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Investigation of a Fe–N–C catalyst for sulfur dioxide electrooxidation[†]

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A Fe–N–C catalyst, synthesized with porous carbon BP2000, the nitrogen source imidazole and iron source FeCl₃, is developed for SO₂ electrooxidation through a series of thermal and pyrolytic disposing processes. The electrochemical measurements of linear sweep voltammograms (LSV) and cyclic voltammograms (CV) are applied to investigate the SO₂ oxidation performance of the catalyst. The results show that the half-wave oxidation potential of Fe–N–C is 283.8 mV lower than that of BP2000 meanwhile the onset oxidation potential reduces 58 mV as well, implying there is a highly improved SO₂ oxidation performance of the catalyst. The structural and physical characteristics of the Fe–N–C catalyst are examined by the methods of TEM, XPS, XRD and Raman spectroscopy. The characterization proves the formation of graphitic carbon, iron carbides, single-layer graphene and defects as well as the existence of FeN/Fe₂N, pyridinic N and Fe–N components on the prepared Fe–N–C catalyst, which are supposed to have significant effects on the SO₂ electrooxidation performance.

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1. Introduction

Investigations on SO₂ electrooxidation have been extensively carried out in the fields of flue gas desulfurization, water splitting for hydrogen production, electrochemical sensing and corrosion.¹⁻³ SO₂ is usually disposed in the electrolytic reactors with hydrogen production. For instance, Struck *et al.*⁴ described a three-compartment electrolytic cell to oxidize SO₂ at the anode directly. Ümran Tezcan Ün *et al.*⁵ conducted an experiment, in which SO₂ was absorbed and oxidized on a Pt expanded mesh anode with the cycled sulfuric acid electrolyte. The gas diffusion cathodes were applied to oxidize SO₂ with the electrogenerative method.⁶⁻⁸ Zhai *et al.*⁹ proposed a gaseous SO₂ electrooxidation process with compact electrode structures, which greatly reduced the mass transfer resistance in the reaction and showed positive prospects in dealing with the low concentration SO₂.

Generally, catalysts play an important role for SO₂ electrooxidation. However, the applied SO₂ oxidation catalysts are basically precious metals such as the platinum and its alloys.^{10,11} The cyclic voltammetries of SO₂ electrooxidation on noble metals normally exhibit two oxidation peaks. One is attributed to the direct electron transfer between SO₂ and catalysts in relatively low oxidation potential regions, and the other is attributed to the oxidation of active oxides and surface oxygen species.¹² Meanwhile, the anode catalysts (Pt, Ru *et al.*) can generate metal oxides at high potentials and further create the passivation layers on their surfaces, preventing them from reacting with the adsorbed species. The partially covered active sites inhibit the continuous oxidation of SO₂.¹³⁻¹⁶ In addition, precious metal catalysts are not acceptable in the application of SO₂ electrooxidation due to their high price and limited resource.

Non-precious metal catalysts display excellent catalytic characteristics in various electrochemical applications,¹⁷⁻¹⁹ but they are seldom reported in the field of SO₂ electrooxidation. Currently, the most popular non-precious catalysts are the metal–nitrogen–carbon series, whose catalysis activities come from the intrinsic active sites and excellent transport properties.²⁰ In this work, we prepared a Fe–N–C catalyst, studied its activity for SO₂ electrooxidation and investigated the active constituents of the catalyst. We hope the results can be referenced to the application of SO₂ electrooxidation and the further flue gas desulfurization.

2. Experimental

The synthesis procedures of the Fe–N–C catalyst were recorded as follows. Firstly, 160 mg imidazole (Tianjin Guangfu fine chemical research institute) was dissolved in 50 mL ethanol (Shenyang Chemical Reagent Factory) with stirring, then 20 mL 0.1 M FeCl₃ (Tianjin Bodi Chemical Co., Ltd.) was added into the mixture drop-wisely. Subsequently, 160 mg BP2000 (Cabot)



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carbon particles were added and well-dispersed in the mixture with continuously stirring. After that, the flask was transferred into a magnetic stirring oil bath boiler and kept stirring under 60 °C for 6 h. Then the temperature of the boiler was ascended to 80 °C, so that the solvent could be evaporated easily and form the target mixture paste. The paste was kept in a vacuum oven under 60 °C until it was sufficiently dried. And the powders were gathered then further pyrolyzed in a tubular furnace at 700 °C in N₂ for 2 h. After cooling down and sufficiently grinding, the Fe–N–C sample was well prepared and ready for SO₂ electro-oxidation tests.

