

Supporting Information for

**Highly durable Pd metal catalysts for the oxygen
reduction reaction in fuel cells; Coverage of Pd metal with
silica**

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METHODS

Preparation of catalysts. Multi-walled carbon nanotubes (CNTs, supplied by Wako Pure Chemical Industries) were immersed into a mixed aqueous solution of 8.0 M H₂SO₄ and 8.0 M HNO₃, and then mixed ultrasonically at 328 K for 2 h to oxidize the CNT surfaces. The CNTs thus obtained were thoroughly washed with distilled water several times and dried in air. The CNTs (0.60 g) were dispersed in 150 ml of an aqueous solution containing PdCl₂ (0.6 mmol) and dried. The samples thus obtained were treated in hydrogen at 623 K for 1 h to reduce the Pd precursors to Pd metal. The Pd loading in Pd/CNT was evaluated to be 5.0 wt% by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Pd/CNT was covered with silica layers by the successive hydrolysis of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES). Pd/CNT (0.10 g) was dispersed in 22 ml of water and the pH of this solution was adjusted to 10 by the addition of triethylamine. APTES (0.10 g) was added to the solution and the solution was stirred at 333 K for 0.5 h. TEOS (0.14 g) was then added to the solution and stirred at 333 K for 2 h. The samples thus obtained were dried in air at 353 K and reduced with hydrogen at 623 K for 3 h. The loading of silica in the silica-coated Pd/CNT (SiO₂/Pd/CNT) was determined to be 20 wt% by ICP-AES.

Structural analysis. TEM images of the samples were recorded on a JEOL JEM-3000F instrument. Specimens were prepared by ultrasonically suspending the samples in 2-propanol. A drop of the suspension was deposited on a carbon-enhanced copper grid and dried in air.

Measurement of CVs. Cyclic voltammograms (CVs) were obtained using a three-compartment electrochemical cell with a Pt mesh and a saturated Ag/AgCl electrode serving as counter and reference electrodes, respectively. The saturated Ag/AgCl electrode was separated from the working electrode compartment by a closed electrolyte bridge. All potentials are given relative to the reversible hydrogen electrode (RHE). A glassy carbon disk electrode (5 mm diameter) was used as a substrate for the catalysts and polished to a mirror finish. Catalyst ink was prepared by ultrasonically blending 10 mg of the catalysts (Pd/CNT or SiO₂/Pd/CNT) and 5 ml of methanol. A 20 μ l aliquot of this ink was deposited on a glassy carbon disk and dried at 333 K. Twenty microlitres of a 1 wt% Nafion solution diluted with methanol was dropped onto the catalysts to ensure that the catalysts attach to the disk. Nafion[®] ionomer (5% Nafion[®] suspension in alcohol, supplied from Aldrich) was diluted with methanol to obtain a 1 wt% Nafion solution before dropping onto the electrode. The working electrode was

immersed in a N₂-purged 0.1 M HClO₄ electrolyte solution at 303 K. A solution containing 0.1 M HClO₄ electrolyte (supplied by Wako Pure Chemical Industries, super special grade) was prepared using deionized water (Millipore, 18 MΩ cm). Before the measurement of CVs for the fresh Pd catalysts, the potential of the catalysts was changed between 0.05 and 1.20 V (ca. 10 cycles). CVs of the catalysts were measured at a scan rate of 50 mV s⁻¹ between 0.05 and 1.20 V. Accelerated durability tests for the Pd catalysts were carried out by cycling the potential of the working electrode by a triangular wave at a scan rate of 50 mV s⁻¹ between 0.05 V and 1.20 V in N₂-purged 0.1 M HClO₄ at 303 K.

Catalytic evaluation using a rotating ring-disk electrode. Electrochemical measurements using a rotating ring-disk electrode were carried out using a three-electrode electrochemical cell. A glassy carbon rod (diameter = 6 mm) was used as a counter electrode and Ag/AgCl was used as a reference electrode. Catalyst ink was prepared by ultrasonically Pd/CNT or SiO₂/Pd/CNT and methanol. The ring-disk electrode was composed of a Pt-ring on a 6-mm diameter glassy carbon core embedded in a Teflon cylinder. The ink was deposited on a glassy carbon disk so that the amount of Pd on the disk was 1.5 μg for all the Pd catalysts. After drying the catalysts at room temperature, 20 μl of a 0.6 wt% Nafion solution diluted with methanol was dropped onto the catalysts to ensure that the catalysts attach to the disk. The catalysts were immersed in 0.1 M HClO₄ at room temperature. The polarization curves for the oxygen reduction reaction (ORR) on Pd/CNT and SiO₂/Pd/CNT were measured in O₂-saturated 0.1 M HClO₄ at room temperature by changing the potential of the working electrode from 0.1 to 1.1 V at a scan rate of 10 mV s⁻¹ with an electrode rotation rate of 1600 rpm. The Pt-ring electrode was polarized at 1.20 V for the oxidation of hydroperoxide intermediates. Accelerated durability tests for the catalysts were also performed using the rotating ring-disk electrode. The potential of the working electrode was cycled between 0.05 and 1.20 V in N₂-purged 0.1 M HClO₄ and then the polarization curve for the ORR on the catalysts was measured in an O₂-saturated 0.1 M HClO₄ electrolyte.

