

Catalyst-directed vibrational frequency disparity for isotopologue sieving in CO₂ electrolysis

In the format provided by the
authors and unedited

Table of Contents

SUPPLEMENTARY NOTE	3
Supplementary Note 1: Materials	3
1.1. Chemicals	3
1.2. Synthesis of pure Sn Catalyst.	3
1.3. Synthesis of N/P/B-Sn Catalysts.	4
1.4. Synthesis of pure Ag/Ni-based Catalysts.	4
Supplementary Note 2: Experimental methods	6
2.1. Material characterizations	6
2.2. Liquid product analysis.	7
2.3. Operando ATR-SEIRAS Measurements	7
Supplementary Note 3: DFT Calculations	10
3.1 Confirmation of (doped) Sn models:	10
3.2 Catalysis calculation on (doped) Sn, Ni, and Ag surface models:	11
3.3 The effect of spin polarization on calculated vibration frequency	13
3.4 Basic vibration frequency formula.	13
3.5 Constant potential <i>ab initio</i> molecular dynamics (AIMD) simulations with slow-growth approach	14
Supplementary Note 4: The definition of the theoretical isotope factor δ	16
4.1 The theoretical derivation of δ	16
4.2 The usage conditions of δ	20
4.3 The connection between δ and experimental KIE	22
4.4 The contribution of specific vibrational modes in HCOO* and COOH*	25
Supplementary Note 5: Techno-economic analysis (TEA)	27

Electricity:	28
Electrolyzer Capital Cost:	29
Catalyst and Membrane Costs:	30
Electrolyte cost:	31
Balance of Plant and Installation:	32
Other operating costs:	32
SUPPLEMENTARY FIGURES	35
SUPPLEMENTARY TABLES	99
REFERENCES	112

SUPPLEMENTARY NOTE

Supplementary Note 1: Materials

1.1. Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 99%), Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; 98%), Nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 98%), Silver chloride (AgCl ; 99.5%), Methanol (CH_3OH ; 99.7%), Ethanol ($\text{C}_2\text{H}_6\text{O}$; 75%), Melamine ($\text{C}_3\text{H}_6\text{N}_6$; 99%), Disodium hydrogen phosphate anhydrous (Na_2HPO_4 ; 99.9%), and Boric acid (H_3BO_3 ; 99.8%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$; 98%) and Nafion® perfluorinated resin solution (5 wt%) were purchased from Aladdin Industrial Corp. (China). All reagents were used without further purification.

1.2. Synthesis of pure Sn catalyst.

The pure Sn material was synthesized via a two-step pyrolysis method. Initially, 5.58 g of zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 150 mL of methanol to prepare the metal salt solution. Simultaneously, 6.15 g of 2-methylimidazole was dissolved in another 150 mL of methanol to prepare the organic ligand solution. The two solutions were then slowly mixed and continuously stirred at room temperature for 12 h to synthesize the Sn-doped ZIF-8 precursor (Sn-ZIF-8) through a coordination reaction. The resulting white precipitate was separated by centrifugation ($6796 \times g$, 5 min), washed three times with methanol to remove unreacted species, and subsequently dried in an oven at 65°C .

for 12 h. The dried precursor was placed in a tube furnace and pyrolyzed under an argon atmosphere at a heating rate of 5 °C min⁻¹ to 900 °C, where it was maintained for 2 h, followed by natural cooling to room temperature, yielding a black powder. The pure Sn catalyst was obtained.

1.3. Synthesis of N/P/B-Sn Catalysts.

Then, through grinding, 200 mg of the above-mentioned pyrolysis product pure Sn was thoroughly mixed with 10 mg of melamine/anhydrous disodium hydrogen phosphate/boric acid, respectively, and the mixture was subjected to N/P/B doping treatment under an argon atmosphere at a heating rate of 2 °C min⁻¹ to 350 °C, where it was held for 2 h. Finally, the resulting product was immersed in 3 M HCl solution for 4 h to remove unstable components, washed with deionized water until neutral, and vacuum-dried at 60 °C to obtain the final N-, P-, B-Sn materials.

The catalyst prepared by pyrolyzing a mixture of 200 mg pure Sn and 10 mg melamine is denoted as 1:20 (N-Sn). Additional catalysts were synthesized under identical processing conditions: 1:10 (N-Sn) using 200 mg Sn with 20 mg melamine, and 1:30 (N-Sn) using 300 mg Sn with 10 mg melamine.

1.4. Synthesis of pure Ag/Ni-based catalysts.

The pure Ag/Ni material was synthesized via a two-step pyrolysis method. Initially, 5.58 g of zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 g of $\text{AgCl}/\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 mL of methanol to prepare the metal salt solution. Simultaneously, 6.15 g of 2-methylimidazole was dissolved in another 150 mL of methanol to prepare the organic ligand solution. The two solutions were then slowly mixed and continuously stirred at room temperature for 12 h to synthesize the Ag/Ni-doped ZIF-8 precursor (Ag/Ni-ZIF-8) through a coordination reaction. The resulting white precipitate was separated by centrifugation ($6796 \times g$, 5 min), washed three times with methanol to remove unreacted species, and subsequently dried in an oven at $65\text{ }^\circ\text{C}$ for 12 h. The dried precursor was placed in a tube furnace and pyrolyzed under an argon atmosphere at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $900\text{ }^\circ\text{C}$, where it was maintained for 2 h, followed by natural cooling to room temperature, yielding a black powder. The Ag-based/Ni-based catalysts were obtained (XRD analysis is shown in Supplementary Fig. 7).

Supplementary Note 2: Experimental methods

2.1. Material characterizations

X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer operated at 40 kV and 20 mA using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The surface morphology and elemental composition of the samples were characterized by a field-emission scanning electron microscope (FE-SEM, ZEISS Sigma 300, Germany) equipped with an energy dispersive spectroscopy (EDS) detector. Microstructural analysis was conducted using a JEM-F200 field-emission transmission electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV, with scanning transmission electron microscopy (STEM) mode enabled. The chemical states of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS) on a Shimadzu AXIS SUPRA spectrometer (Japan) equipped with a pure μ -metal vacuum chamber under an ultrahigh vacuum of $7.0 \times 10^{-8} \text{ Pa}$. XPS analysis was performed without prior in-situ argon ion sputtering, directly characterizing the surface composition and chemical state of the catalysts after synthesis and exposure to ambient conditions. These results are more representative of the surface state under ambient conditions and relevant to the initial state before electrochemical testing. The N content was determined using an oxygen, nitrogen, and hydrogen analyzer (ONH836 Analyzer (LECO)). Synchrotron-based X-ray absorption near-edge structure (XANES) experiments at the Sn K-edge were performed at the high-brightness hard X-ray beamline of the Australian Synchrotron (ANSTO).

2.2. Liquid product analysis.

Liquid products were analyzed by Nuclear magnetic resonance (NMR) spectroscopy on a Bruker AVANCE NEO 400 superconducting NMR spectrometer. The calibration curve was made by measuring standard solutions of formate. The faradaic efficiencies of liquid products were calculated as follows:

$$FE_{\text{HCOO}^-}(\%) = \frac{Q_{\text{HCOO}^-}}{Q_{\text{total}}} \times 100\% = \frac{n_{\text{HCOO}^-} \times N \times F \times 100\%}{j \times t} \quad (1)$$

where n_{HCOO^-} is the measured amount of formate in the cathodic compartment and t is the reaction time. The HCOO^- partial current density at different potentials was calculated by multiplying the overall geometric current density and its corresponding Faradaic efficiency.

2.3. Operando ATR-SEIRAS Measurements

The preparation of working electrodes for operando IR measurements was modified from a previously reported method. Briefly, an Au thin film was chemically deposited onto the reflecting plane of a Si prism, and then drop-coated with the catalyst ink. Before the Au deposition, the Si prism was polished with a slurry of Al_2O_3 powder and cleaned by sonication in acetone and deionized water sequentially. Then, the Si prism was immersed in a piranha solution (30% H_2O_2 : 98%; H_2SO_4 = 1: 3 v/v) for 1 h, and further treated with NH_4F for 180 s to form a hydrogen-terminated surface. Afterwards, the pre-treated Si prism was soaked in 5 ml of the Au plating solution composed of 12 mM HAuCl_4 , 0.5 M KHCO_3 , and 25 mM $\text{C}_6\text{H}_{12}\text{O}_6$

(glucose, PH = 9.3) at 30 °C for 4 h. As soon as the deposition was finished, the Au-coated Si prism coated was taken out, washed and dried in air for further use. The catalyst ink was prepared by mixing 6 mg samples with 50 μ L Nafion (5%) in 250 μ L deionized water and 250 μ L ethanol. The ink dispersion was then uniformly drop-coated onto the above prepared Au film. The working electrode was mounted in a two-compartment, three-electrode spectro-electrochemical cell with a platinum sheet as the counter electrode and a standard Ag/AgCl electrode as the reference. A bare Au film without catalyst loading was served as the background control.

The ATR-SEIRAS spectra were captured using a Nicolet iS 50 FT-IR spectrometer equipped with a MCT detector. The spectral resolution was set to 4 cm^{-1} for the majority of measurements (high-frequency region, 2200-2300 cm^{-1} , an experimental resolution of 1 cm^{-1} was used). All electrochemical tests were controlled using a CHI electrochemical workstation (CHI 660 E) with 0.1 M NaHCO_3 used as the electrolyte. Before the measurements, N_2 gas was bubbled into the electrolyte for at least 30 min to remove the residual air, followed by a continuous CO_2 purge for at least 30 min until the electrolyte is CO_2 -saturated. In a typical test, with CO_2 continuously bubbled into the electrolyte, the activation of the working electrode was first carried out by cycling the potential between -0.5 and -1.8 V vs. RHE until a repeatable CV was

obtained. Then, for electrochemical measurements, the potential was swept between -0.5 and -

1.2 V vs. RHE at 5 mV s⁻¹.

Supplementary Note 3: DFT Calculations

3.1 Confirmation of (doped) Sn models:

The first-principles calculations were performed with the Vienna ab initio Simulation Package (VASP) code.¹⁻³ The Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used for the exchange-correlation functional.⁴ The unit cell of Sn bulk (SG: I41/amd, 141) containing 4 Sn atoms is optimized first. The plane-wave cutoff energy of 550 eV, and k point mesh of $7 \times 7 \times 11$ are used. The convergence criterion for energy and the force tolerance for ionic relaxation were set as 10^{-7} eV and 0.005 eV/Å, respectively. Then a $2 \times 2 \times 3$ supercell (containing 48 atoms) was built, and interstitial and substitutional doping of B, N, and P into Sn bulk were considered, respectively. The spin-polarized first-principles calculations show that the doped structures show no spin polarization. Thus, we do not consider spin in the following calculations. By comparing the doping energy of different kinds of dopants, we found that interstitial doping shows lower total energy than substitutional doping for B and N (Extended Data Fig. 2a). As for P, for a small amount of P doping, the energy of interstitial and substitutional doping is comparable, however, for a larger amount of P doping, it is clear that substitutional doping has lower energy (Extended Data Fig. 2a and inset). Considering the large concentration on the surface of Sn in the experimental results, we considered substitutional doping for further calculation. The XRD simulation results of doped structures are also consistent with the experimental results (Extended Data Fig. 2b).

3.2 Catalysis calculation on (doped) Sn, Ni, and Ag surface models:

The Sn (200), Ag (111), and Ni (111) surfaces are used for calculation based on our experimental characterization. For the Ag and Ni models, the unit cell of Ag and Ni is optimized first. The plane-wave cutoff energy of 550 eV, and k point mesh of $11 \times 11 \times 11$ are used. The convergence criterion for energy and the force tolerance for ionic relaxation was set as 10^{-7} eV and 0.005 eV/Å, respectively. Then four atomic layers are cutoff for calculation. The lower two layers are fixed, while the rest are fully optimized. For the Sn models, three atomic layers are cutoff from optimized (N, B, P-doped) Sn models, which is proved to be accurate enough (Supplementary Fig. 1). The top layer is set free to reduce the affection of surface reconstruction. The STM simulation of Sn (200) model is highly consistent with experimental results (Extended Data Fig. 2c-d). The surface model contains 36 Sn atoms for the pure Sn model, 36 Sn and 2 B/N for B/N-doped Sn model, and 34 Sn and 2 P for P-doped Sn model. A vacuum of more than 15 Å along the z-direction was used in Ag, Ni, and (doped) Sn surface models to avoid the interaction between neighboring images. The vdW correction of Grimme's D3 scheme and dipole corrections were used to treat the weak interaction in the system.⁴ In the catalysis calculations, the plane-wave cutoff energy of 450 eV, and Gamma-only k point mesh are used, which is proven to be accurate enough in our systems. The convergence criterion for energy and the force tolerance for ionic relaxation were set as 10^{-5} eV and 0.02 eV/Å, respectively.

Through such a method, the lattice distortion, Sn atom displacement, and optimized impurity positions are all considered, which ensures the accuracy of the calculation.

To investigate the CO₂RR routes, for each slab model, we tried different initial molecule adsorption positions for optimization and used the one with the lowest total energy (Extended Fig. 2e-f, Supplementary Fig. 2). It needs to be pointed out that in our model, the dopants (N, B, or P) are not placed on the surface, thus, the active sites are the Sn on the surface of slabs.

The Sn atom far away from the impurity shows the optimized energy for all three kinds of (doped) Sn slabs. Then the HCOO*/COOH* intermediates are calculated based on *CO₂ adsorption configurations. The finite differences approach is used for vibrational frequency calculations. The substrates are fixed, and the intermediates can move freely. For each atom and direction, each atom is displaced by a positive and negative 0.015 Å to obtain the Hessian Matrix. Thus, we can obtain 3* (*number of atoms*) frequencies for each intermediate. To avoid the large affection from imaginary frequencies and little frequencies, we keep the first 6 frequencies for *CO₂ intermediate and 9 frequencies for HCOO* for post proceeding. The detailed vibrational frequencies are provided in Table S3-5.

The adsorption energy of the gas molecule was determined by $E_{ad}=E_{sub+gas}-E_{sub}-E_{gas}$, where $E_{sub+gas}$, E_{sub} and E_{gas} were the total energies of the adsorbed system, the substrate and gas molecules, respectively. The Gibbs free energy was calculated as $G = E + ZPE - TS$, where E

was the total energy obtained by DFT calculation, and ZPE was zero-point energy, which was calculated as $ZPE = 1/2 \sum h\nu_i$ (ν_i is the frequency of the intermediate). T is the temperature of the reaction, which is set as 298.15 K, and S is entropy. An energy difference of 6.17 meV is used for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ (see Supplementary Note 4). The detailed DFT-based energy, ZPE, entropy, and Gibbs free energies are provided in Table S6.

3.3 The effect of spin polarization on calculated vibration frequency

To fully understand the effect of spin on the difference of Gibbs free energies of isotopes, we used *OH adsorbed Cu(Ni)CrP₂S₆ (CNCPS) system as an example. *OH adsorbed CNCPS system is proven to have two possible spin states (ground and excited states, marked as CNCPS(g) and CNCPS(e), respectively), while the magnetic moment of Ni greatly affects the adsorption energy of *OH.⁴ However, we found that the Gibbs free energy difference between CNCPS(g)-*OH and CNCPS(g)-*OD is nearly the same as that of CNCPS(e)-*OH and CNCPS(e)-*OD, no matter if considering spin, indicating that the magnetic moment does not domain the Gibbs free energy differences of isotopes (Supplementary Fig. 3). Based on the above results, we can confirm that without considering spin does not affect the accuracy of DFT results.

3.4 Basic vibration frequency formula.

$$v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (2)$$

k: force constant (N/m)

μ : reduced mass (kg)

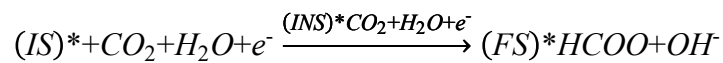
c: speed of light

$$\Delta v = \frac{1}{2\pi c} \left(\sqrt{\frac{k}{\mu_{\text{light}}}} - \sqrt{\frac{k}{\mu_{\text{heavy}}}} \right) \propto \sqrt{k} \quad (3)$$

Variations in force constants (k) across catalyst surfaces, driven by electronic/geometric effects.

3.5 Constant potential *ab initio* molecular dynamics (AIMD) simulations with slow-growth approach

The slow-growth approach implemented in VASP was used to simulate the reaction process of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ adsorption and protonation on N-Sn surface, i.e.,



The AIMD simulations were carried out with the same N-Sn supercell model in catalysis calculation and Γ point at 300 K with a time step of 2 fs.⁵⁻⁷ The constant potential of -1.1 V vs. RHE was set in the simulation via CP-VASP code.^{8, 9} The Nosé-Hoover thermostat was used in the simulation. Due to the forward reaction being uncontrollable in AIMD simulations, we simulated the backward reaction process to obtain reasonable results. Specifically, we started from the HCOO* adsorbed N-Sn surface, and elongated the H-C bonding in the simulation at

a rate of 0.001 Å each simulation step. During the simulation, we found that the $^*\text{CO}_2$ automatically departs from the surface as the increase of H-C distance, indicating that there is no clear “ CO_2 adsorption state” at -1.1 V vs. RHE. Totally 25 H_2O molecules are added to the N-Sn surface to construct the solution environment. Before the slow-growth calculation, the adsorption configuration of HCOO^* and the interfacial aquatic environment have been pre-simulated by a 2 ps AIMD simulation to ensure that the interface has reached energy equilibrium. The same initial position and velocity are used for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ containing systems for slow-growth simulation.

Supplementary Note 4: The definition of the theoretical isotope factor δ

4.1 The theoretical derivation of δ

The reaction rate is defined by both the reaction barrier (E_b) and the Gibbs free energy change (G). For the elemental reaction $^*\text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HCOO}^*$, the forward and backward reaction rates can be defined as functions of the energy barrier of the forward reaction (E_{active}) and the Gibbs free energy change (ΔG):

$$k_{\text{for}} = A_{\text{for}} e^{\frac{-(E_{\text{active}}) - \beta e \eta}{RT}} \quad (4)$$

$$k_{\text{rev}} = A_{\text{rev}} e^{\frac{-(\Delta G + E_{\text{active}}) + (1 - \beta) e \eta}{RT}} \quad (5)$$

Here, β is the symmetry factor, η is the electrode overpotential, e is the charge of electron.

The frequency factors (A_{for} and A_{rev}) are defined mainly by the vibrational partition functions:

$$A_{\text{for}} = \frac{k_B T}{h} \frac{q_{\text{vib } TS}}{q_{\text{vib } ^*\text{CO}_2}} \quad (6)$$

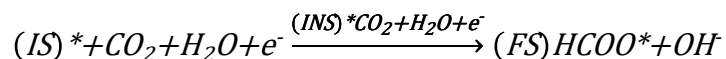
$$A_{\text{rev}} = \frac{k_B T}{h} \frac{q_{\text{vib } TS}}{q_{\text{vib } ^*\text{HCOO}}} \quad (7)$$

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{\frac{-h\nu}{k_B T}}} \quad (8)$$

Due to the physical adsorption properties of CO_2 on the surface of Sn-based catalysts, it is unable to obtain the transition state of CO_2 adsorption and CO_2 protonation. However, we obtained by DFT that the Gibbs free energy change of $^*\text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HCOO}^*$ step is $\sim -0.1 \sim -0.5$ eV, while it is reported that the protonation of CO_2 on metal surface generally has a good Brønsted-Evans-Polanyi (BEP) relationship,¹⁰⁻¹² which shows that the E_{active} is ~ 0.6 eV higher than the ΔG . In our experimental conditions, the overpotential is over 1 V, higher than

the E_{active} , indicating that the reverse reaction ($HCOO^*-e^- \rightarrow ^*CO_2 + H^+$) is extremely inhibited. Furthermore, we also applied AIMD simulation showing that there is almost no energy barrier from solvated CO_2 to the CO_2 adsorption under working potential (-1.1 V vs. RHE), which is consistent with our DFT calculations showing that CO_2 is physically adsorbed. The activation barrier in the process of CO_2 physical adsorption to $HCOO^*$ formation is only about 0.18 eV, which is much smaller than the change in free energy (~1.8 eV). Furthermore, we can see that the kinetic energy barrier difference between $^{12}CO_2$ and $^{13}CO_2$ throughout the entire reaction process is only 0.025 eV, which is less than the solvation energy difference of CO_2 (0.085 eV), indicating that the activation energy barrier has a limited effect on enrichment effects (Extended Data Fig. 3a), indicating the negligible effect of the activation barrier in our system.⁴ Thus, in our definition of δ , it is reasonable to only consider the Gibbs free energy change in CO_2 protonation step.

In such a condition, we can regard the reaction pathway as:



Where IS, INS, and FS indicate initial state, intermediate state, and final state. Thus, the forward and backward reaction rates of such an elemental reaction can be written as:

$$\left\{ \begin{array}{l} k_{for}^{12} = p \frac{q_{vib}^{12} * CO_2}{q_{vib\ sub}^{12}} e^{j(\Delta G_{for}^{12} - \beta e \eta)} \\ k_{for}^{13} = p \frac{q_{vib}^{13} * CO_2}{q_{vib\ sub}^{13}} e^{j(\Delta G_{for}^{13} - \beta e \eta)} \\ k_{rev}^{12} = p \frac{q_{vib}^{12} * CO_2}{q_{vib}^{12} * HCOO} e^{j(\Delta G_{rev}^{12} + \beta e \eta)} \\ k_{rev}^{13} = p \frac{q_{vib}^{13} * CO_2}{q_{vib}^{13} * HCOO} e^{j(\Delta G_{rev}^{13} + \beta e \eta)} \end{array} \right. \quad (9)$$

Here, β is the symmetry factor, η is the electrode potential, e is the charge of electron. Here for the constants:

$$j = \frac{-I}{RT} = const. \quad (10)$$

$$p = \frac{k_B T}{h} = const. \quad (11)$$

and

$$q_{vib} = \prod_i \frac{I}{I - e^{\frac{-h\nu}{k_B T}}} \quad (12)$$

while the forward and backward barriers become the adsorption energy of CO₂ and the Gibbs free energy change of CO₂ protonation, which are defined as:

$$\Delta G_{rev}^{13} = \Delta G_{rev}^{12} - \Delta E_{corr_CO_2} + \Delta E_{corr_CO_2} \quad (13)$$

Where:

$$\Delta E_{corr_CO_2} = G_{*CO_2}^{13} - G_{*CO_2}^{12} \quad (14)$$

$$\Delta E_{corr_CO_2} = G_{CO_2}^{13} - G_{CO_2}^{12} = -6.17 \text{ meV} \quad (15)$$

in which the $\Delta E_{corr_CO_2}$ is defined by the Gibbs free energy of CO₂ isotopologues in vacuum

for the calculation (Table S1-2). The ΔG_{for}^{13} is confirmed by ΔG_{for}^{12} and energy difference

between $\text{H}^{12}\text{COO}^*$ and $\text{H}^{13}\text{COO}^*$:

$$\Delta G_{\text{for}}^{13} = \Delta G_{\text{for}}^{12} + G_{\text{HCOO}^*}^{13} - G_{\text{HCOO}^*}^{12} \quad (16)$$

Except for the reaction barrier difference between isotopologues ($\Delta G_{\text{for}}^{13}$ and $\Delta G_{\text{for}}^{12}$, as well as $\Delta G_{\text{rev}}^{13}$ and $\Delta G_{\text{rev}}^{12}$), we also need to consider the difference between the partition functions of isotopologues (q_{vib}^{12} and q_{vib}^{13}). As we calculated, the C atom-related intrinsic vibrational frequencies in isotopologues have an approximate multiple relationship due to the Hooke's law: the frequencies of ^{12}C intermediates $\times 0.96 \approx$ frequencies of ^{13}C intermediates, while the coefficient of around 0.96 is defined by the square root of the mass ratio ($\sqrt{\frac{12}{13}}$) (Table S2-5, 0.972 for Sn-based catalysts in our work). The frequency has an exponential relationship with q_{vib} , while the C-related frequencies are generally larger than 20 THz, indicating that the q_{vib} is close to 1 (Supplementary Fig. 4a). Thus, we can use a linear relationship to fit q_{vib}^{12} and q_{vib}^{13} :

$$q_{\text{vib}}^{12} = f_{\text{vib, const}} q_{\text{vib}}^{13} \quad (17)$$

Where $f_{\text{vib, const}}$ is a constant and very close to 1 in the same catalytic system for estimation of the intrinsic vibrational frequencies of the carbon isotopologues (Supplementary Fig. 4b)

Thus, we can obtain the ratio of the equilibrium constant ($\frac{K^{12}}{K^{13}}$) for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ participating in the reaction:

$$\delta_{\text{equal}} = \frac{K^{12}}{K^{13}} = \frac{k_{\text{for}}^{12} k_{\text{rev}}^{13}}{k_{\text{for}}^{13} k_{\text{rev}}^{12}} = f_{\text{vib, const, multi}} \frac{e^{j(\Delta G_{\text{for}}^{12})} e^{j(\Delta G_{\text{rev}}^{13})}}{e^{j(\Delta G_{\text{for}}^{13})} e^{j(\Delta G_{\text{rev}}^{12})}} \quad (18)$$

A larger δ_{equil} indicates that $^{12}\text{CO}_2$ takes parts into reaction more completely, leading to more products but less $^{12}\text{CO}_2$ in unreacted gases. Here δ_{equil} is only correlated to the thermodynamic properties of the reaction pathway of isotopologues (Extended Data Fig. 3b). Note that $f_{\text{vib,const,multi}}$ is still very close to 1, j is a negative constant, and all barriers are negative in our system; hence, the $j(\Delta G)$ is very small. Due to the linear increase of the exponential function at a very small change in $j(\Delta G)$, we use the variable (ΔG) to replace the exponential function to simplify the expression:

$$\delta = \frac{\Delta G_{\text{for}}^{12} \Delta G_{\text{rev}}^{13}}{\Delta G_{\text{for}}^{13} \Delta G_{\text{rev}}^{12}} \quad (19)$$

which is the origin δ factor used to indicate the ratio of the equilibrium constant for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in a simpler way. Thus, it can be inferred that the larger the δ , the larger the ratio of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ taking part in the reaction, the more the unreacted $^{13}\text{CO}_2$. It is also worth noting that as $f_{\text{vib,const,multi}}$ is related to the frequencies of intermediates and the substrate. Thus, the benchmark for different catalytic systems should be different. For example, the δ of Sn (220) is 0.9285, which is used as a standard to evaluate other Sn-based catalysts.

Thus, in Sn-based catalysts, it is possible to evaluate the isotope separation performance of each catalyst by comparing their δ (N-Sn: 0.9855, B-Sn: 0.9847, P-Sn: 0.9749) with the δ of pure Sn ($\delta=0.9285$). The larger the δ , the better the isotope separation performance.

4.2 The usage conditions of δ

From a theoretical perspective, δ has a wide range of applications when meet the conditions of (1) large overpotential under which the energy barrier is overcome (Extended Data Fig. 3b), (2) the same catalytic system, and (3) the same reaction pathway.

A few assumptions are made to simplify the ratio of the equilibrium constants of isotopologues in our derivation of δ . We have shown that δ is highly correlated to the experimental ^{13}C enrichment effect and isotope separation performance, but δ cannot be used in a few conditions:

- Kinetic-dominated region: The activation barrier cannot be ignored when the overpotential is small. In other words, the δ is only applicable in the thermodynamic equilibrium-dominated region.
- Comparison among different catalytic systems: the $f_{\text{vib,const,multi}}$ is different for different systems with distinct adsorption configurations and energies of CO_2 , activation energies and Gibbs free energy change of protonation of $^*\text{CO}_2$. Thus, it is unable to compare δ among different catalysts to evaluate the isotope separation performance.
- Comparison among different reaction pathways: Similar reason to “comparison among different catalytic systems”. The $f_{\text{vib,const,multi}}$ for COOH^* and HCOO^* pathways are different.
- Partition function of isotopologues has large differences: the too strong adsorption of intermediates may lead to the invalidation of the multiple relationship between the

frequencies of isotopologues, which also leads to distinct $f_{vib,const,multi}$. In addition, if the low frequencies are dominated by the intermediates (Supplementary Fig. 4a), the ratio of q_{vib}^{12} and q_{vib}^{13} are no longer close to 1 (Supplementary Fig. 4b), which affects the accuracy of δ .

