Applied Surface Science 290 (2014) 246–251

Contents lists available at ScienceDirect

Applied Surface Science

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

Anode electrode with carbon buffer layer for improving methanol oxidation reaction in direct methanol fuel cell

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ARTICLE INFO

Article history:
Received 24 July 2013
Received in revised form
14 November 2013
Accepted 14 November 2013
Available online 22 November 2013

Keywords:
Direct methanol fuel cell (DMFC)
Anode structure
Carbon buffer layer
Methanol crossover

ABSTRACT

An anode electrode with the carbon buffer layer is fabricated to increase the performance of direct methanol fuel cell (DMFC). The carbon buffer layer is located in the middle of the anode catalyst layers, consists of porous carbon and Nafion ionomer. Since the porous and relatively hydrophilic carbon buffer layer absorbs methanol, the flux of the methanol solution in the anode electrode can be controlled. And methanol crossover is decreased by the effect of the carbon buffer layer. Consequently, methanol can be oxidized more efficiently and the performance of DMFC increases. Therefore, the membrane electrode assembly (MEA) with the carbon buffer layer on the anode electrode exhibits higher open circuit voltage (OCV) and maximum power density compared to those of conventional MEA. Especially with 3.0 M methanol solution, the maximum power density is increased by ~60%.

1. Introduction

Direct methanol fuel cell (DMFC) is one of the most promising alternative energy devices because methanol as a fuel has high energy density compared to H_2 gas and is used directly without reforming process. Due to this, DMFC can be used as a power source for mobile electrical devices. Therefore, DMFC has been attracted for portable devices. In order to commercialize DMFC, high concentration of methanol must be used for small volume of portable devices [1–4]. At such a high concentrated methanol solution, however, because of non-reacted methanol solution, methanol crossover occurs in the membrane electrode assembly (MEA) from the anode to the cathode. At the cathode catalyst layer, methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) occur simultaneously due to methanol crossover. This results in mixed potential in the cathode and decreases DMFC performance [5–8]. Therefore, to mitigate methanol crossover and increase DMFC performance, the MEA structures for decreasing methanol crossover have been developed [9–16]. New anode structures have been studied to reduce methanol crossover and to increase DMFC performance [17–20]. Liu et al. fabricated dual-layer anode structure using pore-forming agent and the carbon nanotubes [17]. This morphology controls decreased the rate of methanol crossover and increased DMFC performance. Wan et al. fabricated novel MEA structures with methanol filter using various ratio of Pt-Ru catalyst [19]. This methanol filter suppressed the effect of methanol crossover and increased DMFC performance. These studies mostly focused on new anode structures using pore-forming agent and novel metal. However, the addition of these materials and the high loading of novel metal increase the manufacture cost of DMFC and complexify the MEA fabrication process.

In this work, an anode electrode structure was modified by insertion of the carbon buffer layer. The price of carbon is cheaper than that of novel metal and pore-forming agent and there is no need for new fabrication process.

2. Experimental

Catalyst slurry was prepared by mixing water, ionomer (5 wt% Nafion solution, Aldrich) and isopropyl alcohol (IPA) (Aldrich) with the catalyst. Samples of 75 wt% PtRu/C (Johnson Matthey, the ratio of Pt to Ru is 2:1.) and 60 wt% Pt/C (Johnson Matthey) were used for the anode and cathode catalyst slurries, respectively. The slurries were blended by ultrasonic treatment. In addition, the slurry for the carbon buffer layer was prepared by mixing porous carbon (Vulcan XC-72, Cabot), IPA and 5 wt% Nafion ionomer solution. The

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http://dx.doi.org/10.1016/j.apsusc.2013.11.059

catalyst-coated membranes (CCMs) as MEAs were prepared by direct spray coating method. The amount of Nafion ionomer in the catalyst layer was 30 wt% compared to that of the catalyst. Catalyst layer was fabricated by spraying slurries on Nafion 115 (DuPont) directly. Especially the anode electrode had a layered structure; inner catalyst layer, carbon buffer layer and outer catalyst layer. The carbon buffer layer, its loading is 0.5 mg cm^{-2}, was sandwiched between the anode catalyst layers, with a thickness ratio of 1:1. Inner and outer anode catalyst layer had the same total metal (PtRu) loading of 1.0 mg cm^{-2}. In addition, as a reference, the MEA without carbon buffer layer (conventional MEA) was fabricated. The total anode PtRu loading of two MEAs were identical, 2.0 mg cm^{-2}. To clearly express effect of methanol crossover, two MEAs with cathode Pt loading of 0.5 mg cm^{-2} were fabricated, MEA with the carbon buffer layer on the anode and conventional MEA. After spray coating of catalyst layer, the CCMs were sandwiched between the anode gas diffusion layer (GDL) (Toray TGPH-060) and cathode GDL (SGL 35 BC) without hot pressing process. The active area of the MEAs was 5.0 cm^2 and the serpentine type flow channels were used at the anode and cathode, its total volume is 0.264 ml.

