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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

Chemical Co., Ltd., China) and 1 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99%, National Medicine Group Chemical Reagent Co., Ltd., China) were dissolved in 10 mL of deionized water, followed by dropwise addition of 0.5 mol/L of tetramethylammonium hydroxide aqueous solution (TMAH, 25%, Chemical Reagent Co., Ltd., China) until the pH of the solution was at least 9 (some precipitates were generated when the pH was below 9). The reaction mixture was then sonicated for 40 min. The precursor powder was collected by filtration, washed with deionized water and ethanol, and dried at 80 °C for 2 h. Then, the obtained precursor powder was heated to 700 °C for 5 h at a heating rate of 5 °C/min under argon atmosphere to produce perovskite- LaMnO_3 oxide powder.

Modified carbon black- LaMnO_3 hybrid catalysts with different LaMnO_3 -to-carbon mass ratios of 1:3, 2:3, 3:3, and 4:3 were prepared. In a typical process, a known amount of prepared LaMnO_3 powder and surface chemically modified GCB were respectively added to 20 mL deionized water, followed by addition of 3% Casein X-100 (National Medicine Group Chemical Reagent Co., Ltd., China) and 17% isopropyl alcohol (National Medicine Group Chemical Reagent Co., Ltd., China). Then, the mixture was crushed 99 times using a 1500-W ultrasonic cell crusher (Scientz-2000). The resulting product was collected by centrifugation, dried at 80 °C for 2 h, heated at 300 °C for 2 h under air atmosphere, and naturally cooled to room temperature. A schematic illustration of the synthesis process of carbon black- LaMnO_3 hybrid is shown in Fig. 1.

2.2. Characterization

The lattice structures of the synthesized hybrid catalysts were analyzed on an X-ray powder diffractometer (RINT 2200V/PC, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation operating at 40 kV and 200 mA under a scanning rate of 10°/min. The morphologies of the samples were observed by field-emission scanning electron microscopy (JEOL-6701F, JEOL, Japan) and high-resolution transmission electron microscopy (JEM-3010, JEOL, Japan). The degree of mixing was evaluated using a mapping analysis device attached to the SEM. Raman spectroscopy (LabRam HR800, Horiba Jobin Yvon, France) was used to quantitatively analyze the structural integrity of the carbon materi-

als before and after graphitization. To assess the degree of surface chemical modification of the carbon materials, a specific surface area and pore size analyzer (QUADRASORB SI-MP-9, Quantachrome, America) was used to determine the specific surface area of the carbon materials. Fourier-transform infrared spectroscopy (Spectrum100, PerkinElmer, America) was used to characterize the functional groups on the carbon black surface following treatment with nitric acid. A nano particle analyzer (Nano-ZS90, Malvern, England) was used to assess the dispersion stability of the carbon materials in aqueous solution. To study the chemical states and stability of the carbon materials and catalytically active particles, XPS (Thermo ESCALAB 250, Thermo Scientific, America), thermogravimetric analysis (TG), and differential thermogravimetric analysis (DTA, Thermo plus TG8120, Rigaku, Japan) were conducted. Calibration of the XPS analysis was conducted with respect to the C 1s peak at 284.6 eV.

2.3. Electrochemical measurements

The electrochemical performance of the samples was tested using a rotating ring-disk electrode device (AFCBP1 type, PINE, USA). The measurements were performed in a typical three-electrode system in 1 mol/L NaOH electrolytic solution at room temperature with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrodes were prepared by depositing a thin layer of catalyst ink onto a glassy carbon (GC, area of 0.247 cm^2). The catalyst ink was prepared by dispersing 10 mg of catalyst in a mixture of 1 mL ethanol and 1 mL water, followed by addition of 100 μL of film-forming reagent, i.e., Nafion aqueous solution (5 wt%, DUPONT, USA). The suspension was sonicated for 30 min to form a homogeneous ink, then pipetted onto the surface of the GC electrode and dried at room temperature. The disk potential was scanned at 5 mV/s and the ring potential was constant at 0.5 V (versus SCE). Prior to the experiments, a 1 mol/L NaOH electrolyte solution was saturated with high-purity oxygen. During the measurements, a constant gentle flow of O_2 was bubbled through the electrolyte solution to ensure continuous O_2 saturation.

Fig. 1. Schematic diagram of the preparation procedure of modified carbon black- LaMnO_3 hybrid.

3. Results and discussion

3.1. Structure modification and surface chemical modification of the carbon support

Figure 2 shows HRTEM images of the pristine carbon black and graphitized carbon black. As shown in Fig. 2(a), the pristine carbon black featured a large number of random and short carbon plates that were arranged in a concentric fashion. Moreover, many surface defects on the carbon black particles were observed, indicating a low degree of graphitization. This highly disordered structure leads to not only poor conductivity but also low durability [16]. As shown in Fig. 2(b), after the high-temperature graphitization treatment, the degree of structural integrity and crystallinity of the graphitized carbon black particles improved. A distinct graphite flake structure in the outer layers of the graphitized carbon black particles was observed along with the hollow structure of the carbon black particles. This finding shows that carbon black was converted from a solid-type to hollow-type particles during graphitization at 2600 °C.

To study the lattice structure of the carbon material before and after the high-temperature graphitization treatment, the samples were characterized by XRD. As observed in Fig. 3(a), the XRD pattern of pristine carbon black (CB) displayed diffraction peaks at 24.4°, 43.4°, and 52.7° that were attributed to the (002), (100), and (004) planes of carbon. When compared with CB, the resulting X-ray diffraction peaks corresponding to the (002), (100), and (004) planes of carbon in GCB were sharper. Moreover, the broad peak centered at 26°, corresponding to the (002) plane in GCB, was slightly shifted to higher angles with respect to the corresponding peak in CB, suggesting a high degree of graphitization that was consistent with the TEM analysis. Raman spectroscopy measurements were conducted to further characterize the degree of graphitization in GCB. As observed in Fig. 3(b), both carbon materials (CB and GCB) featured D and G peaks at 1350 and 1580 cm^{-1} , respectively. Unlike CB, GCB exhibited a 2D peak at about 2710 cm^{-1} . In general, the appearance of D peak, which corresponds to the A_{1g} vibration mode of graphite crystallite, is due to the presence of lattice defects and the reduced degree of graphitization in carbon

Fig. 2. HRTEM images of pristine carbon black (a) and graphitized carbon black (b) at 2600 °C.

materials. Unlike D peak, the appearance of 2D peak is indicative of higher graphitic ordering. The G peak corresponds to the vibration mode of E_{2g} of C–C bond stretching vibration within the graphite lattice plane that is inherent in natural graphite [17–19]. As a result, the degree of graphitization of carbon materials can be quantitatively characterized by evaluating the integral peak intensity ratio of either D and G peaks or 2D and G peaks. As evaluated from Fig. 3(b), the I_D/I_G values of CB and GCB were 2.41 and 0.45, respectively. This finding implied that the level of graphitization and crystallinity of the carbon materials significantly improved after the high-temperature treatment. Consequently, high-temperature graphitization can improve the electrochemical properties, durability of the carbon support in alkaline media, and electrical conductivity of CB.

