



The construction of spindle-shaped Ni single-atom catalysts for high-efficiency CO₂-to-CO conversion and Zn-CO₂ battery applications by dual-ligand-driven morphology control

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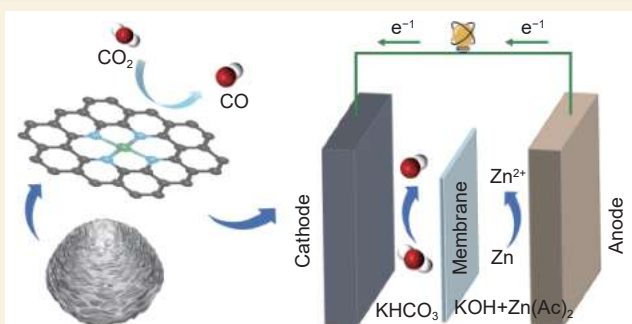
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Abstract: Tailoring the morphology and structure of catalysts is crucial for improving both the accessibility and utilization of single-atom active sites in CO₂ electroreduction. By introducing 5-aminotetrazole (5-AT) as a secondary ligand during the aqueous synthesis of a zeolite imidazolate framework-8 (ZIF-8), a bidentate metal-ligand complex was formed with 2-methylimidazole. The resulting catalyst, Ni-DMC-1, contains open mass-transport paths that expose abundant Ni single-atom sites while facilitating electron transfer. Consequently, Ni-DMC-1 achieves a CO partial current density of 26.2 mA cm⁻² at -1.13 V (vs. RHE) and a maximum CO Faradaic efficiency of 95.7% at -0.93 V (vs. RHE). The high CO current density stems from the hollow layer structure formed by Zn-linking 5-AT and 2-methylimidazole, where interior volatilization during carbonization creates voids that improve atom transport and kinetics. This work provides a novel approach for designing carbon-based catalysts for highly active electrochemical CO₂ reduction reactions. Furthermore, when used in a Zn-CO₂ battery, this catalyst achieves a peak power density of 1.25 mW cm⁻² during discharge, highlighting its potential for use in integrated energy devices.

Key words: Carbon substrate regulation; Ni single atom; Mass transfer optimization; CO₂RR; Zn-CO₂ battery



1 Introduction

The electrochemical reduction of CO₂ to CO offers a straightforward pathway for carbon recycling and negative carbon emissions^[1–3]. Achieving high catalytic activity under industrial-scale current densities is a critical requirement for practical applications^[4–5]. In this context, metal-based single-atom catalysts (SACs) have drawn growing interest, owing to their localized active sites and tunable coordination environments, which are beneficial for en-

hancing catalytic performance^[6–10]. The advantage of metal SACs lies in the fact that their isolated metal sites enable atomic-level uniform dispersion, allowing each metal atom to participate precisely in the catalytic reaction. Precise regulation essentially in-

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volves tailoring the coordination environment, including controlling the types and numbers of coordinating atoms, constructing diatomic sites, and adjusting defects and pore size distributions^[11]. Among these, carrier engineering is capable of enriching accessible active sites and constructing diffusion pathways. However, a significant challenge persists in the precise modulation of metal active sites, especially in enhancing the accessibility of single-atom sites.

Numerous studies have shown that the electrocatalytic CO₂ reduction (CO₂RR) activity of metal SACs is influenced by multiple factors, including pore structure, support morphology, metal coordination environment, and dispersion. Given the high structural sensitivity of metal SACs to CO₂RR, morphological control offers a promising way to framework diffusion pathways and improve the accessible sites of single-atom, enabling precise regulation of SACs and thereby boosting catalytic performance^[12–13]. To date, notable progress has been made toward loading single atoms onto carriers with various morphologies, including one-dimensional (1D) carbon nanotubes, two-dimensional (2D) graphene, and three-dimensional (3D) porous carbon materials. Among these, MOF-derived carbon as a member of 3D porous carbon materials, can be used to prepare M-N-C (metal-nitrogen-carbon) SACs with special morphology^[14–16]. For instance, Tian et al^[17] synthesized a Ni-MOF-derived micro-flower catalyst (Ni NPs@NC-800) with special morphology and hierarchical porosity. It delivered a CO Faradaic efficiency (FE) of 93% at −0.8 V vs. RHE and maintained >90% over 48 h. Yang et al^[18] converted 3D MOFs to monolayer MOFs (monoMOF, ~ 1.8 nm), which achieved a CO Faradaic efficiency of 93% at −0.8 V vs. RHE with a TOF of 10 600 h^{−1} and maintained stability over 47 h.

By controlling MOF-derived carbon morphology, M-N-C-type SACs can develop a unique hollow architecture to anchor metal active sites^[19–23]. Typically, MOF precursors are pyrolyzed at 600–1000 °C to obtain a conductive carbon framework, but such high temperatures often cause framework collapse, necessitating complex processing steps to preserve morpho-

logy^[24–25]. ZIF-8-derived carbon offers a notable exception. As a subclass of MOF-derived carbon, it undergoes Zn volatilization during pyrolysis, leaving behind a stable porous framework that withstands 800–1000 °C. Moreover, it inherits the periodic isolation of metal atoms from the parent MOF structure, effectively suppressing metal agglomeration^[26–30]. Thus, by using the appropriate pyrolysis temperature, a catalyst structure featuring a 3D open architecture with hollow spaces and disperse metal sites can be easily synthesized.

Here, we introduce 5-aminotetrazole (5-AT) as a secondary ligand during the aqueous synthesis of ZIF-8 to fabricate nickel (Ni) single-atom catalysts through a straightforward synthetic approach, with the incorporation of an appropriate amount of 5-AT, the resulting Ni-DMC-1 catalyst exhibits a unique spindle-shaped morphology with loosely bonded layers, generating interlayer gaps and accessible channels that facilitate CO₂ diffusion and adsorption. These interconnected 3D transport pathways provide more efficient access to the active sites than the densely packed framework of conventional ZIF-8. As a result, Ni-DMC-1 achieves a maximum CO Faradaic efficiency (FE) of 95.7% at −0.93 V (vs. RHE) and a CO partial current density of 26.2 mA cm^{−2}. When the amount of added 5-AT is systematically varied, the hollow spindle-shaped carbon substrate induced by the bidentate ligand modulates the active sites and catalytic performance of SACs, providing new insights into the design of carbon substrate morphologies for CO₂RR. Furthermore, when applied to a Zn-CO₂ battery system, the Ni-DMC-1 cathode exhibited a peak power density of 1.25 mW cm^{−2} during discharge, opening new avenues for the conversion and utilization of CO₂ in reduction reactions.

