Electronic Supplementary Information

Electrochemical valorization of captured CO$_2$: recent advances and future perspectives

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Energy analysis

We calculated the total energy cost of state-of-the-art electrochemical CO$_2$ conversion systems, such as gas-fed alkaline flow cells[1] and membrane electrode assembly (MEA) cells,[2] and compared them with electrocatalytic systems that directly upgrade carbonate,[3] carbamate,[4] and bicarbonate solutions (Table S1).[5,6] We selected these examples of electrochemical conversion of gas-fed and captured CO$_2$, which are presented in Table 1 of the main text because they are among the few that provide all the necessary data for conducting a comprehensive energy analysis. Using such reported data from the literature, we evaluated the energy requirements for the overall CO$_2$ electrovalorization, considering three stages that incur the main energy cost for the entire process: CO$_2$ capture/release, electrolysis, and product separation. Although the ultimate economic performance of integrated systems depends on several additional variables, the results obtained allow us to conduct an exploratory analysis of their viability compared to established technology from an energy consumption perspective.

Table S1. Overview of electrochemical CO$_2$ conversion systems analyzed.

System	Product	Ref.
CO$_2$-fed flow cell	CO	[1]
CO$_2$-fed MEA	CO	[2]
Carbonate	CO	[3]
Carbamate	CO	[4]
Bicarbonate	CO	[5]
CO$_2$-fed flow cell	HCOO$^-$	[7]
Bicarbonate	HCOO$^-$	[8]

CO$_2$-fed flow cell	CH$_4$	[9]
Bicarbonate	CH$_4$	[10]
Molten salts	CH$_4$	[11]
CO$_2$-fed flow cell	C$_2$H$_4$	[12]
Carbonate	C$_2$H$_4$	[13]

CO$_2$ capture/release. The energy required to capture the necessary moles of CO$_2$ to produce 1 mol of product is calculated based on the CO$_2$ utilization efficiency and the energy cost associated with the capture technology. In these calculations, we consider the case of direct air capture using hydroxide solutions. The energy required to release CO$_2$ from the formed CaCO$_3$ is 178.3 kJ mol^{-1}, which represents the primary energy cost for this step.[14] Thus, for systems that require a pure CO$_2$ stream for electrolysis (i.e., flow cell and MEA), there is an associated energy cost for its production. In contrast, direct conversion of the resulting CO$_2$ adduct following the capture step eliminates these energy costs.

Since gas-fed CO$_2$ electrolyzers can experience CO$_2$ losses due to crossover, carbonate formation, and low single-pass efficiency, additional CO$_2$ must be provided to generate 1 mol of the targeted product. Based on the reported data from each example, the percentage of each type of loss can be determined, with the remaining percentage representing CO$_2$ utilization. The energy cost associated with the CO$_2$ capture/release step is calculated as follows:

$$\text{Energy for CO}_2 \text{ capture/release} = \frac{178.3 \text{ kJ mol}^{-1}}{\text{CO}_2 \text{utilization efficiency (\%)}} \times 100\%$$

All relevant information regarding the CO$_2$ capture/release step is collected for distinct electrolyzer systems in Table S2.

Table S2. Energy analysis of the CO_2 capture/release step for distinct electrolyzer systems.

System	Product	Outlet CO_2 (%)	CO_2 utilization (%)	CO_2 capture/release (kJ mol-product^{-1})
Flow cell	CO	36	17	1048.8
MEA	CO	50	20	891.5
CO_3^{2-}	CO	0	100	0
Carbamate	CO	0	90	0
HCO_3^-	CO	25	60	0
Flow cell	$HCOO^-$	N.A.	9	1981.1
HCO_3^-	$HCOO^-$	0	99.8	0
Flow cell	CH_4	98.7	1.3	13715.4
HCO_3^-	CH_4	75	25	0
Molten salts	CH_4	0	100	0
Flow cell	C_2H_4	77	5	3566.0
CO_3^{2-}	C_2H_4	0	100	0

CO_2 electrolysis. The energy required for the electroreduction of CO_2 is calculated as follows:

$$\text{Energy for } CO_2 \text{ electrolysis} = \frac{\Delta G^o{}_{product}}{EE}$$

where $\Delta G^o{}_{product}$ is the Gibbs free energy of formation for each corresponding product and EE is the full-cell energy efficiency.

The full-cell energy efficiency of each system was calculated as follows:[15]

$$EE = \sum_i \frac{E_i^o FE_i}{E_{appl}}$$

where E_i^o is the equilibrium cell potential, FE_i is the reported Faradaic efficiency of product i, and E_{appl} is the applied cell potential.

