



Short communication

Study on the membrane electrode assembly fabrication with carbon supported cobalt triethylenetetramine as cathode catalyst for proton exchange membrane fuel cell

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ABSTRACT

An improved fabrication technique for conventional hot-pressed membrane electrode assemblies (MEAs) with carbon supported cobalt triethylenetetramine (CoTETA/C) as the cathode catalyst is investigated. The *V–I* results of PEM single cell tests show that addition of glycol to the cathode catalyst ink leads to significantly higher electrochemical performance and power density than the single cell prepared by the traditional method. SEM analysis shows that the MEAs prepared by the conventional hot-pressed method have cracks between the cathode catalyst layer and Nafion membrane, and the contact problem between cathode catalyst layer and Nafion membrane is greatly suppressed by addition of glycol to the cathode catalyst ink. Current density–voltage curve and impedance studies illuminate that the MEAs prepared by adding glycol to the cathode catalyst ink have a higher electrochemical surface area, lower cell ohmic resistance, and lower charge transfer resistance. The effects of CoTETA/C loading, Nafion content, and Pt loading are also studied. By optimizing the preparation parameters of the MEA, the as-fabricated cell with a Pt loading of 0.15 mg cm^{-2} delivers a maximum power density of 181.1 mW cm^{-2} , and a power density of 126.2 mW cm^{-2} at a voltage of 0.4 V.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) has the characteristics of low-temperature operation and high energy efficiency, and is environmentally friendly, so development of non-precious metal oxygen reduction reaction catalysts is an investigative priority for PEMFC [1–3]. At present, some problems are high-cost raw materials, complex preparation routes, and environmental pollution resulting from fabrication of transition metal macrocycle compound oxygen reduction catalysts [4].

Membrane electrode assemblies (MEAs) are the traditional way to prepare membrane electrodes for PEMFCs. The fabrication method involves a series of catalyst ink spraying or painting operations in combination with hot pressing to bond carbon cloth-supported electrodes to an electrolytic membrane [5,6]. In a fuel cell system, the electrochemical reaction can only occur at “triple-phase boundaries”, where the electrolyte, reaction material, and electrically connected catalyst particles contact together in a MEA [7,8]. The triple-phase-boundary area in turn depends significantly on the fabrication procedure of MEA in addition to other important parameters such as catalyst loading and ionomer loading [9–11].

High-performance MEAs can be obtained by improving the contact between the electrolyte and catalyst layer [12].

The desired high power density from polymer electrolyte membrane fuel cells can only be achieved by speeding up the otherwise slow reaction steps at their low operating temperatures ($\sim 80^\circ\text{C}$) through catalysis. The preparation of efficient and cheap electrodes has become an important research and development direction of PEMFCs nowadays. For the oxygen-reduction reaction (ORR), non-precious metal catalysts (NPMCs), which are potentially less expensive and more abundant, have been outperformed by Pt-based catalysts [13]. Our previous approach in the synthesis of NPMCs for ORR has been to use Co and nitro-containing small molecular ligands to prepare a kind of Co metal small molecular chelate oxygen reduction catalyst [14].

Because of the difference between the carbon supported cobalt triethylenetetramine (CoTETA/C) and the traditional carbon-supported Pt catalyst, the contact between the cathode catalyst layer and the Nafion electrolyte membrane is not satisfactory when the MEA has been prepared by the conventional hot-pressing processes, such as using organic solvents in catalyst ink preparation [15].

In this paper, we report on the application of glycol for the preparation of MEAs with CoTETA/C as the cathode catalyst. Because glycol is a viscous liquid, we anticipate that it would greatly suppress the contact problem between the cathode catalyst and the

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Nafion electrolyte membrane. We also investigated the influence of cathode catalyst loading, ratio of catalyst ink, and effect of the Pt loading at the anode on cell performance.

