



Graphene decorated with multiple nanosized active species as dual function electrocatalysts for lithium-oxygen batteries



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ABSTRACT

Development of an oxygen electrode with high stability and good electrochemical activity is critical to achieve the practical applications of rechargeable lithium-oxygen batteries (LOBs) in our daily life. Here, we report the facile synthesis of a graphene-based composite as an efficient dual function precious-metal-free electrocatalyst for LOBs by applying graphite oxide as the graphene precursor, aniline as the carbon and nitrogen source, FeCl₃ and Co(NO₃)₂·6H₂O as the cation sources and argon as the atmosphere during the pyrolysis. Scanning electron microscope and transmission electron microscope observations demonstrate that the as-prepared electrocatalyst is composed of graphene sheets with nanoparticles mainly in the size of 20–50 nm, while X-ray diffraction characterization confirms that the sample is composed of multiple species such as carbon, cobalt/iron oxide, cobalt/iron sulfide and metallic iron. The cyclic voltammetry and linear sweep voltammograms tests of the electrocatalyst demonstrate favorable electrocatalytic activity for both oxygen reduction and evolution reactions, suggesting its bifunctionality. With the electrocatalyst/Ketjen Black (KB) oxygen electrode applying in LOBs, a specific capacity of 4772 mAh g_{KB}⁻¹ and a discharge plateau potential of ~2.75 V are reached at the density of 100 mA g_{KB}⁻¹ for the related LOBs by discharging to 2.0 V and charging to 4.4 V.

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1. Introduction

With increasing concerns about environmental protection and a sustainable energy supply from the public and governments, electrochemical energy storage and conversion is playing an increasingly important role in our modern energy system. Considering their ultrahigh theoretical energy density (up to 11000 Wh kg⁻¹ [1]), rechargeable lithium-oxygen batteries (LOBs), which have great application potential in electrified vehicles and advanced electronics, have received particular attention during the past several years [2–8]. Unfortunately, the practical application of the rechargeable LOBs in our daily life has still not been realized to date because of the much lower achievable energy density and poor cycling stability of the state-of-the-art LOBs. Insufficient performance of the oxygen electrode is the main cause [9], although the imperfect electrolyte is also not negligible [10].

Both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) are involved in the oxygen electrode of rechargeable LOBs. In the past, considerable research efforts have been directed toward the development of an efficient O₂ electrode with improved activity for both types of reactions [11–15]. Four main types of catalysts are currently under development for ORR/OER, i.e., precious-metal-based materials (Pt, RuO₂ and IrO₂, etc.) [16,17], carbon-based materials (amorphous carbon, doped graphene, etc.) [18–20], transition metal oxides (Fe_mO_n, Co_mO_n, etc.) [21–23], and macromolecules [24]. Pt/C and IrO₂ are the state-of-the-art catalysts for ORR and OER, respectively [17,25,26]. However, a prohibitively high price and scarcity of resources have greatly inhibited their wide use in practical electrochemical devices. Currently, research efforts directed toward the development of noble-metal-free electrode materials for ORR and OER are increasing.

To function as an ideal oxygen electrode for LOBs, in addition to high electrocatalytic activity for oxygen electrocatalysis, the oxygen electrode should also possess sufficient electrical conductivity for efficient current collection. With this consideration, carbon is attractive for its high electrical conductivity and versatile

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properties. The catalytic activity of carbon materials for oxygen electrocatalysis can be tailored through morphology control, surface functionalization and bulk doping [18,27–30]. For example, transition metal(s) (Co or/and Fe) and nitrogen co-doped carbon were recently demonstrated to show promising activity for ORR in an acidic or alkaline aqueous medium [21,22,31], although it is still not clear whether the improved performance was merely due to the promoted formation of more active sites from carbon under the catalysis of a transition metal or resulted from the formation of metal-N_x active sites. The catalytic mechanism of metal-N_x active sites, formed generally by the pyrolysis of nitrogen-rich metal complexes or mixtures containing metal salts, nitrogen-rich organic compounds and carbon, remains largely elusive [32,33].

As an important allotrope of carbon, graphene is an atom thick two-dimensional material that has attracted enormous amounts of attention for functional applications because of its ultrahigh electrical conductivity, outstanding mechanical flexibility, and high surface area, as well as easy surface functionalization [34,35]. The application of graphene or graphene sheets as an electrocatalyst for ORR/OER has recently been well exploited [18–20]. After doping with foreign atoms such as N, S, P and B or a combination of these atoms, very attractive activity for ORR was demonstrated [20,29,30]. However, it is still a major challenge to achieve high activity for both ORR and OER in a single material because different rate limiting steps were usually found for each reaction.

Interestingly, increasingly more experimental results have demonstrated that the formation of a composite electrode from different types of electrocatalysts could lead to improved catalytic activity for ORR/OER compared to the individual components [23,25,31,35], making it possible to develop a bifunctional electrode with high activity for both ORR and OER. This improvement may be related to the complex ORR and OER mechanisms that involve multiple reaction steps, while the formation of a composite electrode may effectively improve the reaction kinetics for the rate limiting step(s) because of the synergistic effects of the different components. For example, we have previously demonstrated a mixture of Pt/C with high activity for ORR and perovskite-type Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} oxide with high activity for OER, and the catalytic activity for both ORR and OER in alkaline media was obviously improved, suggesting the existence of a synergistic effect between the components [36].