In addition, δ needs to be redefined in a few conditions:

- The ΔG of forward and reverse reactions are not two negative values: if two ΔG are both positive (Extended Data Fig. 3e), then a smaller δ indicates better isotope separation performance, because in this case, the absolute value of the ΔG of ^{12}C intermediate is oppositely larger than that of ^{13}C intermediates. On the other hand, if the ΔG for forward and reverse reactions include positive and negative values (Extended Data Fig. 3c-d), then δ cannot be used for evaluation. It is in this case suitable to use revised δ , $\delta' = \Delta G_{for}^{12} + \Delta G_{rev}^{13} - \Delta G_{for}^{13} - \Delta G_{rev}^{12}$ to evaluate the isotope separation performance based on the definition of δ_{equal} .

4.3 The connection between δ and experimental KIE

We specified that a tenfold difference in experimental KIE is related to the cumulative enrichment based on (1) the different onset potential of isotopologues in the kinetic-dominated region, (2) an amplification based on exponential rate sensitivity, and (3) the synergy from other related effects.

1. The lower onset potential of the lighter ^{12}C isotopologues in the kinetic-dominated region:

Discrepancies in the vibrational frequency shifts of ^{12}C - and ^{13}C -containing intermediates serve as a sensitive indicator of binding affinity fluctuations, which subsequently modulate the Gibbs free energy (ΔG) of the adsorbed species. As we noted, the ^{13}C -containing intermediate has lower vibrational frequencies due to the higher mass of ^{13}C , leading to a strong adsorption of ^{13}C -containing intermediates, thereby delaying the onset potential for $^{13}\text{CO}_2$ reduction (Extended Data Fig. 3b). Furthermore, this onset potential is subject to the influences of kinetic effects, including local pH gradients, ionic effects, ion transport, etc.^{13, 14}

Thus, we can infer that the difference between vibration frequencies of isotopologues leads to (1) strong adsorption and (2) a slower kinetic process of ^{13}C intermediates, which together affect the onset potential. Note that we define " δ " as the equilibrium factors between isotopologues affecting the ^{13}C separation most under large overpotential, and the kinetic effect also contributes to the ^{13}C separation.

Such a difference can be further supported by experimental investigation. By measuring the LSV curve for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ reduction and eliminating the influence of HER (Extended Data Fig. 3f), we can observe that the onset potential has a difference of ~ 50 mV (Extended Data Fig. 3g-h), which is tens-fold larger than the energy difference caused by vibrational frequency differences (~ 0.5 meV level). In addition, $^{13}\text{CO}_2$ enrichment rate and $^{13}\text{CO}_2$ separation factor

all have a volcano relationship with applied electrode potential (Fig. 4d-f), precisely indicating that the isotopologues are differently activated with the same voltage, while a proper potential can amplify such a difference to a greater extent.

2. An amplification effect based on exponential rate sensitivity: The rate and Gibbs free energy change have an exponential relationship, which will magnify the subtle differences in the energy barrier (Extended Data Fig. 3b). Compared to the Gibbs free energy change (0.5 eV level) in elemental reaction steps, the free energy difference between isotopologues (0.1~0.5 meV level) is 0.05~0.1% of the Gibbs free energy change (Extended Data Fig. 3b). Thus, the exponential rate sensitivity enlarged the tiny difference for tens even hundreds of times (5% difference in reaction rate).

3. The different inlet concentrations, mass transport and the surface coverage ratios of isotopologues: The inlet concentration of isotopologues also affects the reaction rates. Meanwhile, mass transport of heavier $^{13}\text{CO}_2$ is slower in the interface, which also blocks it from taking part in the chemical reaction. Thus, the concentration in the interface and the surface coverage ratios of isotopologues are both significantly different. According to Van't-Hoff-Arrhenius expression that describes the recovery time of adsorbed isotopologues, the higher adsorption energies of lighter $^{12}\text{CO}_2$ lead to shorter recovery time, indicating that the $^{12}\text{CO}_2$ is easier to take part in chemical reduction reactions.

4.4 The contribution of specific vibrational modes in HCOO* and COOH*

Based on our theoretical analysis, the specific vibrational modes of the key protonation site for $^*\text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HCOO}^*$ step are more correlated with isotope separation performance. As the vibrational frequency difference leads to different correction energy ($E_{\text{corr}} = \text{ZPE} - \text{TS}$) to total energy (E), although the frequency difference of the C-O bond for ^{12}C and ^{13}C is larger in both COOH* and HCOO* intermediates, it leads to similar correction energy differences ($\Delta E_{\text{corr}} = E_{\text{corr}}(^{13}\text{C}) - E_{\text{corr}}(^{12}\text{C})$) in both intermediates (Supplementary Fig. 6a). On the other hand, the vibrational frequency of the protonation sites (C-H bond for HCOO* or O-H bond for COOH*) is the key to C isotope separation, as seen from the large difference of ΔE_{corr} ($\Delta \Delta E_{\text{corr}} = \Delta E_{\text{corr_COOH}} - \Delta E_{\text{corr_HCOO}}$), which is regarded as the main descriptor of isotope separation performance. We also acknowledge that vibrational frequency is the correlation descriptor rather than the sole determinant of isotope separation performance.

(1) Specific vibrational modes in the protonation site are more correlated with the isotope separation performance. Based on simple harmonic vibration and the nearest neighbor model, we can obtain vibrational modes of atoms in the intermediates correlated to the mass of adjacent atoms.⁴ The diverse vibrational modes in COOH* and HCOO* (O-H and C-H bonds, respectively) become the key for comparison.

Our DFT calculations also reveal the difference in vibrational frequencies between COOH* and

HCOO* intermediates containing ^{13}C and ^{12}C (Extended Data Fig. 1a-b). For HCOO*, the C-H bond vibration is significantly affected by the mass of C, while the O-H bond vibration in COOH* shows little difference. We further investigated the correction energy (E_{corr}) to total energy (E) for each vibration mode. The difference in E_{corr} between the ^{12}C -H and ^{13}C -H bonds ($\Delta E_{\text{corr}} = {}^{13}E_{\text{corr}} - {}^{12}E_{\text{corr}} = 0.279 \text{ meV}$) is larger than that of O-H bond in COOH*, which has a negligible effect on isotope separation ($\Delta E_{\text{corr}} = 8.975 \times 10^{-4} \text{ meV}$). We can see that the difference in contribution of the two newly added vibration modes to isotope separation is larger ($\Delta \Delta E_{\text{corr}} = \Delta E_{\text{corr_COOH}^*} - \Delta E_{\text{corr_HCOO}^*} = 0.278 \text{ meV}$, Supplementary Fig. 6a). Therefore, we believe that the C-H bond is the key to C isotope separation from the perspective of vibrational frequency.

(2) While the frequency difference of the C-O bond is larger, it contributes to almost identical correction energy differences (ΔE_{corr}) for HCOO* and COOH*, leading to small $\Delta \Delta E_{\text{corr}}$. The C-O bond contributes correction energy differences of -2.073 and -2.094 meV in COOH* and HCOO*, respectively, a difference between them ($\Delta \Delta E_{\text{corr}}$) of only 0.022 meV (Supplementary Fig. 6a). In contrast, the $\Delta \Delta E_{\text{corr}}$ of C-H/O-H reaches 0.278 meV, more than ten times that of the C-O bond. Therefore, although the C-O bond has a larger frequency difference, it is not as critical as the C-H/O-H bond.

Similarly, the O-C-O vibrational modes of HCOO* and C-O vibrational modes of COOH* contribute a $\Delta \Delta E_{\text{corr}}$ of 0.194 meV. Such value is larger than $\Delta \Delta E_{\text{corr}}$ of C-O vibrational modes

in COOH* and O-C-O modes in HCOO*, which is because the additional H in COOH* affects the C-O vibration, but it is still less than that of $\Delta\Delta E_{\text{corr}}$ of C-H/O-H. Therefore, we believe that the C-H bond is the key to C isotope separation from the perspective of vibrational frequency.

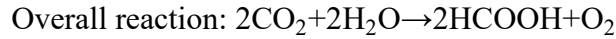
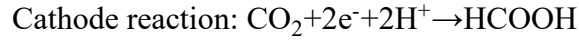
(3) Vibrational frequency is a correlated descriptor of thermodynamic-dominated isotope separation region, not the sole determinant of electrochemical isotope separation performance.

In our analysis of the correlation between “vibrational frequency- ΔG - δ -isotope enrichment”, we found that isotope separation performance is also affected by factors such as the dynamic behavior of isotope particles, surface coverage, and other cumulative effects (Extended Data Fig. 3b), which has been confirmed in isotope separation studies. In our theoretical derivation, we also emphasized that the application condition of δ requires a high overpotential to ensure that the dynamic influence is negligible. Therefore, we believe that vibrational frequency is a correlated descriptor of thermodynamic-dominated isotope separation region, not the only factor for KIE in electrochemical isotope separation.

Supplementary Note 5: Techno-economic analysis (TEA)

Our techno-economic analysis (TEA) model follows a general framework established in prior research. Assuming an isotope enrichment system that concentrates $^{13}\text{CO}_2$ from its natural abundance of 1.1% to 14%, and the costs for producing 1 tonne of 14% $^{13}\text{CO}_2$ per year over a 30-year operational plant lifetime. To estimate the operational voltage for a potential industrial

electrolyzer, we utilized an experimentally derived flow cell voltage of V_{cell} and a total current density of J , as determined from our stability experiments.¹⁵⁻¹⁷



Therefore, producing 1 mole of HCOOH requires 1 mole of CO_2 .

Assuming a system enriching $^{13}\text{CO}_2$ from its natural abundance of 1.1% to 14% with a separation factor α , the Rayleigh equation is used to calculate the initial feed amount.

$$\ln(W_0/W) = (\alpha - 1)^{-1} \left(\ln \frac{X_{W_0}}{X_W} + \alpha \ln \frac{1 - X_W}{1 - X_{W_0}} \right) \quad (20)$$

CO_2 product flow: $G_p = 1$ tonne/year (14% $^{13}\text{CO}_2$)

$$W_0 = \exp \left(\frac{\ln \frac{98.9\%}{86\%} + \alpha \ln \frac{1-86\%}{1-98.9\%}}{\alpha - 1} \right) \quad (21)$$

$$W_0 = \exp \left(\frac{0.1397619 + \alpha \times 2.54747}{\alpha - 1} \right) \quad (22)$$

CO_2 feed flow rate:

$$M_{14\%^{13}\text{CO}_2} = M_{\text{CO}_2} \times 0.86 + M_{^{13}\text{CO}_2} \times 0.14 = 44 \times 0.86 + 45 \times 0.14 = 44.14 \text{ g/mol} \quad (23)$$

$$m_{\text{input } ^{13}\text{CO}_2} = \frac{1 \times 10^6}{44.14} \times 15.59639 \times 44 \times 10^{-6} \text{ tonne} = 15.5469 \text{ tonne} \quad (24)$$

Formic acid production (by-product):

$$m = 15.5469 \times 0.81 = 12.59 \text{ tone/year} \quad (25)$$

Electricity:

The consumption rate of CO₂ (equivalent to the rate of HCOOH production) in moles per second is:

$$\text{CO}_2\text{consumption}\left(\frac{\text{mol}}{\text{s}}\right)=\frac{G_p}{1-c}=\left(\frac{22727}{0.065}\right)\div 8000\div 3600=0.01214\frac{\text{mol}}{\text{s}} \quad (26)$$

Considering the loss of electrons due to FE below 100%, we calculated the current required for the ¹³CO₂ enrichment process (which generates HCOOH) using 90% of the FE:

$$I_{\text{Total}}(\text{A})=\frac{\text{CO}_2\text{consumption}\times n\times F}{90\%}=\frac{2\times 0.01214\times 96485\frac{\text{sA}}{\text{mol}}}{90\%}=2602.9\text{ A} \quad (27)$$

We multiply the experimentally derived flow cell voltage V_{cell} to calculate the power consumption.

$$E(\text{kWh/year})=I_{\text{Total}}(\text{A})\times\frac{V_{\text{cell}}}{1000}\text{ kW}\times 8000\text{ h} / 0.82=25392.7V_{\text{cell}}\text{ kWh/year} \quad (28)$$

To determine the energy consumption for producing 1 tonne of 14% ¹³CO₂, we multiply the power requirement by 8000 hours. We assume the energy efficiency is 82%. The resulting energy consumption is then multiplied by the electricity rate (C_{power}) to calculate the cost per tonne of 14% ¹³CO₂ produced.

$$\text{Cost}_{\text{electricity}}\left(\frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2}\right)=25392.7V_{\text{cell}}\times C_{\text{power}}=2539.27\frac{\$}{14\% \text{ } ^{13}\text{CO}_2} \quad (29)$$

Electrolyzer Capital Cost:

Multiplying by the unit price of the electrolyzer (450 \$/kW) and scaling by the current density, we obtain the total cost of the electrolyzer, according to the reference electrolyzer cost of 450 \$/kW, and current density of 400 mAcm⁻².

$$\begin{aligned}
& \text{Cost}_{\text{Total Electrolyzer}}(\$) \\
& = \text{Power Consumed (kW)} \times \text{Cost}_{\text{Electrolyzer}}(\$) \times \frac{\text{base current density}}{\text{input current density}} \\
& = 468.52 \frac{V_{\text{cell}}}{J} \$
\end{aligned} \tag{30}$$

This method of converting long-term investments into daily costs is applied to all capital expenses, using a capital recovery factor (CRF) calculated based on a discount rate of 7% and a material lifespan of 20 years.

$$\text{CRF}_{\text{electrolyzer}} = \frac{i(1+i)^{\text{lifetime}}}{(1+i)^{\text{lifetime}} - 1} = 0.094393 \tag{31}$$

Next, the total capital cost of the electrolyzer is multiplied by the CRF, then divided by the number of operational days and the daily $^{13}\text{CO}_2$ output. In all calculations, it is assumed that the plant operates at a capacity factor of 0.9.

$$\text{Cost}_{\text{electrolyzer}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} = 49.17 \frac{V_{\text{cell}}}{J} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \tag{32}$$

Catalyst and Membrane Costs:

For the catalyst and membrane costs, we assume they account for 5% of the total electrolyzer cost. The cost per tonne of 14% $^{13}\text{CO}_2$ is calculated based on a catalyst and membrane lifetime of 1 year:

$$\text{CRF}_{\text{C\&M}} = \frac{i(1+i)^1}{(1+i)^1 - 1} = 1.07 \tag{33}$$

$$\begin{aligned}
& \text{Cost}_{\text{C\&M}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} = \frac{\text{CRF}_{\text{C\&M}} \times \text{Cost}_{\text{Total Electrolyzer}}(\$) \times 5\%}{\text{Capacity factor} \times \text{production} \left(\frac{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2}{\text{year}} \right)} \\
& = 27.84 \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2}
\end{aligned} \tag{34}$$

Equation with variables:

$$\begin{aligned} & \text{Cost}_{C\&M} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \\ &= \frac{0.07 \times (1.07)^t}{(1.07)^t - 1} \times \frac{468.52 \frac{\text{V}_{\text{cell}}}{\text{J}} \times 5\%}{0.9} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \end{aligned} \quad (35)$$

Input CO₂:

Based on the above information, to produce 1 ton of 14% ¹³CO₂, 15.46 tonnes of high-purity

CO₂ need to be input. Calculated at a unit price of 50 \$/tonne:

$$\text{Cost}_{\text{Input CO}_2}(\$) = 50 \frac{\$}{\text{tonne CO}_2} \times W_0 \frac{\text{tonne CO}_2}{\text{year}} = \frac{777.35\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \quad (36)$$

Equation with variables:

$$\text{Cost}_{\text{Input CO}_2}(\$) = P_{\text{CO}_2} \times W_0 \quad (37)$$

Electrolyte cost:

Our electrolyte catholyte is 0.1 molar NaHCO₃, and the anode is composed of a 1.0 molar KOH solution. By applying a fixed volume ratio of 100 L of electrolyte per square meter of electrolyzer, we can calculate the total volume of electrolyte required for the system.

$$\text{Volume}_{\text{electrolyte}}(\text{L}) = \text{Surface area}_{\text{electrolyzer}}(\text{m}^2) \times \frac{\text{L}}{\text{m}^2} \quad (38)$$

$$\text{Mass}_{\text{KOH}}(\text{g}) = \text{molarity}_{\text{KOH}} \left(\frac{\text{mol}}{\text{L}} \right) \times \text{Volume}_{\text{electrolyte}}(\text{L}) \times \text{molecular weight} \left(\frac{\text{g}}{\text{mol}} \right) \quad (39)$$

$$\text{Mass}_{\text{NaHCO}_3}(\text{g}) = \text{molarity}_{\text{NaHCO}_3} \left(\frac{\text{mol}}{\text{L}} \right) \times \text{Volume}_{\text{electrolyte}}(\text{L}) \times \text{molecular weight} \left(\frac{\text{g}}{\text{mol}} \right) \quad (40)$$

$$\text{Cost}_{\text{electrolyte}}(\$) = \frac{1.47555}{\text{J}} \$ \quad (41)$$

To determine the cost per tonne of 14% $^{13}\text{CO}_2$, we calculate a new CRF of 1.07, assuming an electrolyte lifetime of one year. This allows us to estimate the electrolyte costs per tonne of 14% $^{13}\text{CO}_2$ produced.

$$\begin{aligned} \text{Cost}_{\text{electrolyte}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} &= \frac{\text{CRF}_{\text{electrolyzer}} \times \text{Cost}_{\text{electrolyte}} (\$)}{\text{Capacity factor} \times 1 \times \text{production} \left(\frac{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2}{\text{year}} \right)} \\ &= \frac{1.7543}{\text{J}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \end{aligned} \quad (42)$$

Balance of Plant and Installation:

All capital costs are adjusted to estimate the price of peripheral equipment surrounding the electrolyzer and separation units. We assume a balance of plants (BOP) at 50% and apply a Lang factor of 1. To calculate the total capital costs, we sum the expenses for the electrolyzer, membrane and catalyst, as well as the cathode separation equipment.

$$\begin{aligned} \text{Cost}_{\text{Total capital}} \left(\frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \right) \\ &= \text{Electrolyzer cost} + \text{Catalyst cost} \\ &= 77.01 \frac{V_{\text{cell}}}{\text{J}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \end{aligned} \quad (43)$$

$$\begin{aligned} \text{Cost}_{\text{Installation}} \left(\frac{\$}{\text{tonne H}_2} \right) &= \text{Lang Factor} \times \text{Cost}_{\text{Total capital}} \\ &= 77.01 \frac{V_{\text{cell}}}{I_{\text{cell}}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \end{aligned} \quad (44)$$

$$\text{BOP} \left(\frac{\$}{\text{tonne } ^{13}\text{CO}_2} \right) = \text{BOP Factor} \times \text{Cost}_{\text{Total capital}} = 38.505 \frac{V_{\text{cell}}}{\text{J}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \quad (45)$$

Other operating costs:

To account for the additional operating expenses related to running the factory (including labor

and maintenance), we have included an extra charge equal to 10% of the electricity cost:

$$\text{Cost}_{\text{other operation}} \left(\frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \right) = 253.927 V_{\text{cell}} \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \quad (46)$$

Total cost for one tonne of 14% $^{13}\text{CO}_2$:

The generated formic acid is treated at a cost of 100 \$ per ton:

$$100\$/\text{t} \times 12.59 \text{ t} = 1259 \$ \quad (47)$$

By adding up all the aforementioned costs, we can determine the total cost of producing one tonne of 14% $^{13}\text{CO}_2$ using an electrolyzer.

$$\text{Cost} = 2036.5 + 192.525 \frac{V_{\text{cell}}}{\text{J}} + \frac{1.7543}{\text{J}} + 2793.197 V_{\text{cell}} \quad (48)$$

The price of 14% $^{13}\text{CO}_2$ is \$210000 per ton. Considering the ^{13}C content at \$15,000 per kg, and adjusting for the low purity to 0.1, the final price is:

$$15000000\$/\text{t} \times 0.14 \times 0.1 = 210000 \$/\text{t} \quad (49)$$

$$\text{Profit} = 210000 - [2793.197 V_{\text{cell}} + 192.525 \frac{V_{\text{cell}}}{\text{J}} + \frac{1.7543}{\text{J}} + 2036.35] \frac{\$}{\text{tonne } 14\% \text{ } ^{13}\text{CO}_2} \quad (50)$$

All experimental conditions were satisfied, yielding a cost of 16209.234 \$ and a profit of 193790.766 \$. $\text{ROI} = \text{Profit} / \text{Cost} = 11.96$.

Based on an in-depth review of existing literature and industry data, the current industrial low-temperature distillation technology can achieve an annual production scale of 500 kg of ^{13}CO (Anhui Zhonghe Tongyuan Technology Co., Ltd.).⁴ Based on an annual operational time of 8,000 hours, the hourly production rate of ^{13}CO is approximately 48.27 L. To achieve this output, our study requires processing approximately 4,388 L of naturally abundant CO_2 (containing 1.1% $^{13}\text{CO}_2$) per hour. With the enrichment efficiency demonstrated in the current research, and

by employing an industrial-scale ten-layer electrolyzer stack (with $10 \times 10 \text{ cm}^2$ catalysts), a configuration of four production lines with five serial enrichment stages is sufficient to achieve the same annual output (Supplementary Fig. 59). Furthermore, by increasing the number of production lines, the annual production capacity of $^{13}\text{CO}_2$ could surpass that of the current cryogenic distillation method (when 8 production lines are constructed, an annual production capacity of 1 t in the TEA calculation can be achieved).

We have found the established qualitative facts to highlight the inherent limitations of cryogenic distillation:⁴

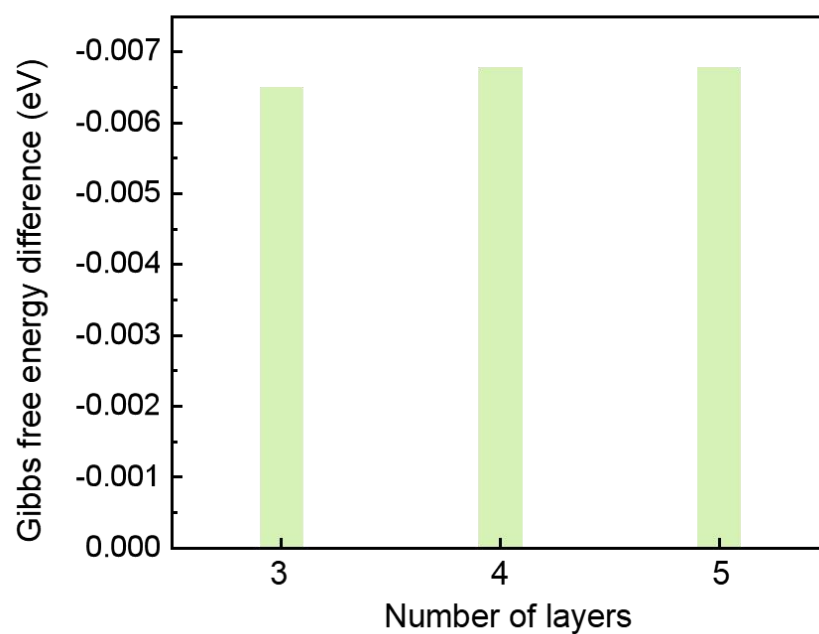
(a) Extremely low temperature limitation: Current industrial production of ^{13}C requires media with extremely low boiling points ($-161.5 \text{ }^\circ\text{C}$ to $-191.5 \text{ }^\circ\text{C}$), imposing stringent demands on both equipment and energy consumption.

(b) Extremely Low Time Efficiency: This represents a core bottleneck of the process. The system requires full reflux to establish the isotopic abundance gradient, and this "start-up" phase lasts from six months to over a year. Any unplanned shutdown would necessitate restarting the entire process, resulting in substantial time and economic losses.

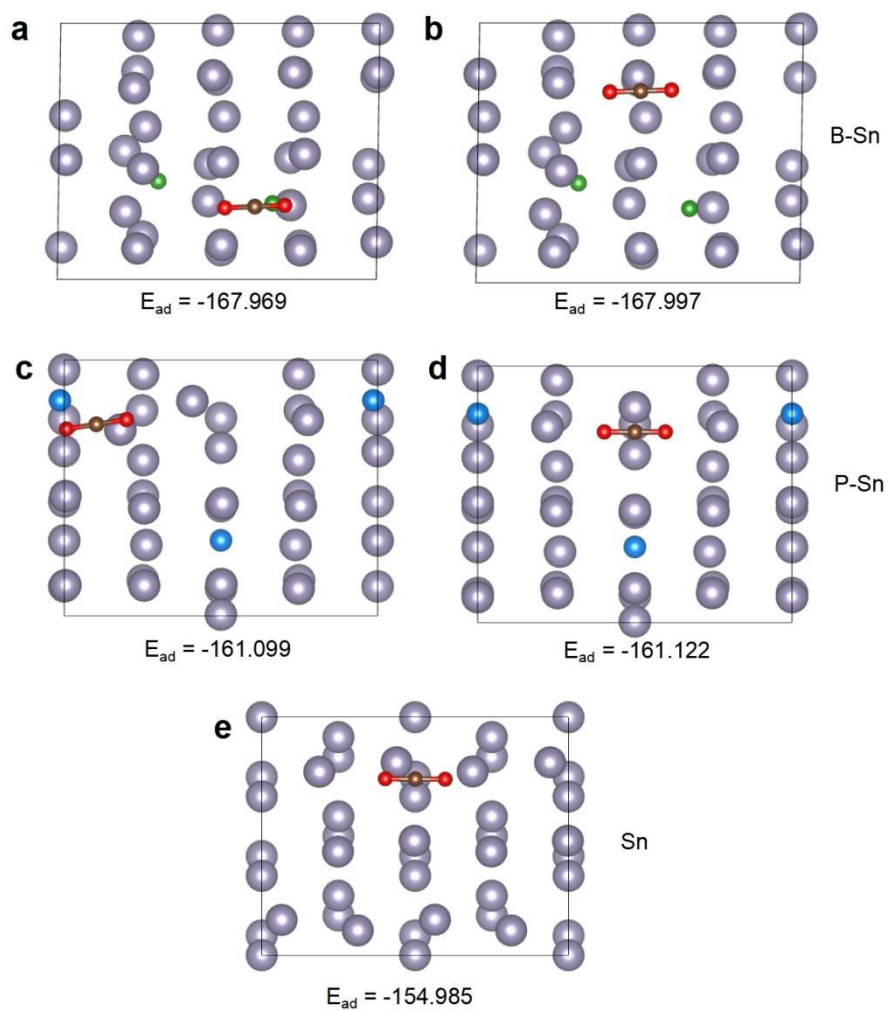
(c) Substantial Capital Investment: The distillation columns used exceed 100 meters in height, far taller than those in conventional industrial systems, leading to exceptionally high investment costs.

These qualitative arguments remain highly persuasive in illustrating the constraints of existing methods.

