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A Highly Active Nitrogen-Containing Non-Precious Metal Catalyst CoHMTA/C for Oxygen Reduction Reaction

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A nitrogen-containing non-precious metal catalyst (NPMC) CoHMTA/C for oxygen reduction reaction (ORR) is prepared by heat-treating a precursor containing acetylene black, hexamethylenetetramine and cobalt chloride. The effects of heat-treating temperature and duration, the content of hexamethylenetetramine and cobalt chloride are all investigated. The results show that the ORR activity of the CoHMTA/C catalyst is not obviously affected by the content of hexamethylenetetramine. But the content of cobalt chloride, heat-treating temperature and duration will significantly influence the performance of the catalyst. More or less content of cobalt chloride both go against the ORR activity. A better catalyst with a 0.58 V (vs. SCE) of ORR onset potential can be obtained by heat-treating a precursor containing 0.1 g of acetylene black, 0.1 g of hexamethylenetetramine and 0.05 g of cobalt chloride at 600 ℃ for 2 hours. The 0.58 V (vs. SCE) of ORR onset potential is closed to the value of a platinum-disc electrode. Cobalt ions are reduced to metallic β-cobalt by carbon black at a higher temperature in the heat-treating process. Then the metallic β-cobalt facilitates nitrogen atoms replace carbon atoms in the graphene sheet of carbon black to form the ORR active sites with the structures of pyrrolic C-N and pyridinic C-N.

Keywords: Oxygen reduction reaction; Electrocatalyst; Nitrogen-containing; Preparation conditions

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) can directly convert chemical energy into electrical energy with a high efficiency and low emission of pollutants. The fuel cells are compact in structure and can fire up at a low temperature, which is important to the design of portable electrical appliances and vehicles. Today, platinum-containing catalysts are widely used to accelerate the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in fuel cells. However, the limited reserves and high cost of platinum block the large scale application of PEMFC and DMFC. Additionally, the small methanol molecules are easy to diffuse across the membrane to the cathode and directly oxidized at the cathode platinum catalysts in a DMFC. This will produce a “mixed potential” and lead to a loss of cell voltage. The oxidized product of methanol will also poison the Pt catalyst and make it lose catalytic activity. The development of a cheap ORR catalyst with good activity and stability is a key to the large scale application of fuel cells [1-4].

In the past decades, many non-precious or non-platinum ORR catalysts were developed [5]. Among these catalysts, heat-treated N_4-macrocycle compounds, such as phthalocyanine and porphyrin with transition metal ions are absorbing special attention. Such catalyst can be labeled as TM-N/C (TM= Co, Fe, Ni, Cr, Mn, etc.) [6-13]. The basic step of the traditional preparation method of TM-N/C catalyst includes: (1) transition metal ions are chelated with nitrogen-containing macrocycle compound to form the TM-N_4 or (TM-N_x) structures; (2) carbon black is added into the solution to adsorb the complex onto its surface; (3) the mixture is dried and heat-treated in an inert atmosphere[14-17]. Recently, the phthalocyanine and porphyrin were also substituted by other nitrogen-containing compounds, such as aniline[18-20], tripyridyl triazine[21], pyrrole[22], ethylene diamine[4,23], amino acids[24], poly-o-phenylenediamine[25], triethylenetetramine[26], hexacyanoferrate[27]. Although the choice of nitrogen source was widen, the preparation is still based on the concept of “generating complex”. That is the coordination bonds must be formed before the necessary heat-treating process.

However, whether the TM-N_4 or (TM-N_x) structure is essential is still questionable, because the TM-N_4 or (TM-N_x) structure must be destroyed at a high temperature. It has been demonstrated that the heat-treatment is key to increase the activity and stability of the catalyst. Based on the method proposed by Zelenay [28,29], the catalytic activity of Co-PPy/C composite was obviously improved by a follow-up pyrolysis. An ORR catalyst can also be synthesized by depositing a certain proportion of TM, C and N atoms on a glass carbon disc and heat-treating the glass carbon disc at a higher temperature[30,31].

Based on the above references, we believe that the TM-N/C catalyst can be synthesized by heat-treating a mechanical mixture of transition metal, nitrogen source and carbon black, regardless of the combination way of the three materials. So we have proposed a facile “solid-state reaction method” to prepare the TM-N/C catalyst in our precious work[32]. The basic step is that a certain proportion of solid nitrogen-rich compound, transition metal and carbon black are grinded in an agate mortars, then the mixture is heat-treated at a high temperature in an inert atmosphere. The advantage of the method is that the traditional impregnation procedure is substituted by a simple mechanical mixing and the expensive nitrogen-containing macrocycle compound is replaced by cheap materials. In this work, a new non-precious metal catalyst CoHMTA/C for oxygen reduction reaction is synthesized by using hexamethylenetetramine as nitrogen source and cobalt chloride as metal source. The preparation process is also optimized to reveal the formation of ORR active sites of the catalyst. The experimental data show the resulted catalyst is excellent in the catalytic activity to ORR.

