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High power direct methanol fuel cell with a porous carbon nanofiber anode layer

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HIGHLIGHTS

- This study demonstrates a novel porous carbon nanofiber anode (PNCF) layer.
- PNFC anode layer DMFC presents power density of 23.0 mW cm^{-2}.
- This unit operates at room temperature and consumes low concentration of methanol.

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ABSTRACT

Three anode electrodes containing Pt–Ru Black as a catalyst were fabricated with a porous layer made with different carbon materials: carbon black (CB), carbon nanofiber (CNF) and a combination of both carbon materials (CB + CNF). The carbon-based porous layer was coated onto a carbon cloth with PTFE pre-treatment for delivering hydrophobic properties and applied in direct methanol fuel cells (DMFCs). Characterisation of electrochemical properties for three different anode electrodes was performed with cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) at room temperature in a half-cell configuration. The evolution of the surface morphology of diffusion layer and electrodes was characterised by using variable-pressure scanning electron microscopy (VP-SEM). The electrochemical results indicate that electrode with CNF layer showed the highest current densities compared to CB and CB + CNF with the same catalyst loading. VP-SEM measurements show the network formation within the structure, which could facilitate the methanol mass transfer and improve the catalyst efficiency. The electrodes were applied to a single-cell DMFC, and the cell performance was experimentally investigated under passive operating mode and room temperature. A maximum power density of 23.0 mW cm^{-2} at a current density of 88.0 mA cm^{-2} with a 3 M dilute methanol solution was achieved. The results show that the electrodes with a CNF layer could improve the performance of DMFC as compared with commercially used CB and prove it's potentially application in DMFC technology especially for portable power source applications due to several advantages as followings: operating at low concentration of methanol, operating at room temperature, low catalyst loading in anode and cathode, cheaper, less hazardous and no parasitic load.

1. Introduction

The direct methanol fuel cell (DMFC) is a power-generating system that converts the energy of a chemical liquid fuel directly into electrical energy without auxiliary devices, making it a promising power source for many mobile and portable applications [1–4]. In the DMFC process, the methanol fuel diffuses to the anode gas diffusion layer and reaches the catalyst layer, where the methanol oxidation reaction takes place [5]. The generated protons diffuse through the polymer electrolyte membrane (PEM) to the cathode catalyst layer and combine with the electrons flowing from external circuit and the oxygen fed to generate water molecules. However, the performance of DMFCs is always restricted by the methanol crossover through the PEM [6] and the sluggish electrochemical reaction at catalyst sites, which results in serious catalyst poisoning and a reduction in the cell efficiency [7].

To overcome these problems and to reduce the catalyst costs, one of the effective approaches used is modification of the diffusion layer in an attempt to increase the mass transfer and catalytic activity. In general, a diffusion layer consist of carbon cloth or carbon paper substrate as backing layer and a layer of carbon-based

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porous layer which provides electronic conductivity to the electrode and controlling the methanol transport through the anode. The CNF is placed between carbon cloth backing layer and the catalyst layer, thus a uniform flat porous layer may reduce the contact resistance between backing layer and the catalyst layer. A good interaction between the catalyst and diffusion layer not only improve the catalyst efficiency but also increase the charge transfer as well as the two-phase transport of methanol and oxygen. In addition, the high surface area of carbon-based porous layer also provide physical support for catalyst where the catalyst always dispersed in the form of nano-particles on the surface of porous layer [8]. It is shown that by properly designing the anode diffusion layer, the catalyst utilization is improved and the methanol crossover is reduced, which in turn enhances the overall cell performance. Basically, the anode porous layer should have a high electronic conductivity, a high surface area for better catalyst dispersion and utilisation, good reactant diffusion properties and good stability under DMFC operating conditions. Carbon materials, such as Vulcan XC-72R carbon black, are preferred materials for porous layer preparation in commercial DMFC application because of their high electronic conductivity, high surface area, easy availability, mechanical and chemical stability and low cost. However, the presence of deep micro-pores in carbon black porous layer which trap the catalyst nano-particles and making them unapproachable to reactants [9,10]. The smaller surface area of carbon black compared with other carbon nano-structure materials (e.g. CNT, CNF) also provides fewer accessible sites for catalyst deposition thus leading to reduced catalyst dispersion and catalyst activity in methanol oxidation.

