



Original article

A non-precious metal catalyst for oxygen reduction prepared by heat-treating a mechanical mixture of carbon black, melamine and cobalt chloride

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ABSTRACT

A non-precious metal catalyst CoMe/C for the oxygen reduction reaction is prepared by heat-treating a mechanical mixture of carbon black, melamine and cobalt chloride at 600 under nitrogen atmosphere for 2 h. The catalytic activity of CoMe/C is characterized by the electrochemical linear sweep voltammetry technique. The onset reduction potential of the catalyst is 0.55 V (vs. SCE) at a scanning rate of 5 mV/s in 0.5 mol/L H₂SO₄ solution. The formation of the ORR activity sites of CoMe/C is facilitated by metallic β -cobalt.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have several advantages as the power sources for electric vehicles. The fuel cells 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 low temperatures, which is important to the design of a vehicle. Platinum-based catalysts are commonly used in the fuel cells to accelerate the rate of the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). Especially, the ORR is kinetically sluggish and the rate of reaction is 6–7 magnitude slower than that of HOR. It is always necessary for more platinum load in the ORR catalyst to make up for this shortage. The limited reserves and high cost of platinum prohibit the large scale application of PEMFCs [1–4]. Additionally, the small methanol molecules in direct methanol fuel cells (DMFCs, as an important type of PEMFCs) can diffuse from anode to cathode across the membrane and be directly oxidized at the cathode catalysts, which produces a “mixed potential” and leads to a loss of cell voltage. The oxidized product of methanol will also poison the platinum catalyst and abolish its catalytic

activity [1]. So an excellent catalyst for ORR in PEMFCs must meet the following requirements: (1) low cost, (2) better catalytic activity, (3) better selectivity for the four-electron reaction route, (4) better methanol tolerance and (5) good stability. High price and poor methanol tolerance are the shortcomings of platinum-based ORR catalysts.

In the past decades, many non-precious or non-platinum ORR catalysts have been developed [5]. Among the catalysts, the pyrolyzed chelates of N₄-macrocycle compounds, such as phthalocyanine and porphyrin, with transition metal ions have attracted much attention [6,7]. The catalyst can be labeled as TM-N/C (TM = Co, Fe, Ni, Cr, Mn, etc.). The traditional preparation method of the TM-N/C catalyst is the “impregnation method”. The basic steps include [8,9]: (1) transition metal ions are chelated with macrocyclic compounds to form a complex; (2) carbon black is added to adsorb the complex onto its surface; (3) the mixture is dried and heat-treated at a high temperature in an inert atmosphere. Recently, the phthalocyanine and porphyrin were also substituted by other nitrogen-containing compounds to synthesize the catalyst, such as aniline [10], tripyridyl triazine [11], pyrrole [12], triethylenetetramine [13], etc.

In this work, a simple and cheap method is introduced to prepare the TM-N/C catalyst. The main materials in the method just involve carbon black, melamine and cobalt chloride. The three reactants were mixed by a solid-state milling method rather than

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generating “complexes”. Then the mixture was heat-treated under nitrogen atmosphere to synthesize a carbon-supported CoMe/C catalyst.

2. Experimental

2.1. Preparation and characterization

Acetylene black (AB) was pre-treated in 1.5 mol/L HNO_3 for 12 h at room temperature. For the preparation of the catalyst, 0.100 g of the treated AB, 0.120 g of melamine ($\text{C}_3\text{H}_6\text{N}_6$, AR) and 0.050 g of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, AR) were mixed in an agate mortars for 30 min. The mechanical mixture was heat-treated at 600 °C for 2 h in a tube furnace in nitrogen atmosphere (the purity of nitrogen was 99.999% and the flow rate was 100 mL/min). The obtained catalysts were marked as CoMe/C600.

The phase of products was characterized by XRD measured using a Shimadzu XRD-6000 diffractometer with $\text{Cu K}\alpha 1$ radiation at a scanning rate of 5°/min.

