Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

Performance and Durability of Pt/C Cathode Catalysts with Various Kinds of Carbons for Polymer Electrolyte Fuel Cells Characterized by Electrochemical and *In-situ* XAFS Techniques

Kensaku Nagasawa,[a] Shinobu Takao,[a] Kotaro Higashi,[a] Shin-ichi Nagamatsu,[a] Gabor Samjeské,[a] Yoshiaki Imaizumi,[a] Oki Sekizawa,[a] Takashi Yamamoto,[b] Tomoya Uruga[ac] and Yasuhiro Iwasawa[*ad]

[a] *Innovation Research Center for Fuel Cells, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan*
[b] *Department of Mathematical and Sciences, The University of Tokushima, Minamijosanjima-cho, Tokushima 770-8502, Japan*
[c] *JASRI/SPring-8, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*
[d] *Department of Engineering Science, Graduate School of Information Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan*

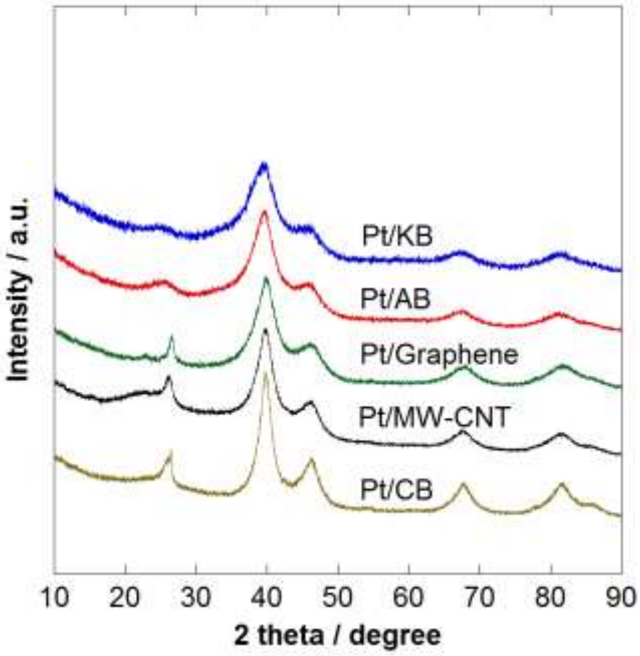

Fig. S1 XRD patterns for as-prepared Pt/KB, Pt/AB, Pt/Graphene, Pt/MW-CNT and Pt/CB catalysts.

