

## Preparation and characterization of carbon composite plates as an electrode for alkaline fuel cell

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### ABSTRACT

Graphite particles (80  $\mu\text{m}$ ) and PTFE particles (40  $\mu\text{m}$ ) were coated with Ni (18–50 wt%) and PTFE fine particles (0.3  $\mu\text{m}$ ; 8 wt%) via electroless Ni–PTFE composite plating. The conductivity of Ni–PTFE plated graphite (C/Ni–PTFE) and PTFE (PTFE/Ni–PTFE) particles increased with the Ni content. At 35 wt% Ni content, the conductivity (300  $\text{Sm}^{-1}$ ) of C/Ni–PTFE particles was about 2 times higher than that of PTFE/Ni–PTFE particles. The particles were pressed into plates under a pressure of 10–500  $\text{kg cm}^{-2}$  and the plates were then subjected to heat treatment at 350°C. The surface of C/Ni–PTFE plates contained infinitely many gaps of 0.01–20  $\mu\text{m}$ ; these gaps are useful as a pathway for reacting gases. The conductivities in a direction perpendicular and parallel to the C/Ni–PTFE plates were respectively about 3.5 times (510  $\text{Sm}^{-1}$ ) and 16 times (48 x 10<sup>3</sup>  $\text{Sm}^{-1}$ ) higher than those of the PTFE/Ni-PTFE plates. Furthermore, the total pore volume (0.145  $\text{cm}^3 \text{g}^{-1}$ ) of C/Ni–PTFE plates was higher than that of PTFE/Ni-PTFE plates, which improved the gas permeability of the former. The current density (84  $\text{mA cm}^{-2}$  at 0.3 V) of C/Ni–PTFE electrode was about 2 times higher than that of PTFE/Ni–PTFE electrode. This increase in the current density might be attributed to the improvement in the total conductivity and gas permeability of C/Ni–PTFE electrode.

### 1. INTRODUCTION

Among various types of fuel cells, alkaline fuel cells (AFCs) are the most matured. The AFCs were the first fuel cell technology to be put into practical use and make the electricity generation from hydrogen fuel. Recently, there has been a resurgence of interest in AFCs [1-4], partly because they have the potential for lower cost in mass production than other types of low temperature fuel cells. The porous gas diffusion layer (GDL) is an essential component of the fuel cell systems. This layer has to be porous for the reacting gases, have good electronic conductivity, and be hydrophobic so that liquid product water does not saturate the material and reduce the permeability of gases [5]. Generally, the structure of the porous GDL is governed by the type of

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carbon and by the hydrophobic resin, typically PTFE that is used in its preparation [6]. The PTFE amount used to coat the carbon in the GDL is important because PTFE addition can reduce the electrical conductivity of the GDL [7].

A previous study [8] investigated the use of electroless Ni plating to produce the Ni-plated PTFE (noted by PTFE/Ni) particles. The PTFE/Ni particles can be converted into the PTFE/Ni plate by heat treatment at 350°C after pressing because the PTFE/Ni particles can be mutually connected via PTFE that is extruded through a Ni film on the PTFE particles. The PTFE/Ni plate is a unique composite material having both properties, such as plasticity or hydrophobicity of PTFE and electrical conductivity of Ni metal. Also it is a new type electrode for AFC that combines two functions of gas diffusion layer and gas distribution channel. As the PTFE/Ni particles are pressed into the PTFE/Ni electrode, the PTFE as a core material in the PTFE/Ni particles, however, reduces the electrical conductivity because it obstructs the connection of Ni networks created between PTFE/Ni particles. There were also presented some Ni-rich and Ni-poor layers in the PTFE/Ni electrodes [9]. Carbon possesses unique electrical and structural properties that can make it an ideal material for use in fuel cell construction. It can also act as a support for the active metal in the catalyst layer [7].

This study explores the utility of carbon material replacing of PTFE as a core material in the PTFE/Ni particle. Especially Ni-PTFE composite plating [10] is examined to produce an electrode containing carbon material for alkaline fuel cells (AFCs).

