

Short communication

A novel proton exchange membrane fuel cell anode for enhancing CO tolerance

Weiyu Shi ^{a,b}, Ming Hou ^{a,*}, Zhigang Shao ^a, Jun Hu ^c,
Zhongjun Hou ^c, Pingwen Ming ^c, Baolian Yi ^a

^a Fuel Cell System and Engineering Research Group, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

^c Sunrise Power Co. Ltd., 1 Huoju Road, Dalian 116025, PR China

Received 26 July 2007; received in revised form 23 August 2007; accepted 30 August 2007

Available online 4 September 2007

Abstract

A novel proton exchange membrane fuel cell (PEMFC) anode which can facilitate the CO oxidation by air bleeding and reduce the direct combustion of hydrogen with oxygen within the electrode is described. This novel anode consists of placing Pt or Au particles in the diffusion layer which is called Pt- or Au-refined diffusion layer. Thus, the chemical oxidation of CO occurs at Pt or Au particles before it reaches the electrochemical catalyst layer when trace amount of oxygen is injected into the anode. All membrane electrode assemblies (MEAs) composed of Pt- or Au-refined diffusion layer do perform better than the traditional MEA when 100 ppm CO/H₂ and 2% air are fed and have the performance as excellent as the traditional MEA with neat hydrogen. Furthermore, CO tolerance of the MEAs composed of Au-refined diffusion layer was also assessed without oxygen injection. When 100 ppm CO/H₂ is fed, MEAs composed of Au-refined diffusion layer have the slightly better performance than traditional MEA do because Au particles in the diffusion layer have activity in the water gas shift (WGS) reaction at low temperature.

© 2007 Elsevier B.V. All rights reserved.

Keywords: PEMFC; CO tolerance; Anode

1. Introduction

Among the various types of fuel cell, proton exchange membrane fuel cell (PEMFC) possesses several highly advantageous features such as a low-operating temperature, sustained operation at high current density, low weight, compactness, potential for low cost and volume, long stack life, fast start-up and suitability for discontinuous operation. Practical PEMFC most likely will use reformat fuel as the primary source for the anode feed. Besides H₂, N₂ and CO₂, the reformat may contain trace amounts of CO which can strongly adsorb on the Pt catalyst surface and cause considerable cell performance losses [1].

In order to overcome the CO poisoning problem, many solutions have been developed. One solution consists of replacing anode Pt catalysts by Pt–M alloys which can improve CO toler-

ance, such as Pt–Ru [2], Pt–Sn [3], and Pt–Mo [4]. The improvement is due to either a lowered CO oxidation potential or a weakened adsorption of CO on these alloy catalysts. However, at the PEMFC operating temperature, this method is unable to completely resolve the CO poisoning issue and the alloy catalysts are not as active as Pt when pure hydrogen is fed. Furthermore, these catalysts are still pending concerning their long-term chemical stability because the non-noble alloying metal has to endure the harsh environment of the catalyst layer [1].

The second potential solution for improving CO tolerance would be to operate the fuel cell at temperature higher than 100 °C. At these temperatures, the CO sticking coefficient on Pt is considerably lower. However, increasing the PEMFC operating temperature might have some adverse impacts. Higher operation temperature greatly increases the resistance of the proton exchange membrane and enhances the aggregation rate of Pt particles as well as the Pt dissolution. Furthermore, when the temperature is above 100 °C, the membrane degrades more quickly [5].

* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.
E-mail address: houming@dicp.ac.cn (M. Hou).

The third solution is to apply composite anode for enhancing CO tolerance. Yu et al. [6] proposed a composite electrode structure which was designed to make the poisonous CO to react at a separate layer with CO active PtRu electrocatalyst in advance and make the hydrogen to react at another layer with Pt electrocatalyst. Wan et al. [7] proposed an anode catalyst layer structure to improve the CO tolerance, and this layered structure was composed of an outer and inner catalyst layer. The outer layer acted as a CO barrier and consisted of a nano PtRu layer and the inner layer was a pure Pt layer. According to their work, this anode catalyst layer structure exhibited a superior performance and CO tolerance which was attributed to the filtering effect of the outer catalyst layer. In this method, the most important point is that the outer catalyst layer should be extraordinarily active for the low temperature electrochemical oxidation of CO.

