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Short communication

A 75-kW methanol reforming fuel cell system

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Abstract

A 75-kW methanol reforming fuel cell system, which consists of a fuel cell system and a methanol auto-thermal reforming fuel processor has been developed at Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS). The core of the fuel cell system is a group of CO tolerant PEMFC stacks with a double layer composite structured anode. The fuel cell stacks show good CO tolerance even though 140 ppm CO was present in the reformate stream during transients. The auto-thermal reforming (ATR) fuel cell processor could adiabatically produce a suitable reformate without external energy consumption. The output of hydrogen-rich reformate was approximately 120 N m^3 h^{-1} with a H_2 content near 53% and the CO concentrations generally were under 30 ppm. The fuel cell system was integrated with the methanol reforming fuel processor and the peak power output of the fuel cell system exceeded 75 kW in testing. The hydrogen utilization approached 70% in the fuel cell system.

Keywords: PEMFC; Auto-thermal reforming; CO tolerance

1. Introduction

Among the various types of fuel cell, the proton-exchange membrane fuel cell (PEMFC) possess 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, rapid start-up, and a suitability for discontinuous operation [1–4]. These features currently make PEMFC technology a promising candidate for a wide variety of power applications that range from portable/micro-power and transportation uses to large-scale stationary power for buildings and distributed generation [5–7]. However, hydrogen fuel faces the challenges of storage and delivery. Therefore, extensive research has been directed towards the development of systems for hydrocarbon reforming to generate hydrogen. Methanol is often considered as one possible fuel since it can be stored as a liquid without any infrastructure change for refueling and can be reformed to hydrogen with relatively mild conditions [8,9]. Therefore, generating hydrogen by reforming of methanol has been frequently considered in the development of hydrogen energy and fuel cells.

Generally, the reformate contains hydrogen, carbon dioxide, carbon monoxide, water, and nitrogen [10–12]. The presence of CO in the reformate causes PEMFC catalyst poisoning, which is attributed to the strong adsorption of CO on the catalyst surface resulting in the reduction of the active catalyst sites for hydrogen electro-oxidation [13,14]. Tests of PEMFC stacks indicate that more than about 10 ppm of CO in the reformate will decrease cell performance [15–21]. Therefore, overcoming the CO poisoning problem is of paramount interest in supplying a viable fuel for PEMFCs.

There are several ways to overcome the CO poisoning of electro-catalysts, namely: (i) oxidant bleeding into the fuel feed stream; (ii) advanced reformer design; (iii) use of CO tolerant catalysts; (iv) membranes for CO separation [22,23]. In addition to these methods, the employment of a double layer (composite) structure anode electrode has also been investigated in recent years. The PEMFC with a composite anode electrodes show good CO tolerance properties and a smaller drop in performance than traditional PtRu electrodes [24].

In our work, double layer composite structured anodes were prepared to overcome CO poisoning. PtRu was used to electro-catalyze the oxidation of CO and Pt was used to catalyze the

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hydrogen oxidation reaction. The CO tolerant PEMFC stacks were assembled using MEAs with double layer composite structured anodes and composite metal bipolar plates. A 75-kW fuel cell system was assembled using three CO tolerance PEMFC stacks. The fuel cell system was integrated with the methanol auto-thermal reforming fuel processor at Dalian Institute of Chemical Physics, CAS.

2. Experimental

2.1. Preparation of the CO tolerant MEA

To improve the CO tolerant performance of PEMFC, a kind of double layer composite structured anode was developed as seen in Fig. 1. The catalyst layer of composite structured anode was made up of two layers. One was a Pt/C catalyst layer to enhance the cell performance in the inner catalyst layer, and the other layer was formed by PtRu/C catalysts to provide CO tolerance in the outer catalyst layer. Hexachloroplatinic acid and ruthenium chloride are used as sources of noble metal, and XC-72 carbon was used. PtRu/C can be prepared similarly to the preparation of Pt/C. The noble metal contents of the catalysts were 20 wt% Pt and 10 wt% Ru. The gas diffusion layers were made of carbon paper (SGL TECHNIK, PE704). The double layer composite structured anodes were prepared by the method in [25]. The Pt loading of the inner catalyst layer was 0.02 mg cm^{-2} Pt. The PtRu loading of inner catalyst layer was 0.28 mg cm^{-2} Pt. A Nafion 112 membrane, the prepared anode and the cathode (Pt/C as catalysts from, Pt loading: 0.5 mg cm^{-2}) were hot pressed at 130 °C and 200 kg cm^{-2} for 90 s to obtain a membrane electrode assembly (MEA).

