

Supplementary Information

Sustainable activation of the $\text{PtCl}_n/\text{Fe-N-C}$ cathode for PEFCs through repeated subnanometer sizing and coarsening

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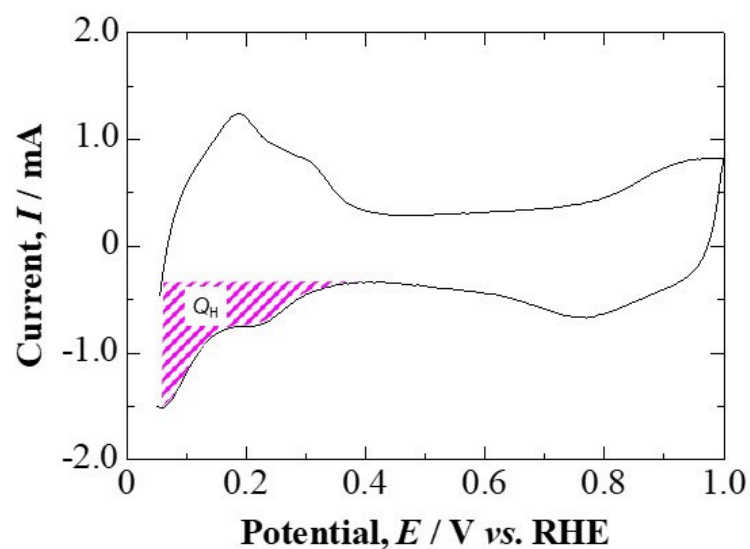


Figure S1. Cyclic voltammograms to determine the ECSA, at a Nafion-coated $\text{PtCl}_n/\text{Fe-N-C}$ electrode in 0.1 M HClO_4 solution purged with Ar at 30°C. Scan rate = 0.05 V s^{-1} .

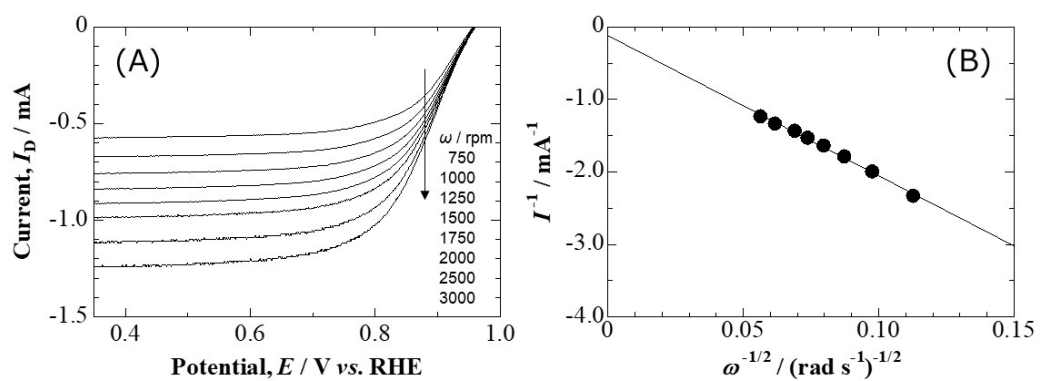


Figure S2. Hydrodynamic voltammograms for ORR in O_2 -saturated 0.1 M $HClO_4$ solution at a Nafion-coated $PtCl_n/Fe-N-C$ electrode at 30 °C. (B) Koutecky-Levich plots at 0.85 V obtained from (A).

