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Guiding research in electrochemical CO_2 conversion strategies through a systems-level perspective†

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Carbon conversion technologies are gaining interest as a solution to utilize captured CO_2 and contribute to efforts to reduce greenhouse gas emissions. This work provides technology developers with a systems-level perspective of the climate impacts of electrochemical CO_2 conversion products. Different uses (polymer production, transportation fuels, and power generation) of three CO_2-based fuels (methane, methanol, and diesel) are compared considering different combinations of electrolyzers (water or CO_2 electrolysis) and thermochemical methods. Additionally, the influence of assumptions and trade-offs between environmental and economic performance are evaluated in sensitivity analyses, using polymer and diesel production as examples. Finally, recommendations are provided based on environmental and economic analyses. The novelty of this work involves the application and communication of LCA methods and insights aimed at helping developers visualize their technology in the full supply chain, providing examples of analyzed systems and a set of recommendations that can be generalized and incorporated into the development of different technologies. Example recommendations include considering that in projects focusing on improving the environmental performance of electrochemical processes, cell degradation and electricity source are major factors. On the other hand, for economic performance, lifetime is more important than cell degradation and electricity source. Electrochemical processes are quite promising from a climate change perspective if the input electricity is from a low-carbon source, if the use phase does not involve combustion, if the product is efficient for the use chosen (*e.g.*, diesel is more efficient for transportation than other fuels), and if the use has a large market size.

1. Introduction

A portfolio of technology solutions will be necessary to keep greenhouse gas (GHG) emissions within limits such as those agreed to in the Paris Agreement.[1] Among them, new ways to produce fuels are being developed, such as carbon conversion technologies (CCTs), which aim to use captured CO_2 as a raw material for manufacturing valuable products. The production of cement,[2] polymers,[3] and fuels from CO_2,[4] as examples, is receiving increasing attention in academic and industrial sectors. Electrolysis is a potentially powerful tool for low-carbon fuel and chemical production. However, aspects such

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as the supply chain environmental impacts and potential trade-offs between environmental and economic performance have not been holistically assessed to date. This is needed to make better decisions about technology investment and development.

Life cycle assessment (LCA) is a tool that is used to evaluate the environmental impacts of a product, process, or service.[5] The inputs and outputs (*i.e.*, materials and energy) involved in providing the product, process, or service are identified and linked to potential environmental impacts. LCA guidelines can be found in ISO (International Organization for Standardization) standards ISO 14040 and ISO 14044.[6,7] LCA studies have mainly been written and used to inform funding[8,9] and policy[10] decisions, and environmental labeling,[11] rather than to inform technology developers. LCAs tend not to be accessible or directly applicable to the decisions made by researchers as they conceptualize and develop a technology at early stages (*e.g.*, lab-scale experiments). However, at this point, the freedom to make changes (and therefore reduce costs and environmental impacts) is highest.[12]

One way to make LCA results more relevant and helpful in informing early-stage technology development is to integrate

LCA with techno-economic assessments (TEAs) to evaluate potential linkages or trade-offs between environmental impacts and economic performance. There has been some recent literature[13–18] exploring this area, but it has not been focused on early-stage technologies and their particular challenges, such as lack of and poor quality data. The technologies considered are mostly at a commercial or mature stage.[16] In addition, the life cycle GHG emissions of equipment manufacturing are sometimes neglected, even though in TEA equipment is considered.[13] An integrated framework proposed by Thomassen *et al.*[19] was applied to diesel production as a case study to evaluate the system, including environmental and techno-economic aspects. The framework provides a helpful operational example of the integration, but it does not explore the influence of LCA methodological choices (*e.g.*, allocation or how input CO_2 is credited) or capital costs, relevant aspects for emerging technologies.

In LCA terminology, the boundaries delimit the system to be analyzed and may influence the results since they determine which phases/processes will be included or excluded from the study.[20] For instance, it is possible to study the life cycle of a product from raw material extraction until its end-of-life in a cradle-to-grave study. Alternatively, the use and end-of-life phases are not considered, and the system is drawn until the "gate" of the factory, called a cradle-to-gate study. In the CCTs field, cradle-to-gate studies are most common and are generally sufficient for comparing different production processes of the same product with the same use and end-of-life phases. However, when there are different potential uses and technology developers seeking to understand the role that their technology could play in different markets, this approach becomes inadequate, and information about the full system or supply chain (including the use phase) is then needed. Additionally, only cradle-to-grave analyses allow assessing whether the CCT can result in negative emissions.[18] Therefore, this systems-level perspective may offer insights that a cradle-to-gate analysis may not provide.

Different approaches have been developed for CO_2 conversion, such as photocatalysis, non-thermal plasma, and electrochemical conversion. Photocatalysis for CO_2 conversion uses low-GHG intensity solar energy but suffers from low efficiency and poor selectivity.[21] Non-thermal plasma is performed in the plasma state of matter (the fourth state) using electrons with high energy. This approach does not use rare materials and allows rapid system response to fluctuating feed (shutdown/start-up), but energy efficiency and CO_2 conversion still cannot be maximized concurrently.[21,22] In electrochemical conversion, selectivity and kinetics can be challenges, depending on the type of electrolyzer used and the desired product.[21,22] However, this approach can provide electricity storage in the form of fuels and chemicals produced from CO_2, especially considering the need for large scale renewable energy storage technologies.

This study provides a bridge between LCA methods and various electrolysis pathways with the aim of informing decisions at early stages of development. For this purpose, this work is focused on Solid Oxide Electrolyzer Cells (SOECs) and Polymer Electrolyte Membrane Electrolyzer Cells (PEMECs) as examples of emerging CCTs, which are considered less mature technologies and therefore offer an opportunity for LCA/TEA to help inform design decisions. In terms of CO_2 conversion strategies, two pathways[22] are considered in this study: electrochemical (only) and a hybrid pathway of electrochemical and thermochemical units, as illustrated in Table 1 and Fig. 1. In the electrochemical pathway, CO_2 is electrochemically converted without the need for H_2, such as achieved by the co-electrolysis of CO_2 and H_2O in SOECs (high-temperature electrolysis), or conversion is carried out in a CO_2–CO-product tandem configuration[23] (CO_2 is converted to CO in a high-temperature SOEC, followed by CO conversion to products in an AEC during low-temperature electrolysis). In the hybrid pathway, H_2 from water electrolysis (in an SOEC or PEMEC) is used as an intermediate, followed by a thermochemical process (*e.g.*, Sabatier reaction) for CO_2 hydrogenation. Table 1 also shows the cases presented in Fig. 1 related to each strategy.

1.1. Past assessments of electrochemical processes

Several products may be generated using CO_2 as a feedstock together with electrochemical and/or thermochemical processes (see Table 1), including methane,[3] methanol,[3] polyoxymethylene,[24] polypropylene,[24] and diesel.[4,25] The hybrid pathway is the most mature and well-studied in LCA,[3,4] with several demonstration projects under development.[26,27] Thus, for CCTs, both CO_2 electrolysis (electrochemical pathway) and water electrolysis (hybrid pathway) are of interest (reactions (1), (2) and (5), (6), Table 1) and are included as potential pathways.

Past LCA studies of fuels production *via* electrolysis have concluded that the intensity of electricity is the biggest driver of GHG emissions from electrochemical processes.[28–30] Wind, hydroelectricity, and solar photovoltaics for electricity generation are attractive sources due to low-GHG intensity.[30] Furthermore, coupling electrolysis with surplus renewable electricity may considerably reduce impacts compared to traditional production processes.[31,32]

In terms of economics, several studies have assessed the costs associated with electrochemical processes. Some of the critical parameters are electricity input and capital costs, and external factors such as local regulations.[33] The lifetime of stacks and electricity prices are also relevant.[14] However, in terms of GHG emissions, stack lifetime was not an influential factor,[14] suggesting that the key factors may differ for environmental and economic performance.

