Electronic supplementary information

Origin of the N-coordinated single-atom Ni sites in heterogeneous electrocatalysts for CO_2 reduction reaction

Yu Wang,[a] Liming You[a] and Kun Zhou*[ab]

[a] Environmental Process Modelling Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 CleanTech Loop, Singapore 637141, Singapore.

[b] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

* kzhou@ntu.edu.sg (KZ)

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1. Supporting Figures

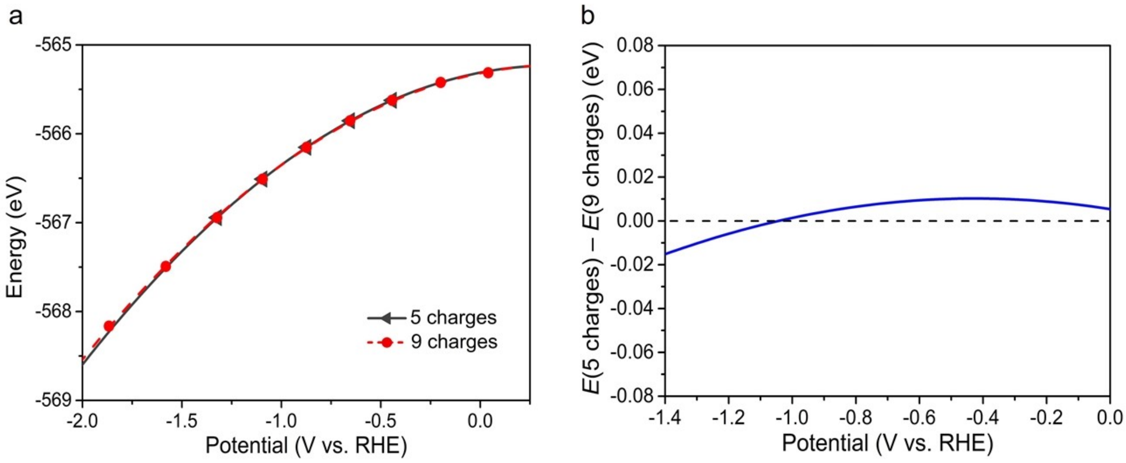

Figure S1. (a) Total energy of clean β-NiN_4 as a function of electrode potential, where the five charge (black) and nine charge (red) samplings are adopted. (b) Energy difference between the two samplings. It can be found that the energy difference is less than 0.01 eV over a wide range of electrode potentials.

