



Rambutan-like CNT-Al₂O₃ scaffolds for high-performance cathode catalyst layers of polymer electrolyte fuel cells



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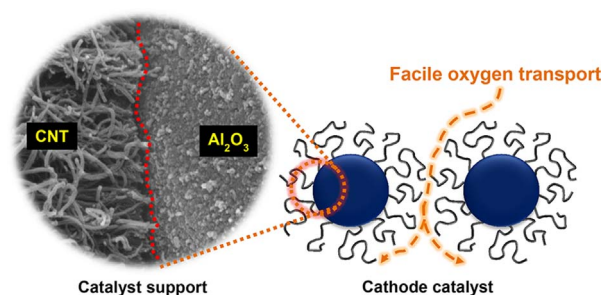
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HIGHLIGHTS

- Rambutan-like CNT-Al₂O₃ is prepared as a catalyst support for PEFCs.
- Pt/CNT-Al₂O₃ MEA show greater performance than Pt/C in the high currents.
- Pt/CNT-Al₂O₃ MEA show better oxygen transport than Pt/C in the catalyst layer.
- Pt/CNT-Al₂O₃ MEA is 3 times more durable than Pt/C against carbon corrosion.

GRAPHICAL ABSTRACT



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ABSTRACT

Rambutan-like CNT-Al₂O₃ scaffolds are introduced as a potential candidate for CNT-based catalyst supports to overcome the CNT issues, such as the easy bundling in catalyst ink and the poor pore structure of the CNT-based catalyst layers, and to achieve high MEA performance in PEFCs. Non-porous α -phase Al₂O₃ balls are introduced to enable the growth of multiwalled CNTs, and Pt nanoparticles are loaded onto the CNT surfaces. In a half-cell, the Pt/CNT-Al₂O₃ catalyst shows much higher durability than those of a commercial Pt/C catalyst even though it shows lower oxygen reduction reaction (ORR) activity than Pt/C. After using the decal process for MEA formation, the Pt/CNT-Al₂O₃ shows comparable initial performance characteristics to Pt/C, overcoming the lower ORR activity, mainly due to the facile oxygen transport in the cathode catalyst layers fabricated with the CNT-Al₂O₃ scaffolds. The Pt/CNT-Al₂O₃ also exhibits much higher durability against carbon corrosion than Pt/C owing to the durable characteristics of CNTs. Systematic analysis of single cell performance for both initial and after degradation is provided to understand the origin of the high initial performance and durable behavior of Pt/CNT-Al₂O₃-based catalyst layers. This will provide insights into the design of electrocatalysts for high-performance MEAs in PEFCs.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are considered one of the most promising energy conversion devices for automotive and residential power applications due to their high efficiency, high power density, and zero pollutant emissions. However, durability and cost

issues are major impediments to commercialization of these fuel cells. An automotive PEFC system typically experiences dynamic power changes including 38,500 start/stop cycles, which leads to high potential excursions of the cathode electrodes up to 1.5 V [1]. Open-circuit voltage (OCV) and idle operation of the fuel cell system also provides approximately 0.95 V and 0.90 V at the cathodes, respectively [1].

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The high potentials accelerate carbon corrosion, particularly at the cathode catalyst layers, with an $11 \pm 2\%$ carbon weight loss resulting in a cell voltage loss of approximately 50 mV at 0.8 A/cm² [1]. It has generally been accepted that fuel cell performance loss arising from electrocatalytic oxidation of carbon is a result of the oxygen reduction reaction (ORR) kinetic loss related to Pt detachment and/or aggregation on the catalyst support and oxygen diffusion loss by porosity decrease of the catalyst layers in the PEFC electrodes.

Many efforts have been directed toward the minimization of carbon corrosion-induced PEFC performance loss. Regarding the material, the surface structure of conventional carbon black (Vulcan XC-72R) has been modified by high-temperature heat treatment [2] to provide durability. Highly durable carbon nanomaterials such as carbon nanotubes (CNTs) [3–7], carbon nanofibers [3,8], and graphenes [9–12] have been introduced to the fuel cell electrodes to improve carbon corrosion durability. Among these, CNTs have been most extensively explored mainly due to their highly graphitized inert structure, as well as their unique physicochemical properties such as high surface area, high thermal and electric conductivities, mechanical strength, and hydrophobicity. Studies have found that Pt catalysts supported on CNTs are much more durable than commercial Pt/C catalysts employing carbon black supports [4–7]. In spite of the excellent properties of CNTs, Pt/CNT catalysts have hardly been applied in real fuel cell systems, as they have poor cell performance characteristics in the cathode catalyst layers used in membrane electrode assembly (MEA) [13]. The one-dimensional morphology of CNTs leads to the formation of densely stacked catalyst layers, whose microporous and mesoporous structures are inefficient for gas diffusion, inducing high oxygen transport resistance. In addition, CNTs tend to form bundles easily during the wet process of catalyst ink preparation [14–16], which results in a non-uniform ionomer-binder distribution in the catalyst layers, leading to low Pt utilization and, therefore, low MEA performance. This indicates that the catalyst layer structure is influenced by the morphology of the electrocatalyst support, which plays a critical role in determining MEA performance. Thus, the morphological design of catalyst supports from the perspective of catalyst layer scaffolds has great importance for realizing the potential of CNTs in fuel cell MEAs. It is notable that vertically aligned CNTs (VACNTs) have demonstrated high performance in MEA, since their structure is efficient for oxygen transport, as well as rapid conduction of protons and electrons [17–19].