1.2. LCA and R&D (research and development) process

In LCA studies, it is common to define a scenario representing a specific technology configuration, such as an electrolyzer with average or typical performance and specifications. From these "base case" results, further analysis may be performed. For example, a contribution analysis can be conducted to

Table 1 Pathways, electrolyzers, characteristics, and reactions involved in each CO_2 conversion strategy in this study

Pathway	Electrolyzer	Characteristics	Reactions (electrolyzer)	Reactions (thermochemical units)	Cases in Fig. 1
Electrochemical (CO_2 is electrolyzed)	SOEC Co-electrolysis	-Not commercialized[41,42] -Temperature: 650-1000°C[43] -Low-cost catalysts[43] - Excellent kinetics at elevated temperatures thus lower potentials needed[44] -At thermoneutral voltage, no additional heat necessary (heat generated via Joule effect is sufficient)[44] -Co-electrolysis mode[44] gives tunable syngas production	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$ $CO_2 + 2e^- \rightarrow CO + O^{2-}$ $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ $(1)^{45}$	Methanation $CO + 3H_2 \rightarrow CH_4 + H_2O$ $(7)^{46}$ Catalytic conversion $CO + 2H_2 \rightarrow CH_3OH$ $(8)^{3}$ Fischer-Tropsch $nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O$ $(9)^{47}$	a.1 (CH$_4$) a.2 (CH$_3$OH) a.3 (Diesel)
	SOEC CO_2 to CO AEC CO to products (in tandem)	SOEC -Early commercialization[44] (The other points for SOECs co-electrolysis apply) AEC -Not commercialized[48] -Temperature: Ambient[49] -Flow cell configuration in this study -CO reduction in flow cells is still in its infancy[50]	SOEC $CO_2 + 2e^- \rightarrow CO + O^{2-}$ $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ $(2)^{51}$ AEC $CO + 5H_2O + 6e^- \rightarrow CH_4 + 6OH^-$ $6OH^- \rightarrow 3/2\ O_2 + 6e^- + 3H_2O$ $(3)^{52}$ $CO + 4H_2O + 4e^- \rightarrow CH_3OH + 4OH^-$ $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$ $(4)^{52}$	N/A	a.4 (CH$_4$) a.5 (CH$_3$OH)
Hybrid (H_2O is electrolyzed to produce H_2; CO_2 and H_2 are converted in a thermochemical unit)	SOEC H_2O electrolysis	-Early commercialization (kW scale) (The other points for SOEC co-electrolysis apply)	$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$ $2O^{2-} \rightarrow O_2 + 4e^-$ $(5)^{48}$	Sabatier reaction $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ $(10)^{3}$ Catalytic conversion $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$ $(11)^{3}$	b.1 (CH$_4$) b.2 (CH$_3$OH) b.3 (Diesel)
	PEMEC H_2O electrolysis	-Early commercialization (MW scale) -Temperature: 50-80°C[43] -Costly catalysts (OER is a problem) -Higher cell voltages required due to OER kinetic limitations[53]	$2H^+ + 2e^- \rightarrow H_2$ $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ $(6)^{48}$	Reverse water-gas shift[22] $H_2 + CO_2 \rightarrow CO + H_2O$ Fischer-Tropsch $nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O$ $(9)^{47}$	b.4 (CH$_4$) b.5 (CH$_3$OH) b.6 (Diesel)

In each pathway, the intermediate products (fuels) are marked in bold. OER: oxygen evolution reaction.

identify the main drivers of impacts. A sensitivity analysis[20] that tests the influence of base case assumptions on results is also common. However, LCA studies directed to the R&D process are scarce, and many discuss the product design phase broadly[34,35] or explain a theoretical framework with specific application examples.[36,37] In these studies, a specific base case is defined, and the conclusions are valid for that system, making it difficult to generalize the insights beyond the base case so that technology developers can apply these insights to their processes.

As examples of LCA applied to electrochemical processes, Griffiths *et al.*,[38] Sharma *et al.*,[39] and Nabil *et al.*[40] employed LCA to guide R&D. The synthesis of a material with superior characteristics or with higher conversion efficiency may not result in lower GHG emissions if the synthesis process is more complex, requires more energy, or if more reagents with high embodied GHG emissions (*e.g.*, palladium's upstream GHG emissions due to extraction and processing) are needed.[38,39]

Nabil *et al.*[40] conducted a cradle-to-gate investigation of strategies for CO_2 conversion, including a tandem[23] approach:

electrolyze CO_2 to CO (in a SOEC) followed by the conversion of CO to products in an alkaline electrolyzer flow cell (AEC-flow). This strategy resulted in lower impacts due to lower energy demand (overall lower cell potential and higher selectivity)[23,40] compared to other strategies. Separation, especially of liquid products, is an important driver of impacts due to the low concentration of products obtained from the electrolyzer. These studies evaluated electrochemical processes but did not include the use phase (*i.e.*, cradle-to-gate). However, when processes are flexible and different products and uses are possible, cradle-to-gate studies should be expanded to include the use phase (*i.e.*, cradle-to-grave).

