Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

Assessing the economic potential of large-scale, carbonate-formation-free CO_2 electrolysis

Xuechen Jing[1,2], Fengwang Li[2,*], Yuhang Wang[1,*]

[1]*Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Soochow University, 199 Ren'ai Road, Suzhou, Jiangsu, 215123, China.*

[2]*School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia.*

[*]Correspondence to: Yuhang Wang (yhwang1988@suda.edu.cn) (Y.W.) and Fengwang Li (fengwang.li@sydney.edu.au).

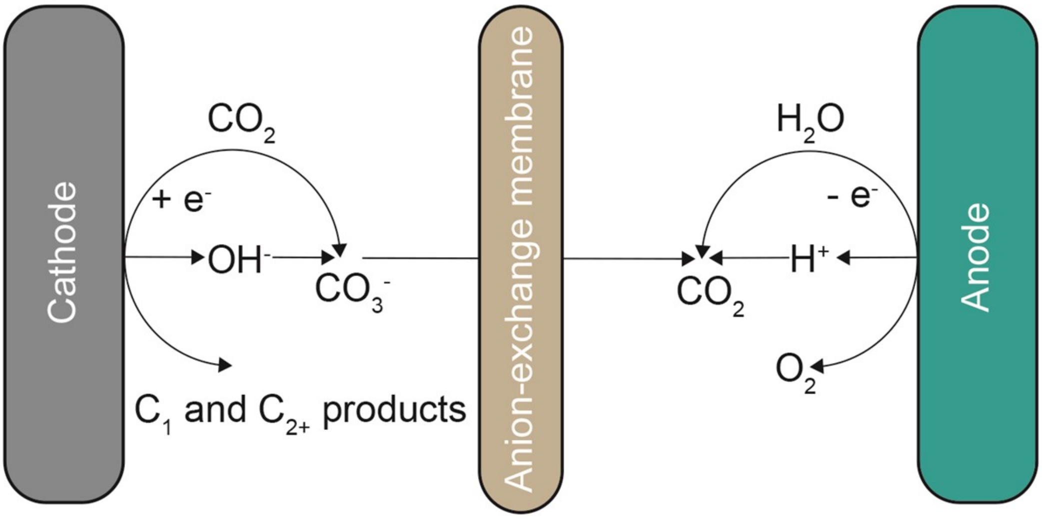

Figure S1. Carbonate formation. A schematic illustration of carbonate formation and crossover during CO_2 electroreduction in an MEA using an anion-exchange membrane.

Note S1. The modeling methods.

We develop the TEA model according to the previous reports,[1,2] and list the related parameters (Table S5) contributing to the ethanol production cost. Furthermore, we compare the results of two situations with and without carbonate formation during CO_2 electroreduction.

The modeling inputs are tabulated below (taking ethanol production as an example):

Table S1. The input parameters of sample calculations.

Parameters	**Value**
Production rate	100 tonne/day
Ethanol molecular weight	46.07 g/mole
Ethanol density	0.789 kg/L
CO_2 molecular weight	44 g/mole
CO_2 ratio	2
Electrons transferred	12
Reference current density	400 mA/cm^2
Balance of plant	50%
Lang factor	1
Capacity factor	0.9
Discount rate	0.07
CO_2 crossover ratio	3
The volume ratio of electrolyte	100
PSA reference cost	1989043 USD
PSA reference scale	1000 m^3/hour
PSA scaling factor	0.7

PSA energy consumed	0.25 kWh/ m^3
Distillation reference cost	4162240 USD
Distillation reference scale	1000 L/min
Distillation scaling factor	0.7
Distillation reference operating cost	9895.17 USD/day
Electrolyte lifetime	1 year
H_2O product ratio	9
H_2O price	1 USD/tonne
CO_2 price	40 USD/tonne
Electricity price	0.05 USD/kWh
Electrolyzer price	550 USD/kW
Cell voltage	3.5 V
Faradaic efficiency	30 %
Single-pass utilization	25 %
Input current density	100 mA/cm^2
System lifetime	10 year
MEA lifetime	1 year

CO_2 and H_2O cost calculation

The CO_2 cost can be calculated using Equation 1:

$$CO_2\ required\ \left(\frac{tonne}{day}\right) = product\ output\ \left(\frac{tonne}{day}\right) \times \frac{CO_2\ molecular\ weight\ (}{Product\ molecular\ weight} \tag{1}$$

Plugging in the model ethanol output rate, CO_2 molecular weight, ethanol molecular weight, CO_2 ratio, and CO_2 single-pass utilization:

$$CO_2\ required \left(\frac{tonne}{day}\right) = 100 \left(\frac{tonne}{day}\right) \times \frac{44 \left(\frac{g}{mol}\right)}{46.07 \left(\frac{g}{mol}\right)} \times \frac{2 \left(\frac{CO_2}{product}\right)}{25\%} = 764.05 \left(\frac{tonne}{day}\right) \tag{1b}$$

The CO_2 purchased cost is:

$$CO_2\ cost\ (\$\ per\ tonne\ product) = CO_2 required \left(\frac{tonne}{day}\right) \times \frac{CO_2\ price\ (\frac{\$}{tonne})}{Production\ rate\ (\frac{tonne\ product}{day})} \tag{2}$$

$$\begin{aligned} &CO_2\ cost\ (\$\ per\ tonne\ product) \\ &\quad = 764.05 \left(\frac{tonne}{day}\right) \times \frac{40\ (\frac{\$}{tonne})}{100\ (\frac{tonne\ product}{day})} = 305.62\ (\$\ per\ tonne\ product) \end{aligned} \tag{2b}$$

The water cost calculation is:

$$\begin{aligned} &H_2O\ required \left(\frac{tonne}{day}\right) \\ &\quad = product\ output \left(\frac{tonne}{day}\right) \times \frac{H_2O\ molecular\ weight \left(\frac{g}{mol}\right)}{Product\ molecular\ weight \left(\frac{g}{mol}\right)} \times molar\ ratio \left(\frac{H}{pro}\right. \end{aligned} \tag{3}$$

$$H_2O\ required\ \left(\frac{tonne}{day}\right) = 100\ \left(\frac{tonne}{day}\right)\ \times \frac{18\left(\frac{g}{mol}\right)}{46.07\ \left(\frac{g}{mol}\right)} \times 9 = 351.64\ \left(\frac{tonne}{day}\right) \tag{3b}$$

$$H_2O\ cost\ (\$\ per\ tonne\ product) = H_2Orequired\ \left(\frac{tonne}{day}\right) \times \frac{H_2O\ price\ (\frac{\$}{tonne})}{Production\ rate\ (\frac{tonne\ product}{day})} \tag{4}$$

$$H_2O\ cost\ (\$\ per\ tonne\ product) = 351.64\ \left(\frac{tonne}{day}\right) \times \frac{1\ \ (\frac{\$}{tonne})}{100\ (\frac{tonne\ product}{day})} = 3.52\ (\$\ per\ tonne\ pr \tag{4b}$$

