Electronic Supplementary Information

Anomalously increased oxygen reduction reaction activity with accelerated durability test cycles for platinum on thiolated carbon nanotubes

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Experimental Section

1) Surface thiolation of MWNTs

MWNTs prepared by chemical vapor deposition (CVD) were acquired from Hanwha Nanotech. The MWNTs were heated at 400 °C in static air for 4 h. They were then mixed with HCl, and the mixture was heated at 70 °C for 12 h. To get purified MWNTs (p-MWNT), the mixture was filtered, washed with deionized water, and dried several times. Surface-thiolated MWNTs were prepared by amidation. p-MWNTs were mixed with H₂SO₄/HNO₃ mixture (3:1 volumetric ratio), and heated at 70 °C for different durations (5, 10, 30, and 60 min) under stirring. The mixture was then washed several times with deionized water, filtered, and air-dried. This process gave carboxylated MWNTs (c-MWNT). For chlorination, c-MWNTs were mixed with SOCl₂ in a two-neck flask with one neck plugged by a septum. The mixture was refluxed for 12 h at 70 °C. The excess SOCl₂ was removed by vacuum evaporation, and anhydrous toluene and H₂CH₂CH₂SH (cysteamine) were injected using a syringe through the septum during stirring to prevent the entry of air in the flask. The reaction was performed at 70 °C for 24 h. After the filtration, thiolated MWNTs (S-MWNTs) were first washed with ethanol and then several times with deionized water and air-dried. Four different S-MWNTs were prepared with different acid-treatment times (5, 10, 30, and 60 min, respectively).

2) Pt catalyst preparation

Impregnation method accompanied by sodium borohydride reduction was used to deposit Pt nanoparticles on each sample of S-MWNTs (5, 10, 30, 60 min). First, 50 mg of S-MWNTs (5, 10, 30, 60 min) from the previous procedure was sonicated with a mixture of 6.25 mL of H₂PtCl₆·6H₂O (2 mg/mL) and 100 mL of deionized water in a beaker. To attach Pt particles, as shown in Scheme 1, NaBH₄ (reducing agent) was introduced into the solution after the sonication. After filtration and evaporation, the solution was oven-dried for 1 d. Finally, 20 wt% Pt-deposited S-MWNTs (Pt-S-MWNT) was obtained. For comparing the performance and properties, Pt/C (20 wt% Pt/C, Premetek) was purchased.

3) Characterization of Pt/C and Pt-s-MWNTs (5, 10, 30, 60 min)

The morphology and polydispersity of the catalysts were determined from the samples prepared on a carboncoated TEM grid by dropping the dispersed particles in ethanol. Pt particle images were obtained by transmission electron microscopy (TEM; JEM-2011, JEOL) with an acceleration voltage of 200 keV. To determine the exact amount of the deposited Pt, inductively coupled plasma atomic emission spectrophotometer (ICP-AES; Ultima 2C HR, HORIBA) was used. An angle-resolved X-ray photoelectron spectrometer (AR-XPS; Theta Probe, Thermo Electron Corporation) was used to investigate the interaction between the Pt nanoparticles and sulfur on the thiol group, and the electronic states of Pt and sulfur.

An Al K α X-ray source (1486.7 keV) was used, and the peaks were shifted with C 1s (284.6 eV) to compensate for charging. The X-ray diffraction was measured with a Philips diffractometer (X'pert PRO MRD, Cu K α) at room temperature.

An in situ XANES measurement was carried out at the beamline of 7D XAFS of the Pohang Accelerator Laboratory (PAL), South Korea, using the facilities and procedure described elsewhere¹⁻³. The Pt L3 edge (11564 eV) XANES spectra were recorded on the BL7D beam line of the Pohang Light Source (PLS), South Korea, with a ring current of 120–170 mA at 2.5 GeV. A Si(111) double-crystal monochromator was employed to monochromatize the X-ray photon energy. The data were collected in the transmission mode with He (50 %) and N_2 (50 %) gas-filled ionization chambers as detectors. Energy calibration was completed using a standard Pt foil. Every experiment on Pt catalysts was conducted on a homemade cell fabricated with an aluminum holder for XAS powder experiments. All spectra were recorded at room temperature. The spectra were processed by using IFEFFIT⁴⁻⁶ program (version 1.2.11c, IFEFFIT Copyright 2008, Matthew Newville, University of Chicago, http://cars9.uchicago.edu/ifeefit/) with background subtraction (AUTOBK)⁷ and normalization. Nitrogensaturated 0.1 M HClO₄ electrolyte was used in the cell and Pt L3 edge was collected in the transmission mode with potential applied from a potentiostat (VSP, Bio-Logic).

