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Article

Thermodynamic and Economic Assessments of Electrochemical CO_2 Conversion to Dimethyl Ether: Trade-off between Hydrogen Gas and Water Vapor as a Proton Source

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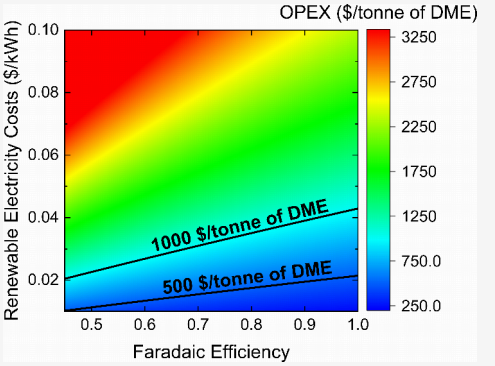
ABSTRACT: Electrochemical conversion of carbon dioxide (CO_2) to valuable products could provide a transformative pathway to produce renewable fuels while adding value to the CO_2 captured at point sources. Here, we investigate the thermodynamic feasibility and economic viability of the electrochemical CO_2 reduction reaction to various carbon-containing fuels. In particular, we explore various pathways for conversion of CO_2 to dimethyl ether (DME), liquid propane gas, and renewable natural gas. We compare and contrast the use of two different proton sources, including hydrogen gas and water vapor at the anode, on the capital and operating costs (OPEX) of electrochemical systems to produce DME. The results indicate that the electrical costs are the most significant portion of OPEX, demonstrating costs of 0.2−0.6 $/kWh per metric ton of DME. DME production using carbon monoxide and formic acid as intermediates proved to be the most cost-effective, demonstrating levelized costs of energy of 0.28 $/kWh with over 0.15 $/kWh of cost recovery possible through renewable hydrogen tax credits and oxygen and hydrogen gas recovery.



INTRODUCTION

Curbing global carbon dioxide (CO_2) greenhouse gas emissions should be of the utmost importance if limiting rising temperatures to 2 °C by the turn of the century is to be achievable. While significant progress is being made in decarbonization, the global reliance on petroleum-based fuels for transportation and industry requires inclusive solutions that fulfill global hydrocarbon needs.

Recycling CO_2 emissions through electrolysis offers a viable solution that can create a circular carbon economy and a pathway to generate renewable carbon-based fuels.[1−3] Electrolysis for industrial applications has been extensively studied for hydrogen (H_2) production.[4−6] Hydrogen gas has a superior energy density by mass but is quite volatile, leading to cost-prohibitive transportation due to its inherent danger.[7] Inspired by water electrolysis, the electroreduction of CO_2 can produce diverse hydrocarbons and intermediates that can be used in transportation and industry. Adopting sustainable pathways to generate fuels and chemicals necessitates detailed analyses of the costs and energy associated with these new processes. Prior work on techno-economic assessments (TEA) of the CO_2 reduction reaction (CO_2RR) primarily focused on producing carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), and ethanol (C_2H_5OH).[8−16] All products have been shown that can be generated via the electrochemical CO_2RR on transition metals such as silver (Ag), gold (Au), nickel (Ni), and copper (Cu). Here, we study electrochemical CO_2RR to dimethyl ether (DME) from the direct route or intermediates. The common intermediates in the electrochemical CO_2RR considered in this study are CO, HCOOH, and methanol (MeOH). The results are also compared with those of liquefied propane gas (LPG) and renewable natural gas (RNG).

