

Graphene-MnO₂ Composite as Electrocatalyst for Oxygen Reduction Reactions.

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Abstract

In recent years, graphene-MnO₂ composites have been demonstrated to be efficient and promising electrocatalyst for oxygen reduction reaction (ORR) in fuel cells application. This brief review summarizes and categorizes the basic requirements, recent progress on the preparation and performance of these systems as ORR catalysts. A concise outline on the challenges and future perspective of this field are also highlighted.

Keywords: graphene-manganese dioxide, nanocomposite, oxygen reduction reaction (ORR), electrocatalyst.

Increasing demand for renewable and sustainable energy has stimulated intense research on energy conversion and storage systems that are highly efficient, cost effective and environmentally friendly. Among the various promising energy conversion technologies available till date, fuel cell, which converts chemical energy from fuels into electricity, is a clean and high-efficiency device with minimum emissions from operation and has drawn a great deal of interest in the recent past in terms of both fundamentals as well as applications [1-2]. In a fuel cell, the fuel (such as hydrogen, methanol, and ethanol, etc) is oxidized at the anode, and the released electrons are transferred to cathode where oxygen is reduced. Because the oxygen reduction reaction (ORR) consisting of 4-e transfer process at the cathode has sluggish reaction

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kinetics, this step limits the cell performance and accordingly, appropriate electrocatalysts are required to facilitate the ORR [3]. Consequently, the electrocatalyst material for the ORR is a key component for fuel cell and plays a vital role in determining the performance of fuel cells, such as power output, open circuit, energy efficiency, and longevity [4-7].

Among the several important factors influencing the ORR kinetics, the requirements of advanced electrode materials with outstanding features, including resourceful storage, plentiful mesoporous variety, potency, long durability, attractive facial chemistry, sustainable as well as wide potential window and environmental friendliness, are crucial points to obtain improved fuel cell performances. Electrode materials for ORR include a variety of metals like platinum, silver, cobalt, iridium, rhodium, etc [6, 8-9]; metal oxides like iron oxides, cobalt oxides and sulfides [10-13] with specific shapes, bimetallic/intermetallic compositions [14-15], and core-shell nanostructures [16-17], all of which have acquired some achievements in optimizing catalytic activity for ORR. Nevertheless some drawbacks, such as high cost, crossover effects and CO poisoning, are unavoidable in present situation, and these problems certainly lead to electrode modification to improve electrocatalytic efficiency [18-20].

Over the past few years, various graphene-based nanomaterials/composites have been extensively designed, prepared, and investigated as efficient electro-catalysts for ORR in fuel cells applications [21-22]. Graphene-based materials/composites are superior to pristine graphene, (which is a thin, single layer of sp^2 carbon atoms that are bonded together in a hexagonal honeycomb lattice) in various fields, such as in electronic or photo detectors, capacitors, transparent electrodes, sensors, electrocatalysis, environmental remediation, and energy applications [23-25]. Generally, when graphene-based nanocomposites are used as electrode materials for ORR, the following advantages are automatically benefited: (1) The

flexibility and immobilization of graphene nanosheets which provide large space to accommodate and support the anchored materials, preventing their agglomeration. (2)The good superficial characteristics of graphene due to large surface area increase the solid-air contact efficiency, resulting in a large amount of oxygen adsorption on graphene layers. (3)The electronic structure of graphene reinforces enhanced electrical conductivity which promotes electron transfer rate on the surface of graphene to be significantly increased. (4)The structural defects of carbon atoms on single layered graphene provide larger number of active sites for the functionalization of active groups, which stimulates the electrocatalytic ORR [24].

Recent leading works in this field includes introduction of various transition metal oxides anchored on graphene. The morphologies of the supported oxides on graphene with various dimensional nanostructures, such as one dimensional nanocrystals, two dimensional nanosheets/nanoplates have also been explored with impressive properties [26-28]. Among the several transition metal oxides, oxides of manganese are particularly more popular due to its easy availability, low production cost and superior redox characteristics. The family of oxides of manganese has complex members such as MnO_2 , Mn_2O_3 , and Mn_3O_4 [29]. Each of these oxides exhibits a variety of crystallographic structures and morphologies; they contribute to different extent in various catalytic activities, particularly for ORR. Amongst these various oxides of manganese, MnO_2 has been found to have impressive catalytic activity in ORR. It is well known that MnO_2 can form many polymorphs such as α , β , γ , δ - types, offering characteristic properties and extensive applications as promising material for electrocatalysts due to its easy preparation, superior electrochemical performance, environmental friendliness, and lower production cost [30-31]. Over the past few years, various nanostructured MnO_2 , including dendritic clusters, nanocrystals with different morphologies including nanowires, nanotubes/rods, nanobelts, and

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nanoflowers, have been successfully synthesized and characterized [32-34]. However, till date pure transition metal oxide electrodes have suffered from poor cyclability and low performances, mainly caused by its poor conductivity and morphological breakdown by the large volume-change during the repeated cycles which has urged the necessity of anchoring them to conducting 2D substrates like graphene.

