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Article

Co₃O₄ nanoparticles assembled on polypyrrole/graphene oxide for electrochemical reduction of oxygen in alkaline media

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ABSTRACT

The development of highly efficient catalysts for cathodes remains an important objective of fuel cell research. Here, we report Co₃O₄ nanoparticles assembled on a polypyrrole/graphene oxide electrocatalyst (Co₃O₄/Ppy/GO) as an efficient catalyst for the oxygen reduction reaction (ORR) in alkaline media. The catalyst was prepared via the hydrothermal reaction of Co²⁺ ions with Ppy-modified GO. The GO, Ppy/GO, and Co₃O₄/Ppy/GO were characterized using scanning electron microscopy, Fourier-transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The incorporation of Ppy into GO nanosheets resulted in the formation of a nitrogen-modified GO porous structure, which acted as an efficient electron-transport network for the ORR. With further anchoring of Co₃O₄ on Ppy/GO, the as-prepared Co₃O₄/Ppy/GO exhibited excellent ORR activity and followed a four-electron route mechanism for the ORR in alkaline solution. An onset potential of −0.10 V vs. a saturated calomel electrode and a diffusion limiting current density of 2.30 mA/cm² were achieved for the Co₃O₄/Ppy/GO catalyst heated at 800 °C; these values are comparable to those for noble-metal-based Pt/C catalysts. Our work demonstrates that Co₃O₄/Ppy/GO is highly active for the ORR. Notably, the Ppy coupling effects between Co₃O₄ and GO provide a new route for the preparation of efficient non-precious electrocatalysts with hierarchical porous structures for fuel cell applications.

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1. Introduction

The research on anion-exchange membrane fuel cells (AEMFCs) is motivated by the ability of alkaline systems to improve their efficiencies without the use of precious metal catalysts, which is the major limitation for the widespread implementation of proton-exchange membrane fuel cells [1,2]. Furthermore, in alkaline medium, AEMFCs have the additional advantages of faster electrode reaction kinetics and flexible fuel choices [3–5]. The development of low-cost oxygen reduction

reaction (ORR) catalysts is one of the major challenges for electrochemical energy conversion and storage devices such as fuel cells and metal-air batteries. In recent studies on transition metal oxides, conducting-polymer-derived materials have been intensively investigated as ORR catalysts because of their greater abundance and lower cost compared with Pt-based catalysts [6–10]. However, most non-precious metal (NPM) catalysts exhibit insufficient ORR activity and stability, which limits their wide application in fuel cell technologies. A better understanding of the nature of the ORR on the catalytic sites

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and the design of new catalysts with optimal activity and durability are needed.

NPM catalysts include non-noble-metal-based oxides and chalcogenides. Jasinski [11] was the first to report that Pt-free metal phthalocyanines (also called metal-N₄ macrocycles, such as Fe- and Co-macrocycles) could catalyze the ORR as effectively as Pt-based materials. Ever since this seminal work, various other N-coordinated transition metals and metal chalcogenides, oxides, oxynitrides, carbonitrides, and transition-metal-doped conductive polymers have been explored, and their potential to catalyze the ORR and other reactions has been evaluated. Among these materials, state-of-the-art nitrogen-doped graphene oxides (N/GOs) with or without transition metals (Fe or Co) are generally accepted as potential substitutes for Pt for both cost reduction and enhancement of the stability of ORR electrocatalysts [7,12–15]. Deliberate nitrogen doping can enhance the electron-donor property of the graphene or carbon matrix, resulting in an improvement of the interaction between carbon and guest molecules. However, the development of a convenient synthesis method for N/GO catalysts remains a challenge [16–20]. Novel Co or Fe composites containing N/GO with high electrical conductivity and a stable structure are also highly desirable for further improvement of the efficiency, stability, and electrochemical activity, as reported in previous investigations [12,21–29].

