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Regular Article

Metallic nanocatalysts for electrochemical CO_2 reduction in aqueous solutions

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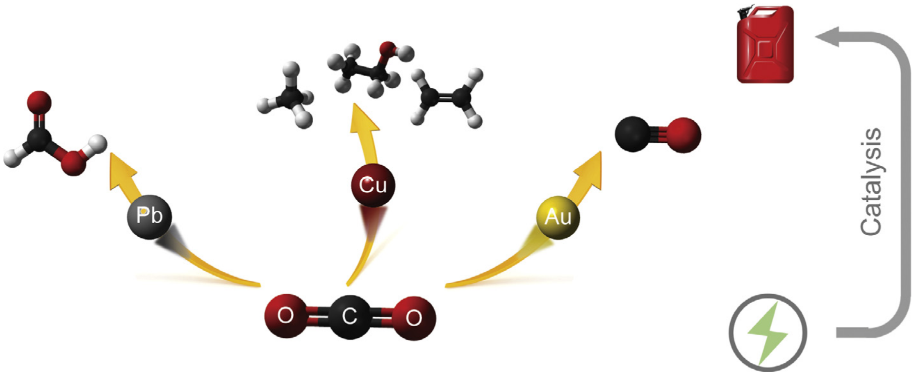
GRAPHICAL ABSTRACT



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ABSTRACT

How to effectively and efficiently reduce carbon dioxide (CO_2) to value-added chemicals represent a frontier in catalysis research. Due to the high activation energy needs and the endothermic nature of CO_2 reduction, the reactions are difficult to carry out. When H_2O is present, hydrogen evolution reactions (HER) often compete favorably with CO_2 reduction reactions. For these reactions, catalysts are of critical importance to CO_2 reduction. In this article, we review the various metal nanocatalysts for electrochemical CO_2 reduction (ECR) reactions. In recognition of the importance of H_2O to CO_2 reduction, we focus our discussions on systems in aqueous solutions. Nanostructured metal catalysts are chosen for the discussions because they represent the most effective catalysts for ECR. After a brief introduction of the fundamental principles of ECR, we devote the rest of the article on the discussions of various types of nanostructured metallic catalysts, which are categorized by their compositions and working mechanisms. Lastly, strategies for improving reaction efficiency and selectivity are discussed.

1. Introduction

1.1. Background of the electrochemical CO_2 reduction

Carbon dioxide (CO_2) is the most stable end products of fossil fuel combustion. Its rapid increase over the past 150 years has

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been regarded as an indication of excessive energy consumption by human activities. The high concentration of CO_2 in our atmosphere is widely agreed as man-made and is a source of recent climate changes [1]. As a way to mitigate the negative impacts by the high concentration of this molecule, the research society has been working hard to convert CO_2 into useful chemicals, particularly liquid fuels [2,3]. On a fundamental level, direct chemical utilization of CO_2 is also interesting because CO_2 represents a low-cost source of C for chemical synthesis. But this conversion is extremely difficult to control due to the rich oxidation states of C in various products, as well as the high activation energies between these products [4–7]. Of the approaches that have been studied, electrochemical CO_2 reduction (ECR) to fuels and value-added chemicals in aqueous solutions is especially appealing since it offers a versatile route toward a wide range of chemicals that can readily meet the thermodynamic energy needs by electricity, which could in principle be supplied by renewable sources such as solar or wind [8].

Exciting progresses notwithstanding, critical issues remain for ECR to become a practicable approach. The main challenges for ECR in aqueous solutions include the high overpotentials, poor catalyst stability, low product selectivity and low faradaic efficiencies (FE) [9]. Moreover, and often more critically, the competing reactions of hydrogen evolution (HER) tend to be kinetically favored due to the relative simplicity of the reactions in comparison with ECR [10]. For these reasons, the goal of selective CO_2 reduction in H_2O at high efficiencies with low hydrogen evolution and good control over the products has attracted tremendous research efforts. Previous research in this area has mainly focused on metal catalysts that are bulk in sizes and morphologies [11]. Recently, nanoscale metal catalysts have emerged as new material platforms for this important reaction due to their unique properties [8,12]. Our purpose of composing this *Article* is to review research activities in this area, with a focus on nanoscale metal catalysts. We aim to summarize research efforts for new insights into how to move forward in this important research area. The article is organized as follows. We first discuss the basic principles of electrochemical CO_2 reduction reactions and then various types of nanostructured metallic catalysts based on primary products and reaction selectivity are discussed. In addition, common strategies for improving reaction efficiency and selectivity are summarized.

