

# Pd-Co/CNT Cathode Catalysts Covered with Silica Layers for Polymer Electrolyte Fuel Cells

Sakae Takenaka<sup>1,2\*</sup> and Masahiro Kishida<sup>1</sup>

<sup>1</sup>Kyushu University, Motoooka 744, Fukuoka 819-0395, Japan

<sup>2</sup>JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

## 1 Introduction

Polymer electrolyte fuel cells (PEFCs) are promising devices used for the direct conversion of hydrogen chemical energy into electricity by the oxidation of hydrogen with oxygen. Pt metal has been used as a catalytically active metal component for the hydrogen oxidation reaction (HOR) at the anode and for the oxygen reduction reaction (ORR) at the cathode in state-of-the-art PEFCs. Large amount of Pt is required at cathode due to the sluggish rate of the ORR on Pt compared with the HOR. Alternative metals to Pt should be used as active cathode catalysts because Pt metal is expensive. However, it is difficult to utilize other metals as cathode catalysts. The cathode catalysts in PEFCs should work under severe conditions, such as low pH, highly positive potential, high temperature and an oxygen atmosphere. Under these severe conditions, most metal species in the cathode catalysts inevitably dissolve, which causes a rapid deactivation of the catalysts at the cathode.

Recently, we developed Pd catalysts covered with silica layers [1]. Pd metal particles supported on carbon nanotubes (Pd/CNT) were covered with silica layers a few nanometers thick. The silica-coated Pd catalysts showed high activity for the ORR. In addition, the silica layers which wrapped around Pd metals prevented the diffusion of dissolved Pd species out of the catalysts. Thus, the silica-coated Pd catalysts showed high durability. However, the catalytic activity of Pd metal for ORR is inferior to that of Pt. Therefore, the catalytic activity of Pd metal should be improved.

In the present study, Pd catalysts were modified with different transition metal species to form their alloys. In addition, highly active Pd-based catalysts were covered with silica layers in order to enhance the durability.

## 2 Experiment

Multiwalled carbon nanotubes (CNTs) were used as supports for Pd metal and Pd-based alloys. Pd/CNT was prepared by impregnation of CNT into an aqueous solution of PdCl<sub>2</sub>, followed by reduction with H<sub>2</sub> at 623 K. For the preparation of CNT-supported Pd-M alloy catalysts (M = V, Fe, Co, Ni and Cu; denoted as Pd-M/CNT), the CNTs were impregnated into a mixed aqueous solution of PdCl<sub>2</sub> and NH<sub>4</sub>VO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub>, and then dried at 353 K. The samples thus obtained were reduced in hydrogen at 773 K for alloy formation.

The Pd/CNT and Pd-Co/CNT catalysts were covered with silica layers by the successive hydrolysis of 3-

aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS).

Cyclic voltammograms (CVs) and polarization curves for the ORR over the Pd-based catalysts were measured using a conventional three-electrode electrochemical cell with a Pt wire and reversible hydrogen electrode (RHE), which served as counter and reference electrodes, respectively. Accelerated durability tests for the Pd-based catalysts were performed by cycling the potential of the working electrode between 0.05 and 1.20 V in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub>. The CVs and polarization curves for the ORR on the catalysts were measured after the durability tests.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the Pd-based catalysts were measured at the Photon Factory of the High Energy Accelerator Research Organization (Proposal No. 2012G593 and 2013G529). Co K-edge XANES/EXAFS spectra for the catalysts were obtained using a Si(111) two-crystal monochromator with beam line BL12C and Pd K-edge spectra were obtained using a Si(311) two-crystal monochromator with beam line NW10A. These spectra were measured at room temperature. Analysis of the EXAFS data was performed using the EXAFS analysis program, REX (Rigaku Co.). Phase shift and amplitude functions derived from FEFF 8.0 were used for the curve-fitting analyses for the EXAFS.