To date, various strategies to introduce N atoms into GO have been intensively employed. Specifically, NH₃, conducting polymers, and methane are effective nitrogen-doping agents [30–33]. Polypyrrole (Ppy) is a well-known electrically conducting polymer and has been used for surface modification of carbon particles, enabling the immobilization of Co ions at the surface via coordination processes [16,17,34]. In this work, Ppy was selected as a multifunctional agent, serving as a crosslinker of Co²⁺ ions with GO and especially as the precursor of nitrogen for the doping of graphene. In our previous work [35], Fe₂O₃/Ppy/GO composites were synthesized using a hydrothermal method, and their effect on the ORR performance was investigated. The decisive factors for improving the electrocatalytic and durable performance of Fe₂O₃/Ppy/GO were the intimate, large interfaces between the Fe₂O₃ nanocrystals and Ppy/GO and the high electron withdrawing/storing ability and high conductivity of GO doped with nitrogen from Ppy. In this work, novel Co and N co-doped graphene networks (Co₃O₄/Ppy/GO) were prepared by the simple pyrolysis of a mixture of pyrroles, cobalt(II) nitrate, and GO. The as-prepared Co₃O₄/Ppy/GO catalysts exhibited comparable catalytic activity and high selectivity for the four-electron ORR in alkaline solutions.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of GO

GO was prepared using the modified Hummers' method [36]. First, 3 g of expandable graphite and 18 g of KMnO₄ were added to a 1-L beaker containing 360 mL of concentrated sul-

furic acid and 40 mL of H₃PO₄. The beaker was placed in an ice-water bath (0 °C) and continuously stirred until the graphite and KMnO₄ were completely dissolved. After cooling the system to ambient temperature, 400 mL of ice water was added to the beaker to keep the solution at 0 °C. Then, 30 mL of 30% H₂O₂ solution was added to the solution with continuous stirring for 4 h. Finally, the suspension was centrifuged and washed several times with deionized water, 30% HCl, and ethanol until a pH of approximately 7 was attained. The black homogeneous supernatant was dried at 30 °C for 48 h to obtain GO.

2.1.2. Preparation of Ppy/GO

The Ppy/GO suspension was prepared according to previously reported procedures [35]. The solution was prepared by mixing 0.2 g GO and 20 mL of H₂O. Another solution of 4 mL of ethanol and 2 mL of pyrrole was then slowly added into the GO solution under continuous stirring. Then, 2 mL of 30% H₂O₂ was added and stirred for 30 min. Finally, the mixture was transferred to an autoclave and stored at 180 °C for 12 h. The resulting product was obtained by washing with water and ethanol five times. The clear product was dried at 60 °C for 24 h in a vacuum drying oven.

2.1.3. Preparation of Co₃O₄/Ppy/GO catalysts

The Co₃O₄/Ppy/GO catalysts were prepared according to previously reported procedures [35]. Briefly, 0.2 g GO was dispersed in 20 mL of water with ultrasonic processing for 1 h to obtain a GO suspension. Then, 4 mL of ethanol and 2 mL of pyrrole were added into the GO solution to form a composite dispersion under vigorous stirring for 30 min. Next, 4 mL of 0.069 mol/L Co(NO₃)₂ was dissolved into the composite solution. The composite solution was then transferred into an autoclave and stored at 180 °C for 12 h. A powder was obtained by washing with water and ethanol three times. The clear product was dried at 60 °C for 24 h in a vacuum drying oven to obtain Co₃O₄/Ppy/GO hybrids. After that, the resulting hybrids were placed into a tube furnace and heated to 400, 600, or 800 °C for 3 h under N₂ flow. The resulting catalysts were labeled Co₃O₄/Ppy/GO-400, Co₃O₄/Ppy/GO-600, and Co₃O₄/Ppy/GO-800, respectively.

2.2. Characterization analyses

The morphology and structure of the as-prepared Co₃O₄/Ppy/GO composites were investigated using scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). Morphological characterization was performed using SEM (QUANTA-450), and all the samples were measured after gold sputter coating. The FT-IR spectroscopy analysis was performed using a Bruker-Tenson 27 FT-IR spectrometer in the 4000–400 cm⁻¹ range to determine the characteristic functional groups of the samples. XPS data were obtained using a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer with a monochromic Al X-ray source. TGA was performed using a TA Instruments

TGA-Q50 in a nitrogen flow (40 mL/min) with a linear heating rate of 10 °C/min to evaluate the thermal stabilities of the samples.

2.3. Electrochemical measurements

2.3.1. Preparation of working electrodes

A glassy carbon electrode (GCE, 5 mm in diameter, geometric area of 0.197 cm²) was used as the working electrode fixed on a rotating apparatus. The GCE was polished with 0.05-mm alumina slurries and sonicated in deionized water three times before the electrochemical measurements. Then, 10 μ L of catalyst ink, prepared by dispersing 2 mg of the catalyst into 1 mL of ethanol containing 10 μ L 5% Nafion, was deposited on the working electrode with a catalyst loading of 0.1 mg/cm².

