

Advanced Circuitual Model for e-Drive Simulation, Including Harmonic Effects and Fault Scenarios

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Perspective

Where to address N₂ and reactive impurities in the CO₂ electrochemical value chain?

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CONTEXT & SCALE The scientific community is moving toward the scale-up of CO₂ electrolyzers. These systems can convert the carbon dioxide released by power plants, steel mills, cement kilns, and other industrial sources back into chemical building blocks using renewable electricity. A major practical hurdle is that these exhaust streams are diluted with N₂ and reactive impurities such as O₂, NO_x, and SO_x. Much recent research has therefore aimed to make CO₂ electrolyzers tolerant of dirty feeds, with the appealing prospect of installing them directly at the source of emissions, without any gas cleanup. But is this approach as sound as it is appealing?

Feeding diluted or impure CO₂ to an electrolyzer does not eliminate the separation problem but displaces it downstream where these species can be even more problematic. For example, downstream separation and synthesis processes are even more sensitive to contamination than the electrolyzer itself, making the trade-off less appealing from a full-system perspective. Viewed across the whole value chain, purifying CO₂ before electrolysis then emerges as the more economical and technologically mature choice, thus relying on separation technologies that are already industrially accessible. These perspectives suggest that prioritization should shift to integrating proven gas-cleanup units with electrolyzers and with emerging CO₂ transport and storage infrastructure and frameworks, which already impose purity specifications.

SUMMARY

The utilization of CO₂ provides a decarbonization pathway for hard-to-abate emissions, with solid-oxide and low-temperature electrochemical CO₂ conversion offering routes to value-added chemicals. Unfortunately, CO₂ sources are dilute and contain reactive impurities (NO_x/SO_x/O₂) that influence electrolyzer performance. Research has then focused on understanding the implications of impurities on operation and designing catalyst structures that tolerate impure feeds. High feed tolerances would be promising as electrolyzers could then be co-located with point-source emissions and avoid pre-processing. However, electrolyzers operated with dilute or impurity-tolerant feeds merely transfer separation burdens downstream. Sulfur limits for methanol or Fischer-Tropsch synthesis are more stringent than the electrolysis step, while separating CO/N₂ downstream is more complex than separating CO₂/N₂ upstream. Last, post-electrolysis oxygen impurities may pose flammability risks with by-product H₂. In this perspective, we critically examine CO₂ feedstocks and invoke a higher-level discussion reflecting where reactive impurities should be addressed in the electrochemical value chain.

INTRODUCTION

Electrochemical conversion of carbon dioxide (CO₂) into value-added products is emerging as a potential pathway in carbon utilization, thus enabling power-to-chemicals routes using renewable electricity.¹ Over the last decade, low-temperature CO₂ electrolysis has evolved from aqueous batch cells to gas-fed, flow-cell, and membrane electrode assembly (MEA) ar-

chitectures that sustain industrially relevant current densities, while enabling the selective production of carbon monoxide, formate, and even multicarbon (C₂₊) products such as ethylene.² Recent reviews and perspectives converge on a lab-scale state of the art in which low-temperature CO₂ electrolysis can exceed current densities greater than 200 mA cm⁻² and high Faradaic efficiencies (FEs) with favorable energetic performance and technoeconomic prospects,³ with CO being one of the most

promising targets.⁴ At the device level, MEA “zero-gap” cells have demonstrated ~100% CO selectivity at up to ~250 mA cm⁻² with >4,500 h stability⁵ and diagnostic tools (e.g., carbon crossover coefficient) that quantify noncatalytic CO₂ losses, thus providing practical guidance to improve designs.⁶ The parallel field of high-temperature solid-oxide CO₂ electrolyzers operating near 600°C boasts similarly attractive current densities (1 A cm⁻²) and stabilities (2,000 h), with the added benefit of >90% energy efficiencies toward CO.⁷

In the best-performing high- and low-temperature CO₂ electrolyzers, however, high-purity CO₂ is used as an input. In the context of CO₂ feedstocks, this implies that heavy pre-processing has taken place prior to the electrochemical devices to concentrate and purify CO₂. For example, all natural and industrial CO₂ sources are initially dilute (0.04%–55%), with most industrial sources containing substantial inert (N₂) and reactive species (O₂, NO_x, SO_x, and H₂S). As these purification and concentration steps add capital and operating expenditures, researchers have naturally asked whether we can operate CO₂ electrolyzers under dilute feeds or with different levels of impurities. The direct operation of electrolyzers with point-source emissions is also naturally appealing to emitters as it shifts purification and separation downstream.

Efforts to operate both low-temperature⁸ and solid-oxide⁹ electrolyzers under dilute CO₂ feedstocks with a N₂ balance have been largely successful. Within low-temperature CO₂ electrolyzers utilizing gas-diffusion electrodes, this is because mass transport-limited behavior is rarely observed unless salt formation or flooding occurs.^{10,11} So a dilution of the CO₂ feed can still enable meaningful CO₂ access to the catalyst layer even at 1 atm. Pressurization to 10 bar of a 10% CO₂ dilute stream, for example, sustained CO production at 2 A cm⁻².¹² While such pressures may be considered moderate in the context of electrochemical operation, they could be more demanding from a process standpoint. A system challenge with dilute operation, however, is a greater need to co-locate CO₂ sources with electrolyzers or risk the energy penalties of transporting a small fraction of CO₂ with inert N₂ over long distances.¹³ Dilute feeds contain many more species than just nitrogen, however, with the presence of other components posing more substantial threats to cell and catalyst performance.