The specific surface areas of CB and GCB were 216 and 73 m^2/g , respectively. The lower specific surface area of GCB may be due to the decrease in the pore structure and presence of defects owing to the improved degree of graphitization during the high-temperature treatment process. To overcome the problem of high hydrophobicity and small specific surface area, as featured by GCB following graphitization, a two-step surface chemical modification of GCB in HNO_3 and ammonia was carried out. The specific surface area of GCB after the surface chemical modification increased to 85 m^2/g . During the surface chemical modification, large amounts of oxygen-containing functional groups (e.g., carboxyl and hydroxyl) are grafted on the surface of GCB that can serve as active points for the depo-

Fig. 3. XRD patterns (a) and Raman spectra (b) of pristine carbon black (CB) and graphitized carbon black (GCB).

Fig. 4. FTIR spectra (a) and zeta potential profiles (b) of the carbon materials. (1) Pristine GCB; (2) Nitric acid-treated GCB; (3) Modified GCB following successive treatments in nitric acid and ammonia solutions.

sition of metal oxide particles. The FTIR spectra of pristine GCB, nitric acid-treated GCB, and ammonia-treated nitric acid-treated GCB are shown in Fig 4(a). All three carbon materials displayed characteristic peaks at 3430, 1220, and 1630 cm⁻¹. The bands at 3430 and 1630 cm⁻¹ were attributed to the stretching and deformation vibration of -OH (in adsorbed water and grafted hydroxyl groups on the surface of carbon black), and the band at 1220 cm⁻¹ was assigned to stretching vibrations of epoxide groups on the carbon black surface. Unlike from the non-treated GCB, the nitric acid-treated GCB and ammonia-treated nitric acid-treated GCB samples displayed a small peak at 1730 cm⁻¹, which was attributed to the stretching vibration of -COO [20]. The presence of these peaks demonstrates the presence of oxygen-containing functional groups grafted onto the surface of GCB. Zeta potential values of GCB, HNO₃-treated GCB, and ammonia-treated HNO₃-treated GCB were +23, -31, and -50 mV, respectively (Fig. 4(b)). This suggests that the surface of the modified GCB after the two-step surface modification treatment in nitric acid and ammonia features larger amounts of functional groups possessing a surface negative charge. Based on these findings, hydrophilic oxygen-containing functional groups can be efficiently grafted on the surface of carbon materials with a high degree of graphitization via surface chemical modification. Consequently, the modification process affords the generation of a large number of active sites for subsequent chemical deposition of rare earth oxide nanoparticles on the surface of the carbon.

3.2. Structure of modified carbon black-LaMnO₃ hybrid

The pure perovskite-type LaMnO₃ nanoparticles were first prepared by co-precipitation of La(NO₃)₃·6H₂O and MnCl₂·4H₂O precursors by accurately controlling the pH of the aqueous solution. The influence of pH on the morphological and crystalline structures of the oxide nanoparticles was investigated by XRD and SEM. The XRD patterns of the samples prepared under different pH conditions and calcined at 700 °C displayed distinct diffraction peaks at 22.3°, 25.1°, 31.3°, 32.3°, 40.1°, 45.7°, 47.2°, 57.7°, and 67.7° (Fig. 5). These distinct peaks correspond to the (110), (111), (020), (200), (202), (220),

(004), (312), and (400) crystalline planes of LaMnO₃, respectively, and are consistent with those of LaMnO₃ (JCPDS 35-1353). Other minor peaks that were observed were also consistent with those of LaMnO₃. No additional peaks associated with impurities were observed regardless of the different pH conditions employed, indicating the presence of pure perovskite-type LaMnO₃ oxides. The morphology of the prepared LaMnO₃, which is shown in Fig. 6, featured rod-like, three bars-like, and bamboo rod-like structures. The average size of the nanoparticles is 40–60 nm in diameter and 200–400 nm in length. Hence, it could be concluded that pH had negligible effects on the morphology of the nanoparticles. However, pH significantly influenced the dispersion of the nanoparticles. When the pH was adjusted to 9, the resulting LaMnO₃ nanoparticles displayed good dispersion on the carbon support, with no apparent agglomeration (Fig. 6(a)). When the pH was higher than 9, the resulting oxide nanoparticles tended to gather together, subsequently growing to larger particles and leading to significant agglomeration (Fig. 6(b)–(d)).

In this work, the carbon-LaMnO₃ hybrid catalysts were first prepared by mixing the previously prepared pure perovskite-type LaMnO₃ with the modified GCB at different LaM-

Fig. 5. XRD patterns of pure perovskite-type LaMnO₃ nanoparticles prepared under different pH conditions.

Fig. 6. SEM images of LaMnO_3 nanoparticles prepared under different pH conditions. (a) pH = 9; (b) pH = 10; (c) pH = 11; (d) pH = 12.

nO_3/C mass ratios, followed by sintering at 300 °C under air atmosphere for 2 h. Figure 7 displays the XRD patterns of the synthesized hybrid material with a LaMnO_3/C mass ratio of 2:3. Based on the XRD analysis, the hybrid material showed a distinct diffraction peak at $\sim 26^\circ$, which is consistent with the diffraction peak of the C(002) plane of the modified GCB. Additional diffraction peaks were consistent with the characteristic diffraction peaks of pure perovskite-type LaMnO_3 (Fig. 7). This shows that the hybrid material maintains the characteristic perovskite-type crystal structure of component LaMnO_3 even at a high sintering temperature of 300 °C. Figure 8 displays the SEM image and corresponding mapping profile (inset) of the synthesized hybrid material. As observed, the La element (green), Mn element (red), and C element (gray) were well distributed on the surface of the modified GCB. The average size of the LaMnO_3 particle is about 40–60 nm.

To further confirm the presence of chemical coupling between the LaMnO_3 nanoparticles and carbon support, thermogravimetric analysis of the GCB- LaMnO_3 hybrid catalysts sin-

Fig. 7. XRD patterns of modified GCB (1), LaMnO_3 (2), and modified GCB- LaMnO_3 hybrid (3).

Fig. 8. SEM and corresponding mapping profile (inset: La, green; Mn, red; C, gray) of modified GCB- LaMnO_3 hybrid.

tered at different temperatures was conducted. As shown in Fig. 9, the onset of oxidation temperature of carbon in the modified GCB is approximately 676 °C. The onset of oxidation temperature of carbon in the GCB- LaMnO_3 hybrid prepared at 250 °C is about 600 °C, whereas that in the GCB- LaMnO_3 hybrid prepared at 350 and 400 °C is about 633 °C. The hybrid material prepared at a sintering temperature of 300 °C displayed an onset oxidation decomposition temperature of about 570 °C,

Fig. 9. TG (a) and DTA (b) curves of modified GCB (1) and modified GCB- LaMnO_3 hybrid prepared at sintering temperatures of 250 (2), 300 (3), 350 (4), and 400 °C (5).

which is the lowest among all the studied samples. According to the literature, the presence of metal oxide can effectively promote the oxidation of carbon materials in metal oxide-carbon hybrid materials at elevated temperatures, provided that the individual components are in close proximity [21]. Based on this reported study, we believe that intimate contact between the loaded LaMnO_3 nanoparticles and carbon support enables the development of chemical interactions between the particles and carbon. Subsequent research results also confirmed that covalent bond connections formed between the metal oxide and carbon black during heat treatment at 300 °C, consequently leading to an improved electrocatalytic activity towards ORR.

