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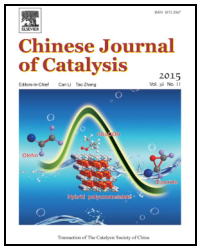

Review

# Graphene derivatives supported nanocatalysts for oxygen reduction reaction

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ABSTRACT

Very recent progress on the graphene derivatives supported variable nanocatalysts for oxygen reduction reaction (ORR) in fuel cell is reviewed. First, common electrochemical techniques to characterize graphene-based electrocatalysts are mentioned. Second, recent updates on graphene-derived electrocatalysts are introduced. In this part, both electrochemical activity and stability of Pt catalysts can be improved when they are supported by reduced graphene oxide (RGO). Other noble-metal catalysts including Pd, Au, and Ag showing comparable performance have been investigated. The stability of Pd catalyst is enhanced by RGO or few-layered graphene support. Synthetic approaches for Au or Ag catalysts supported on graphene oxide are discussed. In addition, non-noble transition metals in $N_4$-chelate complexes can reduce oxygen electrochemically. Fe and Co are cheap alternative catalysts for ORR. In most cases, the stability and tolerance issues are overcome well, but their overall performances don't seem to surpass Pt/C catalyst yet.



## 1. Introduction

Graphene is a 2-D carbon material with one-atom thickness and excellent electrical conductivity, and has been one of the most talented materials in nanotechnology because of its unique chemical and physical properties. Very recently, graphene supported nanocatalysts have been highlighted by high surface area, electrical properties, and thermal stability [1].

We are now facing energy shortages and environmental pollution, and the huge demands for renewable and sustainable energy conversion technologies are emerging because fossil fuels will be depleted in near future [2]. The most important step in solving our energy and environmental concerns would be the development of a practical, safe, and efficient fuel cell. For example, proton exchange membrane (PEM) fuel cell is a non-polluting ecological device and expected to be one of solutions [3]. Fuel cell converts chemical energy from a fuel to electricity through oxidation on anode and reduction on cathode. The most common fuel is $H_2$, which can be produced from steam reforming of natural gas or water splitting. $H_2$ is oxidized at anode to create a current, and hydrogen ions (protons) pass through an electrolyte membrane to cathode. $O_2$ from air is reduced at cathode by the current, and then forms water. Unlike battery, electricity can be produced continuously as long as fuel is supplied [4].

Even though hydrogen fuel is a promising alternative to fossil fuel, the fuel cell still has some obstacles to be more affordable and popular: high costs and the stability of electrocatalysts.

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The splitting of hydrogen molecules is relatively easy when catalyzed by transition metals, but the kinetics of oxygen reduction is too slow to achieve the overall capability. Pt supported on carbon is widely used as a catalyst at both anode and cathode in spite of many drawbacks. Basically Pt is too expensive for commercialization in large-scale production. In addition, Pt suffers from serious issues including activity degradation, methanol crossover, and CO poisoning. Although many alternative catalysts have been investigated for oxygen reduction reaction (ORR), their electrocatalytic activity and stability are insufficient and low in most of cases. Among them, graphene is the best support for electrocatalysts because of large surface area and high conductivity, even though stacking of graphene sheets are prone to lower the surface active sites [1].

In this review, we summarize very recent major research progress on graphene derivatives supported transition metal nanoparticle-based catalysts (nanocatalysts) including their synthetic methods and electrocatalytic performance for ORR. We specifically highlight and discuss the strategies to utilize graphene derivatives as practicable supports for variable nanocatalysts with the investigated ORR electrocatalytic properties. We also explore their synthetic designs, characterizations, prospective applications, advantages, stabilities, durability and challenges of the introduced systems. This article is organized as follows: (1) common experimental techniques for electrocatalytic ORR, (2) graphene-derived electrocatalysts. Especially, we mainly deal with the details of graphene-derived electrocatalyst systems such as Pt-based electrocatalysts enhanced or optimized for ORR in fuel cell, the synthesis and preparation of non-Pt noble metal electrocatalysts, and selected examples of non-noble metal electrocatalysts.

## 2. Experimental techniques in electrocatalytic ORR

In PEM fuel cells, two electrochemical reactions take place at the surface of the two electrodes. Hydrogen oxidizes on anode, while oxygen reduces on cathode. The hydrogen oxidation reaction (HOR) has a lower overpotential and a higher kinetic rate than the ORR. Especially ORR is well known as slow due to high reduction overpotential, so the main focus in PEM fuel cell is related to speed up the ORR kinetics. The commonly used techniques to evaluate ORR performance are cyclic voltammetry, linear sweep voltammetry. polarization curves, Koutecky-Levich plot, and chronoamperometric response, etc [4]. Table 1 summarizes the experimental techniques in electrocatalytic ORR.

