Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society

PERFORMANCE OF MEMBRANE ELECTRODE ASSEMBLY USING Pt/C AND CoFe/N-C CATALYSTS IN PROTON EXCHANGE MEMBRANE FUEL CELLS

(Prestasi Pemasangan Elektrod Membran Menggunakan Pemangkin Pt/C dan CoFe/N-C dalam Sel Bahan Api Membran Pertukaran Proton)

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Received: 16 October 2023; Accepted: 15 February 2024; Published: 29 April 2024

Abstract

The performance of membrane electrode assembly (MEA) hinders fuel cell commercialisation. MEA is greatly affected by humidification, temperature and hydrogen flow rate. In this study, the effects of operating conditions on MEA were determined using Pt/C and CoFe/N-C catalysts in proton exchange membrane fuel cells. Herein, two types of MEAs using the Nafion-212 membrane were prepared and tested. The anode and cathode of the first MEA were coated with Pt/C and CoFe/N-C catalysts, respectively, whereas the second MEA utilised a Pt/C catalyst on both electrodes. The electrode with Pt/C and CoFe/N-C catalysts was characterised using cyclic voltammetry and electrochemical impedance spectroscopy to obtain the electrochemical surface area (ECSA) and electrical conductivity of the electrode, respectively. The performance of two MEAs was tested under different operating conditions, such as various humidifier temperatures (40 °C, 60 °C, 80 °C and 100 °C) and hydrogen flow rates (100, 200, 300 and 400 mL/min). The electrode with a Pt/C catalyst exhibited higher ECSA (0.245 m^2/g) than the CoFe/N-C electrode (0.018 m^2/g). Similarly, the Pt/C electrode possessed higher conductivity (7.2×10^{-3} S/cm) than the CoFe/N-C electrode (4.4×10^{-3} S/cm). Consequently, the open-circuit voltage (OCV) of the second MEA with a Pt/C catalyst on both electrodes showed a higher value (0.890 V) than the OCV of the first MEA (0.790 V). Furthermore, the humidifier temperature was optimum at 80 °C, and it achieved power density levels as high as 10.14 and 3.43 mW/cm^2 for the second and the first MEA, respectively. In addition, the performance of MEA was affected by the hydrogen flow rate. At the optimum hydrogen flow rate of 400 mL/min for the first MEA, a power density of 4.93 mW/cm^2 was achieved. Meanwhile, the second MEA required a lower hydrogen flow rate (200 mL/min) to achieve a maximum power density of 10.14 mW/cm^2.

Keywords: proton exchange membrane fuel cells, MEA performance, Co-Fe/N-C, humidification temperature, hydrogen flow rate

Abstrak

Prestasi pemasangan elektrod membran (MEA) membawa kepada kesesakan pengkomersialan sel bahan api. MEA sangat dipengaruhi oleh pelembapan, suhu, dan kadar aliran hidrogen. Dalam kajian ini, menentukan kesan keadaan operasi pada MEA menggunakan pemangkin Pt/C dan CoFe/N-C dalam sel bahan api membran pertukaran proton (PEMFC). Di sini, dua jenis MEA yang menggunakan membran Nafion-212 telah disediakan dan diuji. Anod dan katod MEA pertama disalut dengan pemangkin Pt/C dan CoFe/N-C, manakala MEA kedua menggunakan pemangkin Pt/C pada kedua-dua elektrod. Elektrod dengan pemangkin Pt/C dan CoFe/N-C dicirikan menggunakan voltammetri kitaran dan spektroskopi impedans elektrokimia (EIS) untuk mendapatkan kawasan permukaan elektrokimia (ECSA) dan kekonduksian elektrik elektrod. Prestasi dua MEA diuji dengan keadaan operasi yang berbeza, seperti pelbagai suhu humidifier (40 °C, 60 °C, 80 °C, dan 100 °C) dan kadar aliran hidrogen (100, 200, 300, dan 400 mL/min). Elektrod dengan pemangkin Pt/C mempamerkan ECSA yang lebih tinggi (0.245 m^2/g) daripada elektrod CoFe/N-C (0.018 m^2/g). Begitu juga, elektrod Pt/C mempunyai kekonduksian yang lebih tinggi (7.2 x 10^{-3} S/cm) daripada elektrod CoFe/N-C (4.4 x 10^{-3} S/cm). Akibatnya, voltan litar terbuka (OCV) MEA kedua dengan pemangkin Pt/C pada kedua-dua elektrod menunjukkan nilai yang lebih tinggi (0.890 V) daripada OCV MEA pertama (0.790 V). Tambahan pula, suhu humidifier adalah optimum pada 80 °C dan mencapai tahap ketumpatan kuasa setinggi 10.14 dan 3.43 mW/cm^2 masing-masing untuk MEA kedua dan pertama. Di samping itu, prestasi MEA dipengaruhi oleh kadar aliran hidrogen. Dengan kadar aliran hidrogen optimum 400 mL/min untuk MEA pertama, ketumpatan kuasa 4.93 mW/cm^2 telah dicapai. Sementara itu, MEA kedua memerlukan kadar aliran hidrogen yang lebih rendah (200 mL/min) untuk mencapai ketumpatan kuasa maksimum 10.14 mW/cm^2.