TEM images were recorded on a transmission electron microscope with the JEOL JEM-2000EX equipment. XRD patterns were acquired on a D/max-2500PC diffractometer with Cu K α (λ = 1.54 nm) radiation. XPS measurements were carried out on an imaging photoelectron spectrometer of Thermo Scientific ESCALab 250Xi (AlK α , 1486.6 eV). Raman spectra were collected on a Raman spectrometer of Jobin Yvon LabRAM HR800 with a 532 nm laser.

Electrochemical measurements were carried out on the CHI730D electrochemical workstation (CHI Instruments, Chenhua Co., China) in a typical three-electrode system. A catalyst modified glassy carbon electrode (GCE, 4 mm in diameter) acted as the working electrode. A saturated calomel electrode (SCE) served as the reference electrode, and a platinum foil was used as the counter electrode. Moreover, the background electrolyte in test was 0.5 M H₂SO₄, and the sulfur dioxide came from 1 g L⁻¹ Na₂SO₃, which was prepared by adding appropriate amount solid Na₂SO₃ into the background electrolyte deoxygenated through N₂ sufficiently bubbling.

The preparation procedures of the thin film electrode on GCE were depicted as follows. First, the catalyst ink was prepared by adding 5 mg catalyst powders into 1 mL isopropyl alcohol (Tianjin Kemiou Chemical reagent Co., Ltd.), then complementing with 50 μ L Nafion (Du Pont Corp., 5 wt%), and further dispersing with ultrasound to form a homogeneous suspension. Second, 10 μ L suspension was evenly coated on the surface of the glassy carbon electrode by a syringe and dried in air to form a catalytic film. The prepared thin film electrode was used as the catalyst modified working electrode in the test. A precious metal (Pt/C (20%, JM)) coated working electrode and a carbon (BP2000 (Cabot)) coated working electrode were also prepared in order to compare the catalytic property with the Fe-N–C catalyst.

Electrochemical measurements for SO_2 electrooxidation were performed and analysed with the linear sweep voltammograms (LSV, 1 g L⁻¹ Na₂SO₃, 1600 rpm, 5 mV s⁻¹), cyclic voltammograms (CV, 50 mV s⁻¹) and LSV-rotating tests (LSV- ω , 1 g L⁻¹ Na₂SO₃, from 400 rpm to 2000 rpm, 20 mV s⁻¹).

3. Results and discussion

The morphology of the prepared Fe–N–C catalyst was characterized by a transmission electron microscope. As shown in Fig. 1(a), tiny grains dispersedly distribute on the carbon matrix, implying the formation of catalytic substances on the Fe–N–C catalyst. The appearance of nanotubes among carbon particles indicates the catalytic role of iron species during the carbonization processes. XRD was applied to analyse the crystal structures of the Fe-N-C catalyst (Fig. 1(b)). The typical peak at around 25° corresponds to the (002) facet of graphite carbon. Differing from BP2000, the Fe-N-C peaks locate at 37.7, 43.8, 44.5, 46.1, 47.9, 49.3, 54.4° and 57.9°, which belong to the constituent of Fe₃C (JCPDS no. 89-2867), verifying the appearance of iron carbides in the catalyst. The typical carbon peaks among iron carbides at 25, 43.8° and 78.4° indicate the encapsulated structures of iron species under graphitic carbon. The 2θ values at 42.8, 61.3° are attributed to the (200) and (220) facets of FeN, and the values at 41.1, 43.8° are referring to the (200) and (121) facets of Fe_2N , which are believed to form the Fe–N_x active sites. The peaks at 44.5° and 65.1° indicate the coexisted metallic iron, according to the α -Fe (JCPDS no. 87-0722) diffraction data. In general, XRD patterns clearly demonstrate the existence of metallic iron, FeN/Fe2N, Fe3C and graphitic carbon structures in Fe-N-C catalyst, which are supposed to be the catalytic active substances for SO₂ electrooxidation. Raman spectroscopy was applied to analyse the carbonization and graphitization properties of Fe-N-C catalyst (Fig. 1(c)). The graphitization value of $I_{\rm D}/I_{\rm G}$ for BP2000 is 2.662. Compared with BP2000, the graphitization value of the Fe-N-C catalyst is 2.926, seemingly exhibiting a worse graphitization property. This may be because the formation of doping substances and tiny carbon structures increase the disorder characteristics of the catalyst, showing a relatively higher I_D/I_G on the Fe-N-C catalyst. However, there is a more notable G' band appearing after the preparation of Fe-N-C in the high displacement of Raman spectra at around 2700 cm⁻¹, owing to the formation of tiny single-layer graphene structures in the carbon matrix. The defects, irregular carbon and graphene structures can serve as the active sites for catalysis. X-ray photoelectron spectroscopy (XPS) was also employed to characterize the chemical compositions of the Fe-N-C catalyst in Fig. 1(d). As expected, the



Fig. 1 Physical characterizations of Fe–N–C and BP2000. (a) TEM image of Fe–N–C. (b) XRD pattern of Fe–N–C and BP2000. (c) Raman spectra of Fe–N–C and BP2000. (d) XPS spectra of Fe–N–C and BP2000.

survey spectrum reveals the presence of N (3.19%, atomic), O (6.34%, atomic), Fe (1.03%, atomic) elements in Fe–N–C catalyst, suggesting the successfully doped elements and well fabricated active structures for SO_2 electrooxidation.

