

Short communication

C₂F₆ plasma treatment of a carbon support for a PEM fuel cell electrocatalyst

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Abstract

To lower Pt loadings for proton exchange membrane fuel cells (PEMFCs), electrocatalytic activity per unit mass of Pt should be improved. In this paper, we report that carbon black treated using C₂F₆ radio frequency plasmas is a good electrocatalyst support for the membrane electrode assembly of a PEMFC. The hydrophobicity of the catalyst support and the affected electronic state of the supported Pt particles, both of which are due to the introduced CF₃ group, are thought to enhance the catalytic activity.

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1. Introduction

The prospect of early practical application and dissemination of proton exchange membrane fuel cells (PEMFCs) is anticipated in the light of their potential high efficiency, small size and moreover, environmental benignity [1]. One challenge to be met in the attainment of this goal is the reduction of Pt loadings in electrocatalysts. Thus far, we have reported that the electrocatalytic activity of carbon-supported platinum (Pt) toward oxygen reduction is dependent on the texture and introduced chemical species of the carbon support [2–4]. In this paper, we discuss the effect of CF₃ group on the carbon support on electrochemical activity.

2. Experimental

The introduction of CF₃ group to carbon black XC-72 was carried out in radio frequency (rf) plasma. A schematic illustration of the reactor is shown in Fig. 1. Hexafluoroethane (C₂F₆) gas was excited by an rf source at 13.56 MHz. The experimental parameters were as follows: inlet gas composition of pure

C₂F₆; gas pressure at 80 Pa; rf power at 40 W; reaction duration of 60 min. Using C₂F₆ rf plasmas, CF₃ group is reported to be introduced to the treated surfaces [5].

The introduction of CF₃ group to carbon black was confirmed using a DM500 goniometer (Kyowa Interface Science Co., Ltd.) to compare the contact angles. The sample powder was spread on a piece of double-sided adhesive tape, which was placed on a glass plate, onto the surface of which water droplets (1 μl in volume) were dropped. To avoid errors, every contact angle in this study was obtained by averaging 10 sets of data. The contact angles of pristine and plasma-treated XC-72 were 79° and 156°, respectively. This suggests that the hydrophobicity was well endowed to the carbon black.

To prepare electrocatalysts with 40 wt.% Pt for this study, the Pt precursor salt Pt(NO₂)₂(NH₃)₂ was dissolved in ethanol and added to the carbon support. The mixture was dried and reduced in a stream of 10 vol.% hydrogen gas at 250 °C.

The oxygen reduction activities of the obtained catalysts were evaluated using a rotating disc electrode (RDE) system. The catalysts were placed atop an RDE of glass-like carbon to which drops of ethanol solution of Nafion® (polyperfluorosulfonic acid from DuPont) were added then allowed to dry. The counter electrode was a Pt wire and the reference electrode was a reversible hydrogen electrode (RHE). Cathodic reduction from 1.1 V versus RHE at a scanning rate of 1 mV s⁻¹ in oxygen saturated 0.1N

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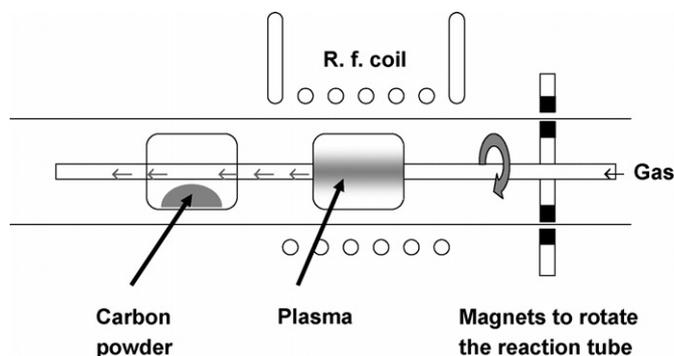


Fig. 1. Schematic illustration of the reactor for rf plasma treatment.

perchloric acid was carried out and the oxygen reduction activity was assessed according to the magnitude of the net kinetic current (i_{kin}) at 0.8 V versus RHE per unit area of Pt. Details of the determination of i_{kin} are described in previous papers [2,6].