2.2. High power PEMFC stacks

The CO tolerant PEMFC stacks were assembled using composite bipolar plates and MEAs with double layer composite structured anode electrodes. The composite metal bipolar plates used 316L grade stainless plate with a surface treatment as the supporting plate and a flexible graphite plate as the flow field plate. This plate was produced by composite molding. Stacks with 180 single cells were assembled with the bipolar plates and MEAs prepared as previously specified. The electrochemical performance of the stacks was tested using pure hydrogen and a simulated reformate. During the stack experiment, saturated humid air was supplied by a water sealed air compressor and the stacks were cooled with water. The operating temperature and pressure were maintained at 60 °C and 1.5 bar, respectively.

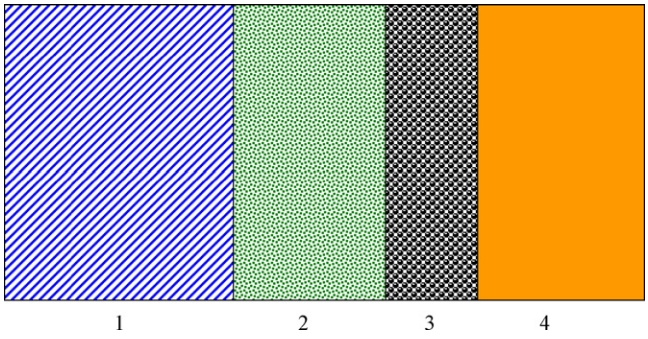

Fig. 1. Schematic structure of a composite anode: (1) gas diffusion layer; (2) outer catalyst layer; (3) inner catalyst layer; (4) Nafion membrane.

2.3. The methanol auto-thermal reforming fuel processor

The methanol auto-thermal reforming fuel processor consisted of three major parts: an evaporation unit, an auto-thermal reforming (ATR) unit, and a CO purification unit as seen in Fig. 2. Fuel, water, and air were fed into the ATR reactor. Using the energy balance for the endothermic reaction of steam reforming (SR) and exothermic reaction of partial oxidation (POX) at a given temperature range, the ATR process can adiabatically produce a suitable H_2/CO ratio without external energy consumption. Then the H_2/CO blend gas was purified by the followed process: CO water gas shift (WGS) and CO preferential oxidation (PROX) to remove CO to avoid fuel cell poisoning by trace amount of CO in reformate. After the electrochemical reaction in the fuel cell, the anode vent gas could be utilized to evaporate and heat the water/alcohol feed, thus achieving an optimal energy balance in the integrated system. The output of hydrogen-rich reformate from the fuel processor was kept near 120 N m^3 h^{-1}, for which the content of hydrogen was about 53% and CO impurity was kept generally under 30 ppm.

2.4. The 75-kw fuel cell system

The fuel cell system in Fig. 3 was composed of four major parts: PEMFC stacks, air supply subsystem, cooling subsystem, and fuel cell control subsystem. The saturated humid air was provided by a water sealed air compressor. The cooling system with water recycling consisted of a recycle pump and heat exchange equipment. The fuel cell control system involved a cell voltage monitor (CVM) and an electronic control unit (ECU) which could control the temperature and pressure of the stack and record the current, potential, power, temperature, pressure, and the CO concentration under the system operating.

Fig. 2. Photograph of 75-kW methanol auto-thermal reforming fuel processor.

Fig. 3. Photograph of 75-kW fuel cell system.

