19 (2026) 100603

Contents lists available at ScienceDirect

Carbon Capture Science & Technology

journal homepage: www.elsevier.com/locate/ccst

Review

From thermal to electrochemical CO_2-to-methanol conversion: A comprehensive review of process technologies, techno-economics, and life-cycle performance

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ARTICLE INFO

Keywords:
Green methanol
Power to methanol
Electrification
Techno-economic analysis
Life cycle assessment

ABSTRACT

Methanol is central to the decarbonisation of chemicals and fuels, yet current production is almost entirely reliant on fossil syngas. This review contrasts mature thermocatalytic routes with three emerging green pathways that incorporate electrolysers: 1). one-step direct electrochemical reduction of CO_2 to methanol, 2). two-step schemes in which CO_2 is hydrogenated using electrolytic hydrogen, and 3). three-step syngas-based system design in which CO_2 is first converted to CO with co-produced H_2, then supplemented with electrolytic H_2 for conventional methanol synthesis. Published data are reconciled consistently across technology readiness, energy and carbon efficiency, levelised methanol cost, and life cycle impacts to identify robust trends rather than case-specific results. The analysis shows that conventional steam reforming remains the lowest-cost option at present, while green electrochemical routes can reduce cradle-to-gate greenhouse gas emissions by >80% at the expense of significantly higher production costs, dominated by electricity prices, electrolyser performance, and capacity factors. Direct electrochemical pathways are at a low level of technological readiness but offer the prospect of compact, modular plants that avoid intermediate hydrogen handling. In contrast, the two- and three-step concepts are closer to deployment but incur the energy penalties associated with separate hydrogen generation and CO_2 capture. By integrating techno-economic, life-cycle, and scale-up considerations, the review delineates the operating windows, renewable energy prices, and methanol premiums required for economic competitiveness. It highlights research priorities in catalyst durability, large-area stack design, system integration, and policy support that are most likely to close the remaining performance and cost gaps.

1. Introduction

Global anthropogenic carbon dioxide (CO_2) emissions remain at record levels, with fossil CO_2 projected at about 36.8 Gt CO_2 in 2023 and total anthropogenic CO_2 (including land-use change) at about 40.9 Gt CO_2, indicating that global decarbonisation has not yet delivered an absolute decline in emissions (Friedlingstein et al., 2023). This sustained burden is driven by hard-to-abate sectors, where the chemical industry alone contributes ~2 Gt CO_2 per year, reinforcing the strategic importance of carbon capture and utilisation as part of near-term mitigation portfolios (Freyman et al., 2023). Developing green and efficient approaches to CO_2 capture and utilisation has become a significant research focus, particularly given the environmental benefits of renewable energy sources. An appealing idea is to produce carbon-based e-fuels from abundant feedstocks, such as CO_2 and H_2O.

Methanol (MeOH) is widely seen as a key platform chemical and energy carrier. Its versatility stems from use as a feedstock for formaldehyde, olefins, and acetic acid, as a solvent and fuel additive (Dalena et al., 2018). Industrial methanol production remains dominated by the syngas route, in which H_2 and CO are generated via natural gas steam

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https://doi.org/10.1016/j.ccst.2026.100603
Received 16 January 2026; Received in revised form 14 March 2026; Accepted 17 March 2026

reforming or autothermal reforming, or via coal gasification, followed by Cu-based catalytic synthesis. Recent biomass-to-methanol routes increasingly rely on integrated process trains that combine feedstock conversion, syngas generation and conditioning, and catalytic methanol synthesis. Representative pathways include biomass gasification to syngas, biochemical routes via biogas or biomethane with subsequent reforming, and pyrolysis to bio-oil followed by upgrading or reforming to syngas before methanol synthesis (Tariq et al., 2025). As this review focuses on CO_2 to methanol via thermocatalytic and electrochemical routes, biomass-related pathways are only outlined here and are not discussed further.

Despite the conventional methanol production route having been commercially dominant for many years, it is strongly reliant on fossil feedstocks, primarily natural gas and coal, resulting in significant greenhouse gas emissions and price volatility (Mehmeti et al., 2018). Electrochemical hybrid methods, which include direct CO_2-to-methanol reduction (Albo et al., 2015; Marlin et al., 2018), CO_2-to-CO conversion followed by hydrogenation with supplemental hydrogen from water electrolysis (Jouny et al., 2018a; Sollai et al., 2023), and direct coupling of CO_2 with green hydrogen (Harris et al., 2021; Wang et al., 2023; Zong et al., 2024), offer potential advantages like operation at ambient conditions and integration with renewable energy sources. As shown in Fig. 1, methanol can be produced in a circular green methanol system that couples carbon capture with renewable energy and water electrolysis. Concentrated CO_2 from industrial point sources is captured and combined with green hydrogen produced using wind and solar power to synthesise methanol. The crude product is purified to high-grade methanol for use as fuel and a chemical feedstock, while unconverted CO_2 is recycled within the loop. This integrated configuration reduces demand for fossil feedstocks and enables partial closure of the carbon cycle at the process level.

Fig. 2 summarises the evolution of research on green methanol and electrochemical methanol synthesis from 2000 to 2025 across five themes: life cycle and sustainability, hybrid renewable systems, renewable hydrogen integration, seasonal storage and grid balancing, and techno-economic optimisation. Research output was limited in the early 2000s, but increased after 2010 and accelerated further over the past decade, reflecting growing interest in methanol as a low-carbon energy carrier and chemical feedstock. Notably, the rise in studies on techno-economic optimisation, renewable hydrogen integration, and system-level sustainability indicates that progress in power-to-methanol systems depends not only on catalytic or process performance, but also on renewable integration, storage strategies, and rigorous economic and environmental assessment.

Recent literature on power-to-methanol (PtM) shows an increasing focus on integrating carbon capture, renewable hydrogen production and renewable electricity to deliver low-emission methanol. An important theme is the optimal design and operation of PtM systems. A research study developed a mixed-integer linear programming model that simultaneously optimises investment and operational decisions for PtM plants (Akram and Kienberger, 2024). Their case study repurposing a coal power plant in Austria showed that using large PEM electrolyser capacities (~434 MW) with flexible part-load operation can reduce methanol costs to about 0.8 EUR kg^{-1} when carbon prices approach 500 EUR t^{-1}. Similarly, another research formulated a dynamic MILP to size and schedule PtM components; the optimised configuration increased hydrogen storage capacity by ~95% while keeping the electrolyser size almost constant, enabling better utilisation of fluctuating renewable

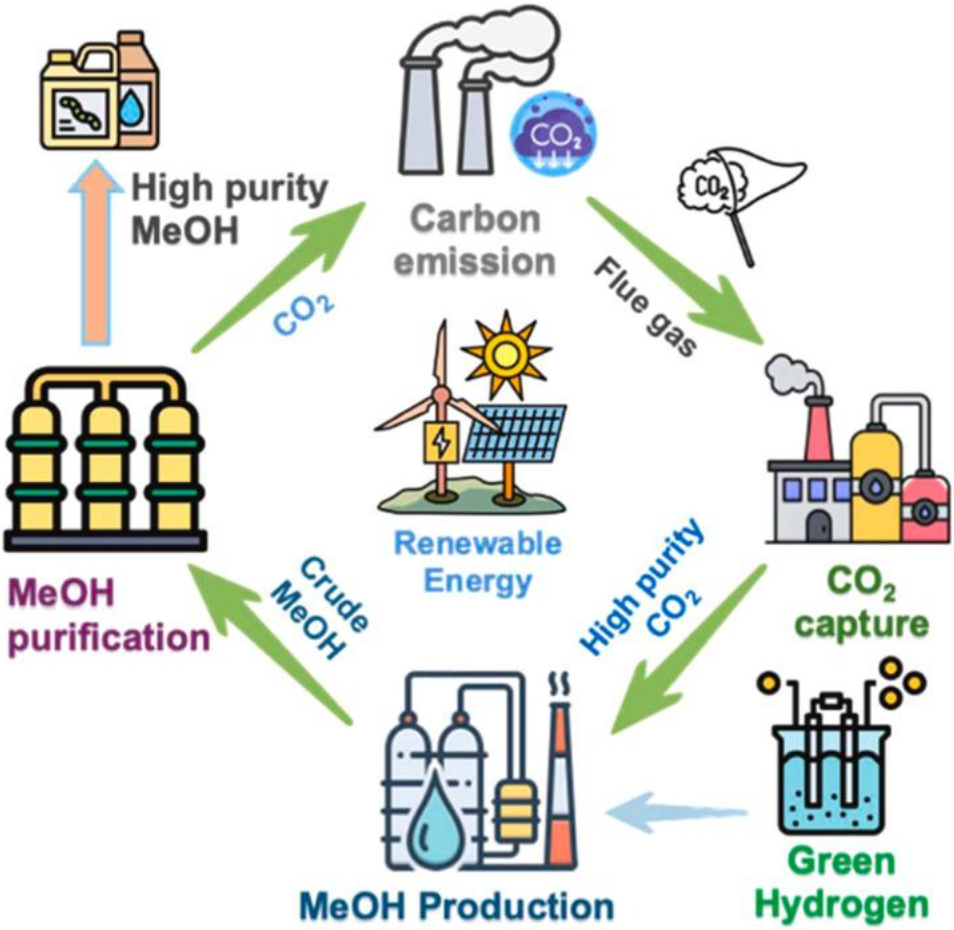

Fig. 1. Integrated green methanol production from captured CO_2 and renewable hydrogen. Icons: www.flaticon.com.

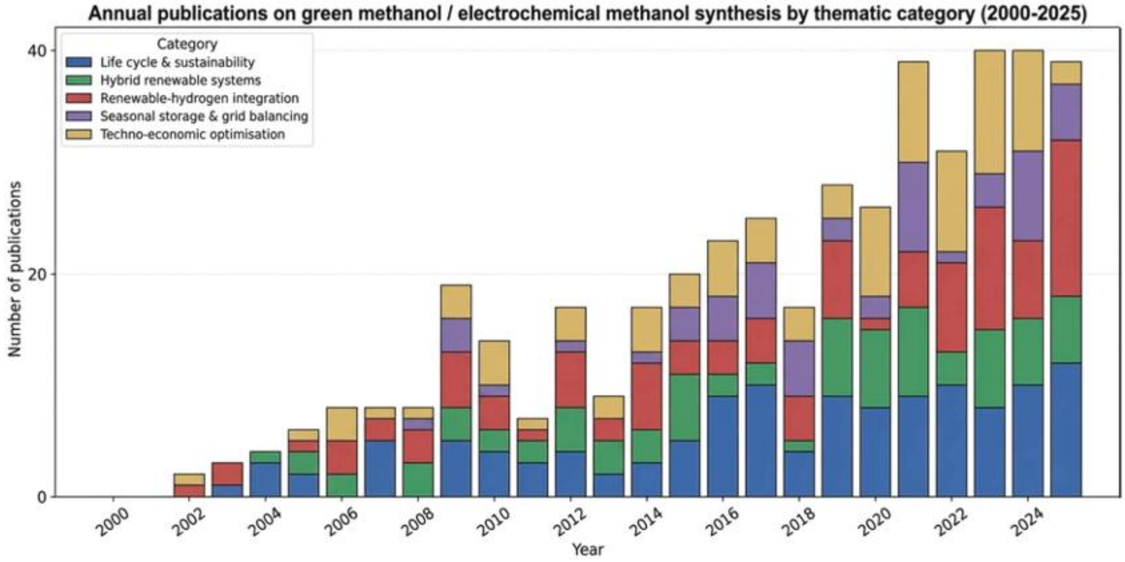

Fig. 2. Evolution of research themes in green methanol and electrochemical methanol synthesis from 2000 to 2025.

energy and mitigating peak loads (Ye et al., 2025). A techno-economic and sustainability assessment showed that an optimised PtM process (with membrane and amine absorption capture) achieved an energy efficiency of 56 % and consumed 1.4 kg CO_2 kg^{-1} MeOH (Pakdel and Eslamloueyan, 2024). Their economic analysis yielded production costs of USD 631–643 t^{-1} and illustrated how declining electrolyser costs could reduce methanol prices towards 2030. The integration of offshore wind and carbon capture is also gaining traction. A recent study assessed offshore wind-powered PtM systems supplying the maritime sector (Du et al., 2025). Their scenario analysis showed that the LCOM varied depending on carbon source and grid connection and electricity accounted for over 60 % of the LCOM, with alkaline water electrolysis consuming about 50 % of the electricity (Du et al., 2025).

Beyond the optimisation and scheduling studies discussed above, several recent contributions could further strengthen this review's positioning within the broader power-to-methanol literature. A recent research examined the integration of e-methanol production with oxy-fuel power plants in an Australian case study and showed that adaptive power management, coupled with large PEM electrolyser capacity and flexible part-load operation, can improve system-level economics while maintaining carbon capture performance (Akbari et al., 2026a). A related line of work introduced the concept of a biomass battery, in which biomass serves as a long-duration energy reservoir for seasonal storage and e-methanol synthesis; this study demonstrated that coupling wind power with biomass-derived heat and CO_2 can substantially improve grid balancing and reduce methanol costs under favourable carbon pricing conditions (Akbari et al., 2026b). In parallel, recent feasibility studies on solar thermochemical hydrogen production for power-to-methanol have highlighted the potential of alternative renewable hydrogen pathways to reduce dependence on grid electricity and enhance overall process efficiency (Akbari et al., 2025). Taken together, these studies address complementary dimensions of PtM development, including techno-economic optimisation, seasonal storage, and renewable hydrogen integration.

Life-cycle studies reinforce the benefits of integrating seasonal renewable energy. A recent LCA of green methanol production based on multi-seasonal renewable configurations found that seasonal wind and solar mixes, coupled with hybrid battery storage, can reduce global warming potential by 24.38–28.26% relative to a conventional grid-powered plant (Güleroğlu and Yumurtacı, 2025). Monte Carlo analysis confirmed the robustness of these environmental gains, while process analysis revealed that hydrogen production accounts for 74–94% of the lifecycle impacts (Güleroğlu and Yumurtacı, 2025). Another study was conducted on a cradle-to-gate LCA of methanol from fossil, biomass, and waste sources. They found that renewable methanol pathways reduced greenhouse gas emissions by 58–226% relative to natural gas-based methanol and that capturing carbon from process emissions could increase the reductions to 327% (Masum et al., 2025).

Fig. 3 shows a clear geographical clustering of methanol pathways, with e-methanol projects concentrated mainly in Europe, North America, and parts of Asia, where strong policy support, renewable electricity deployment, and industrial decarbonisation strategies are already in place. By contrast, biomethanol projects are more widely distributed across biomass-rich regions, particularly in China, Southeast Asia, and parts of Northern Europe, whereas low-carbon methanol is found in fewer locations, associated with established fossil-based infrastructure and transitional carbon management strategies.

In general, green methanol synthesis aims to develop a sustainable, low-carbon alternative that integrates electrolysers powered by renewable energy sources. However, current e-MeOH pathways remain at a low technology readiness level (TRL), posing significant obstacles for large-scale industrial implementation (Chiou et al., 2023; Wang et al., 2023). To address the above challenges, this review proposes a quantitative framework that harmonises system boundaries and benchmarks electrolyser-enabled e-methanol systems against mature thermocatalytic methanol production. The analysis covers one-step direct electrochemical reduction of CO_2 to methanol, two-step power-to-methanol routes combining water electrolysis with catalytic CO_2 hydrogenation, and a three-step hybrid configuration in which a CO_2 electrolyser is embedded to form a syngas-like intermediate. Recent techno-economic analyses and life cycle assessments are synthesised using aligned indicators to assess cost, environmental impacts, technology readiness, and commercial feasibility, with particular emphasis on the hybrid route. By linking electrolyser-level constraints, including efficiency, durability, and scale-up operability, to process integration choices and boundary-consistent outcomes, the review identifies bottlenecks spanning feedstock supply, reactor and stack engineering, and policy and market enablers, and provides a mechanistic rationale for the three-step concept under stoichiometric constraints. Relevant studies were systematically retrieved from Web of Science and Scopus, with supplementary searches in Google Scholar, then screened using predefined inclusion and exclusion criteria. Extracted data were standardised in Excel for pathway classification, key-metric harmonisation, and comparative TEA and LCA analyses. A standardised data extraction

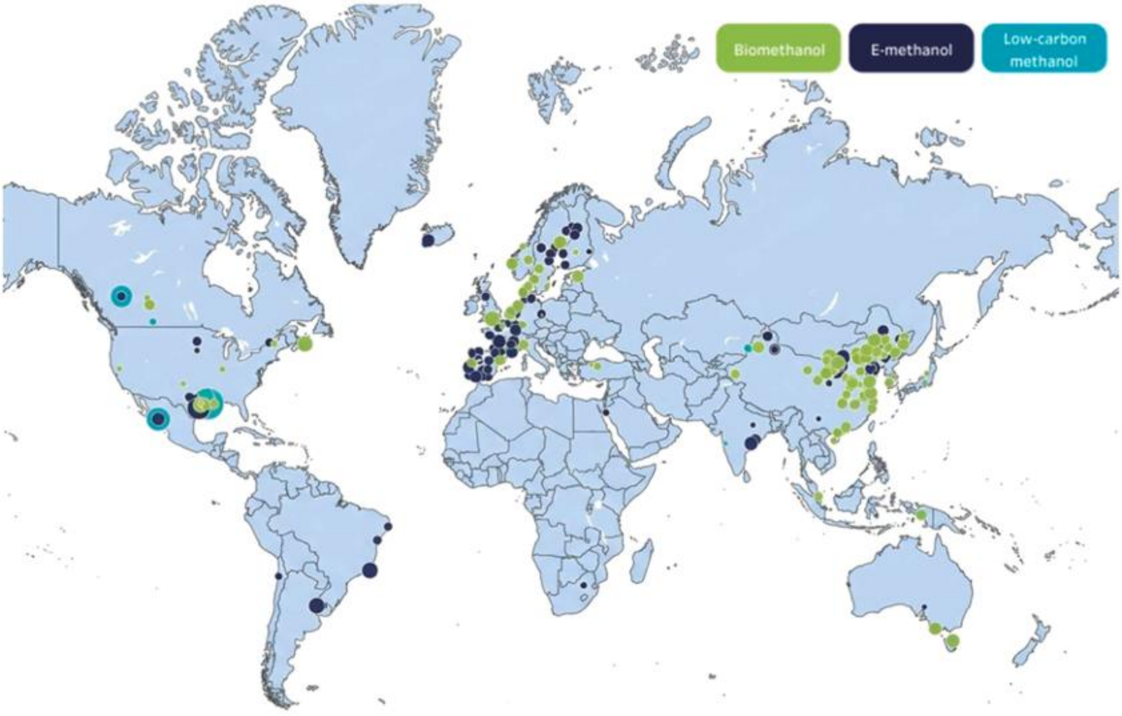

Fig. 3. Distribution map of biological methanol and electronic methanol projects. The data is sourced from MI's official website. https://methanol.org/renewable/.

template was used to record pathway type, key technical and economic assumptions, and Life Cycle Assessment boundary definitions. The extracted data were then synthesised using a structured evidence framework, including techno-economic harmonisation to a common base year, currency, and boundary conditions, and boundary-based grouping to improve comparability across LCA studies.

