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# New trends in the development of heterogeneous catalysts for electrochemical $CO_2$ reduction

Bijandra Kumar*, Joseph P. Brian, Veerendra Atla, Sudesh Kumari, Kari A. Bertram, Robert T. White, Joshua M. Spurgeon*

*Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY, 40292, USA*

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ABSTRACT

The electrochemical conversion of $CO_2$ into energy-rich fuels and chemicals has gained significant interest as a potential strategy for simultaneously mitigating increasing global $CO_2$ concentration and effectively storing intermittent renewable energy from sources such as solar and wind. This process recycles $CO_2$, permitting a carbon-neutral, closed-loop of fuel combustion and waste $CO_2$ reduction to help prevent a rising concentration of this greenhouse gas in the atmosphere. At the same time, intermittent electricity generation can be stored in an energy-dense, portable form in chemical bonds. However, the stability of $CO_2$ makes its conversion kinetically challenging, generally requiring a large overpotential, and thus the efficiency of electrochemical $CO_2$ reduction is strongly dependent on the activity and selectivity of the cathodic electrocatalyst. In this review, we discuss the current state-of-the-art of unconventional heterogeneous catalysts with a focus on activity and product selectivity, even if the $CO_2$ reduction reaction mechanism remains uncertain. Various emerging approaches to enhance the yield of specific products and the overall rate of reaction will also be addressed. Finally, prospects for the development of next-generation catalysts will be discussed.

## 1. Introduction

With the advancement of society, energy consumption is rapidly increasing and is projected to more than double by 2050 [1,2]. Despite extensive efforts to develop renewable, carbon-neutral energy sources, fossil fuels are predicted to remain the leading energy source for the near future. Energy extraction from the combustion of fossil fuels results in significant carbon dioxide ($CO_2$) emissions, as well as other pollutant gases (e.g., $NO_x$, $SO_x$, etc.) [3]. Global $CO_2$ emissions have grown to ~35–40 gigatonnes of $CO_2$ (GtC) per year, and will likely continue increasing in the coming years as developing nations further industrialize [3]. The United Nations Intergovernmental Panel on Climate Change (IPCC) has concluded that a 50–85% reduction of global $CO_2$ emissions by 2050 (compared to 2000 levels) is needed to limit the long-term global mean temperature rise to 2.0–2.4 °C (IPCC, 2007) [4,5]. Achieving this level of $CO_2$ reduction is a major challenge for the scientific community to address [6]. While key efforts are in progress for developing carbon-neutral alternative energy sources, there is also an urgent need to find a solution to store or convert the produced $CO_2$ so that the atmospheric level of $CO_2$ remains constant.

In the quest to deal with $CO_2$ after its production, geological sequestration [7,8] and molecular conversion [7,9–13] of $CO_2$ are the main emerging technologies. However, the long-term impacts of geological sequestration on the environment are uncertain due to the potential for leakage [14]. In contrast, the conversion of $CO_2$ is a more attractive process since it allows the valorization of $CO_2$ as a feedstock to produce useful chemicals (e.g., methane, methanol, ethanol, formate, and syngas) [9–13,15–18]. Therefore, this approach has received considerable attention in recent years (Fig. 1), and substantial progress has been made in this field. $CO_2$ can be converted through a diverse set of processes, including chemical, photochemical [10,16–19], electrochemical [9,12,13,15], biological [7], or inorganic transformations [8]. Among these, electrochemical reduction has numerous advantages over other conversion processes [9,12,13,15,18,20]. For instance, electrochemical conversion is directly controllable by adjustment of the applied electrode potential, and the reaction can be driven by renewably generated electricity to store intermittent, non-dispatchable renewable sources such as wind and solar in the form of chemical bonds in energy-dense hydrocarbon fuels (e.g., ethanol, gasoline).

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* Corresponding authors.
*E-mail addresses:* bijandra.kumar@louisville.edu (B. Kumar), joshua.spurgeon@louisville.edu (J.M. Spurgeon).

