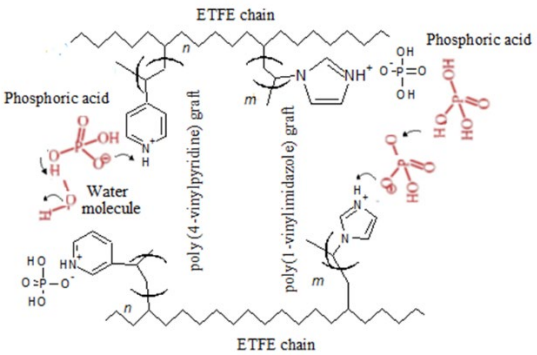

FIG. 2. Preparation of PA doped membranes based on EB irradiated ETFE film grafting with 4-VP/1-VIm.

The obtained ICM has homogenous graft distribution as depicted in Fig. 3. More importantly, the membrane showed a higher PA doping level and a less water dependency than the counterparts obtained by RIGC of 4-VP or 1-VIm alone. The membrane also showed a proton conductivity higher than PA doped PBI membrane at 120 °C. This was accompanied by a power density of 278 mw/cm^2 using partially humified gases of 20% RH when tested in FC compared to 226 mw/cm^2 at dry conditions under the same operating conditions as indicated by polarization curves shown in Fig. 4.

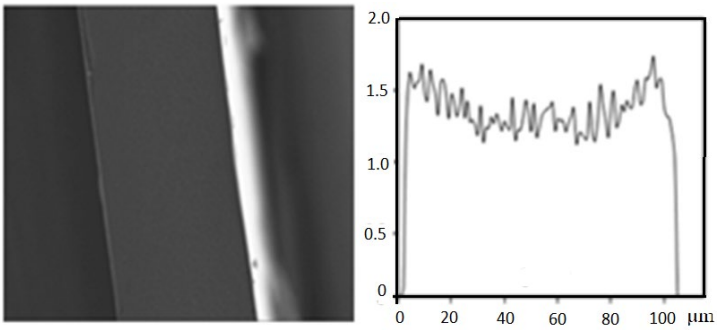

FIG. 3: Cross-sectional SEM image of acid doped ICM with phosphorus profiling across it.

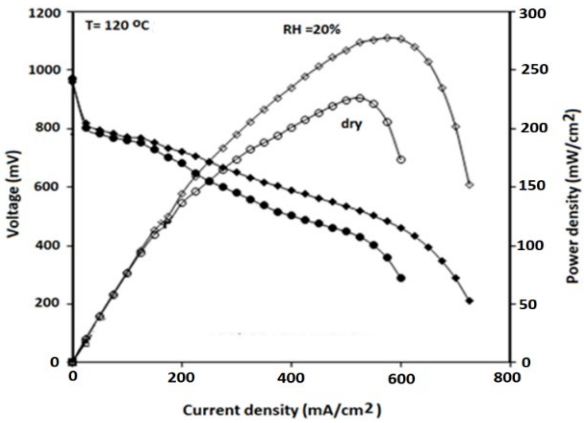

FIG. 4. Polarization curves of HT-PEMFC single cell with PA doped membranes tested under dry and 20% RH. The cell operated at 120 °C with H_2 and O_2 follow rates of 600 and 300 ml/min, respectively.

4. RADIATION GRAFTED ICM FOR AEMFC

Commercial ICMs for AEMFC are mainly challenged by low IEC and -OH conductivity. Radiation grafted membranes offer alternatives with improved properties. An imidazolium (Im) OH conductive containing ICM was prepared by RIGC of VBC onto EB irradiated nanofibrous s-PP sheet at 5 kGy/pass to a total dose of 35 kGy in an emulsion medium composed of a mixture of 5 wt% of VBC and 0.5 wt% of Tween-20 in DI water that was homogenized for 1 h at room temperature and flushed with N_2 gas for 30 min. The reaction vessel was water placed in a water bath at 50 °C for 10 h. The grafted samples were removed and cleaned then crosslinked with 1,8-octanediamine (ODA) and subsequently functionalized with Im groups as illustrated in Fig. 6 [7].

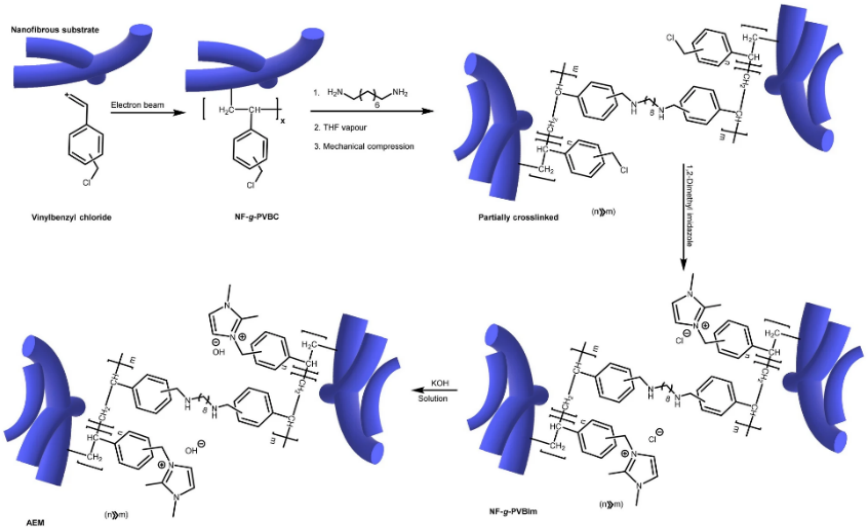

FIG. 5: Preparation of Im-containing membranes based on EB irradiated ETFE film grafting with VBC crosslinking with ODA and alkalisation with KOH [7].

The obtained membrane has a high IEC of 1.9 mmol/g and displayed OH conductivity of 130 mS/cm at 80 °C. The fuel cell performance shown Fig. 7 demonstrated a power density of 440 mA/cm^2 when tested under H_2 and O_2 flow rates of 200 ml/min, RH of 90% and 80 °C.

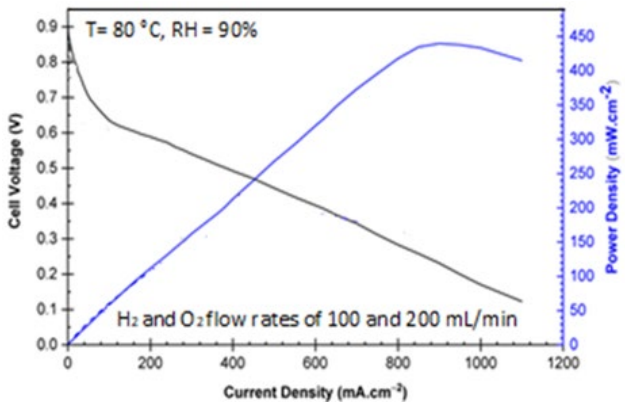

FIG. 6: Polarization curves of AEMFC with of Im-containing membrane [7].

5. CONCLUSIONS

EB was successfully used to initiate the preparation of 3 types of IEMs by RIGC of various monomers onto selected substrates. The adopted RIGC method led to ICMs with improved electrochemical properties and improved performances in fuel cells. The level of properties improvement depends on the amount of grafted moiety when functionalized.

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