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Tailoring ionomer distribution in the catalyst layer via heteroatom-functionalization toward superior PEMFC performance

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1. Experimental

1.1 Synthesis of Pt_3Co/O-C

2 g of commercial 40 wt.% Pt_3Co/C (SSAC-4001) was mixed with 100 mL 1 M HNO_3 in a 250 mL flask. Then, the mixed solution was immersed in a pre-heated 70°C water bath and stirred for 2 h. After that, the reaction solution was filtered and washed with water until the filtrate became neutral. The obtained powder was dried in a vacuum oven at 80°C for 12 hours. Then, the obtained samples were heated at 5% H_2/Ar atmosphere and 300°C for 3h and denoted as Pt_3Co/O-C.

1.2 Synthesis of Pt_3Co/S-C

2 g of commercial 40 wt.% Pt_3Co/C (SSAC-4001) was mixed with 5 g thiourea and 10 g deionized water in a 50 ml mill pot. The pot was ground in a planetary ball mill at 1000 rpm for 2 h. Then, the slurry was turned into solid powder through a freeze-dryer. Finally, the obtained solid powder was heated at 5% H_2/Ar atmosphere and 300°C for 3h and washed twice with water. The obtained catalyst is denoted as Pt_3Co/S-C.

1.3 Synthesis of Pt_3Co/N-C

2 g of commercial 40 wt.% Pt_3Co/C (SSAC-4001) was mixed with 5 g urea and 10 g deionized water in a 50 ml mill pot. The pot was ground in a planetary ball mill at 1000 rpm for 2 h. Then, the slurry was turned into solid powder through a freeze-dryer. Finally, the obtained solid powder was heated at 5% H_2/Ar atmosphere and 300^{o}C for 3h and washed twice with water. The obtained catalyst is denoted as Pt_3Co/N-C.

1.4 Morphological and structural characterization

The X-ray diffraction (XRD) patterns were obtained by a Rigaku D/max-2500B2+/PC powder XRD, using Kα radiation (λ = 1.5406 Å) in a 2θ angle range 5-90°at room temperature. The size of the nanoparticles was calculated according to Sherrer Equation (1):

$$D=\kappa\lambda/B\cos\theta \quad (1)$$

where D is the average size of the grain perpendicular to the direction of the grain plane (nm). B is the half-height width of the diffraction peak (rad). K is Scherer's constant (0.89). θ is the diffraction Angle. λ is the X-ray wavelength (0.154056 nm). Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) (FEI TecnaiG2F20) were performed to evaluate the crystal structure. The X-ray photoelectron spectroscopy (XPS) was carried out by Thermo Electron Corporation ESCALAB 250 XPS spectrometer.

1.5 Ring-disk electrode (RDE) measurements

RDE measurements were performed using a CHI Electrochemical Station (Model 760) in a three-electrode electrochemical cell at room temperature. Ag/AgCl was used as a reference electrode and Pt foil was used as a counter electrode. In this work, all measured potentials were converted to a reversible hydrogen electrode (RHE) according to Equation (2).

$$E(RHE)=0.059*pH + 0.098 +E(Ag/AgCl) \quad (2)$$

where RHE is the reversible hydrogen electrode and Ag/AgCl is the reference electrode.

The catalyst ink was prepared by sonicating the mixture of 5 mg catalyst and 40 μL (5 wt%) Nafion in 5 mL isopropanol. Then, the ink was drop-coated onto the working electrode (a glassy carbon disk with a diameter of 5.0 mm) with Pt loading of 15-20 μg cm^{-2} and dried at room temperature

in air. After drying, the catalysts were electrochemically activated by cyclic voltammetry (CV) scanning between 0.06 and 0.8 V at 50 mV s^{-1} in N_2-saturated 0.1 M $HClO_4$ solution (around 50 cycles). Then the linear scanning voltammetry (LSV) curves were obtained from 0.06 V to 1.0 V at 5 mV s^{-1} in O_2-saturated 0.1 M $HClO_4$ with the rotating speed at 1600 rpm.