2 Experiment

2.1 Materials

Zinc acetate dihydrate (99.0%) and 5-Aminotetrazole monohydrate (99.0%) were purchased from Shanghai Titan Technology Co., Ltd. 2-Methylimidazole (99.0%) was obtained from Shanghai Aladdin

Biochemical Technology Co., Ltd. Ni chloride (99.0%) was purchased from Damas-beta. And hydrochloric acid solution (HCl) was purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2 Preparation of the catalysts

(1) Synthesis of catalysts DMC-1 and Ni-DMC-1: Preparation of DMC-1: Dissolve 2968 mg 2-methylimidazole in 100 mL H₂O, then add 851 mg 5-aminotetrazole and stir thoroughly until dissolved. Dissolve zinc acetate dihydrate (2195 mg) in 100 mL H₂O and stir until completely dissolved. Combine the 2 solutions, stir continuously for 30 min, then place the mixture in 80 °C water bath for 1 h. Subsequently, centrifuge to obtain a solid precipitate. Carbonize the resulting solid powder with a heat-up rate of 5 °C min⁻¹ to 900 °C under an N₂ carrier gas to yield the carbon-based substrate DMC-1. Mix 200 mg of the obtained carbon substrate thoroughly with 20 mg/mL NiCl₂ solution (NiCl₂ solution in ethanol as solvent), dried, and calcined again in a tube furnace at 800 °C for 1 h. Finally, to eliminate the effects of metal particle impurities and metal oxides, the calcined material was washed with 1 mol L⁻¹ HCl solution for 12 h, filtered, and dried to yield the catalyst Ni-DMC-1.

(2) Synthesis of catalyst Ni-DMC-2: Adjust the amount of 5-aminotetrazole to 2252 mg. The quantities of other reagents and the synthesis procedure remain identical to those for Ni-DMC-1, yielding catalyst Ni-DMC-2.

(3) Synthesis of catalyst Ni-MC: The preparation process for Ni-MC is identical to that of Ni-DMC-1, except that 5-aminotetrazole is not added during the synthesis of Ni-MC. The remaining experimental steps followed the procedure for synthesizing Ni-DMC-1, ultimately yielding the catalyst Ni-MC.

2.3 Electrochemical measurement

For catalyst ink preparation, 8 mg of the catalyst powder was mixed with 30 µL of Nafion solution and 370 µL of anhydrous ethanol, followed by ultrasonication to obtain a homogeneous catalyst ink. The resulting ink was uniformly drop-cast onto four 1 cm ×

1 cm carbon paper substrates. For working electrode preparation in a flow cell, 72 mg of the catalyst powder was mixed with 270 µL of Nafion solution and 3830 µL of anhydrous ethanol. The mixture was ultrasonicated for 2 h to form a homogeneous catalyst ink. Subsequently, 1000 µL of the ink was uniformly dispensed onto a 3 cm × 3 cm carbon paper substrate and dried thoroughly before use.

Preparation of ZCB: We conducted preliminary tests on Zn-CO₂ cell using a custom-built experimental setup to assess the exceptional performance of Ni-DMC-1 in the carbon dioxide reduction reaction. The anode was a polished Zn foil (geometric area: 2 cm²), and the cathode was fabricated by depositing Ni-DMC-1 on hydrophobic carbon paper with a mass loading of 2.0 mg cm⁻². A bipolar membrane separated the 2 compartments, with the anodic side filled with 2 mol L⁻¹ KOH containing 0.02 mol L⁻¹ zinc acetate and the cathodic side filled with 0.5 mol L⁻¹ KHCO₃. During testing, high-purity CO₂ was continuously pumped into the cathodic electrolyte at a constant flow rate of 20 mL min⁻¹. Gas-phase products yielded in the electrocatalytic reaction were characterized by gas chromatography. Furthermore, the discharge electrochemical polarization behavior and operational stability of the catalyst were measured by a self-developed experimental platform equipped with a CHI 760e electrochemical working station.

3 Results and discussion

3.1 Catalyst preparation and characterization

In this study, four distinct catalysts were prepared: DMC-1 without Ni metal, Ni-DMC-1 with an appropriate amount of the second ligand, Ni-DMC-2 with an excess of the second ligand, and traditional ZIF-8-derived Ni-MC catalyst without 5-AT. Fig. 1 illustrates the synthesis procedure of the Ni-DMC-1 catalyst. First, by a simple one-pot method, 5-AT and 2-methylimidazole were assembled into a layered precursor, which used Zn²⁺ as a linking agent. Then, prepared precursor was carbonized in a two-step process to yield the target catalyst Ni-DMC-1. Unlike traditional ZIF-8-derived carbon catalysts with a compact

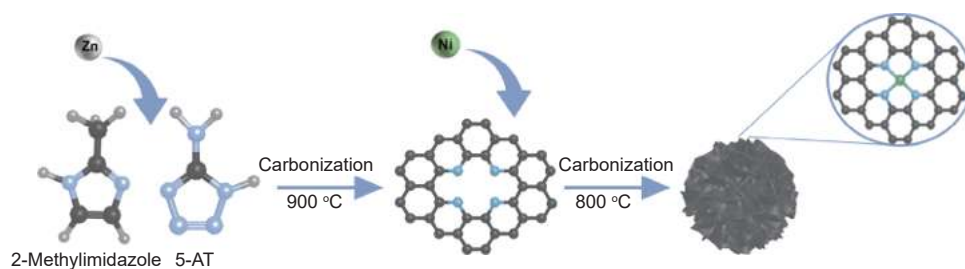


Fig. 1 Illustration of the preparation process of Ni-DMC-1

microporous structure, the present catalyst undergoes removal of internal volatile components (5-AT) during carbonization, yielding a clustered hollow spindle-shaped structure^[31–32]. The addition of an appropriate amount of 5-AT not only enhances the exposed surface area of the layers while preserving the catalyst morphology but also facilitates a single Ni atom loading on the catalyst surface.

Scanning electron microscopy (SEM) characterization revealed that Ni-DMC-1 layers exhibited gaps between their layers, which were no longer tightly stacked. The layers show increased thickness while maintaining a clustered overall structure (Fig. 2a–b). In contrast, Ni-MC exhibits a tightly stacked structure, while Ni-DMC-2 shows a scattered flake-like morphology (Fig. 2c–f). Therefore, the addition of an appropriate amount of bidentate ligand not only increases the exposed surface area of the layers without disrupting the overall morphology, but also facilitates subsequent metal loading on the catalyst surface. Transmission electron microscopy (TEM) further confirmed that Ni-DMC-1 exhibits a distinct layered

structure with clear edges and a well-defined hollow architecture (Fig. 3a). Ni-MC layers exhibit tightly stacked arrangements (Fig. S1a), whereas Ni-DMC-2 shows a more disordered structure without a distinct overall morphology (Fig. S1b). Furthermore, no distinct Ni nanoparticles were observed in the layered structures of Ni-MC, Ni-DMC-1 or Ni-DMC-2. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images confirmed the presence of dispersed Ni single atoms in Ni-DMC-1 (Fig. 3b). Combined with EDS elemental mapping, the results show that C, N, O and Ni coexist uniformly in Ni-DMC-1. Notably, metallic Ni exhibits no clustering, indicating atomic-level distribution within the catalyst (Fig. 3c).