## 3 Results and Discussion

Figure 1 shows XRD patterns of Pd-based/CNT catalysts. The molar ratio M/(M+Pd) in these Pd-based catalysts was adjusted to 0.5 with a fixed Pd loading of 10 wt%. Two diffraction lines appeared at around 2θ = 40 and 47° in the XRD pattern for Pd/CNT. These peaks are assignable to a face centered cubic (fcc) phase of Pd metal. The XRD patterns for all the Pd-M/CNT catalysts also showed a typical fcc pattern. However, the addition of M to Pd/CNT resulted in the shift of the position of diffraction peaks toward higher 2θ values. These results indicate the alloy formation between Pd and M with fcc phases.

Figure 2 shows CVs for Pd-based catalysts in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> electrolyte. Two peak couples were observed in the potential range from 0.05 to 0.3 V and from 0.5 to 1.2 V for all the Pd-based catalysts. The CV features for all the Pd-based catalysts were similar. The former peak couples were assignable to the adsorption and desorption of hydrogen on Pd, whereas the latter peaks were due to the oxidation and reduction of Pd. The

peak positions were slightly different according to the types of metal species (M) added to the Pd/CNT catalyst.

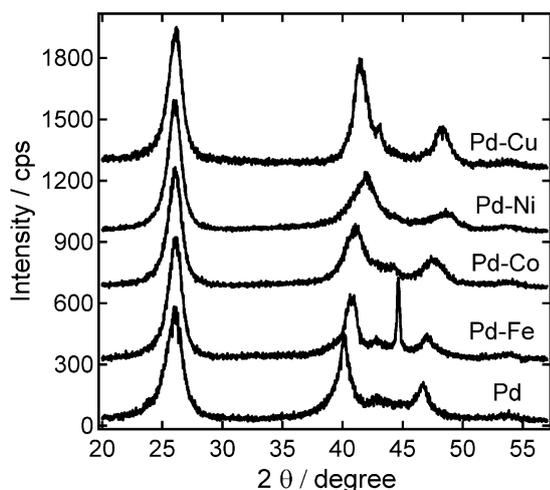


Figure 1 XRD patterns of Pd-based catalysts.

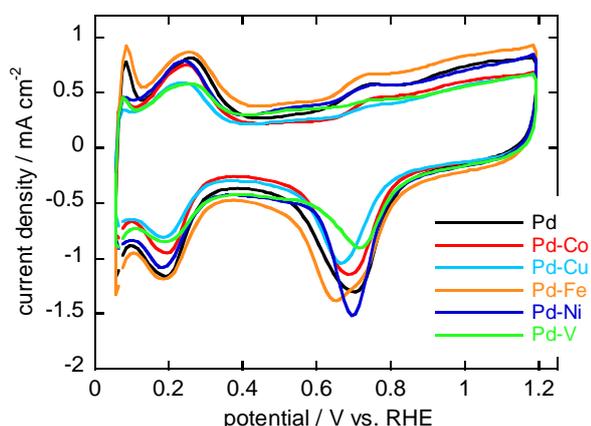


Figure 2 CVs for Pd-based catalysts in N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub>.

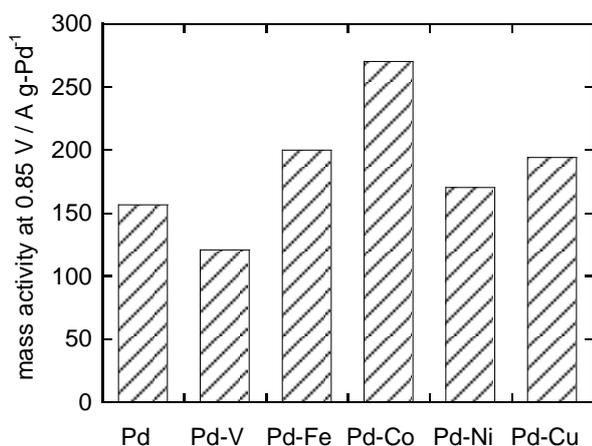


Figure 3 Pd mass-normalized activity of the Pd-based catalysts for the ORR.