Flue gases and biogenic sources of CO₂ inevitably carry O₂, NO_x, SO_x, H₂S, and other volatile compounds in concentrations from ppm to percent levels. Even after conventional purification processes (e.g., scrubbing), residual impurities can persist.¹⁴ Numerous electrochemical experiments in the past decade have now determined the impacts of these various impurities on transport properties, corrosion phenomena, and electrochemical performance.¹⁵ The most destabilizing of these impurities are O₂ and SO_x, which for all intents and purposes have been shown that they should be prevented from reaching the catalyst layer of the electrolyzers.¹⁶ To tolerate some degree of oxygen and sulfur within CO₂ electrolyzers, researchers have aimed to inhibit species transport from the gas channel to the catalyst layer through a mixture of mass transport and catalytic approaches.¹⁷ An underrealized consequence of operating CO₂ electrolyzers with dilute feeds or impurity tolerance, however, is that these undesired species still must be processed within the CO₂ value chain

to supply a purified product and recycle unreacted CO₂. For example, CO products that are eventually used for methanol (CO + 2H₂) or Fischer-Tropsch synthesis must contain only ppb levels of sulfur impurities and limited oxygen.^{18,19}

These observations raise several system-level questions. If downstream processing ultimately requires the removal of reactive impurities from electrolyzer effluents, should impurities be removed earlier in the CO₂ conversion value chain? Furthermore, operating with dilute CO₂ feeds effectively trades CO₂/N₂ separation upstream for CO/N₂ separation downstream. From a system perspective, which is preferred? These questions have large implications for problem ownership, how we design and operate electrolyzers, and what level of impurities must be tolerated throughout the process.

In this perspective, we examine where reactive impurities should be removed within the carbon value chain. We show that, in most cases, the optimal point for addressing impurities and inert species is upstream of the electrolyzer. While our analysis primarily focuses on CO₂-to-CO conversion as a representative case study, we also highlight how the key considerations may differ for other CO₂ reduction products, including other gaseous and liquid species. We first discuss the impurities and CO₂ concentrations expected for various sources and common means of removing each species. We then discuss how impurities and dilute feeds influence cell performance and how researchers have aimed to circumvent these penalties. Last, we conclude with the system consequences of downstream N₂/O₂/SO_x purification and provide our outlook for where N₂ and impurities should be addressed in the carbon value chain moving forward. Briefly, the core three system options for handling CO₂ and other species as shown in Figure 1 are, (1) feeding flue gases directly from the source to a CO₂ electrolyzer without treatment, (2) removing all reactive impurities prior to electrolysis, and (3) a full pre-processing approach where high-purity CO₂ is fed to the electrolyzer unit.

IMPURITIES IN CO₂ FEED: SOURCES AND COMPOSITION

To mitigate carbon accumulation in the atmosphere, electrolyzers can valorize CO₂ captured directly from ambient air through direct air capture (DAC) or from point-source gas streams from industrial processes.²⁰ However, the scientific community broadly agrees that DAC remains prohibitively expensive due to the low concentration of CO₂ in ambient air (~400 ppm).²¹ Consequently, the most realistic strategy is to employ flue gases from hard-to-abate industries as a carbon feedstock. In point sources, CO₂ concentrations typically range from 1% to 44%, depending on the specific industrial process.²² At these starting levels, carbon capture technologies (e.g., amine-based chemical absorption) are significantly less energy intensive compared with DAC.

Understanding the specific composition of various CO₂-containing sources is crucial for designing efficient carbon capture and utilization (CCU) technologies. Table 1 summarizes the molar composition of flue gases produced by oil and gas power plants, as well as steel and cement facilities. In addition to CO₂, N₂, O₂, and H₂O, which constitute the major components of

