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Article

Pyrolyzed titanium dioxide/polyaniline as an efficient non-noble metal electrocatalyst for oxygen reduction reaction

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ABSTRACT

To overcome the prohibitive cost and poor durability of conventional Pt-based catalysts, TiO₂/C was prepared by pyrolyzing a novel titanium dioxide/polyaniline (TiO₂/PANI) composite. The prepared catalysts were characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, cyclic voltammetry (CV), and linear sweep voltammetry. Interaction between PANI and TiO₂ was found to inhibit the aggregation of TiO₂ and its transformation from anatase to rutile. The catalytic activity of the TiO₂/C first increased with increasing PANI content and then decreased; the optimum was achieved when the PANI/TiO₂ mass ratio was 35/100. CV and *i*-*t* curves showed that the prepared composite has a good catalytic stability.

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1. Introduction

The preparation of low-cost, efficient, and stable catalysts as fuel cell cathode materials is currently a hot research topic. Groups 4 and 5 metal oxide compounds have been regarded as promising candidates for polymer electrolyte fuel cell (PEFC) cathode catalysts because they are insoluble in acid media [1]. The use of oxides of zirconium [2–6], tantalum [5–10], niobium [6], titanium [1,5], and hafnium [11–13] as cathode catalysts in oxygen reduction studies has been reported, with varied synthesis methods employed. In particular, TiO₂ is a promising photocatalyst that has received widespread interest [14,15]. Thorough research has been conducted regarding its synthesis, morphology and crystal phase control, modification, and combination with other materials to prepare composite materials.

TiO₂ is often used as the base material for catalysts because of its good stability. Recently, TiO₂ has also been examined as a fuel cell cathode catalyst because it can improve the stability [16] and methanol resistance of cathode catalysts and the selectivity and catalytic activity of 4-electron reactions [17,18]. Non-stoichiometric TiO₂ has also been used as a base material for cathode catalysts [19].

Notably, TiO₂ is an oxygen reduction catalyst. Zhang et al. [20] prepared a cathode catalyst via the hydrolysis of TiCl₄ followed by heat treatment and used the resulting product in zinc–air batteries. Dam et al. [21] used TiO₂ as a precursor to prepare a titanium carbonitride matrix after calcination at high temperature, and the resulting TiCNO product was a mixture of TiO₂ and TiCN catalysts. The initial oxygen reduction potential and the carrying current of the titanium carbonitride catalyst

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were significantly improved compared with those of pure TiO_2 . Additionally, Chisaka et al. [1] prepared a cathode catalyst, in which the main component was rutile TiO_2 , by heat treatment of TiCN . Their studies showed that the residual carbon did not integrate into the TiO_2 lattice to form impurity defects. During heat treatment at elevated temperatures, C was instead incorporated into graphene, which then coated the surface of the TiO_2 ; the coating played a role in the oxygen reduction electron transfer process. Although part of the N and Ti formed TiN , the N atoms did not influence the oxygen reduction activity because they were not integrated into the TiO_2 lattice. Conversely, both oxygen defects generated in TiO_2 during heat treatment at high temperatures and doped N are known to significantly affect the activity of TiO_2 towards oxygen reduction. Recent studies have indicated that the (110) plane of TiO_2 [1] is more conducive to the adsorption of oxygen. Thus, the (110) facets are favorable for oxygen reduction reactions. Despite the research results achieved to date, further investigations are required to adequately determine the mechanism of oxygen reduction over TiO_2 and its performance as a catalyst or catalyst support.

TiO_2 is a semiconductor, and as such its low conductivity limits its application in terms of oxygen reduction. Based on first-principle calculations, Zheng et al. [22] reported that for low-conductivity materials, the electron transfer efficiency is low, the reaction is limited to a small area on the material interface, and oxygen reduction tends to occur via a two-electron mechanism. The accumulation of the resulting products, H_2O_2 and HO_2^- ions, is unfavorable for the reaction to continue. Conversely, the introduction of conductive carbon favors the reduction of oxygen via a four-electron mechanism, thereby improving the oxygen reduction performance of the material. These conclusions have been experimentally confirmed [22]. Chisaka et al. [1] studied TiO_2 prepared via heat treatment of titanium carbonitride at high temperatures in N_2 and H_2 atmospheres. The resulting material exhibited oxygen reduction activity; C was not incorporated into the lattice of TiO_2 but was instead present as a single layer of graphite on the surface of the TiO_2 . C played a primary role in electron transportation [23], and the oxygen defects formed during the heat treatment process had a decisive role in improving the performance of the oxygen reduction catalyst.

In this study, we first prepared a novel TiO_2 /polyaniline (PANI) complex via a hydrothermal route, and a TiO_2 /C catalyst was obtained via subsequent pyrolysis. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the crystal phase composition and morphology of the TiO_2 /C, and its electrochemical performance was assessed. Moreover, the influence of the mass ratio of PANI to TiO_2 and the pyrolysis temperature on the oxygen reduction performance of the catalyst was examined to establish optimum synthesis conditions to provide a reference for the future study of oxygen reduction TiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

First, 2.282 g ammonium persulfate (APS, AR, Tianjin Damao Chemical Reagent Factory, Tianjin, China) was dissolved in HCl (36%, AR, Beijing Chemical Plant, Beijing, China) solution (0.1 mol/L) and held in an ice-water bath. Then, 0.3411 g of cetyltrimethylammonium chloride (CTAC, AR, Tianjin Guangfu Chemical Plant, Tianjin, China) dissolved in HCl solution (0.1 mol/L) was added to a three-necked flask. After adding 0.92 mL aniline (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), the mixture was mechanically stirred in an ice-water bath for 1 h to ensure uniform dispersion of the aniline monomers. The polymerization of the aniline monomers was initiated by the addition of the pre-cooled APS solution. The total volume of HCl solution (0.1 mol/L) used was 100 mL. The reaction solution was kept in an ice-water bath under mechanical stirring for 24 h. After the reaction, the product was centrifuged and washed three times with industrial ethanol, distilled water, and absolute ethanol (AR, Sinopharm) in turn. Finally, the product was redispersed in 80 mL absolute ethanol before use. The 20 mL of polyaniline (PANI) ethanol dispersion was centrifuged and dried in a vacuum dryer at 60 °C for 6 h, and the concentration of the PANI nanofiber dispersion (11.46 mg/mL) was calculated by weighing the resulting solid powder. The yield of PANI was found to be about 97.6%.