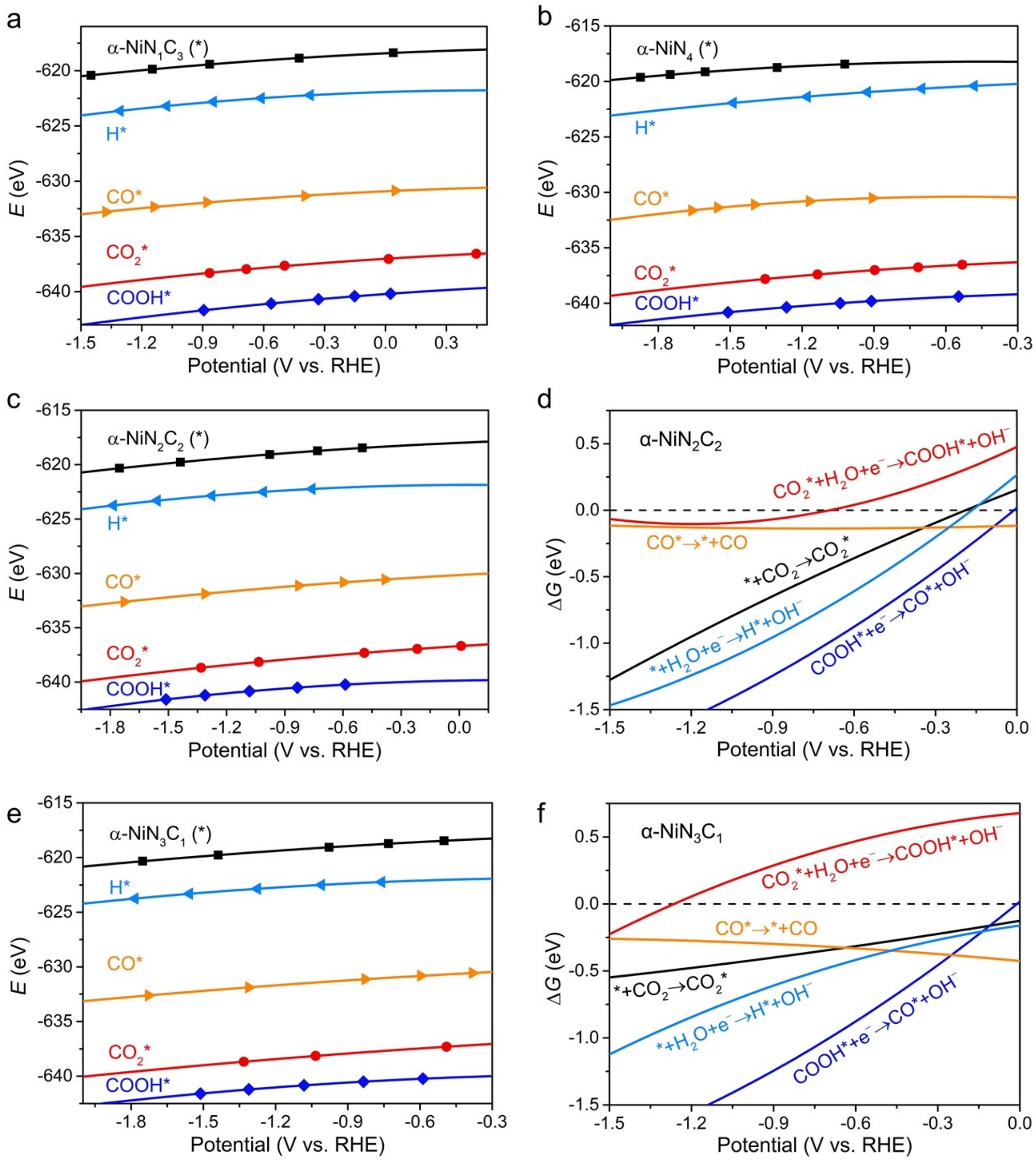

Figure S2. Total energy of the reaction species of (a) α-NiN_1C_3, (b) α-NiN_4, (c) α-NiN_2C_2, and (e) α-NiN_3C_1 as a function of electrode potential. Free energy changes ΔG of the reaction steps of (d) α-NiN_2C_2 and (f) α-NiN_3C_1 as a function of electrode potential.