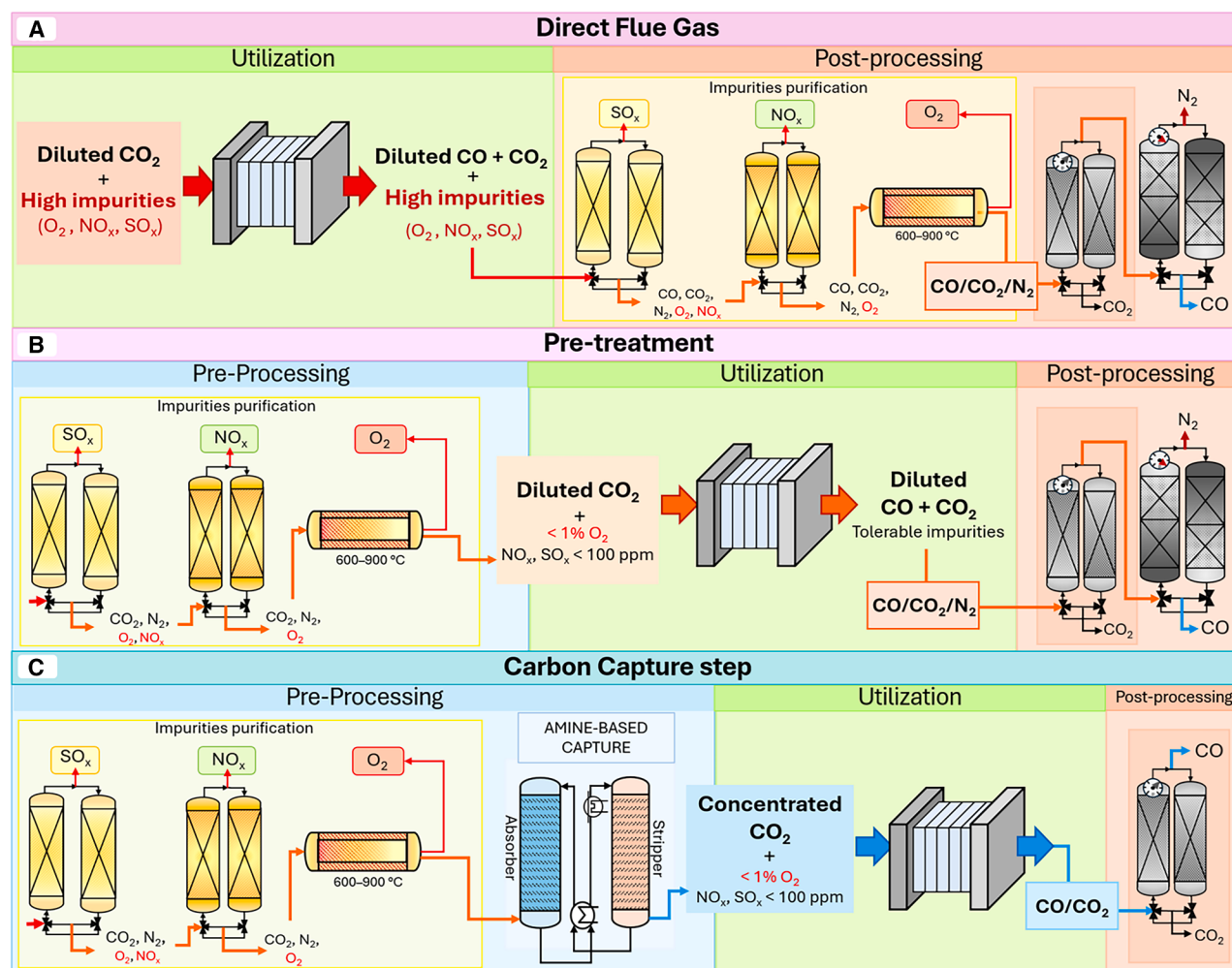


Figure 1. Three scenarios for the valorization of CO₂ sources via electrochemical reduction

(A) Direct use of CO₂ source without treatment, (B) pre-treatment removing SO_x, NO_x, and O₂ leaving an N₂-diluted CO₂ stream, and (C) pre-treatment and purification of CO₂ prior to electrolysis.

typical flue gas, other air pollutants (e.g., SO_x, NO_x, and CO) may also be present, ranging from trace amounts to thousands of ppm. The SO_x species (predominantly SO₂) come directly from fuel sources, while NO_x (mostly NO and NO₂) are formed via high-temperature reactions between atmospheric N₂ and O₂. The presence of CO indicates incomplete combustion.¹⁷

When evaluating the exact composition of CO₂ sources, additional operational factors must also be considered—most notably the pre-existence of denitrification units (DeNO_x) and flue-gas desulphurization (FGD) systems. DeNO_x technologies can reduce NO_x concentrations to below 100 ppm, while FGD systems can lower SO₂ levels to values below 70 ppm. These systems are commonly used in coal and oil combustion processes.^{17,30} Nevertheless, many point sources contain levels of reactive species that can affect downstream processes.

Additional CO₂ sources can be valorized through CO₂ reduction reaction (CO₂R) to generate value-added chemicals. Biogas, produced via the anaerobic biodegradation of organic matter, is a renewable fuel primarily composed of CH₄ and CO₂. A

particularly promising strategy involves upgrading biogas by electrochemically reducing its CO₂ fraction to methane, thereby increasing the overall calorific value of the fuel.³¹ The exact composition of biogas, however, depends on the nature of the feedstock and the digestion system employed. Besides CH₄ and CO₂, biogas can also include minor components such as H₂, N₂, and H₂S (Table 1), but it is overall simpler to purify and concentrate than other feedstocks.^{32,33} In this context, biogas upgrading through CO₂ electroreduction could be particularly attractive, as the CO₂ present in biogas could be further converted to increase the CH₄ content, rather than being simply separated and released.³⁴

IMPACT OF DILUTION AND IMPURITIES ON CO₂ ELECTROLYZER PERFORMANCE

In this section we address what happens when the aforementioned CO₂ sources are fed directly into a CO₂ electrolyzer as described in the first process route shown in Figure 1.

Table 1. Composition of the main carbon waste resources in Europe

Component	Power plant		Steel production	Cement production	Air	Biogas
	Oil	Natural gas				
CO ₂	3%–15%	3%–5%	1%–30%	11%–44%	400 ppm	20%–55%
N ₂	75%	74%–80%	5%–47%	56%–76%	78%	1%–20%
O ₂	3%–6%	12%–15%	<1%	2%–14%	21%	trace
H ₂ O	17%	7%–10%	<5%	7%–18%	1%–4%	saturate
SO ₂	5,000 ppm	trace	trace	100–1,300 ppm	–	–
NO _x	3,500 ppm	50 ppm	trace	100–1,500 ppm	–	–
CO	10,000 ppm	trace	4%–80%	160–1,200 ppm	–	trace
CH ₄	–	–	–	–	–	45%–75%
Ar	–	–	–	–	1%	–
H ₂ S	–	–	–	–	–	0–10,000 ppm

Components present at negligible concentrations have not been included. ^{17,23–29}

Specifically, how will various concentrations of NO_x, SO_x, and O₂ impurities present in the inlet CO₂ stream affect the electrochemical performance, selectivity, and stability of the conversion step (Figure 2A)? And subsequently, what are the catalytic and systemic approaches to suppress the electrochemical

activity of unwanted reactive species to become impurity tolerant? From the literature in this area, we can then conclude both which impurities are most problematic for electrolyzer operation and what concentration levels are acceptable to handle.