3.3. Electrocatalytic performance

Figure 10(a) shows the polarization curves of commercial Pt/C and the synthesized carbon- LaMnO_3 hybrid catalysts prepared at different LaMnO_3/C composition ratios, measured at room temperature in an O_2 -saturated 1 mol/L NaOH solution. The hybrid catalyst prepared at a LaMnO_3/C composition ratio of 2:3 showed the highest oxygen reduction electrocatalytic activity. The onset potential of the catalyst was higher in the positive direction than that of the catalysts prepared at alterna-

tive composition ratios. Also, the resulting ORR limiting diffusion current density of the catalyst was higher, reaching up to 2.8 mA/cm^2 , which was comparable with that of commercial Pt/C (E-TEK, 3.2 mA/cm^2). To further evaluate the ORR efficiency of the hybrid catalyst (LaMnO_3/C composition ratio of 2:3), rotating ring-disk measurements were performed in 1 mol/L O_2 -saturated NaOH solution under different rotation rates. The results are shown in Fig. 10(b). As observed, the ORR limiting diffusion current increases with increasing electrode rotation rates. This suggests that the ORR process, as catalyzed by this catalyst, is entirely controlled by the diffusion of the dissolved oxygen. Moreover, the disk current was much larger than the ring current in the scanning potential region from -0.2 to -1.0 V, relative to the SCE. The electron transfer number (n) and the ORR hydrogen peroxide yields ($Y(\text{H}_2\text{O}_2)$) can be calculated from the measured disk current and ring current as described in the literature [22] according to the following equations:

$$n = 4I_D / (I_D + I_R/N) \quad (1)$$

$$Y(\text{H}_2\text{O}_2) = 2I_R / (I_R + NI_D) \times 100\% \quad (2)$$

where I_D and I_R are the disk current and ring current, respectively, and N is the current collection efficiency of the Pt ring. N was determined to be 0.37.

Fig. 10. (a) Polarization curves of the hybrids prepared at different LaMnO_3/C mass ratios of 1:3 (1), 2:3 (2), 3:3 (3), and 4:3 (4), and commercial Pt/C (5), recorded at room temperature in an O_2 -saturated 1 mol/L NaOH solution at 1600 r/min. (b) Rotating ring-disk electrode voltammograms of GCB- LaMnO_3 hybrid prepared at a composition ratio of 2:3. The disk potential was scanned at 5 mV/s and the ring potential was constant at 0.5 V (versus SCE). (c) ORR electron transfer number of GCB- LaMnO_3 hybrid prepared at a composition ratio of 2:3 at varying potentials under 1600 r/min. (d) Percentage yield of peroxide at varying rotation speeds using GCB- LaMnO_3 hybrid catalyst prepared at a composition ratio of 2:3

Using the disk and ring current values in the diffusion controlled region (Fig. 10(b)), the electron transfer number of ORR was calculated from Equation (1) at different cathodic polarization potentials (i.e., -0.5 , -0.6 , -0.7 , -0.8 , and -0.9 V). The results are shown in Fig. 10(c). The number of transfer electrons in ORR on this catalyst was 3.78, 3.8, 3.82, 3.82, and 3.82, respectively, averaging to a value of 3.81. The corresponding yield of hydrogen peroxide was 9%, 8.9%, 9.1%, 9.9%, and 10.7%, producing an average yield of 9.5%. The above results showed that the ORR catalyzed by the GCB-LaMnO₃ hybrid proceeded mainly via a four-electron reduction pathway. To confirm the pathway of oxygen reduction, the production of hydrogen peroxide intermediate during ORR was measured using Equation (2) at -0.8 V (versus SCE), as shown in Fig. 10(d). As the electrode rotation rate increased from 400 to 1600 r/min, the hydrogen peroxide yields reduced from 14.2% to 9.9%. The lower yields of hydrogen peroxide further confirmed that the ORR on this hybrid catalyst proceeded via a four-electron mechanism, hence leading to the high selectivity for ORR in alkaline media. A reported study suggested that ORR over pure perovskite oxides proceeds via an oxygen ion reaction mechanism [23], whereas that of the carbon-perovskite oxide hybrid catalyst involves a synergistic effect mechanism. Furthermore, Yeager [24] proposed that the oxygen molecules on the surface of carbon materials are first reduced to HO₂⁻ by a two-electron pathway, then catalytically converted to either O₂ or OH⁻ by the perovskite oxide. Thus, the high electrocatalytic activity primarily originated from an oxygen reduction synergistic effect involving carbon black and LaMnO₃, as schematically depicted in Fig. 11.

To investigate the stability of the carbon-perovskite oxide hybrid materials during ORR in an alkaline medium, galvanostatic tests were conducted and the results were compared with that obtained from the commercial Pt/C catalyst. As observed from Fig. 12, the carbon-perovskite oxide hybrid material featured a stable oxygen reduction potential, which was comparable with that of the commercial Pt/C. Moreover, under extended working conditions, the electrode potential of the hybrid catalyst is slightly more stable than commercial Pt/C, showing the high stability of the hybrid catalyst in alkaline media.

3.4. Chemical compound effects analysis of the electrocatalytic materials

Fig. 11. Schematic diagram of the oxygen reduction reaction mechanism of the modified GCB-LaMnO₃ hybrid.

Fig. 12. Chronopotentiometry response of modified GCB-LaMnO₃ hybrid (1) and commercial Pt/C (2) at a constant current density of 1 mA/cm² in 1 mol/L NaOH.

To fully elucidate the factors contributing to the improved electrocatalytic activity for ORR of the carbon-perovskite oxide hybrid materials, the electronic structures generated as a result of interfacial interactions between the carbon and loaded LaMnO₃ nanoparticles were assessed. Figure 13 displays the XPS spectra of the pure modified GCB and corresponding GCB-LaMnO₃ hybrid material prepared at a LaMnO₃/GCB mass composition ratio of 2:3. The XPS results show that the GCB-LaMnO₃ hybrid material is composed of C, O, La, and Mn elements, whereas the pure GCB is composed of C and O elements only. The XPS C 1s curves of the studied samples were fitted with a Gaussian-Lorentzian model following a Shirley background correlation, as shown in Fig. 13(a) and (b). According to the literature [25,26], the C 1s spectra of the pure GCB in Fig. 13(a) indicate the presence of non-oxygenated $-C-C-$ in aromatic rings (284.6 eV), and C in $-C-O-$ (286.1 eV) and $-C=O$ (289.0 eV), respectively. Similarly to pure GCB, the C 1s spectra of the GCB-LaMnO₃ hybrid catalyst indicate the presence of non-oxygenated $-C-C-$ (284.6 eV), $-C-O-$ (285.3 eV), and $-C=O$ (289.0 eV), as depicted in Fig. 13(b). However, the peak corresponding to $-C-O-$ bonds in the hybrid catalyst shows a negative shift relative to that of the pure GCB support, suggesting the presence of the LaMnO₃ nanoparticles in the hybrid material. To further confirm this result, the GCB-LaMnO₃ hybrid sample was subjected to a prolonged hydrochloric acid (2 mol/L) treatment in an attempt to completely etch the LaMnO₃ nanoparticles from the carbon surface—HCl is known to be passive with respect to attack of the carbon atoms in the sample [27]. Interestingly, as observed in Fig. 13(c), the previously observed negative shift of the $-C-O-$ bonds in the GCB-LaMnO₃ hybrid catalyst is no longer apparent in the HCl-treated GCB-LaMnO₃ hybrid catalyst (Fig. 13(b)). This finding provides additional evidence of the presence of interfacial interactions between the carbon support and LaMnO₃, which leads to the chemical shift of the $-C-O-$ bonds in the hybrid catalyst. Moreover, as evident from Fig. 13(c), the content of the $-C-O-$ bonds in the HCl-treated hybrid catalyst is reduced to only ~14.1 at% (non-treated hybrid catalyst: ~38.9 at%), which is comparable with that of the as-synthesized sample (~20.2 at%), as calculated from the relevant peak areas in

