Supporting Information

Harnessing Electrochemical CO_2 Reduction and Assisted Water Electrolysis via Constrained Thermodynamic Modeling

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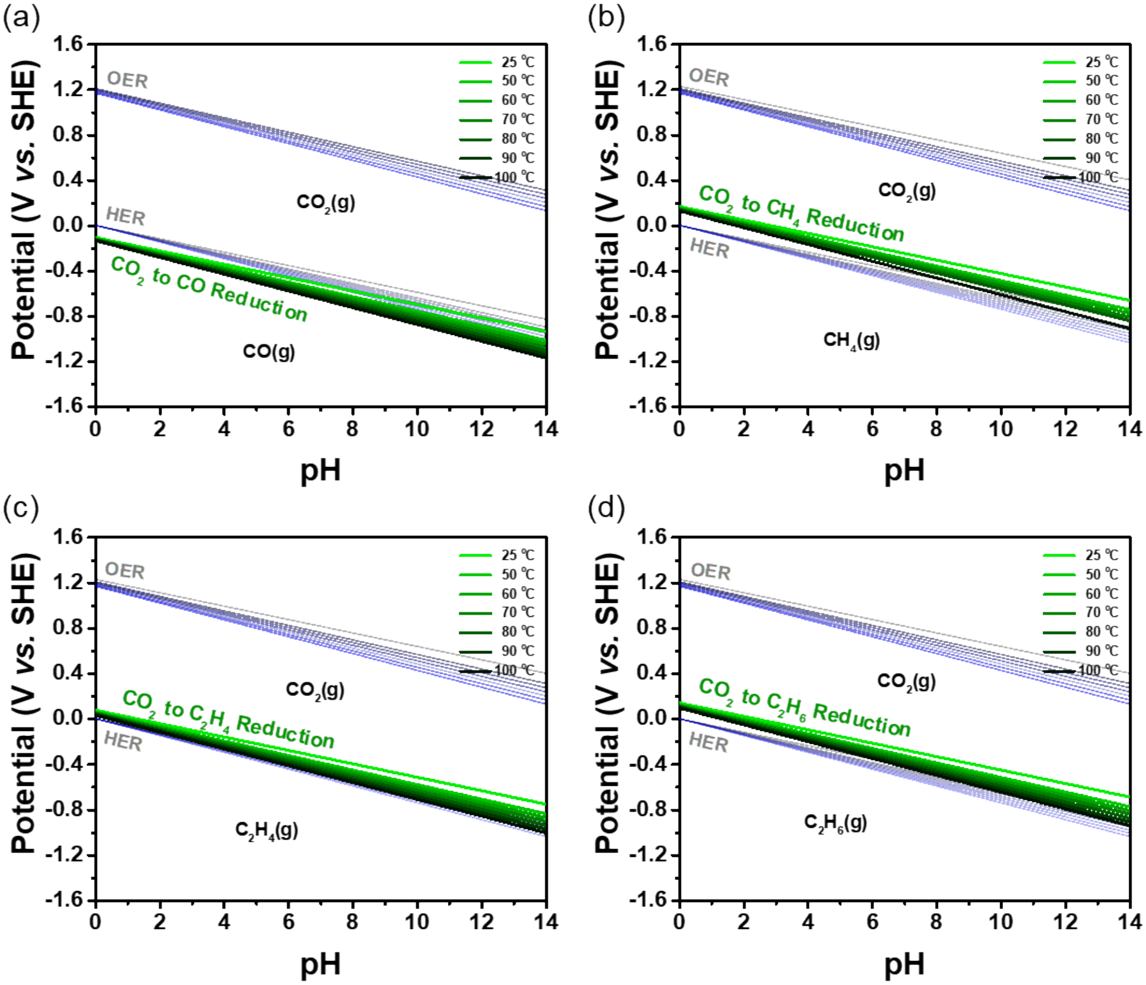

Fig. S1 Pourbaix diagrams of hydrocarbons including (a) CO, (b) CH_4, (c) C_2H_4, and (d) C_2H_6 using CO_2(g) as a function of temperature from 25 to 100 ^oC.

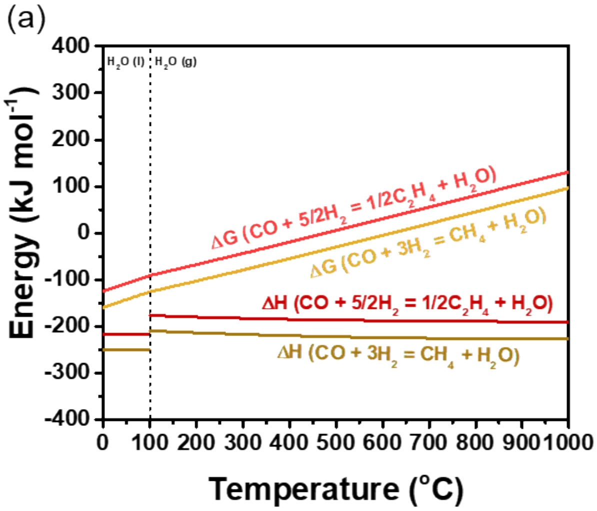

Fig. S2 Gibbs free energy and enthalpy of Fischer-Tropsch process as a function of temperature from 0 to 1,000 ^{o}C.