Kata kunci: sel bahan api membran pertukaran proton, prestasi MEA, Co-Fe/N-C, suhu pelembapan, kadar aliran hidrogen

Introduction

Proton exchange membrane fuel cells (PEMFCs) have high efficiency, high power density, pollution-free properties because they use hydrogen as fuel [1] and flexible source of hydrogen [2]. PEMFCs can be used in electric vehicles [3] and maritime applications [4], as well as for portable and stationary applications [5]. The membrane electrode assembly (MEA) is the most important component in PEMFCs. The performance of MEA's is determined by the catalytic activity, the method of placing the catalyst at the catalyst layer (CL) [1], the effect of supporting a material for the CL [6] and the design structure of the flow field [7]. The ideal catalyst for PEMFCs has good conductivity and high stability [8], particularly the activity and stability of the catalyst at the cathode [9]. In general, the catalyst used in PEMFCs is Pt-based because it is optimum for the hydrogen oxidation reaction at the anode [10], [11]. However, the weakness of the Pt/C catalyst lies in its high cost and susceptibility to CO poisoning, which accelerates platinum particle growth, causing aggregation and structural changes. This phenomenon negatively impacts catalytic activity, which leads to gradual deactivation, thereby reducing fuel cell lifespan and efficiency [12].

Meanwhile, oxygen reduction at the cathode in PEMFCs is relatively slow [13]. Thus, a catalyst that can accelerate the reduction reaction at the cathode is necessary. Pt catalyst alloys with other transition metals is commonly used at the cathode to reduce the interatomic distance in the lattice and energy variations in the d-orbitals, which can facilitate the adsorption of oxygen on the cathode surface [9]. Moreover, the slow reaction at the cathode will lead to the improper occurrence of the stoichiometric equilibrium between the hydrogen and oxygen reactions that are supplied, thereby decreasing the performance of the PEMFC. The oxygen reduction reaction (ORR) of the CoFe/N-C catalyst makes it a good catalyst for the cathode because it increases the reduction reaction in rechargeable zinc–air batteries [14].

Meanwhile, the use of nitrogen graphene with iron fibre can increase the ORR on the membrane, whereas the N-doped cobalt carbon (Co/C) can reduce the oxygen evolution reaction (OER). Thus, the performance of the CoFe/N-C catalyst in PEMFC can be compared with that of the Pt/C catalyst that is often used in the PEMFC cathode. Using a non-platinum FeCo-based catalyst at the cathode has also been carried out using the printing method for catalyst synthesis [15]. Several studies have shown that the alloys of transition metals, nitrogen and carbon synergise with one another to obtain ORR electrocatalytic activity and high performance durability [16]. Based on the evaluation using the rotating disk electrode technique, a significant increase in ORR activity is observed in CoFe/N-C compared with Co/N-C and Fe/N-C (Table 1). This finding indicates a synergistic coupling effect between Co and Fe in alloy metal nanoparticles supported on nitrogen-doped Vulcan carbon. The CoFe/N-C catalyst demonstrates higher current density at the same overpotential, indicating greater electrocatalytic activity [14].

Apart from the catalytic activity, the performance of MEA also depends on operating conditions. Humidification and gas flow rate are the operating conditions of MEA that can affect its performance [8, 17]. In MEA, humidification is important because it will affect the supply of water vapor to the membrane. If the water vapor supply is less, then the membrane will be dehydrated, and the evaporation of water in the membrane increases [18]. Meanwhile, increasing the temperature can increase the reaction kinetics [19]. Increasing the temperature of the humidifier keeps the water passing through the electrode in a vapor state to avoid condensation, which can create a flood condition on the electrode [20].