2. EXPERIMENTAL

Acetylene black (AB) was used as supporter and one of the reactants. The AB was treated in 1.5 mol L^{-1} HNO_3 for 12 hours at room temperature, then filtered, washed and dried at 80 ℃ for 12 hours. For the preparation of the catalyst, the treated AB, hexamethylenetetramine (HMTA, AR) and cobalt chloride ($CoCl_2·6H_2O$, AR) were ground in an agate mortars for 30 minutes to get a precursor labeled as AB+HMTA+$CoCl_2·6H_2O$. The precursor was heat-treated in a N_2 atmosphere at a high temperature for a considerable duration. The effects of heat-treating temperature and duration both were investigated. The influences of contents of HMTA and $CoCl_2·6H_2O$ on the ORR activity of the resulted CoHMTA/C were also checked in this work.

The phase of CoHMTA/C products was characterized by XRD measured using a Shimadzu XRD-6000 diffractometer with Cu Kα1 radiation at a scanning rate of 5° min^{-1}. The states of nitrogen, carbon and cobalt atom in the CoHMTA/C catalyst were characterized by X-ray photoelectron spectroscopy (XPS). The XPS spectrum was acquired using Kratos XSAM800 photoelectron spectrometer equipped with monochromatic Mg source of 1253.6 eV operating at 180 W, and the operating pressure was 2×10^{-7} Pa. The analysis of XPS data were performed using the XPSPEAK (V4.0) software. A Shirley background and a line shape of 20% Gaussian/80% Lorentzian were used in the curve fitting.

The ORR activity of the catalyst was evaluated by the onset potential of ORR from linear sweep voltammetry test. The electrochemical measurements were carried out on a CHI660A workstation. Traditional three-electrode cell was used with a saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the counter electrode. A glass carbon electrode coated with catalyst layer as the work electrode. The work electrode was fabricated as follows: 10 mg of the catalyst, 1 ml of isopropyl alcohol, 1 ml of de-ioned water and 5 drops of diluted Nafion solution (0.5 wt%, with isopropyl alcohol as solvent) were ultrasonically mixed for 20 minutes to form a uniform ink. Then 10 μl of the ink was added on the surface of a glass carbon disk (Φ 5 mm), and was dried over 2 hours before electrochemical tests. The electrolyte was 0.5 mol L^{-1} H_2SO_4 solution saturated by oxygen or nitrogen for 15 minutes before tests. The LSV test was carried out at a scan rate of 5 mV s^{-1} at 30 ℃.

3. RESULTS AND DISCUSSION

3.1 catalytic activity of CoHMTA/C to ORR

A precursor consisting 0.1 g of AB, 0.1 g of HMTA and 0.05 g of $CoCl_2·6H_2O$ was heat-treated at 600 ℃ for 2 hours to prepare a CoHMTA/C600 catalyst. For comparison, a HMTA/C600 catalyst without cobalt was prepared from 0.1 g of AB and 0.1 g of HMTA on the same heat-treating condition. Figure 1 shows the voltammograms of AB, CoHMTA/C600, HMTA/C600 and platinum disc electrode in 0.5 mol L^{-1} H_2SO_4 solution. It can be seen that the reduction process is not obvious in the voltammogram curve of CoHMTA/C600 tested in H_2SO_4 solution saturated by N_2 (Figure 1(a)). However, a significant reduction process can be observed in the curve of CoHMTA/C600 tested in

H_2SO_4 solution saturated by O_2 (Figure 1(b)). The difference shows the reduction process corresponds to the oxygen reduction reaction (ORR). The ORR onset potential of 0.58 V (vs. SCE) of the CoHMTA/C600 catalyst is closed to the value of Pt-disc electrode at the same condition (Figure 1(e)). The results show that the ORR activity of CoHMTA/C600 catalyst is excellent and the CoHMTA/C600 catalyst may be a possible candidate for the expensive Pt-based catalyst in the cathode of PEMFC.