Although there are several reports available in the literature about the combination of transition metal and nitrogen co-doped carbon as an electrocatalyst for ORR in an acidic or alkaline medium [37–39], few studies about two transition metal co-doped carbon for ORR or/and OER are available [40]. In particular, the use of electrocatalysts with multiple active components in rechargeable LOBs with a non-aqueous electrolyte has rarely been reported. Very recently, Song et al. demonstrated that an electrocatalyst composed of reduced graphene oxide modified with oxide nanoparticles, nitrogen dopants and possible metal-N-C sites showed attractive performance for ORR in an aqueous alkaline medium [41]. The reactions of an oxygen electrode in LOBs with a non-aqueous electrolyte are known to be more complicated compared to reactions with an aqueous electrolyte because insoluble Li₂O₂ will be formed during the discharge process, and the insoluble Li₂O₂ will build up in the pores of the electrode, significantly affecting the cycling stability.

In this study, we reported a facile synthesis of a graphene-based composite with multiple active species such as Co, Fe and N co-doped graphene, cobalt/iron oxide, and cobalt/iron sulfide as a new type of bifunctional electrocatalyst for rechargeable LOBs with an organic liquid electrolyte. Under optimal conditions, good bifunctionality of the catalyst was demonstrated with favorable activity for both ORR and OER. The as-developed catalysts were further

investigated as a practical O₂ electrode in an LOB with an organic liquid electrolyte.

2. Experimental

2.1. Sample preparation

Graphite oxide, the raw material for graphene in this study, was prepared from natural graphite powder by oxidation with a mixture of NaNO₃, H₂SO₄ and KMnO₄ in an ice bath according to a modified Hummers method [42]. For a typical synthesis, a suspension composed of 5.0 g pulverized flaky graphite, 3.75 g NaNO₃ and 172.2 mL concentrated H₂SO₄ was added to a beaker under stirring at room temperature for 24 h. Then, 22.5 g KMnO₄ was slowly added to the beaker under stirring and in an ice bath to allow the quick release of the heat from the violent oxidation reaction between the graphite and the oxidants. The resulting mixture was stirred for another 5 days to allow the reaction to go to completion. Afterward, 500 mL of 5 wt.% H₂SO₄ was added to the mixture under stirring for 2 h; then, 50 g of 30 wt.% H₂O₂ was also added, and the mixture was stirred for another 2 h. Finally, the suspension was washed by 2 L of 30 wt.% H₂SO₄/1 wt.% H₂O₂ solution and then purified with deionized water by a centrifuge to remove the impurities until the supernatant showed a pH value of 7. The brown homogeneous graphite oxide suspensions were collected by removing the supernatant. Graphite oxide powder was obtained after the drying of the suspensions, followed by grinding.

Iron and cobalt were added simultaneously for the modification of graphene, and the molar ratio of cobalt to iron was fixed at 1:2. The dual function electrocatalysts were prepared as follows. Graphite oxide powder (100 mg, as prepared by the modified Hummer method) was dispersed into 100 mL hydrochloric acid (0.5 M) by sonication for 30 min to obtain the graphene oxide (GO)/hydrochloric acid suspension. Aniline (1 mL) was dispersed into the hydrochloric acid solution under ice-bath conditions; then, the transition metal precursors of FeCl₃ (1 mmol) and Co(NO₃)₂·6H₂O (2 mmol) were added to the suspension obtained above, followed by the addition of ammonium persulfate (APS) (molar ratio aniline/APS=4/1). The in situ polymerization of aniline was carried out with magnetic stirring at room temperature for 24 h. Then, 200 μL NH₃·H₂O and 40 μL N₂H₄ were sequentially added to this suspension using a pipette at 110 °C to allow the reduction of GO to reduced graphene oxide (rGO). After reduction for 24 h, the suspension containing carbon, polymer and transition metal was dried at room temperature. The as-obtained solid samples were ground into powder, put into a quartz boat, and annealed for 2 h in a tube furnace at 850 °C under a flowing argon atmosphere. The heating rate was fixed at 5 °C min⁻¹, and the Ar flow rate was constant at 200 mL min⁻¹. The sample obtained was treated in 0.5 M H₂SO₄ at 80 °C for 8 h to remove unstable and inactive species (uncarbonized organic components) from the catalyst and then thoroughly washed with deionized water. The catalyst was heat-treated again under an argon atmosphere at 850 °C for 0.5 h. The final product was obtained and is denoted as PANI-Fe₁-Co₂-rGO.

2.2. Basic characterization

The X-ray diffraction (XRD) patterns at room temperature for the prepared samples were characterized by a Rigaku Smartlab (Cu K-alpha radiation, λ = 1.5406 Å) for phase identification. The morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM) images obtained from a Hitachi S-4800. The energy dispersive X-ray spectroscopy (EDX) mapping was obtained using an EDAX GENESIS 2000 to detect the

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