

A Gross-Margin Model for Defining Technoeconomic Benchmarks in the Electroreduction of CO₂

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We introduce a gross-margin model to evaluate the technoeconomic feasibility of producing different C₁–C₂ chemicals such as carbon monoxide, formic acid, methanol, methane, ethanol, and ethylene through the electroreduction of CO₂. Key performance benchmarks including the maximum operating cell potential (V_{\max}), minimum operating current density (j_{\min}), Faradaic efficiency (FE), and catalyst durability (t_{catdur}) are derived. The V_{\max} values obtained for the different chemicals indicate

that CO and HCOOH are the most economically viable products. Selectivity requirements suggest that the coproduction of an economically less feasible chemical (CH₃OH, CH₄, C₂H₅OH, C₂H₄) with a more feasible chemical (CO, HCOOH) can be a strategy to offset the V_{\max} requirements for individual products. Other performance requirements such as j_{\min} and t_{catdur} are also derived, and the feasibility of alternative process designs and operating conditions are evaluated.

Introduction

The development of economically viable technologies that can stabilize and eventually reduce the rising levels of CO₂ in the earth's atmosphere (currently close to 400 ppm)^[1] remains one of the grand challenges of the 21st century.^[2] Earlier, Socolow et al. proposed the stabilization wedge approach to help guide the mitigation of the rise in atmospheric CO₂ levels.^[3] Their strategy entailed the simultaneous implementation of different methods that include increasing the energy efficiency of buildings and vehicles, moving from fossil-fuel-based power plants to renewable energy sources, and the capture and sequestration of CO₂ from point sources such as coal-fired power plants and cement plants. The photochemical or electrochemical reduction of CO₂ to different value-added C₁–C₂ chemicals such as carbon monoxide, formic acid, methanol, methane, ethanol, or ethylene could provide an additional option for a stabilization wedge.^[4] As a result of major technological advances in wind and solar electricity generation, the cost of producing renewable electricity has declined steadily over the last decade, and a recent U.S. Department of Energy (DOE) report indicated that wind energy could be used to generate electricity at

a cost as low as \$0.02 kWh⁻¹.^[5] The use of cheap, readily accessible renewable energy for electrochemical CO₂ reduction provides an attractive approach for the production of carbon chemical feedstocks in a carbon-neutral way. The process can be utilized to solve the intermittency problem of renewables through the storage of excess renewable electricity as chemical energy if grid supply exceeds demand. In addition, the technology has the potential to be implemented on an industrial scale more quickly than some competing technologies such as direct photochemical CO₂ reduction.


In the early 1990s, Hori et al. performed a comprehensive screening of different metal electrodes to determine their selectivity and activity towards different CO₂ electroreduction products.^[6] Transition metals such as Au, Ag, and Zn were selective towards CO production, whereas Pb and Sn exhibited selectivity towards HCOOH production. Cu was the only metal electrode that could produce C₂ chemicals such as C₂H₅OH and C₂H₄ at significant levels of selectivity (> 5%). Since then, numerous research efforts have focused on the development of new catalysts,^[7] the analysis of the effects of different electrolytes,^[8] the development of new electrolyzer designs,^[9] the comparison of different methods of electrode preparation,^[10] and the optimization of process conditions^[11] to identify design rules to improve the selectivity and activity of CO₂ electroreduction towards a particular product.

Herein, we report a technoeconomic analysis for the electroreduction of CO₂ to different value-added chemicals and fuels. The performance of a particular catalyst or a reaction system in the area of CO₂ electroreduction is usually defined in terms of four parameters, namely, (1) the current density (j), which signifies the total productivity or activity of the catalyst; (2) the operating cell potential (V), which signifies the amount of energy required to form a particular product; (3) the Faradaic efficiency (FE), which signifies the selectivity towards a particular prod-

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uct; and (4) the catalyst durability (t_{catdur}). Although some techno-economic analyses for the electroreduction of CO_2 have been reported,^[12] a comprehensive and straightforward analysis tool explicit in terms of different variables (such as catalyst cost, electricity cost, electrolyzer cost, separation cost, interest rate, consumable chemical cost, and the market price of the product) that can provide benchmarks for a variety of CO_2 electroreduction products is still lacking. We report a gross-margin model to fill in this gap. Gross-margin models are often used across the manufacturing and chemicals industries to assess the profitability of different products and processes.^[13] Here, we utilize such a model to evaluate the economic viability of CO_2 electroreduction to different C_1 – C_2 chemicals and fuels. We also use the model to calculate the performance targets required in terms of maximum operating cell potential (V_{max}), minimum operating current density (j_{min}), FE, and t_{catdur} for an economically viable electrochemical CO_2 reduction process. A comparison of the V_{max} values obtained for the different products and operating conditions with the absolute value of the standard cell potential ($|E_{\text{cell}}^0|$) helps answer some key questions: What specific products should be produced? What level of selectivity (FE) is required for such a product? The question of selectivity is rather important for two main reasons. First is the debate between whether to produce CO selectively as a lone product or to produce a mixture of CO and H_2 , that is, syngas, as a product of CO_2 electroreduction. The second issue is the selective production of chemicals such as CH_4 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and C_2H_4 , which is currently difficult to achieve. Existing electrocatalysts exhibit low selectivity owing to the existence of a scaling relationship between the binding energies of rate-limiting intermediates and the commonality in rate-determining steps.^[9d,14] The gross-margin model reported here provides an economic basis to answer the aforementioned questions. We further use the model to study the effects of parameters such as catalyst durability and cost on the j_{min} requirements. Such an analysis of the different parameters that affect the economics of the overall process provides a valuable perspective on research directions that should be pursued and can, thus, help to guide electrochemical CO_2 reduction towards economic viability.

