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*Short Communication*

# Preparation and Catalytic Performance of Ni/NiO@C using Bamboo as source of Porous Carbon

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Hydrogen is the most potential clean energy, because of high combustion heat value and water is the only product after combustion. The method of hydrogen production by water electrolysis will become the main one. However, the energy consumption of hydrogen production by hydrolysis is too large, so appropriate electrode materials are needed to reduce the energy consumption. Bamboo carbon is an important biomass carbon material. Therefore, it is considered that Ni/NiO@C catalytic material can be synthesized by coating a layer of nickel oxide on the surface of bamboo carbon, which may increase the catalytic efficiency. The main raw material is bamboo carbon powder and loaded NiO onto carbon ball through in-situ synthesis to form Ni/NiO@C composite catalytic material. Linear scanning voltammetry, cyclic voltammetry and other methods were used to analyze and characterize the finishedproducts. The catalytic effect of the materials in this experiment can be seen from the linear sweep voltammetry curve. At the current of 0.010 A, the overpotential is 0.249 v.

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**Keywords:** Bamboo carbon, Hydrogen Evolution, Catalytic Performance

## 1. INTRODUCTION

The development of new energy and new materials is an important issue to be solved urgently in the 21st century [1]. In terms of energy materials, lithium ion batteries, fuel cells and other secondary batteries with high capacity in the future have a huge development space. Fuel cells have a wide range of applications. In the electrocatalytic hydrogen production process, hydrogen is generated by hydrogen evolution reaction, which has serious cathodic polarization phenomenon and requires high overpotential. Therefore, we need to find and study some efficient electrocatalysts to reduce the high overpotential during the reaction. Therefore, it is necessary to find electrode materials with lower potential and taffel value, such as platinum. As electrocatalysts, most non-precious metals are not as good as precious metals. However, due to the rarity and high price of precious metals in nature, transition metal nickel and its alloys have become a research hotspot in this field due to their unique electronic structure [2,3].

There are many ways to produce hydrogen, such as fossil fuel production, microbial production and hydroelectricity production [4]. At present, the most important hydrogen production method is fossil fuel, which accounts for more than 90% of the hydrogen production industry each year. The raw materials for hydrogen production from fossil fuels are coal and natural gas. Fossil fuels are mainly non-renewable resources. Therefore, hydrogen production by this method is neither environmentally friendly nor sustainable, and cannot fundamentally solve the contradiction between energy and environment. Microbial hydrogen production method used by the equipment is complex, the preparation process requirements are also relatively demanding. Photodecomposition of water to produce hydrogen is environmentally friendly, but hydrogen takes a long time to produce. The method of hydrogen production by electrolysis with water is not only environmentally friendly and simple, but also has an uninterrupted production cycle, which can produce a large amount of hydrogen in a short time. Hydrogen production from hydroelectricity will gradually replace hydrogen production from fossil fuels and become the most important method for hydrogen production [5-8]. Hydroelectrolysis hydrogen production technology can solve part of the future social life may face energy shortage and ecological environment deterioration and other problems.

Ideally, the calculation by Nernst equation shows that in a reversible electrolytic water reaction, the theoretical value of the overpotential at both ends of the hydrogen evolution reaction is 0V. In the experiment, the overpotential at both ends of the hydrogen evolution electrode is 1.8V-2.0V [9]. As a result, the energy consumption of hydroelectrolysis to produce hydrogen is too high, which is difficult to be widely used in the actual industrial production process. Therefore, appropriate electrode materials are needed to reduce the energy consumption. To be precise, the main reason for limiting the development of hydrogen production from electrolytic water is the high cost. At present, among the major hydrogen preparation methods, the cost of hydrogen production from fossil fuels is the lowest. But the cost of hydrogen production from electrolysis water is much higher than that from fossil fuels [10,11]. Compared with the price of oil, the production of hydrogen from fossil fuels has a certain profit. The production of hydrogen from water has no profit, thus leading to the popularization of the production of hydrogen from water. There are mainly two factors that affect the hydrogen production effect of electrolytic water, namely energy factor and geometric factor [12]. The energy factor mainly refers to the difference in the activity of metal hydrogen evolution due to the bonding energy between metal atoms and hydrogen atoms. The geometric factor mainly refers to the ability of hydrogen evolution affected by the surface morphology and specific surface area of the material. In this experiment, the energy factor mainly depends on the catalytic effect of Ni/NiO, while the geometric factor is enhanced by bamboo-based multi-pore carbon. There are two main ways to prepare hydrogen evolution electrode materials with high catalytic properties. One is to increase the specific surface area of the electrode materials. The second is to find a resource rich and relatively inexpensive catalytic material with high electrochemical activity.