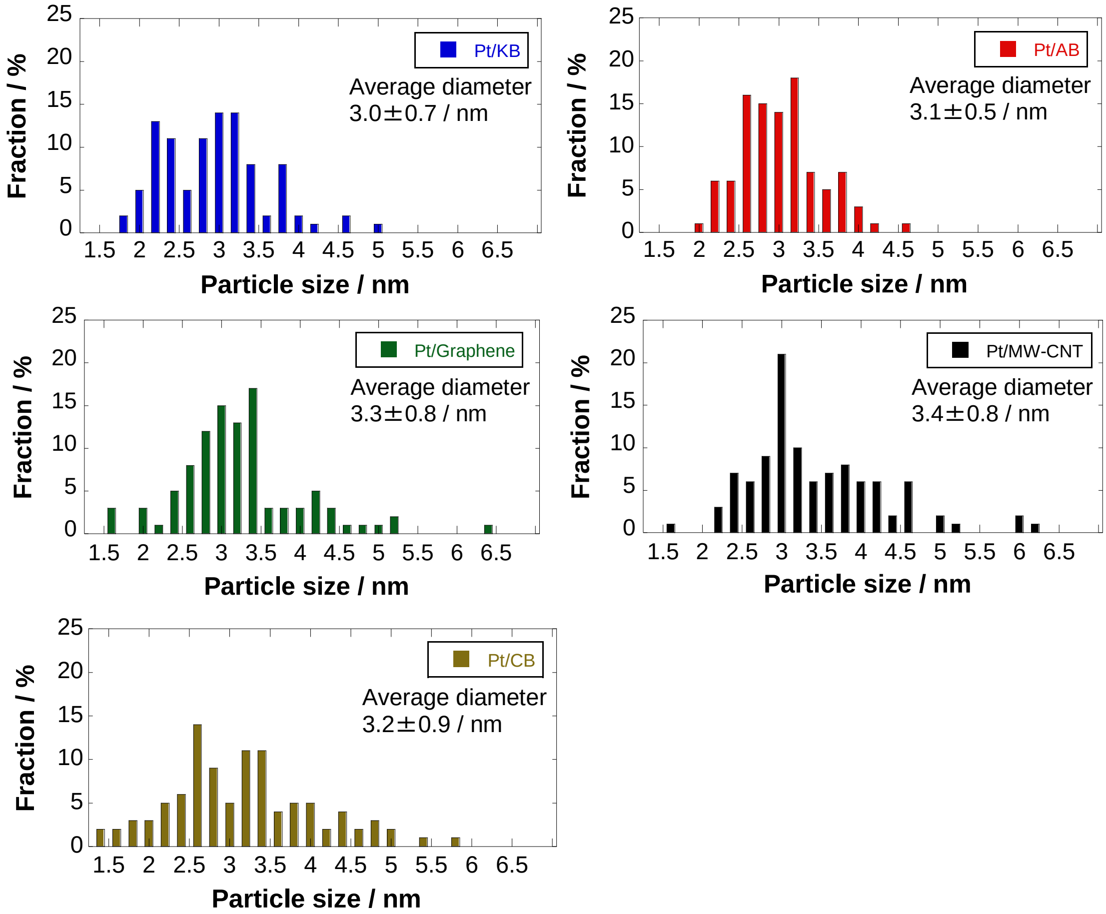

Fig. S2 Histrograms of Pt particle sizes and average particle diameters for the five as-prepared Pt/C catalysts estimated from TEM images.

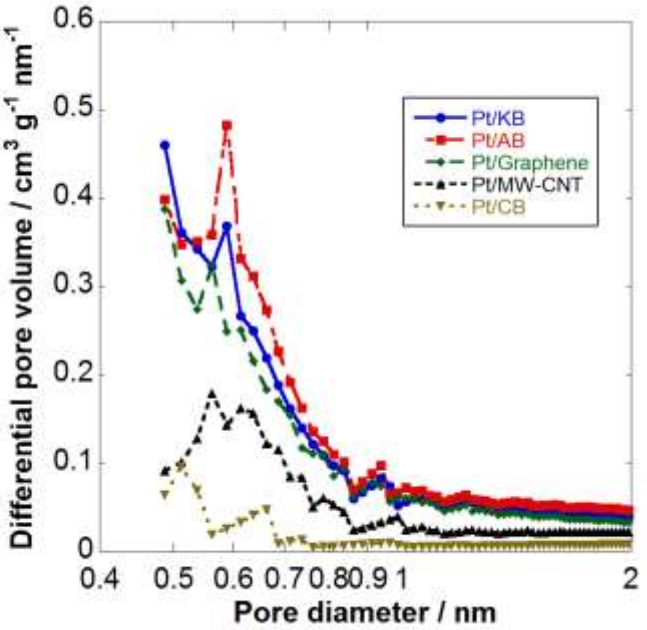

Fig. S3 Pore volume distributions of micropore with HK method for Pt/KB, Pt/AB, Pt/Graphene, Pt/MW-CNT and Pt/CB. The pore size distributions in the micropore region with diameters < 2 nm for Pt/KB, Pt/AB, Pt/Graphene, Pt/MW-CNT and Pt/CB were determined by Horvath Kawazoe (HK) method.

