

Supporting Information for

Bismuth-atom Electrocatalyst for a Stable and Economical Aqueous Zn-CO₂ Battery

Mahboob Alam ^{#a}, Jia Xu ^{#a}, Evan J. Hansen ^a, Ela Nurlaela ^b, Li Tao^a, Alexander R. Uhl
^b, Jian Liu ^{a*}

^a School of Engineering, Faculty of Applied Science, The University of British Columbia,
Kelowna, British Columbia, V1V 1V7, Canada

^b Laboratory for Solar Energy and Fuels (LSEF), School of Engineering, The University
of British Columbia, Kelowna, V1V 1V7 Canada

The authors make equal contributions to this paper.

*Corresponding author's E-mail: jian.liu@ubc.ca (J. Liu)

Experimental Section

Materials. Zinc(II) acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, CAS No: 5970-45-6, $\geq 98.0\%$ purity) was obtained from Ward's Science. N, N-dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$, CAS No: 68-12-2) was sourced from Alfa Aesar. 2-Methylimidazole (2-MIM, $\text{C}_4\text{H}_6\text{N}_2$, CAS No: 693-98-1, $\geq 99.0\%$ purity) and bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, CAS No: 10035-06-0, 98.0% purity) was acquired from Sigma-Aldrich. Sulphuric acid (H_2SO_4 , CAS No: 7664-93-9, 95-98.0% purity) was obtained from VWR. All of the chemical reagents were used as received without further purification.

Synthesis of NC. Under the typical procedure, 0.3 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 10 mL deionized water (DI), which was subsequently added into 10 mL DI containing 1.12 g of 2-MIM under ultrasonication for 10 minutes at room temperature. Subsequently, the Zn-ZIF was grown at room temperature for 24 h. The as-obtained precipitates were isolated from the solution using centrifugation, then washed with methanol three times and dried in a vacuum at $60\text{ }^\circ\text{C}$ overnight. After drying, the Zn-ZIF precursors underwent heating at $900\text{ }^\circ\text{C}$ for 2 hours with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ under an Ar flow. Subsequently, they were treated with 0.5 M H_2SO_4 for 4 hours under continuous stirring to produce the N-doped carbon matrix derived from Zn-ZIF (referred to as NC).

Synthesis of Bi-SAs/NC. First, 100 mg NC and 9.8 mg $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 10 mL DMF. The solution was stirred for 2 h and dried under vacuum at $60\text{ }^\circ\text{C}$ overnight (8 h). Next, the obtained black product was heated to $700\text{ }^\circ\text{C}$ for 2 h at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ under Ar flow to obtain the final material, labeled Bi-SAs/NC.

Characterization Methods. The X-ray diffraction (XRD) experiments were carried out in Cu-K α radiation ($\lambda = 1.5418\text{ \AA}$) at a scan rate of 4° min^{-1} . Scanning electron microscopy (SEM, Tescan Mira 3 XMU) and transmission electron microscopy (TEM, Tecnai F20) analysis were applied to study the morphologies and microstructure of samples. The X-ray photoelectron spectroscopy (XPS) measurements were done using a PHI 5700 ESCA System. The Raman spectra were acquired using a Bruker Sunterra II Raman spectrometer using a 6 mW laser with a wavelength of 532 nm.

Electrochemical characterization

A Biologic electrochemical workstation (model SP-150) was used to measure the electrocatalytic activity of the catalysts. Initially, a three-electrode, single-compartment cell made of Teflon was employed to test the activity of Bi-SAs/NC in neutral (N_2 saturated electrolyte) and CO_2 RR conditions (CO_2 saturated electrolyte). The gas diffusion electrode (GDE Freudenberg H23C3, Model 1590044 at Fuel Cell Store ©) modified with electrocatalyst ink suspension (as Working electrode–WE), Pt wire (as counter electrode), and Ag/AgCl (as Reference Electrode–RF) were used in 0.5 M $KHCO_3$ (potassium hydrogen carbonate–99 to 100% / Thermo Scientific CAS 298-14-6) to collect the data. Double layer capacitance (C_{dl}) was calculated using Cyclic Voltammetry (CVs) at different scan rates.

The H-type cell consists of two glass compartments joined with a metal clamp. The anolyte and catholyte were separated using a Nafion™ membrane (111 Nafion™) during the experimentation. Platinum mesh (as CE), Ag/AgCl (as RE) and GDE cut into a bell shape and modified with electrocatalysts (as WE) were applied with a 0.5 M $KHCO_3$ solution saturated with CO_2 (pH = 7.5). A mass flow controller (ALICAT scientific) was used to control the flow of CO_2 gas between 6 to 8 sccm.

