Applied Energy 147 (2015) 396–401

Contents lists available at ScienceDirect

Applied Energy

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

Structure optimization of cathode microporous layer for direct methanol fuel cells

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HIGHLIGHTS

- Pore-forming technology was introduced to optimize microporous layer microstructure.
- The water removal and gas mass transfer property of diffusion layer were improved.
- The optimum DMFC performance reached 292 mW cm^{-2} at 80 °C.

ARTICLE INFO

Article history:
Received 17 September 2014
Received in revised form 2 March 2015
Accepted 4 March 2015
Available online 19 March 2015

Keywords:
Direct methanol fuel cell
Membrane electrode assembly
Cathode microporous layer
Pore-forming agent
Mass transfer

ABSTRACT

To obtain the cathode microporous layer (CML) with high mass transfer performance and high electronic conductivity, a pore-forming technology was introduced to optimize CML microstructure for direct methanol fuel cells. In this paper, the effects of carbon material type, carbon material loading and pore-forming agent loading in CML on fuel cell performance were discussed systematically. The results indicated that the optimized CML consisted of carbon nanotubes and ammonium oxalate with the loading of 1.5 and 3.5 mg cm^{-2} respectively. The fuel cell performance was improved by 30.3%, from 224 to 292 mW cm^{-2} at 80 °C under 0.3 MPa O_2. Carbon nanotube was found to be the most suitable carbon material for the CML due to its great specific surface area and small particle size, resulting in increasing the number of the hydrophobic sites and the contact area between the support and the catalyst layer. The carbon material and pore-forming agent loading directly influenced the pore distribution and the contact resistance of membrane electrode assembly. The water removal capacity and the gas mass transfer property of diffusion layer were improved by optimizing the amount of micropore and macropore structures.

1. Introduction

The direct methanol fuel cell (DMFC) has gained great attraction as portable electricity sources for portable multi-functional electronic devices and light-duty vehicles due to its easy fuel storage, low operating temperature and simple structure [1–3]. Now the DMFC performance has reached more than 200 mW cm^{-2} after optimization of catalyst layers [4]. Mass transfer property and internal resistance caused by diffusion layer will gradually become key factors to affect the DMFC performance, especially at a high current density. Therefore, the modification of the diffusion layer has attracted more and more scholars to study.

The main function of the diffusion layer consisted of a microporous layer and a support layer is to provide more electronic channels and suitable gas–liquid mass transfer channels [5–7]. The cathode microporous layer (CML) is not only the mass transfer place for oxygen and water, but also the current collector of electrons in fuel cell circuit. The previous optimization researches for CML were focused on the type and loading of carbon material and polymeric binder, and the multilayered structure to improve gas–water management [8–15]. However, few reports referred to the optimization of CML microstructure to enhance gas–water mass transfer by using pore-forming agent.

The CML with high mass transfer performance and electronic conductivity was obtained by adjusting the carbon material type and loading in this paper. Meanwhile, to further enhance oxygen transfer, a pore-forming technology was introduced to optimize

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http://dx.doi.org/10.1016/j.apenergy.2015.03.021
0306-2619/

the CML microstructure. Finally, the DMFC performance reached up to 292 mW cm^{-2} at 80 °C.

2. Experimental

2.1. Preparation of cathode microporous layer

Carbon paper (Toray-H-90, Japan) was employed as support layer, and was treated with 10 wt.% PTFE as described in the previous work [4].

Cathode microporous layer slurry, which consisted of carbon material, PTFE emulsion (20 wt.%), isopropyl alcohol and ammonium oxalate (as pore-forming agent), was dispersed by ultrasonic dispersion method. Then the slurry was sprayed onto the pre-treated carbon paper at uniformly 120 °C to form a thin microporous layer by the Sonotek membrane electrode assembly (MEA) ultrasonic spray system. Among them, there were three kinds of carbon materials: acetylene black (50 $m^2 g^{-1}$, particle size of 45 nm, Hebei Luna Trading Ltd), carbon nanotubes (1500 $m^2 g^{-1}$, particle size of 10 nm, black pearl 2000, Cabot Ltd) and Vulcan XC-72 (250 $m^2 g^{-1}$, particle size of 30 nm, Cabot Ltd). Subsequently, the carbon paper with the microporous layer was dipped into 0.5 mol L^{-1} H_2SO_4 solution to remove the pore-forming agent, and was dried at 80 °C for 0.5 h in vacuum. Finally, the resulting diffusion layer was sintered at 280 °C for 0.5 h.

