

Supporting Information

Single Catalyst Electrocatalytic Reduction of CO₂ in Water to H₂:CO Syngas Mixtures with Water Oxidation to O₂

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I. Experimental

Materials and Methods

All chemicals were purchased from commercial sources if not mentioned otherwise. THF was of HPLC grade and further purified by a Pure-Solv Solvent Purification System (Innovative Technology). Deionized water was further purified by using a Milli-Q Synthesis A10 Water Purification system. Argon was purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves. CO₂ (National Welders, research grade) was of 99.999% purity with less than 3ppm H₂O and used as received. D₂O (Cambridge Isotope) was used as received. Tetrabutylammonium hexafluorophosphate ("Bu₄NPF₆, Fluka, electrochemical grade) was dried at 60 °C under vacuum for 12 h and stored in the glovebox. ELAT-H carbon fiber cloth (10×10 cm) was purchased from FuelCellsEtc (College Station, TX). All other reagents are commercially available and were used without further purification. NMR spectra were recorded on

Bruker AVANCE-400 NMR spectrometer. Complexes **1**(PF₆)₂ and **2**(PF₆)₂ were synthesized according to previous literature reports.^{1,2}

Electrochemistry and Product Analyses

Electrochemical experiments were performed using a custom-made CHI 6012D potentiostats (CH Instruments, Inc., TX). A three-electrode setup for aqueous media consisted of a glassy carbon working electrode (BASi, 7.1 mm²), a coiled Pt wire counter electrode, and a SCE reference electrode (0.244 V vs NHE) in an airtight, glass frit-separated two-compartment cell. In THF, the reference electrode was Ag/AgNO₃ reference electrode (BASi, 10 mM AgNO₃, 0.1 M ⁿBu₄NPF₆ in acetonitrile), and ferrocene was added at the end of the experiment and the potential was converted relative to NHE following a literature protocol.³ Prior to each measurement, the glassy carbon electrode was polished with a 0.05- μ m alumina slurry for 1 min, then sonicated and thoroughly rinsed with Milli-Q water and acetone, and finally dried in an Ar stream. In cyclic voltammetry experiments, the working and counter electrodes were separated from the reference electrode. In controlled potential electrolyses with the three-electrode setup, the reference and working electrodes were separated from the Pt mesh counter electrode with AMI-7001 anion exchange membrane (Membrane International, Inc., Ringwood, NJ). In the two-electrode setup, the cathode compartment was separated from the anode compartment with the same anion exchange membrane, the cathode was connected with the working lead of the potentiostat and the anode was connected with both reference and ancillary leads. Each compartment was added 4 mL electrolyte solution.

Controlled potential electrolyses were performed in 4 mL, 0.5 M NaHCO₃ aqueous solutions in an airtight electrochemical cell under vigorous stirring. The solution was degassed by purging with Ar for 15 min and then saturated with 1 atm of CO₂ for 15 min before sealing the cell. Solution resistance was measured and compensated at 85% level in the bulk electrolyses. At the end of electrolysis, gaseous samples (0.6 mL) were drawn from the headspace by a gas-tight syringe (Vici) and injected into the GC (Varian 450-GC). Calibration curves for H₂ and CO were obtained separately. The liquid phase was doped with a known amount of DMF as internal standard and diluted 1:1 with D₂O for ¹H-NMR analysis.