In recent years, more and more attention has been paid to biomass carbon sources. China's bamboo forest species is very rich, but the treatment of bamboo technology is not high enough to make full use of bamboo. Bamboo carbon is the product of bamboo carbonization and has a continuous three-dimensional network with large pores and micropores, which greatly increases the specific surface area of bamboo carbon [13]. Therefore, it is necessary to synthesize bamboo-based composites based on bamboo carbon. The electrochemical performance of Ni/NiO@C electrode based on bamboo carbon was studied. Potassium hydroxide was added to bamboo carbon by activation method, and it was thoroughly mixed by ultrasonic. Nickel hexahydrate chloride was added to the bamboo carbon after pore expanding to make a solution, which was mixed evenly by ultrasonic and fully adhered to the bamboo carbon in the hydrothermal reaction kettle. The Ni/NiO@C composites were prepared by calcination in a tube furnace. The structural properties of bamboo-carbon composite electrode materials were tested. The cyclic voltammetry and linear voltammetry were used to study the hydrogen evolution properties of bamboo carbon composite electrode materials.

## 2. EXPERIMENTAL SECTION

### *2.1 Materials*

Bamboo powder is made in the laboratory. Ethanol, nickel chloride hexahydrate, hydrochloric acid, potassium hydroxide, Nafion, carbon paper were all analytical reagents purchased from Shanghai Chemical Reagents Corp (Shanghai, China).

### *2.2 Preparation of porous bamboo carbon*

Weigh 3 g bamboo powder and 3.36 g potassium hydroxide into a 25 mL beaker and add 15 mL deionized water. Put it into ultrasonic cleaner, 300 W ultrasonic for 10 min, and stir with glass rod during ultrasonic process. After ultrasonic, pour the solution in the beaker into 20 mL hydrothermal synthesis reactor, put the hydrothermal synthesis reactor into the oven and heat it to 180 ºC for 5.5 h. Cooling to room temperature, and the pure bamboo carbon was obtained.

Pour the solution into a beaker and wash it with 5% HCl solution. 300 W ultrasonic for 10 min, centrifugal speed 4000 R/min rotation for 3 min. Pour away the supernatant and wash with deionized water for 2-3 times in the same way. The black solid was dried in vacuum at 60 ºC for 12 h, and the product was obtained after grinding. The bamboo carbon by pore-enlarging treatment and the porous bamboo carbon was obtained.

### *2.3 Preparation of bamboo carbon loaded* Ni/NiO *composites (*Ni/NiO@C*)*

Weigh 0.8 g bamboo powder and 0.24 g nickel chloride hexahydrate into a 50 mL beaker and add 40 mL deionized water. Put into the ultrasonic cleaner, 300 W ultrasonic half an hour. After the end of ultrasound, the solution was poured into a 50mL hydrothermal synthesis reactor and heated to 110 °C in an oven for 6h. When cooled to room temperature, pour the solution evenly into a centrifuge tube and put it in a centrifuge at a centrifuge speed of 4000 r/min for 10 minutes. Pour out the upper solution and wash it with ethanol for 2-3 times. The centrifuge speed is 4000 r/min for 10 minutes. Put the centrifuged product into a porcelain boat and put it into a tubular furnace, calcining it to 600 °C with a preset program. After cooling, the black powder is obtained. Pour the powder into a mortar and grind it, and it becomes the product Ni/NiO@C.

