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EFFECT OF TEFLON AND NAFION LOADING AT ANODE IN DIRECT FORMIC ACID FUEL CELL (DFAFC)

M. S. MASDAR[1,2,*], N. A. PUAAD[2], N. M. ASLAM[1], S. K. KAMARUDIN[1,2]

[1]Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[2]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia,43600 Bangi, Selangor, Malaysia
Corresponding Author: shahbud@ukm.edu.my

Abstract

DFAFC has extensive hydrophilic nature and will cause problems in a limited mass transport in the anode side of electrode. Thus, the microporous layer (MPL) of DFAFC needs a different in structure and morphology compared with that of PEMFC and DMFC because it will directly affect the performance. Therefore, in this study, the formulation of anode's MPL has been investigated by varying the amount of Teflon and Nafion. Different loading of Teflon in MPL and Nafion in catalyst layer, i.e., 0 to 40% in weight, were used to fabricate the anode's DFAFC. The characteristic of MPLs and anode (MPL with catalyst layer) such as surface morphologies and resistivity, i.e., electrical impedance, have been analyzed using field emission scanning electron microscopy (FESEM) and contact angle measurements as well as electrochemical impedance spectra (EIS). Meanwhile, the performance of fabricated anode was measured using cyclic voltammetry (CV) technique with a half cell of DFAFC. From the result, it was obtained that the optimum content for both Teflon and Nafion on anode's DFAFC was 20 wt% as shown in a highest electro-activity in electrode. The single cell DFAFC with optimum MEA formulation showed a good performance and hence, it is possible to apply the electricity power for electronic devices.

Keywords: Microporous layer, Electrode, Teflon, Nafion.

1. Introduction

Nowadays, other fuel cell types such direct liquid fuel cell (DLFC) including direct methanol fuel cell (DMFC), and direct formic acid fuel cell (DFAFC) have been focused in research and development [1]. For DFAFC, formic acid is one of the liquid fuels that can operate at ambient temperature and could maintain its performance under the certain fuel concentrations. It also has a low rate of fuel crossover through electrolyte membrane compared to DMFC. Therefore, the formic acid fuel at high concentrations can be used to increase the DFAFC performance and improve the mas transport limitation at anode [2]. In addition, it also has a faster electrochemical oxidation compared to methanol [1, 2].

In a membrane electrode assembly (MEA), microporous layer (MPL) serves as an electrical conductor which transport electron through the catalyst layer (CL) and assisting in the management of water [3, 4]. MPL is supported by carbon paper or carbon cloth that acts as diffusion media (DM). The DM plays an important role in the passage of reactant towards the catalyst layer and water/ heat/ gas product removal towards the flow field channels [5]. In a CL, Nafion ionomers used both as a proton conductor and as a binder to facilitate the extension of the three-dimensional reaction zone and an increase in catalyst utilization. Too low Nafion loading will lead to a poor contact between the electrolyte and catalyst particles and thereby a poor cell performance. While at very high Nafion content would cause a decrease in cell performance due to blocking of the catalyst sites, blocking of the electrode pores, reduction of gas permeability and increase in mass transfer resistance [6].

MPLs are usually treated with varying amounts of hydrophobic Teflon or polytetrafluroethylene (PTFE) for the purpose of water management as mentioned earlier. This can change the thermal resistance of a MPL and, consequently heat management [5]. Several studies on the performance of PEMFCs have been implemented by optimizing the diffusion media properties focused on the hydrophobicity and the surface area of carbon black used in MPL. For instance, a few studies performed to date to measure and model the thermal conductivity of gas diffusion layers (GDLs) treated with teflon. Khandelwal and Mench [7] and Burheim et al. [8] reported that teflon treatment leads to a reduction in thermal conductivity from ambient room temperature to higher temperature. On the other hand, the models developed by Yablecki and Bazylak [9] and Bahrami et al. [10] both predict a noticeable increase in thermal conductivity with increasing teflon content with a similar room conditions.