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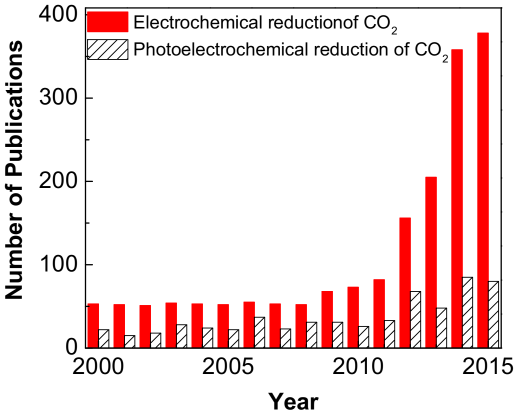

**Fig. 1.** Publications per year on photocatalytic and electrochemical reduction of $CO_2$. The data was extracted from the ISI Web of Science (search: Topic = electrochemical reduction of $CO_2$, photoelectrochemical reduction of $CO_2$).

Additionally, an electrochemical system can have a relatively small footprint, operate near room temperature, require a minimal chemical intake, and be easily scaled-up to suit the application.

The electrochemical $CO_2$ reduction reaction (CO2RR) can be promoted by using either homogenous [12,15] or heterogeneous catalysts [12,13,17,21–25]. However, the two catalyst classes generally have different reaction mechanisms and require distinct electrochemical cell designs and experimental protocols. It is therefore beyond the scope of this review to describe the in-depth studies and current state-of-the-art for both types of catalysts. Hence, this review will mainly focus on the current progress on the electrochemical reduction of $CO_2$ via heterogeneous catalysis. Moreover, strategies are discussed for designing electrocatalyst systems that are selective, efficient, and cost-effective.

### *1.1. Thermodynamics and kinetics of the $CO_2$ reduction reaction*

As the final carbon product of the combustion of organic molecules, $CO_2$ is thermodynamically a very stable molecule [26,27]. It is also kinetically challenging to convert, with a generally high initial activation energy for the reduction process [28]. In particular, the single electron reduction of $CO_2$ to $CO_2^-$ has a very high thermodynamic potential, i.e., $E^\circ = -1.90\,V$ versus the standard hydrogen electrode (SHE) in aqueous media (pH = 7) [15,29–31]. However, electrochemical CO2RR proceeds through multiple proton-coupled electron-transfer steps and occurs at lower potentials due to the formation of thermodynamically more favorable molecules. Various $C_1$ and $C_2$ products (e.g., CO, $CH_4$, $C_2H_4$, etc.) of CO2RR have been identified depending on the catalyst and electrolyte media [18,23,25,32–38]. The thermodynamic redox potentials for different possible reduction half-reactions responsible for different products are given in Table 1. These half-reaction potentials only reflect the minimum thermodynamic potential to enable the reaction and depend on the electrolyte media as well [28,39–42]. However, the reaction kinetics, including the activation energy, reaction rate, and mechanistic pathway cannot be forecast by the thermodynamic potentials alone.

Generally, $CO_2$ reduction competes with the hydrogen evolution reaction (HER), which is also a cathodic half-reaction that occurs at a comparable thermodynamic potential (0 V vs. SHE) but on most surfaces proceeds at lower overpotential [25]. This side reaction introduces a major challenge for efficient and selective $CO_2$ electrochemical reduction [38,40,44–50]. Therefore, ideal electrocatalysts for $CO_2$ reduction should minimize the activation barrier for CO2RR relative to HER, driving $CO_2$ reduction selectively at low overpotential with high reaction rates (i.e., currents). [13,18,40,50–54]

**Table 1**
The electrode potentials for numerous electrochemical $CO_2$ reduction half-reactions in aqueous solution at standard experimental conditions [43].