Factors not related to the performance of electrochemical processes (*e.g.*, sources of feedstock or energy) may play an essential role in the overall environmental impacts but may not be easily identified. This work aims to study the impacts of upstream and downstream choices in systems that involve electrochemical processes, helping to prioritize research areas.
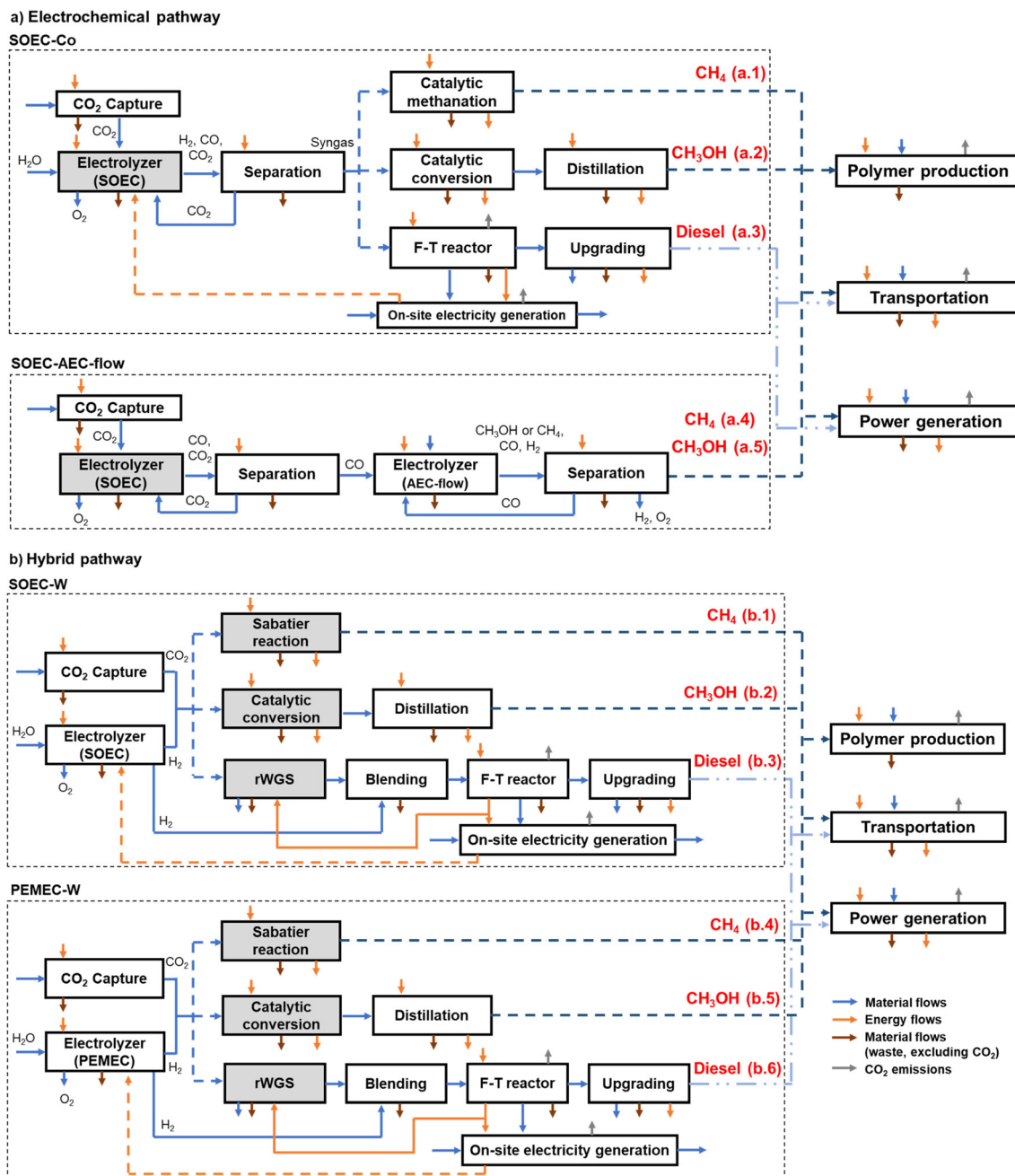
Fig. 1 System boundary and key material flows of CO_2-based fuels production *via* (a) electrochemical and (b) hybrid pathways. Boxes are labeled on the left side with the different combinations of processes and products. The blue dashed lines linking the upstream and midstream to the downstream phases indicate the potential uses for each fuel. Units where CO_2 is converted are shown in gray. SOEC-Co: SOEC co-electrolysis, SOEC–AEC-flow: tandem electrochemical CO_2 conversion in SOEC followed by AEC, SOEC-W: water electrolysis in an SOEC followed by CO_2 hydrogenation, PEMEC-W: water electrolysis in a PEMEC followed by CO_2 hydrogenation. rWGS: reverse water gas shift, F–T: Fischer–Tropsch.

We aim to answer the following research questions:

(1) Do different uses of products (*e.g.*, methane, syngas) generated from CO_2 conversion involving electrolysis (*i.e.*, electrochemical or hybrid pathways) affect the life cycle GHG emissions?

(2) Which factors, if any, drive differences in GHG emissions across the proposed pathways?

(3) What parameters affect the GHG emissions and cost of products? Are there trade-offs?

(4) Are there specific aspects of different strategies (*e.g.*, SOEC co-electrolysis or tandem CO_2 to CO to products) that may be an advantage or disadvantage in terms of GHG emissions?

The answers to the above questions are used to generate a set of recommendations that can help technology developers to consider electrochemical processes from a broader perspective.

A cradle-to-grave LCA is conducted for methane, methanol, and diesel production from CO_2 when produced using different strategies, which may be classified in two pathways (*i.e.*, electrochemical-only and hybrid). The strategies are summarized in Table 1.

Three potential uses for the chemicals are considered (polymer production, transportation, and power generation), and an integrated LCA and TEA is performed for diesel production. Given the effort to achieve climate targets and the potential role that electrochemical processes may play in this context, this paper focuses on GHG emissions. However, other impacts, such as acidification and water consumption, can and should be included for a more comprehensive investigation of environmental impacts. In this study, other impacts are qualitatively discussed in Section S5 in the ESI.† Caution is advised when analyzing the results since the technologies in this study are at different maturity levels, resulting in different levels of uncertainty, which is beyond the scope of this study.

2. Materials and methods

The goal of this study is to provide technology developers with insights and recommendations using LCA as a tool that can be generalized and applied to the R&D process. As LCA studies are rarely written for technology developers, we also provide clarifications about methodological choices in worked examples to help the audience visualize major aspects that influence a reported GHG emissions estimate. The results of this study are not intended to be used as definitive and assertive identification of the lower impact pathways, which would be difficult given the maturity level of the considered technologies. Instead, the characteristics and differences across strategies (*e.g.*, liquid/gaseous products, tunability) are identified and used to recommend potential improvements for development.

The functional units considered are described in Section 2.2. Flows of GHG emissions are the focus of the study (for details, see Sections S1.1–S1.3 in the ESI†), and the characterization factors (*i.e.*, the global warming potential of the various GHGs in relation to the reference CO_2) are defined by the IPCC 6th assessment for 100 years.[54] We also focus on the operations phase of the life cycle, as the operation is often responsible for most impacts especially in processes that have high energy demands (including non-spontaneous processes such as electrolysis). Therefore, we model material and energy flows for CO_2 conversion in more detail, which allows exploring potential associated impacts and effects of CO_2 conversion process improvements.

The pathways, electrolyzers, intermediate products, and general characteristics are shown in Table 1. The last column in Table 1 also references the respective cases in Fig. 1, which shows the flow diagram of each case.

Fig. 1 presents the system boundaries of CO_2-based fuels production *via* electrochemical (Fig. 1a) and hybrid (electrochemical + thermochemical) (Fig. 1b) pathways, as well as

main flows. Each combination of process and product is labeled between parentheses in front of the respective box, *e.g.*, (a.1) for methane produced from SOEC-Co, where "Co" infers the co-electrolysis of CO_2 and water in the same SOEC. Each pathway is explained in detail in Section 2.1.

Three potential uses (polymer production, transportation, and power generation) of the CO_2-based fuels are evaluated to put the electrochemical technologies in context and help technology developers envision the impacts of future use.

General assumptions are made to ensure a consistent analysis and are detailed in Section 2.4.

Previous studies that provide a detailed inventory and are preferably based on process simulations were selected to build the model. This requirement is especially relevant for less mature technologies, given that simulations are useful to estimate their performance more accurately than laboratory estimations or use of proxies,[9] by including aspects such as heat integration and equipment scale-up. As a note, there is active research in the LCA field regarding scale-up methods and ensuring fair comparisons across technologies at different maturity levels.[9]

The base case LCA method to handle multi-product systems is system expansion *via* substitution.[55] Allocation methods are tested in the sensitivity analysis (Section 2.3). Some data for the background system (supporting activities) may also employ allocation, noted in Section S1 in the ESI.†

2.1. Description of the system

This section describes the systems, technologies, uses, incumbent processes (conventional way to produce a product or service), assumptions, and metrics.

For the electrochemical pathway, SOECs operated in the CO_2/H_2O co-electrolysis mode are labeled as SOEC-Co, generating syngas that is further processed into fuels. It is also possible to electrochemically convert CO_2 in tandem (CO_2 to CO in the SOEC and CO to products in an AEC in a flow configuration),[40] identified as SOEC–AEC-flow.

The hybrid pathway involves water electrolysis and thermochemical units (Sabatier reaction for methane,[3] or reverse water gas shift, rWGS, followed by Fischer–Tropsch, F–T, for diesel).[25] In this case, water electrolysis is performed by high-temperature electrolysis in a SOEC (which we identified as SOEC-W) or during low-temperature electrolysis in a PEMEC (PEMEC-W).