2. Experimental

2.1. Preparation of the CoTETA/C

The CoTETA/C cathode catalyst was prepared as follows. First, 0.404 g cobalt chloride was dissolved in 25 ml ethanol and 1.0 ml TETA was added to form CoN_4 chelate. The obtained solution was mixed with 1.0 g carbon support (BP2000) for 1 h under ultrasonic conditions and then 2 h under stirring. After drying to remove the ethanol, the resulting powder was heat-treated at 800°C for 90 min under an argon atmosphere [16]. All chemicals used in this work were of analytical grade purity and were used without further purification.

2.2. Preparation of the catalyst ink

Commercial Pt/C (20 wt.%, E-teck) was used as the anode catalyst. The catalyst ink is composed of 10 mg Pt/C catalyst powder, 0.05 ml double distilled water, Nafion solution (5 wt.%, DuPont) and isopropanol. The ratio of Pt/C catalyst, Nafion and isopropanol was 3:1:300. CoTETA/C was used as cathode catalyst. The catalyst is composed of CoTETA/C catalyst power, Nafion solution (5 wt.%, DuPont), glycol and isopropanol. The ratio of CoTETA/C catalyst, glycol and isopropanol was 1:8:100.

2.3. Preparation of MEA

The MEAs were prepared using Nafion 212 as an electrolyte, and GDL (E-teck) as a support. Before fabrication, the Nafion 212 electrolyte membrane was treated by the following three main steps for removing organic material and activating the membrane. It was first cleaned in boiled deionized water for 1 h and again cleaned in 3% hydrogen peroxide (H_2O_2) to remove organic substances. Then it was boiled in 0.5 M H_2SO_4 to activate the membrane [17]. All treatment processes were conducted at 80°C . The anode catalysts and the cathode catalyst ink were spray-deposited onto each side of the GDL separately by a spraying gun. Finally, the pretreated membrane and electrodes of a 5 cm^2 cross-sectional area were bonded together by the hotpressing method. The temperature of the hotpressing was 130°C , the pressure was 8 MPa and the time was 90 s.

2.4. Fuel-cell testing and analysis

A commercial PEMFC single cell housing with a 5 cm^2 active area, and including Teflon gasket, carbon block, and gold-coated copper current collector (ElectroChem), was used to test the performance of the cells assembled from the MEAs. The test station consisted of two main systems: a control system and gas feed system. The control system was for measuring and controlling the operating conditions of the single cell while the gas feed system was for treating and supplying the fuel and oxidant gases fed to the cell. Before testing the cell, the MEAs had been activated by drawing while keeping cell voltage at 0.5 V. Industrial grade oxygen was supplied as the oxidant at 150 ml min^{-1} as the cathode atmosphere and industrial grade hydrogen as the reactant gas at the anode side at 100 ml min^{-1} , both at ambient pressure. Oxygen was humidified at 55°C and hydrogen was humidified at 70°C before entering the cell. The temperature of the cell was also measured using a thermocouple and was maintained at 60°C by a heating-cartridge located on the external surface of the current collector. The cell performance of each MEA was determined from its polarization curve, plotted

between voltage and current density. A Zahner Im6ex electrochemical working station was used for the impedance measurements and the applied frequency was varied from 0.1 to 10 kHz with an excitation voltage of 5 mV.

2.5. Cyclic voltammetry testing and analysis

The electrochemical measurements were performed with the conventional three electrodes system in 0.5 M H_2SO_4 solution. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All potentials presented in this paper have been transferred to the normal hydrogen electrode (NHE). Ink-type electrode was prepared as follows: 5 mg of the electrocatalyst was mixed with 0.5 ml doubly distilled water and 50 ml 5 wt% Nafion (Du Pont) for 15 min in an ultrasonic bath and 10 ml of this ink was deposited onto the surface of glassy carbon disk ($d = 4.0\text{ mm}$) and then air-dried. The acid electrolyte was saturated with pure oxygen during all of the electrochemical experiments. Cyclic voltammetry was scanned between 0.04 and 1.04 V at a scan rate of 50 mV s^{-1} .