2.3.2. Electrocatalytic measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed on a ZAHNER ZENNIUM electrochemical workstation with a three-electrode system. A glassy carbon rotating disk electrode (RDE) with a 5-mm diameter loaded with as-prepared GO, Ppy/GO, and Co₃O₄/Ppy/GO was used as the working electrode. A Pt gauze electrode was employed as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. All the electrode potentials here are reported versus the SCE. During the electrocatalytic measurements, the working electrode loaded with the as-prepared catalysts was continuously electrochemically looped. O₂ was bubbled into the electrolyte for 10 min before each experiment, and a flow of O₂ was maintained over the electrolyte during the measurements to ensure O₂ saturation. The CV and LSV measurements were

performed at a scan rate of 10 mV/s.

The slopes of Koutecky-Levich (K-L) plots were used to calculate the number of transfer electrons according to Eqs. (1) and (2), where J , J_K , and J_L are the measured current density, kinetic current density, and diffusion-limiting current density, respectively, n is the number of transfer electrons in the ORR, F is the Faraday constant (96487 C/mol), C_0 is the concentration of molecular oxygen in the 0.1 mol/L KOH electrolyte (1.117×10^{-6} mol/mL), D_0 is the diffusion coefficient of O₂ (1.9×10^{-5} cm²/s), ν is the kinetic viscosity of the electrolyte (0.01073 cm²/s for alkaline solution), ω is the angular velocity in rad/s [37].

$$1/J = 1/J_K + 1/J_L = 1/J_K + 1/(B\omega^{1/2}) \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

For the Tafel ($E - \log(J_K)$) plot, the kinetic current was calculated from the mass-transport correction of the RDE using the following equation [12,38,39]:

$$J_K = J \times J_L / (J_L - J) \quad (3)$$

3. Results and discussion

3.1. Morphology and microstructure

The SEM images of the GO and Ppy/GO nanocomposites in Fig. 1(a) and (b) reveal typical layered structures, similar to the layered structure of pure graphene in terms of regularity. The corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum of Ppy/GO in Fig. 1(c) indicates that the systems contained 3.03 at% N. After treatment of Ppy/GO in N₂ for 2 h at 600 °C, the resulting Ppy/GO-600 still exhibited a layered structure, as observed in Fig. 1(d). The images of Co₃O₄/Ppy/GO in Fig. 1(e) and (f) indicate that Co₃O₄ and Ppy

Fig. 1. SEM images of (a) GO, (b) Ppy/GO ((c) corresponding EDS spectrum of Ppy/GO), (d) Ppy/GO-600, (e) Co₃O₄/Ppy/GO, and (f) Co₃O₄/Ppy/GO-600.

were inserted into adjacent GO layers, resulting in large inter-spaces between GO layers with a thickness range of 10–200 nm. The corresponding XPS spectrum of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ in Fig. 2 indicates the presence of 1.3 at% Co and 8.5 at% N in the systems.

The XPS analysis of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ in Fig. 2(a) reveals mainly C, O, N, and Co, as indicated by the presence of the C 1s, O 1s, N 1s, and Co 2p core levels, with no evidence of impurities. A clear N 1s peak is observed, confirming the presence of N (Fig. 2(b)). The N 1s peak can be divided into three components located at 398.4, 399.0, and 400.4 eV, which correspond to pyridinic, pyrrolic, and graphitic nitrogen, respectively [14,16,40]. The estimated N doping level was 8.5 at%, of which 59.48% was pyrrolic nitrogen, indicating that the main form of nitrogen was pyrrolic nitrogen. Importantly, the presence of graphitic N is an indicator of the *in situ* formation of N-doped graphitic carbon.

As shown in Fig. 2(c), two sharp peaks at 780.1 and 794.9 eV were detected for the Co_3O_4 samples, which correspond to the $\text{Co } 2p_{1/2}$ and $\text{Co } 2p_{3/2}$ spin-orbit peaks of Co_3O_4 spinel, respectively. The XPS spectra of the O 1s electronic levels of the Co_3O_4 samples are presented in Fig. 2(d). Two component peaks are observed, which indicates the presence of two types of oxygen species on the surface of the Co_3O_4 samples. The peak with low binding energy (529.8 eV) can be assigned to the lattice oxygen

O^{2-} [38]. The signal at 531.3 eV indicates the presence of surface hydroxyl (OH^-) species, which most likely led to the generation of Co-OH . The higher concentration of surface hydroxyl ions (OH^-) than lattice oxygen in the Co_3O_4 sample indicates that the addition of Co_3O_4 improves the ORR performance [41,42]. The detailed analysis results of each surface species are presented in Table 1.