CO stripping. CO stripping experiments were conducted under the same conditions as the measurement of the CVs described earlier. CO stripping from the SiO₂/Pd/CNT catalysts that were attached to a glassy carbon rod was measured in a N₂-purged 0.1 M HClO₄ solution at 303 K by changing the potential from 0.4 to 1.20 V at a scan rate of 50 mV s⁻¹ after the SiO₂/Pd/CNT was immersed in CO-saturated electrolyte and held at 0.4 V for 30 min.

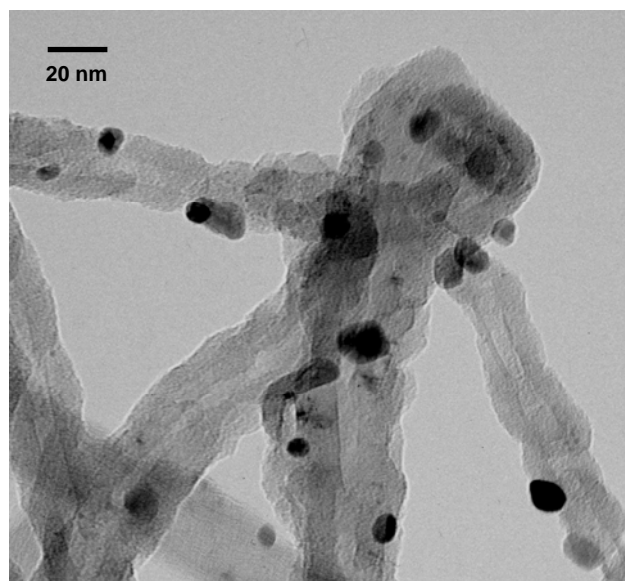


Figure S1. TEM image of silica-coated CNTs after the deposition of Pd.

Pd metal particles were electrochemically deposited on silica-coated CNTs. Pd metal particles were observed on the surface of the silica-coated CNTs indicating that all the CNT surfaces were not covered with the silica insulator.

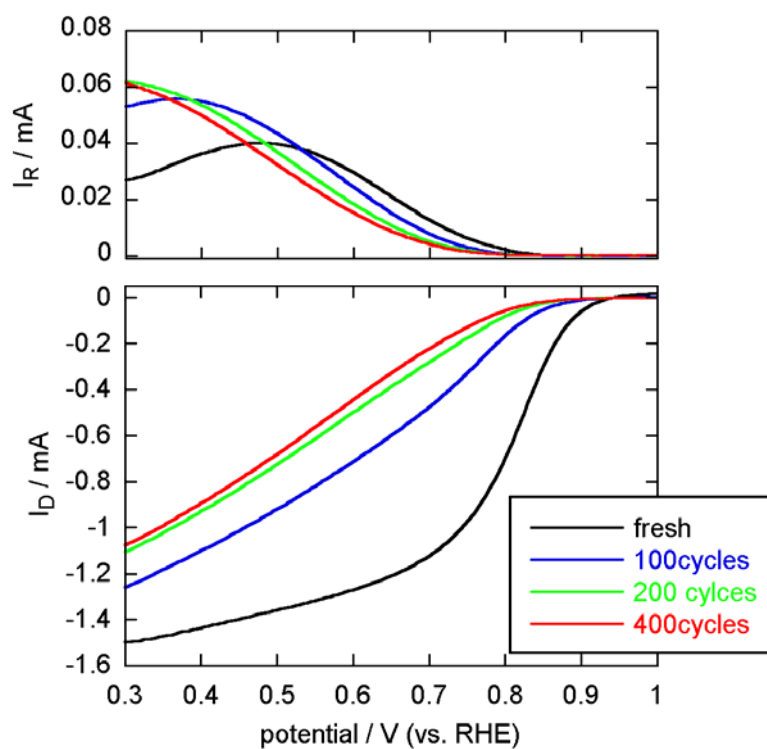


Figure S2. Polarization curves obtained with a rotating ring-disk electrode for the oxygen reduction reaction on the Pd/CNT catalyst in O₂-saturated 0.1 M HClO₄ at room temperature during potential cycling experiments. Sweep rate = 10 mVs⁻¹, rotation rate of the electrode = 1600 rpm.

