



# Porous graphene/carbon nanotube composite cathode for proton exchange membrane fuel cell

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## ABSTRACT

Porous Pt-graphene/multiwalled carbon nanotube (MWCNT) composite cathodes were fabricated for proton exchange membrane fuel cells and their electro-chemical performances were examined. Rod-like MWCNTs with a high aspect ratio induced a porous network structure and Pt-graphene was bound homogeneously to the porous network structure of MWCNTs in the form of a very rough surface, which facilitated simultaneous access between the Pt electro-catalyst and reactant. In addition, the porous MWCNT network enabled the Pt-graphene electrode to overcome the deficiency induced by high electrical resistance by providing an electrical pathway for the oxygen reduction reaction (ORR). Therefore, the ORR charge transfer resistance of the Pt-graphene/MWCNT composite cathode was much smaller than that of the Pt-graphene cathode, and the maximum power density of the Pt-graphene/MWCNT composite cathode was four times higher than that of the Pt-graphene cathode.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) utilizing hydrogen as a fuel are being developed to replace batteries in portable electronic devices and internal combustion engines in automobiles on account of their high energy efficiency, low pollutant emission and low working temperature. In PEMFCs, Pt-based electro-catalysts are widely used as anode and cathode electro-catalysts for hydrogen oxidation and oxygen reduction reaction (ORR), respectively. One important goal for the commercialization of PEMFCs is to reduce the amount of Pt electro-catalysts required without sacrificing the performance. To effectively utilize the Pt electro-catalysts, the Pt must have simultaneous access to the gas, electron-conducting medium, and proton-conducting medium. Therefore, the catalyst layers must be relatively thin to minimize the losses due to the rate of proton diffusion within the catalyst layer and the rate of mass transfer of the chemical reactants and products to and from the active sites. The latter can contribute to a significant overpotential or polarization of the electrodes, which can limit the cell performance, particularly at high current densities [1]. A range of methods, such as modified thin film methods [2], sputter deposition [3], electrodeposition [4], electro-spray techniques [5] and Pt sol methods [6], have been used to

achieve high Pt utilization and better performance. However, many challenges still remain [7].

Various carbon materials with different nanostructures and morphological characteristics have been used as the electro-catalyst supports in PEMFCs [8–12]. The catalytic activity of the Pt based electro-catalysts is strongly dependent on the catalyst support, which plays a very important role in determining the size and degree of catalyst dispersion as well as the distribution and stabilization of catalyst particles [12]. Instead of traditional carbon supports for the electro-catalysts, nano-sized carbon supports can be used effectively to reduce the Pt loading.

Graphene, which is a one-atom-thick two-dimensional layer of sp<sup>2</sup>-bonded carbon, has attracted considerable attention owing to its unique physical, chemical and electrical properties [13–15]. The unique nanostructure and properties have potential applications in electro-chemical devices [16–18]. Graphene sheets used for electro-catalytic ORR showed higher performance and electro-chemical surface areas (ESAs) than the commercial catalyst, E-TEK [19]. However, electrodes prepared by graphene have an obstacle in mass transfer of the chemical reactants and products to and from the active sites due to graphene's morphological characteristics [20]. Therefore, a new strategy for mass transfer of graphene electrodes is required when a thin catalyst layer using graphene sheets is fabricated.

Carbon nanotubes (CNTs) are some of the most promising materials for the design of functional thin films, including those for catalytic membranes [21,22] and for a range of electro-chemical energy conversion and storage devices [23–25] owing to

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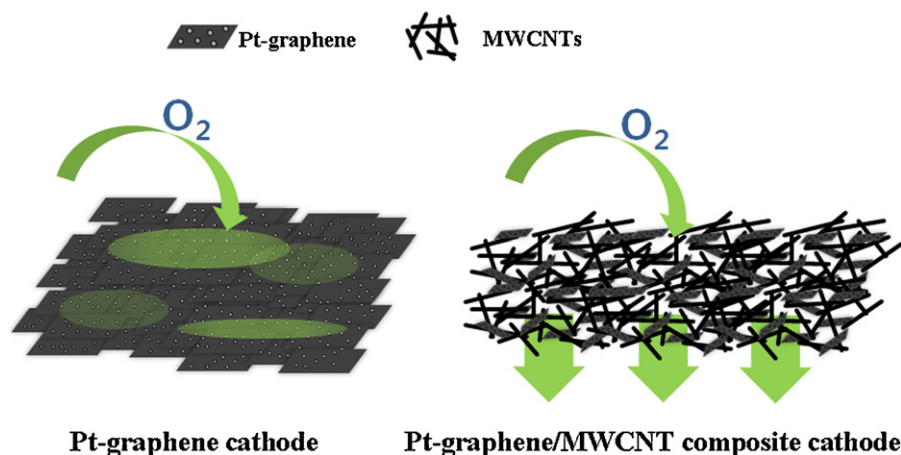


Fig. 1. The structures of the Pt-graphene cathode and Pt-graphene/MWCNT composite cathode.

their unique morphological characteristics and physical properties, including one-dimensional high aspect ratio, large surface area, high electrical conductivity, and superior chemical and mechanical stability [26,27]. Nano-structured membranes fabricated by CNTs, which allow fast mass transfer, were prepared using several methods, such as layer by layer assembly [28], templated growth [29,30], vacuum filtering [31,32] and spinning technology [33].

