Supporting Information

Breaking the Volcano-Plot Limits for Pt-based Electrocatalysts by Selective Tuning Adsorption of Multiple Intermediates

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Experimental Section

Chemicals and materials. Commercialized Pt/C (20 wt.%), PtM/C (20 wt.%, M = Fe, Co, Ni) were purchased from FuelCellStore without further treatment. All the other chemicals used in the experiments were purchased from Sigma-Aldrich Co. LLC.

Fabrication of electrocatalysts. The acid-treated PtM/C samples were fabricated by mixing 10 mg of PtM/C with 30 mL of HClO₄ solution (0.1 M) followed by overnight stirring. The products were then washed several times with deionized water and freeze-dried. The annealed PtM/C samples were fabricated by annealing 10 mg of PtM/C under 900 °C for 5 hours in H₂/Ar (H₂=5 vol.%) atmosphere.

Characterization of materials. Scanning transmission electron microscopy (STEM) images were collected on a Titan G2 80-200 Field-Emission-Gun electron microscope. The Pt L₃ edge X-ray adsorption fine structure (XAFS) spectra of various Pt-based alloys were recorded in transmission mode (Si 111) under mode 2 (8.5 - 18.5 keV) at the Australian Synchrotron. The data were normalized and analyzed using Athena and Artemis. The composition of the dealloyed samples are measured by an Agilent 7900x inductively coupled plasma mass spectrometer (ICP-MS).

The d-band vacancies calculation. The d-band vacancies of Pt in all the alloys and Pt/C samples were calculated using the following equation:

$$(h_J)_{total, sample} = (1 + f_d)(h_J)_{total, reference}$$

where h_J refers to the total number of unoccupied d-states for Pt. The h_J for standard Pt foil reference has been evaluated to be 0.3, and f_d is:

$$f_d = (\Delta A_3 + 1.11\Delta A_2)/(A_{3r} + 1.11A_{2r})$$

where ΔA is:

$$\Delta A = A_s - A_r$$

The term A represents the areas under XANES adsorption edge. The number refers to the L_2 or L_3 absorption edge, 'r' refers to reference material, and 's' refers to the sample.

Electrochemical testing setup. All the electrochemical data were recorded on a CHI 760E bipotentiostat (CH Instruments, INC.). The powdered electrocatalysts were dispersed in distilled water containing 0.05 wt.% of Nafion to form a 2.0 mg/mL homogeneous ink gel. The working electrode was prepared by adding 20 μ L of the ink gel onto the glassy carbon rotating disk electrode (RDE, surface area of the glassy carbon = 0.196 cm², Pine Research Instrumentation) and dried at room temperature. The reference electrode was an Ag/AgCl in 4 M KCl solution. The counter electrode was a pure gold wire. All the potentials were referenced to reversible hydrogen electrode (RHE) by using pure hydrogen calibration and all polarization curves were iR corrected. A flow of Argon was maintained over all the cyclic voltammograms (CVs) tests, while a flow of H₂ was purged during obtaining all the polarization curves. During all the tests, the working electrode was rotated at 1600 rpm. A special cell with water jacket from Pine Research Instrumentation was used for all the tests to achieve controllable temperature.

Exchange current density. The kinetic current densities are worked out through the equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \#$$

where j, j_k and j_d are the measured current, kinetic current and diffusion limit current, respectively. The HER current is commonly considered not limited by H⁺ transport, therefore, the diffusion current is not counted into the calculation. The j_0 of HER was obtained by fitting j_k into the Butler-Volmer equation:

$$j_k = j_0 \left[\exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(\frac{(\alpha - 1)F \eta}{RT}\right) \right] \#$$

where α is the transfer coefficient, η is the overpotential, F is Faraday's constant, R is the universal gas constant and T is the thermodynamic temperature.

ECSA calculation. The ECSA could be calculated using the function below:

$$ECSA_{(m^2/g, metal)} = \frac{Q_{CO}}{M_{metal} \times Q_{CO}^{theo}}$$

In the equation, Q_{CO} is the CO stripping charge, M_{metal} is the mass loading of the metal on the working electrode. Q_{CO} ^{theo} is the theoretical value of Q_{CO} , which is 420 μ C/cm² for a two-electron transfer of one CO molecule to a CO₂ per electrocatalyst atom. The as calculated ECSA of Pt is 92 m²/g_{metal}, within the reported range of Pt ECSA. The detailed ECSAs of Pt/C and other Pt based samples are as Table S2. Before CO stripping, a few cycles of CVs was run for each sample to clear the electrochemical surface. The CO stripping process was conducted in 0.1 M KOH using RDE. CO adsorption was under potential control at 0.06 V/RHE, followed by two cycles of CVs at 0.05 V/s to determine CO-based ECSA.

