

Supporting Information

Cu and Zn promoted Al-fumarate metal organic frameworks for electrocatalytic CO₂ reduction

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S1 Experimental

CO₂ electroreduction product analysis:

Gaseous products: An on-line gas chromatograph (SRI instruments, MG#5 GC, Ar carrier) was employed to quantify C₂H₄, H₂, CO and CH₄ production. Quantification of H₂ was performed by a thermal conductivity detector with a HaySepD precolumn attached to a 3 m molecular sieve column used to separate H₂ from the other gases. Carbon-containing products were analyzed using a flame-ionization detector with CO and CH₄ separated using a 3 m molecular sieve column, and C₂H₄ and C₂H₆ separated using a 5 m HaySepD column. The GC was calibrated with a gas mixture containing H₂, CO, CH₄, C₂H₄, C₂H₆ and CO₂ as the diluent. Calibration curves for each molecule were obtained by further diluting the gas mixture with CO₂ (both provided by mass flow controllers) before injecting to the GC.

Liquid products: Liquid product yields were determined by ionic chromatography (Metrohm™ EcoIC) and proton nuclear magnetic resonance spectroscopy (¹H-NMR; Bruker Avance III 300 MHz, 300 K). 400 μL of reacted catholyte, 100 μL D₂O (Eurisotop, 99.9%) as a locking solvent and 100 μL of 5 mM aqueous terephthalic acid solution (terephthalic acid, Sigma-Aldrich, 98%) as a reference were mixed and water peaks for each spectrum eliminated by a Pre-SAT180 water suppression method.

Faradaic efficiencies for each product was calculated using the following equation:

$$FE_x(\%) = \frac{n_x \times n_{e-x} \times F}{Q} \times 100$$

where n_x is the mols of product x , n_{e-x} is the number of electrons required to generate product x from CO, CO₂ or H₂O, F is the Faraday constant (96500 C.mol⁻¹), and Q the charge passed to generate n_x .

Water adsorption analysis: The samples were placed into a small climate chamber with controlled temperature and relative humidity (TA Instruments, Universal V4.5A). The water adsorption of samples was evaluated at 30 °C and ~90% relative humidity.

