Preparation and Catalytic Performance of Ni/NiO@C and SiO₂@C Composites as using Bamboo as Carbon Source for Hydrogen Evolution Reaction

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With the depletion of traditional fossil energy and the deterioration of the earth's ecological environment, the development of clean and renewable new energy is worthy of attention. Compared with traditional fossil energy, hydrogen energy has the advantages of high combustion calorific value, abundant resources, wide sources, green environmental protection, clean and renewable, easy storage and so on. In the field of hydrogen production, electrolysis of water for hydrogen production has the advantages of simple operation equipment and preparation process, relatively high purity and yield of products, and non-toxic by-products. However, the disadvantage is that in the actual electrolysis process, there is a large overpotential on the electrode, which leads to excessive power consumption, high economic cost and seriously hinders its large-scale commercialization. Therefore, the development of cheap, efficient, stable and low overpotential electrocatalyst is of great significance to improve the economic benefits of electrolytic aquaculture. In this project, Ni/NiO@C and SiO₂@C composite catalytic materials were synthesized by loading nickel oxide on bamboo carbon materials and silica on bamboo carbon materials as electrodes. The main raw material is bamboo carbon powder, which is expanded by chemical activation method. NiO and SiO₂ with the same molar concentration are loaded on the expanded bamboo carbon by hydrothermal method to form Ni/NiO@C and SiO₂@C composite catalytic materials. Scanning electron microscopy, cyclic voltammetry and linear sweep voltammetry were used for analysis. The cyclic voltammetry curves show that the Ni/NiO@C and SiO₂@C composites have symmetrical redox peaks, good cyclic stability and reversibility, and good electrochemical properties. The overpotential at 1mA was obtained from the linear sweep voltammetry curve. The mass ratio of SiO₂ in SiO₂@C composite was 5%, 15%, 30% and 50%, which were 0.563V, 0.577V, 0.584V and 0.586V respectively. The molar concentration of SiO₂ in 1.5% Ni/NiO@C composite was 0.588V. The cyclic voltammetry curves of Ni/NiO@C and SiO₂@C composites with the same molar concentration show that SiO₂@C composites have more obvious symmetrical redox peaks. The linear sweep voltammetry analysis shows that the overpotential at 1mA of SiO₂@C composites is smaller than that of Ni/NiO@C composites, and the Tafel slope is also smaller than that of Ni/NiO@C composites The reversibility and electrochemical performance of SiO₂@C composite are better than that of Ni/NiO@C composite.

1. INTRODUCTION

The rapid consumption and gradual depletion of traditional mineral and other energy sources, as well as the impact of excessive carbon dioxide emission on the earth's climate and the damage to the ecosystem, make the development of clean, renewable and new energy sources appear particularly important [1]. However, solar, wind and tidal energy, which are typical of clean and renewable energy sources, have been severely restricted in their large-scale application due to their intermittent nature, geographical limitations and inconvenient storage and transportation. Therefore, it is extremely urgent to develop efficient, green and sustainable new energy to replace traditional fossil energy. Compared with traditional fossil energy, hydrogen energy has the advantages of high combustion calorific value, sufficient resources, wide source, green environmental protection, clean and renewable, easy to store and so on, and has a good development trend in the future [2-5].

At present, there are many ways to obtain hydrogen in industry. Among them, hydrogen production by electrolysis of water has potential application value in hydrogen production industry in the future because of simple operation equipment and preparation process, relatively high product purity and yield, non-toxic by-product generation and clean and pollution-free in the whole preparation process [6-8]. However, there is a fly in the ointment, in the actual production process, due to the large overpotential on the electrode, resulting in excessive energy consumption, and high cost, which restricts the large-scale promotion and application of water electrolysis hydrogen production technology. Precious metals have special electronic structure with less d orbital electrons, and have appropriate strength to the reaction intermediates, which is conducive to the adsorption and desorption of intermediates. Although platinum (Pt)/carbon (C) catalysts have been used in the commercial water electrolysis and hydrogen production industry, their large-scale commercial application is seriously hindered by the limited reserves and high price of precious metals [9]. Therefore, the development of cheap, efficient, stable and low overpotential electrocatalysts is particularly important for the improvement of economic benefits of electrolysis aquaculture.