However, only a few studies have been reported to investigate the effect of the anode diffusion media on the performance of direct liquid fuel cells especially for DMFC [11-14]. For instance, Nordlund et al. [11] studied the effect of adding teflon to the anode of a DMFC. The authors postulate that when 10% teflon was added to the BL, the performance was lowered and with increasing teflon content till 50%, the performance increased progressively. Oedegaard et al. [12] found that adding teflon to the anode catalyst layer led to better gas transfer in the liquid phase and had a positive effect on the performance of a DMFC. They postulate that 15% teflon content facilitates ideal DMFC performance. Based on our literature, no paper reported the effect or optimization of Teflon at anode's DFAFC. We expect that the structure of the anode must be different due to different in liquid fuel characterization and their electro-oxidation (methanol versus formic acid. Eventhough, studies were for the PEMFC and DMFC, the qualitative results can still apply to DFAFC.

In the case of CL, several studies have involved the optimization of Nafion loading and the development of novel preparation methods for the MEAs including PEMFC, DMFC as well as DFAFC [14-17]. For instance, in PEMFC, Boyer et al. [14] reported that the proton conductivity of a catalyst layer prepared with Nafion solution is directly proportional to the volume fraction of Nafion within the catalyst layer. Moreover, Chenitz and Dodelet obtained that equal volumes of Nafion and catalyst of palladium gave the best performance in DFAFC [16]. However, Thomas and Ren [17] obtained that there are benefits having lower Nafion loadings in the catalyst layer. They conclude that the lower Nafion loading decreases the thickness of the catalyst layer, hence could allow more catalyst particles to fill in contact with the membrane for adequate proton conduction. Moreover, the effects of DFAFC operating conditions have been studied by other researchers. Zhu et al. investigated the effect on the cell of formic acid concentrations from 1 to 10 M, revealing that a concentration of 3 M formic acid generates the highest maximum power density [1]. Ha et al. investigated the effect of a larger range (3–15 M) of formic acid concentrations for a passive DFAFC and found that the optimum concentration is 10 M [18].

In DFAFC point of view, on the basis of the information discussed above, researches focus on the optimization of Nafion loading for preparing CL rather than the teflon loading in MPL. Moreover, based on our review, we could not find any report focus in details the combination of Teflon and Nafion in anode and study the effects of these materials to the anode's structure and DFAFC performance. Therefore, here we present our work on the optimization of Teflon's loading in MPL and Nafion's loading in CL from 0 wt% to 40 wt% for electrode formulation. The effect Teflon's and Nafion's loading at anode will be discussed on the basis of anode's characterization and electrochemical performance of electrode in half cell and real single cell DFAFC.

2. Experimental

2.1. Fabrication of anode's diffusion layer and MEA

For the anode microporos layer (MPL) and MEA preparation, similar and conventional procedures by previous researchers were used. The homogenous carbon ink was prepared by ultrasonication the carbon with carbon black, CB (Cabot), isopropyl alcohol and different loading of Teflon from 0 wt% to 40 wt%. Then, the ink was coated on the backing layer of carbon paper (Toray carbon) with 2 mg cm^{-2} carbon loading. The MPL was dried in oven at 80 °C about an hour. For a cathode's MPL, carbon paper with 20 wt% Teflon and 2 mg cm^{-2} carbon loading were used throughout the study.

Palladium (Pd) black (Alfa Aesar) and Platinum (Pt) black (Alfa Aesar) were used as catalysts for the anode and cathode, respectively. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and Nafion® solution (Wako Pure Chemical Industries, Ltd.) For the anode, the catalyst ink was varied by varying the Nafion loading from 0 wt% to 40 wt%. Pd ink was coated with 4 mg cm^{-2} loading of on the prepared MPL. For the cathode, Pt ink was coated on prepared MPL with fixed Nafion loading at 20 wt% and the catalyst loading at 4 mg cm^{-2}. The MEA was then fabricated by sandwiching the electrolyte membrane, Nafion 117 (DuPont) between the anode and cathode and hot pressing them at 135 °C and 5 MPa for 3 minutes. The active area of the electrode was 4.84 cm^2.

2.2. Characterization of anode's electrode

The characterization studies provide a physical and an electrochemical result for each of developed electrode that influences the performance of DFAFC. The characterization of physical properties was carried out by measuring the hydrophobicity level, field emission scanning electron microscopy (FESEM) image morphology and electrochemical impedance. The physicochemical properties and surface morphology of the electrode were observed with a contact angle measurement (KRÜSS Drop Shape Analysis by KRÜSS GmbH, Germany) and FESEM (Supra 55VP by ZEISS, Germany), respectively.

