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Preliminary Study of Alkaline Direct Ethanol Fuel Cell by Using Crosslinked Quaternized Poly (Vinyl Alcohol)/Graphene Oxide Membrane

(Kajian Awal Sel Fuel Etanol Langsung Beralkali Menggunakan Membran Elektrolit Berasaskan Alkohol Polivinil Terkuaternisasi/Grafin Oksida)

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ABSTRACT

A crosslinked of Quaternized Poly (vinyl alcohol)/Graphene oxide (QPVA/GO) composite membrane was prepared via quaternization and solution casting method. With the main objective is to performed lower ethanol permeability membrane than Nafion 117 membrane thus can be the potential alternative membrane in future. The physical and chemical properties of the QPVA/GO membrane were investigated via the Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction analysis (XRD) and Filed Emission Scanning Electron Microscopy (FESEM). The characterization result shows the good interaction of matrix polymer, GO loading and glutaraldehyde as a crosslinked agent. A maximum conductivity of 1.08 × 10^{-2} S cm^{-1} was obtained for QPVA/10wt% GO membrane at 30°C. The ethanol permeability has been reduced until 2.2 × 10^{-7} cm^2 s^{-1} with increasing of 10 wt.% GO loading which was lower than Nafion 117 (19.5 × 10^{-7} cm^2 s^{-1}). The increasing of GO content in composite membranes has append the hydrophobic region which play role as blocking effect to hinder the ethanol crossover. The cell voltage and power density were analyzed at the temperature 30°C. A maximum power density achieved by QPVA/GO membrane was 6.92 mW cm^{-2} at 10.wt% GO loading which higher than Nafion 117 with only 5.07 mW cm^{-2} using 2 M ethanol + 2 M KOH at 30°C.

Keywords: Quaternized Poly (vinyl alcohol); Graphene oxide, alkaline–DEFC; Nafion 117

ABSTRAK

Membran komposit alkohol polivinil terkuaternisasi/grafin oksida terpaut silang telah disediakan menerusi proses kuaternisasi dan kaedah tebaran pelarut. Dengan objektif utama kajian untuk menghasilkan membran yang mempunyai kebolehtelapan etanol yang lebih rendah berbanding membran Nafion yang mana akan menjadikan membran ini berpotensi untuk menjadi membran alternatif pada masa hadapan. Sifat-sifat fizikal dan kimia membran QPVA/GO telah dikaji menggunakan spektroskopi inframerah transformasian Fourier, pembelauan sinar-X dan Mikroskop Elektron Imbasan Medan Pancaran. Kekonduksian maksimum yang dihasilkan oleh membran QPVA/GO 10wt.% ialah 1.08 × 10^{-2} S cm^{-1} pada suhu 30°C. Kebolehtelapan etanol pula berkurang sehingga 2.2 × 10^{-7} cm^2 s^{-1} dengan peningkatan berat pengisi GO sehingga 10wt.% lebih rendah berbanding Nafion 117 (19.5 × 10^{-7} cm^2 s^{-1}). Peningkatan kandungan GO di dalam membran komposit telah menambahkan kawasan hidrofobik yang di mana bahagian ini bertindak sebagai kesan penghadang kepada lintasan etanol. Prestasi sel dan ketumpatan kuasa juga dianalisis pada suhu 30°C. Ketumpatan kuasa maksimum yang dihasilkan oleh membran PVA/GO mencapai 6.92 mW cm^{-2} dengan bebanan GO sebanyak 10 wt.% yang mana lebih tinggi berbanding membran Nafion yang hanya mencapai 5.07 mW cm^{-2} dengan menggunakan 2 M etanol + 2 M KOH pada suhu 30°C.

Kata kunci: Alkohol polivinil terkuaternisasi; Grafin oksida; DEFC beralkali; Nafion 117

INTRODUCTION

Ethanol has a potential as an alternative power source due to their advantages compared to methanol as known as pioneer alcohol applied in micro fuel cell technologies. For examples, ethanol has higher volumetric energy density of 8.00 kW h kg^{-1} than methanol only 6.09 kW h kg^{-1}, classified as renewable energy due to its natural availability and can be produced in bulk from agricultural bio-processes and nontoxic, which avoids environmental pollution issues and safe for human (An et al. 2015; Badwal et al. 2015; O'hayre et al. 2016).