In the case when the cell potential was not reported and only the potential at the working electrode vs. the reversible hydrogen electrode (RHE) was provided, EE was calculated as follows:

$$EE = \frac{1.23 - E_i^o \text{(vs. RHE)}}{1.23 + \eta_{OER} - E_{appl} \text{(vs. RHE)}}$$

where η_{OER} is the overpotential for the oxygen evolution reaction and a constant value of 350 mV was assumed.[16]

The values of E_i^o, E_i^o (vs. RHE), and $\Delta G^o_{product}$ used in the above formulas were calculated based on previously reported thermodynamic data[17] and are presented in Table S3.

Table S3. Values of equilibrium potentials and Gibbs free energies used in calculating the electrolysis energy and energy efficiency (EE).

Product	E_i^o (V)	E_i^o (V vs. RHE)	$\Delta G^o_{product}$ (kJ mol^{-1})
CO	1.33	−0.10	256.7
HCOO$^-$ (pH = 2)	1.40	−0.17	269.6
HCOO$^-$ (pH = 14)	1.04	0.19	200.7
CH$_4$	1.06	0.17	818.7
CH$_4$ (T = 650 °C)	1.35	−0.12	1042.0
C$_2$H$_4$	1.15	0.08	1332.8

In the case of the molten salts example, where electrolysis was conducted at 650 °C,[11] the energy required to heat the electrolyzer was calculated as follows:

$$W = W_0 + P \times t$$

W_0 is the energy required to heat the molten salts from 25 to 650 °C, P is the power needed to maintain the temperature, and t is the reaction time. W_0 can be theoretically calculated based on the specific heat capacities of the molten salts (Table S4) used and the cell materials as follows:

$$W_0 = \Sigma C_x \times m_x \times \Delta T_x$$

The molten salt used is a mixture of Li_2CO_3-Na_2CO_3-K_2CO_3-LiOH, with LiOH comprising 15% of the total mixture, and the total amount of the salts being 120 g. The cell is constructed from welded titanium alloy tubes with three partitioned chambers. Each chamber was 20 mm in internal diameter, 2 mm in wall thickness, and 40 mm in vertical length. The density (ρ) of titanium alloy is 4.33 g cm^{-3}. Thus, the mass of the cell $= 3\rho V = 3 \times 4.33 \times \pi \times (1.1^2 - 1^2) \times 4 = 34.3$ g and $W_0 = 1.61 \times 120 \times 85\% \times 625 + 2.08 \times 120 \times 15\% \times 625 + 0.526 \times 34.3 \times 625 = 137.3$ kJ.

Table S4. Heat capacities of relevant materials.

Materials	Li_2CO_3-Na_2CO_3-K_2CO_3	LiOH	Ti alloy
Heat capacity (J g^{-1} K^{-1})	1.61	2.08	0.526

Accurately calculating the power to maintain the temperature is challenging, as it is closely tied to heat transfer behavior.[18] To simplify the estimation, we assumed, based on previously reported data,[19] a heat loss rate of 350 K h^{-1} if no heating power is applied to maintain the temperature. Thus, to maintain the temperature, the heating power required equals $(1.61 \times 120 \times 85\% + 2.08 \times 120 \times 15\% + 0.526 \times 34.26)$ J K$^{-1} \times 350$ K h$^{-1} = 77$ kJ h^{-1}

Regarding the measured CH_4 production rate in the molten salts electrolyzer, the time required to generate 1 mol of CH_4 is 415.2 h. Thus, $W = W_0 + P \times t = 137.3$ kJ $+ 77$ kJ h$^{-1} \times 415.2$ h $= 32107.7$ kJ mol-CH_4^{-1}

All relevant information regarding the electrolysis step is collected for distinct electrolyzer systems in Table S5.

Table S5. Analysis of the electrolysis energy for distinct electrolyzer systems.

System	Product	FE (%)	E_{appl} (V)	EE (%)	Electrolysis (kJ mol^{-1})
Flow cell	CO	99	−0.8[a]	53.6	479.9
MEA	CO	77	2.54	40.6	633.2
CO_3^{2-}	CO	25	3.45	35.0	734.4
Carbamate	CO	72	2.38	40.5	634.5
HCO_3^{-}	CO	70	3.70	25.4	1014.5
Flow cell	$HCOO^{-}$	96	4.56	29.4	916.6
HCO_3^{-}	$HCOO^{-}$	85	2.20	40.2	499.5
Flow cell	CH_4	48	−1.4[a]	14.9	5494.8
HCO_3^{-}	CH_4	27	7.2	4.0	20583.5
Molten salts	CH_4	43	2.70	21.4	4880.7
Flow cell	C_2H_4	70	−0.5[a]	33.5	3973.6
CO_3^{2-}	C_2H_4	34	4.10	9.5	13970.6

[a] Half-cell potential vs. RHE

Product separation. Since CO_2 removal is the most energy-intensive downstream step,[20] we only considered the energy cost for separating CO_2 from the products in our calculations. The energy cost varies considerably from 100 to 900 kJ mol^{-1}, depending on the method used for separation. Here, we assumed a fixed cost of 500 kJ mol^{-1} to separate unreacted CO_2 from gaseous products.[3] Thus, the product separation energy is calculated as follows:

$$\text{Separation energy} = 500 \text{ kJ mol-CO}_2^{-1} \times CO_2 \text{ outlet (mol)}$$

In the case when formate must be separated from an aqueous mixture, a value of 265 kJ mol^{-1} was used based on the reported energy consumption for a pressure-swing distillation method.[21]

All relevant information regarding the product purification step is collected for distinct electrolyzer systems in Table S6.