Next, 3 mL of tetrabutyl titanate (AR, Sinopharm) was mixed with a certain amount of ethanol. After ultrasonic dispersion, the PANI ethanol dispersion was added, and the mixture was ultrasonically dispersed for another 10 min. The total volume of the ethanol dispersion was set at 30 mL. Then, under magnetic stirring, 10 mL of distilled water was added dropwise to the above mixture. The mixture was stirred at 70 °C for a further 30 min to ensure complete hydrolysis. The resulting precipitate was centrifuged, washed three times with distilled water, and then dispersed into 60 mL of aqueous HCl solution (1 mol/L). The mixture was transferred to a 250 mL three-necked flask and mechanically stirred at 70 °C for 4 h. The resulting solution was then transferred to a 35 mL autoclave and hydrothermally treated at 150 °C for 18 h. The precipitated powder was centrifuged, washed three times each with industrial ethanol and distilled water, and dried at 60 °C. Finally, the obtained solid was ground and calcined in a tube furnace at 800 °C under flowing N_2 to generate the TiO_2 /C catalyst.

2.2. Catalyst characterization

XRD measurements were performed with a Rigaku D/Max-RB X-ray diffractometer (Japan) using $\text{Cu K}\alpha$ radiation at a tube voltage of 40 kV and operating current of 30 mA. The morphologies of the samples were analyzed with a field emission scanning electron microscope (FE-SEM; Philips FEI-Sirion 200) and a transmission electron microscope (TEM; FEI TECNAI G2). Raman spectra were collected with a Renishaw inVia Raman spectrometer using a He-Ne laser (0.1 mW) at 633 nm. Fourier transform infrared spectra (FT-IR) were collected using a Nicolet Avatar 360 spectrometer (USA). X-ray photoelectron spectroscopy (XPS) measurements were performed with a ULVAC PHI5700ESCA spectrometer. Thermal analysis of the samples was carried out using an SDT Q600 thermogravi-

metric-differential scanning thermal analyzer (TGA-DSC; USA).

2.3. Catalyst performance

The Ti/C catalyst (4 mg) was placed in a 1.5 mL centrifuge tube, and 0.4 mL of absolute ethanol, 0.4 mL of distilled water, and 20 μ L of 0.5 wt% Nafion solution (5% Nafion in isopropyl alcohol, analytically pure, Alfa Aesar Tianjin Chemical Co., China) were then added. Catalyst was dispersed in the mixture by ultrasonication. To obtain the working electrode, 4 μ L of the catalyst dispersion was dripped and uniformly spread onto the surface of a glassy carbon rotating disk electrode (RDE; diameter 4 mm), and naturally dried. After each test, the electrode was successively washed with distilled water and absolute ethanol and then dried in air.

The electrochemical properties of the catalyst were measured with a three-electrode system in KOH (AR, Tianjin Sailboat Chemical Reagent Co., Ltd., Tianjin, China) electrolyte (0.1 mol/L) at room temperature using a Shanghai Chen Hua CHI650D electrochemical workstation. The working electrode was the catalyst-loaded glassy carbon RDE, the counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode. To ensure gas saturation, 30 min of aeration was carried out before each test. The scan range was 0.2 to -0.8 V, and the scan speed was 5 mV/s.

3. Results and discussion

3.1. Influence of the mass ratio of PANI to TiO₂ on the performance of the TiO₂/C composites

TEM images of the synthesized PANI before and after its combination with TiO₂ are shown in Fig. 1. The HCl doped PANI had a fiber-like structure with rough spiculations on its surface, as shown in Fig. 1(b). Fig. 1(a) shows that the TiO₂ nanoparticles were closely and uniformly adhered to the surface of the PANI nanofibers.

The effect of the PANI on the phase composition of the TiO₂ was investigated by XRD. The presence of PANI in the composites was found to change the phase composition and crystal size of the TiO₂. Fig. 2 shows the XRD patterns of TiO₂/PANI composites with different PANI contents (the amount of TiO₂ was calculated according to the theoretical yield). The proportion of anatase TiO₂ in the composites increased, and the pro-

Fig. 1. TEM images of (a) PANI nanofibers and (b) TiO₂/PANI with PANI/TiO₂ = 40/100.

Fig. 2. XRD patterns of TiO₂/PANI composites with different PANI contents. PANI/TiO₂ mass ratio: (1) 5/100; (2) 20/100; (3) 30/100; (4) 40/100.

portion of rutile TiO₂ decreased with increasing PANI content. The rutile phase was the dominant phase in all of the obtained composites. When the mass ratio of PANI to TiO₂ was 5/100, the product was pure rutile-TiO₂. At PANI/TiO₂ = 40/100, the proportion of rutile TiO₂ decreased to 74.6% while that of anatase TiO₂ increased to 25.4%. It is well-known that rutile-TiO₂ is the thermodynamically stable state. Under the hydrothermal synthesis conditions and high concentrations of hydrochloride employed, TiO₂ is expected to completely transform into rutile.

However, the interaction between TiO₂ and the surface of the introduced one-dimensional PANI fibers inhibited the anatase-to-rutile transformation, consequently leading to the formation of anatase TiO₂ in the composite [24]. Moreover, previous studies have shown that the crystal transformation from anatase to rutile occurs at the interfaces of the anatase particles, suggesting that weakened agglomeration of anatase will inhibit the formation of rutile TiO₂. As observed in Fig. 2, the intensity of the characteristic XRD peaks of TiO₂ decreased, leading to peak broadening, with increasing PANI content. These results confirm that higher PANI content increased the attachment of TiO₂ on the surface of the PANI fibers and inhibited the agglomeration and formation of large TiO₂ particles. To support the above analysis, Scherrer's formula was used to calculate the particle size of TiO₂ in the composites, and the results are given in Table 1.