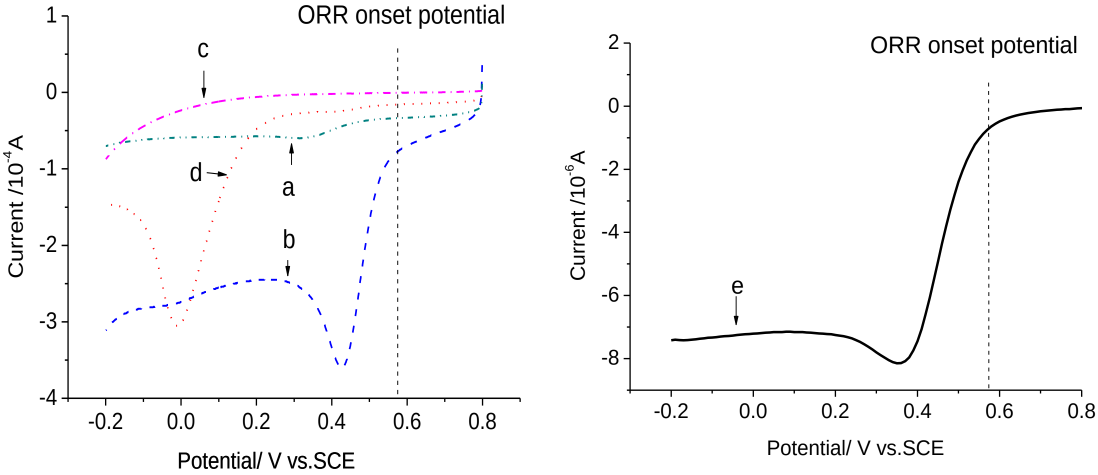

Figure 1. Linear sweep voltammograms of CoHMTA/C600 catalyst in 0.5 M H_2SO_4 solution (a) saturated by N_2, (b) saturated by O_2 and (c) AB, (d) HMTA/C600, (e) Pt-disc electrode (ϕ2mm) in 0.5 M H_2SO_4 solution saturated by O_2.

It can also be seen that the untreated acetylene black (AB) has a little catalytic activity toward ORR with an onset potential of about 0.1 V (vs. SCE, Figure 1(c)). The ORR onset potential HMTA/C600 is about 0.2 V (vs. SCE, Figure 1(d)) which is greater than the value of AB, but is less than the 0.58 V of CoHMTA/C600 catalyst. The result suggests that HMTA or its decomposing products at high temperature would react with carbon black to form the ORR active sites and the cobalt can facilitate this reaction to get the better activity of CoHMTA/C600 catalyst.

3.2 Influences of heat-treating conditions on the activity of CoHMTA/C

The precursor of AB+HMTA+$CoCl_2 \cdot 6H_2O$ was heat-treated at 400 ℃, 500 ℃, 600 ℃, 700 ℃ and 800 ℃ for 2 hours to investigate the effect of heat-treating temperature on the performance of the catalyst. The resulted catalysts were labeled as CoHMTA/C400, CoHMTA/C500, CoHMTA/C600, CoHMTA/C700 and CoHMTA/C800, respectively. Figure 2 and Figure 3 show the catalytic activities and XRD patterns of the series of catalysts. It can be seen that the temperature obviously influences the activity of the CoHMTA/C catalyst. The CoHMTA/C400 shows an ORR activity with a 0.31 V of onset potential, and the ORR onset potentials shift to 0.48 V and 0.58 V when heat-treated at higher 500℃ and 600℃. The activity of the CoHMTA/C catalyst is improved by increasing the heat-treating temperature in the range of 400 ℃ to 600 ℃. This tendency is consistent to the state of metallic β-cobalt as shown in Figure 3, in which the crystal structure of β-cobalt tends to perfect in the same range of temperature. However, the activities of CoHMTA/C obtained at 700 ℃ and 800 ℃ become worse, although the crystal structures of β-cobalt are more perfect than in the catalysts obtained at lower temperatures. The relationship between the ORR activity and crystal structure of β-cobalt reveals that the cobalt ions are reduced to metallic β-cobalt at a high temperature, and then the fresh β-cobalt catalyzes nitrogen atoms to react with carbon black to form the ORR active sites with different C-N structures. But the formed organic C-N structures will also decompose at a higher heat-treating temperature, which will worsen the ORR catalytic activity of the resulted catalyst. That is the reason why the catalytic activities of CoHMTA/C obtained at 700 ℃ and 800 ℃ gradually become worse with the increasing of the heat-treating temperature [21,33,34].