2.1.1. Electrochemical only pathway (SOEC-Co: cases a.1–a.3, SOEC–AEC-flow: cases a.4 and a.5). The first three cases in Fig. 1a (cases a.1–a.3) refer to co-electrolysis processes in a single SOEC unit to produce CO + H_2 (reaction (1), Table 1), followed by subsequent thermochemical units to produce methane, methanol, and diesel (reactions (7)–(9), Table 1). Cases a.4 and a.5 (Fig. 1a) refer to electrochemical CO_2 conversion in CO_2–CO-product tandems, in which CO_2 is converted to CO in an SOEC (reaction (2), Table 1), and the CO is converted to products in an AEC-flow system (reactions (3) and (4), Table 1).

In the co-electrolysis processes (SOEC-Co, cases a.1–a.3), H_2O and CO_2 are fed in the desired ratio and co-electrolyzed to

produce syngas. The reference study[45] considered a scaled-up process to produce syngas at $H_2 : CO$ molar ratio of $2 : 1$[45] (for methane, extra H_2 is necessary to adjust the ratio to $3 : 1$[3] and is assumed to be provided by SOEC water electrolysis). The syngas can be converted to methane, methanol, or F–T diesel in thermochemical units. As in all electrolysis processes discussed here, oxygen is generated as a co-product, and in F–T diesel production, LPG (liquefied petroleum gas), gasoline, wax, and steam are also generated.

Purification of the gaseous stream is assumed to be done by pressure swing adsorption.[40,56] The separation of gaseous streams is a minor contributor to GHG emissions[40] (assumption tested in the sensitivity analysis).

It is assumed that the energy demand for methane and methanol production[3] from CO and CO_2 are equivalent (assumption tested in the sensitivity analysis). In diesel production,[57,58] the fuel gas leaving the F–T unit is used for electricity generation,[57] which offsets part of the electrolyzer's energy consumption. For details, see Section S1.1 in the ESI.†

Cases a.4 and a.5 (SOEC–AEC-flow) involving low-temperature CO_2 conversion in aqueous systems[40] consider a combination of a high-temperature SOEC for CO production from CO_2 and a low-temperature AEC. The reference study[40] assumed optimistic performance, such as 90% selectivity towards methane and methanol (90% faradaic efficiency), and H_2 as the only cathodic by-product (along with oxygen from the anode, with oxygen also generated in the SOEC). A range of by-products is expected,[59] but the favorable assumptions were selected to verify if electrochemical CO_2 conversion, as defined, can be competitive.[40] Data about the core processes (electrolysis and separation) is used, and the remaining parts of the system (CO_2 capture process, energy, and other utilities production, and use phase) are adjusted to align with the boundaries of our study.

We calculate the net GHG emissions resulting from the use of CO_2-based fuels in the uses listed in Table 2. Net GHG emissions are the summation of all GHG sources in the system: CO_2 captured, energy consumption during electrolysis and production process, CO_2 converted, CO_2eq avoided by co-products, and fuel use.

Table 2 CO_2-based fuels and their uses considered in this study, as well as the metrics used for the quantification of impacts to climate

Use	CO_2-based fuels	Metrics
Polymer production	Methane (for POM[a] production)	kg CO_2eq per kg POM
	Methanol (for PP[b] production)	kg CO_2eq per kg PP
Transportation	Methane Methanol Diesel	kg CO_2eq per pkm
Power generation	Methane Methanol Diesel	kg CO_2eq per kW h

[a] POM: polyoxymethylene. [b] PP: polypropylene.

2.1.2. Hybrid pathway (SOEC-W: cases b.1–b.3, PEMEC-W: cases b.4–b.6). CO_2-based fuels production via water electrolysis in a hybrid (electrochemical and thermochemical) pathway is presented in Fig. 1b.

Water is electrolyzed in either an SOEC (reaction (5), Table 1; cases b.1–b.3, Fig. 1b) or a PEMEC (reaction (6), Table 1; cases b.4–b.6, Fig. 1b) to produce H_2, which reacts with CO_2 in a subsequent thermochemical unit, generating methane, methanol, and F–T diesel (reactions (9)–(11), Table 1). For F–T diesel, CO_2 is converted to CO using an rWGS reaction to produce CO.[4] Additional H_2 from the electrolyzer is blended with the product of rWGS to produce syngas with a $H_2 : CO$ molar ratio of $2 : 1$.[25] Oxygen is produced during water electrolysis as a co-product, as well as LPG, gasoline, wax, and steam in F–T diesel production.

The energy demands associated with using SOEC and PEMEC for water electrolysis are taken as 46[48,60] and 54 kW h kg^{-1} H_2,[3,48] respectively, and additional information about steam demand and oxygen production is taken from Zhang et al.[61] Water electrolysis using the SOEC and PEMEC are referred to as SOEC-W and PEMEC-W, respectively.

The same CO_2 conversion units as those described in Section 2.1.1 are employed. For details, see Section S1.2 in the ESI.†

2.1.3. Uses and incumbents. Three uses for the CO_2-based fuels are considered: polymer production, transportation, and power generation.

For polymer production, methane is used to produce polyoxymethylene (POM) and methanol is used to produce polypropylene (PP), which are processed by injection molding.[24] In the base case, polymers are considered to have a lifetime sufficient to maintain CO_2 sequestration. Two alternative end-of-life treatments are considered in the sensitivity analysis (see Section 2.3.1): recycling followed by incineration and direct incineration.[24] The incumbent process (conventional way to produce a product or service) for polymer production is the same but uses fossil feedstocks instead of CO_2-based chemicals. For POM, additional information is provided in Section S1.3.1 in the ESI.†

For transportation, fuels are assumed to be used in medium-size passenger cars.[62,63] The incumbent is assumed to be a gasoline-fueled vehicle complying with Euro 5 standard.[62] For power generation, methane and methanol are used as the input to the solid oxide fuel cells (SOFC), generating heat and power.[64] Diesel is consumed in a heat and power cogeneration unit,[63] and the incumbent is a natural gas combined cycle plant.[65]

Regarding co-products, gasoline and LPG incumbents are assumed to be from fossil sources, and oxygen from cryogenic air separation. For details, see Sections S1.3 and S1.4 in the ESI.†

Multiple incumbents and competitors may exist. The incumbent may be different in different contexts, and future work should consider this aspect.

We focused on three end uses, but technology developers may also consider other uses for the intermediate products. For instance, methane is an important and potent GHG if released at any point in the supply chain. Methane can also be

used for a variety of purposes such as heating[29] or substrate for bioproducts.[66]

2.2. Metrics of evaluation of life cycle GHG emissions and functional units

A functional unit describes the function or service that the process under study intends to fulfill.[20] Each use has a different functional unit. For polymer production, the functional unit is one kg of polymer (POM or PP) produced and used. For transportation, the functional unit is one passenger-kilometer (or pkm), which represents the transportation of one passenger for one kilometer.[67] For power generation, the functional unit is the generation of 1 kW h of electricity. Table 2 summarizes the CO_2-based fuels and their uses, and metrics to support understanding results. Note that polymer production has two units, and diesel is not considered in all end uses.

Net GHG emissions, in CO_2 equivalents, represent the global warming impact indicator, quantifying the potential impact that a process, product, or service could contribute to increasing global temperatures.

Net GHG emissions are organized into two sets of metrics in this study: the first set is related to the use of CO_2-based fuels and is described in the paragraph above.