Table 1
Phase composition and crystallite size of TiO₂/PANI with varied PANI contents.

PANI/TiO ₂ mass ratio	Mass fraction (%)		Diameter (nm)	
	Anatase-TiO ₂	Rutile-TiO ₂	Anatase-TiO ₂ (101)	Rutile-TiO ₂ (110)
5/100	0	100	—	15.31
20/100	7.8	92.2	8.36	12.58
30/100	14.4	85.6	6.82	12.13
40/100	25.4	74.6	6.82	12.02

The interaction between PANI and TiO_2 was further investigated by FT-IR spectroscopy. The FT-IR spectra of the TiO_2 /PANI composites are shown in Fig. 3. The peaks at 3502, 1573, and 1490 cm^{-1} were indexed to the stretching vibration absorptions of N–H single bonds, C=N double bonds, and C=C double bonds, respectively. The peaks at 1305 and 1248 cm^{-1} were assigned to the C–N stretching vibration absorption of benzene rings. The peaks at 1143 and 802 cm^{-1} arise from the IR absorption of quinone and benzene rings in the doped PANI, respectively. The absorption from 400 to 1000 cm^{-1} corresponded to the network structure of O–Ti–O in the TiO_2 component. Furthermore, differences in absorption at and below 802 cm^{-1} could be distinguished among the spectra. At high TiO_2 contents in the composite, the absorption peak corresponding to TiO_2 overlapped with that corresponding to PANI absorption at lower wavenumber owing to the existence of the interaction between them. The gradual disappearance of the absorption peak at 802 cm^{-1} , shift in the O–Ti–O absorption peak, and reduction in the intensity of the remaining PANI absorption peaks confirm the existence of interactions between PANI and TiO_2 . We speculate that the N–H groups of PANI interacted with the surface hydroxy groups of TiO_2 at the interfaces [24].

The TiO_2 /PANI composite with PANI/ TiO_2 = 40/100 was characterized by XPS to analyze the chemical bonds present and their associated energy to further confirm the interaction between TiO_2 and PANI. Fig. 4(a) shows the resulting XPS spectrum of the TiO_2 /PANI composite. The XPS spectrum confirmed the presence of C, O, Ti, and N in the composite. The peaks at binding energy of 284.3, 530.1, 458.8, and 400.1 eV could be well indexed to C 1s, O 1s, Ti 2p, and N 1s, respectively. The fractions of the elements were calculated to be C 49.95%, O 33.35%, Ti 13.20%, and N 3.5%. Fig. 4(b) and (c) shows high-resolution XPS spectra for C 1s and O 1s, respectively. The C 1s XPS spectrum displayed three peaks at 284.6, 286.4, and 288.5 eV following Gaussian fitting, where the carbon atoms with binding energy of 288.5 eV are associated with C–O–Ti bonds in the composite. The O 1s peak could be divided into two peaks at 530.0 and 531.9 eV after deconvolution. The peak at 530.0 eV is associated with Ti–O bonds, whereas the peak at 531.9 eV confirmed a change in the Ti–O bond environment in

Fig. 3. FT-IR spectra of TiO_2 /PANI composites with different PANI contents. PANI/ TiO_2 : (1) 5/100; (2) 10/100; (3) 20/100; (4) 30/100; (5) 40/100.

the TiO_2 . Based on the XRD patterns and FT-IR spectra, we believe that PANI formed hydrogen bond-like interactions with hydroxyl groups on the surface of the TiO_2 via amino or imino groups during the synthesis of the composite materials [24].

Linear sweep voltammetry (LSV) curves were recorded to analyze the catalytic activity of the TiO_2 /C composites for the oxygen reduction reaction before and after pyrolysis of TiO_2 /PANI. The LSV curves obtained before and after pyrolysis are shown in Fig. 5. The performance of the TiO_2 /C catalyst towards oxygen reduction improved with increasing PANI content, reaching a maximum at a PANI/ TiO_2 = 30/100–40/100. This can be ascribed to the extension of the limited conductivity of TiO_2 that enhanced the activity of the catalyst towards oxygen reduction. Moreover, the N in the framework of PANI may also have acted as an active center for the oxygen reduction reaction [25,26]. As the PANI content increased, the content of C–N derived from the pyrolyzation also increased, resulting in a higher catalytic rate of oxygen reduction [25,26]. As noted, further increases in PANI did not lead to further improvement in catalytic activity, indicating the existence of a limitation in the interaction at the interface between PANI and

Fig. 4. (a) XPS spectrum of TiO_2 /PANI with PANI/ TiO_2 = 40/100; (b) High-resolution XPS spectra of C 1s; (c) High-resolution XPS spectra of O 1s.

Fig. 5. LSV plots for TiO_2/C derived from TiO_2/PANI composites with different PANI contents before (a) and after (b) pyrolyzation at $800\text{ }^\circ\text{C}$ for 1 h in N_2 . Electrolyte: O_2 saturated KOH (0.1 mol/L); scanning rate: 5 mV/s; rotation speed: 900 r/min.

TiO_2 at which TiO_2 cannot act as a good cocatalyst. This limitation may have arose from the limited catalytic activity of the N-doped C generated from the pyrolysis of pure PANI, which was lower than that of commercial Pt/C materials. The LSV curve of Pt/C has a wide current plateau and strong limiting diffusion current density, indicating a diffusion-controlled process related to an efficient 4e^- dominated oxygen reduction pathway. Conversely, current stabilization could not be attained in the N-doped C material obtained from pyrolysis of pure PANI. This suggests a likelihood of a transformation process involving 2e^- , namely the transformation of O_2 into OOH^- [22]. This represents a huge step behind the study of N-doped C materials obtained from the pyrolysis of GO-PANI [26]. The LSV curve of the TiO_2/C composite material from pyrolyzed TiO_2/PANI displayed an obvious current plateau, after which the diffusion current density increased continuously, which can be ascribed to the effects of combined 2e^- and 4e^- pathways.

