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Review (Special Issue on Electrocatalysis Transformation)

Recent developments in copper-based, non-noble metal electrocatalysts for the oxygen reduction reaction

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ABSTRACT

The high cost of Pt-based catalysts and the sluggish dynamics of the oxygen reduction reaction (ORR) severely hinder the rapid development of fuel cells. Therefore, the search for inexpensive, non-noble metal catalysts to substitute Pt-based catalysts has become a critical issue in the ORR research field. As an earth-abundant element, the use of Cu to catalyze the ORR has been explored with the ultimate target of finding a replacement for Pt-based catalysts in fuel cells. This review mainly focuses on recent research progress with Cu-based ORR catalysts and aims to aid readers' understanding of the status of development in this field. The review begins with a general update on the state of knowledge pertaining to ORR. This is followed by an overview of recent research based on Cu nanomaterial catalysts, which comprises Cu complexes, compounds, and other structures. Charting the development of Cu-based ORR catalysts shows that designing Cu-based materials to mimic active enzymes is an effective approach for ORR catalysis. By collecting recent developments in the field, we hope that this review will promote further development of Cu-based ORR catalysts and their application in fuel cells.

1. Introduction

Fuel cells are increasingly regarded as an effective tool to address global environmental and energy problems [1,2]. The first fuel cell that transformed chemical energy into electrical energy was developed in 1839 [3]. Since then, an abundance of studies have concentrated on improving the energy conversion efficiency, leading to the development of various fuel cells types (Fig. 1) [4]. Although the materials used for anodes and electrolytes vary between fuel cells, the reaction at the cathode is the same, i.e., the oxygen reduction reaction (ORR). In practice, both the ORR (at the cathode) and the fuel-oxidation reaction (at the anode) need catalysts to yield acceptable reaction efficiencies, but the obstacle for large-scale uptake of fuel cells is the sluggish rate of the ORR. Among the many catalysts developed over the past decades, Pt has shown the best catalytic performance, but its high cost has limited its large-scale application. Pt-alloys have been widely investigated to address the cost issue while making maximum use of Pt, with some alloys exhibiting much better catalytic performance than commercial Pt/C [5–8]. A number of substitutes for Pt have also been considered. These include Pd-based catalysts [9] and non-noble metals and functionalized carbon materials [10–12]. Among the non-noble metal catalysts, Fe [11], Co [13], and Mn [14] are the most studied materials, though the body of work on using Cu-based materials to catalyze the ORR has also been growing.

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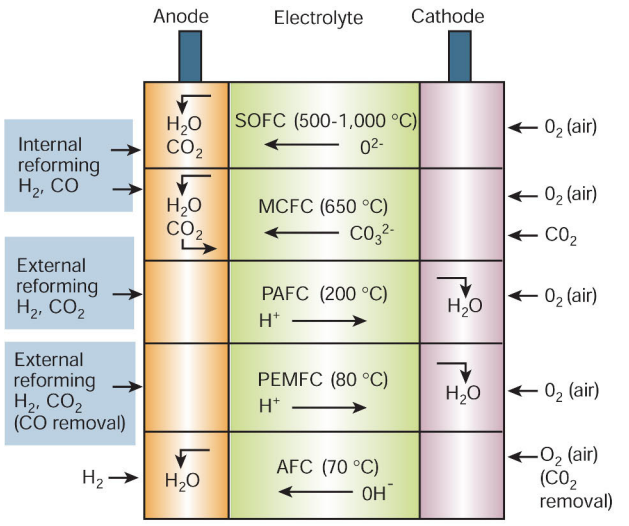

Fig. 1. The scheme of different types of fuel-cells. Reproduced from Ref. [4] with permission from Nature Publishing Group.

As an earth-abundant non-noble metal, Cu has been widely investigated in a number of fields; notably including transparency electrodes [15] and organocatalysis [16]. Indeed, Cu-based nanomaterials have been shown to exhibit excellent electrocatalytic activities in glucose oxidization [17], hydrogen peroxide reduction [17] and methanol oxidization [18]. Early studies reported the ORR kinetic parameters for a bulk Cu electrode [19,20]. Lately, via a one-pot method, our research group synthesized a type of subnanometer-sized Cu clusters with high ORR activity [21]. The catalytic activity of Cu clusters has also been found to depend on their core size [22].