The activation energy (E_a) measurement and calculation. The E_a of the samples are acquired through the natural logarithm of Arrhenius' equation.

$$\ln(k) = \frac{-Ea}{R} \left(\frac{1}{T}\right) + \ln(A)$$

Where k is the rate constant, T is the absolute temperature in kelvin, R is the universal gas constant, A is the pre-exponential factor and E_a is the activation energy. In this work, we considering k as the j_0 of each reaction, and a relationship between j_0 and the temperature of the reaction can be established. The HER polarization curves of each sample were measured under 4 different temperatures (10 °C, 25 °C, 40 °C, 55 °C) in a water jacket cell with H₂ purging. The corresponding j_0 was then acquired by fitting j_k into the Butler-Volmer equation. As a result, a linear relationship could be built between 1/T and ln j_0 . The slope of the plot is considered as $-E_a/R$, from where E_a could be easily calculated. The similar process had been used to acquire the E_a of all the other samples in different solutions.



Fig. S1 HAADF-STEM images of (a) PtFe alloy nanoparticle (b) dealloyed PtFe nanoparticle (c) Fe nanoparticle with Pt skin. (d) PtNi alloy nanoparticle (e) dealloyed PtNi nanoparticle (f) PtNi nanoparticle with Pt skin.



Fig. S2 EDS mapping images of PtM bimetallic samples.



Fig. S3 XRD spectra of the Pt-based samples.



Fig. S4 Pt L_{III} -edge XANES spectra of (a) Fe (b) Ni samples. Pt L_{II} -edge XANES spectra of (c) Fe (d) Ni samples.



Fig S5 CO stripping of PtM samples in 1M KOH. The CO was fully pre-adsorbed on the electrocatalysts by immersing the electrode in 1 M KOH saturated with CO under potential control of 0.06 V (vs. RHE) for 20 minutes.



Fig S6 CO stripping of PtM samples in 0.5 M KOH. The CO was fully pre-adsorbed on the electrocatalysts by immersing the electrode in 0.5 M KOH saturated with CO under potential control of 0.06 V (vs. RHE) for 20 minutes.



Fig. S7 CO stripping investigation on various electrocatalysts in 0.1 M KOH. The CO was fully preadsorbed on the electrocatalysts by immersing the electrode in 0.1 M KOH saturated with CO under potential control of 0.06 V (vs. RHE) for 20 minutes.



Fig. S8 HER polarization curves of (a) PtFe-containing samples and (b) PtCo-containing samples and (c) PtNi-containing samples in 0.01 M KOH solution with their corresponding Tafel plots (d-f). The dotted lines indicate Butler-Volmer fitting results.



Fig. S9 HER polarization curves of (a) PtFe-containing samples and (b) PtCo-containing samples and (c) PtNi-containing samples in 1 M KOH solution.



Fig S10 The experimentally acquired relationship between the d-band vacancies and j_0 for a series of Pt based materials in 0.5M KOH.



Fig S11 HER activity of PtM samples in 0.5 M KOH



Fig. S12 (a), (d), (g), (j) HER polarization curves of the Pt and Pt alloy samples and their corresponding experimental Tafel plots (b), (e), (h), (k). The dotted lines indicate Butler-Volmer fitting results. (c), (f), (i), (l) the relationship between the reaction temperature and j_0 of the corresponding alloy electrocatalysts. All the tests were carried out in 1 M KOH solution.



Fig. S13 (a), (d), (g) HER polarization curves of the Pt dealloyed samples and their corresponding experimental Tafel plots (b), (e), (h). The dotted lines indicate Butler-Volmer fitting results. (c), (f), (i) the relationship between the reaction temperature and j_0 of the corresponding dealloyed electrocatalysts. All the tests were carried out in 1 M KOH solution.



Fig. S14 (a), (d), (g) HER polarization curves of the samples with Pt skin and their corresponding experimental Tafel plots (b), (e), (h). The dotted lines indicate Butler-Volmer fitting results. (c), (f), (i) the relationship between the reaction temperature and j_0 of the corresponding Pt skinned electrocatalysts. All the tests were carried out in 1 M KOH solution.



Fig. S15 (a), (d), (g), (j) HER polarization curves of the Pt and Pt alloy samples and their corresponding experimental Tafel plots (b), (e), (h), (k). The dotted lines indicate Butler-Volmer fitting results. (c), (f), (i), (l) the relationship between the reaction temperature and j_0 of the corresponding alloy electrocatalysts. All the tests were carried out in 0.1 M KOH solution.



Fig. S16 (a), (d) HER polarization curves of the Pt dealloyed samples and their corresponding experimental Tafel plots (b), (e). The dotted lines indicate Butler-Volmer fitting results. (c), (f) the relationship between the reaction temperature and j_0 of the corresponding dealloyed electrocatalysts. All the tests were carried out in 0.1 M KOH solution.



