Future Energy

Tandem and Hybrid Processes for Carbon Dioxide Utilization

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As fossil fuels continue to dominate the energy portfolio, the atmospheric carbon dioxide (CO_2) concentration has exceeded 400 ppm, posing a major threat to our environment. Conventional chemical processes utilize fossil carbon sources to produce chemicals and fuels, which inevitably emit a tremendous amount of the greenhouse gas CO_2. To realize sustainable chemical production and to minimize environmental impacts, CO_2 captured from industrial sources and ambient air can serve as an alternative carbon source. A variety of CO_2 conversion technologies, including thermochemical, biological, and electrochemical approaches, are currently under development. Thermochemical hydrogenation processes are capable of converting CO_2 into single carbon (C_1) products such as methane, methanol, and carbon monoxide. These technologies have high technology readiness levels (TRL) compared to the electrochemical and biological approaches (Figure 1A) but use hydrogen primarily derived from methane through steam reforming, a process that emits CO_2.[1] Biological approaches, such as artificial photosynthesis and algae growth, suffer from high operational costs but are capable of producing long-chain C_2–C_6 products with high selectivity.[2] Electrochemical approaches, such as CO_2 electrolysis, have the unique advantage of being able to operate using solely renewable electricity. With renewable electricity becoming steadily more available and affordable, CO_2 electrolysis can effectively produce C_1 and C_{2+} products directly from CO_2 at rapid and cost-effective rates. Recent techno-economic analyses have found that the CO_2 electrolysis products formic acid, acetic acid, and ethylene are all very close to being economically viable, given the current trajectory of renewable electricity prices.[3] As a result, significant research should be invested in CO_2 electrolysis technologies to improve performance and deploy them for chemical manufacturing.

DIRECT CO_2 ELECTROLYSIS AT LOW TEMPERATURES

The performance of CO_2 electrolyzers has been improved significantly with the operational current density (reaction rate) approaching 1 A cm^{-2}.[4] However, CO_2 electrolyzers still suffer from several practical issues which stem from the reliance of CO_2 electrolyzers on alkaline electrolyte to achieve high reaction rates. The alkaline electrolyte together with locally generated hydroxide anions inevitably reacts with fed CO_2 to form carbonates at the electrode-electrolyte interface, which not only causes flooding issues for the electrodes but also results in low single-pass conversion of CO_2 toward desired products. Furthermore, if anion exchange membranes (AEM) are used, the carbonate (and bicarbonate) anions will cross the membrane and reach the anode chamber, requiring additional recycling and separation steps to be recovered as well as producing unwanted interactions with the anode. This also has the added issue of limiting CO_2 conversion to < 50% toward desired products.[4] Bipolar membrane (BPM) CO_2 electrolyzers could address this issue, as they do not suffer from the same crossover issues as AEM electrolyzers.[5] However, BPM-based electrolyzers suffer from high cell voltages and are still in the early stage of their development (TRL 2-3).

High-temperature CO_2 electrolyzers, using solid oxide (ceramic) based electrolytes, are another potential route for direct CO_2 electroreduction. These systems are mature (TRL 8) and have been demonstrated with thousands of hours of stability.[6] Since solid oxide electrolyzers do not rely on alkaline electrolytes to convert CO_2 to CO, carbonate formation is not an issue. However, these systems are only capable of directly converting CO_2 to CO. Solid oxide electrolyzers also suffer from coke formation at high CO_2 conversion, necessitating recycle loops and separation steps for the production of concentrated CO product streams.

Both low-temperature and high-temperature routes for CO_2 electrolysis suffer from significant limitations. The primary challenges of the two systems are that low-temperature CO_2 electrolysis is limited to < 50% conversion of CO_2 to products, while high-temperature electrolysis is limited to solely producing CO. To overcome these issues, tandem and hybrid processes (Figure 1B) including tandem electrocatalytic, tandem electrocatalytic-biological, tandem electrocatalytic-thermocatalytic, and reactive capture (coupling carbon capture with electrocatalytic conversion) processes are all potential options. Here, we present a brief discussion of each route to provide insights and stimulate more interest in the integration and hybridization of CO_2 electrolysis for practical applications as well as possible future research directions.