S2 Results

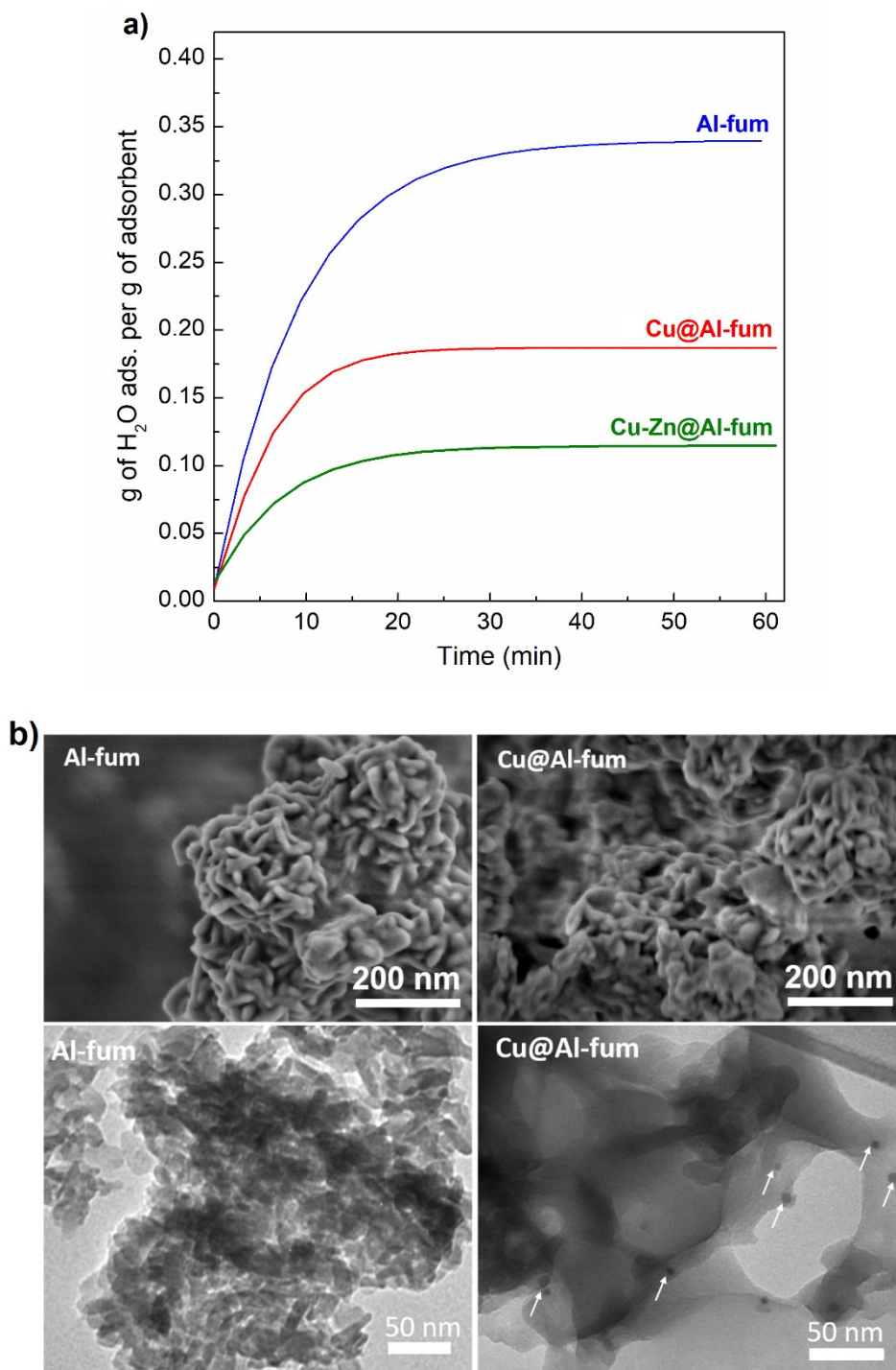


Figure S1. (a) Water adsorption on Al-fum, Cu@Al-fum and Cu-Zn@Al-fum and (b) SEM (top) and TEM (below) images of Al-fum and Cu@Al-fum MOFs.

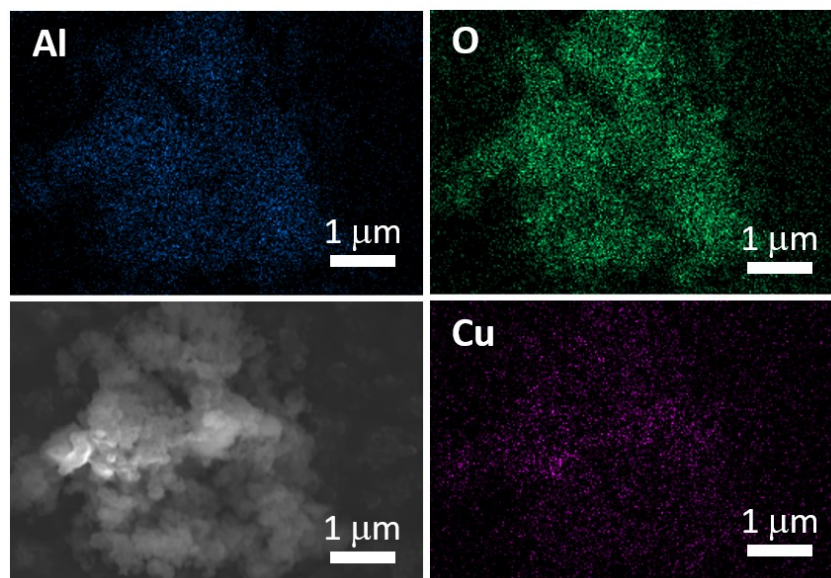


Figure S2. SEM image and corresponding EDX elemental maps of Al, O and Cu for Cu@Al-fum.