Although the influence of metal oxides on the enhancement of catalytic activity of C materials is not considerable, the number of studies on fuel cells involving metal oxides has gradually increased in the last several years owing to the cost-effective use of metal oxides, and more importantly, their dramatic electrochemical stabilization of catalysts and enhancement of the working lifetime of fuel cells [27]. The i - t curves of the pure

Fig. 6. i - t plots of TiO_2/C and C derived from pyrolyzation of TiO_2/PANI composite and PANI, respectively, at $800\text{ }^\circ\text{C}$ for 1 h in N_2 . Electrolyte: O_2 saturated KOH (0.1 mol/L); initial potential: -0.5 V ; rotation speed: 900 r/min.

carbonized PANI and composite prepared at a PANI/ $\text{TiO}_2 = 40/100$ were measured and are shown in Fig. 6. Under similar conditions, the current loss of the composite was only 13% after 5000 s reaction, while the current loss for the N-doped C material obtained from the carbonization of pure PANI reached as high as 32%. Namely, although the product of the carbonization of pure PANI exhibited slightly better catalytic activity than the product from TiO_2/PANI , the stability of the latter was much more superior to that of the former. Further, CV was performed to study the cycle stability of the TiO_2/C catalyst. Fig. 7 shows no apparent fluctuation in the electrochemical response of TiO_2/C after 100 cycles, which is consistent with the results of the above i - t curves. As deduced, the introduction of TiO_2 and the carbonization of the conductive polymer reduced the carbon content in the catalyst and improved the cyclic sta-

Fig. 7. CV plots in (a) N_2 and (b) O_2 of TiO_2/C derived from pyrolyzation of TiO_2/PANI composite at $800\text{ }^\circ\text{C}$ for 1 h in N_2 .

bility of the carbon material as an electrocatalyst or catalyst support.

Additionally, the TG curve of the pre-carbonized composite with PANI/TiO₂ = 40/100 was recorded in air to investigate the real mass ratio of PANI to TiO₂ (Fig. 8). The final mass loss reached 34.8% after heating to 950 °C. The mass loss of 4.0% in the range from 0 to 100 °C can be attributed to the evaporation of absorbed water; the other 30.8% loss can be ascribed to the combustion of PANI in the composite.

3.2. Influence of pyrolysis on the oxygen reduction performance of TiO₂/C composites

Fig. 9 displays a TEM image of TiO₂/C derived from the pyrolysis of the TiO₂/PANI composite with PANI/TiO₂ = 40/100 at 800 °C for 1 h in N₂. Compared with the results in Figs. 1(a) and 3, the fiber-like structure disappeared, and the TiO₂ was coated by carbon material with no obvious morphology. Thus, the pyrolysis converted the PANI into an amorphous carbon material.

FT-IR spectra of the TiO₂/PANI composites with PANI/TiO₂ = 40/100 before and after pyrolysis are shown in Fig. 10. The composite obtained following pyrolysis displayed peaks at 3416 cm⁻¹, assigned to the stretching vibration of N–H bonds in PANI; 1575 cm⁻¹, ascribed to the stretching vibration of C=N in

Fig. 8. TGA curve of TiO₂/PANI with PANI/TiO₂ = 40/100.

Fig. 9. TEM image of TiO₂/C derived from pyrolyzation of TiO₂/PANI composite with PANI/TiO₂ = 40/100 at 800 °C for 1 h in N₂.

Fig. 10. FT-IR spectra of (1) TiO₂/PANI, (2) TiO₂/C (800 °C for 1 h in N₂), and (3) PANI.

the quinone ring; 1487 cm⁻¹, attributed to the stretching vibration of C=C bonds in the benzene ring; and 1301 and 1243 cm⁻¹, ascribed to the stretching vibration of C–N bonds. The absorption peak at 1145 cm⁻¹ was indexed to the quinone ring doped into PANI, and no assignable absorption peaks were observed below 793 cm⁻¹. The samples maintained their infrared absorption in the range of 400–1000 cm⁻¹ before and after pyrolysis, indicating that the network structure of O–Ti–O did not apparently change after carbonization. The small absorption peak at 1585 cm⁻¹ originated from the absorption of water on the surface of the TiO₂. Therefore, the original structure of PANI was damaged during pyrolysis, but the structure of O–Ti–O network was unchanged.

Fig. 11 shows the Raman spectra of the TiO₂/PANI composite with a PANI/TiO₂ = 40/100 before and after pyrolysis. The sample before pyrolysis exhibited strong absorption peaks at 1599, 1464, 1220, and 1165 cm⁻¹, which were assigned to the vibration of quinonediimine groups in PANI. The absorption peak at 1337 cm⁻¹ was indexed to the stretching vibration absorption of the N–C bond in phenylene diamine. Thus, the presence of PANI in the samples before calcination is confirmed. The absorption peaks of PANI disappeared following calcination. Two broad absorption bands at 1336 and 1558 cm⁻¹, corresponding to the D and G bands of graphite carbon, respectively, were observed instead. Ring deformation vibration absorption peaks of PANI were observed at 414 and 522 cm⁻¹ before pyrolysis and disappeared after pyrolysis.

Therefore, we can deduce that the structure of PANI was damaged during pyrolysis, resulting in the formation of graphitic carbon. The conductivity of this carbon material was better than that of the PANI fibers. Accordingly, the conductivity of the composite improved following pyrolysis, inhibiting the localized accumulation of products generated from oxygen reduction and thereby improving the activity of the composite towards oxygen reduction.