TWO-STEP TANDEM CO_2 ELECTROLYSIS PROCESS

The CO_2 electrolysis process can be conducted in two consecutive steps: CO_2 reduction to CO in a non-alkaline environment and then CO reduction to C_{2+} products in an alkaline electrolyte (Figure 2A). CO_2-to-CO in non-alkaline conditions benefits from reduced formation of carbonate species as well as > 90% selectivity toward CO.[4] This CO will then be fed to a CO electrolyzer, which has recently been demonstrated to be capable of reaching > 90% selectivity toward C_{2+} products as well as > 1 A/cm^2 operating current densities.[8] Moreover, the CO electrolyzer also showed a unique ability to produce acetate selectively using a Cu nanosheet catalyst (Figure 2B).[9] This is a significant improvement in selectivity toward C_{2+} products compared to direct CO_2 electrolysis, especially when carbonate formation is

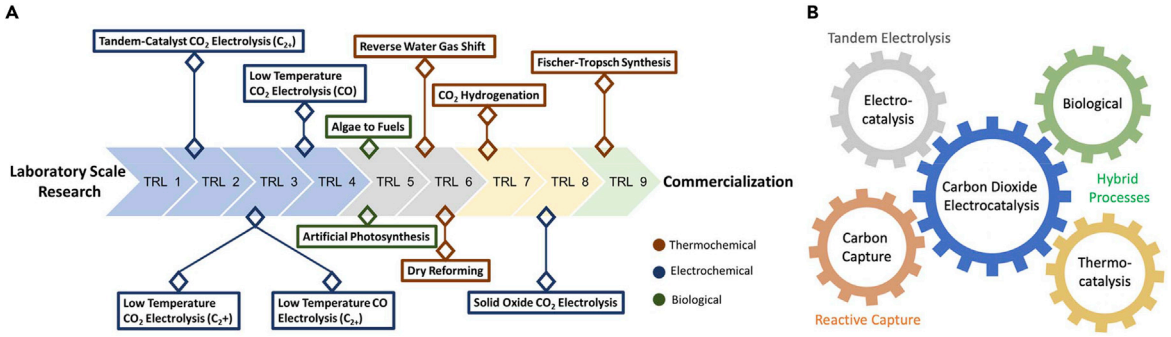

Figure 1. Independent and Tandem Processes for CO_2 Conversion

(A) Current TRL of various CO_2 utilization technologies compiled from Jarvis and Samsalti (2018)[1] as well as Roh et al. (2020).[2]

(B) Concepts of tandem and hybrid processes for CO_2 utilization.

taken into account. Currently, CO_2 electrolyzer and CO electrolyzer have TRLs of 4 and 3, respectively.

The feasibility of two-step tandem CO_2 electrolysis has been demonstrated experimentally by Romero Cuellar and coworkers, who reported a total CO_2 reduction current density of 300 mA/cm^2 with a cumulative Faradaic efficiency of 62% toward C_{2+} products.[10] While this is an excellent proof of concept, the system is far from optimized when compared to standalone CO_2 and CO electrolysis technologies. Low CO_2 conversion in the first reactor led to a scrubber being necessary to remove excess CO_2 before the CO electrolyzer, vastly reducing the conversion of fed CO_2 to C_{2+} products. A CO_2/CO membrane separator could provide a more sustainable option for product stream purification, as CO_2 would not have to be recovered from the scrubber after capturing, thus allowing for steady-state operation. Even with a CO_2/CO separator, a significant improvement in single-pass conversion of CO_2 is still necessary. Most CO_2 research now operates at extremely low single-pass conversion of CO_2, which is not industry viable. Future research efforts should focus on maximizing CO_2 conversion to CO to minimize the energy requirement for separating unreacted CO_2 from the product stream. A potential route for this could be a renewed focus on CO_2 delivery to the catalyst surface. Improvements in flow cell design and catalyst layer design (i.e., porosity) could significantly improve CO_2 conversion by allowing a higher percentage of fed CO_2 to be reacted.