2.2. Evaluation of the electrocatalytic activity of the catalyst

The electrocatalytic activity of the catalyst was evaluated by linear sweep voltammetry (LSV). The electrochemical 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 (the potential values in the paper are referenced to SCE unless otherwise specified) and a Pt wire as the counter electrode. A glass carbon electrode coated with a catalyst layer was the working electrode. The working electrode was fabricated as follows: 10 mg of the catalyst, 0.5 mL of isopropyl alcohol, 0.5 mL of de-ioned water and 2 drops of diluted Nafion solution (0.5 wt%, with isopropyl alcohol as solvent) were ultrasonically mixed to form a uniform ink. Then 10 μL of the ink was dropped onto the clean surface of a glass carbon disk electrode (Φ 5 mm). The coated electrode was naturally dried over 2 h in air before electrochemical tests. The electrolyte was 0.5 mol/L H_2SO_4 solution saturated by oxygen or nitrogen before tests. The LSV tests were carried out at a scan rate of 5 mV/s until getting stable and reproducible curves. The tests were conducted at 30 °C.

3. Results and discussion

The mechanical mixture of carbon black, melamine and cobalt chloride was divided in three quartz boats and orderly placed in a tube furnace to heat-treat simultaneously. The resulting products were labeled as A1, A2 and A3 from the inlet to the outlet of the

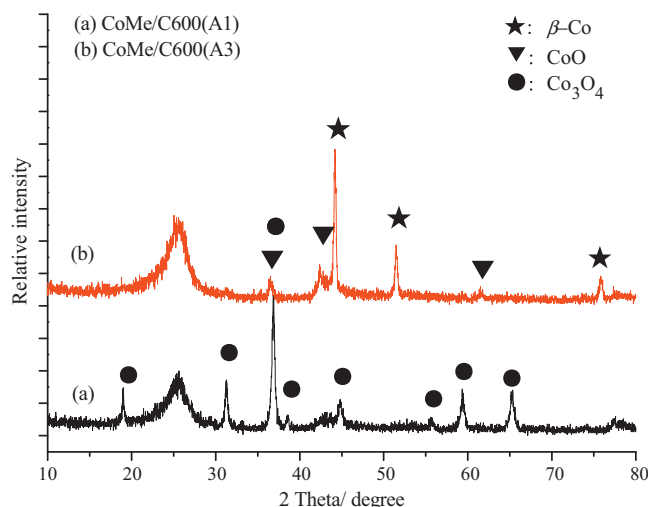


Fig. 2. The XRD patterns of CoMe/C600 heat-treated at different positions in tube furnace.

furnace, respectively. The catalytic activity of the resulting catalyst CoMe/C600 in ORR was evaluated by the onset reduction potential from the linear sweep voltammetry test.

Fig. 1 shows the linear sweep voltammograms of acetylene black (AB), catalyst CoMe/C600(A3) (near the outlet of the furnace) and platinum disk electrode (Φ 2 mm) in 0.5 mol/L H_2SO_4 solution. It can be seen that the acetylene black has little activity in ORR with an onset potential of 0.1 V (vs. SCE). However, the CoMe/C600(A3) exhibits good ORR catalytic activity with an onset potential of about 0.55 V (vs. SCE), which is closer to the value of platinum disk electrode under the same conditions. The results indicate that the acetylene black reacted with the decomposition products of melamine at high temperatures to form the catalytic sites for the ORR.

Fig. 2 shows the XRD patterns of CoMe/C600(A1) near the inlet of the furnace and CoMe/C600(A3) near the outlet of the furnace. It can be seen that the state of the cobalt element is different in these two samples. The cobalt element mostly exists as cobalt oxides CoO and Co_3O_4 in CoMe/C600(A1), but as β -type metallic cobalt in CoMe/C600(A3). This difference is from the impurity of oxygen in nitrogen as a protecting gas. The Co(II) ions would be reduced to lower valence metallic cobalt by carbon black at high temperatures under the nitrogen atmosphere. However, the fresh metallic cobalt in CoMe/C600(A1) would be re-oxidized to cobalt oxides by the residual oxygen in nitrogen gas, which