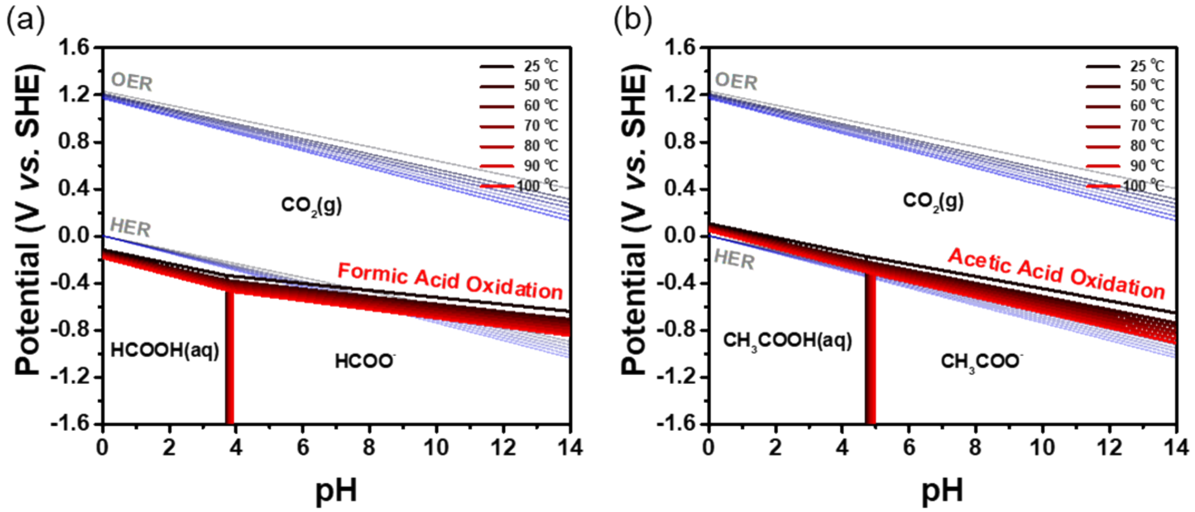

Fig. S3 Pourbaix diagrams of organic acid including (a) formic acid and (b) acetic acid using CO_2(g) as a function of temperature from 25 to 100 ^oC.

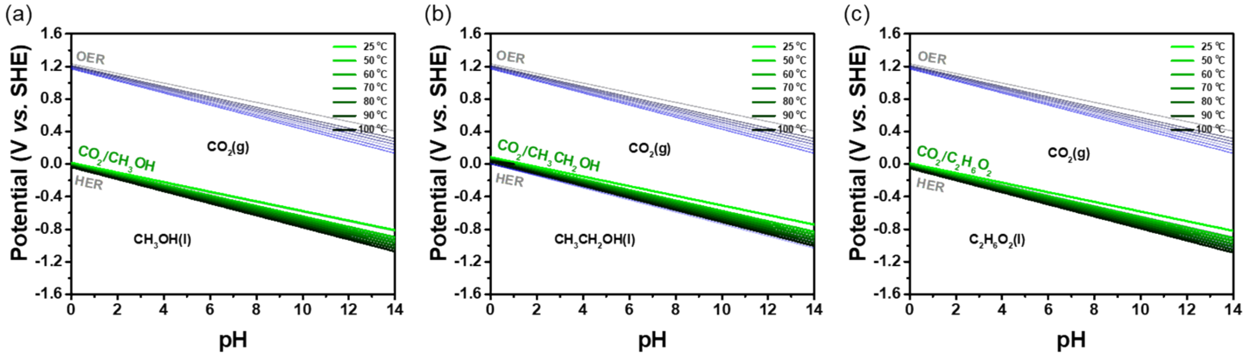

Fig. S4 Pourbaix diagrams of the liquid-phase oxidation of (a) methanol, (b) ethanol, and (c) ethylene glycol as a function of temperature from 25 to 100 °C.