The fourth solution is to utilize pulsing techniques for electrochemical oxidation of CO. Lakshmanan et al. [8] used a PEMFC as a flow reactor for continuous preferential oxidation of CO over H₂ from 1% CO in H₂ under pulse-potential control. By varying the pulse profile, the CO and H₂ oxidation currents were varied independently. Zhang et al. [9] proposed an electrochemical preferential oxidation process (ECPROX) for selectively removing CO from H₂-rich gas by utilizing the anode potential oscillations in a device with a structure similar to that of a PEMFC. Furthermore, this ECPROX unit can simultaneously produce some supplementary power by electrochemical oxidation of CO and H₂.

Another possible solution to the issue of catalyst poisoning by CO is to inject a small amount of oxygen along with the fuel stream which was established in the late 1980s at Los Alamos [10]. Gottesfeld et al. [10] found that the deleterious effect of 100 ppm CO could be completely eliminated by injecting a small amount of O₂ (2%). However, roughly one out of every 400 O₂ molecules oxidizes an adsorbed CO molecule [11] and the remaining oxygen chemically combusts with hydrogen. The combustion reaction not only lowers the fuel efficiency, but might also accelerate the sintering of catalyst particles to

lead to a performance decline with time [7]. In order to enhance the efficiency of the oxygen, some reconfigured anodes have been proposed. Uribe et al. [1] placed a composite film containing inexpensive materials onto the gas diffusion layer and these materials were able to catalyze the oxidation of CO with O₂ to CO₂. Haug et al. [12,13] placed a layer of Ru atop a Pt anode, and this anode structure can increase the CO tolerance when oxygen is added to the fuel stream.

In this paper we report a novel PEMFC anode which can facilitate the CO oxidation by air bleeding and reduce the direct combustion of hydrogen with oxygen within the electrode. Fig. 1 depicts the schematics and functionality of this method. It has been reported that Pt and Au particles are active for catalytic CO oxidation [14], so we placed Pt or Au particles in diffusion layer (called Pt- or Au-refined diffusion layer in this work) by impregnation. Thus, the chemical oxidation of CO occurs at Pt or Au particles before it reaches the electrochemical catalyst layer when trace amount of oxygen is injected. At the same time, this structure can avoid the disadvantageous heating effects to electrocatalyst and membrane caused by the oxygen injection because the CO oxidation and hydrogen oxidation with remaining oxygen occur in the diffusion layer. Furthermore, it was reported that Au catalysts have high activity in the water–gas shift (WGS) reaction at low temperature [15,16], and CO tolerance of the MEAs composed of Au-refined diffusion layer was assessed without oxygen injection in this work.

2. Experimental

For obtaining the Pt-refined diffusion layer by impregnation, Toray carbon paper was dipped in the H₂PtCl₆·6H₂O ethanol solution for several minutes and then the ethanol was evaporated at 80 °C. Then dry impregnated carbon paper was placed in a quartz tube and reduced under a pure hydrogen flow for 2 h at 400, 600 and 800 °C, respectively. Similarly, the Au-refined diffusion layer was obtained by dipping carbon paper in

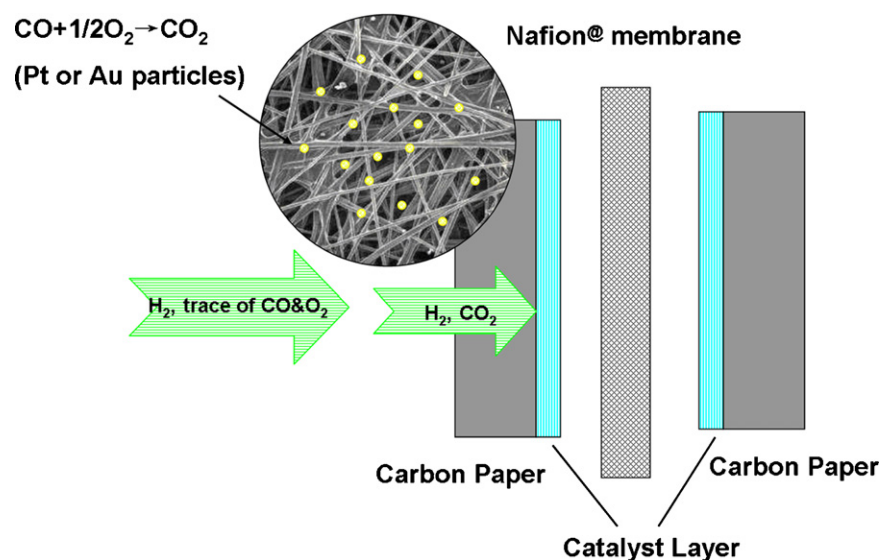


Fig. 1. Schematics and functionality of the novel anode composed Pt- or Au-refined diffusion layer for enhancing CO tolerance.