The ORR activity of the Pd-based catalysts was evaluated using the rotating disk electrode method. The Pd mass-normalized activity of these Pd-based catalysts for the ORR is shown in Fig. 3. The Pd mass-normalized activity was evaluated from the ORR current at 0.85 V of the polarization curves. All the Pd-based catalysts had the catalytic activity for the ORR. The Pd mass-normalized activity of Pd/CNT was improved by modification with the transition metals. It should be noted that the catalytic activity of Pd-Co/CNT was approximately 2 times higher than that of Pd/CNT.

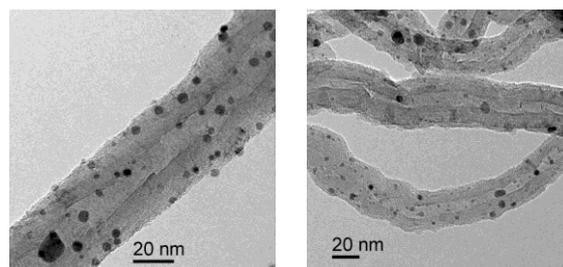


Figure 4 TEM images of Pd-Co/CNT (left) and SiO<sub>2</sub>/Pd-Co/CNT (right).

Pd-based alloys are easily dissolved under PEFC cathode conditions, as described below. Thus, the Pd-based catalysts were quickly deactivated during the durability test. The Pd-Co/CNT and Pd/CNT catalysts were covered with silica layers to improve the durability. Figure 4 shows TEM images of the Pd-Co/CNT and SiO<sub>2</sub>/Pd-Co/CNT catalysts. Many metal particles were observed on the surfaces of the CNT supports in the TEM images for both the Pd-Co catalyst. The metal particles and CNTs in SiO<sub>2</sub>/Pd-Co/CNT seemed to be covered with silica layers a few nanometers thick. The silica loading in SiO<sub>2</sub>/Pd-Co/CNT was evaluated by ICP-AES to be 24 wt%.

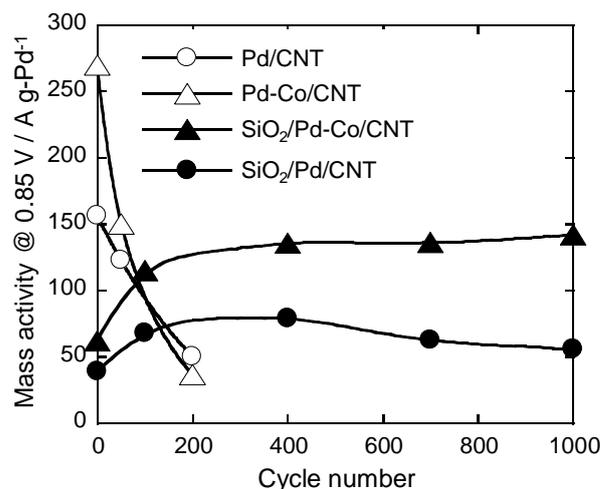


Figure 5 Change of Pd mass-normalized activity for ORR on the Pd-based catalysts during the durability test.

Figure 5 shows the change of the Pd mass-normalized activity for the ORR over the Pd-based catalysts during

the durability test. The activity of the fresh Pd-Co/CNT catalyst for the ORR was approximately 2 times higher than that of the fresh Pd/CNT catalyst. However, both catalysts without silica-coating were rapidly deactivated as the number of the potential cycling increased. The coverage of Pd/CNT and Pd-Co/CNT with silica layers improved their durability during the durability test. Both the silica-coated catalysts showed poor activity for the ORR at early period of the durability tests. However, the activity of these catalysts was gradually improved during the durability test. The catalytic activity of SiO<sub>2</sub>/Pd-Co/CNT for the ORR was significantly higher than that of SiO<sub>2</sub>/Pd/CNT over the durability test. The silica layers in the SiO<sub>2</sub>/Pd-Co/CNT prevent the diffusion of Pd and Co species dissolved from Pd-Co alloys out of the catalysts.

