Journal of Power Sources 273 (2015) 517–521

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

High-temperature passive direct methanol fuel cells operating with concentrated fuels

Xuxin Zhao, Wenxiang Yuan, Qixing Wu*, Hongyuan Sun, Zhongkuan Luo, Huide Fu

College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China

HIGHLIGHTS

- A high-temperature passive DMFC utilizing concentrated fuels was proposed.
- A H_3PO_4-doped PBI membrane was utilized as the electrolyte in this new passive DMFC.
- A peak power density of 37.2 mW cm^{-2} was achieved at 180 °C with 16 M methanol.
- The effects of temperature and methanol concentration on performance were studied.
- The performance of this new DMFC was relatively stable during 132 h stability test.

ARTICLE INFO

Article history:
Received 15 June 2014
Received in revised form
27 August 2014
Accepted 20 September 2014
Available online 28 September 2014

Keywords:
Passive direct methanol fuel cells
Concentrated fuels
Polybenzimidazole membranes
Phosphoric acid
High temperatures

ABSTRACT

Conventionally, passive direct methanol fuel cells (DMFC) are fed with diluted methanol solutions and can hardly be operated at elevated temperatures (>120 °C) because the ionic conductivity of Nafion-type proton exchange membranes depends strongly on water content. Such a system design would limit its energy density and power density in mobile applications. In this communication, a passive vapor feed DMFC capable of operating with concentrated fuels at high temperatures is reported. The passive DMFC proposed in this work consists of a fuel reservoir, a perforated silicone sheet, a vapor chamber, two current collectors and a membrane electrode assembly (MEA) based on a phosphoric acid doped polybenzimidazole (PBI) membrane. The experimental results reveal that the methanol crossover through a PBI membrane is substantially low when compared with the Nafion membranes and the PBI-based passive DMFC can yield a peak power density of 37.2 mW cm^{-2} and 22.1 mW cm^{-2} at 180 °C when 16 M methanol solutions and neat methanol are used respectively. In addition, the 132 h discharge test indicates that the performance of this new DMFC is quite stable and no obvious performance degradation is observed after activation, showing its promising applications in portable power sources.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Over the past decade, direct methanol fuel cells (DMFC) that can convert the chemical energy in the methanol to electricity without reforming, have attracted worldwide efforts of researchers due to their appealing features, including simple system design, ease in fuel handling and high energy density (4800 Wh L^{-1}) [1–5]. Generally, DMFCs can be divided into two types: an active one that utilizes pumps and blowers (or compressors) to supply reactants and remove products, and a passive one that takes advantage of diffusion and natural convection to deliver fuel and oxidant [6]. As the passive DMFC consumes no additional power generated by the fuel cell and consists of fewer auxiliary devices than does the active one, it is more suitable for powering the high-performance portable electronic devices such as smart phones, tablets and laptops.

Conventionally, Nafion® membranes from Dupont® are employed in passive DMFCs to conduct protons from the anode to cathode. Although the proton conductivities of Nafion membranes are good, these membranes are easily permeable to methanol and thus excess methanol in the anode will predominantly permeate through the membrane to the cathode, leading to fuel loss and a mixed potential at the cathode. To minimize the adverse effects of methanol crossover, diluted methanol solutions (<4 M) are usually fed to passive DMFCs directly. Such an operation, however, will significantly lower the energy density of a DMFC system [3,5], sacrificing the most attractive advantage of this type of fuel cell. To increase the energy density, a number of researches have been performed over the past few years, including modifying the

---

* Corresponding author. Tel.: +86 755 2655 7393; fax: +86 755 2653 6141.
E-mail address: qxwu@szu.edu.cn (Q.X. Wu).

http://dx.doi.org/10.1016/j.jpowsour.2014.09.128
0378-7753/© 2014 Elsevier B.V. All rights reserved.

existing Nafion membranes [7–9], developing new proton-conducting membranes [10–13], introducing novel fuel delivery schemes [14–19] and improving the water management [20–29].

In addition to the issue of methanol crossover, the use of Nafion membranes precludes a high-temperature operation (>120 °C) of the passive DMFC. This is because the proton conductivity of a Nafion membrane depends strongly on water; this membrane exhibits a fairly low proton conductivity at elevated temperatures due to the absence of liquid water. In fact, high temperatures can offer several desirable advantages [30–32]: 1) enhancement in the kinetics of electrochemical reactions at each electrode; 2) increase in the CO tolerance of catalysts; 3) improvement in the transport of fuel and oxidant to electrodes. Driven by such favorable features, operating DMFCs at high temperatures has received increasing attentions in recent years [33–41]. The high-temperature DMFC was first proposed by Wainright et al. [33] in the open literature. In their DMFC, a PtRu loading of 4 mg cm^{-2} and a Pt loading of 4 mg cm^{-2} were applied in the anode and cathode, respectively, and a phosphoric acid doped polybenzimidazole (PBI) membrane was used as a proton-conducting membrane for the first time; it was demonstrated that a peak power density of about 120 mW cm^{-2} can be achieved with a water to methanol ratio of 4 (approximately 9 M) and pure oxygen at a temperature of 200 °C. Lobato et al. [36] investigated the effects of the operating temperatures, methanol concentrations and partial pressures on the performance of the high-temperature DMFC based on a H_3PO_4-doped PBI membrane with the help of a reference electrode. It was shown that a power density of 138.5 mW cm^{-2} can still be obtained with a low catalyst loading of 1 mg cm^{-2} at 200 °C. More recently, Mamlouk et al. [37] also studied the influence of operating conditions and found that the presence of phosphate in the anode electrode was a key factor leading to a poor performance. Rather than using H_3PO_4-doped PBI as electrolyte, Fan et al. [38] introduced a silicon carbide matrix to hold H_3PO_4 and apply it to a high-temperature DMFC. A variety of operating and structural parameters including the stream pressure, cell temperature, design of the gas diffusion layer (GDL) and thickness of the silicon carbide were investigated experimentally in this new type of high-temperature DMFC.

