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Review

Exploring the effect of temperature on the stability and scalability of CO_2 electrolysis systems with copper electrodes

Kevin Fernández-Caso, Jurriaan Peeters and Ruud Kortlever

The electrochemical reduction of CO_2 using copper-based catalysts represents a promising pathway for producing multi-carbon products from renewable energy. Temperature is a key parameter that not only determines reaction pathways and product selectivity but also strongly affects catalyst stability, electrolyte composition, and membrane integrity. Despite its importance, most studies have primarily focused on catalytic selectivity, often overlooking the thermal and stability aspects recently emphasized in the literature. This perspective underscores the central role of temperature in governing both catalytic performance and the physical and chemical resilience of electrolyzer components under low-temperature (20–80 °C) conditions. These factors become even more critical during scale-up, where heat management and transfer directly influence efficiency and long-term durability, similar to challenges in hydrogen production systems. A comprehensive understanding of thermal effects on both catalytic and non-catalytic elements is therefore essential for optimizing system performance. This work proposes experimental methodologies to evaluate the thermal and chemical stability of catalysts, electrolytes, and membranes, and outlines future research directions aimed at enabling the practical, efficient, and scalable deployment of CO_2 electrolysis through improved thermal design and integrated heat management.

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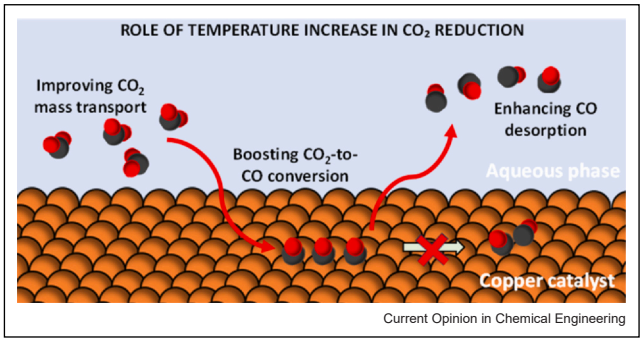
Introduction

The electrochemical reduction of CO_2 into valuable multi-carbon products such as ethylene and ethanol offers a promising path for sustainable energy conversion and carbon utilization [1–4]. Copper-based catalysts are uniquely suited for this task due to their capacity to form C–C bonds, enabling the production of C_{2+} compounds [5–8]. However, these pathways require significantly more electrons than the two-electron processes that yield carbon monoxide [9] or formic acid [10], increasing both charge-transfer limitations and heat generation. Importantly, heat at the catalyst surface scales linearly with current density ($Q \propto j$), while ohmic heating in the electrolyte scales quadratically with current density ($Q \propto j^2$), making thermal effects critical to reaction selectivity and efficiency [11,12].

Given this dependence of heat generation on j, even small variations can lead to significant local temperature changes, which in turn influence product distribution. As illustrated in Figure 1, increases in j are accompanied by both enhanced CO_2 mass transfer and pronounced local heating, making temperature a critical parameter governing selectivity. Consequently, several studies have investigated how temperature affects product selectivity. Vos et al. [13] showed that CO selectivity remains relatively stable with temperature, whereas C_{2+} products reach a maximum selectivity near 48 °C. Similarly, Brandão et al. [14] used SEIRAS to show that CO surface coverage and migration to active sites peak around 45 °C, correlating with observed shifts from C_{2+} to C_1 products. While the enhanced CO_2 mass transfer at higher temperatures observed in Figure 1 can improve reactant availability, elevated temperatures also favor CO desorption over C–C coupling, ultimately lowering the Faradaic efficiency (FE) for C_{2+} product formation [15].

Temperature also plays a central role in scalable CO_2 electrolyzers, influencing ionic conductivity, reaction kinetics, and water management. Giron-Rodriguez et al. [16] found improved performance at elevated temperatures but noted a decline in C_2H_4 FE from 20% to 9% over 290 hours at 60 °C. Complementarily, Ren et al. [17] further confirmed that stability is maximized around 50 °C, whereas higher temperatures rapidly induce flooding and HER dominance, severely limiting durability. Gabardo et al. [18] maintained >40% C_2H_4 FE at 40 °C for 100 hours, whereas She et al.

