Electrochimica Acta 133 (2014) 8–15

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effects of design parameters on the performance of passive direct methanol fuel cells fed with concentrated fuel

Q.X. Wu [a], L. An [b], X.H. Yan [b], T.S. Zhao [b,*]

[a] College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China
[b] Department of Mechanical and Aerospace Engineering, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 20 March 2014
Accepted 28 March 2014
Available online 6 April 2014

Keywords:
Passive direct methanol fuel cells
Concentrated fuel
Water starvation
Operating temperatures
Design parameters.

ABSTRACT

Operating a passive direct methanol fuel cell (DMFC) with concentrated methanol is to achieve its inherently appealing feature of high specific energy. The objective of this work is to understand and identify key system design parameters that influence the performance of the passive DMFC operated with concentrated fuel at different operating temperatures. The design parameters that were investigated include the open ratios of the perforated polytetrafluoroethylene (PTFE) sheet, and the anode gas diffusion layers (GDL) and the cathode filters. Experimental results show that with the neat methanol operation, a medium open ratio is required to achieve high cell performance. It is interesting to find that unlike the passive DMFC operating with diluted fuel, an increase in the operating temperature from 40 to 60 °C results in a decrease in the cell performance due to water starvation. In addition, it is demonstrated that the anode GDL has little influence on the cell performance, but the effect of cathode filters is much more significant. Finally, the constant-current discharge test indicates that the supply of methanol becomes a key factor leading to performance degradation during the long-term operation.

1. Introduction

With the unprecedentedly rapid development of personal mobile electronic devices such as smart phones, laptops and tablets, the use of conventional batteries becomes a bottleneck for powering high-performance devices due to their relatively short runtime and low specific energy. Among various candidates to replace batteries, the direct methanol fuel cell (DMFC) has been recognized one of the strongest contenders because of its simple design, quiet operation, usage of liquid methanol, high energy-conversion efficiency and large specific energy [1–3]. Nevertheless, conventional DMFCs have to utilize diluted fuel (< 4 M) to minimize the cathode mixed potential caused by methanol crossover from the anode to cathode. As a consequence, the specific energy of a conventional DMFC is far away from its theoretical value, about 6000 Wh kg^{-1}.

To realize the high specific energy, concentrated fuel must be utilized in a DMFC system. One solution to operate a DMFC with concentrated fuel is to collect the water produced in the cathode and pump it to the anode mixing chamber where water is mixed with neat methanol to produce diluted methanol solutions [4]. Obviously, such a design will complicate the system and consume additional power. Another way is to vaporize the liquid methanol and take advantage of the carbon dioxide produced from the anode reaction to dilute methanol vapor before it enters into the anode electrode. As compared to the first approach, such a system design is much more attractive due to its simplicity and zero additional power consumption. To vaporize concentrated methanol solutions, a variety of methods have been proposed in the literature [5–16]. These approaches include the usage of hydrogels [5], the introduction of a porous carbon plate with a high methanol transfer resistance [6,7], the modification of an anode flow field [8] and the employment of a pervaporation membrane [9–15].

In addition to developing novel methanol delivery schemes, water management in the DMFCs operating with concentrated methanol solutions is also of critical importance [1,3,16]. In fact, water plays double roles in a DMFC: 1) the Nafion® membrane, the most commonly used proton exchange membrane, needs water to increase its proton conductivity; 2) the methanol oxidation reaction (MOR) taking place in the anode must consume water to form carbon dioxide. The demand of water can be readily met when diluted methanol solutions are fed to a DMFC, while water starvation may happen if concentrated methanol is utilized because no or little water is fed to the anode directly. Recently, increasing efforts [16–26] have been spent on understanding and alleviating the

* Corresponding author. Tel.: +00852 2358 8647; fax: +00852 2358 1543.
E-mail address: metzhao@ust.hk (T.S. Zhao).

http://dx.doi.org/10.1016/j.electacta.2014.03.183
0013-4686/

water starvation problem. Wu and Zhao [17] experimentally investigated the water transport characteristics under various operating conditions and structural designs. Wu et al. [16] developed a chromatography-based method to determine the water concentration in the anode catalyst layer (CL) of a DMFC and studied the effect of water concentration on the MOR performance. Xu and Faghri [18] developed a two dimensional, two-phase, non-isothermal model to investigate the water transport phenomenon in a passive DMFC operating with concentrated fuel. Zhang el al. [20] modified the cathode backing layers (BL) by increasing the polytetrafluoroethylene (PTFE) content to 40 wt. % and an energy density of 438 Wh L^{-1} was attained. Rather than optimizing the cathode gas diffusion layer (GDL), adding a hydrophobic air filter [21] and a perforated cover [22] onto the cathode were also proposed to enhance the back flow of water from the cathode to anode.