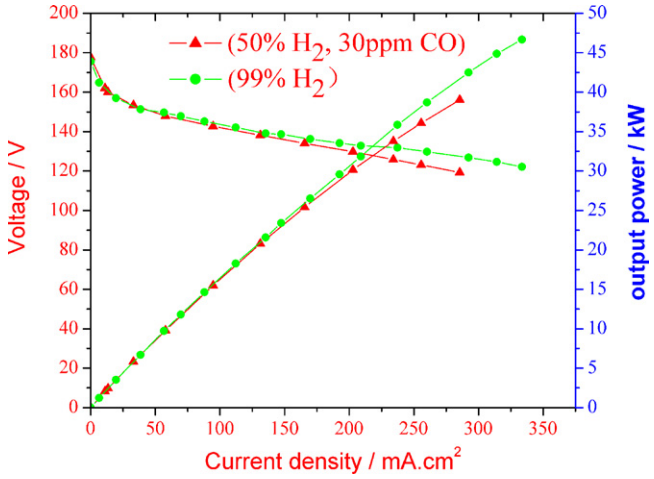

Fig. 4. The performance of fuel cell stack running with pure hydrogen and simulating reformate, operating temperature = 60 °C; operating pressure = 1.5 bar.

2.5. Integrated testing of the fuel processor and fuel cell systems

The methanol reforming fuel cell system consists of a fuel cell system and a methanol auto-thermal reforming fuel processor. This has been developed at Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS). The fuel processor supplied 120 N m^3 h^{-1} of reformate for the fuel cell system. The saturated humid air was supplied by a water sealed air compressor. The operating temperature and pressure were maintained at 60 °C and 1.5 bar, respectively. The current, potential, power, temperature, pressure, and the variation of the CO concentration under the system operating conditions were recorded by the fuel cell control system. After the electrochemical reaction in the fuel cell, the anode vent gas could be used to evaporate and heat the water/alcohol feed to the fuel processor, thus improving the energy efficiency of the integrated system.

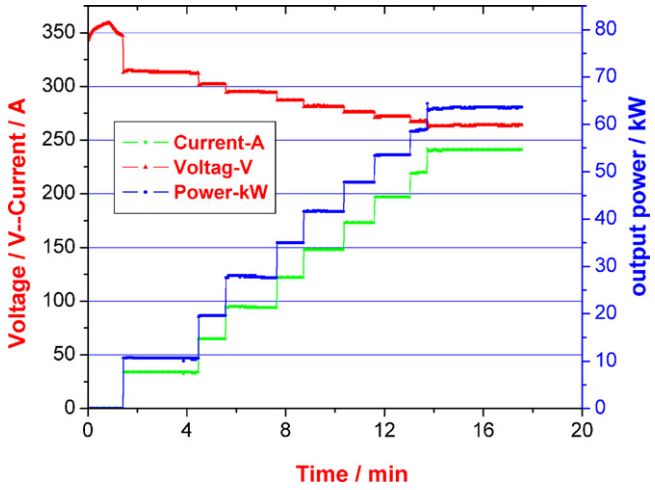

Fig. 5. The power–current–voltage of the fuel cell system during integrated test.

3. Results and discussion

3.1. Performance of the fuel cell stack

The performance of one fuel cell stack is shown in Fig. 4. It can be seen that the power outputs of the stack can reach 47 kW for pure hydrogen and 39 kW for the simulated reformate. Comparing the two cases, the power output of the stack with reformate as fuel, decreased by only 20% as compared to pure hydrogen. This mainly comes from the successful anode structure reformation. In the outer catalyst layer, PtRu/C serves as a CO barrier, and the electro-catalyst Pt/C maintains a high