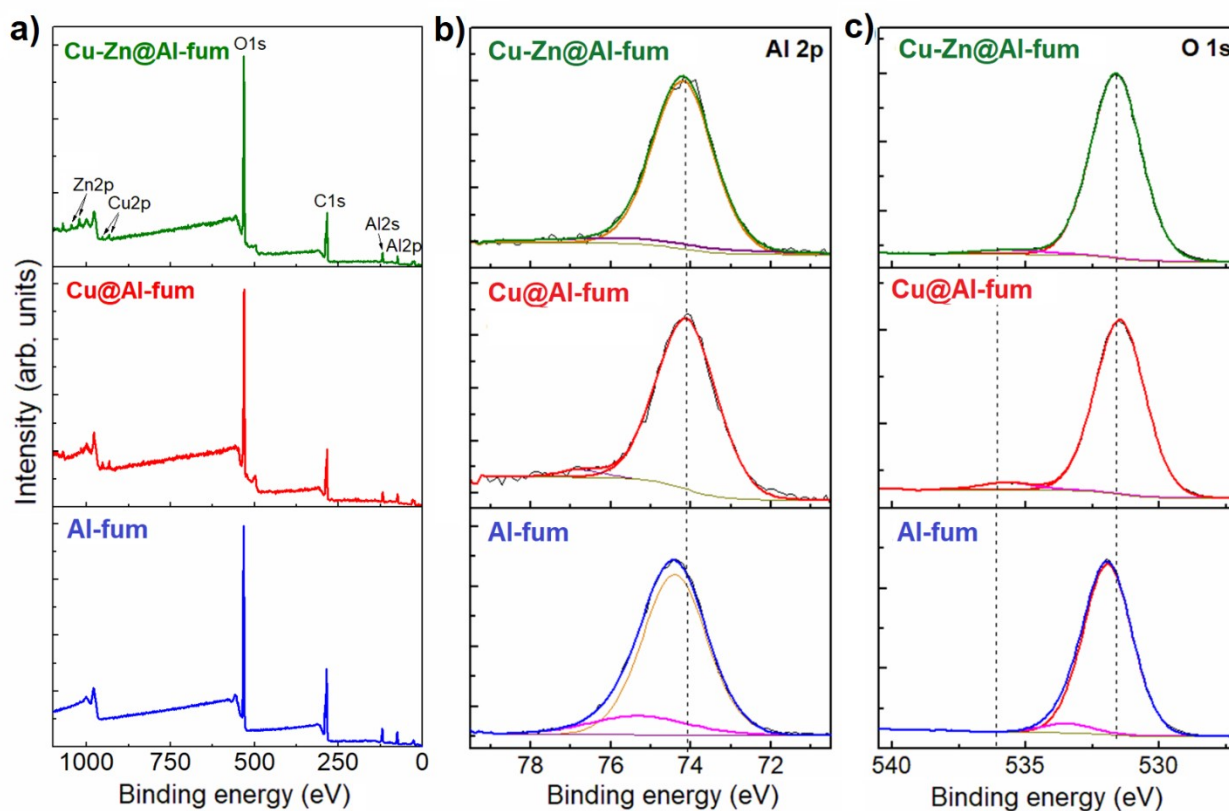


Figure S3. (a) Survey, (b) Al 2p and (c) O 1s XPS spectra of the pristine Al-fum, Cu@Al-fum and Cu-Zn@Al-fum MOFs.

