Composite anode for CO tolerance proton exchange membrane fuel cells

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Abstract

Fuel of proton exchange membrane fuel cells (PEMFC) mostly comes from reformate containing CO, which will poison the fuel cell electrocatalyst. The effect of CO on the performance of PEMFC is studied in this paper. Several electrode structures are investigated for CO containing fuel. The experimental results show that thin-film catalyst electrode has higher specific catalyst activity and traditional electrode structure can stand for CO poisoning to some extent. A composite electrode structure is proposed for improving CO tolerance of PEMFCs. With the same catalyst loading, the new composite electrode has improved cell performance than traditional electrode with PtRu/C electrocatalyst for both pure hydrogen and CO/H_2. The EDX test of composite anode is also performed in this paper, the effective catalyst distribution is found in the composite anode. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: CO tolerance; Composite electrode; PEMFC; Electrode structure

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as high efficiency, low pollution power generators for stationary and transportation applications. Much attention has been devoted to the implementation of the fuel cell for transportation applications in current researches, which develop the economically viable low-temperature fuel cells.

PEMFCs with pure hydrogen as fuel can deliver high power densities to automobiles. It is known that the preparation and storage of pure hydrogen as transportation fuel is too difficult for PEMFC to play the role of automobile power, as the fuel chosen for the electric vehicle needs to be readily available. Though reforming technologies are well established, when reformate is used, CO in fuel gas leads to a drastically decreased power density. Although many attempts have been made in the last few decades to develop non-noble metal electrocatalyst for replacing the platinum catalyst in PEMFC and other low temperature fuel cells, platinum remains as the perfect [1]. Tests in PEMFCs indicate that more than about 10 ppm of CO in the gas stream will decrease cell performance especially in the range between 60–100 °C [2]. The performance of PEMFC will continue to decrease and remain unsteady variation when CO is fed in. The situation in which performance of PEMFC

depends strongly on the CO concentration and cell temperature will make a notable impact on fuel cell performance. At higher temperature, less CO adsorption will happen, less cell performance drop will occur [3].

There are several ways to overcome CO poison problem in PEMFC. The first way is to bleed very low levels of oxidant into the fuel feed stream, for instance, O_2 [4,5] and H_2O_2 [6,7]. The second way is advanced purification of reformate gas by fuel processor [8]. The third way is to develop new CO tolerant electrocatalyst. Regarding the first way, when oxidant is added to the fuel stream, the utilization of the fuel will certainly be decreased, and the safety problem should also be considered and the second method will make the fuel cell system much more complex and expensive. Therefore, most of the researchers believe that new CO tolerant electrocatalyst will be the most hopeful way to solve the CO poisoning problem in PEMFC.

Nowadays, development of CO tolerance electrocatalyst has been concentrated on PtM (M is usually a transition metal) bimetallic catalysts. For example, PtRu binary catalyst shows evidently CO tolerance. The oxidation potential of CO on PtRu is reduced due to bifunctional mechanism. The performance of PEMFCs will be improved when fuel stream contains CO [9–11], but Pt-Ru alloy is not as active as Pt when pure hydrogen is served as the fuel [1].

Based on previous experience, the structure of electrode plays an importance role in improving cell performance. However, there is less effort on CO tolerance electrode structure improving. As we know that the electrode structure

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relates to diffusion process and reaction dynamics, we have an opportunity to decrease the poisoning of PEMFC anode. Compared with new electrocatalyst development, the improvement of electrode structure will be much more attractive for PEMFC popularization.

When the electrode structure is modified, the loading of the precious metal is reduced and the cell performance will not drop. The electrode structure can be designed to make the poisonous CO to react at a separate layer with CO active electrocatalyst in advance, and make the main hydrogen to react at another layer with traditional electrocatalyst platinum. Then there is possibility for us to have a good result on the electrode structure for CO tolerance study.