Fig. 13. C 1s spectra of the pure modified GCB support (a), GCB-LaMnO₃ hybrid catalyst (b), and hybrid catalyst following dissolution of LaMnO₃ in 2 mol/L HCl (c). O 1s spectra of the pure modified GCB support (d), GCB-LaMnO₃ hybrid catalyst (e), and modified GCB and LaMnO₃ blends (before sintering) (f). The hybrid material was prepared at a composition ratio of 2:3.

the C 1s spectra in Fig. 13(a)–(c). This result further confirms that the LaMnO₃ nanoparticles are chemically bonded to the carbon matrix via C–O–M bonds (M = La, Mn) in the hybrid material.

To evaluate the formation of C–O–M bonds in the hybrid material, the O 1s spectra of the GCB-LaMnO₃ hybrid material and pure modified GCB support were fitted accordingly. The results are shown in Fig. 13(d) and (e). From Fig. 13(d), the peaks at 531.9 and 533.3 eV for the pure GCB support were successfully assigned to –O–C=O and –C–O– groups, respectively, consistent with the results available in the literature [25,26]. The GCB-LaMnO₃ hybrid catalyst displayed O 1s peaks at 533.3, 531.9, 532.4, 531.3, and 529.6 eV as depicted in Fig. 13(e). The two peaks at 531.9 and 533.3 eV were attributed to oxygen atoms that are connected to carbon atoms in –O–C=O and –C–O– bonds, consistent with the O 1s spectra analysis of the GCB support (Fig. 13(d)). The remaining three peaks at 532.4, 531.3, and 529.6 eV were ascribed to LaMnO₃ nanoparticles on the GCB support, and respectively assigned to lattice oxygen (O^{2–}), adsorbed atomic oxygen (O[–]), and adsorbed molecular oxygen (O₂[–]) in the LaMnO₃ oxides. The characteristic peaks of the GCB-LaMnO₃ hybrid catalyst are positively shifted when compared with the binding energies of the peaks corresponding to lattice oxygen O^{2–} (528.8–529.0 eV), adsorbed atomic oxygen O[–] (529.2–530.7 eV), and adsorbed molecular oxygen O₂[–] (531.1–532.4 eV) in pure LaMnO₃ according to the literature [28]. This indicates the presence of strong electronic interactions between the oxide and carbon. An additional peak was recorded at 533.2 eV in the O 1s spectra of the hybrid catalyst. According to the literature report [21], the peak is indicative of the formation of C–O–M bonds (M = La or Mn). For proper assignment of the peak, a control study was performed,

whereby XPS analysis of a composite sample that was prepared by physical mixing of the LaMnO₃ particles and GCB support in the absence of sintering at 300 °C was conducted. Only five peaks, as observed in Fig. 13(f), were identified, and the peak centered at 533.2 eV was not detected. This confirmed that the previously observed peak at 533.2 eV corresponded to the presence of C–O–M bonds in the GCB-LaMnO₃ hybrid catalyst sintered at 300 °C.

Therefore, by combining the results obtained from fitting the C 1s and O 1s spectra in Fig. 13, we can conclude that LaMnO₃ nanoparticles were successfully integrated into the carbon surface through covalent C–O–M bonds (M = La, Mn). Furthermore, Hall effect measurements revealed that the nature of the semiconductor changed from n-type (pristine carbon black, CB) to p-type (modified GCB) following high-temperature graphitization and two-step surface chemical modification. The p-type structure of the carbon material should facilitate the formation of covalent C–O–M bonds between the LaMnO₃ particles and modified GCB in the hybrid material. Figure 14 shows the fitted O 1s spectra of the hybrids prepared at different composition ratios (i.e., 1:3, 3:3, and 4:3). The hybrids prepared at varying composition ratios of 1:3, 2:3 (Fig. 13(e)), 3:3, and 4:3 displayed covalent C–O–M bonds (M = La, Mn) contents of 15.9%, 16.3%, 13.3%, and 12.9%, respectively. The hybrid prepared at a composition ratio of 2:3 featured the highest content of covalent C–O–M bonds. The higher contents of covalent C–O–M bonds resulted in higher electrochemical performance, as shown in Fig. 10(a). This result further indicates that the enhanced electrochemical performance of the modified carbon black-LaMnO₃ hybrids can be ascribed to the formation of covalent (C–O–M) bonds between the LaMO₃ nanoparticles and carbon, which in turn improve ORR kinetics.

Fig. 14. O 1s spectra of the hybrids prepared at a composition ratio of 1:3 (a), 3:3 (b), and 4:3 (c).

4. Conclusions

Well-dispersed perovskite-type LaMO_3 nanoparticles supported on modified carbon black were synthesized by physical mixing of carbon and LaMnO_3 nanoparticles, followed by sintering at different temperatures. Modification processes including graphitization, HNO_3 , and ammonia treatments not only improved the structural integrity of the resulting carbon materials but also afforded the generation of a large number of oxygen-containing functional groups on the carbon surface that served as an active site for LaMnO_3 attachment. Morphology analysis of the resulting modified carbon black- LaMnO_3 hybrid catalysts revealed the presence of intimate contacts between the loaded LaMnO_3 and carbon support that were beneficial for the formation of covalent bonds in the current novel hybrid catalyst material. The carbon- LaMnO_3 hybrid catalyst prepared at a mass ratio of 2:3 displayed the highest electrocatalytic activity towards oxygen reduction reaction (ORR) among all the synthesized hybrid catalysts studied. The performance of the optimal hybrid catalyst was comparable with that of the commercial Pt/C catalyst (E-TEK). The remarkably improved electrocatalytic activity for ORR was attributed to the strong electronic interactions (covalent C–O–M bonds) between the metal oxide nanoparticles and carbon support that effectively im-

proved ORR kinetics. The findings provide a new insight into the design of carbon-supported rare earth oxide nanoparticles as highly efficient catalysts for ORR in alkaline media.

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Graphical Abstract

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Facile preparation of modified carbon black- LaMnO_3 hybrids and the effect of covalent coupling on the catalytic activity for oxygen reduction reaction

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The enhanced electrochemical performance of modified carbon black- LaMnO_3 hybrids can be explained by the formation of covalent bonds (C–O–M) between the LaMnO_3 nanoparticles and carbon, consequently improving oxygen reduction reaction (ORR) kinetics.