| Electrochemical thermodynamic half-reactions | Electrode potentials (V vs. SHE) under standard conditions |
|---|---|
| $CO_2(g) + 4H^+ + 4e^- \rightarrow C(s) + 2H_2O\ (l)$ | 0.210 |
| $CO_2(g) + 2H_2O(l) + 4e^- \rightarrow C(s) + 4OH^-$ | −0.627 |
| $CO_2(g) + 2H^+ + 2e^- \rightarrow HCOOH(l)$ | −0.250 |
| $CO_2(g) + 2H_2O(l) + 2e^- \rightarrow HCOO^-(aq) + OH^-$ | −1.078 |
| $CO_2(g) + 2H^+ + 2e^- \rightarrow CO(g) + H_2O(l)$ | −0.106 |
| $CO_2(g) + 2H_2O(l) + 2e^- \rightarrow CO(g) + 2OH^-$ | −0.934 |
| $CO_2(g) + 4H^+ + 4e^- \rightarrow CH_2O(l) + 4OH^-$ | −0.898 |
| $CO_2(g) + 6H^+ + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$ | 0.016 |
| $CO_2(g) + 5H_2O(l) + 6e^- \rightarrow CH_3OH(l) + 6OH^-$ | −0.812 |
| $CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + H_2O(l)$ | 0.169 |
| $CO_2(g) + 6H_2O(l) + 8e^- \rightarrow CH_4(g) + 8OH^-$ | −0.659 |
| $2CO_2(g) + 2H^+ + 2e^- \rightarrow H_2C_2O_2(aq)$ | −0.500 |
| $2CO_2(g) + 2e^- \rightarrow C_2O_4^{2-}(aq)$ | −0.590 |
| $2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_2CH_2(g) + 4H_2O(l)$ | 0.064 |
| $2CO_2(g) + 8H_2O(l) + 12e^- \rightarrow CH_2CH_2(g) + 12OH^-$ | −0.764 |
| $2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_2CH_2OH(l) + 3H_2O(l)$ | 0.084 |
| $2CO_2(g) + 9H_2O(l) + 12e^- \rightarrow CH_2CH_2OH(l) + 12OH^-$ | −0.744 |

### *1.2. Traditional catalysts for $CO_2$ reduction*

Beginning in the early 1980s, preliminary research in this field was in the direction of studying the catalytic activity of bulk metal catalysts. [32,40,44,51,52,55–75] Therefore, most common, single-element metallic electrodes have been investigated for CO2RR electrocatalysis in bulk polycrystalline form [18,76,77]. The distribution of products obtained through electrochemical $CO_2$ reduction depends on various factors, including the physical characteristics and form of the material used as the cathode, the electrolyte, and the operational conditions (e.g., pressure and temperature) [47,48,78–80]. In particular, the intrinsic electronic properties of the cathode surface strongly govern the kinetics and product selectivity of $CO_2$ reduction by affecting the intermediate species binding energies and activation barriers [18,81–83]. The pure metal electrocatalysts for CO2RR generally fall into one of a few different classes. CO is produced as the major carbonaceous product on metals like Pt, Ni, Fe, Al, Ga, and Ti [62,63,76,84]. However, the HER rate on these metals is generally much higher than that of the CO2 reduction rate. A related class of metals such as Au, Ag, and Zn also produces CO but with a higher current efficiency [51,65,67,76]. Another class of metal catalysts including Sn, Pb, In, and Hg produces formate as the primary CO2RR product [39,85–87]. The reduction reaction at these metal surfaces to make formate follows a different mechanism in which there is no breaking of the carbon–oxygen bond. Metallic electrodes of Cr, Mo, and W have been considered poor catalysts due to poor reduction rate and selectivity [11,88]. Cu is in another class as well as it is one of the only known metal catalysts able to reduce CO2 to hydrocarbon and alcohol products (e.g., CH4, CH3OH, C2H4, etc.). However, recent work has illustrated that certain other bulk metal catalysts can also reduce CO2 further into these more energetic species, though at lower faradaic efficiencies than Cu, with the reaction rate influenced by the binding energy of the intermediate CO molecule (Fig. 2). For instance, those catalysts (e.g., Au, Ag) which have a lower binding energy for CO molecules are able to produce CO preferentially, as it can be released from the surface without further reduction [12,37,89]. Therefore, the rate of higher carbon product formation remains very low on these surfaces. Among the pure metals, however, Cu remains a unique catalyst with a more ideal CO binding energy which allows it to produce several more-reduced carbon products (e.g., alcohols and hydrocarbons) with much higher activity (Fig. 2). [90,91]. The findings suggest that by tuning the binding energy of the intermediate reactants on the