Today, passive alkaline direct ethanol fuel cell (alkaline–DEFC) is one of direct alcohol fuel cell types gain attention among the researchers. The passive alkaline–DEFC has promise several advantages compared to conventional power sources for portable devices such as lower temperature operation, compact, flexible in design of cell, faster rechargeable, easier in storage and transportation (Akhairi & Kamarudin 2016). Polymer electrolyte membrane is an important part in the fuel cell development. Basically, the function of this part are separating the chemical reaction of ethanol oxidation in anode and reduction oxygen in cathode, barrier for the ethanol crossover, allow the ionic transfer and obstruct the electron diffuse through the polymer electrolyte membrane (Huang et al. 2016; Zakaria et al. 2016). Wang et al. (2010) fabricate poly (vinyl alcohol)/3-(trimethylammonium) propyl functionalized silica (PVA-TMAPS) composite membrane and use in alkaline DEFC system. The membrane with a ratio of PVA: TMAPS = 90:10 exhibited the highest OH conductivity. Zeng et al. (2012) also studied about PVA based membrane in alkaline DEFC which accompanied with layered double hydroxide with maximum power density achieved of 82 mW cm^{-2} at 80°C. Besides, Huang et al. (2016) also fabricated the membrane which applied in DEFC which consist of graphene and CNT as filler in PVA based membrane, respectively.

Nafion membrane is used as polymer electrolyte membrane commonly in direct alcohol fuel cell due to the higher ionic conductivity performance. Unfortunately, this membrane experienced higher fuel permeability leading to the fuel crossover which cause several problems such as loss of ethanol fuel, poisoning the cathode catalyst and degrade the single cell performance. Besides, the production cost of Nafion membrane is expensive which thus limit the commercialization of fuel cell product. Therefore, to develop an alternative membrane that can replace the conventional membrane is the urgent necessary (Zhao et al. 2010; Zakaria et al. 2016; An & Zhao 2017).

Poly (vinyl alcohol) (PVA) is a particularly interesting and versatile polymer due to low cost, hydrophilic polymer, non-toxic materials, biodegradable and suitable as electrolyte membrane for alkaline–DEFC. Moreover, PVA has high ability in chemical resistance, thermal resistance and high film forming ability. Fortunately, PVA is also low soluble in ethanol that beneficial in reducing the ethanol permeability problem as facing by conventional fuel cell system. On the other hand, PVA has low ionic conductivity and high solution uptake which leading to the swelling problem (Saxena 2004; Zeng et al. 2012). But, the advantages of PVA polymer is high hydrophilicity and availability of free sites for the formation of a stable membrane with good mechanical properties that swelling property can be controlled and thus can be the backbone of the composite membrane (Wang et al. 2010; de Souza Gomes & Dutra Filho 2012).

In this study, the main focus is to explore the potential of PVA based membrane in passive alkaline–DEFC which success in reducing the ethanol permeability as reported in previous study (Zeng et al. 2012). With introduce the quaternary ammonium function group graft to backbone chain of PVA, the quaternization process will build the new functionalized polymer call as quaternized poly (vinyl alcohol) (QPVA). (Xiong et al. 2008) claimed the membrane based QPVA polymer able to increase the ionic conductivity until 7.35 × 10^{-3} S cm^{-1} in deionized water. Besides, in order to increase the conductivity of membrane and maintain the ability to reduce ethanol permeability, the QPVA polymer was blended with the Graphene Oxide (GO) inorganic filler as GO has received great attention among researchers due to the interesting characteristic. Therefore, GO is a promising membrane material for fuel cell technologies (Cao et al. 2011; Shaari & Kamarudin 2017; Farooqui et al. 2018). GO will provide good ionic conductivity due to oxygenic functional group such as hydroxyl, carboxylic, and epoxy groups in the hydrophilic region surrounding of edge GO. Karim et al. (2016) has described the potential of GO that can increase the conductivity of membrane which had achieved nearly 10^{-2} S cm^{-1} that higher than bulk graphite oxide with only 10^{-4} S cm^{-1}. Moreover, the hydrophobic region in the GO nano-sheet structure which consists of sp^2 carbon layer can contribute in ethanol crossover reduction and improve the mechanical strength of the membrane due to the strong covalent bonding. The objective of this present work is to prepare, characterize and determine the performance of crosslinked quaternized poly (vinyl alcohol)/graphene oxide (assigned as QPVA/GO) composite membrane which is expected can effectively reduce the ethanol permeability and improve the ionic conductivity consequently competent to the commercial Nafion membrane in passive alkaline–DEFC.

METHODOLOGY

MATERIAL

Poly (vinyl alcohol) (PVA) (Mw 85,000-124,000, 99 + % hydrolyzed), graphite powder, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and glycidyltrimethyl ammonium chloride (GTMAC) were supplied by Sigma Aldrich. Glutaraldehyde (GA, 25% content in distilled water) provided from Nacalai Tesque/Japan. Potassium hydroxide (KOH), Phosphoric acid (H_3PO_4), bought from J.T. Baker. Pt–Ru and Pt were supplied by Alfa Aesar, USA. All these commercial material are used without any purification.

SYNTHESIS OF QUATERNIZED PVA

The appropriate amount of PVA was dissolve in deionized water under stirring at 90°C for 2 h. The resulting PVA solution became homogeneous, transparent and viscous in appearance. The temperature of viscous solution was reducing to 65°C. Then, the appropriate amount of GTMAC, KOH (GTMAC:KOH = 1:1 in mole ratio) was introduced and the resulting homogeneous and colorless solution, keep stirring for 4 h. The solution was rinsed off with anhydrous ethanol to obtain yellow precipitates of quaternized poly (vinyl alcohol) (QPVA) followed by drying process in vacuum oven.