Even with a 100%-efficient CO_2 electrolyzer, CO_2 conversion to desired products will always be limited to 50% in a low-temperature CO_2 electrolyzer.[4] This issue could be addressed by utilizing CO produced from more mature renewable technologies such as solid oxide electrolysis (TRL 7–8) or the reverse water-gas shift reaction (TRL 6). This would also decrease the risk associated with CO electrolysis, as the CO feed would be from a well-established process. However, these processes will require more complicated integration due to the large differences in operating conditions between the high-pressure and -temperature thermal reactors and the low-temperature and -pressure CO electrolyzer. Improvements on current CO electrolysis technologies, such as increased selectivity toward a single product and long-term stability, will be necessary before it can be considered to be coupled with these mature reactors. Research efforts should be focused on first improving CO electrolysis performance and then on the coupling of the CO electrolyzer with these mature technologies.

BEYOND TANDEM ELECTROLYSIS—HYBRID PROCESSES

A major challenge of CO_2 electrolysis is the production of chemicals containing more than two carbon atoms per molecule in a selective manner. In comparison, biological carbon utilization technologies can selectively produce valuable C_4–C_6 carboxylic acids and their corresponding alcohols as biofuel precursors. However, biological processes often suffer from slow production rates and the complexity of co-culturing multiple organisms. To improve upon these rates, a hybrid approach that combines easily scalable CO_2 electrolysis and biological upgrading could be utilized. Recently, the feasibility of the electrocatalytic-biological hybrid process was reported, where CO_2 and H_2O were electrocatalytically converted into synthesis gas (i.e., a mixture of CO and H_2) followed by a biological upgrading process to produce butanol and hexanol using a bacteria solution containing *C. autoethanogenum* and *C. kluyveri*.[11] The production rate of butanol and hexanol by these microorganisms is significantly boosted in the presence of CO, as compared to CO_2 and H_2 alone. Future efforts in this area will be required to