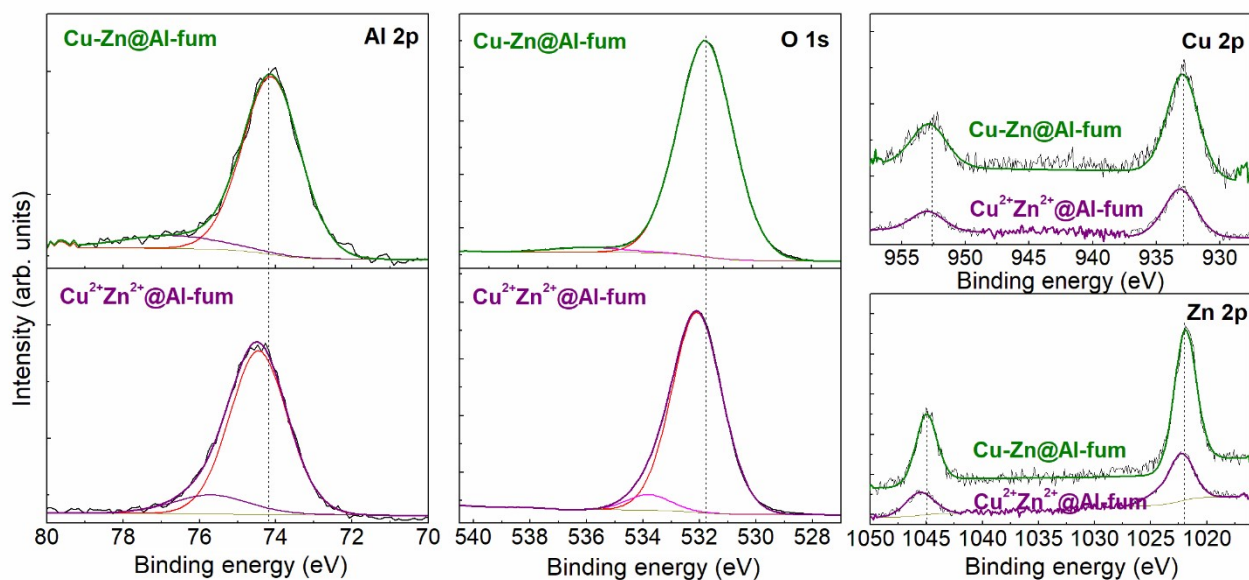


Figure S4. Al 2p, O 1s, Cu 2p and Zn 2p XP spectra of Cu-Zn@Al-fum before (designated Cu²⁺Zn²⁺@Al-fum) and after treatment with NaBH₄.

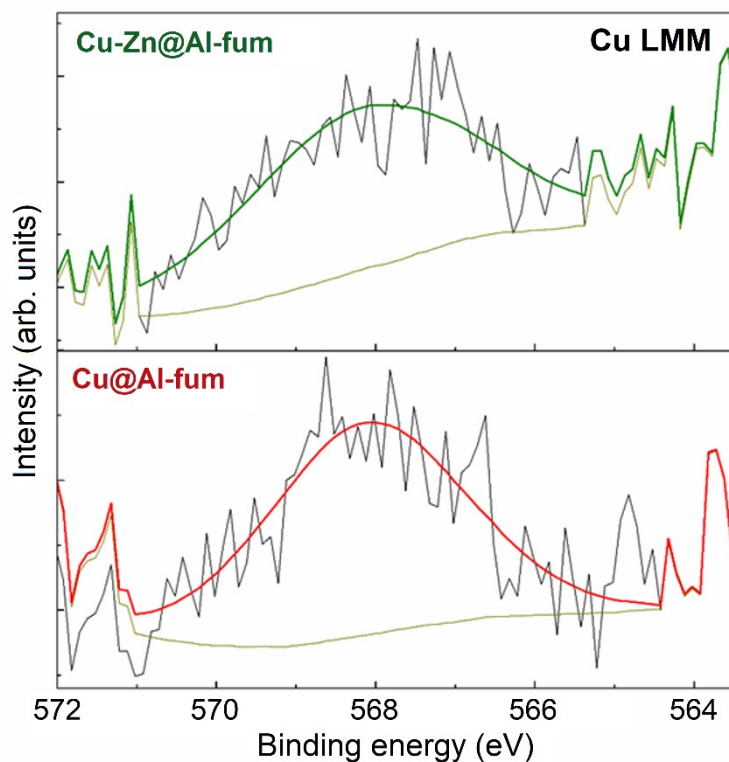


Figure S5. Cu LMM Auger spectra of Cu and Cu-Zn doped Al-fum.

