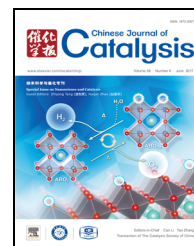


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Review (Special Issue on Nanoscience and Catalysis)

Recent advances in the rational design of electrocatalysts towards the oxygen reduction reaction

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ABSTRACT

The quest for low-cost yet efficient non-Pt electrocatalysts for the oxygen reduction reaction (ORR) has become one of the main focuses of research in the field of catalysis, which has implications for the development of the next generation of greener fuel cells. Here, we comprehensively describe the 'big picture' of recent advances made in the rational design of ORR electrocatalysts, including molecule-based, metal-oxide-based, metal-nanomaterial-based and two-dimensional electrocatalysts. Transition metals can fabricate molecular electrocatalysts with N_4 -macrocycles such as porphyrin-class compounds and the so-formed M–N–C active centre plays a crucial role in determining the catalytic performances towards the ORR. Group-IV and -V Transition metal oxides represent another class of promising alternative of Pt-based catalysts for the ORR which catalytic activity largely depends on the surface structure and the introduction of surface defects. Recent advances in synthesis of metallic nanoparticles (NPs) allow for precise control over particle sizes and shapes and the crystalline facets exposed to enhance the ORR performance of electrocatalysts. Two-dimensional materials such as functionalized graphene or MoS_2 are emerging as novel electrocatalysts for the ORR. This review covers various aspects towards the design of future ORR electrocatalysts, including the catalytic performance, stability, durability and cost. Some novel electrocatalysts even surpass commercial Pt/C systems, demonstrating their potential to be alternatives in industrial applications. Despite the encouraging progress, challenges, which are also described, remain to be overcome before the real-world application of novel ORR electrocatalysts.

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1. Introduction

As an ideal primary-energy device that can directly convert chemical fuels into electricity through electrochemical processes, fuel cells use hydrogen or hydrocarbon fuels in which the chemical energy stored is greater than that in common bat-

tery materials and they can be operated at close to room temperature [1]. Fuel cells are thus considered a promising replacement of traditional energy solutions in terms of providing clean, steady and sustainable power to meet the rising global energy demand [2]. It is expected that highly efficient fuel cells will come into widespread commercial use in the areas of

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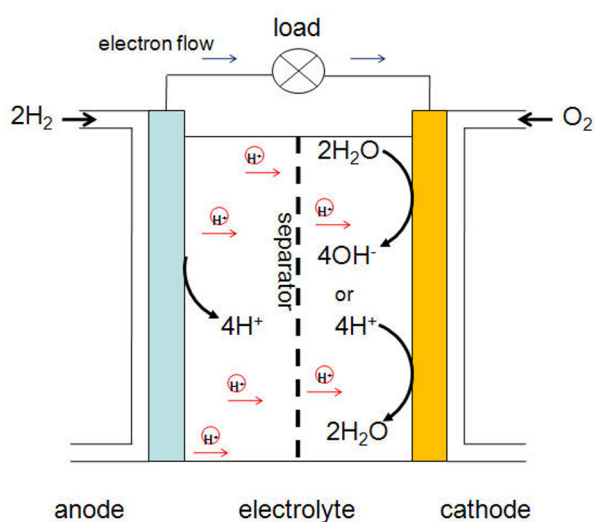
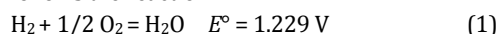


Fig. 1. Representation of a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell.

transportation and stationary and portable power generation [3]. When hydrogen fuel is used, water is the only by-product and there is no carbon footprint on the environment. A typical $\text{H}_2\text{-O}_2$ fuel cell follows the reaction



