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RESEARCH ARTICLE

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The optimization performance of cross-linked sodium alginate polymer electrolyte bio-membranes in passive direct methanol/ethanol fuel cells

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Summary

Consumption of methanol and ethanol as a fuel in the passive direct fuel cells technologies is suitable and more useful for the portable application compared with hydrogen as a preliminary fuel due to the ease of management, including design of cell, transportation, and storage. However, the cost production of commercial membrane is still far from the acceptable commercialization stage. Based to our previous works, the low cost of cross-linked sodium alginate (SA) polymer electrolyte bio-membrane shown the virtuous chemical, mechanical, and thermal characterization as polymer electrolyte membrane in the direct methanol fuel cells (DMFCs). This study will further the investigation of cross-linked SA polymer electrolyte bio-membrane performance in the passive DMFCs and the passive direct ethanol fuel cells (DEFCs). The experimental study investigates the influence of the membrane thickness, loading of catalysts, temperature, type of fuel, and fuel concentration in order to achieve the optimal working operation performances. The passive DMFCs is improved from 1.45 up to 13.5 mW cm^{-2} for the maximum peak of power density, which is obtained by using 0.16 mm as an optimum thick of SA bio-membrane that shown the highest selectivity 6.31 10^4 S s cm^{-3}, 4 mg cm^{-2} of Pt-Ru as an optimum of anode catalyst loading, 2 mg cm^{-2} of Pt at the cathode, 2M of methanol as an optimum fuel concentration, and an optimum temperature at 90°C. Under the same conditions of cells, the passive DEFCs are shown to be 10.2 mW cm^{-2} in the maximum peak of power density with 2M ethanol. Based on our knowledge, this is the first work that reports the optimization works of performance SA-based membrane in the passive DMFCs via experimental studies of single cells and the primary performance of passive DEFCs using the SA-based membrane as polymer electrolyte membrane.

KEYWORDS
membrane, passive DEFCs, passive DMFCs, SA-based bio-membrane

1 | INTRODUCTION

Urban lifestyles today rely heavily on the use of portable devices such as laptops, smartphones, and iPads. The conventional battery application has its limits including the necessity to recharge with external electricity sources many times, small capacity, and narrow locality. An alternative promising power supply for portable electronic device is fuel cells technologies.[1-5] This technology operates via the conversion of fuel in the chemical energy form (eg, hydrogen and alcohols) directly to electrical energy without any combustion process. In addition, this green technology is helpful for reducing air pollution due to the low emission of CO_2 gas.[3,6-8]

Passive direct alcohol fuel cells (DAFCs) use alcohol liquid fuels without involving a reforming system like hydrogen consumption, thus leading to a compact and small-scale structure. In addition, alcohols are easier to handle, transfer and store, and have a higher energy density. The advantages of applying passive DAFCs in portable electronic devices include (a) the potential to offer 10 times higher energy density compared with a rechargeable battery, (b) operation in ambient conditions, (c) quick refuelling and flexibility for system development, (d) the superior specific energy density leads to longer cell life time, and (e) higher efficiency of energy conversion.[2,3,6,9-11] Therefore, these advantages are the large attraction of passive DAFCs in portable electronic devices.

The primary alcohol fuels used in passive DAFCs applications are methanol and ethanol. The energy density of methanol is 6.09 kW h kg^{-1}, and ethanol is 8.0 kW h kg^{-1} that is higher compared with the hydrogen fuel (3.08 kW h kg^{-1}). In addition, both alcohols are easy to handle due to less toxicity and safety for human beings (ethanol is widely used in the medical field). The fuel production is also of low cost, and renewable fuel can be produced via agricultural bioprocesses production form the biomass product form farming, forestry, and community waste via the fermentation process. In addition, ethanol exists naturally leads to increase value added to use the direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs) as portable power supply..[1,10-14]

However, the application of both type DAFCs are still limited due to the sluggish electro-oxidation reaction of fuel on the anodic electrode and fuel crossover issue that caused by the high permeability properties of the commercial Nafion membrane from DuPont. The sluggish reaction of fuel in anode electrode and fuel crossover have cause the reduction of fuel feeding efficiency and degraded the cathode electrode. The mixed potential from fuel oxidation and oxygen reduction on cathode side will generate extra heat and water that leads to the cathodic flooding phenomena. In addition, the production cost of Nafion membrane is expensive, leading to the major limitation of the fuel cells commercialization as portable power sources.[2,11,15-22]

In passive fuel cells system, fuel directly feed via the passive diffusion mechanism to the anode catalyst layer. The fuel may deliver ineffectively and not timely that causes the redox process arise imperfectly. Thus, the polarization of cell voltage will occur and reduce the cell performance. To overcome this issue, the fuel catalytic activity must be maximized to produce the high output of cells through the consumption of high concentration of fuel on the passive fuel cells system. Unfortunately, under the high concentration of fuel consumption on the passive fuel cells system will cause the polymer electrolyte membrane will face the fuel crossover problem. Hence, the loss of fuel through the polymer electrolyte membrane without oxidizing to produce energy and generates extra heat without any power leads to degradation of cells.[22-25] Therefore, the optimum concentration of fuel consumption is the crucial issue to get high performance of passive fuel cell system with the low fuel crossover problem.[1-3,26-28]