CO_2RR to CO is a pathway that has been extensively studied and has shown promising results for industrial production. A wide range of catalysts has been tested and has shown great selectivity toward CO, including surface additive Ag, Ni, and porous Au catalysts.[17−20] In particular, it has been shown using Ni coordination systems improves impurity tolerances on single-atom catalysts (SACs), which favors commercial applications due to impure gas streams.[21] This has also been shown to achieve high selectivities (>95% Faradaic efficiencies (FE)) at high current densities (500 mA/cm^2). In a tandem electrocatalytic CO_2RR, low energy requirements reaction intermediates, such as CO and HCOOH (2 electron transfer processes), could be leveraged to produce more complex carbon-containing fuels. In addition, HCOOH is a viable hydrogen carrier and has been shown to be a potential fuel itself.[22,23] The electrochemical CO_2RR to

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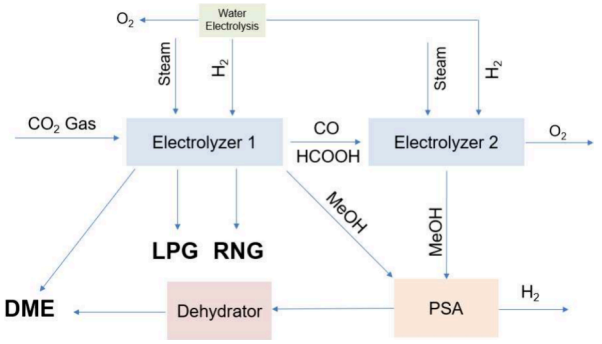
HCOOH occurs at relatively low cell voltages (1.5 V versus the reversible hydrogen electrode (RHE)), at current densities as high as 200 $mAcm^{-2}$.[24] This reaction is fully realized in acidic media (pH < 1), which can negatively affect the mechanical behavior of metal catalysts due to corrosion. Formate ($HCOO^-$) is another viable option that can be fully realized under alkaline conditions. This has been shown on cuprous oxide (Cu_2O) catalysts with over 75% Faradaic efficiencies in H-cells.[25] Electrochemical CO_2RR to MeOH is an evolving topic of interest as methanol is considered to be a viable fuel alternative and additive.[26] Additionally, methanol dehydration will result in the generation of DME, which is an excellent candidate for replacing diesel fuel in engines. DME has a higher cetane number, resulting in higher engine combustibility than diesel, coupled with no carbon-to-carbon bonds and 34.8% oxygen content, leading to virtually no particulate matter (PM) when combusted.[27] DME has a lower energy density than diesel (27.6 MJ/kg compared to 42.6 MJ/kg for diesel), requiring an engine double the size to achieve the same fuel economy as diesel.

Here, we aim to consider the thermodynamics and economics of producing renewable fuels with superior specific energy (kWh/kg) and energy density (kWh/L), such as DME, LPG, and RNG, which could be utilized directly by using current infrastructure in the power, energy, and transportation industries with no or minimal modification to energy conversion systems. The electrochemical CO_2RR to DME can be achieved through four different pathways, two by leveraging the CO_2RR to CO and HCOOH to follow favorable reaction pathways to MeOH followed by dehydration and two through reactions with higher energy requirements *via* direct conversion to MeOH and DME (Scheme 1). We investigate

Scheme 1. Schematic of Various Pathways for the Electrochemical CO_2RR to DME, LPG, and RNG from Direct Routes and Intermediates[a]



[a]There are various direct and multistep pathways that require different energies, impacting OPEX and CAPEX of the electrochemical fuel production system.