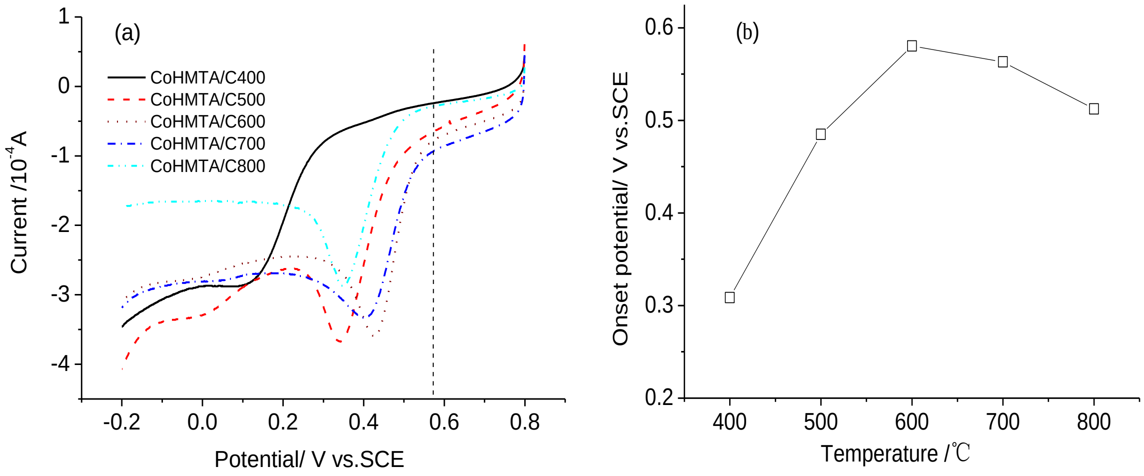

Figure 2. The ORR catalytic activities of CoHMTA/C catalysts heat-treated at different temperatures. (a) Linear sweep voltammograms, (b) Relationships between ORR onset potential and heat-treating temperature

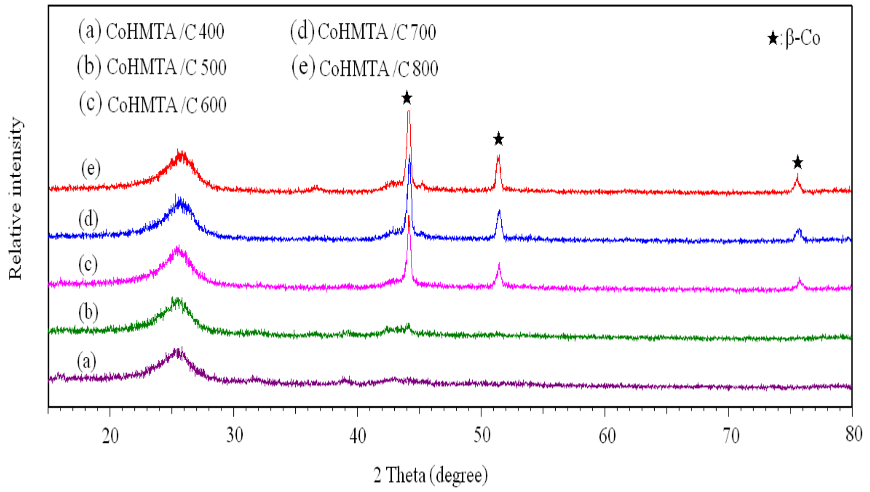

Figure 3. XRD of CoHMTA/C catalysts heat-treated at 400 ℃, 500 ℃, 600 ℃, 700 ℃, 800 ℃.

Figure 4 shows the activities of CoHMTA/C catalysts prepared at 700 ℃ for different durations. It can be seen that the catalyst of heat-treating for 2 hours has better ORR activity. The effect of heat-treating duration is similar to heat-treating temperature. That is the formed active sites will partially decompose in a longer duration, which causes the deterioration of the ORR activity of the catalyst.