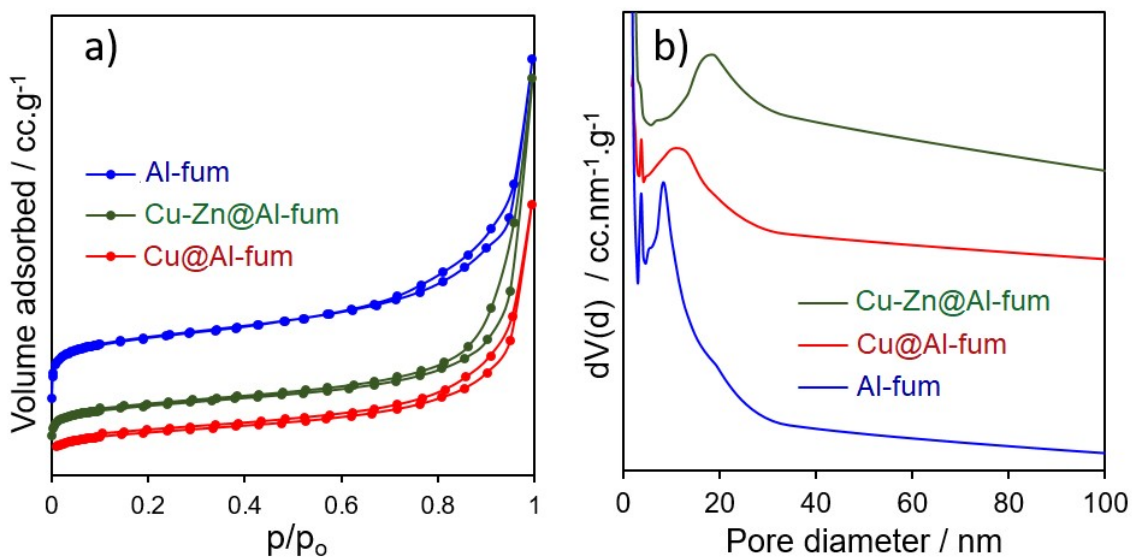


Figure S6. (a) N₂ adsorption-desorption isotherms, and (b) BJH pore size distributions of Al-fum, Cu@Al-fum and Cu-Zn@Al-fum MOFs.

