Viewpoint

Commercialization of electrochemical CO₂ reduction: HCOOH pathway versus CO pathway

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ABSTRACT

The objective of electrochemical CO₂ reduction technologies (ECRs) is notably audacious: to revolutionize the market by generating fuel and essential chemicals at a more competitive price than petrochemicals can offer, all while prioritizing environmental sustainability. To expedite the commercialization of ECR technology, we discuss here how ECR can reshape the industry landscape through 2e⁻ pathways.

1. Introduction

The conversion of CO₂ into fuels and chemicals, utilizing renewable energy sources, presents a compelling strategy to enhance the integration of renewables into chemical bonds. This transformative process can be achieved through biological, thermochemical, photochemical, or electrochemical methods, each of which has been extensively explored. Notably, room-temperature electrochemical carbon dioxide reduction (ECR) technologies have emerged as promising avenues for addressing climate change and reducing reliance on fossil fuels, effectively converting carbon emissions into economically valuable substances. These technologies offer several benefits, such as precise and selective control of the reaction *via* the applied voltage, broad scalability owing to modular electrolyzer configurations, eco-friendly use of electrons as redox agents instead of harmful chemicals, and fast and flexible integration with renewable energy. Despite these merits, it is essential to acknowledge that the electrochemical reduction of CO₂ can follow multiple pathways, resulting in various gaseous products (carbon monoxide (CO), methane, ethylene, etc.) and liquid products (formic acid (HCOOH), methanol, ethanol, propanol, etc.). From a commercialization standpoint, there exists a critical need for a pragmatic and well-defined roadmap to guide ECR goals effectively. This comment aims to contribute to this discourse by exploring how C₁ products derived from electrochemical CO₂ reduction, particularly CO and HCOOH (Fig. 1), are forging distinct paths, transforming the current market

landscape.

2. 2e⁻ Products versus C₂₊ products

Price and large-scale commodity markets serve as apt indicators of enduring prospects for CO_2 electrolysis. An optimal conversion pathway must exhibit scalability and cost-effectiveness in comparison with fossil fuel alternatives, alongside a reduced carbon footprint to facilitate significant emission reductions through the transition from traditional petrochemical production methods to electrosynthesis-based approaches. A quantitative techno-economic analysis (TEA) is normally considered on the basis of capital cost, operational maintenance cost (especially for the cost of CO_2, the electricity price, and the price of the product), and the market demand for certain products [1]. Most financial projections utilize data from the Department of Energy's (DOE) H_2A analysis for water electrolysis as a reference [2]. Among them, electricity pricing and the electrolyzer's capital cost are regarded as primary cost factors. Simultaneously, effective measures could encompass offering financial incentives to spur research and development, extending tax credits or subsidies to facilitate the deployment of ECR systems. In addition to economic considerations, a cradle-to-gate life cycle assessment (LCA) was also suggested for quantifying environmental impacts [3].

Prior research has suggested that the direct production of C_{2+} products may not be the most viable for commercialization because of two primary factors [1,4]. First, considering electricity pricing, an increase in molecular complexity with more carbon atoms (C_{2+}) or electrons (CH_4, CH_3OH) leads to more proton-coupled electron transfers, increasing the kinetic overpotential and decreasing the overall energy conversion efficiency. This may undermine the competitiveness of complex molecules when evaluating revenue per mole of electrons in comparison to 2e⁻ C_1 products [4]. Notably, CO and HCOOH stand out for maintaining the highest normalized market price per electron, as supported by reported data showing current densities and Faradaic efficiencies (FEs) for CO and HCOOH synthesis that already satisfy industrial benchmarks, exceeding 200 mA cm⁻² and 95%, respectively [5–8]. Although the complexity of liquid separation introduces a considerable expense to the manufacturing process of HCOOH, integrating the electrolysis unit with product purification steps, such as membrane separation or adsorption, could reduce energy-intensive purification re-

quirements. Moreover, solid electrolyte cells can directly produce pure HCOOH products, avoiding the additional costs associated with subsequent separation processes. In addition, significant challenges remain in the synthesis of C_{2+} products owing to the low product selectivity or the low-cost thermochemical pathways available for their manufacture [9]. Additionally, from an LCA perspective, the direct production of C_{2+} generates a higher concentration of hydroxide ions per unit of product yield at the reaction interface. This accelerates carbon loss due to carbonate formation, increasing fuel wasting [10]. Consequently, a widely embracing strategy involves the use of CO as an intermediate for the electrochemical production of C_{2+} hydrocarbons and oxygenation *via* cascade catalysis. This entails two key steps: the conversion of CO_2 to CO, followed by the transformation of CO to C_{2+} products (with ethylene being a prominently discussed example) [11,12]. The rationale behind this approach is that the formation of multicarbon compounds requires either the dimerization or hydrogenation of *CO intermediates. This strategic perspective has prompted companies such as LanzaTech and Twelve to focus their efforts on producing CO through electrochemical CO_2 reduction, while a growing body of research has focused on electrochemical CO reduction [13,14].