1.6 Membrane electrode assembly (MEA) preparation

The cathode catalyst ink was made by mixing the catalysts with the ionomer solution (D2020) and a water-n-propanol solvent mixture (the n-propanol to water ratio was 4), followed by sonicating the dispersion in ice water for 30 min. The ionomer-to-carbon ratio (I/C) of 0.9 was screened to obtain optimal performance. The catalyst-coated-membrane (CCM with an active area of 25 cm^2) was prepared on a Nafion membrane (GORE, 12 μm) with ultrasonic spray equipment. The Pt loadings of all MEAs at the cathode and anode were controlled to be 0.15 and 0.05 mg_{Pt} cm^{-2}, respectively.

1.7 Proton exchange membrane fuel cell testing

Fuel cell tests were performed on the Scribner 850e fuel cell test stand linked with a Scribner 885 potentiostat. After activation, the H_2-O_2 polarization curve was set at 80°C, 100% RH, 0.5 bar, and the stoichiometric ratio of H_2/O_2 was set at 1.5/1.5. The H_2-air polarization curve was set at 80 °C, 100% RH, 0.5 bar, and the stoichiometric ratio of H_2/O_2 was set at three different conditions, as 1.5/1.5, 1.5/2.5, and 1.5/3.5. Tafel plots were used to calculate the mass activity and tested at 80 °C, 100% RH, 0.5 bar, H_2/O_2 at flow rates of 0.2/0.5 L min^{-1}. Electrochemical surface area (ECSA) was measured using the hydrogen underpotential deposition method and cyclic voltammetry curves were recorded in a range between 0.1 V and 0.8 V vs RHE at 100 mV/s.

The accelerated durability test in MEA was carried out using a square wave voltage from 0.6 to 0.95 V with a duration of 3s at each voltage level, according to the US DOE MEA accelerated durability test protocol for catalysts. Each test was run up to 30,000 cycles at 80°C, 100% RH, with H_2/N_2 flow 200/75 sccm for the anode and cathode, respectively.

2. Supplemental Figures

Table. S1. Particle Size of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C and Pt_3Co/N-C.

Sample	Particle Size (nm)	
	TEM	XRD
Pt_3Co/C	3.9	4.0
Pt_3Co/O-C	4.1	4.1
Pt_3Co/S-C	4.0	4.0
Pt_3Co/N-C	4.0	4.1

Table. S2. The Pt content of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C and Pt_3Co/N-C.

Sample	ICP Pt Content (wt%)
Pt_3Co/C	38.6
Pt_3Co/O-C	38.2
Pt_3Co/S-C	38.6
Pt_3Co/N-C	38.4

Table. S3. Heteroatomic content of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C and Pt_3Co/N-C.

Sample	Heteroatomic Content (at%)		
	O	S	N
Pt_3Co/C	0.92	0.61	0.79
Pt_3Co/O-C	3.22	0.48	0.95
Pt_3Co/S-C	0.99	1.56	0.78
Pt_3Co/N-C	0.83	0.59	2.96

Table. S4. ECSA via CO stripping at 20 % RH and 100% RH of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C, and Pt_3Co/N-C.

Sample	$ECSA_{CO\text{-}20\%RH}$ ($m^2\ g_{pt}^{-1}$)	$ECSA_{CO\text{-}100\%RH}$ ($m^2\ g_{pt}^{-1}$)	$ECSA_{CO\text{-}20\%RH}$/ $ECSA_{CO\text{-}100\%RH}$
Pt_3Co/C	8.49	50.73	16.74%
Pt_3Co/O-C	25.45	60.73	41.91%
Pt_3Co/S-C	15.85	57.03	27.79%
Pt_3Co/N-C	32.05	69.35	46.21%

