Electronic Supplementary Information

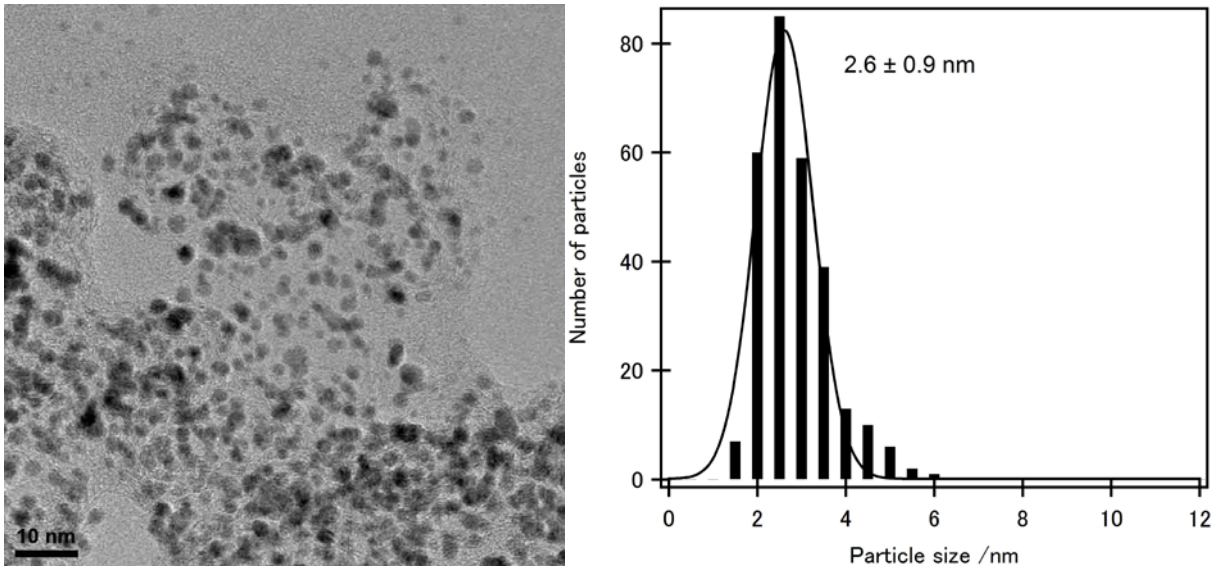

Figure S1. The TEM image of the Pt/C cathode catalyst in a fresh MEA (0.5 $mg_{\text{-Pt}}/cm^2$) and its particle size distribution estimated by the TEM image.