3. Results and discussion

Current density–voltage and current density–power density curves for the hot-pressed MEA under H_2/O_2 are shown in Fig. 1. The cell performance of the MEA with glycol added to the cathode catalyst ink is clearly better than the MEA without. This indicates that the glycol effectively improves the performance of the PEM fuel cell without increasing the catalyst loading. In the electrochemical polarization-controlled region, the slope of the MEA with glycol is also higher than that of the MEA without. This indicates the cathode catalyst layer has close contact with the electrolyte membrane which increases the triple-phase boundaries. In the resistance-controlled region, the slope of the MEA with glycol is lower than that of the MEA without. This is because glycol is a viscous liquid, so it can improve the contact between the cathode catalyst layer and Nafion electrolyte membrane, reducing the resistance of the MEA. Evidence of the improved contact is shown in Fig. 2.

The departure from linearity between potential and current density at high current density is predominantly due to the rapid increase in the contributions of mass transport limitations [18]. Since the diffusion layers used in both test cells are the same, the more rapid decreasing trend in the diffusion-controlled region of

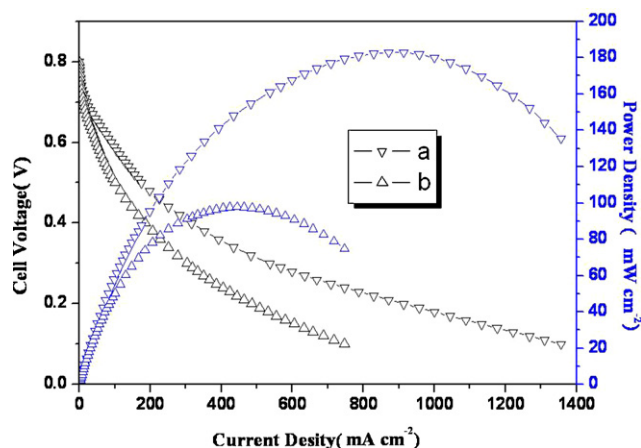


Fig. 1. Current density–voltage and current density–power density curves of single cells made from hot-pressed MEAs with CoTETA/C as cathode catalyst: (a) 0.1 ml glycol added to the cathode catalyst ink (b) without glycol in the cathode catalyst ink. In both cases the loading of CoTETA/C is 2 mg cm^{-2} , the ratio of CoTETA/C to Nafion is 2:1.

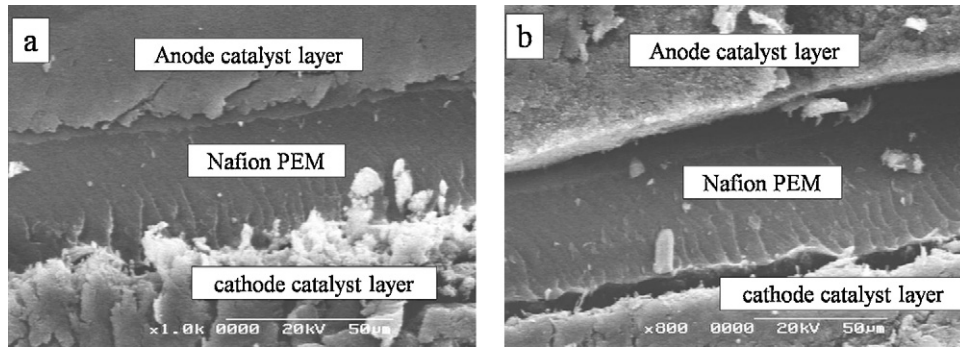


Fig. 2. SEM images of the cross-section of MEA with CoTETA/C as cathode catalyst. (a) 0.1 ml glycol added to the cathode catalyst ink (b) without glycol in the cathode catalyst ink. In both cases the loading of CoTETA/C is 2 mg cm^{-2} , the ratio of CoTETA/C to Nafion is 2:1.