There are much of researchers introduced an alternative membrane to resolving the fuel crossover problem due to the commercial Nafion membrane faced high fuel permeability issues. The Nafion membrane modification with additive materials and the low-cost polymeric materials has improved its properties, such as fuel barrier properties, ionic conductivity, and production costs for DAFC applications.[7,8,28-34] Munjewar et al[35] reviewed passive direct DMFCs application from the material development side. There is various modification of Nafion membrane, and alternative polymeric material has been applied in DMFCs such as poly (vinyl alcohol), polybenzimidazole and poly (ether ether ketone). The bio-polymer like chitosan, alginate, and carrageenan also received attention in fuel cell application due to natural available, low cost, ease preparation, ease modification process, etc.[36,37]

Sodium alginate (SA) is extract from brown seaweed. SA is classified as a bio-polymer based on the polysaccharide type. Thus, the consumption of SA is green for the environment due to it being a natural and biodegradable material. It is widely used in various applications, especially in the packaging industry. SA is safe for human being, easier to prepare and higher capability to form thin film membranes. In addition, the lower cost of production of this biopolymer compared with other polymers, especially the Nafion membrane, is an added value for DAFC applications in which it can function as a polymer electrolyte bio-membrane.[38,39] The SA polymer electrolyte bio-membrane has higher hydrophilic properties, which lead to higher swelling properties and degraded mechanical properties. The mechanical properties of this bio-polymer can be enhance with the introduction of a cross-linking agent, such as calcium chloride, and a plasticizer, such as glycerol, which have been shown in our previous study.[39] The SA bio-membrane has high potential to react as a polymer electrolyte membrane in passive DMFCs application. The SA bio-membrane is cross-linked with the usage of 1.5 g of calcium chloride and 3.5 mL of glycerol to form the cross-linked SA bio-membrane polymer. This process enhanced the mechanical properties, thermal properties, highest selectivity, lowest permeability of methanol, and conductivity of proton and showed the performance of 2.99 mW cm^{-2} for the power density.[39]

This paper gives an optimization work for the self-synthesized SA polymer electrolyte membrane through the various experimental study in the passive DMFCs and DEFCs applications. Based on our knowledge, this is the first work that optimizes the performance DMFCs by using the SA bio-membrane polymer via experimental works and the first study that utilizes the SA bio-membrane in passive DEFCs applications as polymer electrolyte membrane. The membrane thickness, anode catalyst loading, fuel consumption (methanol and ethanol) concentration, and temperature of the cell operation effects to the passive DMFCs and the passive DEFCs were investigated the membrane electrode assemble (MEA) via an «in-house» single cell of DAFCs in 4-cm^2 active area.

2 | EXPERIMENTS

Figure 1 shows the lists of experimental works including the half-cell performance (ie, ion exchange membrane, conductivity of membrane, and permeability of methanol), performance of single-cell DMFCs (ie, membrane thickness, anode catalyst loading, methanol concentration, and temperature), and performance of single-cell DEFCs (ie, ethanol concentration and temperature) by using SA bio-polymer for this paper. All the material used such as SA bio-polymer, glycerol, and alcohols were obtained directly from Sigma-Aldrich. The self-synthesis of the SA (5 wt%) polymer electrolyte bio-membrane with external cross-linking by 1.5 g of calcium chloride and 3.5 mL of glycerol was prepared based on our previous study in which the thickness of membrane was controlled (0.12-0.18 mm).[39] Four different thickness of cross-linked SA bio-membrane fabricated from 0.12 to 0.18 mm. For step 1, all the self-performance of membrane was examined with ion exchange capacity test, conductivity of proton, and fuel permeability before the evaluation of single cell to study the effect of membrane thickness to the cell performance. The ion exchange capacity tested with the titration method and calculated with Equation (1). The potentiostat/galvanosat (WonATech, Seoul, Korea) used to examine proton conductivity with the measure the resistance inside the membrane and calculated with Equation (2) with four-probe electrode conductivity cell. The fuel permeability is obtained with the two-compartment cell that sandwich the SA bio-membrane, one side fill with fuel and water in another side to see the permeability activity of fuel in the membrane and calculated with Equation (3). The details methodology was described in our previous work.[39]

$$\textit{Ionic Exchange membrane}, \frac{V_{\text{NaOH}} \times M_{\text{NaOH}}}{W_d}, \tag{1}$$

where V_{NaOH} is the volume (mL) and M_{NaOH} is the mol concentration (M) of NaOH solution. W_{d} signifies the dried membrane weigh after drying at 100°C for 24 hours in the oven.

$$\textit{Proton conductivity}, \sigma = \frac{L}{RS}. \tag{2}$$

where L is the four electrodes length (cm), R is the ohmic resistance (S^{-1}), and S is the membrane cross-sectional area (cm^2).