the $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ethanol solution. Because the melting point of Au (1063°C) is much lower than that of Pt (1796°C), the HAuCl_4 in the carbon paper was reduced at 400°C for 2 h under a pure hydrogen flow in order to control the size of Au particles. For the Toray carbon paper with fixed surface area, the capacity to the adsorption of catalyst precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ethanol solution) can be considered constant. So Pt or Au loading in the carbon paper can be controlled theoretically by adjusting the concentrations of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ethanol solution. For example, when the concentration of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ is fixed at 0.075 mol L^{-1} , the carbon paper with 0.3 mg cm^{-2} Au loading can be obtained. The accurate Au loading can be confirmed by gravimetric method and the loading error of Au is less than 5%. Then, in order to improve the hydrophobic properties of the diffusion layer, the Pt- and Au-refined carbon paper were immersed in polytetrafluoroethylene (PTFE) emulsion and were sintered at 330°C for 40 min subsequently to give a homogeneous dispersion of PTFE. During the hydrophobic treatment process, partial Pt or Au particles will be covered by PTFE inevitable. As a result, the available metal loading is lower than theoretical loading. Because the available loading is difficult to measure, theoretical loading is used in this paper.

The 50 wt.% Pt on Vulcan XC-72 (from Johnson–Matthey) catalyst, Pt- or Au-refined carbon paper, Nafion solution and PTFE suspension were used to fabricate the anode. Similarly, a 50 wt.% Pt on Vulcan XC-72 (from Johnson–Matthey) catalyst, traditional Toray carbon paper, Nafion solution and PTFE suspension were used to fabricate the cathode. The Pt loading of the catalyst layer were both 0.5 mg cm^{-2} on the anode and the cathode. More details about preparation of the electrodes were reported by our research group [17]. Nafion[®] 212 membrane, anode and cathode were hot pressed at 140°C for 1 min to obtain a membrane electrode assembly (MEA), the active area of each MEA was 5 cm^2 . The MEAs prepared and tested in this work are shown in Table 1.

The polarization curves were performed with fuel and air flows of 50 and 600 sccm (standard cubic centimeter per minute), respectively, and operating pressures P_{fuel} and P_{air} were all 0.1 MPa. The operating temperature of the single cell was kept at 60°C . Humidification temperature of the cathode was 60°C . Scanning electron microscopy (SEM) was applied to investigate

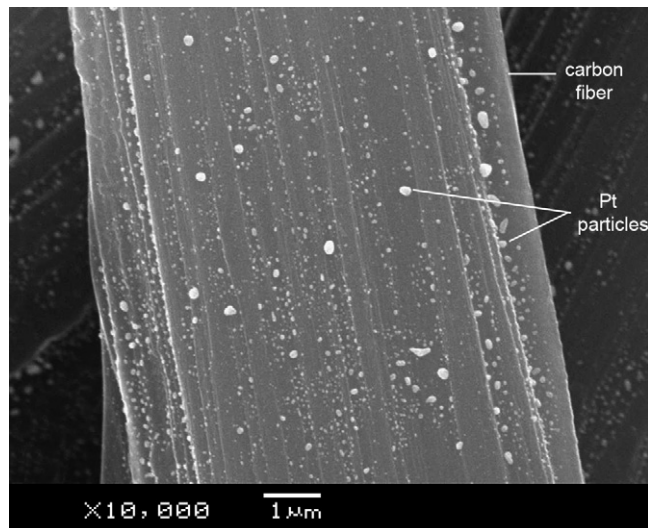


Fig. 2. SEM image of Pt-refined diffusion layer (before the hydrophobic treatment, Pt loading in the diffusion layer: 0.3 mg cm^{-2}); reduce temperature: 600°C .

the Pt or Au particles in carbon paper and SEM characterization was performed on a JEOL (JSM-5600LV).