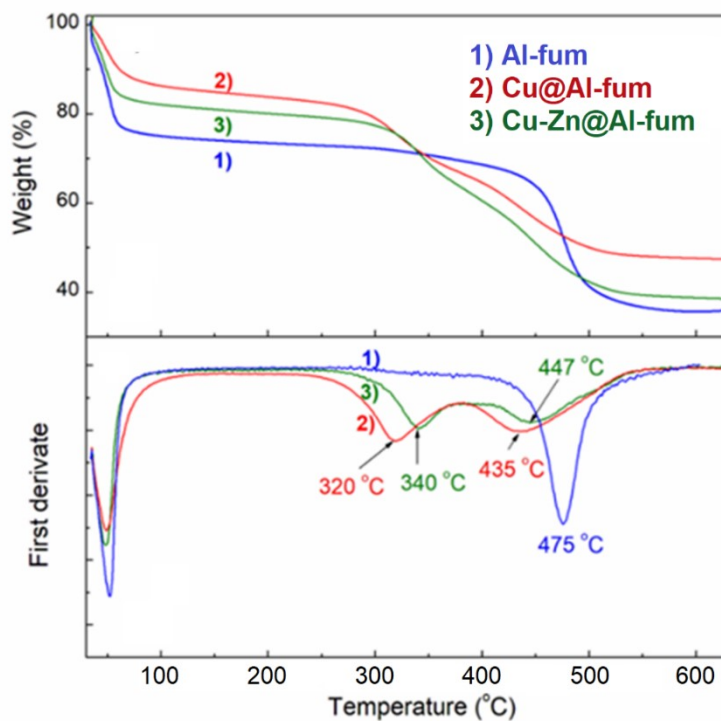


Figure S7. Thermogravimetric analysis profiles and corresponding first derivatives of Al-fum, Cu@Al-fum and Cu-Zn@Al-fum.

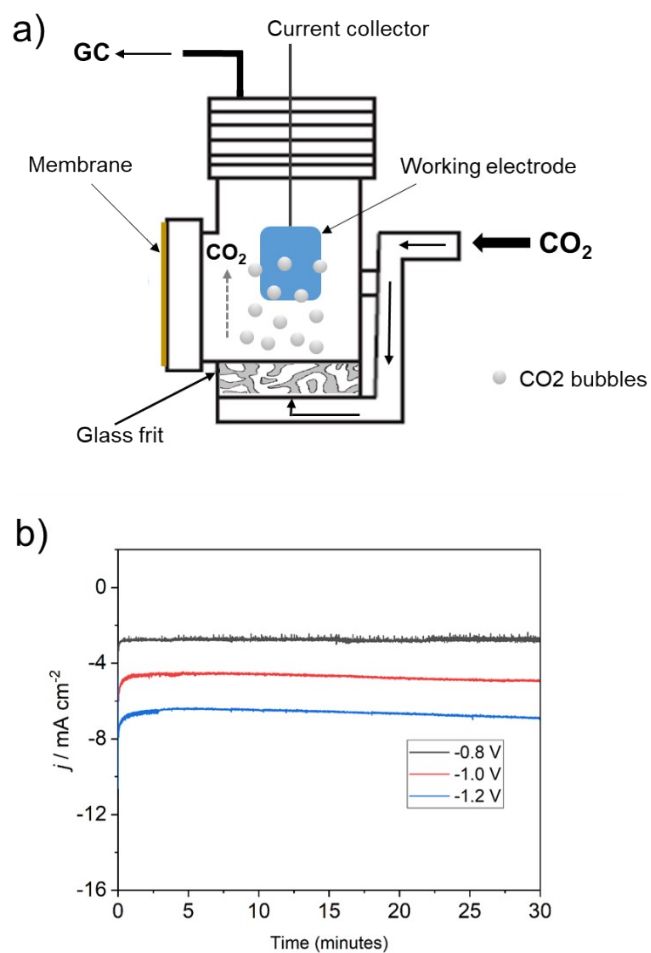


Figure S8. (a) Schematic of cathodic electrochemical cell for CO₂ reduction, (b) time-dependent current density of Cu-Zn@Al-fum/gas diffusion electrode at different cathodic potentials. Measurements made in 0.1 M KHCO₃, saturated with CO₂ bubbled at 7.5 ml/min.