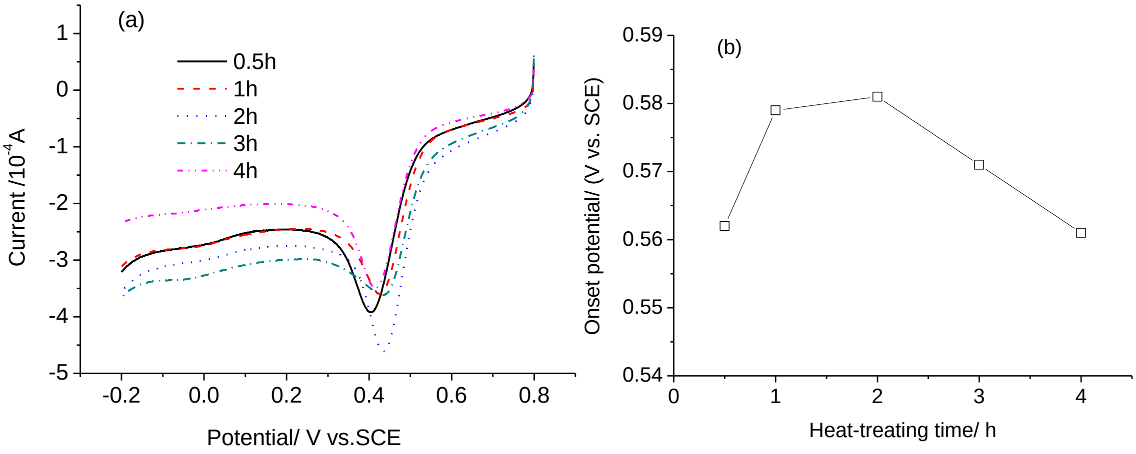

Figure 4. Electrocatalytic activity of CoHMTA/C catalyst heat-treated at 700 ℃ for different durations, (a) Linear sweep voltammograms, (b) Relationships between ORR onset potential and heat-treating temperature.

3.3 Influences of the composition of precursor on the activity of CoHMTA/C

A series catalyst were prepared by heat-treating different precursors containing 0.1 g of AB, 0.05 g of $CoCl_2·6H_2O$ and changing the content of HMTA as 0.06 g, 0.08 g, 0.1 g, 0.12 g and 0.14 g at 600 ℃ for 2 hours. The resulted products were labeled as CoHMTA006/C600, CoHMTA008/C600, CoHMTA010/C600, CoHMTA012/C600 and CoHMTA014/C600, respectively.

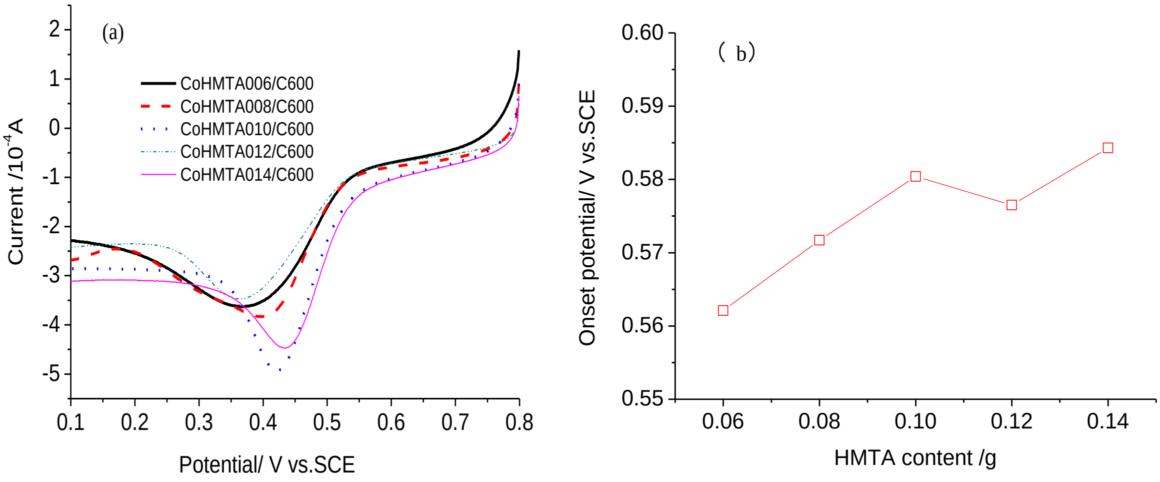

Figure 5. ORR catalytic activity of CoHMTA/C catalysts with different HMTA contents. (a) Linear sweep voltammograms, (b) Relation between ORR onset potential and HMTA content.

Figure 5 shows the ORR activity of the series catalysts. It can be seen that the ORR activity of the series of catalysts change a little with the increasing of HMTA content. The possible reason is that the HMTA is excess in the precursor and the formation process of active site is most controlled by the content of cobalt.