Hydrogen energy has many advantages to become the clean energy of the future mainly reflected in the following three aspects [10-13]. First of all, it has abundant sources and no geographical restrictions. It can be extracted from hydrogen-containing compounds and extracted from renewable or fossil energy sources. Since renewable energy sources such as water are everywhere, it has no geographical restrictions and sources. Secondly, it has high energy density and is convenient for storage. The mass energy density of hydrogen is 122 KJ/g, which has high calorific value. Hydrogen can be stored in large quantities and the storage operation is not complicated [14]. Final green, clean, renewable, hydrogen reaction product is water, there is no pollution of the environment, is the real "zero emissions". The water also can produce hydrogen electrolysis has an infinite loop, hydrogen diffusion ability, when leakage occurs, can spread quickly to avoid harm and no any toxic hydrogen, will not pollute the air, achieves truly for the protection of the ecological environment. Hydrogen energy can be obtained by fossil fuel combustion, biological fermentation, light decomposition of water, electrolysis of water and other methods [15-17]. From the above preparation methods, the fossil fuel combustion hydrogen

production method is the most mature, but obviously this hydrogen production method is very polluting and destructive to the environment and does not have sustainable development. However, although biological fermentation and photodecomposition of water to produce hydrogen are environmentally friendly, they are difficult to be applied on a large scale due to the problems of sustainability, stability and low energy conversion efficiency [18]. In contrast, the method of hydrogen production by electrolysis of water is not only environmentally friendly, but also has simple operation equipment and preparation process, relatively high product purity and yield, non-toxic by-product generation and clean and pollution-free in the whole preparation process. However, there is a large overpotential on the electrode in the actual electrolysis process, resulting in high energy consumption and high economic cost [19]. Therefore, it is important to develop low cost, high efficiency and low overpotential electrocatalysts.

Carbon-based materials (such as graphene, carbon nanotubes, fullerenes, carbon fibers and graphitized carbon nitrification) have been widely used in renewable energy storage and conversion fields such as electrocatalysis, photocatalysis and bio-fuel cells due to their unique properties (such as considerable electrical conductivity, strong corrosion resistance and environmental protection, etc.) [20-24]. Such carbon materials themselves are almost catalytic inert, so they are usually combined with other active materials to be loaded on conductive fluid collectors, or used as structural support to disperse and support catalysts, and can also improve the electron transport performance of catalysts [25]. In addition, since graphene and carbon nanotubes are easy to be functionalized, their surface can be functionalized with functional groups to improve their intrinsic activity, or non-metallic heteroatoms (such as B, N, S, Se and P) can be doped to achieve the goal of regulating the electronic structure of carbon materials and optimizing their electrocatalytic activity [26].

The electrocatalysts on the market are mainly platinum or platinum alloys. However, the price of platinum is very high, and the processing and reuse of platinum is complicated, which makes it difficult to popularize. In order to solve the problem, the low-cost non-(expensive) metal catalyst is proposed to replace the precious metal catalyst, so as to scientifically and efficiently reduce the cost and promote the commercial application. However, various metal catalysts often need to be loaded with various carbon-based materials, and the active position of metal catalysts itself is on the surface of carbon materials. Therefore, the study of carbon composite electrocatalysts plays a key role in the future application and development of electrocatalysts [27].

In this paper, two kinds of Ni/NiO@C and SiO_2@C composites were prepared based on bamboo carbon. Scanning electron microscope (SEM) was used to analyze and characterize the catalytic performance of Ni/NiO@C and SiO_2@C composites with the same molar concentration and SiO_2@C composites with SiO_2 content of 5%, 15%, 30% and 50% respectively. The bamboo-carbon composite electrode material was studied with a scanning electron microscope, cyclic voltammetry and linear sweep voltammetry.

2. EXPERIMENTAL SECTION

2.1 Preparation of porous bamboo carbon material

Grinding the bamboo carbon into about 1 micron. And weigh 5g bamboo toner into a 50ml beaker and add 30ml hydrochloric acid of 36.0-38.0%. The glass rod was used in the fume hood to stir for 30 min and then stood for 12 h. Wash 4-5 times using deionized water for 5 minutes at a centrifugal speed of 2000 r/min. Put into 60 °C oven for 24h drying, drying products with agate mortar grinding is porous bamboo carbon material.