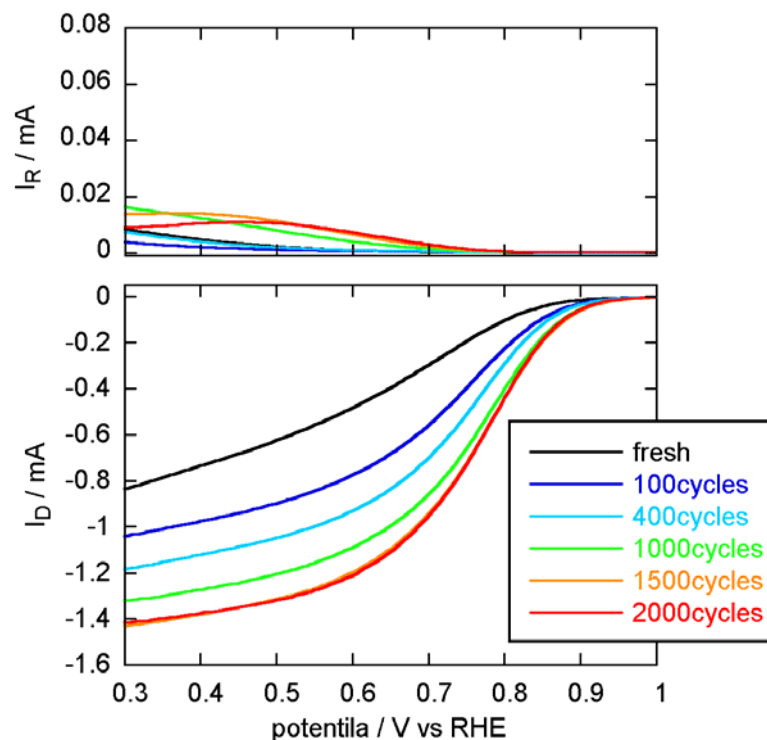


Figure S3. Polarization curves obtained with a rotating ring-disk electrode for the oxygen reduction reaction on the SiO₂/Pd/CNT catalyst in O₂-saturated 0.1 M HClO₄ at room temperature during potential cycling experiments. Sweep rate = 10 mVs⁻¹, rotation rate of the electrode = 1600 rpm.

The H₂O₂ yield at 0.6 V was estimated to be 3% in the oxygen reduction reaction on SiO₂/Pd/CNT after 1500 cycles, while the yield at 0.6 V for the fresh Pd/CNT was estimated to be 12%. (correction efficiency of the ring electrode was 0.38)

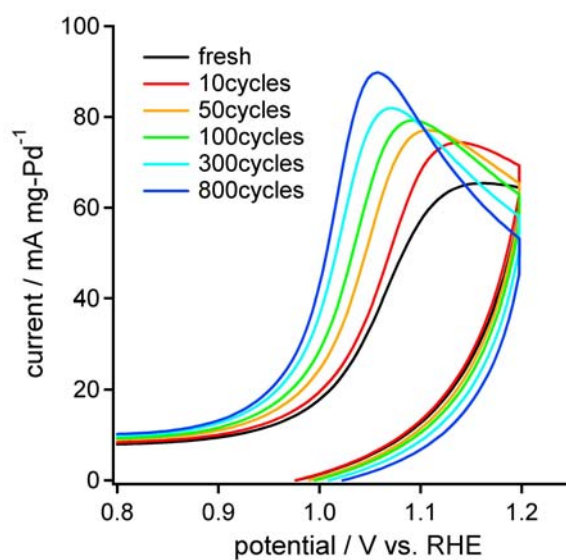


Figure S4. CO stripping voltammograms of SiO₂/Pd/CNT before and after potential cycling between 0.05 and 1.20 V (vs. RHE). CO stripping voltammograms on the catalysts were measured in N₂-purged 0.1 M HClO₄ at 303 K. CO was adsorbed onto SiO₂/Pd/CNT at 0.4 V. After CO was thoroughly purged with N₂ gas the catalyst potential changed from 0.4 V to 1.20 V.