Table 1. Electrocatalytic data at a current density of 10 mA·cm^{-2} (E@10 mA·cm^{-2} for OER)

Materials	**ORR**		
	$E_{on\ set}$ (V $_{vs}$ RHE)	**$E_{1/2}$ (V $_{vs}$ RHE)**	**Tafel slope (mV dec^{-1})**
CoFe/N-C	1.03	0.821	86
Pt/C	1.01	0.817	93
Fe/N-C	0.95	0.764	80
Co/N-C	0.91	0.776	54

Source: [14]

Materials and Methods

Herein, we compared the performance of two MEAs. The electrodes of the first MEA used Pt/C 40 wt.% (Fuel Cell Store) and CoFe/N-C (self-synthesised, refer to paper [14]) catalysts at the anode and cathode, respectively, with catalyst loading of 1 mg/cm^2 of each electrode, whereas the second MEA used a Pt/C catalyst on both electrodes. The electrode size was 5 cm × 5 cm, and the electrolyte membrane used was Nafion-212 (Fuel Cell Store). A pin type flow field and gold-plated current collectors (Electrochem/Fuel Cell Store) were also used. The electrode structure consisted of a backing layer in the form of a carbon paper (Gashub, Singapore) and a microporous layer (MPL) comprising a mixture of carbon Vulcan XC-72R (Fuel Cell Store), ammonium bicarbonate (Sigma-Aldrich) and Teflon DISP 30 Fluoropolymer dispersion (Fuel Cell Store). The electrode structure also consisted a CL comprising a Pt/C catalyst (40 wt%, Fuel Cell Store) at the anode (for both MEA types) and Pt/C and Co-Fe/C-N catalysts (self-synthesised) for each cathode at two types of MEAs. Catalyst loading was 1 mg/cm^2, and the catalyst ink on the catalyst and MPL was stirred using an ultrasonic homogeniser for 15 min. The electrodes were characterised using an Autolab PGSTAT 204 by cyclic voltammetry and electrochemical impedance spectroscopy to determine electrochemically active surface area (ECSA) and electrical conductivity. ECSA and electrical conductivity are calculated using Equations (1) and (2) with modifications.

$$\text{ECSA (cm}^2\text{/g)} \quad = \frac{q}{\Gamma.L} \qquad (1)$$

where q is the charge density (C/cm^2), Γ is the equivalent constant (μC/cm^2), and L is the catalyst loading (mg/cm^2) [21, 22].

$$\text{EIS } (\sigma) \text{ (S/cm)} \quad = \frac{1}{Z_R} \times \frac{1}{A}, \qquad (2)$$

where Z_R is the total resistance = Rp + Rs (Ω) (note: Rp, and Rs are obtained from Nyquist curve fitting), l is the thickness (cm), and A is the surface area (cm^2) [23, 24].

CV and EIS analyses were performed using Potentiostat/Galvanostat PGSTAT204 from Methrom with Nova 2.1.4 software to process the data. CV and EIS were performed by placing Pt/C or Co-FeN/C electrodes, Ag/AgCl and platinum rods as working, reference and supporting electrodes, respectively. In addition, NaOH solution with a concentration of 1 M served as the electrolyte with a potential range of −0.2 V to 0.6 V and a scan rate of 100 mV/s. The measurements were repeated for 5 cycles.

MEA was fabricated from two electrodes and Nafion 212 (NR 212) (Fuel Cell Store) as an electrolyte membrane with hot pressing at 135 °C of 2000 psi for 3 min. The performance of MEA (I-V and I-P's performance) was tested using the fuel cell test station SMART2 WonAtech (South Korea) with varying flow rates of hydrogen gas (UHP, Samator, 100, 200, 300 and 400 mL/min) and oxygen gas (UHP, Samator) at 100 mL/min. The humidifier temperature varied from 40 °C, 60 °C, 80 °C and 100 °C.

Results and Discussion

Electrochemical characterisation

MEAs consisting of Pt/C (anode) and Co-Fe/N-C (cathode), as well as Pt/C catalysts on both electrodes, were arranged in a stack. Before making the MEA, the electrodes were characterised using CV and EIS. These methods were used in electrode characterisation to determine catalytic activity based on the ECSA values from CV analysis and electrical conductivity from EIS analysis. Determining the ECSA value from the voltammogram is a common procedure, and the value depends on the area of the electrode as well as the kinds and the loading of the catalyst [25, 26].