2. Experimental

2.1. Composite electrode structure

In H_2/CO fuel stream, as diffusion coefficients of H_2 and CO are different, it is possible to design a special composite electrode structure according to the fuel component. The anodes can be designed with different electrocatalyst components, different contents and different pore distribution. In this way, the designation of structure can help to solve the CO poisoning problem. Several electrode structures are tested in this paper. The electrode structures and electrocatalyst components are listed in Table 1. Two kinds of electrocatalyst 20% Pt/C and 30% PtRu/C are from Johnson-Matthey Inc. The gas diffusion layers are made of carbon paper (SGL TECHNIK, PE704). The proton exchange membrane is Nafion 112 (DuPont Company) and 5% Nafion solution is purchased from DuPont Company.

In Table 1, the traditional method is a one proposed by Lindstrom [12] and the main difference of these anodes is the inner catalyst layer. The transfer method is described in [13], in which the thin layer is hydrophilic as there is no PTFE in it. The E4 and E5 are prepared by the method in [14]. The composite anode structure is shown in Fig. 1.

2.2. Single cell test

Prepared Nafion 112 membrane, anode and cathode (Pt/C from Johnson-Matthey, Pt loading: 0.5 mg/cm^2) are hot pressed at 10 MPa, 140 °C for 1 min to obtain membrane electrode assembly (MEA). Then the above MEA is
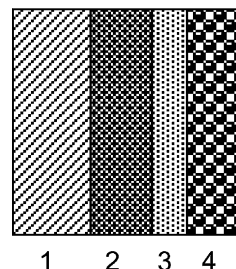

Fig. 1. Schematic structure of a composite anode: (1) gas diffusion layer; (2) outer catalyst layer; (3) inner catalyst layer; (4) Nafion membrane.

mounted in single cell with stainless steel end plates, and mesh flow field is used. The active area of MEA is 5 cm^2.

In PEMFC performance test, both fuel and oxygen are humidified at 80 °C. The operating pressures P_{O_2} and P_{fuel} are all 0.2 MPa. Cell Temperature is 80 °C. The stoichiometric coefficient for hydrogen and oxygen in reaction (1) are 1.25 and 2, respectively. The polarization data is obtained when the vibration of cell voltage is not more than 1 mV in 1 min. Each experiment operates without any oxygen injection:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{1}$$

2.3. EDX analysis

The electrodes are cut to expose their cross-sections. Then the cross-sections are tested by Oxford Instruments X-ray Microanalysis 1350 to have EDX results. The element distribution status is shown in EDX analysis.

3. Results and discussions

3.1. Effect of different catalyst layers on CO poisoning problem

Many researches disclose that the best electrocatalyst in PEMFC is platinum, but when there is more than 10 ppm CO in the fuel, the platinum will be poisoned and the fuel cell performance will decline dramatically. Electrocatalyst in the anode side of E1 and E3 is platinum. When pure hydrogen is served as fuel, E1 and E3 have the similar performance although the total platinum amount in E3 is only 1/15 of that of E1. Since when the mass specific activity