Field emission scanning electron microscopy (FE-SEM) analysis was carried out using a JSM 6701F (JEOL Ltd.) to analyze the morphology of the anode electrode structure. The water drop contact angles were measured with a DSA 100 (KRÜSS) to examine the hydrophilicity of the anode catalyst layer and carbon buffer layer. The porosity of the anode catalyst layer and carbon buffer layer was measured with an AUTOPORE IV 9500 (V.106) (Micromeritics) by mercury intrusion porosimetry.

For single cell performance test and electrochemical impedance spectroscopy measurement, 1.0 M or 3.0 M methanol solution and non-humidified air gas were supplied into the anode and cathode, respectively. Flow rates of methanol solution were 3 ml min^{-1} and 0.5 ml min^{-1} at 1.0 M and 3.0 M methanol solution, respectively. Flow rate of air was 200 ml min^{-1}. Electrochemical impedance spectroscopy (EIS) (IM6, Zahner) of the single cells was conducted at 0.45 V with an amplitude of 10 mV and in the frequency range from 0.1 Hz to 10 kHz. To analyze the quantity of permeated methanol, the limiting current method was used. The cathode was used as working electrode (WE) and the anode was used as reference electrode (RE) and counter electrode (CE). Methanol solution and humidified nitrogen gas were supplied to the anode and cathode, respectively. Meanwhile, a positive potential was applied to WE from 0 V to 0.75 V vs. RE with scan rate of 2 mV s^{-1}. All electrochemical measurement was committed at temperature 70 °C.

The constant current test at 0.15 A cm^{-2} was carried out to prove the effect of carbon buffer layer. During the experiment, 500 ml of 3.0 M methanol solution and dry oxygen gas was supplied to the anode and cathode, respectively at cell temperature 70 °C. Once the methanol supply had been depleted and the electrical load was still on, the cell voltage decreased with time and the elapsed time was measured until the cell voltage reached zero.

3. Results and discussion

Fig. 1 shows the schematic diagram of the MEA with carbon buffer layer on the anode. Cross-section images of the MEAs are shown in Fig. 2. As shown in Fig. 2(a), carbon buffer layer is placed in the middle of anode catalyst layer. As mentioned above, the thickness of the inner and outer catalyst layers was almost the same since the same amount of catalyst was loaded in Fig. 2(a) (9.4 μm (±0.2 μm) for inner catalyst layer and 9.2 μm (±0.2 μm) for outer catalyst layer). In addition, the sum of thickness of inner and outer catalyst layer is almost the same as the thickness of anode catalyst layer of conventional MEA (18.6 μm (±0.4 μm)). From this, it is proved that two MEAs have the same loading of the anode catalyst layer.

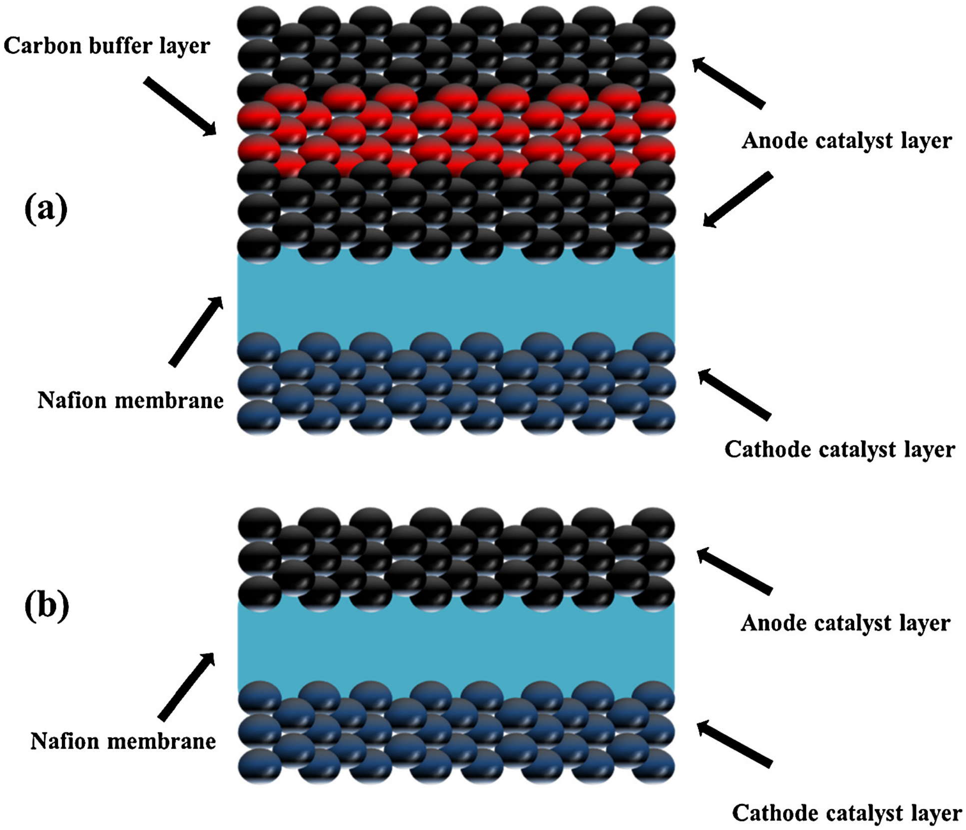

Fig. 1. The schematic diagrams of (a) the MEA with the carbon buffer layer and (b) the conventional MEA.