1.2. Basics of electrochemical CO_2 reduction

For the ease of discussions and to provide a basis for our readers, we first define the commonly used terminologies in the literature.

1.2.1. Onset potential

The onset potential is defined as the applied voltage, at which appreciable current densities can be measured. It is important to note that the measured current densities are thought to produce desired products (such as CO or hydrocarbons). During the reaction, the standard reduction potential is often more positive than the onset potential since the electrochemical CO_2 reduction must overcome a kinetic barrier [13]. Within this context, overpotential is defined as the difference between the standard reduction potential and the onset potential. At what current density should the onset potential be measured, however, is an important point of contentions. In principle, the current density should be determined by measuring the intrinsic exchange current densities; in practice, the exchange current density measurements can be cumbersome. Often, the chosen current density is not based on a meaningful theoretical basis but serves as a reference point for easy comparisons of experimental results by different groups under similar conditions.

1.2.2. Fradaic efficiency

The Fradaic efficiency (FE) refers to the percentage of charges (*i.e.* electrons as we are mostly concerned with reduction reactions) used to produce desired products over the overall charges measured. The FE represents the selectivity of the desired products in a reaction, and the FE can be calculated using Eq. (1).

$$\varepsilon_{FE} = \frac{\alpha nF}{Q} \tag{1}$$

where α is the number of transferred electros, n is the number of mole of a desired product, F represents Faraday's constant (96,485 C mol^{-1}), and Q referrers to the total charge passed [14].

1.2.3. Tafel slope

The Tafel plot referrers to a plot of overpotential versus the logarithm of the current density. The basis for Tafel analysis is the exponential dependence of the current densities on the applied potentials as described by the Butler-Volmer relationship. The analysis is useful for investigating the mechanisms of the reaction and for evaluating the performance of catalysts. For example, a Tafel slope of ~118 mV dec^{-1} is often used to suggest that the formation of the $CO_2^{\cdot -}$ intermediate by the initial one-electron transfer step is the rate-determining step, while a slope of ~59 mV dec^{-1} implies a fast one-electron pre-equilibrium and then a slower chemical reaction as the rate-determining step in the case of ECR [13].

1.2.4. Electrochemical cells

A variety of experimental configurations have been used in the literature for ECR research. For the ease of discussions, we choose one representative lab-scale H-type cell here. The common H-type electrochemical cell in the ECR consists of two compartments, three electrodes, and gas in/out valves. The two chambers are separated by an ion-exchange (commonly proton-exchange) membrane to prevent products cross-over, which would otherwise compromise the desired reactions. Parameters such as CO_2 pressure, reaction temperatures, pH, and the details of the electrolyte chemical composition are all important in defining the electrochemical behaviors of the cell.

1.2.5. Reaction pathways

CO_2 can be converted into a number of products via different electron transfer pathways. Several common transformations by ECR are summarized in Table 1, where the thermodynamic potentials (E^0) associated with the transformations are listed. From these thermodynamic potentials, we can immediately see why ECR is difficult to control – different transformations often feature thermodynamic potentials that are very close. Another important point to make about Table 1 is that although the reduction reactions can

Table 1
Thermodynamic potentials (E^0) for electrochemical CO_2 reduction reaction [15].

Electrode	Reaction	Number of electron transfer	E^0 (V) vs. RHE
Cathode	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	2	−0.106
	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	2	−0.250
	$CO_2 + 4H^+ + 4e^- \rightarrow HCOH + H_2O$	4	−0.070
	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	6	0.016
	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	8	0.169
	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	12	0.064
	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	12	0.084
	$2H^+ + 2e^- \rightarrow H_2$	2	0.000
	$CO_2 + e^- \rightarrow CO_2^{\cdot -}$	1	−1.49
Anode	$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	4	1.230

All potentials are referenced against the reversible hydrogen electrode (RHE).