To analyze the gaseous products, an H-type cell coupled with gas chromatography (Thermo scientific trace 1300 series) employed automatic injection at set potentials after an interval of 30 minutes. To address the limitation of run-off time in the continuous GC product detection, measurements were constrained to two per hour. The GC was equipped with a Pulsed Discharged Detector (PDD) and an oven set with a ramped temperature setting from 50 to 250 °C over 30 mins. The liquid products in the electrolyte were analyzed by *ex-situ* Nuclear Magnetic Resonance (Bruker AVII 600 MHz spectrometer) spectroscopy using 1H -spectra with water suppression (Watergate W5 pulse sequence, 256 scans) after 3 hours of chronoamperometry testing at a constant potential of -0.99 V (vs. RHE). Following experimentation, the electrolyte (686 μ L of the 60 mL total) was combined with an internal standard *d*6-Dimethyl Sulfoxide (DMSO 34 μ L, Sigma Aldrich CAS: 2206-27-1) and D_2O (80 μ L) for NMR testing.

The equation for gas products

$$FE_{\%} = v \times \frac{z_i C_i F}{i} \times 100 \quad E1^1$$

Where v is the volume of gas leaving the H-type cell, z_i is the number of electrons involved in the generation of product, C_i is the concentration of product under consideration, F is the Faraday constant, and i is the applied current.

The equation for liquid products

$$FE_{\%} = V_{total} \times \frac{z_i C_i F}{C_{total}} \times 100 \quad E2^1$$

Where V_{total} is the total volume of collected electrolyte sample, C_{total} is the total charge required to generate the product, z_i is the number of electrons utilized to catalyze the product, C_i is the concentration of product calculated using NMR integrated data, and F is the faraday constant.

The equation for Liquid products

$$C_i = \frac{I_i}{I_{std}} \times \frac{n_{std}}{n_i} C_{std} \quad E3^1$$

Where I_i and I_{std} are the NMR integral of the compound and standard (DMSO), and n_i and n_{std} represent the number of protons in each of the compound and standard, respectively, used to calculate single product concentration.

Zn-CO₂ battery measurement

A custom cell arrangement consisting of two chambers separated by a Nafion™ membrane (111 Nafion™) was used to construct the Zn-CO₂ battery. The electrocatalysts were drop cast onto GDE with an areal loading of 0.5 mg cm⁻² with a cathode area of 1 cm². The anode area was matched at 1 mA cm², using Zn foil (thickness = 100 μm) that was first cleaned with isopropanol. The anolyte chamber was filled with 1 M KOH + 0.2 M zinc acetate solution, the catholyte chamber was filled with a 0.5 M KHCO₃ solution, and the gas chamber on the cathode side was purged with CO₂ at 5 sccm. The CO₂ battery performance was tested using galvanic discharge and charge testing with a Biologic workstation (SP-150). The discharge and charge cycles were set to 20 mins (total 40 mins for 1 cycle) and the Linear Sweep Voltammetry (LSV) was screened at 10 mV s⁻¹ to produce the polarization curves.

Figures

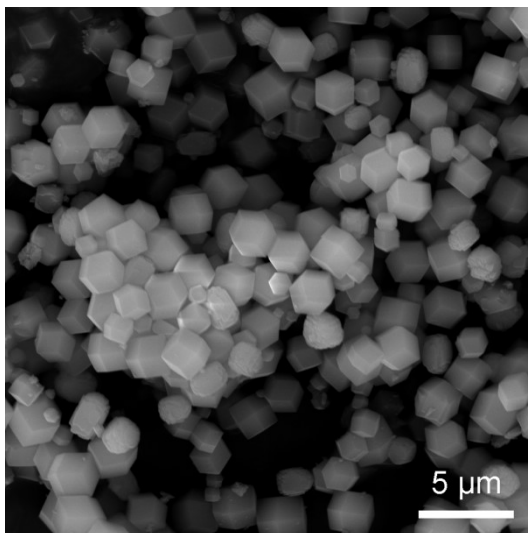


Figure S1. SEM image of ZIF-8.

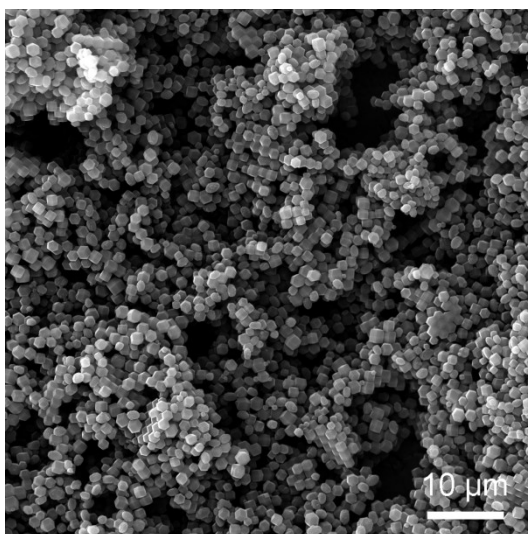


Figure S2. SEM image of NC.

