Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplemental Information

Electrified CO2 valorization in emerging nanotechnologies: A technical analysis of gas feedstock purity and nanomaterials in electrocatalytic and bio-electrocatalytic CO2 conversion

Joshua Jack*[a], Aidan Weber[c], Sara Bolzman[a] , Stephen McCord[b]

[a] Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI, 48109, USA

[b] Global CO_2 Initiative, University of Michigan, Ann Arbor, MI, 48109, USA

[c] Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, 48109, USA

(*) Corresponding author address: Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI 48109, USA

Tel: +1 (734)-764-0452; E-mail: jdjack@umich.edu

Table of Contents

S1.0 Energy inputs and costs calculations……..…..1

S.2.0 Carbon footprint calculations……...…….....…..…3

Table S1: Reported Electrochemical Performance Metrics……...3

Table S2: Reported Bio-electrochemical Performance Metrics……..…….3

References Cited……..…...…….4

S1.0 Energy inputs and costs calculations

Production costs were estimated for various feed gas scenarios using reported performance metrics from recent literature. Three distinct gas feed scenarios were considered for both electrocatalytic and bio-electrocatalytic CO_2 conversion processes. Brief descriptions of each scenario are provided below.

Scenario 1, 20% CO_2: This scenario evaluated the case where a waste gas stream containing 20% (v/v) CO_2 could be used without pretreatment of the gas stream prior to

CO_2 conversion. This scenario is expected to model the emissions that might be available from a coal fired power plant or industrial cement plant or steel mill.

Scenario 2, 99% CO_2: This scenario demonstrated a case where a high purity gas stream of containing 99% (v/v) CO_2 could be used for direct CO_2 conversion without upstream separation. These calculations are relevant to concentrated emissions reported in industrial bioethanol fermentations or ammonia synthesis plants.

Scenario 3, 20% CO_2 + MEA: This scenario evaluated the case where a waste gas stream containing 30% (v/v) CO_2 is first upgraded to a 99% (v/v) CO_2 feedstock using an on-site MEA separation unit prior to CO_2 conversion.This scenario is assumed to be the standard case if significant scientific advancements are not made in CO_2 conversion operation and catalyst design. For bio-electrocatalytic analyses, 30% (v/v) CO2 was used rather than 20%(v/v) for Scenarios 1 and 3.

For each scenario, total production costs were taken as the sum of the estimated energy costs required to produce a kg of CO_2-derived product plus the accompanying separation costs to provide the associated mass of initial CO_2 feedstock (Eq. S1). Capital costs were considered outside the scope of this initial analysis.

$$Production\ cost = \ Energy\ Cost\left(\frac{\$}{kg\ product}\right) + Separation\ Cost\left(\frac{\$}{kg\ product}\right),\ Eq.S1$$

When analyzing electrocatalytic CO_2 conversion processes, representative performance values were taken from literature for Ag nanoparticle-based electrodes[1] as these electrocatalysts show excellent potential for scale-up. Specific literature values are listed in Table S1. The first step in approximating the production costs was to estimate the energy costs per kg product via the reported power demand and production rates from the study via Eqs. S2-S6.

$$Power\ (W) = \ Current\ density\left(\frac{A}{m^2}\right) \times Electrode\ surface\ area\ (m^2) \times\ Voltage(\ V),\ Eq.S2$$

$$Charge\ utilization\ (\frac{e^-}{sec}) = \ Current\ (A) \times \frac{\frac{C}{sec}}{1A} \times \frac{6.25\ x\ 10^{18}\ e^-}{1C}\ \ Eq.S3$$

For electrochemical reduction of CO_2 to CO:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO,\ Eq.S4$$

This means 1 mol of CO demands 1 mol of CO_2 and 2 electrons as reactants:

$$Synthesis\ rate\left(\frac{g\ CO}{sec}\right) = Charge\ \left(\frac{e^-}{sec}\right) \times \left(\frac{1mol\ CO}{2\ e^-}\right) \times \left(\frac{1mol\ CO}{6.022 \times 10^{23}}\right) \times \left(\frac{28\ g}{1\ mol\ CO}\right), Eq.S5$$

$$Unit\ power\ demand\left(\frac{kWh}{kg\ CO}\right) = \frac{1}{Syntehsis\ Rate}\ \left(\frac{day}{kg\ CO}\right) \times\ Power\ (kWh), Eq.S6$$

$$Energy\ costs\left(\frac{\$}{kg\ CO}\right) = Unit\ power\ demand\ \left(\frac{kWh}{kg\ CO}\right) \times\ Electricity\ costs\left(\frac{\$}{kWh}\right), Eq.S7$$

Electricity costs were estimated using levelized costs of energy (LCOE) from a recent U.S. Energy Information Administration (EIA) report [2]. Similar calculations were also used to calculate acetate production costs via a bio-electrocatalytic CO_2 conversion process using values for an RVC NT cathode[3]. Initially the power demand was estimated using Eq.S2. In this case, the total cell voltage was approximated using Eq.S8 assuming an overpotential for the anode oxygen evolution reaction of 0.27V, as commonly reported in literature[4].

$$E_{cell} = E_{cathode} - E_{anode,}\ \ Eq.S8$$

Notably, the acetate synthesis rate was used directly from literature as the columbic efficiency was nearly 100%. As such, the unit power demand and energy costs were calculated using variations of Eq. S6-S7 for acetate production rather than CO.