2. Conventional methanol production: process, economics and environmental performance

The thermal catalytic pathway for methanol production has been widely analysed (Bertau et al., 2014; Olah et al., 2009), hence a detailed discussion lies beyond the scope of this review. In general, the established industrial synthesis route comprises three primary stages: the production of synthesis gas (syngas), the catalytic conversion of syngas to crude methanol, and subsequent distillation to achieve commercial-grade purity. Large-scale plants convert natural gas, coal, or heavy oil into syngas via endothermic steam reforming or autothermal reforming, followed by methanol synthesis over copper-based catalysts. The most widely used route employs steam methane reforming (SMR) to convert natural gas (predominantly methane) into syngas. Methane reacts with steam over a nickel catalyst at 800–950 °C and 20–40 bar to yield H_2 and CO (Prakash et al., 2011). A subsequent water–gas shift reaction adjusts the H_2/CO ratio to approximately 2:1, and the conditioned syngas is then compressed and fed to a methanol reactor operating at 50–100 bar and 220–280 °C (Olah et al., 2009). SMR plants typically achieve high energy efficiency (55–65 %), and because natural gas is relatively inexpensive, methanol production costs range from 0.1 to 0.25 USD kg^{-1} (Pakdel and Eslamloueyan, 2024). The process is mature (TRL of 9), with unit capacities exceeding 5000 t day^{-1} (Blug et al., 2014). Its main drawbacks are vulnerability to gas price spikes and high CO_2 emissions; its cradle-to-gate footprint is approximately 1.4–1.5 kg CO_2-eq per kg methanol (Pakdel and Eslamloueyan, 2024). In recent years, methane pyrolysis has emerged as an alternative to SMR, in which methane is thermally decomposed into hydrogen and solid carbon (Zong et al., 2024). Pyrolysis avoids direct CO_2 emissions from reforming and yields solid carbon that can be sold or sequestered. A techno-economic comparison of nine CO_2-to-methanol routes showed that methane pyrolysis integrated with dry reforming could reduce methanol production costs from 0.296 USD kg^{-1} to 0.990 USD kg^{-1} by 2050 under favourable natural-gas prices and high carbon penalties (Zong et al., 2024). However, this pathway remains at the pilot scale and faces challenges related to reactor design, solid carbon handling, and hydrogen purification (Zong et al., 2024).

Currently, most conventional methanol synthesis pathways employ $Cu/ZnO/Al_2O_3$ as catalysts (Fichtl et al., 2015; Xu et al., 2016; Slotboom et al., 2020). These exhibit high activity and selectivity but deactivate via sintering, copper over-oxidation and ZnO reduction. Indium-based catalysts are attracting attention because they activate CO_2 more effectively than copper. For example, a metal organic framework (MOF)-derived In_2O_3/ZrO_2 heterojunction achieved gas-phase methanol selectivity of 81 % and productivity of 2.64 g MeOH g cat^{-1} h^{-1} by exploiting abundant interfacial oxygen vacancies and a liquid-phase selectivity of 96 % (Koley et al., 2025). Such catalysts operate at milder pressures and are less sensitive to water yet remain at the laboratory scale. Another avenue is doping Cu-based catalysts with Ga, Zr or Ce to modify electronic properties and enhance CO_2 adsorption. Hybrid catalysts that couple the reverse water-gas shift and methanol synthesis functions into a single material have been proposed; they enable conversion of CO_2-rich streams by first producing CO and subsequently methanol. However, managing heat release and preventing undesired methanation remain challenges. Modern large-scale SMR-based units typically consume about 28 to 33 GJ of primary energy per tonne of methanol, corresponding to overall thermal efficiencies of roughly 55 to 65% (Blumberg et al., 2019; Blumberg et al., 2017). The cost of natural gas used as both feedstock and fuel usually accounts for more than half of operating expenditure, typically 50–70%, making the levelised methanol cost of the fossil routes to 100–250 USD t^{-1} under favourable gas prices (Olah et al., 2009) and highly sensitive to gas-price volatility (Jingyun Ye et al., 2025). Power-to-methanol concepts that couple water electrolysis with CO_2 hydrogenation often require about 40 to 60 GJ of electricity equivalent per tonne of product (Daggash et al., 2018).

In summary, the current methanol supply is dominated by fossil-based routes, such as natural gas steam reforming and coal gasification, which operate at a high TRL. These processes provide the techno-economic and environmental baseline for this review. Incremental decarbonisation options, such as carbon capture and storage retrofits, electrified reforming, and methane pyrolysis, can lower the carbon intensity of grey methanol. Still, they do not remove its structural dependence on fossil feedstocks or its exposure to gas price volatility. The following sections, therefore, shift focus to green methanol pathways that integrate water electrolysis and electrochemical CO_2 conversion into the systems and assess the extent to which these routes can overcome the carbon and energy limitations of conventional plants while remaining cost-competitive and scalable.

3. Electrochemical route integrated with renewable systems

3.1. Electrochemical CO_2 reduction

Achieving commercially viable electrochemical routes to methanol requires integrated optimisation of electrolyser architecture, catalyst design and operating conditions. This subsection outlines the key reaction pathways and metrics governing electrochemical carbon dioxide reduction, including methanol yield, selectivity, Faradaic efficiency (FE), current density, energy efficiency, and operational durability. Advances in cell and stack engineering are then assessed, with emphasis on gas-diffusion and membrane-electrode assembly configurations that enable industrially relevant performance. Finally, recent progress in electrocatalysts for carbon monoxide and methanol formation is critically reviewed, spanning state-of-the-art copper-based systems and emerging non-copper alternatives that offer improved selectivity for carbon monoxide or formate at lower cost, while highlighting phthalocyanine-based molecular catalysts for high-purity carbon monoxide production. Through this section, readers can develop a clear understanding of the CO_2 electroreduction process, the current technological status, and the major research barriers that govern the reliable integration of CO_2 electrolysers with downstream methanol synthesis in power-to-methanol systems.

3.1.1. eCO_2R Electrolyser configuration

Electrochemical CO_2 reduction has been studied across a set of increasingly application-relevant cell configurations, as shown in Fig. 4, spanning fundamental mechanistic screening to industrial-scale deployment. Most early electrochemical studies employed H-type cells with two glass compartments separated by an ion-conducting membrane or a salt bridge (Fig. 4(a)) (Hernandez-Aldave and Andreoli, 2020; Tufa et al., 2020). This configuration is well-suited to mechanistic elucidation and to catalyst or electrolyte screening, but its limited mass transport and low CO_2 solubility limit the attainable current densities. This setup limits CO_2 availability because dissolution in aqueous electrolyte is poor (≈ 34 mM). Thick diffusion layers restrict mass transfer, so current densities rarely exceed 20 mA cm^{-2} (Seger et al., 2023). Consequently, the FE for CO is modest and varies with the electrolyte pH and the

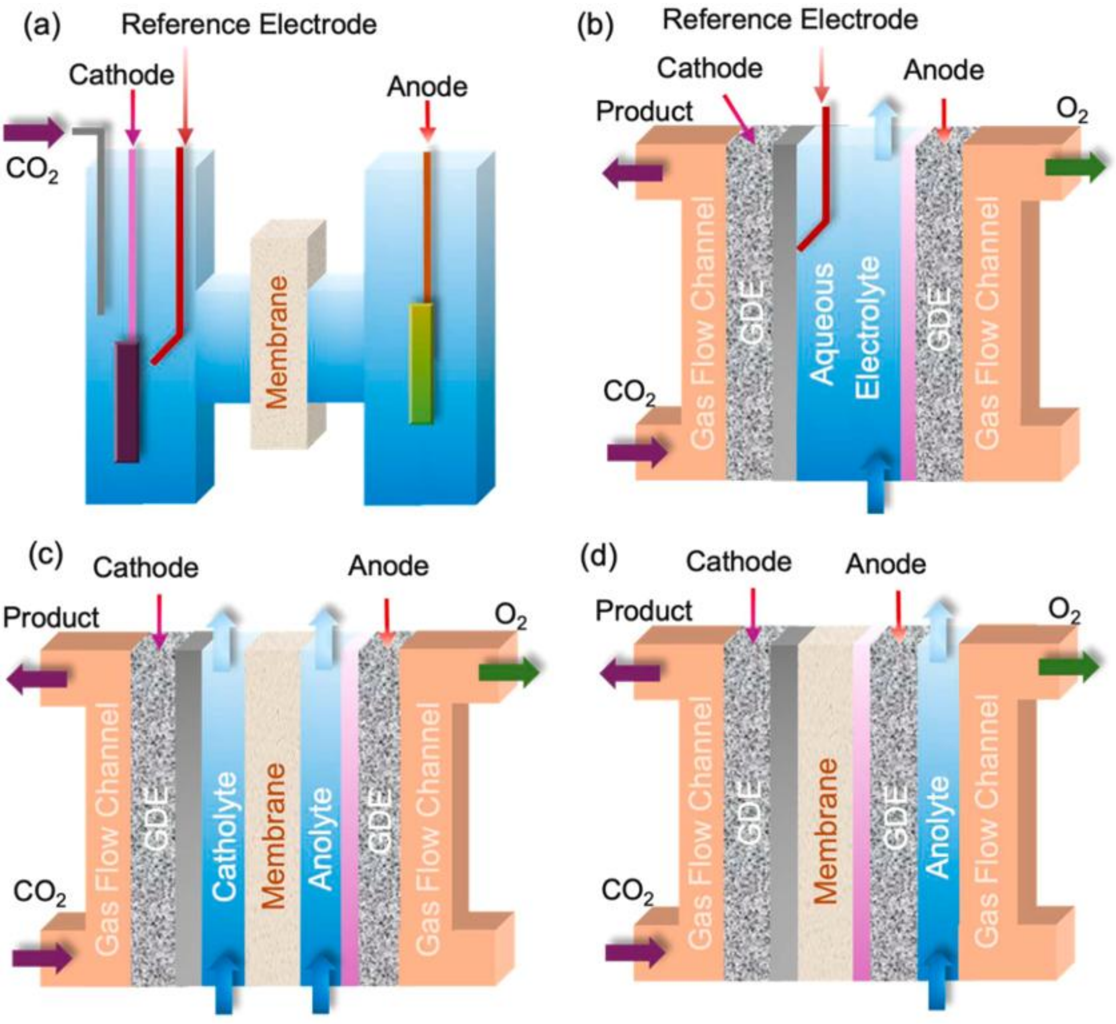

Fig. 4. Schematic comparison of four common CO_2 electrolyser configurations. (a), H-cell architecture. (b), Microfluidic cell. (c), Membrane-separated flow cell with liquid-phase CO_2 supply. (d), Gas-fed membrane–electrode-assembly (MEA) electrolyser / zero-gap using a gas-diffusion electrode (GDE).

catalyst. Nevertheless, H-cells remain useful for mechanistic studies and catalyst screening (Serafini et al., 2023). Nafion membranes are often used to separate catholyte and anolyte but cause proton transport to the cathode, which can favour hydrogen evolution; alternative membranes (anion-exchange or bipolar) reduce this cross-over (Serafini et al., 2023). Meanwhile, microfluidic cells extend laboratory studies to porous catalyst layers and gas diffusion electrodes by using a narrow channel and thin electrolyte film, enabling precisely controlled hydrodynamics and shorter diffusion distances (Fig. 4(b)) (Tufa et al., 2020). As a result, they offer enhanced mass transport and are often used for low flow rate experiments requiring high operational control.

To overcome mass-transfer limitations, researchers moved to flow cells in which CO_2 gas contacts a porous gas-diffusion electrode (GDE) and is fed by a liquid electrolyte on the other side. In the liquid phase CO_2 feed membrane flow cell (Fig. 4(c)), CO_2 is first dissolved into the catholyte and delivered to the reaction interface through a GDE, which provides higher practical current densities and serves as a common transition architecture between benchtop cells and industrial reactors (Gawel et al., 2022). Research has reported that hydrophobic polymer coatings on Cu-based GDEs maintain a balanced CO_2/H_2O ratio and prevent flooding (Chen et al., 2024). However, the gas diffusion layer (GDL) can flood, blocking CO_2 access and allowing electrolyte crossover. Silver nanoparticles modified with hydrophobic ligands similarly retained >90 % FE for CO at 298 mA cm^{-2} (Ko et al., 2024). These examples show that controlling local hydrophobicity is critical. Another flow-cell variant uses Taylor flow in a tubular reactor. Gas bubbles form slugs separated by a thin liquid film; the diffusion layer around each bubble is orders of magnitude thinner than in an H-cell, leading to much higher current densities and improved FE (Bagemihl et al., 2022). Flow-cells therefore represent the work-horse for modern electrochemical CO_2 reduction research and are relevant for scaling up e-methanol production.

The most likely to be industrially aligned platform is the gas phase CO_2 fed membrane electrode assembly (MEA), often implemented as a zero-gap electrolyser (Fig. 4(d)), where GDE sandwich an ion exchange membrane and CO_2 is fed directly to the cathode (Hernandez-Aldave and Andreoli, 2020). This zero-gap configuration minimises ohmic losses, alleviates solubility-limited transport, and enables high-current-density operation, making it the dominant direction for CO_2 reduction scaling towards power-to-methanol and other utilisation routes. Flow-cell and MEA architectures now routinely reach current densities near those required for industrial deployment, often above 200 mA cm^{-2}, with FE for CO_2-derived products exceeding 80–90% (Jouny et al., 2019). Demonstrating long-term durability, however, remains a central challenge, as most systems operate for only hundreds of hours before notable degradation and the conversion rate was limited to <43%, while the total CO_2 consumption rate could reach 95% (Jeng and Jiao, 2020). Membrane choice governs both cell performance and durability. Anion exchange membranes facilitate high-current-density operation, yet the strongly alkaline microenvironment near the cathode promotes rapid reaction between CO_2 and OH^-, leading to substantial formation of bicarbonate and carbonate. These species often become the dominant charge carriers, driving carbonate-mediated CO_2 losses, while the membrane chemistry may also degrade at high pH. Bipolar membranes can partially decouple the anode and cathode pH, lowering cathode alkalinity and mitigating carbonate formation and crossover, but this comes at the cost of a voltage penalty due to water dissociation overpotential and additional ohmic resistance. By contrast, acidic eCO_2R using cation exchange membranes (CEMs) such as Nafion can deliver high carbon utilisation, in some cases exceeding 90%, although proton crossover to the cathode can intensify hydrogen evolution reaction (HER) and thereby reduce CO selectivity and energy efficiency (Kang et al., 2025b, 2025a). GDEs with tuned hydrophobicity, surface modification of cationic polyelectrolytes for substituting alkali metal cations, membranes with enhanced ion transport, resistance to CO_2 crossover and solid-state electrolyte concepts reduce flooding, carbonate accumulation and product crossover (Johnson et al., 2023; Lees et al., 2021; Yang et al., 2021; Zhang et al., 2026). Solid-state electrolyte (SSE) cells, which replace liquid catholytes with ion-conducting polymers or ceramics, show promise in improving stability and simplifying product separation (Wiranarongkorn et al., 2023). A recent study used a Cu_6Sn_5 catalyst and a cation-free SSE membrane to convert CO_2 to formic acid with 91 % FE at 1.2 A cm^{-2}; the single-pass carbon efficiency reached 77 % and 0.36 M formic acid was produced continuously with 37 % energy efficiency (Yu et al., 2024). By preventing carbonate formation and managing water activity, SSEs promise high product concentrations and minimal downstream separation, although long-term stability and scale-up remain challenges. In general, their current densities and scale-up maturity require further development before integration into power-to-methanol systems is feasible.

In addition to other configurations, solid-oxide electrolysers (SOEs) are employed for CO_2R at high temperatures (> 600 °C), a process that has recently gained significant attention in the scientific community. In a typical SOE, the anode and cathode are separated by a solid electrolyte, which can be either an oxygen ion conductor or a protonic conductor. The electrochemical reduction of CO_2 at the interface of electrodes, a solid electrolyte, and reactant gases at high temperatures enables more efficient mass transport of CO_2 and reduces the activation energy barrier (Song et al., 2019). This results in a higher current density for SOEs compared to traditional low-temperature CO_2R in aqueous electrolytes. Despite these benefits, SOEs face significant constraints due to complex electrocatalytic chemistry and substantial degradation of electrodes, electrolytes, and the electrode-electrolyte interface at elevated temperatures (Hanif et al., 2023; Wang et al., 2021; Wang et al., 2023; Wolf et al., 2023).

3.1.2. *eCO_2R Catalysts*

Catalyst design in CO_2 electrolysers is pivotal to the production of green methanol, as it influences both carbon utilisation and the overall process efficiency. This section concentrates on two categories of electrocatalysts: those that directly reduce CO_2 to CO at the cathode and those that produce CO_2-based compounds. Rather than providing an exhaustive review of all reported materials, the discussion emphasises synthesising prior research to identify catalyst systems that demonstrate high selectivity, significant partial current density, and acceptable stability under conditions relevant to industrial CO_2 electrolyser operation.

Metals such as Ag, Au, Pt, Pd, Zn, Ni, Ga and Fe can be used to reduce CO_2 to CO as non-copper metal catalysts. Au and Ag deliver the highest FE (> 90 %) at partial current densities above 200 mA cm^{-2} but are expensive (Serafini et al., 2023). Zn and Ga offer a lower cost and produce CO with FEs up to 87 %. Sn, Pb, Cd, In and Bi favour formate/formic acid (Hu et al., 2023). SnO_2 nanosheets on carbon cloth achieved roughly 87 % FE for formate at 50 mA cm^{-2} (Serafini et al., 2023). Doping Sn with sulfur increased FE to 93 % at 55 mA cm^{-2}, showing that electronic structure tuning is critical. Bi catalysts also exhibit ~95 % FE for formate and have been demonstrated in flow-cells with partial current densities >200 mA cm^{-2} (Serafini et al., 2023).

Nanoparticle size and oxidation state tune product distribution: small nanoparticles or oxide-derived copper favour ethylene, whereas larger particles favour methane. Incorporating tandem catalysts (e.g., Cu with Zn or Ag) can provide an abundant CO intermediate, which is further reduced to C_1 species. Overa et al. (2022) summarised their advances in electrochemical CO_2 conversion, spanning electrocatalyst development, reactor engineering, mechanistic insights and techno-economic considerations. They demonstrated that nanoporous Ag and Cu-based bimetallic catalysts enhance CO and C_1 production. At the same time, gas-fed flow cells and MEA reactors achieve industry-relevant current densities approaching 1 A cm^{-2} with high selectivity (Overa et al., 2022).

Copper has been shown to be unique in its ability to produce multi-carbon products (methane, ethylene, ethanol). Nano structuring enhances selectivity by exposing specific facets and edges. For instance, mesoporous Cu catalysts with hydrophobic polymers achieved > 87 % FE to C_2+ products at 2 A cm^{-2} (Chen et al., 2024). Copper catalysts modified with ligand coatings or alloyed with elements such as In or Ga suppress competing hydrogen evolution and methane formation. Reports of high FE for direct electrochemical methanol synthesis remain scarce, partly because methanol is readily oxidised at the anode and stabilising intermediates are difficult to form. Recently, a milestone was reported where (Chen et al., 2025) developed an In_2O_3-x overlayer and inverse In_2O_3-x/Ni interfacial catalyst formed by in situ surface reconstruction of $Ni_3InC_{0.5}$, delivering 19% CO_2 conversion, 65% methanol selectivity, and a methanol space time yield of 508.4 mg g_{cat}^{-1} h^{-1} at 260 °C and 5 MPa, while maintaining activity over a 250 h stability test.

