Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

1. Particle size distribution of pristine P1 and P2 precursors

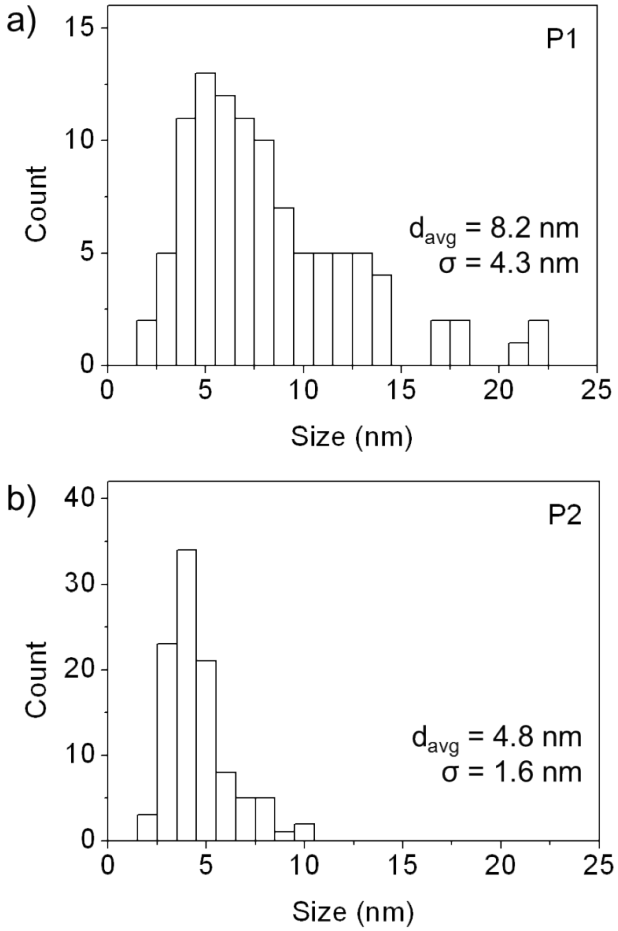

Figure S1. Particle size distribution of (a) pristine P1 and (b) pristine P2 precursors. More than 100 particles of each sample were measured to calculated the average of particle size (d_{avg}) and the standard deviation of particle size distribution (σ).

2. ECSA change before and after 30k cycles

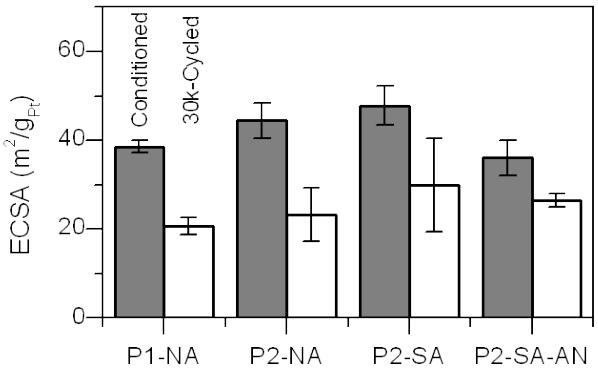

Figure S2. ECSA of MEAs with P1-NA, P2-NA, P2-SA and P2-SA-AN cathodes before and after 30k operation cycles, respectively. The ECSAs were obtained from the H adsorption/desorption (HAD) peaks using cyclic voltammetry. The error bars represent the standard deviations of ECSA measurements among at least 4 MEA samples.

3. Cycling of P2-NA at lower upper voltage limit (UVL)

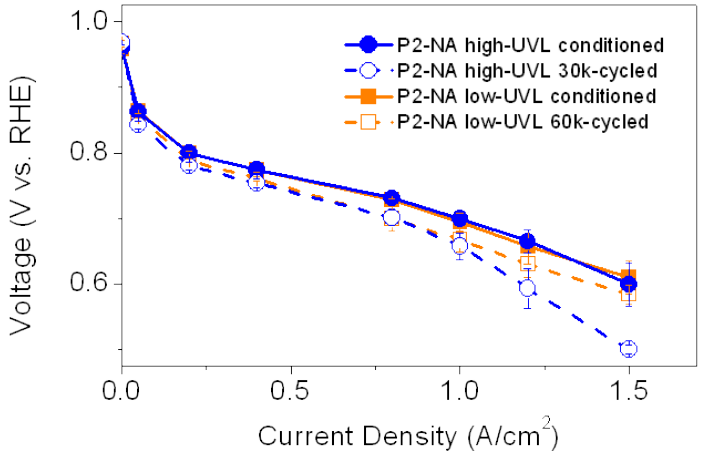

Figure S3. Fuel cell polarization curves of MEAs with P2-NA cathodes at different cycling voltage range (high UVL: 0.6-1.0 V vs. RHE; low UVL: 0.6-0.925 V vs. RHE) and aging stages (conditioned and cycled). Testing conditions of anode/cathode were H_2/air, 100/100% RH, 170/170 kPa_{abs} back pressure, and stoichiometric coefficient of 1.5/2, respectively. The error bars represent the standard deviation of activity measurements among at least 4 MEA samples.