II. Additional Electrochemistry and GC Data

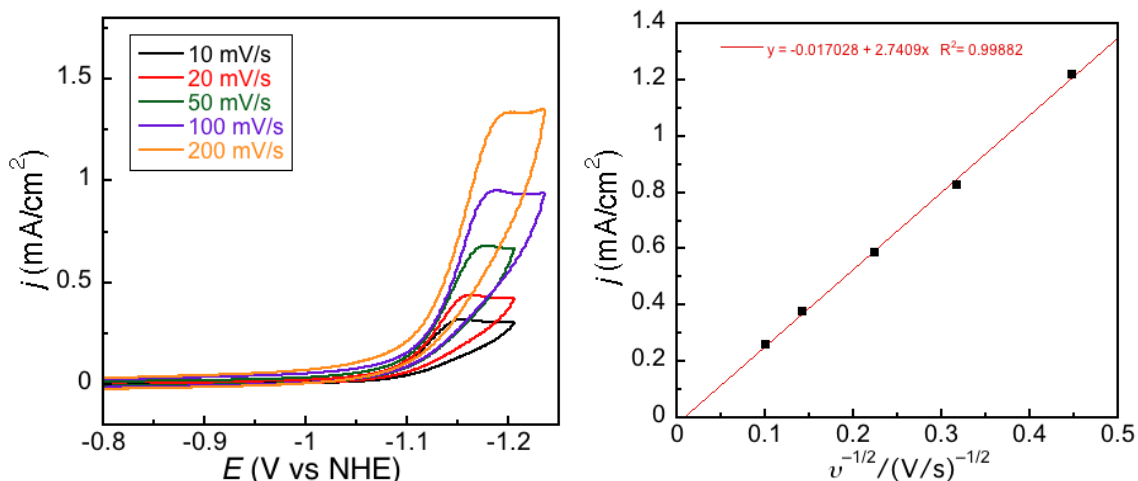


Figure S1. Left: cyclic voltammograms of **1** at various scan rates in water under CO₂. Right: plot of peak current density $j_{p,c}$ under CO₂ vs. the inversed square root of the scan rate ($v^{-1/2}$ in (V/s)^{-1/2}). Conditions: 0.5 M NaHCO₃, glassy carbon electrode, area 0.072 cm², 1 atm CO₂, room temperature.

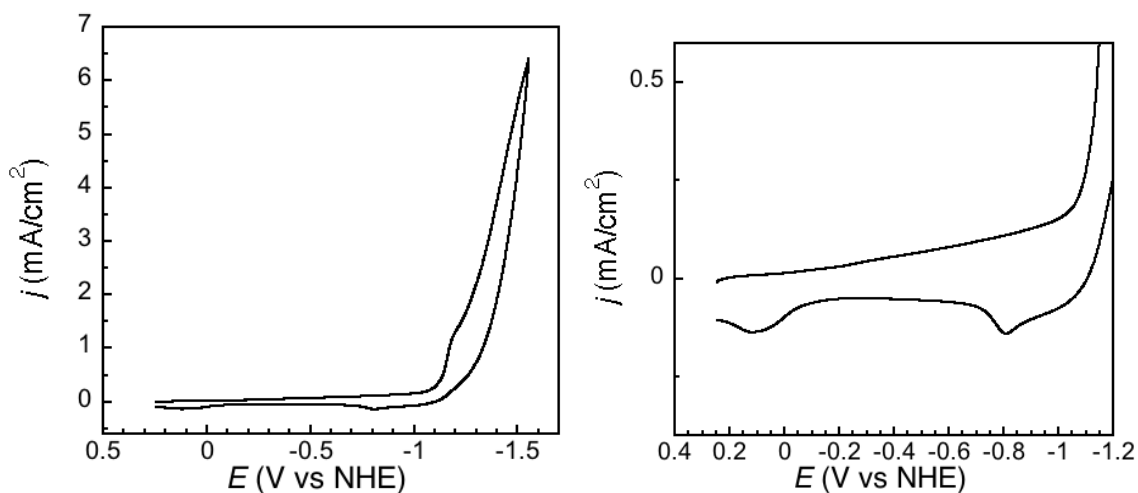


Figure S2. Cyclic voltammograms of 1 mM **1** in water under Ar. Left: Overview. Right: Zoom-in view. Conditions: 0.1 M NaHCO₃, glassy carbon electrode, area 0.072 cm², 100 mV/s scan rate, room temperature.

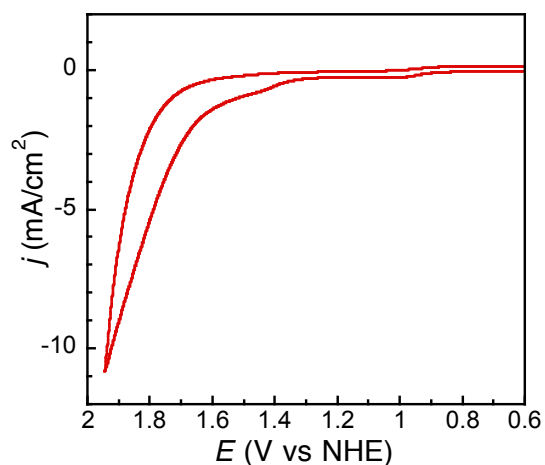


Figure S3. Cyclic voltammograms of 1 mM **1** in water under CO₂. Conditions: 0.5 M NaHCO₃, glassy carbon electrode, area 0.072 cm², 100 mV/s scan rate, room temperature.