## 2. Experimental details

As the plating core material to produce the electrode material, graphite particles (80  $\mu\text{m}$ ; Nippon Kokuen Industries, Ltd.) were selected. And PTFE particles with 40  $\mu\text{m}$  average diameter particle size (KT-300M; Kitamura Industries, Ltd.) were used as a reference material. All particles were sieved to uniform the size and to prevent their mutual cohesion. The graphite and PTFE particles were hydrophilized using a nonionic surfactant (BL-2; Nikko Chemicals, Ltd.) to disperse them in a water-plating bath. As the hydrophilic treatment, all particles were stirred in an aqueous solution of 2 wt% surfactant (BL-2) at 60°C for 30 min and dried in a 70°C air chamber after filtering and washing with ion-exchanged water.

With respect to the sensitizing process used for electroless metal plating, all particles were immersed in an aqueous solution of 2 wt% tin(II) chloride dehydrate (Kanto Chemical Co. Inc.) and 1 vol% hydrochloric acid (12M; Nacalai Tesque Inc.) for 10 min, followed by gentle rinsing with ion-exchanged water. For the activation process, the sensitized particles were immersed in an aqueous solution of 0.1 wt% palladium (II) chloride (Mitsuwa Chemical Co. Ltd.) and 0.5 vol% hydrochloric acid (12 M) for 2 min, followed by gentle rinsing with ion-exchanged water. All particles were re-treated three times using these sensitizing and activation processes. The Pd amount on the activated graphite and PTFE particles was measured from the dissolving Pd in nitric acid by atomic absorption spectrometry (AAS, Z5000-300; Hitachi Ltd.) analysis.

The Ni-PTFE composite plating bath was prepared mixing of (1) a fine PTFE dispersion solution and (2) an electroless Ni plating solution at 60 °C for 10 min. The fine PTFE dispersion solution was produced suspending the PTFE (0.3  $\mu\text{m}$ , Daikin Industries, Ltd.) fine particles with surfactant (F-150, Nippon Ink Industries, Ltd.) in

aqueous solution. The electroless Ni plating bath was prepared using 20 g/dm<sup>3</sup> nickel(II) sulfate hexahydrate (Nacalai Tesque Inc.), 30 g/dm<sup>3</sup> tri-sodium citrate dehydrate (Nacalai Tesque Inc.) and sodium ammonium solution (Kanto Chemical Co. Inc.) as a pH adjuster. Then sodium phosphinate monohydrate (Nacalai Tesque Inc.) was used as a reducing agent. The activated particles, 10 g, were put into the composite plating bath of 1000 ml, which was controlled to 60°C and pH 9.0. Finally, the substrate was rinsed carefully with ion-exchanged water and dried in a 70°C air chamber after filtering. After the Ni-PTFE composite plating process, two kinds of particles, C/Ni-PTFE and PTFE/Ni-PTFE could be acquired. The C/Ni-PTFE particle means that the Ni-PTFE composite plating film was coated on the surface of C (graphite) particle as a core material. In case of PTFE/Ni-PTFE particles, the Ni-PTFE composite plating film was formed on the surface of PTFE particle as a core material. In this paper, the C/Ni-PTFE and PTFE/Ni-PTFE will be noted as the sample name.

The conductivities of Ni-PTFE composite plated graphite (C/Ni-PTFE) and PTFE (PTFE/Ni-PTFE) particles were measured 3 times using the four-terminal dc method with a disk sample ( $\phi$  10 mm) pressed at 3 kg/cm<sup>2</sup>. The particle surface was observed using scanning electron microscopy (SEM, S-2400; Hitachi Ltd.). A cross-section polisher (SM-09010; JEOL) was used to observe the cross-section of particles. The Ni amount was measured from a Ni film on the C/Ni-PTFE and PTFE/Ni-PTFE particles in nitric acid using AAS (Nacalai Tesque Inc.).