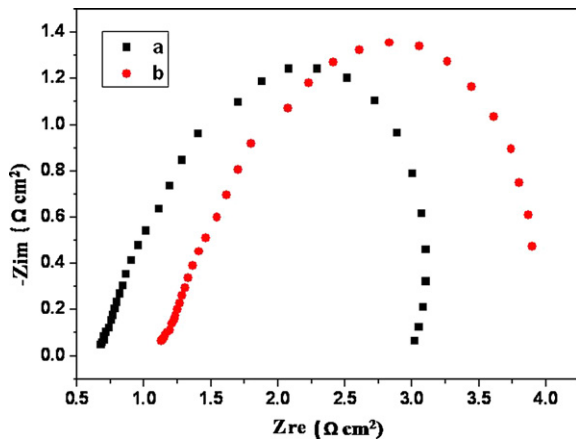


Fig. 3. Impedance curves of the single cells of the MEAs with CoTETA/C as cathode catalyst, measured at 0.5 V. (a) 0.1 ml glycol added to the cathode catalyst ink (b) without glycol in the cathode catalyst ink. In both cases the loading of CoTETA/C is 2 mg cm^{-2} , the ratio of CoTETA/C to Nafion is 2:1.

current–voltage curves of the MEA without any glycol compared to the MEA with glycol suggests that the MEA without glycol is more affected by flooding on the cathode side of the cell.

Fig. 3 shows the impedance responses of the single cells prepared with (cell “a”) and without (cell “b”) glycol in the cathode catalyst ink. Fig. 4 shows the equivalent circuit. In the equivalent circuit, R_1 represents the total ohmic resistance of the cell which includes ohmic resistances of various cell components and also the end plates and the contacts between them. R_2 is usually associated with the charge transfer resistance across the catalyst/electrolyte interface, and CPE is a constant phase element related to the double-layer capacitance of the porous electrode [19]. This equivalent circuit may be applicable even though the real reaction pathways could be very complicated. The fitting results are given in Table 1.

As expected, the ohmic resistance R_1 of cell “a” is smaller than cell “b.” As the electrochemical impedance is kinetically dominated by the oxygen reduction at the cathode [20], the smaller R_2 for cell

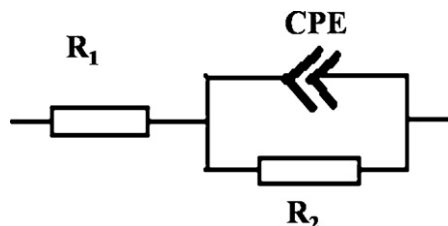


Fig. 4. Equivalent circuit used for the impedance analysis.

Table 1
Fitted impedance parameters of the single cells made from MEA (a) and (b).

MEA	Voltage (V)	R_1 ($\Omega \text{ cm}^2$)	R_2 ($\Omega \text{ cm}^2$)
(a)	0.5	0.71	1.15
(b)	0.5	1.13	1.46

“a” demonstrates that the ORR on the catalyst layer of the CCM (catalyst coated membrane) is significantly faster than that of cell “b.” This is consistent with that of the current density–voltage studies.

Fig. 5 shows the influence of CoTETA/C loading on the performance of the MEA. The comparison of cell performance shows that increasing the cathode catalyst loading can improve the cell performance. But when the load of CoTETA/C was more than 2 mg cm^{-2} , the performance of the cell declined with increasing CoTETA/C loading. This is because for NPMCs, electrode thickness predicts the kinetic current density of the cathode, and mass-transport limitations are also related to electrode thickness [13]. Too-thick cathode catalyst layers also increase the cathode ohmic resistance and the possibility of flooding.

Nafion plays an important role in the electrode performance of the PEMFCs. The proper amount of Nafion within the electrode could greatly expand the amount of electrolyte–electrode–gas triple-phase boundaries where the electrochemical reactions take place [21]. And Nafion is also a good adhesive, which can help to make close contact between the catalyst layer and electrolyte membrane giving reduced contact resistance. Therefore, the effect of Nafion content within the electrode was also investigated. Shown in Fig. 6 are the current density–voltage curves of the single cells with various catalyst-to-Nafion weight ratios in the cathode catalyst ink.