Figure 1



Schematic representation of the impact of temperature increase on CO_2 reduction in copper-based catalysts.

[19] heated the anolyte to 60 °C and achieved over 1000 hours of stable operation in a stack-format zero-gap cell, with C_2H_4 FE decreasing only slightly from 50% to 48%. Recently, Brandão et al. [20] demonstrated in flow cell electrolyzers that elevated temperatures enhance local pH gradients and reduce diffusion boundary layers, shifting product selectivity and underscoring the role of microenvironmental control. Hurkmans et al. [21] addressed non-isothermal behavior during scale-up, identifying 60–70 °C as the optimal range to balance conductivity, reaction kinetics, and CO_2 solubility.

Although CO_2 electrolysis at ambient temperatures (< 25 °C) has achieved high selectivities, practical stack-scale systems inherently experience temperature buildup. Operation in the 40–70 °C range mitigates salt precipitation, improves water handling and voltage efficiency, and enables waste-heat recovery opportunities [22].

Here, we focus on CO_2 electrolysis with copper electrodes in the 20–80 °C range, analyzing how steady-state thermal gradients influence catalyst stability, membrane behavior, and ionic conductivity. Transient thermal effects (temporal gradients) are not considered, as the primary objective is to analyze temperature distributions under steady operating conditions that are most relevant for continuous operation, reactor design, and scale-up, where thermal equilibration is typically achieved. We therefore emphasize steady-state heat transfer as a practical framework for assessing long-term performance and durability and propose integrated modeling and experimental strategies for designing thermally optimized, stable, and scalable CO_2 electrolyzers.

Electrolyzer configurations for CO_2 reduction: temperature and stability

Flow cell and zero-gap architectures

The architecture of a CO_2 electrolyzer critically influences not only electrochemical performance but also thermal behavior, particularly heat generation, dissipation, and the emergence of thermal gradients. Among the most established designs are flow cell and zero-gap configurations, each presenting distinct thermal and operational characteristics (see Figure 2).

Flow cell systems, where the electrodes are separated by a liquid electrolyte and a membrane, allow for independent temperature control of the anolyte and catholyte streams. This setup inherently provides some thermal buffering, as the flowing electrolyte helps dissipate heat uniformly and limits the formation of localized hot spots (Figure 2a). The open architecture also enables external cooling or heating, which makes it easier to maintain isothermal conditions. However, the increased interelectrode distance and contact resistances often reduce energy efficiency and limit scalability.

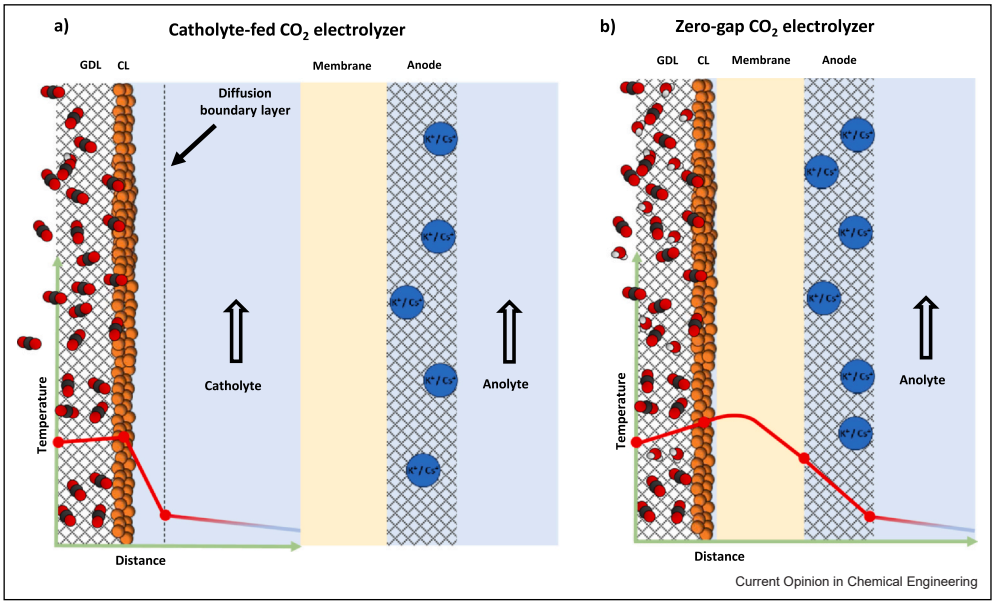
In contrast, zero-gap architectures, where electrodes are pressed directly against the membrane, are favored for their compactness, low ohmic losses, and compatibility with high j (> 200 mA cm^{-2}). Yet, this design introduces significant thermal management challenges [21]. The tight geometry reduces avenues for convective heat dissipation, increasing the likelihood of thermal gradients across the membrane and catalyst layers (Figure 2b). Ohmic heating becomes more concentrated, particularly at high j where $Q \propto j^2$, potentially leading to localized dehydration, membrane thinning, or catalyst deactivation [11].