3. Results and discussion

3.1. Performance of Pt-refined diffusion layer

SEM image of Pt-refined diffusion layer is shown in Fig. 2. Pt particles are prepared on the carbon fiber which can catalyze the reaction of CO oxidation. Pt particles are distributed in a wide range because it is difficult to obtain uniform particles with a good dispersion by impregnation.

Fig. 3 shows the single cell performance comparison of MEAs composed of Pt-refined diffusion layer obtained at different reduce temperature (MEA-1: 400°C ; MEA-2: 600°C ;

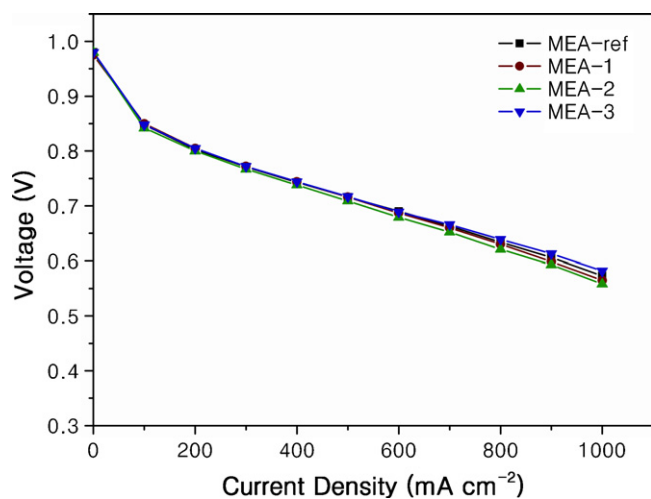


Fig. 3. Single cell performance comparison of MEAs composed of Pt-refined diffusion layer obtained at different reduce temperature with neat H_2 ; $T_{\text{cell}} = 60^\circ\text{C}$; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and 60°C .

Table 1
MEAs prepared and tested

Sample	Catalyst loading in the anode diffusion layer (mg cm^{-2})	Reduce temperature ($^\circ\text{C}$)	Pt loading of the catalyst layer on anode and cathode (mg cm^{-2})
MEA-ref	–	–	0.5
MEA-1	Pt: 0.3	400	0.5
MEA-2	Pt: 0.3	600	0.5
MEA-3	Pt: 0.3	800	0.5
MEA-4	Pt: 0.1	600	0.5
MEA-5	Pt: 0.2	600	0.5
MEA-6	Au: 0.1	400	0.5
MEA-7	Au: 0.2	400	0.5
MEA-8	Au: 0.3	400	0.5

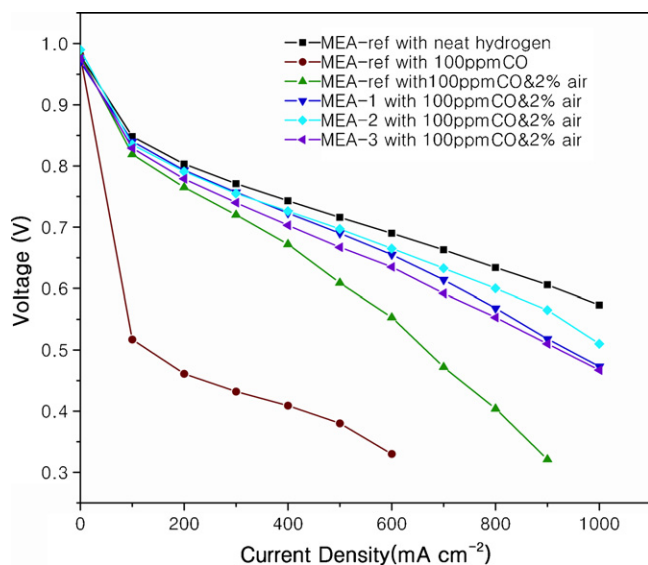


Fig. 4. Single cell performance comparison of MEAs composed of Pt-refined diffusion layer obtained at different reduce temperature with 100 ppm CO/H₂ and 2% air; $T_{\text{cell}} = 60^\circ\text{C}$; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and 60°C .