Thermogravimetric analysis (TGA) was used to evaluate the CO₂ capture performance of the three samples. All samples were first degassed in N₂ at 110 °C to remove adsorbates, and then subjected to multi-cycle adsorption-desorption tests (Fig. 4a), each consisting of isothermal CO₂ adsorption (100 min) at a set temperature, followed by desorption in N₂ at

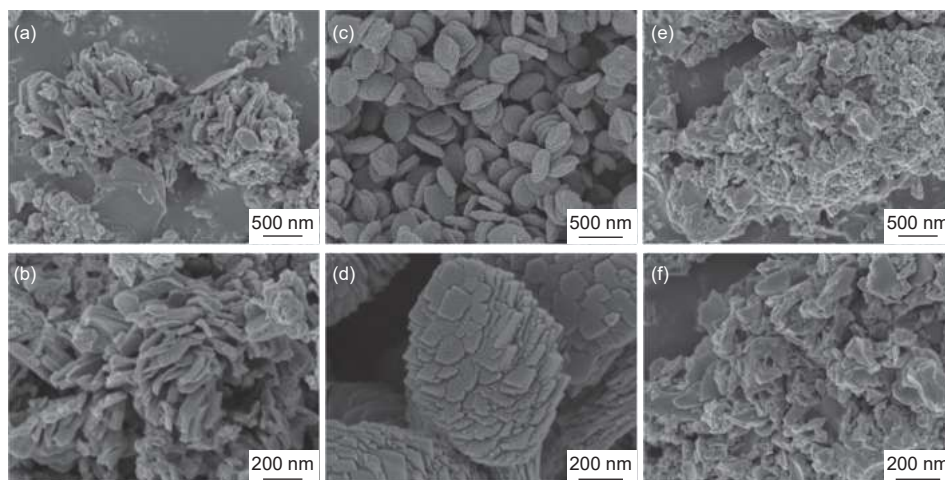


Fig. 2 (a, b) SEM micrographs of Ni-DMC-1. (c, d) SEM micrographs of Ni-MC. (e, f) SEM micrographs of Ni-DMC-2

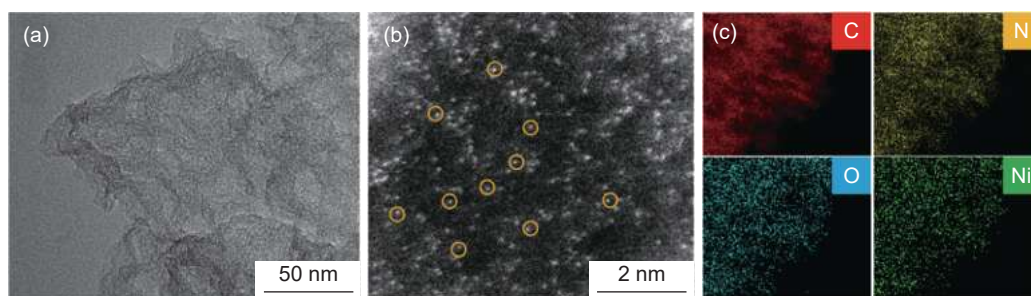


Fig. 3 (a) TEM image of Ni-DMC-1. (b) HAADF-STEM image of Ni-DMC-1. (c) The elemental mappings of C, N, O, Ni for Ni-DMC-1

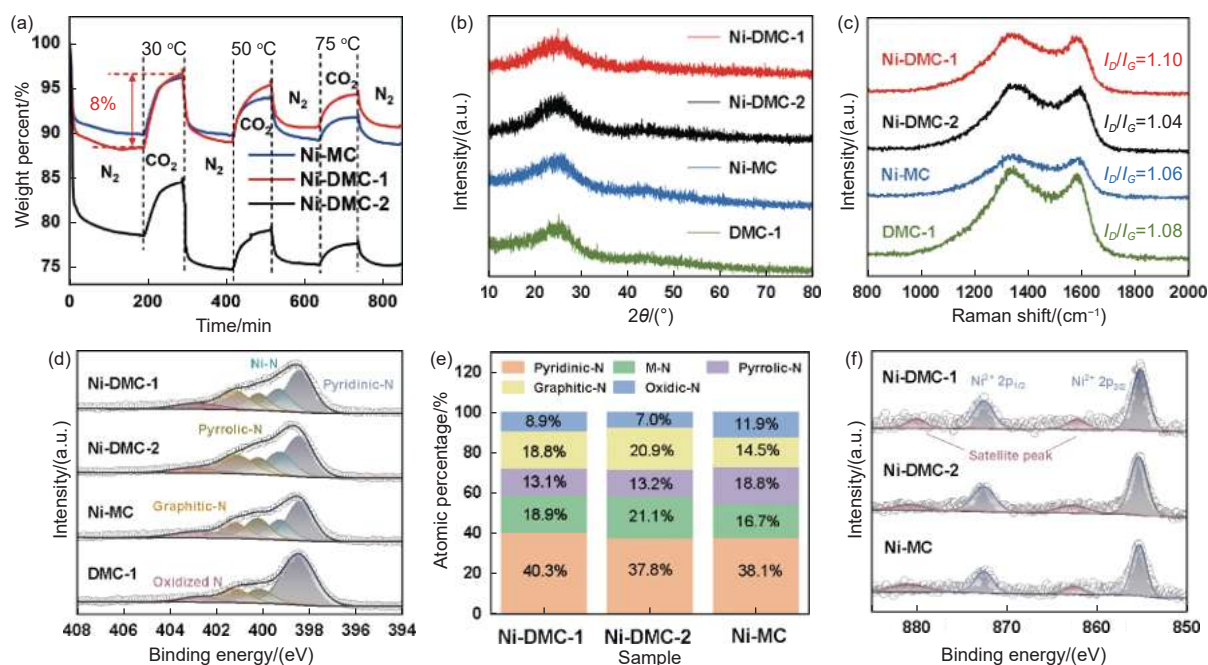


Fig. 4 (a) Typical carbon dioxide adsorption-desorption curves of different catalysts (b) XRD diffractograms of different catalysts. (c) Raman vibrational profiles of different catalysts. (d) N 1s deconvoluted spectra of different catalysts. (e) Quantitative nitrogen species distribution of varied morphologies. (f) Ni 2p orbital splitting patterns of different catalysts

110 °C. The tests were conducted sequentially at 30, 50 and 75 °C. At 30 °C, all samples exhibited weight gains due to physical CO₂ adsorption^[33–34]. Ni-DMC-1 showed the highest saturated uptake (8%), followed by Ni-DMC-2 (6.5%) and Ni-MC (5%). The superior performance of Ni-DMC-1 was attributed to the appropriate 5-AT loading, which created interlayer gaps and interconnected channels, thereby increasing accessible surface area and reducing diffusion resistance. In contrast, Ni-MC (without 5-AT) retained a compact, closed structure with limited pore accessibility. Ni-DMC-2, with excess 5-AT, exhibited the largest mass loss during initial degassing, reflecting that the excess ligand led to a loose, disordered structure that adsorbed more ambient moisture; although

its uptake exceeded that of Ni-MC, confirming that 5-AT indeed opened the structure, this disorder did not confer a CO₂ adsorption advantage. As the temperature was elevated to 50 and 75 °C, the adsorption capacities of all samples decreased, consistent with physisorption thermodynamics, but Ni-DMC-1 still outperformed the others at 75 °C. After three cycles, no significant capacity decay was observed, and the masses returned to baseline after desorption at 110 °C, confirming good regenerability and stability. Overall, Ni-DMC-1 modified with an appropriate amount of 5-AT exhibited the best CO₂ capture performance over a wide temperature range, owing to its moderately open structure.