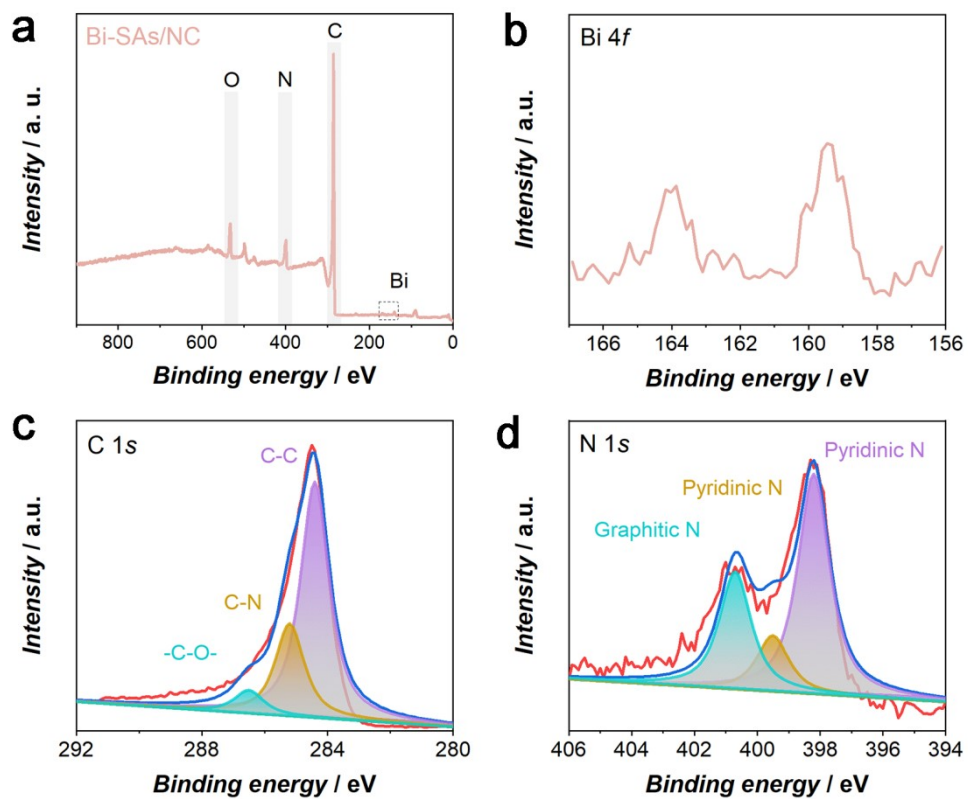


Figure S3. (a) XPS survey spectrum of Bi-SAs/NC; the high-resolution XPS spectra of (b) Bi 4f, (c) C 1s, and (d) N 1s from Bi-SAs/NC.