As observed in Fig. 3, the FT-IR spectrum of GO contains strong bands centered at approximately 3405, 1550, and 1734 cm^{-1} , which are attributed to O–H, carbon double bonds ($\text{C}=\text{C}$), and strong carbonyl ($\text{C}=\text{O}$) stretching vibration, respectively. The peaks at approximately 1056, 1125, and 1250 cm^{-1} can be assigned to the epoxy C–O stretching vibration, C–OH stretching vibration, and carboxy C–O stretching vibration, respectively [43].

With the polymerization process of Ppy within or on the GO film, the peaks related to $\text{C}=\text{C}$ (at approximately 1550 cm^{-1}) and $\text{C}=\text{O}$ (1734 cm^{-1}) stretching vibration were relatively weakened. The epoxy C–O, C–OH, and carboxy C–O stretching vibration almost disappeared, suggesting the introduction of GO. Several new peaks at approximately 1452 cm^{-1} can be observed on Ppy/GO, which can be assigned to symmetric stretching modes of the pyrrole ring, further demonstrating the existence of Ppy in the samples [43–46]. The strong and sharp absorption peaks at ~ 750 and ~ 800 cm^{-1} are attributed to the

Fig. 2. XPS surveys of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ (a) and high-resolution spectra of N 1s (b), Co 2p (c) and O 1s (d).

Table 1Summary of surface concentration (atom percent) of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ determined from XPS analysis.

Species	C	N	Co	O	N species			O species	
					Pyridinic	Pyrrolic	Graphitic	O^{2-}	OH^-
Binding energy (eV)	—	—	—	—	398.4	399.0	400.4	529.8	531.3
Content (at%)	82.0	8.5	1.3	8.2	32.81	59.48	7.71	16.36	83.64

vibrational modes of Co–O and Co=O bonds in Co_3O_4 [42].

TGA curves of GO, Ppy/GO, and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ under a N_2 atmosphere are presented in Fig. 4. GO showed considerable (>40%) mass loss before 250 °C because of the low molecular mass and volatile feature of the adsorbed H_2O molecules. The mass loss of Ppy/GO upon heating to 800 °C was 40%, which was slightly higher than that of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ (25%). Nevertheless, the slow mass loss indicates the high stability of GO/Ppy and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ resulting from the Ppy bonding effect between GO and Co_3O_4 . This high stability is beneficial for the use of these composites as durable ORR catalysts. $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ was subsequently pyrolyzed at various temperatures (400, 600, and 800 °C) in an inert atmosphere for 2 h to produce N-doped porous Co_3O_4 anchored on GO network materials.

3.2. Electrocatalytic activity

The GO sample was selected as a tentative catalyst to examine the ORR activity. The electrocatalytic activity of GO for the ORR was evaluated by CV scanning in KOH aqueous solution (0.1 mol/L) saturated with either N_2 or O_2 gas at room temperature. As observed in Fig. 5(a), the CV scan of GO was featureless in N_2 -saturated KOH (line (1)). The sample exhibited a dramatic increase in current density from the potential –0.18 V vs. SCE in an O_2 -saturated electrolyte compared with that in a N_2 -saturated electrolyte (line (2) in Fig. 5(a)). The cathodic reduction current increase near –0.18 V vs. SCE in the O_2 saturated electrolyte corresponds to the electrochemical reduction of oxygen molecules [47].

The impressive electrocatalytic activity of GO was confirmed by the LSV curves on a RDE (Fig. 5(b)). The potential at a current density of 0.1 mA/cm^2 , also known as the onset potential

[7], was –0.31 V vs. SCE, and the limiting current density at –1.0 V vs. SCE for 1600 r/min reached approximately 0.36 mA/cm^2 , which is higher than that of GO-based materials [48]. However, GO alone exhibited very distinct ORR activity.