Fig. 4b shows the XRD test results for the cata-

lysts. It can be observed that all catalysts exhibit peaks at 28° and 43° , corresponding to the C (002) and C (100) planes of graphitic carbon, respectively. This indicates that all materials possess a certain degree of graphitization. Furthermore, no additional peaks appear in any catalyst, further confirming that the metal dispersion within the catalysts is achieved at the atomic level, highly uniform, and free from metallic crystallization or clustering. Additionally, Raman spectroscopy analysis (Fig. 4c) was performed on the catalysts to assess the degree of carbon defects. The Raman spectra of all catalysts exhibited both *D* and *G* peaks. The Raman *D* peak at 1350 cm^{-1} indicates the formation of intrinsic carbon defects in the lattice; in contrast, the *G* peak at 1580 cm^{-1} originates from in-plane stretching vibrations associated with sp^2 -bonded carbon atoms^[35–36]. The *D* and *G* peaks correspond to disordered carbon and graphitic carbon, respectively, and their ratio I_D/I_G reflects the abundance of carbon defects. With progressive addition of the second ligand, the defect density first rises and then falls. Notably, Ni-DMC-1 possesses the highest defect level among the samples, and its value is also larger than that of DMC-1, confirming that Ni incorporation promotes structural disorder. A comprehensive analysis of the Raman spectroscopy data for all catalysts indicates that metal doping, combined with the introduction of an appropriate amount of a second ligand, can induce a large number of lattice defects within the catalyst, thereby significantly enhancing its catalytic activity and long-term cycling stability^[37].

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that the content of Ni in Ni-DMC-1 was 3.32% (Table S1). To better understand the surface chemistry of the 4 samples (Ni-DMC-1, Ni-DMC-2, Ni-MC and DMC-1) (Fig. S2), survey scans were performed, aiming to reveal the elemental makeup and valence states present on their surfaces. Characteristic peaks for Ni, N, C and O were detected in all 3 catalysts except DMC-1, which exhibited no Ni signal due to the absence of a Ni source. High-resolution analysis of the C 1s orbitals (Fig. S3) reveals 3 characteristic peaks for all catalysts, corre-

sponding to the sp^2 -hybridized C=C bond (284.8 eV), C=N bond (286.2 eV), and O=C–O bond (288.8 eV). In the N 1s orbital region (Fig. 4d), five characteristic peaks were detected for Ni-DMC-1, Ni-DMC-2, and Ni-MC, assigned to pyridine nitrogen (398.4 eV), metal-coordinated nitrogen (399.3 eV), pyrrolic nitrogen (400.2 eV), graphitic nitrogen (401.2 eV), and oxidized nitrogen (402.8 eV). Among these, the relative content of pyridine nitrogen in Ni-DMC-1 was higher than in the other samples. The abundance of pyridine nitrogen provides active sites for anchoring single Ni atoms, increases the electron density around Ni, and thus promotes the activation of CO_2 molecules. Meanwhile, Ni-DMC-2 had the highest metal-nitrogen content (Fig. 4e). This phenomenon confirms the effectiveness of the bidentate ligand strategy: the introduction of bidentate ligands not only significantly increases the effective Ni loading in the catalyst but also results in a marked increase in the metal-nitrogen bond ratio as the amount of bidentate ligands added increases. Analysis of the O 1s fine patterns (Fig. S4) reveals only 2 peaks for all catalysts, with no M-O peak observed, indicating that the metal does not form coordination with oxygen in the catalyst. To further investigate the chemical state of Ni, high-resolution spectrum analysis was performed on the Ni 2p orbital (Fig. 4f). All Ni-containing catalysts exhibited 4 characteristic peaks in the Ni 2p orbital region, attributed to Ni $2\text{p}_{3/2}$, Ni $2\text{p}_{1/2}$, and their corresponding satellite peaks. Peak fitting results reveal that Ni $2\text{p}_{3/2}$ signal has binding energies ranging from 853.0 eV (Ni^0) to 855.7 eV (Ni^{2+}), indicating that the valence state of Ni in the catalysts varied between 0 and 2. In summary, the dual-ligand strategy enhances Ni loading and pyridine nitrogen, metal-N bond formation without Ni-O coordination; Ni exists in mixed valence states (0–2), providing a favorable coordination environment for catalysis.

Multi-scale synchrotron radiation characterization techniques (XANES, EXAFS and WT-EXAFS) were used to further analyze the oxidation states and coordination states of Ni in Ni-DMC-1. Through combined R-space and k-space analysis, the Ni-N coordin-

ation geometry and the arrangement patterns of neighboring atoms were elucidated^[38–39]. In the X-ray absorption near-edge structure (XANES) spectrum, the energy of Ni-DMC-1 absorption edge lies between that of Ni foil and NiO (Fig. 5a), indicating that Ni sites within the sample exhibit a mixed valence state spanning 0 to 2, which is consistent with the results of previous XPS characterization. The K-space EXAFS signal (Fig. S5) was subjected to a Fourier transform to analyze the extended X-ray absorption fine structure (EXAFS) lines, thereby revealing structural details of the Ni-DMC-1 catalyst in R-space (Fig. 5b). The characteristic scattering peaks of Ni-DMC-1 in the *R* region coincide with the signal positions widely reported to be attributed to Ni-N coordination bonds, indicating the presence of nitrogen in the coordination environment of metallic Ni, which is consistent with XPS measurements. Furthermore, no distinct signal for Ni-Ni bonds at ~ 2.10 Å was observed in Ni-DMC-1, indicating the absence of metallic Ni nanoparticles. To further confirm the presence of Ni-N bonds, EXAFS wavelet transform (WT) analysis (Fig. 5d–f) was employed. The maximum signal intensity of Ni-DMC-1 shifted toward the Ni-N bond in NiPc, suggesting the existence of Ni-N bonds in this

catalyst. The XPS peak decomposition results were combined with the R-space Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) curve fitting results for Ni-DMC-1 to determine the coordination structure of metallic nickel more accurately. The fitting results in Fig. 5c (Table S2) confirm that the coordination number of the Ni-N bond is approximately four, indicating the presence of a Ni-N₄ configuration at the Ni center in the Ni-DMC-1 catalyst.