The C/Ni-PTFE particles were pressed into the C/Ni-PTFE plates under a pressure of 10–500 kg/cm<sup>2</sup> to the size of 60 mm × 60 mm × 1 mm using a die with a ditch pattern to facilitate gas flow; subsequently, it was sintered at 350°C under 10% H<sub>2</sub> – 90% N<sub>2</sub> and atmospheric pressure for 1hr. The total schematic image from C/Ni-PTFE particles to C/Ni-PTFE plate is depicted in Fig. 1. The C/Ni-PTFE particles can be mutually connected via PTFE extruded in the Ni-PTFE composite film. The PTFE/Ni-PTFE plates were also prepared pressing the PTFE/Ni-PTFE particles under identical conditions. Consequently, the plates with a gas passage pattern could be prepared.

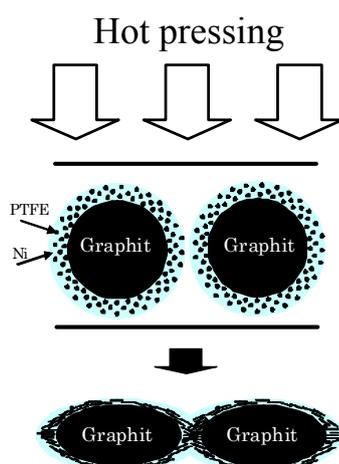


Fig. 1. Schematic image from C/Ni-PTFE particles to C/Ni-PTFE plate using hot pressing.

The gas permeability of C/Ni-PTFE and PTFE/Ni-PTFE plates was measured using two methods: (1) the gas permeability measurement apparatus, explained in detail in a previous paper [16], was used to measure the gas permeability ratio. (2) Automated mercury porosimetry (Auto Pore IV; Micrometrics Inc., Shimadzu Corp.) was used to measure the pore distributions and the porosity in the plates. In addition, EPMA-SEM analysis (S-2400; Hitachi Ltd.) was used to observe the interior structure.

The conductivity of C/Ni-PTFE and PTFE/Ni-PTFE plates was measured using two methods: (1) for a direction perpendicular to the surface of the plates; the conductivity was measured using the four-terminal dc method with a 20-mm diameter disk sample pressed at 3 kg cm<sup>-2</sup>. (2) For a direction parallel to the surface of the plates, the sample surface was measured directly. The conductivity was measured using four-terminal dc method with a 10 mm × 50 mm rectangular sample. In addition, Ag paste was painted to the contact point of the terminal on the sample. The voltage was measured at the current of 3 mA.

In case of electrolyte in AFC, an alkaline aqueous solution has been widely used as an electrolyte. To prevent the liquid leakage, however, a gel electrolyte was used in this study. The gel electrolyte was produced by adding the gelling agent (PW-150; Nihon Junyaku Co. Ltd.) used for nickel/metal hydride battery or alkaline zinc cells to 7 mol/dm<sup>3</sup> potassium hydroxide (Nacalai Tesque Inc.).

The unit fuel cell was operated at room temperature with a fuel cell performance testing equipment (PEFC single-cell testing equipment; Chino Corp.). The reacting gas flow rate was set at 100 cm<sup>3</sup> min<sup>-1</sup> for dried H<sub>2</sub> gas and 200 cm<sup>3</sup> min<sup>-1</sup> for dried O<sub>2</sub> gas. The potential properties of unit fuel cells were measured using a potentio/galvanostat (1287; Solartron Analytical).

### 3. Results and discussion

The Pd is expected to deposit directly on the sample surface through the sensitizing and activation processes. The Pd amount on the activated graphite and PTFE particles was 1.7 and 1.5 wt%, respectively. Using the electroless composite plating method, Ni was plated onto the Pd-activated particles.