The Ppy/GO could impart electrocatalytic activities toward the ORR and was compared with the metal oxides supported on it. A well-defined O_2 reduction peak centered at –0.38 V vs. SCE emerged as the electrolyte solution became saturated with O_2 (the curve (2) in Fig. 6(a)), which is close to the value of other N-doped GO catalysts in alkaline solution [15,49,50]. As observed in Fig. 6(b), the onset potential of the ORR for the Ppy/GO electrode was –0.20 V vs. SCE with the cathodic reduction peak at approximately –0.38 V vs. SCE. As observed in Fig. 7, the cathodic reduction peak started at approximately 0.10 V vs. SCE (Fig. 7(a)), and the onset potential was at –0.10 V vs. SCE (Fig. 7(b)) for the ORR for the Ppy/GO-600 electrode. These findings indicate that nitrogen doping and high-temperature pyrolysis are the primary contributors to the ORR performance, forming active sites and facilitating electron or charge transfer on the electrodes [20].

After the Co_3O_4 nanoparticles were assembled, the $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ catalysts were heated to 400, 600, or 800 °C. To efficiently analyze the effect of temperature on the ORR performance, a comparison between the RDE voltammograms for $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ at a rotation rate of 1600 r/min was made. As observed in Fig. 8(a), the onset potentials of the catalysts at 0.1 mA/cm^2 were –0.20, –0.18, –0.10, and –0.10 V vs. SCE for $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$, $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -400, $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -600, and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -800, respectively. In addition, the diffusion limiting current density for $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -800 was higher than those for $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$, $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -400, and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -600. These results indicate that pyrolytic carbonization of $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ (a necessary step in generating active N-doped

Fig. 3. FT-IR spectra of GO, Ppy/GO, and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$. **Fig. 4.** TGA and DTG analysis of GO (1), Ppy/GO (2) and $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ (3).

Fig. 5. (a) CVs of GO in N_2 - (1) and O_2 -saturated (2) KOH (0.1 mol/L) with a scan rate of 10 mV/s; (b) ORR polarization curves of GO in O_2 -saturated KOH (0.1 mol/L) with different rotation rates and a scan rate of 10 mV/s.

Fig. 6. (a) CVs of Ppy/GO in N_2 - (1) and O_2 -saturated (2) KOH (0.1 mol/L) with a scan rate of 10 mV/s; (b) ORR polarization curves of Ppy/GO in O_2 -saturated KOH (0.1 mol/L) with different rotation rates and a scan rate of 10 mV/s.

Fig. 7. (a) CVs of Ppy/GO-600 in N_2 - (1) and O_2 -saturated (2) KOH (0.1 mol/L) with a scan rate of 10 mV/s; (b) ORR polarization curves of Ppy/GO-600 in O_2 -saturated KOH (0.1 mol/L) with different rotation rates and a scan rate of 10 mV/s.

or Co,N-co-doped carbon species) requires high temperatures.

In Fig. 8(b), the CVs of the $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ -800 catalyst show a reductive peak at -0.18 V vs. SCE in O_2 -saturated KOH (0.1 mol/L), which is close to the value of -0.18 V for commercial

carbon-supported Pt and superior to those of other reduced GO-based catalysts [12]. Therefore, the enhanced ORR on $\text{Co}_3\text{O}_4/\text{Ppy}/\text{GO}$ is due to the excellent dispersion of Co_3O_4 nanoparticles with smaller size and the nitrogen doping effect on

Fig. 8. (a) ORR polarization curves of Co₃O₄/Ppy/GO treated at different temperatures with an electrode rotation rate of 1600 r/min and a scan rate of 10 mV/s; (b) CVs of Co₃O₄/Ppy/GO treated at different temperatures in O₂-saturated KOH (0.1 mol/L) with a scan rate of 10 mV/s.

GO sheets.

To obtain further insight into the ORR involving the Co₃O₄/Ppy/GO-800, LSV curves on a RDE at various rotation rates were constructed. Fig. 9(a) demonstrates that the onset potential for Co₃O₄/Ppy/GO-800 at various rotation rates was almost constant, and more importantly, at a rotation rate of 1600 r/min, Co₃O₄/Ppy/GO-800 exhibited a comparable limit-

ing current density to that of a Pt/C catalyst. These results suggest that the ORR catalytic activity of Co₃O₄/Ppy/GO is closer to that of commercial Pt/C catalysts.