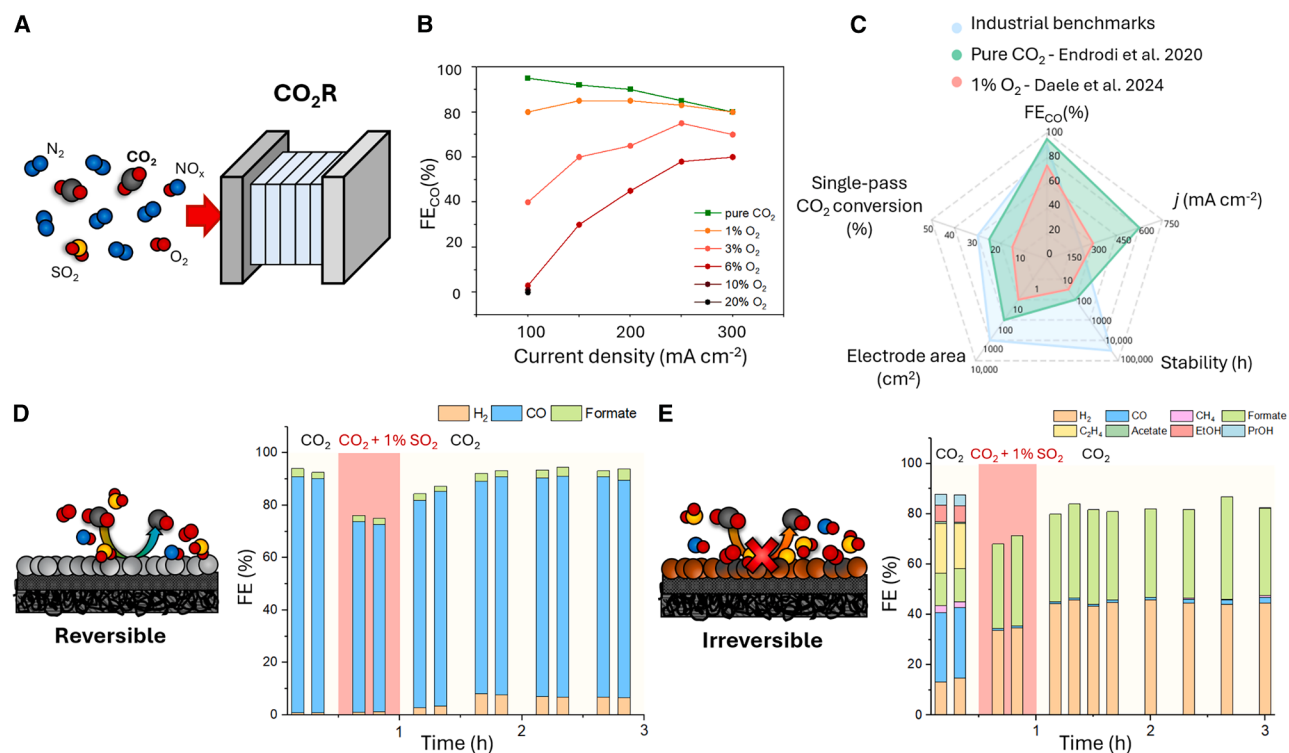


Figure 2. Effects of O₂ and SO_x on CO₂ electrolysis performance

(A) Schematic representation of mixed feeds entering a CO₂ electrolyzer.

(B) Impact of increasing O₂ content in the CO₂ feed on FE_{CO} as a function of current density j (mA cm⁻²). Data from Van Daele et al.¹⁶

(C) Comparison of key performance metrics reported for electrochemical CO₂ reduction to CO: industrial benchmarks, with a state-of-the-art system operating with pure CO₂, and with 1% O₂ in the CO₂ feed stream.^{5,16,35,36}

(D) Demonstration of the effects of SO_x on CO production using a silver cathode. Image re-used with permission from Luc et al.³⁷ Copyright 2019, American Chemical Society.

(E) Demonstration of the effects of SO_x on multicarbon product formation on a copper cathode. Image re-used with permission from Luc et al.³⁷ Copyright 2019, American Chemical Society.

Table 2. Reduction reactions and standard reduction potentials (E°) of common species present in CO₂ source gases compared to CO₂R and HER

	Reactions	Standard potential (V vs. RHE)
HER	$2H^+ + 2e^- \rightarrow H_2$	0
CO ₂ R	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.10
	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.25
	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	0.06
	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	0.09
NRR	$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$	0.09
ORR	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70
SO ₂ R	$SO_2 + 4H^+ + 4e^- \rightarrow S + 2H_2O$	0.50
	$SO_2 + 6H^+ + 6e^- \rightarrow H_2S + 2H_2O$	0.35
NO _x R	$NO_2 + 7H^+ + 7e^- \rightarrow NH_3 + 2H_2O$	0.80
	$2NO_2 + 8H^+ + 8e^- \rightarrow N_2 + 4H_2O$	1.36
	$NO + 3H^+ + 3e^- \rightarrow NH_2OH$	0.38
	$2NO + 4H^+ + 4e^- \rightarrow N_2 + 2H_2O$	1.68
	$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$	1.77

The major effects of impurities in the gas stream can be categorized into three main mechanisms: (1) dilution of CO₂ concentration, (2) competition with CO₂ for electrons via preferential electroreduction (Table 2),^{23,38,39} and (3) adsorption-induced modification or poisoning of the catalyst surface. These effects may occur individually or synergistically, depending on the catalyst composition and operating conditions, and their impacts often propagate beyond electrochemical technology to influence downstream separation, safety, and system integration.