Fig. 2 presents the BSE images ((a), (b)) and mapping images ((c) Ni, (d) F) of the C/Ni-PTFE particles with Ni (35 wt%) and PTFE fine particles (8 wt%). The C/Ni-PTFE surface was covered uniformly with Ni-PTFE composite film as shown in Ni and F mapping images. The conductive path was apparently constructed by connecting Ni deposited on the C/Ni-PTFE particles.

Fig. 3 presents the conductivity of various particles with different Ni contents. The conductivities of the graphite (C/Ni and C/Ni-PTFE) plated with Ni (■) and Ni-PTFE (●), respectively were about 40 times greater than that (7 Sm<sup>-1</sup>) of the original graphite particles. Namely the conductivity of original graphite particles could be improved using the metal plating that makes to reduce the contact resistance between the original graphite particles [11, 12]. The conductivity of C/Ni and C/Ni-PTFE particles mainly increased with the Ni content. The sharp increase near at 20 wt% Ni was reasoned for the connections of dot-like Ni plated on the graphite. Namely it was resulted from the formation of Ni-networks on the particle surface. Comparing with the conductivity behavior of C/Ni particles, the conductivity behavior of C/Ni-PTFE particles was mutually

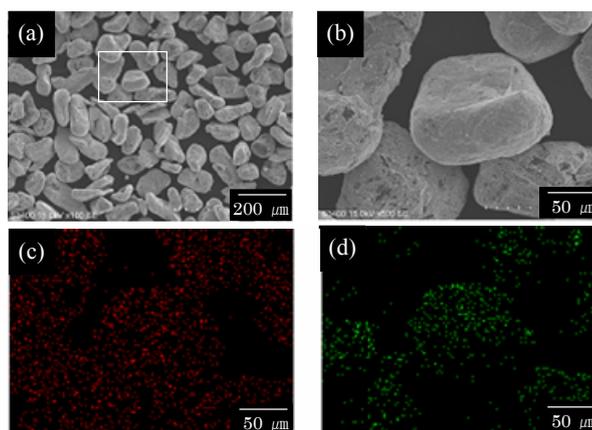


Fig. 2. Surface morphology of C/Ni-PTFE particles: (a) and (b) BSE images; (c) Ni and (d) F mapping images by EPMA.

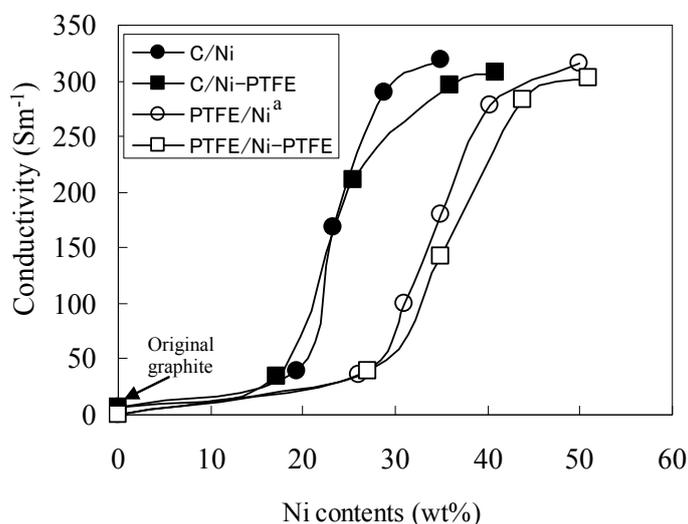


Fig. 3. Conductivity vs. Ni content of graphite (●, ■) and PTFE (○, □) particles treated by Ni-PTFE composite plating and Ni plating: <sup>a</sup> Conductivity data of PTFE/Ni particles was referred [16].

similar except the conductivity loss in 25–40 wt% Ni due to the electrical insulation of the PTFE fine particles in the Ni-PTFE composite film. Especially the PTFE fine particles, however, are essential as a binder for the electrode preparation in this study. When the C/Ni-PTFE and PTFE/Ni-PTFE particles were compared with each other at 35 wt% Ni, the conductivity ( $302 \text{ Sm}^{-1}$ ) of C/Ni-PTFE particles was about 2 times higher than that of PTFE/Ni-PTFE particles. It may be caused that graphite particles play a role to support for the conducting path with Ni-networks. The conductivity of C/Ni-PTFE and PTFE/Ni-PTFE particles was about  $300 \text{ Sm}^{-1}$  at 35 wt% Ni and 50 wt% Ni, respectively and these particles were used for the preparation of C/Ni-PTFE and PTFE/Ni-PTFE plates in this study.