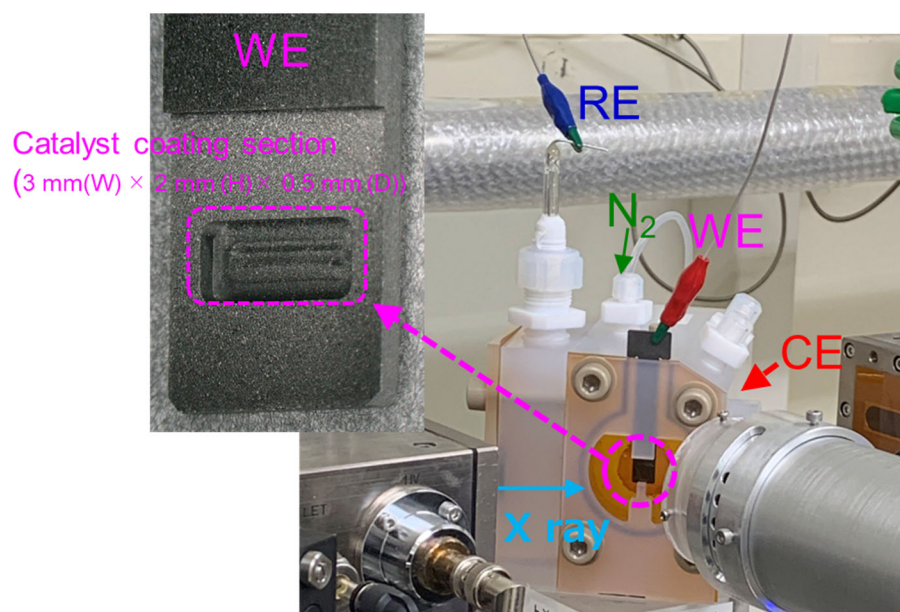


Figure S3. Electrochemical cell and working electrode (WE) for *in situ* XAFS measurements.

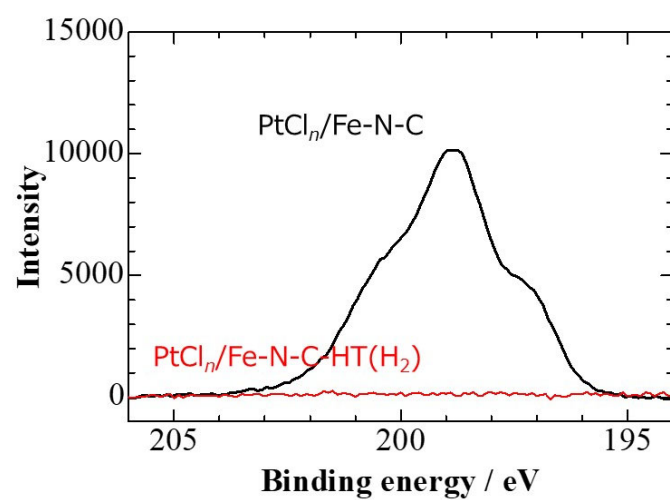


Figure S4. XPS Cl 2p spectra obtained for $\text{PtCl}_n/\text{Fe-N-C}$ and $\text{PtCl}_n/\text{Fe-N-C-HT(H}_2\text{)}$ powders.

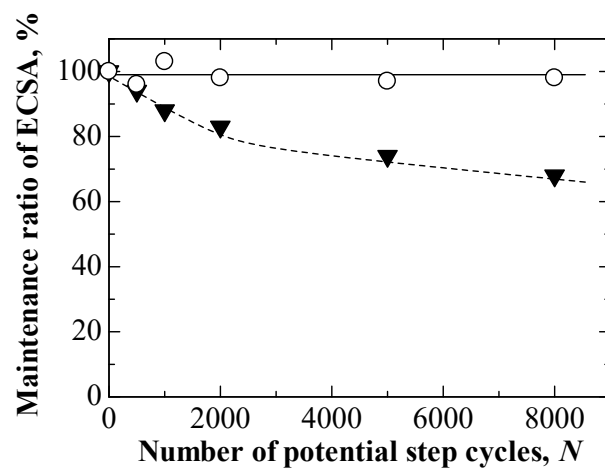


Figure S5. Change in ECSA value for the (○) PtCl_n/Fe-N-C with 0.07 mgPt cm⁻² loading and (▼) commercial Pt/C with 0.14 mgPt cm⁻² loading cathode in single cell with 5 cm × 5 cm MEA. Cell temperature: 80°C. N₂ and H₂ humidifier temperature: 80°C. Cathode flow rate 0.8 L min⁻¹; anode flow rate: 0.2 L min⁻¹.

