



## Effective Utilization of Carbon Nanocoil-supported PtRu Anode Catalyst by Applying Anode Microporous Layer for Improved Direct Methanol Fuel Cell Performance

Yoshiaki SHIMIZU,<sup>a</sup> Yoshiyuki SUDA,<sup>a,\*</sup> Hirofumi TAKIKAWA,<sup>a</sup> Hitoshi UE,<sup>b</sup> Kazuki SHIMIZU,<sup>c</sup> and Yoshito UMEDA<sup>d</sup>

<sup>a</sup> Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan

<sup>b</sup> Fuji Research Laboratory, Tokai Carbon Co., Ltd., 394-1 Subashiri, Oyama, Sunto, Shizuoka 410-1431, Japan

<sup>c</sup> Shonan Plastic Mfg. Co., Ltd., 31-27 Daikan, Hiratsuka, Kanagawa 254-0807, Japan

<sup>d</sup> Corporate Research Department, Toho Gas Co., Ltd., Nagoya, Aichi 456-8511, Japan

\* Corresponding author: [suda@ee.tut.ac.jp](mailto:suda@ee.tut.ac.jp)

### ABSTRACT

The application of a microporous layer (MPL) between the gas diffusion layer and the catalyst layer (CL) plays a crucial role in the performance of the direct methanol fuel cell (DMFC). To this end, this study investigates the effects of carbon loading and the nature of the carbon material used in the anode MPL on the performance of DMFC using transmission and scanning electron microscopy, polarization technique, and electrochemical impedance spectroscopy (EIS). DMFC was indigenously fabricated using 30 wt% PtRu catalyst supported on carbon nanocoil and commercial Pt catalyst as the anode CL and the cathode CL, respectively. Carbon nanoballoon (CNB) and Vulcan XC-72R (Vulcan) were used as the anode MPL. According to polarization studies, a membrane electrode assembly (MEA) with CNB and Vulcan MPLs (loading of 1.5 mg cm<sup>-2</sup>) shows higher power density. This is 1.3 and 1.8 times higher than that without the anode MPL when methanol concentration was 0.5 M (M = mol dm<sup>-3</sup>), respectively. Electrochemical impedance spectra (EIS) results indicate that the MEAs with the anode MPLs have lower high-frequency resistance and charge transfer resistance when compared to those without the anode MPL. Thus, it can be realized that the anode MPL plays a significant role in the effective utilization of CNC-supported PtRu anode catalyst, thereby improving DMFC performance.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Microporous Layer, Carbon Nanocoil, Carbon Nanoballoon, Carbon Loading

### 1. Introduction

Direct methanol fuel cell (DMFC) is a promising energy source for portable and automotive applications, mainly due to their low operating temperature, direct use of liquid fuel, and simple structure without the stringent need for a reformer.<sup>1–3</sup> Nevertheless, issues such as water management and methanol crossover still limit the widespread commercial application of DMFC.<sup>4–8</sup> In particular, the permeation of methanol from the anode to the cathode presents a negative effect on the open circuit voltage, fuel efficiency utilization, and its overall performance.

To this end, several studies have been conducted over the past decade for the effective mitigation of both water and methanol crossover in DMFC.<sup>6–18</sup> Liu et al.<sup>19</sup> reported the design of a membrane electrode assembly (MEA) that consisted of a thin membrane and a backing layer coated with a highly hydrophobic microporous layer (MPL), in order to reduce the rates of both the water and methanol crossover. The MPL, in particular, plays an important role in the water management of DMFC. It significantly contributes to the reduction of water crossover through the membrane, thereby improving the overall performance of the DMFC.<sup>17,18,20</sup>

In our previous study, we analyzed the use of carbon nanocoils (CNCs) as a catalyst support in DMFC.<sup>21</sup> Due to their three-dimensional structure, CNC is considered to be a unique support material for electrocatalyst materials. By using CNCs in the DMFC cathode, the diffusion of fuel and gas, and the removal of reaction products became considerably smoother. Consequently, the DMFC with CNCs showed higher power density when compared to other

carbon nanomaterials, such as Vulcan XC-72R (Vulcan) and arc black (AcB). In addition, we performed electrochemical studies of the PtRu catalysts as an anode catalyst supported on carbon nanomaterials for methanol oxidation using cyclic voltammetry. Results indicate higher catalytic activity of the PtRu catalyst supported on CNC when compared to those on AcB and Vulcan. However, the use of CNCs in the anode of DMFC did not prevent the permeation of methanol across the membrane, and hence resulted in poor DMFC performance. Therefore, to utilize the advantages of CNC as an anode catalyst support, we applied the anode MPL to DMFC for improving the efficiency of utilization of the CNC-supported PtRu catalyst. To the best of our knowledge, there are no studies reported so far on the DMFC performance of a MEA with MPL as the anode using CNCs in the anode catalyst layer (CL). The anode MPL is expected to play a crucial role in preventing the permeation of methanol across CNCs in the anode CL. Therefore, in this study, 30 wt% PtRu (atomic ratio 1:1) supported CNC was used as the anode CL. Carbon nanoballoon (CNB) and Vulcan were used as the anode MPL materials. CNB is a unique material because of its hollow structure and high electrical conductivity, while Vulcan has a high surface area and high electrical conductivity. Furthermore, we investigated the optimization of carbon loading and carbon type in the anode MPL.

### 2. Experimental

#### 2.1 Synthesis of carbon nanomaterials

CNCs were synthesized using an automatic chemical vapor deposition system with a consecutive substrate transfer mechan-