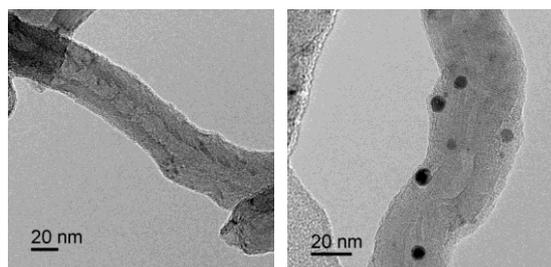


Figure 6 TEM images of Pd-Co/CNT (right) and SiO<sub>2</sub>/Pd-Co/CNT after the durability test.

Figure 6 shows TEM images of the Pd-Co/CNT and SiO<sub>2</sub>/Pd-Co/CNT catalysts after the durability tests. Any metal particles were not found in the TEM image of Pd-Co/CNT after the durability test. In contrast, many metal particles were observed in the TEM image of SiO<sub>2</sub>/Pd-Co/CNT after the durability test. The metal particle size in the used SiO<sub>2</sub>/Pd-Co/CNT was very similar to that of the fresh one. The silica layers which wrapped around Pd-Co particles prevent the diffusion of Pd and Co species that are dissolved from the Pd-Co alloys out from the silica layers.

Figure 7 shows Pd K-edge XANES and EXAFS spectra for Pd-Co/CNT, Pd foil and PdO. The feature of the XANES spectrum for Pd-Co/CNT is very similar to that for Pd foil. These results indicate that most of the Pd species in Pd-Co/CNT is present in the metallic state. A strong peak was observed at around 2.4 Å in the Fourier transform of the k<sup>3</sup>-weighted EXAFS (radial structural function; RSF) spectra for Pd-Co/CNT and Pd foil. The peak for Pd-Co/CNT was assignable to Pd-Pd and Pd-Co bonds since the XRD pattern of the catalysts showed the formation of Pd-Co alloys. Curve-fitting analysis for the peak at around 2.4 Å in the RSF of the Pd-Co/CNT was performed. The peak could be fitted by two types of shells, i.e., Pd-Pd and Pd-Co. The shorter Pd-Pd bond length (2.71 Å) for Pd-Co/CNT compared to that for pure fcc phase Pd metal (2.75 Å) and the presence of Pd-Co bonds (interatomic distance = 2.59 Å) indicate the formation of Pd-Co alloys in the Pd-Co/CNT catalysts. The coordination number of Pd-Pd and Pd-Co for Pd-Co/CNT was evaluated to be 5.8 and 2.3, respectively.

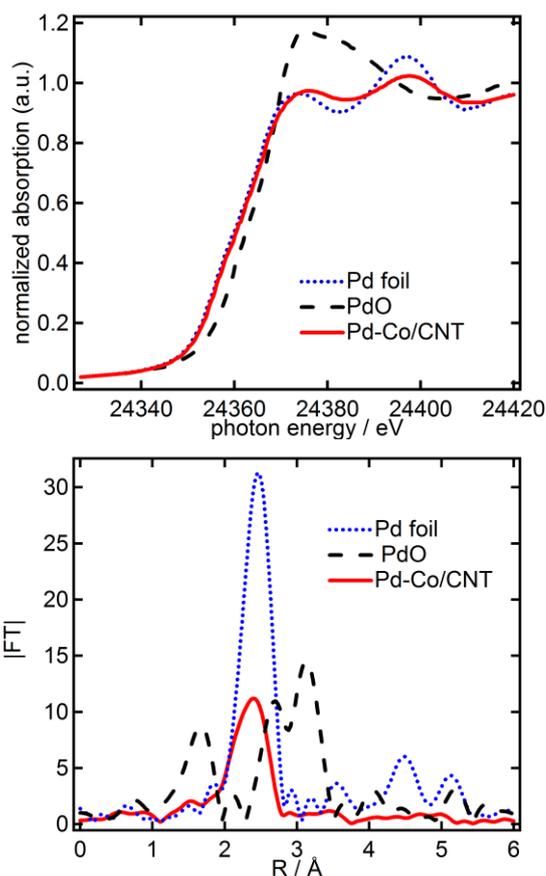


Figure 7 Pd K-edge XANES spectra (upper) and Fourier transforms of k<sup>3</sup>-weighted EXAFS (lower) for Pd-Co/CNT, Pd foil and PdO.