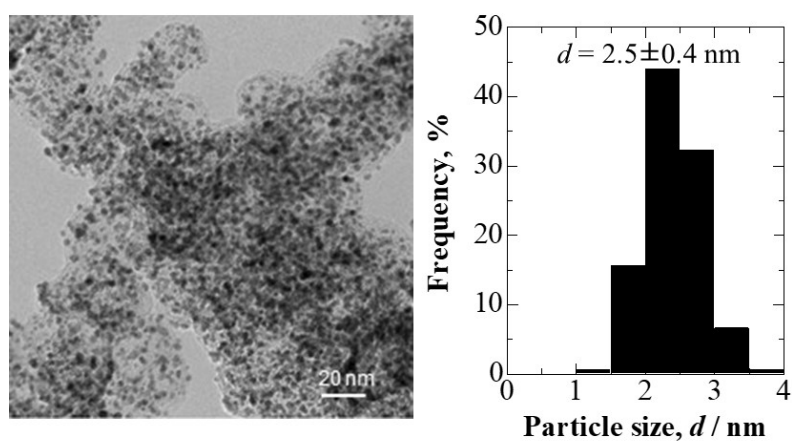


Figure S6. TEM image and particle size distribution histogram for commercial Pt/C.

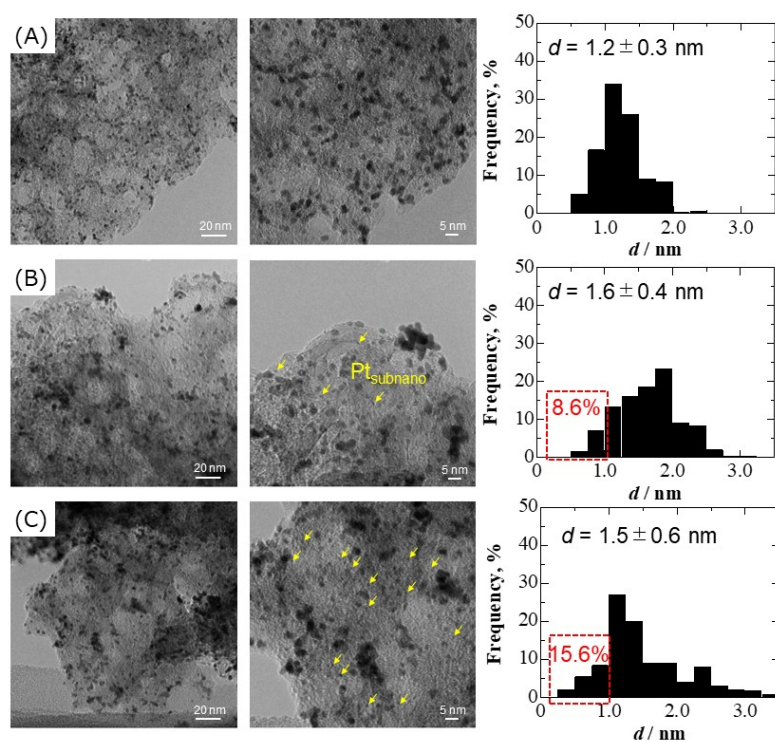


Figure S7. TEM images and particle size distribution histograms for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode after in-situ XAFS measurement at (A) $N = 0$, (B) $N = 25$, and (C) $N = 75$.