Our literature review indicates that both methanol delivery and water management are critical to the performance of a DMFC operating with concentrated fuel. Tackling these two issues relies closely on the enhanced understanding in the effects of fuel cell structural parameters on the transport of methanol and water. However, for passive DMFCs, such knowledge is far less sufficient. In this work, the effects of the structural parameters such as the open ratios of the perforated PTFE sheet, anode GDLs and cathode filters on the performance of a passive DMFC fed with concentrated fuel, are experimentally investigated under different operating temperatures with the assistance of a reference electrode. For the sake of guiding future work on system optimization, special focus is placed to identify the key factors that govern the fuel cell performance and operating stability.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEA)

A 50 μm-thick Nafion® 212 membrane from Dupont® was used to fabricate the MEA in this work. Hispec® 10000 PtRu/C (atomic ratio of Pt to Ru is 1:1 and the total metal content is 60 wt. %) and Hispec® 9100 Pt/C (60 wt. % Pt) from Johnson Matthey® were used as catalysts for the anode and cathode electrodes, respectively. The catalyst loading and Nafion® ionomer content were maintained to be 4 mg cm^{-2} and 20 wt. % for both electrodes. The GDLs used in each electrode consisted of a Toray® 090 carbon paper (280 μm) pretreated with 5 wt. % PTFE and a microporous layer (MPL). Three types of MPLs were applied in the present work: 1) hydrophobic MPL with a carbon loading of 2 mg cm^{-2} and a PTFE content of 20 wt. %; 2) hydrophilic MPL-I with the same carbon loading as the hydrophobic ones and a Nafion® ionomer content of 20 wt. %; 3) hydrophilic MPL-II with the same carbon loading and ionomer content as the hydrophilic MPLs-I and an additional 5 wt. % nanoporous SiO_2 (5-15 nm, Aldrich®). Except for the investigation of the anode GDL, hydrophobic MPLs were employed throughout this work. To form a compact MEA, an anode and a cathode electrode with the active areas of 2.0 cm × 2.0 cm were hot pressed onto two sides of the membrane at a temperature of 135 °C and a pressure of 4.0 MPa for 3 minutes.

2.2. Single cell fixture with a built-in reference electrode

Fig. 1 shows the single cell design of the passive vapor feed DMFC applied in the present work. As shown in Fig. 1, the fixture consists of an anode end plate, a fuel tank with a of volume of 9.2 mL, a pervaporation membrane, a perforated PTFE sheet, a vapor chamber with a CO_2 venting hole, an anode current collector, an MEA, a cathode current collector and a cathode end plate. A Tokuyama® A201 membrane with a thickness of 28 μm was employed as the pervaporation membrane. The perforated PTFE sheet with a thickness of 300 μm was used to control the methanol delivery rate by adjusting its open ratio. To investigate the effect of open ratios, 5 open ratios (6%, 15%, 40%, 60% and 80%) were employed in this work. The combination of the pervaporation membrane and the perforated PTFE sheet can effectively depress the methanol crossover so that concentrated methanol solutions can be directly used. The current collectors applied in the anode and cathode were made of 316L stainless steel with the open ratios of 47.8%. For convenience of temperature control, the cathode end plate was made of aluminum block with 2 holes for electrical heating rods and 1 hole for a thermal couple. It should be mentioned that the cell temperature was controlled only in the study of the temperature effect and the long-term discharge test.

To understand the effect of the structural parameters on the anode MOR, the anode potential was in-situ measured during the performance tests. A reversible hydrogen electrode with an active area of 1.0 × 1.0 cm^2 was used as the reference electrode and was built in the single cell fixture for the measurement of anode potential. The construction of the reference electrode was similar to our previous works [23,26]. The compositions of the GDLs and CLs in the reference electrode were the same as those used in the cathode electrode of the DMFC except that the catalyst loading was 1 mg cm^{-2}. The hydrogen inlet and outlet (not shown in Fig. 1) were located on the top and bottom surfaces of the cathode end plate, respectively. Humidified hydrogen was fed into the inlet by an Omega® FMA-2619A mass flow controller at a flow rate of 10 sccm. The current collectors for the reference electrode were also made of 316L stainless steel and formed with serpentine flow channels; the channel width, rib width and depth were 1.1 mm, 1.1 mm and 1.5 mm, respectively. The voltage between anode electrode of the DMFC and the reference electrode was recorded by an Agilent® 34970A data acquisition unit with a sampling time of 10 seconds.

2.3. Electrochemical instrumentation and test conditions

An Arbin® BT-5HC multiple independent channel test station was employed to control the discharging current, measure the transient voltage and determine the internal resistance of the DMFC under various operating conditions and structural designs. The measurement of internal resistances was based on the current interruption technique. For the test of current-voltage (I-V) or current-power (I-P) characteristic, the passive DMFC was first kept at open circuit condition (OCC) for 40 minutes to attain a stable open circuit voltage (OCV), and then the DMFC was controlled to discharge at each preset current for 1 minute. After each test, the fuel was extracted and the DMFC was kept at OCC for 24 hours to remove the produced water inside the MEA and make it in equilibrium with the ambient water vapor. This was to ensure that the initial water content within the MEA was similar for each test. The ambient temperature and the relative humidity for all the experiments were about 15-17 °C and 50-60%, respectively.

3. Results and discussion

3.1. Effect of methanol concentrations

The feeding methanol concentration is an important parameter that needs to be optimized for the passive DMFC system since it will influence the performance and the specific energy simultaneously. Fig. 2 shows the effect of methanol concentrations on the performance of the passive vapor feed DMFC, in which the open ratio of the perforated PTFE sheet is 40%. It can be seen that at low current densities, the cell performance decreases slightly with an increase in the methanol concentration; the OCV is 0.441 V, 0.433 V, 0.427 V