Table S6. Energy analysis of the product purification for distinct electrolyzer systems.

System	Product	CO_2 outlet (mol)	Product separation (kJ mol-product^{-1})
Flow cell	CO	2.1	1050
MEA	CO	2.5	1250
CO_3^{2-}	CO	0	0
Carbamate	CO	0	0
HCO_3^-	CO	0.4	200
Flow cell	$HCOO^-$	N.A.	265
HCO_3^-	$HCOO^-$	0	265
Flow cell	CH_4	76	38000
HCO_3^-	CH_4	3	1500
Molten salts	CH_4	0	0
Flow cell	C_2H_4	30.8	15400
CO_3^{2-}	C_2H_4	0	0

Product purity. For the calculation of the product purities, we assume that 1 mol of product is produced in each case. The product purities in the gas outlet, as shown in Table 2 in the main text, were calculated as follows:

$$\text{Purity of product} = \frac{1 \text{ mol product}}{CO_2 \text{ outlet (mol)} + H_2 \text{ outlet (mol)} + 1 \text{ mol product}}$$

The number of mol-CO_2 in the outlet was calculated based on the CO_2 utilization efficiency (%) and CO_2 outlet (%) as follows:

$$CO_2 \text{ required (mol)} = \frac{(n_{CO2}) \times 100\%}{CO_2 \text{ utilization efficiency (\%)}}$$

$$CO_2 \text{ outlet (mol)} = \frac{[CO_2 \text{ required (mol)}] \times [CO_2 \text{ outlet (\%)}]}{100\%}$$

where n_{CO2} is the number of CO_2 molecules required per molecule of product. In the case of CO, $HCOO^-$, and CH_4, n_{CO2} equals 1, while in the case of C_2H_4, n_{CO2} equals 2.

For simplicity, we assumed that the rest of the faradaic efficiency goes to the production of H_2. Therefore, the number of moles of H_2 in the outlet was calculated as follows:

$$H_2 \text{ outlet (mol)} = \frac{100 - FE(\text{product})}{FE(\text{product})} \frac{ne_{\text{product}}}{ne_{H2}}$$

where ne_{product} denotes the number of electrons required to form the corresponding product and ne_{H2} is the number of electrons required to produce H_2. Table S7 summarizes the obtained data.

Table S7. Purity of the different products at the outlet of the electrolyzer.

System	Product	CO_2 utilization (%)	CO_2 outlet (%)	CO_2 required (mol)	CO_2 outlet (mol)	FE (%, product)	H_2 outlet (mol)	Purity (vol.%)
CO_2	CO	20	50	5.0	2.5	77	0.3	26
CO_2	CO	17	36	5.9	2.1	99	0	32
CO_3^{2-}	CO	100	0	1.0	0.0	25	3.0	25
Carbamate	CO	90	0	1.1	0.0	72	0.4	72
HCO_3^-	CO	60	25	1.7	0.4	70	0.4	54
CO_2	CH_4	1.3	98.7	76.9	75.9	62	2.5	1
HCO_3^-	CH_4	25	75	4.0	3.0	27	10.8	7
Molten salts	CH_4	100	0	1.0	0.0	43	5.3	16
CO_2	C_2H_4	5	77	40.0	30.8	70	2.6	3
CO_3^{2-}	C_2H_4	100	0	2.0	0.0	34	11.6	8

In the case of formate production using a CO_2-fed electrolyzer, the product purity could not be quantified due to insufficient reported data for the calculation. For the direct conversion of bicarbonate to formate, the product purity was calculated as follows:

$$HCOO^- \text{ production rate} = j_{\text{tot}} \times \text{Electrode area} \times FE(HCOO^-) \times \left(\frac{1 \text{ mol } HCOO^-}{2 \text{ mol } e^-} \right) F^{-1}$$

$$= \left(\frac{0.1\,\text{A}}{\text{cm}^2}\right)(4\,\text{cm}^2)\left(\frac{85\%}{100\%}\right)\left(\frac{1\,\text{mol}}{96485\,\text{C}}\right)\left(\frac{1\,\text{mol HCOO}^-}{2\,\text{mol}\,e^-}\right)$$

$$= 1.8 \times 10^{-6}\,\text{mol HCOO}^-\,\text{s}^{-1}$$

During the 5 h of bulk electrolysis, 0.03 mol of HCOO$^-$ are produced. Given that the catholyte volume is 40 mL, the concentration of HCOO$^-$ becomes 0.8 M.

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