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Renewably powered electrochemical CO_2 reduction toward a sustainable carbon economy

Zhenyu Sun*

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The scale of global energy consumption and manufacturing demands continues to increase, leading to dangerous emission and accumulation of CO_2 from the prevalent use of fossil fuels. The average atmospheric CO_2 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 CO_2 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 CO_2 capture and sequestration technologies, and to implement strategies that improve combustion efficiency to attenuate CO_2 emissions.[1] At the same time, CO_2 is recognized as a nontoxic, inexpensive, and sustainable C_1 carbon source. Converting CO_2 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 CO_2 reduction (ECR) is one such appealing route for driving CO_2 chemical transformation, using water or other low-cost feedstocks as a source of protons without the need for fossil fuels and H_2.[2] CO_2 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 CO_2 conversion.[7]

State-of-the-art ECR performance

Over 16 reduction products have been identified from CO_2 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 catalysts[8] and Bi-based materials,[9] respectively.

Other C_1 or C–C coupled products need transfers of 6–18 or more electrons and protons. A Cu-based metal–organic framework $[Cu_4ZnCl_4(btdd)_3]$ (Cu_4-MFU-4l, H_2btdd = bis(1*H*-1,2,3-triazolo-[4,5-*b*],[4′,5′-*i*])dibenzo-[1,4]-dioxin) was reported to enable selective reduction of CO_2 to methane (CH_4) 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 (CH_3OH) 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 $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ catalyst.[11] In an ionic liquid aqueous solution ($[Bmim]BF_4/H_2O$), the CH_3OH 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 (C_2H_5OH) 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 C_2H_5OH product was up to −423.3 mA cm^{-2} under −0.56 V (*vs.* RHE) on F and K co-modified Cu.[14]

State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: zhenyus@mail.buct.edu.cn

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 $[SiW_9V_3O_{40}]^-$ (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 ($(CH_2OH)_2$) 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 $(CH_2OH)_2$ 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/Cu_2O interfaces in a flow cell.[19] On a nitrogen-doped γ-Fe_2O_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 ($CH_2{=}CHCH_2O$) 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 ∼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 ($C_2H_5CH_2OH$) 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-furanediol 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*-C_4H_9OH,[24] 3-hydroxybutanal ($CH_3CHOHCH_2CHO$),[24] and *t*-C_4H_9OH ($(CH_3)_3COH$)[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 electrolysers. 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 electrolysers 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 CO_3^{2-}/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 *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 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 CH_3COOH/CH_3COO^-) 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 electrolysers 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 electrolysers, 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 bio-catalytic fermentation processes appears attractive for the production of long-chain fuels and chemicals.

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