Molecular catalysts offer tunable active sites and well-defined coordination environments. Cobalt- and nickel-phthalocyanine grafted on carbon have shown industrially relevant current densities and high FE for CO. For example, trimethylammonium-substituted cobalt phthalocyanine generated CO with approximately 95 % selectivity and a partial current density of 165 mA cm^{-2} in a flow-cell (Wang et al., 2019). Graphite-conjugated $Ni(NH_2)_8$ phthalocyanine displayed nearly 100 % FE for CO over a wide potential window and maintained 246 mA cm^{-2} current density (Han et al., 2024). These catalysts benefit from electronic delocalisation between the metal centre and the conjugated carbon support, which facilitates electron transfer and stabilises intermediates. Beyond phthalocyanines, Mn bipyridines and Co porphyrins have been reported with FE of CO approaching 90% (Wang et al., 2019). However, these molecular catalysts often operate in flow cells rather than MEAs and may leach over the long term.

Across catalyst classes, several design principles emerge:

Nanostructuring and morphology control: increasing active surface area and exposing specific crystallographic facets enhances CO_2 activation. SnO_2 nanosheets, Cu nanowires and nanocubes, and hierarchically porous catalysts exemplify this strategy (Serafini et al., 2023). Oxide-derived copper provides a representative example of morphology-driven performance. Jouny et al. (2018b) reported a high-rate CO flow electrolyser based on oxide-derived copper, achieving a FE of 91% for C_2^+ products and partial current densities above 630 mA cm^{-2}.

Electronic tuning: doping or alloying modifies the adsorption energies of key intermediates (e.g., CO*, HCOO*). Sulfur doping in SnO_2 improves FE for formate (Serafini et al., 2023); Cu–Sn alloys suppress hydrogen evolution in acidic SSE cells and reach 91 % FE for formic acid (Yu et al., 2024).

Hydrophobic modifications: polymer coatings or hydrophobic ligands maintain triple-phase boundaries, prevent flooding and enhance local CO_2 concentration. This principle underpins high-performance GDEs using Cu or Ag catalysts (Chen et al., 2024; Ko et al., 2024).

Operando reaction environment: Controlling local pH, the CO_2-to-H_2O ratio, and electrolyte composition directs the formation of intermediates. Cation identity and buffer strength influence both selectivity and current density, while pressurised CO_2 or gas-fed MEAs enhance solubility and mass transfer (Zhang et al., 2025). Recent advances also demonstrate the value of regulating ionic distributions. For example, integrating a π-conjugated covalent organic framework into the catalyst layer modulates local cation and anion arrangements, enabling CO electrolysis to reach a single-pass carbon efficiency of 95%, an energy efficiency of 40% and a sustained current density of 240 mA cm^{-2} over 200 h (Ozden et al., 2023). Complementary advances demonstrate that manipulating acid–base equilibria at the device level can further overcome carbonate limitations. A BPM-enabled architecture that regenerates CO_2 from bicarbonate in situ and employs a nanometre-scale unbuffered catholyte layer surpasses the conventional 25% single-pass utilisation limit, reaching 78% and cutting downstream separation energy by an order of magnitude (Xie et al., 2022).

Table 1 summarises common electrolysers, representative catalysts and performance metrics from recent research. Overall, although Au/Ag, Sn/Bi/In and molecular catalysts each offer distinct advantages in selectivity and mechanistic control, Cu-based and Cu-containing tandem catalysts are currently the most suitable candidates for large-scale industrial deployment because they are the most compatible with high-rate device architectures and remain the only practically relevant platform for advancing beyond C1 intermediates towards methanol synthesis. Among the four configurations, H-cells and microfluidic cells are primarily suited to mechanistic studies and catalyst screening, flow cells offer a practical intermediate platform with improved mass transport, solid-oxide electrolysers provide high-temperature kinetic advantages but remain constrained by materials degradation and system complexity, whereas gas-fed zero-gap MEA electrolysers are currently the most promising option for large-scale industrial methanol production because they best combine high current density, compact architecture, and compatibility with scale-up.

Table 1

Representative CO_2 electrolyser configurations, catalysts and performance metrics.

Configuration	Represent Catalyst(s)	Target Product	Faraday Efficiency	Current density	Comments
H-cell with Nafion membrane	Au, Ag, Cu nanoparticles; SnO_2 nanosheets	CO	FE(CO) ≈ 80–90% (Au/Ag).	10–20 mA cm^{-2} (Seger et al., 2023)	Limited by CO_2 solubility and diffusion layer thickness.
Flow-cell with GDE	Hydrophobic-polymer-coated Cu; hydrophobic-ligand Ag; Zn, Bi	C_2+ products (ethylene, ethanol), CO, formate	FE(C_2+) ≈ 87 % (Cu)(Chen et al., 2024); FE(CO) $>$ 90 % (Ag)(Ko et al., 2024); FE (formate) ≈ 95% (Bi).	Partial current densities 200–300 mA cm^{-2} or total current densities up to 2 A cm^{-2}	Hydrophobic coatings prevent flooding and maintain the triple-phase boundary; improve mass transport over H-cell.
Tubular flow-cell (Taylor flow)	Cu, Ag, Sn catalysts	CO	FE like planar flow-cells; improved due to a thin boundary layer	Significantly higher than H-cell; reported increases by orders of magnitude (Bagemihl et al., 2022).	Gas–liquid Taylor flow forms slugs with thin liquid films and high mass transfer.
Zero-gap MEA	Polymer-modified Cu GDE; Bi/Cu tandem catalysts	C_2+ products, CO	FE(C_2+) ≈ 87 % at 2 A cm^{-2} (Chen et al., 2024).	> 1 A cm^{-2}	Eliminates catholyte, reducing ohmic losses; membrane choice affects pH control and crossover.
Solid-state electrolyte (SSE) MEA	Cu_6Sn_5 alloy on SSE	Formic acid	FE ≈ 91 % at 1.2 A cm^{-2}.(Yu et al., 2024)	Single-pass carbon efficiency 77 % with 0.36 M product concentration: energy efficiency ≈ 37 %.	Prevents carbonate formation, allowing concentrated streams; long-term stability still developing.
Flow-cell with molecular catalyst	Trimethylammonium-substituted Co phthalocyanine; graphite-conjugated Ni phthalocyanine	CO	FE(CO) = 95–100%.(Wang et al., 2019)	Partial current densities around 165–246 mA cm^{-2}.	Molecular catalysts allow precise tuning and high selectivity, but stability and cost are concerns.

3.2. Green hydrogen production

3.2.1. Water electrolyser configuration

Both the two-step and three-step electrochemical methanol synthesis routes inherently depend on the input of green hydrogen. Currently, water electrolysis is the most promising solution for green H_2 production (Hassan et al., 2024). The capital cost, energy efficiency and operational flexibility of the electrolysis step largely dictate the life-cycle cost of green methanol. Four mature or emerging water-splitting technologies are available: proton exchange membrane electrolysis (PEM), alkaline water electrolysis (AWE), solid-oxide electrolysis (SOE) and anion-exchange membrane electrolysis (AEM), as shown in Fig. 3. It should be noted that Fig. 3 was prepared by the authors based on information synthesised from a published report and established common knowledge on water electrolysis technologies (Green Hydrogen Cost Reduction, 2020).

PEM electrolysers, as shown in Fig. 5(a), employ a solid polymer membrane that conducts protons while separating gases, allowing compact designs and rapid load changes (Carmo et al., 2013; Wang et al., 2025). They can deliver high-pressure, high-purity hydrogen but rely on expensive platinum-group catalysts (Krishnan et al., 2023). According to DOE targets, 2022-status PEM stacks operated at ~51 kWh kg^{-1} H_2, with stack capital costs of ~450 USD kW^{-1} and system costs of ~1000 USD kW^{-1} (James et al., 2022). The target electrical efficiency is ~48 kWh kg^{-1} H_2, and the H_2 production cost is likely to drop to 1 USD per kg by 2031 through improvements in efficiency, increased stack

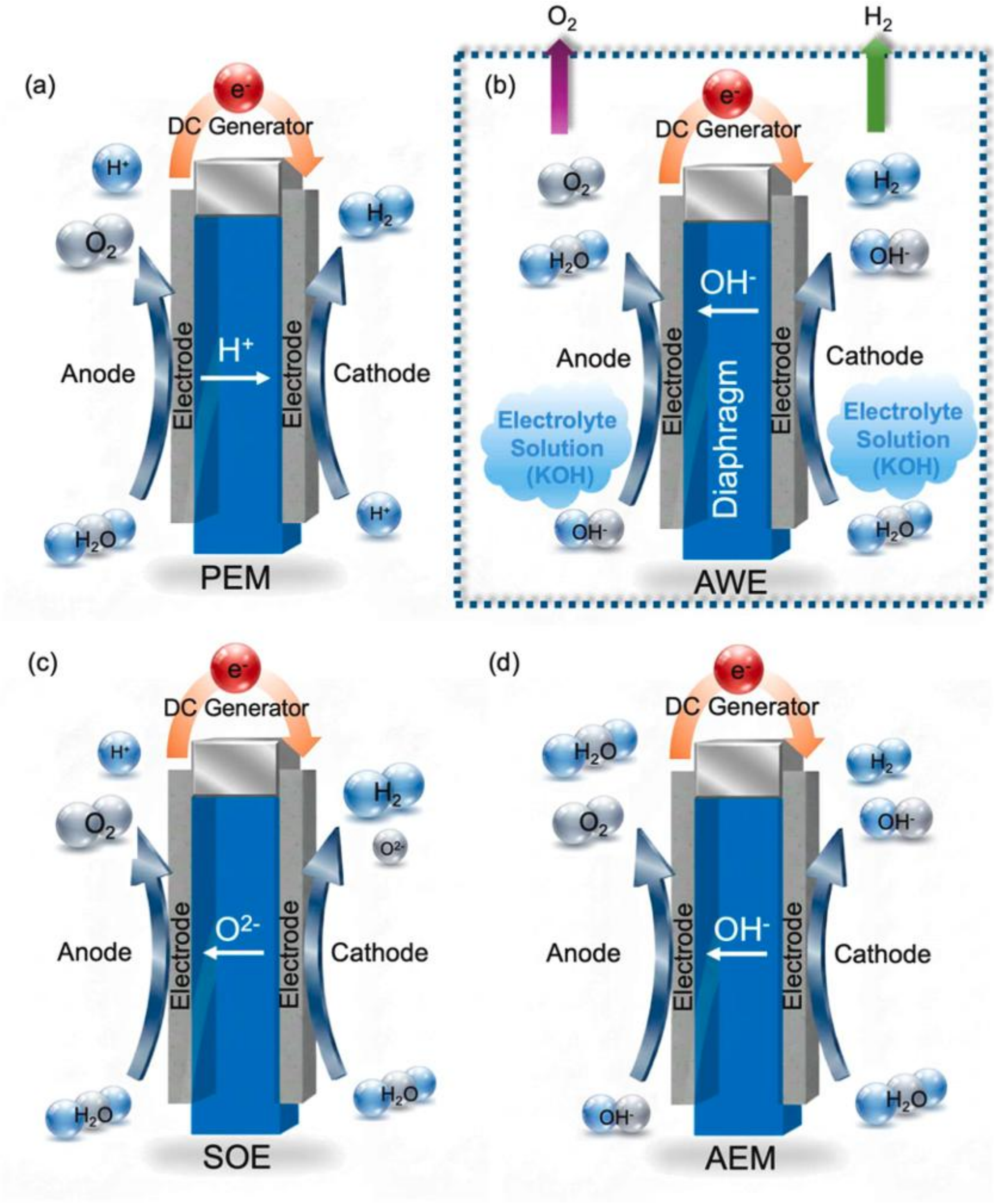

Fig. 5. Configurations of four common water electrolyser technologies. (a), Schematic and reaction mechanism of a PEM electrolyser. (b), Alkaline water electrolysis. (c), Reaction mechanism of an SOEC. (d), Reaction mechanism of an AEM electrolyser.

lifetime, and reduced capital costs (James et al., 2022). It is also reported that commercial analyses place installed costs in the 1400–1700 USD kW^{-1} range and energy consumption at approximately 52 kWh kg^{-1} H_2 in 2023 (Duke et al., 2026). Market forecasts for 2025 suggest prices may fall to 700–1500 USD kW^{-1} (Jaeger and deBiasi, 2023).

AWE, as shown in Fig. 5(b), uses an aqueous electrolyte of potassium hydroxide or sodium hydroxide, separated by a diaphragm (Tüysüz, 2024). The technology has been commercially deployed for decades and benefits from inexpensive nickel-based electrodes and a relatively simple design (Lee et al., 2019). Commercially available systems show that AWE operates at 60–80 °C, typically 30 bar, uses nickel or nickel–molybdenum cathodes and nickel or nickel–cobalt anodes, and has a lifetime of 60,000–100,000 h (Tüysüz, 2024). Matured AWE plants achieve system efficiencies of 68–77% Higher Heating Value (HHV), although current densities remain modest (0.2–0.4 A cm^{-2}) and dynamic response is relatively slow (Ulleberg, 2003). U.S. Department of Energy (DOE) data indicate that mature AWE stacks consumed about 51 kWh kg^{-1} H_2 in 2022 and had stack capital costs around 250 USD kW^{-1} and system costs near 500 USD kW^{-1}. Industry sources cite commercial units costing 800–1000 USD kW^{-1} with efficiencies of roughly 55 kWh kg^{-1} H_2 (Jaeger and deBiasi, 2023). These systems are robust and well-suited to large, steady-state H_2 production, but respond slowly to power fluctuations and operate at lower current densities (Zuo et al., 2023).

SOE, as shown in Fig. 5(c), operates at 600–1000 °C using a solid ceramic electrolyte; high temperatures enable part of the energy input to be supplied as heat, yielding theoretical electricity consumptions as low as ∼40 kWh kg^{-1} H_2 (Rouwenhorst, 2023). When fed with steam, the energy efficiency is approximately 20% higher than in low-temperature electrolysis, and the technology can utilise waste heat from industrial processes, making it attractive for integration with exothermic methanol synthesis (Liu et al., 2024). However, commercial deployment is nascent: Institute for Sustainable Process Technology (ISPT) estimates that a 1 GW SOE plant currently costs about 5200 USD kW^{-1}, and even optimistic scenarios project costs of 1300 USD kW^{-1} by the end of the decade (Rouwenhorst, 2023). SOE cells have long warm-up times and materials challenges but promise high efficiency and synergy with high-temperature methanol reactors or combined heat-and-power systems (El-Shafie, 2023).

AEM electrolysis, as shown in Fig. 5(d), combines alkaline chemistry with polymer membranes and introduces a stack architecture more akin to PEM systems. The anion exchange membrane divides two half-cells; each half-cell contains a thin catalyst layer, a porous GDL and a metallic bipolar plate. Hydroxide ions generated at the cathode migrate through the membrane to the anode, allowing water reduction at the cathode and oxygen evolution at the anode while keeping the gases separate (Petrov et al., 2022a). Dilute electrolytes, typically 1% KOH, circulate only on the anode side, so that the cathode operates dry and hydrogen exits at high purity (≈99.9%) and at pressures up to 35 bar (El-Shafie, 2023). AEM stacks, therefore, use high-surface-area nickel or NiFeCo alloys as anode catalysts and nickel-based materials on the cathode; the porous transport layers and bipolar plates are generally nickel-coated stainless steel, thereby avoiding titanium plates and noble-metal catalysts of PEM systems (Green Hydrogen Cost Reduction, 2020). With renewable electricity priced at approximately 0.03 USD kWh^{-1}, the levelised cost of hydrogen is approximately 2 USD kg^{-1}, potentially falling below 1.5 USD kg^{-1} with scale. AEM electrolysers remain pre-commercial (TRL 6–7) (El-Shafie, 2023).

3.2.2. Water electrolyser catalysts

Electrolysis performance and cost are dictated by the catalysts used for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Traditional PEM electrolysers rely on platinum cathodes and iridium oxide or ruthenium oxide anodes, which deliver excellent activity and durability but are prohibitively expensive. A techno-economic assessment in 2024 reports that PEM systems use 0.5–1 g_{Pt} kW^{-1} and 1.3–2 g_{Ir} kW^{-1}, with global production of Ir at only 7.7 t yr^{-1} and Pt costing ∼33,755 USD kg^{-1} while Ir costs 80,700–161,400 USD kg^{-1} (Shanian and Savadogo, 2024). The extraction of these metals emits 12.5 t CO_2 kg^{-1} Pt and 10 t CO_2 kg^{-1} Ir, adding significant environmental burdens. Consequently, research focuses on low-cost earth-abundant catalysts (Shanian and Savadogo, 2024).

In alkaline and AEM electrolysis, nickel-based catalysts dominate. Reviews report that Ni, Ni–Mo and Ni–Fe alloys are the standard HER cathodes, while NiFe-layered double hydroxide (NiFe-LDH) and CoFe-LDH are widely used OER anodes (Abudureyimu et al., 2025). NiFe-LDH is often regarded as a leading non-noble alternative to precious-metal catalysts owing to its low cost, scalable synthesis, and strong intrinsic stability and activity. In 1.0 M KOH, it delivers an OER overpotential of 175 mV at 10 mA cm^{-2}, an HER overpotential of 185 mV, and an overall cell voltage of 1.52 V at 10 mA cm^{-2} (Li et al., 2025). $NiFe_2O_4$ catalysts are also attractive; they are abundant and low-cost and achieve 10 mA cm^{-2} OER current at 290–342 mV overpotential with low Tafel slopes, and alloying $NiFe_2O_4$ with NiO or Co_3O_4 can further reduce overpotentials to ≈251 mV (Ahmed et al., 2025). These catalysts eliminate the need for noble metals and exhibit good durability, making them suitable for large AWE/AEM systems.

In alkaline environments, Ni–Mo alloys are extensively studied for the hydrogen evolution reaction (HER). NiMo catalysts exploit the synergistic electronic effect between nickel and molybdenum, offering high activity and low cost. A recent study reports that a NiMo alloy on nickel foam achieves an HER overpotential of 127 mV at 100 mA cm^{-2} and maintains high stability for 45 hours (Ding et al., 2025). The authors note that while precious metal catalysts such as platinum offer superior activity, their high cost and limited availability hinder large-scale deployment (Ding et al., 2025). For PEM systems, the most widely used catalysts remain Pt for HER and IrO_2 for OER, but their high cost drives the development of alternatives. Reviews note that transition-metal dichalcogenides (MoS_2, WS_2) and phosphides (Ni_2P, CoP) have been investigated for acidic HER, while perovskite oxides (e.g., $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) and FeCoP nanorods offer promising OER activity (Ding et al., 2025). However, stability under acidic conditions remains a challenge. In SOE, the conventional fuel electrode is nickel-yttria-stabilised zirconia (SOEC fuel electrode) (Ni/YSZ), often modified by infiltration or ALD to enhance the triple-phase boundary length and durability (Abudureyimu et al., 2025). Oxygen electrodes use perovskites such as lanthanum strontium cobalt ferrite (LSCF); high-entropy oxides and doped perovskites are being explored to improve stability and reduce strontium segregation (Abudureyimu et al., 2025).

