Supporting Information

Enhanced Electroreduction of CO₂ to Ethanol via Enriched Intermediates under High CO₂ Pressure

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Experimental Section

Electrochemical testing under ambient and high pressure: CO₂ electrolysis under ambient and high pressure was operated in a custommade high-pressure electrolytic cell with two-compartment PEEK lining separated by a Nafion 117 proton exchange membrane. Pressure-resistant quartz windows for observation of electrochemical system are equipped in the high-pressure electrolytic cell, and PEEK lining with a threeelectrode system could be connected to an electrochemical workstation instrument (CHI 660E). Pt mesh and Ag/AgCl (saturated KCl) were used as the counter electrode and the reference electrode, respectively. 20 mL of 0.1 M KHCO₃ solution was used as the electrolyte in each compartment. The electrolyte in the cathode was bubbled with CO_2 at the rate of 10 mL min⁻¹ for 30 min to form a CO₂-saturated solution before CO₂ reduction test under atmospheric pressure. For the high-pressure test, the inlet of the high-pressure electrolytic cell was linked with a pump, which connects with CO_2 gas cylinders (Figure S2). The electrolyte both in the cathode and anode were bubbled with CO_2 for at least 30 min to remove the dissolved air before pressurization at 35 °C. Subsequently, CO₂ was charged into the high-pressure electrolytic cell equipped with a digital pressure gauge and the flow rate was controlled by a microregulation valve. In all measurements, Ag/AgCl (saturated KCl solution) was used as the reference electrode, the Ag/AgCl electrode is assumed not affected by the pressure unless otherwise noted, and the potential (V vs. Ag/AgCl) was converted to V vs. RHE using

$$E$$
 (vs. RHE) = E (vs. Ag/AgCl) + 0.210 V + 0.0591 × pH

The correlation between current and current density was exhibited below.

Current	density	(mA		cm ⁻²)	=
	Current density (mA)				
			0		

Area of catalysts on the carbon paper (cm^2)

Product analysis: After each electrolysis at controlled potentials, the gaseous and liquid products were detected by gas chromatography (GC) and ¹H NMR, respectively. In particular, liquid products were collected from cathodic, anodic and high-pressure/supercritical CO₂ zones due to the high ethanol solubility under high CO₂ pressure. The Faradaic efficiency (FE) values of different CO₂RR products under both ambient pressure and high pressure were calculated as

$$FE = \frac{n \times F \times amount of the product}{Q} \times 100\%$$

Where n is the number of moles of electrons to participate in the faradaic reaction, F is the Faraday constant (96485 C/ mol), and Q is the amount of charge passed through the working electrode.

Tafel slopes analysis: The Tafel area is essentially far from the thermodynamic equilibrium region. The polarization of the electrode reflects the process of the electrode obstruction. In the electrochemical reaction process, the current density and polarization overpotential of the

apparent reaction through the interface can be described by the Butler-Vollmer formula. The exchange current density and charge transfer coefficient of the electrode reaction can be solved by fitting the measured polarization curve using Butler-Vollmer (B-V) formula, which are important parameters for evaluating the electrode reactivity.

$$i = i_{fd} - i_{rev} = i_0 \exp\left(\frac{\alpha n F \eta}{RT}\right) - i_0 \exp\left(\frac{-(1-\alpha)n F \eta}{RT}\right)$$
(B-V equation)

According to the B-V equation, only part of the electrical energy can cause the change of electrode potential in the electrochemical reaction process, and the overpotential is the regulator of the electrochemical reaction rate. By controlling the overpotential, the electrochemical reaction rate can be changed by several orders of magnitude. Overpotential (η) and current density (*j*) have the following relationship:

 η = a + b log |*j*| (a, b are the Tafel constants)

Calculation Details: All periodic DFT calculations were performed using the VASP software¹, and the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)² generalization function was chosen for all calculations. The plane-wave basis set used a 450 eV truncation energy with a convergence threshold of 0.02 eV/Å for structural optimization, while the Brillouin zone was sampled by a $4\times4\times1$ -Monkhorst-Pack K-point grid. For the structural model, based on the experimental characterization information, we chose the Cu (111) surface and built a flat plate with four atomic layer thicknesses, extending the Z-axis by about 18 Å vacuum layers to avoid the interaction between the mirror images. Grimme's DFT-D3 dispersion correction was used to describe the van der Waals interactions^{3,4}. For the calculation of the free energy, the implicit model was used to deal with the solvation effect of water. The solvation energy values reported by Nørskov were used⁵, which estimated that the energy of some adsorbed intermediates was stabilized by the surface water layer by about -0.25 eV for all OHcontaining intermediates, and -0.1 eV for intermediate species such as CO (not containing hydroxyl groups).