### *2.4 Electrode assembly*

0.04 g solid powder was put into a small centrifuge tube. 0.9 mL ethanol and 0.1ml Nafion solution were added with a pipette, and the mixture was evenly mixed with ultrasonic for 1-2 h. The carbon paper was cut into $1\times1$ cm$^2$, and the mixed slurry was evenly spread on the carbon paper. Under the irradiation of the infrared lamp, each drop was absorbed and then dropped again. After the 1 mL slurry was all spread on the carbon paper and absorbed, linear scanning voltammetry analysis and cyclic voltammetry analysis were performed at the electrochemical workstation. In this paper, a three-electrode battery system is used to test the catalytic performance of the obtained materials. The working electrode holder is the sample made above, Ag/AgCl electrode is the reference electrode, and the electrode is the carbon rod. 100 mL 1mol/L KOH solution was prepared as electrolyte with a voltage range of -0.6-0V [14].

### *2.5 Characterization*

The microstructures were observed on a Scanning Electron Microscope (Hitachi S4000, Japanese), and the bamboo carbon is sprayed with gold.

X-ray diffractometer (X'pert PRO, PANalytical) was used. The test parameters of the instrument are as follows: 36 kV, 30 mA and Cu radiation.

Nitrogen adsorption test (BET) was using the automatic physical adsorption instrument (ASAP2020, mack instruments). Isothermal physical absorption and desorption by static capacity method. The specific surface area and pore size of the sample were measured using a nitrogen desorption apparatus. A small amount of powder, about 0.1g, was vacuumed at 350°C and then tested under liquid nitrogen.

Linear sweep voltammetry is a kind of general electrochemical method. By controlling the increase of voltage over time, the change of potential current curve is recorded and observed. When the current is 10 mA, the corresponding voltage is the overpotential. The closer the voltage is to zero, the better.

In the actual measurement process, the overpotential obtained is converted to the standard hydrogen potential, which requires the use of Nengst for the redox reaction (aA+bB=cC+dD).

The calculation formula is:

$$E = E_0 - \frac{RT}{(\mathrm{n}F)\ln(\frac{[C]c[D]d}{[A]a[B]b})} \tag{1-1}$$

Where, $E_0$ is the standard electrode potential. R is the gas constant of 8.3144 J/(K·mol). T is the temperature. n is the number of electron transfer in the reaction. F is Faraday constant 96.487 J/(V·mol). [A], [B], [C], [D] are the concentrations of substance A, B, C and D, respectively.

When Ag/AgCl is the reference electrode and the reference electrode filling fluid is saturated potassium chloride, the Nenst equation can be obtained into:

$$E_{(RHE)} = E_{(Ag/AgCl)} + 0.0592pH + 0.197 \tag{1-2}$$

Cyclic Voltammetry is a relatively common electrochemical research method. By controlling the change of voltage over time, the potential current curve is recorded and observed. The type of redox reaction occurring at the electrode can be derived from the potential current curve at which the redox peak is located.

The calculation formula of specific capacitance is:

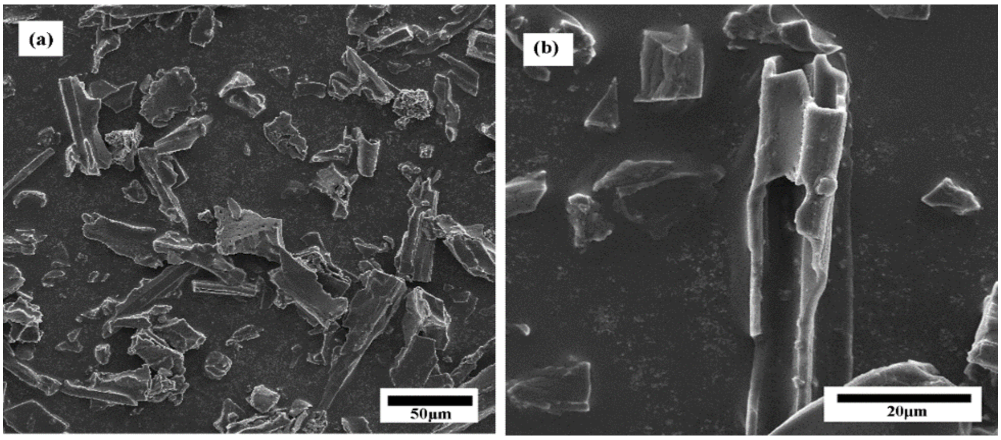
$$Cs = I\Delta t/m\Delta V \tag{1-3}$$

Where I(A) is the charge-discharge current. Δt for discharge time. m is the mass of the active substance in the electrode material. ΔV is the discharge voltage range.

The cyclic voltammetry is to discuss the reaction of capacitor electrode after applying triangular waveform potential. The applied control signal is potential, and the measured corresponding signal is current. It is mainly to study the change rules of I-t and I-U. The relation curve of U-I can be obtained by observing the T-t graph [15].

## 3. RESULTS AND DISCUSSION

The morphology and structure of bamboo carbon were characterized by scanning electron microscopy (SEM) as shown in the figure above. Figure 1 shows that bamboo carbon exhibits a loose structure. Bamboo carbon particles in ethanol solution dispersity is good, the particle size itself is large, basically in micron particles.



**Fiure 1.** SEM photographs of bamboo carbon with different magnification ratios. (a) 500X, (b) 2000X.

X-ray diffraction analysis can be used to further understand the crystal structure of bamboo carbon. In Figure 2, there are two relatively wide graphitized carbon peaks at 25° and 44°, which are most likely characteristic peaks shown on hexagonal lattice (002) and (101) crystal planes, indicating that there are many free carbons in bamboo carbon. According to the Bragg equation 2dsin=n, the d value is 3.52a and 2.02a respectively, indicating that the bamboo carbon is carbon with a six-carbon ring [16].

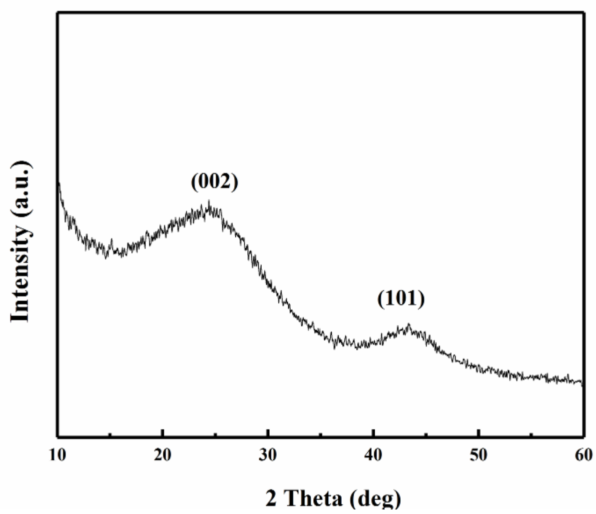


**Figure 2.** XRD analysis of bamboo carbon

From the adsorption/desorption curve of bamboo carbon, it can be seen that bamboo carbon has obvious adsorption effect under low pressure (<0.1, relative pressure P/P0) which indicated that there are a large number of micropores in bamboo carbon particles. In the low pressure area, the adsorption-desorption curves were similar which indicated that the micropores of bamboo carbon were mainly obtained by water heat treatment. In the high pressure area (>0.8, relative pressure P/P0), the nitrogen adsorption effect was obvious, indicating that the specific surface area of bamboo carbon was large.