3. Commercialization pathways of C₁ products

The burgeoning interest in CO for its potential to generate high-value C_{2+} products, which have a substantial market size and value, has overshadowed the role of HCOOH in CO_2 catalysis research. This overshadowing is largely due to the limited market capacity of HCOOH. However, contextualizing this within the broader framework of renewable energy limitations is crucial. Presently, the global production of CO stands at approximately 150 million metric tons per year [15], marked by a predominantly centralized production structure. For example, the world's largest CO production pipeline network, designed by Air Products, has a capacity of 70 million standard cubic feet per day (MMSCFD) [16]. If the entire CO production process was to shift to an electrochemical method—assuming a cell voltage of 3 V and 90% FE—the annual energy consumption would be approximately 950000 GWh. Importantly, although the global cumulative renewable energy capacity is projected to exceed 4500 GW by the end of 2024 [17], these sources are predominantly decentralized. For example, Bhadla Solar Park,

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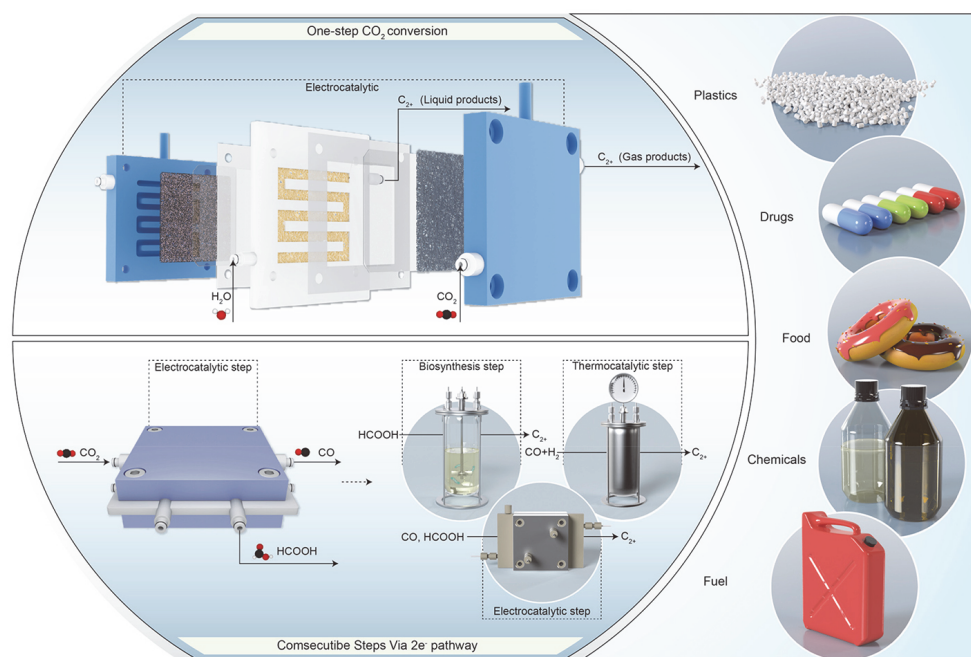
Fig. 1. Key principles and potential applications of electrochemical CO_2 reduction for the production of chemicals and fuels *via* direct ECR (top) and direct $2e^-$ C_1 pathways (bottom).

the world's largest solar power plant, has a capacity of only 2245 MW; when considering a capacity factor of 25%, its effective output falls significantly short of the energy demands required for a 70 MMSCFD CO production plant. Integrating decentralized renewable sources into the grid introduces new complexities, such as maintaining power quality, managing subsynchronous oscillations, and compensating for reactive power, all of which are not considered in the current TEA analysis [18].