Calculation on concentrations of carbon species and protons in 0.1 M KHCO₃ under various CO₂ partial pressures.

In aqueous solutions (35 °C), H₂CO₃ experiences a two steps dissociation process:

$$\begin{split} H_2CO_3 \rightleftharpoons HCO_3^{-+} H^+, \\ k_1 &= ([H^+] \times [HCO_3^{-}]) / [H_2CO_3] = 2.8 \times 10^{-4} \text{ M}; \\ HCO_3^{-} \rightleftharpoons CO_3^{2-} + H^+, \\ k_2 &= ([H^+] \times [CO_3^{2-}]) / [HCO_3^{-}] = 1.3 \times 10^{-10} \text{ M}. \end{split}$$

However, the dissolved CO_2 (noted as CO_2 (*aq*)) exists in equilibrium with H_2CO_3 :

$$\operatorname{CO}_2(aq) + \operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{H}_2\operatorname{CO}_3,$$

k = [H₂CO₃] / [CO₂(aq)] \approx 1/600.

So that the first dissociation process of H₂CO₃ could be described with

an apparent dissociation constant involving $CO_2(aq)$:

$$H_2CO_3 \{ \text{or } CO_2 (aq) + H_2O \} \rightleftharpoons HCO_3 + H^+,$$

$$k_a = ([H^+] \times [HCO_3^-]) / ([H_2CO_3] + [CO_2(aq)]) = 4.66 \times 10^{-7} M.$$

Here, the equilibrium concentrations $[CO_2 (aq)]$ under different pressures at 35 °C were calculated according to our previous work⁶ by using the Stryjek and Vera modification of the Peng-Robinson equation of state instead of the Henry's law⁷.

According to charge conservation in electrolyte:

$$[K^+] + [H^+] = [HCO_3^-] + 2 \times [CO_3^{2-}] + [OH^-],$$

together with the self-ionization equation of water:

$$H_2O \rightleftharpoons [H^+] + [OH^-],$$

 $k_w = [H^+] \times [OH^-] = 2.09 \times 10^{-14}, (35 \text{ °C}),$

the bulk concentrations of carbon species and protons in 0.1 M KHCO₃ electrolyte under various CO₂ partial pressure were calculated using MATLAB⁷. Results are shown in Figure S3; Figure S3(a) indicates that $[CO_2 (aq)]$ under different pressures at 35 °C can be well described by the Stryjek and Vera modification of the Peng-Robinson equation of state⁸ and obviously does not follow the Henry's law.

The techno-economic analysis (TEA)

The techno-economic analysis about the electrocatalytic CO_2 conversion to ethanol under high pressure was displayed as below.

From the technology and its impact on society, the process of electrochemical CO₂ reduction to produce ethanol is the green pathway for CO₂ conversion relevant to carbon reduction/utilization. Among CO₂ conversion, the high-pressure strategy is highly amenable to industrial CO₂ waste streams⁹. Furthermore, large amount of CO₂ in liquid state with high pressure such as about 20-30 bar at saturated state is collected from the coal chemical industry¹⁰. The utilization of this high-pressure stream of CO₂ needs low energy supply by liquid pump although relatively high energy is necessary when using compressor for atmospheric pressure CO₂. The high-pressure CO₂ can also be easily recycled for electrolysis just as the way used in industry supercritical CO₂ extraction which is well-known/typical system in green chemistry (high-pressure tanks such as 1000 to 5000 L are widely used in China)

For simplification without considering product separation process (this depends on product distribution), we analyze the energy consumption cost of the CO_2 electrolysis process at high pressure, which mainly includes the electricity fee for CO_2 electrolysis and the cost of pressurization (CO_2 supply). These calculations were conducted by using current density of -5 mA cm⁻², area of catalyst of 1 cm², cell voltage of

2.3 V, FE_{ethanol} of 35.8%, FE_{HCOOH} of 31.4%, FE_{CO} of 1.1%, testing 12 h at 75 bar and 35 °C was implemented (test started after reaching the conditions). Accordingly, the power for electrolysis is 0.005 A × 2.3 V = 0.0115 W (or 1.15×10^{-5} kW), the ethanol produced calculated to be 2.56×10^{-7} kg h⁻¹ from the current and FE_{ethanol}, and the CO₂ consumed is 1.83×10^{-6} kg h⁻¹ from the current and FE_{ethanol}, FE_{HCOOH} and FE_{CO} (only products of ethanol, formic acid and CO converted from CO₂ can be found). The consumed CO₂ should be charged to the electrolytic cell by the CO₂ supply system.