Contact angle measurements were done by using low, i.e., 1 M and 2 M and high, 10M and 15M, formic acid concentrations. SEM image were taken before and after the catalyst layer were coated to the GDL. Drop shape analysis was used to measure contact angles between water or liquid solution and the carbon backing layer to evaluate the hydrophobicity properties. The impedance spectra were recorded in the constant potential mode at 0.4 V and maximum current at 0.01 A by applying a frequency from 10, 000 to 0.1 Hz. A half-cell technique (similar technique for cyclic voltammetry, CV) was used using electrochemical instrument (Metrohm Autolab) and analysis software of NOVA 1.7 from Netherlands.

2.3. Measurement of electrode performance and single cell DFAFC

The electrochemical reaction for half-cell as well as single cell DFAFC was measured and studied based on cyclic voltammetry (CV) and current – voltage (I-V) testing, respectively. Both tests were used WonATech potentiostat (WMPG1000, Korea). CV test involved three electrodes which are Ag/AgCl as reference electrode and platinum wire as counter electrode. The working electrode used for the measurement was the prepared anode electrode with different Teflon and Nafion loading. For the electrolyte of the half-cell reaction, 0.5 M H_2SO_4 was added to 0.5 M formic acid to maintain a pH and stabilize the reference electrode potential. The scan rate for this electrochemical measurement was set at 50 mV s^{-1}, which in the range of 0 to 1 V.

For real performance of DFAFC, a single cell with optimum MEA, i.e., optimum Teflon and Nafion loading with 20 wt% loading was fabricated and operated passively by injecting a formic acid solution at 8 ml with a certain concentration from 2 M to 12 M into the reservoir under ambient conditions. The electrochemical performance, i.e., current-voltage (I-V), of the cell was carried out by using potentiostat/galvanostat (Wonatech WMPG 1000, Korea) by dropping the voltage at the rate of 1 mV s^{-1} from OCP until 0 V.

In order to activate the MEA for single cell DFAFC testing, the activation process was implemented and the steps were similar to that Rejal et al. [19] using hydrogen gas (H_2) and air. The MEA was conditioned initially within the test fixture at 70 ^oC under the H_2 - air fuel cell operating mode for 1 h with constant cell voltage at 0.6 V. The H_2 flow rate was fixed to 600 mL min^{-1} at anode while air was fixed as 1200 mL min^{-1} at cathode; both streams were humidified at 70 ^oC prior to entering the cell. Cell potential was controlled by a fuel cell testing electric load (Paxitech, France).

3. Results and Discussion

3.1. Characterization of anode

3.1.1. Surface morphology

Figure 1 shows the morphology of anode for different weight of Teflon in MPL with constant 5 wt% Nafion loading in catalyst layer. Based on Fig. 1, it can be observed that different structures at the surface were found at different loading of Teflon in MPL. By comparing the pores in each MPL surface, the sizes of the pores are getting smaller with increasing weight content of Teflon. It is clearly visible on the weight content of 0 wt% to 20 wt% as shown in Fig. 1(a) to (c). A similar observation was found by Labato et al. [20]. They obtained that pore fraction decreases as the Teflon content is increased. It means that the mean pore size will decrease with the Teflon content, as shown the situation in Fig. 1(a) to (c). This also can be explained with Teflon function as hydrophobic agents, which generally works in improving the water management by decreasing the flooding phenomenon.