the operating and capital costs (OPEX and CAPEX) of each electrochemical pathway to convert CO_2 to DME and compare them to the industry-standard method of steam reformation of natural gas to produce methanol.[26] In the steam reformation process, methane reacts with steam to generate syngas (mixture of CO and H_2), which is then followed by a syngas reaction over transition-metal-based catalysts to produce MeOH. Electrochemical oxidation of methane to MeOH is also considered, and a more detailed analysis is provided in the Supporting Information (SI). These pathways to DME will be compared with electrochemical CO_2 conversion to LPG and RNG. Electrochemical LPG generation from CO_2 is another viable option and has produced promising results through different multifunctional catalysts.[28,29] Using functional Mo_3P nanoparticles, direct CO_2 to LPG at -395 mA/cm^2 was demonstrated with an FE of 91%.[29] Electrochemical CO_2RR to CH_4 has been more extensively researched, with different types of catalysts being demonstrated from Cu catalysts achieving FE of 64% at a current density of -192 mA/cm^2 to W_2C catalysts obtaining high FEs (>82%) and current densities of -421.63 mA/cm^2 for 700 h.[30,31] Nanoparticles with various sizes and shapes have also been demonstrated to promote the CO_2RR to CH_4, with 75 nm Cu octahedra nanoparticles reaching 55% FE with the hydrogen evolution reaction (HER) as the primary competing reaction.[32] Zero-gap electrolyzers consisting of a membrane electrode assembly (MEA) will be considered for the CO_2RR. This type of electrolyzer differs from a traditional H-cell by having a gas diffusion electrode (GDE) that allows for direct feeding of CO_2 to the catalyst surface, minimizes mass transport losses, and enhances product selectivity.[33] There have been extensive studies on MEAs exploring electrolyte effects, GDE properties, membranes, specifically anion exchange membranes (AEM) and bipolar membranes (BPM), and optimization techniques such as *iR* compensation and CO_2 flow rate.[34−41] In addition, operating zero-gap electrolyzers consisting of an MEA in a gaseous phase without liquid electrolytes enables the production of primarily gaseous products, minimizing separation and purification steps. Eliminating the hassle and costs associated with the downstream separation and purification of chemicals substantially reduces production costs.[42]

RESULTS AND DISCUSSION

This work will have two major TEA components: OPEX and CAPEX. OPEX is influenced by electrical costs and operations and maintenance (O&M). CAPEX is dependent on the stack costs, balance of the plant (BoP), pressure swing adsorption (PSA), and CO_2 capture costs. Combined together, a levelized cost of energy (LCOE) is produced in $/kWh, which is compared to current market fuel prices, and conclusions regarding the economic viability of electrochemical CO_2RR to DME can be made. In addition, we explore two different proton sources (*i.e.*, water vapor and H_2) on the anodic side of the electrochemical reactor and explore the trade-off between these two proton sources on the OPEX and CAPEX of the electrochemical system for DME, LPG, and RNG production. Raw hydrogen from conventional means (*i.e.*, steam reformation) results in a competitive price of ~$2/kg.[43] However, this method has a significant carbon footprint compared to that of hydrogen production from water electrolysis using renewable energy. Therefore, raw hydrogen from conventional sources was not considered in this study. We also incorporate the values of oxygen (O_2) and H_2 recovered through electrolysis systems and clean H_2 tax credit in our analyses.

Each pathway can be executed with two different sources of protons supplied by the anode side. One option is to supply hydrogen gas to the anode with the following oxidation reaction $H_2 \rightarrow 2H^+ + 2e^-$ with a standard cell voltage of 0.0 V versus RHE.[44] This option requires another electrolyzer to carry out the water electrolysis, which adds to the separate electrical and stack costs. Another option is to supply water vapor directly in the anode where the reaction $2H_2O \rightarrow 4H^+ + 4e^- + O_2$ has a standard cell voltage of 1.23 V versus RHE.

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This option offers an attractive all-in-one pot option but has the extra half-cell voltage attached to it, increasing electrical costs, especially at lower Faradaic efficiencies. All six pathways from captured CO_2 to desired products are summarized in Table 1 with their voltages used for OPEX and CAPEX calculations for hydrogen gas and water vapor at the anode, respectively.[45]

Table 1. Summary of All of the Electrochemical Pathways Studied in This Work[a]

Pathway	Reactions
DME Pathway 1	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ (1.75, 3 V)
	$CO + 4H^+ + 4e^- \rightarrow CH_3OH$ (1.75, 3 V)
	$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
DME Pathway 2	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ (2 V, 3.25 V)
	$HCOOH + 4H^+ + 4e^- \rightarrow CH_3OH + H_2O$ (2 V, 3.25 V)
	$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
DME Pathway 3	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ (3 V, 4.25 V)
	$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
DME Pathway 4	$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3OCH_3 + 3H_2O$ (3.5 V, 4.75 V)
LPG Pathway	$3CO_2 + 20H^+ + 20e^- \rightarrow C_3H_8 + 6H_2O$ (2.5 V, 3.75 V)
RNG Pathway	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ (2.75 V, 4 V)
Methane oxidation to MeOH	$CH_4 + 2OH^- \rightarrow CH_3OH + H_2O + 2e^-$ (3 V)
Oxygen evolution reaction	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ (1.23 V)

[a]The voltages used to calculate OPEX and CAPEX are next to the reactions. The two potentials represent the use of hydrogen gas or steam at the anode, respectively. Approximately 1.25 V was added if water splitting was done at the anode.