Table 2 summarises previous research on water electrolysis technology (Carmo et al., 2013; Chatenet et al., 2022; Du et al., 2022; El-Shafie, 2023; Laguna-Bercero, 2012; Nnabuife et al., 2025). From a systems perspective, the most commercially viable catalysts for large-scale green hydrogen production, and consequently green methanol, are nickel-based catalysts (Ni-Fe, Ni-Mo) for alkaline or AEM electrolysis, owing to their low cost, high abundance, and effective activity. Noble-metal catalysts remain essential for high-performance PEM electrolysis. However, their high cost and limited supply limit scalability. Ongoing research on perovskite and transition-metal catalysts remains vital to decreasing dependence on platinum-group metals. Among the four water electrolysis technologies, AWE is the most mature and cost-effective for large, steady hydrogen production, PEM is best suited to flexible operation with variable renewables but is constrained by noble-metal cost, SOE offers the highest efficiency and heat-integration potential yet remains limited by high temperature materials challenges, and AEM provides an attractive compromise between cost and flexibility but still lacks durability maturity; therefore, AWE and PEM are currently the most credible options for industrial methanol production, while AEM may become highly competitive for large-scale deployment once long-term stability is improved.

Table 2
Comparison of water electrolyser technologies.

Attributes	AWE	PEM	AEM	SOEC
Electrolyte	Aqueous KOH (20–40% solution)	Solid polymer (PFSA membrane)	Anion-exchange membrane (solid) + 1 M KOH support	Ceramic oxide (YSZ solid electrolyte)
Operating Temperature	~60–80 °C	~50–80 °C	~40–60 °C	~700–850 °C
Response Time	Slow start-up; longer ramp (minutes)	Fast response (load-flexible, seconds)	Potentially fast (like PEM), but not yet proven at scale	Slow (thermal startup; suited to steady operation)
Efficiency (HHV)	~60–70% (industrial)	~60–75% (typical)	~55–65% (prototype)	~80–90% (with heat input)
Maturity	Most mature (commercial for decades)	Commercialized (since ~2010s)	Emerging (demonstrations ongoing)	Pilot/early commercial (R&D stage)
Cost (Stack)	Lowest CAPEX (≈ 500–1000 USD kW^{-1})	Higher CAPEX (≈ 700–1400 USD kW^{-1})	Projected low cost (PGM-free design)	High initial cost (small-scale ~ 2, 000 USD kW^{-1})
Ideal Use Case	Large, steady hydrogen production (robust, low-cost, but bulky)	Dynamic operation with renewables (compact, high-purity H)	Future low-cost distributed systems (hybrid of PEM & alkaline)	Industrial heat integration (highest efficiency if waste heat available)
Anode Catalyst (OER)	Ni-based (e.g. Ni oxyhydroxide on Ni or Fe–Ni alloy)	Iridium oxide (IrO_2)-based catalysts	Ni-based (e.g. Ni–Fe (LDH) or Ni–Fe–Co oxide)	Perovskite oxide (e.g. LSM or LSCF oxygen electrode)
Cathode Catalyst (HER)	Ni-based (e.g. Raney Ni or Ni–Mo alloy)	Platinum-based catalysts (Pt on C)	Ni-based (e.g. high-surface Ni or Ni–Mo alloy)	Ni–YSZ cermet (Ni + YSZ composite fuel electrode)

3.3. Renewable system integration and digitalisation

Integrating green methanol synthesis with variable renewable energy sources (such as solar and wind) is widely regarded as both necessary and urgent for the deep decarbonisation of fuels and chemicals. Renewable methanol production enables surplus intermittent renewable power to be converted into a storable liquid fuel, thereby addressing the mismatch between fluctuating renewable generation and steady industrial energy demand (Fulham et al., 2024). Major process steps include CO_2 capture (from point sources or via DAC), water electrolysis to produce green H_2, and methanol synthesis (producing methanol by reacting H_2 with CO_2 over a catalyst in a reactor). Downstream of the reactor, product separation and purification units (e.g. flash separators, heat exchangers and distillation columns) are employed to isolate high-purity methanol from water and unreacted gases (Savva et al., 2025), with heat integration techniques improving overall energy efficiency. Buffer storage of intermediate streams (e.g., compressed H_2 and CO_2 tanks) and flexible operational strategies are often incorporated to manage the intermittency of solar and wind power, enabling continuous or responsive methanol production despite variable energy inputs. Critically, water electrolysis and any electrochemical CO_2 reduction (eCO_2R) steps serve as the core links between renewable electricity and fuel synthesis – they directly transform renewable “electrons” into chemical bonds – and thus play a pivotal role in enabling the power-to-methanol pathway (Sheppard et al., 2023). Advanced digitalisation (e.g. dynamic control systems and process optimisation algorithms) can further enhance this integration, ensuring that the PtMeOH plant operates optimally in tandem with real-time renewable energy availability.

Digital optimisation and advanced control algorithms will enable flexible operation and maximise efficiency. Electrolyser selection must consider multiple performance metrics. Faraday Efficiency (FE) reflects selectivity towards the desired product. Partial current density quantifies how quickly a product forms. Energy efficiency (the ratio of the Gibbs free energy of the products to the electrical energy input) determines economic viability. Researchers should also report cell voltage, total current density, product concentration and continuous stability (Seger et al., 2023). Cross-over of reactants or products through the membrane can depress selectivity; contamination of catalysts by impurities (e.g., chloride, metal ions) can degrade performance and must be controlled. Several studies have systematically investigated these aspects, offering representative insights into the current progress and remaining challenges in this field. Fig. 6 illustrates a surrogate model that integrates electrochemical equations with mass and energy balances to evaluate electrolyser performance under varying operating conditions. Key variables, such as cell voltage, temperature, and pressure, are introduced into the electrochemical framework to resolve intermediate parameters, including the polarisation curve, FE, and single-pass conversion (SPC). These outputs are subsequently coupled with mass and energy balance calculations to quantify system-level metrics, including water consumption, power demand, product yield and energy losses. Overall, the performance of green-methanol pathways is ultimately determined by system-level interactions rather than isolated unit operations (Fig. 6).

Despite this necessity, extant process-modelling research offers only partial depictions of electrolysers. Conventional Aspen modules are unable to accurately portray voltage–current characteristics, transient responses, or degradation phenomena, thereby constraining the robustness of integrated design investigations. Semi-empirical models developed within Aspen ACM, such as that developed by Edwards et al. (2023) indicate that electrochemical performance can be estimated with moderate accuracy; however, their computational demands hinder large-scale scenario evaluations and dynamic optimisation.

An increasing number of studies employ multiphysics modelling to represent unit-level eC O_2R behaviour, yet comparatively few integrate the eCO_2R device with whole system design and operation. For example, Weng et al. (2016a) constructed a 1-D multiphysical model for the GDE in the eCO2R process, quantitatively analysed the wettability and pore structure of CL, and showed how these affect the overall performance of the GDE, providing a modelling framework for designing high-performance GDEs. Subsequently, Weng et al. (2016b) extended this model to encompass the MEA and compared the performance of zero-gap and flow-cell configurations. Their research revealed that zero-gap systems exhibit lower cell potential at high current densities, albeit at the expense of concentration polarisation and membrane dehydration. Expanding on this, Petrov et al. (2022) developed a multi-physics model for AEM that incorporates microchannels within the catalyst layer (CL), addressing concerns regarding K^+ crossover and AEM conductivity. Their work highlighted the potential of membranes with strategically designed channels, offering up to a 40% increase in current density compared to standard AEMs. Furthermore, Kas et al. (2021) delved into a 2-D model that projected a gradual reduction in CO_2 concentration and buffer electrolyte along the channel, leading to significant local variations in current density during high single-pass conversion. In a different approach, Yang et al. (2021) examined five operating and design parameters, namely the applied cathode potential, catalyst loading, porosity, inlet gas composition, and gas velocity. A two-dimensional, steady-state, multiphase gas diffusion electrode model was used to identify optimal conditions, with specific electrical energy consumption and product yield introduced as metrics to evaluate GDE scalability and overall system performance. Building on this work, Xing et al. (2023) developed a data-driven surrogate model coupled with

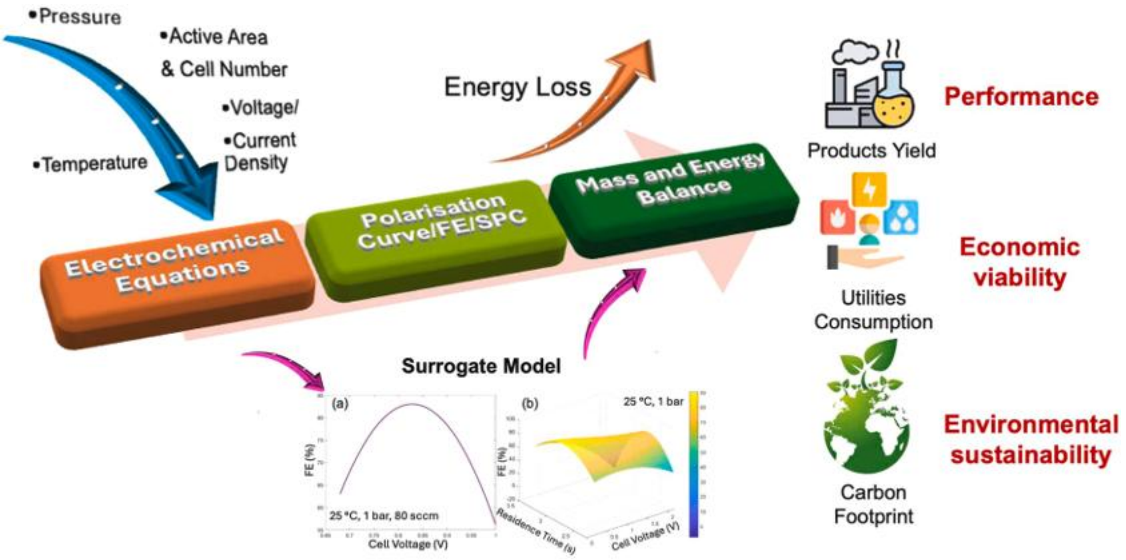

Fig. 6. Modelling framework and performance evaluation of electrolysers.

multi-objective optimisation to quantify trade-offs among product yield, FE, and specific electrical energy consumption. Moreover, Blake et al. introduced computational methods to simplify their 2-D model, revealing challenges associated with poor electrolyte buffering arising from increased boundary-layer thickness during the upscaling of eCO_2R cells (Blake et al., 2021). Qiu et al. (2023) further advanced this field by extending the multi-product 1-D model developed by Weng et al. (2018) to a 2-D model. Their work unveiled the intricate relationship between local carbon dioxide concentration and the selectivity of various reduction products. Wang et al. (2025) developed a 2-D model for acidic MEA-type CO_2 electrolysers that integrates transport and reaction processes. They revealed that CO_2RR overpotential dominates at low-to-moderate current densities, while HER and ionic overpotentials become the main limitations at high current densities. The study found that combined optimisation of the cathode catalyst layer and operating conditions achieved a 40.7% reduction in energy intensity (Wang et al., 2025). In addition, they have recently developed a cross-scale simulation framework that couples first-principles calculations with mass transfer in the interfacial electric double layer (EDL), addressing the challenge that traditional Butler-Volmer (B-V) equations struggle to describe the competitive reaction kinetics of CO_2RR (Wang et al., 2025). This method is expected to be extended to macroscale single-cell simulations in the future, enabling more accurate consideration of the impacts of the interfacial EDL and local microenvironment on reaction kinetics. Tai et al. (2023) presented a multiphysics and deep-learning-coupled framework for the adaptive optimisation of eCO_2R processes under intermittent renewable energy supply, representing a pioneering approach to the integrated planning and adaptive optimisation of eCO_2R reactors coupled with renewable energy systems. However, limited attention has been paid to temporal coupling among renewable power variability, electrolyser dynamics, and multi-step methanol synthesis pathways.

Emerging work therefore integrates digital tools, such as reduced-order surrogate models, data-driven predictors, and plant-wide optimisation frameworks, to investigate system sizing and scheduling strategies. These methodologies facilitate techno-economic and environmental assessments utilising consistent indicators, such as the levelised cost of methanol, specific energy consumption, and global warming potential relative to fossil methanol. Building upon this system's perspective, the subsequent sections offer a structured comparison of three green-methanol pathways and assess their technology readiness, energy efficiency, economic viability, and life-cycle emissions.

4. Electrochemical methanol synthesis system integration

In the 1980s, Hori et al. (1985) discovered high-efficiency hydrocarbon formation on metallic Cu, paving the way for the development of more effective electrocatalysts for the formation of other products. Research in this field has continued to grow since then, with reviews covering various aspects (Centi et al., 2013; Costentin et al., 2013; Jhong et al., 2013). Methanol production has progressed from purely thermocatalytic routes (Bowker, 2019; Graaf et al., 1988) to hybrid configurations (Jouny et al., 2018a; Kiss et al., 2016; Sollai et al., 2023) and, more recently, to electrochemical single-step concepts (De Falco and Capocelli, 2018; Marlin et al., 2018; Overa et al., 2022). The developed framework is subsequently employed to evaluate and compare three methanol production routes in a representative case study.

As shown in Fig. 7, Case (a) presents a one-step CO_2 to methanol pathway. Here, the captured CO_2 is fed to the electrolyser, where it is electrochemically reduced to methanol via a six-electron transfer pathway, and the resulting crude product stream is subsequently subjected to downstream separation and purification. Case (b) presents a two-step electrochemical route, where H_2 is generated via WE and subsequently reacts with CO_2 in a MeOH synthesis reactor to produce MeOH. Case (b) shows a 3-step electrochemical route that involves a water electrolyser (WE) for H_2 production, eCO_2R to generate CO, and subsequent hydrogenation of the CO, CO_2, and H_2 mixture to produce MeOH. These two processes differ from the conventional MeOH synthesis route, in which CO and H_2 are made from natural-gas steam reforming, as shown in case (c).

System-level indicators should reflect capital intensity, operational flexibility, conversion efficiency, and supply-chain risks across electricity, water, and carbon sources. Therefore, comprehensive assessment frameworks are essential for comparing alternative production routes, identifying optimisation priorities, and guiding policy interventions that promote the commercial deployment of e-MeOH technologies. This review adopts a quantitative techno-economic assessment framework based on harmonised system boundaries, a common functional unit, and explicitly defined comparability rules. The assessment is structured around three linked layers: electrolyser performance modelling, process-level mass and energy balance analysis, and discounted cash flow-based economic evaluation. Key electrochemical parameters, including current density, cell voltage, Faradaic efficiency, single-pass conversion, stack lifetime, and capacity factor, are translated into electricity demand, electrolyser area, stack requirements, recycle duty, and separation loads, which then feed the process and cost models.

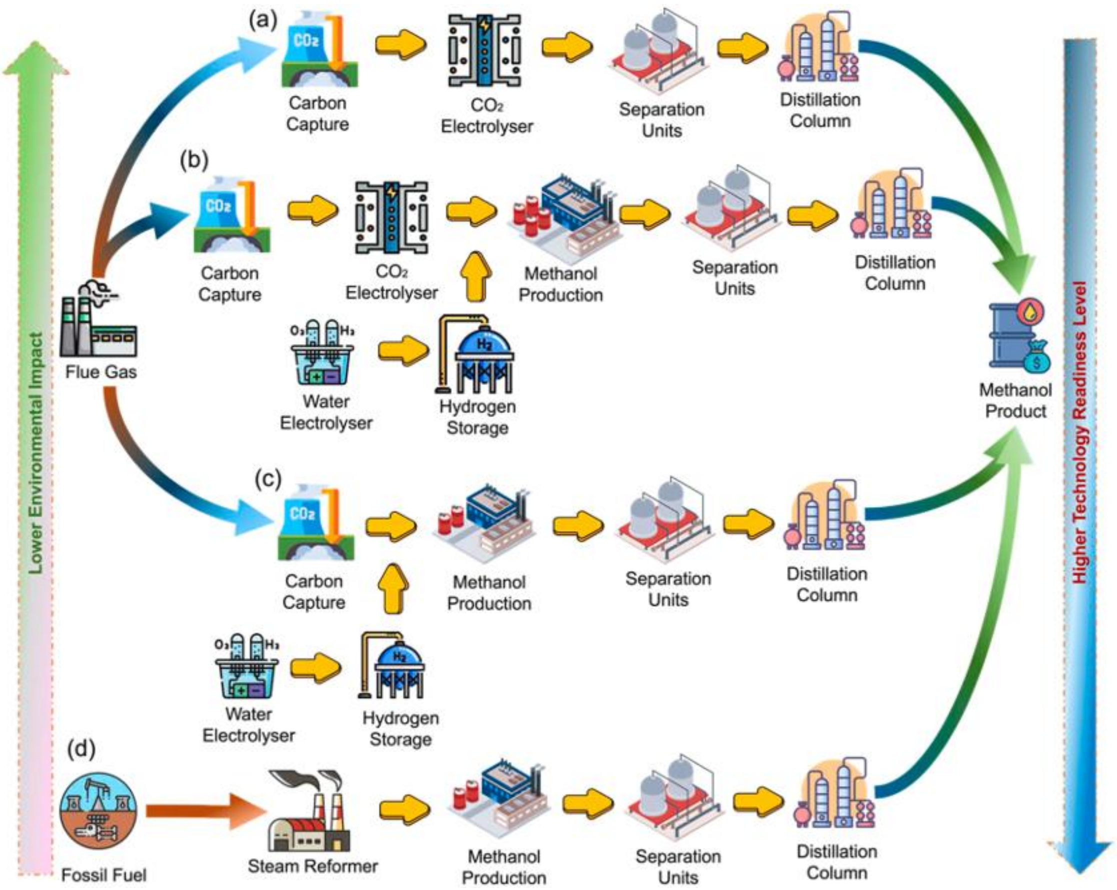

Fig. 7. Process architectures for CO_2-to-methanol conversion across increasing technology readiness levels. www.flaticon.com.

4.1. *One-step CO_2 to methanol pathway*

Electrochemical CO_2 reduction (eCO_2R) electrolysers have emerged as a promising solution for carbon mitigation, capable of converting CO_2 into various fuels and high-value chemicals (Lee et al., 2017; Mistry et al., 2017; Ren et al., 2015). In practice, the reduction proceeds via multiple proton-coupled electron transfer steps and intermediates, such as CO, formate ($HCOO^-$), and formaldehyde, as shown in Fig. 8.