Table 1
Several electrode structures and electrocatalyst loading

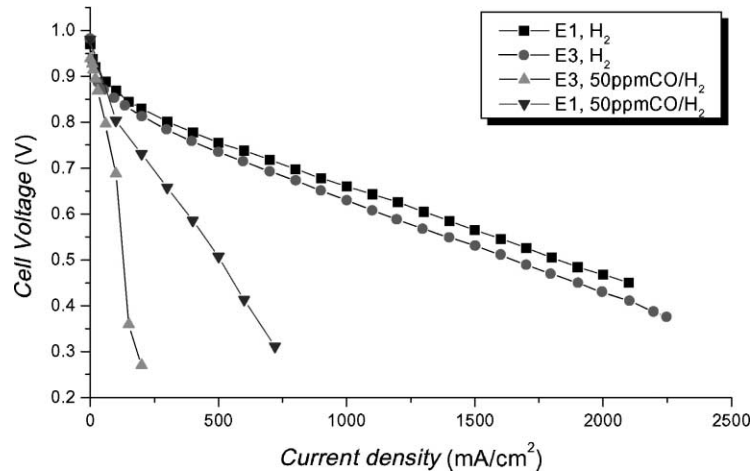| Anode	Inner catalyst layer	Outer catalyst layer
E1	–	Traditional method; Pt/C, 0.3 mg/cm^2 Pt
E2	–	Traditional method; PtRu/C, 0.3 mg/cm^2 PtRu
E3	Transfer method; Pt/C, 0.02 mg/cm^2 Pt	–
E4	Traditional method; Pt/C, 0.1 mg/cm^2 Pt	Traditional method; PtRu/C, 0.2 mg/cm^2 PtRu
E5	Transfer method; Pt/C, 0.02 mg/cm^2 Pt	Traditional method; PtRu/C, 0.28 mg/cm^2 PtRu

Fig. 2. Cell performance of E1 and E3 when H_2 and 50 ppm CO/H_2 serve as fuels.

is considered, the utilization of electrocatalyst E3 is higher than that of E1:

$$i_s = \frac{i}{m_c} \tag{2}$$

where i_s is the specific current density (mA/(cm^2 mg)), i the current density (mA/cm^2) and m_c the electrocatalyst loading (mg). SEM experiment shows that the thickness of the catalyst layer in E1 is about 40 μm, and the catalyst layer of E3 is less than 5 μm [13]. This means that the catalyst layer made by transfer method has less gas transfer distance than that of the traditional method with the same Nafion solution content. Then we can obtain high cell performance with low catalyst loading. But when 50 ppm CO/H_2 is served as fuel, cell performance of E3 drops much more than that of E1 (shown in Fig. 2). Because the diffusion distance and the total electrocatalyst loading in E3 are all less than that of E1, CO will diffuse easily to the surface of the electrocatalyst, it makes the performance of PEMFC to decrease significantly. So when CO containing fuel is fed into a single cell, E3 will be poisoned more easily than E1 as a result of thinner diffusion distance and less electrocatalyst loading in E3. In Fig. 3, it is shown that the mass specific activity of E3 is
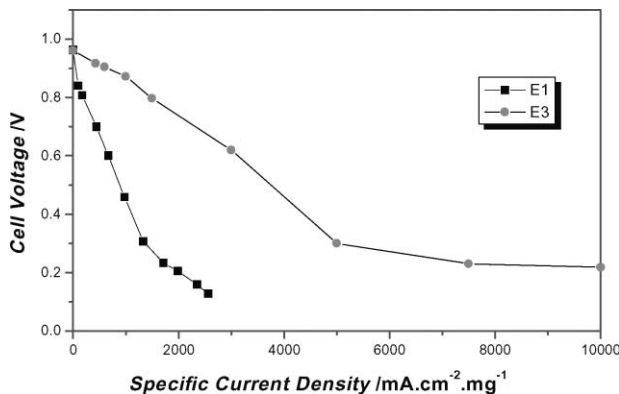
much more higher than that of E1 although total electrocatalyst loading of E3 is less. It indicates that the transfer method could make high catalyst utilization in PEMFC.

From Figs. 2 and 3, it can be seen that each electrode structure has its own characteristic on pure hydrogen fuel and CO containing fuel. The thinner catalyst layer made by transfer method has high catalyst utilization but low CO tolerance, the traditional method is better when CO containing fuel is fed in. It is hopeful to combine the two electrode structures to improve the CO tolerance of PEMFC.

3.2. Composite anode study

At present, Pt–Ru alloy is the most active electrocatalyst for solving CO poisoning problem, but Pt–Ru alloy is not as active as Pt for pure hydrogen, e.g. it makes lower power density than platinum when pure hydrogen is served as fuel. In Fig. 4, it can be seen that E2 is less active than E1 when pure H_2 is served as fuel. When 50 ppm CO/H_2 is used as fuel, the performance of E2 is better than that of E1. The bifunction mechanism of PtRu enhances the CO tolerance of PEMFC.