2.2. Preparation of MEA and single cell assembly

Prior to fabrication of hotpressed MEA, the anode diffusion layer that comprised Nafion (20 wt.%) and carbon powder (80 wt.%, XC-72) was prepared followed the reports [9,15]. The catalysts for anode and cathode were Pt/Ru black (Pt:Ru, 1:1 atomic ratio, Johnson Matthey) of 3.0 mg cm^{-2} and Pt black (Johnson Matthey) of 2.0 mg cm^{-2}. Catalyst inks were formed by mixing catalysts, Nafion ionomer solution, isopropyl alcohol and pore-forming agent, and were treated by sonication and were sprayed on PTFE sheets to form thin catalyst layers. A catalyst coated membrane was obtained by transferring the catalyst layers from Teflon blanks to the pre-treated Nafion 115 by the decal method under the conditions of 135 °C, 750 N cm^{-2} for 3.5 min. Herein, the MEAs with the double anode catalyst layer and pore-forming optimized cathode catalyst layer were prepared, and the preparation process was followed as described in [16,17]. A DMFC was assembled by sandwiching a catalyst coated membrane between anode and cathode diffusion layers for activation [18] and test. The working area of each MEA was 5 cm^2. Three same MEAs were prepared to calculate the average and error value of the polarization curve for every sample shown in Figs. 2, 3 and 7.

2.3. Measurements of DMFCs

Polarization tests were carried out by a VMP2 system (Princeton Applied Research). Methanol solutions (1.5 M, 2.5 mL min^{-1}) and O_2 (0.3 MPa, 520 mL min^{-1}) were fed to anode and cathode, respectively. Electrochemical impedance spectroscopy (EIS) test was carried out at 0.4 V with the frequency varied from 9 kHz to 99 mHz. The polarization and EIS curves of the DMFC were measured at 80 °C.

Surface morphologies of these samples in this experiment were observed by a Cambridge S-360 scanning electron microscope (SEM).

The homemade test device of water seepage pressure based on the principle of communicating vessel is shown in Fig. 1. The diffusion layer was sealed tightly in the left tube with the microporous layer side down. The height differences between the two liquid

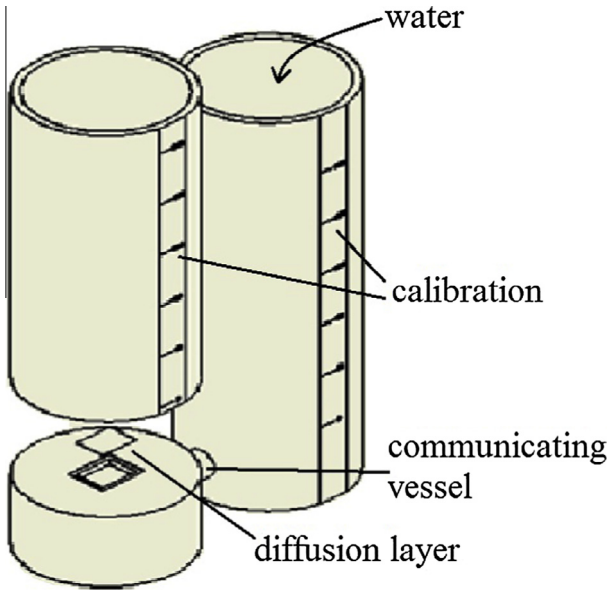

Fig. 1. Schematic diagram of the detection device for water osmotic pressure test of diffusion layers.

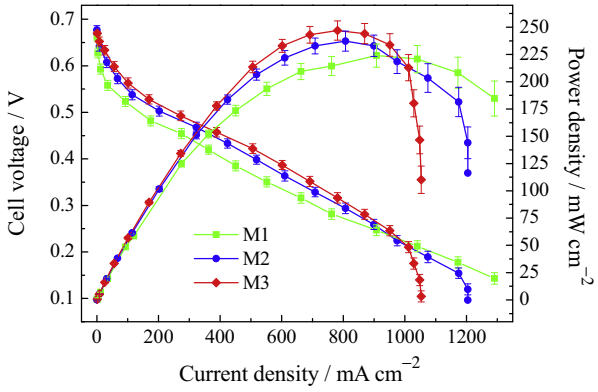

Fig. 2. Effect of the carbon material type in cathode microporous layer on the DMFC performance.

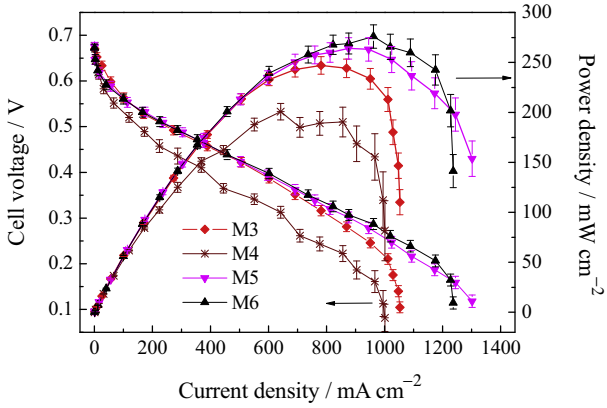

Fig. 3. Effect of the carbon material loading in cathode microporous layer on the DMFC performance.