

Supplementary Information

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

Hiroshi Yano

New Field Pioneering Division, Toyota Boshoku Corp., Kariya, Aichi 448-8651, Japan

Phone: +81 566 26 7714, Email: hiroshi.yano@toyota-boshoku.com

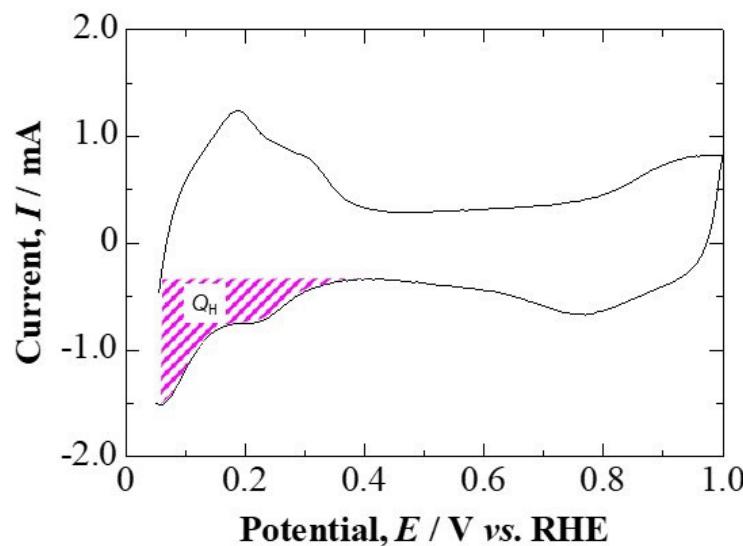


Figure S1. Cyclic voltammograms to determine the ECSA, at a Nafion-coated $\text{PtCl}_n/\text{Fe-N-C}$ electrode in 0.1 M HClO_4 solution purged with Ar at 30°C. Scan rate = 0.05 V s^{-1} .

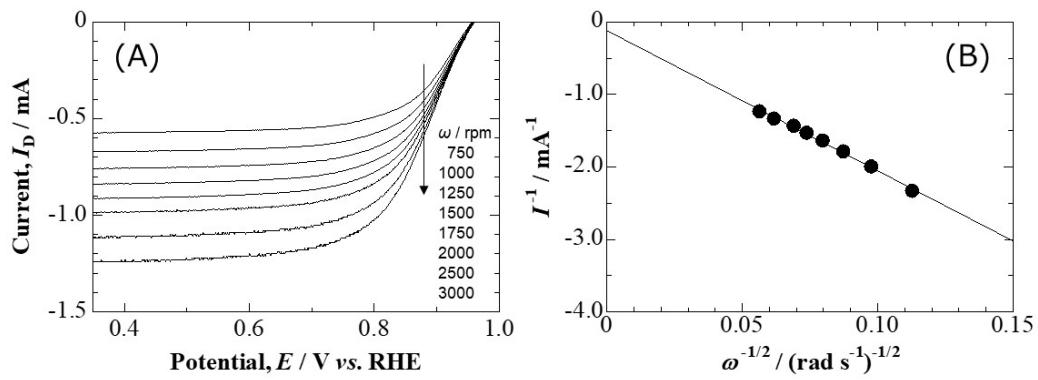


Figure S2. Hydrodynamic voltammograms for ORR in O₂-saturated 0.1 M HClO₄ solution at a Nafion-coated PtCl_n/Fe-N-C electrode at 30 °C. (B) Koutecky-Levich plots at 0.85 V obtained from (A).

