

Highly-durable carbon nanowalls electrodes for fuel cell synthesized employing a C_2F_6/H_2 mixture gas plasma

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Abstract

The carbon nanowalls (CNWs) electrodes synthesized using a C_2F_6/H_2 mixture gas plasma (C_2F_6 -CNWs) showed higher durability than that by the CNWs synthesized using a CH_4/H_2 mixture gas plasma (CH_4 -CNWs). Actually, in the case using the C_2F_6 -CNWs electrodes with Pt nanoparticles, the electrochemical surface area (ECSA) decreased to 48% at 140,000 cycle, although that using the CH_4 -CNWs ones decreased to 55% only at 30,000 cycles. Pt aggregation was observed after 140,000 cycles; however, although the Raman spectra showed a decrease in the intensity ratio of D-band peak to G-band one, there was no change in the FWHM values of these peaks before and after aggregation of the Pt nanoparticles. This indicates that no corrosion occurred on the graphite structure of the C_2F_6 -CNWs.

1. Introduction

The polymer electrolyte fuel cells (PEFCs) have attracted much attention for having the features of low operating temperature (around 80-100°C) and high-power density. Therefore, the PEFCs are expected for the applications on the private power generation, the power for mobile devices, automobile power sources, and so forth. However, there are still serious problems to promote further popularization of PEFCs. The most serious issue high cost and reserve limit of Pt as a catalyst. The other one is low-durability of carbon black (CB), which are commonly used as a support material of Pt nanoparticle catalysts. It is well known that the CB electrodes are easily corroded and degraded only by several thousand times of the start and stop operations.

To realize higher durability fuel cells, the catalyst support materials should have higher resistance toward corrosion. Surface functionalization, metal-based supports, and carbon supports with higher crystallinity including graphitized carbon such as carbon nanotubes and graphene are thus expected [1-4]. The catalysts support for PEFCs requires the utilization of more active sites with high durability and large surface area. Among various types of carbon nanomaterials, carbon nanowalls (CNWs) are one of promising candidates as a novel support material which could have a large surface area and high durability. The CNWs consist of multi-layer graphene

sheets vertically standing on the substrate. In our previous researches, the CNWs, which were fabricated using a CH_4/H_2 gas mixture as a precursor, and its durability have been reported [1]. The CNWs fabricated with the CH_4/H_2 gas mixture (CH_4 -CNWs) maintained 78% performance until 20,000 cycles of the start-stop tests, although that by the CB drastically degraded less than 50% only after several thousand of cyclic tests. Therefore, the CNW supports potentially extend the PEFC lifetime due to the higher durability of the carbon support material. The Fuel Cell Commercialization Conference of Japan (FCCJ) stated that the final target for the durability of start/stop cycles is 60,000 cycles [2]. For CNW supports, the further extension of the lifetime is thus required. In this study, the CNWs were synthesized using C_2F_6/H_2 gas mixture plasma (C_2F_6 -CNWs) were fabricated and then Pt nanoparticles were supported on the C_2F_6 -CNWs (Pt/ C_2F_6 -CNWs). The electrochemical durability of Pt/ C_2F_6 -CNWs was evaluated by start-stop cycling tests and the advantages of CNW supports for application in PEFC electrodes were discussed.

2. Experimental

The C_2F_6 -CNWs were fabricated using a radical injection plasma-enhanced chemical vapor deposition (RI-PECVD) system. In this system, two types of plasmas, which are surface wave excitation plasma (SWP) and capacitively coupled plasma (CCP), are used. H_2 gas is injected into the SWP region, and C_2F_6 gas is injected into the CCP region. 100 sccm of H_2 gas and 50 sccm of C_2F_6 gas were introduced with a total gas pressure of 100 Pa. The power applied to the SWP and CCP regions was 250 and 200 W, respectively. A 0.1 mm thick and 40 mm square titanium plate was placed on the lower electrode as a CNW substrate at a distance of 10 mm from the upper electrode. The deposition time was 30 min and the substrate temperature was kept at 1000°C. The Pt nanoparticles were supported on the CNWs using a supercritical fluid metal organic chemical fluid deposition (SCF-MOCFD) system [3]. 1 wt% of trimethyl (methylcyclopentadienyl) platinum (IV) $[(CH_3C_5H_4)Pt(CH_3)_3]$ in n-hexane $[CH_3(CH_2)_4CH_3]$ was used as the Pt precursor. Pt nanoparticle deposition was performed for 30 min. To evaluate the durability of the Pt/CNWs, PCT was performed. The potential

was changed from 1.0 V to 1.5 V at a scan rate of 500 mV/s, which is the standard protocol suggested by the FCCJ. The potential cycle tests (PCTs) were conducted up to 140,000 cycles, and the electrochemical surface area (ECSA) was calculated from the hydrogen absorption peak that appeared around 0.05 to 0.3 V vs.