SYNTHESIS OF GRAPHENE OXIDE

The Modified Hummers methods was applied to synthesis the graphene oxide (GO) (Leong et al. 2015). 2 g of graphite is mixed with 2 g of $NaNO_3$ in 500 ml volumetric flask. Then, 150 ml of H_2SO_4 is poured and continuous stirring for 30 min in the ice bath (0-5°C). After that, the mixture was added with 12 g of $KMnO_4$ while the reaction temperature should be controlled and maintained below 20°C for 4 h. Remove the ice bath and retain stirring until the solution appear liked pasty brownish for one day at 35°C. Next, the solution was diluted with 100 ml D.I water to form a brown solutions, quickly, the temperature rise until 98°C. Then, add more 200 ml of water to reduce the temperature. Lastly, 10 ml of H_2O_2 was poured to treat the solution and obviously yellow color performed. The centrifuge used to purified the solution with 10% HCl and DI water was used to rinsing which purification step was repeated the for several times.

PREPARATION OF THE CROSS-LINKED QPVA/GO COMPOSITE MEMBRANE

QPVA (8wt.%) was dissolve in deionized (DI) water by magnetic stirrer for 1 h at 75°C to form homogenous and transparent solution. GO solution with 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.% and 10 wt.% was prepared with diluting the GO solution (1 g/L) provided. The solution of QPVA was continuously stirring which then mix with various GO solution wt.% (2:1 = ratio of volume) for 1 h and then produce QPVA/GO solution looks like yellow brown color. The yellow brown solution was continuous stirring then followed by addition of 10wt.% of GA and stirred for 30 min. The solution was cast onto a plastic plate and permits solvent evaporation at ambient temperature for 24 hours and then dried in a vacuum oven at 60°C for 12 hours. The membrane was peeled off from plastic plate and then put on glass plate for annealing process at 100°C for 1 hour. Then, the membrane was conducted by immersing the membrane in 1M of KOH solution at 80°C for 24 hours. The excess of KOH on the membrane surface was removed by repeatedly rinsing with D.I. water and stored in D.I. water at room temperature for prior use.

CHARACTERIZATION

FOURIER TRANSFORMATION INFRARED SPECTROSCOPY

Fourier Transformation Infrared spectroscopy (FTIR) analysis of crosslinked QPVA membrane and crosslinked QPVA/GO composite membrane was recorded on Perkin Elmer FTIR spectrophotometer with an ATR (attenuated total reflection) module. The samples were hold in sample holder and placed in the ATR–FTIR system. The FTIR studies were conduct in ambient temperature and the spectral range was 400-4000 cm^{-1}.

X-RAY DIFFRACTION

X-ray diffraction (XRD) spectrometer (model D8 Advance, Bruker AXS Germany) was used to assess the crystallinity of GO, crosslinked QPVA membrane and crosslinked QPVA/GO composite membranes. Radiation was generated using Cu Kα (wavelength of 0.15406 nm) at anode operating power was 40 kV and 40 mA. The scanning rate was $0.5°s^{-1}$ with a 0.02° resolution. XRD spectra were recorded over 10°-50°.

FIELD EMISSION SCANNING ELECTRON MICROSCOPE

The surface and cross-section morphologies of the crosslinked QPVA membrane and cross-linked QPVA/GO composite membrane was viewed using ZEISS SUPRA 55VP Field Emission Scanning Electron Microscope (FESEM).

PERFORMANCE

ETHANOL PERMEABILITY

The diffusion cell that consists of two glass compartment was built to measure the ethanol permeability through the membrane. Two compartment glasses was separated as the feed compartment was filled with 2M ethanol and another side was the receiving chamber which containing of deionized water. Each compartment contained a magnetic stirring bar for solution agitation. All the samples of crosslinked QPVA/GO composite membrane and Nafion 117 membrane was clamped vertically between two glass compartments. During experiment, the ethanol crossover concentration through membrane was measured with the membrane permeability was calculated by using the following equation (1):

$$\mathrm{P} = \frac{1}{Ca}\left(\frac{\Delta Cb(t)}{\Delta t}\right)\left(\frac{LVb}{A}\right) \tag{1}$$

P is represent the ethanol diffusion permeability of the membrane ($cm^2\ s^{-1}$), C_a is representing the concentration of feeding chamber in cell A ($mol\ L^{-1}$), $\Delta Cb(t)/\Delta t$ is representing the slope of the molar concentration variation of ethanol in cell B as a function of time ($mol\ L^{-1}\ s$), V_b is representing the volume of each diffusion reservoir (cm^3), A is representing the membrane area and L is representing the thickness of the membrane (cm). The ethanol concentration in cell B is calculated from refractometer. The dropwise of solution is taken from second compartment at certain range of time and drop on refractometer. The refractometer than give index of refraction for that ethanol solution to be used in determination of ethanol concentration.

