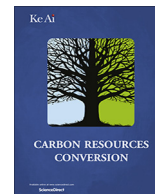




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## Improved performance of direct methanol fuel cells with the porous catalyst layer using highly-active nanofiber catalyst

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## ABSTRACT

PtRu supported on TiO<sub>2</sub>-embedded carbon nanofibers (PtRu/TECNF), which was recently reported as a highly-active catalyst for methanol oxidation, was applied to a direct methanol fuel cell (DMFC), and the power generation performance was compared to that using the commercial PtRu/C. Before the comparison, the effect of the catalyst loading on the power density of the DMFC was investigated using PtRu (18 wt%)/TECNF. The DMFC power density showed a maximum at about a 1.5 mg cm<sup>-2</sup> PtRu loading that corresponds to about an 80 μm layer thickness. A catalyst layer thicker than this value reduced the power density probably due to the concentration overvoltage. The PtRu content in the PtRu/TECNF was then increased to 30 wt% or more to reduce the layer thickness and to increase the power density. The DMFC performance was compared to that of different anode catalysts at a 1 mg cm<sup>-2</sup> PtRu loading. The power density was maximized using the PtRu30 wt%/TECNF, which showed a 173 mW cm<sup>-2</sup> at 353 K and had 66 μm layer thick, that was 26% higher than that of commercial PtRu/C. The current-voltage curve of the DMFC with the PtRu/TECNF suggested an improved mass transport overvoltage, but a little improvement in the activation one despite using the catalyst with about a 2 times higher activity compared to that of the commercial PtRu/C. This was attributed to the lower Pt utilization of the nanofiber catalyst layer.

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### 1. Introduction

A direct methanol fuel cell (DMFC) has been expected to be an attractive power source for mobile and portable applications due to its advantages including a high theoretical energy density, simple system structure, ease of handling of the liquid fuel and low operating temperatures [1,2]. However, the performance of the current DMFC is still far from ideal. One of the major reasons is attributed to the sluggish electrode reactions at both the anode and cathode and the methanol crossover that induces mixed potentials and flooding of the cathode. Pt and Pt-based materials have been used as a catalyst for both the methanol oxidation reaction (MOR) and oxygen reduction reaction at the anode and cathode, respectively. Although a relatively large amount of the precious metal is used, the power density of the DMFC is usually much lower than that of hydrogen fuel cells. In order to increase the power density of the DMFC, it is necessary to develop a highly-active catalyst. It is also important to reduce the loading

of the precious metals, like Pt and Ru, to reduce the DMFC cost for commercialization. Hence, a highly-active catalyst using a lower precious metal loading is strongly required for the DMFCs.

For the anode of the DMFC, PtRu, which is typically an alloy with the atomic Pt:Ru ratio of 1:1, has widely been used [1–4] as the active catalyst for the MOR. The effect of Ru on the activity in the alloy catalyst has been explained by a bifunctional mechanism [3,4] or the ligand effect. It is usually used as PtRu black or nanoparticles supported on carbon black, PtRu/C. In a DMFC, a relatively high PtRu loading of about 3 mg cm<sup>-2</sup> or higher [5–7] is generally used for the anode due to the lower MOR activity.

In order to increase the mass activity and reduce the PtRu loading, support materials that enhance the mass activity [8] and/or durability [9] have recently been investigated. Many reports have revealed that some metal-oxide supports, like TiO<sub>2</sub> [10–13], CeO<sub>2</sub> [12–15] and their composites with carbon [16–20], could enhance the activity of the Pt-based catalyst. The enhanced activity is sometimes attributed to the strong interaction between the metal and support [12,14]. Some of the authors proposed PtRu supported on a TiO<sub>2</sub>-embedded carbon nanofiber (PtRu/TECNF) as the catalyst for the MOR and demonstrated significantly higher MOR activities

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**List of symbols***Latin letters*

<i>L</i>	thickness [ $\mu\text{m}$ ]
<i>i</i>	current density [ $\text{mA cm}^{-2}$ ]
<i>Q</i>	electric charge [C]
<i>W</i>	mass [g]

*Greek letters*

$\varepsilon$	porosity [–]
$\eta$	overpotential [V]

*Sub scripts*

ac	anode catalyst layer
cat	catalyst
co	carbon monoxide
com	commercial
MEA	membrane electrode assembly
-PtRu	PtRu
-Pt	Pt

compared to the commercial catalyst depending on the  $\text{TiO}_2$  content in the carbon nanofiber [17,18]. The optimum  $\text{TiO}_2$  content was found to be  $\text{Ti/C} = 1$ , and the maximized mass activity was about 3 times higher than that of the commercial PtRu/C catalyst. This suggested that a DMFC with the nanofiber catalyst layer will exhibit a high power density compared to that with the conventional PtRu/C catalyst. Although a higher DMFC power density using the PtRu/TECNF anode compared to that with PtRu/C was reported in a previous paper, it was pointed out that the power density of a DMFC using PtRu/C as the comparison target was too low. Since PtRu/C catalysts are generally used by introducing a microporous layer between the gas diffusion layer, usually a carbon paper, and the PtRu/C layer, it would be fair that the comparison should be conducted by introducing a microporous layer for the PtRu/C catalyst layer.