Nitrogen, the most common inert component in flue gas primarily acts as a diluent by lowering the partial pressure of the CO₂, thereby lowering maximum current densities and reducing reaction rates.^{40,41} Due to the strong N≡N triple bond, however, the electrochemical reduction of N₂ (NRR) is kinetically hindered and requires large activation overpotentials.⁴² As a result, N₂ does not directly participate in electrochemical reactions and only acts as a diluting agent. However, by diluting the CO₂ stream, it shifts the system toward higher overpotentials and increased competition from the hydrogen evolution reaction (HER).⁴³ Research has shown that dilution effects can be overcome by increasing gas flow rates and system pressure, which then enables adequate CO₂ to reach catalytic sites without overly substantial penalties.

As a different diatomic molecule, oxygen impurities represent a more severe challenge due to their direct electrochemical competition with CO₂ (Figure 3). Owing to the significantly more positive thermodynamic potential of the oxygen reduction

reaction (ORR) relative to CO₂R pathways, even trace amounts of O₂ in the feed are then preferentially reduced instead of CO₂. This severe electron competition then shows as a rapid loss in CO₂ FE until all oxygen in the catalyst layer is depleted. A feed containing only 1% O₂, for example, already results in nearly 20% of the FE being consumed by the ORR, with losses increasing further at higher O₂ concentrations (Figure 2B).¹⁶ Increased current density operation leads to a greater FE for CO₂ reduction products, but a fixed limiting current density penalty of the ORR remains. Moreover, Breugelmans et al. showed that conventional carbon-based gas-diffusion electrodes can promote the ORR within the porous substrate itself,⁴⁴ which consumes the oxygen before the CO₂ reaches the catalyst layer, thus highlighting the need to reconsider electrode architectures beyond catalyst composition alone.⁴⁵

Nitrogen oxides, including NO, NO₂, and N₂O, represent another class of impurities that primarily affect CO₂R through competitive electrochemistry.⁴⁶ The presence of NO_x up to 0.83% in the CO₂ feed has been shown to cause a decrease in CO₂R FE due to their preferential electroreduction over CO₂.⁴⁷ However, given the overall dilute concentrations of nitrogen oxides in feeds (ppm) compared with O₂ (>1%), in the absence of catalyst poisoning, the overall FE is not penalized as heavily. Furthermore, studies on Cu- and Ag-based electrodes indicate that low concentrations of NO_x in the feed do not significantly alter the metallic state or morphology of the catalysts under CO₂ reduction conditions. Thus, with the present knowledge,

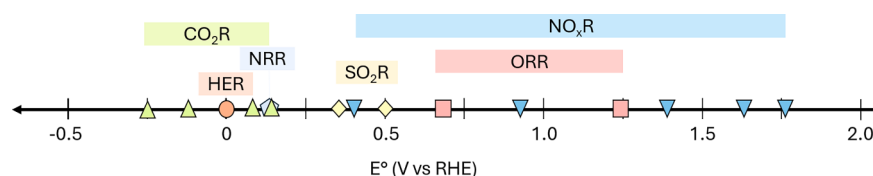


Figure 3. Schematic of standard reduction potential (E°) for common species present in CO₂ source gases compared to CO₂R and HER

nitrate impurities do not seem meaningfully detrimental to electrolyzer operation.

The last impurity to consider in most CO₂ feedstocks is sulfur, which represents one of the most critical challenges for working with impure feeds. Sulfur species simultaneously affect catalytic performance, long-term stability, and process safety due to their reactive and adsorptive behavior. Similar to O₂ and NO_x species, SO_x species (predominantly SO₂) are thermodynamically more favorable to reduce than CO₂ under reductive conditions, with reduction potentials substantially more positive than those of key CO₂R pathways.³³ As observed for O₂ and NO_x, this leads to strong competition for electrons and preferential impurity reduction.

The more challenging effects of sulfur compounds, however, are how they affect the catalysts themselves. Ag-based electrodes exhibit a comparatively high tolerance, with 1% SO₂ concentrations reducing CO selectivity by ~10%–15% while SO₂ is present. Once SO₂ is removed, though, activity is shown to recover (Figure 2D), showing a more reversible trend.⁴⁸ For feeds continuously feeding sulfur-containing gases, though, a fixed penalty then results from sulfur in the feed, as well as a potential long-term build-up in the system. In contrast, Cu-based catalysts are markedly sensitive to sulfur species, as they show severe suppression of C₂+ selectivity even at low SO₂ concentrations (Figure 2E).³⁷ In fact, sulfur becomes incorporated into the Cu structure, thus leading to a product switch toward formate and away from CO, ethylene, and ethanol as the dominant products. These observations indicate that, although SO₂ thermodynamically competes with CO₂ in all systems, its practical implications are strongly material dependent, which poses a minor risk for Ag-based CO₂R while representing a critical barrier for Cu-based systems. Other CO-producing catalysts such as N-doped carbons may exhibit much greater resistances to sulfur feeds than metal-based catalysts, but there is less research with these catalysts.³³ While not discussed in detail here, research into the higher temperature solid-oxide electrolyzer field has shown that sulfur is particularly problematic for the typically used nickel catalysts, thus necessitating SO_x removal prior to electrolysis.⁴⁹

Beyond electrochemical performance, the presence of SO_x introduces additional operational concerns. In humid environments in the presence of H₂ by-products, sulfur oxides can be converted into reduced sulfur species such as H₂S, which additionally poses significant safety, corrosion, and handling risks due to its high toxicity. As a result, the impact of sulfur impurities extends well beyond the catalyst layer, which underscores the need to treat impurity management as an integral component of system design and process operability, rather than as a downstream purification issue alone.⁵⁰ There has also yet to be research into understanding how continued sulfur contamination may affect the electrolyzer's bipolar plates or the rest of the balance of the plant. The challenges of H₂S become more pronounced for solid-oxide electrolysis cells, where it forms nickel sulfide, blocking catalytic sites.⁵¹

Recent advances demonstrate that CO₂R system can operate stably under controlled but non-ideal conditions. For example, the Breugelmans group⁴⁴ reported long-term stable operation of gas-diffusion electrodes under mixed-gas feeds by switching

the carbon-based support for a polytetrafluoroethylene gas-diffusion layer. They were then able to maintain an acceptable performance despite the presence of ~200 ppm SO_x/NO_x contaminants. In a similar approach, Sinton et al.⁵² showed that an electrochemically inert hydrated ionomer layer placed on top of the gas diffusion layer, but before the metal catalyst, can maintain stable operation even with a 4% O₂-containing feed. The hydrated layer adds a mass transport barrier to O₂, while CO₂ is much less impeded due to the ~30-fold higher solubility.