4. TEM Images for Catalysts from Conditioned MEA

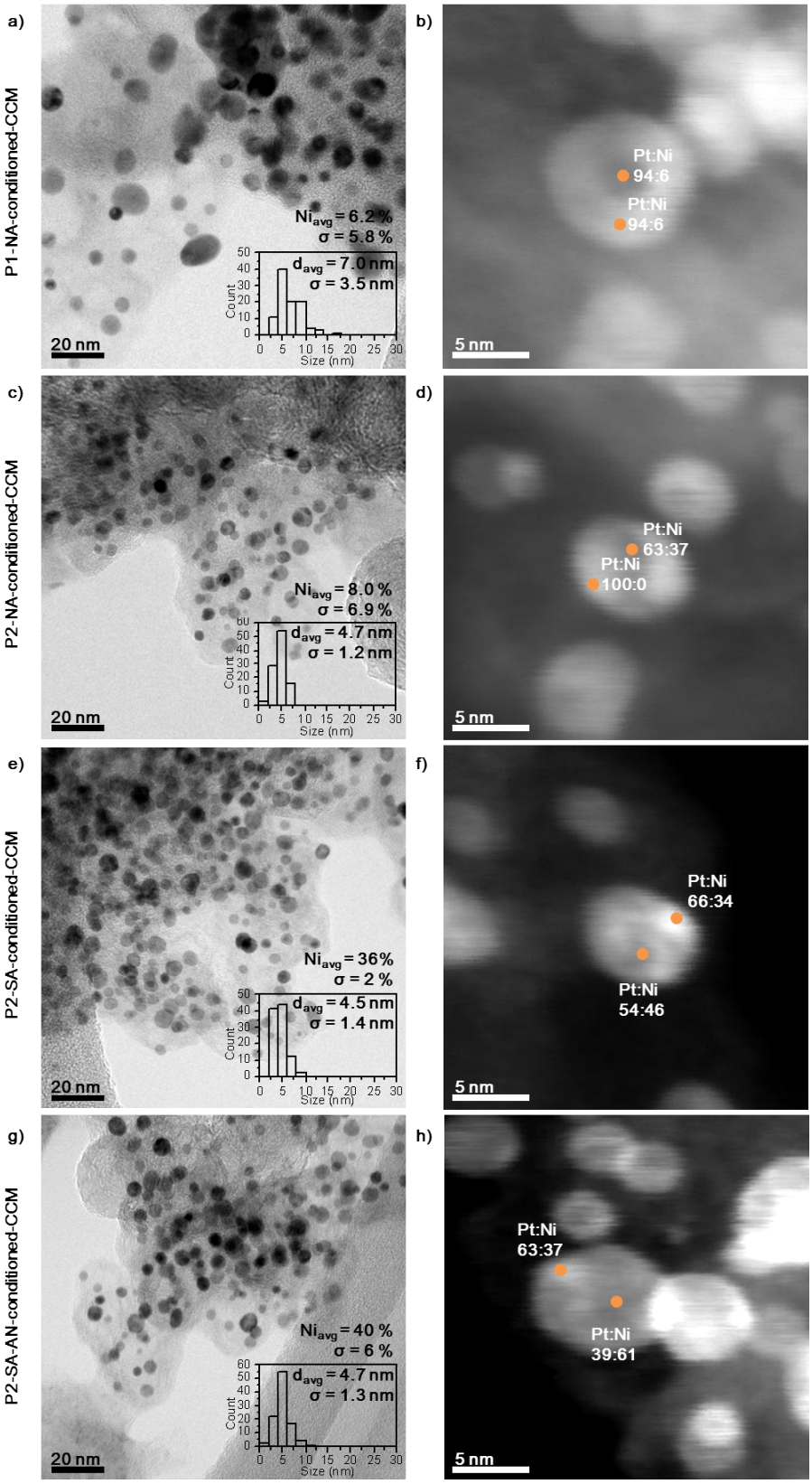

Figure S4. Bright Field diffraction contrast TEM images with PSDs, Ni atomic percentages determined from parallel-beam EDS (left) and HAADF STEM images with point mode EDS (right) for catalysts taken from conditioned MEA. (a)(b) P1-NA, (c)(d) P2-NA, (e)(f) P2-SA, (g)(h) P2-SA-AN. Here σ represents the standard deviation of PSD from at least 100 measurements and the standard deviation of EDS results among 3 different locations.