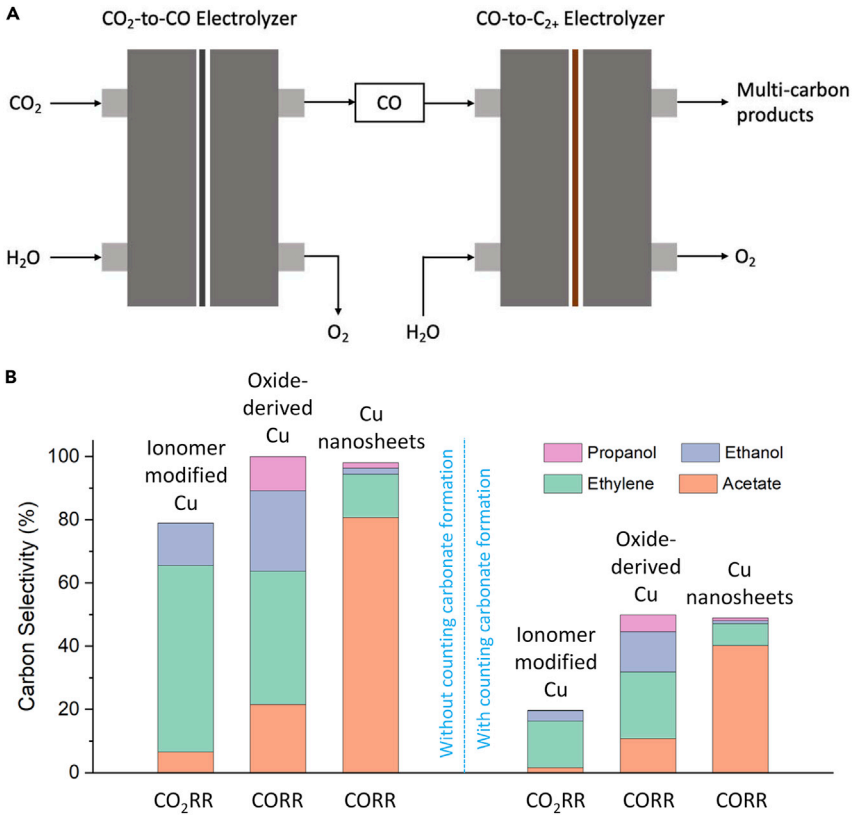

Figure 2. CO_2 Conversion to Multi-Carbon Products

(A) Schematic diagram of the two-step tandem CO_2 electrolysis process and (B) state-of-the-art performances for the CO_2 reduction reaction (CO_2RR) and CO reduction reaction (CORR). Carbon selectivity is defined as the amount of carbon in the desired product(s) divided by the theoretical total amount of CO_2 consumed in the reactor at 100% conversion of fed CO_2. Data originate from García de Arquer et al. (2020),[7] Jouny et al. (2018),[8] and Luc et al. (2019).[9]

address the solubility issue of synthesis gas in the aqueous media of the biological reactor. An alternative CO_2 reduction product, formate, has also been investigated, which overcomes these solubility limitations. However, only a select few bacteria are capable of using formate as their carbon source, emphasizing the need to find a compatible and soluble CO_2 electrolysis product that can be further upgraded through biological means.

The CO_2 electrolysis process can also be coupled with a thermocatalytic process to produce chemicals that cannot be obtained by CO_2 electrolysis alone. For instance, the synthesis gas produced through the CO_2 electrocatalytic process could be fed into the Fischer-Tropsch process for synthetic fuel productions. This process can be done most efficiently by coupling Fischer-Tropsch with a high-temperature solid oxide CO_2 electrolyzer and solid oxide water electrolyzer.[12] With similar operating conditions and high maturity, this system could be rapidly deployed to sustainably convert CO_2 into liquid fuels.

REACTIVE CARBON CAPTURE

Instead of coupling two carbon conversion steps in a tandem and/or hybrid process, a reactive carbon capture approach can be employed to combine a CO_2 capture step with a CO_2 conversion step. In this concept (outlined in Figure 3), once the CO_2 capture materials bind to CO_2, they do not release CO_2 through an energy-intensive desorption process, but rather act as an electrolyte additive to carry the captured CO_2 molecules to the catalytic sites for the subsequent electrochemical CO_2 reduction. After the conversion step, the CO_2 capture materials are regenerated for the next CO_2 capture cycle. By doing so, the overall energy demand for CO_2 capture and conversion could be significantly reduced.

For conventional amine-based solvents that capture CO_2 through the exothermic formation of carbamate species ($\Delta H = -80$ kJ/mol), the resulting carbamates are not electrochemically active. Owing to the high CO_2 capture capacities and charged nature, novel materials such as nanoparticle organic hybrid materials and ionic liquids have been suggested as attractive candidates for reactive carbon capture. They can be designed via CO_2 binding energy optimization. Recent studies have shown that these novel electrolyte materials can improve CO_2 conversion rates as well as product distributions.[13] For example, Park and coworkers showed that the reactivity of nanoparticle organic hybrid materials bound to CO_2 is distinct from free CO_2, illustrating the potential co-catalytic role of nanoparticle organic hybrid materials during electrochemical CO_2 conversion.[14] Further research is required in this direction to gain a better fundamental understanding of the properties of these electrolyte materials and to develop integrated reactive systems that are able to capture CO_2 and *in situ* convert it to desired products in an energy-efficient way.

FINAL REMARKS

Tandem and hybrid processes for CO_2 utilization are promising future directions that have great potential in creating alternative routes in sustainable chemical manufacturing and renewable energy storage sectors.

