

## Electrocatalytic Activity of Pt-Ag-Co/C Alloy Nanoparticles for the H<sub>2</sub>O<sub>2</sub> Reduction Reaction in Direct NaBH<sub>4</sub> - H<sub>2</sub>O<sub>2</sub> Fuel Cell

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**Abstract.** This study explores the catalytic properties of Pt-Ag-Co ternary alloys used for H<sub>2</sub>O<sub>2</sub> reduction. All catalysts are prepared by impregnation reduction method and characterized by XRD and TEM. The electrochemical performance is examined by cyclic voltammetry (CV) at 25°C. The results show that Ag, Co and Pt form ternary alloy and the alloy nanoparticles are 2~4nm in diameter. The electrocatalytic activity increase slightly when Ag instead of part of Pt. If metal Co is introduced into Pt-Ag to form Pt-Ag-Co alloy, the catalytic performance will improved significantly. The best ratio of Pt-Ag-Co is 10%-10%-15% (weight percent).

### Introduction

Direct NaBH<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> fuel cells (DBHFCs), NaBH<sub>4</sub> as the fuel of anode and H<sub>2</sub>O<sub>2</sub> as oxidant of cathode, have been widely studied in recent years, due to their high energy density, unpolluted product, raw materials easy to store and transport [1-4]. H<sub>2</sub>O<sub>2</sub> as the cathode reactant, the cell can react completely out of the air, so this type of fuel cell can be used in some special area, such as underwater and aerospace. Usually, H<sub>2</sub>O<sub>2</sub> can be decomposed into water and oxygen at natural condition. If the oxygen cannot be removed promptly, it will increase the pressure inside the battery, thereby increasing the difficulty of battery design and decreasing the utilization of H<sub>2</sub>O<sub>2</sub>. Therefore, the choice of suitable catalysts for H<sub>2</sub>O<sub>2</sub> reduction is significant. Currently, the catalyst selection of H<sub>2</sub>O<sub>2</sub> reduction is mainly focused on precious metals, such as Pt, Pd, Ir, Au, Ag and their alloys [5-11]. But the limited resources and higher cost of precious metal greatly limit the development of DBHFC. Some researchers selected transition metal oxides[12] and metal macrocyclic compound[13-14] for catalyzing the H<sub>2</sub>O<sub>2</sub>, but the cell performance are not ideal.

In this paper, we prepared different ratio of Pt<sub>x</sub>-Ag<sub>10</sub>-Co<sub>y</sub>/C(x=5,10, y=10,15,20,25) alloy catalysts by impregnation-reduction method, and explored the possibility of Ag and Co instead of Pt. The electrocatalytic activities of Pt<sub>x</sub>-Ag<sub>10</sub>-Co<sub>y</sub>/C are tested by cyclic voltammetry and the optimal alloy ratio of Pt<sub>x</sub>-Ag<sub>10</sub>-Co<sub>y</sub>/C is determined.

### Preparation of electro-catalysts and working electrode

Metal Pt, Ag and Co are prepared by impregnation-reduction method. First, different amounts of AgNO<sub>3</sub> and sodium citrate, which are mixed in deionized water, was added in the XC-72 Carbon suspension, the PH was adjusted to 9-10 with ammonia solution and ultrasound dispersed them for 1.5h. Then excessive NaBH<sub>4</sub> was added in slowly. The different amounts of Ag/C catalysts were got after the above mixture solution being magnetic stirred continually for 2h at room temperature, separated by vacuum filtration, washed with distilled water and dried at 80°C for 24h.

There was a same procedure to prepare Pt-Ag-Co/C. In brief, mixed Ag/C, deionized water and isopropanol firstly, then added in Cobalt nitrate solution and H<sub>2</sub>PtCl<sub>6</sub> solution in order, ultrasound dispersed them for 2h. Adjusted the PH to 8-9 with NaOH solution. Finally, added in the dilute NaBH<sub>4</sub> solution, magnetic stirred them continually for 2h at 80-90°C. The Pt-Ag-Co/C was got after the above mixture solution being magnetic stirred continually for 2h, separated by vacuum filtration, washed with distilled water for 3 times and vacuum dried at 80°C for 24h.