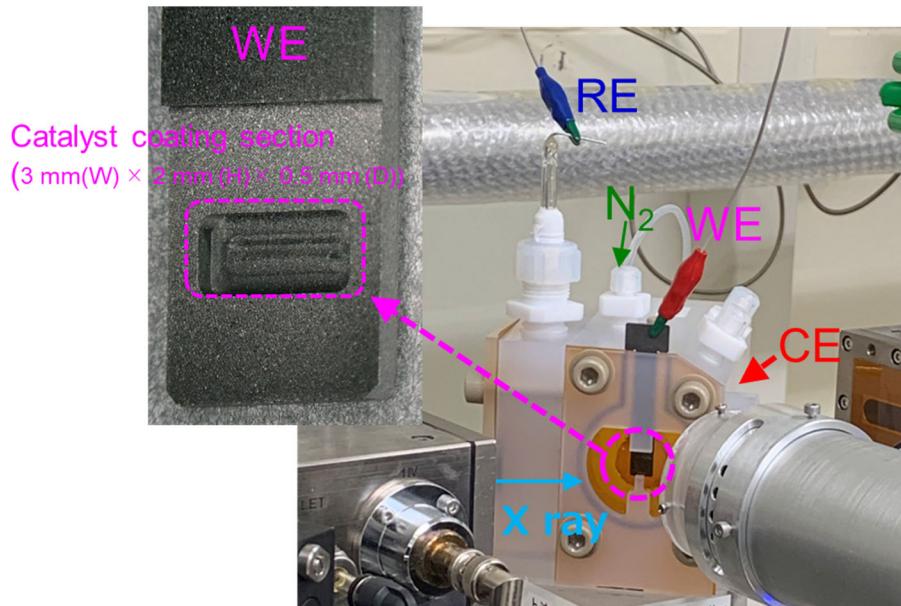


Figure S3. Electrochemical cell and working electrode (WE) for *in situ* XAFS measurements.

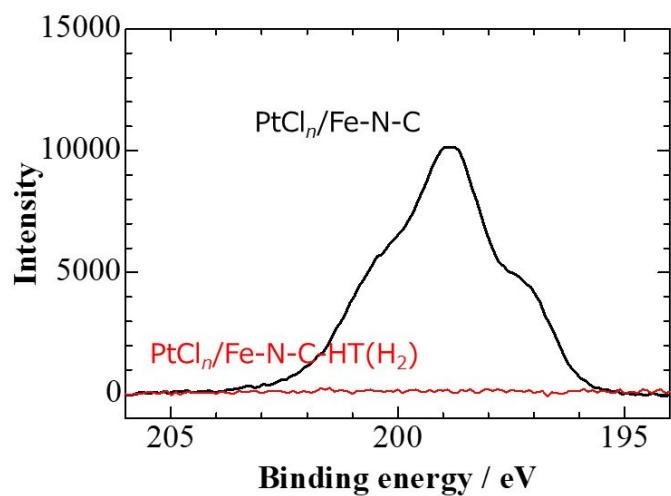


Figure S4. XPS Cl 2p spectra obtained for $\text{PtCl}_n/\text{Fe-N-C}$ and $\text{PtCl}_n/\text{Fe-N-C-HT(H}_2\text{)}$ powders.

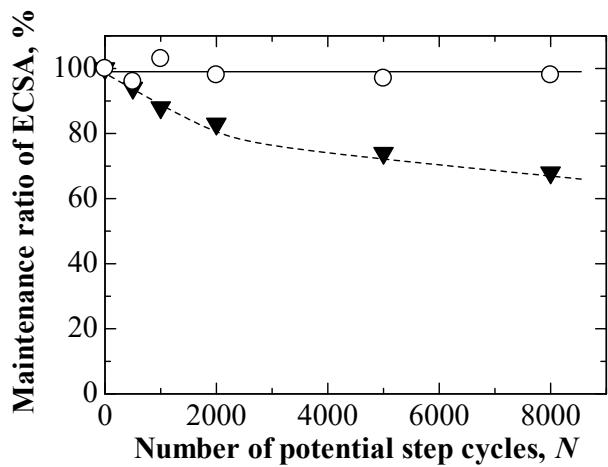


Figure S5. Change in ECSA value for the (○) $\text{PtCl}_n/\text{Fe-N-C}$ with $0.07 \text{ mgPt cm}^{-2}$ loading and (▼) commercial Pt/C with $0.14 \text{ mgPt cm}^{-2}$ loading cathode in single cell with $5 \text{ cm} \times 5 \text{ cm}$ MEA. Cell temperature: 80°C . N_2 and H_2 humidifier temperature: 80°C . Cathode flow rate 0.8 L min^{-1} ; anode flow rate: 0.2 L min^{-1} .