The preparation method of the membrane electrode assembly (MEA) is as follows. The prepared electrocatalysts were made into a thin layer by mixing with 5 wt.% Nafion solution. The Pt loadings were 0.1–0.3 mg cm⁻² on C₂F₆ plasma-treated or pristine XC-72 for the cathode and 0.4 mg cm⁻² on pristine XC-72 for the anode. The electrode-coated polytetrafluoroethylene (PTFE) sheet was placed on both sides of the Nafion 117 membrane and then hot-pressed at 150 °C to form the MEA. Evaluations of cell performance were conducted using a single cell with an active area of 25.0 cm². The cell temperature was maintained at 50 °C.

X-ray photoelectron spectroscopy (XPS) analyses were performed on an S-Probe ESCA Model 2803 (Surface Science Instruments) using Al K α radiation (1486.6 eV). Binding energies were calibrated with respect to C(1s) at 285 eV.

3. Results and discussion

As i_{kin} is directly proportional to the activity, the i_{kin} values per unit area of Pt at 0.8 V versus RHE allow a comparison of the oxygen reduction activity of the electrocatalysts. The i_{kin} values of the electrocatalysts prepared using pristine XC-72 and C₂F₆ plasma-treated XC-72 are 0.076 and 0.301 mA(Pt) cm⁻², respectively. The CF₃ group introduced to the carbon support using C₂F₆ rf plasmas [5] is presumed to enhance the oxygen reduction activity of Pt.

Thus far, enhancements of electrocatalytic activity for oxygen reduction on Pt by alloying with Fe [7] or Ni [8] have been reported. This increase in activity is explained on the basis of the increase in valence electron (5d) vacancy, and the increase in the d-vacancy has been confirmed by XPS. In a similar manner, the high oxygen reduction activity of Pt electrocatalyst loaded on the C₂F₆ plasma-treated XC-72 could be explained. The XPS spectra of Pt loaded on pristine and plasma-treated XC-72 are shown in Fig. 2. The 4d3 and 4d5 peaks of Pt loaded on plasma-treated XC-72 are positively shifted from the peak positions of Pt loaded on pristine XC-72 or standard Pt. The shift evaluated to ca. 0.7 eV suggests the increase in valence electron (5d) vacancy of Pt. The CF₃ group containing electronegative fluorine on XC-

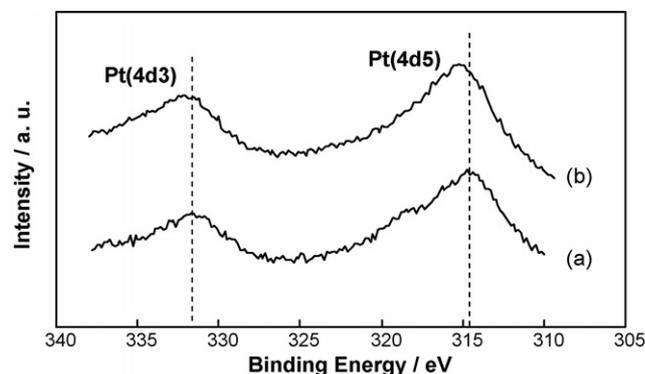
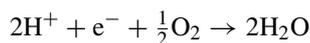


Fig. 2. XPS spectra of Pt loaded on (a) pristine XC-72 and (b) plasma-treated XC-72. Dotted lines show the normal peak positions of the binding energies of standard Pt.

72 is supposed to cause this. The increased d-vacancy of Pt on the electrode surface for oxygen reduction must bring about a strong metal–oxygen interaction, which causes a weakening of the O–O bond, resulting in fast bond scission and a new bond formation between the O atom and H⁺ in the electrolyte.

The oxygen reduction activity of the catalyst determines the single-cell performance, and improved characteristics of PEMFC are expected using the C₂F₆ plasma-treated carbon black. Cell performance, however, is also influenced by the transport condition of the reactant and product gases. In general, the electrode of a PEMFC is constituted by a hydrophobic backing layer of carbon fibre and a porous electrocatalyst layer formed by Pt on carbon as a catalyst agent, PTFE powder and Nafion. The incorporation of PTFE imparts a degree of hydrophobic character to the electrocatalyst layer. PTFE has reduced the propensity of electrode flooding and promotes gas permeable pathways in order to achieve rapid gas transport to catalytic sites [9]. Nevertheless, the existence of PTFE in the catalyst layer lowers the conductivity of both electron and proton, which is considered to deteriorate the cathode reaction:



To reduce this deterioration, an attempt was made to replace the hydrophobicity due to PTFE with that due to the CF₃ group introduced to the carbon support.