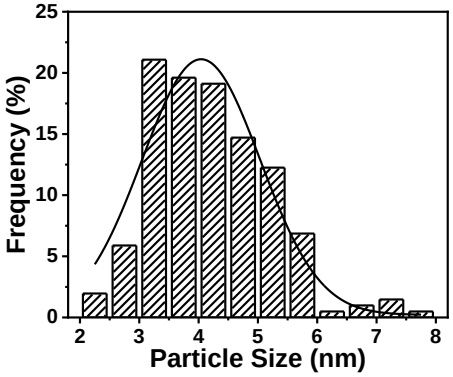

Fig. S1. Histogram of the particle size distribution of Pt_3Co/N-C.

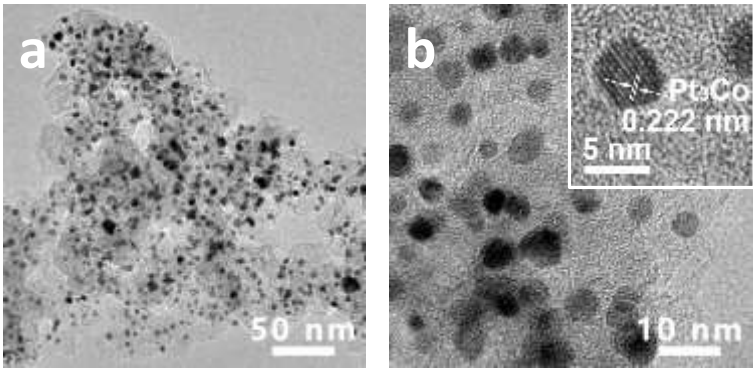

Fig. S2. TEM images of Pt_3Co/C.

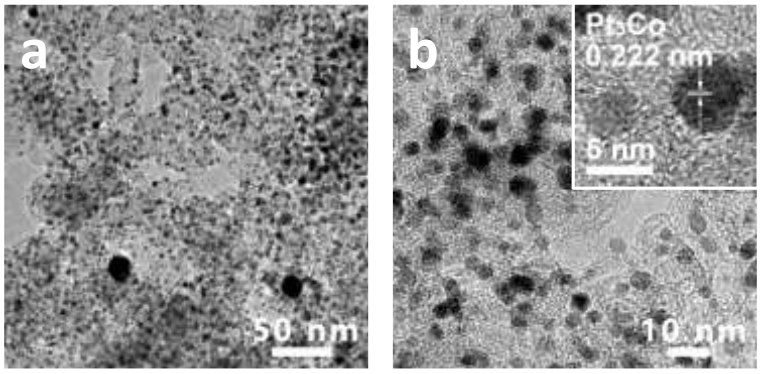

Fig.S3. TEM images of Pt_3Co/O-C.

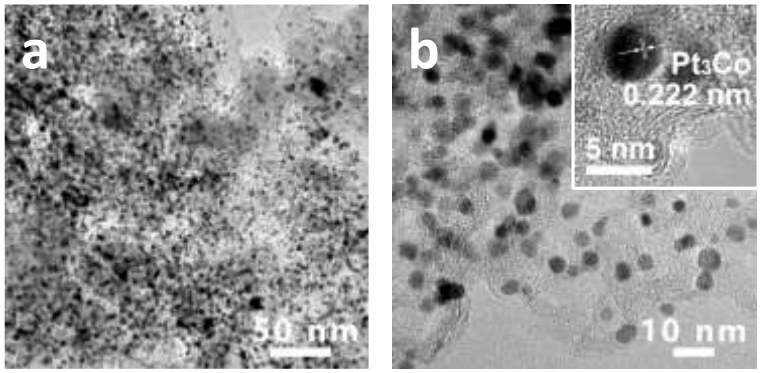

Fig. S4. TEM images of Pt_3Co/S-C.