IONIC CONDUCTIVITY

The ionic conductivity measurement was determined via using an electrode system, which contained a four stainless steel electrodes connected to an impedance analyzer WonATech potentiostat (WMPG1000). The crosslinked QPVA/GO composite membrane were equilibrate in deionized water and conducted at ambient temperature. The membrans were laid in transverse direction and sandwiched by stainless steel electrodes. All measurement was carried out using the equation (2):

$$\sigma = \frac{L}{RS} \tag{2}$$

Where σ, L, R and S are represent the proton conductivity (S cm^{-1}), distance between the counter electrodes (cm), ohmic resistance of the membranes (S^{-1}) and cross section area of the membrane samples (cm^2).

SELECTIVITY FACTOR

The selectivity factor of the crosslinked QPVA/GO composite membrane (the ratio of the proton conductivity to the ethanol permeability) was determined using this following equation (3):

$$\text{Selectivity, } \Phi = \frac{\sigma}{P} \quad (3)$$

PERFORMANCE OF PASSIVE ALKALINE – DEFC

The membrane – electrode assembly (MEA) for passive alkaline–DEFC test cell was fabricated by sandwich the crosslinked QPVA/GO composite membrane between anode and cathode electrodes via hot-pressing machine. For anode, a Pt–Ru catalyst applied was 4 mg cm^{-2} loading and cathode was applied by Pt catalyst with 4 mg cm^{-2} loading which carbon paper act as gas diffusion layer via manual casting technique. DEFC performance was tested through a passive air-breathing with homemade single cell stack which active area of MEA is 4cm^2. The fuel reservoir region of the single cell stack allows fulfilling by 2 mL of fuel. The polarization data were obtained using the potentiostat/galvanostat (WonATech) to measure the voltage response by applying load current for the single cell at ambient condition. 2M KOH + 2M ethanol react as fuel in anode and air diffuse surrounding in cathode.

RESULTS AND DISCUSSION

CHARACTERIZATION OF QPVA AND CROSSLINKED QPVA/GO COMPOSITE MEMBRANE

Figure 1 indicate the FTIR spectra of QPVA and crosslinked QPVA/GO composite membrane from 400 cm^{-1} to 3900 cm^{-1} wavelength. For the crosslinked QPVA membrane, the absorption peak appear at 686 cm^{-1}, 1643 cm^{-1} and 3399 cm^{-1} which belongs to the aliphatic C–H bending, C=C from backbone from matrix polymer and group of hydroxyl (Gu et al. 2008; Han et al. 2011); at 968 cm^{-1} belongs to characteristic of aliphatic of C-N, it is indicate that the quaternary ammonium group was grafted onto the backbone of matrix polymer of QPVA (Xiong et al. 2008); at 1115 cm^{-1} is indicate the C–O–C stretch group appeared after the cross-linking treatment and it proved that the cross-linking reaction by GA was successful (Wang et al. 2010). After modification of matrix polymer of QPVA with GO, all the peak of matrix polymer reduce due to interaction of hydrogen bonding with the GO. The several peak of oxygenic functional group from GO loading are appear in composite membrane, at 1351 cm^{-1} is belongs to epoxy C-O symmetric vibrations (Lin et al. 2017); 1460 cm^{-1} is represent the stretching vibration from O=C–O group (Lin & Lu 2013); 1656 cm^{-1} is attributed to the C=C stretch from aromatic structure corresponding to sp^2 characteristic of GO hydrophobic region (Han et al. 2011); 1720 cm^{-1} singed from –COOH stretching carboxylic group.

The peaks appear at wavelength of 2871 cm^{-1} were attributed to the =C–H stretching vibration and the strong and broad absorption at 3399 cm^{-1} of –OH hydroxyl functional group stretching vibration (Lo et al. 2013). The peak for the cross-linking GA treatment effect can be seen appear at 1115 cm^{-1} that belongs to the C–O–C stretch group thus proved that the cross-linking reaction by GA was successful occurred (Wang et al. 2010). From the FTIR spectra analysis,

