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Polypyrrole nanowire networks as anodic micro-porous layer for passive direct methanol fuel cells

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ABSTRACT

Polypyrrole nanowire networks (PPNNs), as anodic micro-porous layer (MPL) of passive direct methanol fuel cells (DMFCs), are grown *in-situ* on the surface of carbon paper through an electrochemical polymerization. Passive DMFC with the novel MPL achieves a 28.3% increment in maximum power density from 33.9 mW cm^{-2} to 43.5 mW cm^{-2} compared with the conventional layer with similar PtRu(1:1) loading of 2.0 mg cm^{-2} and operating with 4 M methanol solution at 25 °C. When the PtRu loading is decreased to 1.0 mg cm^{-2}, the maximum power density of the DMFC still reaches 34.3 mWcm^{-2}, which shows a comparative value with the conventional layer. The enhanced performance should be ascribed to the introduction of PPNNs, significantly improves catalyst utilization and mass transfer of methanol on the anode.

1. Introduction

Direct methanol fuel cells (DMFCs), as promising power sources for portable applications[1–3], have attracted much attention because of their high-energy density and easy-to-operate liquid fuel. However, the practical development of the DMFCs is limited by several critical challenges, such as the sluggish kinetic of both methanol oxidation and oxygen reduction reactions, which would lead to the use of high noble metal loading (ca. 2 mg cm^{-2} to 4 mg cm^{-2} on each electrode)[4,5]. Therefore, significantly reducing the noble metal loadings within the membrane electrode assembly (MEA) without performance loss is greatly important. The most common approach that has been adopted to achieve better noble metal efficiency can be broadly divided into the following aspects[6]: (i) utilization of high-performance low-Pt electrocatalysts and even Pt-free electrocatalysts to reduce Pt dependency and (ii) development of nanostructured electrode to maximize the triple-phase reaction boundary of the MEA. Recent studies have indicated that the construction of nanostructured MEA could lead to a significant improvement in both catalyst utilization and DMFC performance, thus allowing a dramatic decrease in noble metal loading within the MEA.

The construction of nanostructured electrode is known to maximize the triple-phase boundary and improve the mass transfer of the species within the DMFCs. Investigations have been focused on the development of nanostructured catalytic layer. Debe et al. [7] developed the nanostructured thin film catalyst-based MEA, which constitutes a Pt thin film deposited on nanostructured non-conducting organic whiskers for an H_2-O_2 fuel cell. Pt loadings within the MEA can be significantly decreased without reduced cell performance. Xia et al. [8,9]developed a facile electrochemical polymerization method for the synthesis of a well-ordered vertically aligned nanowire polypyrrole (PPy) on Pd-modified Nafion membranes to form an ordered nanostructured catalyst layer for DMFC, facilitating mass transport and improving catalyst utilization. Chen et al. [10] developed a novel nanofiber network catalyst layer structure for the anode of a passive DMFC by electrospinning, which leads to a dramatic decrease in catalyst loading on the anode. More recently, Huang et al. [11] reported that the addition of magnesium oxide nanoparticles, as a sacrificial pore-former into the catalytic layer (CL) and micro porous layer (MPL) in the anode of an MEA, could lead to the formation of porous anodic structure, greatly enhancing the performance of a passive DMFC. Furthermore, the formation of nanostructured MPL has an important influence on mass transfer and catalyst utilization. Yuan et al. [12] reported that

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the addition of carbon nanotubes (CNTs) into the anodic MPL of an MEA leads to the formation of the network structure, thus improving catalyst utilization and promoting the methanol mass transport. Okada et al. [13] used carbon nanofibers as the material for the interplayer between the PtRu black catalyst layer and the carbon paper to increase catalyst utilization in the DMFC, which enhanced the performance of the cell.

Polypyrrole (PPy) as an attractive conductive polymer has been extensively employed as catalyst support and nanostructured electrode material. Seo et al. [14] synthesized PPy-modified Pd nanoparticles supported on carbon. They found that introducing PPy remarkably suppressed the deactivation of Pd under acidic conditions. Selvaraj et al. [15] reported that using PPy-CNT composite polymer films as catalyst support for Pt and PtRu significantly improve the catalytic activity and stability of methanol oxidation. Similar result has also been reported using PPy-modified CNT as catalyst support[16]. Xia et al. [8,9] constructed well-aligned PPy nanowires-Pt nanostructure as catalytic layer. This novel nanostructured MEA showed an excellent cell performance with 45% enhancement in the maximum power density and enhanced stability, compared with the traditional disordered structure of an MEA. These results are due to the ordered PPy nanowires that significantly facilitated the mass transport and enhance catalyst utilization. However, it has not been reported that the catalyst loading reduces within MEA by constructing polypyrrole nanowire networks (PPNNs) as anodic MPL. In the present study, a nanostructured anodic MPL through PPNNs grown *in-situ* on the surface of carbon paper through an electrochemical polymerization is reported. The PPNNs can enlarge the surface area of the carbon fiber, thus improving catalyst utilization and promoting the methanol mass transports. The performance of passive DMFC with this anode MPL exhibits significantly improvement with relatively low loading of anodic catalysts.