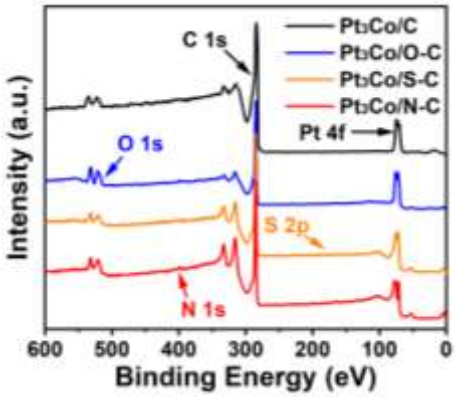

Fig. S5. XPS survey spectrum of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C, and Pt_3Co/N-C.

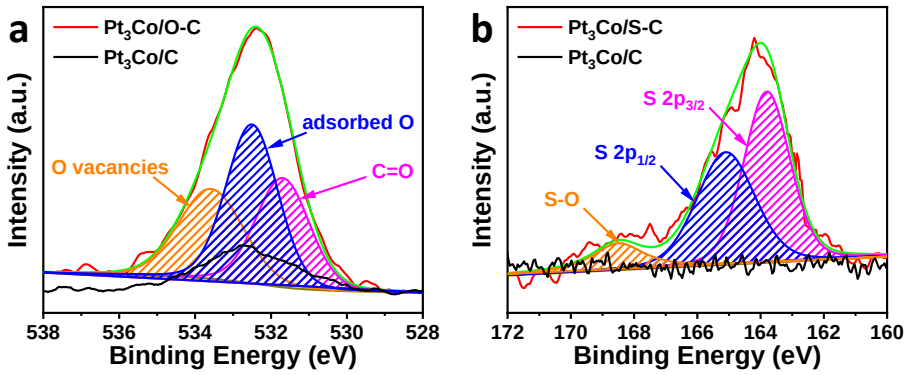

Fig. S6. (a) O 1s spectra of Pt_3Co/O-C, and Pt_3Co/C. (b) S 2p spectra of Pt_3Co/S-C, and Pt_3Co/C.

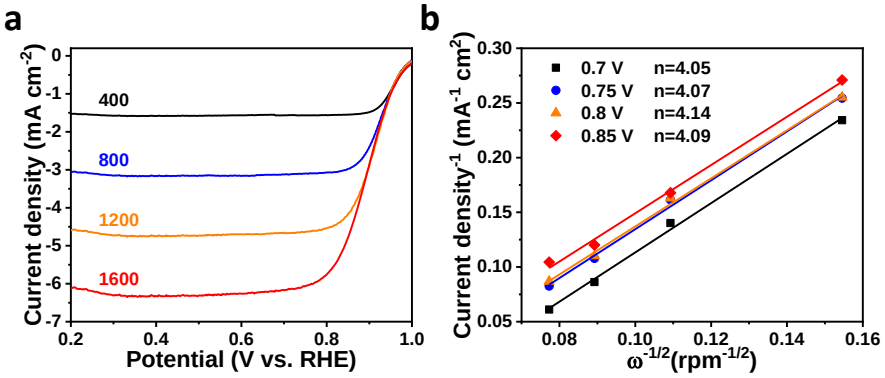

Fig. S7. (a) LSV curves at different rotation rates and (b) the corresponding K–L plots of Pt_3Co/N-C.

The calculation of the number of exchanged electrons (n):

The RDE tests were measured at various rotating speeds from 400 to 1600 rpm with a sweep rate of 5 $mV \cdot s^{-1}$. The electron transfer number (n) and kinetic current density (J_k) can be calculated from the Koutecky-Levich (K-L) Equation (3) and (4):

$$1/J = 1/J_L + 1/J_k = 1/(B\,\omega^{1/2}) + 1/J_k \quad (3)$$

$$B = 0.62\ n\ F\ C_0\ D_0^{2/3}\ V^{-1/6} \quad (4)$$

where J is the measured current density, ω is the angular velocity of the disk, n is the electron transfer number, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.26×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 0.1 M $HClO_4$ (1.93×10^{-5} $cm^2\ s^{-1}$), and V is the kinematic viscosity of the electrolyte (0.01 $cm^2\ s^{-1}$).