Electrolyzer capital cost

Firstly, we need to transfer the unit of production rate from tonne/day to mole/s to calculate the electrolyzer capital cost.

$$Production\ rate\ \left(\frac{mol}{s}\right) = \frac{Production\ rate\ (\frac{g}{day})}{product\ molecular\ weight\ \left(\frac{g}{mol}\right) \times 86400(\frac{s}{day})} \tag{5}$$

$$Production\ rate\ \left(\frac{mol}{s}\right) = \frac{1 \times 10^8\ (\frac{g}{day})}{46.07\ \left(\frac{g}{mol}\right) \times 86400(\frac{s}{day})} = 25.12\left(\frac{mol}{s}\right) \tag{5b}$$

Based on the ethanol production rate, we can obtain total current density by use following equation:

$$Totol\ current\ (A) = \frac{Production\ rate\ \left(\frac{mol}{s}\right) \times electrons\ transferred\ \times 96485\ (\frac{sA}{mol})}{FE/100} \tag{6}$$

$$Totol\ current\ (A) = \frac{25.12\ \left(\frac{mol}{s}\right) \times 12\ \times 96485\ (\frac{sA}{mol})}{30/100} = 96958935.28(A) \tag{6b}$$

The discount rate and system lifetime are already known, so the capital recovery factor (CRF) of electrolyzer can be got:

$$CRF_{electrolyzer} = \frac{Discount\ rate\ \times (1 + discount\ rate)^{:System\ lifetime}}{(1 + discount\ rate)^{System\ lifetime} - 1} \tag{7}$$

$$CRF_{electrolyzer} = \frac{0.07\ \times (1 + 0.07)^{10}}{(1 + 0.07)^{10} - 1} = 0.1424 \tag{7b}$$

Total electrolyzer capital cost is:

$$Total\ electrolyzer\ capital\ cost\ (\$) = Power\ consumption\ (kW) \times Electrolyzer\ price\ (\frac{\$}{kW}) \times \frac{Base\ current\ density\ (\frac{n}{c}}{Input\ current\ density\ (\frac{n}{c}} \tag{8}$$

$$Total\ electrolyzer\ capital\ cost\ (\$) = 96958935.28\ (A) \times 3.5\ (V)\ \div 1000\ (s) \times 550\ \left(\frac{\$}{kW}\right) \times \frac{400\ \left(\frac{mA}{cm^2}\right)}{100\ \left(\frac{mA}{cm^2}\right)} = 746583801.6 \tag{8b}$$

Therefore, electrolyzer capital cost per tonne product is:

$$Electrolyer\ capital\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{CRF_{electrolyzer}\ \times Total\ electrolyzer\ cost\ (\$)}{Capacity\ factor\ \times 365\left(\frac{days}{year}\right) \times production\ rate\ (\frac{t}{}} \quad (9)$$

$$Electrolyer\ capital\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{0.1424\ \times 746583801.6(\$)}{0.9\ \times 365\left(\frac{days}{year}\right) \times 100\left(\frac{tonne}{day}\right)} = 3235.82\left(\frac{\$}{tonne\ p}\right. \quad (9b)$$

Catalyst and membrane (CM) cost:

We assume that the CM cost is equal to 5% of the total electrolyzer capital cost. Thus, it can be obtained using the following calculations.

$$CRF_{CM} = \frac{Discount\ rate\ \times (1 + discount\ rate)^{:CM\ lifetime}}{(1 + discount\ rate)^{CM\ lifetime} - 1} \quad (10)$$

$$CRF_{CM} = \frac{0.07\ \times (1 + 0.07)^1}{(1 + 0.07)^1 - 1} = 1.07 \quad (10b)$$

$$CM\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{CRF_{CM} \times Total\ electrolyzer\ capital\ cost\ (\$) \times 0.05}{Capacity\ factor \times 365\left(\frac{days}{year}\right) \times production\ rate\ (\frac{tonne}{day})} \quad (11)$$

$$CM\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{1.07 \times 746583801.6(\$)\ \times 0.05}{0.9 \times 365\left(\frac{days}{year}\right) \times 100\ (\frac{tonne}{day})} \quad (11b)$$

Electrolyzer operating and other operating cost

The operating cost of electrolyzer is based on the power consumption and electricity price:

$$Electrolyzer\ operating\ cost\left(\frac{\$}{tonne\ product}\right) = \frac{Power\ consumption\ \times 24\left(\frac{hr}{day}\right) \times electricity\ price\ (\frac{\$}{kWh})}{Production\ rate\ (\frac{tonne}{day})} \tag{12}$$

$$Electrolyzer\ operating\ cost\left(\frac{\$}{tonne\ product}\right) = \frac{96958935.28\ (A) \times 3.5\ (V)\ \div 1000\ (s) \times 24\left(\frac{hr}{day}\right) \times e = 0.05\ (\frac{\$}{kWh})}{100\ (\frac{tonne}{day})} = 4072.28\left(\frac{\$}{tonne\ product}\right) \tag{12b}$$

Other operating cost is

$$Other\ operating\ cost\left(\frac{\$}{tonne\ product}\right) = electricity\ cost\ (\frac{\$}{tonne\ product}) \times 0.1) \tag{13}$$

$$Other\ operating\ cost\left(\frac{\$}{tonne\ product}\right) = 4072.28\left(\frac{\$}{tonne\ product}\right) \times 0.1 = 407.23\left(\frac{\$}{tonne\ produ}\right. \tag{13b}$$

Cathode PSA cost

We use pressure swing adsorption (PSA) as the cathode gas separation approach, which is based on a reference cost of \$1989043 of 1000 m^3/hr flowrate (scaling factor 0.7).[3,4]

$$Input\ CO_2\ flow\ rate\left(\frac{m^3}{hr}\right) = \frac{CO_2\ required\left(\frac{tonne}{day}\right) \times 1000\ \times 24.5}{CO_2\ molecilar\ weight\left(\frac{g}{mol}\right) \times 24\left(\frac{hr}{day}\right)} \tag{14}$$

$$Input\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = \frac{764.05\ \left(\frac{tonne}{day}\right) \times 1000\ \times 24.5}{44\ \left(\frac{g}{mol}\right) \times 24\ (\frac{hr}{day})} = 17726.65\ (\frac{m^3}{hr}) \tag{14b}$$

$$Output\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = Input\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) \times (1 - single\ pass\ utilization) \tag{15}$$

$$Output\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = 17726.65\ \left(\frac{m^3}{hr}\right) \times (1 - 0.25) = 13294.99\left(\frac{m^3}{hr}\right) \tag{15b}$$