Gross-margin model

The gross margin (expressed in %) is defined as the difference between the revenue and the cost of goods sold divided by the revenue.^[15] The model does not take into account tax payments, cost of personnel, equity, and other overhead expenses. As most of the products of electrochemical CO_2 reduction are commodity chemicals, we assume a base-case gross margin of 30% (that is, the average value across the commodity-chemicals market)^[13] for the process to be economically viable [Eq. (1)]. Moreover, as the gross margin required for a particular chemical may vary from case to case depending on the market demand, we also performed a sensitivity analysis for gross margins of 15 and 45%.

$$\frac{\text{Revenue} - \text{Cost of goods sold}}{\text{Revenue}} > 0.3 \quad (1)$$

The electrolyzer design we consider here is similar to a polymer electrolyte membrane (PEM) fuel cell. The electroreduction of CO_2 can be performed in such a device by applying an external potential. The production scale is assumed to be of the order of that reported in the DOE H_2A Forecourt analysis for water electrolysis, that is, 1500 kg per day.^[16] The cost of goods sold is given by the sum of the product-manufacturing and product-separation costs. The product-manufacturing cost comprises the cost of the electrolyzer ($\lambda_{\text{electrolyzer}}$), balance of plant (λ_{BOP}), catalyst (λ_{cat}), electrolyte ($\lambda_{\text{electrolyte}}$), and electricity ($\lambda_{\text{electricity}}$). The λ_{BOP} consists of the costs of different auxiliary electrolyzer components such as power electronics, control sensors, gas management, and electrolyte management. The mathematical definitions of these terms are as follows:

$$\lambda_{\text{electrolyzer}} = C_{\text{electrolyzer}} t$$

$$\lambda_{\text{cat}} = \frac{(C_{\text{cat}} W_{\text{cat}} + C_{\text{GDL}}) A t}{t_{\text{catdur}}}$$

$$\lambda_{\text{electrolyte}} = C_{\text{electrolyte}} Q t$$

$$\lambda_{\text{electricity}} = V j A t C_E \times 10^{-6}$$

where $C_{\text{electrolyzer}}$ is the hourly installment payment towards capital investment for setting up the electrolyzer [$\text{\$ h}^{-1}$], C_{cat} is the catalyst cost [$\text{\$ mg}^{-1}$], W_{cat} is the catalyst loading [mg cm^{-2}], C_{GDL} is the cost of the gas diffusion layer [$\text{\$ cm}^{-2}$], A is the surface area of the electrode [cm^2], t_{catdur} is the catalyst durability [h], $C_{\text{electrolyte}}$ is the cost of the electrolyte [$\text{\$ mL}^{-1}$], Q is the purge flow rate of the electrolyte [mL h^{-1}], V is the cell potential (V), j is the current density [mA cm^{-2}], t is the time [h], and C_E is the cost of electricity [$\text{\$ kWh}^{-1}$]. As, by definition, $\lambda_{\text{electrolyzer}}$, λ_{cat} , and $\lambda_{\text{electrolyte}}$ are independent of j , we can combine them to form a single parameter λ . According to the DOE Forecourt analysis, λ makes up 41% of the overall capital cost, and the rest is λ_{BOP} .^[16]

The product-separation costs can be estimated from the Sherwood plot for the separation of dilute streams.^[17] According to the plot, the cost of separating a particular product from a mixture scales inversely with the concentration of the product and can be represented by k_p/w_p ; k_p is the separation constant for the product [$\text{\$ kg}_{\text{mixture}}^{-1}$], and w_p is the weight fraction of the product in the mixture. Thus, the overall cost of separating CO_2 electroreduction products can be obtained by multiplying the cost of separation with the production rate (given by the Faraday electrolysis law) and is defined as follows [Eq. (2)]:

$$\text{Cost of separation} = \frac{36 \times 10^{-6} \times j A t \sum \text{FE}_p \left(\frac{k_p}{z \times w_p} \right) M}{F} \quad (2)$$

where M is the molar mass of the product [g mol^{-1}], F is the Faraday constant (96485 C mol^{-1}), z is the number of electrons transferred in the electroreduction of CO_2 to the product, and FE_p is the Faradaic efficiency for the product [%].