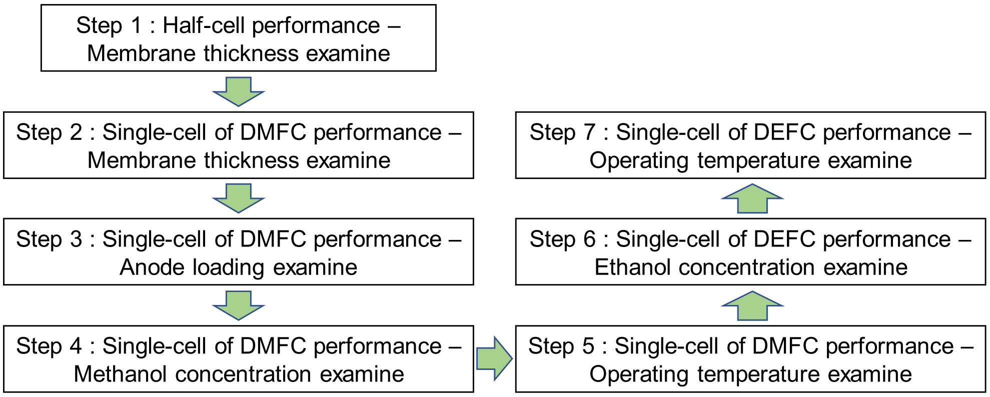

FIGURE 1 The experimental works for the self-synthesis sodium alginate (SA) bio-membrane. DEFC, direct ethanol fuel cell; DMFC, direct methanol fuel cell [Colour figure can be viewed at wileyonlinelibrary.com]

$$\textit{Fuel permeability}, P = \frac{1}{Ca}\left(\frac{\Delta Cb(t)}{\Delta t}\right)\left(\frac{LVb}{A}\right), \qquad (3)$$

where Ca is the fuel concentration, ie, cell A (mol L^{-1}), $\Delta Cb(t)/\Delta t$ is the cell B of fuel molar concentration variation as a function of time (mol L^{-1} s), Vb is the reservoir volume diffusion (cm^3), A is the active area of membrane, and L is the thickness of membrane (cm).

From the half-cell measurement of SA bio-membrane, an optimum membrane will show the high selectivity value with an optimum thickness to be identify. The membrane will prove its potential based on a single-cell test for the second step. The passive DAFCs stack is used for the passive DMFCs and the passive DEFCs testing, as presented in Figure 2A. The active area of MEA is 4 cm^2, the fuel of methanol and ethanol feeding with the atmospheric pressure at anode side and air at cathode side, as presented in Figure 2B. The anode is used Pt-Ru black catalyst (50%:50% ratio) and the cathode with the Pt black, respectively.

Then, an optimum thickness of membrane is used to evaluate the single-cell performance with the best loading of anode catalyst as third step of analysis. The anode catalyst loading is varying from 2 to 8 mg cm^{-2}. All tests are applied the 2 mg cm^{-2} of Pt loading as cathode catalyst. After that, the MEA is developed based on an optimum thickness of SA bio-membrane and anode catalyst loading to evaluate the suitable fuel concentration for the passive fuel cells system with three different concentrations for fourth and sixth steps, 1M until 3M. Finally, the optimum condition of single cell evaluated with different operating temperatures at 30°C, 60°C, and 90°C to enhance the performance of cells for fifth and seventh steps. The methanol fuel is used for earlier testing and followed by ethanol fuel. The WonATech potentiostat/galvanostat electrochemical impedance analyzer (WMPG1000) test station used to conduct all the experimental works.

3 | RESULTS AND DISCUSSION

The results of self-performance cross-linked SA bio-membrane listed in Table 1. All the results shown that the SA bio-membranes with different thicknesses have high ionic exchange capacity for electrolyte membrane applications. The ionic exchange capacity is important to predict the ability of membrane conducting the ionic transfer inside the structure and see the reactivity of membrane with the ionic condition.[4] This condition is useful for obtaining high proton conductivity that exceeds the minimum requirement for use as a polymer electrolyte membrane ($\geq 100 \times 10^{-3}$ S cm^{-1}) in fuel cell application.[10] A thinner membrane has a higher ion exchange capacity and conductivity due to the short pathway for proton transport. However, it is not sufficient to prevent the fuel crossover. Therefore, an optimum membrane thickness is important in order to achieve high conductivity of proton and low permeability of methanol properties that increase the membrane selectivity factor, thus leading to obtain the high performance in passive DMFC application.