$$H_2\ production\ \left(\frac{mol}{hr}\right) = \frac{Total\ current\ (A) \times (1 - FE) \times 3600\ (\frac{s}{hr})}{2\ \left(\frac{electrons}{product}\right) \times 96485(\frac{sA}{mol})} \tag{16}$$

$$H_2\ production\ \left(\frac{mol}{hr}\right) = \frac{96958935.28(A) \times (1 - 0.3) \times 3600\ (\frac{s}{hr})}{2\ \left(\frac{electrons}{product}\right) \times 96485(\frac{sA}{mol})} = 1266189.13\left(\frac{mol}{hr}\right) \tag{16b}$$

$$H_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = 1266189.13\ \left(\frac{mol}{hr}\right) \times \frac{24.5}{1000} = 31021.63\left(\frac{m^3}{hr}\right) \tag{17}$$

$$Output\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = Input\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) \times (1 - single\ pass\ utilization) \tag{18}$$

$$Output\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = 17726.65\ \left(\frac{m^3}{hr}\right) \times (1 - 0.25) = 13294.99\left(\frac{m^3}{hr}\right) \tag{18b}$$

$$Cathode\ PSA\ capital\ cost\ (\$) = PSA\ ref\ cost\ (\$) \times (\frac{Total\ cathode\ flow\ rate\ (\frac{m^3}{hr})}{PSA\ ref\ scale\ (\frac{m^3}{hr})})^{PSA\ scaling\ facor} \tag{19}$$

$$Cathode\ PSA\ capital\ cost\ (\$) = 1989043\ (\$) \times (\frac{44316.62\ (\frac{m^3}{hr})}{1000\ (\frac{m^3}{hr})})^{0.7} = 28264467.66(\$) \tag{19b}$$

$$Cathode\ Captial\ PSA\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{CRF\ electrolyzer\ \times Cathode\ PSA\ capital\ cost\ (\$)}{Capacity\ factor\ \times 365 \times Production\ rate\ (\frac{tonne}{day})} \tag{20}$$

$$Cathode\ Captial\ PSA\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{0.1424 \times 28264467.66(\$)}{0.9\ \times 365 \times 100\ (\frac{tonne}{day})} = 122.50\ \left(\frac{\$}{tonne\ produc}\right. \tag{20b}$$

$$Cathode\ PSA\ operating\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{PSA\ energy\ consumed\ \left(\frac{kWh}{m^3}\right) \times total\ flow\ rate\ \left(\frac{m^3}{hr}\right)}{Production\ rate\ \left(\frac{tor}{dc}\right.} \tag{21}$$

$$Cathode\ PSA\ operating\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{0.25\ \left(\frac{kWh}{m^3}\right) \times 44316.62\ \left(\frac{m^3}{hr}\right) \times 24\left(\frac{hr}{day}\right) \times 0.05\ \left(\frac{\$}{kWh}\right)}{100\ \left(\frac{tonne}{day}\right)} = 132.95\left(\frac{\$}{tonne\ product}\right) \tag{21b}$$

Anode PSA cost

We assume that there are two phenomena in this system, with carbonate formation and without carbonate formation.

For the first situation, we do not need to separate the anode gas, because it only has O_2. However, when the system with carbonate formation, it means that we can get CO_2 and O_2 at the anode side, so we need to separate them by using PSA. Furthermore, when the system has carbonate formation, the maximum CO_2 single-pass utilization is 25%, and all the unreacted CO_2 is going through the membrane to the anode side, so we only need to calculate the anode PSA cost instead of cathode PSA cost.

$$
\begin{aligned}
&Crossover\ CO_2\left(\frac{tonne\ CO_2}{tonne\ product}\right) \\
&= molar\ ratio\ \left(\frac{CO_2}{product}\right) \times crossover\ ratio \times \frac{CO_2\ molecular\ weight\ (\frac{g}{mol})}{Product\ molecular\ weight\ (\frac{9}{mol})} \\
&= 2 \times 3 \times \frac{44\,\frac{g}{mol}}{46.7\left(\frac{g}{mol}\right)} = 5.73\left(\frac{tonne\ CO_2}{tonne\ product}\right)
\end{aligned}
\tag{22}
$$

$$
\begin{aligned}
&Crossover\ CO_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) \\
&= Crossover\ CO_2\ \left(\frac{tonne\ CO_2}{tonne\ product}\right) \times Prodution\ rate\ (\\
&= 5.73\left(\frac{tonne\ CO_2}{tonne\ product}\right) \times 100\left(\frac{tonne}{day}\right) \times \frac{24.5 \times 10}{24\left(\frac{hr}{day}\right) \times 44}
\end{aligned}
\tag{23}
$$

$$
O_2\ flow\ rate\ \left(\frac{m^3}{hr}\right) = \frac{Total\ current\ density\ (A) \times 3600\left(\frac{s}{hr}\right) \times 24.5}{4\left(\frac{electrons}{mole\ O2}\right) \times 96485 \times 1000}
\tag{24}
$$

$$O_2\,flow\ rate\left(\frac{m^3}{hr}\right)=\frac{96958935.28(A)\times 3600\left(\frac{s}{hr}\right)\times 24.5}{4\left(\frac{electrons}{mole\ O_2}\right)\times 96485\times 1000}=22158.31\left(\frac{m^3}{hr}\right) \tag{24b}$$

$$Anode\ PSA\ capital\ cost\ (\$)=PSA\ ref\ cost\ (\$)\times\left(\frac{Total\ anode\ flow\ rate\left(\frac{m^3}{hr}\right)}{PSA\ ref\ scale\left(\frac{m^3}{hr}\right)}\right)^{PSA\ scaling\ facor} \tag{25}$$

$$Anode\ PSA\ capital\ cost\ (\$)=1989043\ (\$)\times\left(\frac{35453.30\left(\frac{m^3}{hr}\right)}{1000\left(\frac{m^3}{hr}\right)}\right)^{0.7}=24177077.42\ (\$) \tag{25b}$$

$$Anode\ Captial\ PSA\ cost\left(\frac{\$}{tonne\ product}\right)=\frac{CRF_{electrolyzer}\times Anode\ PSA\ capital\ cost\ (\$)}{Capacity\ factor\ \times 365\times Production\ rate\ (\frac{tonne}{day})} \tag{26}$$

$$Anode\ Captial\ PSA\ cost\left(\frac{\$}{tonne\ product}\right)=\frac{0.1424\ \times 24177077.42\ (\$)}{0.9\ \times 365\times 100\ (\frac{tonne}{day})}=104.79 \tag{26b}$$

$$\begin{aligned}&Anode\ PSA\ operating\ cost\left(\frac{\$}{tonne\ product}\right)\\&=\frac{PSA\ energy\ consumed\left(\frac{kWh}{m^3}\right)\times total\ flow\ rate\left(\frac{m^3}{hr}\right.}{Production\ rate\ (\frac{to}{d}}\end{aligned} \tag{27}$$

$$Anode\ PSA\ operating\ cost\ \left(\frac{\$}{tonne\ product}\right) = \frac{0.25\left(\frac{kWh}{m^3}\right) \times 35453.30\left(\frac{m3}{hr}\right) \times 24\left(\frac{hr}{day}\right) \times 0.05\ (\frac{\$}{kWh})}{100\ (\frac{tonne}{day})} = 106.36\left(\frac{\$}{tonne\ produc}\right. \quad (27b)$$