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改性炭黑-LaMnO₃复合材料的制备及其共价复合效应对氧还原性能的影响

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摘要: 以Vulcan XC-72炭黑为载体, 通过对炭载体石墨化处理和表面化学修饰, 将其与化学沉淀法制备的纳米级LaMnO₃颗粒共混, 再经特定温度下煅烧, 制备出改性炭黑-LaMnO₃复合材料。X射线光电子能谱和热重分析表明, 当煅烧温度在300 °C时, 炭载体与LaMnO₃纳米颗粒之间形成了大量C—O—M (M = La, Mn)化学键。扫描电子显微镜和高分辨透射电子显微镜分析发现, 纯相LaMnO₃纳米颗粒主要呈现短棒、三支棒或竹节棒的形貌特征, 炭载体则为具有完整石墨层的空心球结构, LaMnO₃均匀分散在炭载体上。在25 °C, 1 mol/L NaOH溶液中的电化学测试结果表明, 成分比(LaMnO₃:C)为2:3的复合材料具有很高的氧还原电催化活性, 氧还原反应电子数为3.81, 中间产物H₂O₂产率为9.5%, 其活性接近商业Pt/C催化剂(E-TEK)。高的氧还原电催化活性主要归因于LaMnO₃纳米颗粒与炭载体之间形成了大量共价键。

关键词: 锰酸镧; 炭材料; 电催化; 共价复合; 氧还原

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1. 前言

氧气还原反应(ORR)是电化学能源转换体系中一个基本的电化学反应, 具有重要的理论研究价值和广泛应用背景。近年来, ORR在清洁能源、污水高级电氧化处理、化工电解工业中的应用进一步激发了人们对高活性ORR电极制备及应用的研究兴趣, 并取得了一些重大研究成果^[1]。然而, ORR过程是一个极其复杂的缓慢动力学过程, 需要高效催化剂参与反应, 以提高ORR的动力学^[2]。目前, 在各种燃料电池、金属-空气电池等电化学储能及能量转换装置中普遍使用的商业Pt/C和Ag/C等贵金属氧还原电催化材料存在价格高、活性低和耐久性不足等缺点。因此开发高效且能长期稳定运行的非贵金属电催化材料成为当前研究热点^[3]。

近年来, 金属氧化物的优良电化学特性引起了许多研究者的兴趣^[4]。由于金属氧化物在碱性介质中具有很

高的选择性和化学稳定性, 其价格低廉, 丰富易得, 很早就被作为催化剂加以研究^[5]。综合文献中的相关报道, 可以将用于氧还原电催化的金属氧化物分为过渡族金属氧化物和稀土氧化物两大类。在上述氧化物中, 由于金属元素具有多种价态, 其氧化物也存在多种整数或非整数变价, 这就为降低氧还原过电位提供了可能。有报道表明, Mg和Ni掺杂改性的MnO_x/C在碱性介质中具有很高的氧还原电催化活性和选择性, 其性能接近于商业化的Pt/C催化剂(E-TEK)^[6]。此外, 一些研究者惊奇地发现, 尽管纯相的Co₃O₄等金属氧化物对氧还原的能力很弱, 但石墨烯负载Co₃O₄复合材料却表现出优异的氧还原电催化活性和稳定性^[7]。进一步研究表明, 将MnO₂, Co₂O₃, NiO₂和TiO₂等氧化物纳米粒子负载到炭载体(炭黑、碳纳米管、石墨烯)表面, 形成类似共价键的结合方式, 可能是这些材料活性高的主要原因^[6,7]。为此, 有学者提出此类复合材料的高电催化活性与金属氧化物对

炭载体价电子的“强电子亲和力”(strong electronic affinity)有关^[8–10]。这种强电子亲和力可以使得金属氧化物纳米晶颗粒与炭载体之间的界面呈现出有别于单一组分材料的独特价电子分布和结构特性^[11,12]。受此启发,由于钙钛矿型稀土复合氧化物(如 LaMO_3 , $M = \text{Mn, Ni, Co}$ 等)同时具有电子和离子导电性,晶格中的氧空位使其能够传导离子,相比于其它过渡金属氧化物导电性能好且在电解液中的稳定性也好,在碱性环境中表现出更高的氧还原电催化活性和耐久性^[13],因此如果将具有较高氧还原电催化活性的稀土复合氧化物负载在炭载体表面上,制备出炭担载型稀土复合氧化物纳米粒子复合材料,可以大幅提高复合材料的氧还原电催化活性。为了实现这一想法,我们采用经典化学沉淀法+高温煅烧的方法制备此类复合材料。前期研究表明,在炭载体存在的条件下,利用化学沉淀法无法合成出具有纯相钙钛矿结构的稀土复合氧化物(如 LaMO_3 , $M = \text{Mn, Ni, Co}$ 等)。这严重阻碍了此类高活性电催化材料的合成及应用。

为了克服制备炭担载纯相钙钛矿型稀土氧化物纳米粒子的难题,本文选择Vulcan XC-72炭黑(CABOT公司)作为载体材料,通过对炭载体进行结构改性及表面化学修饰后,将其与化学沉淀法制备的纳米级 LaMnO_3 粒子共混,然后在特定温度下进行热处理使得炭载体与稀土氧化物活性粒子之间形成共价键而化学复合,简单快速地制备出具有纯钙钛矿相结构的 LaMnO_3 纳米粒子/炭共价复合材料。虽然钙钛矿型复合氧化物 LaMnO_3 与炭复合材料的制备已有报道,但是一般都将其应用于催化醇类转化成酮类的有机反应中^[14,15],对电催化ORR的研究并不多见。因此,本文在制备 LaMnO_3 纳米粒子/炭共价复合材料的基础上系统研究了复合材料成分、结构和形貌与电催化性能之间的定量关系,重点研究了炭与稀土复合氧化物纳米粒子之间的化学复合效应对氧还原电催化性能的影响。该研究对于高效、廉价氧还原电催化材料的制备及其在碱性燃料电池、金属-空气电池以及食盐水电解工业中的应用具有重要意义。

2. 实验部分

2.1. 改性炭黑-LaMnO₃复合材料的制备

为了合成纯相钙钛矿型稀土氧化物纳米粒子/炭复合材料,首先对炭载体进行了结构改性和表面化学修饰处理。炭材料结构改性采用高石墨化处理,目的是提高炭材料晶体结构的完整性及有序化程度,具体过程

如下。将10 g Vulcan XC-72炭黑(简称CB,美国Cabot公司)放入石墨罐中密封,然后将石墨罐置于大型石墨化炉里在保护气氩气气氛下2600 °C保温1 h后随炉冷却到室温,得到高石墨化的Vulcan XC-72炭黑(简称GCB)。针对石墨化处理后炭材料表面疏水性高及比表面积小的问题,需要对炭材料进行表面化学修饰处理。采用特殊的浓硝酸酸化和浓氨水处理两次处理的方法,在尽量避免破坏炭材料表面完整结构的条件下,在炭材料表面接枝上大量含氧官能团(羧基、羟基等),为金属氧化物粒子的沉积提供活性点。典型的炭材料浓硝酸酸化处理如下:称取10 g GCB加入到三口烧瓶中,加入过量浓硝酸在140 °C油浴下冷凝回流10 h,将反应液冷却,用去离子水洗涤过滤至中性,80 °C真空干燥。浓氨水处理过程如下:在5 g酸化GCB粉末中加入过量浓氨水,在空气气氛下290 °C煅烧3 h,得到表面化学修饰的GCB。