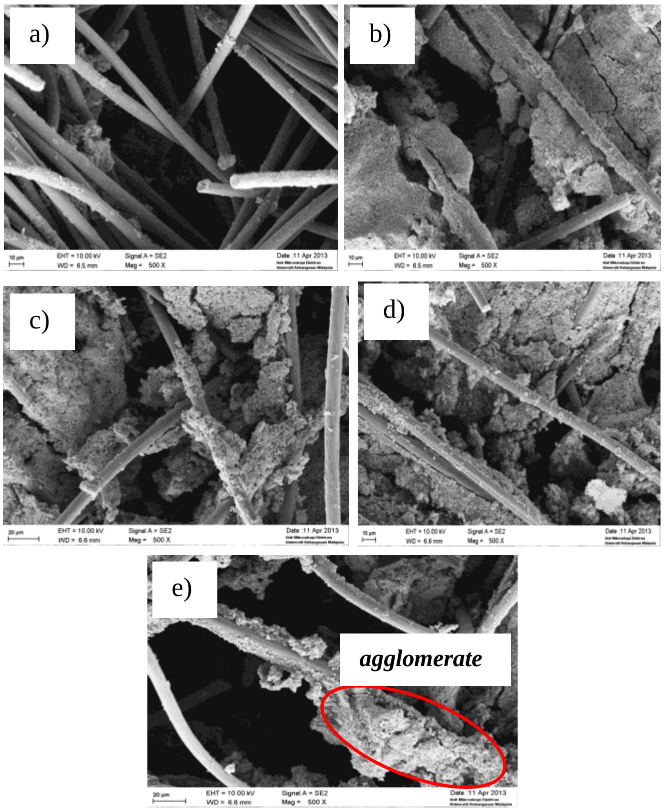

Fig. 1. Morphology of anode surfaces at 500x magnification for different Teflon's loading, a) 0 wt%, b) 10 wt%, c) 20 wt%, d) 30 wt%, e) 40 wt%, with constant Nafion loading at 5 wt%.

In the case of Fig. 1 (d), the morphology of 30 wt% Teflon's loading looks similar to that 20 wt% of Teflon and shows the homogeneous distribution of MPL and catalyst layer in electrode. Meanwhile, the sizing of pores at electrode was observed in increase for 40 wt% loading. It could be due to the agglomerate of Teflon at high loading during MPL preparation, and hence result in non-uniform distribution of MPL as shown in Fig. 1 (d). This non-uniform and high loading of Teflon could be increased the mass transport resistance encountered by the fuel. Hence, it will lead to mass transport limitation problem especially in anode.

Meanwhile, Fig. 2 shows the morphology of anode for different loading of Nafion in catalyst layer with optimum 20 wt% Teflon in MPL. From the figures, it was observed that there are no significant different in morphology surfaces with different Nafion loading. Therefore, it can be concluded that for the morphology surface, the homogeneous distribution of electrode and its structure are significantly influences by the Teflon rather than Nafion. It's could be due to the different properties of both Teflon and Nafion material, i.e., molecular structure, density, etc.

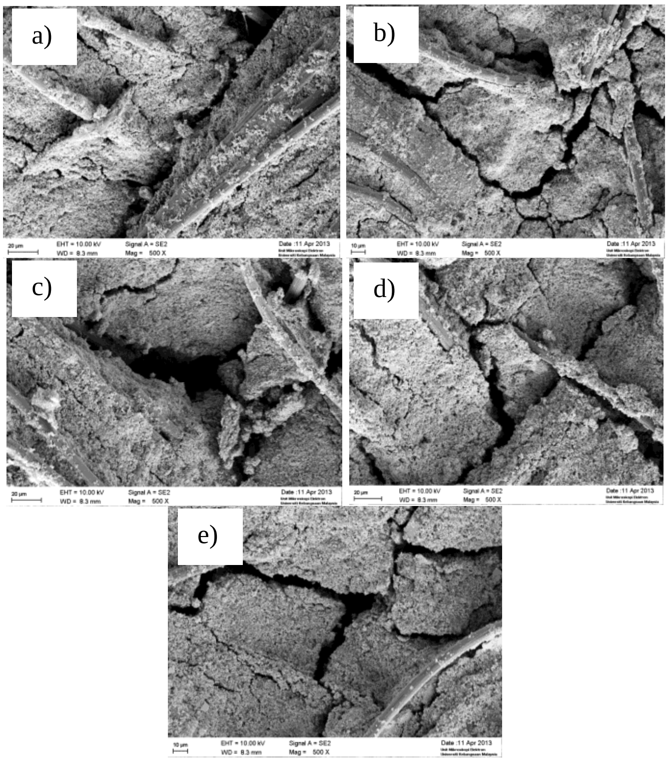

Fig. 2. Morphology of anode surfaces at 500x magnification for different Nafion's loading a) 0%, b) 10%, c) 20%, d) 30%, e) 40%, with optimum Teflon's loading at 20% in weight.