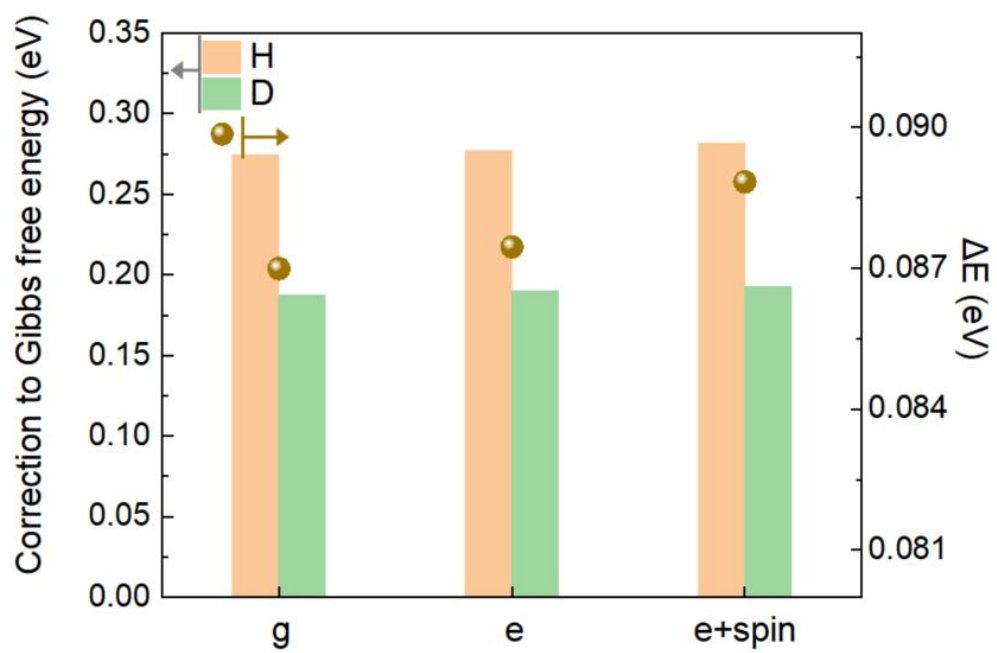
SUPPLEMENTARY FIGURES



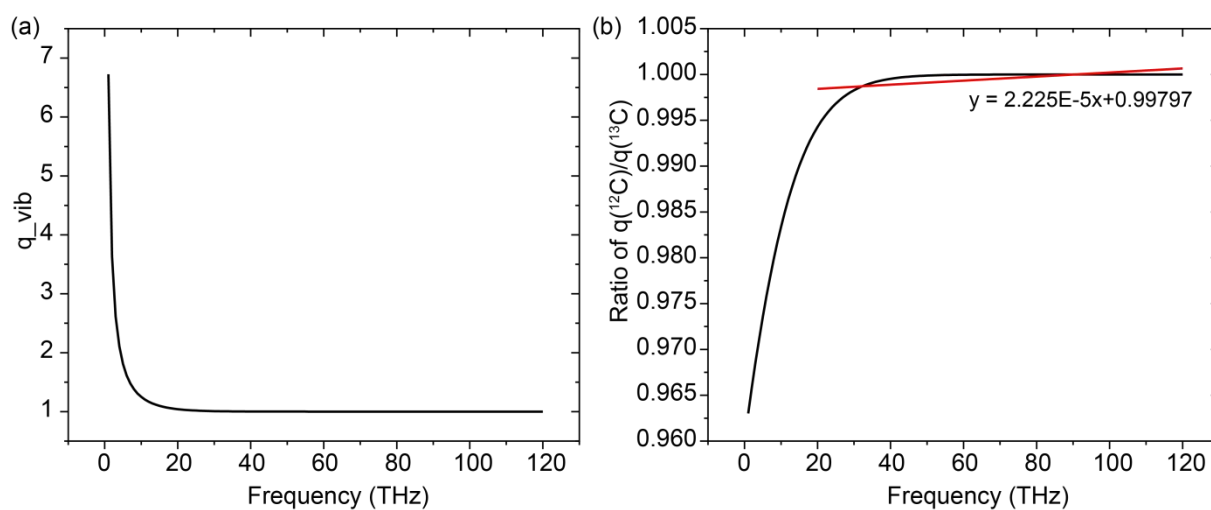
Supplementary Fig. 1. Gibbs free energy differences between $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ adsorbed on Sn model with different atomic layers.



Supplementary Fig. 2. The total energies of CO₂ + catalyst systems when CO₂ is initially set at distinct sites on Sn-based catalyst surfaces: (a-b) B-Sn, (c-d) P-Sn, (e) pure Sn. Only one position is considered for Sn because adsorption sites are identical.

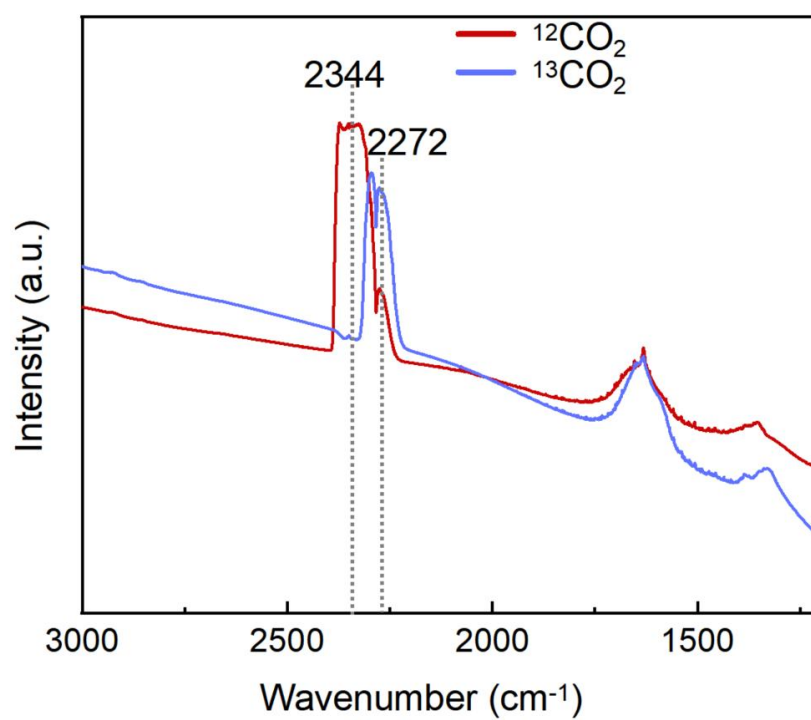


Supplementary Fig. 3. Effect of magnetic moment on isotopic Gibbs Free Energy differences.

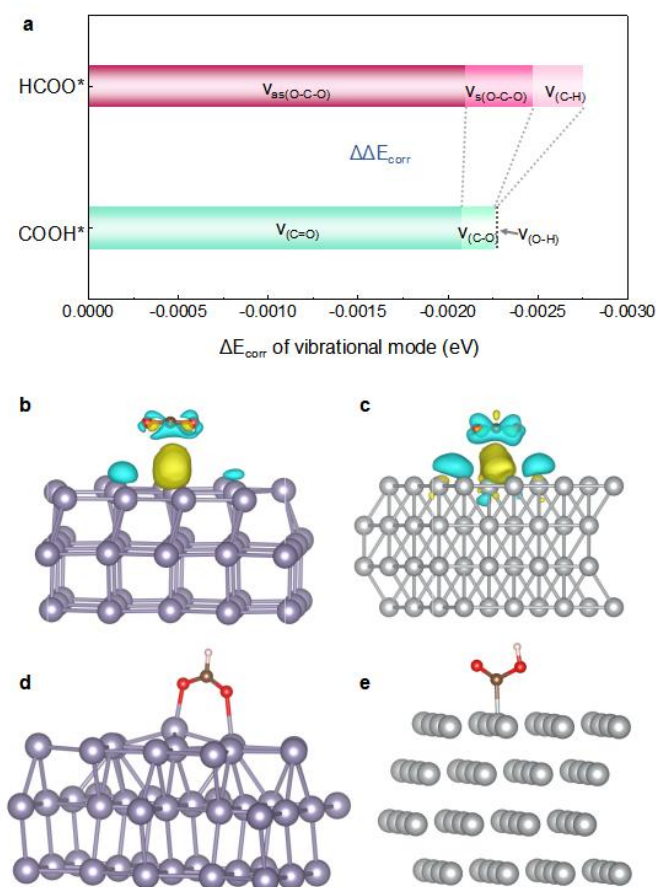


Supplementary Fig. 4. (a) The value of vibrational partition function (q) under different frequencies.

(b) The ratio of q of ^{12}C and ^{13}C intermediates and its fitting when frequencies are over 20 THz.



Supplementary Fig. 5 Experimentally measured infrared absorption peak positions of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$.

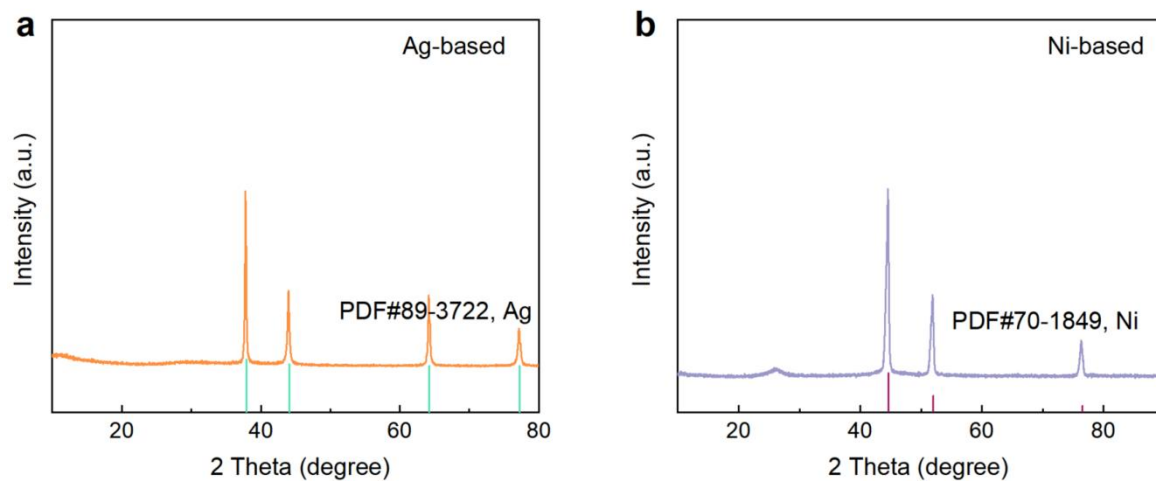


Supplementary Fig. 6. (a) The contribution of main vibrational modes in COOH^* and HCOO^* to the correction energy difference (ΔE_{corr}). Differential charge density diagram of (b) Sn-based and (c) Ag-based catalysts. The schematic diagram of the adsorption configurations of HCOO^* and COOH^* on the (d) Sn-based and (e) Ag-based models.

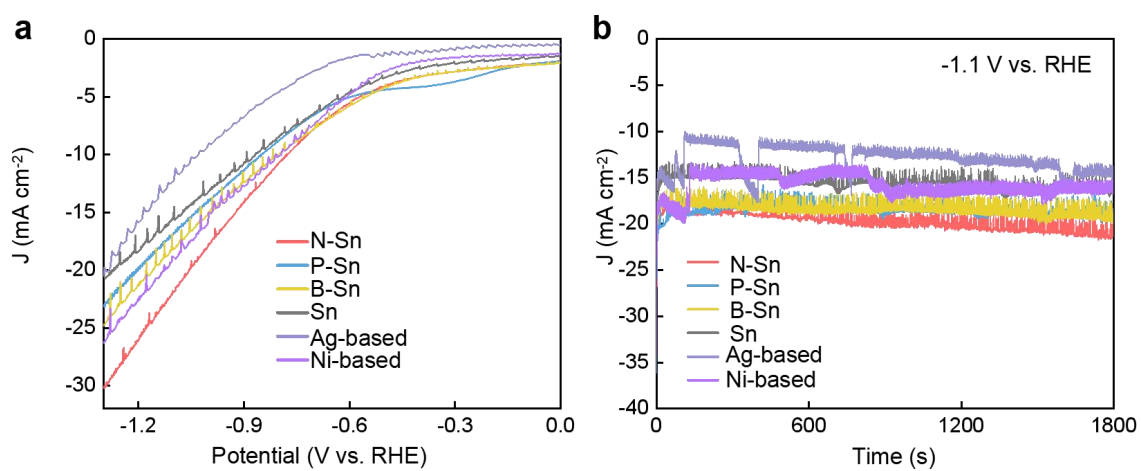
Note: The C affects only C-O bonding in COOH^* , while O-H vibrational mode is not sensitive to C, as evidenced by the negligible difference between the O-H vibration mode in $^{12}\text{COOH}^*$ and $^{13}\text{COOH}^*$ (Extended Data Fig. 1b). On the contrary, HCOO^* formation originates from a CO_2 protonation step that involves C-H bond formation accompanied by significant bending of the O-C-O framework. The C-H vibrational modes exhibit high sensitivity to C isotope mass,

as seen from the remarkable vibrational frequency difference of $^{12}\text{C-H}$ and $^{13}\text{C-H}$ (Extended Data Fig. 1a), as well as the large contribution to the energy difference of isotopologues ($\Delta E_{\text{corr_C-H}}$) (Supplementary Fig. 6a). The C-O vibrational modes also contribute to enlarging the energy difference of isotopologues (Extended Data Fig. 1a-b), but contribute similarly in COOH^* and HCOO^* compared to O-H in COOH^* and C-H in HCOO^* (Supplementary Fig. 6a).

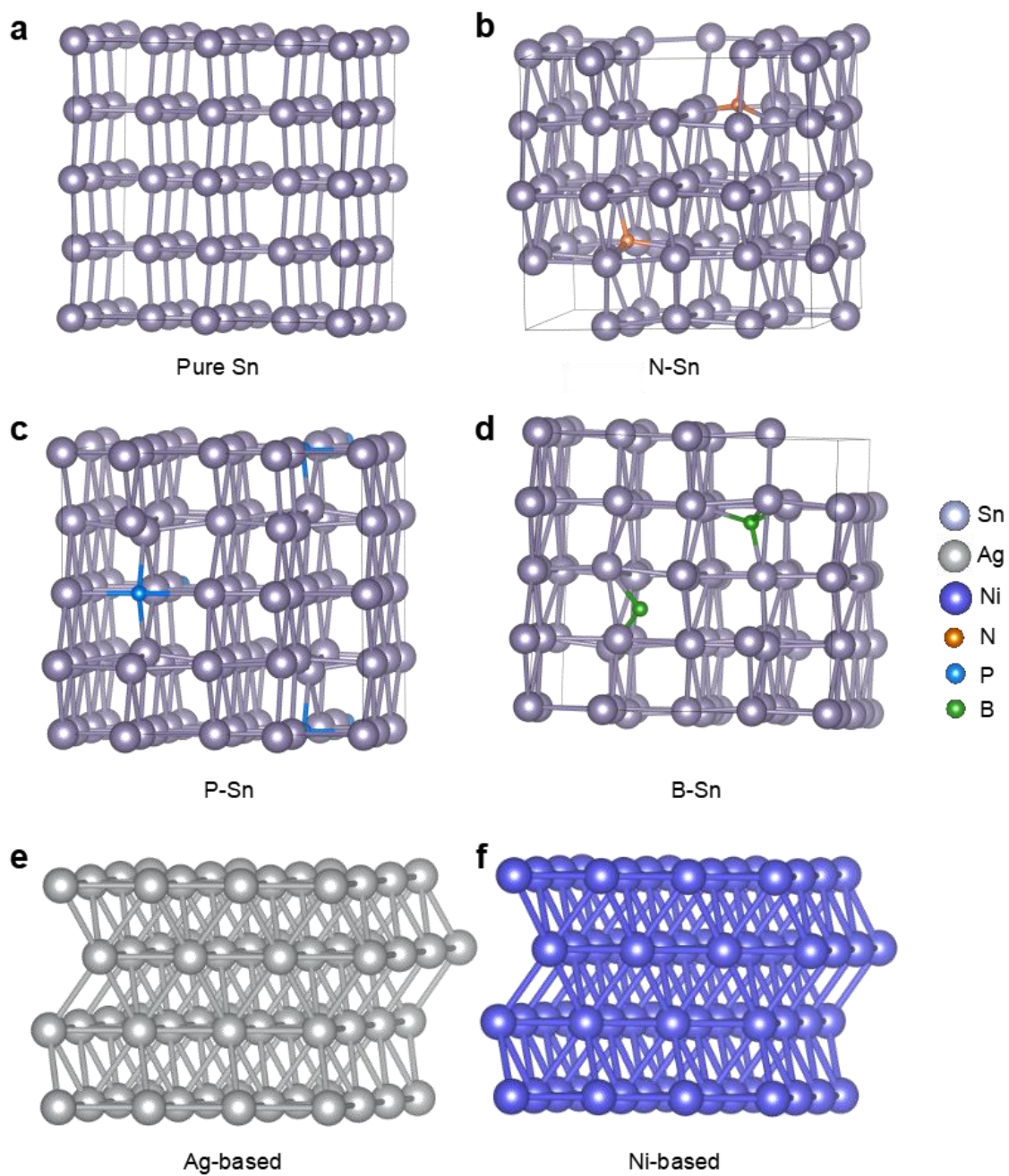
The CO_2 is adsorbed on (doped) Sn, Ag, and Ni surfaces by vdW interaction. C is positively charged due to the polarity of the C=O bond. When CO_2 appears on the metal surface, the positively charged C induces a redistribution of charges on the metal surface through vdW interactions, which can be seen from the differential charge density of metal- CO_2 models (Supplementary Fig. 6b-c). However, we can see in the differential charge density that the O is more negatively charged when CO_2 is on the surface of Ag/Ni, which would greatly enhance proton adsorption, thereby facilitating the formation of COOH^* intermediates. On the contrary, the formation of COOH^* on Sn surface is energetically unfavorable (0.5 eV larger) than that of HCOO^* (Extended Data Fig. 2g-h). And Supplementary Fig. 6d-e show the schematic diagrams of the oxygen adsorption configuration on the Sn-based catalyst and the C adsorption configuration of COOH^* on the Ag-based catalyst.



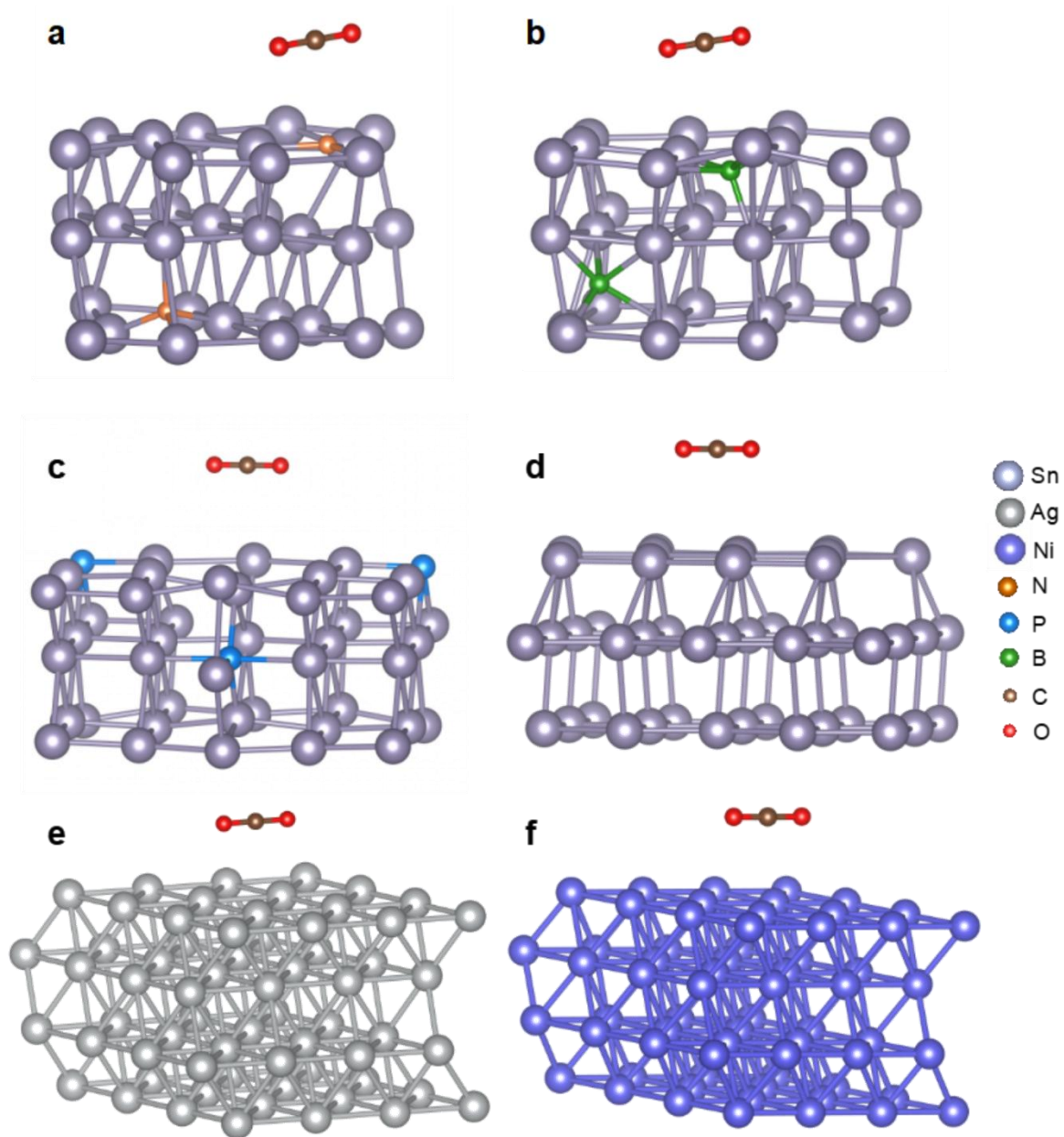
Supplementary Fig. 7. XRD patterns of (a) Ag-based and (b) Ni-based catalysts.



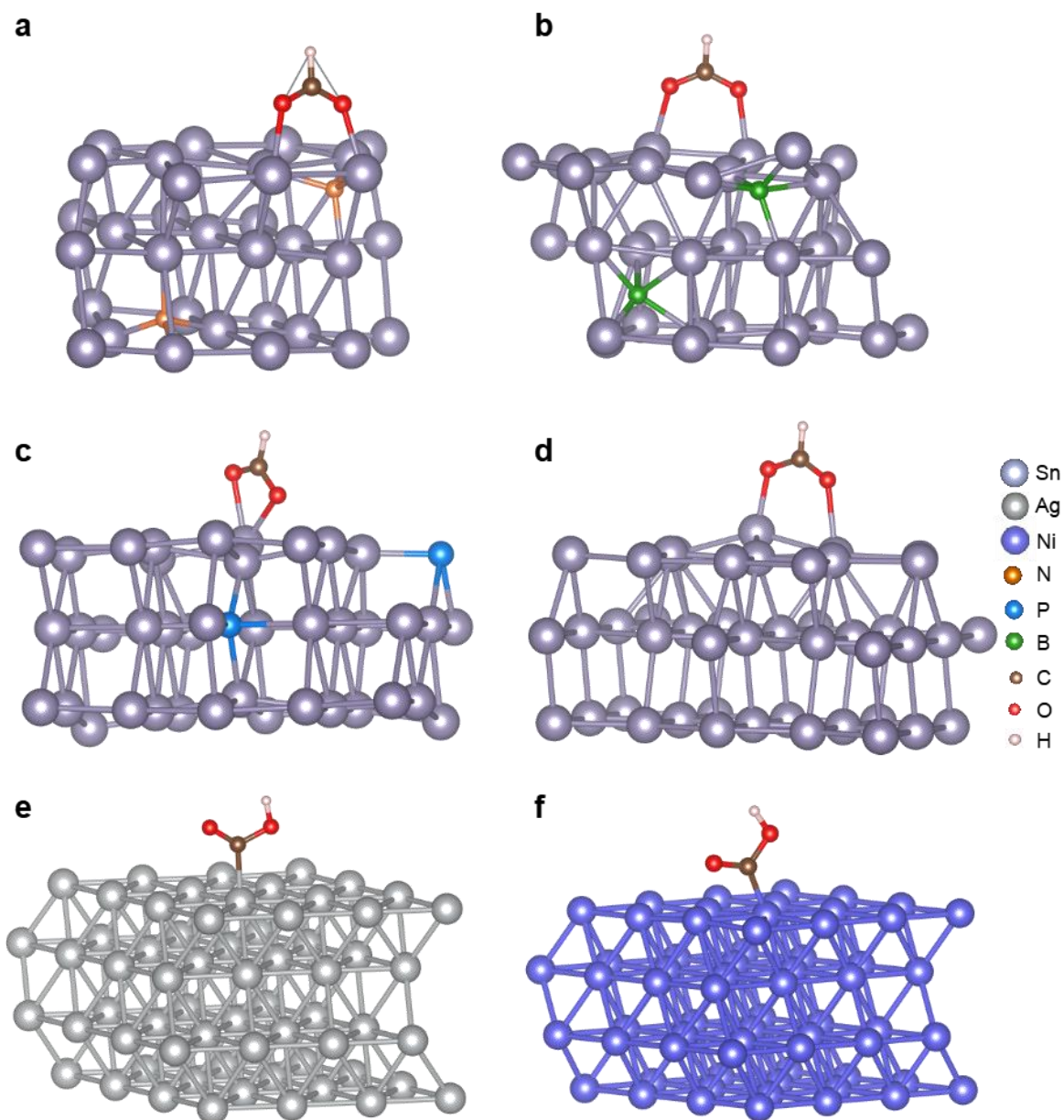
Supplementary Fig. 8. (a) LSV tests and (b) chronoamperometry tests at -1.1 V vs. RHE of Sn-based, Ag-based and Ni-based catalysts in H-cell.



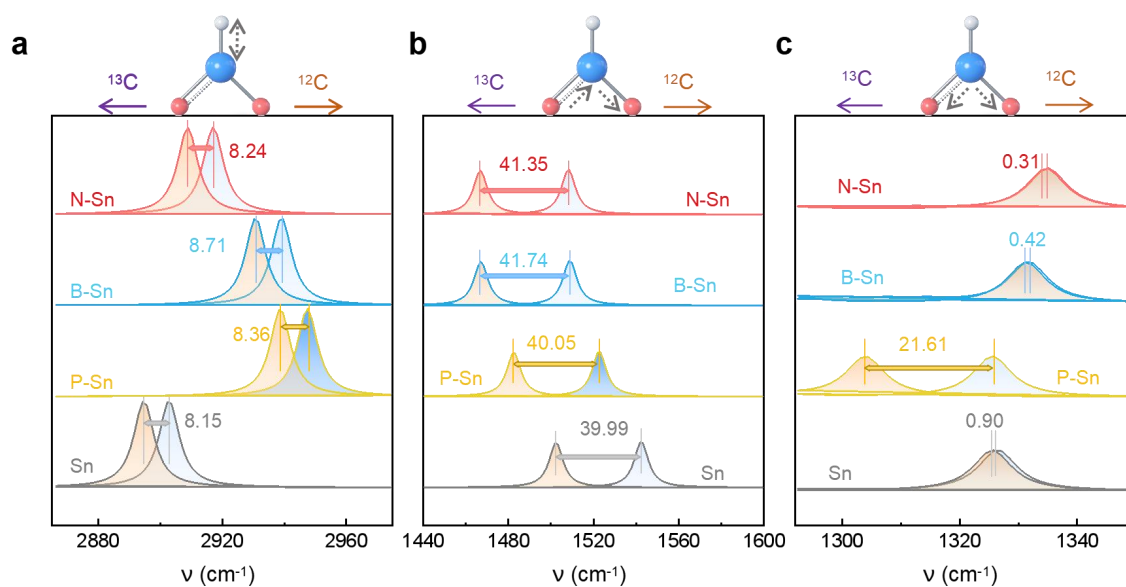
Supplementary Fig. 9. The optimized (a) Sn, (b) N-doped, (c) P-doped, and (d) B-doped Sn catalysts designed through atomic-level doping strategies.



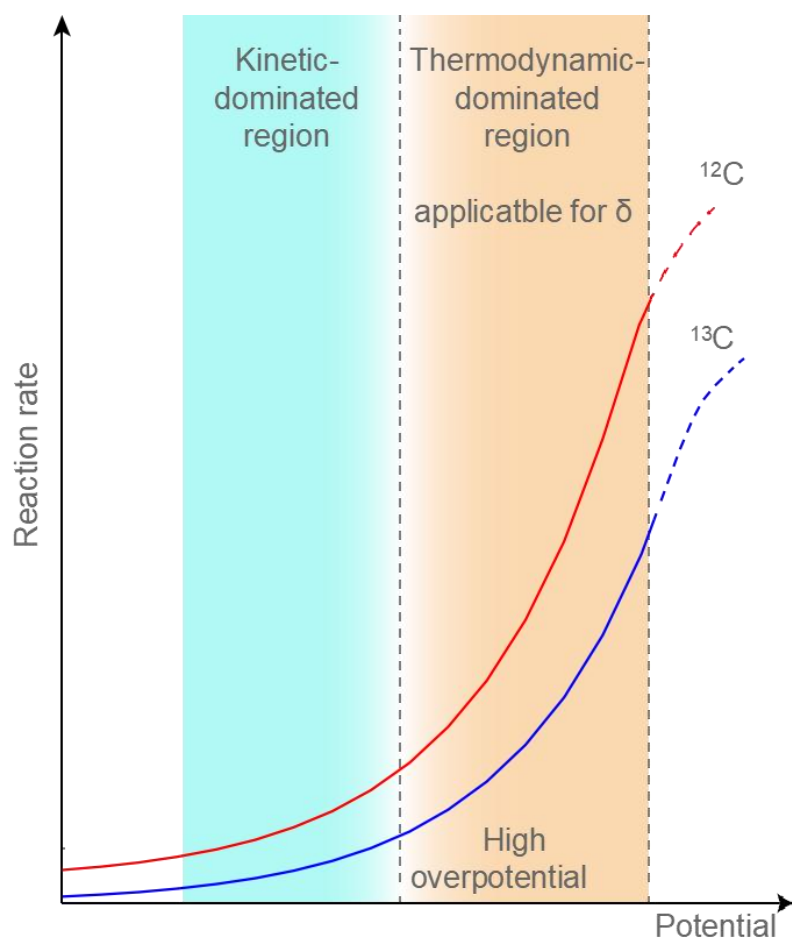
Supplementary Fig. 10. Adsorption configurations of $^{12/13}\text{CO}_2$ on (a) N-Sn, (b) B-Sn, (c) P-Sn, (d) pure Sn, (e) Ag-based, and (f) Ni-based models.