3.2 Electrochemical measurements of CO₂RR

Fig. 6a shows the catalytic performance of the catalyst in an H-type electrolyzer; the tests were conducted over an applied potential range of -0.33 to -1.33 V(vs. RHE). Ni-DMC-1 exhibited the highest selectivity for CO₂ conversion to CO at -0.93 V (vs. RHE) (Fig. 6b), achieving a *FE* of 95.7%. It maintained *FE* above 90% across the voltage range from -0.63 to -1.03 V, demonstrating excellent catalytic selectivity. The electrocatalytic performance of Ni-DMC-2 for CO₂ reduction was evaluated. Although Ni-DMC-2 exhibited a higher maximum *FE*_{CO} at -0.83 V (vs. RHE) than Ni-DMC-1, a comparison of the current densities (Fig. 6c) shows that Ni-DMC-1 consistently exhibited a higher current density than

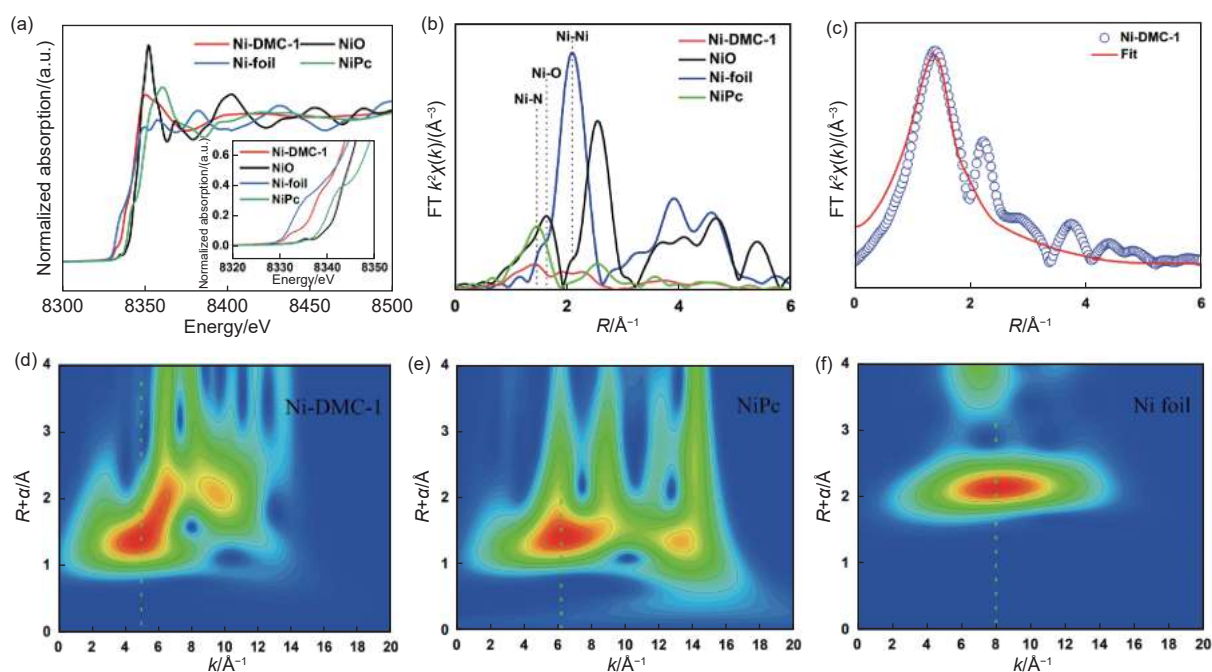


Fig. 5 (a) Ni K-edge XANES spectra of as-prepared samples and references. (b) Fourier transformed curves of Ni K-edge EXAFS spectra. (c) Ni K-edge EXAFS fitting result of Ni-DMC-1. (d–f) WT-EXAFS plots of Ni-DMC-1, NiPc and Ni foil

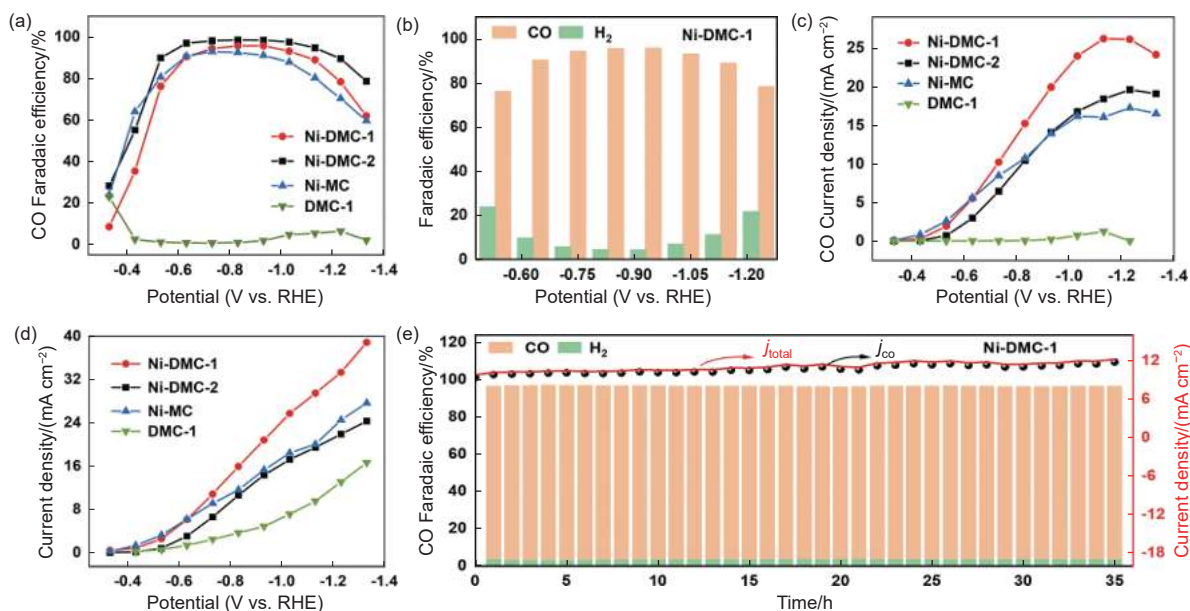


Fig. 6 (a) FE of Ni single atom catalysts with different morphologies. (b) FE of Ni-DMC-1 at different voltages. (c) CO fractional current density with different morphologies. (d) Total current density for Ni single atom catalysts with different morphologies. (e) Stability test of Ni-DMC-1 in H-type electrolytic cell

Ni-DMC-2. At -1.13 V (vs. RHE), the CO partial current density of Ni-DMC-1 reached 26.2 mA cm^{-2} , far exceeding the maximum current density of Ni-DMC-2 at 19.6 mA cm^{-2} , and Ni-DMC-1's total current density reached a maximum of 39 mA cm^{-2} (Fig. 6d). The randomly scattered cluster morphology of Ni-DMC-2 gives high mass transfer, leading to high FE but low active site density and current density. In contrast, the moderately dispersed morphology of Ni-DMC-1 forms an open channel, balancing active sites and mass transfer, resulting in slightly lower FE but the highest current density and yield. Although Ni-MC achieved a CO selectivity of 92.5% (-0.83 V (vs. RHE)), its CO partial current density was limited to 16.18 mA cm^{-2} due to the electrical conductivity and mass transfer resistance of the carbon support. In summary, compared to Ni-MC and Ni-DMC-2, Ni-DMC-1 achieves a superior overall balance between activity and selectivity.