The linearity of the K-L plots (Fig. 9(b)) and near parallelism of the fitting lines suggest first-order reaction kinetics for the concentration of dissolved oxygen and similar electron transfer numbers for the ORR at different potentials [37,51]. The elec-

Fig. 9. (a) ORR polarization curves of Co₃O₄/Ppy/GO-800 in O₂-saturated KOH (0.1 mol/L) with a scan rate of 10 mV/s and different rotation rates; (b) Corresponding Koutecky-Levich plots (J^{-1} vs $\omega^{-1/2}$) of Co₃O₄/Ppy/GO-800 at different potentials; Tafel slopes derived at kinetic regions between -0.2 V and -0.3 V vs SCE (c) and between -0.3 V and -0.6 V vs SCE (d).

Table 2

Electrochemical properties and corresponding experimental data for different samples.

Sample	Cathodic peak potential (V vs SCE)	Diffusion-limiting current density at 1600 r/min (mA/cm ²)	Onset potential (V vs SCE)
GO	—	0.36	−0.31
Ppy/GO	−0.38	1.28	−0.20
Ppy/GO-600	—	1.50	−0.10
Co ₃ O ₄ /Ppy/GO	−0.38	1.40	−0.20
Co ₃ O ₄ /Ppy/GO-400	—	1.50	−0.18
Co ₃ O ₄ /Ppy/GO-600	−0.40	1.78	−0.10
Co ₃ O ₄ /Ppy/GO-800	−0.18, −0.38	2.30	−0.10
Fe ₂ O ₃ /Ppy/GO-800 [35]	−0.24, −0.38	2.60	−0.10
Pt/C	0.0	2.30–2.50	—

tron-transfer number was calculated to be approximately 3.4 between −0.4 V and approximately −0.6 V vs. SCE based on the slopes, indicating that the ORR at the Co₃O₄/Ppy/GO-800 electrode was selected by an approximately four-electron reduction pathway. The Tafel slope calculation was used to analyze the ORR catalyzed by Co₃O₄/Ppy/GO-800 at 1600 r/min, and the kinetic parameters of the reaction were obtained (Fig. 9(c) and (d)). The Tafel slopes ($\partial\eta/\partial \log j_k$) for Co₃O₄/Ppy/GO-800 in the overpotential ranges of −0.2 to −0.3 V vs. SCE and −0.3 to −0.6 V vs. SCE were calculated to be 100 and 160 mV/dec, respectively. These values indicate that the first step involving oxygen adsorption is fast, whereas the reduction of the hydrogen peroxide intermediate is relatively slower. Both these values differed from the Tafel slopes for the ORR on Pt (60 and 120 mV/dec at potentials higher and lower than 0.8 V vs RHE, respectively) [52]. The Tafel slopes for the Pt/C catalyst suggest that the smaller Tafel slope in the low-overpotential region corresponds to the ORR on a Pt surface covered with an oxide and the large slope in the high-overpotential region corresponds to that on a clean Pt surface [53]. For Co₃O₄-Ppy/GO-800, the Tafel slope of 100–160 mV/dec is indicative of a more complicated ORR mechanism, with the rate-determining step likely involving both high activation energy for O–O bond splitting and extremely weak adsorption of the H₂O₂ intermediate molecule on the Co-based active sites. The difference in the Tafel slopes for Co₃O₄-Ppy/GO and Pt/C also implies the different nature of the active ORR site in these two cases. The detailed electrocatalytic activities of the catalysts are listed in Table 2.

To further analyze the experimental results obtained in this

Scheme 1. Reaction scheme of ORR in alkaline solution. **Scheme 2.** Proposed synergetic mechanism for the enhanced catalytic activity of the Co₃O₄/Ppy/GO catalyst for ORR.

study, we used simplified reaction pathways (Scheme 1) [54,55]. Path A shows how O₂ is reduced directly into H₂O through a four-electron transfer. Path B represents the sequential reaction path wherein O₂ is first reduced to H₂O₂ through a two-electron transfer, followed by a two-electron reduction to H₂O (Path C) or the release of the formed H₂O₂ into the bulk solution (Path C'). The latter is less desirable because it is inefficient for fuel conversion; in addition, the H₂O₂ it produces can lead to corrosion of many types of metal-based catalysts. For Co₃O₄/Ppy/GO, the ORR reaction can proceed with the high selectivity of path A; that is, the catalyst yields the more desirable reduced product, H₂O, during the ORR.

Based on these observations, it is postulated that the presence of cobalt oxide assembled nitrogen-GO could be the main contributor to the remarkable capability of Co₃O₄/Ppy/GO to catalyze the ORR with high activity. In our study, the cobalt oxide assembled nitrogen-GO hybrid material was Ppy-stabilized Co₃O₄ clusters embedded in N-doped graphitic carbon materials (Scheme 2). The Ppy chains not only stabilized the Co₃O₄ centers but also aided electron transfer, facilitating the ORR process. The N-doped graphitic carbon formed *in situ* not only directly served as the active site for improved intrinsic activity but also provided robust support to anchor the metal active sites for enhanced corrosion resistance to oxidative attack during the ORR.