A recent study has shown that inadequate heat removal in zero-gap systems can result in temperature differentials exceeding 10 °C across the membrane electrode assembly (MEA) [21], especially in dry cathode operations. This non-uniform thermal distribution promotes localized variations in membrane hydration and ionic resistance, leading to an uneven j distribution and results in the accelerated degradation of both catalyst and electrolyte. Over time, these coupled effects manifest as performance decay and structural instability, even under steady-state operation [16,21,23,24]. Conversely, when properly managed, for example, via humidified gas feeds or heated anolyte reservoirs [19], zero-gap systems can maintain stable operation over extended periods.

This underscores that, beyond electrochemical optimization, the thermal profile of the electrolyzer should be regarded as a key design parameter. Architecture selection thus becomes a trade-off not only between performance and scalability but also between thermal robustness and operational complexity. Future efforts should aim to co-design.

reactor geometry and heat dissipation strategies to ensure uniform temperature fields and long-term stability in CO_2 electroreduction systems [25].

Figure 2



Schematic representation of the temperature profile in flow cells (also called catholyte-fed CO_2 electrolyzer) and MEA cells (also called zero-gap CO_2 electrolyzers). GDL refers to the gas diffusion layer, while CL denotes the catalytic layer.

Beyond these experimental considerations, thermal modeling provides a quantitative framework to describe heat generation and distribution across architectures. The dominant contribution arises from overpotential ($Q_{overpotential}$) calculated as the product of the applied current (I) and the cathodic overpotential ($\eta_{cathode}$):

$$Q_{overpotential} = I\eta_{cathode} \quad (1)$$

where

$$\eta_{cathode} = E_{app} - E_{t,CO2\rightarrow C2H4} \quad (2)$$

The thermoneutral potential ($E_{t,CO2\rightarrow C2H4}$) slightly increases with temperature (1.222 V at 40 °C, 1.224 V at 50 °C, 1.228 V at 60 °C), underscoring the direct link between operating conditions and heat generation.

A second major contribution is ohmic heating (Q_{ohmic}), expressed as:

$$Q_{ohmic} = I^2R \quad (3)$$

where R includes both the membrane and electrolyte resistances:

$$R = R_{membrane} + R_{electrolyte} \quad (4)$$

with

$$R_{membrane} = \frac{\delta_m}{\kappa_m A}, \quad (5)$$

$$R_{electrolyte} = \frac{\delta_e}{\kappa_e A} \quad (6)$$

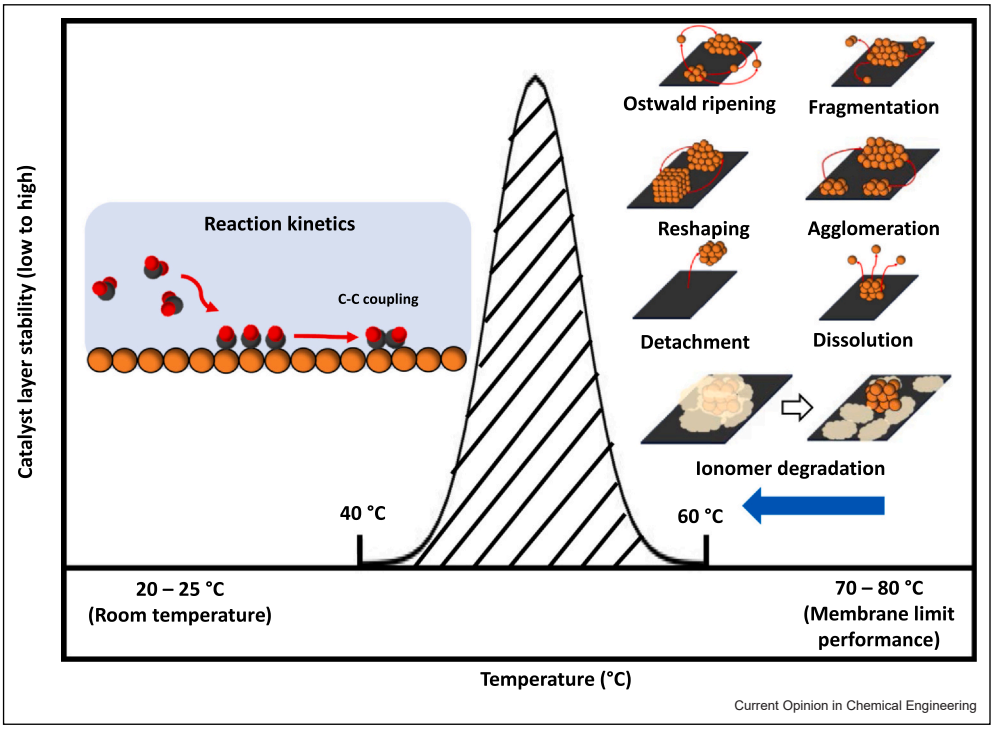
where δ_m and δ_e denote the thickness of the membrane and the catholyte, respectively; κ_m and κ_e represent their corresponding ionic conductivities; and A is the cross-sectional area through which ion transport occurs. According to the equations, increasing the thickness of the electrolyte layer raises the ionic resistance R but also increases the volume available for heat dissipation, while zero-gap configurations reduce ohmic losses. Both membrane and electrolyte ionic conductivities (κ_m and κ_e) increase with temperature, indicating that thermal effects can enhance conductivity, although localized heating may become significant if not properly managed.

Temperature effects on the copper catalytic layer activity and degradation

Temperature strongly influences both the activity and structural stability of copper-based catalysts in CO_2 electroreduction. Elevated temperatures (up to 60 °C [13,16]) can initially enhance reaction kinetics and improve selectivity toward multi-carbon products; however, sustained exposure to elevated temperatures leads to degradation processes that undermine long-term performance (Figure 3).

A major degradation pathway is the restructuring of copper nanoparticles via Ostwald ripening and surface atom migration [26–29]. At higher temperatures, smaller, more active crystallites tend to dissolve and redeposit

Figure 3



Influence of temperature on copper-based catalyst stability during CO_2 electroreduction.

onto larger, less active ones, leading to a loss of high-index facets and defect sites critical for C–C coupling. This restructuring reduces the density of active sites and shifts product selectivity toward less complex (C_1) products and hydrogen over time.