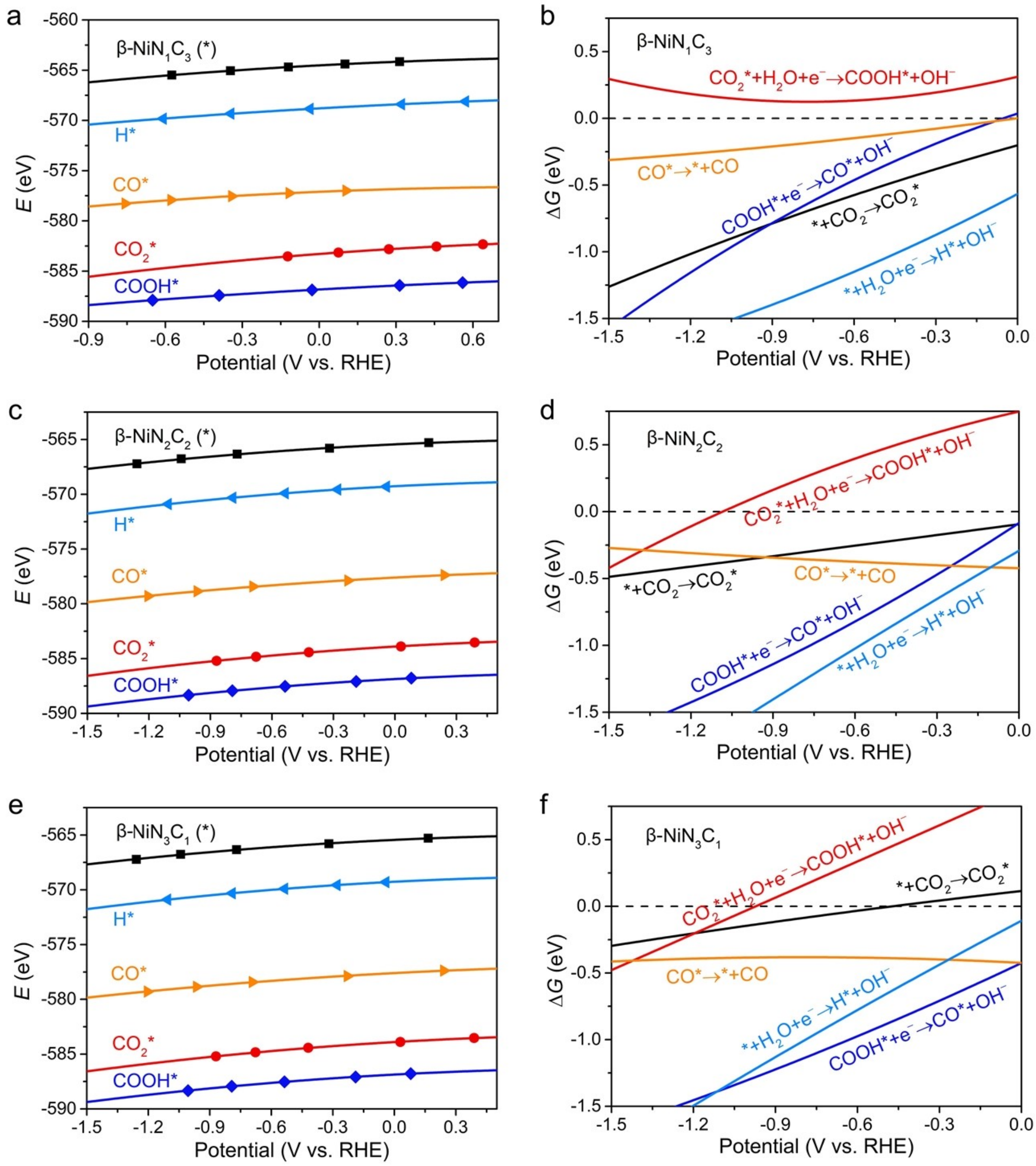

Figure S3. Total energy of the reaction species of (a) β-NiN_1C_3, (c) β-NiN_2C_2, and (e) β-NiN_3C_1 as a function of electrode potential. Free energy changes ΔG of the reaction steps of (b) β-NiN_1C_3, (d) β-NiN_2C_2, and (f) β-NiN_3C_1 as a function of electrode potential.