3. Results and discussion

Figure 1 shows the normalized ECSAs of Pt/C₂F₆-CNWs from 0 cycles to 140,000 cycles. The ECSAs are obtained and normalized with respect to the largest ECSA at 1,000 cycles. The ECSA gradually decreased from 1,000 cycles to 140,000 cycles. At 60,000 cycles, the ECSA of Pt/C₂F₆-CNWs only decreases to 28% of the maximum. The ECSA then decreases to 48% of the maximum at 140,000 cycles. As a comparison, the durability of Pt/CH₄-CNWs is also measured. The ECSA of Pt/CH₄-CNWs is also normalized according to that at 1,000 cycles. The ECSA is almost halved in 30,000 cycles and disappeared after 60,000 cycles. The durability of Pt/CH₄-CNWs is thus lower than that of Pt/C₂F₆-CNWs. The high durability of Pt/C₂F₆-CNWs is significant and a longer lifetime was maintained to reach a half of the initial performance after 140,000 cycles of PCT.

Figure 2 shows SEM and TEM images of Pt/C₂F₆-CNWs before and after 140,000 cycles of potential cycle testing. For the Pt/C₂F₆-CNWs specimen, there is no difference in the wall density and height of the CNWs after the PCT. However, before the potential cycle test, Pt nanoparticles were supported densely over the entire surface of the CNWs; however, after the PCT, the Pt nanoparticles supported on the wall surface of the CNWs are clearly sparse. The average diameter of Pt nanoparticles was 2.3 nm before the potential cycle test. After 140,000 cycles of the potential cycle test, Pt aggregation to form Pt clusters with diameters of more than 10 nm is evident. These differences indicate that the Pt particles aggregate during the PCT, which lowers the performance of the Pt/C₂F₆-CNWs. Figure 3 shows Raman spectra of the Pt/C₂F₆-CNWs before and after degradation. The peak area ratios of the D-band peak (1350 cm⁻¹) to the G-band peak (1580 cm⁻¹) (I_D/I_G ratio) and the full width at half maxima (FWHM) of the G-band peak hardly changed after 60,000 cycles. These results suggest that the degradation of Pt/CNWs is solely determined by Pt aggregation and detachment because no structural corrosion of the carbon support was evident.

4. Conclusions

The C₂F₆-CNWs showed higher durability than that by the CH₄-CNWs. When the C₂F₆-CNWs electrodes with Pt nanoparticles were used, the ECSA decreased to 48% at 140,000 cycle, although that using the CH₄-CNWs ones decreased to 55% only at 30,000 cycles. Pt aggregation was observed after 140,000 cycles; however, although the Raman spectra showed a decrease in the intensity ratio of D-band peak to G-band one, there was no change in the FWHM values of these peaks before and after aggregation of the Pt nanoparticles. This indicates that no corrosion occurred on the graphite structure of the C₂F₆-CNWs. This means controls of crystallinity and surface modification of CNWs are essential

to realize the durability of catalytic electrodes.

References

- [1] S. Imai, H. Kondo, H. Cho, H. Kano, K. Ishikawa, M. Sekine, M. Hiramatsu, M. Ito, and M. Hori, *J. Phys. D* **50** (2017) 40LT01.
- [2] A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida, and A. Daimaru, *ECS Trans.* **41** (2011) 775-784.
- [3] K. Mase, H. Kondo, S. Kondo, M. Hori, M. Hiramatsu, and H. Kano, *Appl. Phys. Lett.* **98** (2011) 193108.

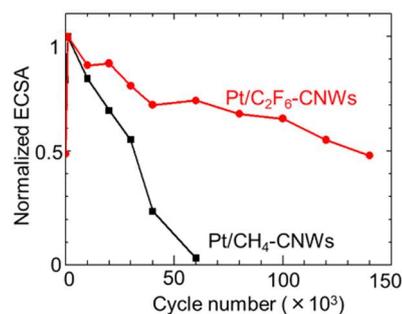


Fig. 1 Normalized ECSA for Pt/CH₄-CNWs (square) and Pt/C₂F₆-CNWs (circle) during potential cycle tests.

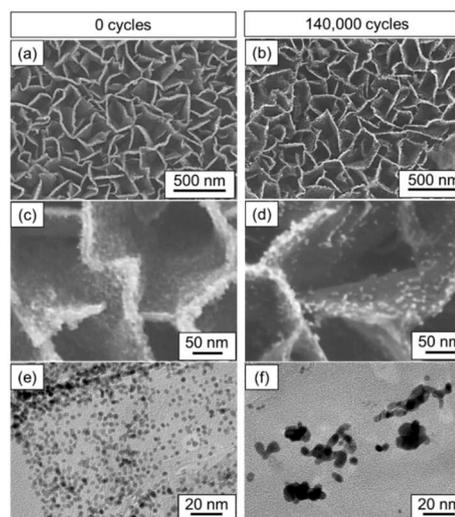


Fig. 2 SEM and TEM images of Pt/C₂F₆-CNWs; top view observed before (left; a, c, e) and after 140,000 cycles (right; b, d, f) of potential cycle testing. Top view observed before (a, c) and after (b, d) the potential cycle test, high magnification TEM image before (e) and after (f) the potential cycle tests.

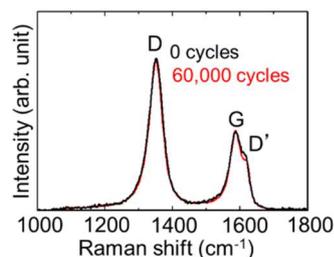


Fig. 3 Raman spectra of Pt/C₂F₆-CNWs before and after potential cycle testing.