4) Electrocatalytic activity and durability test

To evaluate the electrocatalytic activity, a rotating disc electrode (RDE) holder (Modulated speed controller, Pine Research Instrumentation) and a potentiostat (VSP, Bio-Logic) were used. Glassy carbon disc electrode (0.19625 cm²), Pt wire, and Ag/AgCl (3.5 M KCl) were employed as working electrode, counter electrode, and reference electrode, respectively. For potential calibration, the potential of Pt polycrystalline electrode (Fine) as a working electrode was measured in the presence of 0.1 M HClO₄ electrolyte. The acquired potential was referenced to a reversible hydrogen electrode (RHE). To load the electrocatalysts on the RDE, isopropanol (10 mL) and Nafion® solutions (0.2 mL of 5 wt% solution) were mixed in deionized water (39.8 mL). Then, 2 mL of the previously made mixture and 2.5 mg of electrocatalyst were added into a glass container (4 mL) to make the catalyst ink, and the mixture was sonicated. This catalyst ink (20 μ L) was loaded on a glassy carbon electrode and then air-dried.

Cyclic voltammogram (CV) readings were recorded from 0.05 to 1.2 V with a scan rate of 20 mV/s in 0.1 M $HClO_4$ electrolyte saturated with N₂. The oxygen reduction reaction (ORR) was carried out from 0.05 to 1.05 V with different rotating speeds (100, 400, 900, 1600, and 2500 rpm) and a scan rate of 5 mV/s under O₂ bubbling after purging the 0.1 M $HClO_4$ solution for 30 min with O₂. After CV and ORR, an accelerated durability test (ADT) was conducted at the surface oxidation/reduction region between 0.395 and 0.895 V (vs. Ag/AgCl) with a scan rate of 50 mV/S at 100 rpm. After 4000 cycles, CV and ORR were measured; another ADT of 4000 cycles was also measured. Finally, CV and ORR were measured again. From these measurements, the durabilities of the Pt-S-MWNT and purchased Pt/C were evaluated by comparing the electrochemical surface areas (ECSA) and ORR activities.

Results and Discussion 1) TEM



Fig. S1 TEM images of Pt catalysts. (a) Pt/C (b) Pt-S-MWNT (5 min), (c) Pt-S-MWNT (10 min), (d) Pt-S-MWNT (30 min), (e) Pt-S-MWNT (60 min).





Fig. S2 XRD patterns of Pt-S-MWNT (5, 10, 30, and 60 min).

3) Electrochemical test



Fig. S3 ORR polarization curves of Pt catalyst samples before and after durability tests measured in O_2 -saturated 0.1 M HClO₄ at room temperature. Rotation rate: 1600 rpm; sweep rate: 5 mV/s; (a) Pt-S-MWNT (5 min); (b) Pt-S-MWNT (10 min); (c) Pt-S-MWNT (30 min).



Fig. S4. Voltammetry curves of Pt catalyst samples before and after durability tests measured in N_2 -saturated 0.1 M HClO₄ at room temperature. (a) Pt-S-MWNT (5 min), (b) Pt-S-MWNT (10 min), (c) Pt-S-MWNT (30 min).

RDE method was used to evaluate the activity and durability of the synthesized Pt-S-MWNTs (5, 10, 30, and 60 min). All CV measurements were performed using nitrogen-saturated 0.1 M HClO₄ electrolyte at room temperature. The results are shown in Fig. S4. To monitor the changes in the activity, all results were tabulated in Table S1 before ADT, after 4000 cycles, and after 8000 cycles for different electrocatalysts. To obtain the ECSA, Eq. (1) was used; the values are also included in Table S1.

$$ECSA = \frac{Q_H}{[Pt] \times 0.21}$$
(1)

where [Pt] is the platinum loading amount (mg cm⁻²) on the electrode, Q_H is the charge (mC cm⁻²) for hydrogen desorption, and 0.21 is the charge to oxidize the H₂ monolayer adsorbed on Pt.