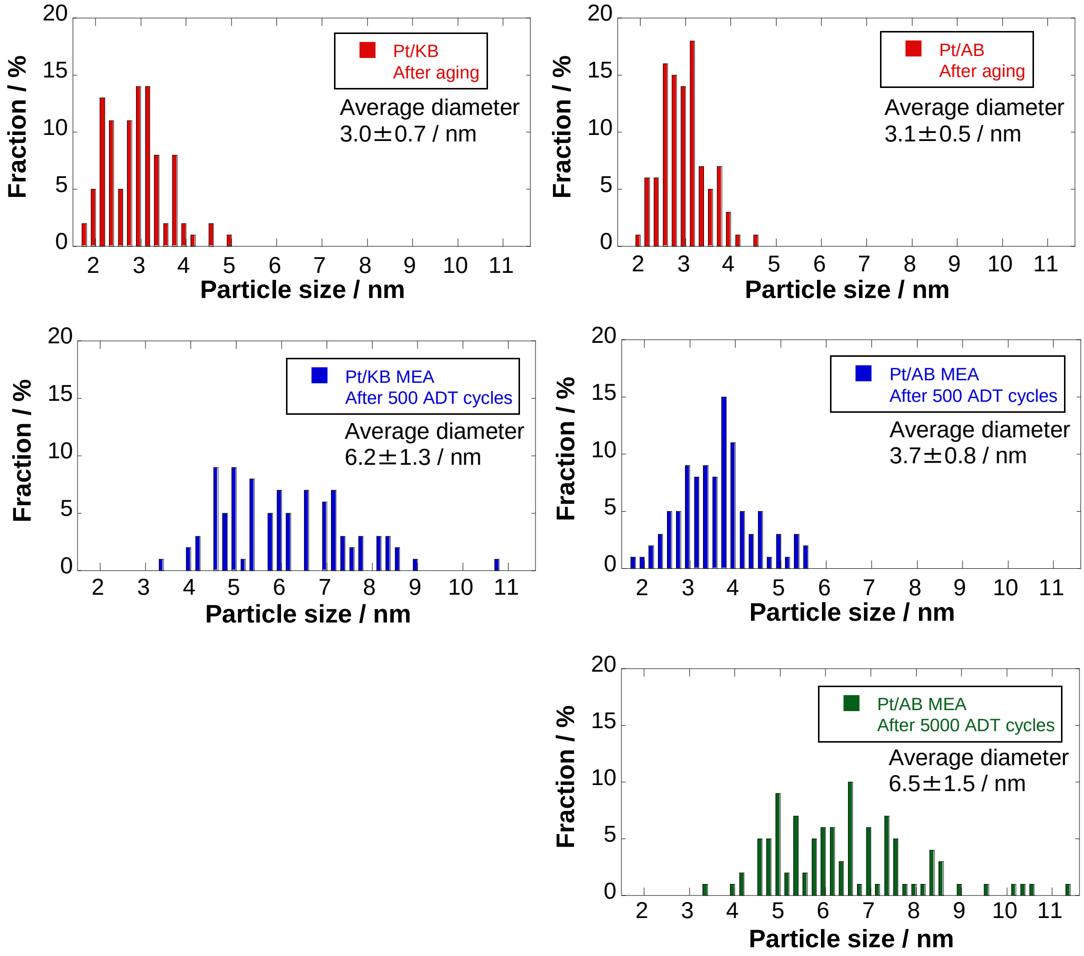

Fig. S4 Size distributions and average diameters of Pt nanoparticles in MEA Pt/KB and Pt/AB catalysts after 500 and 5000 ADT cycles estimated from TEM.

The average diameter of Pt nanoparticles in the MEA Pt/KB increased from 3.0 ±0.7 nm to 6.2 ±1.3 nm by the 500 ADT cycles similar to the previous report.[1] On the other hand, Pt nanoparticles in the MEA Pt/AB did not grow significantly by the 500 ADT cycles (3.1 ±0.5 nm to 3.7 ±0.8 nm). Their average diameter increased to 6.5 ±1.5 nm after 5000 ADT cycles. These results on degradation of carbon supports and growth of Pt nanoparticles explain the variation of the maximum power density with increasing ADT cycles in Fig. 7.