2.2 Preparation of Ni/NiO@C composites as using Bamboo as Carbon Source

0.8g bamboo carbon and 0.24g nickel chloride hexahydrate were respectively weighed by an electronic balance and added to a 50 mL beaker, and 40mL deionized water was added. Cover the beaker with plastic wrap and place it in an ultrasonic cleaner for 30min at 300W. The mixed ultrasonic solution was poured into 50mL hydrothermal synthesis reactor and then put into the oven to heat up to 110°C for 6h. Allow to cool to room temperature, centrifuge with ethanol at 4000r/min for 10 minutes and wash 2-3 times. Put the oven at 60°C for 12h to dry, and grind the dried products with agate mortar. The grinding products were placed in a porcelain boat, placed in a tubular furnace to set the program and calcined to 600°C. After cooling, the black powder obtained was poured into an agate mortar and then ground again to form Ni/NiO@C composites as using Bamboo as Carbon Source.

2.3 Preparation of SiO$_2$@C composites as using Bamboo as Carbon Source

Use A 10 mL measuring cylinder to measure 1.65 mL tetraethyl orthosilicate into 50 mL A beaker, use A 25 mL measuring cylinder to measure 16.5 mL anhydrous ethanol into 50 mL A beaker, use an electronic balance to weigh 0.5g bamboo toner into 50mL A beaker, Add the rotor and cover the top of A beaker with plastic wrap. Then put it into A constant temperature magnetic stirrer and stir at 25°C for 10min. Use a 10 mL measuring cylinder to measure 4.7 mL anhydrous ethanol and 3.5ml ammonia respectively and add them to a 50v mL B beaker; use a 25ml measuring cylinder to measure 19ml deionized water and add them to a 50mL B beaker. Pour the solution of BEaker B into the stirred beaker A and stir it at 25°C for 30min. Add 0.012 mL silane coupling agent to the stirred solution and pour it into 50mL hydrothermal synthesis reactor. Then put it into the oven and heat it to 180°C for 6h. Allow to cool to room temperature, centrifuge with ethanol for 20 minutes at a rate of 4500r/min and wash 2-3 times. Put the oven at 60°C for 12h to dry, and grind the dried products with agate mortar. The grinding products are placed in a porcelain boat, placed in a tubular furnace to set the program and calcined to 600°C. After cooling, the black powder obtained is poured into the agate mortar and then ground again, which is SiO$_2$@C composite material. Above is the preparation method of SiO$_2$@C composites with the same molar concentration as Ni/NiO@C composites, in which the mass percentage of silica is 50%, and then the mass ratio of SiO$_2$@C composites with 5%, 15% and 30% are prepared by the same method.

2.4 Structure and electrochemical properties of the composites

2.4.1 Scanning electron Microscopy (SEM)

SEM is a kind of electron microscope technology that uses the focused electron beam to scan the surface, so as to obtain the morphology, composition, crystal structure, electronic structure and other physical and chemical properties of the sample itself. The microstructure, crystal structure and element distribution of the material were observed by scanning electron microscope.

Test method: The sample is coated with conductive adhesive and sprayed with gold. The scanning electron microscope was used.

In this paper, the microstructures of bambus-carbon porous material, Ni/NiO@C and SiO$_2$@C composites observed on a Scanning Electron Microscope (Hitachi S4000, Japanese) and a Transmission Electron Microscope (JEM-100CX II, Japanese).

2.4.2 Cyclic voltammetry analysis (CV)

CV is a common electrochemical research method, which is used to test the electrode potential with different speeds and times of triangular waveform [28]. This method is mainly used to determine the electrode surface reaction process and reaction reversibility.

Sample preparation: 0.04g sample was weighed and put into the centrifugal tube. 0.9mL anhydrous ethanol and 0.1mL Nafion solution were added into the sample with a pipette gun. Ultrasound was applied for 1-2h to disperse the samples evenly. The carbon paper was cut into a size of 1×1cm^2, and the ultrasonic dispersion solution was uniformly dropped onto the carbon paper under infrared light irradiation until 1mL of the mixed solution was completely absorbed by the carbon paper. The fully absorbed carbon paper was dried in a vacuum oven for 24h and then analyzed by cyclic voltammetry at the electrochemical workstation.