The working electrode is built up as follows: firstly, a 5mg catalyst sample and a small amount of 0.5% nafion solution were ultrasonic dispersed a few minutes until a uniform ink-like formed. Secondly, the catalyst ink was coat on one side of the carbon paper and then was oven dried at 40°C for 30 minutes. The working electrode area is 0.5cm<sup>2</sup> with 2mg/cm<sup>2</sup> loading of catalysts.

The electrochemical performances were examined by Cyclic Voltammetry(CV) Curves. The Pt gauze and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode. Before testing, we need pour high purity nitrogen to the solution about 20 minutes to exclude oxygen.

## Results and discussion

As shown in Fig.1, the alloys(Pt-Ag, Pt-Ag-Co) with good crystal lattice are formed when Ag and Co are added because of the alloy characteristic peak shift to the left of Pt<sub>20</sub>/C obviously. The diffraction peaks at 31.318°, 38.607°, 59.453°, 65.344° correspond to the Co<sub>3</sub>O<sub>4</sub> (220), (222), (511), (440) planes. It indicates that some Co is oxidized to Co<sub>3</sub>O<sub>4</sub> while the ternary alloy is formed.

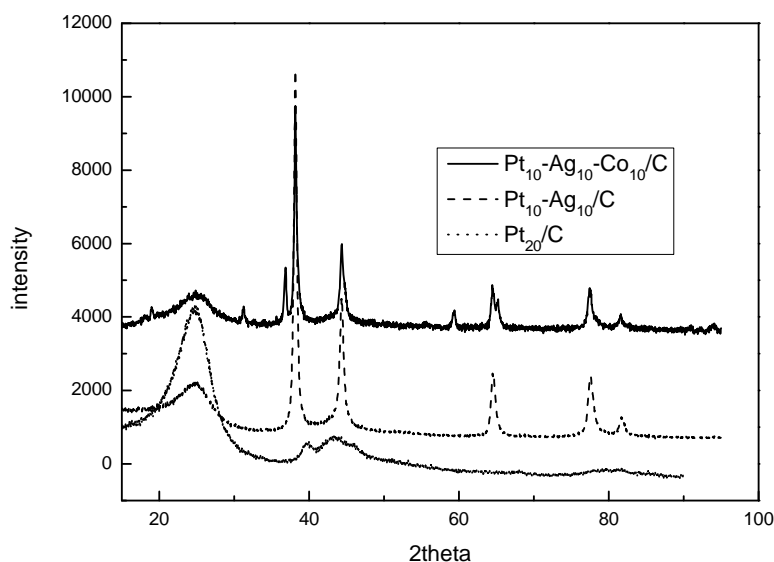


Fig. 1. The XRD spectra of Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>10</sub>/C , Pt<sub>10</sub>-Ag<sub>10</sub>/C and Pt<sub>20</sub>/C catalysts

The TEM images in Fig.2 a ,b, c show the Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>10</sub>/C catalyst which is about 2-4nm in size is distributed on the surface of carrier uniformly. It can be observed obviously in Fig.2d that there are three kinds of crystalline, which lattice line spaces are 0.232nm, 0.226nm and 0.406nm respectively. The 0.232nm is bigger than 0.226nm(Pt(111)) and less than 0.235nm((Ag(111))), thereby indicating the Pt-Ag alloy. The width 0.406nm is narrow than 0.466nm(Co (111)), it can be concluded that there be Pt-Ag-Co alloy being formed, which is consistent with the XRD results.

As shown in Fig. 3, the CV tests of Pt<sub>20</sub>/C, Pt<sub>10</sub>-Ag<sub>10</sub>/C, Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C in 0.5M NaOH +0.06M H<sub>2</sub>O<sub>2</sub> solution were carried at 25°C. It can be seen that three catalysts has a higher catalytic activity for hydrogen peroxide reduction, there peak current densities are 131.9 mA/cm<sup>2</sup>, 135.7 mA/cm<sup>2</sup> and 164.9mA/cm<sup>2</sup> respectively, which confirms that instead of part of Pt by Ag is helpful to improve the electrocatalytic reduction of H<sub>2</sub>O<sub>2</sub>, while the catalytic activity has improved significantly after forming Pt-Ag-Co.