To develop a composite anode, it is important to utilize PtRu to electrocatalyze the oxidation of CO and use Pt to catalyze the hydrogen oxidation reaction (HOR). As hydrogen diffuses faster than CO in gas diffusion layer, the inner catalyst layer should have higher platinum loading, and the outer catalyst layer should be rich in PtRu. Two kinds of composite anode are made: E4 and E5. Fig. 4 shows the PEMFC performance of E4 for pure hydrogen and 50 ppm CO/H_2.

In Fig. 4, it is seen that with the same noble electrocatalyst loading, the composite anode E4 has almost the same performance as that of E1 and is better than E2 when the fuel is pure hydrogen. But when 50 ppm CO/H_2 is served as fuel, the E4 cell performance also drops seriously. It is only a little better than that of E1. Fig. 5 shows the EDX result of the cross-section of E4. Since the electrocatalyst is sprayed

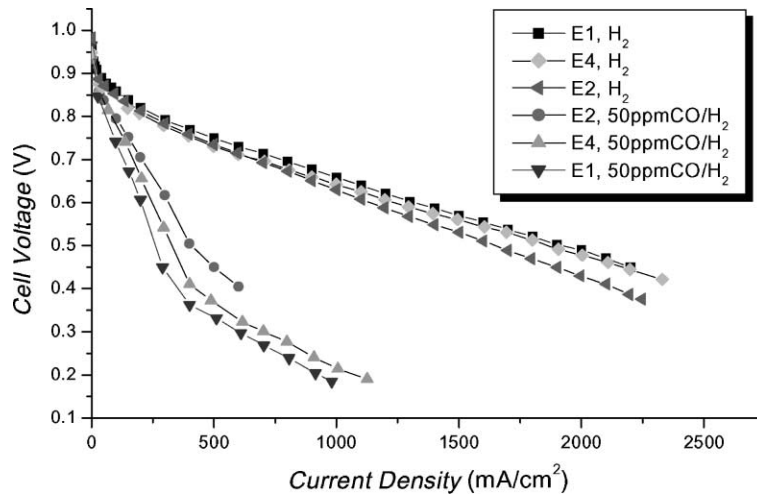Fig. 3. Mass specific activity comparison of E1 and E3.

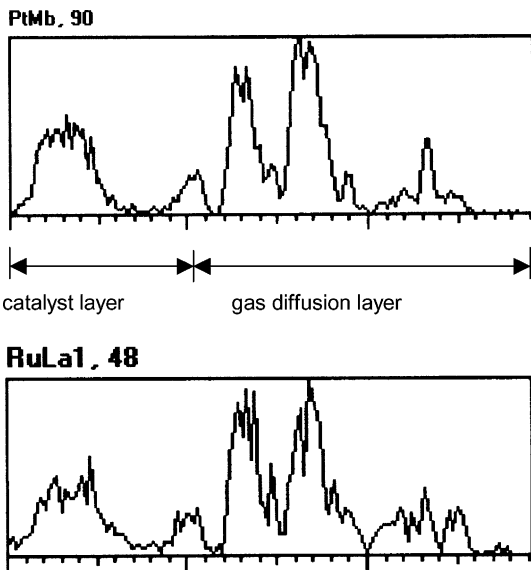Fig. 4. Cell performance of E1, E2 and E4.

