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Renewably powered electrochemical CO₂ reduction toward a sustainable carbon economy

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The scale of global energy consumption and manufacturing demands continues to increase, leading to dangerous emission and accumulation of CO₂ from the prevalent use of fossil fuels. The average atmospheric CO₂ concentration in 2022 was 417.2 parts per million (ppm) and is forecast to be 419.2 for 2023. This will bring about increasingly severe climate change and catastrophic effects for human society in unprecedented and in some cases, irreversible, ways. Note that the last time CO₂ levels exceeded 400.0 ppm was four million years ago, with a global temperature 2.0–4.0 °C warmer and a 10.0–25.0 meter higher sea level than today. To alleviate this continued warming (with an international goal <2.0 °C), a massive concerted effort is ongoing to develop CO₂ capture and sequestration technologies, and to implement strategies that improve combustion efficiency to attenuate CO₂ emissions.¹ At the same time, CO₂ is recognized as a nontoxic, inexpensive, and sustainable C₁ carbon source. Converting CO₂ directly into fuels and useful chemicals by harnessing renewable and clean energy, enables a transition from a fossil-based to a low- or net-zero-emission carbon economy. Electrochemical CO₂ reduction (ECR) is one such appealing route for driving CO₂

chemical transformation, using water or other low-cost feedstocks as a source of protons without the need for fossil fuels and H₂.² CO₂ electro-valorisation also has the benefit of not requiring centralized infrastructure, and thus can provide the ability to store intermittent and distributed renewable sources in a chemical energy product.

ECR was first attempted as early as the 1950s.³ A subsequent work by Hori and co-workers in the 1980s addressed the quantification of the gaseous and liquid products.⁴ After being static for nearly 10 years, the field was re-ignited in 2010 with the decreasing price of renewably generated electricity following the works by Peterson *et al.*⁵ and Schouten *et al.*⁶ Over the past three decades, a large body of research has been concentrated on searching for and developing advanced electrocatalysts to boost the rate (catalytic current density), efficiency (overpotential), selectivity (or faradaic efficiency, FE), and stability of CO₂ conversion.⁷

State-of-the-art ECR performance

Over 16 reduction products have been identified from CO₂ electrolysis. Carbon monoxide (CO) and formic acid/formate (HCOOH/HCOO[−]), which requires two electron/proton transfers, can be selectively produced from ECR with

a corresponding FE approaching 100.0% using single-atom catalysts⁸ and Bi-based materials,⁹ respectively.

Other C₁ or C–C coupled products need transfers of 6–18 or more electrons and protons. A Cu-based metal–organic framework [Cu₄ZnCl₄(btdd)₃] (Cu₄-MFU-4l, H₂btdd = bis(1*H*-1,2,3-triazolo-[4,5-*b*], [4',5'-*i*])dibenzo-[1,4]-dioxin) was reported to enable selective reduction of CO₂ to methane (CH₄) in neutral aqueous electrolytes, yielding an FE of 92.0%/88.0% and a respectable partial current density of −9.8/−18.3 mA cm^{−2} at −1.2/−1.3 V (*versus* (vs.) reversible hydrogen electrode (RHE)).¹⁰ The largest FE for methanol (CH₃OH) formation has been up to 97.0%, albeit with a very low partial current density (∼−0.6 mA cm^{−2}), at −0.98 V (vs. saturated calomel electrode) on a Co(CO₃)_{0.5}(OH)·0.11H₂O catalyst.¹¹ In an ionic liquid aqueous solution ([Bmim]BF₄/H₂O), the CH₃OH partial current density can be improved to −67.0 mA cm^{−2} at −2.0 V (vs. Ag/AgCl) on Sn-modified defective CuO.¹² The maximum FE toward ethanol (C₂H₅OH) also exceeds 90.0% with a small cathodic reduction current density (∼−1.1 mA cm^{−2}) at −0.6 V (vs. RHE) on hydroxyl group-stabilized Cu_{3–4} clusters.¹³ The highest partial current density for the C₂H₅OH product was up to −423.3 mA cm^{−2} under −0.56 V (vs. RHE) on F and K co-modified Cu.¹⁴

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Attaining ECR products with two or more carbons can pose a significant challenge. A conductive two-dimensional copper phthalocyanine-based covalent organic framework was demonstrated to catalyse the ECR to acetate (CH_3COO^-) with an FE of 90.3% at -0.8 V (vs. RHE).¹⁵ Even greater efficiency has been achieved on indium using a Keggin type POM [$\text{SiW}_9\text{V}_3\text{O}_{40}$]⁻ (SiW_9V_3) as a catholyte, with an unprecedented CH_3COO^- FE as high as 96.5% at -0.7 V (vs. RHE).¹⁶ Selective production of acetaldehyde (CH_3CHO) with an FE of 60.0% was obtained at -0.4 V (vs. RHE) using hexagonal-close-packed Co nanosheets.¹⁷ To produce ethylene glycol ($(\text{CH}_2\text{OH})_2$) from ECR, the two oxygen atoms in CO_2 need to be retained. This has been accomplished using an imidazolium ion-terminated self-assembled monolayer-modified Au electrode, affording a $(\text{CH}_2\text{OH})_2$ FE of 87.0% at -0.58 V (vs. RHE).¹⁸ Compared to other C_{2+} products, ethylene (C_2H_4) is more easily fabricated at a high reduction rate, with an FE of 84.5% at -200 mA cm^{-2} on Cu/Cu₂O interfaces in a flow cell.¹⁹ On a nitrogen-doped $\gamma\text{-Fe}_2\text{O}_3$ electrocatalyst, ethane (C_2H_6) was obtained as the major product with an FE of 42.0% and partial current density of -32.0 mA cm^{-2} at -2.0 V (vs. Ag/Ag^+) in an H-cell.²⁰