The deconvolutions of XPS fine spectra were employed to characterize the element bonding configurations and reveal the structures and functional groups in the F-N-C catalyst (Fig. 2). The C 1s fine spectra, as shown in Fig. 2(a), manifest the typical structure of sp² hybridization carbon (284.4 eV, Peak 1), implying the good conductivity of the catalyst. The sp² carbon plays an important role in the Fe-N-C catalyst and its content increases obviously comparing with raw material BP2000 (Table S1[†]), owing to the formation of graphite carbon during the preparation. The 284.7 eV peak (Peak 2) in Fe-N-C also belongs to the sp² carbon structures. Carbon bounded with O or N element leads to the elevated binding energy. In addition, the O percentage of the Fe-N-C catalyst increases by 2.3 times than that of BP2000. The proportion of oxygen functional groups are obviously changed during the preparation (Fig. 2(b)). The O functional groups on BP2000 are mainly in the forms of C=O (531.7 eV, Table S1[†]), O-C=O (532.5 eV, Table S1[†]), C-O (H) (533.4 eV, Table S1[†]) structures. While for the Fe-N-C catalyst, the O element is largely binging at 530.4 eV (O-physical absorbed or carbonates,²¹ 31.6%, Peak 1) and 531.6 eV (49.1%, C=O, Peak 2). There is no C-O (H) structure for the Fe-N-C after the preparation. The oxygen functional groups binding at 530.4 eV play an important role for SO₂ oxidation due to the weak interaction of the oxygen functional groups on catalysts, and the positive influence of oxygen for SO₂ electrooxidation.^{14,15,22,23} What's more, the C=O and O-C=O may also be the active constituents for SO₂ electrooxidation for their better interaction with water. Fig. 2(c) is the complex N 1s deconvolution spectra. The pyridinic N, Fe-N, pyrrolic N, graphitic N, and oxidized N are centred at around 398.2 eV, 399.0 eV, 400.3 eV, 401.1 eV, and the displacement between 402.7 eV and 405 eV, respectively.^{21,24,25} For the Fe-N-C catalyst (Table S1[†]), most of the N element is in the form of the pyridinic N (27.7%) and Fe-N



Fig. 2 Deconvolution of (a) C 1s XPS spectra, (b) O 1s XPS spectra, (c) N 1s XPS spectra and (d) Fe 2p XPS spectra of the Fe–N–C catalyst.

(36.7%) structures, demonstrating a better combination of Fe and N bonds and the well-developed catalytic structures in the catalyst. They are of great importance for SO₂ electrooxidation.²⁶ The other N compositions such as the pyrrolic N (17.6%), graphitic N (14.7%), and oxidized N (3.3%) are relatively less in the catalyst. The Fe 2p spectra display that there is a weak doublets for Fe $2p_{3/2}$ signalling at 711.3 eV and 724.6 eV, demonstrating the presence of iron carbides or metallic iron (Fig. 1(d)). The Fe $2p_{3/2}$ signals at 710.7 eV and 712.5 eV indicate the existence of metallic iron and the influence of N structures. The peaks at around 711.3 eV and 718.6 eV further confirm that Fe coordinating to N element forms the Fe–N bonding structure, which exhibits good electrochemical activity. These coordinated nitrogen structures are supposed to act as the active components for SO₂ electrooxidation.