The development of CO_2 electrolysis technology in this domain has transitioned from initial proof-of-concept demonstrations focusing on selectivity at milliamps per square centimetre to gas-fed configurations that approach viable partial current densities. Current progress is concentrated on three primary thrusts. The first involves heterogeneous copper chemistry that integrates CO- and formate-mediated pathways. Copper-based catalysts remain the most studied due to their unique ability to form C–C and C–O bonds. A notable breakthrough is the Cu/$Cu_2P_2O_7$ hybrid catalyst, which exhibits FE exceeding 50% and partial current densities over 100 mA cm^{-2} for methanol electro-synthesis (Kim et al., 2025). In GDE-based cells, the catalyst achieves an FE of up to 70.1% in caesium bicarbonate electrolytes and remains stable for >48 h (Kim et al., 2025). The enhanced performance arises from synergy between metallic Cu(111) facets, which absorb CO intermediates, and copper pyrophosphate ($Cu_2P_2O_7$), which promotes the formation of formate via the HCOOH pathway, thereby guiding the reaction towards methanol. In addition to copper, indium oxide has been explored. A heterojunction of In_2O_3 and ZrO_2 with interfacial oxygen vacancies achieved gas-phase methanol selectivity of 81% and productivity 2.64 g MeOH g cat^{-1} h^{-1} (Koley et al., 2025). A supplementary approach

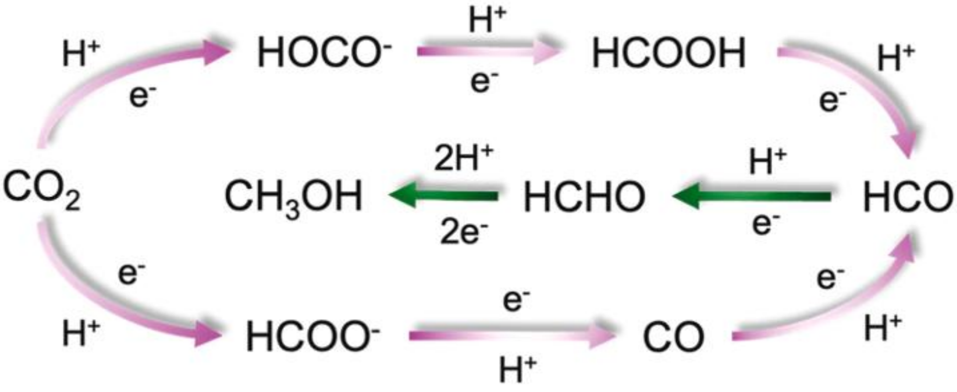

Fig. 8. Mechanism of CO_2 electrochemical reduction to methanol (Albo et al., 2015).

involves molecularly defined catalysts and organo–inorganic hybrids that modulate the microenvironment. Monolayer-engineered noble metal surfaces have also been considered again. A palladium monolayer on Pt(111) yielded methanol at ambient temperature with explicit liquid-product quantification, although the selectivity remained low at approximately one to three per cent faradaic efficiency (Wawrzyniak and Koper, 2025). These findings emphasise that improvements in activity on well-defined model surfaces still trail behind those of copper-based and molecular systems for methanol. Yet, they provide mechanistic insight into C—O bond hydrogenation processes.

The third approach involves photoelectrocatalytic and framework-based architectures that manipulate light fields, ionomers, and pore networks to enhance the local availability of CO_2 and H_2. Reviews of metal–organic framework derivatives summarise strategies to manipulate adsorption and intermediate stability for alcohol generation, while recent photoelectrochemical studies report methanol faradaic efficiency around 58% on tailored heterojunction photocathodes, suggesting that photovoltage can help distribute the overpotential budget more efficiently between charge generation and interfacial kinetics (Gholampour et al., 2024).

Having outlined materials-centric advances, we now consider device architectures and system constraints that govern translation. Across these thrusts, device-level learning remains decisive. GDE and MEA mitigate CO_2 mass-transfer limitations and enable operation at hundreds of milliamps per square centimetre. However, carbonate formation, methanol crossover, and anodic oxygen-evolution losses reduce energy efficiency. Strategies to curb these penalties are therefore essential. System-wide appraisals indicate that one-step CO_2-to-methanol must exceed approximately 64% FE at cell voltages below approximately 2.3 V to outperform two-step H_2-based power-to-methanol on climate grounds, thereby setting a clear performance target for materials and reactors (Wyndorps et al., 2021). Yet at present, most devices deliver current densities of 200–400 mA cm^{-2} and FE below 80%, and their energy efficiency is often below 50% due to high overpotentials (Lin et al., 2024; Overa et al., 2022; Xie et al., 2022).

Two cross-cutting insights emerge. Firstly, many of the most selective catalysts operate at low current densities, whereas industrial relevance demands partial methanol currents of at least 0.2 A cm^{-2} with thousand-hour durability. The $Cu|Cu_2P_2O_7$ study is therefore notable because it couples selectivity and partial current in the same experiment and begins to address durability. However, further scale-up and impurity-tolerance tests are needed (Kim et al., 2025). Secondly, the field benefits from explicit techno-economic and commercialisation metrics that convert electrocatalyst descriptors into stack and plant requirements, including single-pass carbon utilisation, crossover management, and balance-of-plant energy losses. The most recent concise review correlates laboratory metrics with levelised cost boundaries. It emphasises the necessity of integrated capture-to-electrolyser process models for methanol, rather than two-electron product considerations (Kumar et al., 2024). A review emphasises that the TRL still remains at 3, and that substantial advancements in selectivity, cell voltage, CO_2 mass transfer, and long-term stability are imperative for achieving commercial viability (Wiranarongkorn et al., 2023). Direct electrochemical production of liquid fuels like methanol involves multi-electron, deeply reducing pathways with multiple surface intermediates and strongly competing reactions, which makes it intrinsically difficult to sustain high selectivity and FE at technologically relevant current densities. Liquid products also degrade the gas diffusion architecture by altering wettability, viscosity and interfacial transport, so that CO_2 delivery becomes rate-limiting and large concentration overpotentials arise, while the resulting mixed liquid products are strongly coupled to the electrolyte and require energy-intensive downstream separation and purification.

4.2. Two-step power-to-methanol pathway

One of the forerunners in two-step hybrid green methanol synthesis is CO_2 hydrogenation with green hydrogen (Kourkoumpas et al., 2016), enabled by the commercialisation of water electrolysis (Ursua et al., 2012) and advanced carbon capture technologies (Martin et al., 2024; Peres et al., 2022). The carbon source may be industrial flue gases, biogenic streams or direct air capture (DAC) (Bos et al., 2020). The challenge lies in integrating electrolyser stacks with methanol synthesis and managing dynamic operation. According to Section 3.2.1, PEM electrolysers deliver high current densities and can ramp quickly, but they use scarce iridium catalysts (Han et al., 2015; Hernández-Gómez et al., 2020; Shiva Kumar and Himabindu, 2019). Alkaline electrolysers are lower-cost but have lower current density and slower dynamics (El-Shafie, 2023; Jang et al., 2021). SOE cells offer higher efficiency; however, they operate at elevated temperatures and face durability challenges. Yousaf et al. (2022) utilised a high-temperature SOE for the direct hydrogenation of CO_2, reporting a 22.3% decrease in hydrogen costs relative to an AWE, corresponding to approximately a 30% reduction in methanol price.

Green methanol chains that combine water electrolysis, CO_2 capture, and catalytic hydrogenation generally require approximately 40–60 GJ t^{-1} MeOH of electricity-equivalent energy, even under optimistic electrolyser efficiencies and with extensive heat integration, highlighting the intrinsic energy penalty of replacing fossil syngas with electrolytic hydrogen (Fasihi and Breyer, 2024). A recent study advanced the concept of integrated CO_2 capture and conversion by demonstrating that CO_2-laden alcohol–amine solvents can be directly hydrogenated to methanol with a $Cu/ZnO/Al_2O_3$ catalyst, the authors reported that a 10:1 hexanol–triethylamine system delivered a methanol formation rate of 5.6 mmol g^{-1} h^{-1} at 250 °C and 5 MPa, corresponding to 48% CO_2 conversion and 80% selectivity. It indicated that the potential of solvent-integrated pathways to reduce process complexity and energy demand while sustaining high methanol productivity (Guan et al., 2025).

The feasibility of integrating a syngas-to-methanol system with various hydrogen production units has been successfully demonstrated. Several pilot plants have been built, including Carbon Recycling International's George Olah plant in Iceland, which produces around 4000 tonnes per year, and the Carbon2Chem project in Germany, which uses blast furnace gas containing over 20 million tonnes of CO_2 (Marlin et al., 2018). The first PtMeOH pilot plants operate at multi-megawatt scale, demonstrating TRL of 6–7. Scaling to hundreds of megawatts is necessary to achieve cost reductions and supply meaningful amounts of methanol to the market.

4.3. Three-step hybrid green methanol pathway

From a systems perspective, it is more rational to employ electrochemical conversion only for the first step, that is, CO_2 to CO or syngas, and to rely on mature thermocatalytic technology for the subsequent synthesis of methanol. Low-temperature CO_2-to-CO or syngas electrolysers operate through simpler two-electron pathways, can reach high current density and selectivity with relatively robust gas diffusion electrodes, and deliver a gaseous product that is straightforward to separate, compress, and integrate. The subsequent conversion of CO and H_2 to methanol can then be carried out in conventional high-pressure Cu-based fixed-bed reactors, for which catalyst performance, reactor hydrodynamics, heat management, and distillation-based purification are already optimised at the million-tonne scale. This division of functions allows the electrochemical unit to focus on efficient CO_2 activation and syngas generation, while exploiting decades of industrial know-how in thermocatalytic methanol synthesis, typically yielding a lower system-level energy demand and production cost than attempting a one-step route directly to methanol.

Biomass gasification offers carbon-neutral options but is resource-limited (Masum et al., 2025; Tariq et al., 2025), and one-step CO_2-to--methanol conversion remains at the laboratory scale with low energy efficiency, underscoring trade-offs among maturity, cost, and sustainability (Zhao et al., 2025). Accordingly, beyond water electrolysers, the 3-step route includes an additional CO_2 electroreduction module compared to the 2-step green methanol pathway, which produces a gas mixture (CO and small amounts of H_2 and CO_2) before hydrogenation to methanol. Direct hydrogenation of CO_2 (two-step) requires a 3:1 H_2/CO_2 ratio and produces water, resulting in high hydrogen consumption and equilibrium limitations. By adding a CO_2-to-CO electrolyser, part of the CO_2 is electro-reduced to CO via a two-electron reaction. The resulting syngas improves methanol synthesis because CO hydrogenation to methanol is faster and less equilibrium-limited than CO_2 hydrogenation (Adnan and Kibria, 2020; Wiranarongkorn et al., 2023). The CO_2-to-CO electrolyser also operates at a lower voltage and requires only two electrons, reducing energy input and electrolyser area compared with the six-electron CO_2-to-methanol electrolysis. Consequently, hydrogen demand and water formation decrease, the methanol reactor performs better, and the overall energy consumption drops from ~0.056 GJ kg^{-1} (one-step) to ~0.038 GJ kg^{-1} (Adnan and Kibria, 2020). Progress in eCO_2R is assessed using FE, partial current density, cell voltage, single-pass carbon efficiency, and stability. A recent comprehensive review defined these metrics and suggested that commercial viability requires FE above 80%, partial current density above 200 mA cm^{-2}, cell voltage near 2 V, and stable operation for >10,000 h (Kumar et al., 2024).

However, the current efficiencies of the CO_2 electrolyser still fall short of commercial targets. Although it has the advantage of low carbon emissions, its low conversion rate and high investment and operating costs have made it less attractive for commercialisation (Yang et al., 2019; Zhai et al., 2017; Zhu et al., 2017) . While CO can be produced selectively at high efficiency and with favourable separation economics, liquid products such as methanol remain challenging due to low selectivity, high separation energy and estimated costs of about 0.705 USD kg^{-1} compared with a market value of 0.350 USD kg^{-1} (Lu and Jiao, 2016). Many catalysts exhibit good selectivity at low current densities (< 50 mA cm^{-2}), but performance declines at higher current densities due to mass-transfer limitations and competitive hydrogen evolution. Achieving high single-pass carbon efficiency requires efficient gas diffusion electrodes and membrane architecture. Durability remains a key barrier; many catalysts undergo dissolution, surface reconstruction, or poisoning during prolonged operation, leading to declines in selectivity and activity. There is also a trade-off between cell voltage and selectivity. Lowering cell voltage reduces energy consumption but may decrease FE due to slow kinetics. Operating at elevated pressures can increase CO_2 solubility and shift the equilibrium, but it also adds complexity. In addition, calling electrolysers to gigawatt capacity while improving efficiency is central.

5. Techno-economic analysis

It is essential to review advances in electrolysers, catalysts, and electrolytes to identify key mechanistic, mass-transfer, and economic barriers to future commercialisation (Wiranarongkorn et al., 2023; Zheng et al., 2025). When making cross-study techno-economic comparisons, it's important to note that costs for the same process vary due to differences in configurations, time-based assumptions, and volatility in energy and feedstock prices. A reproducible evaluation framework was developed to compare methanol production pathways across technical, economic, and environmental dimensions. Some studies have conducted comparative analyses of various routes for the electrochemical conversion of CO_2 to methanol, considering their process performance from technical, economic, and environmental perspectives (Adnan and Kibria, 2020; Harris et al., 2021; Kim et al., 2022; Li et al., 2023). For a comparative benchmark assessment, Zong et al. conducted a side-by-side TEA of nine CO_2-to-methanol routes, including conventional autothermal reforming, SMR/dry methane reforming (DMR), methane pyrolysis with dry reforming, and electrolysis-based pathways (Zong et al., 2024). Their results showed that while SMR/DMR remains the lowest-cost option at 0.277 USD kg^{-1}, pyrolysis–dry reforming configurations achieve near-parity at 0.296 USD kg^{-1} and could drop to 0.099 USD kg^{-1} by 2050 under low natural gas and electricity costs, with high carbon penalties. State-of-the-art SMR-based plants achieve levelised costs of around 0.28 USD kg^{-1} methanol under European gas prices around 7.5 USD GJ^{-1}, with advanced gas-switching reformers slightly lower at 0.27 USD kg^{-1} (Arnaiz Del Pozo et al., 2022).

Direct electrochemical conversion of CO_2 to methanol remains economically infeasible, with a reported levelised cost of around 11.2–12.7 USD kg^{-1} (Dees et al., 2021; Harris et al., 2021). Modelling studies suggest that to compete with the reverse water-gas shift and hydrogenation route, CO_2 electrolysers need to deliver total current density around 1.5 A cm^{-2}, SPC above 54%, the FE of CO exceeding 90% and cell voltage near 2 V; electricity prices must be <42 USD MWh^{-1} with CO_2 capture costs around 0.1 USD kg^{-1} and the carbon tax is between 0.1 and 0.3 USD kg^{-1} (Almajed et al., 2023). Wiranarongkorn et al. (2023) noted that the overall energy efficiency for the one-step route is only 30–45%, with methanol production costs up to 13 USD kg^{-1}. Notably, Wang et al. (2023) demonstrated that, in the absence of crossover and carbonate formation, methanol production costs in an alkaline flow cell and a neutral membrane electrode assembly cell could be reduced to below 0.4 USD kg^{-1}, provided that the overall energy efficiency exceeds 70% and 50%, respectively. Adnan et al. (2020) also pointed out a 1.73 USD kg^{-1} levelised cost of the direct-to-methanol pathway with a DAC capital cost of 0.375 USD per kg CO_2 per year, and electricity emission intensity (< 275 kg-CO_2 MWh^{-1}). These findings indicate that the economic viability of the single-step route is highly sensitive to electrolyte management and system-level losses, rather than to intrinsic catalytic activity alone.

In the two-step process, the cost of renewable hydrogen is the primary factor influencing the overall process cost (Egli et al., 2018). Kim et al. compared two-step methanol routes based on hydrogen from SMR, coal gasification, and water electrolysis, showing that the electrolysis pathway has the highest H_2 cost at 5.28 USD kg^{-1} yet offers the strongest sustainability benefits (Kim et al., 2024). Another techno-economic assessment found that the minimum selling price of PtMeOH produced from high-purity CO_2 is 0.61–0.64 USD kg^{-1} when the H_2 price is 2 USD kg^{-1} (Zang et al., 2021). The methanol cost rises to 1.24–1.28 USD kg^{-1} with H_2 at 5 USD kg^{-1}, although carbon credits can reduce it to 0.56–0.59 USD kg^{-1} (Zang et al., 2021). The breakeven hydrogen price to match the average market price of methanol (0.38 USD kg^{-1}) is 0.77–0.95 USD kg^{-1} without carbon credits and 2.09–2.24 USD kg^{-1} with a 0.2 USD kg^{-1} CO_2 credit, with the energy efficiency of 51.8% (Zang et al., 2021). The carbon-based negative-emission pyrolysis and co-electrolysis process also shows that coupling pyrolysis with a solid oxide electrolysis cell (SOEC) can reduce costs. The method achieves an energy efficiency of approximately 67% and a levelised cost of between 0.706 and 0.922 USD kg^{-1} (Nogueira Nakashima et al., 2025). Another TEA analysing an integrated bio-electrochemical system reported an energy efficiency of 56% and production costs of 0.631–0.643 USD kg^{-1} in 2023 (Pakdel and Eslamloueyan, 2024). This study notes that small-scale demonstration plants have high costs (2.66 USD kg^{-1}) due to the lack of economies of scale. Furthermore, another study analysed six alternative power-to-methanol configurations with an annual capacity of approximately 20 kt, indicating that the methanol selling price remains at 0.998 USD kg^{-1} when the hydrogen cost is 2.4 USD kg-^{1}, and the internal rate of return (IRR) is 15% (Chiou et al., 2023).

Advances in CO_2 electrolyser technology have reduced system costs and are accelerating the development of three-step pathways for green methanol production. For example, Shin et al. (2021) conducted a techno-economic assessment of low-temperature CO_2 electrolysis using polymer-membrane systems for CO production, where CO is already approaching cost competitiveness, with a levelised production cost of

0.44 USD kg^{-1}. For the three-step hybrid pathway, the reported unit cost of methanol remains in the order of 10^3 USD per tonne. Harris et al. reported a cost of approximately 1050 USD t^{-1} for methanol (Harris et al., 2021), whereas Adnan et al. (2020) suggested a broader cost range of approximately 1180 USD t^{-1} under comparable near-term assumptions. Later on, Adnan and Kibria (2020) also indicated that the levelised cost of methanol (LCOM) varies markedly across the four routes. In the base case, conventional SMR is lowest at approximately 371 USD t^{-1}, whereas the electrified options are substantially higher, ranging from approximately 861 USD t^{-1} to 1585 USD t^{-1}. However, under optimistic assumptions, the electrified routes converge to a similar cost band of 427–433 USD t^{-1}.

A study indicated a methanol selling break-even point of 491 USD t^{-1} via water electrolysis and tri-reforming (Shi et al., 2020). The levelised cost of methanol can further decline to 356 USD t^{-1}, achieving a seven-year payback, if hydrogen costs fall to 2 USD kg^{-1} (Tariq et al., 2025). Sustained research on catalysts, membranes and reactor design will be essential to improve efficiency and durability. At the system level, sitting green methanol plants adjacent to existing renewable power facilities and downstream large industrial emitters would facilitate access to low-carbon electricity and enable direct capture of concentrated CO_2 streams. Demonstration projects in Europe already integrate alkaline and PEM electrolysers with captured CO_2, achieving energy efficiencies of approximately 50% and highlighting a clear trajectory towards commercial viability (Nemmour et al., 2023).

The underlying drivers of the differences in green methanol synthesis pathways are detailed in Table 3. Significant power costs, limited economies of scale, and substantial capital expenditures for carbon capture and electrolysers are the primary drivers of the cost disparity. Power-to-methanol schemes using green hydrogen and captured CO_2 typically yield production costs in the range 600–1450 t^{-1}, primarily because electricity and electrolysers dominate both OPEX and CAPEX (Nizami et al., 2022). When CO_2 is electrochemically reduced directly to methanol, current TEAs indicate even higher costs: Adnan et al. (2021). estimated around 1600 USD t^{-1} for direct CO_2-to-MeOH electrolysis, compared with 850–1000 USD t^{-1} for two- and three-step electrolysis-assisted routes under optimistic electricity prices of 0.04 USD kWh^{-1}. Another study assesses offshore wind-based green methanol production at major EU ports. It shows that the levelised cost of methanol ranges from 953 to 1214 USD t^{-1} in 2025, with > 95.9% emission reductions under wind-only supply (Du et al., 2025). Although green hydrogen, which uses renewable energy, may not currently be as economically competitive, its environmental benefits, such as significantly lower carbon emissions than conventional hydrogen production methods, are substantial.