4. Conclusions

In this study, Co₃O₄/Ppy/GO nanocomposites were prepared, and their performances as ORR electrocatalysts were evaluated and compared with those of GO and Ppy/GO. Unexpectedly, Co₃O₄/Ppy/GO exhibited excellent electrocatalytic performance in terms of higher catalytic activity and selectivity for the ORR in alkaline media. This finding can be attributed to the bridging of Co₃O₄ nanoparticles and GOs with Ppy as well as the effective N doping of GO. The fine distribution of Co species and their excellent activity in the ORR will enable the wide application of Co₃O₄ in fuel cells and other energy conversion

devices.

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Graphical Abstract

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Co₃O₄ nanoparticles assembled on polypyrrole/graphene oxide for electrochemical reduction of oxygen in alkaline media

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Co₃O₄/Ppy/GO demonstrated excellent electrocatalytic performance in terms of higher catalytic activity, and four-electron selectivity for ORR. This can be attributed to the bridging of Co₃O₄ nanoparticles and graphene oxides with Ppy, as well as the effective N doping of GO.

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Co₃O₄/聚吡咯/石墨烯碱性溶液中电化学还原氧

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摘要: 燃料电池具有较高的能量密度和发电效率, 以清洁能源为原料, 零污染排放, 是一种具有发展前景的能量储存和转化装置。阴极氧还原反应(ORR)在燃料电池中起着关键作用。ORR广泛采用贵金属铂基催化剂, 但是它们价格昂贵, 电子动力学转移速率慢, 碱性条件下易团聚, 这些亟需解决的问题阻碍了燃料电池商业化进程。近期, 一些非贵金属催化剂被广泛研究, 例如氮掺杂碳材料、Fe/N/C和Co/N/C材料等, 它们有可能在未来替代铂基催化剂。我们的目标是合成新型高催化活性的Co/N/C及其衍生非金属材料, 用于ORR催化反应。

由于石墨烯具有独特的形貌、较大的比表面积和良好的导电性, 其表面含有功能化的官能团, 所以我们选择石墨烯作为碳载体。首先, 用改性休克尔方法合成了氧化石墨烯(GO), 为了提高其催化活性, 采用聚吡咯作为氮源对其进行了氮掺杂, 制备了聚吡咯/氧化石墨烯(Ppy/GO)。通过ORR催化性能测试发现, GO对ORR具有一定的催化活性, 它的起始电位和阴极电流电位分别为−0.31 V vs SCE和−0.38 V vs SCE; Ppy/GO的起始电位和阴极电流电位分别为−0.20 V vs SCE和−0.38 V vs SCE, 氮掺杂对GO的催化活性有所提高。

采用水热法沉积氧化钴合成了Co₃O₄/聚吡咯/氧化石墨烯(Co₃O₄/Ppy/GO)。其形貌为Co₃O₄分散在氮掺杂GO表面。在KOH电解质(0.1 mol/L)中测试, Co₃O₄/Ppy/GO的起始电位和阴极电流电位分别为−0.20 V和−0.38 V vs SCE。经过800 °C高温煅烧处理后, Co₃O₄/Ppy/GO-800的催化活性明显提高, 起始电位和阴极电流电位分别达到−0.10 V和−0.18 V vs SCE。ORR电子转移数为3.4, 接近于4电子反应途径。Co₃O₄/Ppy/GO对ORR的催化活性及4电子催化选择性较高, 可能是由于纳米形态的Co₃O₄和Ppy/GO之间具有较强的表面作用力, 聚吡咯掺杂的氧化石墨烯具有较强的电子储存及释放能力。

综上, 我们通过水热法制备了钴、氮共掺杂的GO, 并研究了其对ORR的催化活性和电子转移选择性。结果表明Co₃O₄/Ppy/GO是一种高效的非贵金属电催化剂, 在碱性电解质中具有很高的ORR催化活性, 在燃料电池阴极催化剂方面很有前景。

关键词: 非贵金属电催化剂; 四氧化三钴; 聚吡咯; 氧化石墨烯; 氧还原反应; 质子交换膜燃料电池

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