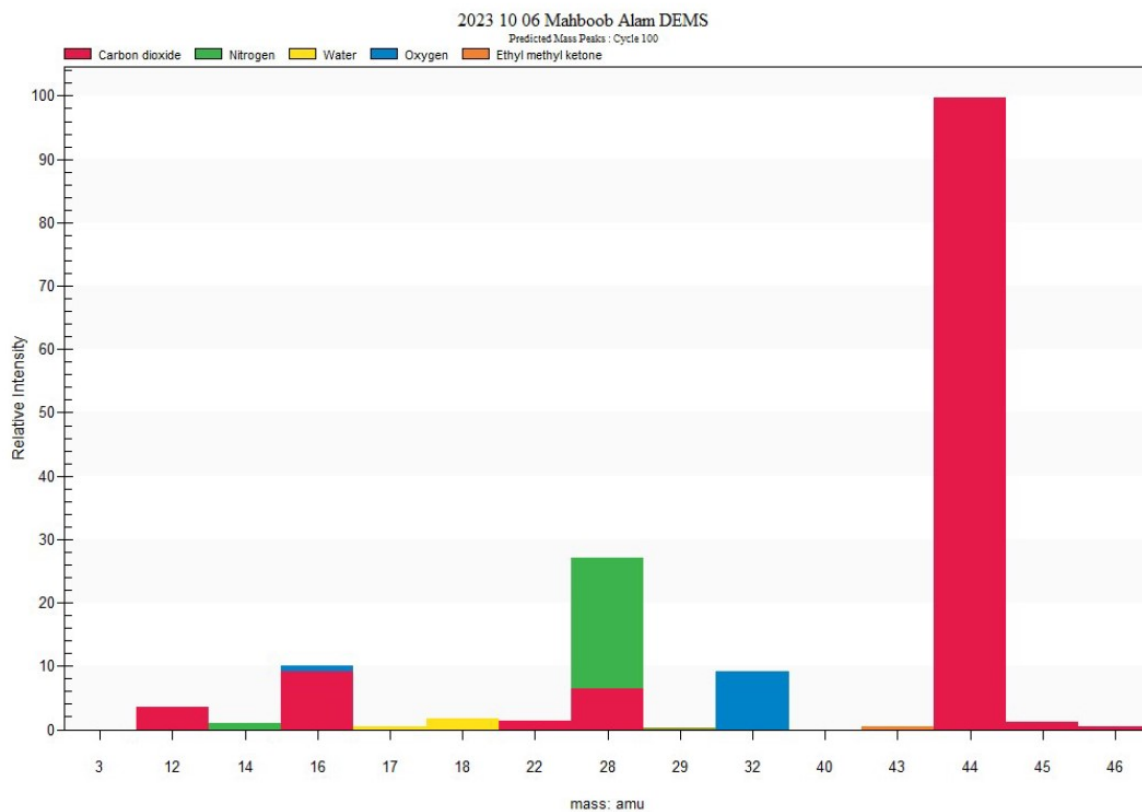


Figure S4. Electrochemical activity of Bi-SAs/NC towards CO₂RR measured in Differential Electrochemical cell emulating Zn-CO₂ system coupled with MS.