As shown in Fig. 9, panel (a) benchmarks the levelised costs of methanol across four routes against 2025 regional market prices (Methanex Corporation, 2025) and a projected cost band for CO_2-derived methanol (International Renewable Energy Agency (IRENA), 2021). Conventional methanol remains the lowest-cost option at present, whereas CO_2-based routes are substantially higher; the direct electrochemical single-step route is the most expensive, followed by the three-step hybrid and the two-step route. With continued advances in clean energy and electrolyser technologies, electrochemical pathways could plausibly reduce the cost of methanol to approximately 430 USD t^{-1} in the near term under optimal conditions (Adnan and Kibria, 2020), approaching current European and Asia-Pacific market levels and falling within the projected competitive range. Panel (b) complements this cost view by comparing normalised performance across reliability, technology readiness level, energy efficiency, capital efficiency, and electrolyser or catalyst cost contribution, showing conventional and two-step pathways as the most balanced, the three-step hybrid as intermediate, and the single-step route limited primarily by low maturity and reliability alongside weaker energy and capital performance. Fig. 9 was constructed using TEA data harmonised to a common base year and currency through inflation adjustment and exchange rate conversion, with explicit inclusion rules applied to exclude studies lacking the minimum cost year or boundary information required for consistent

Table 3
Comparative techno-economic performance, energy demand, capital intensity, and technology readiness for methanol production pathways.

Pathway	Conventional SMR (NG reforming)	CO_2 + Green H_2 ("Power-to-MeOH" two-step)	Direct eCO_2-to-MeOH (Electrochemical single-step)	$CO_2 \rightarrow CO$ (eCO_2R) + $H_2 \rightarrow$MeOH (Three-step hybrid)
MeOH Cost (USD t^{-1})	≈ **100–300** (widely applied)	≈**2660** (small scales: 4 kt yr^{-1}) ≈**600–1450** (larger scales: 50–285 kt yr^{-1})	**1585–1730** (varies with different configurations)	**>1050** (if efficient co-electrolysis of CO_2 and H_2O is used)
Energy Use (MWh t^{-1} MeOH) (like two-step)	≈**8–9** MWh t^{-1} (modern plant efficiency) (~30–33 GJ t^{-1})	**~9–10** MWh t^{-1}, mostly electricity for H_2 (0.188 t H_2 t^{-1} MeOH)	**~15–22** MWh t^{-1} (lab performance);	**~9** MWh t^{-1}
CAPEX Intensity (USD t^{-1} y^{-1})	**~470** (100 kt yr^{-1} plant)	**~500** (100 kt yr^{-1} plant, slightly higher than SMR)	**>1000** – No commercial-scale data (only lab-scale reactors to date)	**700–1000** – First-of-a-kind design only (would require two electrolyser units)
Electrolyser/ Catalyst Cost Contribution (1–5)	**Negligible (1)** – Low catalyst cost (methanol synthesis unit contributes only ~30–50 USD t^{-1}); feedstock fuel dominates overall cost	**High (4)** – H_2 production (electrolyser CAPEX + power) contributes ~60% of total cost; methanol synthesis unit/catalyst is a small fraction (~35 USD t^{-1})	**Dominated by OPEX (3)** – Electricity and electrolyte management dominate cost. E.g., >60% of the cost is in KOH regeneration in the alkaline system; capital (electrolyser stack, membrane, catalyst) accounts for a much smaller share.	**Very High (5)** – Two electrolysers dominate capital and operating costs (>50%). Tandem setup aimed at efficiency gain but adds equipment complexity.
Tech Maturity TRL (1–9)	**9** – Fully commercial, widely deployed	**8** – Technology proven (industrial pilot plants running)	**1–3** – Experimental R&D stage.	**5–7** – Partial mature, CO_2-to-CO electrolysis (TRL ≈ 4); overall process not yet demonstrated (assume in mid-range).
Reliability (1–5)	**5** – **Very high** (mature process with decades of stable operation)	**4** – **Good overall** (comparable to conventional; minor catalyst deactivation due to H_2O, and electrolyser maintenance)	**1** – **Very low** (short catalyst lifetimes and stability issues (e.g. flooding, carbonate build-up))	**3** – **Moderate** (Split steps may improve stability (avoids carbonate flooding, etc.), but the new CO_2–CO electrolyser and system integration are unproven in long-term operation.)

Assumptions: All costs are levelised production costs (excluding carbon taxes/credits). SMR assumes natural gas at 2.3–7.5 USD GJ^{-1} (Arnaiz Del Pozo et al., 2022). The 2-step route assumes renewable electricity (e.g., 0.02–0.07 USD kWh^{-1}) and CO_2 from point (Nishikawa et al., 2023). Direct e CO_2-to-MeOH values based on lab-scale techno-economic analysis (neutral/alkaline CO_2 electrolysers). The three-step route is speculative, combining a CO_2-to-CO electrolyser (e.g., a solid-oxide or gas-diffusion cell) and a water electrolyser; no full-system economic data are yet available (expected to resemble the two-step route in cost structure). All novel routes assume a green CO_2 feed (captured from air or flue gas) and aim to produce carbon-neutral methanol. Sources: TEA studies and reports from 2020 to 2025 as cited in the main text.

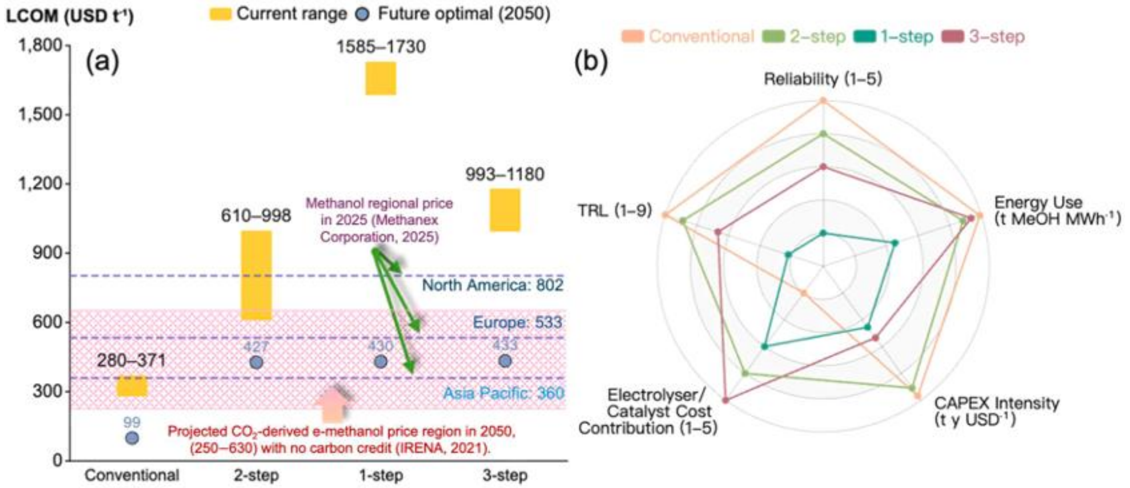

Fig. 9. Techno-economic benchmarking of methanol production pathways. (a) Levelised methanol cost ranges for conventional and CO_2-based routes, benchmarked against regional market prices in 2025. (b) Normalised multi-criteria performance radar comparing key indicators across pathways.

comparison.

The development of one-step electrochemical CO_2-to-methanol electroreduction has progressed from initial demonstrations focused on selectivity to the achievement of credible partial currents on hybrid copper and molecularly tailored electrodes. Nevertheless, current performance levels remain considerably distant from industrial applicability. The current densities predominantly from the one-step route remain below 120 mA cm^{-2}, significantly below the industrial requirement of over 1 A cm^{-2}, with methanol selectivity $<50\%$ (Wiranarongkorn et al., 2023). Another study indicated that direct CO_2-to-MeOH electrolysis must substantially improve its performance to be economically viable, with necessary current densities exceeding 300 mA cm^{-2}, energy efficiency above 45%, and stack stability over 2 years (Adnan et al., 2020). These conditions necessitate extensive recycling processes and high-cost separation techniques such as pressure swing adsorption (PSA) and distillation. However, the reported cost of the one-step pathway is not primarily driven by DAC. Instead, the electrolysis unit itself dominates the overall cost, particularly due to low current density, large active-area requirements, stack replacement, and balance-of-plant costs. Although improvements in cell voltage and FE lower electricity demand, these gains alone are insufficient to offset the inherently high capital intensity of the direct electrochemical route (Keith et al., 2018; Azim et al., 2021; Wang et al., 2023). Achieving stable operation at elevated current densities under realistic gas-fed conditions, enhancing single-pass carbon efficiency, and integrating electrolysers with separation units in techno-economically viable configurations remain the primary challenges before this method can attain maturity comparable to the two-step hydrogenation pathway.

On the other hand, the two-step pathway with water electrolysers and conventional $Cu/ZnO/Al_2O_3$ CO_2-hydrogenation reactors still remains the most developed and easily scalable electrochemical pathway to methanol. Its energy consumption of approximately 0.03 GJ kg^{-1} methanol is comparable to that of the conventional fossil-based route, and the plant design is relatively simple owing to the use of commercialised electrolyser and reactor technologies. However, the requirement for large quantities of low-carbon hydrogen, along with reduced reactor performance in the absence of CO, imposes notable equilibrium limitations and necessitates extensive recycling loops. Capital expenditure is primarily driven by water electrolysis, and the overall climate advantage hinges on access to low-emission electricity. Hydrogen compression, storage, and handling further increase system complexity. Future advancements will need CO_2-hydrogenation catalysts that remain active under high water loadings, sorption-enhanced or membrane-assisted reactor concepts that shift the equilibrium towards methanol, and versatile electrolysers capable of dynamic operation with variable renewable power.

Overall, the green methanol pathways are unlikely to compete with fossil-derived methanol on economic grounds in the near term. The three-step route offers a promising compromise between maturity and efficiency, since the presence of CO in the syngas lowers hydrogen demand and improves reactor performance, while the two-electron CO_2-to-CO step is relatively energy-efficient and already available at about TRL of 8 (Detz et al., 2023). Nevertheless, this configuration still requires around 38 GJ t^{-1} methanol of energy (Adnan et al., 2021), and the plant is more complex because two electrolysers and additional compression stages must be integrated with tight control of H_2 and CO flow rates and pressures. The economic case depends on continued reductions in CO_2-to-CO electrolyser capital cost toward and below about 920 USD m^{-2}, together with gains in efficiency and durability (Bagemihl et al., 2023; Jouny et al., 2018a, 2018b). Future research should prioritise low-overpotential, long-lived CO_2-to-CO catalysts; operating strategies that enable dynamic responses to variable renewable power; and tightly integrated syngas and methanol synthesis sections that can maintain optimal compositions under fluctuating loads.

6. Life cycle assessment

Methanol is both a cornerstone commodity chemical and a prospective low-carbon fuel vector. Early LCA studies, therefore, focused on quantifying energy use and emissions from fossil-based pathways before expanding to systems that integrate carbon capture and utilisation and renewable-electricity-driven synthesis (Badger et al., 2024; Savva et al., 2025). Current estimates indicate that fossil-based methanol production still emits approximately 0.3 Gt CO_2 per year, making large-scale substitution via renewable routes a material mitigation option (Nemmour et al., 2023). Although green methanol is commonly framed as a circular carbon pathway, its climate benefit is contingent on a low-carbon energy supply, and by 2050, associated CO_2 utilisation could reach approximately 1–4.2 Gt per year, enabling system-level emissions reductions through the displacement of fossil fuels (Hepburn et al., 2019). Accordingly, to enable a like-for-like comparison across routes, studies should be interpreted under harmonised assumptions regarding the system boundary, the functional unit, and the carbon accounting for captured, utilised, and stored CO_2. Here, cradle-to-gate is used as the primary comparison basis because the aim of this section is to compare route-level production performance up to the methanol plant gate under a common functional unit, whereas the stages after the gate depend strongly on whether methanol is used as a fuel or as a chemical intermediate. This treatment is also consistent with comparative methanol LCAs that exclude application and waste-treatment stages when those downstream stages are assumed to be identical across routes or are outside the immediate production comparison (Guzmán et al., 2021).

A cradle-to-gate LCA integrating operational data from >120 companies worldwide with mainstream life cycle inventory databases indicates that coal-based and natural gas-based methanol exhibit the highest carbon footprints among the major routes, at approximately 1.79 and 0.95 kg CO_2-eq per kg methanol, respectively (Fig. 10(a)) (Gu et al., 2025). This unfavourable performance is fundamentally driven by fossil carbon entering the system as feedstock and being released as CO_2 across syngas generation, shift conversion, synthesis, and utilities. Contribution analysis further shows that, in conventional fossil routes, the methanol production stage accounts for 72.8–77.9% of the GWP, indicating a structural lock-in associated with syngas preparation and energy supply (Li et al., 2018). Against this backdrop, introducing low-carbon hydrogen and carbon capture and utilisation can reduce the carbon footprint of traditional routes by 15–45% (Gu et al., 2025), but the mitigation benefit diminishes due to constraints imposed by the fossil carbon source and the underlying energy mix (Nemmour et al., 2023).

In contrast, as shown in Fig. 10, bio-based methanol has a markedly lower footprint, typically 0.14–0.46 kg CO_2 eq per kg methanol, primarily owing to biogenic CO_2 uptake during biomass growth and the circulation of biogenic carbon within the system (Douglas et al., 2026). In other words, the lower gate-level GWP of bio-methanol mainly reflects the inclusion of biogenic carbon within the short-term biomass carbon cycle, rather than an automatic permanent removal of atmospheric CO_2. Variability across bio-methanol studies is largely explained by feedstock choice (residues vs dedicated crops), conversion technology, and whether land-use change, residue credits, and avoided waste treatment are included. This distinction is important because the apparent climate benefit is sensitive to how biogenic carbon is accounted for and whether the downstream carbon release is included in the boundary. Under certain scenarios in which separated CO_2 is additionally stored, the life-cycle GWP can shift from positive to strongly negative, reaching approximately −1.04 to −3.61 kg CO_2-eq per kg methanol (Galusnyak et al., 2023). Therefore, strongly negative values should be interpreted as storage-coupled cases rather than as an intrinsic property of all bio-based methanol pathways. Power to methanol routes also tend to yield comparatively low footprints, in the range of 0.28 to 0.65 kg CO_2-eq per kg methanol (Fig. 10(b)) (Nemmour et al., 2023). Among the electrochemical-derived pathways, the two-step configuration that couples mature water electrolysis with thermocatalytic hydrogenation achieves the lowest emissions, supported by high conversion and reduced separation duty. The three-step route, which includes a CO_2-to-CO electrolyser, can exploit favourable CO hydrogenation kinetics. However, this advantage is often offset by the added complexity and electricity demand of operating two electrolysers, resulting in a slightly higher carbon footprint than the two-step route (Adnan and

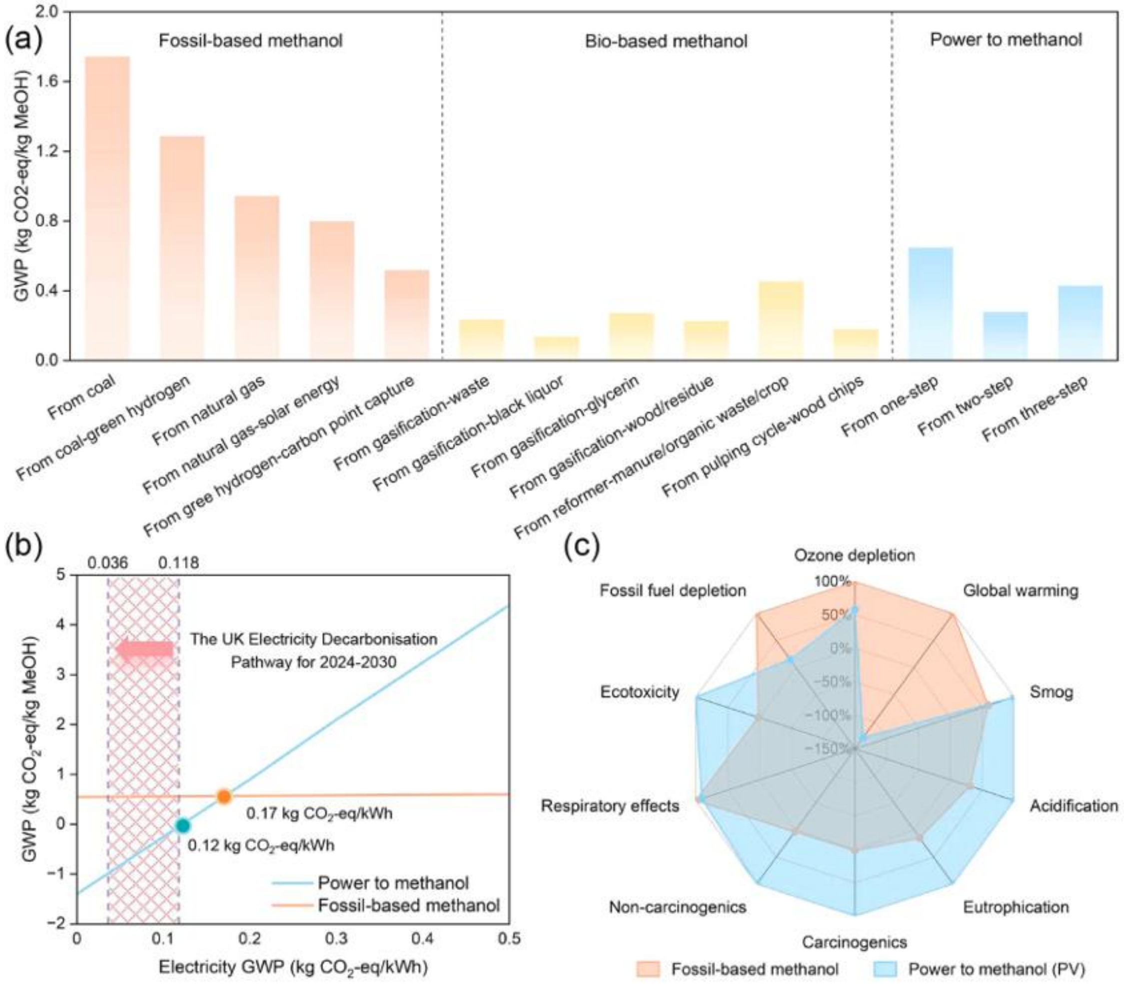

Fig. 10. Life cycle assessment of methanol production pathways. (a) Carbon emissions associated with methanol production (Gu et al., 2025). (b) Influence of electricity carbon intensity on the global warming potential of different methanol production routes (Khojasteh-Salkuyeh et al., 2021). (c) Comparison between photovoltaic electricity-based e-methanol and fossil fuel-derived methanol using the TRACI 2.1 methodology (Badger et al., 2024).

Kibria, 2020). By comparison, the one-step electroreduction route is less environmentally favourable, as the high energy barrier to the six-electron transfer and low Faradaic efficiency yield dilute methanol (Adnan and Kibria, 2020; Guzmán et al., 2021). This necessitates energy-intensive downstream purification, and the implied carbon burden of separation can exceed that of electrolysis itself.

