

# Electrocatalytic CO<sub>2</sub> Conversion in Flow Cells

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## ABSTRACT

The electrocatalytic conversion of CO<sub>2</sub> at ambient temperatures and pressures provides a potential means to convert excess renewable electricity into useful fuels and chemicals. Targeting liquid fuel precursors is particularly compelling because seasonal energy storage and distribution could be achieved with minimal overhaul of our existing fuel infrastructure. CO<sub>2</sub> electrolyzer development is, however, still in the very early stages, and requires innovative chemical and engineering strategies to achieve the high current densities with inexpensive materials that would be needed in a commercial unit. We herein survey some of the fundamental studies that have been performed on lab-scale CO<sub>2</sub> flow cells that offer the next tangible stepping stone towards electrolyzer commercialization.

**Keywords:** electrolysis, CO<sub>2</sub> conversion, power-to-gas, flow cells, energy storage

## 1 CO<sub>2</sub> TO SOMETHING USEFUL

Reliable, cost-effective energy storage systems are required in order to support the growing global production of clean electricity.[1] Several storage technologies are now well developed (e.g., flywheels, batteries, flow batteries), but as yet there are no viable platforms able to accommodate the broad variance in seasonal and geographical energy demand that exists in many parts of the world.[2] Electrolysis has the potential to meet this challenge by utilizing excess clean

electricity to drive the formation of fuels and chemicals that are typically derived from fossil fuels. Water electrolyzers, for example, provide a means of storing energy as clean-burning dihydrogen (H<sub>2</sub>) in “power-to-gas” schemes.[3] The economic case for this process is, however, challenged, by the much lower cost of H<sub>2</sub> extraction from natural gas, as well as a lack of infrastructure to support the deployment of H<sub>2</sub> as a transportation fuel.[4,5] These observations provide impetus to develop alternative strategies for converting electricity into chemicals, and a “CO<sub>2</sub> electrolyzer” is a particularly appealing candidate for producing high-demand fuels (e.g., syngas, alcohols, hydrocarbons) that can leverage our existing infrastructure (Figure 1).[6]

The market viability of a CO<sub>2</sub> electrolysis product is contingent on a number of techno-economic factors that encompass the design and performance of the electrolyzer, the cost and source of inputs (i.e., CO<sub>2</sub>, water, electricity) and the choice and number of products produced.[7] The economic landscape is further convoluted when considering auxiliary factors such as carbon pricing and fluctuating supply chains, and generally speaking there is no one model that can accurately define which CO<sub>2</sub> conversion product(s) should be pursued with absolute certainty. Notwithstanding, there are certain metrics that figure prominently in analyses of *any* type of electrolyzer—such as high current densities ( $J > 200$  mA cm<sup>-2</sup>), prolonged operation (>8000 h), low overpotential and high product selectivity—that can be targeted at the fundamental scientific and engineering level. Herein, we will touch on some of the strategies that have been applied in an effort to improve CO<sub>2</sub> electrolysis systems.

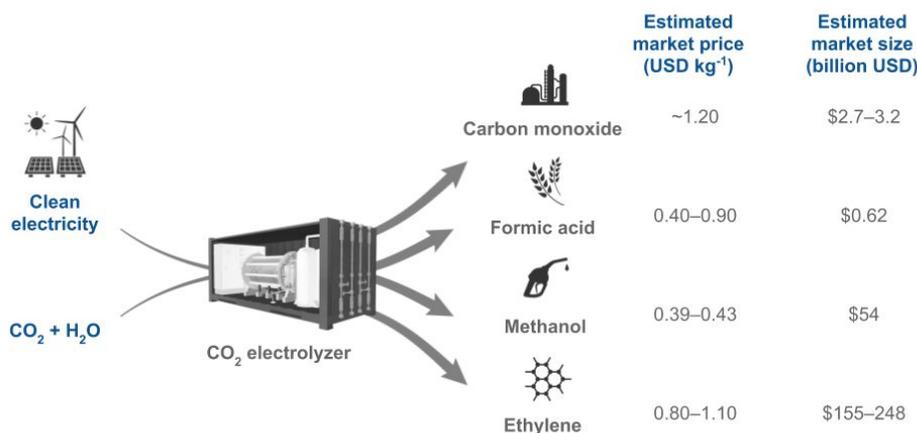


Figure 1: Overview of approximate global market sizes (in United States dollars (USD)) and prices (USD-per-kilogram) for chemicals accessible *via* CO<sub>2</sub> electrolysis. Reprinted with permission from ref 6. Copyright 2018 American Chemical Society.