其次,采用化学沉淀法制备具有单一钙钛矿结构的 LaMnO_3 金属氧化物纳米粒子。将1 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%,天津阿法埃莎化学有限公司)和1 mmol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99%,国药集团化学试剂有限公司)溶于10 mL去离子水中,逐滴加入0.5 mol/L的四甲基氢氧化铵水溶液(25% TMAH水溶液,国药集团化学试剂有限公司)至溶液的 $\text{pH} \geq 9$ (低于9时几乎不生成沉淀),超声分散40 min后将反应物分别用去离子水和乙醇洗涤,抽滤,80 °C干燥2 h得到前驱体粉末。将前驱体粉末在氩气气氛下以5 °C/min的速率升到700 °C保温5 h得到钙钛矿氧化物 LaMnO_3 粉末。

最后,将 LaMnO_3 粉末与表面化学修饰的GCB以质量比为1:3, 2:3, 3:3和4:3分别加入到20 mL去离子水中,加入3%曲拉通X-100 (国药集团化学试剂有限公司)和17%异丙醇(国药集团化学试剂有限公司)后,在1500 W功率下用超声波细胞粉碎机(Scientz-2000)粉碎99次,离心,在80 °C下干燥2 h,最后在空气气氛下于300 °C煅烧2 h,然后随炉冷却,得到一系列不同成分比的改性炭黑-LaMnO₃复合材料。该材料制备的具体流程示于图1。

2.2. 材料表征

对制备的复合材料成分、结构和形貌进行系统表征。采用X射线粉末衍射仪(XRD, RINT 2200V/PC, 日本理学)对制得的材料进行晶型结构分析。XRD衍射条件: Cu靶 K_α 射线,管电压40 kV,管电流200 mA,扫描速率10°/min。采用场发射扫描电子显微镜(SEM, JEOL-6701F, JEOL)和高分辨透射电子显微镜(HRTEM, JEM-3010, JEOL)观察材料的微观形貌,用电镜附带的

Mapping分析装置表征复合材料的共混情况. 为了定量分析炭材料石墨化结构, 采用拉曼光谱仪(LabRam HR800, 法国Horiba Jobin Yvon)对高石墨化处理前后炭材料的结构完整性进行分析. 在此基础上, 为了进一步确定炭材料的比表面积和其表面化学修饰程度, 采用比表面积和孔径分析仪(QUADRASORB SI-MP-9, 美国康塔)表征炭材料的比表面积, 采用傅里叶红外光谱仪(FTIR, Spectrum100, 美国PerkinElmer)表征经过浓硝酸处理后炭黑表面官能团, 采用纳米粒度分析仪(Nano-ZS90, 英国马尔文)分析炭材料在水溶液中的分散稳定性. 采用X射线光电子能谱仪(XPS, Thermo ESCALAB 250, 美国Thermo Scientific)分析炭材料与催化活性粒子之间的化学结合状态, XPS的C1s校准结合能为284.6 eV. 采用热分析仪(Thermoplus TG8120, 日本理学)分析复合材料的稳定性.

2.3. 电化学测试

采用美国PINE公司的AFCBP1型旋转圆环圆盘电极装置测试样品的电化学性能. 采用三电极体系, 其中工作电极为涂有复合材料的圆环圆盘电极(面积为 0.247 cm^2), 其制作过程如下. 将10 mg复合材料分散在1 mL乙醇和1 mL水的混合溶液中, 加入100 μL 成膜物质5% Nafion水溶液(美国杜邦公司), 超声分散30 min后取20 μL (其中Nafion的质量分数为0.25%)滴在圆环圆盘电极表面, 常温干燥; 辅助电极为铂丝; 参比电极为饱和甘汞电极(SCE). 测试温度为 $25\text{ }^\circ\text{C}$, 电解液为1 mol/L的NaOH溶液, 扫描速率为5 mV/s, 环电位恒定在0.5 V(vs SCE). 测量前溶液中通高纯氧30 min至饱和, 测量时溶液上方通氧气保护.

3. 结果与讨论

3.1. 炭载体的结构改性和表面化学修饰

图2是CB和GCB在不同放大倍数下微观结构的高分辨透射电镜图. 由图2(a)可知, CB炭黑由大量取向非常无规且短小的炭层大致平行于球的表面排列而成, 表面和内部存在大量缺陷, 石墨化程度很低. 这种高度无序结构既不利于金属氧化物纳米粒子的附着, 同时也容易遭受氧化腐蚀而破坏^[16]. 由图2(b)可见, 经高温石墨化处理后GCB炭黑颗粒结晶性和有序化程度大幅提高. 炭黑颗粒外层的石墨片层结构已经非常清晰而完整, 在炭黑颗粒内部观察不到炭材料的存在. 由此可见, 经 $2600\text{ }^\circ\text{C}$ 高温石墨化处理炭材料已经从实心的炭黑颗粒转变成类似于空心的结构.

为了研究高温石墨化处理后炭材料的结构, 对上述样品进行了XRD表征, 结果见图3(a). 与CB相比, GCB的(002), (100)和(004)面的衍射峰均变得更加尖锐. 此外, 在 26° 处表征炭层之间距离的C(002)面的峰向高角度明显偏移. 这说明石墨化处理后炭材料的有序度和结晶度得到很大提高, 这与TEM结果一致. 采用拉曼光谱对GCB的石墨化程度进行了表征, 结果见图3(b). CB和GCB两种炭材料在拉曼光谱的一级序区($1000\text{--}3000\text{ cm}^{-1}$)都出现了 1350 cm^{-1} 处的D峰和 1580 cm^{-1} 处的G峰. 与CB不同, GCB还在 2710 cm^{-1} 左右出现一个明显的2D峰. 一般而言, D峰是由于炭材料晶格缺陷和石墨化程度降低导致的, 属于石墨微晶的 A_{1g} 振动模式, 与D峰不同2D峰是由于较高的石墨化有序度引起的; 而G峰是天然石墨结构所固有, 属于石墨晶格面内C–C键的伸缩振动, 振动模式为 E_{2g} ^[17–19]. 因此, 炭材料结构的有序化程度可以用代表无序结构的D峰与石墨结构的G峰的积分强度比 I_D/I_G 以及2D峰与G峰的积分强度比 I_{2D}/I_G 来定量表征. 由图3(b)可见, CB和GCB的 I_D/I_G 值分别为2.41和0.45. 可知通过高温改性处理后炭材料的有序度和结晶度得到较大提高. 这不仅可以提高CB炭载体在碱性介质中的电化学性能和耐久性能, 而且也能获得良好的导电性.