Anolyte cost (only for water)

$$Electrolyzer\ surface\ area\ (m^2) = \frac{Total\ current\ (A) \times 1000}{Current\ density\ (\frac{mA}{cm^2}) \times 10000} \quad (28)$$

$$Electrolyzer\ surface\ area\ (m^2) = \frac{96958935.28(A) \times 1000}{100\ (\frac{mA}{cm^2}) \times 10000} = 96958.94\ (\ m^2) \quad (28b)$$

$$Electrolyte\ weight\ (tonne) = Electrolyzer\ surface\ area\ \left(m^2\right) \times Volume\ ratio\ of\ electrolyte\ (\frac{L}{m^2}) \times \frac{1\ (\frac{kg}{L}}{1000\ (\frac{}{to}} \quad (29)$$

$$Electrolyte\ weight\ (tonne) = 96958.94\ (\ m^2) \times 100\left(\frac{L}{m^2}\right) \times \frac{1\left(\frac{kg}{L}\right)}{1000\left(\frac{kg}{tonne}\right)} = 9695.89\ (tonne) \quad (29b)$$

$$Anolyte\ cost\ (\$) = Electrolyte\ weight\ (tonne) \times water\ price\ (\frac{\$}{tonne}) \quad (30)$$

$$Anolyte\ cost\ (\$) = 9695.89\ (tonne) \times 1\left(\frac{\$}{tonne}\right) = 9695.89(\$) \quad (30b)$$

$$CRF\ anolyte = \frac{Discount\ rate\ \times (1 + discount\ rate)^{Anolyte\ lifetime}}{(1 + discount\ rate)^{Anolyte\ lifetime} - 1} = 1.07 \tag{31}$$

$$\begin{aligned} &Anolyte\ cost\ \left(\frac{\$}{tonne\ product}\right) \\ &= \frac{CRF\ anolyte\ \times anolyte\ cost\ (\$)}{Capacity\ factor \times 365\ \left(\frac{days}{year}\right) \times Productionrate\ (\frac{tonne}{day})} = \frac{}{0.9 \times} \\ &= 0.3158\left(\frac{\$}{tonne\ product}\right) \end{aligned} \tag{32}$$

Distillation cost

$$\begin{aligned} &Liquid\ product\ solution\ flow\ rate\ \left(\frac{m^3}{hr}\right) \\ &= Liquid\ product\ flow\ rate\ \left(\frac{m^3}{hr}\right) + water\ solvent\ flow\ rate\ \left(\frac{m^3}{hr}\right) \\ &= \frac{Production\ rate\ \left(\frac{tonne}{day}\right) \times 10}{Product\ desity\ \left(\frac{kg}{L}\right) \times 24(\frac{hrs}{day})} = \frac{100\ \left(\frac{tonne}{day}\right) \times 10}{0.789\left(\frac{kg}{L}\right) \times 24(\frac{hrs}{day})} = 52.81\left(\frac{m^3}{hr}\right) \end{aligned} \tag{33}$$

$$\begin{aligned} &Distillation\ capital\ cost\ (\$) \\ &= Distillation\ ref\ cost\ (\$) \times \left(\frac{Liquid\ product\ solution\ flow\ rate\ \left(\frac{m}{h}\right.}{Distillation\ ref\ scale\ \left(\frac{L}{min}\right) \times 6}\right. \\ &= 4162240\ (\$) \times \left(\frac{52.81\ \left(\frac{m^3}{hr}\right) \times 1000\ \left(\frac{L}{m^3}\right)}{1000\ \left(\frac{L}{min}\right) \times 60\ \left(\frac{mins}{hr}\right)}\right)^{0.7} = 3806444.24(\$) \end{aligned} \tag{34}$$

$$\mathit{Distillation\ capital\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) = \frac{\mathit{CRF\ electrolyzer}\ \times \mathit{distillation\ capital\ \ cost}\ (\$)}{\mathit{Capacity\ factor}\ \times 365 \times \mathit{Production\ rate}\ (\frac{\mathit{tonne}}{\mathit{day}})} = \frac{0.1424\ \times 3806444.24(\$)}{0.9\ \times 365 \times 100\ (\frac{\mathit{tonne}}{\mathit{day}})} = 16.50\left(\frac{\$}{\mathit{tonne\ product}}\right) \tag{35}$$

$$\mathit{Distillation\ operating\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) = \frac{\mathit{Distillation\ ref\ operating\ cost}\ (\frac{\$}{\mathit{day}}) \times \frac{\mathit{Liquid\ product\ solution}\ \mathit{j}}{\mathit{Distillation\ ref\ sc}}}{\mathit{Production\ rate}\ (\frac{\mathit{tonne}}{\mathit{day}})} = \frac{9895.17\ (\frac{\$}{\mathit{day}}) \times \frac{52.81\left(\frac{m^3}{hr}\right) \times 1000\ (\frac{L}{m3})}{1000\left(\frac{L}{min}\right) \times 60\left(\frac{mins}{hr}\right)}}{100\ (\frac{\mathit{tonne}}{\mathit{day}})} = 87.09\left(\frac{\$}{\mathit{tonne\ product}}\right) \tag{36}$$

Balance of plant and installation cost without carbonate formation

$$\mathit{Total\ captial\ cosst}\left(\frac{\$}{\mathit{tonne\ product}}\right) = \mathit{Electolyzer\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{CM\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{C}\ \left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{Distillation\ capital\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) = 3235.82 + 1215.90 + 122.50 + 16.50 = 4590.72\left(\frac{\$}{\mathit{tonne\ product}}\right) \tag{37}$$

$$BoP\left(\frac{\$}{tonne\ product}\right) = BoP\ factor\ \times Total\ capital\ cost\left(\frac{\$}{tonne\ product}\right) = 0.5 \times 4590.72\left(\frac{\$}{tonne\ produ}\right. = 2295.36\left(\frac{\$}{tonne\ product}\right) \tag{38}$$

$$Installation\ cost\left(\frac{\$}{tonne\ product}\right) = Lang\ factor\ \times Total\ capital\ cost\left(\frac{\$}{tonne\ product}\right) = 1 \times 4590.72\left(\frac{\$}{tonne\ produ}\right. = 4590.72\left(\frac{\$}{tonne\ product}\right) \tag{39}$$