1 H. Schulenburg, B. Schwanitz, N. Linse, G. G. Scherer and A. Wokaun, *J. Phys. Chem.* C, 2011, **115**, 14236.

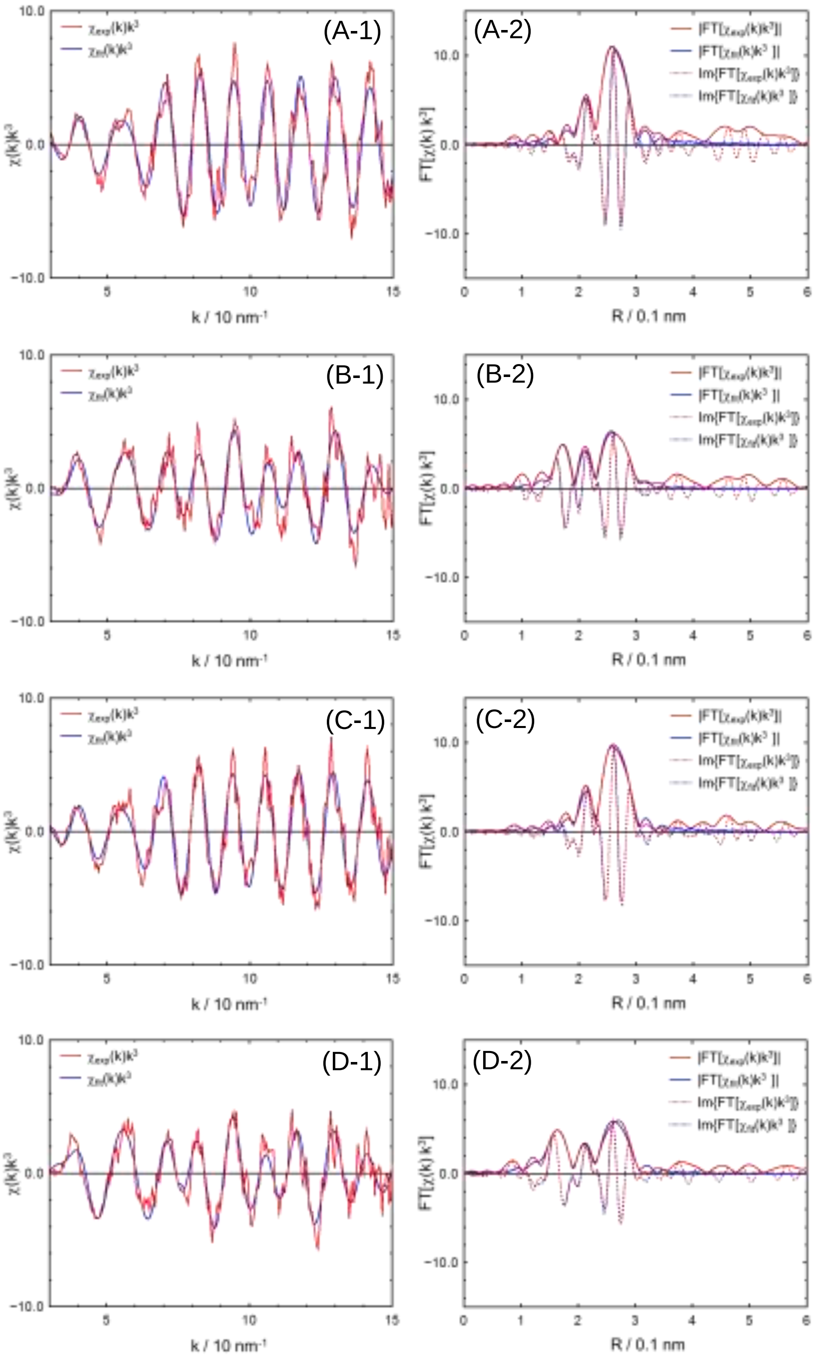

Fig. S5 EXAFS oscillations and associated Fourier transforms for the MEA Pt/KB aging catalyst at 0.4 V_{RHE} (A-1 and A-2) and 1.2 V_{RHE} (B-1 and B-2), respectively and for the MEA Pt/AB aging catalyst at 1.0 V_{RHE} (C-1 and C-2) and 1.4 V_{RHE} (D-1 and D-2), respectively in the increasing potential operation. Red lines: observed; Blue lines: fitted. Anode: H_2; Cathode: Air.

The curve-fittings for the EXAFS data were performed with both oscillations and Fourier transforms. The Fourier transform peak intensity around R = 0.2–0.3 nm due to Pt-Pt contribution reduced by increasing voltages from 0.4 V_{RHE} to 1.4 V_{RHE}, while the Fourier transform peak around R = 0.15 nm due to Pt-O contribution evolved at the higher voltages.