The combination of the definitions above provides an expression for the cost of goods sold as in Equation (3):

$$\text{Cost of goods sold} = \frac{\lambda}{0.41} + jAt \times 10^{-6} \times \left[VC_E + \frac{36 \sum \text{FE}_p \left(\frac{k_p}{z \times w_p} \right) M}{F} \right] \quad (3)$$

The revenue for the electrochemical CO_2 reduction process is given by the sale price of the product [Eq. (4)].

$$\text{Revenue} = \frac{jAt \times 36 \times 10^{-6} \times \sum \frac{\text{FE}_p C_p M}{z}}{F} \quad (4)$$

where C_p is the market price for the product [$\text{\$ kg}^{-1}$]. The combination of Equations (3) and (4) with Equation (1) gives Equation (5):

$$jAt \times 10^{-6} \times \left[\frac{36 \times \sum \frac{\text{FE}_p}{z} \left(0.7C_p - \frac{k_p}{w_p} \right) M}{F} - VC_E \right] > \frac{\lambda}{0.41} \quad (5)$$

As the right-hand side is a positive quantity, the left-hand side should also be a positive quantity. The terms between the brackets in Equation (5) can be rearranged to form an expression for the maximum operating potential (V_{max}) that can be used to drive the CO_2 electroreduction process in an economically viable manner [Eq. (6)]:

$$V_{\text{operating}} < V_{\text{max}} = \frac{36 \times \sum \frac{\text{FE}_p}{z} \left(0.7C_p - \frac{k_p}{w_p} \right) M}{FC_E} \quad (6)$$

The minimum operating current density (j_{min}) required for an economically viable CO_2 electroreduction process can be derived by rearranging the left-hand side of Equation (5) to give Equation (7):

$$j_{\text{operating}} > j_{\text{min}} = \frac{\lambda}{0.41 \times 10^{-6} \times AtC_E [V_{\text{max}} - V]} \quad (7)$$

Results and Discussion

Identifying suitable operating cell potentials

Before deriving the V_{max} requirements for the different products of CO_2 electroreduction, we validated the gross-margin model against H_2 production by water electrolysis. The C_p value for H_2 was assumed to be $\text{\$}4.5 \text{ kg}^{-1}$,^[18] and C_E was assumed to be $\text{\$}0.06 \text{ kWh}^{-1}$, that is, the average price in the U.S.^[19] As H_2 production by water electrolysis requires minimal product separation from the exiting gas stream, we chose a value of $k_p = 0$ for the calculations. From Equation (6), it is predicted that a V_{max} of 1.96 V will be required for economically viable H_2 production by water electrolysis. The state-of-the-

art water electrolyzers operate at a cell potential of 1.6 V, which is lower than the V_{max} predicted by our model.^[20] In other words, this analysis shows that the model provides a realistic upper limit for the operating potential for water electrolysis.

The V_{max} defined by this model should be utilized as the first criterion for economic feasibility. If the absolute value of the standard cell potential ($|E_{\text{cell}}^0|$) to form a particular product is higher than the V_{max} required for the same process under a particular set of operating conditions, then the identification of catalytic systems that can produce such products directly through CO_2 electroreduction will not be possible. Therefore, this criterion should be used to examine what products could feasibly be produced under certain operating conditions.

To estimate the V_{max} values required for different electrochemical CO_2 reduction products, we consider three different scenarios that correspond to three different C_E values. These include $\text{\$}0.06 \text{ kWh}^{-1}$ (corresponding to the current average grid electricity price in the U.S.), $\text{\$}0.04 \text{ kWh}^{-1}$ (corresponding to hydroelectric power generation in the state of Washington and the cheapest electricity price in the U.S.),^[19] and $\text{\$}0.12 \text{ kWh}^{-1}$ (the grid electricity price after the inclusion of a CO_2 capture cost of $\text{\$}60 \text{ tonne}^{-1}$).^[22]

Six major CO_2 electroreduction products (that is, HCOOH , CO , CH_3OH , CH_4 , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$) were analyzed by the gross-margin model. For the base-case analysis, the C_p values for CO and HCOOH were taken from the literature, and the C_p values for CH_3OH , CH_4 , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ were obtained from different industrial and government price indices by averaging the data over a three year time period from 2012 to 2014. The values were taken as $\text{\$}1.2$, $\text{\$}1.2$, $\text{\$}0.51$, $\text{\$}0.21$, $\text{\$}1.2$, and $\text{\$}0.8 \text{ kg}^{-1}$ for HCOOH ,^[23] CO ,^[23] CH_3OH ,^[24] CH_4 ,^[25] C_2H_4 ,^[26] and $\text{C}_2\text{H}_5\text{OH}$,^[27] respectively. As the C_p values for the products fluctuate with time, we also considered a sensitivity analysis with $C_p \pm 30\%$. Furthermore, we assumed a FE_p of 100% for all the calculations. To estimate the cost of product separation, we considered a k_p value of $\text{\$}0.001 \text{ kg}_{\text{mixture}}^{-1}$ for the separation of the gaseous products from the exit gas stream, as calculated previously by Dahmus et al.^[28] Similarly, a linear fit in the commodity chemical (water, ethanol, and citric acid) section of the Sherwood plot reveals a k_p value of $\text{\$}0.006 \text{ kg}_{\text{mixture}}^{-1}$ for the separation of liquid products from the exit electrolyte stream.^[17b] Furthermore, we assumed that the exit streams are dilute in the CO_2 electroreduction products; hence, a weight fraction (w_p) of 0.1 was utilized for our calculations.