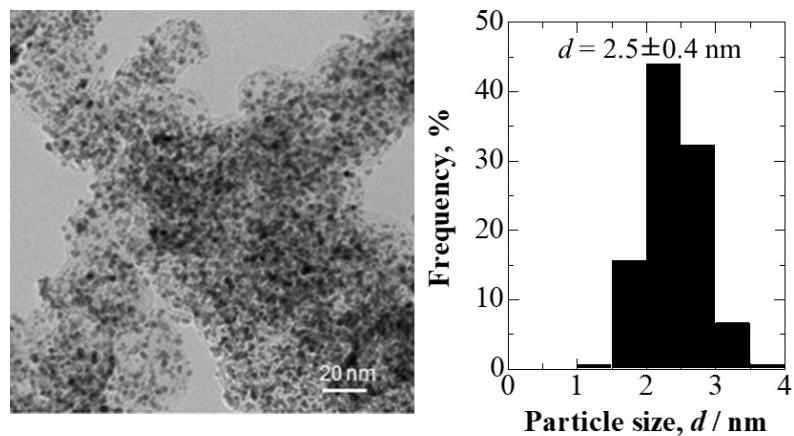


Figure S6. TEM image and particle size distribution histogram for commercial Pt/C.

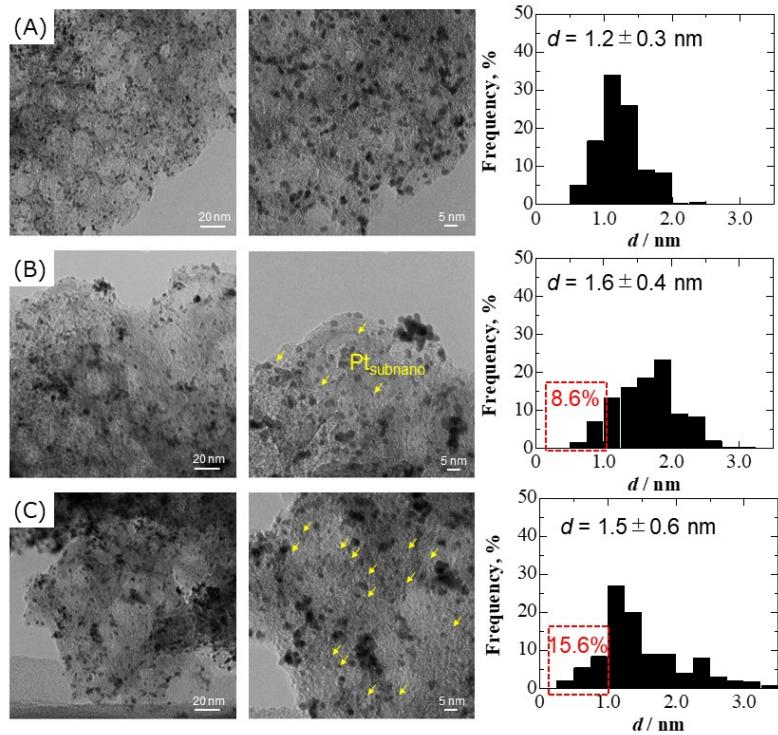


Figure S7. TEM images and particle size distribution histograms for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode after in-situ XAFS measurement at (A) $N = 0$, (B) $N = 25$, and (C) $N = 75$.