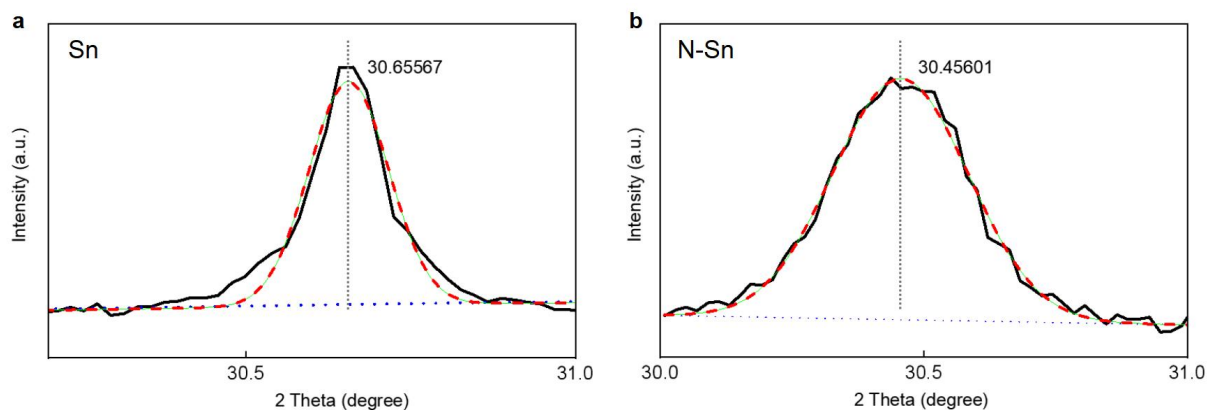
Supplementary Fig. 11. Adsorption configurations of $\text{H}^{12/13}\text{COO}^*$ on (a) N-Sn, (b) B-Sn, (c) P-Sn, (d) pure Sn and adsorption configurations of $^{12/13}\text{COOH}^*$ on (e) Ag-based and (f) Ni-based models.



Supplementary Fig. 12. The vibration frequencies of $\text{H}^{12}\text{COO}^*$ and $\text{H}^{13}\text{COO}^*$ on N-, B-, P-Sn and pure Sn models.



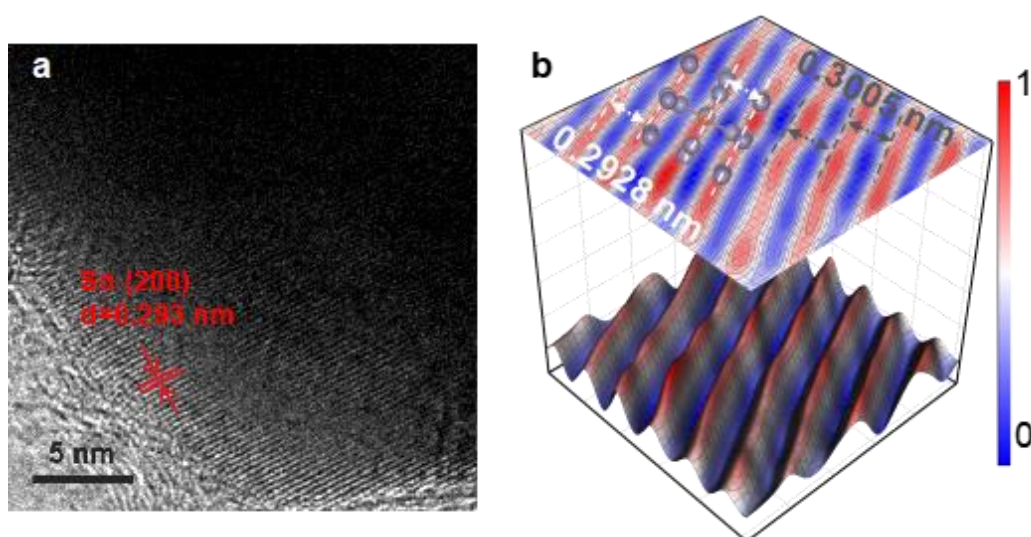
Supplementary Fig. 13. The specific electrochemical conditions under which δ is applied.



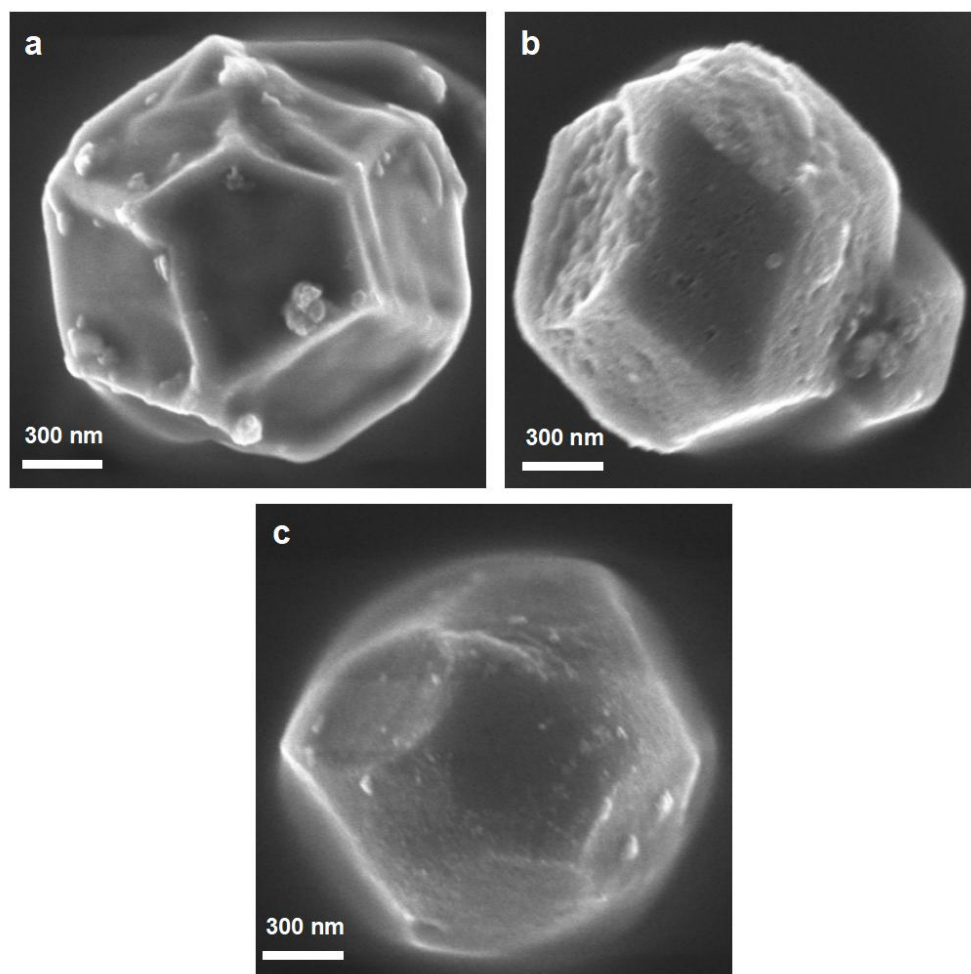
Supplementary Fig. 14. XRD Gaussian fitting patterns of the main peaks of Sn and N-Sn.

Note: The interplanar lattice spacings (d) were calculated based on Bragg's law using the formula: $d = \lambda / (2\sin\theta)$, where λ represents the X-ray wavelength (0.154 nm for Cu K α radiation).

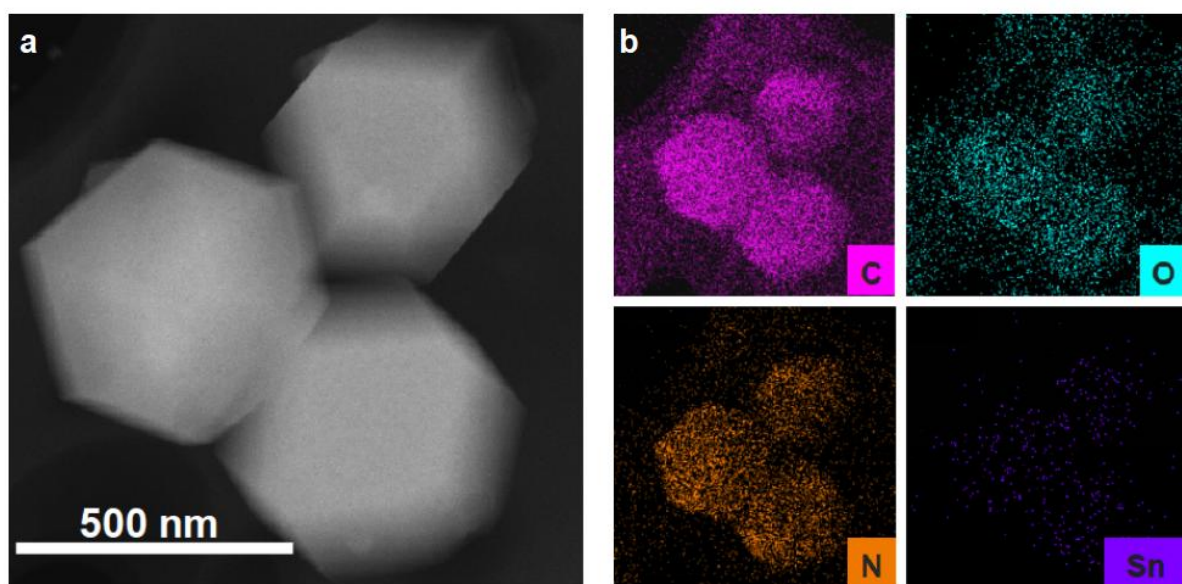
The Gaussian-fitted XRD diffraction peaks for pristine Sn and N-doped Sn (N-Sn) were located at $2\theta = 30.6557^\circ$ and 30.4560° , respectively. Through calculation, the corresponding lattice spacings were determined to be 0.2913 nm and 0.2932 nm. This discernible increase in lattice spacing after nitrogen doping provides clear evidence of lattice expansion, confirming the structural modification induced by nitrogen incorporation into the Sn lattice structure.



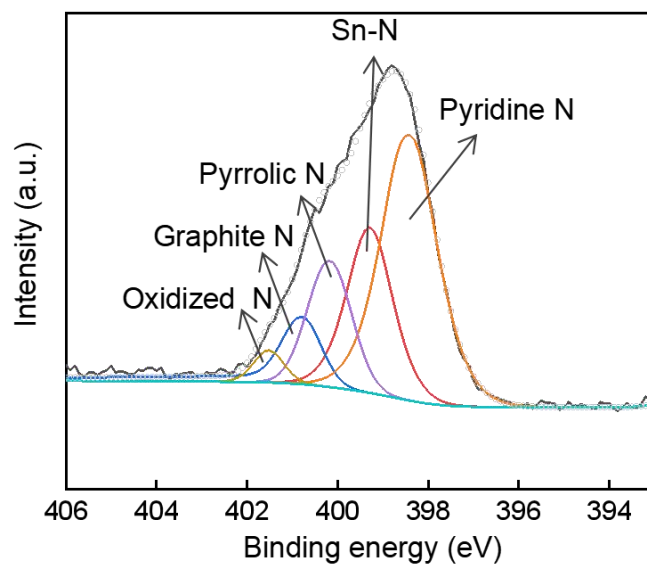
Supplementary Fig. 15. (a) TEM images of N-Sn, (b) 3D atomic overlap Gaussian fitting results.



Supplementary Fig. 16. SEM images of (a) P-Sn, (b) B-Sn, and (c) pure Sn.

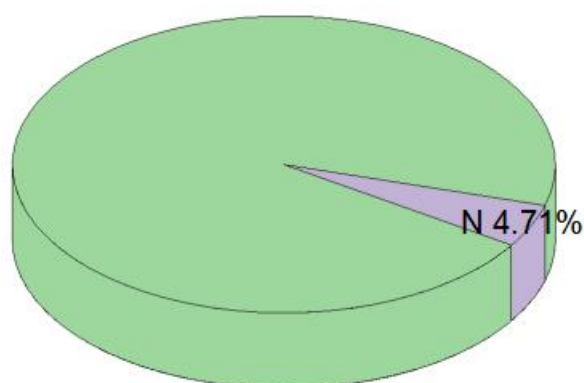


Supplementary Fig. 17. (a) HR-TEM images of N-Sn. (b) The EDS mapping images for C, O, N, and Sn of N-Sn.



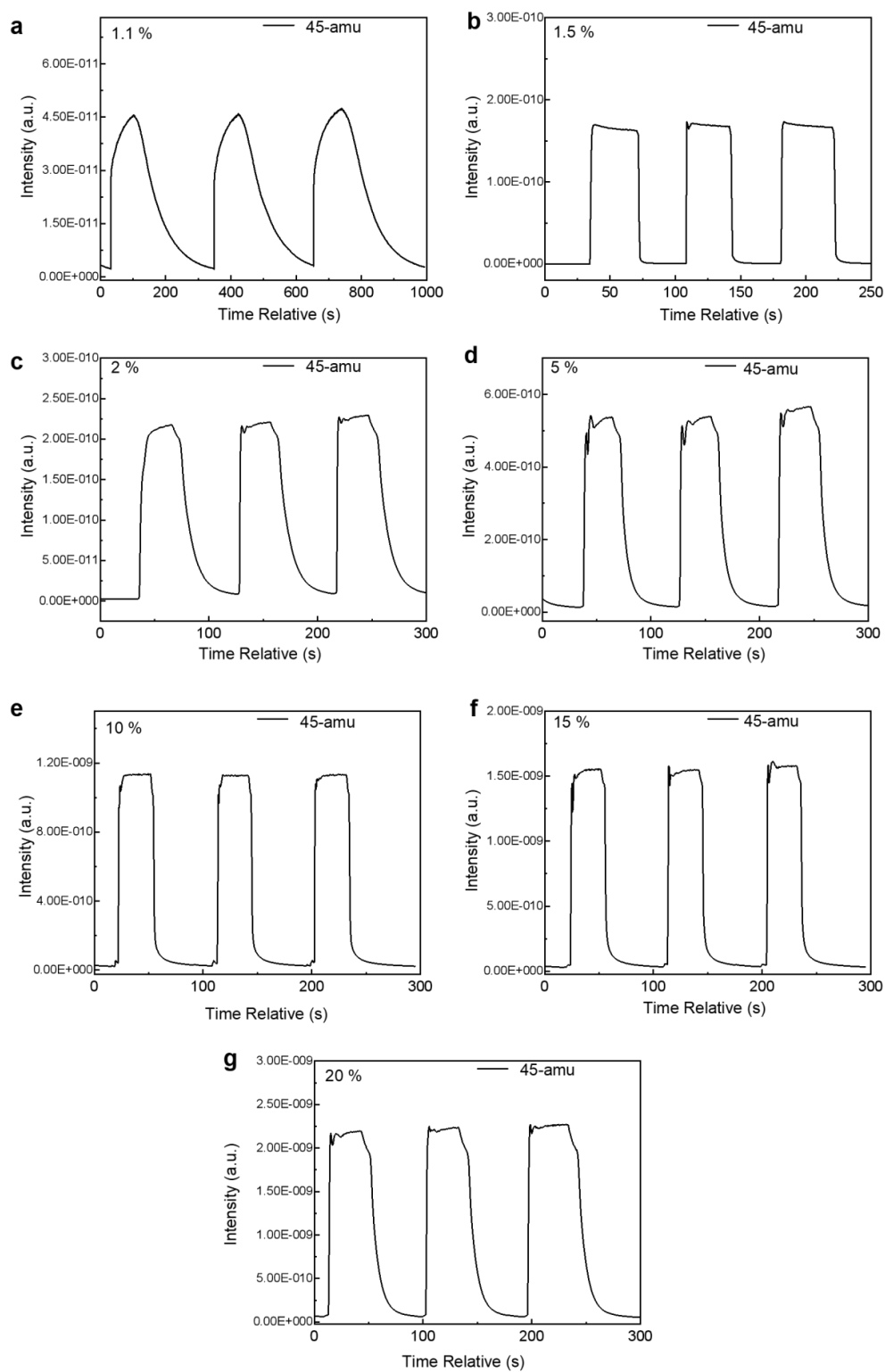
Supplementary Fig. 18. N 1s XPS spectrum of the N-Sn catalyst.

Note: N 1s XPS analysis reveals a distinct Sn-N bonding contribution at 399.3 eV (Supplementary Fig. 18).



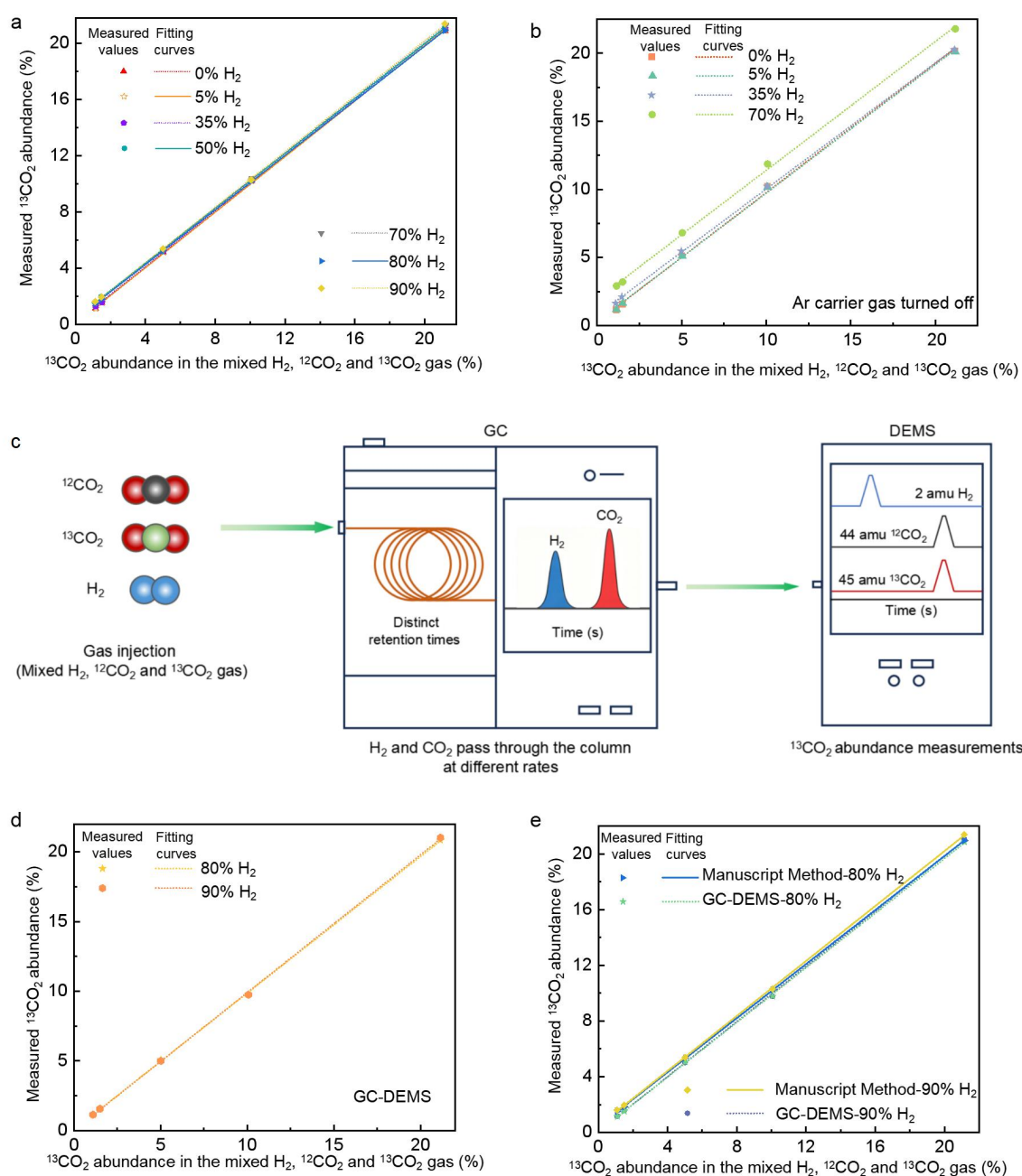
Supplementary Fig. 19. N content analysis of the N-Sn catalyst by the Oxygen, Nitrogen, and Hydrogen (ONH) Analyzer.

Note: The Oxygen, Nitrogen, and Hydrogen (ONH) Analyzer confirms a N content of approximately 4.71% in the catalyst (Supplementary Fig. 19). XPS and ONH analysis demonstrate the successful incorporation of N into the Sn, which precisely modulates the electronic environment of the active Sn sites. This electronic modification enhances CO₂ adsorption and activation, thereby ultimately rationalizing the exceptional ¹³CO₂ enrichment performance, in full agreement with DFT predictions.



Supplementary Fig. 20. (a-g) Differential electrochemical mass spectrometry (DEMS) spectra of $^{13}\text{CO}_2$ standard gas at different concentrations.

Note: Peak profiles do not affect quantitative conclusions: due to the off-line measurement setup, fluctuations in sample introduction flow rate across different catalysts led to variations in peak profiles. To validate the accuracy of this analytical method, calibration curve measurements were conducted. It was observed that the peak profiles of $^{13}\text{CO}_2$ varied slightly across different concentrations (Supplementary Fig. 20); however, a highly linear relationship was consistently maintained between concentration and peak height/area, confirming the reliability of our quantitative analysis (Extended Data Fig. 4a).

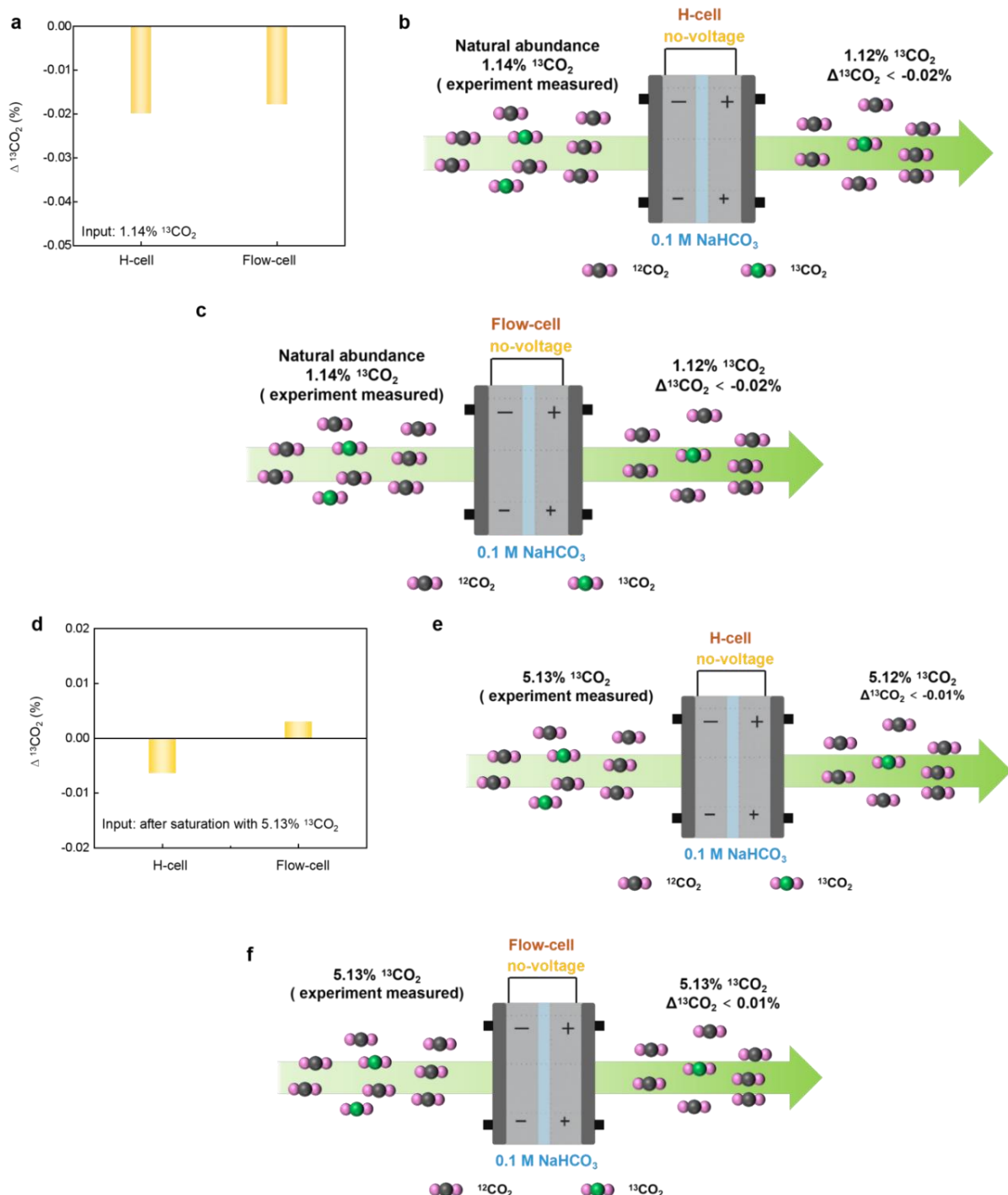


Supplementary Fig. 21. Measured isotopic abundance (y-axis) versus actual abundance (x-axis) for mixed H_2 , $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ gas under (a) standard measurement conditions and (b) the conditions without the Ar dilution strategy. (c) Schematic diagram of the GC-DEMS system. GC column is employed to temporally separate H_2 and CO_2 based on their distinct retention times; then, H_2 and CO_2 gases sequentially elute from the GC into the DEMS. (d) Results measured by coupled GC-DEMS

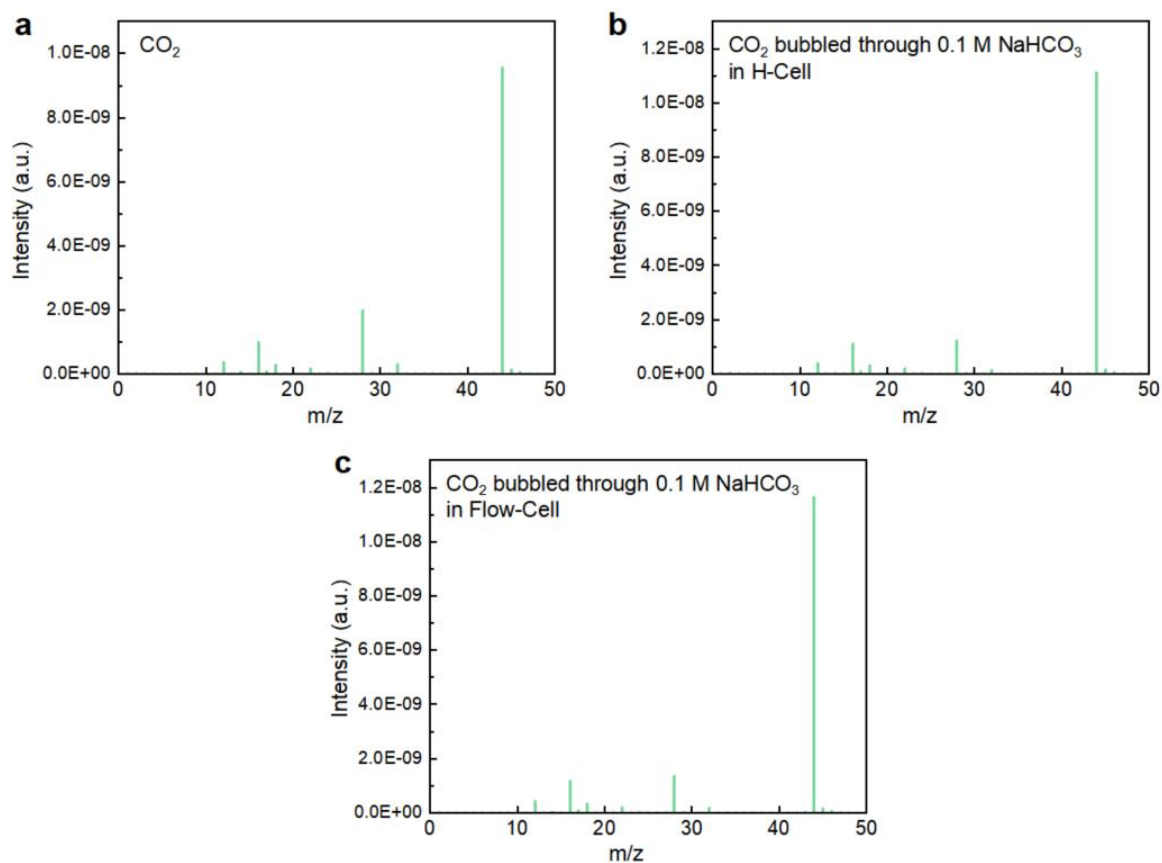
without the Ar dilution strategy. (e) Comparison of two measurement methods for the calibration curves of 80-90% H₂.