Fig. 4 shows the SEM images of the surface (a) and cross-section (b) of C/Ni-

PTFE plate with Ni (35 wt%) and PTFE fine particles (8 wt%). To prepare the C/Ni-PTFE plate, the content of PTFE fine particles in the Ni-PTFE composite film should be needed more than 8 wt%. Below 5 wt% of PTFE fine particles in the Ni-PTFE composite film, the C/Ni-PTFE plate could not be obtained even though the pressure value was increased to  $500 \text{ kg cm}^{-2}$ . Comparing with the PTFE/Ni-PTFE, there were found many gaps of  $0.01\text{--}20 \text{ }\mu\text{m}$  on the C/Ni-PTFE surface. Reacting gases might transfer through such gaps. The Ni (c) and F (d) mapping images showed that the graphite particles were densely connected via PTFE and Ni was plated uniformly on the graphite particles.

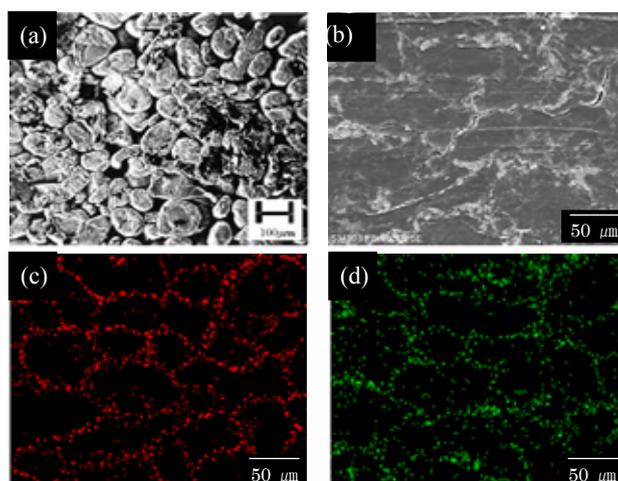


Fig. 4. SEM images of surface (a) and cross-section (b) of C/Ni-PTFE plate, and mapping images of (c) Ni and (d) F.

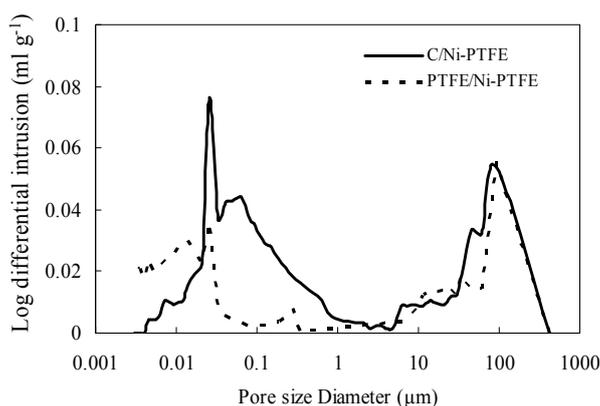


Fig. 5. Pore diameter vs. log differential intrusion by mercury porosimetry for C/Ni-PTFE and PTFE/Ni-PTFE plates.