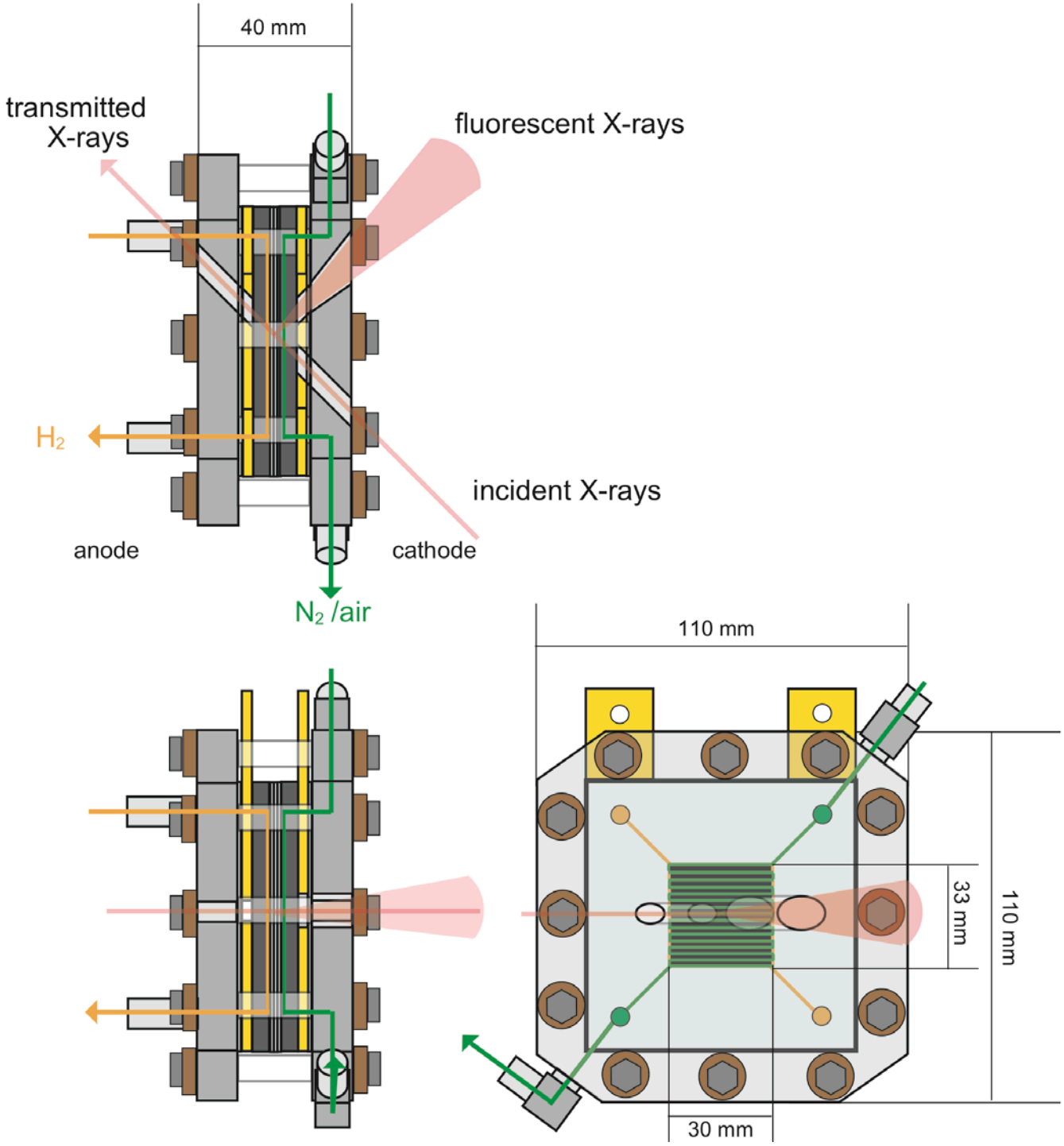

Figure S2. Schematics of an in situ XAFS cell for PEFCs: overhead view (top), side view (bottom left), and front view (bottom right).

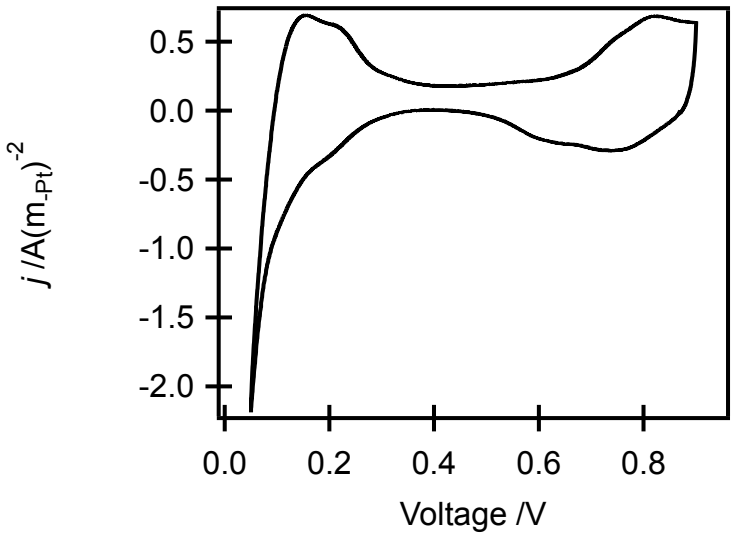

Figure S3. Cyclic voltammogram of the Pt/C electrocatalyst recorded before the in situ time-resolved QXAFS measurements at SPring-8 BL40XU. The voltage was swept between 0.05 and 0.9 V at 50 mV s^{-1} under H_2 flow (anode) and N_2 flow (cathode).