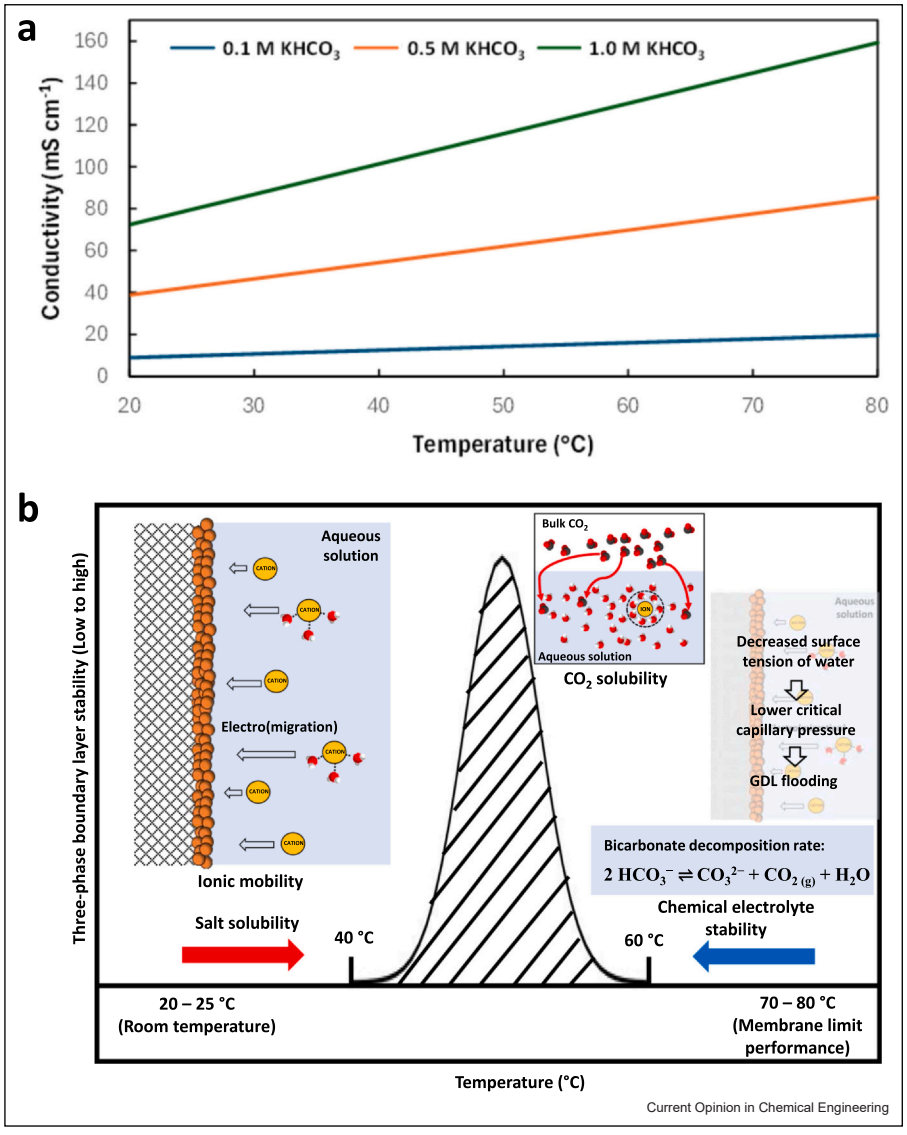
Additionally, copper surfaces evolve through facet-dependent stability: high-index facets and low-coordination sites (steps, edges, corners) are thermodynamically less stable and tend to reconstruct into lower-energy (111), (100), or (110) surfaces under heating [30,31]. Likewise, grain boundaries and extended defects undergo migration or faceting transitions at elevated temperatures, which further reduces the density of catalytically active sites [32]. Importantly, these grain-boundary phase transformations, originally identified in bulk metals [33], have strong implications for copper nanoparticles, which often consist of multiple crystalline domains separated by internal boundaries. Under reaction or annealing conditions, these internal interfaces can reorganize or absorb point defects, analogous to bulk systems, thereby contributing to the loss of highly defective, catalytically favorable sites. For nanoparticulate copper, the combined effects of surface facet smoothing and grain boundary phase transitions synergistically drive the system toward more stable, less active configurations, ultimately explaining the observed shift toward simpler products and reduced C–C coupling activity [34,35].

Moreover, cathodic corrosion, the reductive dissolution of copper under strongly negative potentials [36,37], is exacerbated at elevated temperatures due to enhanced metal ion mobility and local pH fluctuations. This results in physical loss of catalyst mass and morphological changes that impair selectivity and FE stability.

In parallel, ionomer degradation within the catalyst layer becomes a critical issue. Since the catalyst layer is the main site of reaction-induced heating, local temperatures can exceed the average cell temperature. This promotes mechanical breakdown, chemical decomposition, and ionic conductivity loss of the ionomer, compromising both gas transport and charge transfer [38]. Combined, these effects highlight the importance of precise thermal management (with particular focus on humidity fluctuations in the CO_2 cathode stream under zero-gap architecture [38]) within the catalyst layer to preserve both catalytic performance and structural integrity over extended operation.