Fig. 5. EDX result of composite anode E4.

or brushed onto a gas diffusion layer directly in the traditional method, some of the electrocatalyst immerse into the gas diffusion layer. In Fig. 5, it can be seen that there is no distinct interface between the inner catalyst layer and the outer catalyst layer, and in the gas diffusion layer some electrocatalyst exits. This reduces the utilization of electrocatalyst especially the inner catalyst layer seriously. As the inner catalyst layer is combined with the Nafion membrane with Nafion solution, Nafion makes effective three-dimensional reaction zone [15]. It is possible that the inner catalyst layer with Nafion solution has high electrocatalyst utilization than outer layer. From the EDX test on element distribution, it is disclosed that the traditional electrode preparation method cannot provide an effective electrocatalyst distribution in a composite anode and at the same time, the mass specific activity of the traditional method is not as high as that of the transfer method.

Figs. 6 and 7 show the fuel cell performance with E5 and E2 for pure H_2 and CO containing fuel, respectively. It can
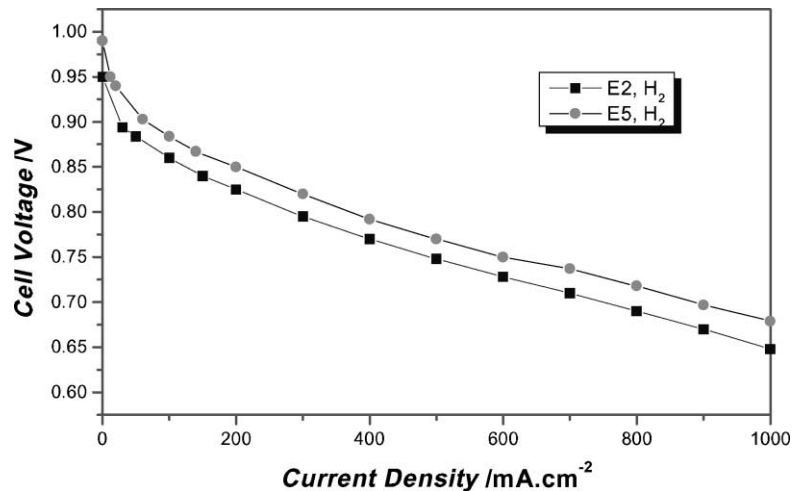

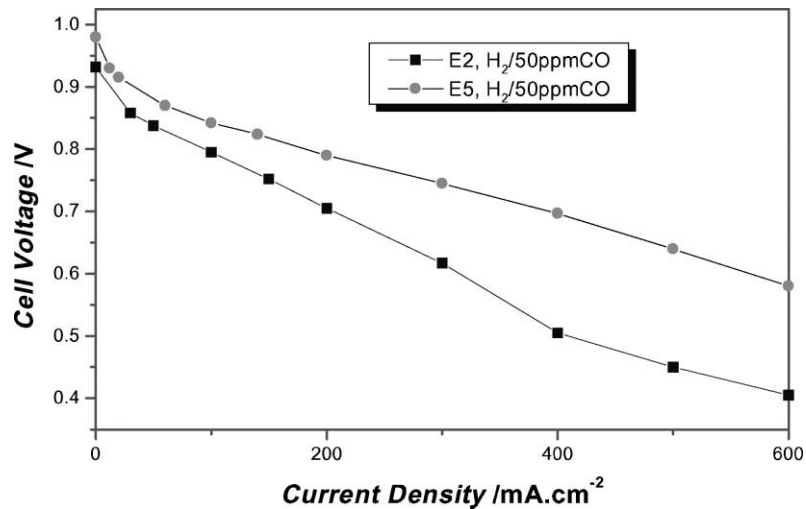Fig. 6. Comparison between E5 and E2 in pure hydrogen.

Fig. 7. Comparison between E5 and E2 in 50 ppm CO/H_2.

be seen that with pure hydrogen and 50 ppm CO/H_2, cell performance of E5 is better than that of E2. In the case, where CO/H_2 is served as fuel, E5 is much better than E2 with about 100 mV improvement on cell performance when the operating current density is over 500 mA/cm^2.