Alongside the technology development trajectory, further mitigation from power to methanol is primarily driven by electricity decarbonisation (Ye et al., 2025). A research first reported that a clear climate advantage for CO_2 hydrogenation to methanol emerges only when the electricity emissions factor falls below approximately 0.13 kg CO_2-eq kWh^{-1} (Adnan and Kibria, 2020). Khojasteh-Salkuyeh et al. (2021) reached a similar threshold of around 0.17 kg CO_2-eq per kWh and further showed that under the current grid mixes in Brazil and Norway, power to methanol can already deliver net negative GWP of roughly -0.1 and -1.3 kg CO_2-eq per kg methanol, respectively. For the UK, the current electricity mix may already support net-negative e-methanol under low-carbon power (below 0.12 kg CO_2-eq kWh^{-1}, subject to the assumed boundary and CO_2 source) (Fig. 10(b)). By 2030, e-methanol produced in the UK is projected to deliver a net CO_2 capture of 0.99 kg CO_2 per kg MeOH under the stated assumptions. In contrast, under carbon-intensive electricity, the GWP of electro methanol can exceed that of conventional natural gas-based methanol by more than a factor of eight, as illustrated for China and Australia (Khojasteh-Salkuyeh et al., 2021). Beyond grid decarbonisation, improving electrolyser efficiency directly reduces electricity demand per unit of methanol produced and the associated indirect emissions. Increasing electrolyser efficiency from 40% to 60% has been reported to reduce net CO_2 emissions by approximately 57% and, under a renewable electricity supply, to confer a pronounced mitigation advantage over fossil-based routes (Adnan and Kibria, 2020). Finally, co-product handling and substitution credits can materially shift net outcomes. For example, assigning some oxygen by-product credit can yield a GWP credit of up to -2.03 kg CO_2-eq per kg of methanol, substantially improving the net emissions profile of power-to-methanol (Badger and Amini, 2025). It should be noted, however, that these comparisons are still primarily made on a cradle-to-gate basis. If the use stage is considered further, the interpretation needs to be applied with caution: for methanol used as a fuel, the carbon embodied in the product is eventually released again, and complete combustion corresponds to 1.38 kg CO_2 per kg MeOH (Douglas et al., 2026). Accordingly, very low or even negative cradle-to-gate values do not automatically translate into net-negative cradle-to-grave performance.

Overall, the high emissions of fossil-based routes are structurally locked in by fossil carbon inputs and the associated syngas and utility energy supply, leaving limited scope for improvements beyond incremental ones. Bio methanol can deliver substantial mitigation through its circular carbon character, with further reductions achievable when coupled with robust CO_2 management strategies. The environmental advantage of power-to-methanol is more conditional, as both the sign and magnitude of its footprint are governed primarily by the carbon intensity of electricity and by the energy demand of electrolysis and capture units. At present, the two-step configuration offers the most credible balance of engineering maturity and environmental performance (Gu et al., 2025). For the three-step route, improved competitiveness depends on step changes in CO_2-to-CO electrolysis efficiency to curtail embodied electricity emissions and to fully exploit the more favourable thermodynamics of CO hydrogenation, thereby reducing recycling and separation duties. By comparison, the long-term viability of the one-step route hinges on mechanistic breakthroughs that decouple dilute product formation from energy-intensive downstream purification.

Looking ahead, as green methanol moves towards large-scale deployment, assessment should extend beyond GWP to address burden-shifting risks. Pathways that perform well on climate metrics may shift burdens toward land occupation, mineral resource use, toxicity-related indicators, or water stress, depending on feedstock and electricity infrastructure (Fig. 10(c)). For instance, biomass cultivation and the siting of renewable energy technologies such as photovoltaics may intensify land competition. For e-methanol, although catalysts and sorbents often contribute little to GWP, typically below 0.02 kg CO_2-eq per kg methanol, they can dominate other impact categories, particularly resource depletion and ecotoxicity, and therefore require explicit constraints (Badger and Amini, 2025; Duke et al., 2026). Finally, the spatiotemporal evolution of power systems will continue to reshape deployment prospects. Near-term implementation is most attractive where low-carbon electricity and near-zero-carbon CO_2 sources are available, whereas medium- to long-term potential will depend on the pace of grid decarbonisation and on reductions in the energy intensity of electrolysis and capture. Emerging and integrated methanol concepts may further reduce net emissions, with hybrid bio- and electro-methanol pathways already reported to approach near-complete greenhouse gas abatement (Tariq et al., 2025).

7. Future perspective

7.1. Scale-up of CO_2 electrolyser

Most CO_2 electrolysis studies remain confined to laboratory cells with geometric electrode areas below about 10 cm^2, typically around 5 cm^2 and operating at only a few watts of electrical power, which simplifies control of mass transport and product analysis but offers limited insight into scale-dependent phenomena such as current distribution, thermal management and pressure drop (Burdyny and Mulder, 2024; Lee et al., 2024). As the field continues to advance, Jouny et al. (2018a) adopted a 25 cm^2 electrode area in their techno-economic analysis of CO_2 electrolysis systems, which remains a common benchmark for performance evaluation. Jeanty et al. (2018) demonstrated the scale-up of Ag-based gas diffusion electrodes in a three-compartment aqueous CO_2 electrolyser, achieving stable operation at 150 mA cm^{-2} with a CO Faradaic efficiency of ~60% on a 100 cm^2 electrode area. Furthermore, El-Shafie et al. (2020) reported an FE of 56% and a current density of 10 mA cm^{-2} using a 10 cm^2 gas diffusion electrode and Cu_2O/ZnO-based catalysts for methanol synthesis from CO_2. These are well-suited to mechanistic studies but provide a weak basis for extrapolating to industrially relevant reactors and stacks (Ge et al., 2022). As a result, many TEA and LCA studies treat electrolyser performance as linearly scalable with electrode area, an assumption that can lead to unrealistic estimates of active area, electricity demand and product fluxes and hence significant uncertainties in material and energy balances and levelised costs (Shin et al., 2021; Somoza-Tornos et al., 2021). Several studies on large-scale electrolyser architectures show that scale-up introduces nonlinear three-dimensional effects in current distribution, mass transport, pressure drop, and thermal management that must be captured explicitly in both reactor design and cost models (Endrődi et al., 2019; Yuan et al., 2023). Recent engineering analyses further underscore that the transition from these small-area cells to large-area electrodes assembled in multi-cell stacks is essential to validate realistic capital costs, operating strategies, and durability targets for industrial implementation, highlighting that current research still predominantly relies on such small-scale devices (Q. Li et al., 2025).

Typical laboratory cells employ electrode areas of only a few square centimetres, whereas commercial electrolysers operate with per-cell electrode areas of hundreds of square centimetres, typically 100 to 1000 cm^2 (Edwards et al., 2023; Nelson et al., 2024). Scaling up electrochemical CO_2 reduction stacks while maintaining uniform current and CO_2 distributions and effective heat management is a significant engineering challenge. Membranes and catalysts must withstand long-term operation. Scaling the CO_2 electrolyser to m^2-scale industrial stacks exposes a set of non-linear bottlenecks, including non-uniform current distribution, uneven CO_2 diffusion across the electrode surface, steep heat and concentration gradients, flooding and drying of gas-diffusion layers, carbonate formation that depletes accessible CO_2, product and ion crossover, and limited long-term stability under high single-pass conversion. These effects are manifold, complicated sealing and pressure management, and undermine the common assumption in techno-economic and life-cycle models that performance can be linearly extrapolated from active area and stack count. Milestone contributions have begun to address these gaps. Another research mapped system-level requirements for terawatt-scale CO_2 electrolysis and highlighted the central role of scalable stacks and balance-of-plant design (Smith et al., 2019). Moreover, research reported the first multilayer CO_2 electrolyser stack operating at high pressure with partial current densities above 250 mA cm^{-2}, demonstrating that multi-cell operation can approach the sum of optimised single cells (Endrődi et al., 2019). A pilot-scale CO_2-to-CO electrolyser and a semi-empirical model that links 5 cm^2 cell data to stack-level performance and costs (Edwards et al., 2023). Complementary reviews by Ge et al. (2022) on MEA architectures, Yuan et al. (2023) on large-scale CO_2 electroreduction, and Burdyny and Mulder (2024) on scale-up strategies have systematised these challenges and set quantitative targets for voltage, current density, CO_2 utilisation and stability that future industrial modules must meet.

Recent scale-up demonstrations have started to define a target range for industrial employment. Several pilot-scale demonstrations provide practical benchmarks: for instance, VoltaChem deployed a 15-cell AEM CO_2 electrolyser stack with a total active area of approximately 500 m^2 (Liu et al., 2018), while Siemens Energy's CO_2EXIDE project operated a 10-cell stack comprising 300 cm^2 cells (European Commission, 2021). In larger-format systems, such as OCOchem's pilot plant for formate production (OCOchem, 2023), only four high-surface-area cells were assembled per stack. These examples suggest that industrially relevant electrolyser stacks typically comprise 10 to 20 cells, each with an active area of 100 to 500 cm^2. Moreover, Kiyota et al. (2025) developed a hydrophilic porous membrane zero gap design that operates a 16 cm^2 cell at 1000 mA cm^{-2} and extended this architecture to a ten cell stack with 100 cm^2 per cell for 500 h, while Ha et al. (2024) reported a large scale four cell CO_2 to CO stack with a total active area of 100 cm^2 and stable operation with CO selectivity above 80%. Together with flow cell work that employs 4 × 100 cm^2 electrodes at tens of amperes and recent perspectives that systematise scale up requirements (Sun et al., 2023; Wei et al., 2023), these studies identify this regime as pilot-plant scale and indicate that cell areas of the order of 10^2–10^3 cm^2 are required to achieve practical throughput (Nelson et al., 2024).

Table 4 consolidates major international projects over the past decade that have advanced the scale-up of CO_2 electrolyser technologies from laboratory and pilot scales to pre-commercial and industrially relevant systems, detailing their funding levels, lead institutions, and technological milestones. Collectively, these initiatives demonstrate clear progress in increasing electrolyser power, active area, and operational stability, while integrating CO_2 electrolysis with downstream fuel, chemical, and biological conversion pathways under realistic industrial conditions. The single most significant engineering showstopper is maintaining spatially uniform local operating conditions across a large active area and across many repeating cells within a very narrow multiphase stability window. The fundamental issue is not that flooding, drying, salt deposition, pressure imbalance, electrical nonuniformity, or thermal gradients are absent at 100 cm^2, but that, at the m^2 scale, small local deviations in flow, pressure, compression, current distribution, hydration, and temperature become strongly coupled and self-amplifying. Once this uniformity is lost, some regions become CO_2-starved and shift towards hydrogen evolution, others overheat or dry out, and salt crystallisation and pore blockage further destabilise transport, leading to selectivity loss, voltage rise, accelerated degradation, and premature stack failure. In practice, therefore, the barrier to industrial scale-up is not a single isolated phenomenon such as flooding alone, but large-area stack operability, namely the ability to sustain uniform reactant delivery, wetting state, current density, and heat management across the entire stack for long-term stable operation.

Overall, Fig. 11 summarises recent progress in scaling the electrode area of representative CO_2 electrolyser configurations from laboratory scale to industrially relevant dimensions, using a small set of illustrative examples from studies employing zero-gap and MEA configurations. When assembled into multi-cell stacks at the kilowatt scale, CO_2 electrolysers reach a realistic minimum scale at which genuine industrial application becomes feasible. In addition, early-stage development has begun for stacks assembled from multiple single cells, and continued improvements in catalyst performance are expected to further reduce stack cost. It follows that the large-scale deployment of stacks, together with enhanced durability, could materially lower the cost of CO_2-to-CO conversion.

7.2. *Improving electrified green methanol economic competitiveness*

The current production costs of e-methanol remain higher than those of the conventional route, largely driven by hydrogen and CO_2 prices, ranging from 0.860 to 1.585 USD kg^{-1} (Adnan and Kibria, 2020). However, all routes could reduce costs to approximately 0.430–0.435 USD kg^{-1} while cutting carbon emissions by 172% relative to the fossil-based route when powered by low-carbon electricity (Adnan and Kibria, 2020). Cost projections indicate that the global price of green methanol could fall substantially as electrolysis technologies scale and renewable electricity becomes cheaper. Continued reductions in green hydrogen prices and improvements in multi-step synthesis efficiency are expected to narrow this gap and enhance the competitiveness of green methanol. When a carbon price of 0.17 USD kg^{-1} CO_2 is included, natural gas-based methanol costs around 0.33 USD kg^{-1}, indicating that e-methanol could become competitive by the 2040s (Fasihi and Breyer, 2024). Projections indicate reductions to 0.25–0.63 USD kg^{-1} by 2050 as renewable electricity and electrolyser costs decline (Nemmour et al., 2023). Du et al. (2025) also indicate potential cost-parity with traditional marine fuels by 2030–2035, driven by falling renewable-electricity and hydrogen prices alongside tightening carbon-pricing frameworks.

Narrowing the cost gap between electrochemical and conventional methanol production will require coordinated advances in technology, energy markets and policy design. Closing this gap requires progress on several fronts simultaneously. Firstly, reductions in renewable electricity and green hydrogen prices, together with higher current density, lower cell voltage, and longer stack lifetime, can cut both energy use and the capital cost (CAPEX) of electrolysers, with system-level studies showing that electricity prices and current density are the dominant cost levers. Fasihi and Breyer (2024) estimate that the e-methanol cost in 2020 was 1.32–1.65 USD kg^{-1} and will drop to 0.66–0.75 USD kg^{-1} by 2030 and 0.35–0.39 USD kg^{-1} by 2050. The projections account for declining electrolyser costs, higher capacity factors and lower electricity prices. Secondly, policy instruments such as carbon pricing and capturing subsidies on the order of 0.116–0.174 USD kg^{-1} CO_2, combined with premium methanol prices in maritime fuels and chemical markets, can bring PtMeOH plants towards breakeven, as illustrated by scenarios where plants become viable when methanol sells above about 580 USD kg^{-1} even without carbon credits. Thirdly, integrated process designs that monetise co-products and reduce energy penalties, for example by selling oxygen, utilising low-grade heat, or pairing CO_2 reduction with value-added anodic oxidations, have been shown to improve electrolysis economics significantly and should be prioritised in future electrocatalytic methanol concepts. Projections suggest that green methanol costs will decline to 0.367–0.407 USD kg^{-1} by 2050 (Fasihi and Breyer, 2024). Achieving hydrogen costs below 2 USD kg^{-1} is critical. Integration of co-electrolysis and pyrolysis shows that negative emissions can be monetised through carbon credits (Nogueira Nakashima et al., 2025). Hybrid bio-electrochemical routes offer intermediate costs and can produce high-value coproducts. Markets for low-carbon fuels and chemicals will expand, providing premium prices.

Table 5 summarises representative global projects that have

Table 4
Projects advancing the scale-up of CO_2 electrolyser technologies over the past decade.

Project acronym and duration	Project title	PI) and Co-Is	Total project funding	Research objectives
ECO2Fuel (2021–2026)	Large-Scale Low-Temperature Electrochemical CO_2 Conversion to Sustainable Liquid Fuels	Coordinated by DLR (German Aerospace Center)	€20.1 million	Develop the world's first 1 MW low-temp CO_2 electrolyser system for direct CO_2-to-fuels. Upscale from a 5 kW prototype to a 1 MW industrial unit producing C_1–C_4 alcohol e-fuels, operated under industrial conditions at TRL7 (Rwe, 2026).
LOTER.CO2M (2018–2022)	CRM-free Low Temperature Electrochemical Reduction of CO_2 to Methanol	Coordinated by DLR (Germany)	€4.26 million	Developed new non-critical catalysts and membranes for direct CO_2/H_2O co-electrolysis to methanol. Scaled the CO_2 electrolyser from lab-scale to a ~2–3 kW *pilot stack* (~30 cells × 100 cm^2 each) tested at RWE's Niederaussem site, demonstrating CO_2-to-methanol fuel production at ~atmospheric pressure. Findings fed into the 1 MW ECO2Fuel project (RWE Innovation Centre, 2022).
CO2EXIDE (2018–2021)	CO_2-based Electrosynthesis of Ethylene Oxide	Coordinated by Fraunhofer (Germany)	€5.42 million	Built an integrated *paired* electrolyser: cathodic CO_2 reduction to ethylene and anodic water oxidation to H_2O_2, with subsequent coupling to ethylene oxide synthesis. Advanced the technology from TRL 4 to TRL 6 by constructing a ~1 kW PEM CO_2 electrolyser (five 10-cell stacks, 800 cm^2 cells) with projected capacity ~100 kg CO_2/day conversion to C_2H_4. Achieved >60% FE in pilot tests and ~2400 h cumulative operation (Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e. V., 2021).
OCEAN (2017–2022)	Oxalic Acid from CO_2 using Electrochemistry at Demonstration Scale	Prof. Siglinda Perathoner (University of Messina, Italy), Coordinator	€8 million	Demonstrated a *pre-pilot* electrochemical CO_2 conversion process for making formate and oxalic acid. Developed a 6 kW electrolysis stack (~40,000 cm^2 total area) operating >0.15 A/cm^2, converting ~250 *g* CO_2/hour into formate, which is then converted to oxalate. The largest CO_2-reduction cell (0.2 m^2) was operated for ~1040 hours at RWE's site, validating the scale-up (TRL6) of the CO_2-to-chemical technology (European Research Institute of Catalysis A.I.S.B.L., 2022).
Rheticus (I/II) (2017–2021)	Artificial Photosynthesis Platform (Electrolysis–Bioreactor)	Jointly led by Evonik (Thomas Haas) & Siemens Energy (Karl-J. Kuhn)	€3.5 million (BMBF)	Developed a test plant combining a CO_2 electrolyser and microbial fermentation to make speciality chemicals. Phase II built a fully automated CO_2 electrolyser (10 cells, 3000 cm^2 total) producing syngas (CO + H_2) at ~25 kW, feeding an 8 m^3 bioreactor where microbes convert CO_2-derived syngas to butanol/hexanol. Demonstrated flexible "artificial photosynthesis" using CO_2 + water + renewable power to produce 1 tonne of chemicals per batch, proving feasibility for industrial scale-up (Siemens Energy, Evonik Industries AG, 2019).
Kopernikus P2X (2016–2022)	Kopernikus "Power-to-X" Integrated Pilot	Consortium (Sunfire, KIT, Climeworks, Ineratec, et al.), funded by BMBF (Germany)	~€30 million (est.)	A national flagship project integrating CO_2 electrolysis with downstream synthesis to create carbon-neutral fuels. Built a compact pilot plant combining high-temperature co-electrolysis of CO_2/H_2O (Solid Oxide electrolyser) with downstream fuel synthesis. Aimed to produce 200 L/day of synthetic fuel by 2022, demonstrating rapid-response electrolysis and complete Power-to-Liquid conversion from captured CO_2 under industrial conditions (DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V, 2024).
Opus 12 (Twelve) (2020–2022)	PEM CO_2 Electrolyser Scale-Up to Enable MW-Scale Modules	Dr. Kendra Kuhl (CTO, Twelve) – PI	$2.5 million (DOE EERE)	U.S. DOE-backed project to scale PEM CO_2 electrolysers from lab to pilot. Focused on enlarging MEA active area >750 cm^2 and assembling multi-cell stacks. Fabricated and tested several pilot-scale PEM electrolysis cells and stacks (with partner Nel), demonstrating performance and efficiency needed for eventual MW-scale CO_2-to-CO systems. Outcomes included design of robust large-area MEAs and

(*continued on next page*)

Table 4 (*continued*)