The undiscussed challenges with both impurity-tolerant approaches, however, are that if oxygen and sulfur species do not react in the electrolysis cell, they do not disappear but are instead transferred downstream in the process.

WHERE SHOULD N₂ AND REACTIVE IMPURITIES BE ADDRESSED IN THE PROCESS?

While many works have discussed the use of impure feedstocks for CO₂ electrolysis, little effort has gone into asking how N₂ and reactive impurities would be dealt with after the electrolyzer. At this stage it is important to ask whether shifting these species downstream (Figures 1A and 1B) is more beneficial than species removal in a pre-electrolysis step (Figure 1C). As such, an assessment may vary if a gaseous or liquid product is formed; we break this discussion in two. First, we focus on gaseous products, using the electrochemical reduction of CO₂ to CO as the case study for downstream impurity treatment, as this is the most advanced and industrially mature CO₂R pathway.⁵³

In CO formation, downstream of the electrolyzer contains a mixture of unreacted CO₂, product CO, inert N₂, and the reactive impurities, O₂, SO_x, and NO_x (Figure 4A). Additionally, the feed will contain H₂, which is produced as an unwanted electrolysis by-product.

First, we consider the presence of O₂ in the downstream process, which poses both safety considerations and complicates CO utilization. From a safety perspective, O₂ in the outlet stream may then fall within flammable or explosive regions (Figure 4B), which depends on the H₂ and CO₂ concentrations that are present.⁵⁵ If O₂ is kept below 5%, it is likely that safe conditions could exist. However, if O₂-tolerant systems are used, the amount of O₂ downstream stays the same, while half of the CO₂ entering the reactor will be converted to carbonate and cross to the anode.^{56,57} Oxygen partial pressures can then increase as a function of current density and operating conditions. A second issue with O₂ in the downstream process, though, is that once CO is produced, it will almost assuredly be paired with H₂ for methanol or Fischer-Tropsch synthesis. These thermocatalytic reactions are highly sensitive to oxygen species, much more so than electrolyzers, and ideally contain little water and O₂. Specifically, O₂ oxidizes the cobalt and iron in Fischer-Tropsch catalysts, thus blocking active sites and requiring re-reduction of the catalysts.⁵⁸ Within methanol synthesis, the copper phase of Cu/ZnO/Al₂O₃ is susceptible to oxidation.⁵⁹ While these metal sites can be reduced with H₂ during operation, continuous oxidation and reduction can lead to restructuring and subsequent degradation. Thus, regardless of the oxygen tolerance of the upstream electrolyzer processes, O₂ will eventually need to be removed to further valorize CO. This provides a strong

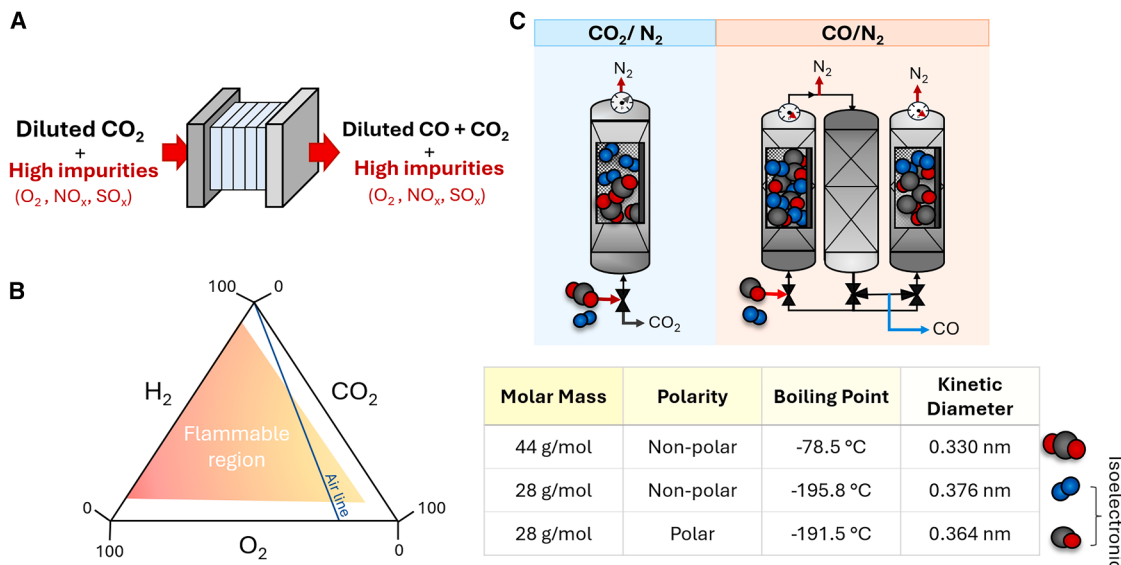


Figure 4. Downstream impacts of an electrolyzer tolerant to dilute feeds and oxygen

(A) Schematic of the inputs and outputs of a direct flue-gas-fed electrolyzer.

(B) Flammability diagram for H₂, O₂, and CO₂ mixtures, highlighting the flammable region.

