Energy Conversion and Management 126 (2016) 697–703

Contents lists available at ScienceDirect

Energy Conversion and Management

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

A study on anode diffusion layer for performance enhancement of a direct methanol fuel cell

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ARTICLE INFO

Article history:
Received 28 May 2016
Received in revised form 25 July 2016
Accepted 22 August 2016
Available online 26 August 2016

Keywords:
Direct methanol fuel cell
Anode supporting layer
Microporous layer
Sintering treatment
Surficial decoration

ABSTRACT

To optimize mass transfer property and electronic conductivity for direct methanol fuel cells with high discharge current density, in this paper, the influence of the modified components in anode diffusion layer on fuel cell performance has been investigated systematically. The modifications include binder type, carbon powder loading and sintering treatment in microporous layer, and surficial decoration of supporting layer. The fuel cell based on the hydrophilic diffusion layer which consisted of the microporous layer with Nafion binder and the supporting layer modified by Nafion emulsion, has shown the highest performance of 272.6 mW cm^{-2} at 80 °C and 0.3 MPa oxygen. The results indicate that the Nafion binder and sintering treatment are favorable for improving transfer properties of methanol solution and electron in anode microporous layer. The optimal carbon powder loading, 1.0 mg cm^{-2}, balances the conflict between mass transfer property and the contact area of the supporting and catalyst layers. The order mass transfer is also realized by the surficial decoration with 5 wt.% of Nafion in supporting layer. In short, the hydrophilic anode diffusion layer is suitable for the fuel cell with high performance.

1. Introduction

In recent years, technology developments have driven interest around the direct methanol fuel cell (DMFC) application in small power device for portable electric and APU systems [1]. All of portable energy devices, fast recharging and hundred-watt-class DMFC systems, designed to supply power for medium-size electrical applications, have been developed [2]. Therefore, as one of the most promising proton exchange membrane fuel cell, DMFCs have received more and more attention because of easy fuel storage, high energy efficiency and simple structure [3]. Barbera et al. [4] designed a simple and functional DMFC stack with planar and monopolar ministack structure for portable applications as a power supply, and run it under various operation temperatures (30–90 °C). Using a 5-cell DMFC stack, Lohoff et al. [5] provided a data for DMFC modeling to the scientific community to simulate experiment results and response surface methodology to the fuel cell characterization. Both of them tried their best to promote practical application of the DMFC device. It's clear that the determining factor is the DMFC performance. In order to improve the DMFC performance, a lot of efficient research works have been explored. Many modification researches, for example, Pd-SiO_2 nanofiber/Nafion membrane, were studied for development of the new proton exchange membrane with low methanol permeability and high dimensional stability [6]. Plenty of papers introduced many kinds of novel catalysts with high activity for methanol oxidation reaction and oxygen reduction reaction [7]. Structure optimizations of the catalyst layer were also developed, for example, application of the porous carbon nanofiber layer in membrane electrode assembly by Zainoodin et al. [8]. The rest of researchers analyzed effects of assembly and operating parameters on the DMFC performance [9]. Until now, the peak power density of the modified DMFC has reached up to more than 200 mW cm^{-2} [10]. In the case of high current density, for example, more than 1000 mA cm^{-2}, the balance of mass transfer of CO_2 gas and methanol needs to be

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http://dx.doi.org/10.1016/j.enconman.2016.08.067
0196-8904/

re-explored and re-established in anode diffusion layer. Therefore, the mass transfer property and internal resistance caused by anode diffusion layer need to be studied systematically, which becomes more and more urgent.

It's well known that diffusion layer is composed of microporous layer and supporting layer, as shown in Fig. S1. Currently, many optimization works have been researched to enhance the property of anode diffusion layer efficiently. Via 1D, two-phase transport model, Shaffer and Wang [11] discovered that a hydrophobic anode microporous layer reduced the water crossover from anode to cathode, resulting in a lower methanol crossover. Combining with a simulation method, Yuan et al. [12] discussed the effect of emulsion binder types (Nafion and PTFE) on fuel cell performance, and obtained a similar conclusion that the anode microporous layer with 10 wt.% of PTFE was the optimal structure for the micro DMFC with limiting current density of less than 150 mA cm^{-2}. As well, Sudaroli et al. [13] also believed that the introduction of PTFE into anode diffusion layer could reduce methanol crossover, and their experimental result showed that about 20% of methanol crossover current density was reduced by 10% PTFE loading, leading to enhancement of fuel cell performance by 50%. Instead, Kang et al. [14] designed an anode diffusion layer with spatial variation of hydrophobicity along the through-plane direction, and found that the hydrophilic anode microporous layer fabricated with an ionomer binder was more beneficial than conventional hydrophobic one fabricated with PTFE. Yuan et al. [15] reported the positive effect of sintering treatment for the anode diffusion layer based on copper-fiber felt with a gradient porous structure on seepage pressure and fuel cell performance. Kim et al. [16] found that carbon black (50 vol%) and platelet carbon nanofiber (50 vol%) was the best content in anode microporous layer, and got the maximum power density of 67.7 mW cm^{-2} under operation with a 7 mol L^{-1} methanol. About material selection of supporting layer, Oliveira et al. [17] verified that the DMFC performance increased with a decrease of carbon paper thickness (340–110 μm) due to a decrease of the anode overpotential achieved by a facilitated access of reactants. So, as for the research of anode diffusion layer, the main effort has been concentrated on type and loading of carbon powder material and binder emulsion in microporous layer, material selection of supporting layer for the DMFC with limiting current density of lower than 750 mA cm^{-2}, since now.