4. Conclusions

We prepared TiO₂/C cathode catalysts and examined the in-

Fig. 11. Raman spectra of TiO_2/PANI composite with $\text{PANI}/\text{TiO}_2 = 40/100$ before (1) and after (2) pyrolyzation at $800\text{ }^\circ\text{C}$ for 1 h in N_2 .

fluence of the PANI-to- TiO_2 mass ratios on the properties of the resulting composite materials. The influence of high-temperature treatment on the properties of the composite materials was also investigated. The results show the presence of bonding between the amidogen (or imido) of PANI and the hydroxy groups on the surface of TiO_2 in the composite materials. The presence of this interaction prohibits the anatase-to-rutile TiO_2 transformation and promotes adhesion of the TiO_2 particles to the surface of PANI fibers, thereby inhibiting aggregation of TiO_2 . The catalyst prepared at $\text{PANI}/\text{TiO}_2 = 35/100$ and pyrolyzed displayed the best activity. The carbon material generated from the carbonization of PANI after the high-temperature treatment was found to coat the surface of the TiO_2 . The TiO_2/PANI composite was transformed into TiO_2/C , leading to increased oxygen reduction activity. Concurrently, the high-temperature treatment caused N from the PANI framework to dope into the lattice of the graphitized carbon, further contributing to the increased oxygen reduction activity of the composite catalyst.

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Graphical Abstract

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Pyrolyzed titanium dioxide/polyaniline as an efficient non-noble metal electrocatalyst for oxygen reduction reaction

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To overcome the prohibitive cost and poor durability of conventional Pt-based catalysts, TiO_2/C was prepared by pyrolyzing a novel TiO_2/PANI composite. This non-noble metal electrocatalyst exhibits good ORR catalytic activity owing to the beneficial interaction between PANI and TiO_2 .

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热解二氧化钛/聚苯胺制备高效非贵金属氧还原电催化剂

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摘要: 为了克服传统Pt系催化剂价格昂贵、稳定性差的缺点, 采用热解新型TiO₂/聚苯胺(PANI)复合物的方法合成了TiO₂/C催化剂. 用扫描电子显微镜、X射线光电子能谱、X射线衍射、傅里叶变换红外光谱、拉曼光谱、透射电子显微镜、循环伏安法和线性扫描伏安法等方法研究了热处理和PANI复合比例对复合物的形貌、成键、晶相组成及氧还原性能的影响. 结果表明, PANI与TiO₂间存在相互作用, 可以抑制TiO₂的团聚和锐钛矿向金红石的转变. 热处理制得TiO₂/C的氧还原活性随着PANI载体含量增加先升高后降低, PANI和TiO₂质量比为35/100时, 催化剂的氧还原活性最高. 同时, 循环伏安和时间-电流曲线测试表明, 已制备的复合材料在催化氧还原反应进行时具有较好的稳定性.

关键词: 聚苯胺; 二氧化钛; 热解; 阴极催化剂; 氧还原

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1. 前言

目前, 制备廉价、高效、稳定的催化剂是燃料电池阴极材料研究的热点. 第IV、V副族金属氧化物因其在酸中不可溶, 被认为是具有前景的燃料电池阴极催化剂备选材料^[1]. 以锆^[2-6]、钼^[5-10]、铌^[6]、钽^[5,11]和钨^[11-13]的氧化物作为阴极氧还原催化剂的研究已见报道, 合成方法也多种多样. TiO₂是一种前景广阔、研究广泛的光催化剂, 有关其合成、形貌及晶相控制、改性及与其他材料复合方面的研究已十分深入^[14,15]. 近来, TiO₂也被用作燃料电池阴极催化剂. 由于TiO₂具有良好的稳定性, 常被作为催化剂基底材料. TiO₂能够提高阴极催化剂的稳定

性^[16]、抗甲醇性能、4电子反应的选择性和催化活性^[17,18]. 此外, 非化学计量比TiO₂也被用作基底材料^[19].

值得注意的是, TiO₂本身也是一种氧还原催化剂. Zhang等^[20]通过TiCl₄水解后高温热处理的方法制备阴极催化剂, 并将其用于锌-空气电池. Dam等^[21]用TiO₂制备的钛的碳氮化物, 再经过高温煅烧, 得到的TiCNO是一种由TiO₂和TiCN混合而成的催化剂, 与纯TiO₂相比, 其氧还原初始电位和极限电流都有明显变化. Chisaka等^[1]也采用热处理TiCN的方法制备了以金红石相TiO₂为主体的阴极催化剂. 他们发现材料中残留的C并没有掺杂到TiO₂中形成杂质缺陷, C在高温热处理过程中结合成石墨烯后包覆在TiO₂表面, 在氧还原过程中起到了传递电

子的作用. 部分N与Ti形成TiN, 这部分N原子由于没有掺杂到TiO₂, 故对氧还原活性没有影响, 但高温热处理过程中在TiO₂中产生的氧缺陷和掺杂N对TiO₂氧还原活性的提高具有很大作用. 近年研究表明, TiO₂(110)晶面由于更容易吸附氧气, 对氧还原反应有利^[11]. 尽管已经取得一定的研究成果, 但是无论是TiO₂氧还原机理, 还是TiO₂作为催化剂或催化剂载体的性能仍需进行深入探讨. 目前在TiO₂合成、改性及与其他材料复合等方面已取得的研究成果具有借鉴意义.

二氧化钛是一种半导体, 电导率低限制了其在氧还原反应中的应用. Zheng等^[22]通过第一性原理计算发现, 对于电导率低的材料, 电子转移效率低, 反应被限制在物质界面处的小区域内, 氧还原反应倾向于发生2电子过程, 生成物为H₂O₂和HO₂⁻离子, 生成物会不断积累, 不利于反应的继续进行; 导电碳材料的引入, 有利于氧气通过4电子过程还原, 提高了材料的氧还原性能. 以上结论在实验上也得到了证实^[22]. Chisaka等^[1]通过在N₂-H₂混合气的气氛中高温热处理钛的碳氮化物制备了具有氧还原活性的TiO₂, 研究发现C并没有掺入TiO₂晶格中, 而是以单层石墨的形式存在于TiO₂表面, C在其中的主要作用为传输电子^[23], 结果高温热处理过程中形成的氧缺陷在提高氧还原催化剂性能方面有决定性作用.