In this study, porous Pt-graphene/multiwalled carbon nanotubes (MWCNTs) composite cathodes were prepared for PEMFCs and their electro-chemical performance was examined. A porous network structure of a Pt-graphene/MWCNT composite cathode was formed by spray coating from a Pt-graphene and MWCNT dispersion. The porous network structure induced by the MWCNTs acted as a pathway for mass transfer of the chemical reactants and products and as an electrical bridge. Therefore, Pt-graphene/MWCNT composite cathodes showed higher performance for PEMFC than did Pt-graphene cathodes. Fig. 1 shows a schematic diagram of the structures of the Pt-graphene cathode and the Pt-graphene/MWCNT composite cathode.

## 2. Experimental

### 2.1. Fabrication of acid treated MWCNTs and graphene oxides (GOs)

The as-received MWCNTs (NCT, Japan) were treated with acid using a procedure reported elsewhere [32]. Briefly, the MWCNTs were treated in an acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 60 °C for 18 h.

The GOs were prepared from natural graphite (Sigma–Aldrich) using the Hummers method. Aqueous GO suspensions were frozen in liquid nitrogen and then freeze-dried using a lyophilizer (LP3, Jouan, France) at –50 °C and 0.045 mbar for 72 h. After lyophilization, low density, loosely packed GO powders were obtained.

### 2.2. Fabrication of the Pt-graphene

The graphene supported Pt catalysts were prepared by the modified microwave-assisted polyol process described by Fang et al. [12]. In particular, 5.0 mL of an aqueous solution of 0.05 M  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was mixed with 150 mL of ethylene glycol in a 250 mL beaker. A total of 1.75 mL of 0.4 M KOH was then added dropwise to a vigorously stirred solution to adjust the pH to approximately 8–9. The required amount of GOs was added to the mixture and ultrasonicated for 30 min. The beaker containing the mixture of Pt salts and GOs was heated in a household microwave oven

(SAMSUNG RE-C20DV, 2450 MHz, 700 W) for 100 s. The resulting suspension was stirred vigorously overnight and filtered. The residue (mainly graphene-supported Pt catalyst) was washed thoroughly with deionized water and dried overnight at 80 °C.

### 2.3. Preparation of the Pt-graphene cathode and the Pt-graphene/MWCNT composite cathode

The fabricated Pt-graphene was dispersed in isopropyl alcohol by an ultrasound treatment for 30 min and then mixed with a 5 wt% Nafion solution. The mixture was then ultrasonicated for another 30 min and sprayed onto a carbon cloth. In the case of the Pt-graphene/MWCNT composite cathode, both the fabricated Pt-graphene and MWCNTs were dispersed in isopropyl alcohol by ultrasound treatment for 30 min and then mixed with a 5 wt% Nafion solution. The mixture was then ultrasonicated for a further 30 min and then sprayed onto a carbon cloth. A 50 wt% Pt loaded carbon black catalysts (J&M) was also prepared using a similar method.

### 2.4. Preparation of membrane electrode assembly (MEA)

The 50 wt% Pt loaded carbon black catalysts (J&M) were used as the anode catalysts. The electrodes had a geometric area of 4 cm<sup>2</sup> with a Pt loading of 0.2 mg/cm<sup>2</sup>. The Pt-graphene cathode and Pt-graphene/MWCNT composite cathode had geometric areas of 4 cm<sup>2</sup> with a Pt loading of 0.13 mg/cm<sup>2</sup>. The MEA was prepared by hot-pressing a pretreated Nafion 212 (DuPont) sandwiched by the anode and cathode.

### 2.5. Characterization

The morphologies of the MWCNTs and electrodes were observed by field emission scanning electron microscopy (FESEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV after pre-coating the samples with a homogeneous Pt layer by ion sputtering (E-1030, Hitachi, Japan). The morphologies of GO and Pt-graphene were observed by transmission electron microscopy (TEM, CM200, Philips, USA) and atomic force microscopy (AFM, a Digital Instrument Nanoscope IVA). X-ray diffraction (XRD, Rigaku DMAX 2500) of the Pt-graphene was carried out using Cu K $\alpha$  radiation (wavelength  $\lambda = 0.154$  nm) operated at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA) was performed using monochromated Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). To estimate the ESA of Pt in the carbon-supported Pt catalysts, a three-electrode electrochemical cell was employed, and cyclic voltammetry (CV)

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