Another series of catalysts were prepared from series of precursors by keeping the contents of AB and HMTA both as 0.1 g and 0.1 g, and changing the content of $CoCl_2·6H_2O$ as 0.03 g, 0.04 g, 0.05 g, 0.06 g and 0.07 g. The precursors were also heat-treated at 600 ℃ for 2 hours. The resulted catalysts were labeled as Co003HMTA/C600, Co004HMTA/C600, Co005HMTA/C600, Co006HMTA/C600 and Co007HMTA/C60, respectively. Figure 6 shows the ORR activity of this series of catalysts. It can be seen that the content of cobalt significantly influences the ORR activity of the catalyst. A good catalyst can not be obtained at a low level of cobalt content. The reason is that the formation process of active sites of the catalyst is also a catalytic reaction, in which the nitrogen atoms enter the lattice of graphene sheet of carbon black and replace some carbon atoms to form new C-N structures, such as pyrrolic and pyridinic C-N structures. The process is believed to be facilitated by the metallic β-cobalt. So a lower content of cobalt can not effectively promote the formation of ORR active sites. On the other hand, a good catalyst can not be obtained at excessive cobalt content. The reason is that the excess Co will transformed into metallic clusters with a smaller specific surface area and worse catalytic activity for the formation of the active sites of CoHMTA/C catalyst[9,35]. The optimal content of $CoCl_2·6H_2O$ is 0.05 g in series of the precursors.

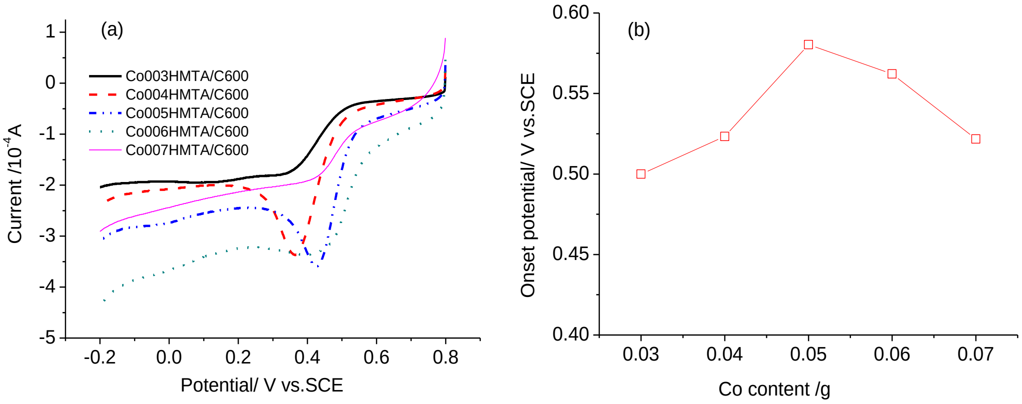

Figure 6. The ORR catalytic activities of CoHMTA/C catalysts with different Co contents, (a) Linear sweep voltammograms, (b) Relation between ORR onset potential and Co conent

3.4 XPS Spectrum of CoHMTA/C600 catalyst

Figure 7 shows the XPS spectra of Co2p, N1s and C1s from CoHMTA/C600 catalyst. The resolution of Co2p spectrum shows spin-orbit splitting into $2p^{1/2}$ and $2p^{3/2}$ components and both components contain the same chemical information. Therefore only the higher intensity $2p^{3/2}$ component was curve-fitted. This component can be fitted by four peaks at 785 eV, 783 eV, 781.8 eV and 780.5 eV. The peaks at 785 eV and 783 eV might be either Co salts or $Co(CO)_4$ species obtained as minor pyrolysis byproducts. The peak at 780.5 eV is due to cobalt oxides. The new formed $Co-N_x$

structure is assigned to the peak at 781.8 eV. But the Co-N_x structure is not the ORR active site. The XPS spectrum of N1s can be fitted by three peaks near 400.7 eV, 399.0 eV and 398.1 eV which are assigned to nitrogen atoms in pyrrolic C-N structure, Co-N structure and yridinic C-N structure, respectively. The C-N structure is also observed in the XPS spectrum of C1s at the 285.8 eV. In the XPS spectrum of C1s, the main peak at 284.6 eV is resulted from aromatic structures of the graphene sheet in carbon black. The information from XPS spectra confirms that there are new C-N structures formed, and the pyrrolic C-N and pyridinic C-N structures are believed as the active sites of TM-N/C catalyst.