For the CO₂ supply, the energies consumed for high-pressure CO₂ (75 bar, 35 °C) from liquid CO₂ (for example, 30 bar and -5.6 °C, saturated) by using pump (efficiency of 80%) and gaseous CO₂ (for example, 1 or 30 bar and 20 °C) by using compressor (efficiency of 80%) are calculated by using Aspen plus V12 (Figure S19, Table S1). For the process, the heat exchange energy can be neglected since only 35 °C is necessary and the recycled tap water can be used.

From Table S1, when 0.03 USD kWh⁻¹ and 0.1 USD kg⁻¹ (commercial saturated liquid CO₂) are assumed, the cost of ethanol from the high-pressure process is 2.06 USD kg⁻¹ (ethanol) if considering the raw material cost $(1.83/2.56 \times 10 \times 0.1 = 0.715 \text{ USD kg}^{-1})$, the electricity fee for CO₂ electrolysis $(1.15/2.56 \times 100 \times 0.03 = 1.35 \text{ USD kg}^{-1})$ and the cost of pressurization/CO₂ supply $(0.0436 \times 10^{-2} \text{ USD kg}^{-1})$. If industrial CO₂

waste stream (free) is applied, then the cost of ethanol from the highpressure process is determined by the electrolysis energy cost (1.35 USD kg⁻¹).

When using the 1 bar gaseous CO_2 and assuming this gas is free, the cost of ethanol from the high-pressure process is 1.40 USD kg⁻¹ (ethanol) if considering the raw material cost (0 USD kg⁻¹), the electricity fee for CO_2 electrolysis (1.35 USD kg⁻¹) and the cost of CO_2 supply (4.59 × 10⁻² USD kg⁻¹).

From the above simplified analysis, we can draw conclusion that the high-pressure strategy does not obviously depend on the pressurization/CO₂ supply cost but mainly on the electrolysis energy cost (high $FE_{ethanol}$ can highly reduce this cost).



Figure S1. XRD pattern of the HS-Cu electrode.



Figure S2. Schematic description of the high-pressure electrolytic cell systems in detail.



Figure S3. Calculation of active carbon species concentrations (a) $[CO_2(aq)]$ (b) $[CO_2(aq)] + [H_2CO_3]$ and pH in 0.1 M KHCO₃ under different CO₂ pressures at 35 °C.



Figure S4. LSV of HS-Cu in 0.1 M KHCO₃ aqueous solution under different CO₂ pressures.



Figure S5. Faradaic efficiencies of different CO_2RR products on HS-Cu electrode in 0.1 M KHCO₃ aqueous solution under 1 bar CO_2 pressure for 1 h electroreduction at various potentials from -1.2 V vs. Ag/AgCl to -2.1 V vs. Ag/AgCl.



Figure S6. Faradaic efficiencies of different CO_2RR products on HS-Cu electrode in 0.1 M KHCO₃ under 25 bar CO_2 pressure for 1 h electroreduction at various potentials from -1.0 V vs. Ag/AgCl to -1.8 V vs. Ag/AgCl.



Figure S7. Faradaic efficiencies of different CO_2RR products on HS-Cu electrode in 0.1 M KHCO₃ under 50 bar CO_2 pressure for 1 h electroreduction at various potentials from -1.0 V vs. Ag/AgCl to -1.8 V vs. Ag/AgCl.



Figure S8. Faradaic efficiencies of different CO_2RR products on HS-Cu electrode in 0.1 M KHCO₃ under 75 bar CO_2 pressure for 1 h electroreduction at various potentials from -0.8 V vs. Ag/AgCl to -1.6 V vs. Ag/AgCl.



Potential (V vs. Ag/AgCI)

Figure S9. A comparison of the current density on HS-Cu under 1 bar, 25 bar, 50 bar, 75 bar and 100 bar CO_2 pressures.



Figure S10. Faradaic efficiencies for different products on HS-Cu electrode under 1 bar at various potentials for one hour test. a) 0.1 M KHCO₃ aqueous solutions of pH \sim 7.0 as the electrolyte, b) 0.1 M KHCO₃+H₂SO₄ aqueous solutions of pH \sim 5.0 as the electrolyte.



Figure S11. CORR performance under different CO pressures. a) Faradaic efficiencies for different products on HS-Cu electrode under 1 bar at various potentials for one hour test, b) Faradaic efficiencies for different products on HS-Cu electrode under 3 bar at various potentials.



Figure S12. XRD patterns of the HS-Cu electrode after CO₂RR under 1bar and 100 bar CO₂ pressure.