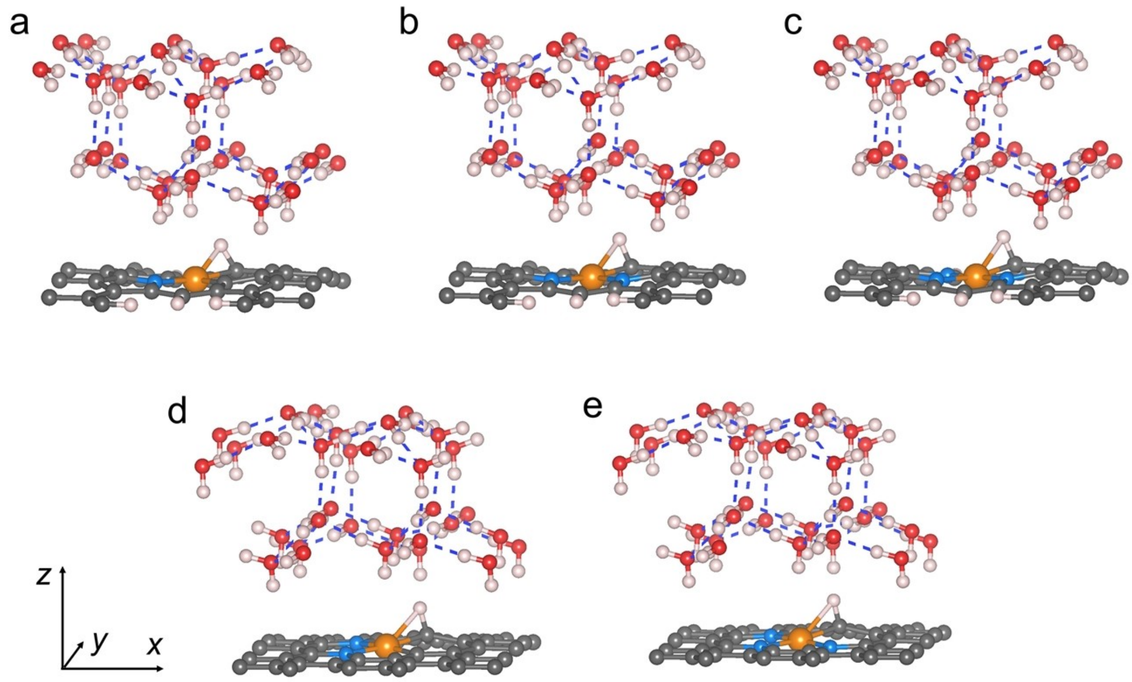

Figure S4. Views of H* adsorbed on (a) β-NiN_1C_3, (b) β-NiN_2C_2, (c) β-NiN_3C_1, (d) α-NiN_2C_2, and (e) α-NiN_3C_1. It can be found that these hybrid moieties prefer the bridge configuration that exhibits a strong binding to H*.

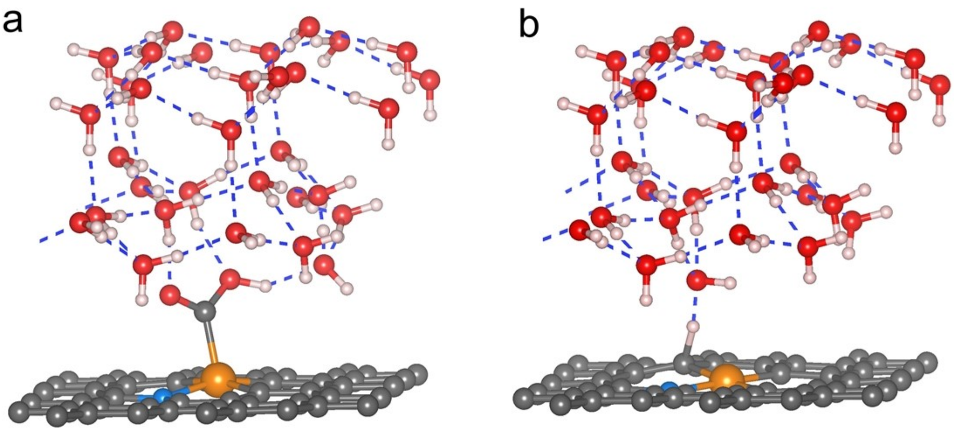

Figure S5. Views of the geometrical structures of transition states for (a) the conversion of CO_2* to COOH* and (b) the formation of H*.