3.1.2. Hydrophobicity

The optimum hydrophobicity level is needed to ensure a good MPL structure for a good fuel mass transport, water and heat management and affect in improving the DFAFC performance. The hydrophobicity characteristic of anode was analysed by measuring the contact angle on the electrode surface. Figure 3 shows the hydrophobicity level at different loading of Teflon in MPL, Fig. 3(a), and Nafion in catalyst layer, Fig. 3(b), from 0 wt% to 40 wt% using different concentration of formic acid. From the figure, it was clearly shown that different level of hydrophobicity was obtained at different loading and different formic acid concentration concentrations. In case of effect of Teflon loading at constant 5 wt% of Nafion in catalyst layer (Fig. 3(a)), the contact angle values varied from $62^0 \pm 2^0$ to $118^0 \pm 2^0$ which depends on formic acid concentration and Teflon's loading in MPL.

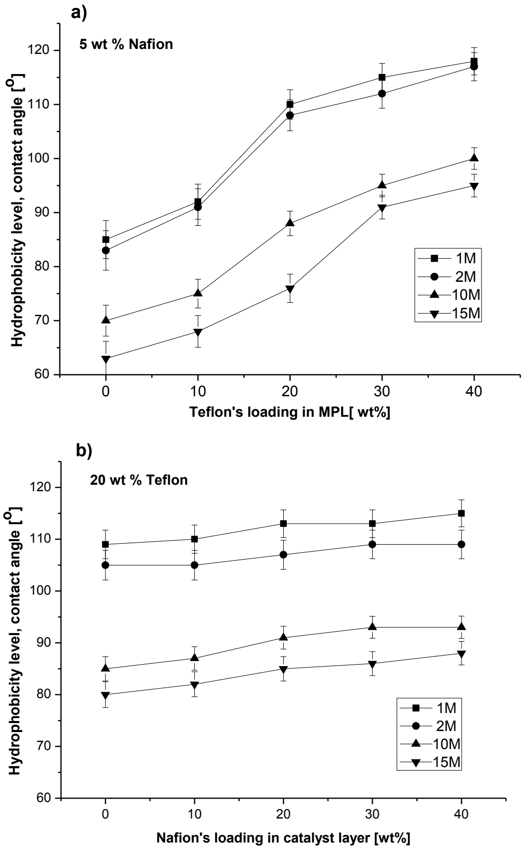

Fig. 3. Hydrophobicity level at anode with different materials loading; a) Teflon; b) Nafion, using different formic acid concentrations.

In general, the contact angle increased with the increasing of Teflon's loading from 0 to 40 wt% and decreasing with formic acid concentration from 1 M to 15 M. The increasing of hydrophocity level with Teflon loading has been expected as results in the morphology of anode structure as shown in Fig. 1. By increasing the Teflon loading, the pore size of electrode would be decreased, and hence it would increase the contact angle and hydrophobic property.

A similar tendency of contact angle decreased with the increasing in the concentration of formic acid was also obtained by Uhm et al. [5]. Nevertheless, the values of the contact angle with greater than 90^0 (as shown in Fig. 3) indicate that the hydrophobic surface layer in the backing layer. Chen et al. [21] listed a static contact angle between 0º to 90º was hydrophilic while contact angle above the 90º was hydrophobic. This is probably due to the nature of formic acid with hygroscopic characteristics and hydrophilic properties. On the other hand, it was suggested that the mass transport limitation phenomena in the MPL and catalyst layer occurred in the presence of hygroscopic characteristics at the high formic acid concentrations.

In case of different in Nafion loading (Fig. 3 (b)), there are no significant changes in hydrophobicity level as shown in almost constant contact angle value with Nafion loading at similar formic acid concentration. It can be also related with the morphology of electrode in Fig. 2. Since, the structure of electrode, i.e., pore size, is almost similar for each Nafion loading, it can be expected that the hydrophocity level is almost constant with Nafion loading. However, the hydrophocity level decreased with increasing the formic acid concentration. This tendency is similar to that Teflon loading as shown in Fig. 3(b) which is due to the hygroscopic characteristics of formic acid as mentioned previously.