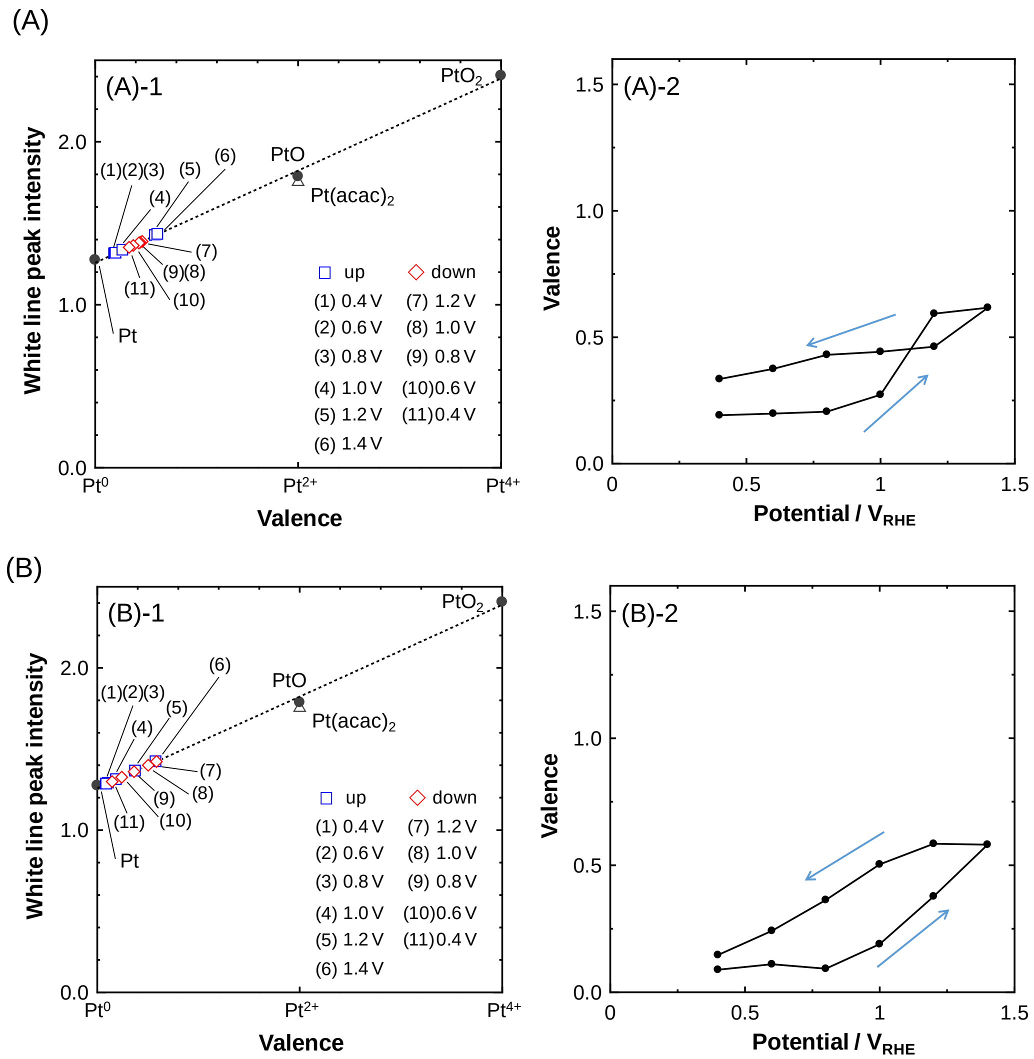

Fig. S6 The linear relationship of Pt valences for Pt foil, PtO, $Pt(acac)_2$ and PtO_2 with their white line peak intensities (A-1 and B-1), and plots of the white line peak intensities at each poteneial vs RHE for the Pt/KB (A-1) and Pt/AB (B-1) after ADT-triangle 1000 cycles and 5000 cycles, respectively on the linear relationship line, and the variation of the estimated Pt valences with the increasing and decreasing operating potentials (A-2 and B-2). The white line peak intensities are taken as the values when the edge height was normalized to the unity.

Table S1 Curve-fitting results of the Pt L_{III}-edge EXAFS data for Pt/KB after the aging treatment

No.	Potential / V	Scat.At.	CN	(e.s.d.)	R / 0.1 nm	(e.s.d.)	σ^2 / 10^{-5} nm^2	(e.s.d.)	ΔE_0 / eV	(e.s.d.)	R-factor / %
1	0.4	Pt	9.1	0.7	2.74	0.00	7.2	0.3	3.4	0.9	0.78
2	0.6	Pt	9.6	1.2	2.74	0.01	7.5	0.5	3.8	1.5	2.91