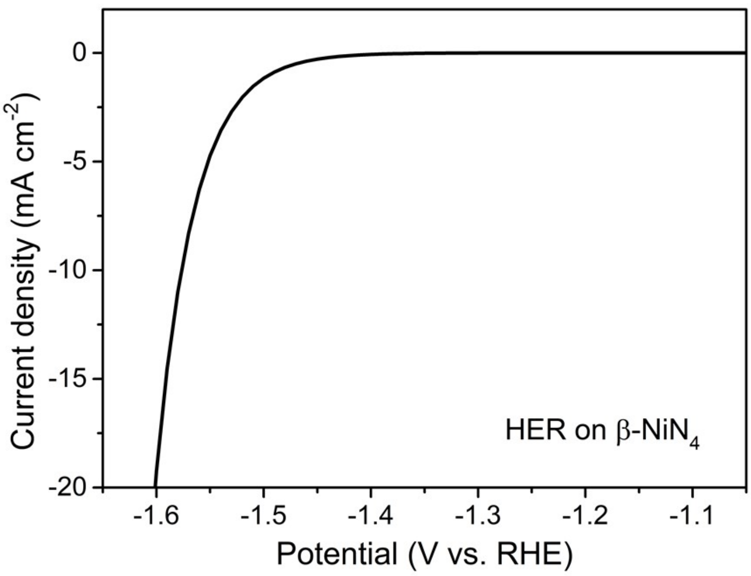

Figure S6. Simulated polarization curve of HER on β-NiN_4.

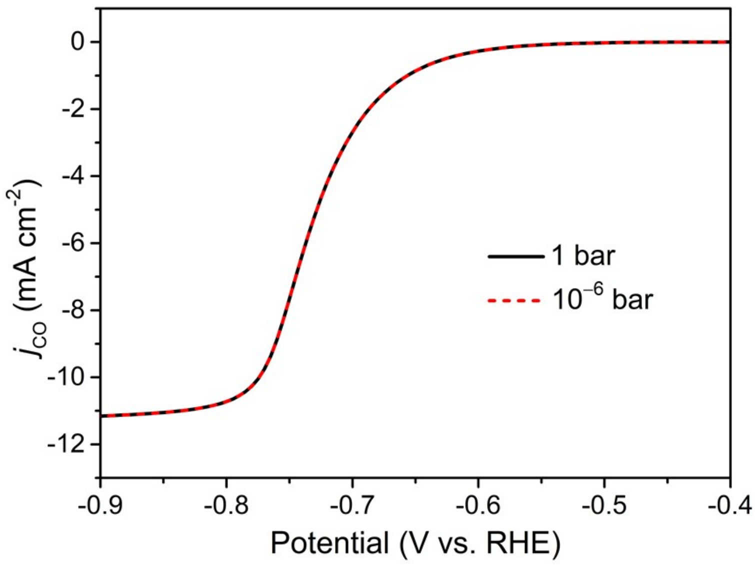

Figure S7. Simulated partial CO current density of β-NiN_4 with p_{CO} = 1 bar and p_{CO} = 10^{-6} bar.

2. Supporting Tables

Table S1. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the β-NiN_4 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	E or ΔG (eV)	R^2
β-NiN_4 (*)	$E = -0.604U^2 + 0.436U - 565.311$	0.999
CO_2*	$E = -0.491U^2 + 1.084U - 583.723$	0.999
COOH*	$E = -0.458U^2 + 1.079U - 586.800$	0.999
CO*	$E = -0.914U^2 + 0.407U - 577.452$	0.997
H*	$E = -0.493U^2 + 1.007U - 567.754$	0.999
* + CO_2 → CO_2*	$\Delta G = 0.112U^2 + 0.649U + 0.161$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = 0.033U^2 + 0.995U + 0.767$	N.A.
COOH* → CO* + OH^-	$\Delta G = -0.456U^2 + 0.328U - 0.340$	N.A.
CO* → CO	$\Delta G = 0.283U^2 + 0.029U - 0.438$	N.A.
* + H_2O → $1/2H_2$ + OH^-	$\Delta G = 0.110U^2 + 1.572U + 1.269$	N.A.