In this paper, the beaker type three electrode battery system was used to test the bamboo carbon porous material, Ni/NiO@C and SiO$_2$@C composites by cyclic voltammetry at room temperature. The sample was prepared by working electrode, the Ag/AgCl electrode was the reference electrode, the carbon rod was the counter electrode. Using 50mL 1mol/L KOH solution as electrolyte, the scanning rates of 0.5V/S, 0.1V/S, 0.05V/S, 0.02V/S and 0.01V/S were used, and the voltage range was -0.2-0.6V.

2.4.3 Linear Sweep Voltammetry (LSV)

LSV is a linear change of voltage applied to the electrode. That is electrode potential, recording the linear change of electrolytic current and applied voltage [29]. The potential current curve is recorded and observed through a linear relationship. The purpose of the test is to verify the catalytic performance of the prepared sample by comparing the overpotential of the material at the current density of 10 mA.

Sample preparation: 0.04g sample was weighed and put into the centrifugal tube. 0.9mL anhydrous ethanol and 0.1ml Nafion solution were added into the sample with a pipette gun. Ultrasound was applied for 1-2h to disperse the samples evenly. The carbon paper was cut into a size of 1×1cm^2,

and the ultrasonic dispersion solution was uniformly dropped onto the carbon paper under infrared light irradiation until 1mL of the mixed solution was completely absorbed by the carbon paper. The fully absorbed carbon paper was dried in a vacuum oven for 24h and then analyzed by linear sweep voltammetry at the electrochemical workstation.

In this paper, the beaker type-three electrode battery system was used at room temperature to test the bamboo carbon porous material, Ni/NiO@C and SiO$_2$@C composites by linear sweep voltammetry. The sample was prepared by working electrode, Ag/AgCl electrode reference electrode, carbon rod as the counter electrode. 50mL of 1mol/L KOH solution was used as electrolyte, the scanning rate was 0.001V/S, and the voltage range was -0.6-0V.

3. RESULTS AND DISCUSSION

All the samples obtained in the experiment are black powder. In order to observe the surface morphology, structural characteristics and catalytic performance of the samples, Scanning electron microscope analysis (SEM), cyclic voltammetry analysis (CV) and linear voltammetry analysis (LSV) were used to test the samples. The results are as follows:

Figure 1 is the SEM diagram of the sample, in which Figure (a) and (b) are the bamboo carbon materials with reaming at different magnification, and Figure (c)-(f) are 5%, 15%, 30% and 50% SiO$_2$@C composites, respectively. It can be seen from the figure that bamboo carbon particles are at the micron level, while silica and nickel oxide are at the nanometer level. It can be seen from Figure (b) that the surface of bamboo carbon with reaming holes is rough, which is conducive to increasing the loading rate of nickel oxide and silica, as well as the specific surface area of the material itself. From Figure (c)-(f), it can be clearly seen that with the increase of silica content in the formula, the sio2 load on the bamboo carbon surface gradually increases. Due to the increase of silica, the surface morphology of bamboo carbon changes greatly, and the surface of SiO$_2$@C composite is concave and convex. It can be predicted that the specific surface area of the composite will also increase.
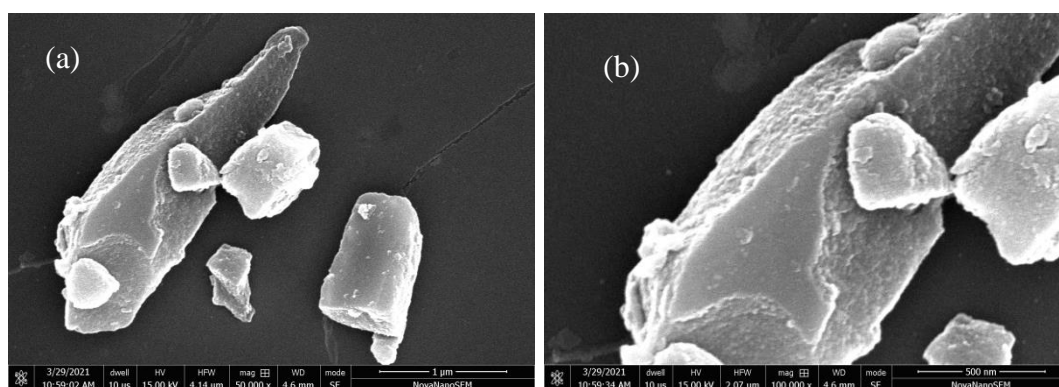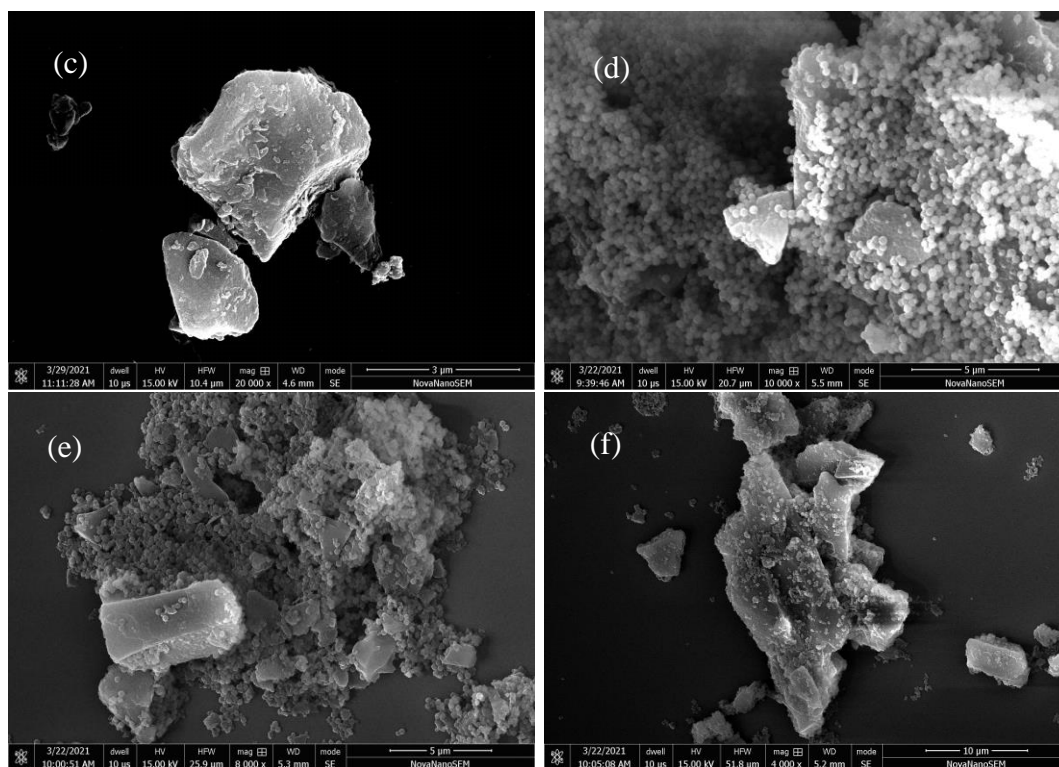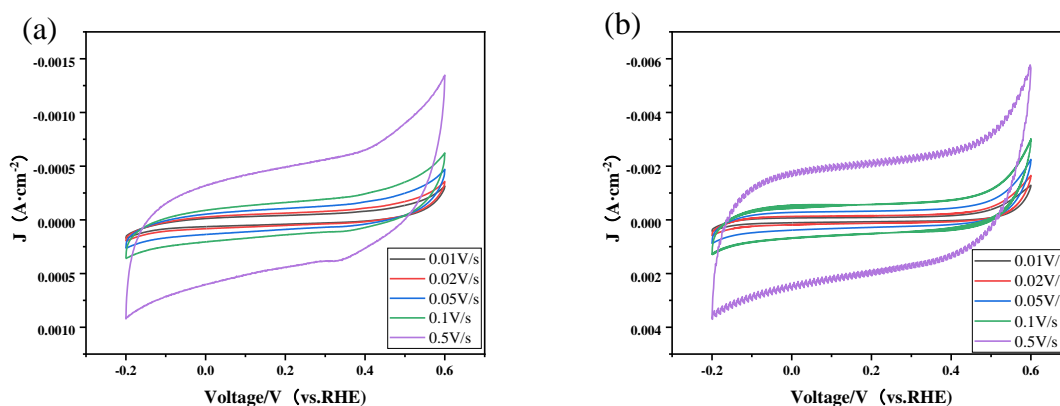
Figure 1. SEM of bamboo carbon composites: (a-b) are the bamboo carbon materials. (c-f) are 5%, 15%, 30% and 50% SiO$_2$@C composites, respectively.