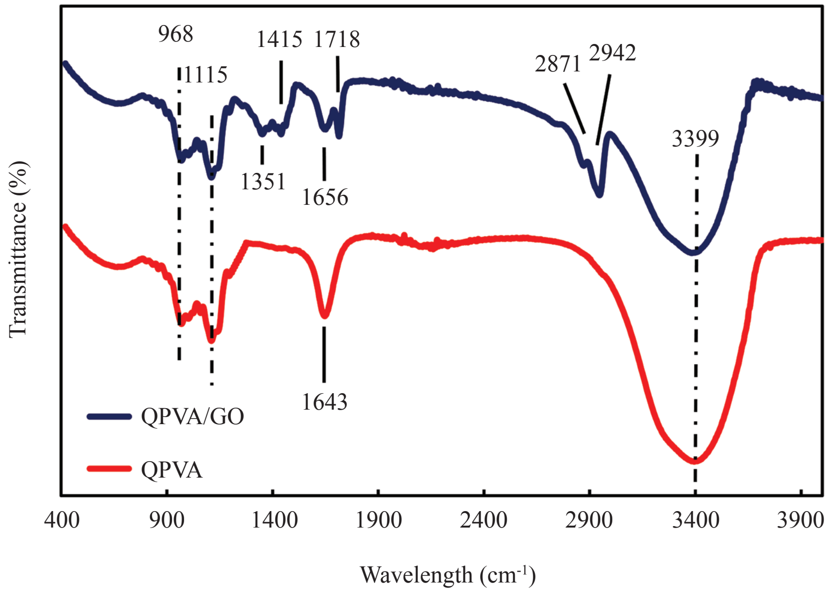

FIGURE 1. FTIR spectra of crosslinked QPVA membrane and crosslinked QPVA/GO composite membrane

the peak of crosslinked QPVA membrane and crosslinked QPVA/GO composite membrane obviously demonstrate similar functional group as reported in previous work (Xiong et al. 2008; Lo et al. 2013; Lee et al. 2014);

X-ray diffraction was perform to observe the crystallinity of the GO, PVA, crosslinked QPVA membrane and crosslinked QPVA/GO composite membranes. The illustrations of the diffraction pattern for the XRD analysis peak is present in Figure 2. Lee et al. (2014) reported that the crystallite peak of graphite was observed at 25.6°, while synthesized GO showed the progressive phase change from graphite to GO due to the crystallite peak appeared at new 2θ value which was at 10.92°. The peak of GO has high intensity at 10.92° due to the interaction of hydrophobic sp2 region with the oxygen functional group of GO that has been produced through the oxidation process of graphite (Lee et al. 2014). The large peak at 19°-20° and the small peak at 39°-40° appeared were indicators of PVA spectra that the semi-crystalline structure of this polymer (Wang et al. 2010). After the quaternization process of PVA, the peak intensity of crosslinked QPVA membrane at 19°-20° has been decreased compared to pure PVA. Introduction of ammonium function group has disturb the semi-crystalline structure of PVA polymer. This implies that the domain phase exist in the QPVA polymer matrix was the amorphous phase perhaps can enhance the ionic conductivity of the AEM. The amorphous phase contribute in facilitate the transport of anions in a polymer matrix by hopping mechanism between coordinate sites due to their less boundaries structure compared to the crystallite phase (Liao et al. 2015; Rajesh Kumar et al. 2015). After modification of matrix polymer QPVA with addition of GO, the large diffraction peak of GO was invisible, which indicates that GO is homogenously dispersed in the QPVA due to the physical interaction. Notably, the invisible GO peak at 2θ = 10.92° is due to the complete exfoliation and destruction of the regular stack by incorporation in QPVA. This result confirmed that the synthesis of a crosslinked QPVA/GO composite membrane was contribute by the formation of hydrogen bonding and the interactions at the ionic level between the polymer chains and the functional group in GO (Xue et al. 2014; Lin et al. 2017; Shaari & Kamarudin 2017).

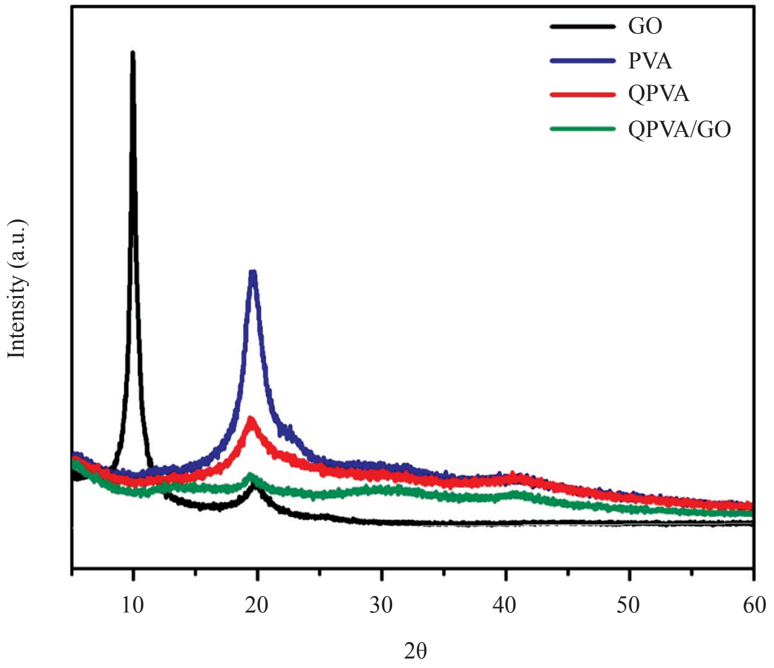

FIGURE 2. XRD spectra of GO, PVA film membrane, crosslinked QPVA membrane and crosslinked QPVA/GO composite membrane