Note: We constructed calibration curves using gas flow mixtures containing 0%-90% H₂, ¹²CO₂ and ¹³CO₂ to validate the accuracy of our results. Higher H₂ concentrations induce increasingly pronounced asynchronous shifts between the m/z 44 and 45 peak profiles owing to H₂ ionization, thereby resulting in larger measurement errors. For gas mixtures containing 50%-90% H₂, the measured deviation was still within the measurement error margin (within ±0.50%, Supplementary Fig. 21a). It is noted that the measurement of ¹³CO₂ abundance under H₂ concentrations above 70% would show significant overestimation errors (over 1.8%, Supplementary Fig. 21b) when shutting off the Ar carrier gas. This error is because of the formation of protonated ¹²CO₂ (¹²CO₂ + H⁺) at m/z 45 due to high concentration of H₂-derived protonic species from secondary ionization.

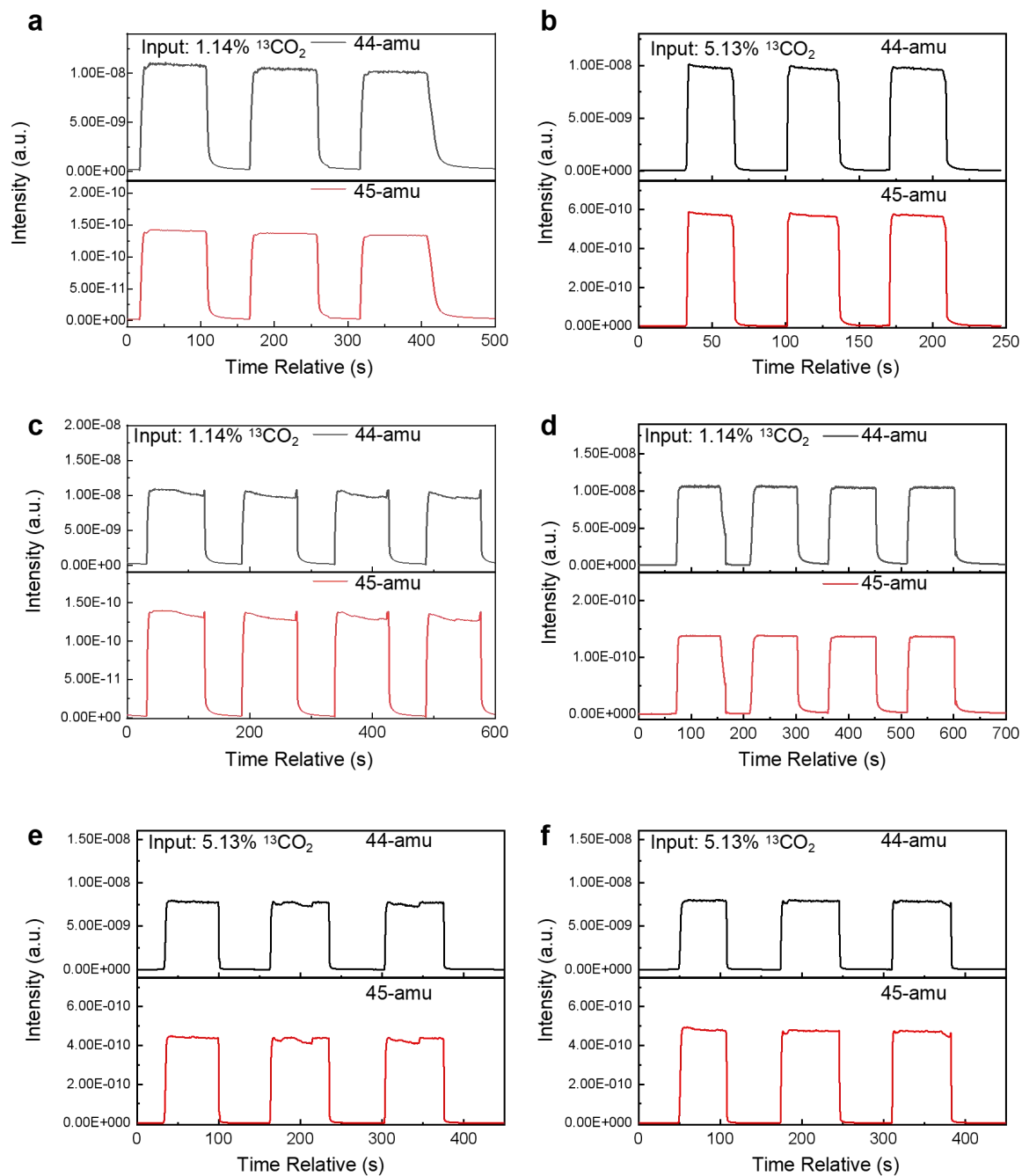
Gas Chromatography-DEMS (GC-DEMS) was used as an orthogonal method to assess the Ar-diluted DEMS measurements under high-H₂ conditions, in which H₂ and CO₂ are temporally separated by the GC column according to their different retention times, then vented from GC and entered the DEMS sequentially to avoid the effect of protonated ¹²CO₂ (¹²CO₂ + H⁺) at m/z 45 (Supplementary Fig. 21c). This approach is accurate and can essentially eliminate the interference of high-concentration H₂ (Supplementary Fig. 21d). Therefore, by comparing the calibration curves (containing 80% and 90% H₂, respectively) measured with the two methods, our Ar dilution strategy is proven to be accurate at certain ranges of H₂ concentration (Supplementary Fig. 21e).



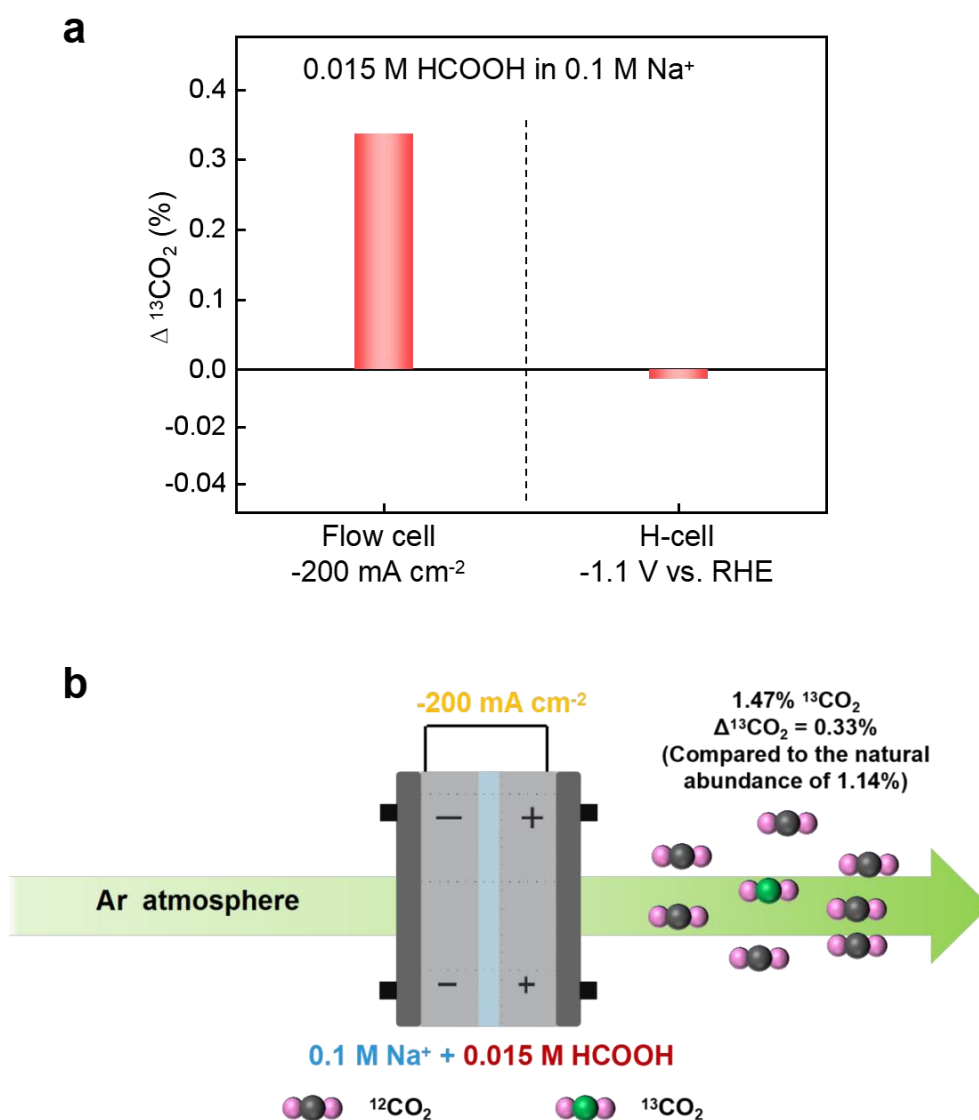
Supplementary Fig. 22. (a) The absorption effect of the cathode electrolyte (0.1 M NaHCO_3) in the H-cell and flow cell for 1.1% $^{13}\text{CO}_2$. Schematic of $^{13}\text{CO}_2$ effluent concentration without applied voltage in (b) H-cell and (c) flow cell. (d) The absorption effect of the cathode electrolyte (0.1 M NaHCO_3) in the H-cell and flow cell for 5.1% $^{13}\text{CO}_2$. Schematic of $^{13}\text{CO}_2$ effluent concentration without applied voltage in (e) H-cell and (f) flow cell.



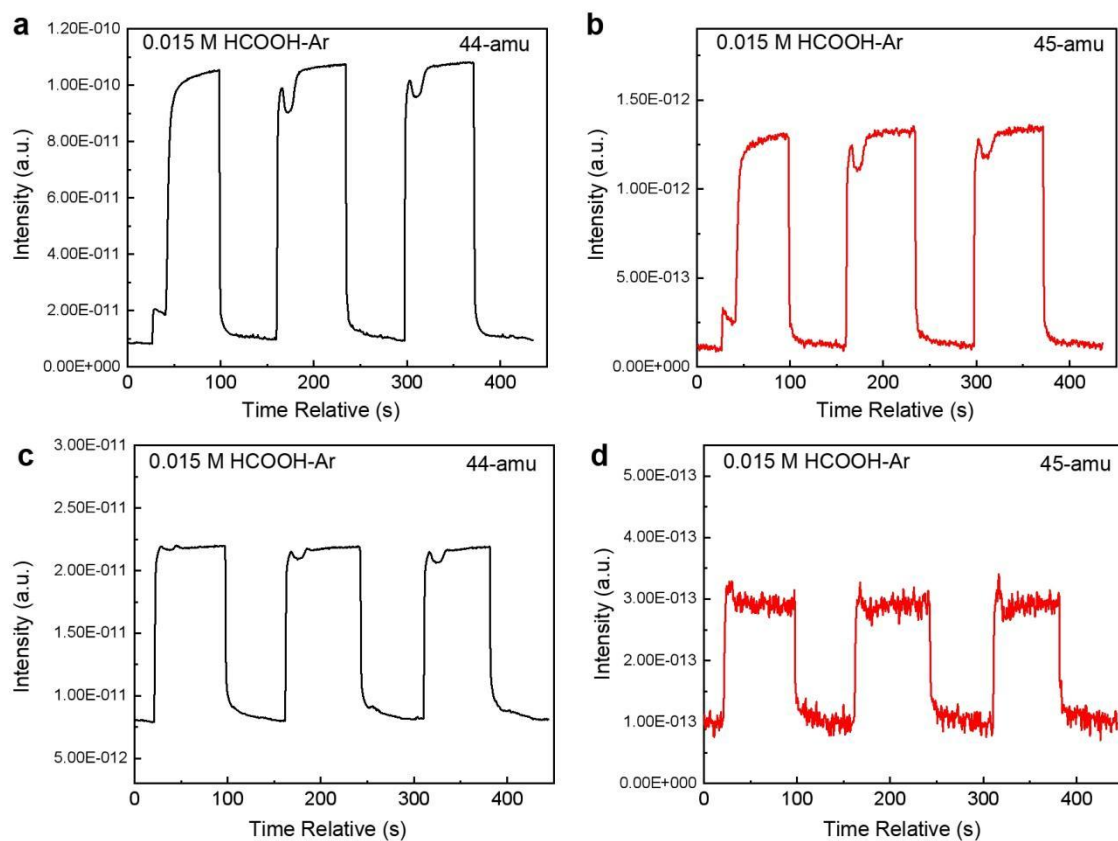
Supplementary Fig. 23. Signals from DEMS full-spectrum analysis of (a) pure CO₂, (b) CO₂ passing through 0.1 M NaHCO₃ catholyte in an H-cell, (c) CO₂ passing through 0.1 M NaHCO₃ catholyte in a flow cell.



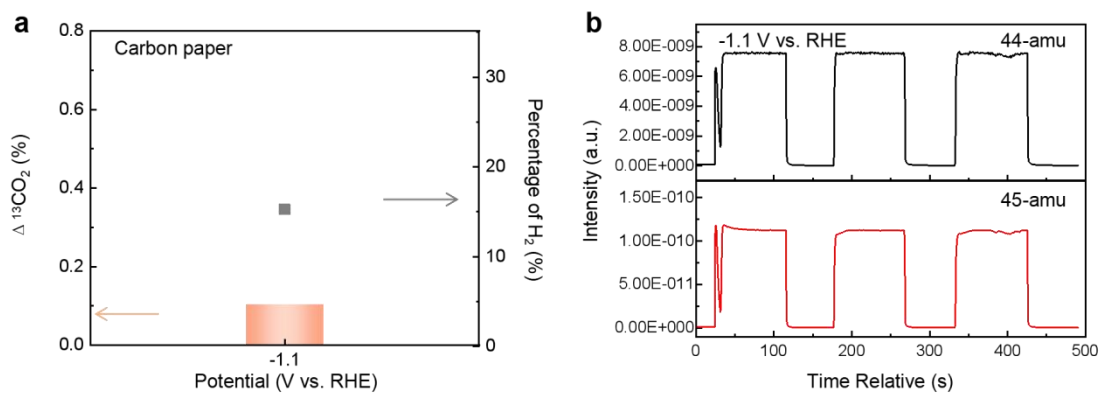
Supplementary Fig. 24. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for (a) CO_2 with 1.14% $^{13}\text{CO}_2$, (b) CO_2 with 5.13% $^{13}\text{CO}_2$. (c, e) CO_2 with 1.14% and 5.13% $^{13}\text{CO}_2$ passing through 0.1 M NaHCO_3 catholyte in the H-cell, (d, f) CO_2 with 1.14% and 5.13% $^{13}\text{CO}_2$ passing through 0.1 M NaHCO_3 catholyte in a flow cell.



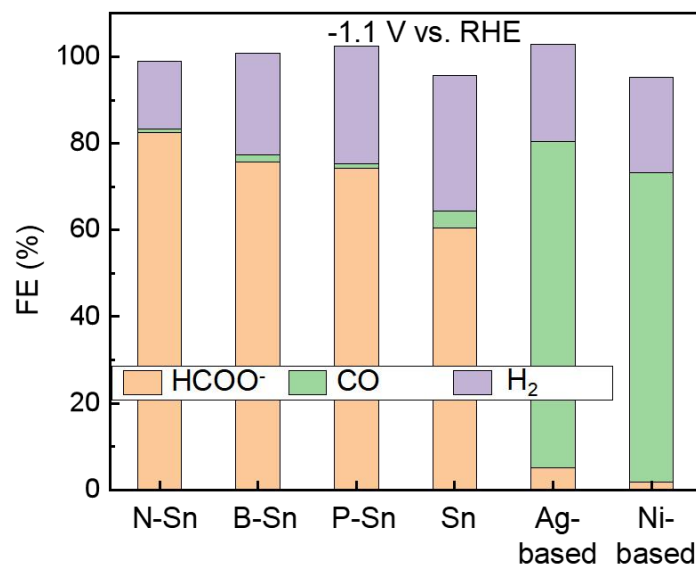
Supplementary Fig. 25. (a) The $\Delta^{13}\text{CO}_2$ caused by electrolysis of the electrolyte containing 0.015 M HCOOH in the H-cell and flow cell under Ar atmosphere. (b) Schematic diagram of the $^{13}\text{CO}_2$ discharge concentration during electrolysis of the electrolyte containing 0.015 M HCOOH in the flow cell.



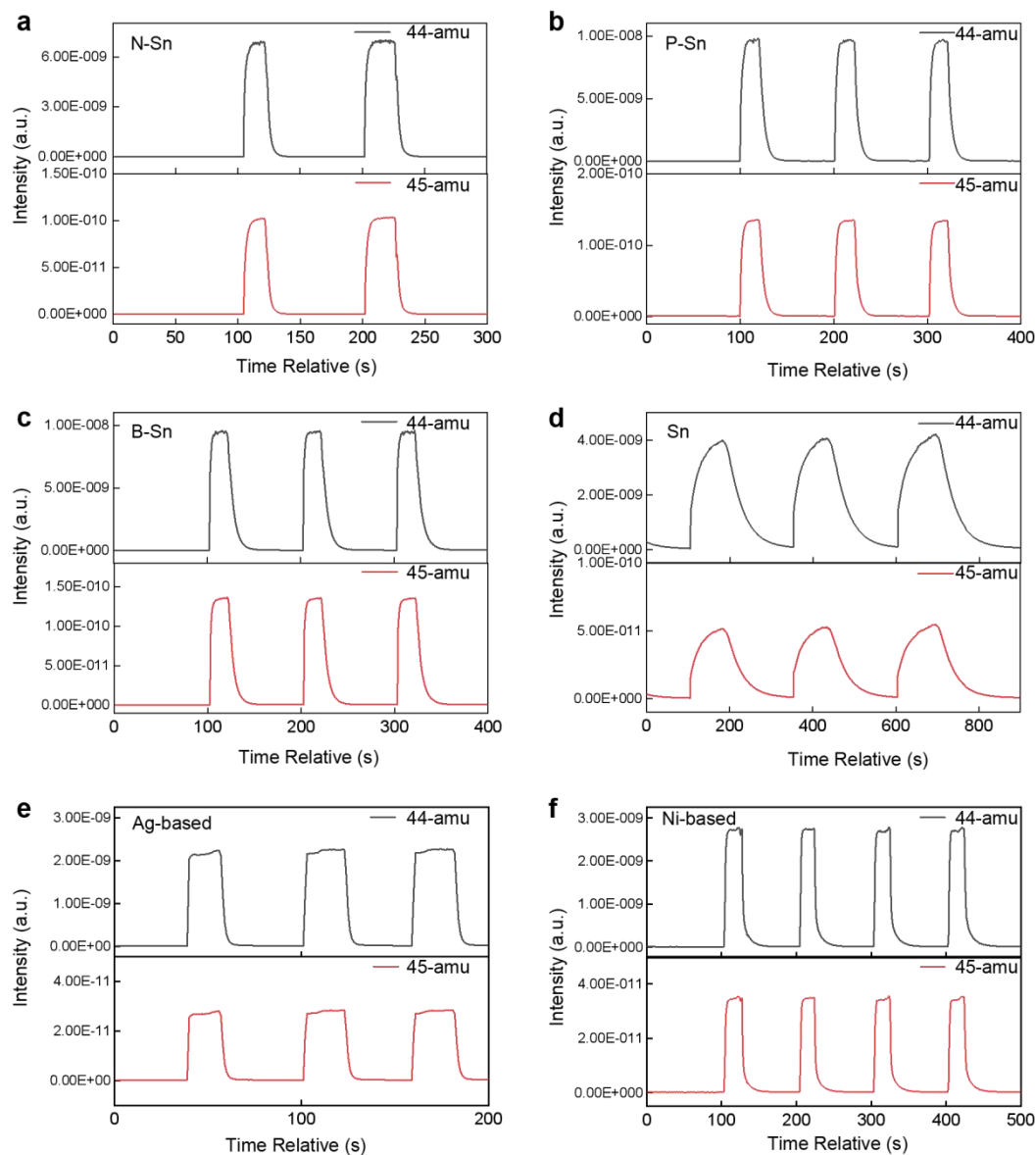
Supplementary Fig. 26. DEMS profiles of 0.015 M HCOOH electrolysis under Ar, H-cell (-1.1 V vs. RHE): (a) $^{12}\text{CO}_2$ ($m/z = 44$), (b) $^{13}\text{CO}_2$ ($m/z = 45$); flow cell (-200 mA cm^{-2}): (c) $^{12}\text{CO}_2$ ($m/z = 44$), (d) $^{13}\text{CO}_2$ ($m/z = 45$).



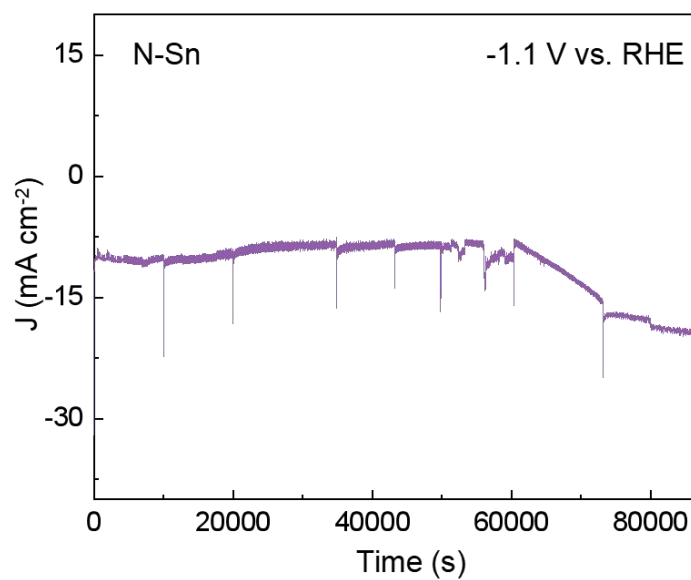
Supplementary Fig. 27. (a) The $\Delta^{13}\text{CO}_2$ of the carbon paper in the H-cell. (b) DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for -1.1 V vs. RHE.



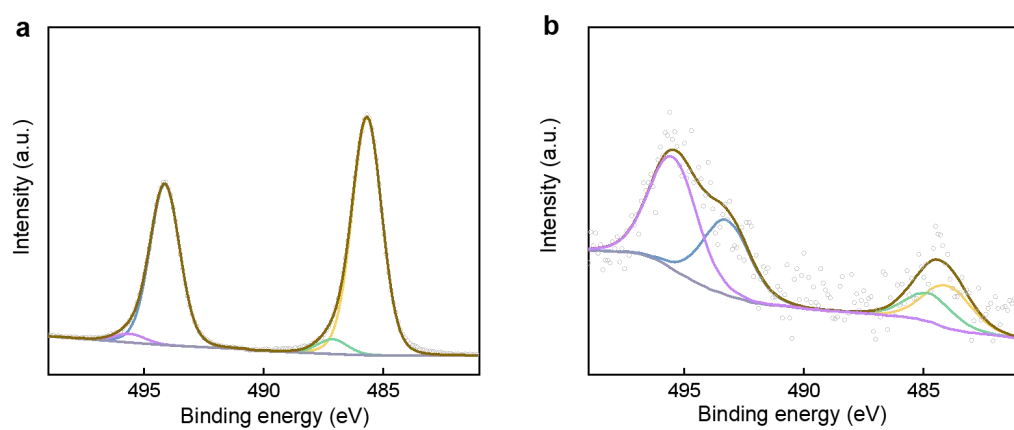
Supplementary Fig. 28. Faradaic Efficiency (FE) of Sn-based, Ag-based and Ni-based catalysts at -1.1 V vs. RHE in H-cell.



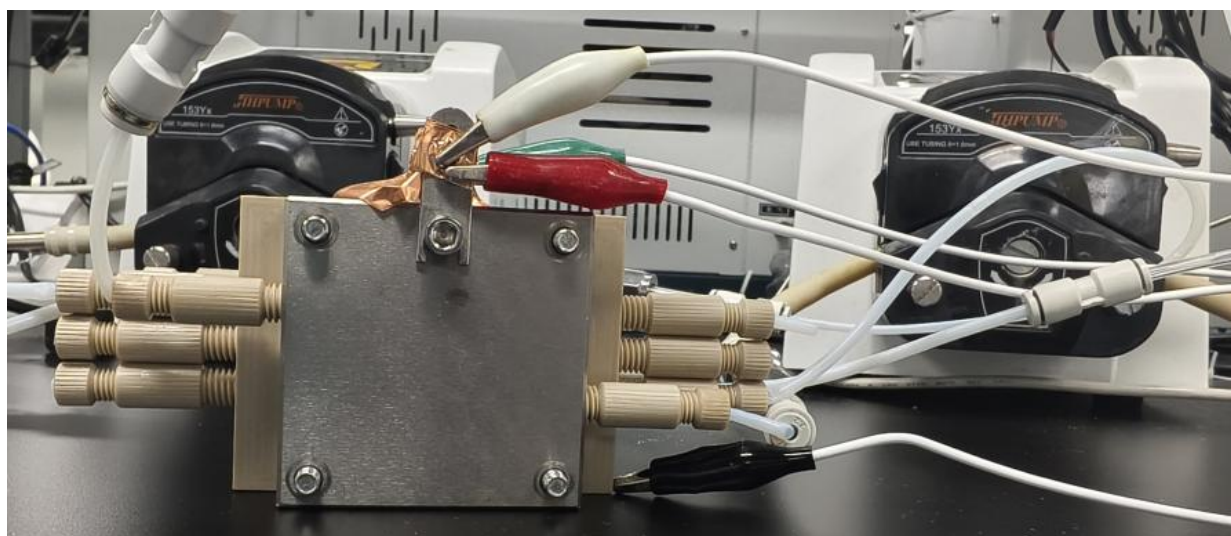
Supplementary Fig. 29. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for (a) N-Sn, (b) P-Sn, (c) B-Sn, (d) pure Sn, (e) Ag-based, and (f) Ni-based catalysts.



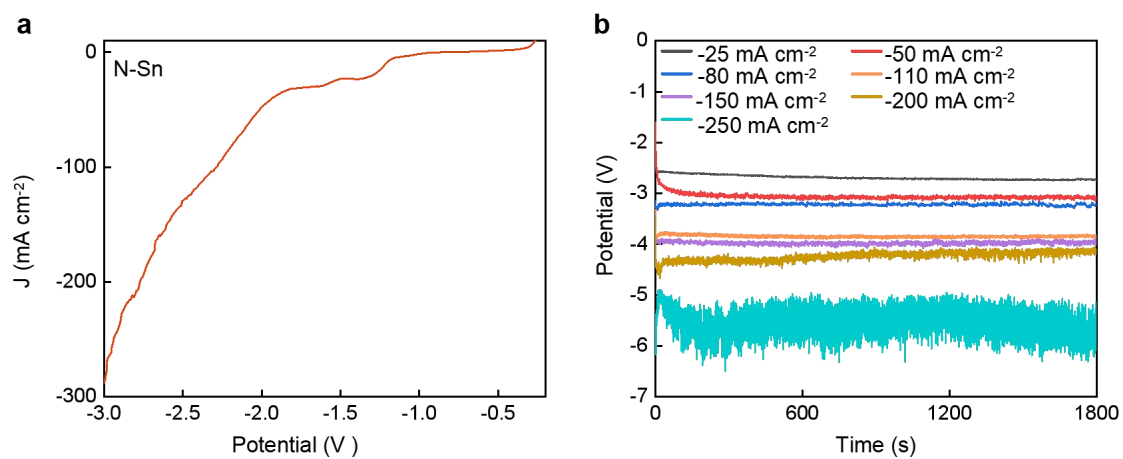
Supplementary Fig. 30. The stability test of N-Sn for 24 hours in the H-cell at -1.1 V vs. RHE.