To identify the key factors governing Ni-DMC-1's catalytic activity, a catalyst DMC-1 without the metal source was synthesized and evaluated for its electrocatalytic performance in CO_2RR . DMC-1 showed almost no selectivity for CO across the entire voltage range (Fig. 6a), and its maximum CO partial current density was only 1.05 mA cm^{-2} (Fig. 6c). Over

35 h of electrocatalytic reaction, the Faradaic efficiency of the catalyst remained virtually unchanged. This indicates that Ni-DMC-1 possesses the capability for long-term catalytic reduction of carbon dioxide, indicating its activity in the electrocatalytic reduction of CO_2 is negligible. The data above indicate that the Ni added is the dominant active site of Ni-DMC-1. The electrocatalytic stability of Ni-DMC-1 was evaluated at -0.93 V (vs. RHE) (Fig. 6e).

Ni-DMC-1 was operated at -0.93 V for 0.5 h to investigate whether liquid-phase products were generated during the electrochemical CO_2 reduction reaction. After the reaction, the electrolyte was collected and analyzed by proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy (Fig. S6). The $^1\text{H-NMR}$ spectrum showed only signals corresponding to H_2O and DMSO, with no detectable peaks attributable to other liquid-phase products^[40–41]. These results indicate that no detectable peaks attributable liquid-phase products were generated during CO_2RR over Ni-DMC-1, confirming its high selectivity toward gaseous products under tested conditions. The electrocatalytic performance of catalyst Ni-DMC-1 for CO_2RR was evaluated using a flow cell within a current density range of 40 to 320 mA cm^{-2} (Fig. 7d). Within the current density range of 120 to 320 mA cm^{-2} , the catalyst consist-

ently maintained a selectivity of 99% or higher for converting CO₂ to CO, demonstrating robust catalytic activity and selectivity. Notably, the Ni-DMC-1 catalyst exhibits excellent catalytic selectivity even at high current densities of 300–320 mA cm⁻², indicating its significant application potential.

In order to evaluate the reactivity of Ni-DMC-1 in the CO₂RR and the HER, we carried out Linear sweep voltammetry (LSV) experiments with electrolytes saturated by carbon dioxide and argon separately (Fig. 7a). Ni-DMC-1 exhibited remarkably higher current responses in CO₂-purged system than the Ar-purged system within the applied potential window of -0.2 to -1.20 V (vs. RHE). By comparing the LSV curves of Ni-DMC-2 with excess ligands added under CO₂ atmosphere (Fig. S7a), Ni-DMC-1 with appropriately doped ligands exhibits higher current density. This further demonstrates that Ni-DMC-1's dispersed, clustered spindle-shaped carbon substrates deliver superior electrochemical performance. The LSV scan curves of other catalysts under Ar and CO₂ atmospheres also indicate that all catalysts exhibit higher current densities in the CO₂ atmosphere than in

the Ar atmosphere (Fig. S7b-c). Nevertheless, Ni-DMC-1 still exhibits the highest current density, demonstrating superior reactivity toward CO₂ reduction compared to other catalysts. Notably, Ni-free DMC-1 exhibits a current density in the CO₂ atmosphere that falls below that in the Ar atmosphere at high potentials, further confirming the superior performance of Ni monometallic active sites for CO₂RR. Fig. 7a shows that the initial potential of catalyst Ni-DMC-1 is -0.5 V (vs. RHE), while Ni-DMC-2 and Ni-free DMC-1 exhibit relatively higher initial potentials. This indicates that the Ni-DMC-1 catalyst exhibits a lower reaction energy barrier during the electrocatalytic reduction of carbon dioxide to carbon monoxide. This superior performance can be attributed to the open 3D structure of Ni-DMC-1. The transport channels formed facilitate mass transfer between CO₂ and the electrolyte, allowing reactants to efficiently reach the nickel active sites within the micropores. Consequently, the reaction can be initiated at a lower overpotential.

Cyclic voltammetry and double-layer capacitance measurements further support this analysis. Cyc-

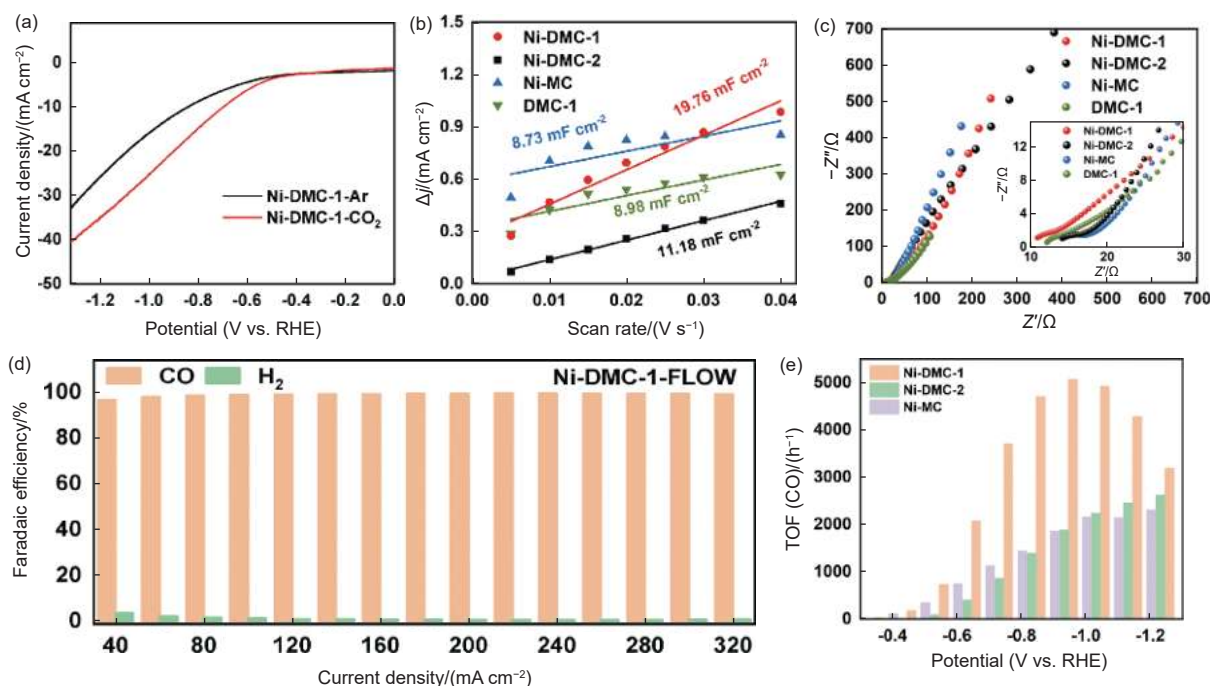


Fig. 7 (a) LSV curves of Ni-DMC-1 under different atmospheres. (b) Double-layer capacitance of samples with different morphologies. (c) EIS curves of Ni single-atom catalysts with different morphologies. (d) FE of Ni-DMC-1 in a flow cell. (e) CO turnover frequency of various catalysts at different operating potentials under low-loading conditions