MEA-3: 800°C) with neat H₂. From Fig. 3, when neat hydrogen is fed, MEA-1, MEA-2, MEA-3 and the traditional MEA (MEA-ref) have the similar performance. But when the hydrogen contains 100 ppm CO, the performance of traditional MEA degrades dramatically because the strong adsorption of CO at the Pt electrode can directly block the surface active sites used for H₂ electro-oxidation, as shown in Fig. 4. The cell voltage decreased to 0.33 V at 600 mA cm^{-2} . Though oxygen injection has some perceived weaknesses, such as low oxygen utilization ratio and disadvantageous heating effects, this method remains to be a useful tool for enhancing PEMFC CO tolerance. When 2% air was injected, the performance of the traditional MEA recovered obviously and the voltage recovered to 0.553 V at 600 mA cm^{-2} . Comparing the traditional MEA, the MEAs composed of Pt-refined diffusion layer have much higher performance with 100 ppm CO/H₂ and 2% air because this anode structure can enhance the efficiency of oxygen bleed into the anode. Furthermore, MEA-2 (reduce temperature: 600°C) shows the greatest CO tolerance which may be relative to size distribution of Pt particles in the diffusion layer because the mean particle size of Pt increases slightly with increasing pyrolysis temperature [18]. Pt particles obtained at 400°C are comparatively smaller and can be easily covered by PTFE during the hydrophobic treatment process which results in lower available Pt loading. On the contrary, Pt particles obtained at 800°C are relatively bigger and distributed in a wider range which may result in low catalytic activity.

Fig. 5 shows performance comparison of MEAs composed of Pt-refined diffusion layer with different Pt loading, and the Pt loading of MEA-4, MEA-5 and MEA-2 in the diffusion layer is 0.1, 0.2, and 0.3 mg cm^{-2} , respectively. When 100 ppm CO/H₂ and 2% air are fed, all MEAs composed of Pt-refined diffusion layer do perform better than the traditional MEA. Theoretically speaking, CO tolerance of a MEA can be enhanced by increasing

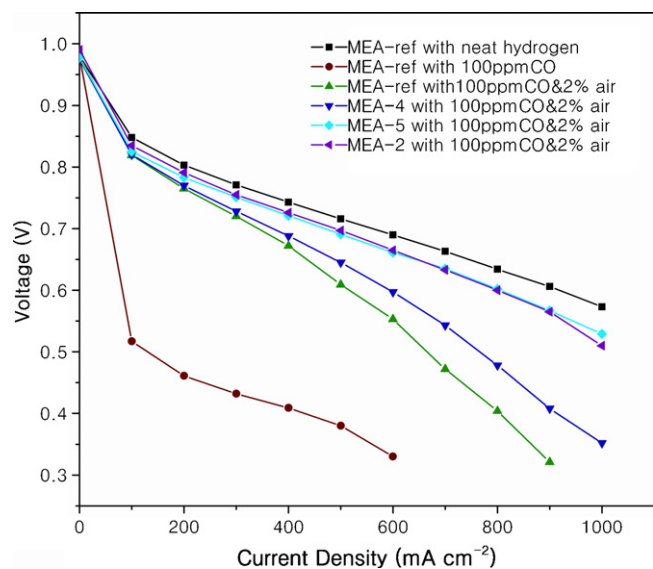


Fig. 5. Single cell performance comparison of MEAs composed of Pt-refined diffusion layer with different Pt loading with 100 ppm CO/H₂ and 2% air; $T_{\text{cell}} = 60^\circ\text{C}$; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and 60°C .

Pt loading in the diffusion layer, thus this refined MEA can provide more Pt particles for catalyzing the chemical reaction of CO before CO reaches the electrochemical catalyst layer. However, excessive Pt loading in the diffusion layer will not only increase cost but also affect the hydrophobic nature of the diffusion layer because of hydrophilic Pt particles. From Fig. 5, MEA-5 has almost the same performance as that of MEA-2 and is better than MEA-4.

3.2. Performance of Au-refined diffusion layer

The catalysis of gold had received little attention until Haruta et al. reported in 1987 that some gold catalysts were extraordinarily active for the low temperature oxidation of CO. Because Au catalysts are more active for CO oxidation than for H₂ oxidation, in applications to the selective removal of CO from the reformate gas, Au catalysts are more advantageous than the Pt catalysts which are more active for H₂ oxidation. Furthermore, Au catalysts are usually enhanced by moisture in catalytic activity for CO oxidation [14]. So, Au particles were prepared in the diffusion layer to enhance the cell tolerance to CO in this work.