### 2.1. Cyclic voltammetry

Cyclic voltammetry is a very common technique in electrochemistry and shows the electrochemical response and catalytic activity of the catalysts for the reactions in a three-electrode electrochemical cell. ORR is measured mostly in an $O_2$-saturated electrolyte solution in reversible potential range

**Table 1**
Summary of experimental conditions and techniques in electrocatalytic oxygen reduction reaction.

| Metal | Graphene type | Dopant or linker | Electrolyte | Reference electrode | Cyclic voltammetry | RDE, Tafel slope | Durability test | Tolerance test | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Pt | Graphene | Perfluoro-sulfonic acid | 0.5 mol/L $H_2SO_4$ | SCE | 0–1.2 V vs. RHE, 50 mV/s | RDE | 4000 cycles | CO | [12] |
| Pt | RGO | — | 0.1 mol/L $HClO_4$ | Ag/AgCl | 0–1.1 V vs. RHE, 100 mV/s | RDE | 20000 cycles | — | [13] |
| Pt | RGO | — | 0.5 mol/L $H_2SO_4$ | SCE | 0–1.2 V vs. RHE, 50 mV/s | RDE | 4000 cycles | — | [14] |
| Pt | RGO | Polydopamine | 0.1 mol/L KOH | Ag/AgCl | –0.8–0.4 V vs. Ag/AgCl, 10 mV/s | RDE | 10000 s | — | [15] |
| Pt | RGO | Nanodendrite | 0.1 mol/L $HClO_4$ | Ag/AgCl | 0–1.4 V vs. RHE, 50 mV/s | RDE | 10000 cycles | — | [55] |
| Pt | Graphene | — | 0.5 mol/L $HClO_4$ | SCE | 0–1.2 V vs. NHE, 20 mV/s | RDE | 1000 cycles | — | [56] |
| Pt | Graphene | $TiO_2$ | 0.5 mol/L $H_2SO_4$, 0.1 mol/L KOH | RHE | 0–1.4 V vs. RHE, 50 mV/s | RDE, Tafel | — | — | [57] |
| Pt | Graphene | — | 0.5 mol/L $H_2SO_4$ | SCE | 0–1.2 V vs. RHE, 50 mV/s | RDE, Tafel | 500 cycles | Methanol | [58] |
| Pt | RGO | — | 0.5 mol/L $HClO_4$ | Ag/AgCl | 0.1–1.1 V vs. Ag/AgCl, 5 mV/s | RDE | — | — | [59] |
| Pt | GO | — | 0.1 mol/L $HClO_4$ | Ag/AgCl | 0–1.4 V vs. RHE, 50 mV/s | RDE | 10000 cycles | — | [60] |
| Pt | Graphene | Perfluoro-sulfonic acid | 0.5 mol/L $H_2SO_4$ | Ag/AgCl | 0–1.2 V vs. NHE, 50 mV/s | RDE | 2000 cycles | — | [61] |
| Pt | RGO | — | 0.1 mol/L $HClO_4$ | Ag/AgCl | 0–1.1 V vs. RHE, 100 mV/s | RDE | 20000 cycles | — | [62] |
| Pd, Pt | Graphene | — | 0.1 mol/L NaOH | Ag/AgCl | 0.2–1.2 V vs. RHE, 50 mV/s | RDE | — | — | [16] |
| Pd, Pt | RGO | — | 0.5 mol/L $H_2SO_4$ | $Hg/Hg_2SO_4$ | 0–1 V vs. NHE, 20 mV/s | RDE, Tafel | — | — | [63] |
| Pd | RGO | — | 0.1 mol/L KOH | Ag/AgCl | 0.1–1.2 V vs. RHE, 5 mV/s | RDE | 4000 cycles | — | [18] |
| Pd | FLG | — | 0.1 mol/L KOH | Hg/HgO | 0–1.2 V vs. RHE, 10 mV/s | RDE, Tafel | 2500 cycles | Methanol | [19] |
| Pd | Graphene | — | 0.5 mol/L $H_2SO_4$ | Ag/AgCl | –0.2–1.1 V vs. Ag/AgCl, 50 mV/s | — | — | — | [64] |
| Au | RGO | — | 0.1 mol/L KOH | Ag/AgCl | –1–0.2 V vs. RHE, 5 mV/s | RDE | 1000 cycles | Methanol | [28] |
| Au | RGO | — | 0.1 mol/L KOH | SCE | –0.8–0.2 V vs. $Hg/Hg_2Cl_2$, 5 mV/s | RDE | — | — | [31] |
| Au | Graphene | N | 0.1 mol/L KOH | Hg/HgO | –0.8–-0.5 V vs. Hg/HgO, 10 mV/s | RDE, Tafel | — | — | [32] |
| Au | RGO | — | 0.1 mol/L KOH | Ag/AgCl | –1.2–0.2 V vs. Ag/AgCl, 50 mV/s | RDE | 4500 s | — | [33] |
| Au | GO | S | 0.1 mol/L KOH | Ag/AgCl | –0.7–0.4 V vs. Ag/AgCl, 50 mV/s | RDE, Tafel | 36000 s | — | [34] |
| Au | Graphene | — | 0.1 mol/L $H_2SO_4$ | Ag/AgCl | –0.4–1.2 V vs. Ag/AgCl, 20 mV/s | RDE | 50000 s | Methanol | [35] |

(To be continued)