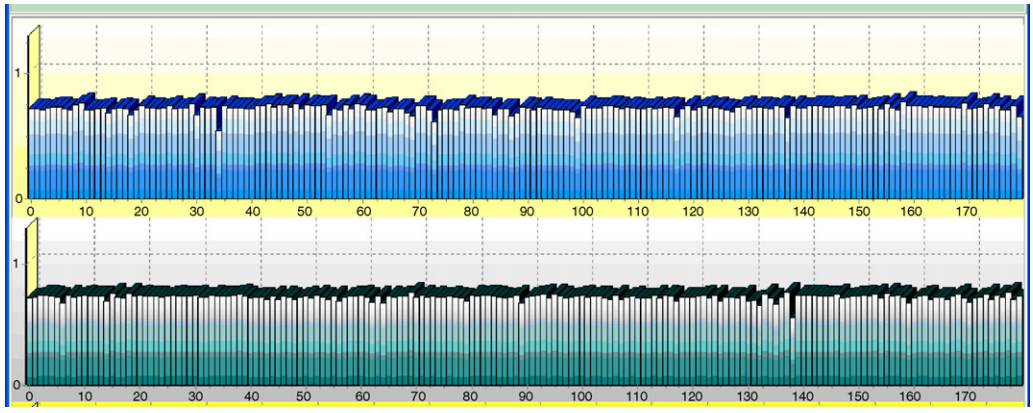

Fig. 6. The uniformity of every single cell in the stacks at 63 kW.

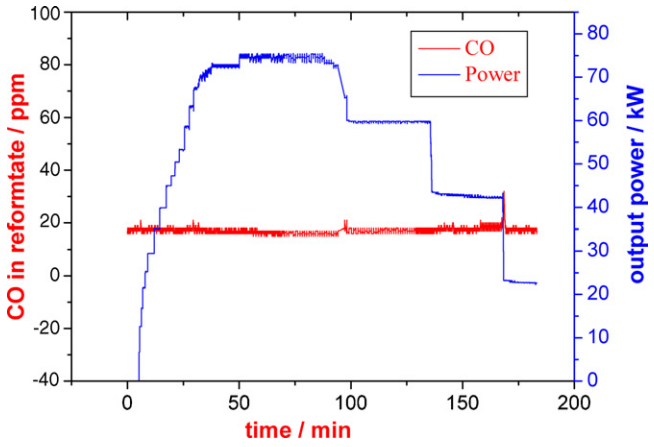

Fig. 7. The output power of the fuel cell system during integrated test.

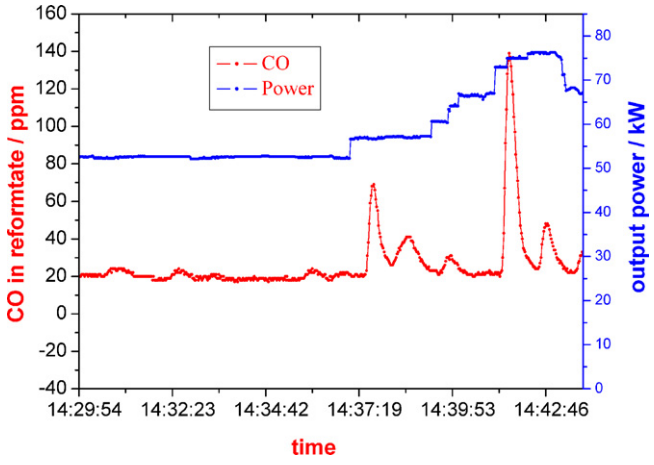

Fig. 9. The variety of CO concentration when quick load.

activity for hydrogen oxidation reaction in the inner catalyst layer.

3.2. Integrated reformer/fuel cell system testing

The fuel processor provided 120 N m^3 h^{-1} reformate. The concentration of hydrogen in the reformate was approximately 53%. The CO concentration was generally kept to less than 30 ppm. There were two stacks running during the integrated system tests. The reformate was provided by a fuel processor and the saturated humid air was provided by an air compressor. The output power of the fuel cell system reached 63 kW as seen in Fig. 5. The hydrogen utilization showed only 60%. But the potentials of several single cells decreased when the output of the fuel cell system was 63 kW—shown in Fig. 6. This indicates that the gas distribution in the stack was not uniform.

To improve the power output and utilization rate of H_2 in the fuel cell system, three stacks were used in the system. Parallel and series reactor configurations were used to supply gas to the stacks. The reformate was first fed to two PEMFC stacks, then the vent gas from the two stacks was fed into the third one. The peak power output of the fuel cell system exceeded 75 kW, as seen in Fig. 7. The hydrogen utilization was maintained about 70% at 75 kW in the fuel cell system. The performance uniformity of every single cell in the stacks was improved due to parallel and series reactor configurations used as seen in Fig. 8.