The permeability of methanol test was examined with the consumption of 2M methanol. Table 1 shows that increasing the SA bio-membrane thickness effectively reduces the permeability of methanol due to the large fuel obstacle area provided by a thick membrane to obstruct the methanol diffusion. Nevertheless, it also affected the SA bio-membrane conductivity of proton. Therefore, the measurement of selectivity has been calculated to estimate an optimum SA bio-membrane that performs well in permeability of methanol and conductivity of proton.[28] Hence, the 0.16 mm of membrane thickness shows the

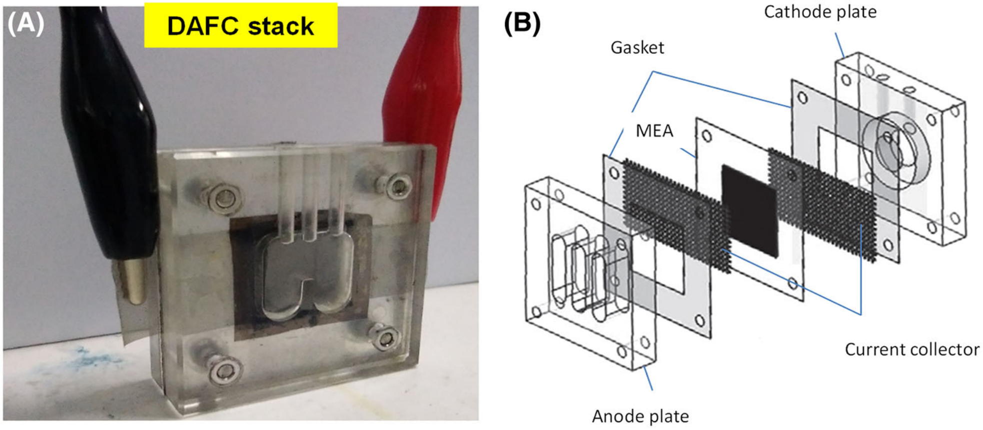

FIGURE 2 (A) The passive direct alcohol fuel cell (DAFC) stack; (B) illustration of the DAFCs stack component [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Performance of self SA bio-membrane with different thickness

Thickness of Membrane, mm	Ionic Exchange Capacity, meq g^{-1}	Conductivity, mS cm^{-1}	Permeability, $\times 10^{-7}$ $cm^2\ s^{-1}$	Selectivity, $\times 10^4$ S s cm^{-3}
0.12	0.41 ± 0.002	12.4 ± 0.21	2.45 ± 0.4	5.06
0.14	0.39 ± 0.005	11.6 ± 0.12	1.98 ± 0.2	5.86
0.16	0.37 ± 0.009	10.1 ± 0.13	1.68 ± 0.3	6.31
0.18	0.34 ± 0.012	9.7 ± 0.15	1.57 ± 0.3	6.18

highest selectivity, which we believe will provide the highest performance for a passive DMFC cell.

3.1 | Performance of the passive DMFCs

The self-synthesized SA bio-membrane is examined in the passive DMFCs. The cell polarization and power density curves are examined to evaluating the SA bio-membrane thickness, loading of anode catalyst, concentration of methanol consumption and cell temperature operation influences on the performance of passive DMFCs.

Figure 3 shows the cell voltage and power density of a passive DMFCs with different thickness of SA bio-membranes. The parameters of the experimental design were 1M methanol and 30°C cell temperature with 2 mg cm^{-2} of Pt-Ru anode catalyst loading and 2 mg cm^{-2} of Pt cathode catalyst loading. The 0.16 and 0.18 mm of the SA bio-membranes are shown 0.72 V open-circuit voltage (OCV), there are represented the lower methanol crossover due to the lower permeability of methanol as presented in Table 1.[39-41] Although, the SA bio-membrane was achieved highest proton conductivity with 0.12 mm thickness. However, the OCV is the lower 0.61 V value and power density only 0.95 mW cm^{-2} by using 0.12 mm membrane thickness because the thin layer of membrane challenged with the high methanol permeability that reduces the performance of the cells.[42] While, the highest selectivity value of the 0.16 mm of the SA bio-membrane is shown the highest performance of the passive DMFCs which achieved 1.45 mW cm^{-2}.

The effects of Pt-Ru catalyst loading were examined on the passive DMFCs performance by using the SA bio-membrane with 2, 4, 6, and 8 mg cm^{-2}, respectively. The parameters of the experimental design were 2 mg cm^{-2} of Pt catalyst as the cathode catalyst, 1M methanol, and 30°C operating temperature with an SA bio-membrane thickness of 0.16 mm. Figure 4 represented the performance of the SA bio-membrane in passive DMFCs with the effect of anode catalyst loading in term of cell voltage and power density. The crucial properties of the electrodes that usually affect their performance are the catalyst loading. To get an optimum of anode catalyst loading for the large and effective active surface area is important for the catalytic activity. The increase of catalyst loading gives the benefit to increase the catalyst active surface area and reduces the resistivity and consequently increases the ionic conductivity of the electrode. Hence, wider active sites with more space are available for the fuel oxidation process on the anode side. The anode overpotential phenomena can also be lowered, and consequently, the passive DMFC performance is enhanced due to the high fuel oxidation activity.[43-45]