The second set of metrics focuses on evaluating CCT alternatives consistently, regardless of the use or the product generated, and identifying potential benefits of CCT alternatives compared to incumbent processes. This set of metrics includes kg CO_2eq emitted per kg CO_2eq converted, avoided emissions in kg CO_2eq avoided per kg of polymer (for polymer production, for example), and global emissions reduction potential in Gt CO_2eq per year. Avoided emissions compare the GHG emissions from CCTs with incumbent technologies, while the global reduction potential incorporates the market size to understand the potential to reduce emissions according to different uses and markets. For details, see Section S3.4 in the ESI.†

2.3. Sensitivity analyses

In LCA studies, sensitivity analyses are useful tools to evaluate the effect that assumptions or decisions made have on results. They are also helpful for identifying the most influential parameters (*e.g.*, electricity source) on the calculated metrics (*e.g.*, net GHG emissions). Therefore, we employ sensitivity analyses to understand which decisions and parameters are most influential, supporting the generation of a set of recommendations that may be considered during R&D. Two sensitivity analyses are performed: one to evaluate the assumptions (for the CO_2-based polymer production) and another to identify the most influential parameters in diesel production. The greater the sensitivity (*e.g.*, the wider the bar in Fig. 5), the more influential that parameter is on the outcome of that analysis.

2.3.1. Sensitivity analysis to test assumptions. CO_2-based polymer production was selected for this sensitivity analysis because it facilitates testing assumptions made for other end uses (*e.g.*, electricity source, allocation) in addition to the end-of-life treatment. The base case is CO_2-based polymer production by SOEC-W water electrolysis (cases b.1 and b.2, Fig. 1) with natural gas-based energy inputs. The tested parameters include the electricity source (renewable and coal-based), allocation method (no allocation and mass allocation), credits for CO_2 used (full credit and no credit, see Section 2.4), electrolyzer energy demand, CO_2 sources (DAC, direct air capture, powered by low-carbon and natural gas energy), methanol synthesis energy demand for PP, and end-of-life treatment (incineration and recycling with incineration). Polymer produced in the recycling process is assumed to be burden-free,[24] and a total of three recycling cycles (four uses) are assumed, with all polymer incinerated after the useful life. For details, see Section S1.3.1 in the ESI.†

Sensitivity to methanol synthesis energy demand was tested by varying the input by ±50% and evaluating the influence on final impacts. The same procedure was used to evaluate the sensitivity to energy demand for separation in the SOEC-Co case.

2.3.2. Sensitivity analysis for influential parameters. For diesel production, an integrated[19] environmental and a simplified economic sensitivity analysis is conducted. The work of Okeke *et al.*,[57] Okeke and Mani,[58] Van Der Giesen *et al.*,[4] and Zhang *et al.*[61] were used as the basis for the process, and the factors listed in Table S9 (ESI†) were varied to identify the most influential factors and potential trade-offs. The lower and higher values represent the best and worst cases of each parameter. Electricity and CO_2 source are based on the low-carbon, natural gas, and high carbon scenarios (see Section 2.4). For the degradation rate, a wider range of values than reported for SOFCs was assumed (0.1% to 2.0%) since SOECs are a less mature technology.[45,68,69] The base case LCA method to handle multi-product systems is system expansion *via* substitution,[55] but other methods are available and discussed in detail in Section S5 (ESI†). For the sensitivity analysis, two extreme cases are considered: no allocation (which attributes all GHG emissions to diesel, ignoring co-products) and mass allocation (which attributes GHG emissions to each co-product according to the relative mass of each product, reducing GHG emissions attributed to diesel). Ranges for the other parameters are based on the low and high values found in the literature. For details, see Section S3 in the ESI.†

2.4. General assumptions

General assumptions are made to harmonize the boundaries of the system, ensuring a consistent analysis across reference studies and data sources. First, the CO_2 capture unit is assumed to deliver a CO_2 stream with the required purity in all cases. Processes based on absorption by monoethanolamine from flue gases may reach high purity, and CO_2 capture *via* DAC is comparable to the absorption process.[3] The sources of CO_2 considered in this study were also used in CCT projects in Europe:[26,27] coal and natural gas power plants, and DAC. The impact of CO_2 source is tested in the sensitivity analysis for polymer production and in the LCA and TEA study of diesel production.

The CO_2 captured and utilized is assumed to receive full credit, and its use generates a negative emissions credit (-1 kg CO_2eq per kg CO_2 used), which can be subtracted from the total GHG emissions throughout the life cycle of the CO_2-based products. When CO_2 is captured from a power plant, for example, there are two product streams, power and CO_2, generating the question of who should get credit for the captured CO_2 (*i.e.*, the avoided emissions). By assuming that CO_2 feedstock can be credited as -1 kg CO_2eq per kg CO_2 used, we implicitly give full credits of the emissions avoided (in the power plant) to the CO_2 product stream. An implication of this assumption is that when negative net GHG emissions are obtained, net CO_2 is not necessarily removed from the atmosphere, but that using the systems under study results in lower GHG emissions compared to the incumbent system (*e.g.*, a power plant releasing all CO_2 produced to the atmosphere); therefore, we use the term GHG-emissions-reducing[18] in this case. In the sensitivity analysis (see Section 2.3.1), we test the extreme high case of this assumption, *i.e.*, the CO_2 from the power plant receives no credits for the avoided emissions (with all the credits for avoiding the GHG emissions attributed to the power plant). In this case, instead of subtracting 1 kg CO_2eq from the total GHG emissions per each kg CO_2 used, no credit is given.

CO_2-based fuel transportation and distribution transfer the produced fuel from the supplier to the end user.[20] Those phases are assumed to be similar in all cases and small relative to other emissions sources,[62] and thus they are not included in the calculations.[4]

We assume that the SOECs operate at the thermoneutral voltage, where the Joule heating from the electrolysis cell operation maintains the cell temperature;[44] therefore, no additional heat is needed once the electrolyzer reaches its operating temperature.

Regarding the deployment context, the natural gas-based scenario assumes that natural gas is the source for utilities. Electricity is assumed to be generated in a natural gas power plant (0.49 kg CO_2eq per kW h),[70] heat in a natural gas industrial furnace, and H_2 from water electrolysis powered by natural gas-based electricity. CO_2 is assumed to be obtained by absorption by monoethanolamine from a natural gas power plant. In the low-carbon scenario, electricity is provided by low-carbon sources (0.024 kg CO_2eq per kW h),[70] and the emission factor used is an average of various sources (hydropower, solar photovoltaics, wind, and nuclear). Low-carbon electricity may vary depending on local contexts, and by assuming a mix of sources, we acknowledge this diversity and the potential intermittent supply. Heat generation is assumed to be from geothermal energy, H_2 from water electrolysis powered by low carbon electricity, and the CO_2 is captured from ambient air *via* DAC and powered by low carbon energy. A high carbon scenario was also considered for the LCA and TEA study of diesel production, where electricity is assumed to be generated in a coal power plant, while heat is produced from a combined heat and power plant. The CO_2 is assumed to be captured from air *via* DAC but using natural gas-based electricity and heat. Table S8 (ESI†) presents the emissions factors of each utility in all scenarios.

3. Results and discussion

3.1. Life cycle GHG emissions

This study estimates the GHG emissions from cradle-to-grave of CO_2-based fuels with three different uses. Fig. 2–4 present the life cycle GHG emissions of different uses of each CO_2-based fuel, with items (a) referring to natural gas-based inputs and (b) referring to low carbon-based inputs. Methane use in the natural gas-based case was not shown because electricity and CO_2 sources are already based on natural gas (main constituent is methane). The natural gas-based case for power generation (Fig. 4) is grayed out because natural gas power plants provide CO_2 and electricity (shown to illustrate potential results). Fig. 2 presents the life cycle GHG emissions in kg CO_2eq per kg polymer (PP, polypropylene for methanol, and POM, polyoxymethylene for methane), Fig. 3 in kg CO_2eq per pkm (passenger-kilometer), and Fig. 4 in kg CO_2eq per kW h.