Table S2. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the α-NiN_1C_3 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	E or ΔG (eV)	R^2
α-NiN_1C_3 (*)	$E = -0.356U^2 + 0.852U - 618.422$	0.999
CO_2*	$E = -0.363U^2 + 1.151U - 637.021$	0.997
COOH*	$E = -0.369U^2 + 1.308U - 640.212$	0.999
CO*	$E = -0.371U^2 + 0.839U - 630.907$	0.998
H*	$E = -0.560U^2 + 0.574U - 621.925$	0.999
* + CO_2 → CO_2*	$\Delta G = -0.007U^2 + 0.299U - 0.027$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = -0.006U^2 + 1.157U + 0.654$	N.A.
COOH* → CO* + OH^-	$\Delta G = -0.002U^2 + 0.531U - 0.387$	N.A.
CO* → CO	$\Delta G = 0.015U^2 + 0.013U - 0.095$	N.A.
* + H_2O → 1/2H_2 + OH^-	$\Delta G = -0.204U^2 + 0.722U + 0.208$	N.A.

Table S3. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the α-NiN_2C_2 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	$\boldsymbol{E}$ **or** $\boldsymbol{\Delta G}$ **(eV)**	$\mathbf{R^2}$
α-NiN_2C_2 (*)	$E = -0.616U^2 + 0.208U - 618.616$	0.999
CO_2*	$E = -0.722U^2 + 1.000U - 637.034$	0.999
COOH*	$E = -0.316U^2 + 0.972U - 640.402$	0.999
CO*	$E = -0.654U^2 + 0.150U - 631.079$	0.999
H*	$E = -0.279U^2 + 0.867U - 622.061$	0.999
* + CO_2 → CO_2*	$\Delta G = -0.107U^2 + 0.793U + 0.154$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = 0.406U^2 + 0.971U + 0.477$	N.A.
COOH* → CO* + OH^-	$\Delta G = -0.338U^2 + 0.178U - 0.369$	N.A.
CO* → CO	$\Delta G = 0.039U^2 + 0.058U - 0.116$	N.A.
* + H_2O → $1/2H_2$ + OH^-	$\Delta G = 0.336U^2 + 1.660U + 0.266$	N.A.

Table S4. Energy of reaction species (*E*) and free energy change of reaction steps (ΔG) on the α-NiN_3C_1 moiety, with dependence of applied electrochemical potential *U*.

Species or reaction steps	*E* or ΔG (eV)	R^2
α-NiN_3C_1 (*)	$E = -0.315U^2 + 0.784U - 617.991$	0.999
CO_2*	$E = -0.277U^2 + 1.123U - 636.688$	0.999
COOH*	$E = -0.558U^2 + 0.304U - 639.855$	0.999
CO*	$E = -0.264U^2 + 0.972U - 630.145$	0.999
H*	$E = -0.554U^2 + 0.068U - 621.863$	0.999
* + CO_2 → CO_2*	$\Delta G = 0.038U^2 + 0.339U - 0.125$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = -0.281U^2 + 0.181U + 0.678$	N.A.
COOH* → CO* + OH^-	$\Delta G = 0.295U^2 + 1.668U + 0.018$	N.A.
CO* → CO	$\Delta G = -0.052U^2 - 0.188U - 0.425$	N.A.
* + H_2O → $1/2H_2$ + OH^-	$\Delta G = -0.238U^2 + 0.284U - 0.161$	N.A.

Table S5. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the α-NiN_4 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	E or ΔG (eV)	R^2
α-NiN_4 (*)	$E = -0.685U^2 - 0.605U - 618.348$	0.998
CO_2*	$E = -0.536U^2 + 0.551U - 636.085$	0.999
COOH*	$E = -0.568U^2 + 0.316U - 639.046$	0.999
CO*	$E = -0.994U^2 - 1.088U - 630.690$	0.996
H*	$E = -0.464U^2 + 0.616\ U - 619.990$	0.999
* + CO_2 → CO_2*	$\Delta G = 0.150U^2 + 1.156U + 0.835$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = -0.033U^2 + 0.765U + 0.883$	N.A.
COOH* → CO* + OH^-	$\Delta G = -0.426U^2 - 0.403U - 1.336$	N.A.
CO* → CO	$\Delta G = 0.308U^2 + 0.482U - 0.237$	N.A.
* + H_2O → 1/2H_2 + OH^-	$\Delta G = 0.222U^2 + 2.221U + 2.069$	N.A.