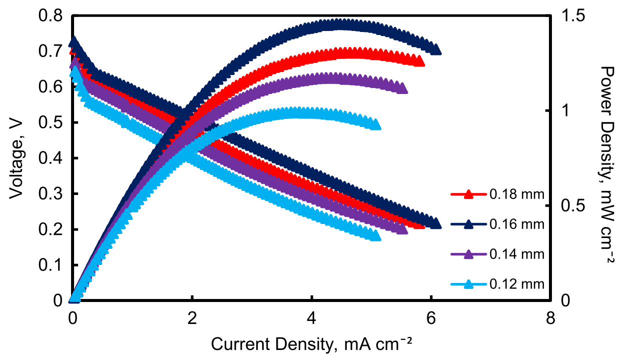

FIGURE 3 Influence of the sodium alginate (SA) bio-membrane thickness on the passive direct methanol fuel cells (DMFCs) performance [Colour figure can be viewed at wileyonlinelibrary.com]

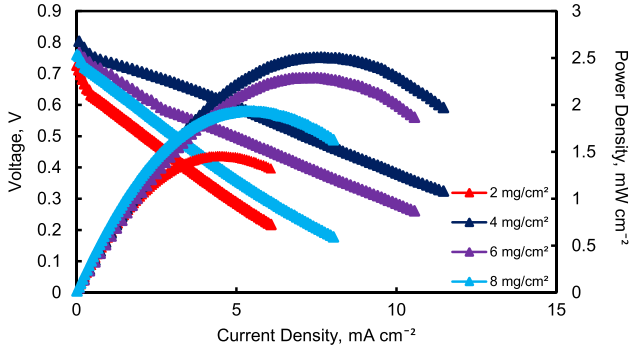

FIGURE 4 Influence of anode catalyst loading to the sodium alginate (SA) bio-membrane on the passive direct methanol fuel cells (DMFCs) performance [Colour figure can be viewed at wileyonlinelibrary.com]

From Figure 4, the increase of the anode catalyst loading showed the increasing OCV value from 2 to 4 mg cm^{-2} and 7.2 to 0.8 V, respectively. This would be caused the dispersion of anode catalyst is homogenous and enough for an optimum MEA development with size 4 cm^2 active area. The higher OCV values shows the reducing the methanol permeability because the high methanol oxidation activity successfully obtained with the 4 mg cm^{-2} anode catalyst loading.[46,47] The increasing of anode catalyst loading more than 4 mg cm^{-2} shown the reduction of OCV value because the high amount of loading catalyst leads to high relative for the surface-active area that causes the agglomerates formed on the electrode. Hence, the methanol catalytic oxidation reaction decreased and reduced the OCV value..[48,49] The increasing of the anode catalyst loading is increased the cell performance from 1.45 mW cm^{-2} to maximum power density 2.51 mW cm^{-2}. The anode catalyst loading with 4 mg cm^{-2} appeared as the optimum level of for this work due to the higher cell voltage and power density performance achieved compared with the other catalyst loadings. The high value of OCV attributed to the well dispersion of catalyst with enough catalyst loading to cover all active area. The high mass transport resistance is sufficient to controlling the rate of methanol reaching the SA bio-polymer and reducing the crossover of methanol. Hence, this condition will reduce the parasite current formation which the methanol oxidizes occurred at the cathode side and attributed the reducing the mixed potential.[3,50]

If anode catalyst loading is over than the optimum level, an overloaded catalyst will cause a limited active surface area due to agglomeration formation and sluggish catalyst catalytic activity. Thus, the cell polarization and power density curves reduced, and this could be from a high internal cell resistance and the ohmic losses, as presented in Figure 4. In addition, an overloaded catalyst will cause a limited active surface area, which is due to agglomeration and a sluggish catalyst.[43,51] Consequently, the cell voltage and power density performance reduced significantly from 0.8 (4 mg cm^{-2}) to 0.74 V (8 mg cm^{-2}) and 2.51 to 1.75 mW cm^{-2}, respectively. Therefore, the anode catalyst loading is a one of imperative factors in controlling the single cell of DMFCs performance. Hence, 4 mg cm^{-2} of Pt-Ru catalyst is an optimum anode catalyst loading is for this work.

The performance of SA bio-membrane on the passive DMFCs studied under the different of methanol concentration to evaluate an optimum fuel concentration with the optimum of SA bio-membrane thickness and loading of anode catalyst, the operating temperature at 30°C and 2 mg cm^{-2} loading of cathode catalyst, respectively. The effects of the concentration of methanol consumption on the passive DMFCs performance are presented in Figure 5. The maximum power density of SA bio-membrane is 3.62 mW cm^{-2} by usage 2M methanol in passive DMFCs. The result confirms that the 2M methanol is appropriated fuel concentration for this cell to optimize the catalyst electrochemical activity and increasing the limitation of current density.