3.3. The effect of CO concentration in the integrated reformer/fuel cell system testing

During the integrated tests, the CO concentration in the reformate generally was maintained under 30 ppm but did change under rapid load changes as seen in Fig. 9. This was due to pressure changes during rapid load changes, resulting in a CO concentration change. One should decrease the rate of load change to avoid CO concentration increases.

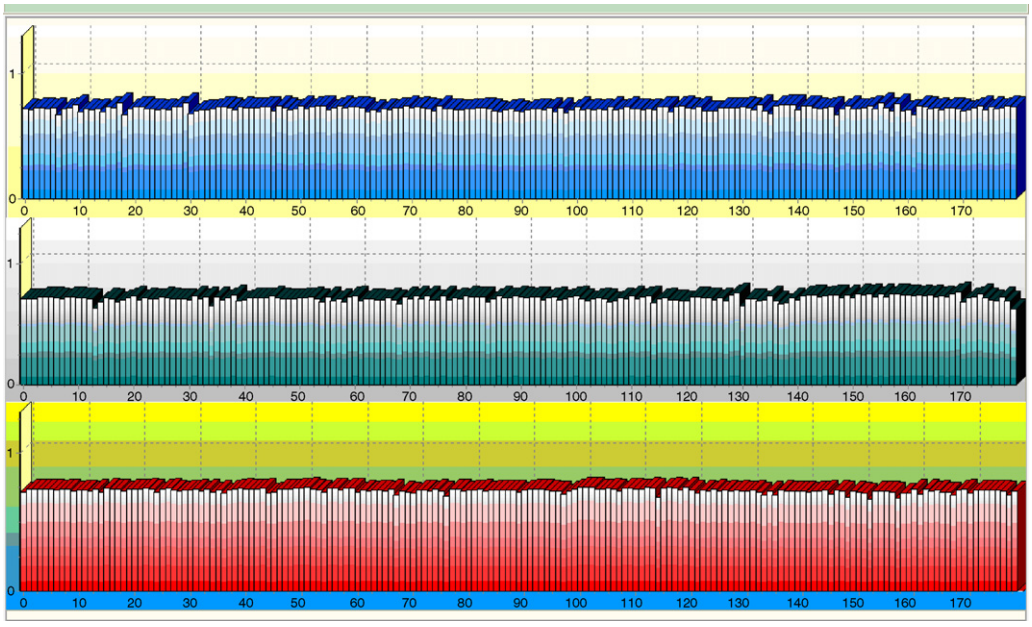

Fig. 8. The uniformity of every single cell in the stacks at 75 kW.

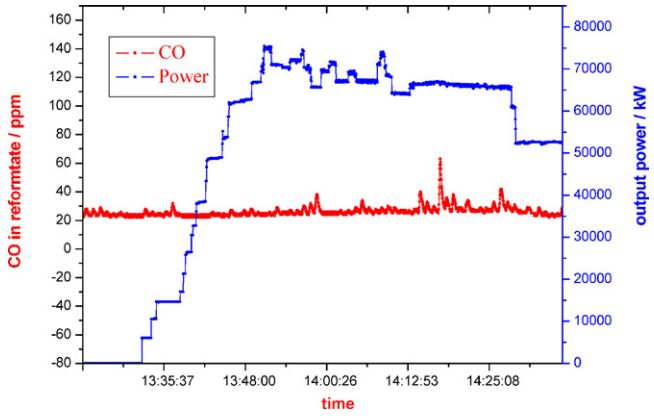

Fig. 10. The effect of CO concentration in the reformate during integrated test.

The integrated tests showed the fuel cell stacks exhibited CO tolerance. The stack performance was not affected when the CO concentration was changed under 80 ppm as seen in Fig. 10. Therefore, the double layer anode has a good CO tolerance and can overcome CO poisoning in an integrated reformer/fuel cell system.