Balance of plant and installation cost with carbonate formation

$$Total\ captial\ cosst\left(\frac{\$}{tonne\ product}\right) = Electolyzer\ cost\left(\frac{\$}{tonne\ product}\right) + CM\ cost\left(\frac{\$}{tonne\ product}\right) + A \left(\frac{\$}{tonne\ product}\right) + Distillation\ capital\ cost\left(\frac{\$}{tonne\ product}\right) = 3235.82 + 1215.90 + 104.79 + 16.50 = 4573.00\left(\frac{\$}{tonne\ product}\right) \tag{40}$$

$$BoP\left(\frac{\$}{tonne\ product}\right) = BoP\ factor\ \times Total\ capital\ cost\left(\frac{\$}{tonne\ product}\right) = 0.5 \times 4573.00\left(\frac{\$}{tonne\ produ}\right. = 2286.50\left(\frac{\$}{tonne\ product}\right) \tag{41}$$

$$\begin{aligned} &Installation\ cost\ \left(\frac{\$}{tonne\ product}\right) \\ &\quad = Lang\ factor\ \times Total\ capital\ cost\ \left(\frac{\$}{tonne\ product}\right) = 1 \times 4573.00\left(\frac{\$}{tonne\ produ}\right. \\ &\quad = 4573.00\left(\frac{\$}{tonne\ product}\right) \end{aligned} \tag{42}$$

Total production cost of ethanol based the model we developed (without carbonate formation):

$$\begin{aligned} &Total\ production\ cost\ \left(\frac{\$}{tonne\ product}\right) \\ &\quad = CO_2\ cost\left(\frac{\$}{tonne\ product}\right) + H_2O\ cost\left(\frac{\$}{tonne\ product}\right) + electrolyzer\ operating \\ &\quad \left(\frac{\$}{tonne\ product}\right) + electrolyzer\ capital\ cost\left(\frac{\$}{tonne\ product}\right) + other\ operating\ c \\ &\quad \left(\frac{\$}{tonne\ product}\right) + cathode\ PSA\ capital\ \&\ operating\ cost\left(\frac{\$}{tonne\ product}\right) \\ &\quad + distillation\ capital\ \&\ operating\ cost\left(\frac{\$}{tonne\ product}\right) + BoP\ cost\left(\frac{\$}{tonne\ produ}\right. \\ &\quad + installation\ cost\left(\frac{\$}{tonne\ product}\right) \\ &\quad = 305.62 + 15.24 + 4072.28 + 3235.82 + 407.23 + 255.45 + 103.59 + 2295.36 + \\ &\quad = 15281.31\left(\frac{\$}{tonne\ product}\right) \end{aligned} \tag{43}$$

Total production cost of ethanol based the model we developed (with carbonate formation):

$$
\begin{aligned}
&\mathit{Total\ production\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right)\\
&\quad = CO_2\ \mathit{cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + H_2O\ \mathit{cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{electrolyzer\ operating}\\
&\quad \left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{electrolyzer\ capital\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{other\ operating\ c}\\
&\quad \left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{anode\ PSA\ capital\ \&\ operating\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right)\\
&\quad + \mathit{distillation\ capital\ \&\ operating\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right) + \mathit{BoP\ cost}\left(\frac{\$}{\mathit{tonne\ produc}}\right.\\
&\quad + \mathit{installation\ cost}\left(\frac{\$}{\mathit{tonne\ product}}\right)\\
&\quad = 305.62 + 15.24 + 4072.28 + 3235.82 + 407.23 + 211.15 + 103.59 + 2286.50 +\\
&\quad = 15210.43\left(\frac{\$}{\mathit{tonne\ product}}\right)
\end{aligned}
\tag{44}
$$

Table S2. The input parameters for the univariate analysis

Parameters	**Highly optimized**	**Optimized**	**Base**
Faradaic efficiency (%)	90	60	30
Current density (mA/cm^2)	1000	500	100
Electricity cost (cent/kWh)	1	3	5
Cell voltage (V)	1.5	2.5	3.5
Single-pass utilization (%)	50	25	10
System lifetime (year)	10	20	30
Electrolyzer cost ($/kW)	250	400	550
CO_2 price ($/tonne)	20	30	40
MEA lifetime (year)	5	3	1

Table S3. The result of the univariate analysis for methanol production.

Methanol production cost (USD/tonne)			
Variate	**Highly optimized**	**Optimized**	**Base**
Faradaic efficiency	996.6	1335.6	2340.9
Current density	1223.3	1335.6	2233.9
Electricity price	856.4	1335.6	1814.8
Cell voltage	969.7	1335.6	1701.5
Single-pass utilization	1211.9	1335.6	1690.3
System lifetime	1287.8	1335.6	1501.7
Electrolyzer price	1251.4	1335.6	1419.8
CO_2 price	1280.7	1335.6	1390.5
MEA lifetime	1326.8	1335.6	1379.4

Table S4. The result of the univariate analysis for ethanol production.

Ethanol production cost (USD/tonne)			
Parameters	**Highly optimized**	**Optimized**	**Base**
Faradaic efficiency	1327.5	1795.7	3185.9
Current density	1639.5	1795.7	3045.2
Electricity cost	1129.2	1795.7	2462.2
Cell voltage	1286.8	1795.7	2304.6
Single-pass utilization	1627.6	1795.7	2279.5
System lifetime	1732.7	1795.7	2014.8
Electrolyzer cost	1678.6	1795.7	1912.9
CO_2 price	1719.3	1795.7	1872.1
MEA lifetime	1783.6	1795.7	1856.7

Table S5. The result of the univariate analysis for n-propanol production.

n-Propanol production cost (USD/tonne)			
Parameters	**Highly optimized**	**Optimized**	**Base**
Faradaic efficiency	1501.1	2038.1	3633.2
Current density	1858.5	2038.1	3475.1
Electricity cost	1271.6	2038.1	2804.7
Cell voltage	1452.9	2038.1	2623.4
Single-pass utilization	1846.6	2038.1	2590.1
System lifetime	1967.2	2038.1	2284.8
Electrolyzer cost	1903.4	2038.1	2172.8
CO_2 price	1950.3	2038.1	2126.0
MEA lifetime	2024.2	2038.1	2108.3

Table S6. The result of the univariate analysis for ethylene production.

Ethylene production cost (USD/tonne)			
Parameters	**Highly optimized**	**Optimized**	**Base**
Faradaic efficiency	2053.4	2839.1	5173.1
Current density	2563.9	2839.1	5040.9
Electricity cost	1734.9	2839.1	3943.4
Cell voltage	1988.8	2839.1	3689.5
Single-pass utilization	2573.4	2839.1	3610.3
System lifetime	2738.6	2839.1	3188.7
Electrolyzer cost	2633.0	2839.1	3045.3
CO_2 price	2805.9	2839.1	3006.1
MEA lifetime	2713.7	2839.1	2964.6

Table S7. The summary of production costs in the base, optimized, and highly optimized cases.