OPEX examines the electrical cost of executing the reactions in Table 1. Electrical costs depend on Faradaic efficiency, cell voltage, and renewable electricity costs. In our analyses, we assume a renewable electricity cost of \$0.02 kWh^{-1}-\$0.03 kWh^{-1}, the 2030 goal set forth by the US Department of Energy (DOE).[46] The current is calculated using a scheme where the electrical costs are inversely proportional to the Faradaic efficiency leading to higher costs at lower Faradaic efficiencies.[12] Due to the high thermodynamic and kinetic requirements for DME pathways 3 and 4, their overall OPEX increases per kWh (Figure 1). Please refer to Tables S1−S12 in the SI for detailed calculations for each pathway.

The results are calculated under the assumption of 1 tonne of fuel being produced per day. At lower Faradaic efficiencies, hydrogen gas at the anode becomes more cost-effective. This is generally seen at low Faradaic efficiencies of <50% for different pathways to DME, LPG, and RNG (Figures S1−S6). Target costs of \$500 per tonne of DME can still be achieved at these low Faradaic efficiencies, but renewable electricity costs of \$0.01−0.02 per kWh would be necessary (Figures S7 and S8). For the two-electron transfer of CO_2 to CO, voltages have been reported to be as low as −1.0 V versus RHE.[47] For industrial purposes, where current densities of 1−5 A/cm^2 are essential, cell voltages of 2−3 V versus RHE are more realistic.[48] For the electrochemical CO_2RR to MeOH, the reaction requires a higher activation energy and is shown to need a total cell voltage of at least 3 V.[12,49] In the scenario where water vapor is used at the anode instead, the cell voltage would increase by a minimum of 1.23 V due to the standard half-cell voltage of water splitting, leading to increased electrical costs (Figures S9 and S10). Electrical costs can be minimized by reducing the cell voltage and lowering renewable electricity costs. Figure 2 suggests that at lower cell voltages, an OPEX of under a dollar per kg of DME is feasible if Faradaic efficiencies of >40% for H_2 gas and >80% using water vapor could be achieved. This indicates that with the larger required cell voltages needed for water vapor at the anode, an OPEX of under a dollar per kilogram is possible when optimizing experimental conditions (Figure 2b). When total cell voltage stays constant, at renewable electricity prices less than \$0.02 per kWh, the market price of DME at \$500 per tonne is feasible (Figure 3). Within the next decade, the US Department of Energy has targeted achieving \$0.02 per kWh from renewable electricity sources. It is important to note that this benchmark depends on the location, climate, infrastructure, population, and policy, all of which dictate electricity prices. At first glance, these results would indicate that the electrochemical CO_2RR is not competitive with fuels generated through conventional thermochemical processes. Indeed, the market price of fossil fuels is hard to compete with; however, there is cost recovery within the electrochemical CO_2RR through hydrogen and oxygen gas recovery and tax credits. Hydrogen gas recovery is dependent on the gas separation phase through PSA. Oxygen gas is also recovered as it is produced from water electrolysis. Tax credits have been used in the United States as the popularity of residential solar panels has increased. A 10% tax credit has been given to homeowners who have installed solar panels.[50] The U.S. Department of the Treasury has conceptualized tax credits in the form of green