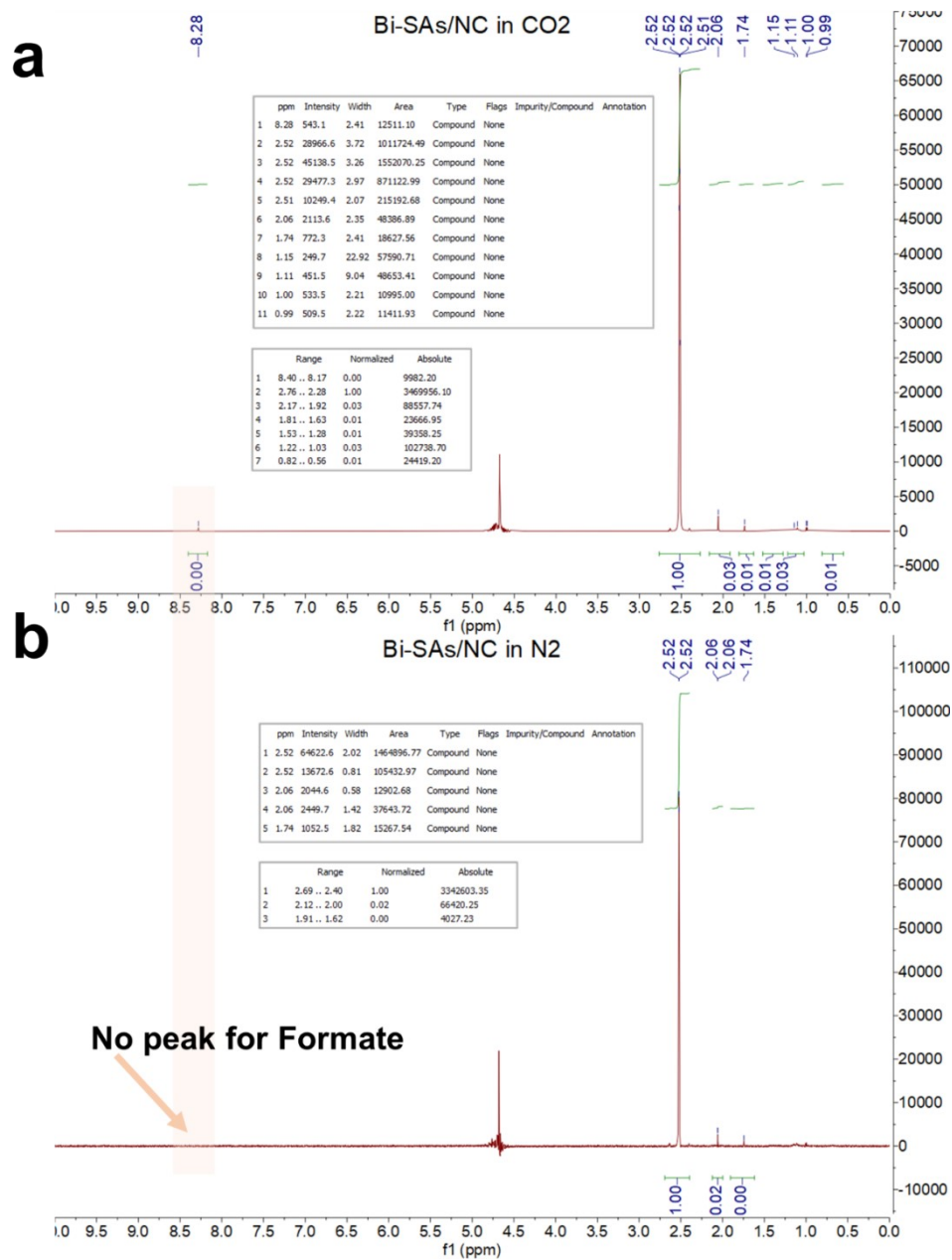


Figure S5. ¹H-NMR spectra of the 0.5 M KHCO₃ catholyte (a) purged with CO₂ (b) purged with N₂, containing expected liquid products after 3 h of chronoamperometry test at -0.99 V (vs. RHE) on GDE modified with Bi-SAs/NC

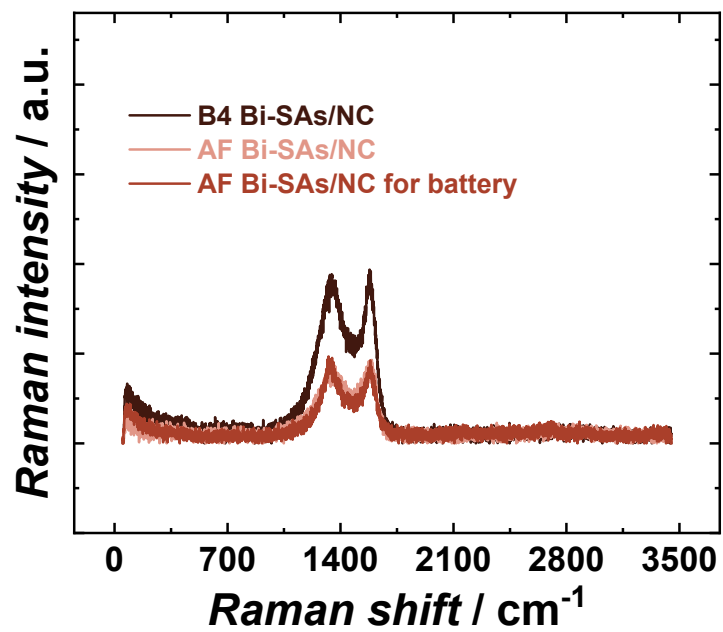


Figure S6. Raman spectra of Gas Diffusion Electrodes (GDE) modified with Bi-SAs/NC before (B4) the CO₂RR test, after (AF) CO₂RR test in H-type cell and after Zn-CO₂ battery discharge-charge cycling.