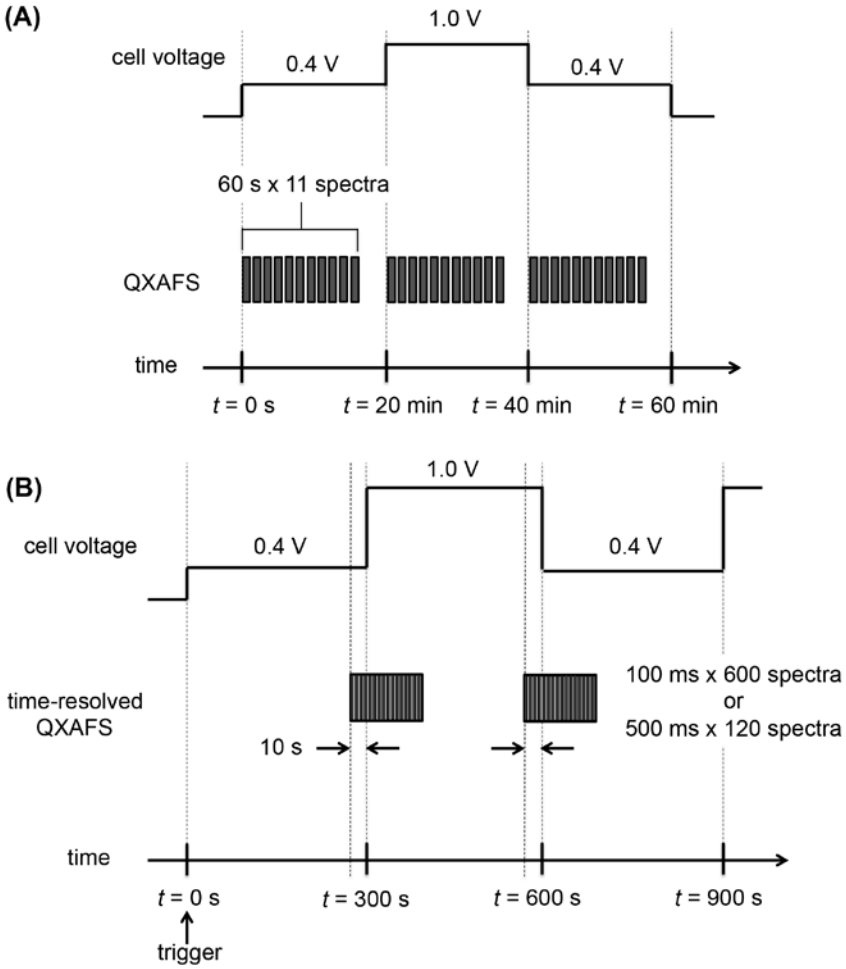

Figure S4. Schematics of (A) the in situ QXAFS measurements (60 s) at SPring-8 BL01B1 and (B) the in situ time-resolved QXAFS (100 or 500 ms) measurements at SPring-8 BL40XU.

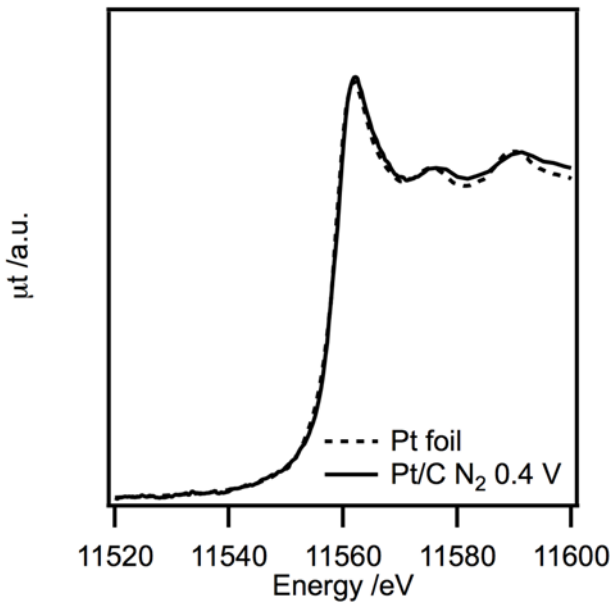

Figure S5. Pt L_{III}-edge XANES spectra of Pt foil (Pt(0)) and Pt/C at 0.4 V (N_2 flow).