Fig. 8 shows the EDX results of E5. Although there is electrocatalyst immersion into gas diffusion layer, the catalyst distribution in Fig. 8 differs from that in Fig. 5. We can see that most of PtRu is distributed near to the gas diffusion layer, while platinum concentrates in the inner catalyst layer with its thickness less than 5 μm and adjacent to Nafion membrane. Such a catalyst distribution can electrocatalyze the reaction for both H_2 and CO when CO/H_2 fuel is fed into PEMFC. As Nafion solution could make the

Fig. 8. EDX result of composite anode E5.

three-dimensional reaction zone in electrode. Because the very thin inner catalyst layer containing Nafion solution, then electrochemical reaction will take place in outer catalyst layer with Nafion conducting protons, while the thin inner catalyst layer maintains high platinum utilization for hydrogen electro-oxidization. From structure point of view, it is important to maintain the distinct interface between inner and outer catalyst layer.

This means that the composite anode ensure both high activity of hydrogen and decrease of CO poison to the platinum. It indicated that the new composite anode E5 improves the diffusion status of hydrogen to enhance CO tolerance of PEMFC with its performance improved when pure hydrogen is served as fuel.

The improvement of PEMFC performance mainly comes from the successful anode structure reformation. In the thick outer catalyst layer, PtRu/C serves as a CO barrier, and electrocatalyst Pt/C maintains high activity to HOR although the platinum loading is low in the inner catalyst layer.

4. Conclusions

The preparation method of anode catalyst layer is very important to the performance of PEMFCs with pure hydrogen and CO containing fuel. The thin-film catalyst layer made by transfer method exhibits high electrocatalyst utilization and low CO tolerance with the same electrocatalyst, while it is different from the traditional method. The advantages of both electrodes are combined in the composite anode design. When H_2/CO acts as the fuel, the PEMFCs exhibit less performance drop with the new composite electrode structure, while pure hydrogen acts as the fuel, the fuel cell posses almost the same performance as that of Pt/C electrocatalyst. It is important for catalyst layer preparation that the inner catalyst layer should be rich in platinum and
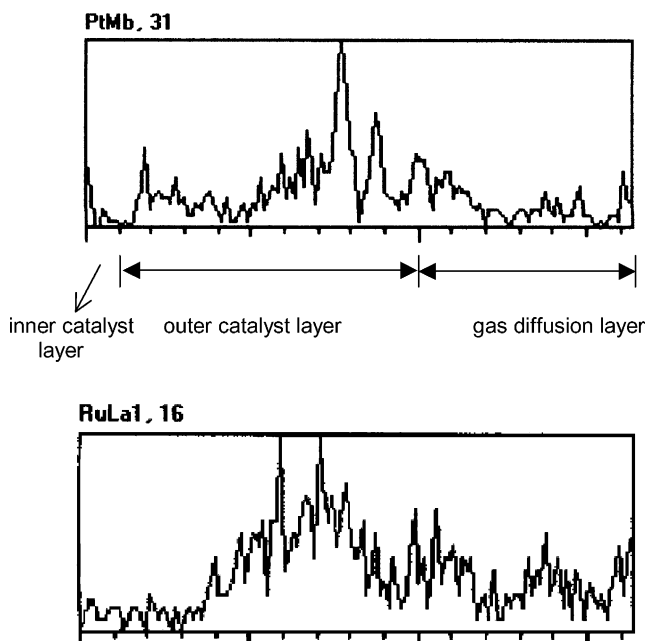
that the outer catalyst layer should be rich in CO tolerance electrocatalyst, e.g. PtRu/C. The outer catalyst layer should have a distinct boundary with the inner catalyst layer. In this way, the effective gradient of the electrocatalyst could be formed and CO could be electro-oxidized in the outer catalyst layer, then HOR is able to have high activity in the inner catalyst layer. The composite anode can improve the CO tolerance of PEFMC with neither increasing the amount of electrocatalyst loading nor oxygen injection.

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