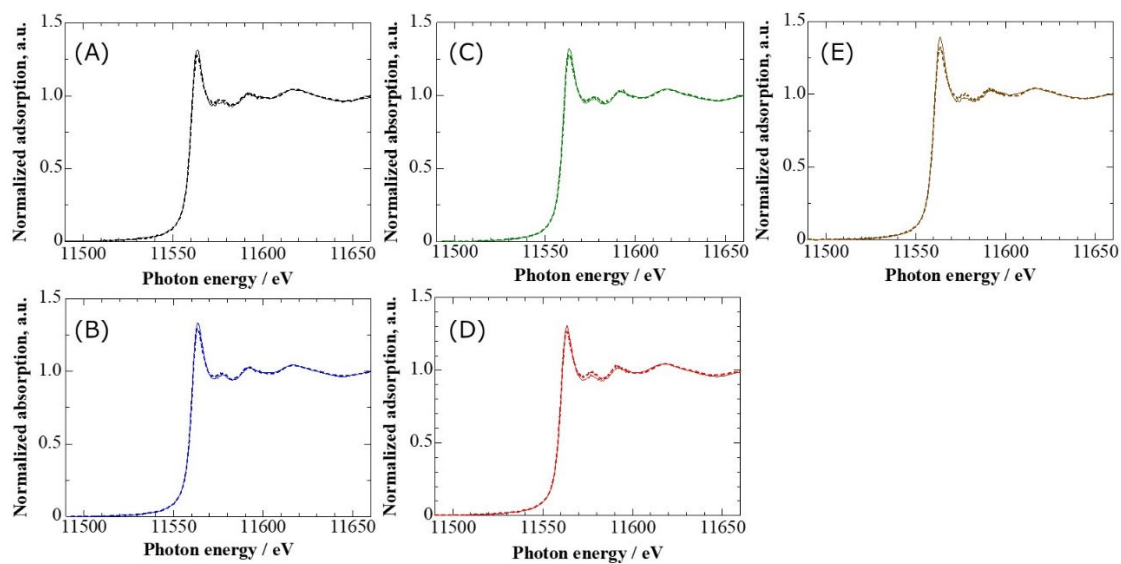


Figure S8. XANES spectra for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode with (A) $N = 0$, (B) $N = 5$, (C) $N = 25$, and (D) $N = 75$ and for the (E) commercial Pt/C electrode ($N = 0$) at (----) 0.4 and (—) 1.0 V in N_2 -purged 0.1 M HClO_4 .

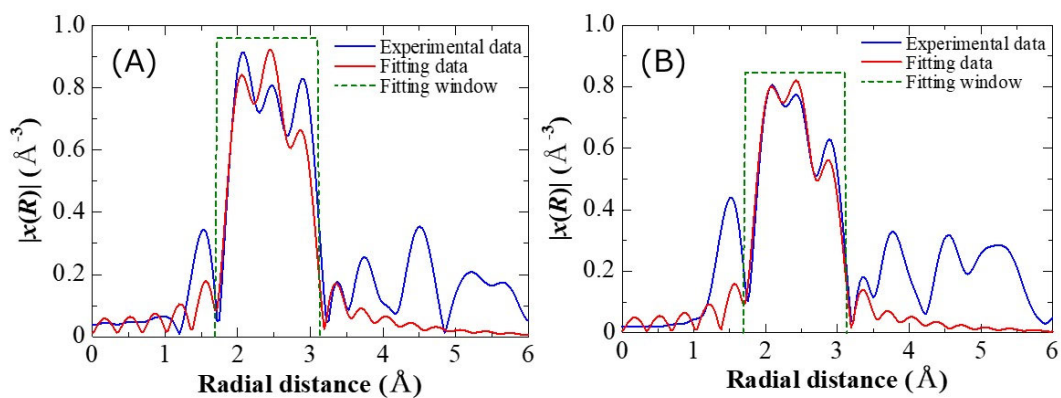


Figure S9. The EXAFS, $\chi(R)$, for $\text{PtCl}_n/\text{Fe-N-C}$ electrode before ($N = 0$) at the potential of (A) 0.4 V and (B) 1.0 V vs. RHE in 0.1 M HClO_4 deaerated with N_2 .

