

Reduction of Pt usage in fuel cell electrocatalysts with carbon nanotube electrodes

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The 12 wt% Pt-deposited carbon nanotube electrode gives 10% higher voltages than 29 wt% Pt-deposited carbon black and reduces the Pt usage by 60% in polymer electrolyte fuel cells with hydrogen and oxygen.

The high price and limited supply of Pt constitute a high barrier to commercialization of fuel cells. Reduction of Pt usage can change fuel cells to a more popular energy source with low environmental load. Carbon black (CB) has been widely used as an electrode which disperses Pt nanoparticles, but many of them are trapped in the pores of the carbon electrodes.¹ These Pt particles are not involved in the electrochemical reactions on electrodes because the triple-phase boundaries (gas–electrolyte–electrode) are essential for PEFC (polymer electrolyte fuel cells). At the triple-phase boundary on the anodes, for example, the following elementary steps may take place; dissociative adsorption of H₂ on the electrode or the electrode catalysts, electron transfer from adsorbed H atoms to the electrode with formation of protons, and proton transportation from the electrode to the electrolyte polymer. An electrode with higher population of the triple-phase boundary is important for the development of efficient electrode catalysts. We report here that a Pt-deposited carbon nanotube (CNT) is a better electrode for PEFC than Pt-deposited CBs, and the 10% higher voltages are achieved with 40% Pt by using Pt/CNT at 0–400 mA cm⁻².

CNTs (Shenzhen Nanotech Co. Ltd.) produced by catalytic decomposition of hydrocarbons were sonicated in 14 M HNO₃ for 1 h, refluxed at 423 K for 2 h, and filtered through a 200 nm membrane after adding distilled water as purification. 1 g CNT stirred in a mixture of HNO₃ (14 M, 50 ml) and H₂SO₄ (98%, 50 ml) for 12 h to make CNT defects^{2,3} was added into HNO₃ (14 M, 50 ml), sonicated, dissolved in 400 ml distilled water, and filtered. The oxidized CNTs were stirred in distilled water with the addition of 30 wt% K₂PtCl₄ in ethanol, and refluxed at 373 K for 2 h in a dark room. The K₂PtCl₄ solution became colorless from brown, with Pt deposition. A commercial 29 wt% Pt-deposited CB (Tanaka Kikinokogyo)^{4,5} was used to compare the performance. The same amount of Pt/CNT and Pt/CB catalysts were dispersed in ethyl acetate, mixed with Nafion® 112 in ethyl acetate, and cast into two electrodes to be pressed with a Nafion® membrane in the same way. *I*–*V* curves were measured with air and hydrogen bubbled in water for the cathode and anode at 353 K, respectively. The *I*–*V* curves were measured several times, and always showed good reproducibility. This performance was the best among our Pt/CNT catalysts.⁶ Transmission electron microscope (TEM) images and X-ray photoelectron (XP) spectra were acquired with JEM-2010F (JEOL) and Escalab 220i-XL (Vacuum Generator) with using a Mg Kα X-ray source, respectively. A Perkin-Elmer 2400 CHN Element Analyser was used for elementary analysis.

Fig. 1 (a) shows the *I*–*V* curves for the Pt/CNT and the Pt/CB electrodes. The voltages of the Pt/CNT electrodes were higher than those of the Pt/CB electrodes at 0–400 mA cm⁻² by 10%. The power densities of the Pt/CNT and the Pt/CB electrodes are calculated from Fig. 1 (a), and shown in Fig. 1 (b). The maximum power density of the Pt/CNT was 0.41 W cm⁻² recorded at 600 mA cm⁻². The voltage drop above 400 mA cm⁻² was ascribed to the proton diffusion. That is, the spaces produced by CNTs may be too small to pass the proton to the Nafion rapidly.

TEM images were acquired for the CNTs and the Pt-deposited CNTs as shown in Fig. 2 (a), (b) and (c), respectively. MWCNTs (multi-walled CNTs) with 20–50 nm diameters were used as carbon supports. The Pt particles were deposited with sizes of 2–4 nm mainly on the CNT surfaces. This is considered to contribute to more efficient Pt usage than the Pt/CB electrodes with forming more triple-phase boundaries. The SWCNTs (single-walled CNTs) generally form bundles,⁷ which decreases their surface area available for supporting Pt particles. Our MWCNTs were dispersed well in ethanol after treatment with mixed acid, and Pt nanoparticles were attached on all the MWCNTs. The high conductivity