The efficient use of the catalyst in its layer is another important issue, because the catalyst is used in the form of a catalyst layer in the membrane electrode assembly (MEA). The structure of the catalyst layer, i.e., the metal loading [5,6,27], thickness [21], pore structure [22], hydrophobicity [23,24], ionomer content [25,26] and their distributions [28–30], affect the electrode performance related to the catalyst utilization and mass transport including the methanol crossover. Improvements in the electrode structure [5,21,29] and optimization of the layer structure [24–26] have been reported. Although DMFCs usually generate a higher power output at a higher pressure, such an optimization of the catalyst layer structure can exceed the relatively high value of  $100 \text{ mW cm}^{-2}$  even under atmospheric pressure with a small amount of PtRu loading. Kyungmun et al. obtained  $120 \text{ mW cm}^{-2}$  at 333 K with a  $2 \text{ mg cm}^{-2}$  PtRu loading in both the anode and cathode by introducing a micro porous layer [23] in anode. Yun et al. provided a carbon buffer layer in anode with a  $2.0 \text{ mg PtRu}$  loading, and obtained  $130 \text{ mW cm}^{-2}$  at 343 K [29].

Some superior performances of a nanofiber-structured catalyst in polymer membrane electrolyte fuel cells (PEMFCs) have recently been reported [30–34]. They can be categorized into (1) uniform distribution of catalyst particles and ionomer in a nanofiber layer [33], (2) an improved mass transport property in the nanofiber layer [11,30,33], (3) a higher electrical conductivity of the nanofiber layer [31,34] and (4) a chemically-modified nanofiber surface [32]. Zhang et al. [33] achieved an exceptionally high mass activity for Pt in the cathode of a PEMFC by preparing a nanofiber-structured Pt/C catalyst using an electrospinning technique, and revealed that the accessible electrochemical surface area (ECSA) of the nanofiber electrode was twice that for a conventional catalyst layer. The higher ECSA and mass activity were attributed to a more uniform distribution of the Pt/C particles and Nafion polymer in a nanofiber mat that allows better proton transport and oxygen diffusion to the catalyst sites. In spite of the strong effect of the catalyst layer structure on the power generation performance as already mentioned, the properties of the nanofiber catalyst layer

were rarely reported in most of the studies. It is important to specify the features of the superior catalyst layer structure.

In this study, DMFCs were prepared using the highly-active nanofiber catalyst, PtRu/TECNF, for the anode, then the power generation performance was compared to the DMFCs with different catalysts including the commercial PtRu/C. Before the comparison, the effect of the catalyst loading on the power density of the DMFC was investigated using the PtRu(18 wt%)/TECNF. The PtRu content of the PtRu/TECNF was then adjusted to have a maximum mass activity. The DMFC performance was compared to the different anode catalysts at a  $1 \text{ mg cm}^{-2}$  PtRu loading. The structure of each catalyst layer, i.e., thickness and porosity, was also studied and compared to each other to specify the features of the nanofiber catalyst layer structure.

## 2. Experimental

### 2.1. Preparation of PtRu/TECNF catalyst

The PtRu/TECNF was prepared in the same way as described in previous papers [17,18]. Briefly, a mixture of specific amounts of  $\text{TiO}_2$  nanoparticles (P25, Nippon Aerosil Co., Ltd.), dimethylformamide (DMF, Wako Pure Chemicals Ind., Ltd.) and polyacrylonitrile (PAN, Sigma–Aldrich Co., Ltd.) was electrospun followed by stabilization (in air, 523 K for 10 h), carbonization (in nitrogen, 1273 K for 1 h) and steam treatment (1123 K for 1 h). Two hundred mg of the obtained nanofibers, TECNf, was then milled for 5 min to normalize the fiber length.

The different contents of the Pt–Ru (18, 20, 30, 40 and 50 wt%, atomic ratio of 1:1) were deposited on the TECNf by the microwave polyol method [35]. A specific amount of the nanofiber was dispersed in ethylene glycol under ultrasonic agitation for 30 min. Specific amounts of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (98.5% Wako Pure Chemicals Ind., Ltd.) and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (99.9% Wako Pure Chemicals Ind., Ltd.) were dissolved in the solution by stirring for 3 h. A 100 mL portion of the mixture in a beaker was heated at 600 W for 3 min in a microwave oven, and the solution was stirred overnight. The slurry was then filtered and washed with a sufficient amount of distilled water and methanol. Finally, the catalyst powder, PtRu/TECNf, was dried overnight at 343 K under vacuum. The PtRu/TECNfs with the different PtRu contents were denoted by adding the weight percent of PtRu like PtRu18/TECNf for the PtRu18 wt%/TECNf.

### 2.2. Characterization of the catalyst

The chemical composition of the catalyst was analyzed by energy dispersive X-ray spectroscopy (EDX, SEDX-500, SHIMADZU Co. Ltd.). X-ray diffraction (XRD) measurements of the samples were conducted to determine the crystal structure using an X-ray

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