Fig. S17 (a), (d), (g) HER polarization curves of the samples with Pt skin and their corresponding experimental Tafel plots (b), (e), (h). The dotted lines indicate Butler-Volmer fitting results. (c), (f), (i) the relationship between the reaction temperature and j_0 of the corresponding Pt skinned electrocatalysts. All the tests were carried out in 0.1 M KOH solution.



Fig. S18 (a) CO stripping of PtFe-containing bimetallic samples in 0.1 M KOH solution, (b) CVs of PtFe-containing bimetallic samples in 0.1 M KOH.



Fig. S19 Fitted EXAFS spectra of the Pt alloy samples. Left: Forward Fourier transform of the EXAFS after correction for phase shifts. Right: Fits in K-space for the Pt alloy samples.



Fig. S20 Fitted EXAFS spectra of the Pt dealloyed samples. Left: Forward Fourier transform of the EXAFS after correction for phase shifts. Right: Fits in K-space for the Pt alloy samples.



Fig. S21 Fitted EXAFS spectra of the samples with Pt skin. Left: Forward Fourier transform of the EXAFS after correction for phase shifts. Right: Fits in K-space for the Pt alloy samples.



Fig S22 The relationship between the OH interaction ability and the HER activity of the catalysts in 0.1 M KOH, (a) PtFe, (b) PtCo and (c) PtNi series. No obvious relationship between the two parameters can be found.

	Pt	PtFe	PtCo	PtNi	dealloyed PtFe
d-band vacancies	0.28286	0.28054	0.28242	0.28369	0.27987
	dealloyed PtCo	dealloyed PtNi	PtFe with	PtCo with	PtNi with
			Pt skin	Pt skin	Pt skin
d-band vacancies	0.28157	0.28761	0.28455	0.28246	0.28689

 Table S1. The d-band vacancies of the Pt-based bimetallic samples.

Table S2. ECSAs of the Pt based samples.

	PtC	PtFe	PtCo	PtNi	dealloyed PtFe
$\frac{\text{ECSA}}{(\text{m}^2/\text{g}_{\text{metal}})}$	92	87	90	82	45
	dealloyed PtCo	dealloyed PtNi	PtFe with Pt	PtCo with Pt	PtNi with Pt
			skin	skin	skin
ECSA	43	50	58	82	52
(m^2/g_{metal})					

Coordination	EXAFS	Fe		Со			Ni			
shell	parameter	Alloy	Dealloy	Pt skin	Alloy	Dealloy	Pt skin	Alloy	Dealloy	Pt skin
R factor		0.0019	0.0026	0.002	0.0031	0.004	0.0038	0.0009	0.001	0.0009
Pt-Pt	R (Å)	2.70(8)	2.70(6)	2.71(1)	2.70(4)	2.70(7)	2.70(2)	2.69(5)	2.69(6)	2.69(5)
	CN	6.24(8)	6.90(6)	8.02(3)	8.02(7)	9.22(0)	9.75(7)	7.97(8)	8.10(5)	7.60(4)
	$\Delta \sigma^2$	0.0075	0.00667	0.0061	0.00788	0.00806	0.0068	0.00806	0.00796	0.00601
	$\Delta E_0(eV)$	4.091	4.528	4.616	3.898	3.424	4.888	3.998	3.61	5.113
Pt-M	R (Å)	2.66(9)	2.67(2)	2.66(7)	2.65(7)	2.66(4)	2.64(4)	2.64(0)	2.65(3)	2.62(2)
	CN	2.39(3)	2.65(9)	5.12(2)	2.20(6)	2.34(9)	5.04(7)	2.75(2)	2.42(9)	4.69(0)
	$\Delta \sigma^2$	0.00774	0.00743	0.00688	0.00913	0.00862	0.00874	0.00912	0.00889	0.00744
	$\Delta E_0(eV)$	8.371	8.055	7.082	9.926	9.387	7.276	9.997	9.687	7.014
Pt-O	R (Å)	2.00(4)	2.00(2)	2.01(6)	2.00(2)	2.00(4)	1.96(6)	1.99(7)	2.00(1)	\
	CN	1.25(2)	2.06(5)	0.42(6)	1.36(0)	2.23(2)	0.82(1)	1.17(9)	2.27(2)	\
	$\Delta \sigma^2$	0.0068	0.00568	0.00304	0.00318	0.00463	0.00134	0.00383	0.00485	\
	$\Delta E_0(eV)$	9.395	9.629	9.192	9.946	9.734	2.601	7.714	9.877	\

Table S3. EXAFS fitting results for the Pt-based bimetallic samples.