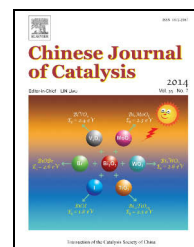


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Article

Facile preparation of modified carbon black-LaMnO₃ hybrids and the effect of covalent coupling on the catalytic activity for oxygen reduction reaction

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ABSTRACT

Covalent coupling between LaMnO₃ nanoparticles and carbon black to produce a composite catalyst for oxygen reduction reaction (ORR) was achieved by physical mixing of modified carbon and perovskite-type LaMnO₃ nanoparticles, followed by sintering at different temperatures. Perovskite-type LaMnO₃ nanoparticles were first synthesized via chemical precipitation, and the carbon support (Vulcan XC-72) was modified using graphitization, followed by HNO₃ and ammonia treatments. The morphology and electronic states of the carbon black-LaMnO₃ hybrid catalyst were characterized by scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The loaded LaMnO₃ particles featured rod-like, three bars-like, and bamboo rod-like structures and were homogeneously dispersed in the carbon matrix that featured a hollow spherical structure. At a sintering temperature of about 300 °C, C–O–M (M = La, Mn) bonds formed at the interface between the carbon and LaMnO₃ nanoparticles. Electrochemical measurements in 1 mol/L NaOH showed that the carbon-LaMnO₃ hybrid prepared at a LaMnO₃/GCB mass ratio of 2:3 displayed the highest electrocatalytic activity towards ORR among all the synthesized hybrid catalysts. The electrocatalytic activity was comparable with that obtained by commercial Pt/C catalyst (E-TEK). The average electron transfer number of ORR was ~3.81, and the corresponding yield of the hydrogen peroxide intermediate was ~9.5%. The remarkably improved electrocatalytic activity towards ORR was likely because of the formation of covalent bonds (C–O–M) between the LaMnO₃ nanoparticles and carbon that can effectively enhance the ORR kinetics. This information is important to understand the physical origin of the electrocatalytic activity of carbon-supported rare earth oxides as catalysts for ORR.

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1. Introduction

Oxygen reduction reaction (ORR) has long been considered one of the key electrochemical reactions in electrochemical energy storage and conversion devices such as fuel cells and

metal-air batteries. Moreover, ORR plays a significant role in the sewage advanced electrolytic oxidation treatment and chemical electrolysis industries [1]. However, ORR kinetics are slow. Hence, to afford practical application of ORR in these industries, efficient ORR electrocatalysts are essential [2]. To

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date, carbon-supported platinum (Pt) and the corresponding alloys have been regarded as the best catalyst for ORR. Thus, a commercial carbon-supported Pt catalyst (Pt/C, E-TEK) has been developed and is currently widely used in various fuel cells and metal-air batteries. However, the high cost and limited supply and durability of non-renewable resource Pt severely restrict the commercial application of Pt-based catalysts. Therefore, much effort has been devoted to substituting Pt-based catalysts by designing new oxygen reduction electrocatalytic materials with high catalytic activity, strong durability, and low cost for ORR; this is currently receiving much attention [3].