Fig. 5 presents the pore diameter distribution of the C/Ni-PTFE and PTFE/Ni-PTFE plates using mercury porosimetry. The porosity of two plates has two distinctive regions in which the pore volume increases sharply: those of  $10\text{--}100 \text{ }\mu\text{m}$ , which are

designated as macropores; and 0.01–1  $\mu\text{m}$ , which are micropores. Comparing with the PTFE/Ni–PTFE plates, the pore volume of micropores in the C/Ni–PTFE plates increased drastically. It may be caused that the fine pores between graphite grain boundary was created after hot pressing (350  $^{\circ}\text{C}$ , 400 $\text{kg}/\text{cm}^2$ ). Apparently, the macropores correspond to pores along the boundary between two particles and those among several particles. The pore volume of macropores in the PTFE/Ni–PTFE and C/Ni–PTFE plates was similar to each other because the Ni–PTFE film was identically deposited on the graphite and PTFE particles under same conditions.

Fig. 6 shows the change of voltage with current density obtained from the C/Ni–PTFE and PTFE/Ni–PTFE electrodes. The open circuit voltages (OCVs) of the unit cells containing electrodes were 950–980 mV. The OCV values were found to be similar for all electrodes. However, the polarization behavior at each electrode differed greatly. The current density (84  $\text{mA cm}^{-2}$  at 0.3 V) of C/Ni–PTFE electrodes was about 2 times higher than that of PTFE/Ni–PTFE electrodes, which might be attributed to (1) the improvement of total conductivity and (2) the improvement of gas permeability attributable to the expanded total pore volume, as presented in Fig. 5.

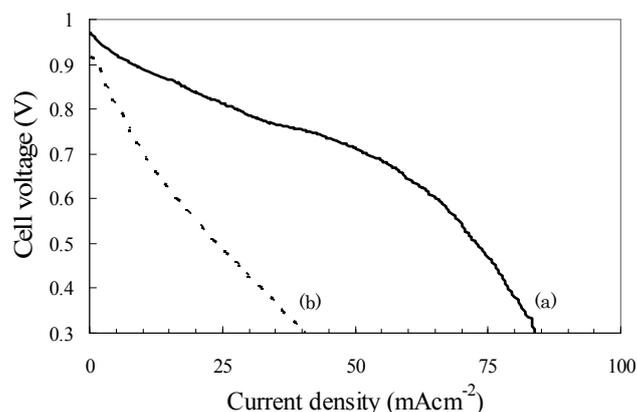


Fig.6. Voltage – current density curves of (a) C/Ni–PTFE and (b) PTFE/Ni–PTFE electrodes.

#### 4. CONCLUSIONS

The Ni–PTFE composite film with Ni (35–36 wt%) and PTFE fine particles (8 wt%) were fabricated uniformly on the graphite and PTFE particles. The conductivity of C/Ni–PTFE particles increased concomitantly with the Ni content and reached about 300  $\text{Sm}^{-1}$  at 35 wt% of Ni content, while the conductivity of PTFE/Ni–PTFE particles reached about 150  $\text{Sm}^{-1}$  at 36 wt% Ni. The C/Ni–PTFE particles were pressed into the C/Ni–PTFE plates under 400  $\text{kg cm}^{-2}$  pressure. Comparing with the PTFE/Ni–PTFE plates, there were detected many gaps of 0.01–20  $\mu\text{m}$  on the C/Ni–PTFE surface. The conductivities in a perpendicular direction and in a parallel direction of C/Ni–PTFE plates were respectively about 3.5 times (510  $\text{Sm}^{-1}$ ) and 16 times ( $48 \times 10^3 \text{Sm}^{-1}$ ) higher than those of PTFE/Ni–PTFE plates. The total pore volume (0.145  $\text{cm}^3 \text{g}^{-1}$ ) and total pore area (10.3  $\text{m}^2 \text{g}^{-1}$ ) in C/Ni–PTFE plates were about 1.1–1.3 times higher than those of PTFE/Ni–PTFE plates, which improved the gas permeability of C/Ni–PTFE

plates. In the unit fuel cell performance, compared with the PTFE/Ni–PTFE electrodes, the current density of C/Ni–PTFE electrodes was drastically improved because of the improved electrical conductivity and gas permeability. Consequently, the C/Ni–PTFE electrodes must be useful as an electrode for alkaline fuel cells.

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