此外, CB和GCB的比表面积分别为216和 $73\text{ m}^2/\text{g}$. 可见, 经石墨化处理后炭材料的比表面积减小. 这是由于高温热处理大幅度提高了炭材料的石墨化程度, 导致炭材料内部缺陷减少. 针对石墨化处理后炭材料表面疏水性高及比表面积小的问题, 需要对炭材料进行表面化学修饰, 目的是在尽可能避免破坏炭材料内部结构完整性的条件下, 在材料表面接枝上大量含氧官能团(羧基和羟基等), 为金属氧化物粒子的沉积提供活性点并且提高其比表面积. 经过硝酸酸化+氨水处理后GCB的比表面积增加到 $85\text{ m}^2/\text{g}$. 原始GCB、硝酸酸化GCB、硝酸酸化+氨水处理后GCB的红外光谱测试见图4(a). 由图可知, 三种炭材料均在 3430 , 1630 , 和 1220 cm^{-1} 处出现了特征峰. 3430 和 1630 cm^{-1} 处的峰分别为羟基的伸缩振动峰和变形振动峰(其中羟基包括炭黑表面吸附水中的羟基和硝酸酸化处理后炭黑表面接枝上的羟基), 在 1220 cm^{-1} 处的峰为炭黑表面产生的脂或环氧化物的伸缩振动峰. 与GCB显著不同, 酸化GCB和氨水处理的GCB样品皆在 1730 cm^{-1} 处出现了一个小峰, 为羧基的伸缩振动峰^[20]. 该峰的出现表明GCB表面接枝上了含氧官能团. 原始GCB、硝酸酸化GCB、硝酸酸化+氨水处理

理后GCB的Zeta电位分别为+23, -31和-50 mV (图4(b)). 这说明硝酸酸化+氨水两步表面修饰处理的GCB表面具有更多的带负电的官能团. 这种表面化学修饰方法能够有效地在石墨化程度很高的炭材料表面接枝上大量的亲水性含氧官能团. 这为后续稀土复合氧化物纳米粒子在炭载体表面的化学沉积提供了大量的活性位点.

3.2. 改性炭黑-LaMnO₃复合材料的结构性质

首先以La(NO₃)₃·6H₂O和MnCl₂·4H₂O为前驱体, 通过精确控制水溶液合成体系的pH值, 采用共沉淀法制备出纯相钙钛矿型LaMnO₃纳米粒子. 重点考察了反应体系中pH值对稀土复合氧化物纳米粒子形貌、晶型以及粒径尺寸的影响, 并对产物进行了XRD表征, 结果见图5. 可以看出, 在pH = 9–12条件下制备的前驱体经700 °C煅烧后在22.3°, 25.1°, 31.3°, 32.3°, 40.1°, 45.7°, 47.2°, 57.7°和67.7°处出现了明显的衍射峰, 分别对应于LaMnO₃复合氧化物的(110), (111), (020), (200), (202), (220), (004), (312)和(400)特征晶面. 其它不明显的小峰也与LaMnO₃ (JCPDF-35-1353)标准谱图完全一致. 此外, 不同pH条件下制得的产物衍射谱没有其它杂峰出现, 说明在不同pH值下均获得了纯相的钙钛矿型LaMnO₃复合氧化物. 制备得到的纯相LaMnO₃的形貌如图6所示. 由图可知, LaMnO₃纳米颗粒的形貌主要呈现出短棒、三支棒或竹节棒等形貌特征. 氧化物纳米颗粒的平均直径为40–60 nm, 长度为200–400 nm. 从图中还可以看出, 尽管合成体系pH值对材料的形貌影响不大, 但对其纳米颗粒的分散性影响显著. 当pH控制为9时, 得到的氧化物纳米颗粒具有良好的分散性, 颗粒之间团聚现象不严重(图6(a)). 当pH大于9时, 随着pH值的增大, 氧化物纳米颗粒开始倾向于聚集在一起, 甚至一部分粒子与粒子之间发生融合长成较大的颗粒, 粒子间团聚的趋势变大(图6(b)–(d)).

在合成出纯相LaMnO₃的基础上, 将其与表面化学修饰后的GCB以不同质量比进行共混, 然后在空气气氛下300 °C保温煅烧2 h, 最终制得改性炭黑-LaMnO₃复合材料. 当LaMnO₃与炭载体质量比为2:3时, 制备出的改性炭黑-LaMnO₃复合材料的XRD如图7所示. 可以看出, 复合材料在26°附近出现了一个明显的衍射峰, 该峰与纯GCB炭黑(002)面衍射峰的位置一致. 该样品其余衍射峰均与纯钙钛矿型LaMnO₃的特征衍射峰完全重合. 这说明LaMnO₃完全保持了复合之前的特征晶体结构, 300 °C高温煅烧没有对催化活性粒子的晶型产生影响. 图8为复合材料的SEM图和Mapping图(插图). 从中可看

出La (绿色)、Mn (红色)和C (灰色)分布很均匀, 说明在复合后的电催化材料中40–60 nm的LaMnO₃纳米颗粒均匀分散在表面化学修饰的GCB表面. 为了进一步研究LaMnO₃纳米颗粒与炭载体之间的复合作用, 对表面化学修饰的GCB和不同温度煅烧的复合材料进行了热重分析, 结果见图9. 可见, 表面化学修饰GCB的初始氧化温度为676 °C, 经过250 °C煅烧处理的样品炭初始氧化温度在600 °C左右, 350和400 °C煅烧处理的样品在633 °C附近. 而300 °C热处理的共混材料其炭载体在空气气氛下初始氧化分解温度为570 °C左右, 均低于上述其他样品. 根据文献报道可知, 对于金属氧化物/炭复合材料, 在高温条件下金属氧化物对炭材料的热氧化分解过程具有强烈促进作用, 特别是二者之间存在紧密连接时, 金属氧化物对炭的刻蚀愈加显著^[21]. 根据这一结论, 我们认为LaMnO₃纳米颗粒与炭载体之间形成某种方式的紧密连接, 且这种紧密连接是材料经过300 °C煅烧后形成的. 后面的研究结果也证实, 金属氧化物与炭黑载体之间在300 °C热处理过程中确实形成了共价键连接, 从而使材料具有高的氧还原电催化活性.

3.3. 复合材料的电催化性能

图10(a)为不同成分比改性炭黑-LaMnO₃复合材料和商业Pt/C催化剂于室温下O₂饱和的1 mol/L NaOH溶液中的氧还原反应极化曲线. 可以看出, 成分比为2:3(LaMnO₃:C)的样品表现出最高的氧还原电催化活性. 该样品的氧气还原起始电位相对于其它成分比的复合材料正移了40 mV左右, 而且该样品的氧还原极限扩散电流密度也比其它复合材料大得多, 达到2.8 mA/cm², 接近商业Pt/C (E-TEK, 3.2 mA/cm²). 为了进一步研究材料的氧气还原反应路径, 在O₂饱和的1 mol/L NaOH溶液中, 对LaMnO₃:C为2:3的样品进行了旋转圆盘测试, 不同转速下的结果见图10(b). 可以看出, 随着电极转速的增大氧还原极限扩散电流升高; 在同一转速下, -0.4至-1 V扫描电位区间内氧还原极限扩散电流均基本保持不变. 这说明此时氧还原反应处于完全扩散控制阶段. 此外, 在一定电位条件下盘电流比环电流大得多. 由测定的盘电流和环电流的相对大小, 可以进一步计算出此时氧还原反应的传递电子数 n 和H₂O₂产率, 计算公式如下^[22]:

$$n = 4I_D / (I_D + I_R / N) \quad (1)$$

$$Y(\text{H}_2\text{O}_2) = 2I_R / (I_R + NI_D) \times 100\% \quad (2)$$

其中 I_D 为盘电流, I_R 为环电流, N 为圆环圆盘的收集效率值0.37.

由图10(b)扩散控制区中对应于1600 r/min时-0.5, -0.6, -0.7, -0.8和-0.9 V的盘电流和环电流通过公式(1)计算了氧还原反应的传递电子数 n , 结果见图10(c). 可见, 氧气还原反应电子数分别为3.78, 3.8, 3.82, 3.82和3.82, 平均值为3.81, 用公式(2)计算得到相应的 H_2O_2 产率分别为9%, 8.9%, 9.1%, 9.9%和10.7%, 平均值为9.5%. 这表明复合材料催化ORR是按照四电子反应路径进行的.