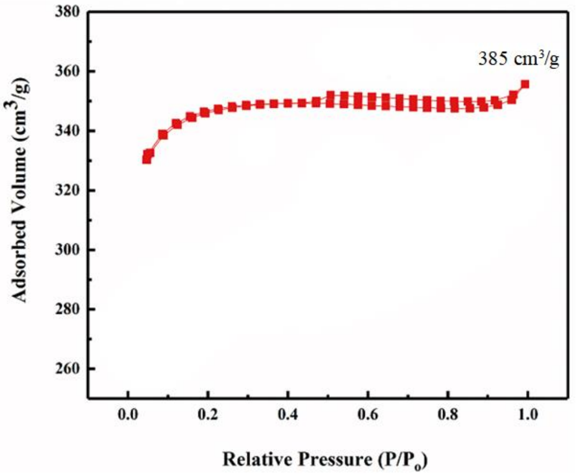


**Figure 3.** Nitrogen adsorption/desorption curves of bamboo carbon

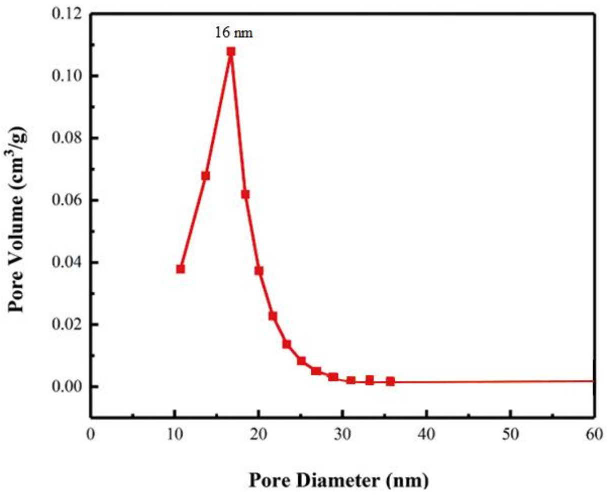


**Figure 4.** Aperture distribution of bamboo carbon

The pore structure of bamboo carbon can be clearly seen from the pore diameter distribution of bamboo carbon in Figure 3 and 4. It can be seen from the figures that bamboo carbon particles have a large nitrogen adsorption peak at about 16 nm. Nitrogen adsorption and desorption results showed that the adsorption volume of bamboo carbon was up to 385 cm$^3$/g. Compared with other mesoporous carbon materials reported in the literature [17-19], the specific surface area of bamboo carbon is relatively small and the number of electrochemical activity points provided by bamboo carbon is also small. This point needs to be further improved in the later study.

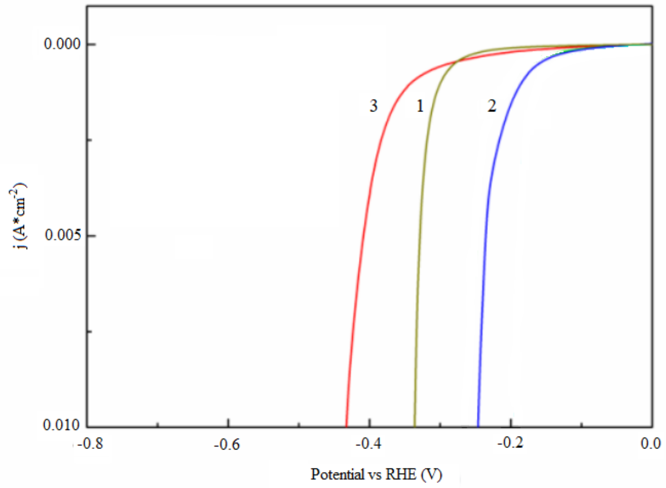


**Figure 5.** LSV analysis diagram of bamboo carbon and loaded Ni/NiO composites. 1-Bamboo carbon by pore-enlarging treatment. 2-Ni/NiO@C. 3-Pure bamboo carbon. The reference electrode was Ag/AgCl standard electrode. Electrolyte was 1 mol/L KOH solution, and the scanning rate was 0.01V/S.

It can be seen from the figure 5 that the LSV hydrogen evolution curve of pure bamboo carbon, bamboo carbon by pore-enlarging treatment and Ni/NiO@C is obtained. The potential at the current of 0.010 A is taken as the overpotential, and the overpotential is 0.431V, 0.345V and 0.249V from large to small. It can be seen from the figure that the bamboo carbon material loaded with Ni/NiO has the optimal catalytic activity. In the electrocatalytic process, the abundant active sites on the surface of bamboo carbon materials accelerate the reaction rate of HER and further reduce the hydrogen evolution reaction should overpotential, thus has a better catalytic activity.