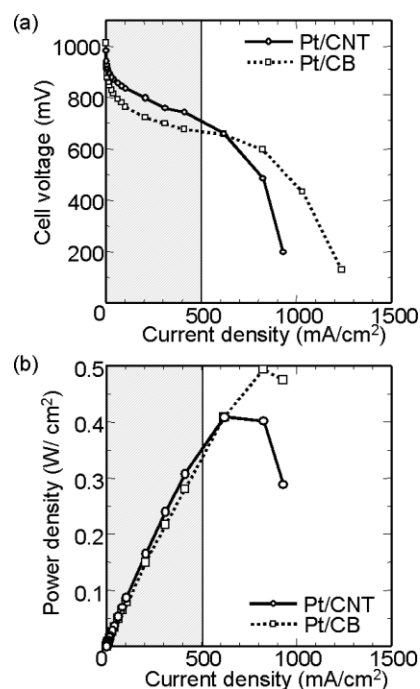


Fig. 1 Performance of the Pt/CNT and the Pt/CB electrodes. (a) *I*–*V* curves. (b) Power density–current density curves.

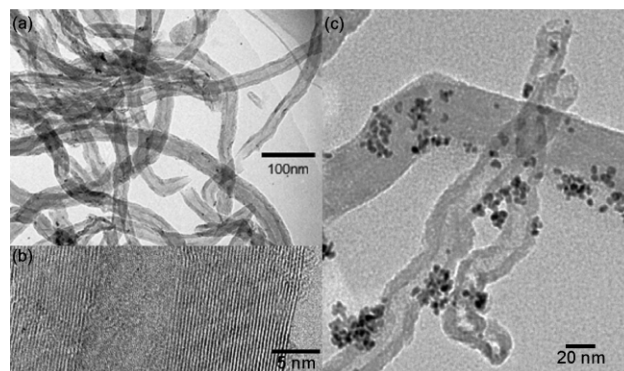


Fig. 2 TEM images of CNTs and Pt/CNTs. (a) CNT. (b) Magnified view of CNT. (c) Pt/CNT.

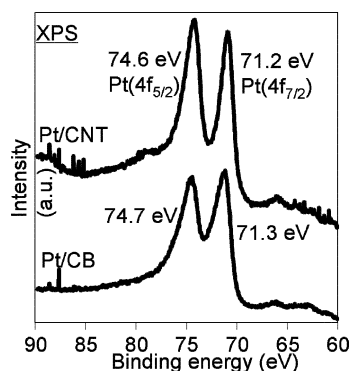


Fig. 3 XP spectra of Pt/CNT and Pt/CB.

of CNTs might be also important for high performance with a low Pt load. The Pt particles agglomerated locally suggesting that the Pt particles were produced in a chain reduction. The mechanism of the Pt deposition will be discussed elsewhere.⁶ TEM images showed well dispersed Pt particles with diameters of 2–3 nm on 20–70 nm CBs, but look more dense than Pt/CNT.^{4–6}

XP spectra were measured for the Pt/CNT and the Pt/CB catalysts as shown in Fig. 3. The Pt particles gave the Pt 4f_{7/2} peaks at 71.2 and 71.3 eV indicating that Pt was deposited as the metal.⁸ This indicates that the Pt ions were fully reduced during the deposition. Metallic Pt is considered to catalyze the reduction of Pt ions with ethanol because Pt nanoparticles agglomerated.

The Pt content was estimated to be 12–13 wt% by elemental analysis.⁶ The Pt content was also estimated to be ~12 wt% considering the escape depth of photoelectrons from the XPS results.⁹ The Pt loads of the Pt/CNT and the Pt/CB per electrode area were roughly calculated to be below 0.2 and 0.5 mg cm⁻², respectively, with the cast catalyst weight and the electrode area. This indicates that the Pt/CNT showed 2–3 times higher voltages per Pt atom below 600 mA cm⁻² compared to the Pt/CB. The power density per Pt atom of the Pt/CNT electrode is also twice better than that of the Pt/CB electrode.

The XP spectrum also suggests that 0.23 Pt particles are attached on the CNTs per nm.¹⁰ This is consistent with the TEM result that ~0.26 Pt nanoparticles are found per nm in Fig. 2 (c). The peak ratio of Pt to C for Pt/CB was 2.3 times larger than that for Pt/CNT. It is hard to estimate the Pt content from the XP spectra exactly since the CBs showed irregular shapes, but TEM images of Pt/CB were also roughly consistent with the Pt content from the XPS results. The results thus indicate that Pt on the CNTs works efficiently compared to the CBs, which is due to the different locations of the Pt catalysts on the CNTs and CBs.

