

Preparation and Performance of a Non-Precious Metal Catalyst CoMe/C for Oxygen Reduction Reaction from Modified Carbon Black Using Melamine as Nitrogen Source

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A non-precious metal catalyst for oxygen reduction reaction is prepared by heat-treating a precursor containing acetylene black, melamine and cobalt chloride. The result shows that the method is effective, and a best catalyst can be obtained by heat-treating the precursor at 600°C for 2 hours. In heat-treating, the cobalt ion is reduced to metallic β -cobalt and the metallic cobalt simultaneously facilitates the nitrogen source reacting with acetylene black to form the active sites to oxygen reduction reaction. The nitrogen source can also react with acetylene black to prepare a metal-free catalyst without the existence of cobalt at a higher temperature, but the activity of resulted catalyst is worse.

Keywords: Oxygen reduction reaction; electrocatalyst; carbon-based; preparation

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) can directly convert chemical energy into electrical energy with a high efficiency and low emission of pollutants. The fuel cells are also compact in structure and can fire up at a low temperature, which are important to the design of an electrical vehicle. Platinum-containing catalysts are widely used to accelerate the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in fuel cells. Especially, the ORR is sluggish in kinetics and the reaction rate is slower than HOR at 6~7 order on the Pt catalyst. It always needs more Pt loading in the ORR catalyst to make up for this shortage. However, the limited reserves and high cost of platinum block the large scale application of PEMFCs and DMFCs[1-4]. Additionally, the methanol molecule is easy to diffuse from the anode to the cathode and directly oxidized at the 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 deactivate the Pt catalyst. So an excellent catalyst for ORR in PEMFCs must meet the following items: (1) low cost; (2) better catalytic activity; (3) better selectivity to four-electron reaction route; (4) better methanol tolerance; (5) good stability. The first and fourth items are exactly the shortage of the Pt-based catalyst.

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 (such as Co(II), Fe(II)), have attracted special attentions[6-9]. The catalyst can be labeled as TM-N/C (TM= Co, Fe, Ni, Cr, Mn, etc.). The structure of N_4 -macrocycle of the compounds can be destroyed in the heat-treating process, so the active site of the catalyst to ORR is still unclear. Studies on Fe-based compounds indicated that FeN_2 or/and FeN_4 fragments in the catalyst are the active sites according to the information from Tof-SIMS [10-13]. A new pyridine-type, pyrrolic type or/and graphite-type C-N structures have been detected by XPS in the TM-N/C catalyst after heat-treatment due to the modification of nitrogen to carbon black. These C-N structures, especially pyridine-like structure at the edge of carbon black, are also widely regarded as the active site of TM-N/C catalyst [14-19].

For the preparation of the TM-N/C catalyst, the $TM-N_4$ (or $TM-N_x$) structure is necessary in a traditional viewpoint. The basic step is: (1) transition metal ions are chelated with macrocycle compound to synthesize a complex; (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 [4, 10, 20, 21]. Recently, the phthalocyanine and porphyrin were also substituted by other nitrogen-containing compounds, such as aniline [22], tripyridyl triazine [19], pyrrole [23], ethylene diamine [4,24], amino acids [25], poly-*o*-phenylenediamine [26], triethylenetetramine [17], hexacyanoferrate [27], etc. Although the choice of nitrogen source was widen, the synthesis of TM-N/C catalyst was still based on the concept of “generating complex”. The catalyst can also be synthesized by a direct metal reduction method [28, 29]: metallic Co was deposited on polypyrrole/carbon to form a cobalt-polypyrrole-carbon composite. The obtained catalyst has good activity and remarkable stability.

Three conclusions can be summarized from the previous researches: (1) Heat-treatment is necessary to improve the ORR activity, and the active site is formed in this process. (2) The active site is not the initial $TM-N_4$ or $TM-N_x$ structure, but is a new structure formed in the heat-treating process, such as FeN_2 or FeN_x fragment, pyridine-type or/and graphite-type C-N structures, etc[14,30,31]. During the heat-treatment, the transition metal facilitates the incorporation of pyridinic and graphitic nitrogen groups into the carbon matrix to form the active sites. (3) Macrocycle compound complex is not necessary to the preparation of the catalyst.