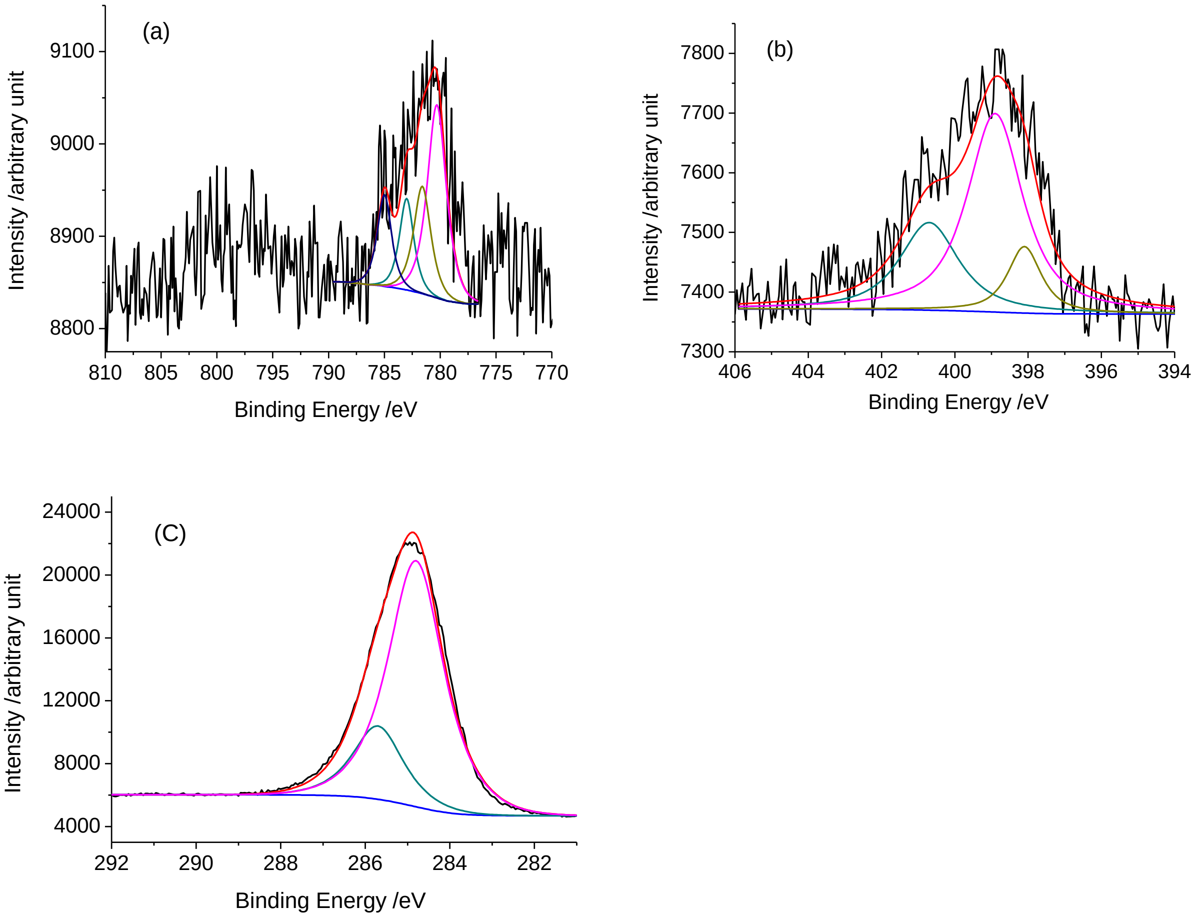

Figure 7. XPS spectra of CoHMTA/C600 catalyst. (a) Co2p, (b) N1s, (c) C1s

4. CONCLUSIONS

A non-precious metal catalyst CoHMTA/C to oxygen reduction reaction can be prepared by heat-treating a mechanical mixture containing acetylene black (AB), hexamethylenetetramine (HMTA) and cobalt chloride ($CoCl_2 \cdot 6H_2O$). A catalyst prepared at 600 ℃ for 2 hours using a precursor from 0.1 g of AB, 0.1 g of HMTA and 0.05 g of $CoCl_2 \cdot 6H_2O$ exhibits best catalytic activity with an ORR onset potential of 0.58 V(vs. SCE) which is closed to the value of a Pt-disc electrode. Two new C-N structures, pyrrolic C-N and pyridinic C-N structures were checked in the catalyst. These new C-N structures are believed to be the ORR active sites of the catalyst. The formation of the active sites can be promoted by metallic β-cobalt from the reduction of Co(II) ions by carbon black at a high temperature. The catalytic activity of CoHMTA/C is mainly affected by the content of cobalt in the precursor, heat-treating temperature and duration.