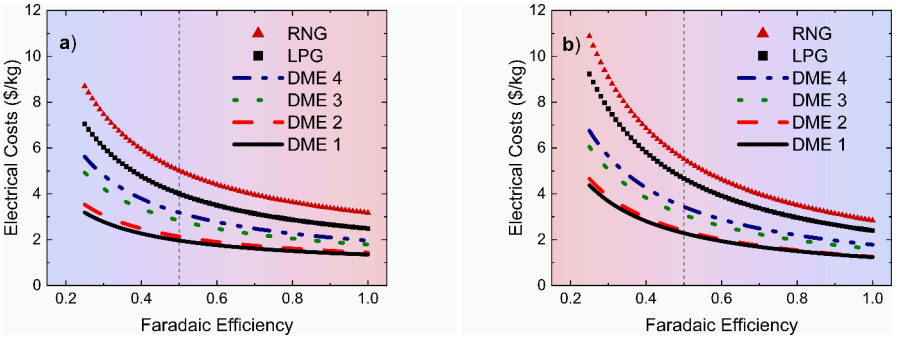

Figure 1. Electrical costs for all electrochemical CO_2 conversion pathways with hydrogen gas supply for (a) and water vapor in the anode for (b). At 45% FE, using water vapor at the anode becomes a more attractive option cost-wise compared to using hydrogen gas at the anode.

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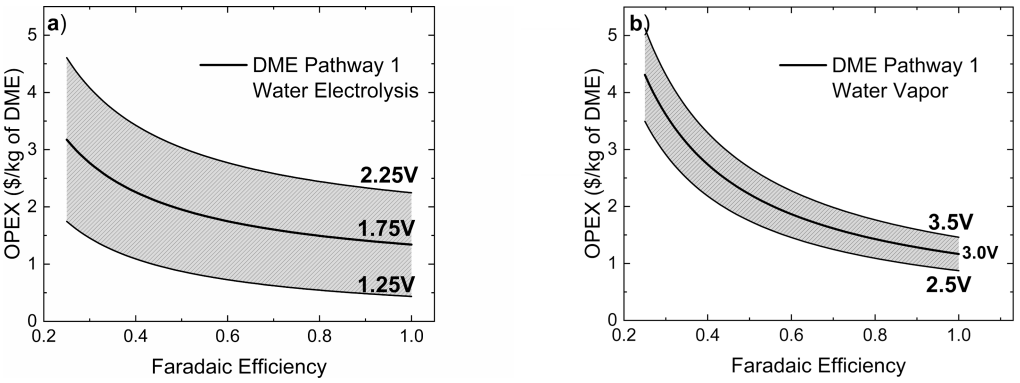

Figure 2. OPEX of DME pathway 1 from CO_2 to CO, which is then electrochemically hydrogenated to MeOH followed by dehydration using hydrogen gas (a) or water vapor (b) at the anode for varying voltages including the potential used in major calculations in this work (middle line) and optimistic (−0.5 V) and pessimistic (+0.5 V) potentials. The wider range of OPEX for the case of using water electrolysis compared to water vapor at the anode is due to the potential being a much greater percentage of the OPEX calculation.