In recent years, some metal oxides have attracted research interest owing to their good electrochemical performance [4]. Because of the high selectivity, high chemical stability, and low-cost attributes of metal oxides, they have been used as catalysts for ORR in alkaline media [5]. Such metal oxides used as ORR catalysts can be categorized as transition metal oxides and rare earth oxides. Because these metal elements have variable valencies when linked with oxygen atoms in different oxides, it is possible to reduce the overpotential of ORR catalyzed by metal oxides. Studies have shown that carbon-supported MnO_x nanoparticles doped with either Mg or Ni exhibit high electrocatalytic activities and selectivity towards ORR in alkaline media that are comparable with those of commercial Pt/C catalysts [6]. Moreover, graphene-supported Co_3O_4 composites exhibit unexpectedly high electrocatalytic activities and stability towards ORR, considering the respective low electrocatalytic activities of the individual Co_3O_4 nanoparticles and carbon components [7]. Chemical coupling of carbon (carbon black, carbon nanotube, and graphene) and metal oxides (such as MnO_2 , Co_2O_3 , NiO_2 , and TiO_2 nanoparticles) that results in interfacial interactions between the nanoparticles and carbon support can potentially lead to high catalytic activities of the resulting hybrid catalysts [6,7]. Hence, researchers proposed that the high electrocatalytic activities for ORR on metal oxides are related to the strong electronic affinity between the metal oxide and carbon support [8–10]. Such strong electronic affinities result in unique valence electron distribution and electronic structure characteristics of the hybrid catalyst that differ from those of the single material component [11,12]. When compared with transition metal oxides, perovskite-type rare earth oxides (such as LaMO_3 , $M = \text{Mn}$, Ni , and Co) exhibit superior stability, higher conductivity (electronic, ionic, and lattice oxygen vacancy conductivity), and higher electrocatalytic activity towards ORR in alkaline media [13]. Based on previous findings, we propose the synthesis of highly efficient carbon-supported LaMO_3 nanoparticles (perovskite-type rare earth oxide nanoparticles loaded on carbon) hybrid catalysts for ORR. However, classical chemical precipitation does not afford the synthesis of carbon-supported LaMO_3 with a pure perovskite structure (e.g., LaMO_3 , $M = \text{Mn}$, Ni , and Co) owing to the presence of carbon in the synthesis system, thereby considerably limiting the synthesis and application of such highly active electrocatalytic materials.

To address this issue, modified carbon black-supported LaMnO_3 nanoparticles with a perovskite-type structure were

prepared by mixing carbon and pure LaMnO_3 nanoparticles followed by sintering at different temperatures to achieve chemical coupling between the carbon support and LaMnO_3 particles. Prior to mixing and sintering, the pure perovskite-type LaMnO_3 nanoparticles were synthesized in aqueous solution via chemical precipitation. The carbon support (Vulcan XC-72) underwent graphitization at an elevated temperature, and the resulting graphitized carbon was subjected to successive surface chemical modification in HNO_3 and ammonia. The morphological and electronic structure of the resulting carbon black- LaMnO_3 hybrid catalysts was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The relationship between the electrochemical performance and composition of the hybrid catalysts was examined in an alkaline solution. The effect of the electronic interaction between the LaMnO_3 nanoparticles and carbon support on the ORR activity was investigated. Although the preparation of perovskite-type LaMnO_3 -carbon black hybrids for the ketonization of alcohols has been reported [14,15], the application of such hybrids in the area of electrocatalytic ORR is rarely reported. This work is important for understanding the origin of the ORR electrocatalytic activity of modified carbon black- LaMnO_3 hybrids.

2. Experimental

2.1. Preparation of modified carbon black- LaMnO_3 hybrids

For the synthesis of carbon-supported LaMnO_3 with a perovskite-type structure as covalent hybrid catalysts, the carbon support was first prepared. Vulcan XC-72 carbon (CB, CABOT Corporation) underwent graphitization, and the graphitized carbon was then subjected to successive surface chemical modification in HNO_3 and ammonia. Optimum graphitization treatment of the carbon support was performed to improve the integrity of the graphite structure. In a typical process, 10 g of CB was placed in a graphite container and sealed, and then heated in a furnace at 2600 °C for 1 h under an argon atmosphere, followed by cooling to room temperature. Then, the graphitized carbon black (GCB) underwent surface chemical modification in HNO_3 , then in ammonia to generate large amounts of oxygen-containing functional groups (e.g., carboxyl and hydroxyl) on the carbon surface. These can then provide active points for the deposition of the metal oxide particles. In a typical nitric acid acidification of the carbon material, 10 g of GCB was first introduced into a three-neck flask. Then, excessive amounts of concentrated nitric acid were added, and the mixture was refluxed in an oil bath at 140 °C for 10 h, then cooled to room temperature. The treated GCB powder was washed with deionized water until the pH of the filtrate was neutral, then dried at 80 °C under vacuum. The subsequent ammonia treatment process was as follows: 5 g of acidified GCB powder was added to excess amounts of concentrated ammonia, and heated at 290 °C for 3 h under an air atmosphere.

The perovskite-type LaMnO_3 nanoparticles were synthesized in aqueous solution by chemical precipitation. In a typical process, 1 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%, Tianjin Afar Sally

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