(C) Comparisons of the CO₂/N₂ vs. CO/N₂ separation, considering key physicochemical properties of CO₂, N₂, and CO.⁵⁴

argument for removing most of the O₂ prior to electrolysis (Figure 1C) and then allowing the electrolyzer unit to purify the last remnants of oxygen.

A similar conclusion can be made for sulfur-containing species. While electrolyzers are sensitive to sulfur, both methanol and Fischer-Tropsch synthesis require sulfur levels in the ppb range or lower.⁶⁰ Thus, even after a CO₂ electrolyzer, sulfur species will need to be removed, which suggests that removal pre-electrolysis is more favorable from a performance perspective.

The final remaining gas to address is N₂. While N₂ only dilutes CO₂ concentrations in the electrolyzer, which does not penalize the system too much, the N₂ must still be separated from unreacted CO₂ and CO. In essence then, by operating an electrolyzer with a dilute CO₂ feed, we are forced into separating CO/N₂ (Figures 1A and 1B) instead of a pre-electrolysis separation of CO₂/N₂ (Figure 1C). It is then worth investigating which of these two separations is more challenging practically and energetically as a metric for assessing where N₂ removal is best addressed in the overall process.

When comparing the molecular and thermodynamic properties (Figure 4C) of CO₂, CO, and N₂, we can see that CO and N₂ are much more similar to each other than CO₂ and N₂. Notably, CO and N₂ have the same molar mass and almost identical boiling points and kinetic diameters. They are also isoelectronic with one another, as they share the same number of total electrons and an electron configuration. The only difference observed is that CO is polar while N₂ is nonpolar. Conversely, CO₂ is much more distinct from N₂, as it contains a quadrupole moment, a higher boiling point, a lower kinetic diameter, and is able to interact strongly with sorbents and selective media (Figure 4C). These property differences make CO/N₂ separation technically more challenging⁶¹ and potentially more energy intensive than CO₂/N₂. Thus, similar to our conclusions for

both oxygen and sulfur, our analysis implies that it is more beneficial for N₂ to also be removed in a pre-electrolysis step (Figure 1C) as a similar or larger penalty is incurred post-electrolysis (Figures 1A and 1B). To avoid CO₂/N₂ separation, an alternative could be CO₂-N₂ co-electrolysis to urea.⁶² However, this route is still at an early stage of development, and it would not be ruled out by the upstream removal of other reactive impurities.

The implications of impurity management for other gaseous products are similar to that of CO. When producing ethylene, for example, a large product mix is now present (e.g., C₂H₄, CH₄, CO, and H₂), implying multiple separation steps, which increase downstream separation complexity and energy demand.⁶³ More so, there is then a large number of absorption steps likely to be poisoned by oxygen and sulfur contaminants. While C₂H₄/N₂ separation is likely less onerous than CO/N₂ separation from a molecular perspective, the fact that both species would be present in a product mix is itself problematic. For example, a FE of 60% to ethylene and 10% to CO leads to a 1:1 molar ethylene/CO gas product mix to be separated from N₂. Thus, C₂H₄/N₂ separation will always be combined with some measure of CO/N₂ separation, leading to the aforementioned challenges.

For liquid products such as formate, acetate, or ethanol, the impact of dilution and impurities manifests differently as the product is typically generated in the electrolyte phase. This provides an inherent separation step from the gaseous impurities. The trade-off then becomes that the liquid products start at an initially low concentration and must be built up over time until they can be removed in a batch-wise process. As ~55 M of water are present in an electrolyte, liquid product recovery is energy and process intensive if a pure product is desired. However, recent advances in electrolyzer design illustrate how these

limitations may be addressed. Wang and co-workers⁶⁴ have demonstrated systems capable of producing high-purity liquid products via engineered configurations that decouple product formation from the electrolyte phase. A caveat of liquid products operated with impure feeds is that unlike O₂ and N₂, SO_x is highly soluble in water, thus implying that a sulfur-tolerant electrolyzer system would still be needed.

In a manner similar to how liquid product formation indirectly separates impurities from products, fully liquid reactors without a CO₂ gas feed can similarly remove O₂ and N₂ with downstream separation. For example, Berlinguette and co-workers⁶⁵ have developed bicarbonate-fed systems enabling operation with dilute CO₂ streams and oxygen tolerance due to oxygen's low solubility. Such impurity tolerance is achieved through a CO₂-to-bicarbonate pre-treatment that is viable for a sub-class of CO₂ sources. Thus, the process favors upstream purification steps.

Overall, these scenarios highlight that the optimal point for addressing impurities and inert species is upstream of the electrolyzer, with potential exceptions for some liquid products. While partial impurity removal is necessary to ensure stable operation, early-stage CO₂ capture and N₂ removal are also critical to avoid severe dilution penalties, enable efficient electrolysis, and minimize the energy intensity of downstream separations. Having contrasted the overall scenarios in Figure 1, it is worth stating that real-world purification technologies cannot fully remove contaminants; therefore, some impurities could remain in the feed.^{66–68} Thus, examining the sensitivity of these components under long-term electrolyzer operation is still critical to the future of the research field.

OUTLOOK

Most research in the electrochemistry community to date has treated impurity and dilute CO₂ feeds as a device-level challenge. Here, we show that a more holistic approach across the entire value chain is needed to assess where and when CO₂ feedstocks should be processed, as solving a problem in one part of a plant simply shifts the issue upstream or downstream. For instance, the development of an oxygen- or sulfur-tolerant electrolyzer may alleviate feedstock constraints but then necessitates downstream oxygen and sulfur removal to ensure product purity and valorize CO₂R products. As a result, the central question is not whether impurities should be removed, but where this removal is most effective.