Figure 3 present the FESEM image at a magnification of 100 × for surface image and cross section image, respectively. All the membrane has produce the dense structure that useful for reduce the ethanol permeability issue. From the top view of FESEM photographs, the image reveal the crosslinked QPVA membrane in Figure 3(a) showed a few bulges presence, which attributed to the grafted aliphatic ammonium functional group and Figure 3(b) showed a compact and rugged texture (Ye et al. 2013). While the surface of QPVA/GO composite membrane looks homogeneous and smooth which might be due to the quaternary ammonium group has been grafted into polymer matrix. Besides, the random distribution of exfoliated GO throughout the electrolyte membrane also leads in dense membrane structure formation which required for electrolyte membrane. From the cross-sectional view in Figure 3(d), the composite membrane exhibit compact structure and high homogeneity, indicate that the unification of QPVA and GO in the composite membrane exist without any holes thus benefits for separation phenomena and reduce the ethanol permeability. Hence, the uniform distribution of exfoliated GO has improve the membrane performance (Xiong et al. 2008; Han et al. 2011).

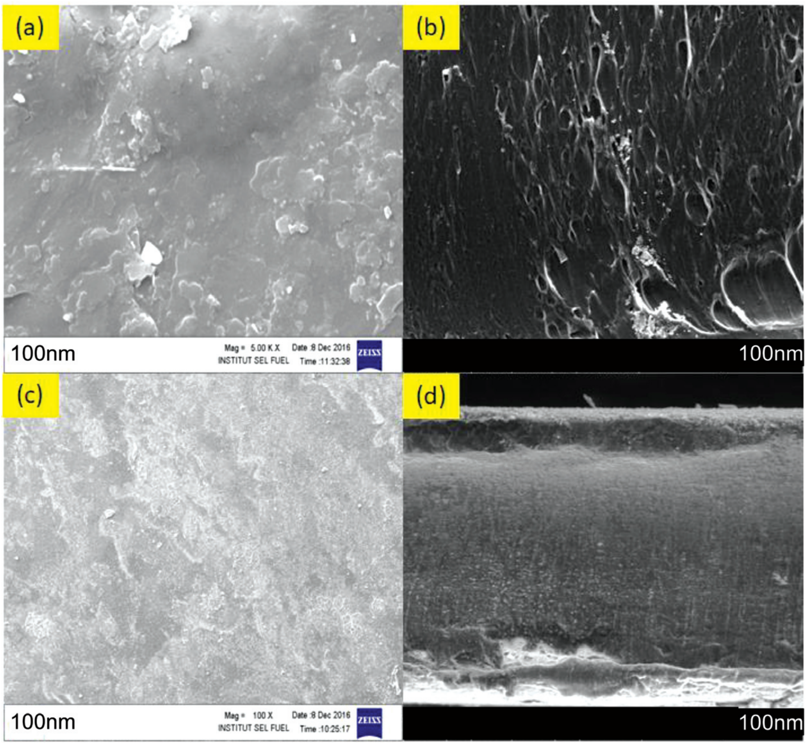

FIGURE 3. FESEM images of (a) QPVA membrane surface (b) QPVA membrane cross section, (c) crosslinked QPVA/GO membrane surface and (d) crosslinked QPVA/GO membrane cross section.

PERFORMANCE OF CROSSLINKED QPVA/GO COMPOSITE MEMBRANE

Figure 4 showed the ionic conductivity and ethanol permeability comparison of the QPVA membrane and crosslinked QPVA/GO composite membrane with 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.% and 10 wt.% loading of GO, respectively. After the crosslinking of membrane, all the membrane were soak in 2 M KOH solution for 24 h before all the samples stored in the deionized water to provide the alkaline electrolyte medium. From Figure 3, all membrane showed very low ethanol permeability which in range of $\times 10^{-7}$ cm^2 s^{-1}. This result prove that PVA based membrane has low fuel permeability due to their properties that low solubility in ethanol and it is the advantage in ethanol crossover issue (Saxena 2004). Subsequently, the modification of QPVA matrix with GO filler also leads in reducing the ethanol permeability.

The increasing of GO content in composite membranes has append the hydrophobic region which play role as blocking effect to hinder the ethanol crossover. This result proved that the exfoliation of GO provide three-dimensional network between GO, GA and QPVA which leads in compact structure formation as shown in FESEM images that show compact and dense structure, which consequently increasing the resistance to ethanol permeability. The lowest ethanol permeability was performed by crosslinked QPVA/GO 10 wt.% composite membrane of 2.2×10^{-7} cm^2 s^{-1} which was seven times better compared to Nafion 117 membrane (1.95×10^{-6} cm^2 s^{-1}) (Leong et al. 2015; Lin et al. 2017).