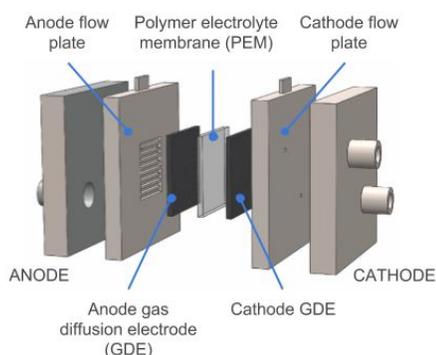
## 2 FLOW CELLS

Anodic and cathodic electrocatalysts are required in order to drive the efficient conversion of electricity and  $\text{CO}_2$  to products. The vast majority of R&D studies carried out on  $\text{CO}_2$  conversion electrocatalysts utilize a three-compartment “H-cell” geometry to quantify catalytic activity.[8,9] However, these experiments rarely report on factors that are relevant to the dynamic environment of a full-scale electrolyzer. Flow reactors, conversely, are lab-scale devices that can readily account for mass transport factors to more closely resemble commercial units. These systems operate by continuously circulating reactants and products to and from the electrodes, and incorporate components that can reliably scale to large electrolyzer stacks. Despite the importance of flow cells to the translation of electrocatalysts to commercial systems, the science and engineering communities are only very recently starting to perform the necessary experiments that help understand the challenges for electrolytic  $\text{CO}_2$  conversion at scale.[6,10]

Two primary cell architectures have emerged in recent years as platforms to design and test reactor components in continuous-flow environments: Membrane-based flow cells (Figure 2A), and microfluidic reactors (Figure 2B). Membrane-based flow cells take much

of their inspiration from highly-developed fuel cell technologies,[11] while electrolytic microfluidic devices were more recently pioneered by Kenis and coworkers.[12,13] Each invoke different dynamic mechanisms for the delivery of  $\text{CO}_2$  to the cathode, and both have been demonstrated to reach reasonable performance metrics for  $\text{CO}_2$  conversion.[14,15] Some similarities exist between the two geometries: For example, both incorporate a highly-porous carbon-based gas diffusion layer (GDL) as the catalyst substrate, which serves to increase the concentration of  $\text{CO}_2$  at electrocatalytic sites and drive up current densities. Both are also amenable the use of gas-phase  $\text{CO}_2$ , which has emerged as a highly-promising strategy for further increasing current density by overcoming mass transport limitations associated with water-solubilized  $\text{CO}_2$ .[6,14] Conversely, membrane chemistry has understandably been scrutinized more rigorously in membrane-based reactors, although there exists a recent study in which a membrane was included in a microfluidic cell to help separate products.[16] We reserve judgement on type of flow cell architecture that will eventually go on to resemble commercial units at this early stage of development, but both can be used to garner valuable evidence on the fluid dynamic aspects of continuous-flow  $\text{CO}_2$  electrolyzers, as well as the impacts of certain materials used therein.

**A) Membrane Reactor**



**B) Microfluidic Reactor**

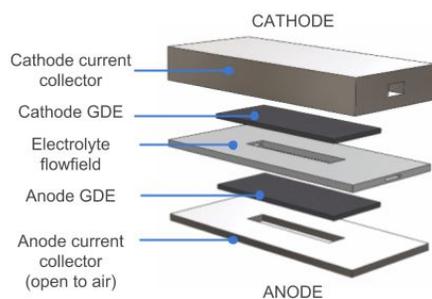


Figure 2: Exploded (left) and cross-sectional (right) diagrams of two lab-scale devices for continuous-flow electrochemical  $\text{CO}_2$  conversion: A) A membrane-based reactor, that bares many of the hallmarks of a fuel cell; B) a microfluidic reactor that typically operates in the absence of a membrane. Reprinted with permission from ref 6. Copyright 2018 American Chemical Society.

## 3 REACTOR OPTIMIZATION

### 3.1 Electrocatalysts

The tendency for a CO<sub>2</sub> electrolysis reaction to proceed efficiently and selectively is contingent on finding catalytic materials that can drive kinetically-challenging electron transfer reactions in a controlled and robust manner. A rapidly-growing body of research now exists exploring catalyst structure-composition-activity relationships for a variety of classes of materials including metals,[8] metal oxides,[17] alloys[18,19] and molecular catalysts[20] in CO<sub>2</sub> conversion schemes. Our own research, for example, has sought to better quantify a correlation between metal stoichiometry and CO<sub>2</sub> conversion activity in mixed metal materials derived from inexpensive precursors.[17] This research forms the basis for the accelerated discovery of functional materials that is now central to our program.