本文使用水热法合成了新型TiO₂/PANI复合物, 再经过高温热解, 制备了TiO₂/C催化剂. 采用X射线衍射(XRD)和扫描电子显微镜(SEM)等技术研究了TiO₂/C的形貌和晶相组成, 并对催化剂进行了电化学测试. 着重研究了聚苯胺(PANI)和TiO₂的比例和热解温度对催化剂氧还原性能的影响, 寻找最佳实验条件, 为TiO₂在氧还原催化剂方面的研究提供一定的借鉴.

2. 实验部分

2.1. 催化剂的制备

将2.282 g过硫酸铵(APS, A.R., 天津大茂化学试剂厂)用HCl(36%, A.R., 北京化工厂)溶液(0.1 mol/L)溶解后预冷却备用. 称取0.3411 g十六烷基三甲基氯化铵(CTAC, A.R., 天津光复精细化工厂), 用HCl溶液(0.1 mol/L)溶解后加入到三口烧瓶中, 再加入0.92 mL苯胺(A.R., 国药集团化学试剂有限公司), 体系在冰水浴条件下机械搅拌1 h, 使苯胺单体分散均匀. 加入预先冷却的APS溶液, 使苯胺单体发生聚合反应, 体系仍保持冰水浴, 继续机械搅拌24 h. 反应过程中, 使用的HCl溶液(0.1 mol/L)总体积为100 mL. 反应结束后, 将产物离心, 用工

业乙醇、蒸馏水和无水乙醇(A.R., 国药集团化学试剂有限公司)各离心洗涤三次, 最后用无水乙醇分散并定容至80 mL备用. 准确量取20 mL PANI乙醇分散液, 离心后置于真空干燥箱中60 °C干燥6 h, 由固体粉末质量计算PANI纳米纤维分散液质量浓度为11.46 mg/mL, PANI收率约为97.6%.

取3 mL钛酸正四丁酯(A.R., 国药集团化学试剂有限公司)和适量无水乙醇混合, 超声分散均匀后, 向混合物中加入适量的PANI无水乙醇分散液, 继续超声分散10 min, 反应中加入无水乙醇和PANI无水乙醇分散液的总体积为30 mL. 磁力搅拌下, 向混合均匀的溶液中滴加10 mL蒸馏水, 将反应体系置于70 °C水浴中继续搅拌30 min, 使钛酸正四丁酯充分水解. 得到的沉淀物经过离心, 用蒸馏水洗涤三次. 用60 mL HCl溶液(1 mol/L)溶解沉淀物, 转移到250 mL三口烧瓶中, 70 °C水浴条件下机械搅拌4 h. 将溶液转移到35 mL的水热釜中, 150 °C反应18 h. 然后离心, 用工业乙醇洗三次, 蒸馏水洗三次, 60 °C烘干. 将得到的固体研磨, 之后在N₂保护下用管式炉800 °C高温处理即得到TiO₂/C.

2.2. 催化剂的表征

样品的XRD谱测试在日本Rigaku D/Max-RB型X射线衍射仪上进行, Cu靶, K_α辐射, 管电压为40 kV, 工作电流30 mA. 利用飞利浦公司FEI-Sirion 200场发射SEM和FEI TECNAIG2透射电子显微镜(TEM)分析材料的形貌. 采用Renishaw inVia拉曼光谱仪采集样品的拉曼响应信号, 激光器为氦氖激光器, 波长为633 nm, 功率为0.1 mW. 使用美国Nicolet公司Avatar 360傅里叶变换红外光谱仪(FT-IR)测试样品的红外吸收峰. 利用ULVAC公司PHI5700ESCA型X射线光电子能谱(XPS)分析样品的元素和成键状况. 样品的热分析在美国TA公司SDT Q600型热重-差示扫描热分析以上进行.

2.3. 催化剂的性能

称取4 mg催化剂置于1.5 mL离心管, 依次加入0.4 mL无水乙醇、0.4 mL蒸馏水和20 μL质量分数为0.5%的Nafion溶液(由5% Nafion溶液分散于异丙醇(分析纯, 阿法埃莎天津化学有限公司)制得), 超声分散均匀后得催化剂分散液. 用移液器量取4 μL催化剂分散液滴于玻碳RDE表面(电极直径为4 mm), 使催化剂在玻碳电极表面均匀铺展, 自然晾干即得所需工作电极. 测试后, 电极依次用蒸馏水和无水乙醇清洗干净, 晾干方可进行下一次测试.

实验使用上海辰华CHI650D电化学工作站采集数

据. 测试在三电极体系中进行: 工作电极为滴有催化剂分散液的玻碳旋转圆盘电极; 对电极是铂丝; 参比电极是Ag/AgCl电极; KOH(A.R., 天津市风船化学试剂科技有限公司)溶液(0.1 mol/L)作为电解质溶液. 为保证气体饱和, 每次测试前需要通入气体30 min左右. 扫描范围是0.2到-0.8 V, 扫描速度是5 mV/s.

3. 结果与讨论

3.1. PANI与TiO₂复合比例对TiO₂/C催化性能的影响

图1为PANI与TiO₂复合前后的TEM照片. 从图1(b)可以发现, 盐酸掺杂PANI呈现纤维状结构, 并且纤维表面不光滑为毛刺状. 图1(a)中TiO₂紧密均匀包覆在PANI纳米纤维表面.