When the discharge current density increases to a big value, anode diffusion layer will be filled by the product gas, CO_2, with vast volume. The transmission of methanol solution from flow field to catalyst layer will be a controlling factor to limit DMFC performance. Our previous work found that the hydrophilic anode diffusion layer prepared by a nitrated treatment method and Nafion binder was helpful to enhance the performance of DMFC with the limiting current density of more than 1300 mA cm^{-2} [18]. But beyond that, to our knowledge, few reports have focused on the optimization research of anode diffusion layer to adapt the DMFC with high performance (for example, discharge current density greater than 1000 mA cm^{-2}).

Herein, in the case of high peak power density, the anode diffusion layer has been explored for the DMFC. The effects of sintering treatment, binder type and carbon powder loading in microporous layer, and emulsion type and loading in supporting layer on fuel cell performance at 80 °C have been discussed systematacially.

2. Experimental

2.1. Preparation of anode diffusion layer

Anode microporous layer slurry composed of carbon powder (XC-72R, Johnson Matthey, USA) of 80 wt.%, PTFE binder emulsion with the solid content of 20 wt.%, and isopropyl as solvent, was dispersed by ice-ultrasonic method. Prior to prepare microporous layer, the carbon paper (Toray-H-90, Japan) was pretreated with 5 wt.% PTFE, then sintered at 280 °C for 0.5 h as supporting layer, as described in our previous work [19]. As shown in Fig. S2, the microporous layer slurry was sprayed onto surface of the obtained supporting layer at uniformly 120 °C to form a thin microporous layer by the sono-tek membrane electrode assembly ultrasonic spray system [20]. Subsequently, the anode diffusion layer was obtained by sintering the resulting microporous layer at 280 °C for 0.5 h.

Followed the above-mentioned preparation process, the component parameters such as binder type and carbon powder loading in microporous layer, and emulsion type for surficial decoration of supporting layer, of anode diffusion layer were optimized, as listed in Table 1. The binder type and sintering temperature were changed from PTFE and 280 °C to Nafion and 120 °C, respectively. The carbon powder loading decreased from 1.5 mg cm^{-2} to 1.0 and 0.5 mg cm^{-2}. Nafion emulsion was employed for surficial decoration of supporting layer instead of PTFE, and its contents in supporting layer were 0, 5 wt.% and 10 wt.%. Finally, the sintering temperature for Nafion modified supporting layer was changed to 120 °C.

2.2. Preparation of membrane electrode assembly

Commercial gas diffusion layer (H2315T10AC1 NOL, Japan) composed of carbon cloth and an active carbon powder layer was employed as cathode diffusion layer. The Nafion® 115 membrane was pretreated by reported method [21]. The catalyst slurries, consisting of Pt-Ru (1:1 atomic ratio of Pt to Ru, Johnson Matthey)/Pt black (Johnson Matthey), Nafion solution (5 wt.% solution, EW1000, Dupont), isopropanol and pore-forming agent, were prepared in ice-bath with ultrasonic dispersion for 1 h, then uniformly sprayed by the sono-tek ultrasonic spray system onto Teflon decal blanks until to the noble metal loadings of 3.0 mg cm^{-2}/2.0 -

Table 1
Anode diffusion layers with different components and the corresponding MEA-numbers.

No.	Microporous layer			Supporting layer		
	Binder emulsion type (20 wt.% of microporous layer)	Carbon loading (80 wt.% of microporous layer) (mg cm^{-2})	Sintering temperature (°C)	PTFE loading (wt.%)	Nafion loading (wt.%)	Sintering temperature (°C)
A-1	Nafion	1.5	–	5	–	280
A-2	Nafion	1.5	120	5	–	280
A-3	PTFE	1.5	–	5	–	280
A-4	PTFE	1.5	280	5	–	280
A-5	Nafion	1.0	120	5	–	280
A-6	Nafion	0.5	120	5	–	280
A-7	Nafion	1.0	120	–	–	–
A-8	Nafion	1.0	120	–	5	120
A-9	Nafion	1.0	120	–	10	120