



Electrochemical Reduction of CO₂: Overcoming Chemical Inertness at Ambient Conditions

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Abstract: Electroreduction allows for the transformation of a chemically inert molecule such as CO₂ into a wide variety of useful carbon products. Unlike other approaches operating at higher temperatures, electrochemical reduction holds great promise since it achieves reduction under ambient conditions, thereby providing more control over the reaction selectivity. By controlling basic parameters such as the potential and the composition of the electrode, CO₂ can be transformed into a variety of products including carbon monoxide, syngas (CO/H₂), methane, and methanol. This reduction process takes place without external hydrogen, since water can be used as a source of both electrons and protons. Furthermore, this technology, when combined with renewable wind- or solar-derived electricity, has the potential to serve as a storage system for excess electricity. Despite these advantages, a number of challenges need to be overcome before reaching commercialization. New (and cheaper) electrocatalyst formulations with high faradaic selectivities are required. Impressive progress has been made on carbon-doped materials, which, in certain cases, have outperformed expensive noble metal-based materials. Research is also needed on new electrochemical reactor configurations able to overcome kinetic/mass transport limitations, which are crucial to reduce overpotentials. Fine control over the nature of the active sites and the reaction conditions is important to avoid parasitic reactions such as the hydrogen evolution reaction (HER), and therefore increases the faradaic efficiency towards the desired products.

Keywords: electroreduction; CO₂; electrocatalysis; renewable energy; carbon products; faradaic efficiency

Fossil fuels provide most of the energy consumed worldwide and serve as a carbon source for preparing the fuels, chemicals, and multitude of carbon-based materials we use on a daily basis. However, massive utilization of fossil fuels involves a number of economic, political, and environmental issues. Consumption of fossil fuels results in net emissions of CO₂ (a powerful greenhouse gas) into the atmosphere, which is associated with global warming and its related climatic issues. The combustion of fossil fuels is predicted to produce ca. 496 gigatonnes of CO₂ within the next 50 years, which can result in a significant increase of the concentration of this gas in the atmosphere. Since CO₂ is the final product of the combustion of fossil fuels, its capture and subsequent conversion into useful products have become an area of interest for researchers worldwide [1,2]. Catalytic, biological, photocatalytic, and electrochemical routes have been proposed to achieve this paradigmatic conversion. Heterogeneous catalysis is useful for performing this transformation, although harsh temperature and pressure conditions are normally required to overcome the high chemical inertness of the CO₂ molecule. In addition, the reduction process ultimately requires large amounts of external (and typically fossil-fuel derived) hydrogen. Biological and photocatalytic routes operate at much milder conditions, but they suffer from sluggish reaction

kinetics and efficiencies. Electrochemical reduction is highly promising because the reduction process can be carried out at ambient conditions and without the need of external hydrogen, since water can be used as a source of electrons and protons [3]. Electroreduction of CO₂ has become a hot topic worldwide, and the number of papers published on this discipline has increased exponentially within the last few years. According to the Web of Science (Figure 1), the number of publications on electrochemical reduction of CO₂ has increased exponentially within the last five years. The relevance of these publications, measured by the number of citations received by these papers, has also increased substantially in recent years.

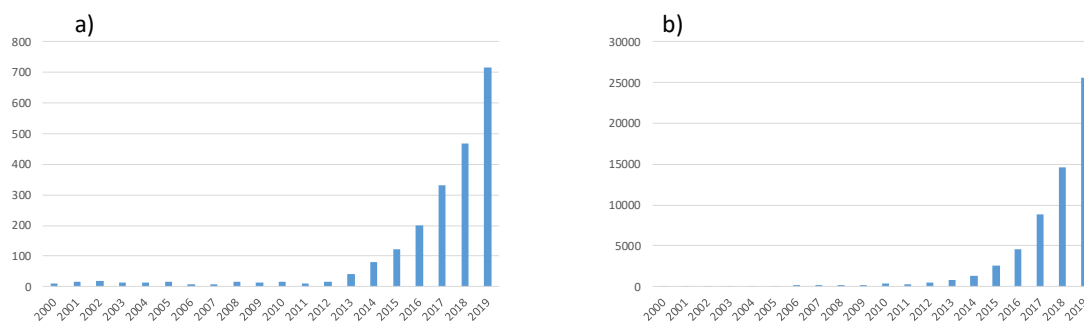


Figure 1. (a) Number of scientific publications containing the topic “electroreduction of CO₂” and (b) total number of citations of these publications within the last 20 years. Source: Web of Science.

Despite recent progress, this technology still has much room for improvement. The main challenge lies in developing low-cost electrocatalysts able to achieve active, selective, and stable electroreduction of CO₂ to a single target product [4]. Thus, despite some recent efforts, electrochemical reduction of CO₂ normally results in a complex mixture of C₁ and C₂ species, including carbon monoxide, methane, methanol, formic acid, ethylene, and ethanol, which limit the applicability of this reaction. The nature/composition of the cathode is crucial in determining the distribution of products. In this sense, a large variety of metals have been used as cathodes including noble metals such as Au, Pt, Ag, and Pd and transition metals such as Ni, Zn, Fe, and Cu. Literature indicates that metals can be classified into four categories depending on the main product obtained: formic acid, carbon monoxide, hydrocarbons (e.g., methane and ethylene), and hydrogen (via paratactic reduction of protons or hydrogen evolution reaction (HER)) [5]. Therefore, most studies have focused on producing these basic carbon feedstocks selectively and with large current densities.

In recent years, carbon-based materials (e.g., graphene, diamond, carbon nanotubes, carbon nanofoams) have been used as cathodes in replacement of expensive metals [6]. Apart from their low cost and abundancy, heteroatom-doped carbon materials present a number of characteristics (e.g., high electronic conductivity, high stability, strong tolerance to acidic/alkaline media) that make them particularly attractive for electrocatalysis. In addition, the preparation methods available today allow generating carbon materials with a wide variety of catalytically-active sites by introducing different dopants and structural defects in the carbon structure. In addition, these materials can be produced from biomass sources [7,8]. These carbon-based materials are typically doped with trivalent heteroatoms such as N or B. The introduction of an element with different electronegativity and size than C causes important changes in the carbon lattice (i.e., charge density redistribution and structural defects), thereby creating new catalytic sites and modifying the performance of carbon materials in a number of processes. For instance, N-doped carbon materials have shown improved redox kinetics because of the presence of nitrogen functional groups on its surface [9]. The incorporation of pyridinic and pyrrolic N sites within the carbon network of aerogels increased the electrochemical performance (capacitance and current density) of supercapacitors and the oxygen reduction reaction (ORR) performance of fuel cells [10,11]. With regards to the electroreduction of

CO₂, doped carbon materials have expanded the range of chemicals produced via this route while providing a new family of cheap electrocatalysts with tremendous potential and wide applications. Various doping strategies have been developed in the past few years, allowing a high degree of control over the location of the doping heteroatom in the carbon lattice [12]. It is expected that a wide range of catalytically-active sites can be generated on the surface of the carbon material upon doping. Rather than being an issue, this wide variety of catalytically active species can provide an opportunity for simultaneously producing several products in the cathodic chamber, as recently demonstrated by Huan et al. [13].

Electroreduction of CO₂ is a topic that has evolved very rapidly. New materials and reactor configurations are developed every year, making it necessary to compile the most recent and relevant works in this field. We expect that this Special Issue can bring together some of the most important advances on this fascinating topic.

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