Fig. 3 shows the potentiodynamic steady-state polarization curves of three samples. Compared with the control XC-72, the addition of 10 wt.% PTFE results in an improvement in cell performance, especially in the high current-density region. This means that the flooding phenomenon is solved by the hydrophobicity of PTFE. Cell performance is similarly improved in the case of C₂F₆ plasma-treated XC-72 used as the catalyst support. This strongly suggests that the CF₃ group introduced to XC-72 reduced the cathode flooding. The amount of Pt loaded in the cathode catalyst layer was 0.17 mg cm⁻², which is less than 70% based on the amount of Pt loaded in the catalyst layer containing PTFE. Even though the amount of Pt is small, the cell performance is equivalent. The introduced CF₃ on the carbon support effectively prevents the platinum catalyst, on the carbon support in the vicinity of CF₃, from being coated with and deactivated by water which is generated in the oxygen reduction reaction.

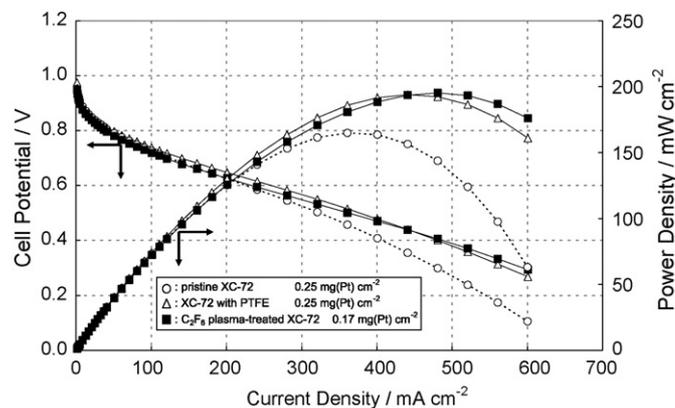


Fig. 3. Polarization curves and power density data. Catalyst support and Pt loading: pristine XC-72 and $0.25 \text{ mg(Pt) cm}^{-2}$ (\circ); XC-72 with 10 wt.% PTFE and $0.25 \text{ mg(Pt) cm}^{-2}$ (Δ); C_2F_6 plasma-treated XC-72 and $0.17 \text{ mg(Pt) cm}^{-2}$ (\blacksquare).

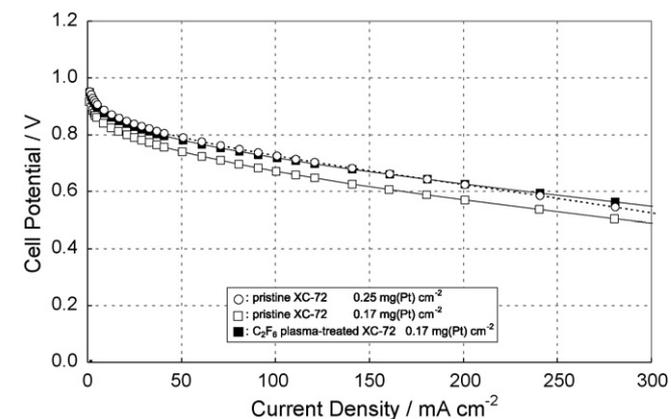


Fig. 4. Polarization curves in the region of higher cell potential. Catalyst support and Pt loading: pristine XC-72 and $0.25 \text{ mg(Pt) cm}^{-2}$ (\circ); pristine XC-72 and $0.17 \text{ mg(Pt) cm}^{-2}$ (\square); C_2F_6 plasma-treated XC-72 and $0.17 \text{ mg(Pt) cm}^{-2}$ (\blacksquare).

Fig. 4 shows polarization curves of MEAs with different amounts of Pt loading at the region of higher cell potential. As mentioned above, C_2F_6 plasma-treated XC-72 with a Pt loading of 0.17 mg cm^{-2} resulted in a polarization curve comparable

to that of pristine XC-72 with a Pt loading of 0.25 mg cm^{-2} . In other words, the generated current density at the region of higher cell potential is superior to that obtained by pristine XC-72 with a Pt loading of 0.17 mg cm^{-2} . This superiority can be attributed to the high oxygen reduction activity endowed by the substituent CF_3 group.

In this manner, introduction of CF_3 group employing rf plasmas serves as an efficient method for introducing hydrophobicity on carbon black and affects the electronic state of supported Pt particles. These phenomena should prove effective to lower Pt loadings in PEMFCs.

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