CO₂ electroreduction to valuable chemicals: State-of-the-art materials and processes
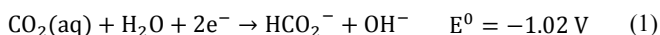
Amin Taheri Najafabadi*

Department of Chemical and Biological Engineering
The University of British Columbia,
2360 East Mall Vancouver BC Canada V6T 1Z3

CO_2 chemical conversion is one of the most strategic urgencies of the 21st century. Undue reliance on fossil fuels in the contemporary human civilization has caused enormous CO_2 emissions which is believed to be one of the main culprits for the climate change and global warming. To address this issue, long term strategies are based on developing sustainable alternatives for the human energy thirst. However, the versatilities of the carbonaceous fuels still uphold them as the main energy supply for a wide variety of applications. Therefore, evolving effective solutions to battle the environmentally detrimental nature of the CO_2 release to the atmosphere is crucial.

Current carbon management measures on large scale emitters (e.g. power stations and cement works) are mainly based upon carbon capture and storage (CCS) with three major solutions: post-combustion capture, pre-combustion capture, and oxy fuel combustion; where the separated carbon dioxide is physically stored afterwards. However, CCS approach does not resolve the problem permanently, just shifting that from the atmosphere to other ecosystems. In fact, long-term ecological impacts of using the earth as a gigantic reservoir for CO_2 are not comprehended. Additionally, this approach is associated with the potential hazards of CO_2 leakage to the earth surface which significantly deteriorates its perspective. Considering all the facts, the cogent solution of this challenging problem is chemical conversion of CO_2 to valuable chemicals [1].

Electroreduction of CO_2, as one of the leading methodologies, was first examined in the 19th century with formic acid production using zinc as the cathode. It drew an intense attention in the 1980s following the oil embargoes of the 1970s. Experimental studies are mostly performed in the neutral to alkaline solutions (pH>7) where the formation of formate ions (HCO_2^-) is facilitated via the reaction shown in Eq. 1. Competitive reduction of water to hydrogen is the main bottleneck of this process (Eq. 2). On the other hand, the pH above 9 causes CO_2 dissolution as bicarbonate/carbonate which avoids CO_2 participation in the reduction reactions.

$$CO_2(aq) + H_2O + 2e^- \rightarrow HCO_2^- + OH^- \quad E^0 = -1.02\,V \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^0 = -0.83\,V \quad (2)$$

The reaction in Eq. 2 is more thermodynamically favored over that of Eq. 1. However, formate can be efficiently produced on specific cathode materials where the water reduction to hydrogen (Eq. 2) is kinetically suppressed comparing with Eq. 1. The recommended materials are Hg, In, Pb, and Sn which are also suitable candidates for the acidic mediums. However, they still suffer from slow turnover rates, high overpotential, poor product selectivity, or low stability. Recently, novel classes of the organometallic complexes are explored with high affinity toward carbon dioxide activation. Electron-rich and earth-abundant metal complexes have shown noticeable stability in a wide range of pH with the presence of

reactive ligands. Moreover, their modular framework allows more control over structural or electronic properties. Fig. 1 depicts a sample Ni, Fe-cluster for the CO_2 electroactivation.
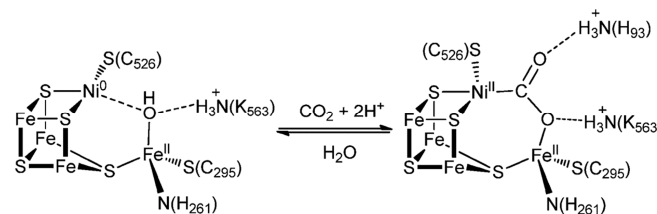

Fig.1: Carbon dioxide activation at the Ni, Fe-cluster of anaerobic carbon monoxide dehydrogenase [2].

From process design viewpoint, any feasible CO_2 electroreducer reactor must address the mass transfer issue of carbon dioxide to the cathode surface. CO_2 has a low water solubility (~30 mM at 1 atm and 293 K), and aqueous electrolytes decrease it significantly where the ionic strength can go up to 10 M. Generally, geometric current densities (based on the superficial electrode area) below 0.1 kA m⁻² are not economically sound. Therefore, following the successful employ of gas diffusion electrodes (GDEs) in the gas-fed fuel cells, recent researches suggested their application for CO_2 electroreduction with promising results. However, they suffer from two major problems which are temporal stability and liquid-phase products accumulation in the GDE pores. Thus, the researchers elevated preciseness to the microfluidics level where any water management issue at the electrodes (flooding or dry-out) can be minimized with enhanced stability. Furthermore, microfluidics offers a versatile analytical prospect for electrosynthesis diagnosis. Fig. 2 shows the schematic of microfluidics approach in carbon dioxide electroreduction [2].

In this work, a technical overview on the state-of-the-art technologies for CO_2 electroreduction is presented. A detailed understanding of some of the most advanced experiments in this field will be elaborated. Importantly, green energy incorporation in CO_2 chemical transformation is vital in order to meet the carbon-neutrality criterion. This necessitates subsidizing more research on sustainable energies coupled with CO_2 conversion practices considering the growing worldwide concerns on carbon management.
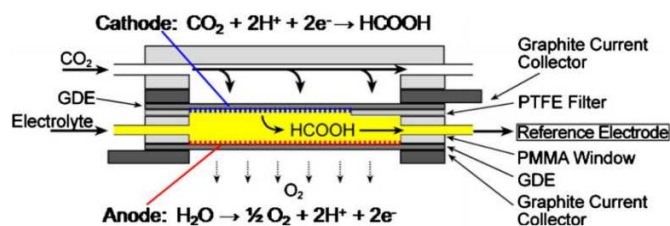

Fig. 2: Schematic of the microfluidic approach for CO_2 electroreduction to formic acid [3].

References

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* Corresponding author: ataheri@chbe.ubc.ca