



Durable Marimo-like carbon support for Platinum nanoparticle catalyst in polymer electrolyte fuel cell



Koki Baba^a, Mikka Nishitani-Gamo^b, Toshihiro Ando^c, Mika Eguchi^{a,*}

^a Department of Biomolecular Functional Engineering, College of Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki, 316-8511, Japan

^b Department of Applied Chemistry, Graduate School of Engineering, Toyo University, 2100 Kujirai, Kawagoe, Saitama, 350-8585, Japan

^c National Institute for Material Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

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ABSTRACT

This study deals with the electrochemical stability of carbon-based catalyst supports as the cathode material of a polymer electrolyte fuel cell (PEFC). The platinum catalyst on the carbon black supports (Pt/CB) was investigated for use in the PEFC. Marimo-like carbon (MC) was used for the catalyst support. Electrochemical surface oxidation of the Marimo-like carbon was compared to that of conventional carbon black during simulated start-stop cycles. We observed a different durability of the electrocatalytic activity between the carbon black and the Marimo-like carbon based on the CV measurements and the XPS. In case of the carbon black, the electrochemical active surface area (ECA) decreased and the electric double layer current density increased with increasing number of cycles in the accelerated degradation test (ADT). These results indicated oxidation of the carbon in the Pt/CB by the ADT. In case of the Marimo-like carbon, the ECA decreased less than in the case of the carbon black, and no change was observed in the XPS. These results indicated that surface oxidation of the Marimo-like carbon proceeded less than that of the conventional carbon black.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) can function with a high efficiency for fast starting motion devices. These properties allow the PEFC to be used as the power sources for automotive, stationary and portable applications [1,2]. To construct a smart grid system using a hydrogen fuel, efficient and durable PEFC systems are required. The hydrogen PEFC required a catalyst promoting chemical reactions in anode and cathode. Platinum is generally used as a catalyst. The Pt catalyst usually consists of Pt nanoparticles dispersed on the surface of carbon black (Pt/CB). The carbon blacks are well known to be a catalyst support for the PEFCs. In recent years, fibrous carbon materials are attracting attention due to their high electric conductivity and water repellency. Carbon blacks have indefinite structures and many fine and deep pores that produce large specific surface areas. However, the carbon black does not have a durable electrochemical property under the PEFC operation conditions. It has been reported that oxygen containing groups (e.g., carboxyl, carbonyl, hydroxyl, phenol, etc.) are formed on the carbon surface at the reaction

temperatures (>65 °C) or operating potentials (>1.0 V vs. RHE) [3–5]. The produced oxygen containing groups cause a decreased conductivity of the carbon and detachment of the Pt nanoparticles from the carbon surface [6–8]. These phenomena decrease the catalytic activity and drastically reduce the performance of the PEFC.

To endure the catalytic electrode activity, it is essential to study the stability of the catalyst and carbon support structures. Some studies have reported durability of carbon materials. Zana et al. investigated the corrosion of high surface area carbons under the start/stop PEFC conditions [9]. Shanahan et al. reported that the graphitized carbon shows a higher stability as a catalyst support [10]. Yuan et al. described a high performance PEFC using fibrous graphite “carbon nanotubes” [11]. Recently, we used a new type of carbon material, i.e., the Marimo-like carbon (Fig. 1). We found that the Marimo-like carbon supported platinum catalyst improved the PEFC performance [12]. Especially, in the high current density range, the MEA efficiently worked. It caused the reactant gases and product water to easily diffuse between the carbon nanofilaments. The optimum ionomer content for the carbon black was about 30 wt%. However, in the case of using the Marimo-like carbon, the ionomer content of 10 wt% gave the best performance because the Marimo-like carbon has a lower surface area of inner pore than the carbon black. The Marimo-like carbon consists of many carbon

* Corresponding author.

E-mail address: eguchi@mx.ibaraki.ac.jp (M. Eguchi).

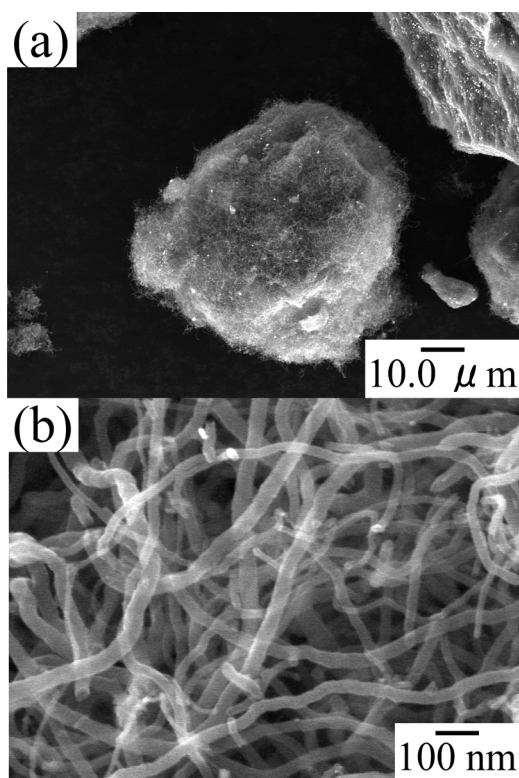


Fig. 1. SEM images of (a) the Marimo-like carbon and (b) the carbon nanofilaments constructed the Marimo-like carbon.

nanofilaments [13,14]. The carbon nanofilaments were interwoven to form a spherical secondary shape. The carbon nanofilaments have a small diameter and long length that form large specific surface areas. They have few pores inside, and their surface areas are due to the outside of the fibers. The fibrous structure simultaneously produces both an increasing surface area and increasing mass transportation. The carbon nanofilaments can contact each other to form a conductive network and provide a good electric conductivity. This structure should be favorable for supplying reactant gases and removing the product water. The carbon nanofilaments have a cup-stack primary structure. The edges of the graphene sheets are exposed to the carbon nanofilaments surface and they act as anchoring sites for the Pt nanoparticle catalyst. Marimo-like carbon does not require any heat pretreatments or any mechanical pretreatments for supporting the Pt particles on their surfaces. The Marimo-like carbon has a superior stability as a support material for the PEFC.