Figure 4 also present the ionic conductivity of membrane. The introduced ammonium functional group has increased the ionic conductivity of PVA based membrane in range of $\times 10^{-2}$ S cm^{-1} (Yang et al. 2014). Moreover, the introduction of GO loading was also successful enhance the ionic conductivity. The increasing in the ionic conductivity of the crosslinked QPVA/GO composite membrane was directly proportional to the increasing of GO loading from 0.52×10^{-2} Scm^{-1} for 2 wt.% to 1.08×10^{-2} Scm^{-1} for 10 wt.%, respectively. The modification of QPVA with GO loading has provide the oxygenic functional group such as carboxyl, hydroxyl and epoxy which functions as anion pathways for hoping mechanism inside the electrolyte membrane. Besides, the strong interaction between GO, GA and QPVA has form three dimensional network that can hold water molecules in Grottus mechanism (Lin & Lu 2013; Lee et al. 2014; Lin et al. 2017). However, this values is considered lower than Nafion 117 membrane that present conductivity until 7.5×10^{-2} Scm^{-1}.

Figure 5 show the highest selectivity was presented by crosslinked QPVA/GO composite membrane with GO loading of 10 wt.%. This composite membrane was selected for the further studies in single cell of passive alkaline–DEFC. The crosslinked QPVA/GO 10 wt.% composite membranes selectivity was of 5.1×10^4 Ss cm^{-3} which higher than Nafion 117 of 3.84×10^4 Ss cm^{-3}. Nafion 117 performed higher ionic conductivity compared to crosslinked QPVA/GO 10 wt.% composite membranes, but, the ethanol permeability of crosslinked QPVA/GO 10 wt.% composite membranes was more excellent compared to Nafion 117. Therefore, the selectivity of crosslinked QPVA/GO 10 wt.% composite

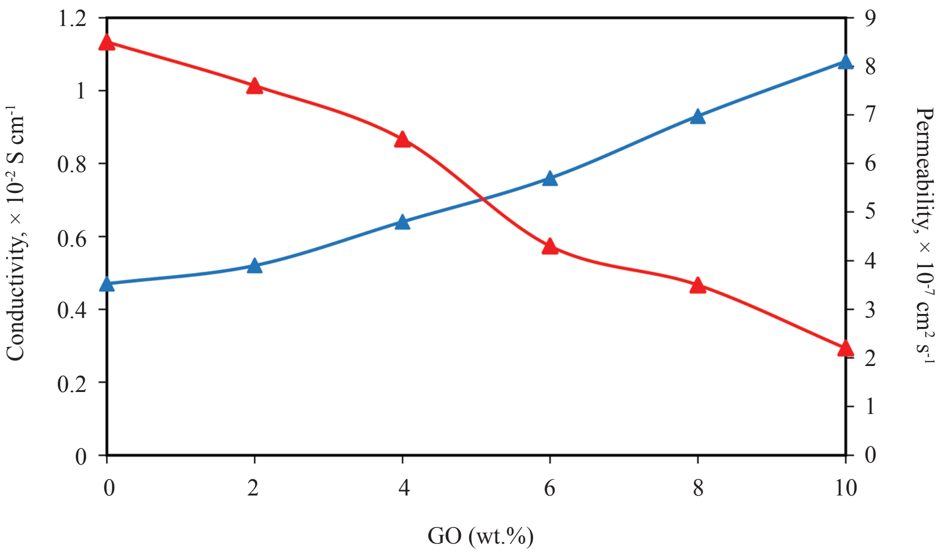

FIGURE 4. Ionic conductivity and ethanol permeability of QPVA membrane and crosslinked QPVA/GO composite membrane with different GO loading (wt.%).

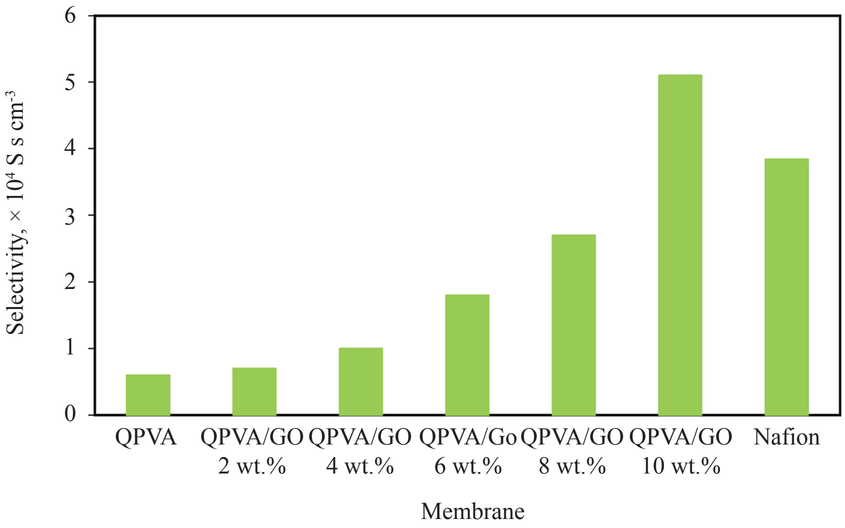

FIGURE 5. Selectivity membrane of QPVA membrane, crosslinked QPVA/GO composite membrane with different GO loading (wt.%) and Nafion 117.

membranes higher than Nafion 117. As a hypothesis, the performance of passive alkaline – DEFC with crosslinked QPVA/GO 10 wt.% composite membranes should be better than Nafion 117 (Thiam et al. 2013).