At a C_E of $\text{\$}0.12 \text{ kWh}^{-1}$ including the cost of CO_2 capture, the model shows that CO and HCOOH are the only products that are economically viable, as the V_{max} values are much greater than the required $|E_{\text{cell}}^0|$ values (Table 1). As the cost of CO_2 feed is not considered explicitly in our model, a C_E of $\text{\$}0.12 \text{ kWh}^{-1}$ seems most relevant for the assessment of practical application. However, if the electrolyzer is placed next to a CO_2 point source and, hence, can utilize the flue gas directly^[11b] or the CO_2 capture process can be combined with CO_2 conversion,^[8] then lower C_E values of $\text{\$}0.06$ and $\text{\$}0.04 \text{ kWh}^{-1}$ become relevant. Such process-design considerations are im-

Table 1. Maximum operating cell potential (V_{\max}) that can be utilized to form different products of CO_2 electroreduction.

Product	C_p [\$ kg ⁻¹]	M [g mol ⁻¹]	Cathode reaction	z	$E^{\circ[\text{a}]}$ [V]	Anode reaction	$E^{\circ[\text{a}]}$ [V]	$ E^{\circ}_{\text{cell}} $ [V]	$C_E^{[\text{c}]}$ = 0.04	$V_{\max}^{[\text{b}]}$ [V] 0.06	0.12
H_2	4.5	2	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	2	0.00	$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$	-1.23	1.23	2.94*	1.96*	0.98
HCOOH	1.2	46.02	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	2	-0.25			1.48	16.74*	11.16*	5.58*
CO	1.2	28.01	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	2	-0.11			1.34	10.84*	7.23*	3.61*
CH_3OH	0.51	32.04	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	6	0.02			1.21	1.48*	0.99	0.49
CH_4	0.21	16.04	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	8	0.17			1.06	0.26	0.17	0.09
C_2H_4	1.20	28.05	$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	12	0.06			1.17	1.81*	1.21*	0.60
$\text{C}_2\text{H}_5\text{OH}$	0.8	46.07	$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	12	0.08			1.15	1.79*	1.19*	0.60

[a] E° values are reported under standard conditions [1 atm (0.1 MPa) and 25 °C; vs. reversible hydrogen electrode (RHE)] in aqueous media; according to Ref. [21]. [b] Values marked by * represent economically viable conditions ($V_{\max} > |E^{\circ}_{\text{cell}}|$); all other values represent economically unfavorable conditions ($V_{\max} < |E^{\circ}_{\text{cell}}|$). [c] C_E in [\$ kWh⁻¹].

portant for exploration as CH_3OH , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ (larger market size!) become economically viable.

Recall that we mentioned earlier that the market prices of the products are subject to fluctuations and the gross margin required to make a particular chemical economically viable may vary from case to case. A sensitivity analysis showed the changes that might be expected in the V_{\max} requirements as a result. We considered a $\pm 30\%$ fluctuation in C_p for the different products. The gross margins were assumed to vary from 15 to 45%, and 30% was our base case. The C_E value was assumed to be $\$0.12 \text{ kWh}^{-1}$ for the calculations to account for the cost of CO_2 capture. As shown in Table 2, even for a gross margin of 15% and a C_p value 30% above the base case, the

V_{\max} values for CH_3OH , CH_4 , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ are below the $|E^{\circ}_{\text{cell}}|$ values. Therefore, to make the electroreduction of CO_2 to CH_3OH , CH_4 , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ price-competitive with existing technologies, alternative process-design strategies such as starting with different raw materials (e.g., CO)^[29] or increasing the temperature and pressure of the electrocatalytic system to enter a different Gibbs free energy of formation regime should be pursued as research directions.^[11a] Owing to the significantly larger market demand for CH_3OH , CH_4 , C_2H_4 , and $\text{C}_2\text{H}_5\text{OH}$ than for HCOOH and CO, such approaches have the potential to provide a much larger stabilization wedge^[3] to reduce CO_2 emissions.

Analyzing the effect of Faradaic efficiency

To provide an answer to whether the selective production of CO from CO_2 electroreduction is a better strategy than the production of a mixture of CO and H_2 , that is, syngas, we considered different ratios of CO and H_2 and calculated the corresponding V_{\max} values with our economic model. A C_E of $\$0.12 \text{ kWh}^{-1}$ was chosen for the analysis to incorporate the cost of CO_2 capture, and a gross margin of 30% was used. The V_{\max} shows a linear relationship with FE_{CO} , and the value is larger for a higher CO content (Figure 1). As a consequence, the coproduction of H_2 with CO can be a good strategy from an economic perspective, as the low V_{\max} requirements for the production of H_2 by water electrolysis are offset. However, if H_2 is derived from natural-gas reforming, then a lower production cost of $\$1.97 \text{ kg}^{-1}$ can be achieved.^[30] For such cases, the selective production of CO followed by combination with H_2 obtained from natural-gas reforming can be an economically viable strategy as well.