At present, there are many types of carbon nanostructure materials being studied as the catalyst support or applied as diffusion layer that have a higher specific surface area compared with the conventional carbon black [11,12]. These materials include single-walled carbon nano-tubes (SWCNTs), multi-walled carbon nano-tubes (MWCNTs), carbon nanofibers (CNFs), fullerenes and carbon nano-horns. Santasalo-Aarnio et al. found that by using Pt–Ru/graphitised CNFs, better stability was achieved, although the cell performance was poor compared with Pt–Ru/Vulcan [13]. In addition, the application of non-carbon materials as catalyst supports has also shown some improvement in the dispersion of catalyst particles in DMFC [14–16]. Gharibi et al. [17] use a thick layer of polyaniline-supported Pt with a low activation energy to improve the catalyst dispersion and utilisation. Among all these carbon nanostructure materials, carbon nanofibers offer several additional beneficial properties, such as a high electrical conductivity, high oxidation resistance, high purity, high thermal conductivity and good permeability to reactants. The meso-pore geometry of CNF porous layer can enhance the reactant mass transport and its high surface area advantageous for catalyst deposition, which is important for DMFC electrochemical reactions.

Besides that, several researches like, Abdelkareem et al. [18,19] had presented porous carbon plate (PCP) to improve the performance of DMFC and obtained a power density of 24–30 mW cm^{-2}. Later, Park et al. [20] presented multi-layer electrodes for DMFC and obtained a power density of 10.7 mW cm^{-2}. While Yuan et al. [21] had invented integrated porous methanol barriers (PMFSF) and obtained a 5.2 mW cm^{-2} of power density. Apparently, it is observed that the PCP [18,19] gives the highest power density for DMFC by reducing the methanol crossover. However, a proper storage system is essential due to the toxicity of methanol to human being. There are also several other researcher adopted the vapor feed methanol to improve the performance of DMFC, however extra vaporizer component is needed to vaporize the liquid methanol [22]. This will affect the water needed in anode side for reaction that will lead to water management problem that would affect the power generation [23,24].

Due to that, this study will focus on the improvement of the performance of passive DMFC by focusing on low concentration of methanol operating at room temperature. In this paper, we report a simple technique to prepare the anode porous layer with different carbon structure materials (CB, CNF, CB + CNF) with the aim to compare the effects of different anode porous layer on the performance of DMFC. The carbon porous layer was applied on a sheet of macro-porous carbon cloth, which contains hydrophobic and hydrophilic properties. The electrodes performance was studied in a half cell and single cell DMFC. The morphologies of the diffusion layer were examined with scanning electron microscopy (SEM). The electrochemical characteristics of electrodes were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) measurements. MEA preparation with different carbon structure porous layer with similar catalyst (Pt–Ru Black) loading was tested in passive air-breathing DMFC single cell.

Furthermore, various methanol concentrations (2 M, 3 M, 4 M, and 5 M) were used to investigate the effect of methanol concentration on the performance of CNF layer in DMFC. Finally, the experimental results of our study for single cell proves that the CNF layers gives a significant effect on the DMFC performance at low concentration of methanol operating at room condition with other several advantages.

2. Experimental

2.1. MEA preparation

The anode porous layers were prepared by the simple precipitation method on a 5 wt% polytetrafluoroethylene (PTFE) pre-treatment carbon cloth (E-TEK, USA). The CNF (Platelet GNF) used in this study was supplied by Catalytic Materials, and CB (Vulcan XC-72R) was supplied by Cabot Corporation with the detail specification is stated in Table 1. Nafion® Solution 5 wt% (Wako Pure Chemical Industries, Ltd.) was used as an ionomer. Pt–Ru Black (HiSPEC 6000, Alfa Easer, USA) acted as a catalyst for anode, while Pt Black (HiSPEC 1000, Alfa Easer, USA) for cathode and isopropyl alcohol (IPA) as a solvent.

Preparation method for electrode is a determination step in a MEA and need to be optimized. The porous layer should be uniformly distributed on the carbon backing layer without blocking the macro-pores of carbon cloth for reactant transport. For the preparation of anode porous layer, firstly the carbon-based materials (CB or CNF or CB + CNF) is mixed with IPA and ionomer solution, secondly the carbon ink is deposited onto one side of carbon cloth pre-treated with PTFE suspension. Then the diffusion layer is heat-treated and results a smooth surface of porous layer (2 mg cm^{-2}) on carbon cloth. A cathode diffusion layer was similarly prepared with the PTFE coated carbon cloth and the carbon black porous layer.

The catalyst ink was prepared by the dispersion mixing of Pt–Ru Black with a 5.0 wt% Nafion solution, deionised water and isopropyl alcohol in an ultrasonic bath. After casting, the electrodes were

Table 1
Properties of porous layer based material.

Based material	Product name	Specific surface area ($m^2 g^{-1}$)	Weight (%)	Electrical conductivity (S cm^{-1})	Particle size (nm)	Porosity (nm)
Carbon black	Vulcan XC-72R	254	>99	4	30	<2
Carbon nano fiber	Platelet GNF	10–300	>99.9	10^2–10^4	80	2–50