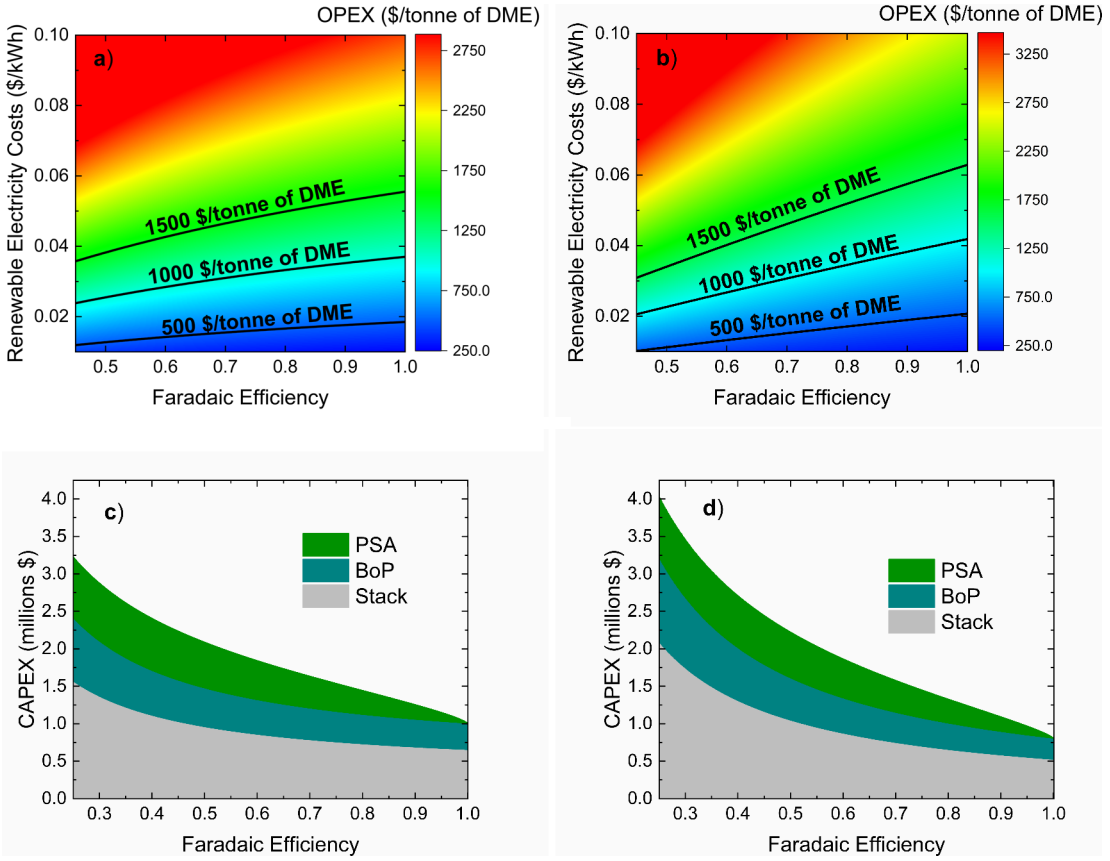

Figure 3. OPEX costs (per tonne of DME) for (a) DME pathway 1 with hydrogen gas used at the anode and (b) DME pathway 1 with water vapor at the anode. Color map includes the consideration of Faradaic efficiency and renewable electricity costs (in terms of $/kWh) at a constant total cell voltage of 1.75 and 3.0 V for (a) and (b) respectively. To achieve market price of 500 $/tonne of DME, a minimum renewable electricity price of under $0.02 per kWh is needed, which is feasible within the next decade. CAPEX is considered for DME pathway 1 for hydrogen gas (c) and water vapor (d) at the anode. Stack costs include the electrolyzer costs, balance of plant (BoP) includes costs of all nonelectrolyzer parts, and PSA is the gas separation costs. PSA is dependent on Faradaic efficiency, which results in a zero cost for PSA at 100% Faradaic efficiency. Using hydrogen gas at the anode requires extra electrolyzer area due to the need for water electrolysis, whereas water vapor at the anode requires one electrolyzer, reducing stack costs.

hydrogen production through the Inflation Reduction Act.[51] Each of these fuels comprises 10−35% hydrogen, which is rewarded through the use of OPEX tax credits. Catalyst and electrolyte costs were not considered in this work, as the variability of the cost of materials would make unclear results; this work aims to offer the minimum baseline needed to execute these reactions.

The overall lifetime of these electrochemical systems was concluded to be 20 years. The first factor determined for CAPEX is the stack costs. DOE targets proton exchange membrane (PEM) electrolysis to have a reference stack cost of

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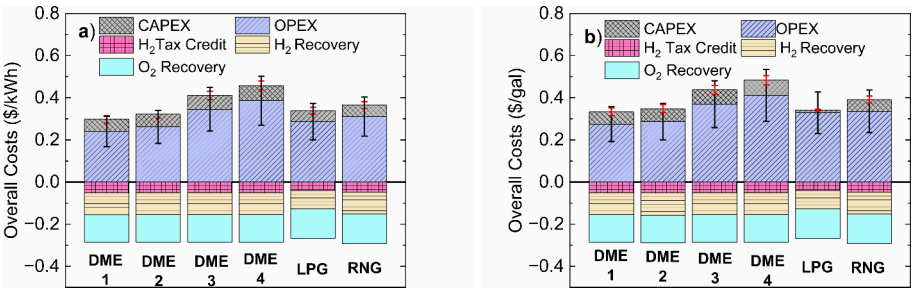