Additionally, we considered binary mixtures of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ with CO (Figure 1). In all cases, the presence of CO as a side-product relaxed the V_{\max} requirement for the products, as V_{\max} tends to scale linearly with FE_{CO} . Moreover, the coproduction of a liquid product such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ with a gaseous product, that is, CO, does not pose a difficult product-separation problem. As a result, the coproduction of an economically less feasible product (CH_3OH , CH_4 , $\text{C}_2\text{H}_5\text{OH}$, C_2H_4) with a more feasible product (CO or HCOOH) present in a dif-

Table 2. Sensitivity analysis to study the effects of fluctuations in product price (C_p) and gross margin.^[a]

Product	C_p [\$ kg ⁻¹]	$V_{\max}^{[\text{b}]}$ [V]			$ E^{\circ}_{\text{cell}} ^{[\text{c}]}$ [V]
		GM ^[d] = 15	30	45	
HCOOH	0.84	4.68*	3.78*	2.88*	1.48
	1.20	6.87*	5.58*	4.29*	
CO	1.56	9.06*	7.38*	5.71*	1.34
	0.84	3.07*	2.52*	1.97*	
	1.20	4.40*	3.61*	2.83*	
CH_3OH	1.56	5.73*	4.71*	3.69*	1.21
	0.36	0.40	0.32	0.23	
	0.51	0.62	0.49	0.37	
CH_4	0.66	0.84	0.67	0.51	1.06
	0.15	0.07	0.06	0.04	
	0.21	0.11	0.09	0.07	
C_2H_4	0.27	0.14	0.11	0.09	1.17
	0.84	0.51	0.42	0.33	
	1.20	0.73	0.60	0.47	
$\text{C}_2\text{H}_5\text{OH}$	1.56	0.96	0.79	0.62	1.15
	0.56	0.50	0.40	0.30	
	0.80	0.74	0.60	0.45	
	1.04	0.98	0.80	0.61	

[a] $C_p \pm 30\%$ and gross margins of 15, 30, and 45% were used for the calculations; for all values, it was assumed that $C_E = \$0.12 \text{ kWh}^{-1}$. [b] Values marked by * represent economically viable conditions ($V_{\max} > |E^{\circ}_{\text{cell}}|$); all other values represent economically unfavorable conditions ($V_{\max} < |E^{\circ}_{\text{cell}}|$). [c] $|E^{\circ}_{\text{cell}}|$ values are reported under standard conditions [1 atm (0.1 MPa) and 25 °C] in aqueous media, and it is assumed that the O_2 evolution reaction at the anode has $E^{\circ} = -1.23 \text{ V}$ versus reversible hydrogen electrode (RHE). [d] Gross margin in [%].

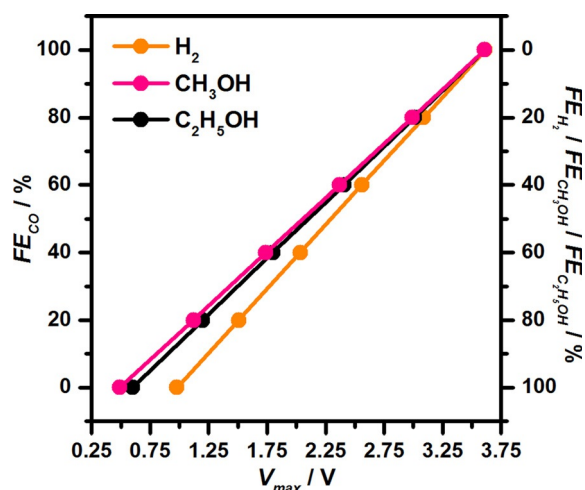


Figure 1. Calculated maximum operating cell potential (V_{\max}) for the production of binary mixtures of CO with H_2 , CH_3OH , and C_2H_5OH through the electroreduction of CO_2 ; $C_E = \$0.12 \text{ kWh}^{-1}$, gross margin = 30%.

ferent phase can be used as a process-design strategy to offset V_{\max} requirements.

