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Preparation of Arc Black and Carbon Nano Balloon by Arc Discharge and Their Application to a Fuel Cell

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Arc black (AcB) was prepared in N_2 gas using the twin-torch arc discharge apparatus, and a hollow capsule with graphite layers named a carbon nano balloon (CNB) was obtained by heat treatment of the AcB in Ar gas at 2400 °C. Transmission electron microscopy, Raman spectroscopy, thermogravimetric analysis, and compressive resistivity measurement confirmed that the CNB was well graphitized. In the direct methanol fuel cell (DMFC) application of these carbon nanomaterials, catalyst metal nanoparticles were supported on the AcB, and a membrane-electrode assembly (MEA) was formed from the catalyst-supported AcB and the CNB by hotpressing them on an electrolyte film. The MEA containing the CNB resulted in a higher DMFC performance than that without the CNB, indicating that the CNB with lower compressive resistivity than the AcB works as a material for the improvement of electric conductivity in an MEA.

1. Introduction

There are several types of carbon nanomaterial, such as carbon nano-onions, carbon nanocapsules, carbon nanohorns, and carbon nanotubes, which are grown by various techniques.[1–3] We synthesized arc black (AcB) by arc discharge using graphite electrodes in N_2 gas and interestingly found that a carbon nano-balloon (CNB), a hollow capsule with graphite layers, was formed by heat treatment of the AcB.[4–9] In this study, we characterized the AcB and CNB by transmission electron microscopy, Raman spectroscopy, thermogravimetric analysis, and compressive resistivity measurement, and evaluated the performance of the direct methanol fuel cell (DMFC), in which the AcB and CNB were used as a catalyst support and material for the improvement of electric conductivity, respectively.

2. Experimental Methods

2.1 Syntheses of AcB and CNB

The twin-torch arc discharge apparatus was used for AcB synthesis.[4] In the discharge chamber, the anode and cathode of 6- and 10-mm-diameter, respectively, graphite rods (Tokai Carbon) contact with an acute angle, and arc discharge occurred between the electrodes with a DC current of 200 A in N_2 gas at 80 kPa. AcB was heat treated in a Tammann oven in Ar gas at 2400 °C for 2 h, and a CNB was obtained.

AcB and CNB were characterized using a transmission electron microscope (TEM; JEOL JEM-2100F), laser Raman spectroscope (JASCO NRS-1000, excitation wavelength = 532 nm), thermogravimetric/differential thermal analyzer (TGA/DTA; Shimadzu DTG-60/60H), and compressive resistivity meter.

2.2 Supporting catalyst metals and fabrication of membrane-electrode assembly (MEA) in DMFC

In the catalyst supporting process, PtRu-supported AcB, PtRu-supported CNB, and Pt-supported AcB were prepared by the following procedure. Sodium hexachloroplatinate ($Na_2(PtCl_6)$, Nacalai Tesque) and/or ruthenium chloride hydrate ($RuCl_3$, Nacalai Tesque) were dissolved in ethylene glycol and the solution was dropped into acid-treated-AcB or a CNB that was dispersed in ethylene glycol.

As for the MEA fabrication process, we have developed the dry-squeeze method to form a catalyst layer.[5] Briefly, PtRu-supported AcB and Pt-supported AcB, were respectively used as anode and cathode catalysts, and a CNB was used as an additive in the catalyst layers for improvement of electric conductivity. The catalyst and additive were thoroughly mixed and evenly laid on a carbon paper (anode: Toray Industries TGP-H-090, and cathode: SGL Carbon GDL35BA). The CNB content was 10%, which was determined by our previous experiments.[10] After dropping 5% Nafion solution (Sigma-Aldrich), an electrolyte, onto the catalyst/additive layer, this layer and Nafion115 (Sigma-Aldrich) were jointly hot-pressed at 2 MPa at 120 °C in order that a three-phase interface, where catalysts on the carbon nanomaterial, methanol-water solution, and Nafion exist simultaneously, was formed. Protons and electrons are generated by methanol oxidation reaction on the surface of the anode catalyst metal (PtRu), and only protons can penetrate Nafion115 toward the cathode catalyst metal (Pt) to be reacted with oxygen and form water molecules.

2.3 DMFC performance

The MEA was built into a DMFC standard cell (Japan Automobile Research Institute, JARI). Methanol-water solution (concentration = 3%) was introduced into the anode with a flow rate of 0.15 ml/s, and dry air was introduced into the cathode with a flow rate of 300 ml/min. The DMFC cell was operated at 60 °C. The polarization property was measured with an FC impedance meter (Kikusui Electronics KFM2030).

3. Results and Discussion

Figure 1 shows the TEM micrographs of the AcB and CNB. The particle diameters of the AcB and CNB were measured to be ∼25 and ∼30 nm, respectively. The CNB was hollow and the shell was formed with graphite multilayers.

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