Figure 4. Overall costs of each pathway including the mean OPEX and CAPEX costs where the error bars represent the lower end performance (41% Faradaic efficiency) and the optimistic case (85% Faradaic efficiency). Hydrogen recovery costs from PSA ($5 kg^{-1}), oxygen recovery costs from water electrolysis ($0.5 kg^{-1}), and a tax credit of $3 per kg of hydrogen according to the proposed protocol by the U.S. Department of the Treasury. a) Overall costs of the electrochemical CO_2RR to DME, LPG, and RNG using hydrogen gas at the anode and b) using water vapor at the anode.

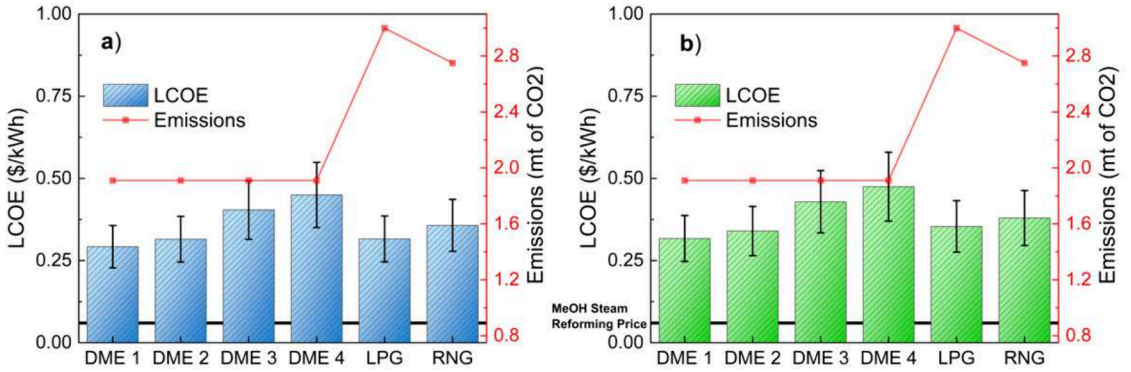

Figure 5. Mean LCOE for all pathways compared to the emissions each fuel emits in metric tonnes (mt) upon a theoretical perfect combustion. a) uses water electrolysis and b) uses water vapor at the anode.

450 $/kW in 2022 and has an ultimate target of 50 $/kW.[52] These costs include the cost of commonly used platinum group metals. These materials are a major contributor to stack costs and are expected to decrease as cheaper materials are discovered. Based on this estimation, this model will use a conservative reference stack cost of 500 $/kW. The second factor is the balance of plant (BoP) costs, which will account for 35% of all CAPEX.[13] BoP accounts for the essential components of the CO_2RR that are not directly accounted for in the stack costs. The third factor considered in CAPEX is PSA. PSA is determined by a reference cost and scaled by flow rate by a factor of 0.7.[12,53,54] PSA CAPEX is modeled by

$$\mathrm{PSA_{CAPEX}} = \$1.9 \times 10^6 \times \left(\frac{\text{Gas Flow Rate} \times (1 - \mathrm{FE})}{\text{Reference Flow Rate}}\right)^{0.7} \quad (1)$$

where the Gas Flow Rate is the combination of the flow rate of carbon species and hydrogen gas in m^3 per hour, and the reference flow rate is 1000 m^3/h. From eq 1, the amount of hydrogen gas recovered can be estimated by knowing the Faradaic efficiency. Currently, hydrogen costs, from renewable means, is $5 kg^{-1} with the current goal of $1 kg^{-1} in the next ten years.[55] The final CAPEX factor is the captured CO_2 costs. This work assumes $100 per tonne of captured CO_2 while not considering CO_2 transportation costs as it is assumed the CO_2 is captured directly from point sources such as oil refineries or coal power plants. (Please refer to the SI for the exact quantity of reactants needed for each pathway.)