3.1.3. Electrochemical Impedance

The impedance of electrochemical analysis was implemented to ensure a good characterisation of the resistance level in anode with different loading of Teflon and Nafion. As a result, Nyquist plot was recorded with the electrochemical resistance magnitude. Figure 4 shows the Nyquist plots of impedance data measured at constant 0.4 V under half-cell of DFAFC with different loading of; a) Teflon, and; b) Nafion, using frequency at 10,000 to 0.1 Hz. For all cases in Fig. 4, semi-circles profiles show almost the same impedance behavior. These profiles were almost similar to that previous reported [22, 23]. Based on Fig. 4, it shows that the diameters of the arcs are affected by the Teflon and Nafion loading. In general, the arcs diameters show in Fig. 4(a) are bigger than in Fig. 4(b) except for 0 wt%. These results could be due to the different in Nafion loading, i.e., too low Nafion loading at 0 and 5 wt%, which Nafion can be contributed to enhance the proton conduction, and hence reduce the electrochemical resistance.

Moreover, as can be seen in Fig. 4, at 0 wt% of Teflon and Nafion, the diameter shows a biggest value almost 3 to 4 times compared to other Teflon and Nafion loading. It was obtained that the diameter increased with the increasing of Teflon or Nafion from 10 wt% to 40 wt% loading as shown in Fig. 4 except for 20 wt%. It can be easily understood that the electrochemical resistance increase with the increasing of Teflon and Nafion loading. However, at 20 wt% loading, the diameter shows the lowest value which means a lowest electrical resistance than others. Therefore, it can be concluded that 20 wt% of Teflon and Nafion are the optimum loading for preparing the electrode. Meanwhile, the electrode preparation without Teflon and Nafion indicate very poor proton conduction.

Based on all samples analysed, it was found that the optimum weight percentage of Nafion is at 20%, for which it shows the best performance because it have the smallest resistance value and the smallest of Nyquist plot compared to other gas diffusion electrode (GDE). Hence, it results in the increase in conductivity as well helping in reducing the problem of mass transport that occurred in DFAFC.

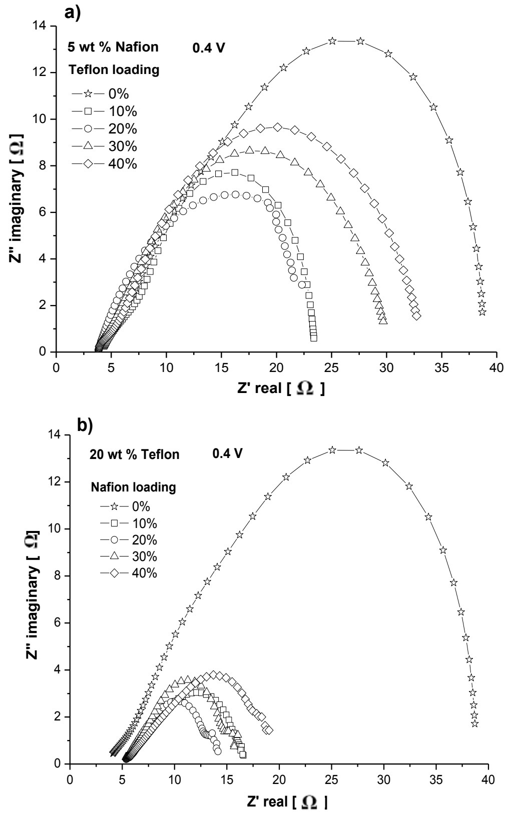

Fig. 4. Nyquist plot for different loading of; a) Teflon; b) Nafion, at anode using constant 0.4V and frequency from 10,000 to 0.1 Hz.

In other point of view, for higher loading of Teflon and Nafion, i.e., 40 wt%, the impedance profiles could be influenced by the limitation of mass transport in the anode DFAFC [23, 24] and can be related the electrode structure as shown in Figs. 1 and 2. The agglomeration tendency at high loading of material, especially for Teflon, would increase the thickness of electrode and increase the electrical resistance. At optimum 20 wt% loading, the morphology characteristic provides a very compact surface structure thus decreasing the electrical resistance at the electrode, and hence increasing the conductivity of the sample.

3.2. Electrode performance

3.2.1. Anode's electro-activity

Cyclic voltammetry (CV) analysis is one of common technique that been used to determine the electro-activity of electrode. A half-cell technique was used to implement CV analysis from 0V to 1.0V. Figure 5 shows a graph of CV profiles at different loading of; a) Teflon; b) Nafion. As shown in Fig. 5, it was obtained that the profile showed a relatively reversible peak in this CV analysis.