4. Conclusion

High power PEMFC stacks with CO tolerance were successfully assembled and electrochemical tests were performed using pure hydrogen and a simulated reformate. A single stack can generate 39 kW using a simulated reformate. The fuel cell system was assembled and integrated with a methanol auto-thermal reforming fuel processor. The peak power output of the fuel cell system exceeded 75 kW in the integrated tests. The hydrogen utilization in the fuel cell system was greatly improved by adopting a parallel and series mode to supply feed gas to the stacks. The double layer anode had good CO tolerance properties and overcame CO poisoning for successful integration in a fuel cell system.

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References

[1] S. Srinivasan, D.J. Manko, H. Koch, M.A. Enayetullah, J.A. Appleby, J. Power Sources 29 (1990) 367–387.
[2] V. Mehta, J.S. Cooper, J. Power Sources 114 (2003) 32–53.
[3] A.F. Ghenciu, Curr. Opin. Solid State Mater. Sci. 6 (2002) 389–399.
[4] P. Costamagna, S. Srinivasan, J. Power Sources 102 (2001) 242–252.
[5] R.A. Lemons, J. Power Sources 29 (1990) 251–264.
[6] C. Pan, R. He, et al., J. Power Sources 145 (2005) 392–398.
[7] J. Hana, S.-M. Leea, H. Chang, J. Power Sources 112 (2002) 484–490.
[8] J. Mathiak, A. Heinzel, et al., J. Power Sources 131 (2004) 112–119.
[9] J.C. Amphlett, K.A.M. Creber, J.M. Davis, R.F. Mann, B.A. Peppley, D.M. Stokes, Int. J. Hydrogen Energy 19 (1994) 131–137.
[10] J.C. Amphlett, R.F. Mann, B.A. Peppley, Int. J. Hydrogen Energy 21 (1996) 673–678.
[11] G. Xu, X. Chen, Z. Zhang, Chem. Eng. J. 121 (August (2–3)) (2006) 97–107.
[12] J. Pasel, P. Cremer, B. Wegner, R. Peters, D. Stolten, J. Power Sources 126 (2004) 112–118.
[13] Z. Hou, B. Yi, H. Yu, Z. Lin, H. Zhang, J. Power Sources 123 (2003) 116–125.
[14] H.-F. Oetjen, V.M. Schmidt, U. Stimming, F. Trila, J. Electrochem. Soc. 143 (12) (1996) 3838–3842.
[15] N. Wagner, E. Gülzow, J. Power Sources 127 (2004) 341–347.
[16] S.J. Lee, S. Mukerjee, E.A. Ticianelli, J. McBreen, Electrochim. Acta 44 (1999) 3283–3293.
[17] L.G.S. Pereira, F.R. dos Santos, M.E. Pereira, V.A. Paganin, E.A. Ticianelli, Electrochim. Acta 51 (2006) 4061–4066.
[18] R.K. Ahluwalia, Q. Zhang, D.J. Chmielewski, K.C. Lauzze, M.A. Inbody, Catal. Today 99 (2005) 271–283.
[19] S. Jiménez, J. Soler, R.X. Valenzuela, L. Daza, J. Power Sources 151 (2005) 69–73.
[20] J.-D. Kim, Y.-I. Park, K. Kobayashi, M. Nagai, J. Power Sources 103 (2001) 127–133.
[21] J.-D. Kim, Y.-I. Park, K. Kobayashi, M. Nagai, M. Kunimatsu, Solid State Ionics 140 (2001) 313–325.
[22] W.A. Adams, J. Blair, K.R. Bullock, C.L. Gardner, J. Power Sources 145 (2005) 55–61.
[23] T. Iorio, K. Yasuda, Z. Siroma, N. Fujiwara, Y. Miyazaki, J. Electrochem. Soc. 150 (2003) 1225–1230.
[24] H. Yu, Z. Hou, B. Yi, Z. Lin, J. Power Sources 105 (2002) 52–57.
[25] H.M. Yu, B.L. Yi, Z.J. Hou, CN ZL, Appl. 01110538.0 (2001).