Fig.4 and Fig.5(a) show that increasing the content of Pt in Pt-Ag-Co/C (from 5% to 10%), the peak current density increases; while holding the Pt-Ag unchanged, the peak current density of Pt<sub>5</sub>-Ag<sub>10</sub>-Co<sub>x</sub>/C, Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>x</sub>/C will increase first and then decrease when enlarged the Co content. The maximum of the peak current density appear at the 15% Co content. We analyst and believe that

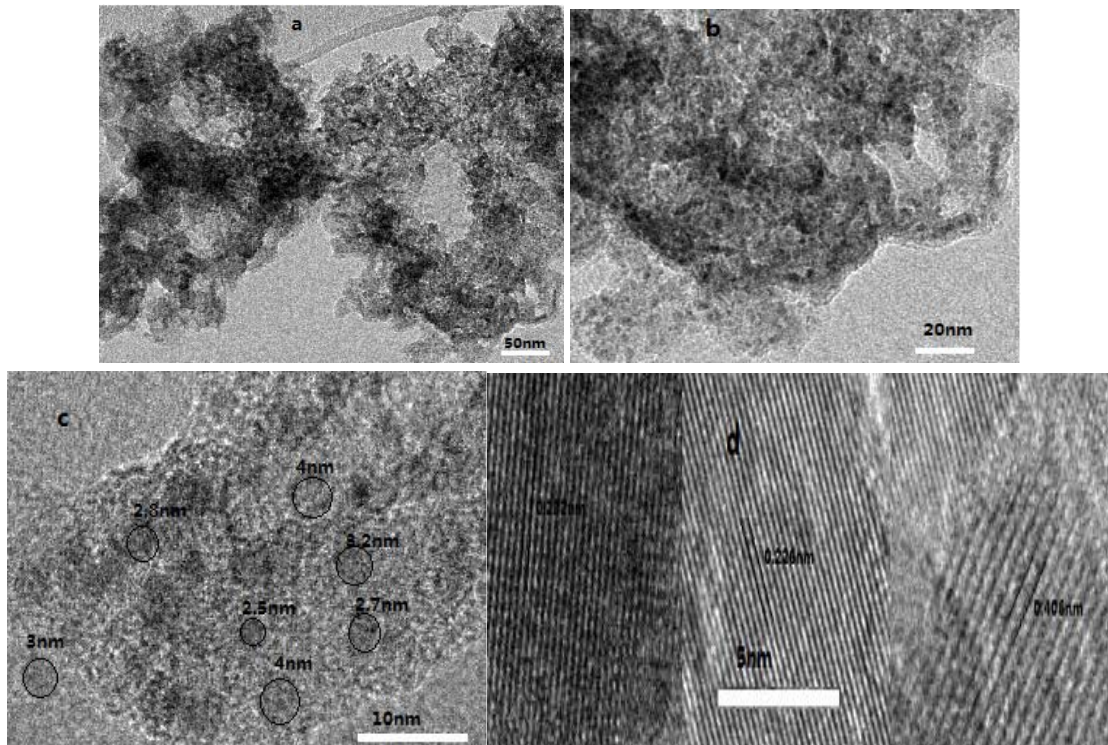


Fig. 2. TEM images of Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>10</sub>/C catalyst

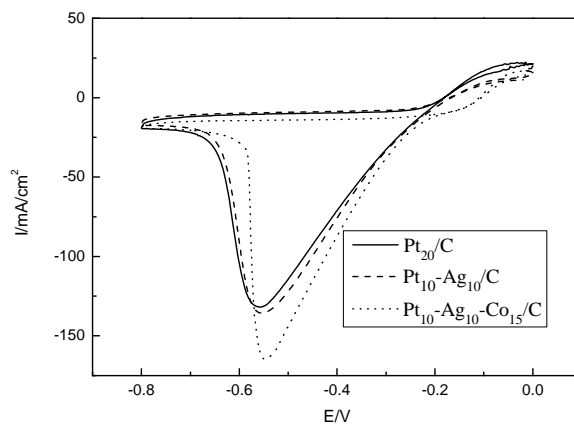


Fig. 3. CV curves of Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C, Pt<sub>10</sub>-Ag<sub>10</sub>/C and Pt<sub>20</sub>/C in 0.5M NaOH and 0.06M H<sub>2</sub>O<sub>2</sub>