A similar profile trend was reported by previous researchers [6, 23]. The anodic peak varied from 0.6 V to 0.7 V for both cases Teflon and Nafion loading. For instance, the anodic peaks of 0 wt%, 30 wt% and 40 wt% were almost similar at 0.6 V, while 20 wt% shows peak at 0.65 V. The result clearly demonstrates that the 20 wt% loading has a strong electro-catalytic characteristic towards the oxidation of formic acid as shown in highest current density at 23.4 mA cm^{-2} and 24.5 mA cm^{-2} at anodic peak for Teflon and Nafion, respectively. These highest electroactivity at 20 wt% loading of Teflon and Nafion can be expected since the EIS results show a lowest resistance using this loading.

As mentioned previously, it was suggested the morphology structure of electrode influenced the characteristic of electrochemical performance. Based on this study, it can be concluded that the electrode with Teflon and Nafion loading at 20 wt% is the most optimal for the electrode in DFAFC and also showed good performance in each analysis such as morphology structure, electrochemical resistance and electro-activity. Therefore, a real single cell DFAFC was fabricated with MEA using optimal Nafion and Teflon loading and then, the DFAFC performance was tested using different fuel concentrations.

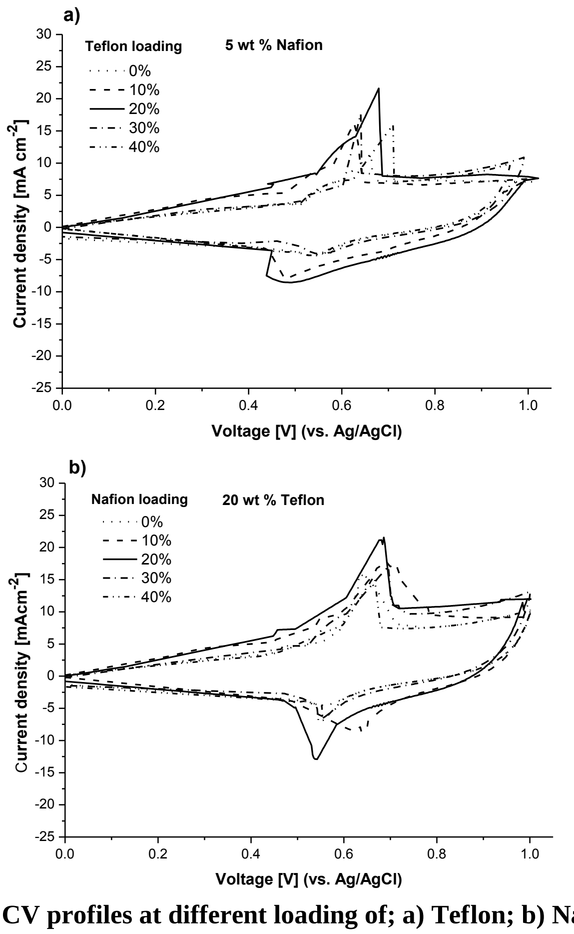

Fig. 5. CV profiles at different loading of; a) Teflon; b) Nafion; in half-cell preparation from 0 to 1 V in 0.5M H_2SO_4 + 0.5 M formic acid.

3.2.2. Single cell DFAFC performance

Figure 6 shows the DFAFC performance using optimum 20 wt% loading of Teflon and Nafion with different formic acid concentrations from 2 M to 12 M at ambient room temperature; a) polarization curve, b) power-current profile. In general, the polarization and power-current show a similar profile for each fuel concentration and the performance of DFAFC was depended on the fuel concentration.

As noted from Fig. 6(a), the open circuit voltage (OCV) was obtained in the range of 0.57 V to 0.64 V. The OCVs decreased with increasing formic acid concentrations from 2 M to 12 M, i.e., the OCV at 2 M and 12 M obtained at 0.64 V and 0.57 V, respectively. This tendency was similar to previous study by Zhu et al. [1]. It was suggested that the decrease in OCVs with formic acid concentrations due to the mixed potential caused by fuel crossover, i.e., OCVs decreased with increasing fuel concentration as shown in Fig. 6(a). The flux of formic acid crossover would increase with the increasing of formic acid concentrations, and hence decreased the OCVs.