The mass-related kinetic current density (J_k) of the catalyst at 0.9 V vs. RHE was calculated according to Equation (5):

$$J_k = J \times J_L/((J_L - J) \times L_{Pt}) \quad (5)$$

where J, J_L, and L_{Pt} represent the measured current density, the diffusion-limited current density, and Pt loading, respectively. Capacitance-correction and IR-correction were performed for the MA calculation in 0.1 M $HClO_4$ solution from 0.1 Hz to 10,000 Hz with an amplitude of 5 mV, the initial potential was set as 0.05 V.

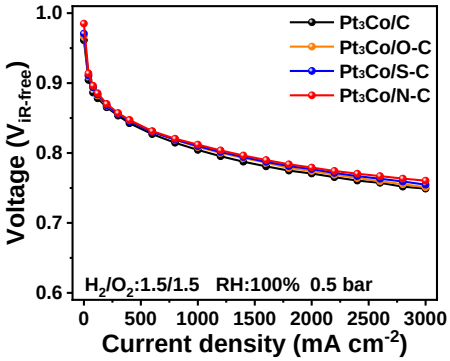

Fig. S8. Polarization curves with HFR corrected of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C, and Pt_3Co/N-C with O_2 as cathode feed at 1.5 stoichiometric ratios.

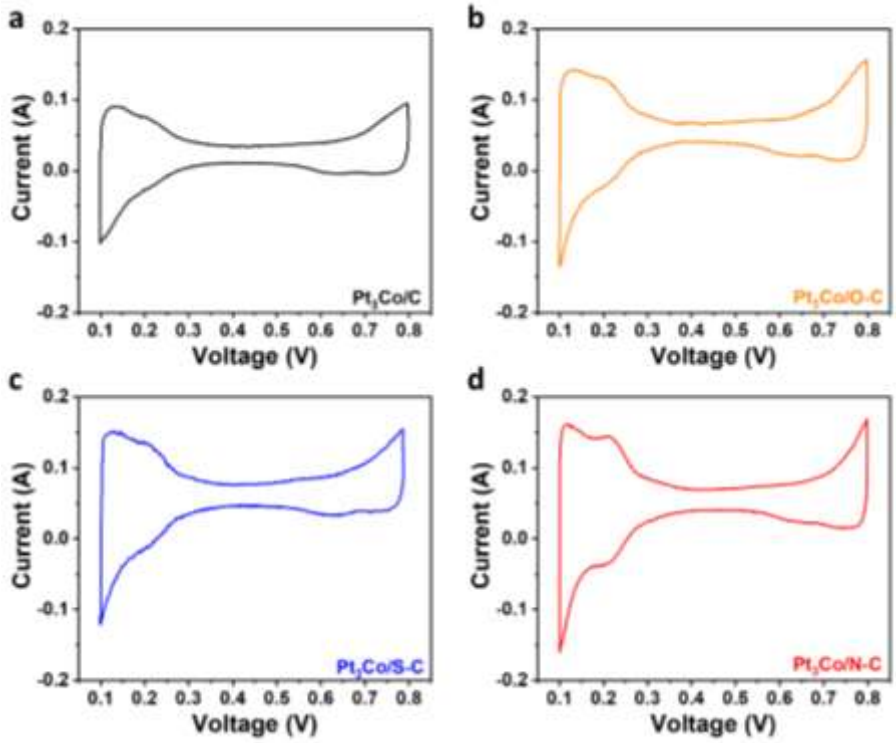

Fig. S9. Evaluation of hydrogen underpotential deposition by PEMFC.