用XRD研究了复合物中TiO₂的晶相组成及PANI对TiO₂的作用. 结果显示, PANI的存在使TiO₂的晶相组成和晶体尺寸发生了变化. 图2为不同PANI/TiO₂质量比(其中TiO₂的质量按照理论产量计算)时TiO₂/PANI复合物的XRD谱. 可以看出, 随着PANI含量的增加, 复合物中锐钛矿TiO₂的含量逐渐增加, 金红石相TiO₂的含量逐渐减少, 但金红石始终是复合物中TiO₂的主要晶相. 当PANI/TiO₂ = 1/100时, 复合材料中的TiO₂全部以金红石相存在; 当PANI/TiO₂ = 40/100时, 金红石所占的比例降低为74.6%, 而锐钛矿的比例增加到25.4%. 这是因为从热力学角度分析, 金红石相是TiO₂最为稳定的晶相, 在水热和高浓度盐酸的条件下, TiO₂应该全部转化为金红石相. 然而, 在TiO₂结晶过程中引入一维PANI纳米纤维后, 生成的TiO₂会和PANI纤维表面形成相互作用, 这种相互作用的存在抑制了TiO₂从锐钛矿相向金红石的转变, 使得复合物中有锐钛矿相TiO₂存在^[24]. 此外, 也有研究表明, 锐钛矿向金红石的转变发生在锐钛矿颗粒间接触的地方, 抑制锐钛矿纳米颗粒的团聚将有利于抑制其向金红石转变. 从图2中还可发现, XRD衍射峰的强度随着PANI含量的增加而减弱, 并且峰出现宽化现象, 可以推测随着PANI含量增加, 复合物中TiO₂附着在PANI纤维表面, 减少了TiO₂团聚, 也抑制了TiO₂颗粒尺寸增长, 使得TiO₂晶粒尺寸减小. 为证明这一点, 根据谢乐公式计算出复合物中TiO₂的晶粒尺寸, 结果见表1.

PANI与TiO₂间相互作用的存在从FT-IR谱中也可得到证明. 图3为PANI和TiO₂质量比不同时TiO₂/PANI的红外吸收光谱. PANI的主要特征峰如下: 位于3502 cm⁻¹处为N-H单键的伸缩振动吸收峰; 1573 cm⁻¹处为C=N的伸缩振动吸收峰; 1490 cm⁻¹处为C=C双键的伸缩振动;

1305和1248 cm⁻¹处是苯环中C-N单键的伸缩振动吸收峰; 1143和802 cm⁻¹处吸收峰则分别归属于掺杂聚苯胺中的醌环和苯环. 在复合物的红外吸收光谱中, 400–1000 cm⁻¹范围内的红外吸收是由TiO₂组分中的O-Ti-O网状结构引起的, 而PANI组分位于802 cm⁻¹及更低波数处的小吸收峰仍能分辨. 当复合物中TiO₂含量较高时, 虽然复合物的主要成分是TiO₂, 但由于相互作用的存在, 导致这一吸收峰和PANI低波数的吸收峰重合, 802 cm⁻¹吸收峰逐渐消失, O-Ti-O吸收峰的位置发生偏移, 并且聚苯胺的其余吸收峰减弱, 由此可以证明, PANI和TiO₂间存在相互作用. 我们推测是PANI中的N-H与TiO₂表面的羟基在二者界面间发生了相互作用^[22].

为进一步印证TiO₂与PANI间存在相互作用, 对PANI/TiO₂ = 40/100的TiO₂/PANI复合物进行了XPS测试, 分析复合物中各元素的结合能和元素之间的成键状况. 图4(a)为PANI/TiO₂ = 40/100时TiO₂/PANI复合物的XPS全谱. 从图可知, 复合物中含有C, O, Ti和N四种元素, 其中光谱信号分别对应于C 1s, O 1s, Ti 2p和N 1s, 结合能分别为284.3, 530.1, 458.8和400.1 eV. 经计算可知, 这四种元素所占比例由大到小依次为C 49.95%, O 33.35%, Ti 13.20%, N 3.5%. 图4(b)和(c)分别为C 1s和O 1s的高分辨XPS谱. 经过高斯拟合, C 1s谱可以细分为284.6, 286.4和288.5 eV处的三个峰. 其中结合能为288.5 eV的碳原子说明体系中C-O-Ti化学键的存在. O 1s峰去卷积计算后可以分为两个峰, 分别位于530.0和531.9 eV, 其中530.0 eV对应于Ti-O键中O 1s轨道的结合能, 而531.9 eV处的O 1s峰则说明了TiO₂中Ti-O键环境发生变化. 结合XRD与FT-IR的分析结果, 我们认为, 在复合材料制备过程中, PANI通过氨基(或亚氨基)与TiO₂表面的羟基形成了类似氢键的化学键^[22].

在此基础上, 用线性扫描伏安法测试了TiO₂/PANI热解前后TiO₂/C催化氧化还原反应的能力. 图5为PANI与TiO₂质量比不同时TiO₂/PANI复合物热解前后的LSV曲线. 随着PANI含量增加, TiO₂/C催化氧化还原反应能力增大. 当PANI/TiO₂ = 100/30–100/40时, 得到的TiO₂/C氧化还原活性最高. 这是由于TiO₂的导电性差, 引入导电性较好的物质可以提高TiO₂的氧化还原活性. 同时, 聚苯胺骨架中的氮元素也是氧化还原反应的活性中心^[25,26], 随着复合物中PANI含量增加, 热解后得到的C-N含量增加, 因而电催化氧化还原反应速率加快^[25,26]. 我们发现, 复合材料中PANI含量的进一步增加并不能带来催化活性的持续增加, 说明PANI与TiO₂二者界面间的相互作用受到限制,

不能很好发挥 TiO_2 作为助催化剂的作用. 通过与纯PANI热解后的样品进行对比, 我们推测复合材料中氧还原活性提高的瓶颈主要源于纯PANI热解后氮掺杂碳材料本身的催化活性, 这些样品的催化活性均与商业Pt/C存在一定差距. Pt/C的LSV曲线有一个很宽的电流稳定平台, 且有很强的极限电流密度, 其催化机理为 $4e^-$ 主导的扩散电流控制的ORR机理. 纯PANI热解后制得的氮掺杂碳材料在LSV曲线中几乎观察不到电流稳定平台, 暗示这可能是 $2e^-$ 转移过程, 也就是说, O_2 只能转化为 OOH^- [22], 其性能与文献报道的氧化石墨烯(GO)-PANI热解后得到的氮掺杂石墨烯材料相距甚远 [26]. TiO_2 /PANI热解形成的 TiO_2 /C复合催化剂在LSV曲线中有一段明显的电流稳定平台, 此后电流密度持续增加, 故推测是 $2e^-$ 和 $4e^-$ 共同作用的结果.

