

## Continuous-flow electroreduction of carbon dioxide



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### ABSTRACT

Solar fuel generation through electrochemical CO<sub>2</sub> conversion offers an attractive avenue to store the energy of sunlight in the form of chemical bonds, with the simultaneous remediation of a greenhouse gas. While impressive progress has been achieved in developing novel nanostructured catalysts and understanding the mechanistic details of this process, limited knowledge has been gathered on continuous-flow electrochemical reactors for CO<sub>2</sub> electroreduction. This is indeed surprising considering that this might be the only way to scale-up this fledgling technology for future industrial application. In this review article, we discuss the parameters that influence the performance of flow CO<sub>2</sub> electrolyzers. This analysis spans the overall design of the electrochemical cell (microfluidic or membrane-based), the employed materials (catalyst, support, etc.), and the operational conditions (electrolyte, pressure, temperature, etc.). We highlight R&D avenues offering particularly promising development opportunities together with the intrinsic limitations of the different approaches. By collecting the most relevant characterization methods (together with the relevant descriptive parameters), we also present an assessment framework for benchmarking CO<sub>2</sub> electrolyzers. Finally, we give a brief outlook on photoelectrochemical reactors where solar energy input is directly utilized.

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**Abbreviations:** BID, Barrier ionization discharge detector; CO<sub>2</sub>, Carbon dioxide; R<sub>cell</sub>, Cell resistance; R<sub>ct</sub>, Charge transfer resistance; CB, Conduction band; CV, Cyclic voltammetry; DEMS, Differential electrochemical mass spectrometry; EIS, Electrochemical impedance spectroscopy; EC, Electrochemical; EDX, Energy-dispersive X-ray spectroscopy; FE, Faradaic efficiency; FT-IR, Fourier transform infrared spectroscopy; GC, Gas chromatography; GDEs, Gas diffusion electrodes; GDL, Gas diffusion layer; LSV, Linear sweep voltammetry; MEAs, Membrane electrode assemblies; NMR, Nuclear magnetic resonance; OER, Oxygen evolution reaction; PC, Photochemical; PEC, Photoelectrochemical; PV, Photovoltaic; PVA, Poly(vinyl alcohol); PEM, Polymer electrolyte membrane; SEM, Scanning electron microscopy; SC, Semiconductor; STH, Solar-to-hydrogen; SOE, Solid-oxide electrolyzers; Rs, Solution resistance; SCCM, Standard cubic centimeters per minute; SPEEK, Sulfonated poly(ether ether ketone); 3D, Three-dimensional; TEM, Transmission electron microscopy; UV, Ultraviolet; R<sub>u</sub>, Uncompensated resistance; VB, Valence band; XRF, X-ray fluorescence spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray powder diffraction

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## 1. Introduction

Finding adequate solutions for a diversified and sustainable energy supply is undoubtedly one of the grand challenges of our society today [1]. It is imperative that renewable energy sources and solar/wind energy in particular, are increasingly used to improve the security of energy supplies and also ameliorate the environmental impact from carbon-based energy production and consumption. While solar and wind electricity generation already enjoy an important, and impressively increasing role in the global (and especially European) energy mix, *storage* is still an issue because of the intermittency of most renewable energy sources [2]. At the same time, the steeply rising level of carbon dioxide (CO<sub>2</sub>) in the atmosphere calls for conceptually new approaches to capture and utilize this greenhouse gas. A solar fuels-based economy tackles the above parallel challenges admirably well, although many challenges remain before widespread use of such energy carriers (e.g., H<sub>2</sub>, methanol, ethanol, and methane) sees the light of day.

CO<sub>2</sub> is a greenhouse gas; therefore using renewable energy to convert CO<sub>2</sub> to transportation fuels and commodity chemicals is a value-added approach to simultaneous generation of products and environmental remediation of carbon emissions. The large amounts of chemicals produced worldwide (Fig. 1) that can be potentially derived from the hydrogenation of CO<sub>2</sub>, highlights further the importance of this strategy. Several industrial entities are interested in such technologies, ranging from energy/utilities companies through cement producing and processing firms to oil and gas companies.

There are numerous routes for converting CO<sub>2</sub> to transportation fuels and other chemicals. The following three major pathways delineate how *sunlight* can be used to generate such products (e.g., CH<sub>4</sub> or CH<sub>3</sub>OH) from CO<sub>2</sub> (Fig. 1) [2–7].