Fig. 6 shows single cell performance comparison of MEAs composed of Au-refined diffusion layer with neat H₂ and the Au loading of MEA-6, MEA-7 and MEA-8 in the diffusion layer is 0.1, 0.2, and 0.3 mg cm^{-2} , respectively. From Fig. 6, when neat hydrogen is fed, MEA-6, MEA-7, MEA-8 and the traditional MEA (MEA-ref) have almost the same performance. However, when 100 ppm CO/H₂ and 2% air are fed, all MEAs composed of Au-refined diffusion layer do perform better than the traditional MEA and the MEA-6 shows a slightly better performance than that of MEA-7 and MEA-8 in the high current density region, as shown in Fig. 7. Though Au catalysts have some advantageous characteristic features,

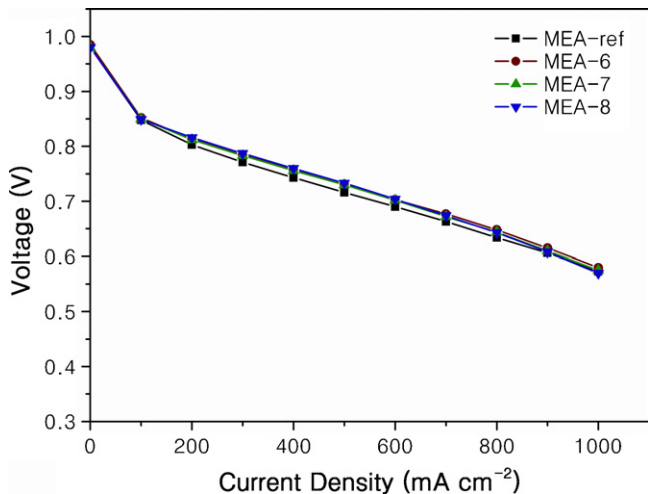


Fig. 6. Single cell performance comparison of MEAs composed of Au-refined diffusion layer with different Au loading with neat H_2 ; $T_{cell} = 60^\circ C$; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and $60^\circ C$.

the catalytic properties of Au markedly depend on the size of Au particles and the interaction with supports [14,19]. In this work, Au particles in the diffusion layer were prepared by impregnation and it is difficult to get Au particles with good dispersion. Au particles are distributed in a much wider range than Pt particles as shown in Fig. 8, because the melting point of Au ($1063^\circ C$) is much lower than that of Pt ($1796^\circ C$).

It can be concluded from the above discussion that the CO tolerance of MEAs composed of Pt- or Au-refined diffusion layer is good but strongly depends on the oxygen injection. According to the work of Andreeva et al. [15,16], Au catalysts have high activity in the WGS reaction at low temperature. If so, CO can

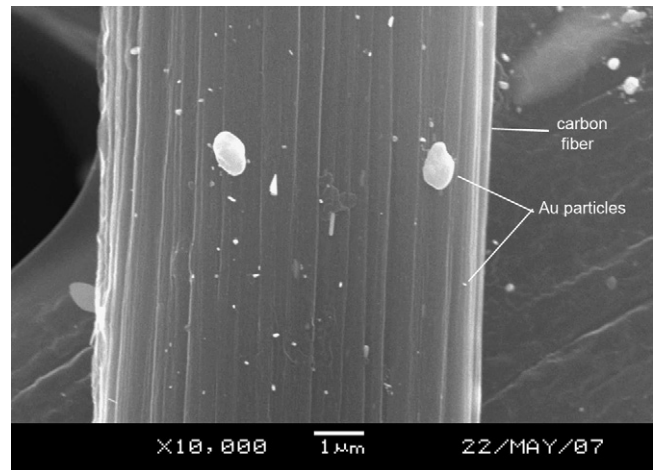


Fig. 8. SEM image of Au-refined diffusion layer (before the hydrophobic treatment, Au loading in the diffusion layer: 0.3 mg cm^{-2}); reduce temperature: $400^\circ C$.