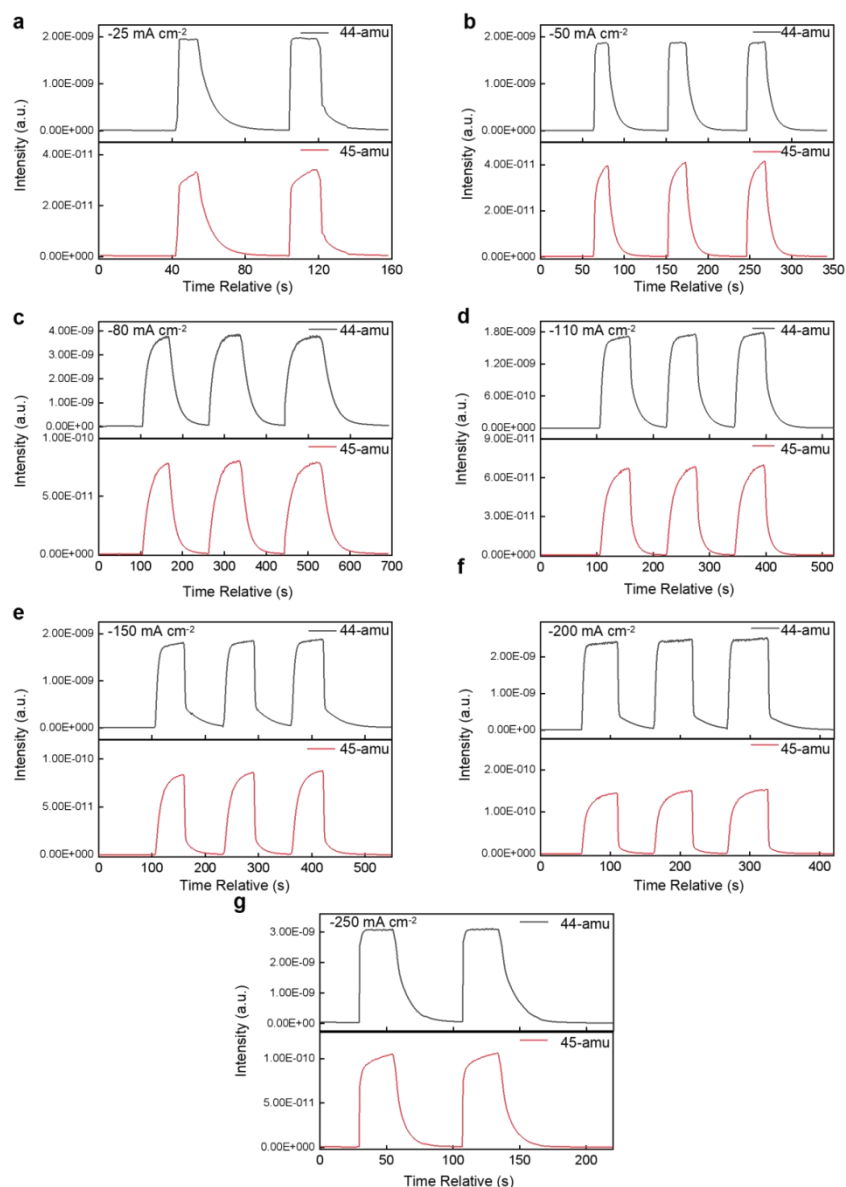
Supplementary Fig. 31. The XPS of (a) N-Sn and (b) N-Sn after the reaction.



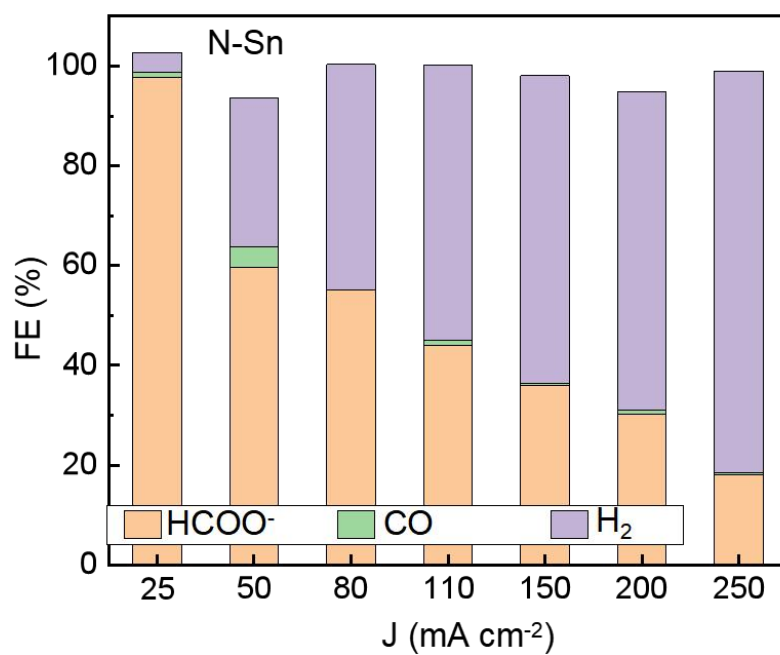
Supplementary Fig. 32. Schematic diagram of a high-throughput flow electrolyzer.



Supplementary Fig. 33. (a) LSV tests and (b) chronopotentiometry tests at -25--250 mA cm^{-2} for N-Sn in a flow cell (the tests were conducted without iR correction).

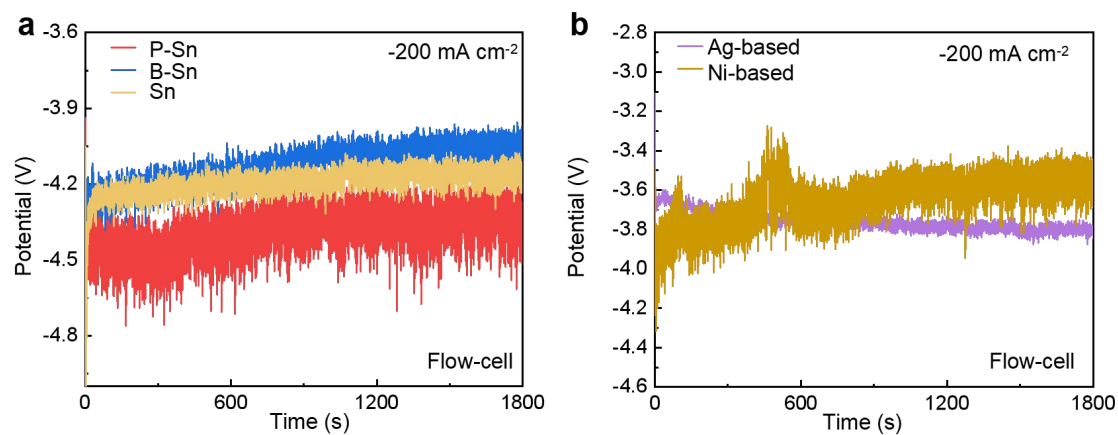


Supplementary Fig. 34. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for (a) -25 mA cm^{-2} , (b) -50 mA cm^{-2} , (c) -80 mA cm^{-2} , (d) -110 mA cm^{-2} , (e) -150 mA cm^{-2} , (f) -200 mA cm^{-2} and (g) -250 mA cm^{-2} in N-Sn. Increased H_2 content causes asynchronous shifts in the m/z 44 and 45 peak profiles owing to H_2 ionization. However, standard gas tests and systematic studies (Supplementary Fig. 21a) confirm that after Ar dilution, low H_2 partial pressure is maintained for inlet H_2 concentrations $< 90\%$, providing accurate and repeatable integrated quantification with the measurement error margin within $\pm 0.5\%$.¹⁸⁻²⁰

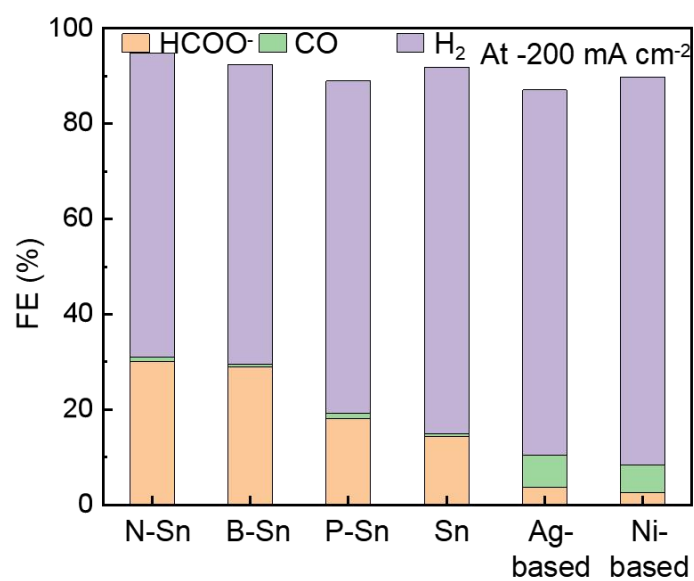


Supplementary Fig. 35. FE for N-Sn at -25--250 mA cm⁻².

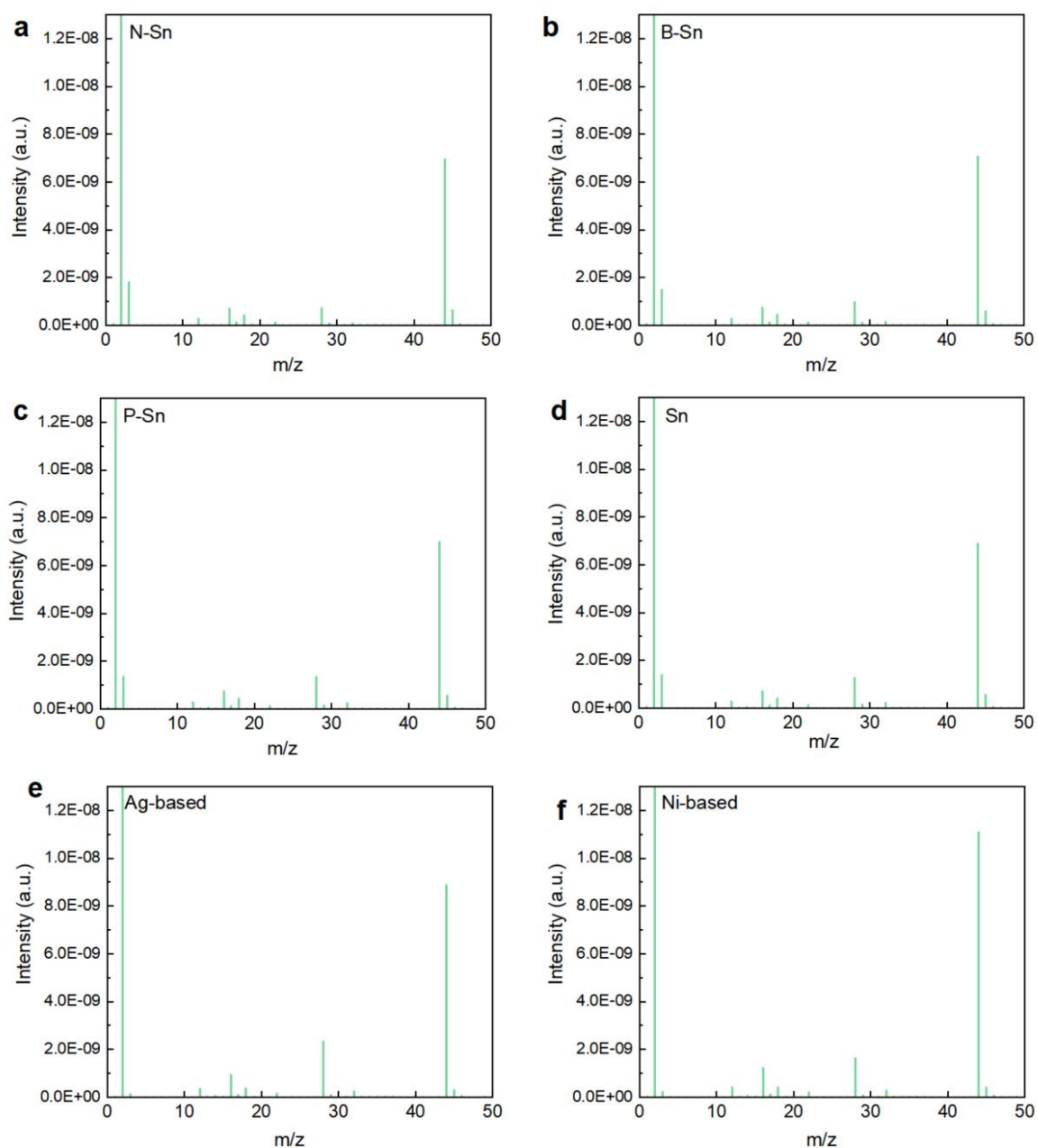
Note: At a high current density, the unoptimized CO₂ feed flow rate of 8 sccm was insufficient, which led to a decline in the FE_{HCOOH} due to inadequate carbon source supply.



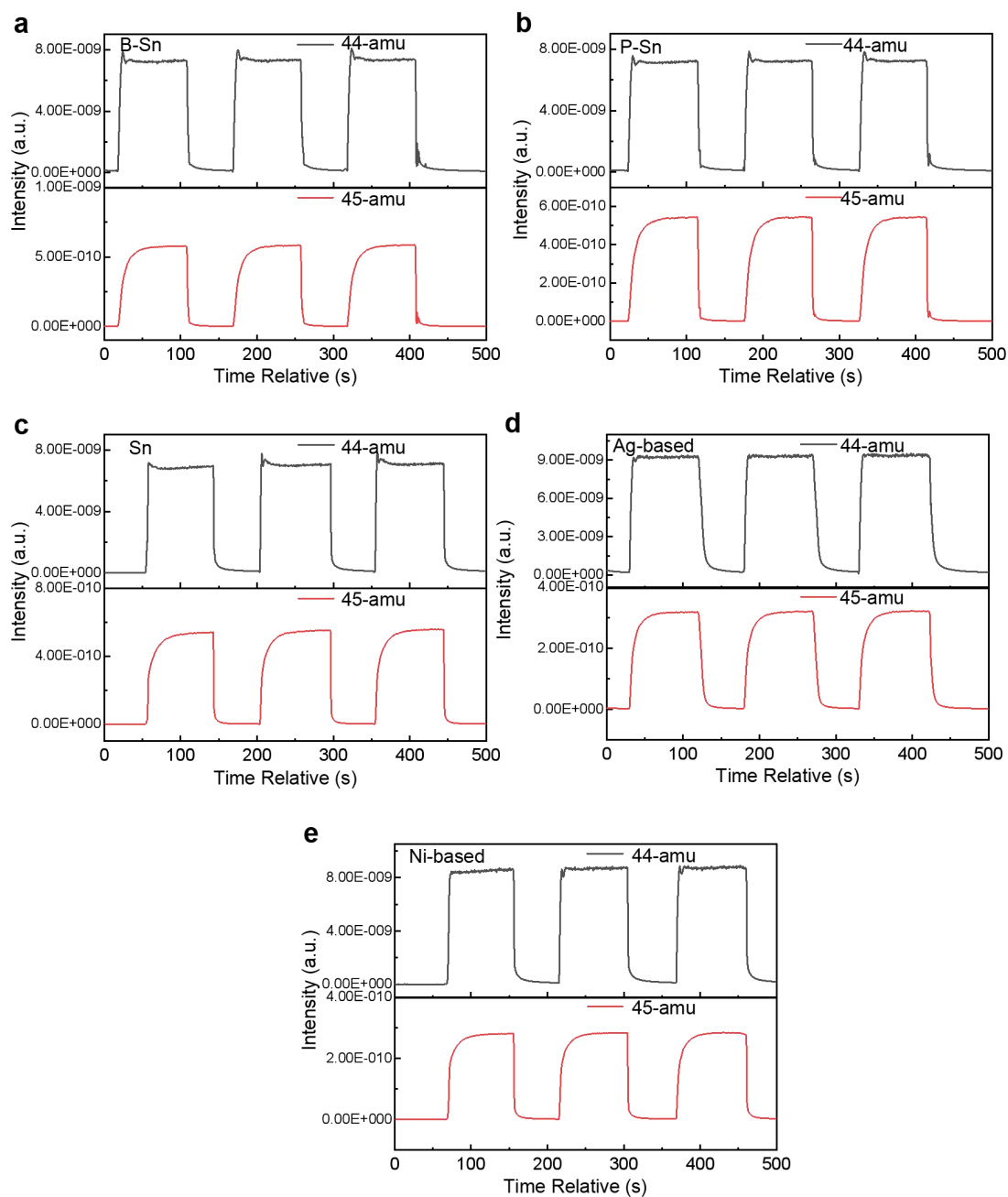
Supplementary Fig. 36. Chronopotentiometry tests at -200 mA cm^{-2} for Sn-based, Ag-based and Ni-based catalysts in the flow cell (the tests were conducted without iR correction. (The E-t curve recorded for N-Sn is already presented in Supplementary Fig. 33b and is therefore not duplicated here.)



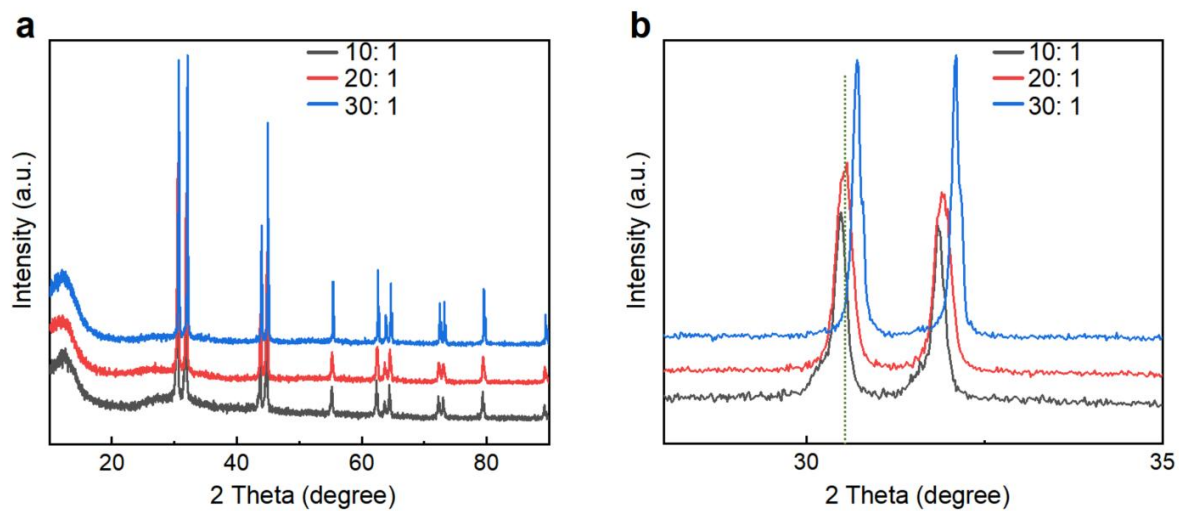
Supplementary Fig. 37. FE of Sn-based, Ag-based and Ni-based catalysts in the flow cell at -200 mA cm⁻².



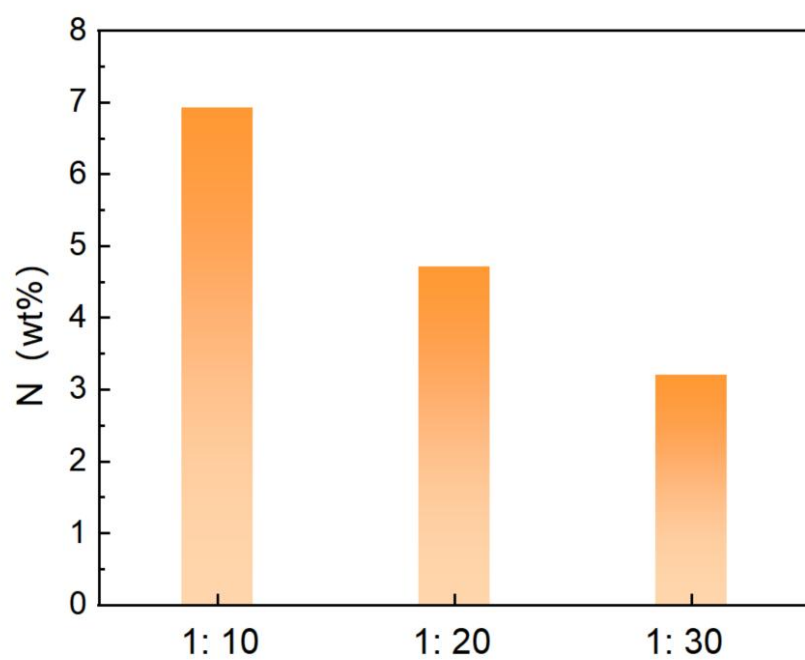
Supplementary Fig. 38. Signals from DEMS full-spectrum analysis of (a) N-Sn, (b) B-Sn, (c) P-Sn, (d) Sn, (e) Ag-based and (f) Ni-based catalysts after reaction at -200 mA cm^{-2} .



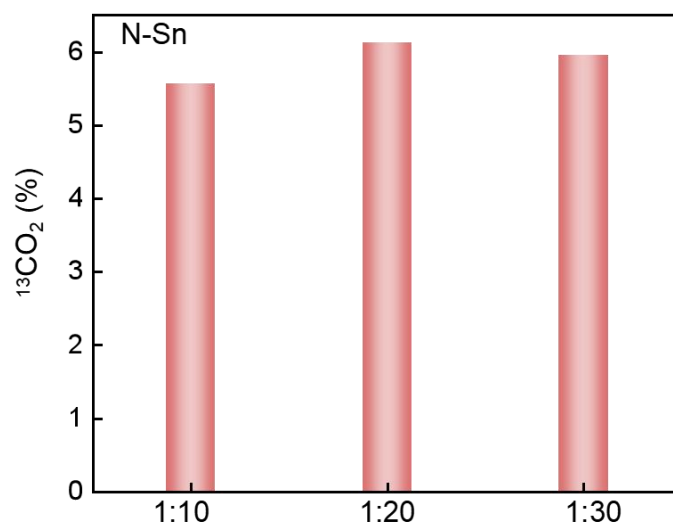
Supplementary Fig. 39. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for (a) B-Sn, (b) P-Sn, (c) Sn, (d) Ag-based and (e) Ni-based catalysts after reaction at -200 mA cm^{-2} . Increased H_2 content causes asynchronous shifts in the m/z 44 and 45 peak profiles owing to H_2 ionization. However, standard gas tests and systematic studies (Supplementary Fig. 21a) confirm that after Ar dilution, low H_2 partial pressure is maintained for inlet H_2 concentrations $< 90\%$, providing accurate and repeatable integrated quantification with the measurement error margin within $\pm 0.5\%$.¹⁸⁻²⁰



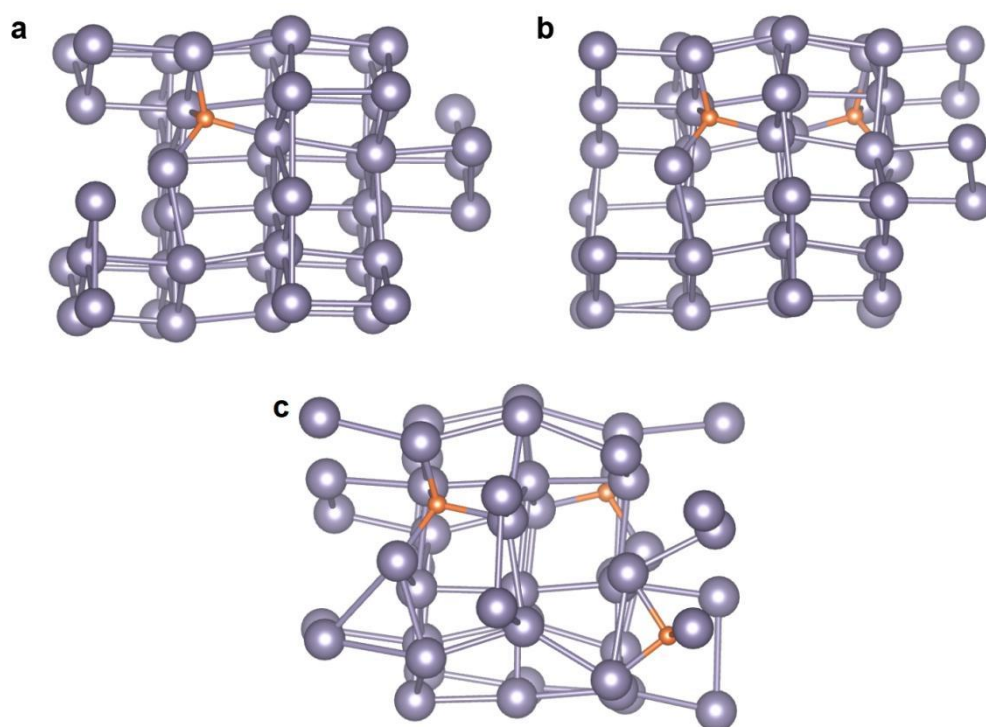
Supplementary Fig. 40. XRD patterns of N-Sn catalysts with different N doping concentrations (a) and their peak shifts (b).



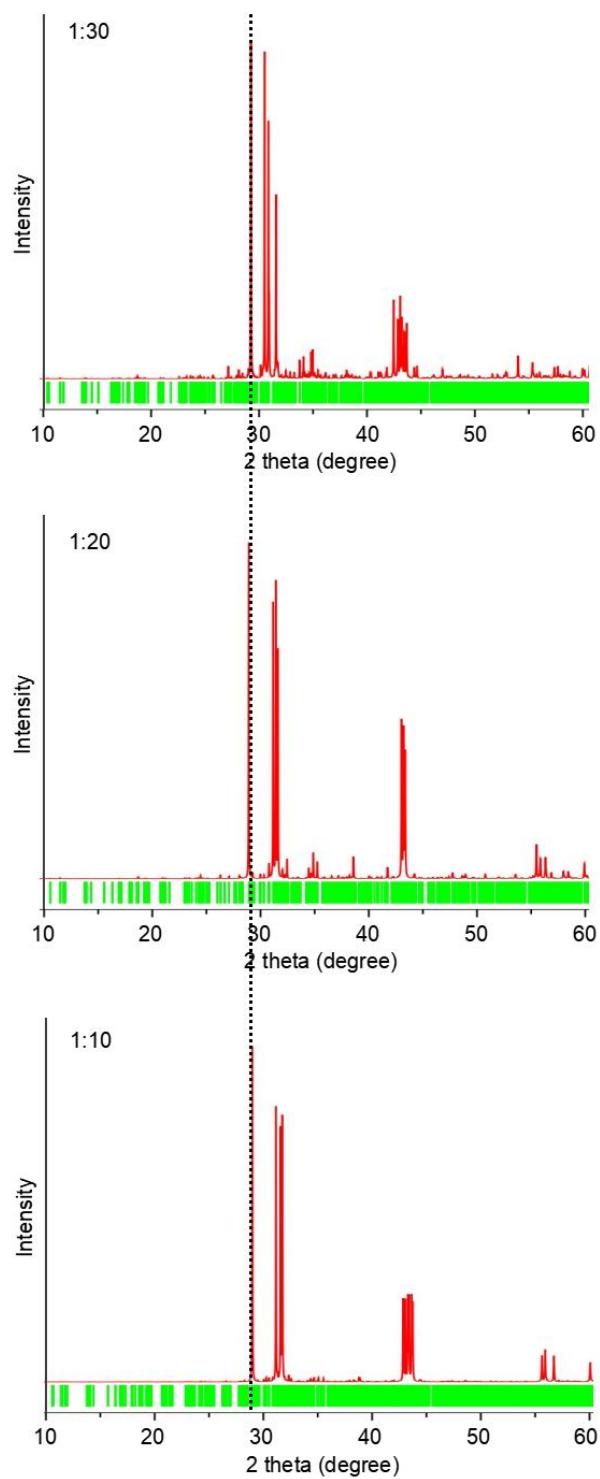
Supplementary Fig. 41. N content analysis (by NHO Analyzer) for catalysts with N gradients (1:10, 1:20, 1:30).