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EIS is a well-established diagnostic method in electrochemistry [27]. The voltammogram and Nyquist curve of the electrodes are shown in Figure 1. As shown in Figure 1, the performance of the electrode with a Pt/C catalyst was better than that with a CoFe/N-C catalyst. Figure 1(a) shows a voltammogram from CV analysis with a scan rate of 100 mV/s. The electric charge can be determined on the basis of the area of the peak curve of the voltammogram and the scan rate data. If the electric charge is observed from the voltammogram curve in Figure 1(a), then the area of the electrode with the CoFe/N-C catalyst is smaller than that with the Pt/C catalyst. This result was confirmed through a smaller ECSA value compared with the Pt/C catalyst.

Figure 1(b) represents the impedance characteristics of the electrode with Pt/C and CoFe/N-C catalysts. Electrodes with a Pt/C catalyst had an impedance value of 3.12 Ω, whereas CoFe/N-C electrodes had a real impedance value of 5.54 Ω. The electrical conductivity of the electrode can be determined with the known equation based on the impedance values [24]. The ability of an electrode to conduct electricity can be determined from the conductivity value. The electrical conductivity value in electrodes coated with Pt/C was 7.2 × 10^{-3} S/cm, whereas that in electrodes coated with CoFe/N-C catalysts was 4.4 × 10^{-3} S/cm (Table 2).

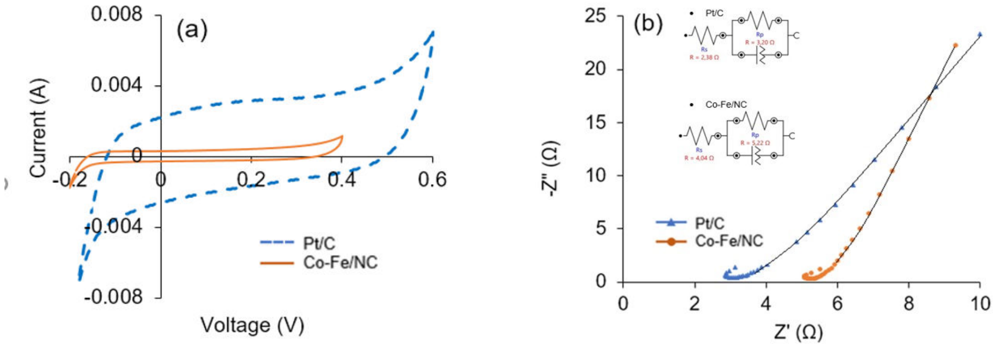

Figure 1. Electrode characterisation result using (a) CV and (b) EIS

Table 2. The electrical conductivity with Pt/C and CoFe/N-C catalysts

No.	Electrode	Impedance Parameters		Electrical Conductivity (S/cm)
		Rs (Ω)	Rp (Ω)	
1.	Pt/C	4.0357	5.2236	7.2 × 10^{-3}
2.	CoFe/N-C	2.3826	3.2046	4.4 × 10^{-3}

ECSA shows the active surface area of the catalyst, which is the response of the electrode in the form of current to the applied voltage. In turn, ECSA can be determined through the existing equations [28, 29] by considering the loading of the catalyst and the surface area of the electrode. Apart from the catalyst loading and surface area, ECSA also used a correction factor [30]. Moreover, based on the calculations, the ECSA value of the electrode with Pt/C and CoFe/N-C catalysts was 0.245 and 0.019 m^2/g, respectively. The distribution and surface area of the catalyst in the CL are the factors influencing the ECSA value of an electrode. Adding conductive carbon to the catalyst can lead to the even distribution of the catalyst [31, 32]. The even distribution of the catalyst in carbon may increase the active site of the catalyst. The carbon matrix in the catalyst is a factor affecting the ECSA value on a fuel cell electrode, which can make the catalyst spread more evenly. The more even the distribution of the catalyst in the carbon is, the larger the active site of the catalyst will be. A large surface area allows the distribution of Pt and CoFe metals amongst the carbon pores and even distribution on the surface of the CL [30].

The particle size of CoFe/N-C was more than 10 nm and uneven [14], whereas the particle size of Pt/C was approximately 3–4 nm [33]. The relatively smaller particle size of Pt/C led to a larger surface area of the Pt/C catalyst. Thus, it became a factor that led to a larger Pt/C ECSA value. Electrodes with Pt/C catalysts have an impedance value of 3.12 Ω, whereas CoFe/N-C electrodes have a real impedance value of 5.54 Ω. A high impedance value indicates the low conductivity of the electrodes. Moreover, EIS was used to analyse the electrochemical performance of an electrode, which will produce data from the sample response to a given frequency range in the form of real independence (Z') and imaginary independence (Z'') values [34, 35]. The Nyquist curve can determine the impedance of electrodes through fitting to simulate the equivalent circuits.