Figure 6 illustrates the cell voltage and power density vs current density curve of crosslinked QPVA/GO 10 wt.% composite membrane and Nafion 117 for passive alkaline–DEFC at temperature 30°C. Obviously this crosslinked QPVA/GO 10 wt.% composite membrane had reach an open-circuit voltage (OCV) of 0.47 V higher than Nafion 117 only of 0.42 V which attributed to the lower ethanol permeability of composite membrane compared to Nafion 117 (Yang et al. 2012). The value of OCV in this study was similar to the OCV value reported in previous study that used the passive cell for the single test performance which in the range of 0.4V to 0.5V (Esquivel et al. 2008; Zhao et al. 2010; Verjulio et al. 2014). The lower concentration of ethanol and KOH consumption can affect the OCV result. For the best result of OCV, the concentration of ethanol and KOH used passive cell must be higher than 4 M (Yuan et al. 2018). Verjulio et al. (2014) also reported that the OCV will be increased when the fuel concentration used increased.

A maximum power density of crosslinked QPVA/GO 10 wt.% composite membrane was 6.92 mW cm^{-2} higher than Nafion 117 of 5.09 mW cm^{-2}. The higher selectivity factor will give higher cell performance of single cell passive alkaline–DEFC. As a conclusion, this membrane has high potential to be developed in passive alkaline–DEFC. For the future works, we plan to enhance the OH$^-$ conduction with increase the loading of GO filler inside the QPVA matrix in order to increase the ionic conductivity and lowered the ethanol permeability. Optimistically, it leads in better performance of whole alkaline-DEFC systems.

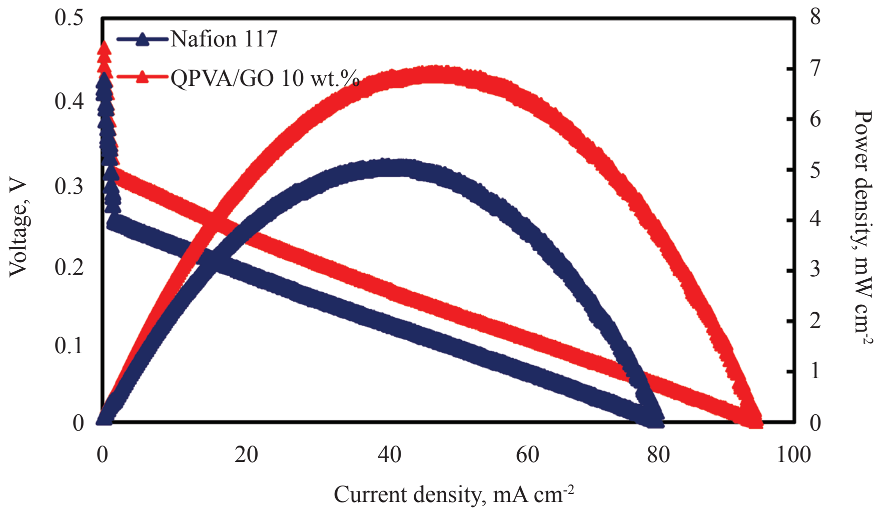

FIGURE 6. Cell voltage and power density vs current density curve of crosslinked QPVA/GO 10 wt.% composite membrane and Nafion 117 (30°C and 2 M Ethanol + 2 M KOH).

CONCLUSION

The crosslinked QPVA/GO composite membrane was prepared for the passive alkaline-DEFC application. The presence of introduced quaternary ammonium group on PVA and existence of GO in polymer matrix was confirmed by FTIR and FESEM analysis. With the formation of three dimensional networking through reaction between QPVA polymer matrix, GO and GA cross-linked agent, the crosslinked QPVA/GO 10 wt.% composite membrane show the highest ionic conductivity which achieve 1.08×10^{-2} S cm^{-1} and their ethanol permeability show great reduction of 2.2×10^{-7} cm^2 s^{-1} compared to the Nafion 117 membranes that only performed about 1.95×10^{-6} cm^2 s^{-1} at room temperature. The membrane with highest selectivity which crosslinked QPVA/GO 10 wt.% composite membrane is further test in single cell part and it achieved maximum power density of 6.92 mWcm^{-2} which higher than Nafion 117 of 5.09 mW cm^{-2} at 30°C. Therefore, the cross-linked QPVA/GO composite membrane has high potential to be apply and performed in DEFCs system in future.

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