

Study on Preparation Process of Pd-Ni Alloy Nano-catalyst for Cathode reduction in Direct NaBH₄ - H₂O₂ Fuel Cell

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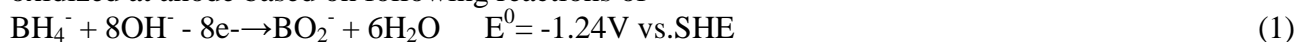
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Keywords: Pd-Ni binary alloy; cathode catalyst; impregnation reduction method; hydrogen peroxide

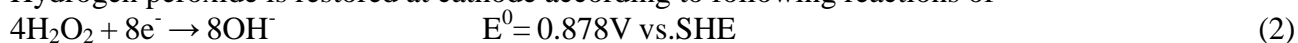
Abstract. In this paper, we prepared Ni/C, Pd/C and Pd-Ni/C binary alloy nano-catalysts by the impregnation-reduction method. The structures of all catalysts were characterized by XRD and TEM. The electro-catalytic performance of all catalysts on H₂O₂ reduction were studied by cyclic voltammetry(CV) and linear sweep voltammetry(LSV). The results show that Pd-Ni binary alloy nano-catalyst is obtained, whose catalytic activity is extremely close to pure palladium catalyst with the same metal loading, and it has better catalytic performance when palladium was reduced preferentially in prepare process.

Introduction

H₂O₂ has a lower activation energy and a higher energy density than O₂ and is easy to transport and storage. Therefore, in recent years, researchers have started to develop fuel cells using H₂O₂ as the oxidant, such as the Direct NaBH₄-H₂O₂ fuel cell(DBHFC), which is attractive as a new, clean alternative power source for portable electronic devices[1-4]. In DBHFC, sodium borohydride is oxidized at anode based on following reactions of



Hydrogen peroxide is restored at cathode according to following reactions of



Accordingly, the net cell reaction in DBHFC is



The theoretical fuel cell potential and specific energy of DBHFC are 2.118V and 17.06Kwh/kg respectively.

At present carbon supported Pt or Pt-based alloys is widely used as cathode catalyst in this type of fuel cell [5-8], however, the limited resources and higher cost of Pt greatly limit the development of DBHFC. Finding a new type of catalyst, which is low-cost and maintains the high catalytic activity to H₂O₂ electro-reduction, is important for promoting the DBHFC technology and commercial process.

In this paper, Ni/C10%, Ni/C20%, Pd/C10% and Pd/C20% were prepared by impregnation reduction method. Meanwhile, the catalysts Pd-Ni/C and Ni-Pd/C with different mass ratio (10%-10%, 15%-15%, 20%-20%, in weight percent) were obtained by the similar way(Pd-Ni/C indicates Pd was prepared preferentially, Ni-Pd/C indicates Ni was prepared preferentially)[9-12].

Preparation of electro-catalysts

Pd₁₀-Ni₁₀/C was prepared by impregnation-reduction method. Firstly, the 80mg XC-72 Carbon, 50mL isopropanol and 50mL deionized water were added into 250mL flask, and the mixture was dispersed for 0.5h by ultrasound. The 2mL chloropalladic acid solution, in which the content of palladium was 5mg/mL, was added dropwise into the above well dispersed suspension and then ultrasonically dispersed for 1h. At a continuous stirring condition, the suspension was adjusted to weak alkaline(pH:9-10) with NaOH solution, it reacted for 2h at constant temperature (80-90°C) after excessive NaBH₄ being added in that mixture slowly and ultrasonic 20 minutes. After cooling, the 49.53mg Ni(NO₃)₂·6H₂O and 15mg sodium citrate, which were mixed in 4mL deionized water, were added dropwise into the above scattered suspension. The PH value of system was adjusted to weak

alkaline (pH:8-9) with NaOH solution, and the suspension reacted for 2h under continuous magnetic stirring at constant temperature (44-46°C) after excessive NaBH₄ being added in that mixture slowly and ultrasonic 20 minutes. The mixture solution was separated by vacuum filtration, washed with distilled water and dried at 60°C for 12h.