3	0.8	Pt	9.3	1.1	2.74	0.01	7.3	0.5	2.8	1.3	1.85
4	1.0	Pt	7.8	0.5	2.74	0.00	7.3	0.3	3.8	0.9	0.44
		O	0.2	0.1	2.02	0.02	-3.4	1.5	7.7	8.1	
5	1.2	Pt	6.1	0.6	2.74	0.00	7.8	0.5	4.9	1.2	0.82
		O	1.0	0.2	2.03	0.01	-0.2	0.8	9.4	2.2	
6	1.4	Pt	5.7	1.1	2.75	0.01	8.7	1.0	6.2	2.5	2.42
		O	1.4	0.3	2.02	0.01	0.1	0.9	8.8	3.0	
7	1.2	Pt	5.0	0.6	2.76	0.01	8.1	2.3	8.7	2.4	4.94
		O	1.7	0.4	2.03	0.01	0.8	1.0	8.7	2.4	
8	1.0	Pt	4.8	0.8	2.76	0.01	7.7	1.9	7.6	2.5	4.77
		O	1.7	0.5	2.03	0.01	1.0	1.0	7.6	2.5	
9	0.8	Pt	5.4	0.4	2.75	0.01	6.8	1.8	7.2	1.5	2.58
		O	1.2	0.3	2.03	0.01	0.3	1.2	7.2	1.5	
10	0.6	Pt	5.9	0.8	2.74	0.00	6.4	0.6	4.4	1.4	1.11
		O	0.7	0.2	2.04	0.01	-1.3	1.1	11.0	4.2	
11	0.4	Pt	7.7	0.8	2.75	0.00	7.1	0.5	6.3	1.2	0.82
		O	0.5	0.2	2.03	0.01	-1.4	1.5	2.7	6.0	

k-range = 30 - 150 nm^{-1}, k-weight = 3, R-range = 0.14 - 0.31 nm
Coordination number (CN), Debye-Waller factor (σ^2), e.s.d. = Estimated standard deviation