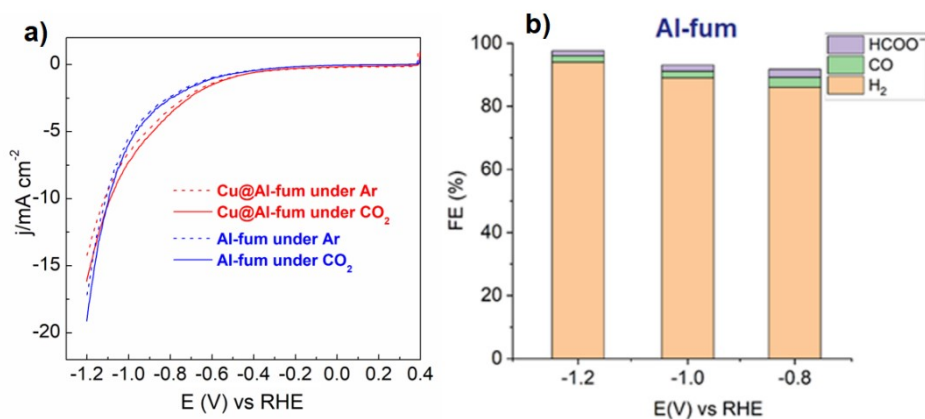


Figure S9. (a) Linear sweep voltammetry curves of Al-fum MOF/GDE and Cu@Al-fum in 0.1 M KHCO₃ aqueous solution saturated with CO₂ or Ar, and (b) Faradaic efficiencies for CO₂ reduction products in 0.1 M KHCO₃-saturated CO₂ at different cathodic potentials of Al-fum MOF/GDE. CO₂ was continuously bubbled at 7.5 mL.min⁻¹ during electrolysis.

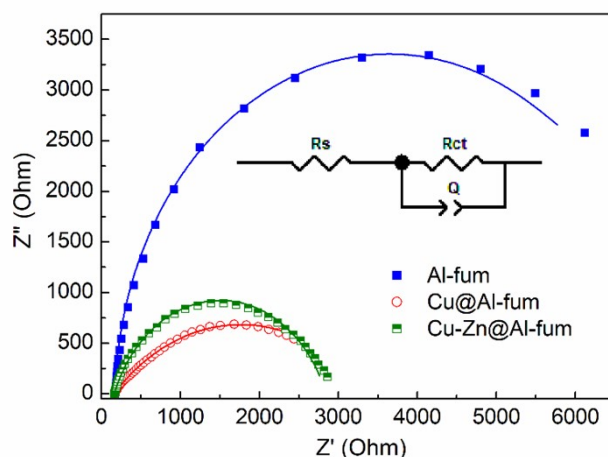


Figure S10. Nyquist plots, with fitting curves (solid lines), of Al-fum MOF, Cu@Al-fum, and Cu-Zn@Al-fum samples in CO₂-saturated 0.1 M KHCO₃ with a frequency $10^5 \div 10^{-1}$ Hz at 10 mV of amplitude. The equivalent circuit model is shown on the insert. R_s stands for the contact resistance, R_{ct} for the charge transfer resistance.

Table S1. Quantification of products formed after 30 min CO₂ electroreduction over Al-fum derived electrocatalysts at -1.2V vs RHE.

| Sample | H₂ (μmol) | CO (μmol) | HCOOH (μmol) | CH₄ (μmol) | C₂H₄ (μmol) | C₂H₅OH (μmol)^a | Selectivity to C products (%) |
|---------------------|--|-------------------------------------|--|---|---|---|--|
| Al-fum | 112.4 | 1.23 | 1.08 | - | - | - | 2 |
| Cu@Al-fum | 58.5 | 6.64 | 6.9 | 0.49 | 0.78 | - | 20 |
| Cu-Zn@Al-fum | 23.21 | 14.91 | 4.45 | 2.22 | 0.77 | 0.68 | 50 |

^aFor ethanol analysis, electrolysis sample was collected after 60 min to enable detection by NMR.

Table S2. Fitted contact resistance (R_s) and charge transfer resistance (R_{ct}) values from Nyquist plots.

| Electrode | R_s (Ohm) | R_{ct} (Ohm) | Q (Farad) | n |
|------------------|----------------------------|-----------------------------|------------------|----------|
| Al-fum | 175.38 | 6943.4 | 0.00010948 | 0.9837 |
| Cu@Al-fum | 160.13 | 3208.3 | 0.0002241 | 0.5134 |
| Cu-Zn@Al-fum | 163.42 | 2681.2 | 0.00003986 | 0.76914 |