In this study, we report a CNT scaffold with rambutan-like morphology for application in the cathode catalyst layers of PEFC MEA. It was expected that the three-dimensional structure of the rambutan-like CNT scaffold, which was established by large alumina balls supporting the CNTs, would provide high gas transport efficiency. Since the CNTs were tethered to alumina balls, CNT bundling problems during catalyst ink preparation were also expected to lessen, easing the formation of uniform catalyst layers. Multiwalled CNTs (MWCNTs) were grown on the surface of non-porous, micrometer-sized Al₂O₃ balls (CNT-Al₂O₃), establishing a rambutan-like microstructure. Pt nanoparticles were loaded onto the outer surface of the chemically functionalized MWCNTs via a microwave-polyol process, producing Pt/CNT-Al₂O₃ catalysts. The performance and durability of Pt/CNT-Al₂O₃ were assessed in both a half-cell and a single cell. For the single-cell study, the MEA was prepared by the conventional decal process. The performance and durability of Pt/CNT-Al₂O₃ in a single cell is systematically analyzed to understand the usefulness of the CNT-Al₂O₃ scaffolds for cathode catalyst layers of PEFCs.

2. Experimental

2.1. Chemicals

Cobalt nitrate hexahydrate (Junsei Chemical, 98%), Ammonium heptamolybdate (Wako Chemical, 99%), anhydrous citric acid (Daejung Chemical, 99.5%), spherical α -Al₂O₃ (Ditto technology, Denka

Chemical), platinum (II) chloride solution (RTX, 10% in water), ethylene glycol (Daejung Chemical, 99%), sodium hydroxide (Sigma Aldrich, anhydrous 97%), and deionized water (DI water, 18 M Ω cm, Millipore) were used without further purification.

2.2. Characterizations

CNT yield was estimated from the weight difference or thermal gravimetric analysis (TGA, Scinco) of the product and the used catalyst. BET surface area, pore size distribution (PSD), and N₂ adsorption/desorption isotherms were determined using a Micrometrics ASAP2020 analyzer. The electric conductivity of the carbon materials was analyzed by a powder conductivity measurement system (ECT-200 K, HUBIS). The morphologies of the Pt nanoparticles on the CNT support were investigated using a transmission electron microscope (TEM, Tecnai TF30 ST) operated at 300 kV. An ethanol solution of ultrasonically dispersed Pt/CNT-Al₂O₃ was cast on the lacey carbon films on a 200-mesh Cu grid. After ethanol evaporation in an oven at 70 °C for 20 min, the grid with dispersed catalyst particles was placed into the TEM. The average catalyst particle size was estimated from the measurement of over 200 particles. The images of the CNT-Al₂O₃ and the catalyst layers in MEAs were obtained by scanning electron microscopy (SEM, S-4800, Hitachi) at an acceleration voltage of 5.0 kV. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical state of the catalyst using the Multilab 2000 (VG, UK) with a non-monochromatic Al K α x-ray source ($E = 1486.6$ eV). The prepared powders were mounted on the sample holder using a small piece of carbon tape. No significant charging effects were detected. All the data were processed using the XPSPEAK software program. The background correction was performed by using a Shirley method, and the binding energy (BE) of the C 1s peak from the support at 284.6 eV was used as an internal standard. Peak areas were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak by a combination of Lorentzian/Gaussian (L/G) curves in varying proportions. Raman spectra were measured by Raman spectroscopy (Horiba Jobin Yvon, France), using a continuous-wave argon-ion laser with an excitation wavelength of 514.5 nm and a maximum power of 40 mW at the sample.

2.3. Preparation of Pt/CNT-Al₂O₃

Cobalt nitrate (0.87 g), ammonium heptamolybdate (0.12 g), and anhydrous citric acid (0.07 g) were dissolved in 20 mL of distilled water. Three grams of spherical alumina support (BET surface area: 0.5 m²/g, D50 = 4 μ m) was added to the metal precursor solution and stirred for 30 min. Water was removed from the solution by rotary evaporation at a pressure of 20 mbar pressure and a temperature of 60 °C. The catalyst was then dried overnight in a drying oven at a temperature of 120 °C to remove residual moisture. The dried catalyst was calcined at 750 °C for 4 h in a muffle furnace in an air atmosphere. The ramping rate was 10 °C/min. Half a gram of the calcined catalyst was placed in a quartz tube reactor (20 mm length) with a microporous glass frit, and then heated to 700 °C under a nitrogen atmosphere. For CNT synthesis, the sample was exposed to a gas mixture of ethylene, hydrogen, and nitrogen in equal volumes, with an upflow rate of 120 mL/min, for between 5 and 60 min.

To obtain hydroxyl- and carboxyl-functionalized CNT-Al₂O₃, CNT-Al₂O₃ composite was ultrasonically dispersed in a mixed solution of nitric (69%) and sulfuric (96%) acid (1:3, v/v) at 60 °C for 30 min. Pt nanoparticles supported on CNT-Al₂O₃ were synthesized via a microwave-assisted polyol method. The acid-treated CNT-Al₂O₃ was ultrasonically dispersed in ethylene glycol (EG) for 1 h. Next, PtCl₂ solution was added, to obtain a metal loading of 40%, and stirred for 1.5 h at 25 °C. Since the sodium hydroxide content of the ethylene glycol has an influence on the size uniformity and distribution of Pt nanoparticles prepared by polyol synthesis, the pH of the suspension was adjusted to a

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