2. Experimental

2.1. PPNNs grown in-situ on carbon paper

A typical electrochemical polymerization process was conducted to fabricate the PPNNs using an electrochemical workstation (SI1287, Solartron Co.). The Toray® carbon paper, rectangular Pt sheet, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The electrolyte comprised phosphate buffer solution (pH = 6.86), 0.1 M distilled pyrrole and 0.1 M p-toluene sulfonic acid sodium. To grow PPy electrochemically on the carbon fiber matrix, a constant potential of 0.75 V versus SCE was applied to the working electrode and maintained for 30 min[9,17,18]. After polymerization, the carbon paper with the as-produced PPNNs was removed from the electrolyte, rinsed with deionized water, and finally stored in deionized water for later use.

2.2. Preparation of membrane electrode assembly

The anode catalyst layer was prepared by spraying the catalyst (60 wt.% PtRu/C, Johnson Matthey) ink on the PPNNs with the PtRu(1:1) loading of 1.0 or 2.0 mg cm^{-2}.The cathode catalyst layer that consisted of carbon-supported Pt (60 wt.% Pt, Johnson Matthey) mixed with 20 wt.% Nafion was prepared by blade-coated method with the Pt loading of ca. 4 mg cm^{-2}. Finally, the well-treated electrolyte membrane (Nafion®115 membrane, DuPont Co.) with the classical processing procedure [16] was sandwiched between the two electrodes by hot-pressing at 130 °C and 2 MPa for 3 min to form an MEA with an active area of 4 cm^2. For comparison, a conventional MEA with 2.0 mg cm^{-2} of carbon-supported PtRu (1:1) was also fabricated in the anode catalyst layer.

2.3. Physical characterization

The surface morphology of the prepared samples was characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800).

2.4. Electrochemical characterization

The polarization performance of the passive DMFCs was evaluated using an Arbin Fuel Cell test station (Arbin Instrument Inc., USA). Each data point was recorded after 180 s waiting time. All tests were performed at room temperature and with the relative humidity of 30% to 40%. The as-prepared MEA was activated under ambient conditions by immersing into 2 M methanol aqueous solution for 24 h before evaluation.

Cyclic voltammograms (CV), linear scan voltammograms (LSVs), and electrochemical impedance spectroscopy (EIS) were measured in the fuel-cell configuration using an electrochemical workstation (SI1287, Solartron Co.). During the CV test, the anode was fed with N_2-purged de-ionized water as the working electrode, whereas the cathode was supplied with humidified H_2 that served as the counter electrode and dynamic hydrogen electrode (DHE). The CV curves were recorded by applying the potential between 0 and 0.7 V versus DHE at a scan rate of 20 mV s^{-1}. Furthermore, the methanol oxidation currents at the anode were measured in the LSV mode at a scan rate of 20 mV s^{-1}. During the test, the cathode was fed with humidified H_2 and the anode with 1 M methanol solution. Finally, electrochemical impedance measurements were conducted for the DMFCs by feeding the anode with 4 M methanol and the cathode with flowing H_2 at a constant potential of 0.4 V versus DHE in a frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

The typical morphology of Toray® carbon paper coated with 20 wt.% PTFE is shown in Fig. 1a. The hydrophobic open pores within the carbon fiber matrix usually promote the mass transfer of the produced CO_2 better than the methanol aqueous solution. The PPNNs only grown *in-situ* on the surface of the carbon fiber matrix are shown in Fig. 1b and 1c. Specifically, no PPNN was observed within the space of the carbon fiber matrix. The average diameter and length of the PPNNs were approximately 80 nm and 10 μm, respectively. The PPNNs obviously enlarged the surface area of the carbon fiber. The surface morphology of the as-prepared anode catalyst layer is shown in Fig. 1d.

The polarization performance curves of passive DMFCs with different anode MPLs are shown in Fig. 2. The DMFC with the novel MPL obviously yields better performance than the traditional one, whether with the maximum operating current density or the highest power density. It achieves a 28.3% increment in maximum power density from 33.9 mW cm^{-2} to 43.5 mW cm^{-2} compared with the conventional one, with similar PtRu loading of 2.0 mg cm^{-2} and 4 M methanol solution. When the PtRu loading is decreased to 1.0 mg cm^{-2}, the maximum power density of the DMFC is 34.3 mW cm^{-2}, which shows a comparative value with the conventional one. This result indicates that introducing PPNNs can effectively reduce PtRu loading without sacrificing DMFC performance. Moreover, the three DMFCs have similar kinetic and ohmic polarization behavior in the low current density region. However, the DMFC with the new MPL exhibits the smallest concentration polarization in the high current density region, which may be caused by the improved methanol mass transport.