Identifying suitable operating current density

As shown in Equation (7), j_{\min} is a function of λ , V , V_{\max} , C_{Er} and FE_p . Estimates for $\lambda_{\text{electrolyzer}}$ were obtained from the capital-cost analysis for a 25 kW direct H_2 PEM fuel cell stack in Ref. [31]. The overall electrolyzer design was assumed to consist of 70 individual stacks. Each individual stack (Figure 2) was made of

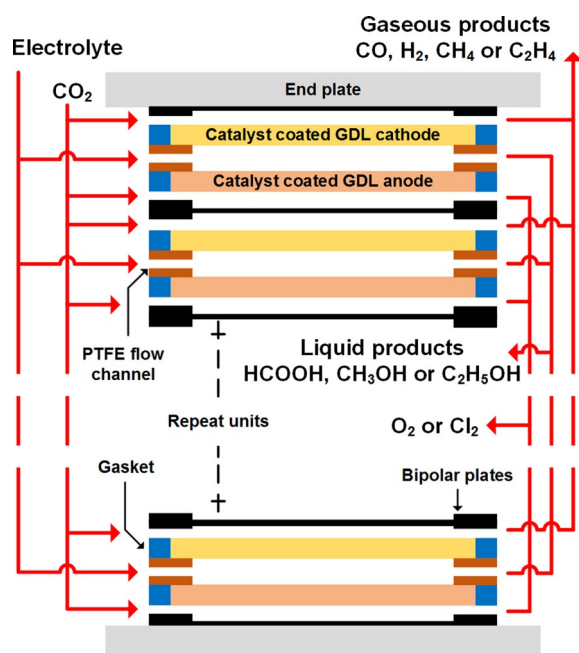


Figure 2. Schematic illustration of a CO_2 electrolyzer stack. Each stack consists of two aluminium end plates and 106 cells connected in series. Each cell is made up of two bipolar graphite plates that sandwich a catalyst-coated gas diffusion cathode, a PTFE electrolyte flow channel, and a catalyst-coated gas diffusion anode layer.

Parameter	Value
Active area per cell [cm^2]	400
Total number of cells in a stack	106
Total active area per stack [m^2]	4.24
Total number of stacks in the electrolyzer	70
Total active area of electrolyzer [m^2]	296.8
Plant runtime per year [h]	8000
Interest rate [%]	5
Loan term [years]	20

106 cells. As a result, the net active surface area of the electrolyzer was estimated to be 296.8 m^2 (Table 3). Liquid electrolytes were used for our analysis instead of the Nafion membrane used in in Ref. [31]. The use of liquid electrolytes is important for CO_2 electroreduction, especially if the desired result is the production of liquid products such as $HCOOH$, CH_3OH , or C_2H_5OH . To account for this change, a polytetrafluoroethylene-based (PTFE-based) electrolyte flow channel with a thickness of $0.0625''$ was added to the design to replace the Nafion membrane.^[32] The change in the electrolyzer cost as a result of this modification was considered in the model. The electrolyzer was estimated to run for 8000 h per year. If it is assumed that the capital required to set up this CO_2 electrolyzer is taken as a loan at an interest rate of 5% for a period of 20 years, $C_{\text{electrolyzer}}$ is $\$1.73 \text{ h}^{-1}$ (Table 4).

Part	Part total [\$]	Stack count	Stack total [\$]
Aluminium end plate	40.24	2	80.48
Bipolar graphite plate	6.81	107	728.67
PTFE flow channel	–	–	1095.21
Gaskets	2.62	212	555.44
Tie Rods	–	–	40
Capital cost per stack			2499.8
Total electrolyzer cost			174986
$C_{\text{electrolyzer}}$ [h^{-1}]			1.73

The cathode catalysts used in the analysis were Sn, Au, Ag, and Zn, and the anode catalyst was Pt. A loading (W_{cat}) of 0.5 mg cm^{-2} was used for the analysis. The C_{cat} values for Sn, Au, Ag, Zn, and Pt were assumed to be $\$1.5 \times 10^{-5}$,^[33] $\$4.06 \times 10^{-2}$,^[34] $\$5.5 \times 10^{-4}$,^[35] $\$1.7 \times 10^{-6}$,^[36] and $\$3.6 \times 10^{-2} \text{ mg}^{-1}$,^[37] respectively. A 2.0 M KOH solution at a purge flow rate (Q) of 5 mL min^{-1} through each stack was used as the electrolyte, and the $C_{\text{electrolyte}}$ was $\$1.465 \times 10^{-4} \text{ mL}^{-1}$.^[38] The gas diffusion layers (GDL) for the stacks were assumed to be 2 mm thick carbon paper dip-coated with PTFE, and the C_{GDL} value was taken as $\$0.006 \text{ cm}^{-2}$.^[31]

To validate the j_{\min} values predicted by the model, we again analyzed water electrolysis for H_2 production. A C_E value of $\$0.06 \text{ kWh}^{-1}$, t_{catdur} of 4000 h, $|V|$ of 1.6 V, and k_p of 0 (as no product separation required) were chosen as the design pa-

rameters. Pt was used as both the cathode and the anode catalyst. The model gave a j_{\min} of 465 mA cm^{-2} to break even (gross margin = 0%) over 20 years. The current state-of-the-art electrolyzers operate at a $j \approx 1 \text{ A cm}^{-2}$, which corresponds to a gross margin of 23%.