Pd₁₅-Ni₁₅/C, Pd₂₀-Ni₂₀/C, Pd/C (without nickel salt), Ni/C (without palladium salt) were synthesized by the method described above. Ni₁₀-Pd₁₀/C, Ni₁₅-Pd₁₅/C and Ni₂₀-Pd₂₀/C (Ni was prepared preferentially) were obtained by the similar way.

Preparation of working electrode

Generally, our working electrode area is 1.0cm² with 2mg/cm² loading of catalysts. The method of preparing working electrode is as follows: firstly, a 8 (6、10) mg catalyst sample prepared above 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 4 (3、5) cm² carbon paper, and then was put in a 40°C oven for 30 minutes.

Electrochemical test

Electrochemical tests were examined by using CHI660C electrochemical workstation and three-electrode system. The electrochemical performance tests of these catalysts were examined by CV. The Pt gauze and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode. The working electrode prepared above, the Pt gauze and SCE electrode worked together to complete the circuit in 0.5mol/L NaOH and 0.06mol/L H₂O₂. Before testing, we need pour high purity nitrogen to the solution for about 20 minutes to exclude oxygen.

Results and discussion

The XRD spectra of Pd₁₀/C、Pd₂₀/C、Pd₁₀-Ni₁₀/C catalysts is showed in Fig.1, we can see that, with respect to the Pd₁₀/C and Pd₂₀/C, the diffraction peak of Pd-Ni alloy catalyst has shifted to the left, which indicates Pd-Ni binary alloy is formed. On the one hand, the diffraction peak intensity of Pd-Ni alloy catalyst was obviously decreased, which means that the introduction of Ni can decrease the crystallinity of catalyst, and more lattice defects will be generated on the surface. The lattice defects are often highly active, which will increase the active site, and that is beneficial to the reaction. On the other hand, decreasing the grain size will increase the specific surface area of the catalyst and improve the catalytic activity. TEM shows us that Pd-Ni particles with diameters from 8 to 16 nm are