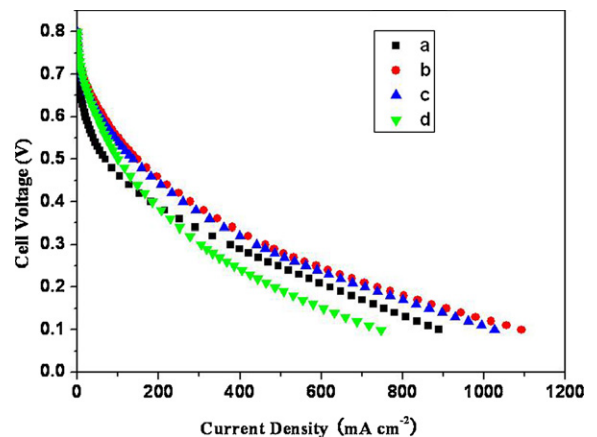


Fig. 5. The effect of CoTETA/C loading on the performance of the MEA with CoTETA/C loadings of (a) 1 mg cm^{-2} , (b) 2 mg cm^{-2} , (c) 3 mg cm^{-2} , and (d) 5 mg cm^{-2} . The CoTETA/C to Nafion weight ratio is 3:1.

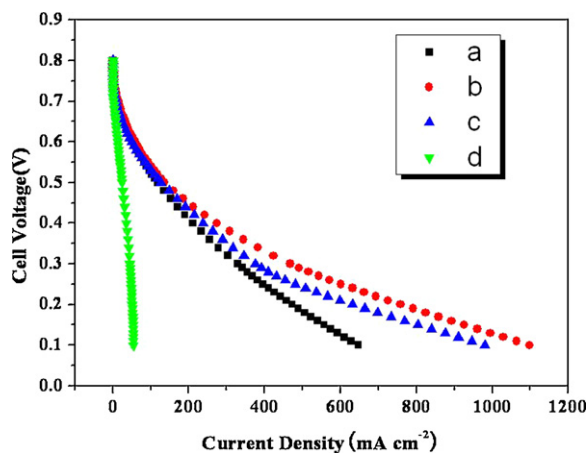


Fig. 6. The effect of Nafion content in the cathode catalyst layer on the performance of the MEA with CoTETA/C to Nafion weight ratios of (a) 3:1, (b) 2:1, (c) 1.5:1, and (d) 1:1. The CoTETA/C loading is 2 mg cm^{-2} .

The optimal Nafion content in the porous electrodes depends on the electrode morphology, which relies on the nature of the catalyst and the fabrication technique of the electrode. In this study, the CoTETA/C and Nafion weight ratio ranged from 3:1 to 1:1. At low Nafion loading (a 3:1 weight ratio of CoTETA/C to Nafion), the protonic conductivity of the electrode was not high enough. There was not sufficient conducting polymer to provide adequate ionic conductance. On the other hand, too much Nafion additive, for example a 1:1 weight ratio of CoTETA/C to Nafion, will lead to a deterioration of the cell performance at high current density. Two possible explanations are as follows. First, the excessive Nafion might cover the surface of CoTETA/C catalyst, leading to a decrease in the active area of CoTETA/C. Second, the percolation path for gas diffusion would be cut off since more water would be produced at high current density and adsorbed by the Nafion resin in the electrode layer [22].