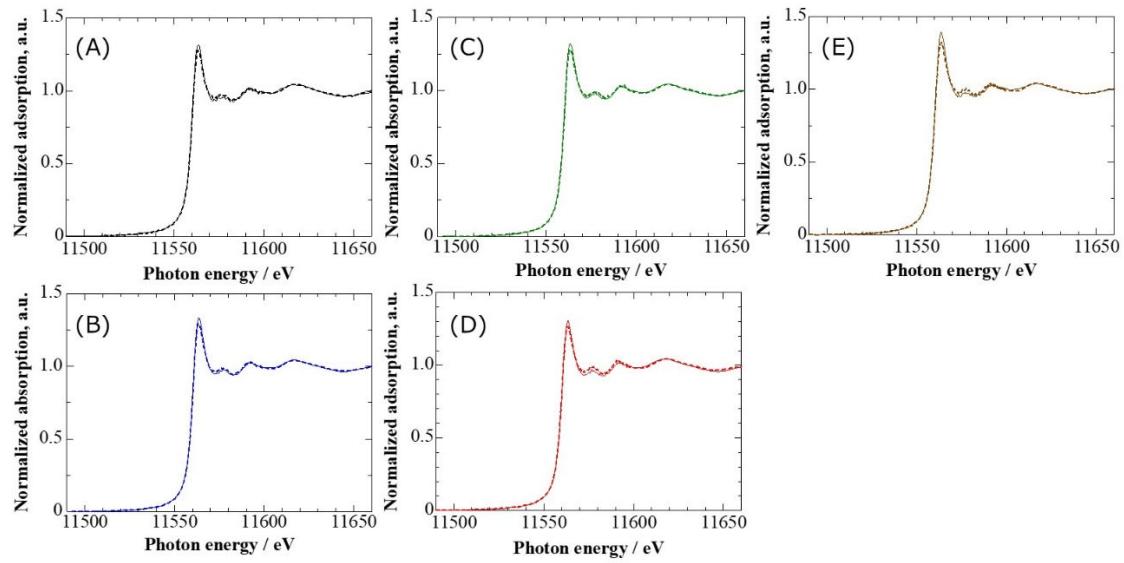


Figure S8. XANES spectra for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode with (A) $N = 0$, (B) $N = 5$, (C) $N = 25$, and (D) $N = 75$ and for the (E) commercial Pt/C electrode ($N = 0$) at (----) 0.4 and (—) 1.0 V in N_2 -purged 0.1 M HClO_4 .

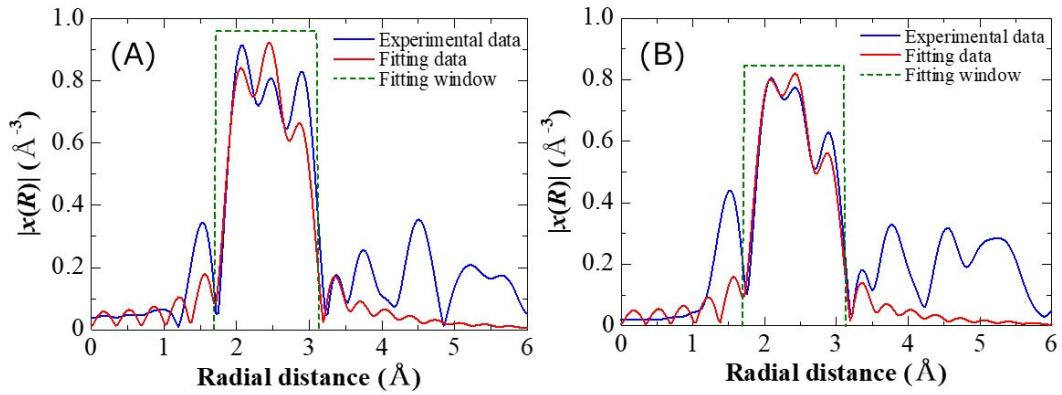


Figure S9. The EXAFS, $x(R)$, for $\text{PtCl}_n/\text{Fe-N-C}$ electrode before ($N = 0$) at the potential of (A) 0.4 V and (B) 1.0 V vs. RHE in 0.1 M HClO_4 deaerated with N_2 .