Across the scenarios considered here, a consistent trend emerges. Operating electrolyzers on untreated or partially treated streams may reduce upstream processing requirements, but it inevitably transfers complexity downstream. While CO₂/N₂ separation upstream is relatively mature and energetically manageable, downstream separations involving CO/N₂ mixtures are more immature and intrinsically more difficult due to their similar physicochemical properties. Likewise, impurity-tolerant operation does not remove the need for purification, as stringent specifications for downstream processes such as methanol or Fischer-Tropsch synthesis still require near-complete removal of sulfur- and oxygen-containing species. These factors lead to more energy-intensive separations, increased process complexity, and additional safety considerations.

From a system perspective, impurity management can also be viewed as an energy allocation problem across capture, conversion, and separation. Conventional CO₂ capture processes already impose substantial penalties, typically around 0.7 GJ per ton of CO₂ of equivalent electrical energy ($\sim 30 \text{ kJ mol}^{-1}$)⁶⁹ for amine-based capture and 40–100 USD per ton,^{16,70,71} but it enables more efficient electrolysis and substantially simplifies downstream processing. In contrast, electrolyzer strategies operating with dilute CO₂ feeds shift N₂ separation downstream. Here CO physisorption energies via π - π interactions or zeolites are ~ 10 – 40 kJ mol^{-1} for concentrated streams (>15%). The adsorption energy does not reflect the process energies associated with heat losses, compression, and cycling, however, thus making these numbers a lower bound for a full process. For more dilute CO/N₂ streams using chemisorption, adsorption energies increase to 80–400 kJ mol^{-1} for dilute mixtures.⁵⁴ A direct energy comparison of CO₂/N₂ vs. CO/N₂ is then challenging given the immaturity of CO/N₂.

Additionally, it has been shown that the electrolyzer energy demand dominates the separation energy requirements, independently of where they are addressed.⁷² For example, CO₂ electroreduction to CO typically requires ~ 15 – 30 GJ/t CO_2 , while downstream gas separation is an order of magnitude less energy intensive.⁷³ This gap becomes even more pronounced when considering multicarbon products, for which the higher electron and energy requirements drive overall process demands beyond $\sim 50 \text{ GJ/t CO}_2$, and in some cases above 100 GJ per ton of product. Therefore, even if CO₂/N₂ and CO/N₂ separations were comparable, which is not the case, any improvement to electrolyzer efficiency that CO₂/N₂ separation brings to CO₂ electrolysis would remain highly relevant.

A separate argumentation that motivates pre-separation over post-separation is the comparative maturity and multi-use of CO₂/N₂ separation technologies. CO₂ recovery is at a deployment stage and relevant not just for electrochemical conversion but also for sequestration and thermocatalytic conversions. Conversely, CO/N₂ and C₂H₄/CO/N₂/H₂ separations still require substantial research investments and time before they could be deployed. Thus, regardless of energy or capital cost differences, CO₂/N₂ has a substantial time and diversity advantage. Taken together, both technological maturity and applicability indicate that upstream impurity removal and CO₂ purification are the most effective approaches.

As these considerations are not specific to CO₂R, impurity management emerges as a system-level constraint across all carbon conversion technologies (low-temperature electrolysis, high-temperature electrolysis, and thermochemical conversion), which often exhibit similar impurity sensibilities. This reinforces the importance of processing steps and highlights a key point: rather than an electrolyzer-centric challenge, impurity management is fundamentally an energy allocation problem across the value chain.^{74–76} Such a conclusion then motivates that CO₂ purification steps should occur on-site at point sources, but this naturally brings about additional land, energy, and resource demands that may not be viable in many places. Thus, the number of viable sites for CO₂ capture and conversion decreases.

A secondary outlook is that over time the composition and availability of the point-source emissions discussed in Table 1

will change. Specifically, emissions from the power sector are expected to decline with increasing renewable energy penetration, while industrial sectors such as steel and cement have potential pathways for emissions reductions.⁷⁷ For example, steel production is projected to reduce CO₂ intensity from ~1.8 t CO₂/t steel to 0.4–0.5 t CO₂/t steel in the mid-to-long term,⁷⁸ yet growing global demand—particularly in India and parts of Africa⁷⁹—will maintain it as a significant CO₂ source. Cement production, with process emissions intrinsically tied to clinker formation, will continue to generate hundreds of millions of tons of CO₂ annually, making it a key target for carbon utilization. At the same time, biogas upgrading offers near-term deployment opportunities and is expected to play a strategic role in European energy independence and its defossilization pathway. Biomethane from biogas upgrading currently accounts for only ~6% of European Union (EU) natural gas consumption, but the REPowerEU Plan targets 35 billion cubic meters (bcm) by 2030 (up from 4.9 bcm in 2023),⁸⁰ with tens of billions in private investments committed.⁸¹ These developments clearly indicate that substantial investments will be directed toward biomethane production in the coming years. The ratios of different impurities will then change with sources over time, and as technology changes, our conclusions should be adapted with changing conditions as well.

Ultimately, impurity management is not a challenge unique to CO₂ electrolysis but one persistent in all chemical conversion steps. Understanding where and how N₂ and reactive impurities should be addressed is then a unifying design principle across all carbon valorization strategies, from electrochemical reduction to thermocatalysis and biological fixation. By taking this approach, cost reductions can be gained by the utilization of common equipment under hopefully future large-scale deployments.

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AUTHOR CONTRIBUTIONS

Conceptualization, L.G. and T.B.; visualization, L.G., T.B., and A.M.; funding acquisition, A.S.; supervision, A.S. and T.B.; writing—review and editing, L.G., T.B., A.S., and A.M.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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