be oxidized by H_2O on the Au particles in the Au-refined diffusion layer without oxygen injection. Therefore, CO tolerance of the MEAs composed of Au-refined diffusion layer was also assessed without oxygen injection. In order to promote CO oxidation by the WGS reaction, the humidification temperature of anode was increased to $60^\circ C$. Fig. 9 shows performance comparison of MEAs composed of Au-refined diffusion layer with 100 ppm CO/H_2 , but without oxygen injection. When 100 ppm CO/H_2 is fed, all MEAs composed of Au-refined diffusion layer (MEA-6, MEA-7 and MEA-8) have the slightly better performance than traditional MEA. However, their tolerance to CO is much weaker than the traditional MEA with 2% air injection, as shown in Fig. 9. These observations suggest that Au particles in the diffusion layer may not work effectively and do not

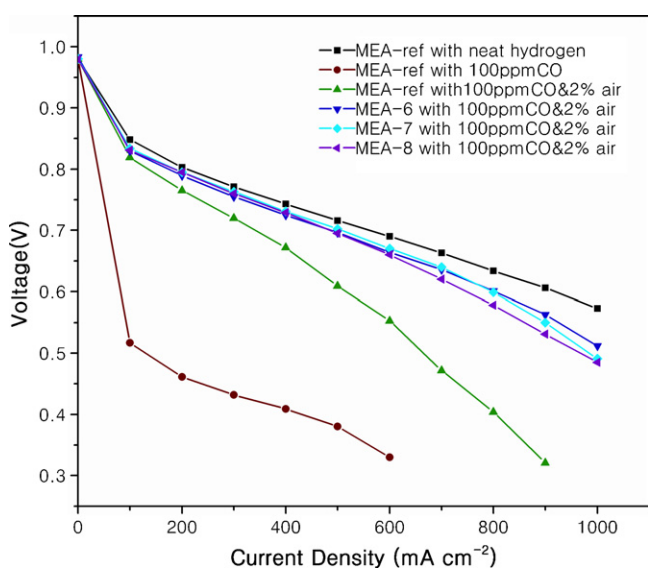


Fig. 7. Single cell performance comparison of MEAs composed of Au-refined diffusion layer with different Au loading with 100 ppm CO/H_2 and 2% air; $T_{cell} = 60^\circ C$; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and $60^\circ C$.

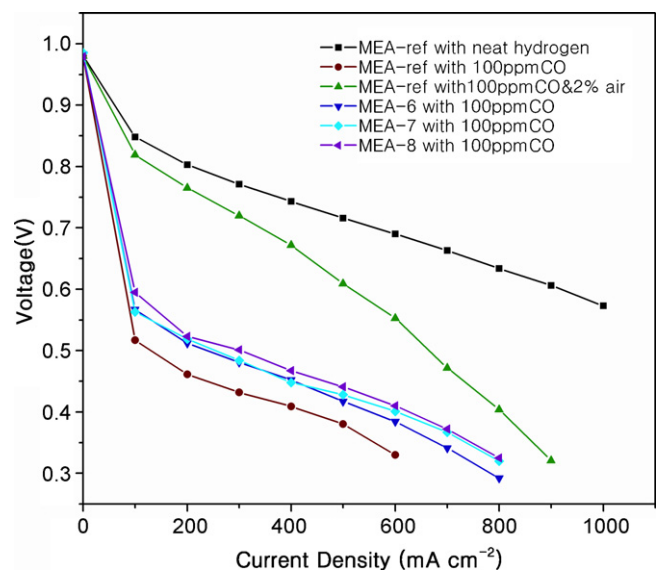


Fig. 9. Single cell performance comparison of MEAs composed of Au-refined diffusion layer with different Au loading with 100 ppm CO/H_2 ; $T_{cell} = 60^\circ C$; operating pressure: 0.1 MPa; humidification temperatures of both anode and cathode: $60^\circ C$.

possess excellent activity in the WGS reaction. And the cause is most probably to be the bad dispersion and wide distribution of Au particles in the refined diffusion layer. Under such conditions, it is reasonable that MEA-8 shows a little better performance than MEA-6 and MEA-7 because of higher Au catalyst loading.

As mentioned above, the catalytic properties of Au markedly depend on the size of Au particles and the interaction with supports, and only gold in a finely divided state exhibits high catalytic activity [14–16,19]. In the future work, preparation of uniform Au particles with good dispersion in the diffusion layer is rather important. If some catalysts which have high activity in the electrochemical oxidation reaction of CO (WGS reaction) at low temperature (about 80 °C) can be prepared uniformly in the anode diffusion layer, the CO tolerance of the PEMFC will be improved dramatically without air injection.