It is well known that the performance of electrodes is controlled by the ORR [23–25]. So it may be possible to reduce the overall loading of Pt in the MEA that uses CoTETA as the cathode catalyst, reducing the costs of PEMFCs. Fig. 7 shows the impact of anode Pt loading on the performance of the MEA. When the Pt loading increased from 0.08 mg cm^{-2} to 0.15 mg cm^{-2} , the performance of the MEA increased significantly. But when it was further increased to 0.35 mg cm^{-2} , the performance of the MEA was a little bit improved. And when the Pt loading was more than 0.35 mg cm^{-2} , the performance of the MEA even declined with the increasing of the Pt loading. That may be because when the Pt loading is high enough (more than 0.08 mg cm^{-2}), ORR is the controlling step of

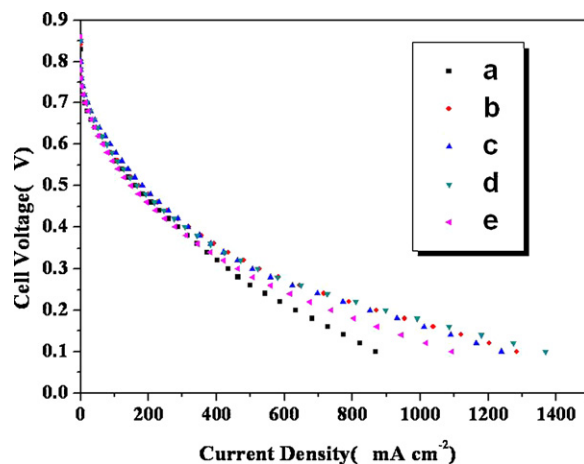


Fig. 7. The effect of Pt/C loading on the performance of the MEA at Pt loadings of (a) 0.08 mg cm^{-2} , (b) 0.15 mg cm^{-2} , (c) 0.25 mg cm^{-2} , (d) 0.35 mg cm^{-2} , and (e) 0.45 mg cm^{-2} . The cathode catalyst CoTETA/C loading is 2 mg cm^{-2} , and the weight ratio of CoTETA/C to Nafion is 3:1.

the membrane electrode. Increasing the Pt loading beyond this will not appreciably accelerate the electrode reaction rate. Increasing the Pt loading also increases the thickness of the electrode and, hence, the mass transport barrier and the electronic impedance of the electrode, both of which are detrimental effects [26].

Since the CoTETA/C catalyst always keep in contact with acidic Nafion membrane, it is quite important to test its stability in the acidic media. Fig. 8(a) shows cyclic voltammograms of the CoTETA/C in oxygen-saturated $0.5 \text{ M H}_2\text{SO}_4$ solution after 100, 300, 500, 1000 circles, respectively. Fig. 8(b) demonstrates the oxygen reduction peak observed at about 600 mV decreased slowly with the increasing of operating circles, which is the same as what could be revealed in the case of Pt/C ORR catalyst [27].

We have taken 20 h durability test of the single cell with the CoTETA as cathode catalyst and with Pt/C as cathode catalyst, respectively. Fig. 9 shows that the performances of both single cells have a little degradation, which could be attributed to crystallite growth, agglomeration of catalyst particles, or catalyst dissolution. Since smaller crystallites have higher surface tension, they have a higher driving force to assemble themselves into larger crystallites to reduce the overall surface energy of the total catalyst mass [27]. As operation continues, the driving force for crystallite growth decreases due to increased average crystallite size and reduced surface energy. Additionally, weak bonding of catalyst particles with the carbon support in a fresh catalytic layer facilitates agglomeration of the nanoparticles at the initial stage of the operation [28].