A clear general trend is that source of utilities is a major factor influencing the net GHG emissions of electrochemical processes given the difference in net GHG emissions in the low-carbon and natural gas scenarios. The use also influences the net GHG emissions.

In Fig. 2 (polymer production), in the low-carbon case, GHG-emissions-reduction, relative to a baseline in which CO_2 is not captured, is possible (-0.53 kg CO_2eq per kg POM and -2.7 kg CO_2eq per kg PP, SOEC-W) because there is no associated combustion of the fuels, and electricity and CO_2 are both obtained from low-carbon sources. The GHG-emissions-reduction is a result of the assumption that the CO_2 utilized can be treated as -1 kg CO_2eq per kg CO_2 used as feedstock (*i.e.*, receives full credit from capture, see Section 2.4), and is a result of the credits given for the co-products, which are also included as negative values. GHG-emissions-reduction means that the GHGs emitted throughout the life cycle is lower than cases when CO_2 is not captured (just released from the emitting source, *e.g.*, power plants) and the co-products (*e.g.*, oxygen) are produced by traditional (or incumbent) processes (*e.g.*, cryogenic separation).

In LCA, in systems that generate more than one product, the burdens can be shared among the products by using a partitioning method or a method called system expansion.[20] There is no consensus about which method to use, but ISO standards[6,7] and Guidelines for CO_2 Utilization[18] recommend using system expansion whenever possible (*i.e.*, "credits" are given to the production of co-products, avoiding traditional processes). Thus, the impacts of these traditional processes are subtracted from the impacts of our system.

In general, for CO_2-based fuels applied to transportation and power generation, further GHG-emissions-reduction is more difficult to achieve due to the combustion step in both cases. Therefore, as one clear message of this work, uses that do not require combustion are more promising to reduce GHG

Fig. 2 Life cycle GHG emissions of polymer production with (a) natural gas-based and (b) low-carbon-based energy inputs, in kg CO_2eq per kg polymer, for electrochemical and hybrid pathways. White diamonds represent the net GHG emissions which are the GHG emitted minus the CO_2 converted and the credits. x-Axis: SOEC-Co: SOEC co-electrolysis, SOEC–AEC-flow: CO_2 conversion in SOEC followed by AEC, SOEC-W: SOEC water electrolysis followed by CO_2 hydrogenation, PEMEC-W: PEMEC water electrolysis followed by CO_2 hydrogenation. Incumbent: conventional way to produce or generate a service. POM: polyoxymethylene, PP: polypropylene. Note the y-axis scale difference between (a) and (b).

emissions. In transportation (Fig. 3), CO_2-based diesel in natural gas-based case presents slightly higher GHG emissions than the incumbent (0.35 kg CO_2eq per pkm for SOEC-W diesel, versus 0.21 kg CO_2eq per pkm for the gasoline incumbent); however, compared to CO_2-based methanol (1.2 kg CO_2eq per pkm, SOEC-W) it is considerably lower. Diesel is much more efficient than methanol for this use (diesel energy content is approximately 43 MJ kg^{-1}, versus 20 MJ kg^{-1} for methanol), and as a result, each kg of methanol can deliver only 4.8 pkm, versus 29 pkm per kg diesel. Therefore, fuel efficiency in the considered use is a factor that should be considered. For power generation, all fuels resulted in similar emissions, except for methanol from SOEC–AEC-flow but it is still lower than natural gas-based power in a low-carbon scenario. In this use, the difference in efficiency between diesel and methanol is not as large as for transportation, with methanol delivering 3 kW h kg^{-1} and diesel delivering 5 kW h kg^{-1}.

Another important outcome of this analysis is that in terms of the different pathways and technologies involved, electrochemical CO_2 conversion via SOEC co-electrolysis (SOEC-Co,

cases a.1–a.3) and hybrid pathways (SOEC-W, cases b.1–b.3; and PEMEC-W, cases b.4–b.6) appear to result in lower net GHG emissions than processes involving low-temperature electrochemical CO conversion (SOEC–AEC-flow, cases a.4 and a.5). In these SOEC–AEC-flow cases, the total energy requirements for methane and methanol production were 31 kW h kg^{-1} methane and 39 kW h kg^{-1} methanol. In our study, for SOEC-W, the energy requirements are 22 kW h kg^{-1} methane and 9.0 kW h kg^{-1} methanol. The large difference between these pathways for methanol production is mainly due to the separation energy needed, which for SOEC–AEC-flow is 27 kW h kg^{-1} methanol (while the energy for conversion in the electrolyzers is 10 kW h kg^{-1} methanol).[40] In AEC-flow, liquid products are formed in the solution and are recirculated to increase the product concentration (the single pass accumulation is low); however, high concentrations of liquid products in the electrolyte can affect local parameters (e.g., pH),[71] impacting the electrolyzer performance[40,72] (e.g., instability and increasing cell potential).[71] Therefore, the relatively low concentration of liquid products elevates the energy demand for separation.

Fig. 3 Life cycle GHG emissions of transportation, with (a) natural gas-based and (b) low-carbon-based energy inputs, in kg CO_2eq per pkm, for electrochemical and hybrid pathways. White diamonds represent the net GHG emissions which are the GHG emitted minus the CO_2 converted and the credits. x-Axis: SOEC-Co: SOEC co-electrolysis, SOEC-AEC-flow: CO_2 conversion in SOEC followed by AEC, SOEC-W: SOEC water electrolysis followed by CO_2 hydrogenation, PEMEC-W: PEMEC water electrolysis followed by CO_2 hydrogenation. Incumbent: conventional way to produce or generate a service. Pkm: passenger-kilometer. Note the y-axis scale difference between (a) and (b).

The hybrid pathway (SOEC-W, case b.2) also requires energy for separation, but this strategy has the advantage of heat integration within the system. The methanol synthesis process is exothermic, which allows the heat generated to be used in the distillation process,[73] reducing the external energy input. Regarding the AEC-flow, improvements in the electrochemical process itself (e.g., faster kinetics, improved stability, and higher selectivity)[22] and integration with other industrial processes that generate surplus heat that can be reused in liquid products separation may help the process become more competitive in terms of GHG emissions.

It is also seen that SOEC-Co (cases a.1–a.3) tends to result in slightly lower GHG emissions than the hybrid pathway, even for methane (case a.1) that in this study uses additional H_2 from water electrolysis to adjust the ratio of H_2 : CO (from 2 : 1 in the scaled-up simulation[45] to the 3 : 1[3] needed to produce methane). In the case of tuning the composition from the co-electrolyzer by adjusting the H_2O : CO_2 ratio, we estimate that the GHG emissions may be further decreased between 4% (transportation) to 19% (power generation) compared to the non-tuned case (see Section S1.1 in the ESI†). Regarding the

hybrid pathway, it is clear that SOEC-W resulted in lower emissions than PEMEC-W because PEMEC electrolyzers are less efficient and require more electricity to produce the same amount of H_2 as SOEC water electrolyzers. The estimates in Fig. 2–4 are uncertain, and while outside the scope of this work, uncertainty should be considered when interpreting the results. The comparisons are an indication of trends, not definitive conclusions. Nonetheless, the results indicate that under certain conditions, CO_2 utilization may be more promising than the current incumbent process. For instance, in PP production (Fig. 2), SOEC-Co (a.2) or SOEC-W (b.3) with low-carbon-based energy inputs may result in net GHG emissions almost 3 times lower than the incumbent.