Based on the above understanding, 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. So we have proposed a facile “total solid-state reaction method” to prepare the TM-N/C catalyst [32]. The basic step of the method 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 compounds are replaced by cheap materials. In this work, a new non-precious metal catalyst CoMe/C

for oxygen reduction reaction was synthesized by using melamine as a nitrogen source. The preparation process was optimized to reveal the formation process of ORR active sites of the catalyst. The experimental data show the prepared catalyst has excellent catalysis activity to ORR.

2. EXPERIMENTAL

2.1 Preparation and characterization

Acetylene black (AB) was used as one of the reactants and the supporter of the catalyst. The AB was pre-treated in 1.5 mol L⁻¹ HNO₃ for 12 hours at room temperature, then filtered, washed and dried at 80 °C. For the preparation of the catalyst, 0.100 g of the treated AB, 0.120 g of melamine (C₃H₆N₆, AR) and 0.050 g of cobalt chloride (CoCl₂·6H₂O, AR) were mixed and grinded in an agate mortars for 30 minutes to get a precursor containing AB+C₃H₆N₆+CoCl₂·6H₂O. Then the precursor was heat-treated in a tube furnace in N₂ atmosphere. The temperature was elevated to a desired value at 10 °C min⁻¹ of ramping rate, and was kept for a series of duration at a desired temperature. The heat-treating temperature in this work was 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and the obtained catalysts were labeled as CoMe/C500, CoMe/C600, CoMe/C700, CoMe/C800, CoMe/C900, respectively. A series of catalysts were also prepared at 600 °C for 30min, 60min, 120min 180min and 240min to investigate the effect of heat-treating duration on the activity of the CoMe/C catalyst.

A precursor containing 0.100g of AB and 0.120g of melamine was heat-treated at 600 °C, 700 °C, 800 °C, 900 °C for 2 hours using the same procedure. The obtained products were labeled as Me/C600, Me/C700, Me/C800, Me/C900, respectively.

The phase of CoMe/C was characterized by XRD measured using a Shimadzu XRD-6000 diffractometer with Cu Kα1 radiation at a scanning rate of 5 ° min⁻¹.

2.2 Evaluation of the catalytic activity of the catalyst

The catalytic activity of the catalyst was evaluated by linear sweep voltammetry (LSV). The measurements were carried out on a CHI660A workstation. The 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 catalyst layer was used as the work electrode. The work electrode was fabricated as follows: 10 mg of the catalyst, 1 ml of isopropyl alcohol, 1 ml of deionized water and 5 drops of diluted Nafion solution (0.5 wt%, with isopropyl alcohol as solvent) were ultrasonicated for 20 minutes to form a uniform ink. Then a drop of ink was dropped on the clean surface of the glass carbon disk (Φ5mm). The coated electrode was dried for 2 hours before electrochemical tests. The basic electrolyte was 0.5 mol L⁻¹ H₂SO₄ solution saturated by oxygen or nitrogen for 15 minutes before tests. The methanol tolerance test was conducted in (0.5 mol L⁻¹ H₂SO₄ + 1.0 mol L⁻¹ CH₃OH) solution by cyclic voltammetry (CV) test. The LSV and CV tests were carried out at a scan rate of 5 mV s⁻¹ at 30 °C.

3. RESULTS AND DISCUSSION

3.1 Catalytic activity of CoMe/C toward ORR

Fig.1 shows the voltammograms of acetylene black, CoMe/C600 catalyst and platinum disc electrode in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. It can be seen that the acetylene black has a little activity to ORR with an onset potential of 0.1 V (vs SCE). However, the CoMe/C600 catalyst exhibits good ORR catalytic activity with an onset potential of 0.55 V (vs SCE, or 0.79 V vs. RHE) which is close to the 0.60 V (vs. SCE) of the platinum disc electrode ($\Phi 2 \text{ mm}$). The 0.79 V (vs. RHE) of onset potential of the CoMe/C600 catalyst is also close to the onset potential of other N-doped catalysts, such as the 0.87 V (vs. RHE) in reference [4], the 0.81 V (vs. RHE) in reference [29] and the 0.76 V (vs. NHE) in reference [31], etc. These comparisons indicate that the CoMe/C600 catalyst is very effective to oxygen reduction reaction.