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Table S2 Curve-fitting results of the Pt L_{III}-edge EXAFS data for Pt/AB after the aging treatment

No.	Potential / V	Scat.At.	CN	(e.s.d.)	R / 0.1 nm	(e.s.d.)	σ^2 / 10^{-5} nm^2	(e.s.d.)	ΔE_0 / eV	(e.s.d.)	R-factor / %
1(*1)	0.4	Pt	9.9	1.5	2.75	0.01	7.3	0.8	3.3	1.4	1.87
2(*2)	0.6	Pt	8.9	1.5	2.77	0.01	7.2	1.0	7.5	2.2	2.06
3	0.8	Pt	8.8	0.5	2.75	0.00	7.0	0.2	3.5	0.7	0.44
4	1.0	Pt	8.4	0.8	2.75	0.00	7.4	0.4	4.0	1.2	1.57
5	1.2	Pt	6.4	0.7	2.75	0.00	8.1	0.5	4.0	1.2	0.95
		O	1.2	0.3	2.01	0.02	4.1	1.9	4.7	3.5	
6	1.4	Pt	5.6	0.8	2.76	0.01	7.7	0.6	7.1	1.9	1.20
		O	1.8	0.4	2.00	0.01	3.2	1.2	2.1	3.1	
7	1.2	Pt	4.9	0.5	2.75	0.01	7.8	0.8	5.7	1.6	2.47
		O	2.2	0.3	2.01	0.01	4.7	1.0	5.7	1.6	
8	1.0	Pt	5.0	0.4	2.75	0.01	7.5	0.7	5.7	1.4	2.21
		O	1.9	0.3	2.02	0.01	4.1	1.2	5.7	1.4	
9	0.8	Pt	5.7	0.2	2.75	0.00	7.3	0.5	4.3	0.8	0.66
		O	1.6	0.2	2.02	0.01	4.5	1.2	4.3	0.8	
10	0.6	Pt	6.8	0.8	2.75	0.00	7.0	0.5	3.7	1.4	0.73
		O	0.6	0.3	2.06	0.03	3.6	3.2	13.0	6.0	
11(*3)	0.4	Pt	9.6	1.6	2.75	0.01	7.2	0.7	4.0	3.3	3.49

k-range = 30 - 150 nm^{-1}, k-weight = 3, R-range = 0.14 - 0.31 nm ((*1) k-range = 30 - 130 nm^{-1}, k-weight = 3, R-range = 0.14 - 0.31 nm, (*2) k-range = 30 - 130 nm^{-1}, k-weight = 3, R-range = 0.18 - 0.31 nm, (*3) k-range = 30 - 150nm^{-1}, k-weight = 3, R-range = 0.18 - 0.31 nm), Coordination number (CN), Debye-Waller factor (σ^2), e.s.d. = Estimated standard deviation

Table S3 Curve-fitting results of the Pt L_{III}-edge EXAFS data for Pt/KB after 1000 triangle ADT cycles