5. Analyzing the Porosity Using HAADF Images

Since the intensity in the HAADF images is proportional to the product of the thickness and Z^2 (Z being the atomic number), we can calculate the relative thickness of different positions on the Pt-Ni particles, using point EDS data and point intensity from HAADF images. Here the relative thickness is defined as $t = I / (c_{Ni}Z_{Ni}^2 + c_{Pt}Z_{Pt}^2)$, where I is the HAADF image intensity, c_{Ni} and c_{Pt} are the atomic composition of Ni and Pt, Z_{Ni} and Z_{Pt} are the atomic number of Ni and Pt.

For example, in Figure S4b, the intensity between center and edge point $I_{center}:I_{edge} = 130:195$, while the center and edge have the same Pt:Ni ratio, therefore we have $t_{center}:t_{edge} = 130:195 = 0.67:1$, implying there is a hole in the center of the particle (porosity). In contrast, in Figure S4d, although it also shows less image intensity in the center, $I_{center}:I_{edge} = 167:203$, since the center has less Pt (63 at.%) than the edge (100 at.%), the calculation shows the relative thickness $t_{center}:t_{edge} = 1.21:1$. Therefore, in Figure S4d, the center "hole-like" low-image-intensity region is caused by less Pt concentration rather than porosity.

Table S1: The relative thickness of centers and edges in all the HAADF images in this paper. The ratios below 1 implying the porosity.

		P1-NA	P2-NA	P2-SA	P2-SA-AN
$t_{center}:t_{edge}$	Pristine CCM (Figure 4)	0.49	0.86	1.43	1.18
	Conditioned MEA (Figure S1)	0.67	1.21	1.05	1.39
	30k-cycled MEA (Figure 5)	0.72	0.92	1.09	1.02

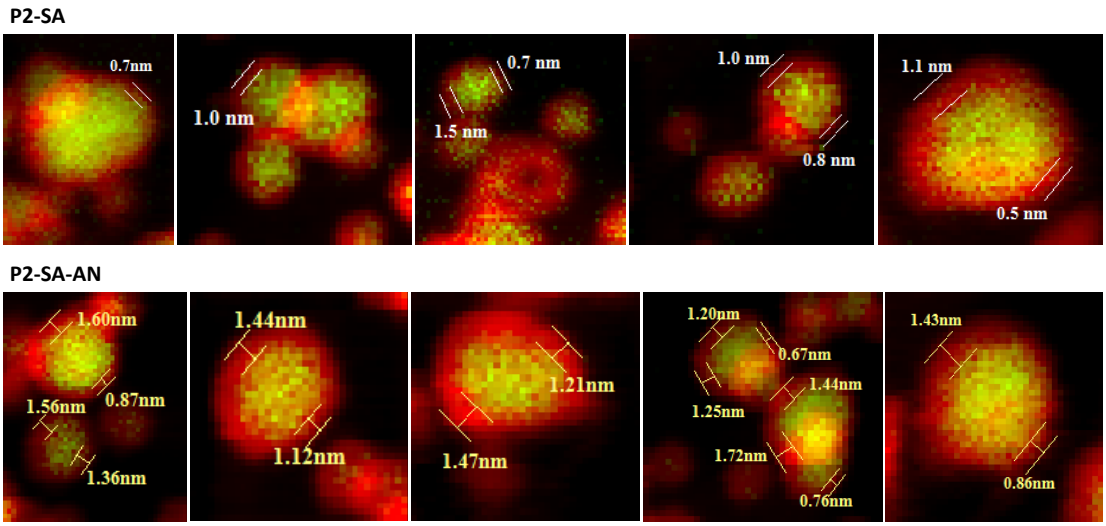

Figure S5. Typical elemental mapping images of P2-SA and P2-SA-AN for Pt shell measurements using HAADF for Pt and EELS for Ni intensities. Shown images are from conditioned MEA cathodes. Measurements were done over 100 measurements across the thickness of the cathode.