The comparsion of bamboo carbon and loaded Ni/NiO composites and other electrode materials were added in table 1.

**Table 1.** The specific capacity comparison of several common cathode materials

| Cathode materials | Overpotential (V) |
|---|---|
| Pure bamboo carbon | 0.431 |
| Bamboo carbon@Ni/NiO | 0.345 |
| Lignin carbon fibre [20] | 0.442 |
| Lignin carbon fibre@Ni/NiO[20] | 0.326 |
| VA-NCNT[21] | 0.302 |
| NOMGAs[22] | 0.317 |
| C-PDDA[23] | 0.358 |
| Traditional petroleum carbon | 0.514 |

As can be seen from table 1, the traditional petroleum carbon have a higher overpotential but bamboo carbon has a low overpotential. The degree defects and activity points of electrochemistry in bamboo carbon are much higher than that in petroleum carbon.

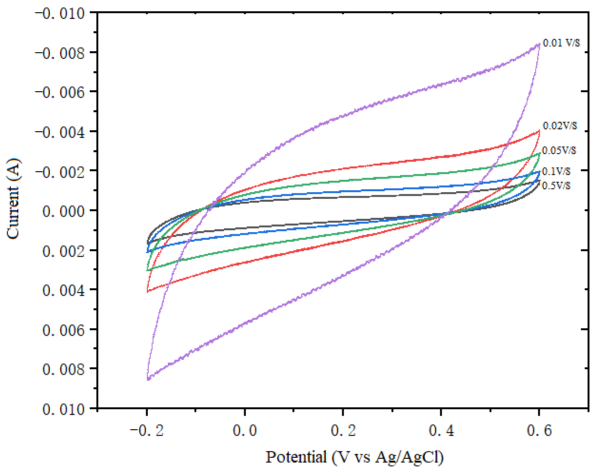


**Figure 6.** Cyclic voltammograms of pure bamboo carbon. Scanning rate: 0.01V/S, 0.02V/S, 0.05V/S, 0.1V/S, 0.5V/S. Scanning voltage 0-0.7 V. The reference electrode was Ag/AgCl standard electrode. Electrolyte was 1 mol/L KOH solution

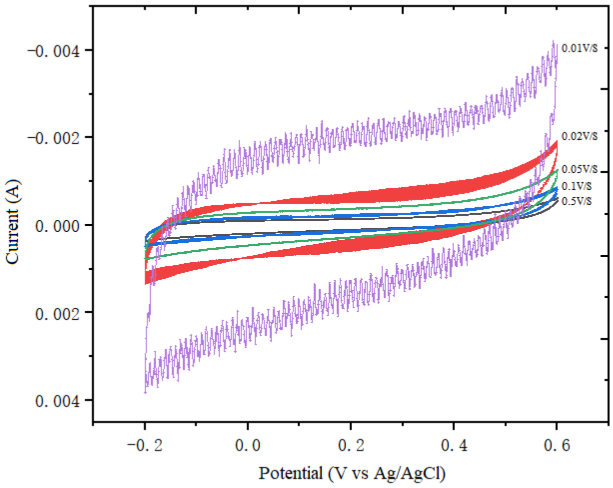


**Figure 7.** Cyclic voltammetry of bamboo carbon by pore-enlarging treatment. Scanning rate: 0.01V/S, 0.02V/S, 0.05V/S, 0.1V/S, 0.5V/S. Scanning voltage 0-0.7 V. The reference electrode was Ag/AgCl standard electrode. Electrolyte was 1 mol/L KOH solution