The use of Cu-based catalysts for the ORR has clearly progressed and this review highlights the recent relevant advances. We first detail a general introduction to the ORR and measuring and evaluating the impact of electrocatalysts on it. The main section of this article then summarizes the recent development of Cu-based catalysts for ORR, disaggregating the catalysts according to whether they are Cu complexes, Cu compounds or other Cu-based nanostructures. Finally, we discuss the potential directions for future development of Cu-based ORR catalysts.

2. ORR fundamentals

Although enormous effort has been devoted globally to the study of ORR, the complexity of dynamic processes mean the reaction is not yet fully understood at the atomic level [23]. Nonetheless, it is widely accepted that the ORR involves the net transfer of four electrons. This transfer results in zero-valent O_2 being reduced to various negatively charged, bivalent oxygen species, depending on the reaction conditions. Under acidic conditions, O_2 can be converted to H_2O through a direct $4e^-$ process, which is the most favorable path for the creation of useful electrical power. However, O_2 may also be converted to H_2O_2, a common intermediate product during ORR, and then reduced to H_2O through a $2e^- + 2e^-$ pathway, which is less desirable. Similar observations can be made for the ORR under basic conditions: O_2 can be totally reduced through a direct $4e^-$ pathway or via a $2e^- + 2e^-$ pathway but with an intermediate product of HO_2^- instead. The theoretical reaction paths are as follows:

In acid:

$$\text{Direct pathway: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$

$$\text{Indirect pathway: } O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (3)$$

In base:

$$\text{Direct pathway: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (4)$$

$$\text{Indirect pathway: } O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (5)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (6)$$

For the most common Pt-based catalysts, O_2 is usually reduced through the most efficient $4e^-$ pathway under normal conditions. Nevertheless, O_2 can be reduced via the $2e^-$ pathway in many cases, especially when less understood non-Pt catalysts are used. Although theoretical calculations can be used to predict the various reaction intermediates [24], their direct detection is still limited and this is the main obstacle to fully understanding the ORR mechanism and effectively designing ORR catalysts. Recently, however, a number of ORR intermediates have been directly identified experimentally by *in situ* spectroscopic techniques [25,26].

The activity of ORR catalysts is usually evaluated by fabricating a membrane electrode assembly (MEA) or by depositing the catalyst on a rotating disk electrode (RDE). A MEA includes electrodes (anode and cathode), a diffusion media (also called substrate), and a proton-exchange membrane [27]. Although a MEA is more suitable for testing the performance of a catalyst for practical applications, it is complicated by the fabrication of apparatus required for carrying out the measurements. Conversely, RDE activity tests are very easily conducted making them a popular option for most ORR research groups. Testing ORR activity by the RDE method requires the prepared catalysts to first be dispersed in a mixture of water, isopropanol/ethanol and Nafion (5 wt%) according to a volume ratio of 4:1:0.025 [28]. However, the proportion and components of the catalyst ink need not be fixed and mixtures with other ratios are also acceptable if the catalyst ink can be uniformly deposited on a glassy carbon (GC) electrode by forming a thin film. Controlling the mass-loading of catalyst in the thin film formed on GC is very important for obtaining accurate activity results (see further experimental details in Ref. [29]). Normally, two electrolytes—an acidic solution and a basic solution—are used, but buffer solutions with different pH values can also be used for some complex catalysts [30]. In general, the electrolyte is chosen according to the properties of the catalyst being tested.

An electrocatalyst's ORR activity can be evaluated qualitatively by different electrochemical techniques. The kinetics of the reaction are usually measured by linear sweep voltammetry (LSV). Here, a RDE is used in an O_2-saturated electrolyte with a low sweep-rate to avoid any interruption from capacitive currents [31]. Fig. 2 shows the typical LSV curve for the ORR [31]. The kinetic data can be obtained using the following K-L (Koutecky-Levich) equation [27]:

$$1/i = 1/i_k + 1/i_d \quad (7)$$

where i refers to the experimental current, i_d is the diffu-