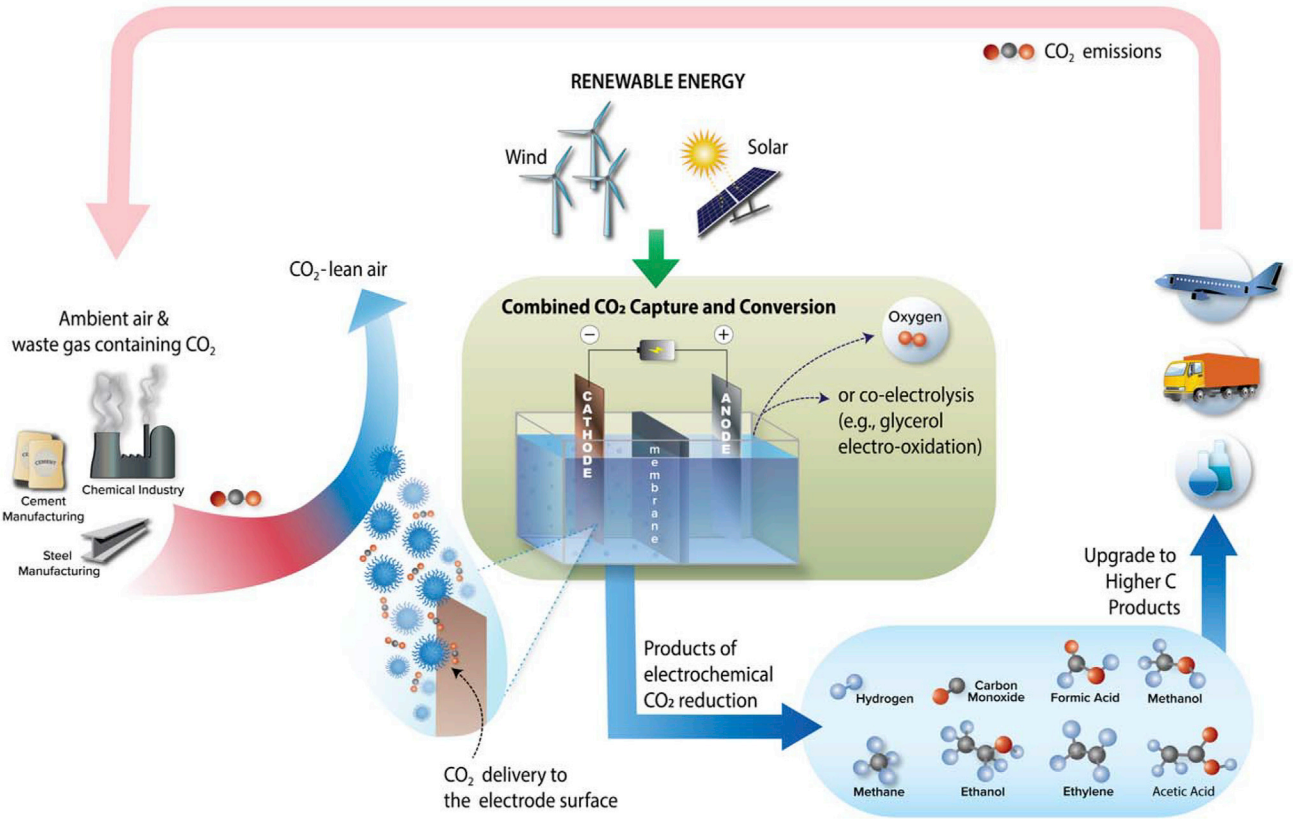

Figure 3. Combined CO_2 Capture and Conversion Approach Using Novel Electrolyte Materials

However, the present readiness level of the electrochemical components, besides solid oxide electrolysis, is relatively low. As a result, significant work needs to be done to address critical challenges such as long-term stability, product selectivity, and cost-competitiveness over existing industrial processes. Combining CO_2 electrolysis, a low TRL process, and a more mature process (e.g., thermochemical CO_2 hydrogenation and high-temperature CO_2 electrolyzer) could substantially accelerate the research and development process to reach a high TRL. Additionally, the tandem and hybrid strategy also creates new opportunities and flexibility to target more valuable products that cannot be produced through a single-step process.

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DECLARATION OF INTERESTS

A.-H.A. Park is an Advisory Board member of *Joule*.

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