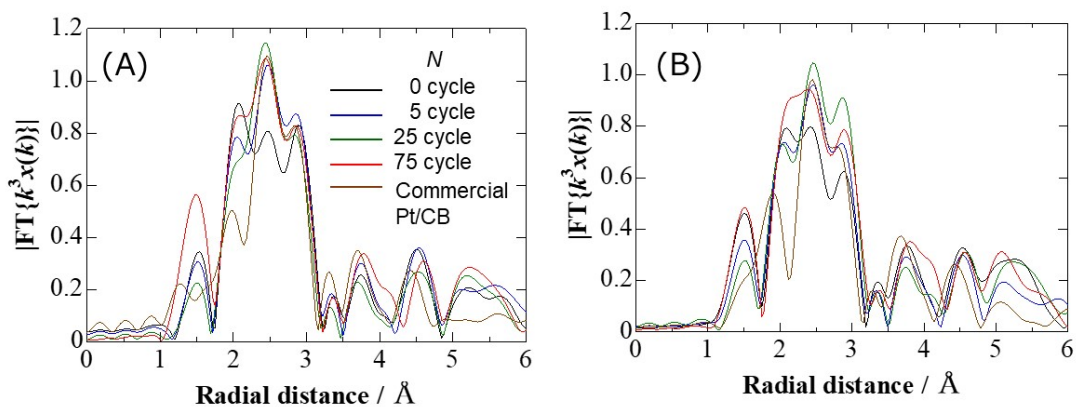


Figure S10. Pt- L_3 edge Fourier transformed EXAFS for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode at $N = 0$ and after $N = 5, 25$, and 75 cycles. EXAFS spectra acquired at potentials of (A) 0.4 V and (B) 1.0 V vs. RHE in 0.1 M HClO_4 deaerated with N_2 .

Table S1. EXAFS fitting results for Pt-Pt bond at 0.4 V

N (cycle)	Path	CN	R (Å)	σ^2 (Å ²)	R factor
0	Pt-Pt Pt-Cl	6.1 ± 1.0 1.4 ± 0.5	2.752 ± 0.009 2.421 ± 0.046	0.0043 ± 0.0009 0.0040	0.037
5	Pt-Pt Pt-Cl	7.2 ± 2.1 1.0 ± 0.4	2.748 ± 0.004 2.418 ± 0.027	0.0041 ± 0.0016 0.0040	0.010
25	Pt-Pt Pt-Cl	8.7 ± 2.3 0.7 ± 0.5	2.743 ± 0.004 2.438 ± 0.029	0.0052 ± 0.0015 0.0040	0.007
75	Pt-Pt Pt-Cl	6.6 ± 2.3 1.4 ± 0.8	2.746 ± 0.008 2.440 ± 0.028	0.0039 ± 0.0032 0.0040	0.029
0 (commercial Pt/CB)	Pt-Pt	7.7 ± 1.6	2.748 ± 0.009	0.0043 ± 0.0013 0.0040	0.006

Table S2. EXAFS fitting results for Pt-Pt bond at 1.0 V

N (cycle)	Path	CN	R (Å)	σ^2 (Å ²)	R factor
0	Pt-Pt Pt-Cl	5.9 ± 2.3 1.3 ± 0.4	2.754 ± 0.006 2.430 ± 0.027	0.0050 ± 0.0022 0.0040	0.045
5	Pt-Pt Pt-Cl	6.6 ± 1.3 1.0 ± 0.3	2.751 ± 0.003 2.431 ± 0.012	0.0043 ± 0.0011 0.0040	0.016
25	Pt-Pt Pt-Cl	8.4 ± 1.7 0.7 ± 0.3	2.749 ± 0.003 2.402 ± 0.028	0.0048 ± 0.0012 0.0040	0.008
75	Pt-Pt Pt-Cl	6.6 ± 3.9 1.3 ± 1.0	2.750 ± 0.010 2.441 ± 0.032	0.0046 ± 0.0040 0.0040	0.046
0 (commercial Pt/CB)	Pt-Pt	6.0 ± 1.3	2.740 ± 0.005	0.0036 ± 0.0013 0.0040	0.014