Figure 2 shows the cyclic voltammetry curves of the samples, where Figure (a)-(d) are bamboo carbon material, bamboo carbon material with reaming and Ni/NiO@C and SiO$_2$@C composites with the same molar concentration respectively. From The 0.2-0.4V in Figure (a), (c) and (d), an obvious REDOX peak can be seen.
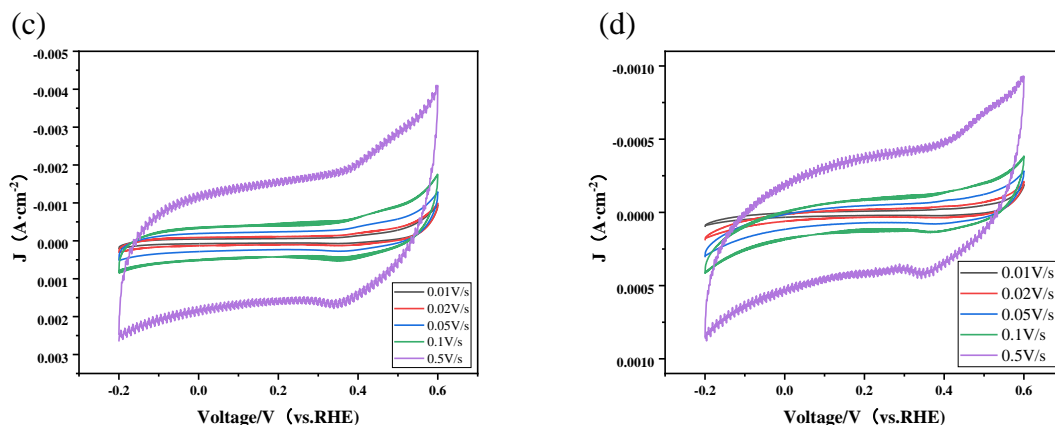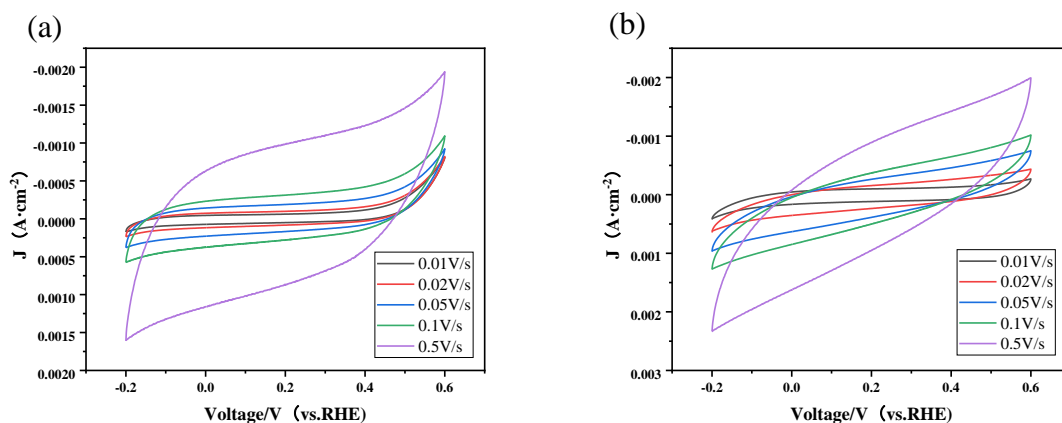
Figure 2. Cyclic voltammetric curve of bamboo carbon composites. (a) bamboo carbon. (b) bamboo carbon with reaming. (c) Ni/NiO@C composites. (d) SiO$_2$@C composites.