The production of propylene (C_3H_6) has been rarely reported, which is due to the kinetic barriers associated with transferring the necessary 18 electrons and the easy desorption of the allyl alkoxy ($\text{CH}_2=\text{CHCH}_2\text{O}$) intermediate in an alkaline microenvironment, causing an unfavourable yield of C_3H_6 .²¹ A partial current density of ~ -5.5 mA cm^{-2} toward C_3H_6 formation with an FE of $\sim 1.2\%$ was achieved at -0.65 V (vs. RHE) on Cu nanocrystals consisting of Cu(100) and Cu(111) facets.²¹ To date, the FE toward *n*-propanol ($\text{C}_2\text{H}_5\text{CH}_2\text{OH}$) is less than 30.0%, with an absolute partial current density < 26.2 mA cm^{-2} .²² C_3 and C_4 oxyhydrocarbons of methylglyoxal (CH_3COCHO) and 2,3-furandiol have been produced on nickel phosphides with FEs reaching 84.0% and 70.0%, respectively.²³ But the absolute partial reduction current densities in both cases are lower than 1.0 mA cm^{-2} . Likewise, although high-value *n*- $\text{C}_4\text{H}_9\text{OH}$,²⁴ 3-

hydroxybutanal ($\text{CH}_3\text{CHOHCH}_2\text{CHO}$),²⁴ and *t*- $\text{C}_4\text{H}_9\text{OH}$ ($(\text{CH}_3)_3\text{COH}$)²⁵ products have been detected from ECR with an FE of 42.0%, 23.0%, and 14.8%, respectively, the corresponding absolute cathodic current densities in all cases is less than 0.5 mA cm^{-2} .

What's next for CO_2 electrolysis

Given the strikingly rapid decrease in the price of renewable electricity, CO_2 electrolysis could be a cost-competitive technology to produce desired commodity chemicals in future global markets. Currently, the conversion of CO_2 into CO is close to commercialization with designed pilot-scale electrolyzers. A zero-gap cell enables a CO FE of 97.0% at -200.0 mA cm^{-2} for over 3500.0 h at room temperature. The cathodic currents can be further improved to -1.5 A cm^{-2} by mildly lifting the electrolyser pressure and circulating alkaline aqueous solution through the anode. To enable this commercial transition, there are several threads of development that should be considered:

(i) Practically, waste CO_2 from steel and cement fabrication and power plant flue gas (containing SO_x and NO_x impurities), or even atmospheric CO_2 , would likely need to be utilized instead of pure CO_2 . As a result, efficient and robust catalysts that can continue to function effectively in the presence of inevitable contaminants need to be developed.

(ii) To facilitate large-scale application of CO_2 -to- C_{2+} electrolysis, the energy penalties associated with electrolyzers and downstream separations need to be substantially reduced. To this end, boosting the selectivity for a target product and coupling with an alternative anode reaction with a lower positive equilibrium potential compared to the oxygen evolution reaction (OER) is desirable. Replacing the OER with a liquid-phase anodic process, such as the oxidation of 5-hydroxymethylfurfural, glycerol, other biomass polyols, and glucose, are especially preferred. This can result in high-purity re-generated CO_2 at the anode, allowing for its direct recycling to the cathode to increase carbon

utilization. However, for these alternative anodic reactions to be practically used, the separation of the anode products from the anolyte needs to be considered.

(iii) Performing ECR with acidic electrolytes would help alleviate $\text{CO}_3^{2-}/\text{HCO}_3^-$ formation and the loss of carbon efficiency that is found with alkaline and neutral electrolytes. This necessitates the design of a bimetallic Cu catalyst by maximizing the co-adsorption of CO and CO_2 while suppressing H binding, or creating asymmetric $\ast\text{CO}$ adsorption and coverage on binary sites.

(iv) Membrane-electrode assemblies (MEAs) can greatly reduce ohmic resistance (from the catholyte) and improve current density permitting an industrial scale-up. Membranes that possess stability and high conductivity, while also maintaining highly selective diffusion, need to be developed for MEAs.

(v) A cascade reactor could be utilized to convert CO_2 first to CO in an electrolyser, with the CO then further reduced to C_{2+} products (such as $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$) in a second electrolyser. This can enhance CO_2 conversion and enable a high C_{2+} selectivity at industrially relevant current densities.

(vi) Fundamental research, which diagnoses the reaction kinetics and pathways, microenvironments, and the nature of catalytic active sites will aid in the design of electrolyzers and the optimization of operation conditions.

To expedite the commercialization of CO_2 electrolysis, a system sustaining over 1000.0 h of stable operation at high current densities should be realized before implementation of a pilot plant. Note that for industrial-scale CO_2 electrolyzers, the electrode areas are usually larger than 5.0 cm^2 , causing heating issues at high current densities. This effect on stability needs to be considered when looking at industrial scale-up of laboratory level reactors. Beyond C_2 and C_3 products, the conversion of CO_2 to C_{4+} products remains a challenge, however the coupling of electrolysis and biocatalytic fermentation processes appears attractive for the production of long-chain fuels and chemicals.



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