In summary, uses that do not involve combustion may be GHG-emissions-reducing compared to a system that employs incumbent production processes and no CO_2 capture. Furthermore, these non-combustion options emit about 2 times less GHG than end uses that result in combustion, on a per kg of CO_2 converted basis in the low-carbon scenario (Fig. S4 in the ESI†). When shifting from natural gas-based to a low-carbon scenario, the pathways become similar in terms

Fig. 4 Life cycle GHG emissions of power generation, with (a) natural gas-based and (b) low-carbon-based energy inputs, in kg CO_2eq per kW h, for electrochemical and hybrid pathways. White diamonds represent the net GHG emissions which are the GHG emitted minus the CO_2 converted and the credits. *x*-Axis: SOEC-Co: SOEC co-electrolysis, SOEC−AEC-flow: CO_2 conversion in SOEC followed by AEC, SOEC-W: SOEC water electrolysis followed by CO_2 hydrogenation, PEMEC-W: PEMEC water electrolysis followed by CO_2 hydrogenation. Incumbent: conventional way to produce or generate a service. Pkm: passenger-kilometer. Note the *y*-axis scale difference between (a) and (b). The natural gas-based case is grayed out because CO_2 and power are provided by natural gas power plants, which is also the end use; therefore, this chain is unlikely to be realized.

of GHG emissions. The electrochemical CO_2 conversion option that involves low-temperature electrolysis (SOEC–AEC-flow, cases a.4 and a.5) in the low-carbon scenario appears to be competitive with high-temperature electrolysis (SOEC-Co, cases a.1–a.3) and the hybrid pathway for methane production.

Comparing the CO_2-based options with the incumbent processes does not capture the GHG mitigation potential that each use presents globally. Thus, including the market sizes of each use in the analysis provides a sense of scale. Fig. S6 and S7 in ESI† presents the avoided emissions and global reduction potential for the base case and low-carbon scenarios. Polymer production appears to be a promising use in a low-carbon scenario according to Fig. 2 compared to the incumbent production process. However, considering the smaller market size compared to transportation and power generation, this use results in a lower potential to reduce emissions globally.

3.2. Sensitivity analyses

In this section, two sensitivity analyses are discussed: (1) influence of assumptions on the results (CO_2-based chemicals in

polymer production was selected as this case includes the end-of-life assumption) and (2) exploring the influence and trade-offs of certain parameters on the net GHG emissions and cost of diesel.

3.2.1. Sensitivity analysis to test assumptions. Fig. 5 presents the sensitivity analysis of assumptions made to calculate the net GHG emissions of CO_2-based methanol used to produce and use PP. The *y*-axis crosses the *x*-axis in the base case value for net GHG emissions, which is 12 kg CO_2eq per kg PP. The bars represent the distance from the base case result, namely water electrolysis in an SOEC (SOEC-W) with natural gas-based inputs.

In this figure, known as a tornado graph, parameters are ranked according to influence. One parameter is varied at each time, and its effect on the net GHG emissions is calculated. The electricity source is the most influential parameter. The use of renewable electricity may decrease net GHG emissions up to 115% compared to the base case, while the use of coal may increase net GHG emissions by 77% from the base case. In this analysis, electricity was evaluated alone, whereas in the former

Fig. 5 Sensitivity analysis of CO_2-based PP production and use. The base case is assumed to be SOEC-W water electrolysis with natural gas-based electricity, CO_2, heat, and steam. The dashed black vertical line indicates the GHG emissions of incumbent production processes. SOEC-W: SOEC water electrolysis, PP: polypropylene, DAC: direct air capture, NG: natural gas. The allocation methods (mass and no allocation) are applied to co-products O_2 and fuels. For the CO_2 source parameter on the left, in DAC (low-carbon) and DAC (NG), the terms between parenthesis refer to the source of energy inputs to DAC.

results (Fig. 2), the impact of electricity was combined with the impact of other utilities and feedstocks (*e.g.*, CO_2 source). The CO_2 source, end-of-life treatment, and energy demand in thermochemical units appears at the bottom of the graph, indicating a weaker influence than the electricity source.

For each parameter, the calculations were repeated with a lower and a higher input compared to the base case. The low and high values are labeled close to their respective bars. For instance, for electricity source, the lower input is low-carbon electricity labeled as "Low-carbon," and the net GHG emissions calculated is −1.8 kg CO_2eq per kg PP, as depicted by the blue bar. The same process was done with the higher input (coal-based electricity, labeled as "Coal"), which resulted in 21 kg CO_2eq per kg PP as can be seen in the *x*-axis.

Methodological choices in LCA, including allocation method and credits for CO_2 use, also resulted in appreciable influence. The allocation method chosen to handle the co-products may affect the net emissions, with mass allocation resulting in lower emissions (66% compared to the base case) and no allocation resulting in higher emissions (3% compared to the base case).

The base case employs system expansion, as recommended by ISO standards.[6,7] However, other methods are available to handle co-products (see Section S4 in ESI† for an explanation about each method and reasons to consider or discard the methods). The base case assumes all credits for CO_2 use are attributed to the CO_2 as feedstock, but when no credits are attributed to the CO_2 captured and used, net GHG emissions increased 31%.

For the assumption regarding the energy requirement for syngas purification in the SOEC-Co case, the base case input of 0.25 kW h m^{-3} was varied by ±50%, with the final net GHG emissions for PP production varying by ±0.20%. Thus, this assumption has a low influence on the results.

In Section S2 in ESI,† additional sensitivity analyses are presented, including a breakeven analysis for CO_2-based polymers with varying electricity emissions intensity, and a sensitivity analysis for the market penetration assumption to estimate the global emissions reduction potential. For PP production from SOEC-W, electricity emissions intensities below 0.075 kg CO_2eq per kW h will likely result in lower net GHG emissions than the current incumbent (2.0 kg CO_2eq per kg PP). The electricity emissions intensity in the provinces of Quebec (0.002 kg CO_2eq per kW h)[74] and Ontario (0.03 kg CO_2eq per kW h)[74] in Canada, for example, are sufficient to achieve lower net GHG emissions for production and use of CO_2-based PP compared to the incumbent. In the province of Quebec, over 94% of the grid is from hydroelectricity and only 0.7% from fuels such as natural gas and diesel.[74]

3.2.2. Sensitivity analysis for influential parameters. The impact of various parameters on GHG emissions in kg CO_2eq per kg diesel, and on cost in $ per kg diesel, for diesel production by water electrolysis (SOEC-W) is presented in Fig. 6. The base case considers natural gas-based electricity and CO_2, a SOEC degradation rate of 0.5%/1000 h,[45,75] and system expansion *via* the substitution method (for handling co-products).

In the LCA sensitivity, net GHG emissions in the base case are 5.4 kg CO_2eq per kg diesel, and costs are $2.5 per kg diesel. The most influential LCA parameters appear at the top of the graph; economic parameters are arranged in the same order as the LCA to highlight the trade-offs between the two dimensions. One parameter was varied at a time, and its effect on the net GHG emissions and production costs was estimated. This is not an optimization exercise or a rigorous TEA, but a tool to identify opportunities for improvement and potential trade-offs between environmental and economic performance.