Next, we estimated the j_{\min} required for an economically viable CO and HCOO^- production process at a FE_p of 100%. A C_E value of $\$0.12 \text{ kWh}^{-1}$ (to account for the cost of CO_2 capture), t_{catdur} of 4000 h, and a $|V|$ of 2.25 V were considered for this analysis. Au was chosen as the cathode catalyst for CO production, and Sn was chosen as the cathode catalyst for HCOO^- production; Pt was the anode catalyst for both cases. With these inputs, the j_{\min} values required to produce CO and HCOO^- at a 30% gross margin are 212 and 56 mA cm^{-2} , respectively. In addition, other j_{\min} values that meet our criteria for economic viability as a function of $|V|$ and C_E for the production of CO and HCOO^- can be determined from Figure 3.

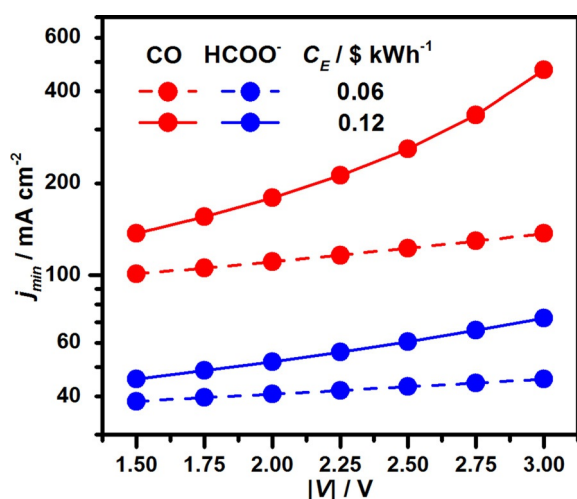


Figure 3. Minimum operating current density (j_{\min}) required for the production of CO and HCOO^- (assuming FE_{CO} , $\text{FE}_{\text{HCOO}^-} = 100\%$ respectively) as a function of cell potential ($|V|$) and electricity price (C_E). Cathode catalyst = Au for CO and Sn for HCOO^- production, anode catalyst = Pt, and $t_{\text{catdur}} = 4000 \text{ h}$. A 30% gross margin was assumed for the analysis.

As a significant fraction of the cost of CO and HCOO^- production is due to the catalyst, we derived j_{\min} as a function of t_{catdur} . The results shown in Figure 4 indicate that j_{\min} increases significantly for catalysts that show durabilities of approximately 2000 h or less. A catalyst durability of approximately 3000 h or more should be targeted because the j_{\min} value starts to level off after that. Typically, laboratory-scale studies of catalyst durability for the electroreduction of CO_2 to CO and HCOOH have lasted less than 10 h.^[7a-c] Thus, research should focus on the design of catalysts that are stable over several thousand hours. Different catalytic support materials should be explored as research directions to improve the stabilities of the current state-of-the-art catalysts. However, electrocatalytic systems that show very high activities but low durabilities might still be economically viable as long as the system meets the j_{\min} requirements derived from Equation (7).

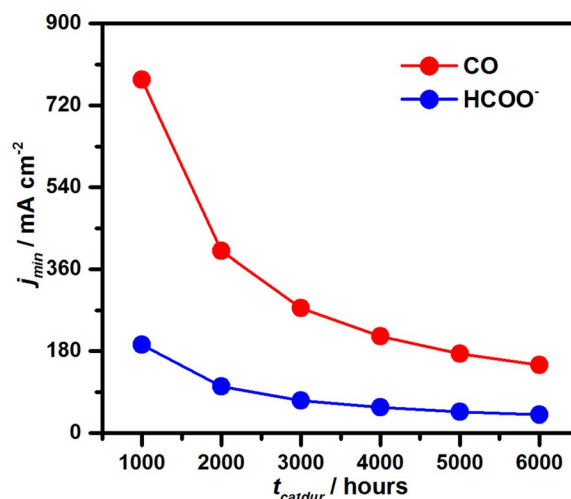


Figure 4. Minimum operating current density (j_{\min}) required for the production of CO and HCOO^- (assuming FE_{CO} , $\text{FE}_{\text{HCOO}^-} = 100\%$, respectively) as a function of catalyst durability (t_{catdur}). Cathode catalyst = Au for CO and Sn for HCOO^- production, anode catalyst = Pt, $C_E = \$0.12 \text{ kWh}^{-1}$, and $|V| = 2.25 \text{ V}$. A 30% gross margin was assumed for the analysis.