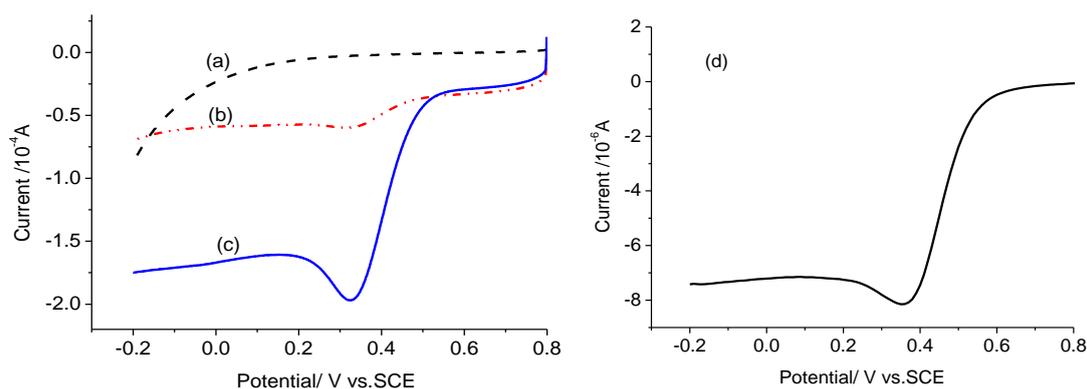


Figure 1. Linear sweep voltammograms of different electrodes. (a) AB in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution saturated by O_2 , (b) CoMe/C600 catalyst in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution saturated by N_2 , (c) CoMe/C600 catalyst in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution saturated by O_2 , (d) Pt-disc electrode ($\Phi 2 \text{ mm}$) in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution saturated by O_2 .

3.2 Effects of heat-treating temperature and duration on the ORR catalytic activity

The precursor of $\text{AB} + \text{C}_3\text{H}_6\text{N}_6 + \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was heat-treated at 500°C , 600°C , 700°C , 800°C and 900°C for 2 hours to synthesize a series of CoMe/C catalyst to investigate the effect of heat-treating temperature on the activity of CoMe/C catalyst. Fig.2 shows the ORR catalytic activity of these samples. The temperature obviously influences the catalytic activity of the resulted catalysts. The catalytic activity can be obtained when the precursor was heat-treated at 500°C , but the ORR onset potential and peak potential are both most negative. The ORR catalytic activity of CoMe/C600 heat-treated at 600°C is the better, and then the catalytic activity gradually worsens with increasing the heat-treating temperature.

The XRD patterns of the catalysts heat-treated at different temperature are shown in Fig.3. It can be seen that the cobalt element mainly exists as cobalt oxides when heat-treated at 500°C , but exists as metallic $\beta\text{-Co}$ when the temperature is up to 600°C . Based on the results presented in Fig.2 and Fig.3, it can be judged that there exists a close relationship between the ORR catalytic activity and

the metallic β -Co. The catalyst exhibits good activity when the metallic β -Co appears. However, the appearance of the metallic β -Co is not the only indicator to judge the ORR catalytic activity of CoMe/C catalyst, since the ORR catalytic activity decreases when the temperature is above 700 °C and the crystal structure of β -Co tends to perfect.

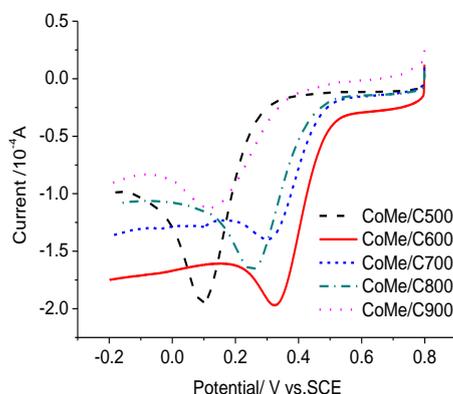


Figure 2. Linear sweep voltammograms of CoMe/C catalysts obtained at different temperatures in 0.5 mol L⁻¹ H₂SO₄ solution saturated by O₂.