Measurement of open-circuit voltage (OCV)

The OCV testing of the two MEAs showed their initial performance. The MEA with a Pt/C catalyst on both electrodes had a higher OCV of 0.890 V compared with that with a CoFe/C-N catalyst on one of the electrodes, which had an OCV of 0.720 V. Although the OCV value suggests an opportunity to use CoFe/C-N catalyst as a catalyst for PEMFC, the performance of the MEA is largely determined by its ability to maintain voltage with increasing load and not just under OCV conditions.

Performance testing of MEA at various humidifier temperatures

The performance of MEA was measured by testing the influence of humidifier temperature at 40 °C, 60 °C, 80 °C and 100 °C with a hydrogen flow rate of 200 mL/min. In addition, MEA treatment at high temperatures can increase the electrochemical kinetics, reduce the susceptibility to contamination and facilitate good water management [8]. Moreover, the performance of MEA at various humidifier temperatures is shown in Figure 2.

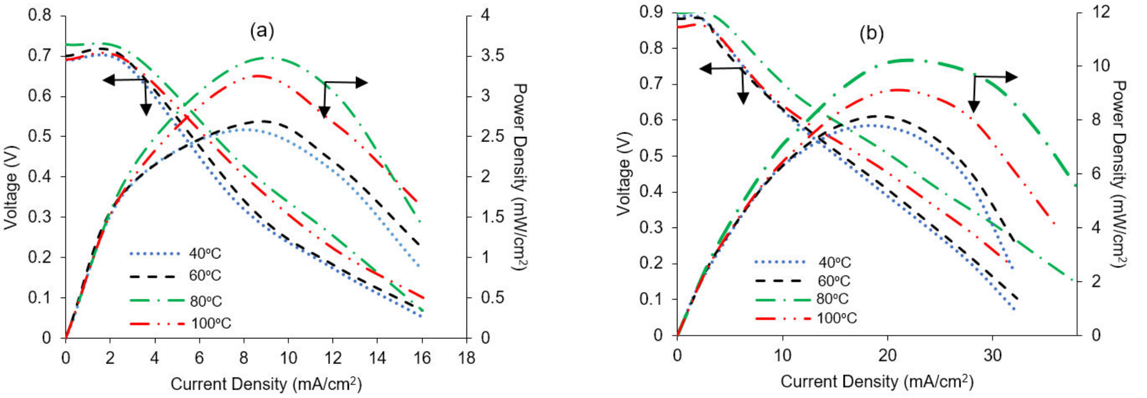

Figure 2. Effects of humidifier temperature on the performance of MEA with (a) CoFe/N-C and (b) Pt/C catalysts

The polarisation curve shows that the voltage decreases with the increase of load implemented as the electric current density [36]. Figure 2 shows that 80 °C is the optimum humidifier temperature because it can maintain voltage against an increase in current density, which is greater than those of other humidifier temperatures. The performance of MEA with CoFe/NC and Pt/C catalysts on the cathode and anode side (Figure 2[a]) was lower than that with a Pt/C catalyst on both sides (Figure 2[b]). This fact strengthened the OCV data. The MEA with a COFe/N-C catalyst in the cathode (Figure 2[a]) cannot support the performance of the Pt/C catalyst in the anode. However, in zinc–air batteries [14], the COFe/N-C catalyst is superior to Pt/C. The MEA shown in Figure 2(a) produced a maximum power density of 3.42 mW/cm^2 at a current density of 8.04 mA/cm^2, whereas the MEA with a Pt/C catalyst on both sides (Figure 2[b]) obtained a maximum power density of 10.14 mW/cm^2 at a current density of 20.04 mA/cm^2. Prior studies have investigated the impact of humidifier temperature on the performance of MEA in PEMFCs, using Pt catalysts on the anode and cathode. The humidifier temperature set at 80 °C delineates the boundary for high-temperature PEMFCs [37].

MEA performance test on various hydrogen flow rates

After obtaining the optimum humidifier temperature of 80 °C, the performance of MEA on PEMFCs was continuously tested on the basis of the effect of varying hydrogen flow rates (100, 200, 300 and 400 mL/min). The I-P and I-V performances are shown in Figure 3.