The LSV measurements on the Fe-N-C catalyst for SO₂ electrooxidation were performed in the Na₂SO₃ aqueous solution and the results were shown in Fig. 3(a). The Fe–N–C catalyst displays a good SO₂ electrooxidation performance. Its onset oxidation potential for SO2 is 0.525 V and the half-wave oxidation voltage is 0.641 V. Before 0.8 V, the oxidation current on the Fe-N-C catalyst rises rapidly with the elevation of working potentials. When the potential is above 0.8 V, the electrooxidation of SO₂ on the Fe-N-C catalyst enters into a platform region with mitigatory increase of the oxidation currents. The current densities for SO2 oxidation at this region are 10.19 mA cm^{-2} @0.8 V, 10.74 mA cm^{-2} @1.2 V and 11.92 mA cm^{-2} @1.4 V respectively, indicating the high activity of the Fe-N-C catalyst for SO₂ electrooxidation. Fig. 3(b) is shown the comparison of the SO₂ oxidation performances of Fe-N-C with 20% Pt/C and BP2000. As we can see, they display very different Faraday characteristics for SO₂ electrooxidation. The onset oxidation potentials of Pt/C, Fe-N-C and BP2000 are 0.456 V, 0.525 V and 0.583 V respectively. The onset potential of the Fe-N-C catalyst is 58 mV lower than that of BP2000, implying an obvious improvement of the SO₂ oxidation performance, but it is still 69 mV higher than that of Pt/C. With regard to the half-wave oxidation voltage, the Fe-N-C is 283.8 mV lower than that of BP2000, and it is only 70.6 mV higher than that of Pt/C. So the SO₂ oxidation performance of the Fe-N-C is highly improved than that of BP2000, but it is still slightly lower than the Pt/C.



Fig. 3 LSV tests of SO₂ electrooxidation. (a) LSV test of Fe–N–C; 1 g L^{-1} Na₂SO₃; rotating rate 1600 rpm; scanning rate 5 mV s⁻¹. (b) SO₂ electrooxidation comparison of BP2000, Pt/C and Fe–N–C.

Fig. 4 Kinetic analysis of SO₂ electrooxidation. (a) LSV- ω tests of the Fe–N–C; (b) Koutecky–Levich analysis of the Fe–N–C and Pt/C. LSV- ω : 20 mV s⁻¹, 1 g L⁻¹ Na₂SO₃, rotation rates: 400, 600, 800, 1200, 1600, 2000 rpm.

LSV-rotating tests were performed to clarify the kinetic property of the Fe-N-C catalyst for SO₂ electrooxidation (Fig. 4(a)), and its kinetic property was compared with Pt/C in Fig. 4(b). The SO₂ oxidation currents for the Fe-N-C catalyst show no obvious changes below 0.637 V with the increase of rotation rates in LSV-w tests, indicating an electrochemical controlling process in this region. While above 0.637 V, the oxidation current is obviously elevated with the increase of rotation rates, implying the significant influence of mass transfer process. Comparing with Pt/C (Fig. 4(b)), Fe-N-C catalyst shows the similar linear Koutecky-Levich (K-L) plots at 0.8 V, 1.2 V and 1.4 V, when the rotation rates are above 600 rpm. But there is a slight deviation under 400 rpm possibly due to the strong interaction between oxidation products and the Fe-N-C catalyst under low rotation rates. Nevertheless, the kinetic currents for the Fe-N-C catalyst are gradually close to Pt/ C with the elevation of oxidation potentials. Accordingly, the Fe–N–C catalyst displays a good SO₂ electrooxidation capability.

To sum up, the TEM images present many dispersedly distributed tiny grains on the carbon matrix, implying well fabrication of catalytic substances on the Fe–N–C. The XRD patterns demonstrate the existence of FeN_x, Fe₃C and graphitic carbon in Fe–N–C catalyst. The Raman spectra prove the production of irregular carbon, graphene and defects in the catalyst. The XPS analyses provide the information about different heterogeneous doping elements, as well as the developed active structures of the pyridinic N and Fe–N in the catalyst. Comparing the SO₂ electrooxidation performances with BP2000, the pyridinic N²⁶ and iron–nitrogen constituents in the prepared Fe–N–C catalyst are regarded as the main effective active sites for the electrooxidation of SO₂. With these active components, Fe–N–C catalyst exhibits a much better SO₂ oxidation performance than the carbon catalyst.

4. Conclusions

In summary, a non-precious Fe–N–C catalyst for SO₂ electrooxidation is developed by disposing and pyrolyzing the raw materials of porous carbon BP2000, nitrogen source imidazole and iron source FeCl₃. The precursors are transformed and then carbonized at 700 °C under N₂ for 2 h to obtain the desired SO₂ electrooxidation catalyst. The physical characterizations prove the formation of graphitic carbon, graphene, iron carbides, FeN and Fe₂N in the Fe–N–C catalyst. The developed pyridinic N, Fe– N and carbides play important roles on SO₂ electrooxidation. What's more, the existence of high content O-physical absorbed oxygen functional groups or carbonates, as well as the C=O, O–C=O structures of the Fe–N–C catalyst take effective interactions with SO₂. Herein, this study provides a preparation method of a non-precious Fe–N–C catalyst and investigates its physical characteristics and catalysis performances for SO₂ electrooxidation. The Fe–N–C catalyst displays good SO₂ oxidation performances, notably distinguishing it from the carbon material. We hope this study can make positive contribution to the application of non-noble catalyst for SO₂ electrooxidation, though its performance is slightly lower than Pt/C.

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