lic voltammetry analysis (Fig. S8) combined with double-layer capacitance measurements (Fig. 7b) reveals that Ni-DMC-1 exhibits a C_{dl} value of 19.76 mF cm^{-2} , significantly higher than other samples ($8.73\text{--}11.18 \text{ mF cm}^{-2}$). This advantage stems from its hierarchical porous structure, which enhances mass transfer kinetics and exposes abundant active sites, leading to a substantial optimization of its electrochemical active surface area. Electrochemical impedance spectroscopy (EIS) plots of the catalyst are presented in Fig. 7c. The absence of a semicircular arc at high frequencies manifests the existence of mass transport restriction. Meanwhile, Ni-DMC-1 displays a diminished semicircle radius, which corresponds to suppressed charge transfer barrier and boosted electron delivery efficiency, further enhancing its CO_2 reduction activity. This is attributed to the synergistic effect between the interconnected conductive carbon framework and open pores within the material, which facilitates rapid electron transport to active sites. Collectively, these electrochemical characterization results demonstrate that the judicious introduction of bidentate ligands increases the exposure of active sites while maintaining a low reaction energy barrier, thereby achieving higher catalytic activity and se-

lectivity. To eliminate mass transfer limitations and the active site burial effect caused by thick catalyst layers^[42], we evaluated the catalytic kinetics of all samples at an ultra-low loading of 0.1 mg cm^{-2} . Crucially, the turnover frequency (TOF) of the Ni-DMC-1 catalyst (Fig. 7e) reached 5100 h^{-1} , which considerably outperforms the counterparts of Ni-MC and Ni-DMC-2. This demonstrates that Ni-DMC-1 delivers optimal atomic utilization efficiency when operated under identical electrocatalytic test conditions.

In-situ Fourier-transform infrared (FTIR) spectroscopy of the Ni-DMC-1 catalyst during CO_2RR reveals that as the operating potential increases, the absorption peaks of *COOH and *COO^- both intensify, indicating enhanced catalytic activity for CO production within a certain potential range (Fig. 8a). The peaks at 1260 , 1386 and 1660 cm^{-1} correspond to *COOH (OH bending, C—O stretching, C=O stretching), while the peak at 1405 cm^{-1} arises from *COO^- symmetric stretching^[43]. Due to rapid protonation of *COO^- to *COOH , the *COO^- signal is relatively weak^[44–45]. These results confirm *COOH and *COO^- as key intermediates. Additionally, the 1660 cm^{-1} peak has a partial contribution from adsorbed water (OH_2). From -0.53 to -1.03 V , the *OH_2

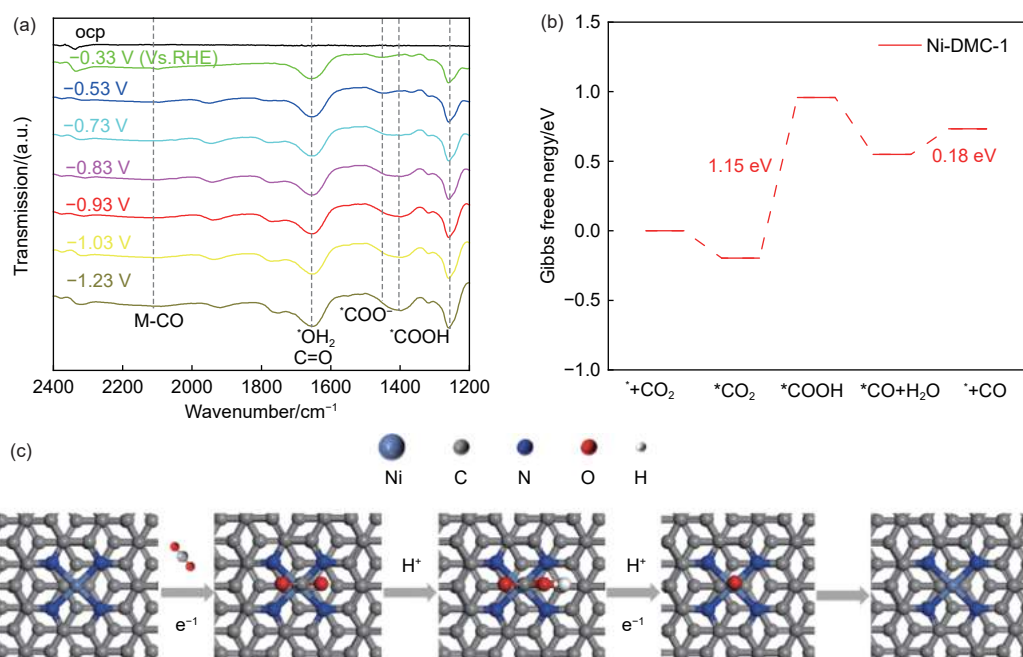


Fig. 8 (a) In-situ TFIR characterizations of Ni-DMC-1 under open-circuit potential and catalytic working potentials. (b) Free energy diagram for CO_2RR to CO on Ni-DMC-1. (c) The reaction pathways for CO_2RR to CO using Ni-DMC-1 as a model

peak remains weaker than the $\ast\text{COOH}$ peak, reflecting high selectivity for CO_2 conversion. At more negative potentials, $\ast\text{OH}_2$ surpasses $\ast\text{COOH}$, indicating increased water adsorption and hydrogen evolution reaction (HER), which lowers selectivity. Overall, Ni-DMC-1 stably generates $\ast\text{COO}^-$ and $\ast\text{COOH}$ intermediates, demonstrating excellent activity and selectivity.

A reaction mechanism for the electrochemical reduction of CO_2 to CO was proposed based on in situ FTIR spectroscopy (Fig. 8c). This mechanism was applied to theoretical calculations of the catalytic reaction process. First-principles density functional theory (DFT) calculations indicate that on the Ni-DMC-1 catalyst, the Gibbs free energy change (ΔG) for the rate-determining step of $\ast\text{COOH}$ formation is 1.15 eV (Fig. 8b), requiring the overcoming of a high energy barrier, which is consistent with the potential dependence of the characteristic $\ast\text{COOH}$ peak observed by FTIR. In contrast, the ΔG for CO desorption is only 0.18 eV, allowing for rapid release of active sites, preventing catalyst poisoning, and suppressing the hydro-

gen evolution side reaction, thereby explaining the high activity and selectivity of Ni-DMC-1.