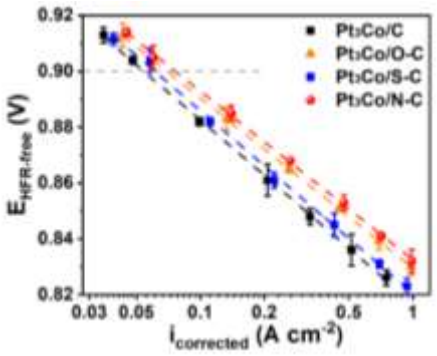

Fig. S10. Tafel slopes of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C, and Pt_3Co/N-C evaluated by PEMFC at 80°C, 100% RH, 0.5 bar, H_2/O_2 at flow rates of 0.2/0.5 L min^{-1}, and the values of Tafel slopes were calculated at 0.9 V.

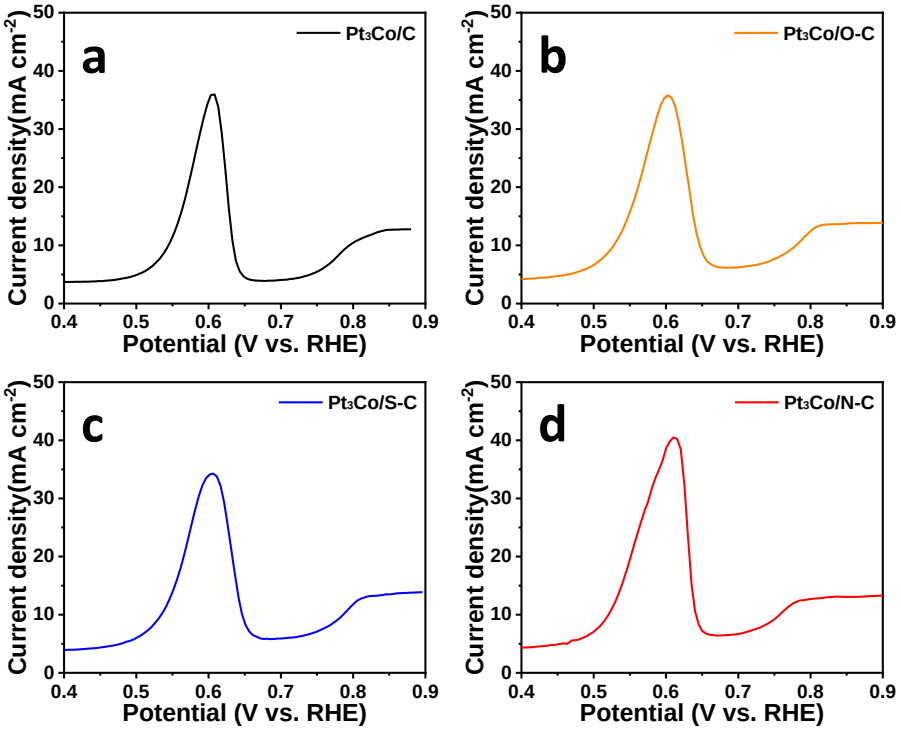

Fig. S11. ECSA via CO stripping of (a) Pt_3Co/C, (b) Pt_3Co/O-C, (c) Pt_3Co/S-C, and (d) Pt_3Co/N-C at 80 °C, 100% RH, 0.5 bar, H_2/N_2 at flow rates of 0.2/0.005 L min^{-1}.