From a modeling perspective, the copper catalytic layer is precisely where overpotential heating (Eqns 1–2) is most intense, since electrochemical reactions occur at the electrode–electrolyte interface. Finite-element simulations consistently predict local hot spots within the catalyst layer, particularly under high j. These thermal gradients correlate with experimentally observed phenomena such as Ostwald ripening, ionomer degradation,

Figure 4



Effect of temperature on electrolyte parameters. **(a)** Influence of temperature on the ionic conductivity of aqueous electrolytes based on $KHCO_3$. **(b)** Effect of temperature on the three-phase boundary layer stability during CO_2 electroreduction.

and accelerated cathodic corrosion. Thus, predictive thermal maps can both rationalize degradation pathways and suggest mitigation strategies, for instance, by incorporating thermally conductive supports or graded porosity to dissipate heat.

Electrolyte and membrane selection under varying thermal conditions

Electrolyte choice, particularly in flow cell systems, often centers on aqueous bicarbonates such as $KHCO_3$ or $CsHCO_3$, which buffer pH and supply CO_2 near the catalyst. These liquid catholytes provide good ionic conductivity, which is particularly pronounced for 1.0 M $KHCO_3$ solutions, as shown in Figure 4a, highlighting the influence of concentration on solution conductivity. CO_2 solubility in these electrolytes, illustrated in Figure 4b, is sufficient at moderate temperatures but decreases as temperature rises, potentially limiting reactant availability at the catalyst surface. Nevertheless, as Figure 4 emphasizes, optimized flow rates combined with gas diffusion electrodes (GDEs) can mitigate the effects of reduced CO_2 solubility, ensuring that electrolyte limitations do not necessarily hinder overall performance [22].

$KHCO_3$ and $CsHCO_3$ exhibit distinct cation effects in CO_2 electroreduction. The Cs^+ cation, being larger and less strongly hydrated than K^+, can enhance C–C coupling and improve ionic conductivity by approaching the

catalyst surface more closely and stabilizing reaction intermediates [39]. Its weaker interaction with bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions can also reduce the local accumulation of carbonates near the membrane or in the catalyst–membrane region under typical operating conditions [39]. At elevated temperatures (60–70 °C), CO_2 solubility in water decreases, shifting the equilibrium ($2\ HCO_3^- \rightleftharpoons CO_3^{2-} + CO_{2\ (g)} + H_2O$) toward CO_2 release and accelerating bicarbonate decomposition [40]. Additionally, increased temperatures lower the catholyte surface tension, which can disrupt gas–liquid–solid contact in the GDE and promote flooding. This flooding blocks gas pathways and can trigger sudden drops in FE [24,41,42]. This effect is more pronounced in flow cells owing to the greater catholyte mass. Using hydrophobic PTFE (polytetrafluoroethylene) substrates or nanoparticles can help maintain proper wetting and reduce the risk of flooding [43]. Although temperature-induced flooding is modest at typical electrolysis temperatures, it can increase local carbonate concentrations near the membrane or in the catalyst–membrane region, placing additional demands on membrane durability.

Membrane hydration and ionic conductivity are equally critical in governing stable CO_2 electrolyzer performance, especially for zero-gap electrolyzer configurations, as both depend strongly on temperature and relative humidity (RH). In flow cell configurations, membranes are fully immersed in HCO_3^- /CO_3^{2-} electrolytes on both sides, ensuring near complete hydration. Under these conditions, ionic conductivity increases with temperature up to ~60 °C due to enhanced ion mobility and reduced solution viscosity, before stabilizing or slightly decreasing at higher temperatures as partial dehydration begins [24]. Cation-exchange membranes (CEM) such as Nafion 117 provide excellent mechanical and thermal stability above 80 °C, but conductivity in bicarbonate or alkaline media is lower as hydroxide and carbonate ions have limited mobility in the sulfonic-acid network, reducing ion-exchange efficiency and local proton availability. Nonetheless, Nafion remains preferred in flow cells, where full hydration minimizes dehydration and its cation selectivity reduces product crossover and local carbonate precipitation near the cathode.