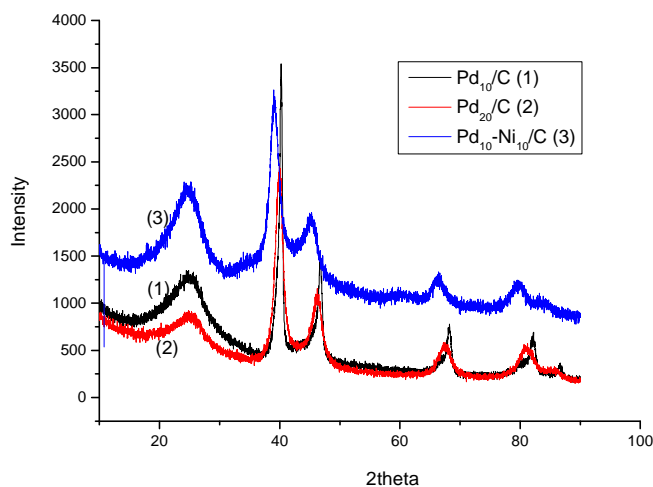


Fig.1. The XRD spectra of Pd₁₀/C、Pd₂₀/C、Pd₁₀-Ni₁₀/C catalysts

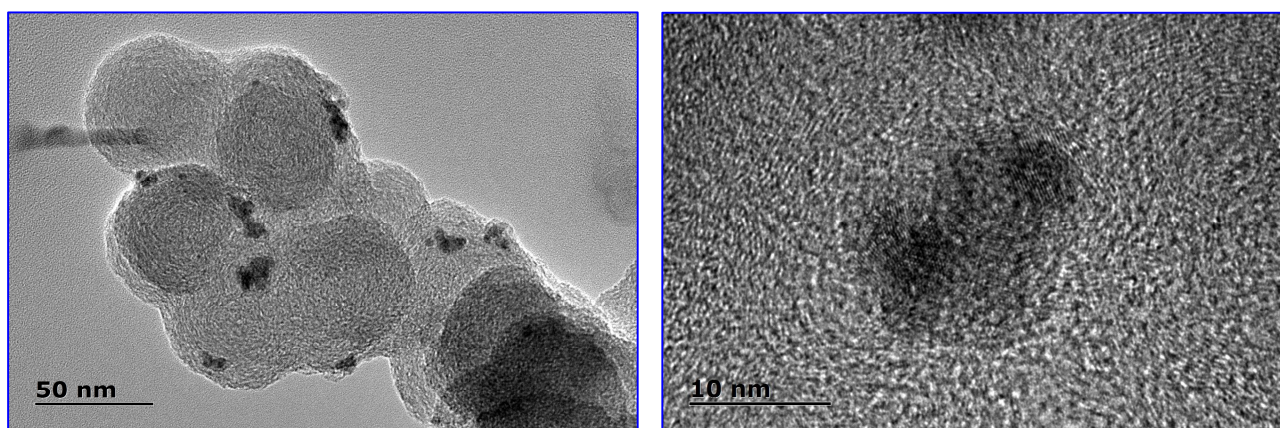


Fig.2. The TEM of Pd-Ni/C catalyst

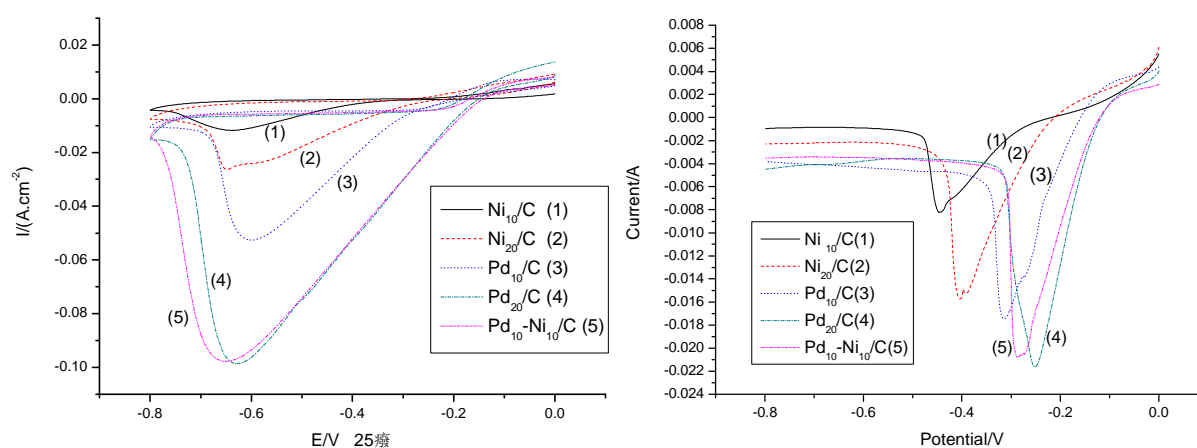


Fig.3.CV and LSV of Ni₁₀/C、Ni₂₀/C、Pd₁₀/C、Pd₂₀/C、Pd₁₀-Ni₁₀/C catalysts at 25°C in 0.5 M NaOH+0.06M H₂O₂ solution.

dispersed uniformly on the support in Fig.2.