Project acronym and duration	Project title	PI) and Co-Is	Total project funding	Research objectives
				insights for MW-scale module integration (U.S. Department of Energy, Opus 12 Inc., 2021).
OCOchem Pilot (2023–2025)	CarbonFlux CO_2-to-Formate Pilot Plant	Todd Brix (CEO, OCOchem)	~$5 million (public–private)	Company-built pilot plant converting CO_2 and water to formate at industrial scale. Commissioned in 2025, it uses a 4-cell stack of 1.5 m^2 GDE-based CO_2 electrolyser cells (world's largest) operating at ambient conditions. The system produces ~60 tons/year of formate. This modular skid-mounted design proved that numbering up large CO_2 electrolyser cells can achieve continuous chemical production, paving the way toward multi-ton scale systems (OCOchem, 2023).
RenewCO$_2$ (2020–2025)	RenewCO$_2$ Containerised MEG Electrolyser	Karin Calvinho (CTO) & Prof. C. Dismukes – co-founders	$1.1 million (DOE SBIR Phase II)	U.S. startup project to scale CO_2 electroreduction to mono-ethylene glycol (MEG). Developed from a wallet-sized lab device to a pilot electrolyser (suitcase-sized, ~1 ton/year MEG) and targeting a 40 ft container module by 2025. Each container unit will process ~3 tons of CO_2 per day into MEG using proprietary catalysts. The project emphasises modular design for deployment at emissions sources, demonstrating a path from milligrams-per-day lab cells to multi-ton-per-day commercial reactors (Argonne National Laboratory, 2023).
Carbon-to-eFuels (2022–2024)	Technology for Electroreduction CO_2 to Gaseous Fuels	Prof. Qian Fu (Chongqing University)	8 million RMB	Funded by China Energy Engineering Corporation (CEEC) and developed a 100-kW-scale CO_2 electroreduction stack. Under industrial current densities, the demonstration unit achieves stable operation with a high CO Faraday efficiency (>90%). Meanwhile, an integrated demonstration device and system for CO_2 enrichment and reduction to syngas with a capacity of 100 tons/ year has been constructed.
C-Circ (2025–2027)	Accelerating the translation of CO_2 Electrolysers	Prof. Alexander Cowan (University of Liverpool), Prof. Eileen Yu (University of Southampton), Dr Ashly Fly (Loughborough University), Dr Lei Xing (University of Surrey)	£800k	Funded by EPSRC in the UK, project is to develop and demonstrate a new generation of CO_2 electrolysers capable of operating efficiently and stably under acidic conditions. Building on recent advances in electrode, membrane, and device technologies, the project aims to translate fundamental discoveries into integrated and scalable systems, e.g., 100–500 cm^2 single cells. Using real-world captured CO_2 from industrial sources, the research will validate performance beyond laboratory conditions and quantify system-level metrics such as carbon utilisation, energy efficiency, and durability. In parallel, the project will evaluate environmental and economic impacts to de-risk industrial deployment and accelerate net-zero, circular carbon applications (UKERC, 2020).

advanced the scale-up of CO_2 electrolyser–enabled methanol production, spanning pilot, demonstration, and commercial scales, and highlighting their funding levels, lead organisations, and integration of electrolysis with downstream methanol synthesis. Collectively, these projects illustrate the transition from decentralised and pilot-scale systems to large-scale, industrial and commercial e-methanol plants, particularly in Europe and China, underscoring the growing technological maturity of CO_2-to-methanol pathways.

In general, although a limited number of methanol plants have reached practical deployment, most research efforts remain confined to the laboratory scale. However, interest is growing due to the potential for modular and distributed production, integration with renewable power and direct utilisation of captured CO_2. Novel materials, advanced reactor designs such as membrane electrode assemblies and gas-fed flow cells, and system integration with renewable energy sources are active areas of research. The path to commercialisation requires breakthroughs in catalysis, materials, device design and system integration. For example, in terms of the future gigawatt-scale production of CO and C_{2+} products, scalable deployment will necessarily rely on a nanoparticle-based catalyst architecture coupled with continuous coating processes (Moon et al., 2026).

7.3. Worldwide policy support

Achieving widespread adoption of green methanol will require coordinated efforts across technological development, policy and market creation. Reductions in the costs of water electrolysis and carbon capture are essential; government targets aim for hydrogen at 1–2 USD kg^{-1} (Hubert et al., 2024). Carbon pricing, renewable electricity subsidies and mandates for low-carbon fuels can accelerate uptake.

Government policies concerning circular economy, carbon emission reduction and green energy have substantially advanced the

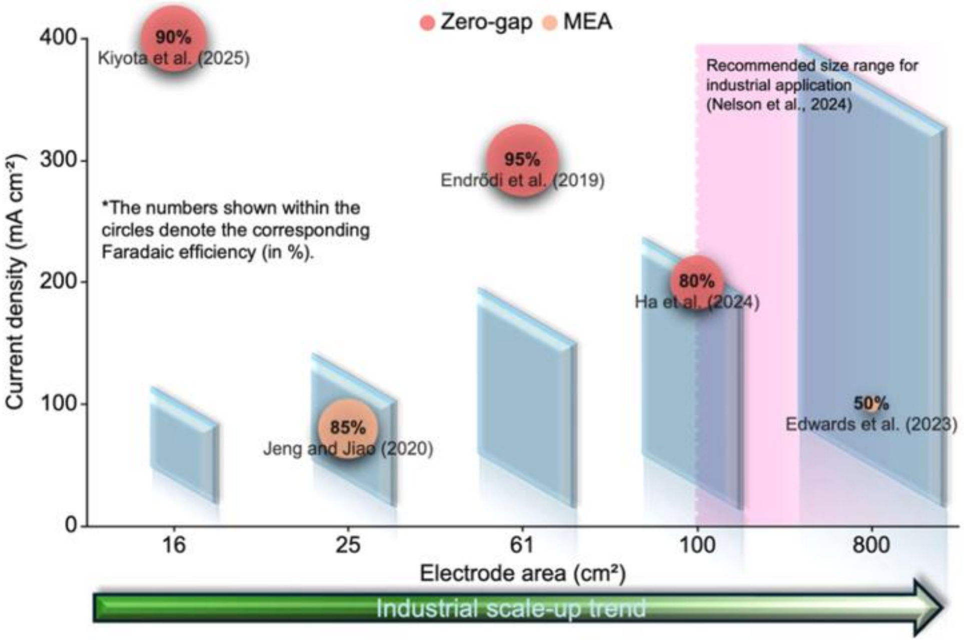

Fig. 11. Industrial scale-up of electrode area in CO_2 electrolysis.

Table 5
Representative global projects on CO_2 electrolyser scale-up for methanol production.

Project acronym and duration	Project title	PI / Lead organisation(s)	Total project funding	Research objectives and scale-up focus
MefCO$_2$ (2014–2019)	Methanol Fuel from CO_2	i-DEALS (Coordinator); RWE; Carbon Recycling International; Cardiff University	~€11 million (EU Horizon 2020)	Demonstration of flexible CO_2-to-methanol production using captured flue-gas CO_2 and renewable H_2. Integrated ~1 MW PEM electrolysis with methanol synthesis. Pilot plant at Niederaussem (Germany) producing ~1 t MeOH day^{-1} (RWE Innovation Centre, 2023).
FReSMe (2016–2021)	From Residual Steel Gases to Methanol	i-DEALS; SSAB; CRI; TNO; Stena Line	~€11.4 million (EU Horizon 2020)	Pilot-scale methanol production from steel mill off-gases. Combined CO_2 capture, residual H_2 recovery and electrolysis-derived H_2. Demonstrated ~50 kg MeOH h^{-1} at Luleå (Sweden) (I-DEALS Innovation and Technology Venturing Services SL, 2021).
UP-TO-ME (2022–2025)	Unmanned Power-to-Methanol Production	VTT Technical Research Centre of Finland	~€2.7 million (EU + UKRI)	Development of decentralised, fully autonomous CO_2-to-methanol units. Coupled small-scale electrolysis with CO_2 capture from biogas. Demonstrated at wastewater treatment sites in Spain (Teknologian Tutkimuskeskus VTT Oy, 2025).
Carbon2Chem® (2016–2024)	Carbon2Chem Industrial CCU Programme	thyssenkrupp; Fraunhofer; MPI; multiple industrial partners	>€135 million (BMBF, Phase I–II)	Industrial pilot converting steelworks off-gases into chemicals including methanol. Integrated large-scale hydrogen electrolysis with catalytic synthesis at Duisburg (Germany) (Thyssenkrupp, 2020).
Project AIR (2021–2026)	Sustainable Methanol from Circular Feedstocks	Perstorp Group; Uniper; Fortum	€97 million (EU Innovation Fund) + national funding	Construction of a commercial-scale methanol plant using captured CO_2 and renewable H_2. Includes ~200 MW electrolysis. Located at Stenungsund, Sweden. Target capacity ~200 kt MeOH yr^{-1} (Johnson Matthey Plc, 2024).
Shunli Project (2021–2022)	CO_2-to-Methanol Plant, Anyang	CRI; Henan Shuncheng Group	~$90 million (industrial)	World-scale commercial CCU plant converting coke-oven CO_2 to methanol. Located at Anyang, China. Capacity ~110 kt MeOH yr^{-1}. Demonstrates industrial replication of electrolyser-enabled CO_2 utilisation (Carbon Recycling International, 2023).
Tianying e-Methanol (2023–2025)	Renewable CO_2-to-e-Methanol Project	CRI; Tianying Group	Not disclosed (industrial)	Large-scale power-to-methanol plant using renewable H_2 from electrolysis and biogenic CO_2. Located at Liaoyuan, China. Phase-I capacity ~170 kt MeOH yr^{-1} (Carbon Recycling International, 2025a).
George Olah Plant (2011–present)	Renewable Methanol Demonstration Plant	Carbon Recycling International	Private and public support	First commercial CO_2-to-methanol plant. PEM electrolysis powered by geothermal electricity. Located at Svartsengi, Iceland. Capacity scaled from 1.3 kt yr^{-1} to ~4 kt yr^{-1} (Carbon Recycling International, 2025b).

development of green electrochemical methanol technology. Stringent emission-reduction targets and rising demand for clean maritime fuels have elevated green methanol as a promising, low-cost alternative, supported by mature technology. Green methanol synthesis can comply with EU renewable fuel regulations and is expected to become cost-competitive with conventional fuels after 2030. The EU Emissions Trading System (ETS) now requires ships above 5000 GT to purchase allowances covering 40% of emissions in 2024, rising to 100 % in 2026 (Du et al., 2025). The FuelEU Maritime Regulation (European Commission, 2023) sets emission-intensity reduction targets, starting at 2%

in 2025 and reaching 80% by 2050. These policies raise the cost of fossil fuel use and incentivise the use of low-carbon fuels. Analysts note that green methanol has emerged as one of the most balanced alternative fuels for the shipping sector, accounting for 41% of the total tonnage of global new ship orders, including 49 methanol-powered ships worldwide in the first half of 2024 (Du et al., 2025). By combining robust policy support, cheap renewable electricity from offshore wind, mature methanol synthesis technology and AI-driven optimisation, integrated power-to-methanol systems could deliver cost-competitive green methanol while meeting ambitious decarbonisation targets.

In summary, the next-generation renewable system integration for methanol synthesis requires a holistic approach that combines intermittent renewable energy with efficient electrochemical processes, utilises artificial intelligence for catalyst discovery and process optimisation, and employs multi-criteria decision frameworks to balance techno-economic and environmental objectives. Policy measures such as the EU ETS and FuelEU Maritime Regulation create market incentives for green methanol; integrated PtMeOH plants powered by renewable electricity and guided by AI-enhanced optimisation could thus become central to a low-carbon chemical industry. Broader policy and regulatory measures that could enable the effective scale-up of CO_2 utilisation include establishing carbon tax in the range of 40–80 USD t^{-1} of CO_2, with scheduled increases over time to strengthen the penalty on emissions.

As shown in Fig. 10, future green methanol production is likely to evolve toward dynamically integrated energy and chemical systems that coordinate variable renewables, such as wind and solar, with firm power and flexibility options to maintain stable plant operation, since a fully renewable electricity supply cannot yet be assumed for continuous industrial duty. CO_2 feedstocks will increasingly combine point source capture with direct air capture, followed by purification to meet electrochemical conversion requirements, while real-time optimisation and control will rely on data-driven methods to reconcile fluctuating power availability with methanol demand and to support accelerated catalyst and electrode development. System design should be evaluated through multi-criteria decision-making frameworks that jointly consider techno-economic performance, environmental impacts, and social outcomes, with policy instruments remaining critical to closing the cost gap relative to fossil-based methanol. On this basis, a staged technology trajectory is plausible: in the near term, declining costs and improving maturity of alkaline water electrolysis and proton exchange membrane electrolysis are expected to favour two-step routes based on renewable H_2 and CO_2 hydrogenation; in the medium term, scale up of CO_2 electrolysers through larger active areas and higher performance, lower cost stacks could enable competitive electrolytic syngas and raise the technology readiness of three-step pathways; in the longer term, direct one-step electrochemical conversion of CO_2 to methanol is expected to remain a focal research direction, but with technology readiness level likely to lag for an extended period (Fig. 12).

7.4. Limitations and recommendations

This review is subject to several limitations that should be considered when interpreting the comparative TEA and LCA findings. First, the evidence base remains uneven across pathways because one-step direct CO_2-to-methanol and three-step routes that embed upstream CO_2 to CO or syngas via electrolysis are still largely pre-commercial, meaning that many assessments depend on projected electrolyser performance, stack durability, and replacement schedules rather than operational data. Second, flue gas realism is insufficiently represented, as only a limited number of studies quantify the effects of impurities such as O_2, SO_x, NO_x, and H_2O, as well as gas conditioning requirements, on electrolyser selectivity, degradation, and downstream separation burdens. Third, residual incomparability persists across TEA studies despite cost-year and currency harmonisation because several reports do not fully disclose key boundary conditions, including plant scale, capacity factor, weighted average cost of capital, stack replacement assumptions, and CO_2 delivery pressure and purity. Fourth, LCA comparisons are

Fig. 12. A systems-level vision for an ai-enabled renewable-driven and carbon-capture-integrated green methanol economy..

constrained by heterogeneous system boundaries and carbon accounting conventions, particularly regarding cradle-to-gate versus cradle-to-grave scope, treatment of captured CO_2, and end-of-life assumptions. Finally, unresolved uncertainty remains where primary studies omit critical inputs such as CO_2 conditioning energy, stack lifetime distributions, or future electricity carbon intensity. To strengthen future work, standardised TEA reporting should be adopted, joint performance and cost models should be used to capture trade offs among current density, Faradaic efficiency, cell voltage, and CO_2 utilisation, LCA studies should provide transparent inventories and boundary definitions, pilot scale demonstrations under simulated or real flue gas should report long duration durability and impurity tolerance, and policy support should de risk first of a kind deployment through robust monitoring and certification frameworks, carbon accounting rules, and financial instruments such as contracts for difference, tax credits, and low carbon power purchasing.

8. Conclusions

Electrochemical methods for green methanol provide a way to decarbonise the chemical and transport sectors, although they vary significantly in maturity, efficiency, and sustainability. One-step CO_2 electro-reduction, though conceptually elegant, is constrained by six-electron kinetics, low selectivity and high energy demand. While two-step synthesis couples mature water electrolysis with CO_2 hydrogenation and is currently the most deployable option, it relies on low-carbon hydrogen and is constrained by high hydrogen consumption and equilibrium limitations. Adding a CO_2-to-CO electrolyser to the three-step route reduces hydrogen requirements and improves reactor thermodynamics, at the cost of additional complexity. Across all routes, the key levers for sustainability are low-carbon electricity (emission factor $<$ 130 g CO_2 kWh^{-1}), high electrolyser efficiency and low stack cost, and advanced catalysts and reactor designs.

For a large-scale three-step methanol system, the water electrolysis section would most plausibly be based on AWE, or, in the medium term, PEM electrolysers, and, in the longer term, AEM electrolysis. In particular, AWE and AEM systems employing Ni or NiMo cathodes for the HER and NiFe-based anodes for the OER are especially attractive, as they offer a strong balance of low cost, material abundance, durability, and scalability for bulk green hydrogen production. In parallel, the CO_2 electrolysis section is more suitably configured as a gas-fed zero-gap MEA electrolyser equipped with a GDE cathode, since this architecture is the most compatible with industrially relevant current densities and compact stack design. For catalyst choice, Ag-based catalysts are most suitable when the target is CO-rich syngas, while Cu-based tandem catalysts become relevant only if deeper reduction beyond CO is desired. Overall, the most practical large-scale configuration is a Ni-based alkaline or AEM water electrolyser coupled with an Ag-based zero-gap MEA CO_2 electrolyser, because this pairing aligns low-cost hydrogen generation with high-rate CO_2 conversion and integrates well with downstream thermocatalytic methanol synthesis.

The emerging consensus is that industrial deployment will not follow a single-step CO_2-to-methanol route, but rather a layered architecture built on stable C_1 product lines and longer-term research into multi-carbon products. Techno-economic studies show that synthetic methanol remains more expensive than fossil-derived methanol. Across all routes, electrolyser capital costs and renewable electricity prices remain key cost drivers, and the environmental benefit depends on the use of low-carbon power. However, reductions in electrolyser costs and falling renewable electricity prices are expected to make e-methanol competitive by mid-century.

Future research should priorities (i) development of selective and durable electrocatalysts for multi-electron CO_2 reduction, (ii) integrated capture-electrolysis models that optimise mass transport and product separation, (iii) hybrid sorption-enhanced or membrane reactors to overcome equilibrium limits, and (iv) system-level optimisation using AI-driven modelling to balance energy, environment and economics. As renewable electricity prices fall and electrochemical technologies mature, green methanol could become a viable carbon-neutral fuel and chemical feedstock. Projected near-term advancements from 2025 to 2028 are expected to focus on commercial electrochemical CO_2-to-CO systems and on the increasing integration of direct air capture technologies. Between 2028 and 2032, hybrid syngas routes are expected to reach technological maturity, enabling modular power-to-methanol systems that integrate CO_2 electrolysis with established thermocatalytic units. Beyond 2032, advances in methanol and higher hydrocarbon production may alter the role of electrochemical synthesis in the chemical industry. From both engineering and commercial perspectives, the primary challenge in CO_2 electroreduction lies not in maximising selectivity for complex products but in enhancing system-level energy efficiency, modular integration, operational stability, and reducing balance-of-plant costs.

CRediT authorship contribution statement

Yuanjing Zhao: Writing – original draft, Investigation, Data curation. **Shiyu Wang:** Writing – original draft, Investigation, Data curation. **Grazia Leonzio:** Supervision, Methodology, Formal analysis. **Qian Fu:** Resources, Funding acquisition, Formal analysis. **Yang Wang:** Writing – original draft, Formal analysis. **Jin Xuan:** Supervision, Resources. **Lei Xing:** Writing – review & editing, Supervision, Methodology, Conceptualization.

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.

Acknowledgements

The authors acknowledge the financial support provided by C-Circ: Accelerating the translation of CO_2 Electrolysers (UKRI781) funded by the Engineering and Physical Sciences Research Council (EPSRC) of the UK and the University of Surrey Library and Learning Services Open Research team through approval of the article processing charge for this publication. This work was also supported by the National Natural Science Foundation of China (No. 52394202, 52476056). Any associated research data and metadata are available via the University of Surrey Open Research Repository. Dr Lei Xing is an editor of the journal; however, the editor had no access to the peer review or editorial process for this article at any point.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccst.2026.100603.

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