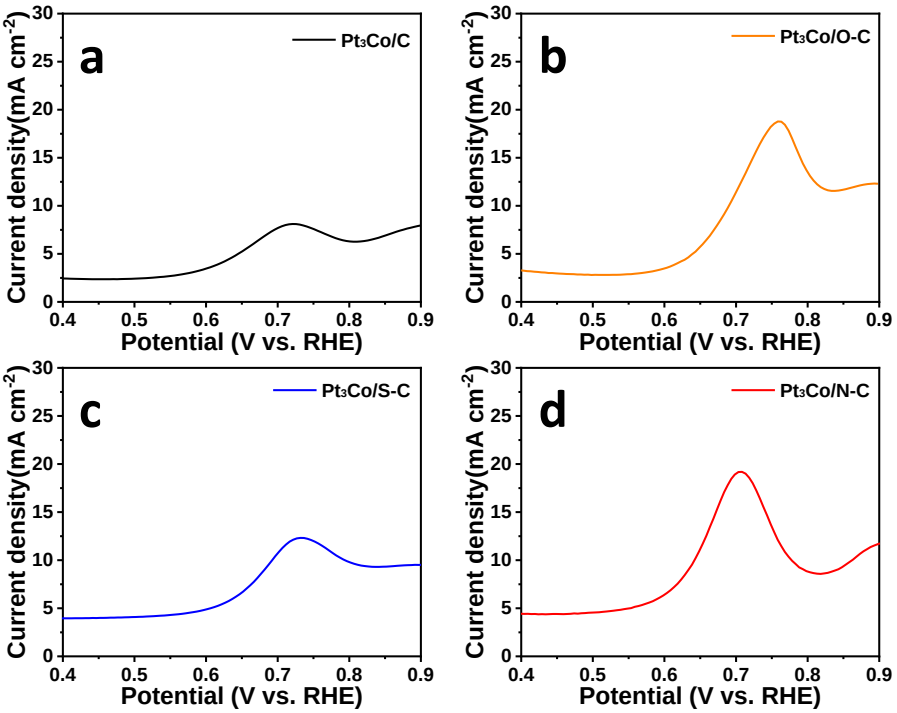

Fig. S12. ECSA via CO stripping of (a) Pt_3Co/C, (b) Pt_3Co/O-C, (c) Pt_3Co/S-C, and (d) Pt_3Co/N-C at 80 °C, 20% RH, 0.5 bar, H_2/N_2 at flow rates of 0.2/0.005 L min^{-1}.

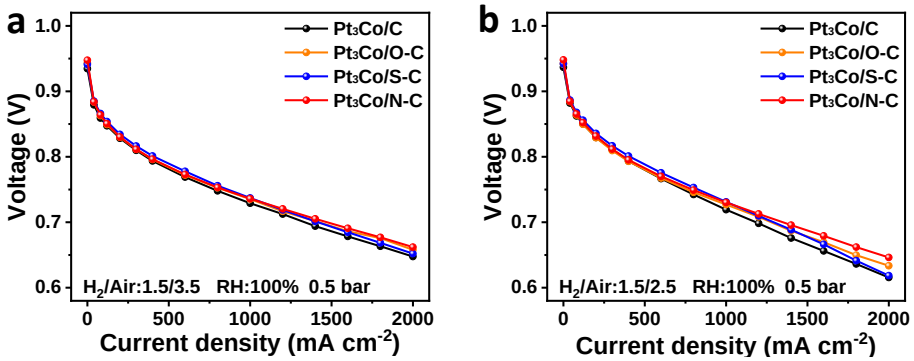

Fig. S13. Polarization curves of Pt_3Co/C, Pt_3Co/O-C, Pt_3Co/S-C, and Pt_3Co/N-C with air as cathode feed at (a) 3.5 and (b) 2.5 stoichiometric ratio.

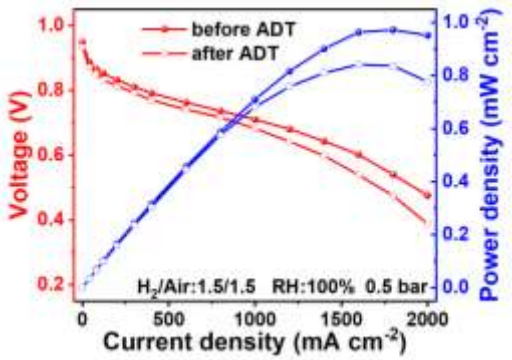

Fig. S14. Polarization curves and power density curves of Pt_3Co/N-C before and after 30000 cycles square wave accelerated stress test.