The electron transfer reactions that mediate the conversion of CO<sub>2</sub> to products within a flow reactor take place at the interface between the electrocatalyst supported on a GDL and an electrolyte (either a solid polymer membrane or a flowing liquid electrolyte). The development of electrocatalysts for CO<sub>2</sub> conversion is an active area of research, but far less consideration is attributed to the chemistry of the GDL and membrane materials. These materials warrant close scrutiny particularly with the delivery of gas phase CO<sub>2</sub> wherein the challenge of well-controlled water and ion management is augmented.

### 3.2 Membranes

In membrane-based reactors the polymer electrolyte membrane (PEM) separates the anode and the cathode and mediates the flow of ions and water across the cell while simultaneously attenuating product crossover. Three classes of membranes have been deployed in CO<sub>2</sub> flow cells: cation exchange membranes (CEMs), anion exchange membranes (AEMs) and bipolar membranes (BPMs). Each membrane type invokes a different ion transport pathway across the cell. Understanding how membrane properties affect CO<sub>2</sub> conversion efficiency and selectivity has motivated studies that explore the relationship between membrane functional groups, membrane thickness, water uptake and conductivity.[21]

CEMs (e.g., Nafion), drive the flow of positive ions from anode to cathode and are widely-studied for their compatibility with gas-phase hydrogen fuel cell systems. In CO<sub>2</sub> reactors, however, CEMs have proved less successful because of their tendency to promote cathodic hydrogen evolution in lieu of the formation of CO<sub>2</sub> conversion products.[22] AEMs promote the flow of anions from cathode to anode, a mechanism which may be more suitable for CO<sub>2</sub> conversion because the forward reactions are promoted without the deliver of H<sup>+</sup> ions to the cathode. Indeed, an

AEM-based flow cell reported in 2017 by Masel and coworkers was able to achieve high current densities and selectivities for CO<sub>2</sub>-to-CO conversion continuously over >4000 h.[23] Our own studies are currently underway to better understand how AEMs can be further improved. Finally BPMs, which facilitate the dissociation of water in OH<sup>-</sup> and H<sup>+</sup> under reverse bias, may offer a distinct over CEMs and AEMs by allowing the use of non-corrosive neutral conditions on either side of the cell.[24] Our research in collaboration with Mallouk has demonstrated the utility of BPMs in CO<sub>2</sub> conversion flow cells,[14,25] but it should be noted that these membranes cannot currently operate at the highest efficiencies due to the large voltage drop that evolves across the cell under reverse bias.[26] It is apparent from the above examples that there is significant room for improvement in the design and synthesis of membrane materials in order to favour conditions within a CO<sub>2</sub> electrolyzer flow cell.

### 3.3 Gas Diffusion Layers

Gas diffusion layers (GDLs) are porous materials composed of a dense array of carbon fibres. GDLs are typically functionalized with: a mesoporous layer, which comprises a more densely packed carbon nanofiber material; the electrocatalyst; and a hydrophobic additive such as polytetrafluoroethylene (PTFE). One of the most recognized limitations to the translation of CO<sub>2</sub> electrolysis results from H-cells to flow cells is the capacity to deposit the electrocatalyst upon a GDL substrate, which is considered integral to achieving reasonable current densities. In gas-phase reactors these materials mediate a triple-phase boundary electron transfer reaction where gaseous CO<sub>2</sub> and liquid H<sub>2</sub>O react at a solid catalyst to form products. There are a number of GDL properties (e.g., porosity, hydrophobicity, conductivity, robustness, catalyst loading) that can be tailored through the judicious selection of materials and fabrication methods.[27] A series of recent studies by Kenis and coworkers demonstrated the effects of manipulating these properties on CO<sub>2</sub> conversion current density and product selectivity in a microfluidic cell.[28–30] The results from these studies provide important guidelines for the ongoing development of GDL materials for both types of flow cell reactor.

## 4 CONCLUSIONS AND OUTLOOK

Electrochemical flow cells for converting CO<sub>2</sub> into useful products provide valuable testing platforms for materials and components relevant to CO<sub>2</sub> electrolyzer commercialization. The influence of non-catalytic components (e.g., GDL, PEM) on overall CO<sub>2</sub> conversion is of equal importance to flow cell performance as the nature of the active electrocatalysts. It is worth noting that there are a number of other considerations for electrolyzer development

that fall outside the scope of this document, including optimization of the anode reaction,[31] improved product separation[32] and tolerance towards CO<sub>2</sub> purity levels.[33] Flow cell reactors provide a critical stepping stone for testing and optimizing these factors in the translation of fundamental laboratory discoveries into real-world practice.

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