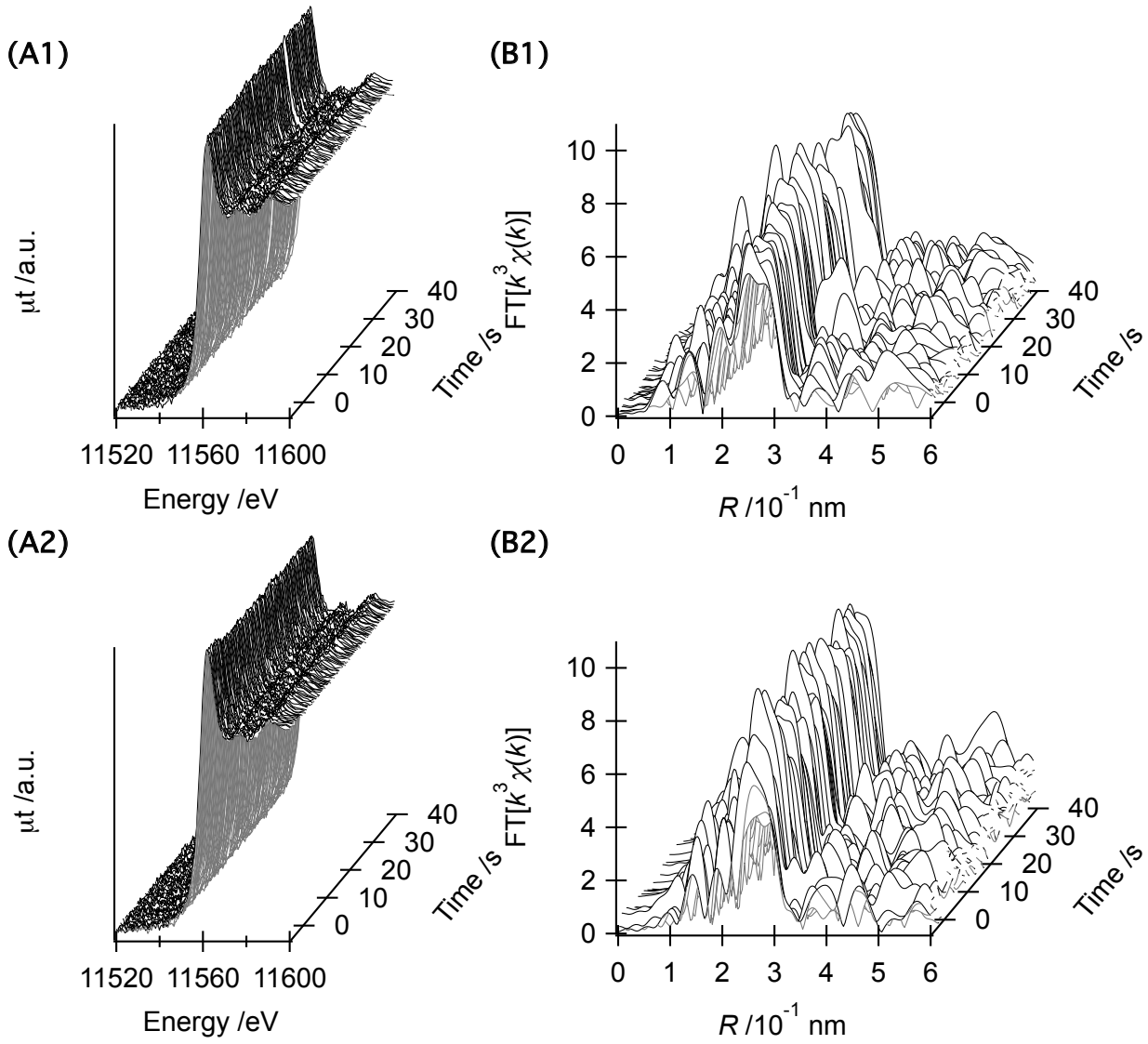

Figure S6. A series of in situ time-resolved Pt L_{III}-edge XAFS spectra for Pt/C MEA under air flow at the cathode. (A) A series of in situ time-resolved Pt L_{III}-edge XANES spectra, recorded at 100 ms intervals. (B) A series of k^3-weighted EXAFS Fourier transforms at k = 30–120 nm^{-1}, recorded at 500 ms intervals. Spectra for the voltage steps of (1) 0.4 V → 1.0 V and (2) 1.0 V → 0.4 V.