Product	**Condition**	**Chemicals (CO_2 and H_2O)**	**Electrolyzer cost (capital and operating)**	**Other operating cost**	**PSA**	**Distillation**	**BoP**	**Installation**	**Total cost**
Methanol	**Highly optimized case**	69	92	8	16	96	16	33	**331**
	Optimized case	179	707	63	68	98	73	147	**1336**
	Base case	564	5254	293	288	103	1676	3352	**11530**
Ethanol	**Highly optimized case**	91	128	12	20	96	20	40	**408**
	Optimized case	244	984	87	90	98	97	195	**1796**
	Base case	779	7308	407	383	104	2319	4638	**15939**
n-Propanol	**Highly optimized case**	103	147	13	23	95	22	44	**447**
	Optimized case	279	1132	100	101	96	110	220	**2038**
	Base case	894	8404	468	432	102	2662	5324	**18287**
Ethylene	**Highly optimized case**	151	214	19	50	-	32	63	**529**
	Optimized case	403	1653	143	172	-	156	312	**2839**
	Base case	1287	13996	669	674	-	3798	7596	**28020**

Table S8. The results of the waterfall analysis for methanol.

Methanol production cost roadmap (USD/tonne)			
Parameters	**Before optimization**	**After optimization**	**Cost reduction**
Faradaic efficiency	11048.4	3955.6	7092.8
Current density	3955.6	1817.4	2138.2
Cell voltage	1817.4	1255.5	561.9
Single-pass utilization	1255.5	1073.2	182.3
Electrolyzer operting cost	1073.2	572.3	500.9
Electrolyzer capital cost	572.3	498.2	74.0
System lifetime	498.2	432.8	65.5
MEA lifetime	432.8	424.0	8.8
CO_2 price	424.0	369.1	54.9

Table S9. The results of the waterfall analysis for ethanol.

Ethanol production cost roadmap (USD/tonne)			
Parameters	**Before optimization**	**After optimization**	**Cost reduction**
Faradaic efficiency	15281.3	5432.9	9848.4
Current density	5432.9	2458.8	2974.1
Cell voltage	2458.8	1677.2	781.6
Single-pass utilization	1677.2	1430.6	246.6
Electrolyzer operting cost	1430.6	733.8	696.8
Electrolyzer capital cost	733.8	630.8	103.0
System lifetime	630.8	550.1	80.7
MEA lifetime	550.1	537.9	12.2
CO_2 price	537.9	461.5	76.4

Table S10. The results of the waterfall analysis for n-propanol.

n-Propanol production cost roadmap (USD/tonne)			
Parameters	**Before optimization**	**After optimization**	**Cost reduction**
FE	17536.1	6217.9	11318.2
Current density	6217.9	2797.6	3420.3
Cell voltage	2797.6	1898.8	898.8
Single-pass utilization	1898.8	1618.4	280.4
Electrolyzer operting cost	1618.4	817.1	801.3
Electrolyzer capital cost	817.1	698.6	118.5
System lifetime	698.6	610.2	88.4
MEA lifetime	610.2	596.2	14.0
CO_2 price	596.2	508.3	87.9

Table S11. The results of the waterfall analysis for ethylene.

Ethylene production cost roadmap (USD/tonne)			
Parameters	**Before optimization**	**After optimization**	**Cost reduction**
FE	26968.6	9434.0	17534.7
Current density	9434.0	3949.9	5484.1
Cell voltage	3949.9	2638.1	1311.8
Single-pass utilization	2638.1	2254.1	384.0
Electrolyzer operting cost	2254.1	1094.0	1160.1
Electrolyzer capital cost	1094.0	904.1	189.9
System lifetime	904.1	776.5	127.6
MEA lifetime	776.5	743.1	33.4
CO_2 price	743.1	617.7	125.5

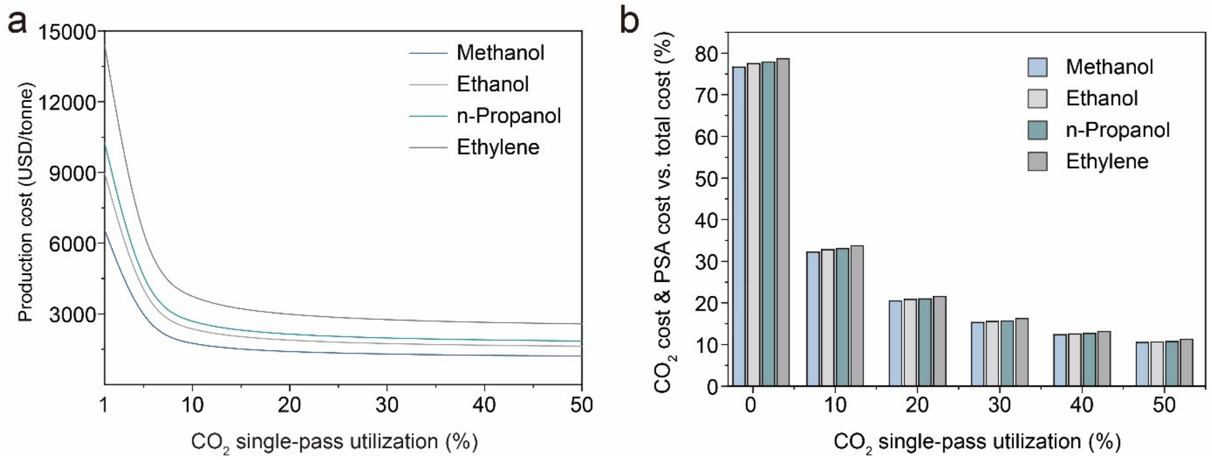

Figure S2. The impact of single-pass utilization on (a) production cost (b) the ratio of CO_2 cost & PSA cost to total production cost. We used the optimized case parameters for other modeling inputs.