4. Conclusions

A novel PEMFC anode which can considerably enhance the efficiency of oxygen bled into the anode is described. We placed Pt or Au particles in diffusion layer by impregnation (called Pt- or Au-refined diffusion layer). Thus, the chemical oxidation of CO occurs at Pt or Au particles before it reaches the electrochemical catalyst layer when trace amount of oxygen is injected. At the same time, this structure can avoid the disadvantageous heating effects to electrocatalyst and membrane caused by the oxygen injection. MEAs composed of Pt- or Au-refined diffusion layer perform better than the traditional MEA when 100 ppm CO/H₂ and 2% air are fed and have the performance as excellent as the traditional MEA with neat hydrogen. Though Au catalysts are extraordinarily active for WGS reaction, the catalytic properties of Au markedly depend on the size and distribution of Au particles, and the interaction with supports. In this work, performance of MEAs composed of Au-refined diffusion layer is only a little better than that of traditional MEA with 100 ppm CO/H₂ because of bad dispersion and wide distribution. So, in the future work, preparation of uniform Au particles with good dispersion in the diffusion layer is crucial.

Acknowledgements

This work was financially supported by the National High Technology Research and Development Program of China (863 Program no. 2005AA501660, no. 2006AA11A141 and no. 2006AA05Z146) and the National Natural Science Foundation of China (no. 20636060).

References

- [1] F.A. Uribe, J.A. Valerio, F.H. Garzon, T.A. Zawodzinski, *Electrochem. Solid-State Lett.* 7 (2004) A376–A379.
- [2] H.A. Gasteiger, N.M. Markovic, P.N. Ross Jr., *J. Phys. Chem.* 99 (1995) 8290–8301.
- [3] H.A. Gasteiger, N.M. Markovic, P.N. Ross Jr., *J. Phys. Chem.* 99 (1995) 8945–8949.
- [4] B.N. Grgur, G. Zhuang, N.M. Markovic, P.N. Ross Jr., *J. Phys. Chem. B* 101 (1997) 3910–3913.
- [5] C. Huang, R. Jiang, M. Elbaccouch, N. Muradov, J.M. Fenton, *J. Power Sources* 162 (2006) 563–571.
- [6] H. Yu, Z. Hou, B. Yi, Z. Lin, *J. Power Sources* 105 (2002) 52–57.
- [7] C.H. Wan, Q.H. Zhuang, C.H. Lin, M.T. Lin, C. Shih, *J. Power Sources* 162 (2006) 41–50.
- [8] B. Lakshmanan, W. Huang, W. John, Weidner, *Electrochem. Solid-State Lett.* 5 (2002) A267–A270.
- [9] J. Zhang, R. Datta, *J. Electrochem. Soc.* 152 (2005) A1180–A1187.
- [10] S. Gottesfeld, J. Pafford, *J. Electrochem. Soc.* 135 (1988) 2651–2652.
- [11] R.J. Bellows, E. Marucchi-Soos, R.P. Reynolds, *Electrochem. Solid-State Lett.* 1 (1998) 69–70.
- [12] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, *J. Electrochem. Soc.* 149 (2002) A862–A867.
- [13] A.T. Haug, R.E. White, J.W. Weidner, W. Huang, S. Shi, N. Rana, S. Grunow, T.C. Stoner, A.E. Kaloyeros, *J. Electrochem. Soc.* 149 (2002) A868–A872.
- [14] M. Haruta, *Catal. Surv. Jpn.* 1 (1997) 61–73.
- [15] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, R. Giovanoli, *Appl. Catal. A: Gen.* 134 (1996) 275–283.
- [16] D. Andreeva, T. Tabakova, V. Idakiev, P. Christov, R. Giovanoli, *Appl. Catal. A: Gen.* 169 (1998) 9–14.
- [17] J. Wu, B. Yi, Z. Hou, H. Zhang, *Electrochem. Solid-State Lett.* 7 (2004) 1–4.
- [18] T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, *J. Catal.* 229 (2005) 176–184.
- [19] G.R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, *Catal. Lett.* 44 (1997) 83–87.