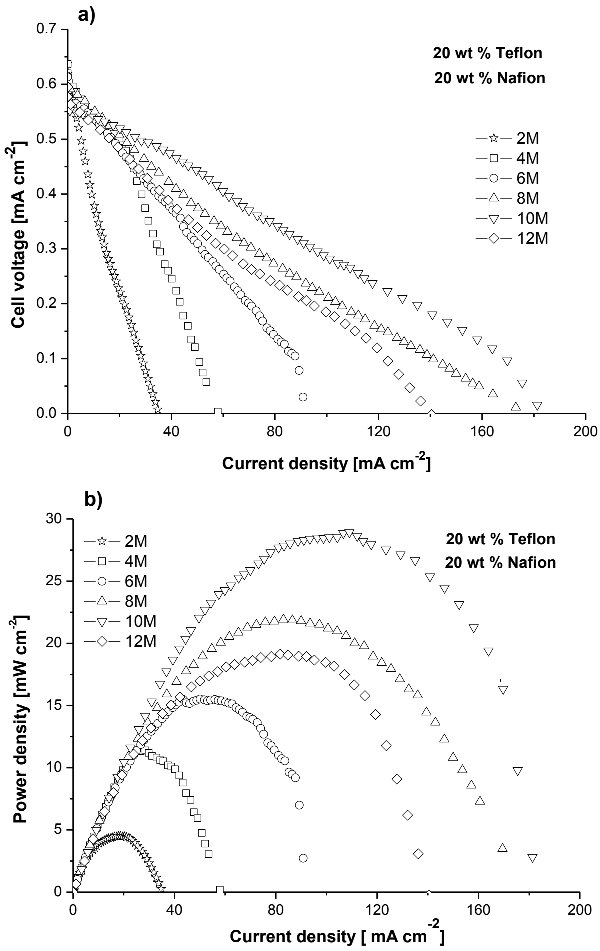

Fig. 6. Single cell DFAFC performance; a) Polarization curve; b) Power profile; at different formic acid concentration.

On the other hand, the maximum power increased with the increasing of the methanol concentration from 2 M to 10 M before it decreased at 12 M. It can be seen that the optimum concentration for DFAFC is 10 M. The performance drop after the optimum concentration achieved. For instance, form Fig. 6(b), the maximum power output for the single cell DFAFC can be up to 29.0 mW cm^{-2}, while the limiting current was obtained at 183 mA cm^{-2} using 10M concentration. However, the power density for DFAFC decreased for the operation of formic acid at 12 M and the maximum power density decreased to 19.2 mW cm^{-2}.

At low concentration, formic acid cannot accommodate fuel operation at high current density due to the presence of mass transport limit [24]. Formic acid concentration 10 M is the optimum concentration that is acquired which meet the study result of few past researchers [1, 19]. However, when the concentration increases from optimum concentration, i.e., 12 M, DFAFC performance will decrease due to low catalyst activity and occurrence of the fuel flux crossing [19]. The decline in performance at high formic acid concentration may also be caused by the very nature of formic acid which is hydrophilic that dries layer near membrane that can inhibit proton transfer [23].

4. Conclusion

The formulation of MPL and CL for anode has been investigated. Different loading of Teflon in MPL and Nafion in CL, i.e., 0 to 40 wt%, were used to fabricate the anode's DFAFC. The characteristic of MPLs and anode (MPL with catalyst layer) such as surface morphologies and resistivity were analyzed using field emission scanning electron microscopy (FESEM), contact angle measurements as well as electrochemical impedance spectra (EIS). By comparing the pores in each MPL surface, the sizes of the pores are getting smaller with increasing weight content of Teflon and Nafion. Based on results, the Teflon and the Nafion content of 20 wt% were found the optimum value or suitable for electrode in DFAFC because of their potential and well performance through some analysis conducted especially low in electrochemical resistance and high electro-activity on CL. The single cell DFAFC with optimum MEA formulation and 10M fuel concentration showed a good performance with 29.0 mW cm^{-2} of power density, hence, it's possible to apply the electricity power for electronic devices.

Acknowledgments

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