Although promising, all the above-mentioned high-temperature DMFCs are based on the active supply of reactant and oxidant, which results in a complex system design and a parasitic power consumption. As a result, such DMFCs may not be suitable for the applications in portable devices. In addition, it has been known that for a passive DMFC operated with neat methanol, due to water starvation, its optimal operating temperature is rather low, typically lower than 50 °C [42], when a Nafion membrane is used as a polymer electrolyte. Obviously, such a low operating temperature would limit its improvement in performance. In this work, to simultaneously increase the energy density and the operating temperature, a passive vapor feed DMFC capable of operating with concentrated fuels at high temperatures was designed and tested. Particular focus was paid to its performance characteristic and the feasibility of a H_3PO_4-doped PBI membrane under passive operation.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEA)

A 40 μm-thick PBI membrane was used as a polymer electrolyte in this work. To make the PBI membrane conduct protons, it was immersed in a 75 wt.% H_3PO_4 solution (Acros Organic) at a temperature of 80 °C for at least 24 h until a doping level of approximately 6 was achieved. Toray® 090 carbon papers with the thickness of 280 μm and 10 wt.% polytetrafluoroethylene (PTFE) content were used as backing layers for both anode and cathode electrodes. To reduce the contact resistance and the loss of catalysts, a microporous layer (MPL) made of Vulcan® XC-72 carbon black and PTFE was brushed onto one side of the backing layer; the carbon loading and PTFE content in the MPL were 2 mg cm^{-2} and 15 wt.%, respectively. Commercially available catalysts from Johnson Matthey®, Hispec® 10000 PtRu/C and Hispec® 9100 Pt/C, were employed respectively in the anode and cathode with the same loading of 2 mg cm^{-2}. The catalyst binder used in this work was PTFE, the content of which was 10 wt.% for both electrodes. To increase the triple phase boundaries in the catalyst layers, both electrodes were loaded with 10 mg cm^{-2} H_3PO_4 by pipetting 5 M H_3PO_4 solutions onto the surface of the catalyst layer. The active area of the electrode was 2.0 × 2.0 cm^2 and the MEA was tested without hot pressing.

2.2. Single cell design of a passive vapor feed DMFC

Fig. 1 shows the single cell fixture of the passive vapor feed DMFC used in this work. This single cell was composed of a cathode end plate, a cathode current collector, a MEA based on a H_3PO_4-doped PBI membrane, an anode current collector, a methanol vapor chamber with a built-in CO_2 venting hole, a perforated silicone sheet, a fuel reservoir with a volume of 13.8 mL and an anode end plate, all of which were clamped together with 8 bolts. In order to control the operating temperature, the cathode end plate was built in with two holes for electrical heating rods and one hole for temperature sensing. It should be mentioned that the electrical heating was added to mimic the high-temperature operation and it may be unnecessary in a practical passive DMFC as a high temperature can be attained by proper thermal insulation. Both the anode and cathode current collectors were made of 316L stainless steel and were perforated to form 36 holes with the diameter of 2.6 mm, which resulted in an open ratio of 47.8%. The 10 mm thick silicone sheet was also drilled to gain an open ratio of 15.7% and was employed to control the delivery of methanol vapor.

2.3. Electrochemical instrumentation and test conditions

An Arbin® BT-5HC multiple channel test station was applied as an external electrical load and to record the performance results of

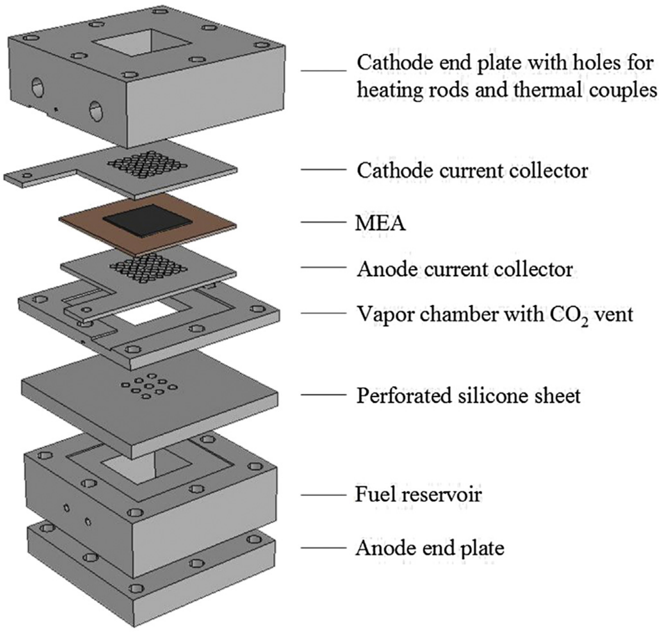

Fig. 1. Single cell design of a passive vapor feed DMFC based on a H_3PO_4-doped PBI membrane.

Download English Version:

https://daneshyari.com/en/article/7734418

Download Persian Version:

https://daneshyari.com/article/7734418

Daneshyari.com