虽然金属氧化物对碳材料催化活性的增强作用并非令人满意, 但是近几年有关金属氧化物用于燃料电池的研究逐渐增多. 原因在于, 金属氧化物不仅可以降低燃料电池的成本, 更为重要的是, 可以显著提高催化剂的电化学稳定性, 延长燃料电池的使用寿命 [27]. 因此, 我们测试了 $\text{PANI/TiO}_2 = 40/100$ 时的复合物以及纯PANI碳化后样品的电流-时间曲线, 如图6所示. 从图中可以看出, 在相同条件下经过5000 s反应之后, 复合材料的电流损失仅为13%, 而对于PANI碳化所得的氮掺杂碳材料, 该损失高达32%. 也就是说, 直接热解PANI制备的氮掺杂碳材料虽然在活性上略优于 $\text{PANI/TiO}_2 = 40/100$ 的碳化产物, 但前者在反应过程中的稳定性却比复合物低很多. 另外, 对复合材料进行了循环伏安(CV)测试以研究所得 TiO_2 /C的循环稳定性, 如图7所示. 从图上可直观地看出, 在100次循环后, TiO_2 /C复合材料的电化学响应并没有明显变化, 这与上述电流-时间曲线的结果一致. 因此, 将 TiO_2 引入导电聚合物再一起碳化, 一方面可以降低催化剂中的碳含量, 另一方面有利于碳材料作为电催化剂或载体的循环稳定性.

此外, 对未碳化的 $\text{PANI/TiO}_2 = 40/100$ 复合物进行了热重分析, 确定其中PANI和 TiO_2 的真实含量. 图8为 $\text{PANI/TiO}_2 = 40/100$ 时复合物在空气中的热稳定性. 复合材料加热到 950°C 后, 总失重是34.8%, 其中在 $0\text{--}100^\circ\text{C}$ 范围内失重4.0%, 这一失重是由吸附水蒸发引起的, 其余30.8%的失重是由于复合材料中的PANI在空气中燃烧.

3.2. 热解对 TiO_2 /C材料氧还原性能的影响

图9为 $\text{PANI/TiO}_2 = 40/100$ 时的复合物在氮气中

800°C 热解1 h后得到的 TiO_2 /C的TEM照片. 对比图1(a)和图3, 可以发现纤维状结构消失, TiO_2 被没有固定形貌的碳材料包覆. 热解的作用是使PANI碳化成为碳材料.

图10为 $\text{PANI/TiO}_2 = 40/100$ 时复合物热处理前后的FT-IR谱. 热处理后PANI在 3416 cm^{-1} 处N-H单键的伸缩振动, 在 1575 和 1487 cm^{-1} 处醌环和苯环中C=N和C=C双键的伸缩振动, 在 1301 和 1243 cm^{-1} 处C-N单键的伸缩振动, 在 1145 cm^{-1} 处掺杂PANI中的醌环吸收峰和 793 cm^{-1} 以下的吸收峰均消失. 热处理前后的样品在 $400\text{--}1000\text{ cm}^{-1}$ 范围内都有红外吸收, 证明碳化前后O-Ti-O网状结构基本没有变化, 并且在 1585 cm^{-1} 处出现一个小吸收峰, 这一吸收峰被认为是由 TiO_2 表面吸附水分产生的. 可见, 高温处理的过程中, 破坏了PANI的原有结构, 而 TiO_2 中O-Ti-O网状结构没有发生较大变化.

图11为 TiO_2 /PANI = 100/40时复合物碳化前后的拉曼光谱. 碳化前样品在 1599 , 1464 , 1220 和 1165 cm^{-1} 等处有强吸收峰, 这些吸收峰显然来自PANI中醌二亚胺基团的振动. 1337 cm^{-1} 处的峰为苯二胺中N-C单键伸缩振动. 由此确定煅烧前样品中PANI的存在. 碳化后样品中PANI的吸收峰消失, 取而代之的是以 1336 和 1588 cm^{-1} 为中心的宽吸收峰. 这两个吸收峰分别为石墨相碳材料的D带和G带. 此外, PANI在 414 和 522 cm^{-1} 处有环变形的吸收峰; 碳化后, 这一变形振动吸收峰也消失.

由此, 我们可以确定碳化后材料中的PANI结构被破坏, 形成了石墨相结构的碳. 碳材料的导电性优于PANI纤维. 因此, 碳化改善了材料的导电性, 避免了氧还原反应产物在局部积累, 提高了材料的氧还原活性.

4. 结论

合成了 TiO_2 /C阴极催化剂, 研究了复合物中PANI和 TiO_2 比例和热处理对材料性能的影响. 结果表明, 在 TiO_2 /PANI复合物中, PANI中的氨基(或亚氨基)与 TiO_2 表面羟基间有键合作用. 由于这种相互作用的存在, 抑制了 TiO_2 由锐钛矿向金红石的转变, 并且使 TiO_2 颗粒附着在PANI纳米纤维表面, 减少了 TiO_2 的团聚. 当复合物中 $\text{PANI/TiO}_2 = 35/100$ 时, 热解后得到的催化剂活性最好. 高温热处理可以使PANI发生碳化生成的碳材料包覆在 TiO_2 表面, 材料由 TiO_2 /PANI变为 TiO_2 /C, 氧还原活性明显提高. 同时, 在高温热处理过程中, PANI骨架中的氮元素在碳化过程中掺杂入石墨化碳的晶格, 有利于氧还原活性的提高.