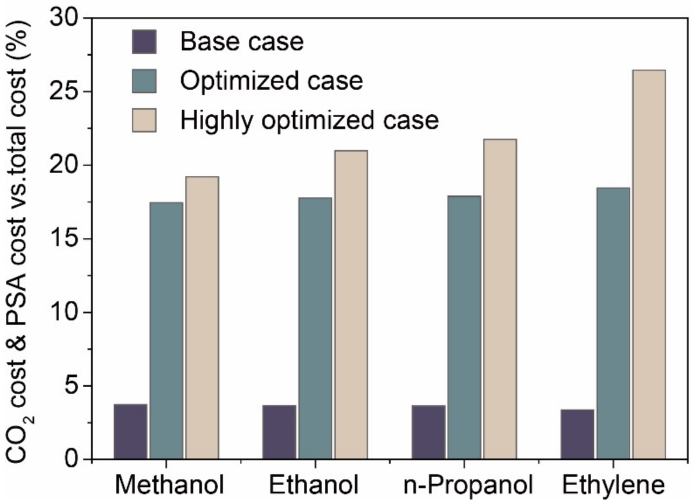

Figure S3. The ratio of CO_2 cost & PSA cost to total production cost under the condition of the base, optimized, and highly optimized case. In the base case, the CO_2 and PSA costs contribute to less than 4% of the total production cost due to the extremely high cost of electrolyzer installation and operation. The CO_2 single-pass utilization is 10% in the base case, 25% in the optimized case, and 50% in the highly-optimized case.

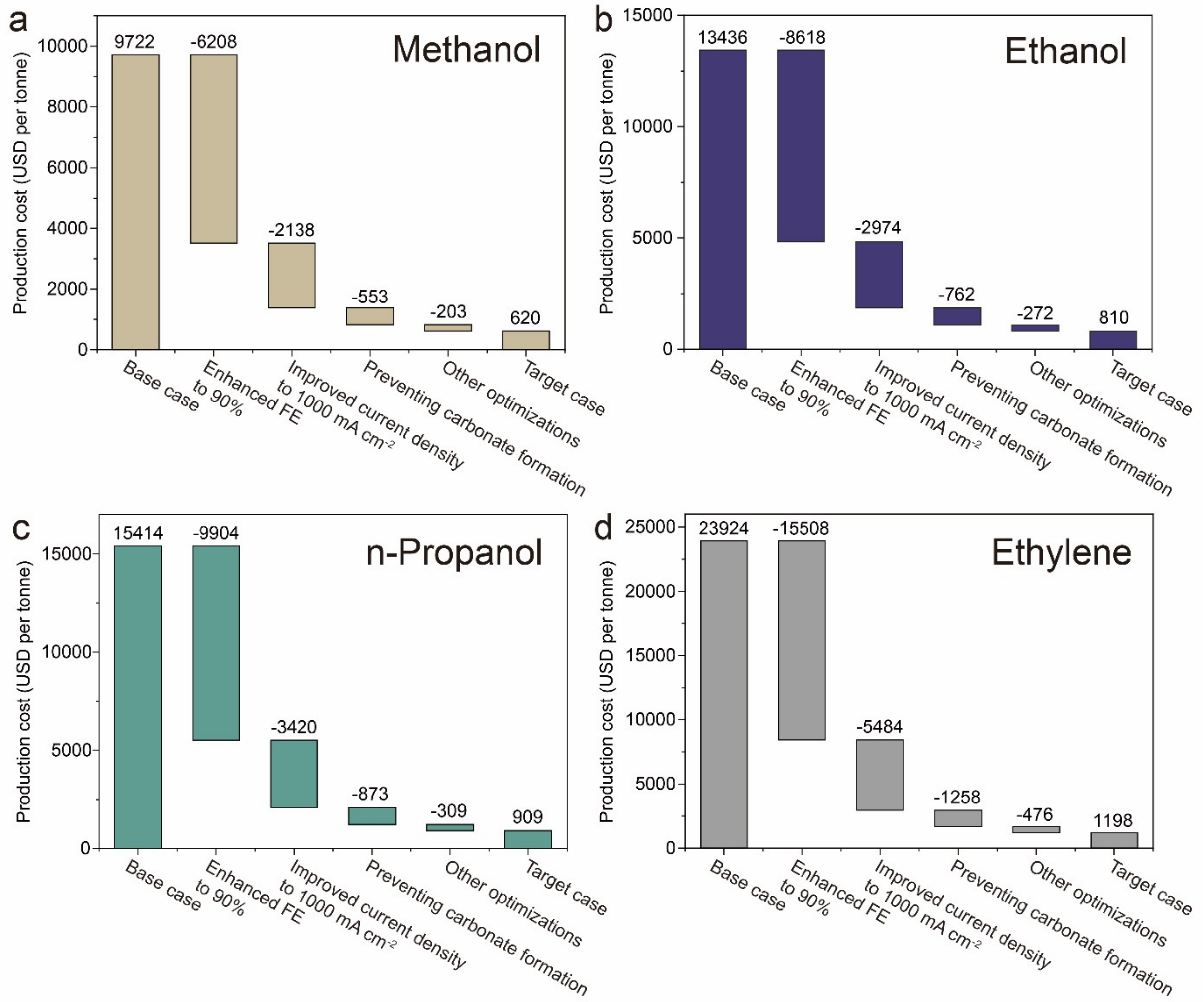

Figure S4. Waterfall analyses at a constant electricity price of 3 cents per kWh. The cost reductions caused by preventing carbonate formation are 553, 762, 873, and 1258 USD per tonne for methanol, ethanol, n-propanol, and ethylene.