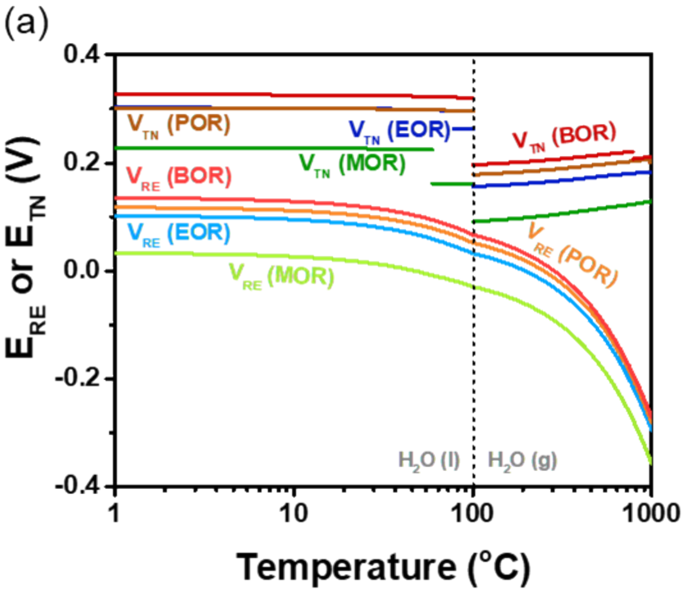

Fig. S5 Theoretical potentials (V_{TN} and V_{RE}) of assisted water splitting using alcohols including methanol (MOR), ethanol (EOR), propanol (POR), and butanol (BOR) as a function of temperature from 0 to 1,000 °C.

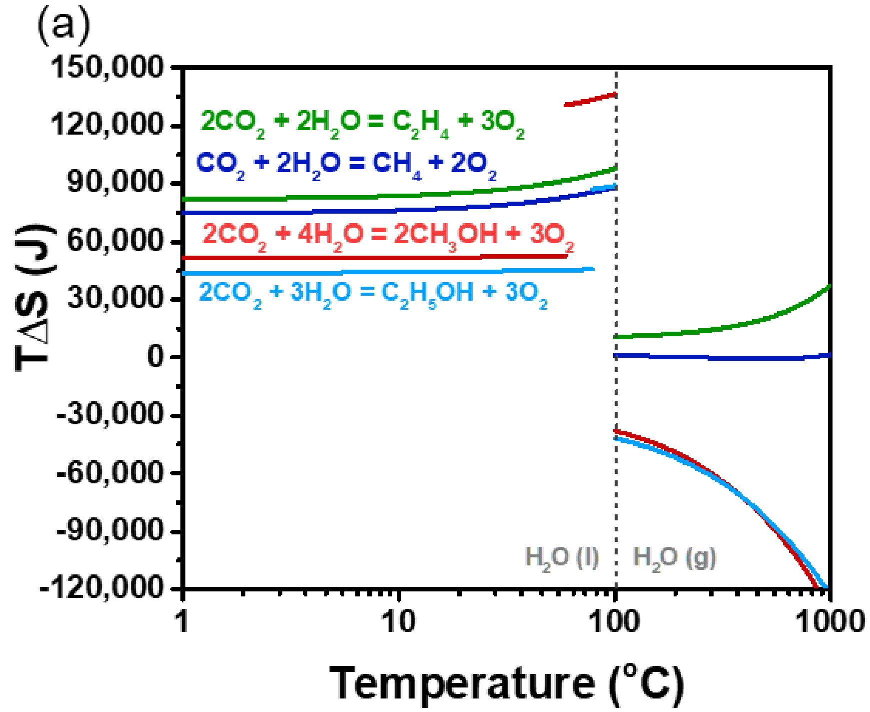

Fig. S6. TΔS of the reaction.

Table S1. Thermodynamic data used for calculations at 1 atm, obtained from the FactPS database.

Species	ΔG_f^0 (kJ)						
	25 ^oC	50 ^oC	60 ^oC	70 ^oC	80 ^oC	90 ^oC	100 ^oC
CH_4(g)	-50.801	-48.751	-47.914	-47.068	-46.213	-45.350	-44.478
C_2H_4(g)	68.388	69.756	70.320	70.894	71.476	72.067	72.667
C_2H_6(g)	-32.896	-28.502	-26.716	-24.916	-23.101	-21.273	-19.432
CO(g)	-137.147	-139.385	-140.283	-141.183	-142.083	-142.985	-143.888
CO_2(g)	-394.422	-394.496	-394.526	-394.555	-394.584	-394.614	-394.642
CH_3OH(g)	-162.497	-159.217	-157.885	-156.542	-155.189	-153.826	-152.452
CH_3CH_2OH(g)	-168.717	-162.942	-160.607	-158.260	-155.901	-153.531	-151.149
HCOOH(g)	-350.998	-348.662	-347.715	-346.763	-345.805	-344.842	-343.873
CH_3COOH(g)	-383.216	-377.096	-374.629	-372.151	-369.663	-367.165	-364.658
$(CH_2OH)_2$(l)	-323.231	-312.215	-307.817	-303.423	-299.033	-294.647	-290.263
CH_4(aq)	-34.498	-30.147	-28.507	-26.910	-25.350	-23.826	-22.337
C_2H_4(aq)	81.215	85.053	86.630	88.231	89.854	91.499	93.167
C_2H_6(aq)	-17.181	-9.955	-7.007	-4.027	-1.015	2.027	5.099
CO(aq)	-119.868	-119.753	-119.693	-119.627	-119.553	-119.472	-119.384
CO_2(aq)	-386.008	-383.639	-382.670	-381.689	-380.697	-379.693	-378.679