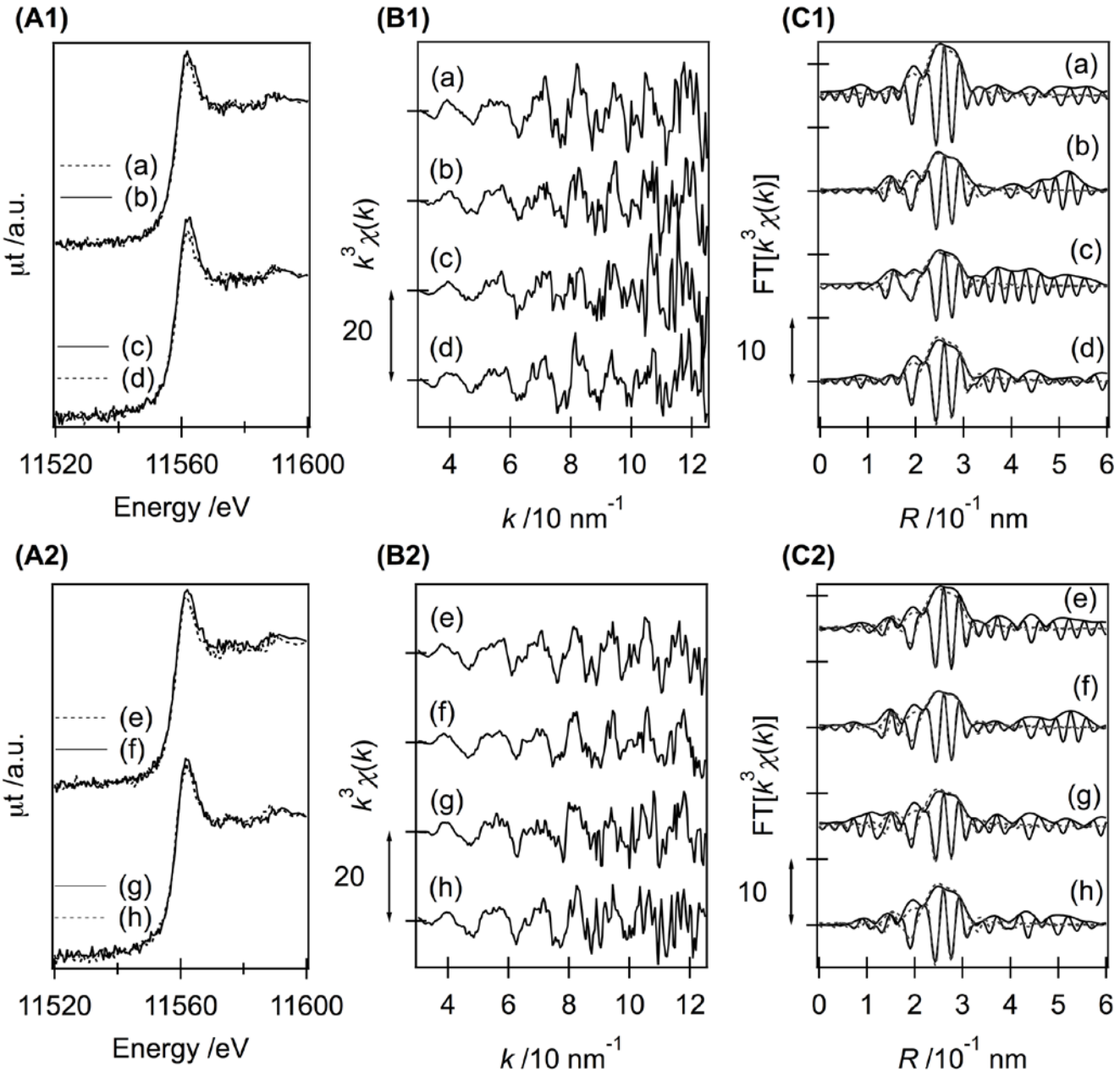

Figure S7. In situ time-resolved XAFS spectra at 0.4 and 1.0 V for the Pt/C MEA. (A) Pt L_{III}-edge XANES spectra, recorded every 100 ms, (B) k^3-weighted Pt L_{III}-edge EXAFS oscillations, recorded every 500 ms, and (C) their k^3-weighted EXAFS Fourier transforms at k = 30–120 nm^{-1}. Solid line: experimental data; solid line: fitted data. (1) Cathode: N_2 flow, (2) cathode: air flow. (a) t = 296.5 s (0.4 V in N_2), (b) 335.0 s (1.0 V in N_2), (c) t = 597.5 s (1.0 V in N_2), and (d) t = 644.5 s in N_2 (0.4 V in N_2), (e) t = 298.0 s (0.4 V in air), (f) 344.0 s (1.0 V in air), (g) t = 592.0 s (1.0 V in air), and (h) t = 643.0 s (0.4 V in air).

Table S1. Structural parameters estimated by curve fitting analysis of the Fourier transforms of the in situ time-resolved Pt L_{III}-edge EXAFS at 0.4 and 1.0 V for the Pt/C MEA (see Figure S7)

Sample	Shell	CN	R /nm	ΔE_0 /eV	σ^2 /10^{-5} nm^2
(a) t = 296.5 s in N_2 (0.4 V)	Pt-O	-0.1 ± 0.1	0.199	2	0.1