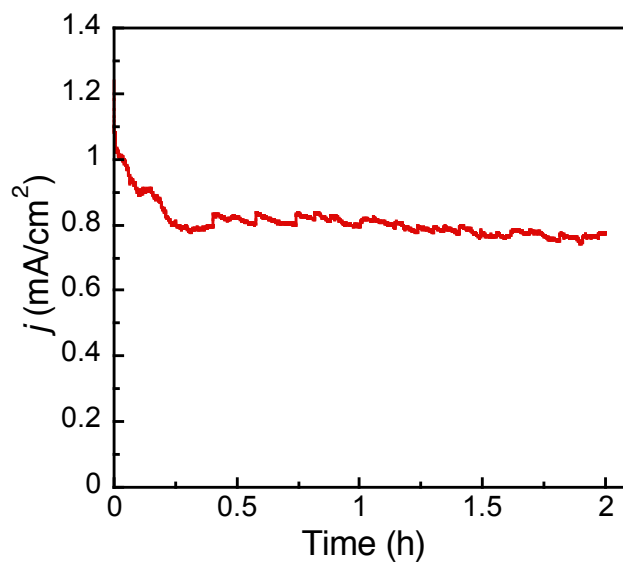


Figure S4. Bulk electrolysis over time using the three-electrode setup with applied potential of -1.2V vs NHE at the cathode. Conditions: 1 mM **1**, 0.5 M NaHCO₃, carbon cloth electrode, area 1.0 cm², 1 atm CO₂, room temperature.