*Photochemical (PC) or photosynthetic methods:* Directly use sunlight to photochemically convert CO<sub>2</sub> to fuels using molecular- or suspended semiconductor (SC) photocatalysts [8–10].

*Electrochemical (EC) approaches:* Here sunlight is first converted to electricity by a photovoltaic solar cell (PV) and CO<sub>2</sub> is then reduced electrochemically [11,12].

*Photoelectrochemical (PEC) route:* Photogenerated electrons are utilized to reduce CO<sub>2</sub> either directly at a SC/electrolyte interface or indirectly employing a redox mediator [13].

With the recent rapid drop in the cost of Si solar cells, the price of solar electricity has decreased to a level that in over 20 countries translates to grid parity. A recent study concluded that on a 20–25 year term it is not likely that any solar energy utilization pathways other than Si solar photovoltaic panels will have an industrially-relevant role [14]. Another techno-economic analysis suggested that PV+EC conversion setups may attain ~14% solar to H<sub>2</sub> efficiency (20% PV, 70% EC) in an economically feasible manner as the electricity price drops (which is clearly the case for both solar and wind power) [4]. These factors suggest that CO<sub>2</sub> conversion, at least on a short to intermediate term, will be driven in an EC configuration (note also the availability of other renewable electricity sources, such as wind). On a longer term basis, the PEC strategy also cannot be ruled out and in fact, further extensive research work is highly encouraged [4].

Electrochemical (EC) and photoelectrochemical (PEC) conversion of CO<sub>2</sub> are multi-electron in nature (up to 8 e<sup>-</sup> for conversion to methane) with considerable kinetic barriers to electron transfer. It therefore requires the use of carefully designed electrode surfaces to accelerate electron transfer rates to levels that make practical sense. In this vein, much has been written about the electrochemical, solid-state physics, theoretical, catalytic, and general materials science aspects of EC/PEC CO<sub>2</sub> reduction [15–17]. During the past 5 years, however, an accelerated progress has occurred, reflected in the number of published research articles and the citations they attracted (Fig. 2). Most of this work has focused on the development of new catalysts [18] and the enhancement of product selectivity [11,19]. Excitingly, we appear to be at the very cusp of a new era of electrochemical CO<sub>2</sub> conversion studies, which hopefully will lead to efficient CO<sub>2</sub> electrolyzers on a practical scale.

At this juncture, however, it has to be noted that CO<sub>2</sub> reduction is a lot more complex than water splitting, simply because many different products can be formed via proton-coupled multi-electron transfer [20]. To drive this process in an economically attractive way, it is important to produce (i) any product as selectively as possible; (ii) products of economic value; and (iii) products that are easy to separate. A recently-performed techno-economic analysis on the process suggested that the picture is even murkier, because co-producing a low value product (such as methanol or ethylene) together with a high value product (such as formic acid or carbon-monoxide) can be a better strategy than producing them alone. In fact, the optimal scenario would be to co-produce two products that are in different phases (i.e., one in the liquid phase and the other in the gas phase) as the separation process becomes straightforward in this case [21].

In addition, since the redox potential for proton to H<sub>2</sub> transformation is very close to the redox potential of the desired CO<sub>2</sub> reduction processes, there is always a competition between these two processes. Furthermore, although thermodynamic considerations would allow reduction of CO<sub>2</sub> at moderately negative potentials, electrochemical reduction of CO<sub>2</sub> is kinetically daunting with high overpotentials needed for its conversion to hydrocarbons and alcohols. Finally, in a simple batch reactor, the maximum achievable rate

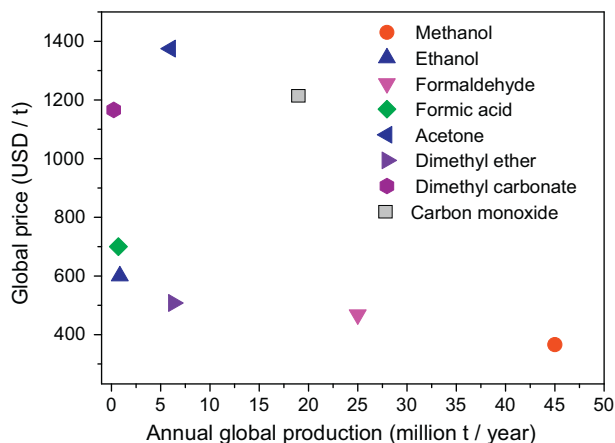


Fig. 1. Global market of the most important CO<sub>2</sub>-utilization products.

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