CAPEX and OPEX for multiple pathways to DME, LPG, and RNG were calculated (Figure 4, Figures S9−S13, and Tables S13−S14). The bars represent the OPEX and CAPEX values for each pathway with a mean in Faradaic efficiency from 0.25 to 1.00 (*i.e.*, 0.63), and the error bars represent the standard deviation of the Faradaic efficiency, giving lower-end and optimistic case scenarios (Figure 4). The first and second DME pathways offer the cheapest routes to fuel and are very viable in industry production. Due to the higher required activation energies for DME pathways 3 and 4, the overall OPEX dominates, even with the lack of need for an extra electrolyzer. LPG and RNG pathways also suffer due to the large activation energies, high number of electrons for electrochemical reactions, and relatively high cell voltage (See SI for detailed calculations). The cost recoveries offer relief and make these production pathways more viable (Figures S14). The electrochemical oxidation of methane to methanol could also provide a promising route to generate methanol and DME with remarkably lower OPEX (Figure S16). This route could also be considered as a short-term alternative, as new advances are being made in the electrochemical CO_2RR to fuels.

Levelized cost of energy (LCOE) offers an opportunity to incorporate falling costs in CAPEX and renewable electricity prices. LCOE is modeled by[56]

$$\mathrm{LCOE}\left(\frac{\$}{\mathrm{kWh}}\right) = \mathrm{CAPEX} \times (1 - \mathrm{CRF}) + \mathrm{O\&M} + \mathrm{OPEX} \quad (2)$$

where O&M is operations and maintenance, which is estimated to be 2% of CAPEX costs.[57,58] CRF is the cost recovery factor, which is defined as

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$$\mathrm{CRF} = \frac{i \times (1+i)^j}{(1+i)^j - 1} \quad (3)$$

where i is the interest rate, and j is the lifetime in years. Using conservative estimates, i is 10%, and j is 20 years. For the most optimal systems, lifetimes should be approaching 30 years.[59]

LCOE makes a better estimate over time when it is compared with the current market price of fuels. The LCOE, along with the emissions from 1 tonne of fuel combusted, which assumes a theoretical 100% efficiency in combustion, is modeled in Figure 5. DME offers the lowest emissions from combustion and generates the fewest PM emissions, making it a great candidate among the three fuels (*i.e.*, DME, LPG, and RNG). It can be reasonably concluded that generating natural gas from the CO_2RR will not be economically competitive with methane market prices within the next few decades. The availability and ease of natural gas processing make it unobtainable for green natural gas production.

DME production is certainly viable compared to the steam reformation of the methanol process. If high Faradaic efficiencies are achieved and cheaper and stable catalysts are used over long periods of time, DME pathways 1 and 2 would be the most cost-competitive pathways to produce DME. If cell voltages improve, DME pathway 3 can compete directly with steam reforming of methane to methanol. One considerable pitfall with DME pathway 2 is the use of acidic media to generate formic acid (pH < 1), which may considerably affect the mechanical performance of the catalysts over time, especially compared to the DME generation occuring in neutral pH in pathway 1 through syngas generation. LPG generation does seem possible, certainly, as single-pot catalyst technology trends to mature over time, leading to cheaper catalysts.

CONCLUSION

As the electrochemical conversion of CO_2 advances, it is important to consider emerging technologies' industrial applicability and economic feasibility. Considering long catalytic lifetimes and the viability to be replaceable in uniformity is the cornerstone to industrial scale-up of novel technologies. The issue of warming climate must involve solutions of different natures, one of which is recycling emissions through electrochemical conversion of CO_2. A TEA allows us to evaluate the economic viability of electrochemical CO_2RRs in generating diverse types of fuels. By benefiting two fields, including renewable hydrocarbons and green hydrogen production, with the addition of government incentives regarding tax credits, the electrochemical CO_2RR could offer an attractive pathway to generate energy-dense fuels such as DME and contribute to combating rising greenhouse gas emissions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c01675.

OPEX calculations, CAPEX calculations, compounds tables, cost recovery calculations, methane to methanol pathway OPEX (PDF)

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Notes

The authors declare no competing financial interest.

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