选取-0.8 V极化电位, 根据公式(2)计算出不同转速下ORR中间产物 H_2O_2 的产率, 结果如图10(d)所示. 随着电极转速从400 r/min增加到1600 r/min时, H_2O_2 产率从14.2%减少到了9.9%. 这一结果进一步证实了复合材料催化ORR为四电子反应过程. 因此, 该材料在碱性介质中对ORR路径具有高选择性. 有研究表明^[23], 纯钙钛矿氧化物上的氧还原机理是氧离子反应机理, 而在含炭材料的复合材料上则主要是以协同反应机理为主. Yeager^[24]进一步提出在炭材料表面氧分子主要经二电子途径被还原为 HO_2^- , 然后再被钙钛矿氧化物催化剂催化成 O_2 和 OH^- . 由此可见, 炭黑-LaMnO₃复合材料的高电催化活性主要起源于二者之间的氧还原协同电催化作用(见图11).

为进一步研究复合材料在碱性介质中电催化ORR中的稳定性, 又进行了计时电位测试并与商业Pt/C催化剂进行了比较, 结果见图12. 由图可知, 复合材料的氧还原过电位与商业Pt/C较接近, 而且在外加恒定电流条件下两种电催化材料的电极电位均十分稳定. 这说明该复合材料在碱性介质中与商业Pt/C具有类似的稳定性能.

3.4. 电催化材料的化学复合作用分析

为了探究炭黑-LaMnO₃复合材料氧还原电催化活性高的原因, 重点研究了炭载体与LaMnO₃纳米颗粒之间的化学复合状态及其对氧还原电催化性能的影响. 选择成分比为2:3的改性炭黑-LaMnO₃复合材料进行了XPS测试, 结果见图13. 由图可知, 对炭载体和复合材料的C 1s谱进行了分峰拟合, 发现炭载体的C 1s谱中出现了C-C (284.6 eV), C-O (286.1 eV) 和 O-C=O (289.0 eV) 三个峰^[25,26]; 复合材料的C 1s中同样出现了C-C (284.6 eV), C-O (285.3 eV)和O-C=O (289.0 eV)三个峰, 但复合材料中的C-O峰位置相对于炭载体的C-O向低结合能方向发生了位移. 有趣的是, 当采用对炭黑惰性的2 mol/L HCl溶液^[27]完全溶解复合材料中的LaMnO₃后, 该峰的化学位移现象完全消失(图13). 这表明炭载体与LaMnO₃之间形成了某种化学键合, 导致复合材料中的C-O峰发

生了化学位移. 此外, 通过计算该峰的面积发现, 炭载体、复合材料和去除LaMnO₃之后的样品中C-O键所占的比例分别为10.9%, 38.9%和14.1%. 这进一步说明复合材料中大量的C-O键是经煅烧后新产生的, 而且这些新产生的化学键与LaMnO₃纳米颗粒有关.

为了进一步证实炭载体与氧化物在煅烧后形成了新的化学键, 分别对炭载体和复合材料的O 1s谱进行了分峰拟合, 结果见图13(d-e). 从图13(d)可以看出, 在炭载体O 1s谱中出现了两个拟合峰, 分别对应于C-O (533.3 eV) 和 O-C=O (531.9 eV), 与文献结果基本一致^[25,26]. 从图13(e)可以看出, 在复合材料的O 1s谱中出现了C-O (533.9 eV), O-C=O (531.9 eV), O_2^- (532.4 eV), O^- (531.3 eV)和 O^{2-} (529.6 eV)五个峰. 与图13(d)比较可知, 前两个特征峰为炭载体的; 后三个特征峰则必定是LaMnO₃纳米颗粒引起的, 分别对应于LaMnO₃氧化物的晶格氧、原子吸附氧和分子吸附氧. 与文献中LaMnO₃纯物质的晶格氧 O^{2-} (528.8–529.0 eV)、原子吸附氧 O^- (529.2–530.7 eV)和分子吸附氧 O_2^- (531.1–532.4 eV)结合能相比^[28], LaMnO₃三个氧结合态特征峰的位置均向较高结合能方向发生了偏移, 这可能是由于炭载体和氧化物颗粒之间存在一定的化学作用. 此外, 除了上述五个峰之外, 在复合材料O 1s谱中结合能为533.2 eV处还出现了一个未知的明显的峰. 据文献报道^[21], 该峰可能是C-O-M (M = La或Mn)引起的. 为了证实这一判断, 对炭载体与LaMnO₃共混样品(未煅烧)的O 1s谱进行了分峰拟合, 结果见图13(f). 值得注意的是, 该样品只出现了上述已知的五个峰, 在O 1s谱中结合能为533.2 eV处的未知峰消失了. 这进一步说明复合材料中形成了C-O-M (M = La或Mn)共价键. 因此, 根据上述复合材料的C 1s和O 1s谱分析结果, 可以确定复合材料中LaMnO₃与炭载体之间确实形成了共价键. 通过C-O-M键的氧桥作用, 金属氧化物纳米颗粒与炭载体之间发生了化学复合. 霍尔效应测试结果也表明, CB经过高温石墨化和表面化学修饰处理后炭载体材料的半导体类型由n型转变成p型. 这种炭材料的p型结构可能是导致复合材料中产生共价键的原因. 对其它三种成分比复合材料(1:3, 3:3, 4:3)的O 1s谱进行了分峰拟合, 结果见图14. 成分比为1:3, 2:3, 3:3和4:3的复合材料中C-O-M (M = La或Mn)共价键所占的百分比分别为15.9%, 16.3%, 13.3%和12.9%. 其中, LaMnO₃:C比为2:3的复合材料具有最高的共价键含量, 与极化曲线测试结果比较发现随着共价键含量的增加, 氧还原活性提高. 这进一步表明高电催

化活性主要归因于 LaMnO_3 纳米颗粒与炭载体之间形成了大量的 C-O-M ($\text{M} = \text{La}$ 或 Mn)共价键。

4. 结论

Vulcan XC-72炭黑经过 $2600\text{ }^\circ\text{C}$ 石墨化处理后从实心的炭黑颗粒转变成类似于空心的结构, 颗粒的结晶性和有序化程度也得到了很大提高。经表面化学修饰后石墨化炭黑表面接枝上了羧基和羟基等含氧官能团, 为 LaMnO_3 的附着提供了大量活性位点。采用化学沉淀法

制备 LaMnO_3 时反应溶液的 $\text{pH} = 9$ 时得到了分散性最好的纳米颗粒, 其主要形貌为短棒、三支棒或竹节棒。将其与改性后的炭黑在 $300\text{ }^\circ\text{C}$ 下保温煅烧得到了不同成分比的复合材料。当 $\text{LaMnO}_3\text{:C}$ 比为2:3时其氧还原活性最高, 平均电子传递数为3.81, 催化氧还原反应中间产物过氧化氢的产率也较低(9.5%), 其活性接近于商业 Pt/C 催化剂(E-TEK)。这是因为成分比为2:3的复合材料中炭载体与 LaMnO_3 纳米颗粒之间形成了最多的 C-O-M ($\text{M} = \text{La, Mn}$)共价键。