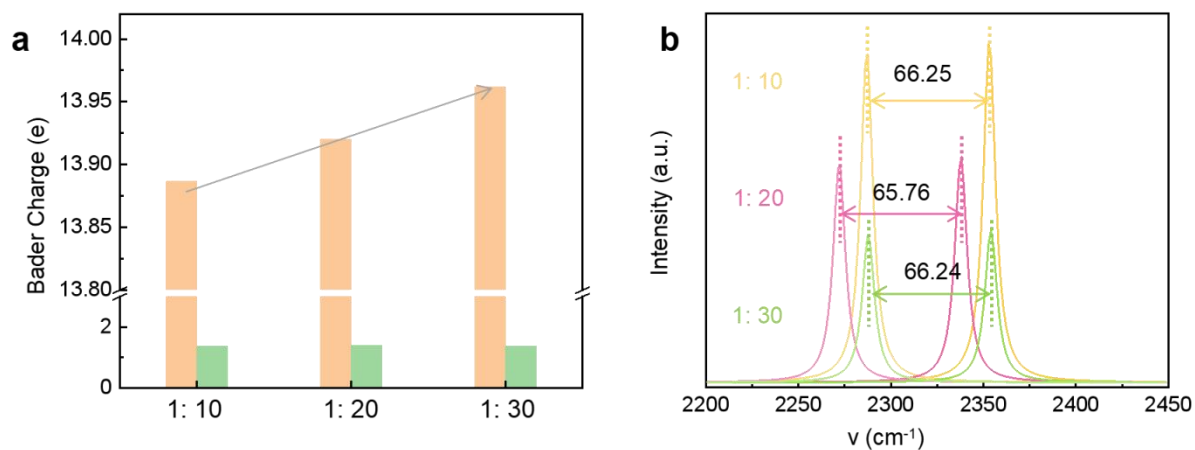
Supplementary Fig. 42. The $^{13}\text{CO}_2$ of N-Sn with different N gradients (1:10, 1:20, 1:30).



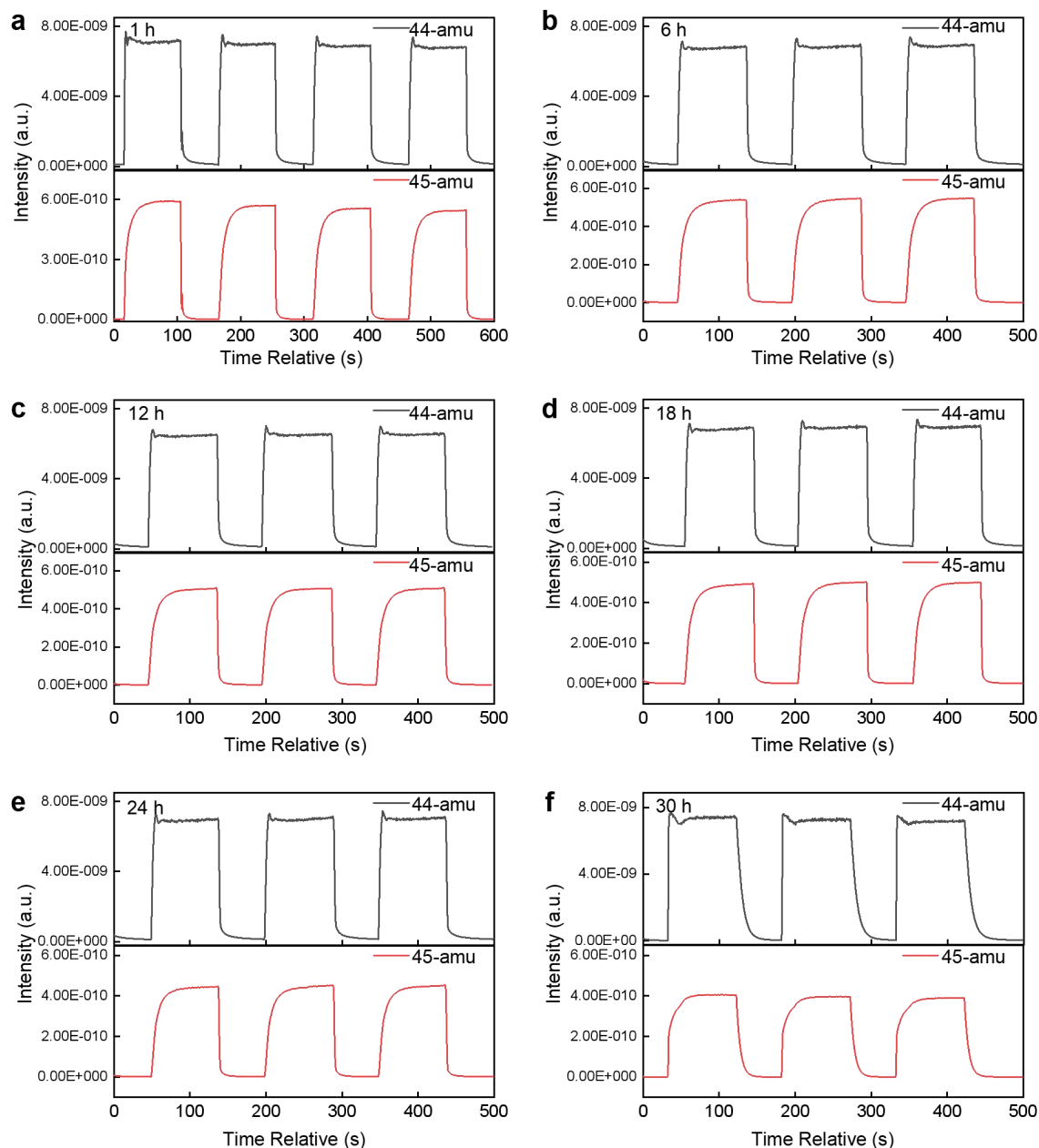
Supplementary Fig. 43. N-Sn models with different concentration gradients: (a) 1:30, (b) 1:20, (c) 1:10 (named according to the ratio of ingredients).



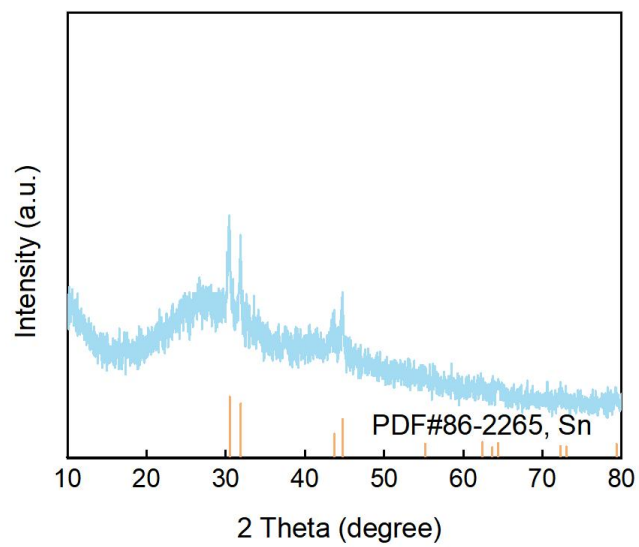
Supplementary Fig. 44. XRD patterns of N-Sn models with different concentration gradients based on DFT calculations.



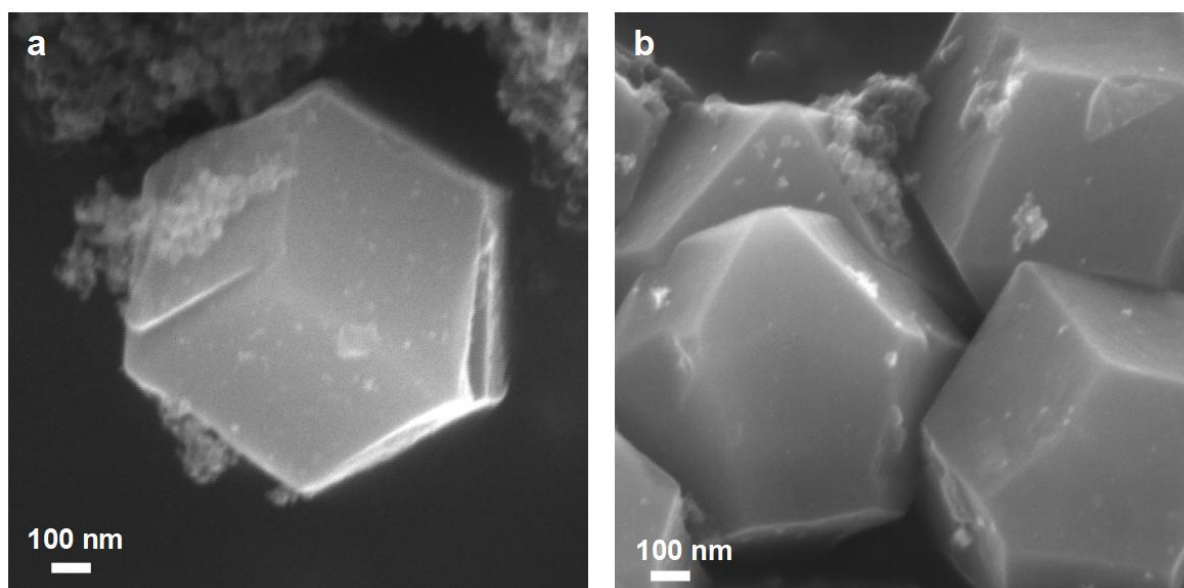
Supplementary Fig. 45. (a) the Bader charge analysis of N-Sn and (b) the vibration frequencies of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ on N-Sn with different N gradients (1:10, 1:20, 1:30) models (named according to the ratio of ingredients). The average charge amount of Sn and average charge gained by N are shown in (a).



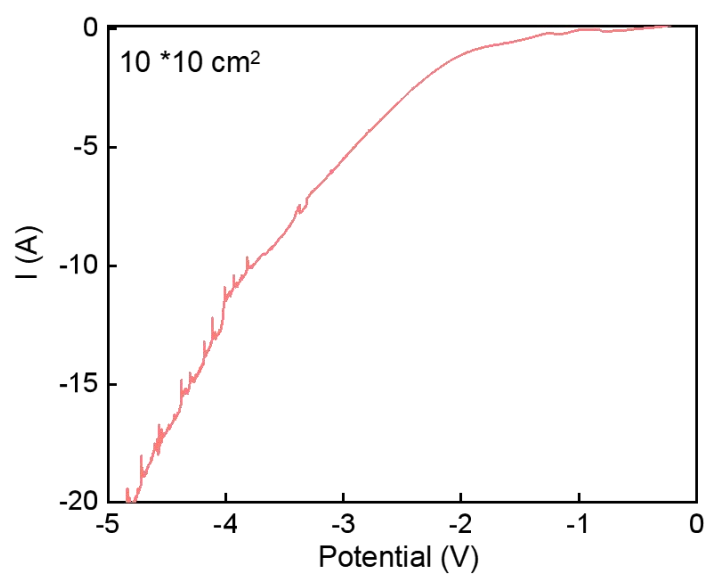
Supplementary Fig. 46. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for N-Sn at -200 mA cm^{-2} , measured at (a) 1 h, (b) 6 h, (c) 12 h, (d) 18 h, (e) 24 h, and (f) 30 h. Increased H_2 content causes asynchronous shifts in the m/z 44 and 45 peak profiles owing to H_2 ionization. However, standard gas tests and systematic studies (Supplementary Fig. 21a) confirm that after Ar dilution, low H_2 partial pressure is maintained for inlet H_2 concentrations $< 90\%$, providing accurate and repeatable integrated quantification with the measurement error margin within $\pm 0.5\%$.¹⁸⁻²⁰



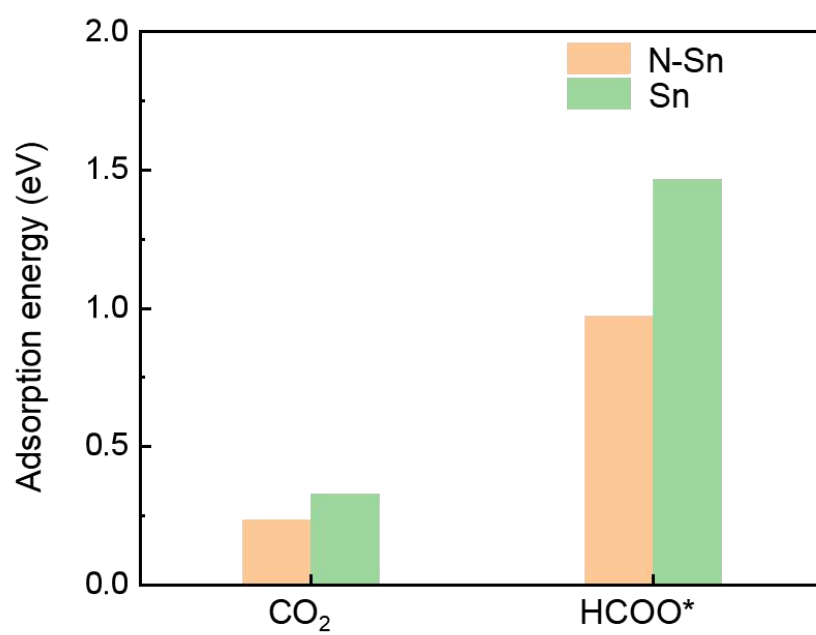
Supplementary Fig. 47. XRD of N-Sn after $^{13}\text{CO}_2$ electrocatalytic enrichment reaction.



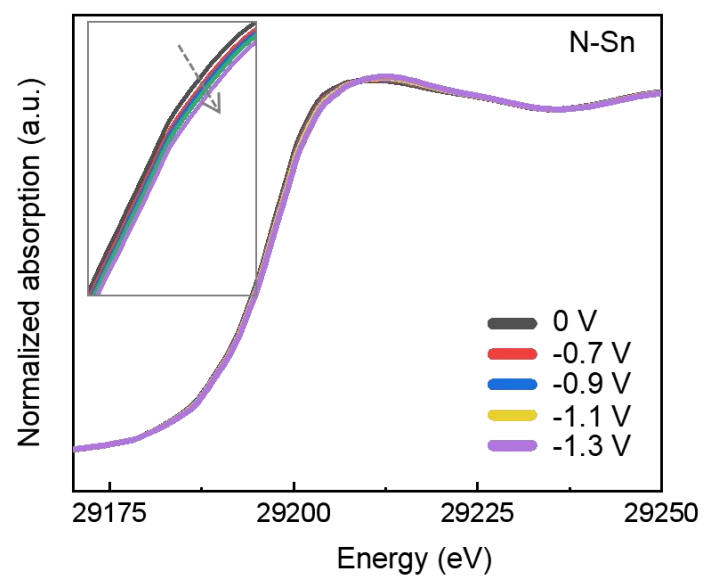
Supplementary Fig. 48. SEM images of N-Sn after $^{13}\text{CO}_2$ electrocatalytic enrichment reaction.



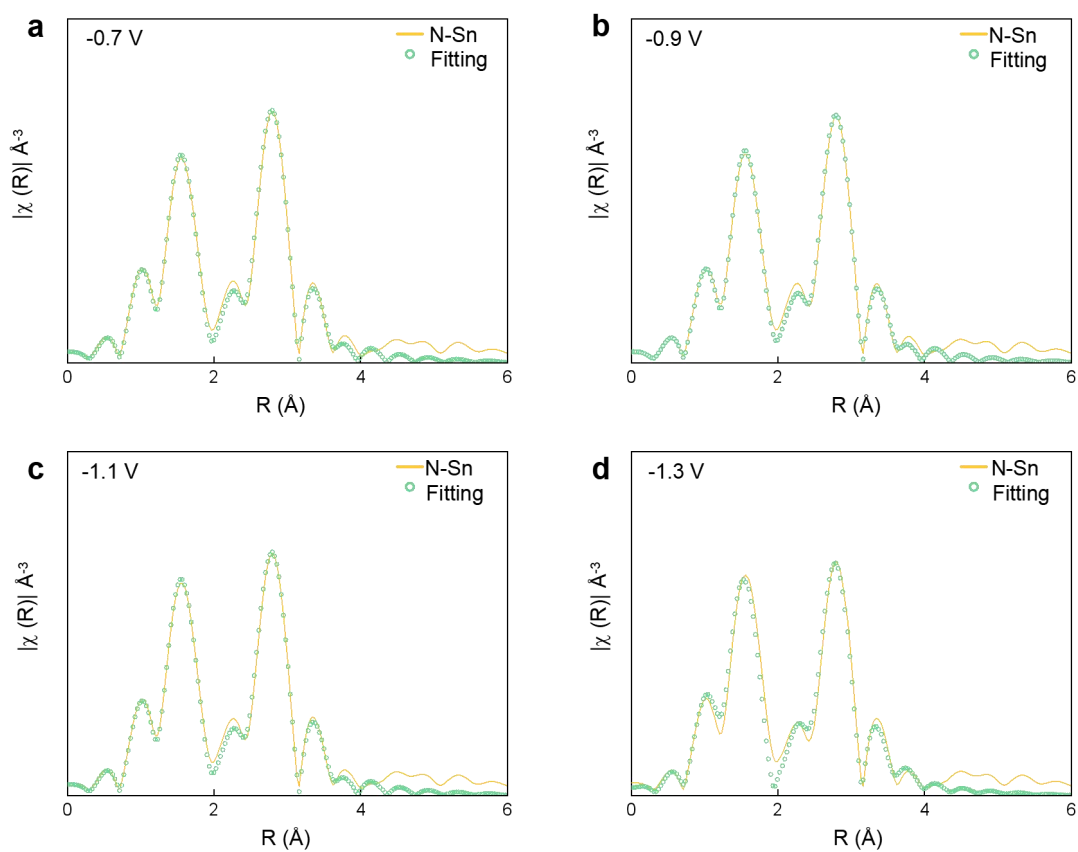
Supplementary Fig. 49. The I-V test ($10 \times 10 \text{ cm}^2$, with iR correction) for N-Sn in a large-scale flow cell.



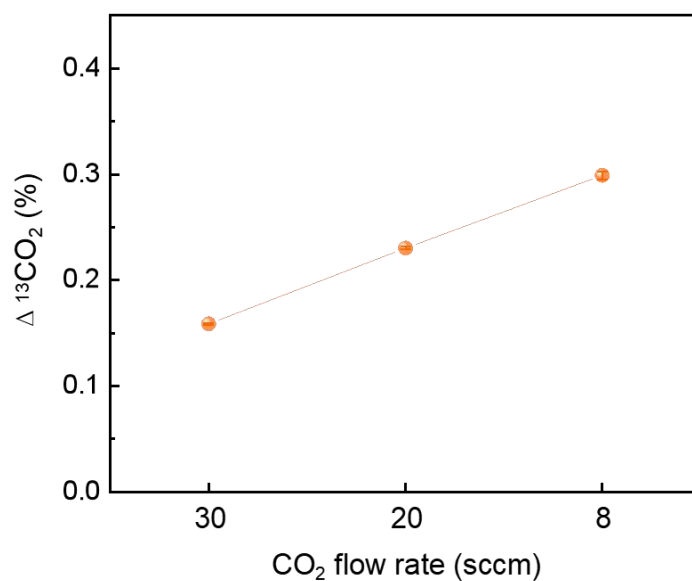
Supplementary Fig. 50. “Corrected” adsorption energies of CO₂ and HCOO* on N-Sn and Sn surfaces.



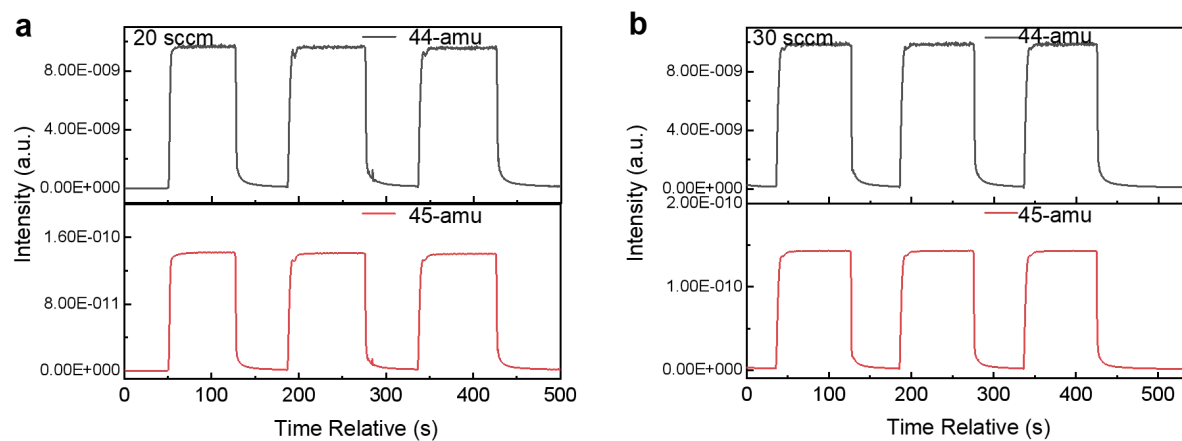
Supplementary Fig. 51. In-situ XANES spectra of N-Sn.



Supplementary Fig. 52. In situ FT-EXAFS fitting curves of N-Sn under varying applied potentials during CO₂RR.

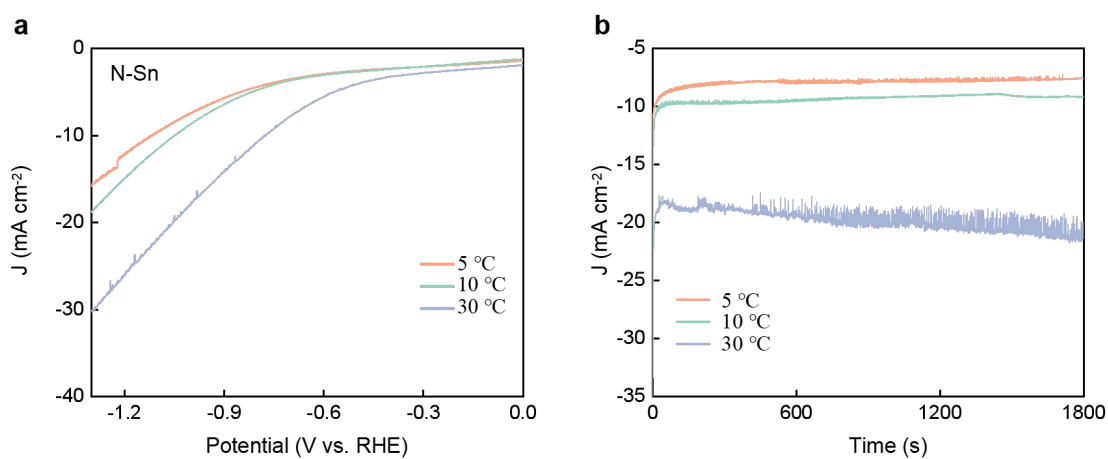


Supplementary Fig. 53. The $\Delta^{13}\text{CO}_2$ for N-Sn at -1.1 V vs. RHE and CO₂ flow rates of 8, 20, and 30 sccm. Error bars represent s.d. All data are presented as mean $\pm$ s.d. from three independent experiments per condition, with values typically falling within ± 0.004 .

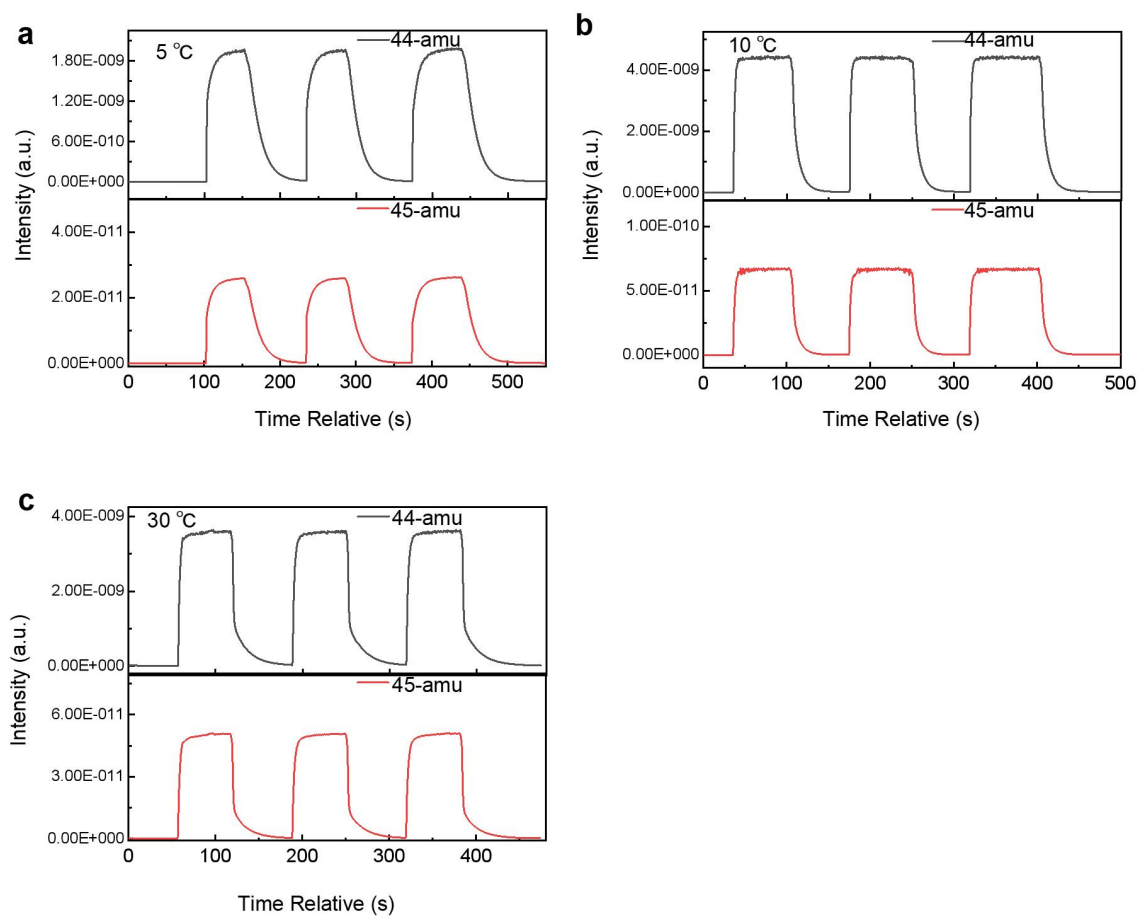


Supplementary Fig. 54. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for N-Sn at -1.1 V vs. RHE and CO_2 flow rates of (a) 20, and (b) 30 sccm. (The DEMS curve recorded at a flow rate of 8 sccm is already presented in Supplementary Fig. 29a and is therefore not duplicated here.)

