Efficient electroreduction of CO into acetate by a metal-azolate framework with dicopper active sites

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Supplementary Index

Experimental details.

Figure S1. PXRD patterns of CuBpz.

Figure 2. Thermogravimetric analysis of CuBpz.

Figure S3. CV curve of CuBpz in non-aqueous solution in Ar atmosphere.

Figure S4. C_{dl} calculation of CuBpz.

Figure S5. GC profiles of gas products for eCORR in liquid-phase flow cell and standard gas.

Figure S6. ¹H NMR spectra of liquid products for eCORR in liquid-phase flow cell and standard samples.

Figure S7. Duration experiment of CuBpz in electrolysis.

Figure S8. TEM images of CuBpz.

Figure S9. XPS spectra of CuBpz.

Figure S10. ¹H NMR spectra of the non-aqueous electrolyte after electrolysis and stripping voltammogram.

Table S1. Acetate selectivity of various catalysts for eCORR reported in literature.

References

Experimental Details

Materials and General Methods. All reagents were commercially available and used without further purification. The ligand 4,4'-Bispyrazole (H₂Bpz) was synthesized according to literature method.¹ Thermogravimetry analysis was performed using a TGA55 system. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu $K\alpha$). Scanning electron microscopy (SEM) images were recorded by a SU8010 system. Transmission electron microscopy (TEM) images were recorded by a JEM-ARM200P system. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer. Nuclear magnetic resonance (NMR) measurement was performed on a Bruker advance III 400 MHz NMR spectrometer. Operando ATR-FTIR tests were performed on a Thermo Fisher Nicolet iS5 spectrometer.

Synthesis of CuBpz was carried out according to a previous report.² A mixture of H_2Bpz (26.8 mg, 0.2 mmol) and 30 mL of acetonitrile was firstly heated at 45 °C. Copper acetate (36.3 mg, 0.2 mmol) was subsequently added into the dispersion. The solution was subsequently stirred at room temperature for one day. The brownish powder was collected by filtration and washed by methanol, and dried at 70 °C under vacuum. Yield: 35.5 mg, 75.1% based on H_2Bpz .

Electrochemical measurements were carried out in a three-electrode flow cell, in which the Pt foil served as counter electrode and Ag/AgCl electrode served as reference electrode. Briefly, 5 mg sample was dispersed in 0.9 mL ethanol and 0.1 mL Nafion solution, following by sonication for half an hour at 25 °C. Then 50 μ L mixture was dropped onto the gas diffusion electrode (GDE) and dried in vacuum at 70 °C. The CO flow rate (20 sccm) was controlled through a mass flow controller. Linear sweep voltammetry (LSV) curves were obtained with a scan rate of 10 mV s⁻¹ on a CHI660E electrochemical workstation.

CO electroreduction reaction measurements were carried out in a three-electrode flow cell. Two chambers in the reactor were separated by a Fumasep FAB-PK-130 anion membrane. Pure CO gas was continuously delivered into the flow cell, and the tail gas was delivered into an 8890B gas chromatography system to achieve the online detection. The Faradaic efficiency of a certain gas product was calculated by the equation:

$$FE = \frac{PV}{T} \times \frac{\nu NF}{I}$$

in which P, V and T represent the pressure (1 atm), gas flow rate (30 mL min⁻¹) and room

temperature, and v (vol %), N, F, and I represent the volume concentration of gas product, number of the electron transfer in electrocatalysis, Faradaic constant, and current, respectively.

Liquid products of eCORR in catholyte were quantitatively detected using ¹H nuclear magnetic resonance spectroscopy (¹H NMR). 100 μ L of D₂O was employed as the deuterated solution, and 100 μ L of 6 mM non-deuterated dimethyl sulfoxide (DMSO) aqueous solution was used as the internal standard to qualify the concentration of liquid products. Both of the liquids were added into 500 μ L of catholyte to prepare the ¹H NMR sample. Then the sample was analyzed using a Bruker AVIII 400 MHz NMR spectrometer.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements were carried out on a Nicolet 6700 spectrometer. The data were collected for the same sample at -1.1 V vs. RHE after purging with high purity carbon dioxide gas for 20 min, and 8 curves from 0 s to 1800 s were recorded.



Figure S1. Powder X-ray diffraction (PXRD) patterns of CuBpz after different treatments.



Figure S2. Thermogravimetric analysis (TGA) of CuBpz.



Figure S3. CV curve of CuBpz in acetonitrile solution in Ar atmosphere.



Figure S4. (a and c) Cyclic voltammetry (CV) curves and (b and d) capacitive behaviors of CuBpz and bare electrode at variousscanrate $(10 \sim 50 \text{ mV s}^{-1})$, respectively.



Figure S5. GC profiles of (a) gas products at -1.1 V *vs*. RHE and standard mixed gas at different concentrations: (b) 100, (c) 500, and (d) 1000 ppm.



Figure S6. 1 H NMR spectra of standard samples of (a) 10, (b) 50 (c) 100, (d) 500, and (e) 1000, and the liquid products atthepotentialsof(f)-1.1Vvs.RHE.



Figure S7. Long-term durability test of CuBPz at the potential of -1.1 V vs. RHE.



Figure S8. TEM images of CuBpz (a, c, and e) before and (b, d and f) after electrolysis.



Figure S9. (a) XPS and (b) auger spectra of CuBpz before and after electrolysis. (c) and (d) are the survey spectra of CuBpz before and after electrolysis, respectively. The F1s peak in (d) is generated from the mixing of Teflon from electrolyzer and the K2p3 one is attributed to KOH electrolyte.



Figure S10. (a) ¹H NMR spectra of the non-aqueous electrolyte after electrolysis and standard sample. The existence of TBABF₄ result in the difficulty of lock field, and thus the broadening of resonance peaks of acetate and ethanol. (b) Stripping voltammogram of **CuBpz**.

Catalyst	Electrolyte	Potential (V vs. RHE)	FE of acetate (%)	Partial current density for acetate (mA cm ⁻²)	Ref.
Cu-Pd alloy	1 M KOH solution	-1	70	425	3
			65	130	4
Cu nanosheets	2 M KOH solution	-0.6	48	131	5
Cu nanocube		-2.24	43	86	6
Cu(I)-imidazole coordination polymer	3 M KOH solution	-0.59	61	244	7
Cu@8%PMMA- MS	1 M KOH solution	-0.53	~15	~6	8
CuBpz	1 M KOH solution	-1.1	51.3	95.6	This work

Table S1. Acetate selectivities of various reported electrocatalysts for eCORR.

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