In zero-gap electrolyzers, hydration is asymmetric: the cathode is exposed only to humidified CO_2, while the anode contacts liquid anolyte, yielding a lower average RH (~60%). Membrane conductivity is highly sensitive to both RH and temperature under these conditions. Higher operating temperatures improve salt solubility, thereby mitigating salt precipitation, but intensify water transport through the membrane, increasing the risk of GDE flooding in copper electrodes [44]. Anion-exchange membranes (AEM) such as Sustainion X37–50 and PiperION TP-85 maintain high ionic conductivity and carbonate tolerance if hydration is preserved and water transport is balanced. However, Sustainion tends to lose conductivity and structural stability above ~70 °C due to imidazolium degradation and dehydration, whereas PiperION, featuring a thermally robust piperidinium backbone, maintains stable performance up to ~90 °C under humidified CO_2 conditions [24,41]. Therefore, a final selection between $KHCO_3$ or $CsHCO_3$ catholytes and AEM versus CEM must balance thermal stability, ionic transport, carbonate management, and water flux, considering the architecture and heat dissipation characteristics of the electrolyzer.

The resistance framework described in Eqns 3–6 quantifies the ohmic losses in both the electrolyte and membrane. Increasing the thickness of the catholyte (δ_e) or membrane (δ_m) raises the ohmic resistance, leading to greater local heating. Conversely, higher ionic conductivities (κ_m, κ_e), which increase with operating temperature, directly reduce ohmic losses. However, higher temperatures may also accelerate chemical degradation of the.

polymer backbones. This trade-off explains why AEMs (such as Sustainion X37–50) excel at low-to-moderate temperatures, yet fail above ~70 °C, while CEMs provide stability but at the cost of reduced CO_2RR selectivity. Integrating thermal modeling with conductivity measurements, therefore, provides a predictive basis for selecting membrane–electrolyte combinations that balance performance and durability under realistic operating conditions.

Materials and operational strategies for enhanced stability

Enabling long-term stability in CO_2 electrolyzers begins with the careful selection of thermally robust catalyst materials and supports. For instance, copper alloys and core–shell Cu@M (M = Ag, Au) nanoparticles help stabilize surface atoms against sintering and Ostwald ripening at elevated temperatures [45–47]. When these catalysts are dispersed on porous, high-surface-area carbon supports, heat generated at the reaction sites is more effectively conducted away, minimizing local hot spots that accelerate degradation [48].

Equally important are advanced membrane–ionomer composite structures. Hybrid laminates combining anion and cation exchange layers leverage the high ionic conductivity of AEMs while benefiting from the superior thermal resilience of CEM backbones [19]. Within the catalyst layer (CL), incorporating inorganic additives, such as zirconia nanoparticles, reinforces mechanical strength, enhances water management, and mitigates both flooding and salt precipitation [49].

At the cell level, integrated thermal management is critical. Embedding microchannel cooling plates adjacent to the MEA ensures a uniform temperature profile [25], while thermally conductive passive heat–pipe architectures

embedded in the cell body transport excess heat to external sinks efficiently, minimizing the need for pumping power and avoiding electrical interference with the cell. Together, these approaches prevent thermal runaway and maintain consistent operating conditions. Li and co-authors[25] implement a non-isothermal CO_2 electrolysis strategy by cooling the cathode and heating the anode, leveraging the Soret effect to drive cations away from the cathode. This thermal gradient mitigates salt precipitation and enhances CO_2 solubility and oxygen evolution reaction kinetics, leading to improved performance and stability. Increasing CO_2 partial pressure compensates for the reduced solubility at elevated temperatures, as shown by Vos et al.[50], maintaining higher reactant availability under conditions where thermal effects alone would limit it. Complementing this, the very recent work of Vos et al.[51] employed a high-temperature, high-pressure electrochemical cell to demonstrate that under extreme conditions, the dominant C–C coupling mechanism on copper shifts from CO dimerization to a Fischer–Tropsch-like chain growth pathway, highlighting the combined influence of temperature and pressure on reaction pathways and product distributions.