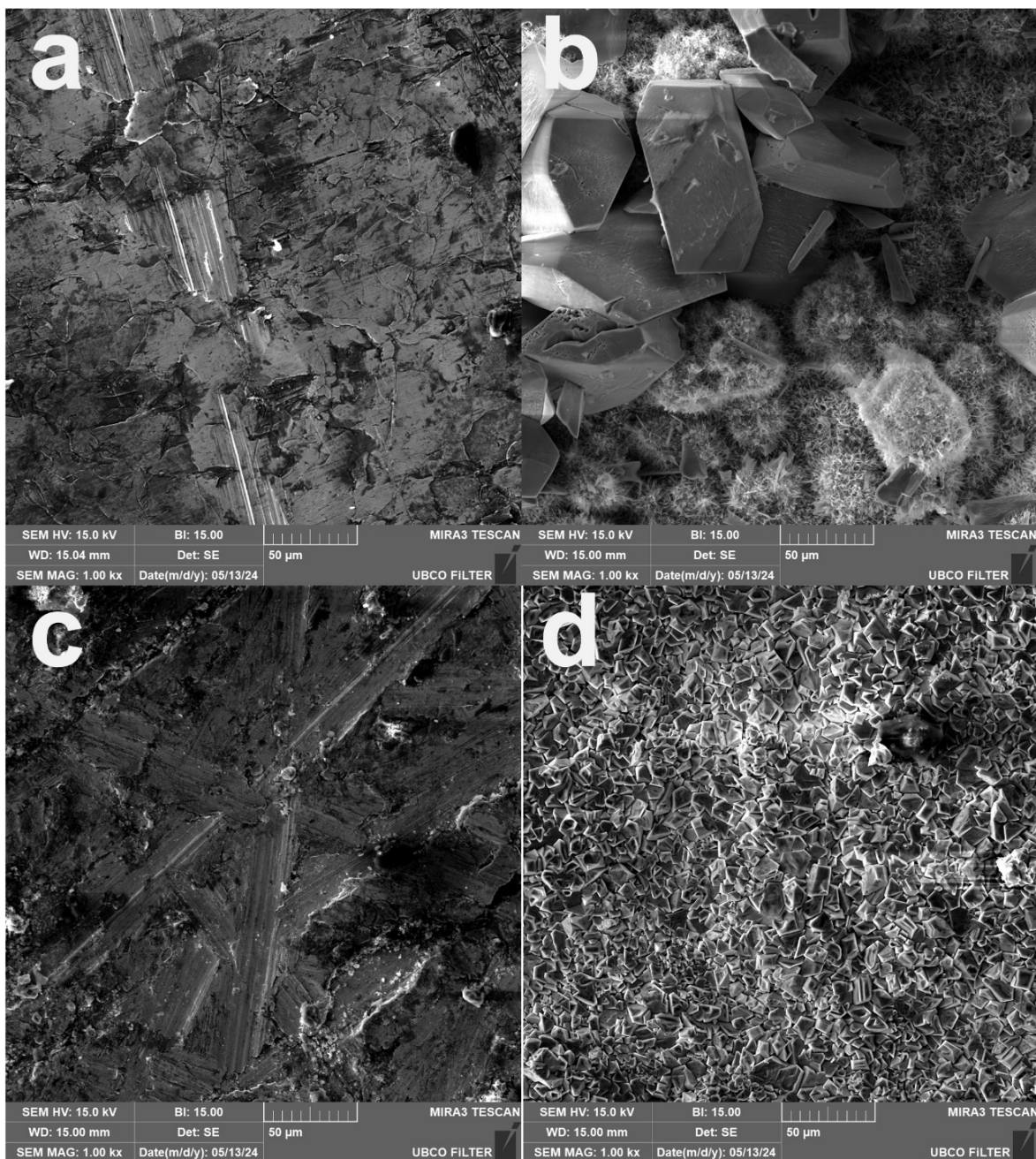


Figure S7. SEM images of the cross-section for both fresh Zn foil electrodes (a) before and (b) after cycling; Recycled Zn electrodes (c) before and (d) after cycling.