3.3 Zn- CO_2 battery

In order to realize the dual-functional application of Ni-DMC-1 material in carbon dioxide conversion and energy storage, this study designed a homemade Zn- CO_2 battery (ZCB) comprising a zinc foil anode and a Ni-DMC-1 cathode. The battery employs a bipolar membrane to separate the cathode compartment ($0.5 \text{ mol L}^{-1} \text{ KHCO}_3$) and the anode compartment (a mixture of $2 \text{ mol L}^{-1} \text{ KOH}$ and 0.02 mol L^{-1} zinc acetate) as the electrolyte (Fig. 9a). During discharge, the zinc anode dissolves to form Zn^{2+} and release electrons, while the cathode undergoes CO_2 reduction^[46]. Conversely, during charging, Zn^{2+} is reduced back to metallic zinc at the anode, and the cathode undergoes oxygen evolution reaction (OER)^[47–49]. Polarization curves were acquired via LSV measurements with a scanning speed of 2 mV s^{-1} (Fig. 9b). Based on performance testing, the Ni-DMC-1-based ZCB achieves a peak power density of 1.25 mW cm^{-2} (Fig. 9b). Simultaneously, the cathode

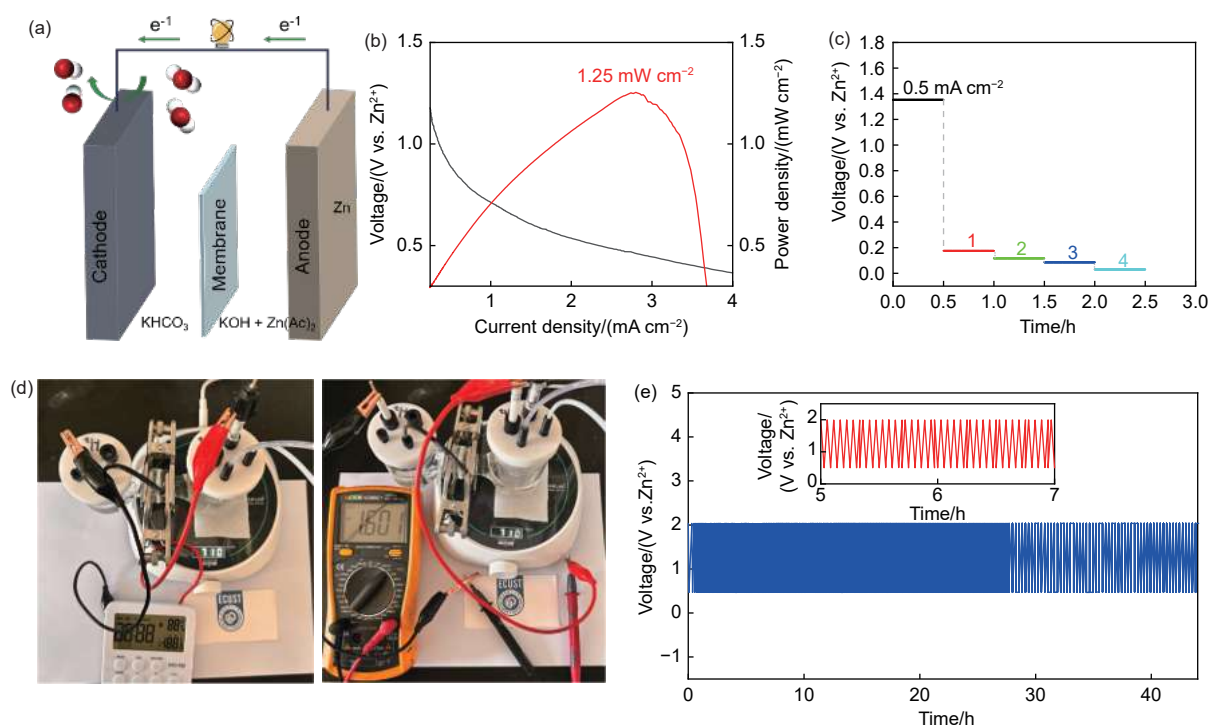


Fig. 9 (a) Schematic configuration of ZCB with Ni-DMC-1 cathode. (b) Discharge polarization plot and power density of ZCB. (c) Discharge stability curves at different current densities of ZCB with Ni-DMC-1 cathode. (d) Photograph of an indoor time display unit ($\sim 1.6 \text{ V}$) powered by Ni-DMC-1. (e) Cycling charge-discharge curves at a current density of 0.5 mA cm^{-2}

material Ni-DMC-1 exhibits stable voltage plateaus during discharge at different current densities (Fig. 9c). Through constant-current charge-discharge testing (Fig. 9e), a 45-hour constant-current charge-discharge cycle test was conducted at a current density of 0.5 mA cm^{-2} , with a charge potential of 2 V and a discharge potential of 0.5 V. In practical applications, the Ni-DMC-1-based ZCB battery can power a small indoor time display unit (Fig. 9d), demonstrating its potential for energy conversion applications.

4 Conclusions

We successfully synthesized a hollow, lamellar-stacked Ni-cluster catalyst (Ni-DMC-1) by introducing a secondary ligand during the aqueous synthesis of ZIF-8 to regulate the morphology of the carbon framework. Ni-DMC-1 achieves a maximum FE_{CO} of 95.7% at a current density of 19.9 mA cm^{-2} in an H-type electrolyzer, outperforming the unmodified carbon substrate catalyst. Moreover, Ni-DMC-1 exhibits excellent catalytic stability, maintaining a stable CO selectivity over 35 h of continuous operation. In a flow-type electrolyzer, Ni-DMC-1 delivers FE_{CO} of 99% across a broad current density range from 120 to 320 mA cm^{-2} , demonstrating its robust catalytic performance under industrially relevant current densities. The ligand-controlled synthesis highlights the critical role of carbon substrate morphology in catalytic performance, offering guidance for designing carbon-supported metal catalysts. Furthermore, when the Ni-DMC-1-based catalyst was engineered into a practical ZCB cell, it exhibits a maximum power density of 1.25 mW cm^{-2} during discharge and can undergo 45 h of cyclic charge-discharge at a current density of 0.5 mA cm^{-2} . A battery connected as a power source can drive a small indoor clock display, demonstrating its practical application value in real-world applications. Simultaneously, the developed methodology is versatile and can be extended to synthesize catalysts with different metal sites (e.g., Ni, Fe) for CO_2 reduction. This work provides both a design strategy for efficient catalysts and a promising platform for CO_2 conversion and utilization.

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