The electricity source, SOEC degradation rate, and allocation method are the most sensitive environmental parameters as changes in any of these factors could result in appreciable variation in the net GHG emissions. The source of electricity is one of the main parameters impacting net GHG emissions, which are higher for coal-based electricity and lower for the low-carbon source. This is due to the higher emission factor for coal-fired electricity (0.80 kg CO_2eq per kW h) compared to electricity produced from natural gas (0.49 kg CO_2eq per kW h) and low-carbon sources (0.024 kg CO_2eq per kW h). A substantial reduction in GHG emissions could be achieved using low-carbon electricity instead of natural gas. However, using renewable electricity may lead to higher costs due to the cost of renewable electricity. The price of renewable electricity in this study was based on the levelized cost, which includes costs for construction and operation, but does not account for intermittency explicitly. In the case of surplus renewable electricity, the electricity is not counted as a cost; however, the operation time (or load factor) depends on when electricity is available, which may lead to higher operational costs per unit produced since production will be lower than a continuous operation with the same capital expense.[14] A more detailed discussion about the effect of intermittency on prices

Fig. 6 Parameter sensitivities to net CO₂ emissions from the base case for (a) LCA and (b) Economic analysis. The base case scenario is related to SOEC-W, natural gas-based electricity, CO₂, heat, and steam, SOEC degradation of 0.5%/1000 h, F−T conversion of 80%, and system expansion *via* substitution. SOEC-W: SOEC water electrolysis, F−T: Fischer−Tropsch. The allocation methods (mass and no allocation) are applied to co-products O₂ and fuels.

may be found in Ganzer and Mac Dowell,[76] who concluded that intermittency may account for up to 2/3 of the price of renewable electricity, depending on the location due to additional costs of storage in batteries or in the form of H₂. Conversely, coal electricity is being phased out in many developed countries, increasing its cost.[77,78] This result may change in the near future since trends in electricity prices show that renewable energy may be cost-competitive in the future.[79] Nevertheless, electricity source and price will continue to be crucial for electrolysis performance.

In terms of SOEC degradation, the higher degradation rate (2.0%/1000 h) than the base case has a notable impact on the net emissions (~65% higher) compared to the base case (SOEC-W, natural gas-based electricity, CO₂, heat, and steam, SOEC degradation of 0.5%/1000 h, F−T conversion of 80%, and system expansion *via* substitution). We assume that the production of diesel would be the same throughout the lifetime of the SOEC (water electrolysis). To compensate for degradation, electricity demand will need to increase with degradation to maintain output. The SOEC would thus consume more electricity than the base case, resulting in higher net GHG emissions with time. However, as the technology matures, emissions are expected to decrease as degradation rates decrease. Promising work is targeting issues that may lead to lowered degradation rates, such as minimizing Ni migration[44] and coking,[80] and replacement of metal catalysts with more stable metal oxides.[81] Cost follows the same trend as the GHG emissions due to the cost of electricity.

Allocation method is another influential parameter for GHG emissions, reinforcing the importance of LCA methodological choices on the results. Mass allocation shares the GHG emissions among the co-products based on their mass, and since the mass of oxygen produced is relevant, a substantial portion of GHG emissions is attributed to oxygen, resulting in lower GHG emissions attributed to diesel (12%). For the no allocation case, 100% of the GHG emissions are attributed to diesel.

Lastly, the lifetime of stacks appeared to be the least relevant factor for the LCA portion, with a lower lifetime of

12 000 hours (12 kh) only slightly increasing emissions. Infrastructure typically has lower impacts than operational factors, being commonly assumed to have negligible impacts.[3] Conversely, stack lifetime is one of the most influential cost drivers. If a research project aims to improve environmental performance, stack lifetime appears to be of minor importance but is relevant if the goal is to reduce costs. In this study, we consider lifetime and degradation separately and having different effects on GHG emissions, even though they are related.[14] Degradation is assumed to only increase electricity demand, maintaining the base case lifetime (48 000 hours), while the stack lifetime parameter considers the GHG emissions of replacing the electrolyzer in terms of infrastructure (*e.g.*, steel for interconnects and sealings) when the end-of-life voltage of the base case is achieved.

Most factors in the sensitivity analysis have the same effect on environmental and economic indicators, except for electricity and CO₂ source. Renewable sources (with lower GHG emissions) are currently more expensive than fossil options and lead to higher production costs. Thus, these factors are especially important to consider in decision-making processes.

The other tested parameters (energy demand for H₂ production, stack cost, electrolysis pathway, the CO₂ source, and the F−T conversion) are discussed in Section S3 in the ESI.† The technologies involved in this study are at different maturity levels. For instance, F−T is a mature technology, whereas SOECs are in the early stages of commercialization, and assessment of uncertainty is therefore relevant. However, uncertainty analysis is beyond the scope of this study.

3.3. Recommendations

Based on the analysis and results of this study, we formulated the following recommendations for technology developers of electrochemical CO₂ conversion solutions. It is worth noting that our intention is not to predict which technology or strategy is the most preferred but, from an analysis considering a broader scope, to generate insights and provide suggestions about applications and conditions that should be prioritized in research.

• Pair with renewables or look for low-carbon grids to decrease GHG emissions, keeping in mind that costs may increase.

• Avoid combustion wherever possible.

• In terms of the magnitude of global GHG emissions reduction, the difference between the alternative (*e.g.*, CO_2 conversion) pathway and incumbent is as important as the market size of the use.

• Consider the efficiency of the product-use relation (such as diesel, which is more efficient than the other fuels in transportation).

• In low-temperature electrochemical CO_2 conversion, pathways that produce liquid products and need more energy for the separation process than gaseous products, reusing waste heat in the separation unit may help decrease the overall energy requirement.

• Minimize degradation and energy demand, especially if the grid is carbon-intensive or if the electricity price is high.

• Better characterize the long-term behavior of high temperature electrolyzers (especially co-electrolysis) with dynamic loads to understand the degradation pattern, if any, and better assess their lifetime.

• In high temperature dry CO_2 or co-electrolysis, issues with carbon deposition or electrode microstructure change that can increase degradation should be minimized, as degradation rate is a relevant parameter for LCA.

• Stack lifetime is more relevant to economic performance than environmental performance. Thus, if the goal is to reduce climate impacts, energy demand is more relevant.

• Where high-temperature co-electrolysis is possible, it may be more promising than low-temperature electrolysis technologies and may even be competitive against thermochemical pathways. Also, tuning the intermediate products composition (*e.g.*, syngas) according to the use may be beneficial.

4. Conclusions

Our study provides a systems-level perspective to technology developers, highlighting the most relevant factors for improvement in the R&D process of electrochemical systems involving CO_2 conversion. The results indicate that electricity source and consumption during operation are the main drivers of GHG emissions. Other influential parameters include those related to the processing unit, such as SOEC degradation rates (which are still uncertain), energy demand for H_2 production, electrolyzer type, and F–T conversion (diesel case). External parameters also considerably influence the results, including the electricity source, as mentioned above, and the CO_2 source, reinforcing the notion that the overall emissions are heavily affected by factors beyond the electrochemical process itself. The LCA methodology may also have an appreciable effect (*e.g.*, the method to handle multiple co-products in diesel production). In terms of costs, stack lifetime, electrochemical process, and thermochemical units (*e.g.*, F–T reactor for diesel) are shown to be relevant factors.

Based on the results of each metric and the sensitivity analyses, a list of recommendations was provided with the intent of helping technology developers prioritize research areas of focus, considering environmental and economic performance.

It is worth emphasizing that this study does not aim to compare different technologies or strategies to define which one has the lowest GHG emissions. We use the comparison, which is subject to uncertainty, to investigate characteristics or sources of differences across strategies, and potential improvements that could support decisions during R&D. Additionally, we provide relevant LCA fundamentals to help technology developers identify aspects of LCA studies that influence a reported value, or what assumptions and methodological choices are behind a GHG emissions estimate.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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