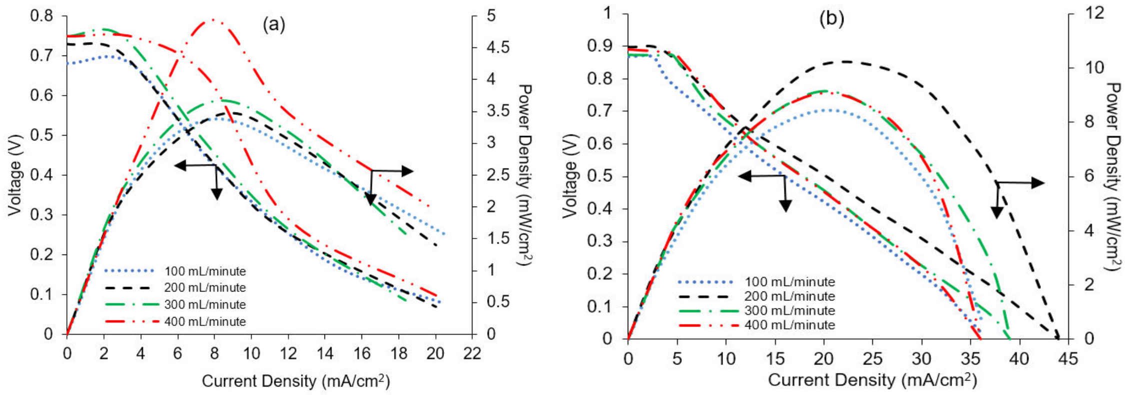

Figure 3. Effects of the hydrogen flow rate on the performance of MEA with (a) CoFe/N-C and (b) Pt/C catalysts

The ability of MEA to maintain a high voltage for a given current at a hydrogen flow rate of 400 mL/min compared with other hydrogen flow rates was shown on the basis of the I-V curve depicted in Figure 3(a) (MEA with CoFe/N-C and Pt/C catalysts). The hydrogen flow rate can well maintain the voltage during activation and ohmic polarisation; hence, the voltage does not decrease drastically with the increase of current density. However, MEA with a Pt/C catalyst on both sides (Figure 3[b]) at a hydrogen flow rate of 400 mL/min could not maintain the resulting voltage with increasing current density. This result was particularly true in the region of concentration polarisation because of an imbalance in the ratio between the supply of reactants and the supply of products. Meanwhile, at a hydrogen flow rate of 200 mL/min, MEA in PEMFC can better maintain the resulting voltage with increasing current density. The resulting I-V curve was gentler than the curves of other hydrogen flow rates.

Figure 3(a) shows that MEA with a CoFe/N-C catalyst on the cathode side had a fairly good performance with increasing hydrogen flow rate. This result was due to the maximally distributed hydrogen supply on the anode side, which increased the number of protons produced. The increase can be seen from the resulting power density of 4.93 mW/cm^2 at a current density of 7.72 mA/cm^2. However, it did not affect MEA with Pt/C catalysts on both sides (Figure 3[b]). Thus, this finding indicated that a hydrogen flow rate of 400 mL/min produced a lower power density than a hydrogen flow rate of 200 mL/min, that is, 10.14 mW/cm^2 at a current density of 20.04 mA/cm^2. MEA with a Pt/C catalyst on both sides of the electrode showed better performance than MEA with CoFe/N-C and Pt/C catalysts at the cathode and anode side, respectively. Thus, Pt/C was the best catalyst for MEA of PEMFCs, and adequate hydrogen flow rate can lead to a good performance.

Conclusion

The characterisation of electrodes with a Pt/C catalyst showed a higher ECSA and electrical conductivity value compared with electrodes with a CoFe/N-C catalyst. Furthermore, a humidifier temperature of 80 °C produced the best performance on PEMFC for both MEAs with a Pt/C catalyst on both sides as well as Pt/C and CoFe/N-C catalysts on the anode and cathode sides, respectively. Meanwhile, increasing the hydrogen flow rate improved the performance of MEA. A hydrogen flow rate of 400 mL/min produced the highest performance for MEA with Pt/C and CoFe/N-C catalysts on the anode and cathode side, respectively. However, for MEA with a Pt/C catalyst on both sides (anode and cathode), the optimum hydrogen flow rate was 200 mL/min. Therefore, the CoFe/N-C catalyst can be an alternative for a Pt/C catalyst in fuel cells, especially PEMFCs.

Acknowledgement

We would like to thank Sriwijaya University for facilitating this research and the authors who assisted in the research and publication process, especially to Prof. Dr. Edy Herianto Majlan and Dr. Afriayanti Sumboja for the best collaboration in this research.

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