In Scenario 3, separation costs were included using unit separation costs estimates from a recent IPCC Special Report on Carbon Dioxide Capture and Storage[5] . Assuming the theoretical 1:1 molar ratio of CO_2 to CO (Eq. S7) can be achieved and the separation energy demands can be calculated using Eq. S9. Similar equations can also be derived for acetate production.

$$Unit\ separation\ energy\left(\frac{kWh}{kg\ CO}\right) = Capture\ energy\left(\frac{kWh}{kg\ CO_2}\right) \times MW_{CO_2}\left(\frac{kgCO_2}{mol}\right) \times \left(\frac{1\ molCO_2}{1\ mol\ CO}\right) \times \frac{1}{MW_{CO}}\left(\frac{kg}{mol\ CO}\right), Eq.S9$$

The unit separation energy values were then multiplied by EIA levelized costs of energy to estimate the total separation costs for Scenario 3. This value was then added directly to the energy costs for CO_2 conversion via Eq. S1.

Table S1: Reported electrochemical performance metrics

Parameter	Value	Units
V_{cell}	3.0	V
$J_{co,}$ 20% (v/v)	39	$\frac{mA}{cm^2}$
J_{co}, 99% (v/v)	52	$\frac{mA}{cm^2}$
Surface Area	1	cm^2

Table S2: Reported bio-electrochemical performance metrics

Parameter	Value	Units
$V_{cathode}$	-0.45	V

$J_{co,}$ 30% (v/v)	34	$\frac{A}{cm^2}$
J_{co}, 99% (v/v)	35	$\frac{A}{cm^2}$
$Synthesis\ Rate$ 30% (v/v)	275	$\frac{g}{m^2\ day}$
$Synthesis\ Rate$, 99% (v/v)	300	$\frac{g}{m^2\ day}$
Surface Area	1.36	cm^2

2.0 Carbon footprint calculations

The expected carbon footprint was predicted for each feedstock scenario described in section S1.0. Overall, the unit power demand (Eq. S6) and unit separation energy (Eq. S9) were used to estimate the energy demand per mass of product generated (e.g. kWh per kg CO) for both the CO_2 conversion and separation processes. The total unit energy demands were then calculated by summing these values (Eq. S10).

$$Total\ unit\ energy\left(\frac{kWh}{kg\ product}\right) = Unit\ power\ demand\left(\frac{kWh}{kg\ product}\right) + Unit\ separation\ energy\left(\frac{kWh}{kg\ product}\right), Eq.S10$$

The carbon footprint was then calculated for various energy sources using the carbon intensity for energy source from a recent IPCC Special Report on Carbon Dioxide Capture and Storage via Eq.S11.

$$Carbon\ footprint\left(\frac{kg\ CO_2\ eq^-}{kg\ product}\right) = Total\ unit\ energy\left(\frac{kWh}{kg\ product}\right) \times Carbon\ intensity\ of\ energy\left(\frac{kg\ CO_2\ eq^-}{kWh}\right), Eq.S11$$

3.0 Energy source abbreviations

Abbreviation	**Power Source**
Biomass	Conventional biomass energy
CC	Natural gas fired combined cycle energy
Coal	Ultra-supercritical coal energy
GT	Large-scale geothermal energy
Offshore	Off-shore wind energy
Onshore	On-shore wind farm energy
Solar	Solar photovoltaics

References:

1. Kim B, Ma S, Molly Jhong HR, Kenis PJA. Influence of dilute feed and pH on electrochemical reduction of CO2 to CO on Ag in a continuous flow electrolyzer. Electrochim Acta. 2015;166.
2. U.S. Energy Information Administration (EIA). Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2020. US EIA. 2020;(February).
3. Jourdin L, Freguia S, Flexer V, Keller J. Bringing High-Rate, CO2-Based Microbial Electrosynthesis Closer to Practical Implementation through Improved Electrode Design and Operating Conditions. Environ Sci Technol. 2016;50(4).
4. Jack J, Zhu W, Avalos JL, Gong J, Ren ZJ. Anode co-valorization for scalable and sustainable electrolysis. Vol. 23, Green Chemistry. 2021.
5. Mathieu P. The IPCC special report on carbon dioxide capture and storage. In: ECOS 2006 - Proceedings of the 19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. 2006.