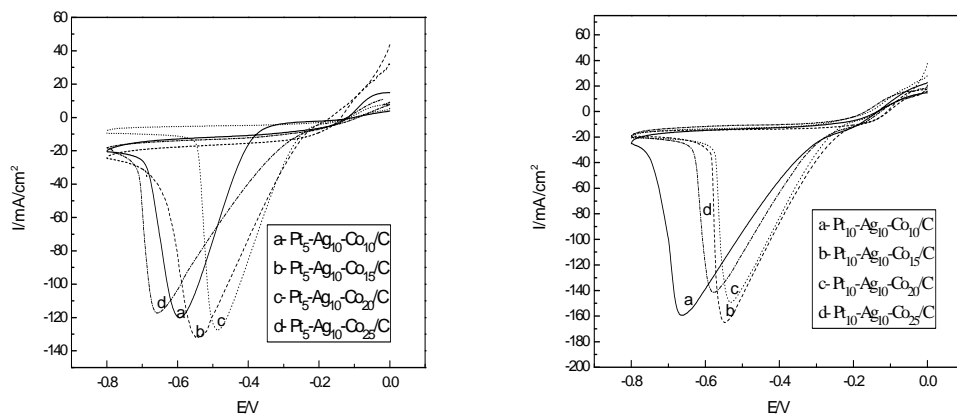


Fig.4. CVcurves of Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>x</sub>/C and Pt<sub>5</sub>-Ag<sub>10</sub>-Co<sub>x</sub>/C in 0.5M NaOH+0.05MH<sub>2</sub>O<sub>2</sub>

there will be less Pt-Ag-Co/C formed with relatively small amount of Co, so the catalytic activity is not ideal. On the contrary, the excessive Co can attach on the surface of Pt-Ag-Co alloy which hinder the reactant contact effectively with the catalyst. It is only when the ratio of Pt/Ag/Co is within a certain range, for example 10%-10%-15%, the better catalytic effect will be achieved.

Fig.5(b) shows us the difference impedance of Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C and Pt<sub>5</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C. It indicates that the Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C catalytic electrode has a smaller contact resistance than that of Pt<sub>5</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C. That means the catalytic reaction on the Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C surface is easier and the catalytic activity is higher. All of these verify the previous results.

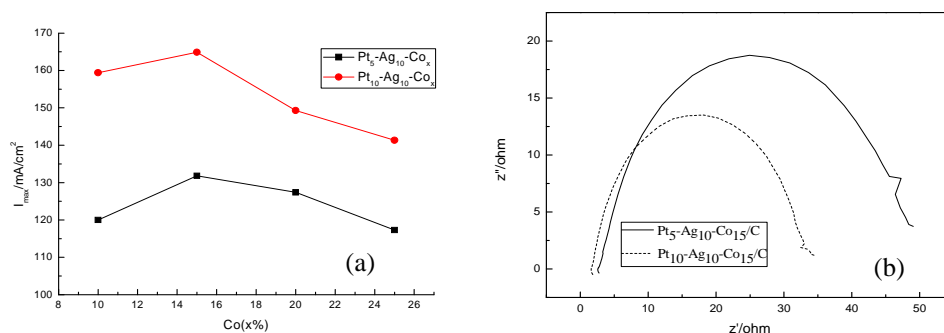


Fig.5. The effect of Co on  $I_{\max}$ (a) , EIS curves of Pt<sub>5</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C and Pt<sub>10</sub>-Ag<sub>10</sub>-Co<sub>15</sub>/C (b)

## Conclusion

We prepared a series of Pt-Ag-Co ternary alloy catalysts for H<sub>2</sub>O<sub>2</sub> reduction reaction. The test results indicate the ternary alloy can be distributed uniformly on the surface of carrier, and the catalytic activity of Pt-Ag-Co has a significant improvement than that of Pt-Ag. The best proportion of Pt-Ag-Co is 10%-10%-15% in weight percent.

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