If we assume a current density of 500 mA/cm² and an FE of 90%, the production of the required amount of CO would necessitate an electrolyzer area exceeding 60 million square meters; such a vast land area could potentially cause cropland loss [19], and the cost becomes significant. Given the challenges associated with scaling up modularly designed electrolyzers, if the size of one electrolyzer is taken to be 10 × 10 cm², it requires more than 6 billion electrolyzers. Even with the possibility of scaling up electrolysers and adapting designs from current water electrolysers, considerable challenges remain. Specifically, to achieve this transition, nearly half of the anticipated global electrolyzer capacity, which is projected to potentially reach 170–365 GW by 2030 [17], would need to be allocated to CO electrolysis within the next five years. This substantial allocation does not even consider the broader and more complex transition needed for the entire petrochemical industry, especially for C_{2+} products involving more electron transfers and exhibiting a much lower FE. Moreover, this challenge is compounded given that the current focus on hydrogen decarbonization itself is growing and that water electrolysis technology is more mature than CO electrolysis. Moreover, the scenario is further complicated because of the superior energy conversion efficiency and the current market price of H_2 compared with those of CO [20]. Therefore, while the interest in CO is under-

standable, the feasibility of its large-scale electrochemical production must be critically assessed in the context of near-term renewable energy capabilities and competing demands. In addition, developing scalable catalyst synthesis methods, optimizing reactor designs for better gas-liquid contact and creating robust membranes to withstand harsh operating conditions are all significant challenges in later stages.

The annual production of HCOOH is approximately 1300 kilotons [21], equating to an energy consumption of approximately 5460 GWh (cell voltage of 3 V, 90% FE). This production level utilizes a comparatively smaller portion of the current market's electrolyzer capacity. Consequently, given the limitations of electricity and electrolyzer capacity, HCOOH has emerged as a compelling option to showcase the industrial viability of CO_2 electrolysis. Diverging from CO production, which is focused primarily on centralized production, the commercialization and research of HCOOH production lean towards applications in fine chemicals. This strategic shift treats CO_2 as a valuable C_1 resource, targeting the development of higher-value products, even though these may cater to smaller market sizes. This orientation also makes HCOOH production less susceptible to fluctuations and policies in energy markets, offering a more stable and predictable pathway for profit maximization with decentralized CO_2 electrolyzers.

HCOOH, in its liquid form known for its safety and high energy density, holds substantial promise in fuel cell applications. HCOOH is considered a promising hydrogen carrier, which is significant in the context of the growing hydrogen economy. The last decade has seen remarkable progress in developing catalysts for efficient hydrogen generation from HCOOH under ambient conditions [22]. In addition, the increasing demand for formic acid as a preservative, its role in silage preservation, and the rising demand for natural rubber, which utilizes formic acid

in its production process. However, the full realization of formic acid's potential in large-scale applications, such as transportation and stationary power generation, is currently hampered by the pricing barrier, which is a consequence of its saturated production capacity. Advancing the production of HCOOH through CO_2 electrolysis could effectively address this bottleneck, facilitating broader application and opening new avenues for commercial exploitation.

Another promising area for downstream applications of HCOOH lies in biological upgrading. For example, 3-methyl-1-butanol, a fuel compatible with internal combustion engines, is produced from electrogenerated HCOOH [23]. Additionally, the efficient conversion of HCOOH into the fundamental cellular component of *Escherichia coli* has been successfully demonstrated [24]. The results showed that the use of microbial cell factories to efficiently utilize HCOOH as a feedstock and for the synthesis of target compounds offers a promising avenue for promoting sustainable agricultural practices. Using HCOOH as a source of hydrogen, various biomass-derived platform molecules, such as levulinic acid, furfural, 5-hydroxymethylfurfural, and glycerol, can also be converted into an array of valuable chemicals and fuels [25]. With the rapid growth of the synthetic biology market, additional explorations of artificially engineered HCOOH-utilizing microbes are needed. Furthermore, the recent demonstration of electrochemically upgrading HCOOH to formamide through the co-reduction of nitrite exemplifies the potential of HCOOH as a starting point for producing a diverse array of appealing products and building blocks. Delving into various reactions, such as formylation, methylation, hydrogenation, deoxygenation, and cyclization, enabled by the unique chemical structure of HCOOH, opens up the possibility of its electrochemical transformation into a multitude of valuable compounds.

4. The perspective

In the landscape of commercializing CO_2 electrolysis, C_1 products such as CO and HCOOH stand out as the most promising candidates. However, a critical assessment is needed to determine the most effective way to commercialize CO_2 electrocatalysis: does it align better with large-scale chemical production or decentralized, smaller-scale fine chemical manufacturing? Large-scale chemical production is characterized by lower profit margins per unit, necessitating expansive, centralized production to achieve substantial financial returns. Conversely, a strategic alternative might be to target the production of high-value downstream products that, while moderate in scale, offer a higher profit per unit. In this context, the CO and HCOOH approaches represent two distinct but viable commercialization pathways. A dual approach could be the linchpin for fully unlocking the potential of CO_2 electrocatalysis, paving the way for a more sustainable and economically viable future.