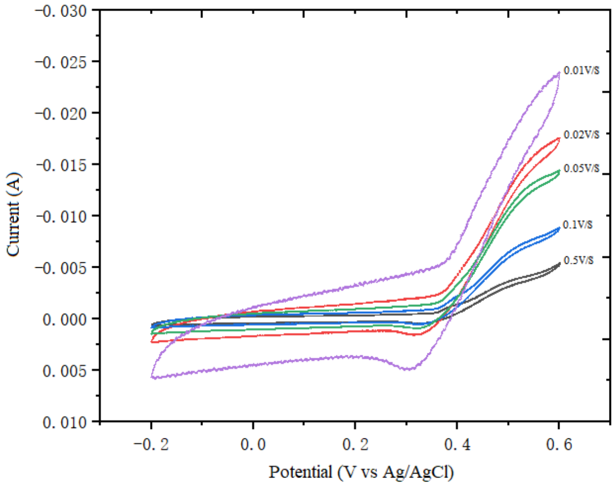


**Figure 8.** Cyclic voltammograms of Ni/NiO@C. Scanning rate: 0.01V/S, 0.02V/S, 0.05V/S, 0.1V/S, 0.5V/S. Scanning voltage 0-0.7 V. The reference electrode was Ag/AgCl standard electrode. Electrolyte was 1 mol/L KOH solution

The introduction of transition metals and their oxides significantly reduce the electrochemical degree of composite materials and provide a prerequisite for hydrogen evolution reaction. It can be seen from the table that carbon fiber materials and special structural carbon materials, showing a lower degree in overpotential, which provide a new ideas for the design of electrochemical hydrogen evolution electrode.

CV test in this subject is mainly used for activating electrodes. The electrode scanning rates were 0.01 V/S, 0.02 V/S, 0.05 V/S, 0.1 V/S and 0.5 V/S, respectively. By comparing the overpotential of the current density at 0.010 A, it can be seen clearly that the CV curves of several groups of samples show obvious rectangular characteristics and conform to the cyclic voltammetry curve of carbon materials. It can also be seen from the figure 6 that there is a redox peak between 0.2-0.4V. It can be concluded that redox reaction occurs when the material is tested by cyclic voltammetry. There is also electrode reaction occurring [24]. As can be seen from the above three figures, the overall area of the reaming bamboo carbon loaded with Ni/NiO is obviously smaller than that of pure bamboo carbon, and the reaming bamboo carbon loaded with Ni/NiO is not only stable, but also has increased electrochemical activity. The cyclic voltammetry curves of bamboo carbon samples have obvious rectangular characteristics. Since it does not contain nickel oxide, there is no oxidizing return during the cycle. Therefore, there is no redox peak in the cyclic voltammetry curve, which is in sharp contrast to the cyclic voltammetry curve of nickel oxide supported. As can be seen from figure 8, due to the addition of nickel oxide, the cyclic voltammetry curve presents a symmetric redox peak. There are oscillations in CV curves, which indicate that the electron transfer is reversible. The anodic peak occurs because of the oxidation reaction. NiO and $OH^-$ combine to lose electrons and become NiOOH, while the cathode peak occurs in the opposite way.

## 4. CONCLUSIONS

Bamboo carbon was used as raw material, and its powder were expanded by activation method. Then Ni/NiO was loaded on the porous bamboo carbon to form Ni/NiO@C composites. Using biomass bamboo carbon as raw material, SEM, BET and other characterization methods showed that bamboo carbon particles had a high specific surface area, up to 385 $m^2/g$. The XRD results show that bamboo carbon is a six-member carbon ring structure, which contains not only a large number of free carbon, but also nitrogen doping successfully. It is found that nickel oxide or nickel oxide loaded on carbon has relatively excellent performance as catalytic electrode materials, but there are few reports that both of them are loaded on carbon materials at the same time. The final results of this experiment show that the superpotential at a current of 0.010 A is only 0.249 V, as can be obtained from the linear scan voltammetry curve. It can be seen from the linear scanning voltammetric curve and cyclic voltammetric curve that the properties and stability of bamboo carbon materials by pore-enlarging treatment are better than without reaming, indicating that the activation of potassium hydroxide improves the properties of bamboo carbon.

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