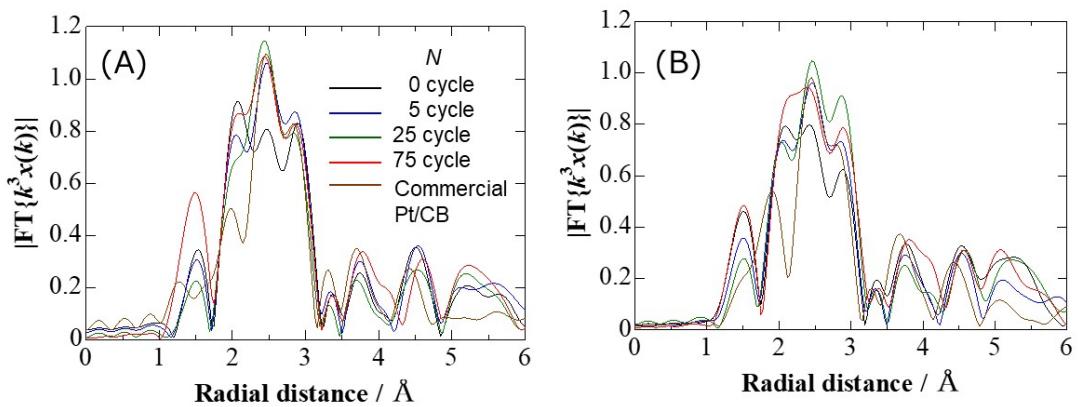


Figure S10. Pt-L_3 edge Fourier transformed EXAFS for $(\text{PtCl}_n)_{0.9\text{nm}}/\text{Fe-N-C}$ electrode at $N = 0$ and after $N = 5$, 25, and 75 cycles. EXAFS spectra acquired at potentials of (A) 0.4 V and (B) 1.0 V vs. RHE in 0.1 M HClO_4 deaerated with N_2 .

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	6.1 ± 1.0	2.752 ± 0.009	0.0043 ± 0.0009	0.037
	Pt-Cl	1.4 ± 0.5	2.421 ± 0.046	0.0040	
5	Pt-Pt	7.2 ± 2.1	2.748 ± 0.004	0.0041 ± 0.0016	0.010
	Pt-Cl	1.0 ± 0.4	2.418 ± 0.027	0.0040	
25	Pt-Pt	8.7 ± 2.3	2.743 ± 0.004	0.0052 ± 0.0015	0.007
	Pt-Cl	0.7 ± 0.5	2.438 ± 0.029	0.0040	
75	Pt-Pt	6.6 ± 2.3	2.746 ± 0.008	0.0039 ± 0.0032	0.029
	Pt-Cl	1.4 ± 0.8	2.440 ± 0.028	0.0040	
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	5.9 ± 2.3	2.754 ± 0.006	0.0050 ± 0.0022	0.045
	Pt-Cl	1.3 ± 0.4	2.430 ± 0.027	0.0040	
5	Pt-Pt	6.6 ± 1.3	2.751 ± 0.003	0.0043 ± 0.0011	0.016
	Pt-Cl	1.0 ± 0.3	2.431 ± 0.012	0.0040	
25	Pt-Pt	8.4 ± 1.7	2.749 ± 0.003	0.0048 ± 0.0012	0.008
	Pt-Cl	0.7 ± 0.3	2.402 ± 0.028	0.0040	
75	Pt-Pt	6.6 ± 3.9	2.750 ± 0.010	0.0046 ± 0.0040	0.046
	Pt-Cl	1.3 ± 1.0	2.441 ± 0.032	0.0040	
0 (commercial Pt/CB)	Pt-Pt	6.0 ± 1.3	2.740 ± 0.005	0.0036 ± 0.0013 0.0040	0.014