As shown in Fig. 1, H_2 is oxidized at the anode while O_2 is reduced at the cathode, and current thus flows through the circuit [4]. A hydrogen fuel cell can work under alkaline or acidic conditions. In comparison with the hydrogen oxidation reaction, the oxygen reduction reaction (ORR) has much slower kinetics for either alkaline or acidic media [1]. As summarized in Table 1, in acid media, the ORR can proceed by a direct four-electron and four-proton reaction with O_2 to yield H_2O , or can proceed by consecutive two-electron and two-proton steps to yield H_2O_2 followed by H_2O . In basic media, the four-electron direct reduction produces four equivalents of hydroxide, while the two-electron reduced product is one equivalent of hydroxide and one hydroperoxyl anion. The hydroperoxyl anion can then be further reduced by two electrons to three hydroxide ions. The performances and costs of fuel cells therefore largely depend on the ORR electrocatalysts used [5].

Besides slow kinetics, a substantial overpotential arises from the high bond strength of the dioxygen double bond (498 kJ), which prevents the full delivery of the predicted 1.229 V for a hydrogen fuel cell [6]. Platinum (Pt) has an overpotential of ~ 300 mV for the ORR, and has been regarded as the most promising and practical ORR catalyst for hydrogen fuel cells [7]. However, the scarcity and high cost of Pt are primary barriers in the commercial world [8–10]. In addition, the Pt-based elec-

trode suffers from other issues, including poor long-term stability and the tendency to be deactivated by a catalyst poisoner (e.g., CO) [1,2,11,12].

Attempts to reduce/replace Pt for the electrochemical reduction of oxygen in fuel cells began in the 1960s [13] and have been increasing intensively in recent decades. Even though the amount of Pt needed to achieve the desired catalytic effect can now be reduced by using Pt alloys [14,15] or making core-shell structures with supporting materials [16], the commercial scale-up of production at low cost remains challenging. In this context, much recent effort has been devoted to developing alternative ORR electrocatalysts, including molecular electrocatalysts [5,17–19], metal-nanomaterial-based electrocatalysts [20–25], metal-oxide-based electrocatalysts [2,26] and newly emerging two-dimensional electrocatalysts [27–30]. Although a few outstanding review papers have been published in the field of ORR electrocatalysts recently [2,3,6,12,21–23], a comprehensive coverage of various facets, particularly those investigated in the past 10 years, is still lacking.

The purpose of this review is to give a comprehensive picture of state-of-the-art non-Pt ORR electrocatalysts. The review covers recent developments of various materials used, compares the pros and cons of each material selection, and projects future directions of the development of ORR electrocatalysts.

2. Molecule-based electrocatalysts for the ORR

There have been numerous studies on transition-metal organic complexes as ORR catalyst alternatives since the investigation of transition-metal macrocyclic complexes in the 1960s [13]. Subsequently, the drive to replace expensive noble Pt catalysts for the ORR has led to a large number of molecular electrocatalysts comprising transition metal ions combining with nitrogen functional groups on carbonaceous supports [31]. The performance of these catalysts is directly related to the preparation conditions, such as the synthesis method, metal precursor, ligand structure and carbon support, because nitrogen-containing precursors as well as the metal centre play important roles in forming an active catalyst [32,33]. Later studies have indicated that the pyrolysis of these transition-metal macrocycles can generally improve both the activity and stability of the electrocatalysts [34,35].

2.1. Molecule-based electrocatalysts with N_4 -macrocycles

Research on metal complexes as oxygen reduction catalysts has produced metal macrocycle compounds with many different structures that can promote catalysis for the ORR in acidic, alkaline and neutral conditions [34,36]. The higher ORR cata-

Table 1
Electrochemical reactions for the ORR under different conditions.

| Media | | Acidic | Alkaline |
|---------------------------|---------|--|---|
| Electrochemical reactions | anode | $\text{H}_2 - 2\text{e}^- = 2\text{H}^+$ (2) | $\text{H}_2 - 2\text{e}^- = 2\text{H}^+$ (6) |
| | cathode | $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$ (3) | $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{HO}_2^- + \text{OH}^-$ (7) |
| | | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$ (4) | $\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- = 3\text{OH}^-$ (8) |
| | overall | $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$ (5) | $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ (9) |

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