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### Short communication

# Effect of platinum amount in carbon supported platinum catalyst on performance of polymer electrolyte membrane fuel cell

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#### Abstract

The performance of polymer electrolyte membrane fuel cells fabricated with different catalyst loadings (20, 40 and 60 wt.% on a carbon support) was examined. The membrane electrode assembly (MEA) of the catalyst coated membrane (CCM) type was fabricated without a hot-pressing process using a spray coating method with a Pt loading of  $0.2 \text{ mg cm}^{-2}$ . The surface was examined using scanning electron microscopy. The catalysts with different loadings were characterized by X-ray diffraction and cyclic voltammetry. The single cell performance with the fabricated MEAs was evaluated and electrochemical impedance spectroscopy was used to characterize the fuel cell. The best performance of 742 mA cm<sup>-2</sup> at a cell voltage of 0.6 V was obtained using 40 wt.% Pt/C in both the anode and cathode. © 2007 Elsevier B.V. All rights reserved.

Keywords: Polymer electrolyte membrane fuel cell; Catalyst coated membrane; Membrane electrode assembly; Spray coating; Platinum loading

#### 1. Introduction

Fuel cells are a promising energy source on account of their high efficiency and low pollutant emission. Polymer electrolyte membrane fuel cells (PEMFC) have attracted considerable attention as a transport and portable power source for low operation temperature and rapid start-up [1]. However, it is believed that PEMFC are not competitive enough to rechargeable lithium ion battery with respect to the cost price because of the expense of the rare metals used such as platinum in PEMFC. Therefore, reducing the amount of platinum used in fuel cells is very important for their commercialization [2].

Generally, there are two approaches to reduce the amount of platinum in fuel cell. One method is to develop an alloyed catalyst based on platinum, which has a better catalytic activity, or to discover a new catalyst [3–5]. The other is to invent a new catalyst layer fabrication method such as pulse electrodeposition, electrospray technique, sputter deposition, pulsed

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laser deposition and ion-beam deposition [6–10]. With respect to the thin catalyst film formation in a fuel cell, supported catalysts and polymer ionomers within the catalyst layer has been used to reduce the amount of catalyst from  $4 \text{ mg cm}^{-2}$ to approximately  $0.4 \text{ mg cm}^{-2}$ . A supported catalyst has a much larger surface area compared with an unsupported catalyst, and a mixed polymer ionomer containing catalyst within the catalyst layer has tremendously increased the number of electrochemical reaction sites, so-called three-phase boundary [11].

It was reported that the catalyst particle size increases and the electrochemical active area (ECA) decreases with increased loadings of the supported catalyst [12]. When the supported platinum loading was increased from 20 to 40 and 60 wt.%, the amount of carbon particles for given amount of platinum was lower, and the structure of the catalyst layer with the polymer ionomer was changed. Structural modification affects the mass transport of the reactant gas and water produced during the reaction. The ion and electron transfer was also affected and the single cell performance was changed in the end. Then, catalysts with several different platinum loadings (20, 40, and 60 wt.%) were used to investigate the effects of

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the loading on the performance of a fuel cell. The MEAs were examined by scanning electron microscopy (SEM) and single-cell test. The electrochemical properties were also studied using electrochemical impedance spectroscopy.

#### 2. Experimental

#### 2.1. Characterization of the catalysts and catalyst layer

The size of the platinum particles in the catalyst powder was examined by X-ray diffraction (XRD) (D/MAX2500 PC, Rigaku Corp.) before applying them to the membrane electrode. Catalyst ink was prepared by mixing the catalyst powder (20, 40 and 60 wt.% platinum on carbon) with an ionomer (5 wt.% Nafion solution, DuPont) in de-ionized water and isopropyl alcohol. The Nafion loading in both electrodes was 30 wt.%, and the ink was ultrasonicated.