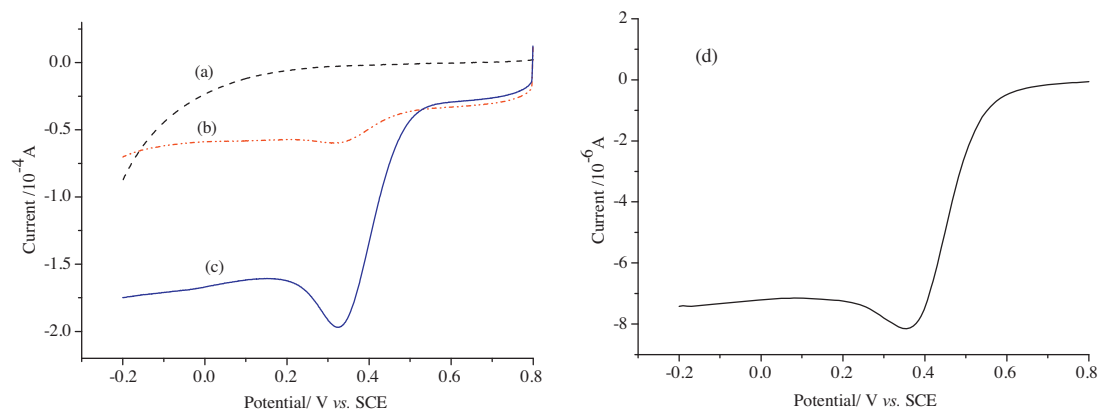


Fig. 1. The activities to oxygen reduction reaction of AB in 0.5 mol/L H_2SO_4 solution saturated by O_2 (a), CoMe/C600 catalyst in 0.5 mol/L H_2SO_4 solution saturated by N_2 (b) and saturated by O_2 (c), and Pt-disk electrode (Φ 2 mm) in 0.5 mol/L H_2SO_4 solution saturated by O_2 (d).

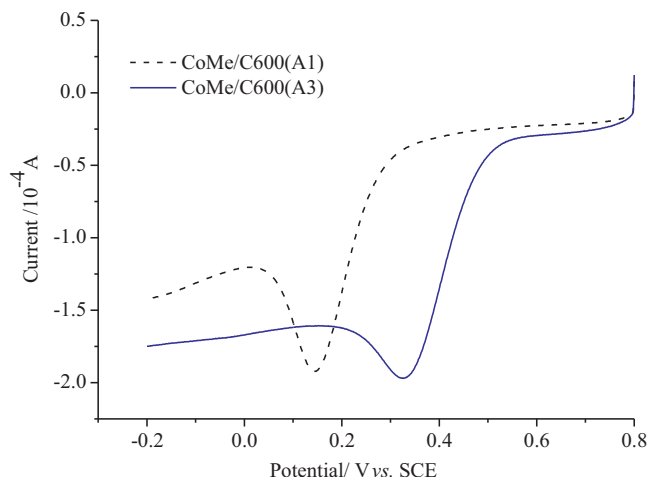


Fig. 3. The difference in the ORR catalytic activity of CoMe/C600(A1) and CoMe/C600(A3).

consumes the oxygen and protects the metallic cobalt in CoMe/C600(A3) from oxidation.

Fig. 3 shows the catalytic activity of CoMe/C600(A1) and CoMe/C600(A3) in ORR. The 0.32 V of ORR onset potential of CoMe/C600(A1) is more negative than the 0.55 V of CoMe/C600(A3), and the catalytic activity of CoMe/C600(A3) is better than that of CoMe/C600(A1). According to the existing literatures, the role of metal element in TM-N/C is to facilitate the formation of ORR active sites in metallic state. The correlation between the XRD pattern and the ORR activity from Figs. 2 and 3 supports the hypothesis that the existence of metallic cobalt facilitates the formation of the ORR catalytic sites between the decomposition products of melamine and carbon black.

4. Conclusion

A non-precious metal catalyst CoMe/C600 for oxygen reduction was synthesized by a convenient procedure and cheap materials including metal salt, nitrogen source and carbon black. The three reactants were mixed by a mechanical method rather than generating coordination bonds as in the traditional “impregnation method” before the heat-treating process. The catalytic activity of CoMe/C was found to depend on the state of cobalt element. The Co(II) ions would be reduced to metallic cobalt by carbon black at

high temperatures under the nitrogen atmosphere, then the fresh metallic cobalt facilitates the formation of ORR active sites of catalyst CoMe/C.

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