Generally, the increase of fuel concentration in fuel cell stack is improved the performance of cell because the addition of fuel molecules to convert to electrical energy. However, there are limitation levels of fuel concentration to achieve the maximum efficiency of energy conversion and to prevent the fuel crossover phenomena due to the excessive methanol molecules. If the methanol crossover occurs through the SA bio-membrane, the oxidation of fuel will degrade the cathode catalyst layer activity and performance due to the reducing of oxygen reduction activity, creates a mixed potential problem and the occurrence of flood phenomena caused by excessive water production. This problem happened when the increasing the methanol concentration is more than 2M. Additionally, the high-water content at the cathode side that comes from the crossover and water produced due to the cathode reaction may cause a flooding issue, which degrades the passive DMFC performance. Consequently, the power density of cells reduced from 3.62 to 2.92 mW cm^{-2} when the fuel increase to 4M from 2M. Besides, the higher OCV value of SA bio-membrane shows 0.8 V with 2M methanol, which is higher than other methanol concentrations. This is affected by lower fuel crossover phenomena and high catalytic activity of fuel oxidation reaction in an optimum methanol concentration for this cells.[11,52,53] Hence, 2M of methanol is the optimum concentration for this work with the best passive DMFCs performance.

Finally, the operation temperature effect on the passive DMFCs system is evaluated to enhance the SA bio-membrane performance. With the constant parameter of optimum condition the membrane thickness, anode catalyst loading, and methanol concentration, three different

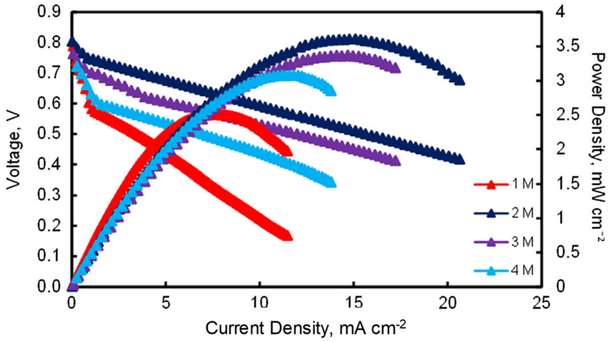

FIGURE 5 Influence of methanol concentration to the sodium alginate (SA) bio-membrane on the passive direct methanol fuel cells (DMFCs) performance [Colour figure can be viewed at wileyonlinelibrary.com]

temperature are tested, as presented in Figure 6. The OCV value of SA bio-membrane performance is improved from 0.8 V at 30°C to 0.84 V at 90°C, and the power density of cells is 3.6 mW cm^{-2} at 30°C, rising up to maximum value of 13.5 mW cm^{-2} at 90°C. There are several reasons for this condition, the increase of operating temperature is led to the improvement of methanol oxidation electrochemical catalytic activity and the oxygen reduction.[51,52] Second, the proton conductivity is increased when the cell operating temperature is increased, thus lowering the ohmic loss and enhancing the cell performance.[10,54] Third, the enhancement of redox reaction is reducing the fuel concentration losses through the SA bio-membrane. Hence, the efficiency of fuel conversion is increased and maximized the fuel consumption to produce energy.[32,34]

3.2 | Performance of the passive DEFC

Ethanol is an emerging renewable fuel that is promising as high energy density, inexpensive, and safe for human beings. The passive DEFCs appear as a power source for microscale portable application due to high energy density compared with methanol, naturally existing and flexible in design of system.[10,12] To evaluate the potential of SA bio-membrane in passive DEFCs system, the cell designed with constant of membrane thickness (0.16 mm), 4 mg cm^{-2} Pt-Ru catalyst as an anode catalyst layer, and 2 mg cm^{-2} Pt catalyst as cathode catalyst layer. The ethanol concentration and operating temperature are changed to get the best performance of passive DEFCs with SA bio-membrane.

The ethanol concentration influenced the SA bio-membrane performance in the passive DEFCs, as presented in Figure 7A. The increase of ethanol concentration is reduced the OCV value of the passive DEFCs from 0.82 (1M) to 0.76 V (3M) because of the excess of fuel molecules on the anode side affecting the fuel cross-over as explained before in passive DMFCs section. The highest power density of the SA bio-membrane in passive DEFCs achieved was 2.89 mW cm^{-2} by using 2M of ethanol. This indicated that the 2M ethanol is an optimum concentration for the passive DEFC in this work. Under the same ethanol concentration and the amount of catalyst loading, the result of SA bio-membrane in passive DEFCs is advanced compared with previous study by Pereira et al[55] who attained 1.33 mW cm^{-2} of power density in the passive DEFC by using a commercial Nafion 117 membrane. The minimum ethanol concentration 1M only gives 1.37 mW cm^{-2} of power density due to low ethanol molecule for the energy production in oxidation catalytic activity in anode side. Meanwhile, over an optimum ethanol concentration, the power density also showed the reduction from 2.89 to 2.14 mW cm^{-2} for 3M ethanol due to the efficiency of fuel utilization usually reduced because of crossover issues.