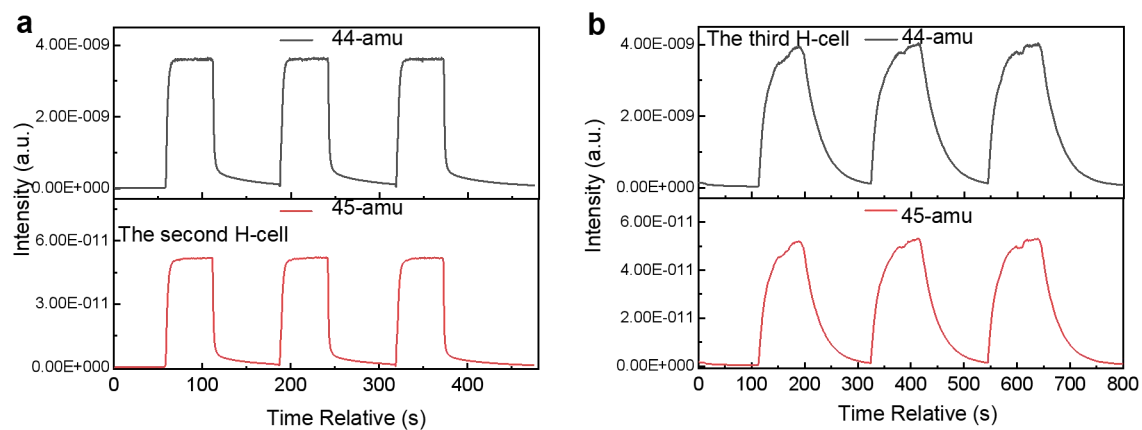
II



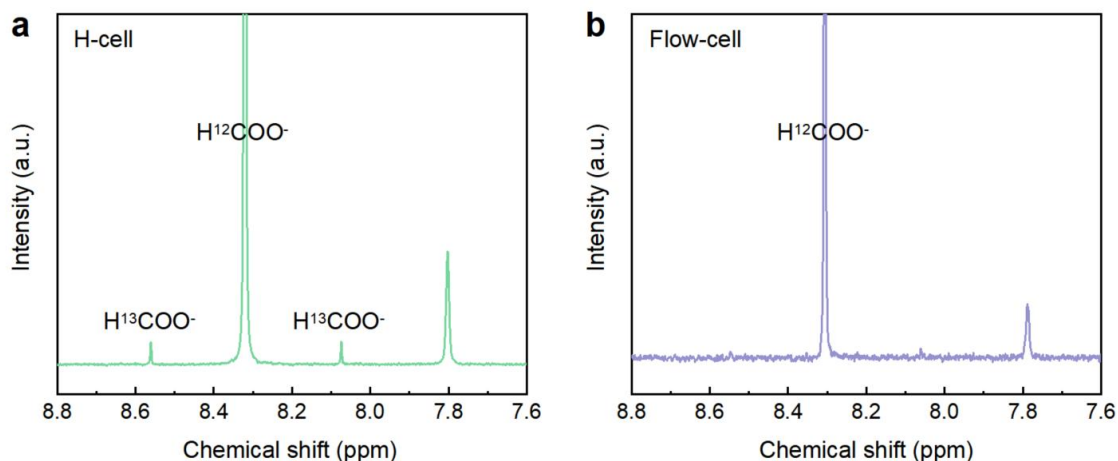
Supplementary Fig. 55. (a) LSV tests and (b) chronoamperometry tests at -1.1 V vs. RHE for N-Sn in a H-cell at different temperatures. (The LSV and I_t curves recorded at 20 °C are already presented in Supplementary Fig. 8 for N-Sn and are therefore not duplicated here.)



Supplementary Fig. 56. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) for N-Sn at -1.1 V vs. RHE and different reaction temperatures of (a) 5, (b) 10, and (c) 30 °C. (The DEMS curve recorded at 20 °C is already presented in Supplementary Fig. 29a and is therefore not duplicated here.)



Supplementary Fig. 57. DEMS of 44 ($^{12}\text{CO}_2$) and 45 ($^{13}\text{CO}_2$) of the domino-type tandem H-cell system with N-Sn catalyst at -1.1 V vs. RHE. (The DEMS curve recorded in the first H-cell is already presented in Supplementary Fig. 29a and is therefore not duplicated here.)



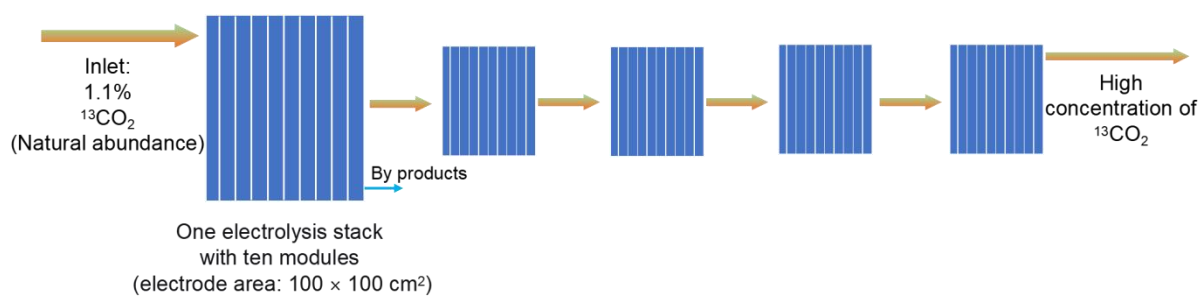
Supplementary Fig. 58. (a) H-cell and (b) flow cell liquid products analysis by ^1H -NMR in N-Sn.

Note : In a single-pass reaction, the utilization of ^{13}C in the gas phase reached 98.78%, while approximately 1.22% of ^{13}C was lost into the liquid phase and could not be recovered.

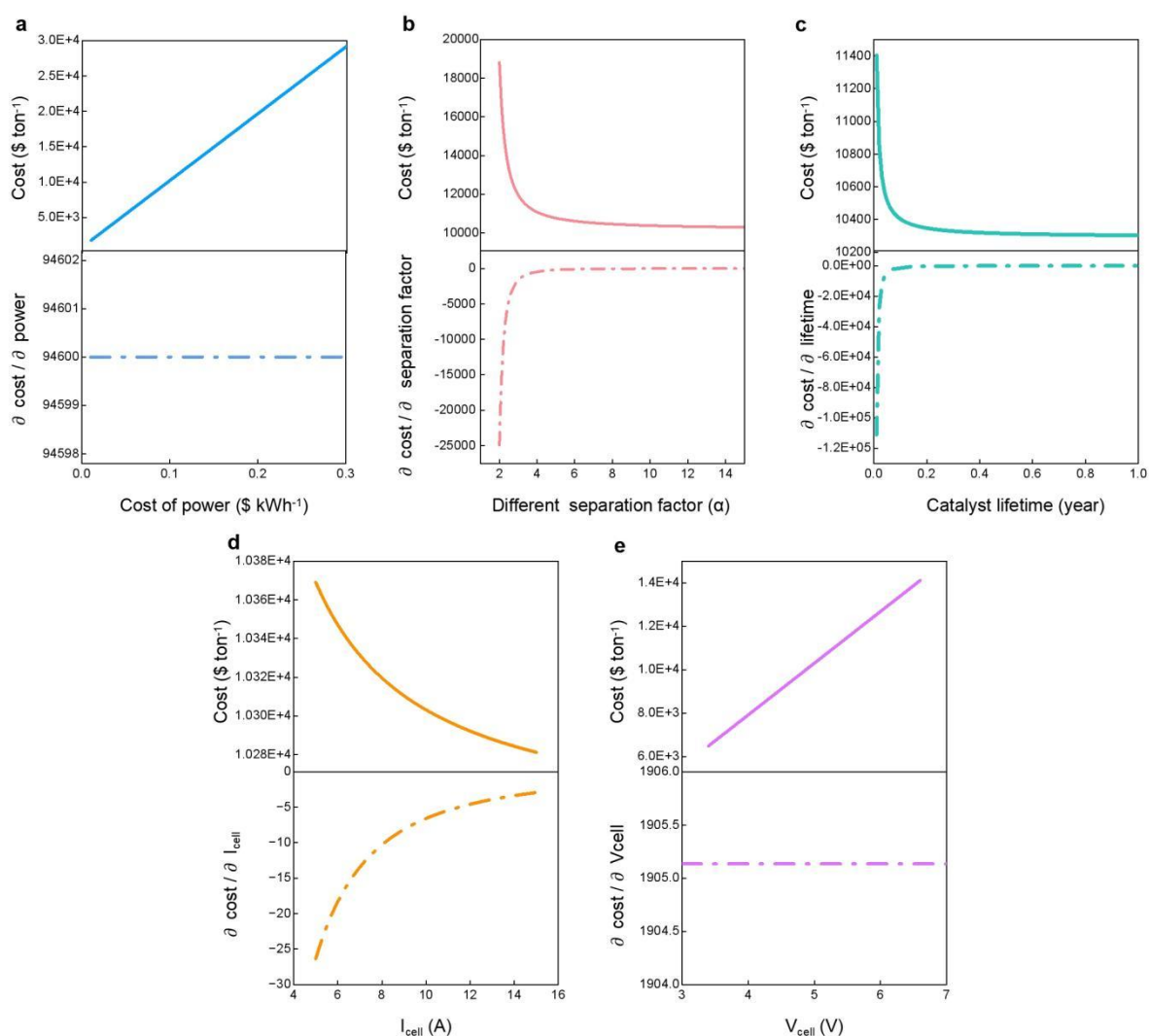
Firstly, the electrolyte was pre-saturated with CO_2 , effectively preventing gas loss through absorption by the electrolyte during the reaction. Secondly, a Nafion 117 proton exchange membrane was used between the anode and cathode, and any minimal gas crossover through the membrane to the anode is assumed to be negligible.

Under these conditions, we observed noticeable ^{13}C loss in the H-cell, primarily in the form of the liquid-phase product $\text{H}^{13}\text{COO}^-$ (Supplementary Fig. 58a). It should be noted that all gaseous products were collected using a gas bag and can be further purified and separated; therefore, these are not considered as losses but rather as enriched ^{13}C sources for subsequent processing. In contrast, such loss was barely detectable in the flow cell configuration (Supplementary Fig. 58b).

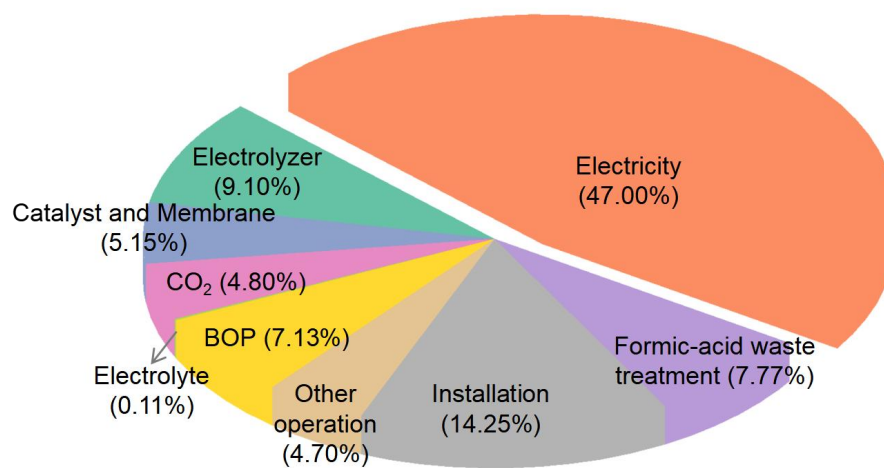
In the H-cell, the calculated FE for H^{13}COOH formation was below 1%, corresponding to a molar loss of $\sim 1.43 \times 10^{-6}$ mol of ^{13}C . Compared to the total molar amount of $^{13}\text{CO}_2$ fed over 30 minutes (1.18×10^{-4} mol), the utilization rate of ^{13}C in the gas phase reaches 98.78%, indicating that the loss via liquid products is minimal.



Supplementary Fig. 59. Schematic of one typical production line for $^{13}\text{CO}_2$ electrochemistry isotope enrichment, which is one of four identical lines in the system.



Supplementary Fig. 60. Sensitivity analysis of key operating parameters on the overall process economics. The total cost analysis (top) and the partial derivatives (bottom) for each parameter during fabricating 1 ton $^{13}\text{CO}_2$ with other factors under the baseline conditions: (a) cost of power, (b) separation factor, (c) catalyst lifetime, (d) I_{cell} , and (e) V_{cell} . Baseline conditions: cost of power = 0.1 \$ kWh⁻¹, separation factor = 14, lifetime = 1 year, V_{cell} = 5 V, and I_{cell} = 10 A.



Supplementary Fig. 61. Detailed cost breakdown of the entire process for electrocatalytic enrichment of 14% $^{13}\text{CO}_2$ at -100 mA cm^{-2} current density ($10 \times 10 \text{ cm}^2$), 3 V cell voltage.

SUPPLEMENTARY TABLES

Supplementary Table 1. The energies of each molecule based on DFT calculations.

Molecular	Energy (eV)
CO ₂	-22.9553 (E)
¹² CO ₂	-23.2132 (G)
¹³ CO ₂	-23.2190 (G)
H	-3.4080 (G)

Supplementary Table 2. Intrinsic vibrational frequencies of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ bonds (real frequencies) based on DFT calculation.

Molecular	Vibration frequency group (THz, keep four decimal places)					
$^{12}\text{CO}_2$	70.6846	39.6427	18.9270	18.9155	4.6799	3.6143
$^{13}\text{CO}_2$	68.7526	39.5499	18.4954	18.4779	5.0985	4.1129

Supplementary Table 3. Intrinsic vibrational frequencies of $^{12}\text{COOH}$, $^{13}\text{COOH}$ and H^{12}COO , H^{13}COO bonds (real frequencies) based on DFT calculation.

Molecular	Vibration frequency group (THz, keep four decimal places)							
$^{12}\text{COOH}$	101.3772	45.8790	37.7274	22.5823	19.8761	17.8558	12.4512	5.1422
$^{13}\text{COOH}$	101.3767	44.8779	37.6379	22.1908	19.7693	17.6252	12.1674	5.1288
H^{12}COO	76.1924	43.4574	34.2919	30.3043	26.2604	9.2450	3.4367	1.7440
H^{13}COO	76.0576	42.4466	34.1096	30.1805	25.8259	9.1321	3.4324	1.7436

Supplementary Table 4. The vibration frequency groups (real frequency) of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ bonds on Sn models based on DFT calculation.

Model	Molecular	Vibration frequency group (THz, keep four decimal places)					
Sn	$^{12}\text{CO}_2$	70.6345	39.4744	18.6287	18.2135	1.4794	1.2259
Sn	$^{13}\text{CO}_2$	68.6476	39.4744	18.1038	17.7001	1.4634	1.2171
N-Sn	$^{12}\text{CO}_2$	70.0871	39.1303	18.9370	18.4896	2.1083	2.0384
N-Sn	$^{13}\text{CO}_2$	68.1156	39.1299	18.4056	17.9703	2.1070	2.0381
B-Sn	$^{12}\text{CO}_2$	70.6395	39.5024	18.5238	17.8470	2.0226	1.4156
B-Sn	$^{13}\text{CO}_2$	68.6516	39.5024	18.0011	17.3453	2.0075	1.4016
P-Sn	$^{12}\text{CO}_2$	70.5734	39.4515	18.6257	18.1503	1.5274	1.46291
P-Sn	$^{13}\text{CO}_2$	68.5887	39.4515	18.1021	17.6394	1.5106	1.4471
Ag	$^{12}\text{CO}_2$	70.3331	39.2744	18.3750	17.7524	1.8798	0.6264
Ag	$^{13}\text{CO}_2$	68.3546	39.2744	17.8577	17.2528	1.8651	0.6202
Ni	$^{12}\text{CO}_2$	70.2312	39.2910	18.4318	17.5594	1.7572	0.9914
Ni	$^{13}\text{CO}_2$	68.2560	39.2905	17.9120	17.0695	1.7268	0.9869

Supplementary Table 5. The vibration frequency groups (real frequency) of the H¹²COO and H¹³COO bonds on Sn-based models based on DFT calculation.

Model	Molecular	Vibration frequency group (THz, keep four decimal places)								
Sn	H ¹² COO	87.0252	46.2399	39.7665	38.2083	29.8951	21.6687	8.1276	7.4764	5.0402
Sn	H ¹³ COO	86.7810	45.0410	39.7395	37.5698	29.4673	21.4454	8.0856	7.3760	5.0121
N-Sn	H ¹² COO	87.4523	45.2147	40.0222	38.9128	29.8173	21.5090	7.6368	7.2572	5.5678
N-Sn	H ¹³ COO	87.2052	43.9749	40.0128	38.3003	29.3890	21.2852	7.5492	7.2119	5.5352
B-Sn	H ¹² COO	88.1122	45.2344	39.9243	39.0914	29.6927	21.5243	7.3374	7.1442	6.5260
B-Sn	H ¹³ COO	87.8617	43.9830	39.9117	38.4915	29.2591	21.3009	7.2970	7.0709	6.4761
P-Sn	H ¹² COO	88.3627	45.6467	39.7394	38.3052	30.0799	23.0347	8.7286	5.8132	3.9342
P-Sn	H ¹³ COO	88.1017	44.4459	39.0916	38.2857	29.6551	22.7944	8.6291	5.7584	3.9342

Supplementary Table 6. DFT-calculated energies of all intermediates.

Model	Intermediate	E_DFT	Total ZPE	Entropy ($\times 10^{-4}$, eV/T)	G (eV)
Sn	*	-131.8788			-131.8788
Sn	$^{12}\text{CO}_2$	-154.9852	0.3094991	2.912	-154.7626
Sn	$^{13}\text{CO}_2$	-154.9852	0.3031911	2.934	-154.7695
Sn	H^{12}COO	-158.8080	0.5861882	1.123	-158.2553
Sn	H^{13}COO	-158.8080	0.5801284	1.136	-158.2617
N-Sn	*	-149.4174			-149.4174
N-Sn	$^{12}\text{CO}_2$	-172.6396	0.3118447	2.26	-172.3951
N-Sn	$^{13}\text{CO}_2$	-172.6396	0.3055904	2.268	-172.4016
N-Sn	H^{12}COO	-176.8403	0.5860688	1.109	-176.2873
N-Sn	H^{13}COO	-176.8403	0.5800169	1.122	-176.2937
B-Sn	*	-144.8876			-144.8876
B-Sn	$^{12}\text{CO}_2$	-167.9971	0.3101082	2.571	-167.7636
B-Sn	$^{13}\text{CO}_2$	-167.9971	0.3038184	2.593	-167.7705
B-Sn	H^{12}COO	-172.2174	0.5885439	1.053	-171.6602
B-Sn	H^{13}COO	-172.2174	0.5824738	1.066	-171.6667
P-Sn	*	-138.0339			-138.0339
P-Sn	$^{12}\text{CO}_2$	-161.1218	0.3097779	2.752	-160.8941
P-Sn	$^{13}\text{CO}_2$	-161.1218	0.3034664	2.777	-160.9011
P-Sn	H^{12}COO	-165.1259	0.5865952	1.356	-164.5797
P-Sn	H^{13}COO	-165.1259	0.5804971	1.367	-164.5862

Supplementary Table 7. Structural parameters extracted from the quantitative EXAFS curve-fitting.

Catalyst	Path	CN	ΔE_0 (eV)	σ^2 ($\text{\AA}^2$)	R ($\text{\AA}$)	R-factor
N-Sn	Sn-N	1	2.620 $\pm$ 0.821	0.0053 $\pm$ 0.0011	2.04	0.020
	Sn-Sn	1	2.620 $\pm$ 0.821	0.0048 $\pm$ 0.0007	2.99	
	Sn-Sn	2	2.620 $\pm$ 0.821	0.0179 $\pm$ 0.0038	3.14	

Note: CN, coordination numbers; R, bonding distance; σ^2 , Debye-Waller factor; ΔE_0 , inner potential shift.

Supplementary Table 8. The composition of the mixed gas including H₂, ¹²CO₂, ¹³CO₂ for calibrations.

Standard calibration sample	Gas concentration (%)			The abundance of CO ₂ (%)	
	H ₂	CO ₂		¹² CO ₂	¹³ CO ₂
		¹² CO ₂	¹³ CO ₂		
1	0.00	98.90	1.10	98.90	1.10
		98.50	1.50	98.50	1.50
		94.98	5.02	94.98	5.02
		89.93	10.07	89.93	10.07
		78.84	21.16	78.84	21.16
2	5.00	93.96	1.05	98.90	1.10
		93.58	1.43	98.50	1.50
		90.23	4.77	94.98	5.02
		85.43	9.57	89.93	10.07
		74.90	20.10	78.84	21.16
3	35.00	64.29	0.72	98.90	1.10
		64.03	0.98	98.50	1.50
		61.74	3.26	94.98	5.02
		58.45	6.55	89.93	10.07
		51.25	13.75	78.84	21.16
4	50.00	49.45	0.55	98.90	1.10
		49.25	0.75	98.50	1.50
		47.49	2.51	94.98	5.02

		44.97	5.04	89.93	10.07
		39.42	10.58	78.84	21.16
5	70.00	29.67	0.33	98.90	1.10
		29.55	0.45	98.50	1.50
		28.49	1.51	94.98	5.02
		26.98	3.02	89.93	10.07
		23.65	6.35	78.84	21.16
6	80.00	19.78	0.22	98.90	1.10
		19.70	0.30	98.50	1.50
		19.00	1.00	94.98	5.02
		17.99	2.01	89.93	10.07
		15.77	4.23	78.84	21.16
7	90.00	9.89	0.11	98.90	1.10
		9.85	0.15	98.50	1.50
		9.50	0.50	94.98	5.02
		8.99	1.01	89.93	10.07
		7.88	2.12	78.84	21.16

Supplementary Table 9. The $\text{Sn}^0/\text{Sn}^{2+}$ ratio of N-Sn and N-Sn after the reaction.

Sn 3d	Sn^0 3d_{5/2}	Sn^0 3d_{3/2}	Sn^{2+} 3d_{5/2}	Sn^{2+} 3d_{3/2}
N-Sn	56.27%	38.16%	3.51%	2.07%
N-Sn after the reaction	11.01%	28.99%	16.51%	43.49%

Supplementary Table 10. The vibration frequency groups (real frequency) of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ bonds on N-Sn models with different N concentration gradients (1:10, 1:20, 1:30) (named according to the ratio of ingredients).

Model	Molecular	Vibration frequency group (THz, keep four decimal places)					
N-Sn (1:10)	$^{12}\text{CO}_2$	70.5732	39.4285	18.5805	18.2317	1.7500	1.2090
N-Sn (1:10)	$^{13}\text{CO}_2$	68.5875	39.4284	18.0584	17.7172	1.7341	1.2016
N-Sn (1:20)	$^{12}\text{CO}_2$	70.0871	39.1303	18.9370	18.4896	2.1083	2.0384
N-Sn (1:20)	$^{13}\text{CO}_2$	68.1156	39.1299	18.4056	17.9703	2.1070	2.0381
N-Sn (1:30)	$^{12}\text{CO}_2$	70.5477	39.4635	18.5014	18.0940	1.8029	1.1303
N-Sn (1:30)	$^{13}\text{CO}_2$	68.5617	39.4635	17.9791	17.5817	1.7851	1.1214

Supplementary Table 11. Structural parameters extracted from the quantitative EXAFS curve-fitting.

The applied voltage of N-Sn	Path	CN	ΔE_0 (eV)	σ^2 ($\text{\AA}^2$)	R ($\text{\AA}$)	R-factor
0 V	Sn-N	1	2.620 $\pm$ 0.821	0.0053 $\pm$ 0.0011	2.04	0.020
	Sn-Sn	1	2.620 $\pm$ 0.821	0.0048 $\pm$ 0.0007	2.99	
	Sn-Sn	2	2.620 $\pm$ 0.821	0.0179 $\pm$ 0.0038	3.14	
-0.7 V	Sn-N	1	2.578 $\pm$ 0.761	0.0048 $\pm$ 0.00096	2.04	0.015
	Sn-Sn	1	2.578 $\pm$ 0.761	0.0051 $\pm$ 0.0006	2.99	
	Sn-Sn	2	2.578 $\pm$ 0.761	0.0191 $\pm$ 0.0038	3.14	
-0.9 V	Sn-N	1	2.772 $\pm$ 0.739	0.0046 $\pm$ 0.00091	2.04	0.015
	Sn-Sn	1	2.772 $\pm$ 0.739	0.0052 $\pm$ 0.0006	2.99	
	Sn-Sn	2	2.772 $\pm$ 0.739	0.0192 $\pm$ 0.0037	3.15	
-1.1 V	Sn-N	1	2.957 $\pm$ 0.722	0.0044 $\pm$ 0.00088	2.04	0.014
	Sn-Sn	1	2.957 $\pm$ 0.722	0.0053 $\pm$ 0.0006	3.00	
	Sn-Sn	2	2.957 $\pm$ 0.722	0.0193 $\pm$ 0.0037	3.15	
-1.3 V	Sn-N	1	3.305 $\pm$ 0.700	0.0040 $\pm$ 0.00082	2.04	0.014

	Sn-Sn	1	3.305±0.700	0.0054±0.0006	3.00	
	Sn-Sn	2	3.305±0.700	0.0195±0.0036	3.16	

Note: CN, coordination numbers; R, bonding distance; σ^2 , Debye-Waller factor; ΔE_0 , inner potential shift.

REFERENCES

1. Kohn W, Sham LJ. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140(4A): A1133-A1138.
2. Hohenberg P, Kohn W. Inhomogeneous Electron Gas. *Phys. Rev.* 1964, 136(3B): B864-B871.
3. Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54(16): 11169-11186.
4. Bai H, Liu D, Zhou P, Feng J, Sui X, Lu Y, *et al.* Spin evolution and flip in the oxygen reduction reaction: a theoretical study of Cu(Ni)_xP₂S₆ (X = In, Bi and Cr). *J. Mater. Chem. A* 2022, 10(42): 25262-25271.
5. Oberhofer H, Dellago C, Geissler PL. Biased Sampling of Nonequilibrium Trajectories: Can Fast Switching Simulations Outperform Conventional Free Energy Calculation Methods? *J. Phys. Chem. B* 2005, 109(14): 6902-6915.
6. Jarzynski C. Nonequilibrium Equality for Free Energy Differences. *Phys. Rev. Lett.* 1997, 78(14): 2690-2693.
7. Woo TK, Margl PM, Blöchl PE, Ziegler T. A Combined Car-Parrinello QM/MM Implementation for ab Initio Molecular Dynamics Simulations of Extended Systems: Application to Transition Metal Catalysis. *J. Phys. Chem. B* 1997, 101(40): 7877-7880.
8. Yu S, Levell Z, Jiang Z, Zhao X, Liu Y. What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe-N-C Catalysts? *J. Am. Chem. Soc.* 2023, 145(46): 25352-25356.
9. Bai X, Zhao X, Zhang Y, Ling C, Zhou Y, Wang J, *et al.* Dynamic Stability of Copper Single-Atom Catalysts under Working Conditions. *J. Am. Chem. Soc.* 2022, 144(37): 17140-17148.
10. Bao Y, Tang Z, Wang Y, Li S. Scaling relations of CO₂ hydrogenation and dissociation on single metal atom doped In₂O₃ catalysts with promoted oxygen vacancy sites. *RSC Adv.* 2025, 15(10): 7832-7842.
11. Dietz L, Piccinin S, Maestri M. Mechanistic Insights into CO₂ Activation via Reverse Water-Gas Shift on Metal Surfaces. *J. Phys. Chem. C* 2015, 119(9): 4959-4966.
12. Polynski MV, Kozlov SM. Reaction network of CO₂ hydrogenation into C₁₋₂ oxygenates and its BEP relationships. *EES Catal.*, 2026, 4(3): 660-672.
13. Huang J, Wang R, Sheng H, Zhu X, Dominic Ross R, Hua D, *et al.* Isotope-dependent Tafel analysis probes proton transfer kinetics during electrocatalytic water splitting. *Nat. Chem.*, 2026, 18: 669-676.
14. Kim H, Seo Y, Park J, Lee E, Oh H. A Gate-Opening Control Strategy via Nitrate-Chloride Anion Exchange for Enhanced Hydrogen Isotope Separation in Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* 2025, 64(11).

15. Fang W, Guo W, Lu R, Yan Y, Liu X, Wu D, *et al.* Durable CO₂ conversion in the proton-exchange membrane system. *Nature* 2024, 626(7997): 86-91.
16. Hao S, Elgazzar A, Zhang S-K, Wi T-U, Chen F-Y, Feng Y, *et al.* Acid-humidified CO₂ gas input for stable electrochemical CO₂ reduction reaction. *Science* 2025, 388(6752).
17. Gu Y, Tan Y, Tan H, Han Y, Cheng D, Lin F, *et al.* Industrial electrosynthesis of hydrogen peroxide over p-block metal single sites. *Nature Synthesis* 2025, 4(5): 614-621.
18. Merritt, D. A. *et al.* Factors Controlling Precision and Accuracy in Isotop-Ratio-Monitoring Mass Spectrometry. *Anal. Chem.* 1994, 66: 2336-2347.
19. Sacks, G. L. *et al.* Fast Gas Chromatography Combustion Isotope Ratio Mass Spectrometry. *Anal. Chem.* 2007, 79: 6348-6358.
20. Al-Ghoul, H. & Elsner, M. Nickel Wall-coated Microreactors for Enhanced Sensitivity and Peak Resolution in Compound-specific Carbon and Nitrogen Isotope Analysis. *Anal. Chem.*, 2026, 98: 15565-15575.