Acknowledgments

Declaration of interests

The authors declare no competing financial interests.

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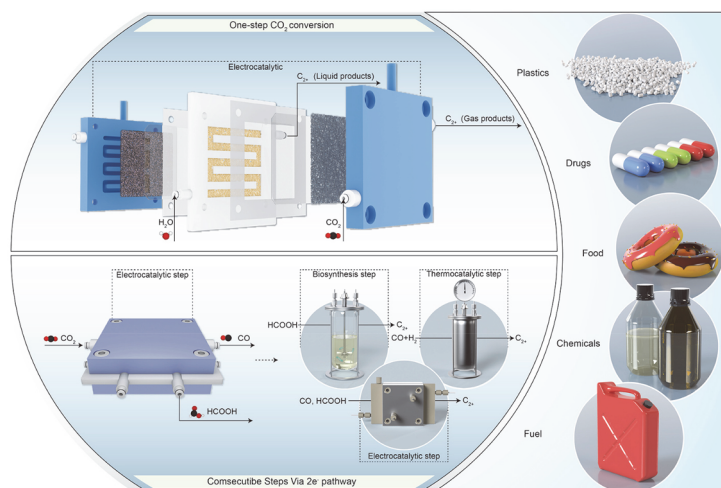
The article highlights the potential of converting CO₂ into valuable chemicals and fuels *via* electrochemical reduction, suggesting that a dual approach targeting CO and HCOOH could unlock the full potential of CO₂ electrocatalysis for a sustainable future.

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电化学二氧化碳还原的甲酸与一氧化碳商业化途径对比

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摘要: 电化学二氧化碳还原技术(ECRs)是一种利用可再生电能驱动CO_2转化为多种高值化合物的技术, 具有广阔的应用前景. 该技术有望以比石化产品更具竞争力的成本生产人类所需的燃料和关键化学品, 同时最大程度降低对环境的污染. 然而, 直接利用该技术将CO_2直接转化为多碳产物仍然面临着目标产物选择性低和催化剂稳定性差等难题. 为了推动ECRs技术的进一步商业化应用, 本文探讨了ECR技术中两电子($2e^-$)路径在商业化应用过程中的各自优劣及其商业化前景.

本文首先利用定量的技术经济分析(TEA), 比较了通过ECRs直接生产C_1产物相较于直接生产C_{2+}产物的优势. 从能量效率和经济性角度考虑, C_{2+}产物的转化过程中涉及更多的电子转移和质子耦合过程, 通常会有更高的反应动力学过电位, 因此整个过程具有更低的整体能量转换效率和单位摩尔电子经济性. 另一方面, 从生命周期评估(LCA)的角度来看, 直接生产C_{2+}产物会导致在反应界面上每单位产品会产生更高浓度的氢氧根离子, 加速由于碳酸盐形成导致的碳损失. 其次, 本文系统分析了两种主流C_1产品的商业化应用前景. 文章从长期市场容量和短期市场盈利两个角度分别分析了两种C_1产品在商业化过程中可能存在的问题. 其中, CO的大规模商业化应用要盈利的话, 需要大面积的电解槽. 考虑到目前对氢能的

关注日益增加, 且水电解技术比CO电解更为成熟, CO电解槽可能会面临产能不足的问题. 相较于CO, HCOOH的年产量约为1300千吨, 相当于约5460 GWh的能耗 (电池电压为3 V, FE为90%). 因此, 商业化产HCOOH仅需利用相对较小部分的当前市场电解槽产能. 其次, HCOOH下游应用的另一个有前景的领域在于生物升级. 例如, 从电生HCOOH中可进一步生产出与内燃机兼容的燃料3-甲基-1-丁醇. 利用HCOOH作为氢源, 还可以将各种生物质衍生的平台分子, 如戊二酸、糠醛、5-羟甲基糠醛和甘油, 转化为一系列有价值的化学品和燃料. 其次, 还可以深入研究HCOOH独特化学结构所支持的各种反应, 如甲酰化、甲基化、氢化、脱氧和环化等, 将为其电化学转化为多种有价值化合物提供更多可能性.

最后, 展望了两种路径分别在大规模化工合成和去中心化化学品生产两方面各自的独特优势. CO和HCOOH各自开辟了独特的商业化道路, 综合考虑其CO_2电催化的优劣势才能引领我们走向一个更可持续、经济效益更佳的未来.

关键词: 二氧化碳转化; 电化学还原; 两电子路径; 商业化前景