Figure S13. Cu 2p and Cu LMM XPS spectra of the electrode after CO₂RR under 100 bar CO₂ pressure.



Figure S14. SEM images of the electrode after CO_2RR a) under 1 bar CO_2 pressure, b)under 100 bar CO_2 pressure.



Figure S15. Schematic illustration of the custom-made high pressure in-situ Raman cell setup.



Figure S16. In-situ Raman spectra for HS-Cu catalyst at different potentials during CO_2RR a) under 1 bar CO_2 pressure, b) under 25 bar CO_2 pressure, c) under 80 bar CO_2 pressure.



Figure S17. DFT-optimised structures of (a) *CCH and (b) *CHCHOH on a Cu(111) surface range from 0/9 to 4/9 *CO coverage. Yellow, copper; grey, carbon; red, oxygen; white, hydrogen.



Figure S18. Free energy of *CHCOH to *CCH (cyan) or *CHCHOH (red) at different *CO coverage on the Cu (111) surface.



Figure S19. Process flow diagram of the CO_2 supply (a) for liquid CO_2 to CO_2 at 75 bar and 35 °C; (b) for gaseous CO_2 to CO_2 at 75 bar and 35 °C.

Initial CO ₂	CO ₂ supply flow rate, ×10 ⁻⁶ kg h ⁻¹	Power of pump or compressor, ×10 ⁻⁷ kW	Cost of CO ₂ supply, $\times 10^{-2}$ USD kg ⁻¹ (ethanol)	Ratio of power of CO_2 supply to that of electrolysis, $\times 10^{-2}$
Liquid, 30 bar, -5.4 °C	1.83	0.0373	0.0436	0.0324
Gaseous, 30 bar, 20 °C	1.83	0.468	0.545	0.407
Gaseous, 1 bar, 20 °C	1.83	3.92	4.59	3.41

Table S1. The cost of pressuring liquid or gaseous CO_2 to CO_2 at 75 bar and 35 °C.

Note: 0.03 USD kWh⁻¹ and commercial ethanol ~1 USD kg⁻¹ are assumed; produced ethanol is 2.56×10^{-7} kg h⁻¹.

Catalysts	FE of ethanol	Potential (V vs. RHE)	Potential (V vs. Ag / AgCl)	Electrolyte	Pressure (bar)	Current density (mA cm ⁻²)	Ref.
SW-Cu ₂ O/Cu	9.5%	-1.25	-1.8	0.5 M KHCO ₃	45	~ -62.3	J. Am. Chem. Soc. ¹¹
Cu electrode	8.2-13.9%	n. r.	-1.55 V vs. Ag/AgPF ₆	1.0 M CsHCO ₃	80	~ -9	ChemSusChem ¹²
Oxide-derived Cu	33.2%	-0.35	-1.35	0.1 M KOH	2.4*	-1.28	Nature ¹³
Silver	1.154%	n. r.	-3	0.5 M KOH	60*	n. r.	Angew. Chem., Int. Ed.14
OD Cu/C	34.8%	-0.5	-1.2	$0.1 \mathrm{M} \mathrm{KHCO}_3$	1	-1	ACS Appl. Mater. Interfaces. ¹⁵
Cu sandwich	31%	-0.3	-0.97	0.1 M KHCO3	1	-1.25	Adv. Sustain. Syst.16
Cu-Cu ₂ O-3	39.2%	-0.4	-1.0	0.1 M KCl	1	-7.3	Nat. Commun. ¹⁷
Cu/Cu ₂ O aerogel	41.2%	-1.1	-1.7	0.1 M KCl	1	-79	Adv. Funct. Mater.18
GB-Cu	31.74%	-1.3	-2.3	1 M KOH	1	-45	J. Am. Chem. Soc. ¹⁹
3D Cu nanostructures	51%	-0.3	-1.3	1 M KOH	1*	~-2.4	ACS Catal.20
Cu/CNT	37%	-0.3	-1.3	0.1 M KOH	1*	-0.37	ACS Cent. Sci.21
HS-Cu	36.6%	-0.48	-1.0	0.1 M KHCO3	100	-7.1	This work
HS-Cu	35.8%	-0.48	-1.0	0.1 M KHCO3	75	-6.3	This work
HS-Cu	22.8%	-0.67	-1.2	0.1 M KHCO3	50	-5.3	This work
* Stand for electrochemical CO reduction reaction. n.r. = not reported.							

Table S2. The performance comparison of representative catalysts for the conversion CO₂ (CO)-to-ethanol under ambient and high pressure in H-typed cell.

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