Table S1. ECSA of Pt ca	talysts						
C		[Pt]	Q'	Q"	Q _H	Q _H /[Pt]	ECSA
Sampre		(µg cm ⁻²)	$(mC cm^{-2})$	$(mC \ cm^{-2})$	$(mC cm^{-2})$	(mC mg ⁻¹)	$(m^2 g^{-1})$
	initial		3.545	2.904	3.249	127.553	60.739
Pt/C	4000 cycles	25.477	2.595	1.861	2.228	87.486	41.660
	8000 cycles		2.223	1.565	1.894	74.356	35.408
	initial		4.325	2.672	3.499	137.353	65.406
Pt-S-MWNT (5 min)	4000 cycles	25.477	3.493	2.383	2.938	115.337	54.922
	8000 cycles		3.067	2.021	2.544	99.871	47.558
	initial		3.262	1.551	2.406	94.476	44.988
Pt-S-MWNT (10 min)	4000 cycles	25.477	2.615	1.434	2.024	79.479	37.847
	8000 cycles		2.283	1.217	1.750	68.694	32.711
	initial		2.012	0.933	1.473	57.817	27.532
Pt-S-MWNT (30 min)	4000 cycles	25.477	2.018	0.751	1.384	54.356	25.884
	8000 cycles		1.686	0.880	1.283	50.397	23.999
	initial		4.040	2.364	3.202	83.791	40.006
Pt-S-MWNT (60 min)	4000 cycles	25.477	2.993	1.946	2.469	64.626	29.027
	8000 cycles		2.180	1.182	1.681	44.002	20.880

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Fig. S5 Cyclic Voltammetry curves of Pt-S-MWNT(60 min) before and after durability tests measured in N_2 -saturated 0.1 M HClO₄ at room temperature.



Fig. S6 ORR polarization curves of Pt-S-MWNT(60 min) before and after durability tests measured in O_2 -saturated 0.1 M HClO₄ at room temperature. Rotation rate: 1600 rpm; sweep rate: 5 mV/s

Pt-S-MWNT(60 min)	$ECSA(m^2 g^{-1})$	Error (%)	ORR onset Potential (V)	Error (%)
Initial	40.006	0.265	0.962	0.207
After 2000 cycles	34.439	6.043	0.966	0.283
After 4000 cycles	29.027	6.012	0.965	0.377
After 6000 cycles	22.499	3.986	0.964	0.519
After 8000 cycles	20.880	0.349	0.961	0.433
After 10000 cycles	18.087	3.411	0.960	0.610
After 12000 cycles	17.002	6.693	0.958	0.147

Table S2 ECSA and ORR activity of Pt-S-MWNT(60 min)

4) TEM (after ADT of 8000 cycles)



Fig. S7 TEM image of Pt catalysts after 8000 cycles. (a) Pt/C, (b) Pt-S-MWNT (5 min), (c) Pt-S-MWNT (10 min), (d) Pt-S-MWNT (30 min), (e) Pt-S-MWNT (60 min).





Fig. S8 Comparison of XPS Pt 4f peak of Pt-S-MWNTs samples.

Sample	Assigned chemical state (Pt 4f _{7/2})	Binding Energy (eV)	Relative intensity (%)
Pt-S-MWNT (5min)	Pt (0)	71.0	10.6
	Pt (II)	71.8	17.0
	Pt (IV)	72.7	13.5
Pt-S-MWNT (10min)	Pt (0)	71.0	10.2
	Pt (II)	71.8	12.0
	Pt (IV)	72.7	21.4
Pt-S-MWNT (30min)	Pt (0)	71.0	0.2
	Pt (II)	71.8	19.7
	Pt (IV)	72.7	20.6
Pt-S-MWNT (60min)	Pt (0)	71.0	0.3
	Pt (II)	71.8	12.2
	Pt (IV)	72.7	36.7

Table S3 Distribution of Pt species and relative intensities in Pt-S-MWNT samples.



Fig. S9 Comparison of XPS S2*p* peak of S-MWNT and Pt-S-MWNT. Acid treatment times: (a) 5 min, (b) 10 min, (c) 30 min, (d) 60 min.





Fig. S10 In situ XANES spectra obtained for Pt catalysts at 0.4 and 1.0 V in 0.1 M HClO₄. (a) Pt-S-MWNT (5 min), (b) Pt-S-MWNT (10 min), and (c) Pt-S-MWNT (30 min).

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