Figure 8 shows Co K-edge XANES and EXAFS spectra for Pd-Co/CNT, CoO and Co foil. The XANES spectrum for Pd-Co/CNT was consistent with that for the Co foil, rather than that for CoO, i.e., the spectrum for the Pd-Co/CNT had a pre-edge peak at around 7710 eV, similar to that for Co foil, and the absorption at around 7730 eV (white line) for Pd-Co/CNT was significantly lower than that for CoO. However, the intensity of the pre-edge peak for Pd-Co/CNT was lower than that for Co foil, and the white line for Pd-Co/CNT was stronger in intensity than that for Co foil. Thus, some of the Co species in Pd-Co/CNT catalysts were oxidized, although most of the Co species were present as the metallic form. In the RSF for Pd-Co/CNT, a strong peak was found at 2.1 Å in addition to a small peak at around 1.6 Å. The peaks in the R range from 1.0 to 2.8 Å for Pd-Co/CNT could be fitted by three shells of Co-O, Co-Co and Co-Pd. Therefore, the Co species in Pd-Co/CNT is present in the Pd-Co alloy and as oxidized Co species. It is likely that the oxidized Co species in Pd-Co/CNT would not be covered with silica layers during the successive hydrolysis of APTES and TEOS, whereas the Pd-Co alloy particles were covered with silica layers. During the coverage with silica layers, APTES and TEOS are successively hydrolyzed in the presence of Pd-Co/CNT. It is likely that APTES molecules do not adsorb on the

oxidized Co species in the Pd-Co/CNT. Therefore, the oxidized Co species are not covered with silica layers and the oxidized Co species in SiO<sub>2</sub>/Pd-Co/CNT are lost during the durability test, while the Co atoms in the Pd-Co alloy cannot be diffused out through the silica layers.

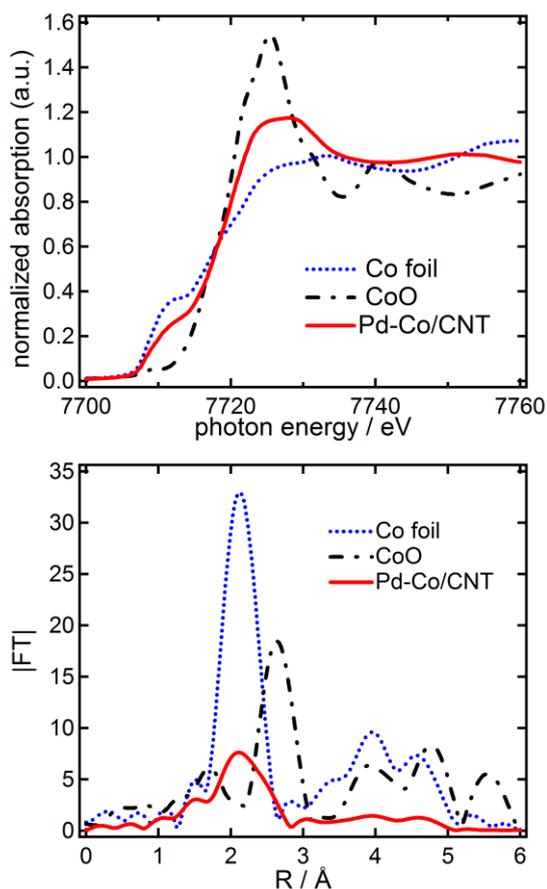


Figure 8 Co K-edge XANES spectra (upper) and Fourier transforms of  $k^3$ -weighted EXAFS (lower) for Pd-Co/CNT, Co foil and CoO.

#### References

- [1] S. Takenaka *et al.*, *Chem. Commun.*, **46**, 8950 (2010).

\*takenaka@chem-eng.kyushu-u.ac.jp