CO_3^{2-}	-674.066	-514.821	-509.386	-503.830	-498.161	-492.385	-486.505
CH_3OH(aq)	-175.478	-169.488	-167.047	-164.581	-162.091	-159.577	-157.040
CH_3CH_2OH(aq)	-181.785	-172.734	-169.048	-165.325	-161.567	-157.774	-153.947
$HCOO^-$	-351.184	-344.893	-342.343	-339.772	-337.180	-334.568	-331.935
HCOOH(aq)	-372.391	-367.999	-366.272	-364.560	-362.864	-361.186	-359.529
CH_3COO^-	-369.589	-359.701	-355.681	-351.624	-347.528	-343.394	-339.223
CH_3COOH(aq)	-396.615	-389.178	-386.219	-383.269	-380.330	-377.404	-374.495
HCO_3^-	-586.773	-577.884	-574.285	-570.661	-567.010	-563.333	-559.630
H_2(g)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O_2(g)	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O(g)	-228.607	-227.487	-227.034	-226.578	-226.119	-225.657	-225.192
H_2O(l)	-237.190	-233.144	-231.543	-229.951	-228.369	-226.795	-225.231
H^+	0.000	0.006	0.011	0.018	0.026	0.036	0.047
H_2(aq)	17.531	19.191	19.775	20.319	20.826	21.300	21.742
O_2(aq)	16.359	18.533	19.307	20.029	20.702	21.326	21.904
OH^-	-157.248	-150.990	-148.403	-145.773	-143.099	-140.384	-137.628
e^-(aq)	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Efficiency Calculations for Electrochemical CO_2RR and Assisted Water Electrolysis

1. Faradaic efficiency (FE)

$$FE_{Product}\,(\%) = \frac{Q_{Product}}{Q} = \frac{n_{Product} \times V \times c_{Product} \times F}{Q} \qquad \text{(Eq. S1)}$$

2. Voltage efficiency (VE)

$$VE_{Cell}\,(\%) = \frac{E^{0}_{Oxidation} - E^{0}_{Reduction}}{E_{Oxidation} - E_{Reduction}}$$

(Eq. S2)

3. Energy efficiency (EE)

$$EE_{Product}\,(\%) = VE_{Product} \times FE_{Product}$$

(Eq. S3)

$$EE\ of\ half-cell\,(\%) = \frac{\left(E^{0}_{Oxidation} - E^{0}_{Reduction}\right) \times FE}{E_{Oxidation} - E_{Reduction}}$$

(Eq. S4)

$$EE\ of\ full-cell\,(\%) = \frac{\left(E^{0}_{Oxidation} - E^{0}_{Reduction}\right) \times FE}{E_{Cell}}$$

(Eq. S5)

Where Q represents the total applied charge (C), and Q_{Product} denotes the charge required to synthesize the desired product. n is the number of electrons transferred per reaction, V is the volume of the catholyte, c_{Product} is the product concentration in the catholyte, and F is the Faraday constant (96,485 C mol^{-1}). E^{0}_{Product} and E^{0}_{OER}

represent the theoretical potentials for electrochemical CO_2RR and the OER, respectively, while E_{Product} and E_{OER} are the applied potentials for CO_2RR and OER, respectively. EE is defined as the product of FE and VE. The EE of a half-cell considers only the reduction reaction, whereas the EE of a full-cell accounts for both the reduction and oxidation reactions.

Specific Energy Consumption Calculations

The specific energy consumption (SEC) is a key parameter used to evaluate and compare the energy requirements of different CO_2RR-to-product pathways. It represents the amount of energy input required per kilogram of the desired product and is calculated using the following equation:

$$SEC\,(kWh\,kg^{-1}) = \frac{n \times F \times E_{cell}}{T \times FE \times M_P}$$

(Eq. S6)

where n denotes the number of electrons transferred per reaction, F is the Faraday constant (96,485 C mol^{-1}), E_{cell} is the applied cell voltage, T is the operating time, FE is the Faradaic efficiency, and M_P represents the molar mass of the product. This metric facilitates a direct comparison of energy efficiency among different ammonia production methods and aids in optimizing operating conditions for a more sustainable and cost-effective electrochemical CO_2RR process.