(R_f = 1.7%)	Pt-Pt	10.3 ± 0.5	0.273 ± 0.001	1 ± 1	7.7
(b) t = 335.0 s in N_2 (1.0 V)	Pt-O	0.5 ± 0.1	0.199	2	0.1
(R_f = 3.1%)	Pt-Pt	7.8 ± 0.5	0.274 ± 0.001	2 ± 1	7.7
(c) t = 597.5 s in N_2 (1.0 V)	Pt-O	0.6 ± 0.1	0.199	2	0.1
(R_f = 4.1%)	Pt-Pt	7.1 ± 0.6	0.273 ± 0.001	1 ± 1	7.7
(d) t = 644.5 s in N_2 (0.4 V)	Pt-O	-0.0 ± 0.1	0.199	2	0.1
(R_f = 2.5%)	Pt-Pt	9.0 ± 0.5	0.274 ± 0.001	2 ± 1	7.7
(e) t = 298.0 s in air (0.4 V)	Pt-O	0.5 ± 0.1	0.199	2	0.1
(R_f =2.9%)	Pt-Pt	8.1 ± 0.5	0.274 ± 0.001	2 ± 1	7.7
(f) t = 344.0 s in air (1.0 V)	Pt-O	0.6 ± 0.2	0.199	2	0.1
(R_f = 4.7%)	Pt-Pt	7.4 ± 0.6	0.275 ± 0.001	1 ± 1	7.7
(g) t = 592.0 s in air (1.0 V)	Pt-O	0.6 ± 0.2	0.199	2	0.1
(R_f = 5.7%)	Pt-Pt	7.3 ± 0.7	0.274 ± 0.001	2 ± 1	7.7
(h) t = 643.0 s in air (0.4 V)	Pt-O	0.5 ± 0.1	0.199	2	0.1
(R_f =3.5%)	Pt-Pt	8.4 ± 0.6	0.274 ± 0.001	3 ± 1	7.7

S_0^2 = 0.94, k = 30–120 nm^{-1}, R = 0.12–0.35 nm. R, ΔE_0, and σ^2 of Pt-O and σ^2 of Pt-Pt were fixed at the values for Pt/C at 1.0 V under N_2 flow in Table 1.