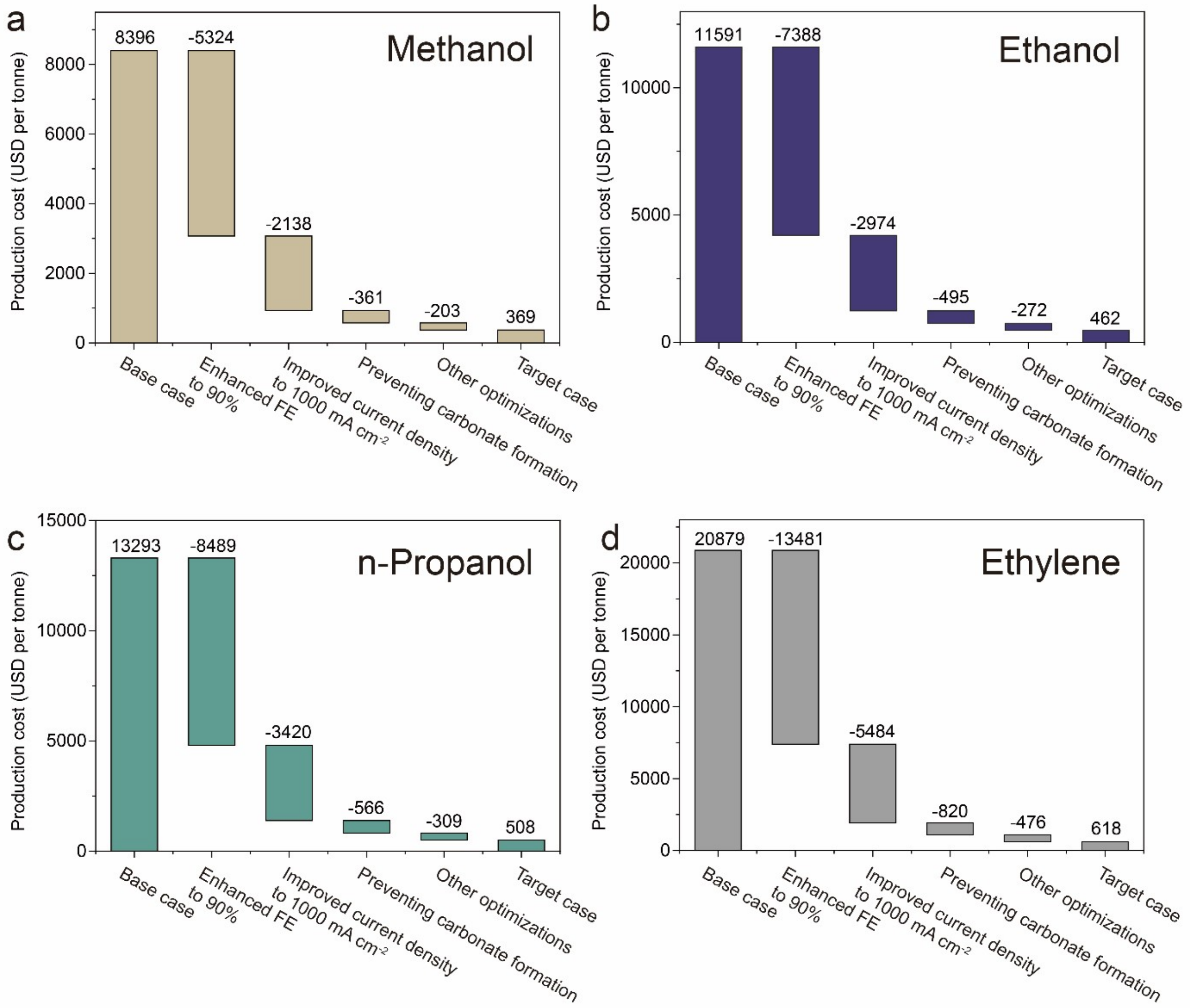

Figure S5. Waterfall analyses at a constant electricity price of 1 cent per kWh. The cost reductions caused by preventing carbonate formation are 361, 495, 556, and 820 USD per tonne for methanol, ethanol, n-propanol, and ethylene.

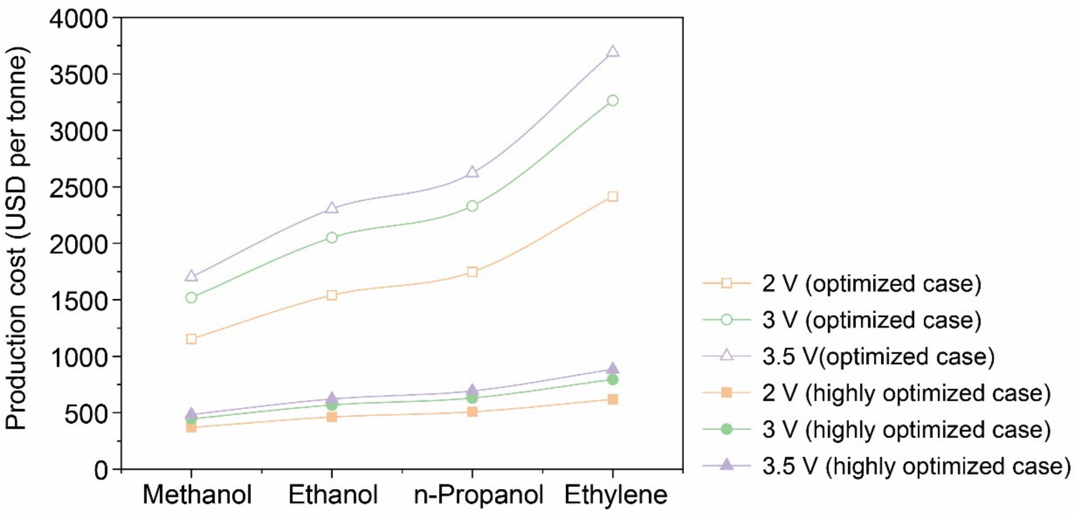

Figure S6. The analysis of acidic CO_2RR. The modeling was performed by screening the impact of cell voltages on the production costs in the optimized and highly optimized cases without carbonate formation.

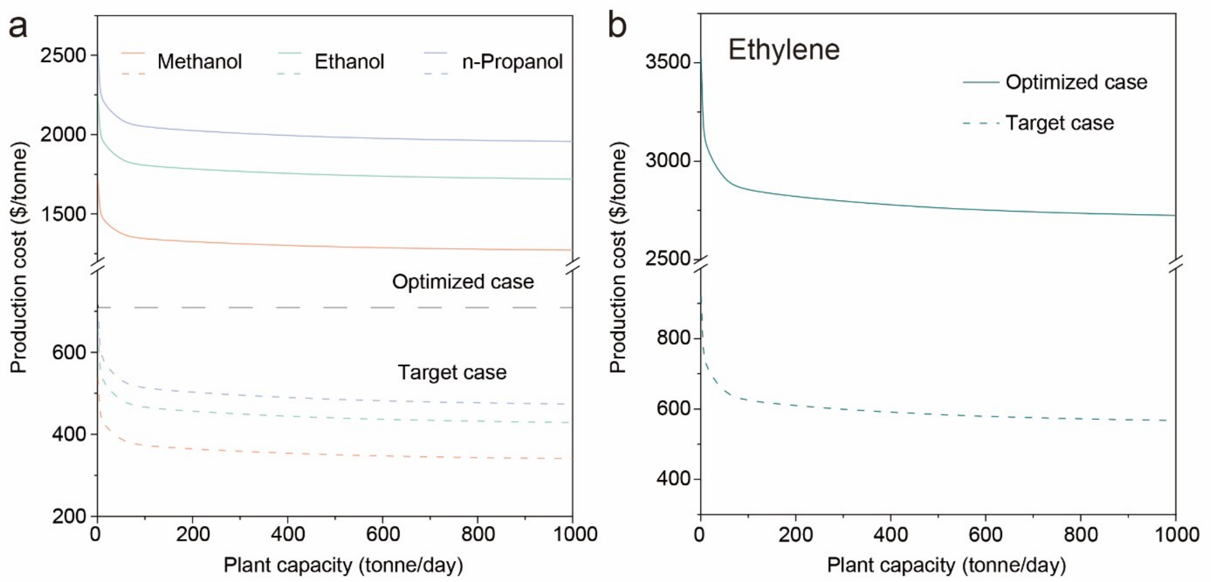

Figure S7. The impact of plant capacity. The correlations between production costs and plant capacities at the optimized and target cases for (a) methanol, ethanol, n-propanol, and (b) ethylene.

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