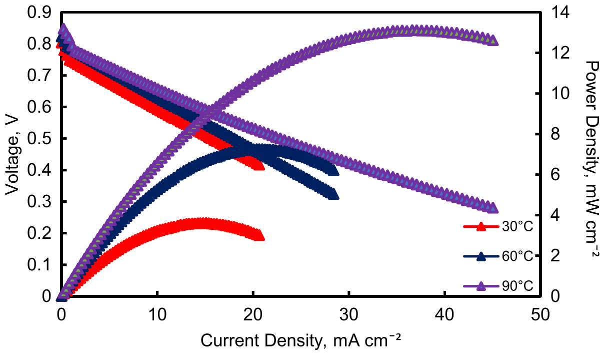

FIGURE 6 Influence of temperature to the sodium alginate (SA) bio-membrane on the passive direct methanol fuel cells (DMFCs) performance [Colour figure can be viewed at wileyonlinelibrary.com]

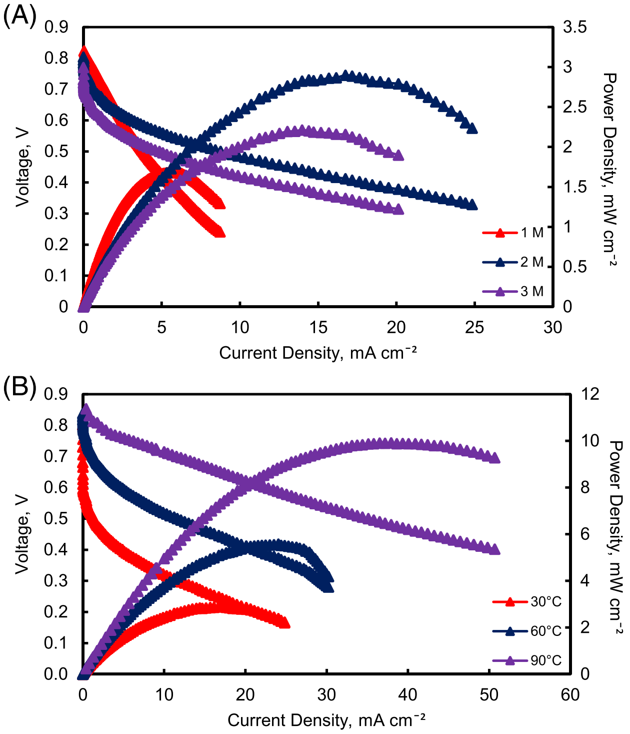

FIGURE 7 (A) Influence of ethanol concentration and (B) influence of temperature to the sodium alginate (SA) bio-membrane on the passive direct ethanol fuel cells (DEFCs) performance [Colour figure can be viewed at wileyonlinelibrary.com]

The performance of SA bio-membrane in the passive DEFCs is low compared in the passive DMFCs at the same condition because the electrochemical activity of ethanol oxidation is more tough compared with methanol oxidation due to the much of chemical bonding in ethanol molecule than to methanol.[33,56] As presented in Equation (4) for methanol oxidation and Equation (5) for ethanol oxidation, the ethanol oxidation is necessary to break more chemical bonding compared with methanol oxidation. Therefore, the electro-oxidation activity of ethanol is low compared with methanol.

$$\text{Anode:} \, CH_3OH + H_2O \rightarrow \; CO_2 + 6H + +6e^-, \quad (4)$$

$$\text{Anode:} \, C_2H_5OH + 3H_2O \rightarrow \; 12CO_2 + 12H + +12e^-. \quad (5)$$

The operating temperature of passive DEFCs is evaluated, as presented in Figure 7B. At 90°C, the SA bio-membrane shows a maximum power density of 10.2 mW cm^{-2} and maximum OCV of 0.85 V. As explained in the passive DMFCs, the increase of temperature leading to enhancement of electrochemical catalytic activity that utilized the fuel in maximum condition and improves the efficiency of energy conversion. The present results indicate that the SA bio-membrane has a good potential to apply as a polymer electrolyte membrane in DEFCs applications. Indeed, this is first attempt work applied the SA bio-membrane in passive DEFCs system and for the future work this membrane is recommend to modify with the any additive to propagates membrane capability.

The SA bio-membrane shown the high potential to utilize in passive DMFCs and passive DEFCs. The high chemical stability makes this membrane allowed the high catalytic activity occurred as discuss in OCV value before. Besides, the high mechanical strength of SA bio-membrane has allowed to this membrane is evaluated in single-cell test performances because actually the bio-polymer based membrane was faced the problem in the MEA production stage due to low mechanical strength of bio-polymer which usually makes the membrane will break during this stage. Furthermore, based on our previous works, the thermal stability of this membrane shown the good result that suitable for fuel cell application and it proved that the passive single cell of this work can be operated until 90°C without failure.[39] The cross-linked and plasticized process through this self-preparation membrane contributed to enhancing the potential of this membrane in passive DMFCs and passive DEFCs, as presented in Figure 8.