Finally, dynamic operational protocols help limit cumulative thermal stress in CO_2 electrolyzers. Pulsed current operation reduces [52,53] the average heat load and introduces brief recovery periods, mitigating temperature gradients within the cell and slowing catalyst sintering, thereby enhancing durability and operational stability. Periodic reverse-polarity cleaning cycles dissolve carbonate deposits [52] *in situ* and rejuvenate ion exchange sites, all without requiring a complete system shutdown. Implementing these combined material and operational strategies enables CO_2 electrolyzers to sustain high j and multi-carbon product selectivities over hundreds to thousands of hours of continuous use.

Modeling tools allow these stability strategies to be evaluated virtually before implementation. By combining the overpotential (Eqns 1–2) and ohmic (Eqns 3–6) heating models with experimental operating protocols, one can predict long-term temperature profiles and identify stress points within the MEA. For example, simulations of pulsed current operation show how intermittent cooling periods reduce average heat accumulation, slowing copper sintering. Likewise, reducing catholyte channel thickness from 2 mm to 1 mm has been modeled to cut ohmic heating nearly in half, extending catalyst and membrane lifetimes. In this way, modeling acts as a design compass, complementing experimental validation and accelerating the development of robust CO_2 electrolysis systems.

Conclusions and future outlook

Temperature acts as both a driver and a risk in scaling Cu-based CO_2 electrolyzers: it accelerates kinetics and mass transport but may induce catalyst sintering, ionomer degradation, and membrane failure. In this context, and by analogy with systems based on Ag or Au (CO-selective) and p-block metals such as Sn and Bi (formate-selective), which involve comparatively simple reaction networks, copper-based electrolyzers operate through far more complex C_{2+} pathways, making robust thermal management especially critical for stability and scale-up. Integrating thermal modeling into cell and stack design enables prediction of gradients, prevention of hot spots, and uniform current and reactant distribution, unlocking the benefits of operation within 20–80 °C.

The key priorities moving forward involve developing coupled thermal–electrochemical models to ensure fully isothermal operation in both flow and zero-gap configurations. This requires the use of thermally robust copper catalysts, such as alloys, supported nanostructures, or conformal coatings, to minimize sintering and degradation. Equally important is the implementation of active temperature management, enabled through real-time diagnostic tools (for instance, thermocouples or infrared mapping) combined with adaptive control of flow conditions. Long-term durability testing must take a holistic approach by integrating calorimetric measurements with extended operation under representative thermal loads. Finally, successful scale-up will depend on modular design principles, utilizing standardized thermal units to enable predictable performance at pilot and commercial scales.

In addition, actionable strategies to address temperature-related challenges include optimizing electrode architecture and catalyst placement to minimize local hot spots, employing temperature-tolerant ionomers and membrane materials to extend operational life, implementing dynamic flow control and cooling strategies to actively manage gradients, integrating predictive thermal–electrochemical modeling to guide design and operation, and performing accelerated aging tests under controlled thermal gradients to validate long-term stability.

Ultimately, durable CO_2 electroreduction requires coupling materials innovation, architecture design, and proactive heat management into an integrated thermal–electrochemical framework.

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- •• of outstanding interest

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This study explores how temperature affects CO_2 electroreduction on copper. Two regimes were identified: from 18 to ~48 °C, multicarbon (C_{2+}) products showed higher selectivity, while methane and formic acid decreased, and H_2 remained constant. Above 48 °C, hydrogen evolution dominated and CO_2RR activity declined, favoring C_1 products like CO and formic acid. The low-temperature behavior is linked to CO coverage, local pH, and kinetics, while high temperatures likely induce structural changes in the copper surface, shifting product distribution.

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This study examines how temperature affects zero-gap CO_2 electrolyzers with Cu-based electrodes. Testing from room temperature to 80 °C showed that higher temperatures improve CO_2 transport, conductivity, and water management, boosting catalytic activity. Above 50 °C, selectivity shifted toward CO production, with SEIRAS revealing lower surface CO coverage. Heating method also influenced performance and product distribution. These results highlight the critical role of thermal management in optimizing CO_2 electrolysis, particularly for commercial systems expected to operate at elevated temperatures.

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