No.	Potential / V	Scat.At.	CN	(e.s.d.)	R / 0.1 nm	(e.s.d.)	σ^2 / 10^{-5} nm^2	(e.s.d.)	ΔE_0 / eV	(e.s.d.)	R-factor / %
1	0.4	Pt	9.7	0.5	2.75	0.00	7.4	0.2	3.9	0.7	0.49
2	0.6	Pt	9.7	0.7	2.75	0.00	7.3	0.3	4.2	0.9	0.71
3	0.8	Pt	9.9	0.8	2.75	0.00	7.3	0.3	4.7	1.3	1.39
4	1.0	Pt	8.8	0.6	2.75	0.00	7.4	0.3	4.5	0.9	0.45
		O	0.6	0.3	2.04	0.04	4.6	3.6	3.6	6.7	
5	1.2	Pt	7.2	0.9	2.76	0.00	7.4	0.5	5.0	1.4	1.18
		O	1.7	0.7	2.01	0.03	7.2	3.6	2.0	4.4	
6	1.4	Pt	7.0	0.6	2.76	0.00	7.4	0.4	7.1	1.3	0.95
		O	1.5	0.5	2.01	0.02	5.7	2.7	3.7	4.3	
7	1.2	Pt	7.6	0.6	2.75	0.00	7.4	0.3	3.6	1.1	0.63
		O	0.9	0.3	2.04	0.02	4.1	2.2	8.3	4.2	
8	1.0	Pt	7.9	0.5	2.75	0.00	7.2	0.3	4.6	0.8	0.34
		O	0.9	0.2	2.03	0.01	3.1	1.6	4.0	3.5	
9	0.8	Pt	8.9	1.0	2.75	0.01	7.6	0.4	5.0	1.7	1.40
		O	0.5	0.3	2.04	0.03	-0.8	2.4	7.5	10.3	
10	0.6	Pt	8.0	1.2	2.75	0.01	7.4	0.6	4.7	1.7	1.55
		O	0.8	0.5	2.04	0.05	4.3	3.8	6.3	8.7	
11	0.4	Pt	8.2	0.7	2.75	0.00	7.6	0.4	4.9	1.0	0.62
		O	0.9	0.7	2.02	0.06	8.7	7.8	2.9	9.0	

k-range = 30 - 150 nm^{-1}, k-weight = 3, R-range = 0.14 - 0.31 nm
Coordination number (CN), Debye-Waller factor (σ^2), e.s.d. = Estimated standard deviation

Table S4 Curve-fitting results of the Pt L_{III}-edge EXAFS data for Pt/AB after 5000 triangle ADT cycles

No.	Potential / V	Scat.At.	CN	(e.s.d.)	R / 0.1 nm	(e.s.d.)	σ^2 / 10^{-5} nm^2	(e.s.d.)	ΔE_0 / eV	(e.s.d.)	R-factor / %
1	0.4	Pt	10.9	1.6	2.76	0.01	6.8	0.7	4.8	1.6	1.09
2	0.6	Pt	10.0	1.6	2.76	0.00	6.6	0.7	4.7	1.2	1.44
3	0.8	Pt	9.7	1.2	2.75	0.00	6.4	0.5	4.0	1.4	1.27
4	1.0	Pt	9.8	1.8	2.75	0.01	6.6	0.8	3.7	1.8	1.96
5	1.2	Pt	8.2	2.3	2.76	0.01	6.6	1.1	5.4	2.3	3.15
		O	1.7	1.5	1.99	0.08	10.2	10.3	1.3	11.7	
6	1.4	Pt	7.1	1.6	2.76	0.01	6.7	0.9	5.7	1.9	1.48
		O	1.0	0.4	2.06	0.02	2.6	3.3	10.7	5.2	
7	1.2	Pt	7.6	1.1	2.76	0.01	6.8	0.5	6.0	1.7	1.44
		O	1.6	1.1	2.02	0.06	7.7	6.0	2.4	9.0	
8	1.0	Pt	7.0	1.2	2.76	0.01	6.5	0.6	5.8	1.6	1.42
		O	1.2	0.6	2.04	0.04	5.7	4.2	7.3	6.9	
9	0.8	Pt	7.9	1.0	2.76	0.00	6.6	0.5	5.6	1.6	1.22
		O	1.2	0.6	2.03	0.05	7.2	5.1	4.0	8.1	
10	0.6	Pt	9.2	1.3	2.76	0.00	6.8	0.6	5.1	1.3	1.75
11	0.4	Pt	10.6	1.3	2.75	0.01	7.5	0.6	4.1	1.5	1.68

k-range = 30 - 150 nm^{-1}, k-weight = 3, R-range = 0.14 - 0.31 nm
Coordination number (CN), Debye-Waller factor (σ^2), e.s.d. = Estimated standard deviation