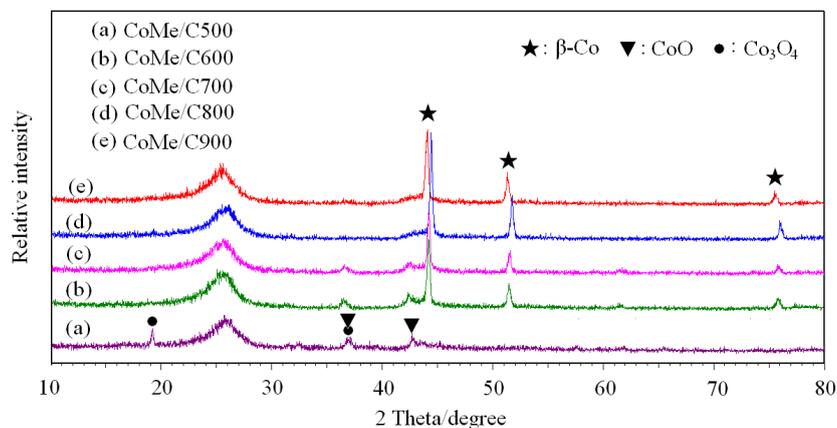


Figure 3. XRD patterns of CoMe/C catalysts obtained at different temperatures. (a) CoMe/C500, (b) CoMe/600, (c) CoMe/C700, (d) CoMe/C800, (e) CoMe/C900.

The effect of heat-treating duration on the ORR activity of CoMe/C catalyst was also investigated at 600 °C with the same precursor. Fig.4 and Fig. 5 show the catalytic activities and XRD patterns of the CoMe/C catalysts obtained at 600 °C for 30min, 60min, 120min, 180min and 240min. It can be seen that the ORR activity of the catalysts gradually improves with the heat-treating duration prolonging in the range of 30 min ~ 120 min. Then the activity of catalysts heat-treated for 180 min and 240 min decreases. This regularity is similar to the heat-treating temperature as shown in Fig.2 and Fig.3. The XRD patterns also show the same regularity as the results of heat-treating temperature. The crystal structure of β -Co also tends to perfect with prolonging the heat-treating duration.

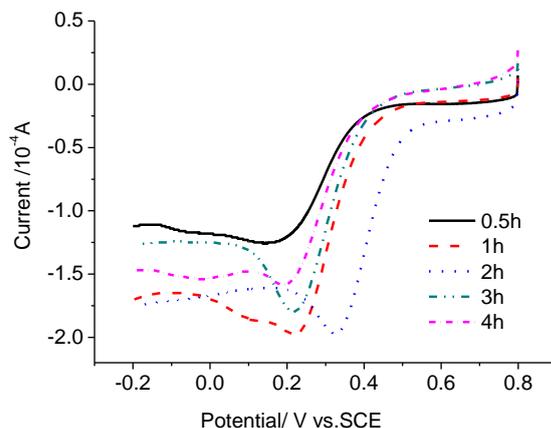


Figure 4. Linear sweep voltammograms of CoMe/C catalysts obtained at 600 °C for different durations in 0.5 mol L⁻¹ H₂SO₄ solution saturated by O₂.

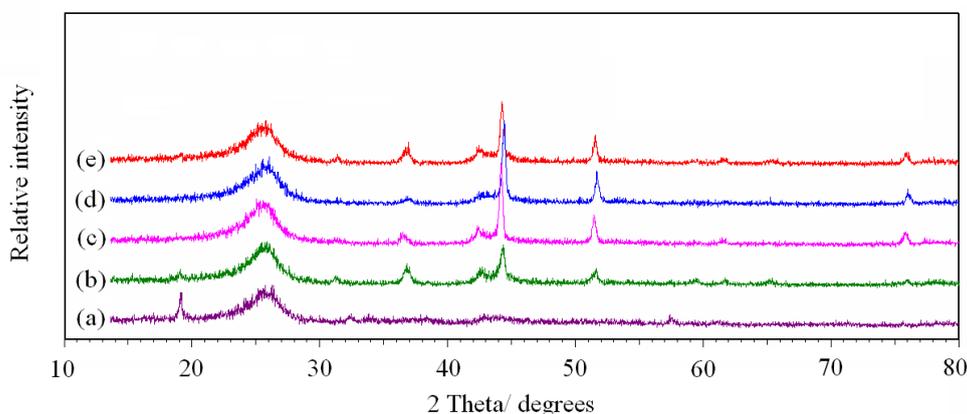


Figure 5. XRD patterns of CoMe/C catalysts heat-treated at 600 °C for different duration, (a) 30min, (b) 60min, (c) 120min, (d) 180min, (e) 240min.