Table S6. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the β-NiN_1C_3 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	E or ΔG (eV)	R^2
β-NiN_1C_3 (*)	$E = -0.576U^2 + 1.355U - 564.518$	0.999
CO_2*	$E = -0.670U^2 + 1.921U - 583.293$	0.999
COOH*	$E = -0.351U^2 + 1.411U - 586.826$	0.999
CO*	$E = -0.620U^2 + 1.080U - 577.098$	0.999
H*	$E = -0.409U^2 + 1.427U - 568.797$	0.999
* + CO_2 → CO_2*	$\Delta G = -0.094U^2 + 0.566U - 0.202$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = 0.319U^2 + 0.490U + 0.312$	N.A.
COOH* → CO* + OH^-	$\Delta G = -0.269U^2 + 0.670U + 0.036$	N.A.
CO* → CO	$\Delta G = 0.044U^2 + 0.275U + 0.001$	N.A.
* + H_2O → $1/2H_2$ + OH^-	$\Delta G = 0.167U^2 + 1.072U - 0.567$	N.A.

Table S7. Energy of reaction species (E) and free energy change of reaction steps (ΔG) on the β-NiN_2C_2 moiety, with dependence of applied electrochemical potential U.

Species or reaction steps	E or ΔG (eV)	R^2
β-NiN_2C_2 (*)	$E = -0.309U^2 + 1.273U - 565.363$	0.999
CO_2*	$E = -0.303U^2 + 1.544U - 584.030$	0.999
COOH*	$E = -0.517U^2 + 1.002U - 587.126$	0.999
CO*	$E = -0.331U^2 + 1.342U - 577.519$	0.999
H*	$E = -0.362U^2 + 1.086U - 569.366$	0.999
* + CO_2 → CO_2*	$\Delta G = 0.006U^2 + 0.271U - 0.094$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = -0.214U^2 + 0.458U + 0.748$	N.A.
COOH* → CO* + OH^-	$\Delta G = 0.186U^2 + 1.340U - 0.085$	N.A.
CO* → CO	$\Delta G = 0.022U^2 - 0.068U - 0.423$	N.A.
* + H_2O → 1/2H_2 + OH^-	$\Delta G = -0.053U^2 - 1.188U - 0.292$	N.A.

Table S8. Energy of reaction species (*E*) and free energy change of reaction steps (ΔG) on the β-NiN_3C_1 moiety, with dependence of applied electrochemical potential *U*.

Species or reaction steps	***E* or Δ*G* (eV)**	**R^2**
β-NiN_3C_1 (*)	$E = -0.415U^2 + 0.871U - 564.442$	0.999
CO_2*	$E = -0.446U^2 + 1.100U - 583.899$	0.999
COOH*	$E = -0.446U^2 + 1.003U - 586.864$	0.999
CO*	$E = -0.350U^2 + 0.976U - 577.597$	0.998
H*	$E = -0.480U^2 + 0.949U - 569.262$	0.999
* + CO_2 → CO_2*	$\Delta G = -0.030U^2 + 0.229U + 0.115$	N.A.
CO_2* + H_2O → COOH* + OH^-	$\Delta G = -0.001U^2 + 0.903U + 0.879$	N.A.
COOH* → CO* + OH^-	$\Delta G = 0.097U^2 + 0.974U - 0.425$	N.A.
CO* → CO	$\Delta G = -0.066U^2 - 0106U - 0.424$	N.A.
* + H_2O → $1/2H_2$ + OH^-	$\Delta G = -0.065U^2 + 1.078U - 0.108$	N.A.