The electrochemical performance test results were showed in Fig.3. Relative to Ni₁₀/C and Pd₁₀/C, Pd₁₀-Ni₁₀/C has a higher reduction peak current, which shows that the electrocatalytic activity of Pd₁₀-Ni₁₀/C (on the reduction of H₂O₂) is higher than that of Pd₁₀/C or Ni₁₀/C. The electrochemical properties of Pd₁₀-Ni₁₀/C and Pd₂₀/C were very close, showing that it is effective to substitute 10%Ni for 10%Pd. From the LSV curve it can be seen that the limiting diffusion current density and catalytic activity of Pd₁₀-Ni₁₀/C catalyst are close to those of the Pd₂₀/C, which verifies the previous inference.

The Fig. 4 shows that reduction peak current of Pd₁₀-Ni₁₀/C(97.78 mA) is 62.67% higher than reduction peak current of Ni₁₀-Pd₁₀/C(60.11mA); the reduction peak current of Pd₁₅-Ni₁₅/C(103.8 mA) is 38.45% higher than that of Ni₁₅-Pd₁₅/C(74.97mA); the reduction peak current of Pd₂₀-Ni₂₀/C(100.7 mA) is 25.34% higher than that of Ni₂₀-Pd₂₀/C(80.31mA). We found that the catalytic performance of Pd-Ni alloy catalyst which was synthesized by preparing Pd preferentially is better than Ni-Pa alloy(preparing Ni preferentially). With the increase of Pd and Ni content, the catalytic performance of Pd-Ni/C also increases, but the content of Pd and Ni continues to increase, the catalytic activity decreases. Therefore the best content of Pd-Ni/C is Pd 15% and Ni 15%.

Conclusions

The XRD spectra peak of Pd-Ni alloy catalyst is shifted compared with that of pure Pd, which indicates Pd-Ni binary alloy is formed. Pd-Ni alloy catalyst has higher catalytic activity than pure nickel catalyst with the same metal load. The electrochemical performance of Pd₁₀-Ni₁₀/C is very close to that of Pd₂₀/C, which indicates that it is effective to substitute 10%Ni for 10%Pd. Three sets

of experiments have proved that Pd-Ni/C with the reduction of preparing Pd preferentially has much higher electrochemical performance than that with the reduction of preparing Ni preferentially, so the preparation process of Pd-Ni alloy catalyst was established.

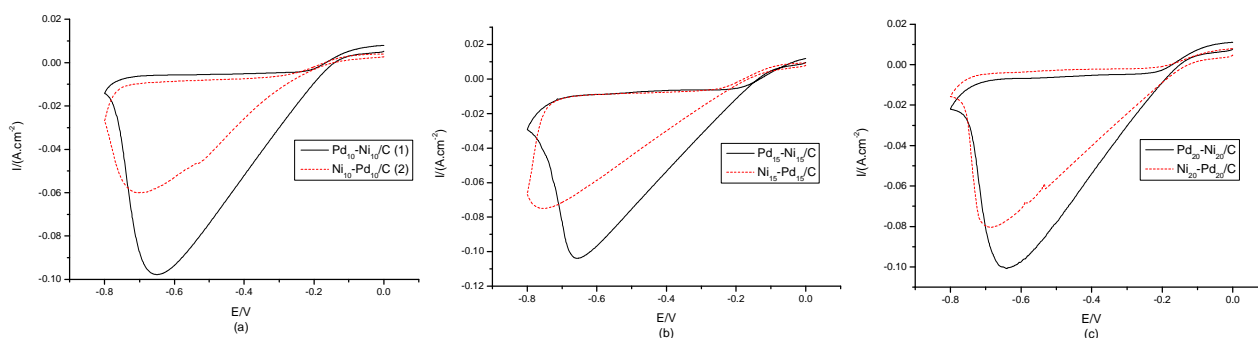


Fig.4. CV of Pd₁₀-Ni₁₀/C、Ni₁₀-Pd₁₀/C、Pd₁₅-Ni₁₅/C、Ni₁₅-Pd₁₅/C、Pd₂₀-Ni₂₀/C、Ni₂₀-Pd₂₀/C catalysts at 25° C in 0.5 M NaOH+0.06M H₂O₂ solution.

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