It can be concluded that the formation of β -Co play a key role in the formation of active site of the CoMe/C catalyst from the results of the effect of heat-treating temperature and duration. The active site is formed by the facilitation of β -Co, but the β -Co itself would not be a part of the active sites, because the catalysts with a perfect crystal structure of β -Co prepared at a higher temperature and in a long heat-treating duration do not exhibit better ORR catalytic activity. It can also be deduced that there are two competitive reactions in the heat-treating process, one is the formation of catalytic active site by the facilitation of metallic β -Co, and the other is the decomposition of the formed active site which deteriorates the ORR catalytic activity of CoMe/C catalyst. The formation of active site is quicker than the decomposition of active site when the temperature is below 700 °C for 2 hours. So the catalytic activity of the CoMe/C improves with increasing heat-treating temperature from 500 °C to 600 °C. The decomposition of active site will significantly increase when the temperature is above

700°C and be greater than the formation, which leads to the deterioration of ORR activity of CoMe/C catalyst.

The effect of heat-treating duration can also be explained by the two competitive reactions. The formation of active site dominates the process in short duration and the catalytic activity of the CoMe/C improves with the duration prolonging. The number of decomposition of active site will be greater than the formation of active site when the heat-treating duration is surpass 120min, which leads to the deterioration of the catalytic activity of resulted CoMe/C catalyst.

3.3 Catalytic activity of Me/C catalyst without the existence of cobalt element

In order to further determine the effect of cobalt element in the CoMe/C catalyst, a precursor just containing AB and melamine was heat-treated at 600°C, 700°C, 800°C, 900°C for 2 hours, and the product was labeled as Me/C600, Me/C700, Me/C800 and Me/C900, respectively. The catalytic activities of Me/C catalysts to ORR are shown in Fig.6. It can be seen that an ORR catalyst can be prepared by heat-treating a mechanical mixture of AB and melamine without the existence of cobalt element. However, the activity of the resulted Me/C catalyst is worse than that of the CoMe/C catalyst. The greatest onset potential of 0.35V of Me/C800 in the Me/C series is more negative than the 0.55V of CoMe/C600 in the CoMe/C series. According to the common rule in chemistry, higher temperature is beneficial to a reaction rate while without the existence of a catalyst. The Me/C catalysts show the best catalytic activity by heat-treated at 800°C. However, the CoMe/C catalysts exhibit the best activity by heat-treated at 600°C with the existence of cobalt, which shows the catalytic effect of metallic cobalt to the formation of the active sites in CoMe/C catalysts.

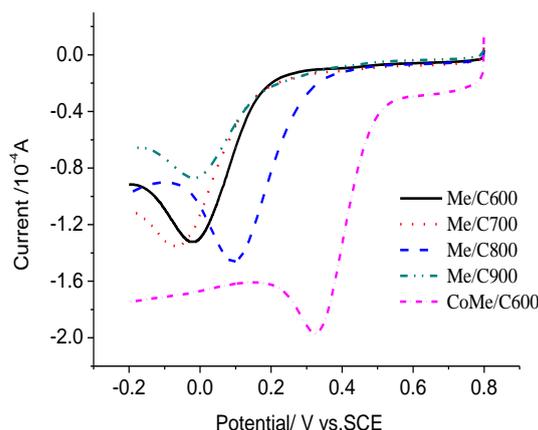


Figure 6. The linear sweep voltammograms of Me/C catalysts without cobalt element obtained at several temperature