In this study, we examined the durability of the Pt nanoparticle catalyst supported on the Marimo-like carbon (Pt/MC) to investigate changes in the electrochemical property and chemical structures during simulated start/stop cycles [15,16].

2. Experimental

2.1. Catalyst preparation

We used the Marimo-like carbon for the catalyst support. The Marimo-like carbon was synthesized by the decomposition of hydrocarbons using the thermal chemical vapor deposition method [13]. The decomposition of methane was carried out in a flow reactor. Using 100 mg of an oxidized diamond supported Ni catalyst, 30 SCCM CH_4 was introduced at 823 K and heat-treated for 3 h. Since the Ni catalyst was not detected by XPS and EDX analyses, we consider that cell performance and/or durability was not

influenced by the Ni catalyst. The Pt nanoparticles were loaded on the Marimo-like carbon support by the modified nanocolloidal method (Pt/MC) [17,18]. The Pt nanoparticles were directly deposited on the carbon nanofilaments of the Marimo-like carbon from the solution. NaOH (2.76 mol l^{-1} , 5 ml) was added to deionized water (80 ml), followed by the addition of the Marimo-like carbon (100 mg). The carbon-included solution was stirred for 30 min and then irradiated with an ultrasonic vibration for 30 min. Next, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.36 mol l^{-1} , 250 ml) and citric acid (0.56 mol l^{-1} , 5 ml) were added to the carbon-included solution. The solution was stirred for 30 min and then irradiated with an ultrasonic vibration for 30 min. Finally, NaBH_4 ($167.58 \text{ mol l}^{-1}$, 5 mL) was added to the solution and Pt complex ions were reduced to generate Pt metallic nanocolloidal particles. The yielded Pt particles were separated from the solution by centrifugation. After the supernatant solution was removed by the centrifugation, the precipitation products composed of the Pt particles on the Marimo-like carbon.

2.2. Electrochemical measurements

Catalyst inks ($5.4 \text{ g}_{\text{cat}} \text{ l}^{-1}$) were prepared by mixing the 8.4 mg of catalysts (prepared 20 wt% Pt/MC or commercial 20 wt% Pt/CB (TANAKA HOLDINGS Co., Ltd., TEC10E20E)) with 0.043 ml of 5 wt% Nafion solution (E.I. Du Pont de Nemours & Co., Inc., DE521), 0.5 ml of reagent grade 2-propanol (Kanto Chemical Co.) and 1 ml of deionized water under ultrasonic irradiation. 20 μl of the catalyst ink was dropped onto a platinum disk electrode, then the electrode was dried in a nitrogen atmosphere at room temperature for 30 min. The prepared electrode on a platinum disk was used as the working electrode for a triple electrode cell system consisting of a platinum electrode as the counter electrode and a Ag/AgCl as the reference electrode. To remove the influence of oxygen, all the electrochemical measurements were carried out in a deoxygenated $0.1 \text{ mol l}^{-1} \text{H}_2\text{SO}_4$ solution.

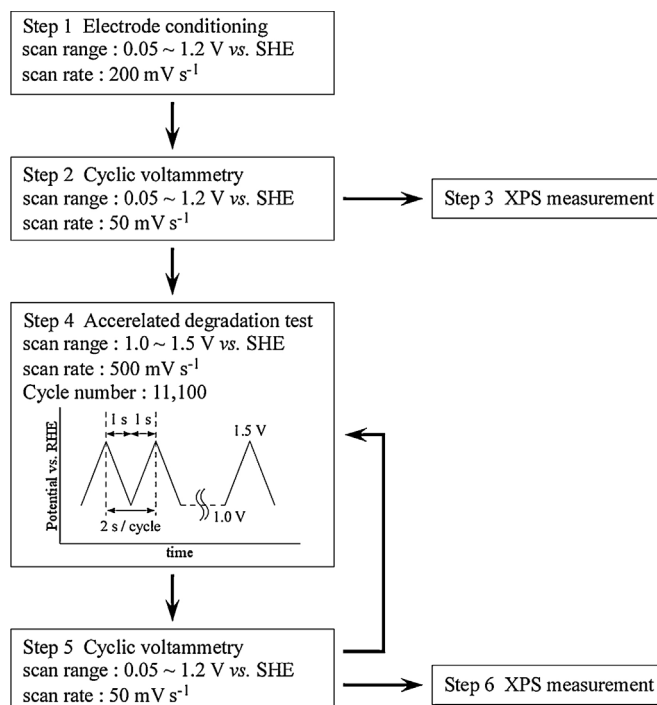


Fig. 2. Procedure for evaluating degradation of Pt/MC and Pt/CB catalysts.

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