Cyclic voltammetry (CV) (Autolab PGSTAT 30, Eco Chemie. Co.) measurements were carried out to calculate the electrochemical active area of the catalyst [13]. A saturated calomel electrode (SCE) was used as the reference electrode and platinum wire was used as the counter electrode. The catalyst ink was dropped onto glassy carbon as the working electrode. The electrodes were immersed in an argon purged  $H_2SO_4$  solution at room temperature and the measurement was carried out at a scan rate of 10 mV per second.

A Nafion 112 membrane (DuPont) was used as the polymer electrolyte membrane. The membrane was treated with 3 wt.% H<sub>2</sub>O<sub>2</sub> (Junsei Chemical Co. Ltd.) for 1 h and boiled in deionized water for another 1 h. The above process was repeated twice. The treated membrane was immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> (Sigma–Aldrich, 95–98%, A.C.S. reagent grade) at 100 °C for 1 h and washed in de-ionized water for 1 h [14].

## 2.2. Fabrication of MEA with different platinum loading on electrodes

The membrane electrode assembly was fabricated via the catalyst-coated membrane by spraying the platinum catalyst on both sides of the polymer membrane. This was followed by just physically placing GDLs without the need for a hotpressing process. A treated Nafion 112 membrane was fixed on a proper plate during fabrication of the catalyst coated membrane by the spraying method. The amount of platinum catalyst used in the spraying method was  $0.2 \text{ mg cm}^{-2}$ , which is approximately a half of the conventional platinum usage (ca.  $0.4 \text{ mg cm}^{-2}$ ) in a PEM fuel cell [18]. The fabricated catalyst coated membrane was dried for approximately 1 h [15].

The effect of different supported platinum loadings on the anode electrode performance was investigated by fixing the catalyst loading on the cathode electrode to 20 and 40 wt.% for various anode-supported catalyst loadings. The anode catalyst loading used was 20, 40 and 60 wt.%. The effect of the different catalyst loading on the cathode electrode was investigated by fixing the amount of the catalyst loading on the anode and varying the cathode catalyst loading.

#### 2.3. Single cell performance measurements

The performance of the fabricated MEA with the different catalyst loading was evaluated using a single cell (CNL-PEM005-01, CNL Energy) and electronic loader. The active area of the MEA was  $5 \text{ cm}^{-2}$  and the MEA was placed between the graphite plates with serpentine flow-field. Two GDLs were also placed between the graphite plate and MEA, and the whole unit was tightened between the metal plates with the proper pressure. The single cell performance was characterized using humidified hydrogen gas at 75 °C on an anode electrode and humidified air gas at 70 °C on a cathode electrode with a stoichiometric ratio of 1.5/2 for the anode and cathode. The cell temperature during the single cell test was maintained at 70 °C and ambient pressure [16]. The current–voltage characteristics were measured using an electronic loader (WFCTS, WonATech Co., Ltd.).

The electrochemical properties of the prepared MEA were examined by electrochemical impedance spectroscopy (Gamry Instruments). The DC current of the single-cell was set to 1 A, and the AC current was maintained at 0.1 A root-mean-square during the impedance measurement. The measurement was carried out at frequencies ranging from 10 kHz to 1 Hz and ten points per logarithmic decade were recorded.

#### 3. Results and discussion

#### 3.1. XRD, CV, and SEM measurements

X-ray diffraction was used to show the changes in particle size as a function of the catalyst loading on carbon. From Fig. 1, the particle size of the platinum catalyst was calculated to 3.4, 4.0 and 5.4 nm at a catalyst loading 20, 40 and 60 wt.% on the carbon support, respectively.

Fig. 2 shows cyclic voltammetry measurements of the surface areas of the 20, 40 and 60 wt.% carbon supported platinum. The results indicate that the surface area decreases with increasing platinum loading. The surface area of the 20, 40 and 60 wt.% of the carbon supported platinum was calculated to be 42.09, 33.40 and  $28.02 \text{ m}^2 \text{ g}^{-1}$ .



Fig. 1. X-ray diffraction (XRD) patterns of 20, 40, and 60 wt.% Pt/C catalysts.

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