3.4 Methanol tolerance of CoMe/C catalyst

Fig.7 show the cyclic voltammograms of a Pt disc electrode and CoMe/C600 catalyst in 0.5 mol L⁻¹ H₂SO₄ and (0.5 mol L⁻¹ H₂SO₄ + 1.0 mol L⁻¹ CH₃OH) solution. It can be seen that methanol was oxidized on the platinum electrode at 0.7 V (vs. SCE) in the process of negative scanning and the

oxidization potential is more positive than the onset potential of oxygen reduction in the blank H_2SO_4 solution. After the oxidization of methanol, the current of oxygen reduction on platinum electrode in ($0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 1.0 \text{ mol L}^{-1} \text{CH}_3\text{OH}$) solution is smaller than that the value in $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. The result shows the platinum electrode was poisoned by the oxidization product of methanol and deactivated. However, the cyclic voltammogram of CoMe/C600 catalyst in $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and ($0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 1.0 \text{ mol L}^{-1} \text{CH}_3\text{OH}$) solution are similar to each other, and the oxidation of methanol cannot be observed on the CoMe/C600 catalyst. This result shows the CoMe/C catalyst is good at the methanol tolerance.

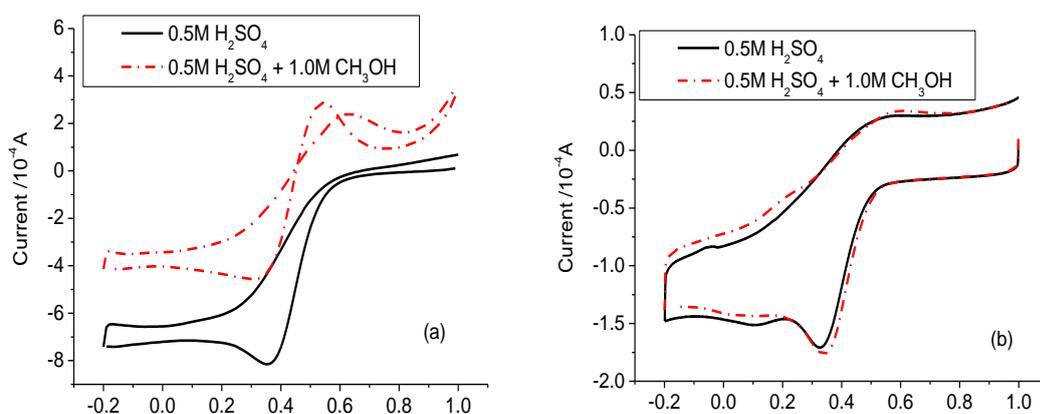


Figure 7. Cyclic voltammograms of (a) Pt disc electrode and (b) CoMe/C catalyst in $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ and ($0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 1.0 \text{ mol L}^{-1} \text{CH}_3\text{OH}$) solution.

4. CONCLUSIONS

A non-precious metal catalyst CoMe/C to oxygen reduction reaction (ORR) was prepared by heat-treating a mechanical mixture of acetylene black, melamine and cobalt chloride. Heat-treating temperature and duration are both important factors influence the catalytic activity of catalyst. There are two types of competitive reactions in the heat-treating process: the formation and decomposition of active site in the CoMe/C catalyst. The formation of active site is slow at low temperature, and the total number of active site is small in short duration. The formed active site will also decompose at high temperature and in long duration, and deteriorates the ORR activity of the resulted catalyst. A good CoMe/C catalyst can be obtained by heat-treating the precursor at 600°C for 2 hours. This temperature is lower than the most reports in which the heat-treating temperature is always above 800°C . When the temperature is 600°C , the cobalt ions are reduced to metallic β -cobalt by carbon black in the process of heat-treating, and the metallic cobalt simultaneously facilitates the reaction of nitrogen source with acetylene black to form the ORR active site. The nitrogen source can also react with acetylene black to form ORR active site to synthesize a Me/C catalyst without the existence of cobalt, but the best activity of Me/C catalyst must be obtained at a higher temperature upper to 800°C . The activity of Me/C catalyst is also less than CoMe/C catalyst. This result further indicates the

facilitation effect of metallic cobalt to the formation of ORR active site in CoMe/C catalyst. In addition, the CoMe/C catalyst is good at the methanol tolerance.

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