References 11–13 are reports on DMFC (direct methanol fuel cells), and the fuels for these are methanol, not hydrogen which we used. Their systems are different from ours. However, they also obtained similar results in that CNT or CNH (carbon nanohorn) improved the performance compared to CB, and only results are mainly shown in their reports. The higher performance of the Pt/CNT electrodes compared to the Pt/CB electrodes can be ascribed to the following: (i) the well-dispersed Pt particles on the CNT surfaces form more triple-phase boundaries. (ii) The networks and interiors of CNTs might consist of spaces for gas diffusion at 0–400 mA cm⁻². (iii) CNTs possess high electric conductivity.

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- $N_e(z)$, the number of emitted photoelectrons from the depth z of CNTs with the inelastic mean free path (IMFP) λ is given by

$$dN_e(z) = -dzN_e(z)/\lambda$$

The contribution ratio of electrons to the depth z is given by

$$I(z) = 1 - \exp(-z/\lambda).$$

This leads to the conclusion that photoelectrons emitted in the range of the surface and the 2.3λ depth give 90% of the detected electrons.

$N_{\text{Pt-XPS}}(z)$, the number of atoms in a Pt particle multiplied by the sensitivity due to the escape depth (1 for surface atoms) from the surface to the depth $r_{\text{Pt}} - r$ is calculated as follows, where the average radius, atomic weight, density and IMFP are $r_{\text{Pt}} = 1.43$ nm, $M_{\text{Pt}} = 195$ and $\sigma = 2.15 \times 10^{-20}$ g nm⁻³ and $\lambda_{\text{Pt}} = 0.404$ nm (71.2 eV), respectively.

$$dN_{\text{Pt}}(r) = 4\pi r^2 dr \sigma_{\text{Pt}} \exp((r - r_{\text{Pt}})/\lambda_{\text{Pt}})$$

and the atom number density $\sigma_{\text{Pt}} = 6.02 \times 10^{23}$ σ/M_{Pt} . Therefore,

$$N_{\text{Pt-XPS}}(2.3\lambda_{\text{Pt}}) = 407$$

after integrating between $r = 2.3\lambda_{\text{Pt}}$ and r_{Pt} .

The number of Pt atoms in a Pt particle is calculated by

$$N_{\text{Pt}} = (4/3)\pi r_{\text{Pt}}^3 \sigma = 812$$

S_{Pt} , the sensitivity of Pt in a particle due to the escape depth is given by

$$S_{\text{Pt}} = N_{\text{Pt-XPS}}(2.3\lambda_{\text{Pt}})/N_{\text{Pt}} = 0.501$$

When the layer separation and IMPF of CNTs are $s_{\text{CNT}} = 0.34$ nm and $\lambda_{\text{C}} = 1.08$ nm (284.5 eV), respectively, the 7th layer from the surface corresponds to the $2.3\lambda_{\text{C}}$ depth.

$N_{\text{C}}(x)$, the number of C atoms in the x th layer of a 1 nm CNT is calculated as follows, where the average radius and the C–C bond length of CNTs are $r_{\text{CNT}} = 12.5$ nm and $d_{\text{C}} = 0.213$ nm, respectively.

$$N_{\text{C}}(x) = 2(r_{\text{CNT}} - x s_{\text{CNT}})\pi / ((3\sqrt{3}/4)d_{\text{C}}^2)$$

$N_{\text{C-XPS}}(x)$, the number of C atoms in CNTs per nm multiplied by the sensitivity due to the escape depth for the x th layer is given by

$$N_{\text{C-XPS}}(x) = N_{\text{C}}(x)\exp(-x s_{\text{CNT}}/\lambda_{\text{C}}).$$

S_{C} , the C sensitivity in the CNTs with the average of 25 layers due to the escape depth is given by

$$S_{\text{C}} = N_{\text{C-XPS}}(1 - 7)/N_{\text{C}}(1 - 25) = 4.30 \times 10^3 / 2.24 \times 10^4 = 0.192.$$

The atomic sensitivity factor ratio of Pt to C is 0.0531,⁶ and the Pt content is derived from the peak area ratio of Pt to C, R_{XPS} as follows.

$$(195R_{\text{Pt}}/S_{\text{Pt}})/((195R_{\text{C}}/S_{\text{C}}) + (12/S_{\text{C}})) = 12 \text{ wt\%}$$

$$\text{and } R_{\text{Pt}} = R_{\text{XPS}}/0.0531 = 1.17 \times 10^{-3}/0.0531 = 0.022..$$

- The number of Pt particles on the CNTs per nm is given by

$$R_{\text{Pt}}N_{\text{C-XPS}}(1 - 7)/N_{\text{Pt-XPS}}(2.3\lambda_{\text{Pt}}) = 0.23.$$

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