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References

1. S.C. Thomas, X. Ren, S. Gottesfeld, P. Zelenay, *Electrochim. Acta,* 47 (2008) 3741.
2. S. Alexey, K. Chan, *Appl. Catal. B: Environ.*, 90 (2009) 313.
3. E. Yeager, *Electrochim. Acta*, 29(1984) 1527.
4. V. Nallathambi, J.W. Lee, S.P. Kumaraguru, G. Wu, B.N. Popov, *J. Power Sources*, 183 (2008)34.
5. B. Wang, *J. Power Sources*, 152 (2005) 1
6. Y.Y. Shao, J.H. Sui, G.P. Yin, Y. Gao, *Appl. Catal. B: Environ.*, 79 (2008) 89.
7. J.H. Zagal, F. Bedioui, J.P. Dodelet, *N_4-Macrocyclic Metal Complexes.* New York, Springer, (2006).
8. R. Jasinski, *Nat.*, 201 (1964) 1212.
9. C.W.B. Bezerra, L. Zhang , K. Lee, H. Liu, A.L.B. Marques, E.P. Marques, H. Wang, J. Zhang, *Electrochim. Acta*, 53(2008) 4937.
10. S. Li, Y. Hu, Q. Xu, J. Sun, B. Hou, Y. Zhang, *J. Power Sources*, 213 (2012)265.
11. S.H. Lim, Z. Li, C.K. Poh, L. Lai, J. Lin, *J. Power Sources*, 214 (2012)15.
12. H.C. Kong, X. Yuan, X.Y. Xia, Z.F. Ma, *Int. J. Hydrogen Energy,* 37 (2012) 13082.
13. C.Z. Guo, C.G. Chen, Z.L. Luo, *J. Power Sources*, 245 (2014) 841.
14. G. Faubert, R. Cote, D. Guay, J.P. Dodelet, G. Denes, P. Bertrand, *Electrochim. Acta*, 43 (1998) 341.
15. J. Herranz, M. Lefevre, N. Larouche, B. Stansfield, J.P. Dodelet, *J. Phys. Chem. C,* 111 (2007) 19033.
16. F. Charreteur, F. Jaouen, S. Ruggeri, J.P. Dodelet, Electrochim. Acta, 53 (2008) 2925.
17. H. Niwa, M. Saito, M. Kobayashi, Y. Harada, M. Oshima, S. Moriya, K. Matsubayashi, Y. Nabae, S. Kuroki, T. Ikeda, K. Terakura, J. Ozaki, S. Miyata, *J. Power Sources*, 223 (2013) 30.
18. W.M. Millan, T.T. Thompson, L.G. Arriaga, M.A. Smit, *Int. J. Hydrogen Energy*, 34 (2009) 694.
19. Y. Hu, X. Zhao, Y. Huang, Q. Li, N.J. Bjerrum, C. Liu, W. Xing, *J. Power Sources,* 225(2013) 129.
20. Z. Mo, R. Zheng, H. Peng, H. Liang, S. Liao, *J. Power Sources*, 245 (2014) 801.
21. C.W.B. Bezerra, L. Zhang, K. Lee, H. Liu, J. Zhang, Z. Shi, A.L.B. Marquesc, E.P. Marques, S. Wu, J. Zhang, *Electrochim. Acta*, 53 (2008) 7703.
22. A. Garsuch, R. d'Eon, T. Dahn, O. Klepel, R.R. Garsuch, J.R. Dahn, *J. Electrochem. Soc.*, 155 (2008) B236.
23. N.P. Subramanian, S.P. Kumaraguru, H. Colon-Mercado, H. Kimc , B.N. Popov, *J. Power Sources*, 157 (2006) 56.

24. J. Maruyama, N. Fukui, M. Kawaguchi, I. Abe, *J. Power Sources*, 182 (2008) 489.
25. P. Wang, Z. Ma, Z. Zhao, L. Jia, *J. Electroanal. Chem.*, 611 (2007) 87.
26. H.J. Zhang, X. Yuan, W. Wen, D.Y. Zhang, L. Sun, Q.Z. Jiang, Z. F. Ma, *Electrochem. Commun.*, 11 (2009) 206.
27. K. Sawai, Y.S. Maeda, *J. Electrochem. Soc.*, 155 (2008) B27.
28. R. Bashyam, P. Zelenay, *Nat.*, 443 (2006) 63.
29. K. Lee, L. Zhang, H. Lui, R. Hui, Z. Shi, J. Zhang, *Electrochim. Acta*, 54 (2009) 4704.
30. A. Garsuch, R. Yang, A. Bonakdarpour, J.R. Dahn, *Electrochim. Acta*, 53 (2008) 2423.
31. R. Yang, K. Stevens, J.R. Dahn, *J. Electrochem. Soc.*, 155 (2008) B79.
32. Y.J. Si, C.G. Chen, W. Yin, H. Cai, *Chin. Sci. Bull.*, 56 (2011) 1086.
33. J.Y. Choi, R.S. Hsu, Z.W. Chen, *J. Phys. Chem. C*, 114 (2010) 8048.
34. K. Artyushkova, S. Levendosky, P. Atanassov, J. Fulghum, *Top Catal.,* 46 (2007) 263.
35. M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B*, 104 (2000) 11238.