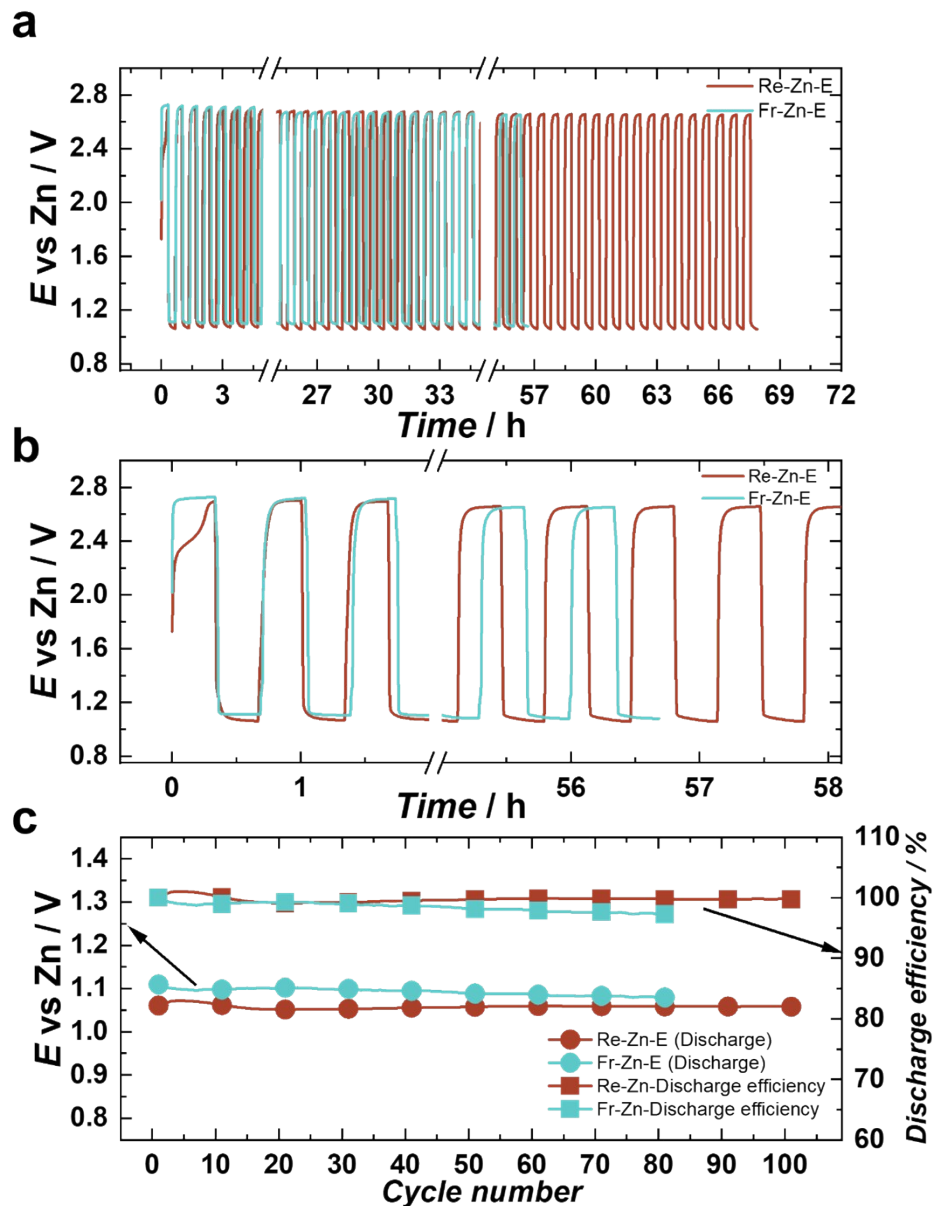


Figure S8 (a) The galvanic discharge and charge cycling of a Bi-SAs/NC modified gas diffusion electrode (GDE) at a current density of 0.5 mA cm^{-2} using fresh Zn (cycling for 57 h) and recycled Zn (cycling for 67 h) as anode (b) Isolated galvanic discharging and charging cycling for Bi-SAs/NC showing differences between specific cycles (c) comparison of the discharge potential and efficiency of both reversible Zn-CO₂ batteries for 100 cycles.