Consequently, the SA bio-membrane has high potential to be applied in passive DAFCs for the portable device application. The portable device application such as laptop, table lamp, and hearing aids operated below than 60°C, the usage of methanol and ethanol are suitable due to easier for handling and safe for human's consumption with low concentration of fuel consumption and there are remains as liquid form at the range of operating temperature.[3,57] Towards the commercialization stage, the SA bio-membrane is necessary to further the

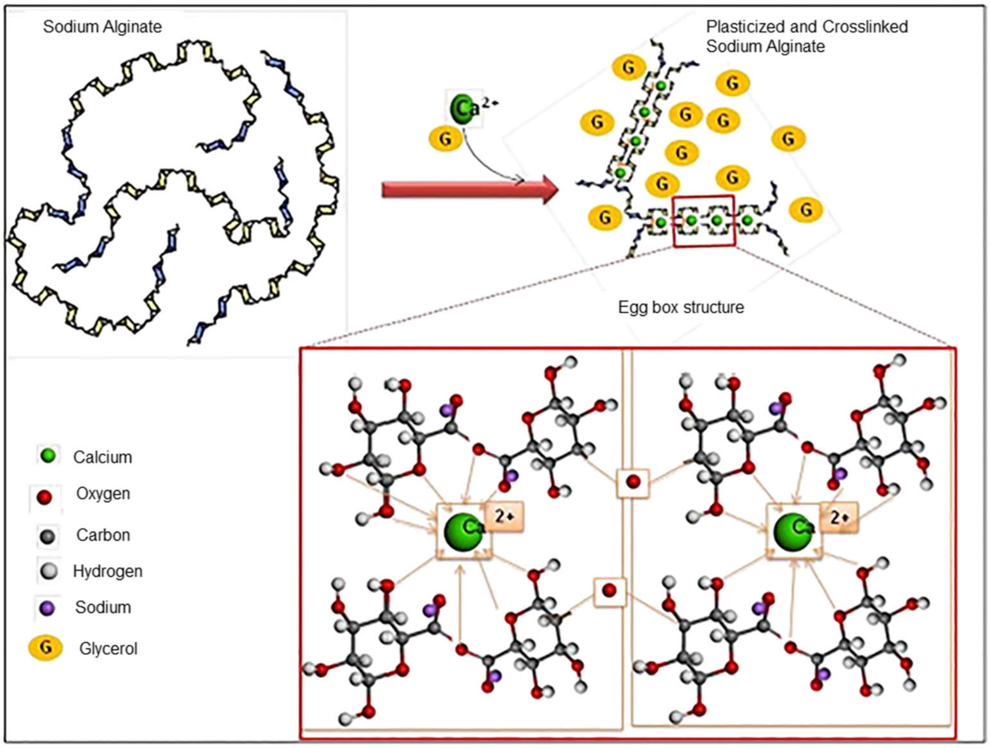

FIGURE 8 Illustration of the inner structure of cross-linked and plasticized sodium alginate (SA) bio-membrane[39] [Colour figure can be viewed at wileyonlinelibrary.com]

investigation process to improve in term of the durability of membrane and maintain the performance. The modification with the other low-cost synthetic polymer like poly (vinyl alcohol) or the additional of additive materials such as graphene-based reinforcement, boron nitrite nanosheet, and carbon nanotubes drive to enhanced the conductivity, permeability, mechanical, and thermal properties of SA bio-membrane is believed able to expand the SA bio-membrane ability to various industries such as household appliance and transportation.

4 | CONCLUSION

Based on previous works, the SA bio-membrane has good potential to be applied in the passive DMFCs.[39] The high selectivity of the SA bio-membrane is essential to ensure that the great performance of the passive DMFCs and DEFCs has proven. This parameter can be obtained through the equilibrium condition between the membrane conductivity activity and fuel permeability. A thinner membrane is given the higher proton conductivity. However, it leads to higher fuel permeability. Therefore, the ideal point of proton conductivity and fuel permeability is crucial for obtaining a higher selectivity. From the result, an optimum membrane thickness is approximately 0.16 mm, which shown high selectivity and achieved high power density 1.45 mW cm^{-2} compared with the other thickness. Besides, understanding the effects of different designs and operating parameters is important to achieving the higher single-cell performance. The loading of anode catalyst, concentration of fuel, type of fuel, and operating temperature were studied in this work. Based on the result, an optimum loading of anode catalyst to give the high catalytic activity is 4 mg cm^{-2} which adequate for 4-cm^2 active area; 2M methanol and 2M ethanol are an optimum fuel concentration for passive fuel feeding system. A low fuel concentration reduces the energy density, and high fuel concentrations will generate higher ethanol crossover, lowering the fuel cell performances. The high operating temperature is helpful to increase the cells performance due to excellent of the kinetic activity of fuel and oxidant to achieve high redox activity. In this work, a maximum power density of the SA bio-membrane in passive DMFCs is 13.5 mW cm^{-2} with 0.84 V of OCV value and 10.2 mW cm^{-2} in the passive DEFCs. An optimum design of single-cell conditions is obtained using a 0.16-mm-thick SA bio-membrane, Pt-Ru as anode catalyst (4 mg cm^{-2}), Pt as cathode catalyst (4 mg cm^{-2}), and 2M of fuel concentration (methanol and ethanol) at 90°C. For the future work, the stability and durability test will be performed to further the potential of SA bio-membrane in passive DAFCs application.

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