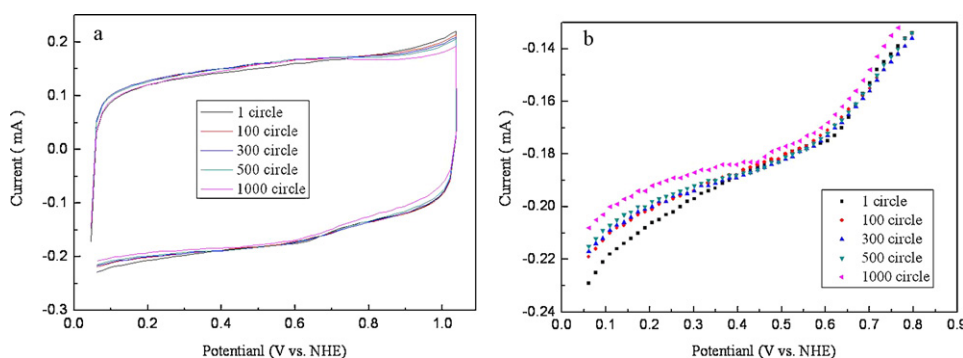


Fig. 8. Cyclic voltammograms for the ORR on the CoTETA/C in $0.5 \text{ M H}_2\text{SO}_4$ solution saturated with O_2 , respectively. Potential scan rate: 50 mV s^{-1} . (a) Overall, (b) part of CV which current is from -0.14 mA to -0.24 mA .

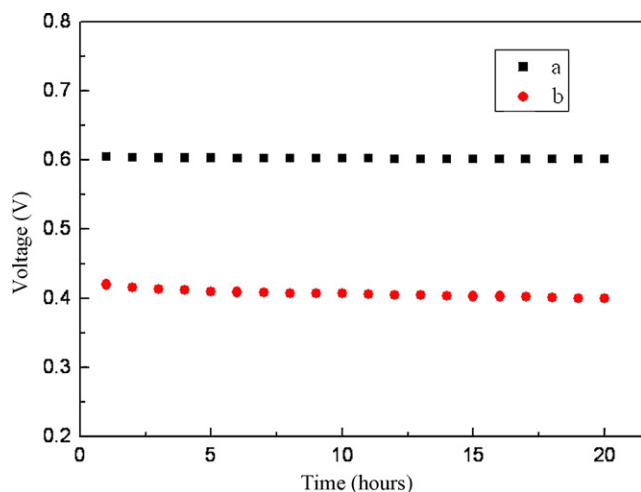


Fig. 9. The performance of single cell at the current density of 300 mA/cm^2 within 20 h. (a) Pt/C as both of cathode and anode catalyst. (b) CoTETA as cathode catalyst and Pt/C as anode catalyst. In both cases, the loading of Pt is 0.15 mg/cm^2 and the ratio of Pt/C to Nafion is 3:1. The loading of CoTETA/C is 2 mg/cm^2 , the ratio of CoTETA/C to Nafion is 2:1.

4. Conclusions

In this paper, we fabricated MEAs that use CoTETA/C as the cathode catalyst by hot-pressing. Because of the difference properties between this carbon-containing cobalt metal chelates and the traditional carbon-supported Pt catalyst, the performance of MEAs that use CoTETA/C as the cathode catalyst is poor when prepared by the method based on the traditional Pt/C cathode catalysts. This is because a CoTETA/C catalyst layer prepared using the traditional method cannot achieve good contact with the Nafion electrolyte membrane. We successfully solved this problem by addition of a certain proportion of glycol.

The effect of the weight ratios of CoTETA/C and Nafion on the cell integrity and performance was studied. By optimizing the fabrication parameters, the catalyst layer adhered to the Nafion electrolyte membrane homogeneously and firmly without any crack formation. We also investigated the effect of the loading of both CoTETA/C and Pt/C. The best cathode CoTETA/C load is 2 mg/cm^2 through our research.

We found that when the anode Pt loading reaches a certain value (Pt content is more than 0.08 mg/cm^2), the oxygen reduction in cathode is the determining step for electrode reaction rate. Within this context, increasing the Pt loading the performance of the MEA

will not be significantly increased. On that basis, we can minimize the use of precious metal Pt to reduce the cost of the PEMFC.

The as-fabricated cell with a Pt loading of 0.15 mg/cm^2 and a CoTETA/C loading of 2 mg/cm^2 delivered a maximum power density of 182.1 mW/cm^2 . Compared to traditional MEAs where the Pt loading of the cathode and anode are both 0.4 mg/cm^2 , we reduced the amount of Pt by 81%.

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