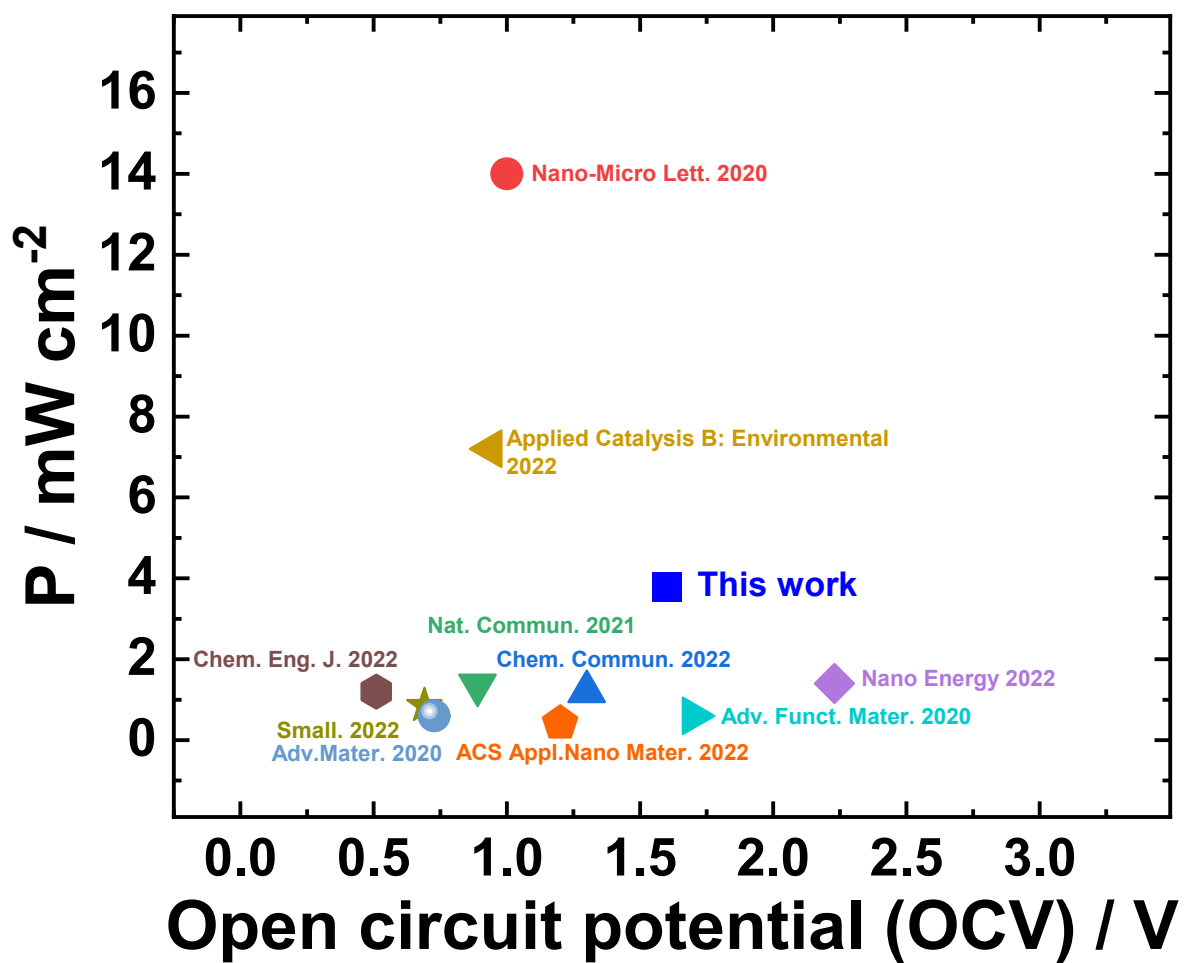


Figure S9. Comparison of power densities against open circuit voltage towards non-precious metal-based Zn-CO₂ batteries.

Tables

Tables S1. The elemental composition of the Bi-SAs/NC.

<i>Elements</i>	<i>Content (at %) by XPS</i>
C	85.8
N	6.2
O	7.8
Bi	0.2

Tables S2. Zn-CO₂ battery performance with those reported electrocatalysts.

Catalysts	Electrolyte	Discharge products	OCV (V)	Power density (mW cm⁻²)	Stability	Ref.
Bi-SAs/NC	0.5 M KHCO₃	HCOOH CH₃CH(OH)₂ CH₃COOH	1.6 V	3.8 and 3.2 mW cm⁻²	67 h	This work
Ni-N ₄ sites	0.5M KHCO ₃	CO (g)	1.37 V	1.4 mW cm ⁻²	20 h	Nano-Micro Lett. 2020, 12, 108
Metal Bi with abundant defects	2M KHCO ₃ +0.02 HCOO ⁻	HCOOH (l)	1.3 V	1.2 mW cm ⁻²	22 h	Chem. Commun. 2022, 58, 3621
Ni and Fe single atoms in N-doped graphene	2M KCl	CO (g)	0.89 V	1.36 mW cm ⁻²	90 h	Nat. Commun. 2021, 12, 4088
Bi nanoparticles in N-doped carbon	2M KHCO ₃ +0.02 HCOOH	HCOOH (l)	2.23 V	1.4 mW cm ⁻²	20 h	Nano Energy 2022, 92, 106780
BiC/HCS	0.1 M KHCO ₃	HCOOH (l)	0.94 V	7.2 ± 0.5 mW cm ⁻²	10 h	Applied Catalysis B: Environmental 307 (2022) 121145
Cu-N ₂ on graphene matrix	0.5M KHCO ₃	CO (g)	1.7 V	0.6 mW cm ⁻²	40 h	Adv. Funct. Mater. 2020, 30, 1907658
Single Fe atom on B and N codoped carbon	0.8M KHCO ₃	CO (g)	0.51 V	1.2 mW cm ⁻²	27 h	Chem. Eng. J. 2022, 437, 135294
Fe-P@NCPs	0.1 M KHCO ₃	CO (g)	0.691 V	0.85 mW cm ⁻²	168 h	Small. 2022, 18, 2104965
FeNC NSs-1000	0.5 M KHCO ₃	CO (g)	-	1.05 mW cm ⁻²	30 h	Nano Energy. 113 (2023) 108568
BiPdC	0.1 M KHCO ₃ with 0.1 M HCOONa	HCOOH (l)	1.2 V	0.42 mW cm ⁻²	45 h	ACS Appl.Nano Mater. 2022,5, 12387-12394
Ni-N ₃ -NCNFs	0.5 M KHCO ₃	CO (g)	-	1.05 mW cm ⁻²	46 h	Adv. Funct. Mater.2021, 31, 2008146
Zn/NC NSs	0.5 M KHCO ₃	CO (g)	-	1.8 mW cm ⁻²	25 h	Angew.Chem.Int.Ed. 2022,61,e202111683
Fe1NC/S ₁ -1000	0.8 M KHCO ₃	CO (g)	0.727 V	0.6 mW cm ⁻²	25 h	Adv.Mater. 2020, 32, 2002430
Ni@N-C	0.5 M KHCO ₃	CO (g)	-	1.64 mW cm ⁻²	43 h	Small 2023, 19, 2301128

References

1. H.-P. Iglesias van Montfort, S. Subramanian, E. Irtem, M. Sassenburg, M. Li, J. Kok, J. Middelkoop and T. Burdyny, *ACS Energy Letters*, 2023, **8**, 4156-4161.