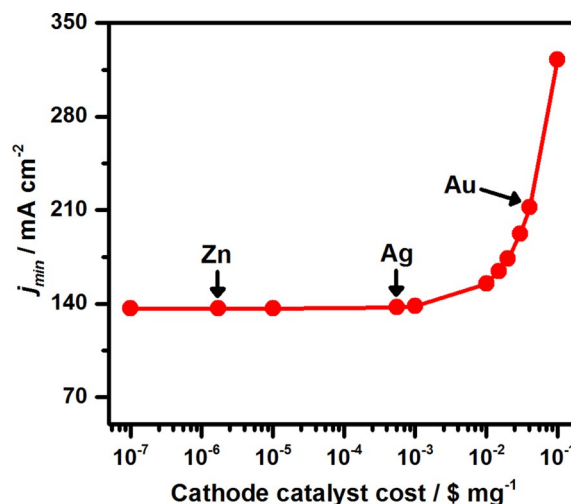


Figure 5. Minimum operating current density (j_{\min}) required for the production of CO (assuming $\text{FE}_{\text{CO}} = 100\%$) as a function of cathode-catalyst cost. $C_E = \$0.12 \text{ kWh}^{-1}$, $t_{\text{catdur}} = 4000 \text{ h}$, $|V| = 2.25 \text{ V}$, and anode catalyst = Pt. A 30% gross margin was assumed for the analysis.

We also analyzed whether the utilization of a cheaper cathode catalyst might be a better strategy for reducing the j_{\min} requirements for CO_2 reduction. As shown in Figure 5, the required j_{\min} shows the following trend: $\text{Zn} \approx \text{Ag} < \text{Au}$. As a result, for the same or even lower current density, a cheaper and more durable catalyst might be more economical. Caution should be exercised if the catalytic performance of an expensive catalyst is compared with that of a cheaper alternative, as other factors need to be taken into account. For CO_2 conversion to CO, the j_{\min} required for Zn is comparable to that for Ag for two reasons. First, the anode utilizes Pt, which becomes a major cost driver if a cathode catalyst cheaper than Ag is used. If the electrocatalytic system were to utilize an inexpen-

sive anode, that is, an O₂ evolution catalyst with a cost comparable to that of Zn, a j_{\min} as low as 69 mAcm⁻² would be required for an economically viable CO production process with Zn as the cathode catalyst and at a C_E of \$0.12 kWh⁻¹, t_{catdur} of 4000 h, and a $|V|$ of 2.25 V. The second reason behind the comparable j_{\min} requirements for Zn and Ag is the cost of the GDL (\$0.006 cm⁻²), which is 3.38× cheaper than that for Au but 21.8× more expensive than that for Ag and 7058× more expensive than that for Zn (assuming $W_{\text{cat}} = 0.5 \text{ mg cm}^{-2}$). Therefore, the GDL becomes a major cost driver if Zn and Ag are used as the catalysts. Further research into the development of inexpensive and durable GDLs will be required to lower the overall system cost and, hence, the j_{\min} required for an economically viable process.

Summary and Outlook

Although a significant amount of prior research has focused on the design of new catalysts, electrolytes, and electrocatalytic systems to tailor the electroreduction of CO₂ towards a particular product at low overpotentials, a comprehensive techno-economic insight into what performance levels are required for a commercially viable process is still lacking. The gross-margin model reported here defines such benchmarks for several different products of CO₂ electroreduction under different process conditions. Performance targets in terms of maximum operating cell potential (V_{max}), Faradaic efficiency (FE), catalyst durability (t_{catdur}), and minimum operating current density (j_{\min}) were derived using the model. The values of V_{max} obtained from the model indicate that the production of CO and HCOOH could soon be commercialized successfully. However, as the market for chemicals such as CH₃OH, CH₄, C₂H₅OH, and C₂H₄ is significantly larger than the market for CO and HCOOH, different process-design strategies such as coproduction with CO and HCOOH to offset V_{max} requirements, the use of CO as the raw material instead of CO₂, the direct utilization of flue gas, or the combination of the CO₂ capture and CO₂ conversion processes will be required for the electroreduction of CO₂ to become a significant stabilization wedge for the reduction of CO₂ emissions.

Unsurprisingly, an analysis of the catalyst durability and cost shows that the durabilities of CO₂ reduction catalysts need to be improved so that they last for thousands of hours. Optimized designs for the gas diffusion layer will also be required to further decrease the stack cost once cheap and durable catalysts have been identified. In addition, the utilization of cheap and durable catalysts for the anode reaction, that is, O₂ evolution, should also be considered in overall system performance studies.

Although some recent studies, especially those focusing on HCOOH production, have achieved current density values close to the j_{\min} values calculated here, very high cell potentials were often required to achieve these current densities; thus, the energy efficiency was reduced significantly. Moreover, the analyses of the commercial viabilities of the state-of-the-art systems are often hampered by the lack of information on durability and cell potentials.

Other researchers in the field can utilize the gross-margin model introduced here to analyze a variety of scenarios (such as different products combinations, selectivity ratios, and process designs) for the electroreduction of CO₂ to different value-added products or product mixtures. The model presented here uses the product price as the input and provides the associated required performance levels as the output. The model can also be used in reverse to estimate the cost of a product produced (in \$kg⁻¹) with the performance parameters (e.g., V , j , t_{catdur} , FE) as the inputs. Furthermore, with appropriate modifications, the model reported here could be applied more generally to other sustainable electrochemical processes (such as electrochemical CH₄ oxidation or NH₃ synthesis through N₂ and H₂O electrolysis) as a tool to identify the minimum performance levels needed for economic viability.

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