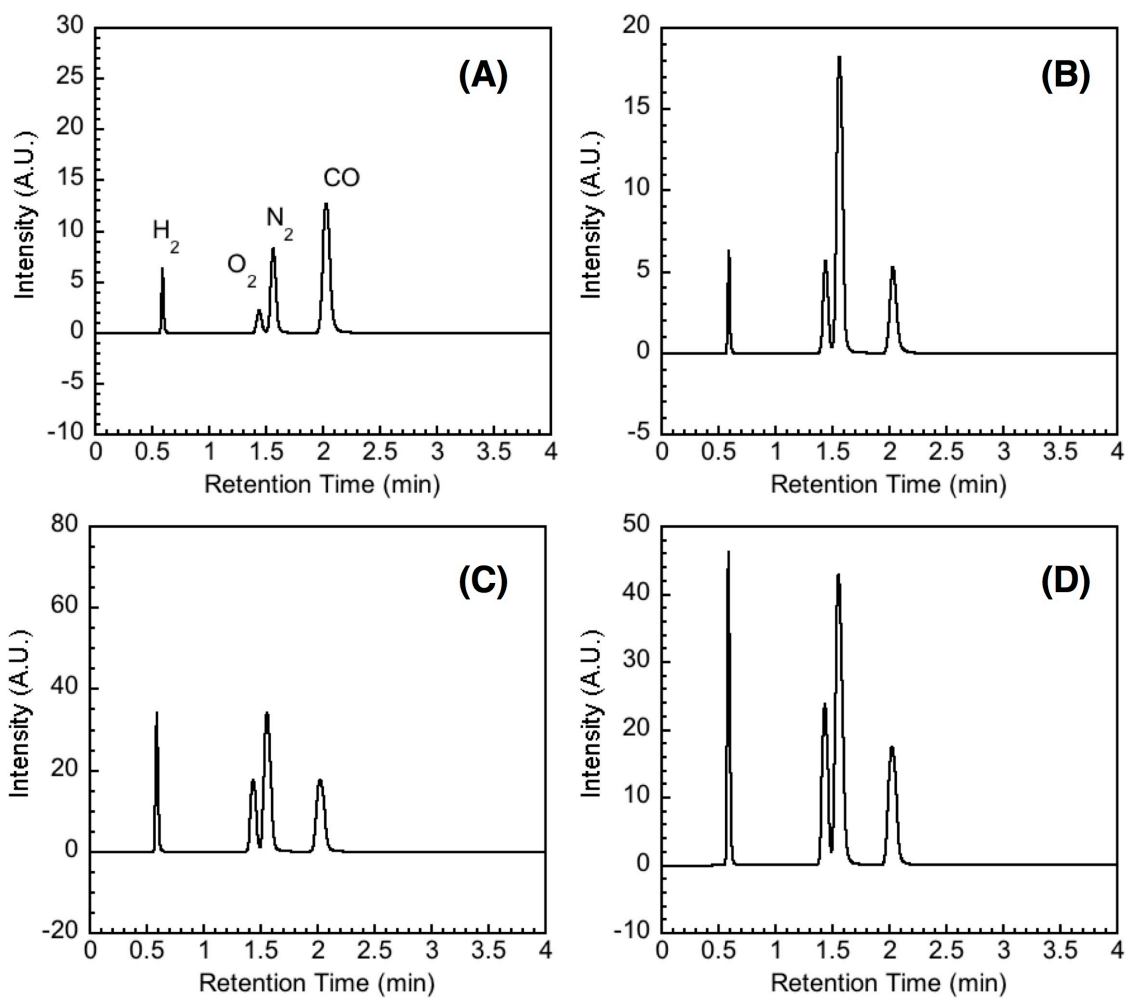


Figure S5. GC analysis of the cathode headspace after bulk electrolysis of **1** using three-electrode setup. Applied potential vs NHE: (A) -1.2 V; (B) -1.3 V; (C) -1.4 V; (D) -1.5 V. Conditions: 1 mM **1**, 0.5 M $NaHCO_3$, carbon cloth electrode, area 1.0 cm^2 , 1 atm CO_2 , room temperature.

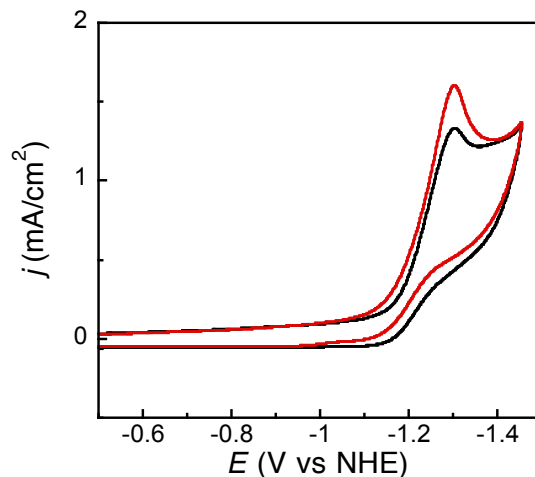


Figure S6. Cyclic voltammograms of 1 mM **2** in water under Ar (black) and 1 atm CO₂ (red). Conditions: 0.5 M NaHCO₃, glassy carbon electrode, area 0.072 cm², 100 mV/s scan rate, room temperature.

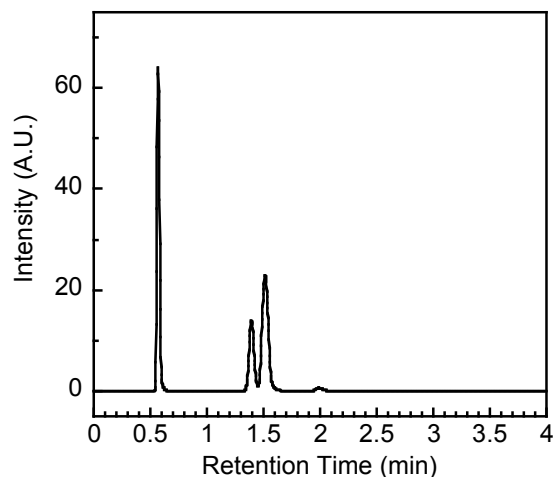


Figure S7. GC analysis of the cathode headspace after bulk electrolysis of **2** using three-electrode setup. Conditions: 1 mM **2**, 0.5 M NaHCO₃, carbon cloth electrode, area 1.0 cm², applied potential -1.2 V, 1 atm CO₂, room temperature.

III. Energy Efficiency Calculation

The calculation of energy efficiency ε follows a modified approach in ref. 4 based on heating values.





$$\varepsilon = \frac{\eta_{\text{CO}}\Delta H_{\text{CO}}^0 + \eta_{\text{H}_2}\Delta H_{\text{H}_2}^0}{V} \quad (3)$$

in which η_{CO} and η_{H_2} are the current efficiencies for CO and H₂, respectively, V the applied cell voltage and ΔH^0 the enthalpy change per 1e⁻ for the separate reactions.

IV. References

1. J. J. Concepcion, J. W. Jurss, M. R. Norris, Z. F. Chen, J. L. Templeton and T. J. Meyer, *Inorg. Chem.*, 2010, **49**, 1277-1279.
2. J. J. Concepcion, J. W. Jurss, J. L. Templeton and T. J. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 16462-16463.
3. V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97-102.
4. C. Delacourt, P. L. Ridgway, J. B. Kerr and J. Newman, *J. Electrochem. Soc.*, 2008, **155**, B42-B49.