Graphene–MnO₂ composite as an effective ORR catalyst is based on the following rationales: firstly, manganese oxides are desirable ORR catalysts because of their low price, environmentally friendly nature and intrinsic activity towards ORR. Secondly, graphene sheets, even in functionalized forms are sufficiently conductive to facilitate rapid electron transport for ORR. Thirdly, the dispersion of MnO₂ clusters on graphene sheets would provide better electrocatalytic performance for ORR. Finally, the direct growth of MnO₂ on graphene sheets without disrupting the conductive network would significantly reduce the contact resistance usually caused by conventional carbon-supported catalysts via simple absorption and/or mixing. Therefore, the synergistic effect of MnO₂ clusters and graphene sheets is expected to offer superior catalytic activities in comparison with the pristine components [20, 35].

Few years back, microwave-irradiated synthesis process of MnO₂/graphene nanosheets (MnO₂/GNs) hybrids as electrocatalysts for ORR [36]. The prepared MnO₂ particles (size of 5~10nm) were uniformly coated on the surface of GNs. The nanocomposites displayed a distinctive oxygen reduction peak at –0.43 V in alkaline solution, which is more positive than that of MnO₂ (–0.71 V) and even better than that of Pt/C (–0.44 V), demonstrating that MnO₂/GNs qualified as a significant ORR accelerator. To increase the solubility of graphene for processing purposes, many researchers proposed the usage of graphene oxide or/and reduced graphene oxide as supporting substrate instead of pure graphene. Current reports shows that

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MnO₂/reduced graphene oxide (MnO₂/rGO) composites were synthesized by a facile chemical reduction method assisted by poly(sodium 4-styrene sulfonate) [37]. There are two functional aspects used in this synthesis. The first is aimed at increasing the solubility of graphene in aqueous solutions thereby using the modification- reduced graphene oxide (rGO); the second is for tethering Mn²⁺ precursor onto graphene. The polymer-assisted synthetic strategy was adopted to create 3D MnO₂/rGO nanocomposites, which displayed good electrocatalytic activity toward the four-electron reduction of oxygen. Lately, three-dimensional flower-like manganese oxide was directly grown on reduced graphene oxide (RGO) sheets via a chelation-mediated method, exhibiting good catalytic activity, higher selectivity and better stability towards oxygen reduction reaction [35]. They showed that hierarchical structure generated from 3D MnO₂ clusters and RGO thin sheets is likely to facilitate the mass transfer of oxygen molecules to improve the diffusion limit for an efficient oxygen reduction synergistically. Moreover, RGO–MnO₂ composite is not able to catalyze the oxidation of the crossover methanol to reduce the oxygen reduction current, leading to higher selectivity toward ORR. Our group is also exploring the influence of different shapes of MnO₂ decorated on hydroxyl-functionalized graphene on ORR in a systematic approach [38]. Very recently, S. Khilari group developed graphene supported α -MnO₂ nanotubes (MnO₂-NTs/graphene composite) exhibiting impressive electrocatalysis in ORR reaction [39]. They indicated that the material had minimum charge transfer resistance value which facilitates excellent charge transport. This faster electron transport increases the oxygen reduction rate in accordance to the highest reduction current obtained from the MnO₂-NTs/graphene composite. Kumar group lately reported nano-tubular shaped α -MnO₂/graphene oxide nanocomposites were synthesized via a simple, cost and time efficient hydrothermal method. The growth of hollow structured MnO₂ nanotubes preferentially occurred along the

[001] direction as evidenced from the morphological and structural characterizations. The tunnels of α -MnO₂ nanotubes with increased surface area easily accommodated molecular oxygen and exhibited outstanding catalytic activity towards the oxygen reduction reaction over the rod structure and was further enhanced with the effective carbon support graphene oxide [40]. Another group reported a new electrocatalyst based on a graphene oxide-intercalated layered manganese oxide (GO-HLMO), which was prepared by inserting graphene oxide sheets within the interlayers of protonated layered manganese oxides (HLMO); its catalytic activity towards ORR was subsequently evaluated in alkaline media. They claimed that the aforesaid electrocatalyst had more accessible Mn(III)/Mn(IV) sites which probably resulted in the large enhancement in ORR activity in alkaline media [41].

Thus, we observe from the above studies that, the role of Graphene-MnO₂ composites in ORR is still in a very promising stage and the challenges, until now, remain to be realized in a scientific and technical way. The fundamental mechanism of the kinetic process in these graphene-based nanocomposites is yet to be fully understood/explored, especially with respect to their surface functionalities/defects and hierarchical electrode structures. More systematic exploration and deeper understanding of the different catalytic mechanisms of these types of graphene-based materials for ORR are required for optimum material design and device performance optimization. The durability and stability of these nanocomposites, too, of course, are of crucial importance for their practical application in real fuel cells. Obviously, the development of facile, green, cost-effective, and controllable preparation method is still also a significant issue, because the current assembly process usually needs rigorous reaction conditions (such as high temperature or pressure) and/or involves tedious procedures, which complicates its synthetic methodology. Thus, much further research is needed to understand the

ultimate objective of final industrial implementation, large scale, low cost, and simple production of these graphene-based materials with high catalytic activity and practical durability for ORR. This short review, nonetheless, is anticipated to encourage more future opportunities to achieve the aim and promote sustainability in this field of research.

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