It can be concluded that the electrode reaction occurs when the material is tested for cyclic voltammetry, and the cyclic scanning rate increases to 0.5V/S. The current of oxidation peak and reduction peak on the curve increases, and the peak type becomes sharper. The cyclic voltammetry curves of Figure (c) and (d) show symmetric REDOX peaks, which indicate that the electron transfer is reversible [30]. Figure (d) shows a more obvious symmetric REDOX peak, from which it can be concluded that the cyclic stability and reversibility of SiO$_2$@C composites are better than that of Ni/NiO@C composites.

Figure 3 shows the cyclic voltammetry curves of the sample, in which Figure (a)-(d) are 5%, 15%, 30%, 50% SiO$_2$@C composites with silica content respectively. The REDOX peak can be seen from 0.2-0.4V in Figure (c) and (d), and it can be concluded that the electrode reaction occurs when the material is tested for cyclic voltammetry. The REDOX peak in Figure (d) is the most obvious and shows symmetry. Therefore, it can be concluded that 50% SiO$_2$@C composite material has good cyclic stability and reversibility. It also has the best electrochemical performance.
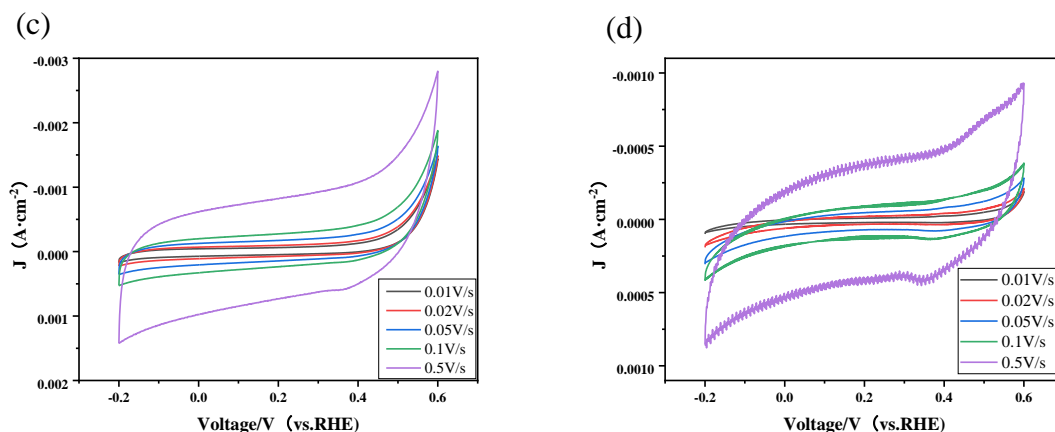
(c)

(d)

Figure 3. Cyclic voltammetric curve of bamboo carbon composites. The silica contents are: (a) 5%. (b) 15%. (c) 30%. (d) 50%.

Figure 4 is the linear sweep voltammetric curve of the sample, in which Figure (a) and (c) are the linear sweep voltammetric curve of the initial test, and Figure (b) and (d) are the linear sweep voltammetric curve of the sample after 100 cycles. In Figure (a), the overpotential at current 1mA is 0.563V, 0.577V, 0.584V and 0.586V from 5%-50%, and 0.593V, 0.588V, 0.599V and 0.599V in Figure (b), respectively. In Figure (c), the overpotential at current 1mA from $SiO_2@C$ bamboo carbon compsites are 0.586V, 0.578V, 0.575V and 0.576V successively, and in Figure (d), 0.599V, 0.593V, 0.591V and 0.591V successively. By comparing the overpotential at 1mA before and after 100 cycles, it can be found that the overpotential gap of 15% content of $SiO_2@C$ composite is the least, which indicates that 15% $SiO_2@C$ composite has more stable catalytic performance and longer catalytic life. According to the overpotential comparison at current 1mA before and after 100 cycles in Figure (b) and (d), it can be concluded that the overpotential gap of $SiO_2@C$ composites with the same molar concentration of Ni/NiO@C and $SiO_2@C$ composites is smaller, which indicates that the catalytic performance of $SiO_2@C$ composite is more stable than that of Ni/NiO@C composite. Longer catalytic life.
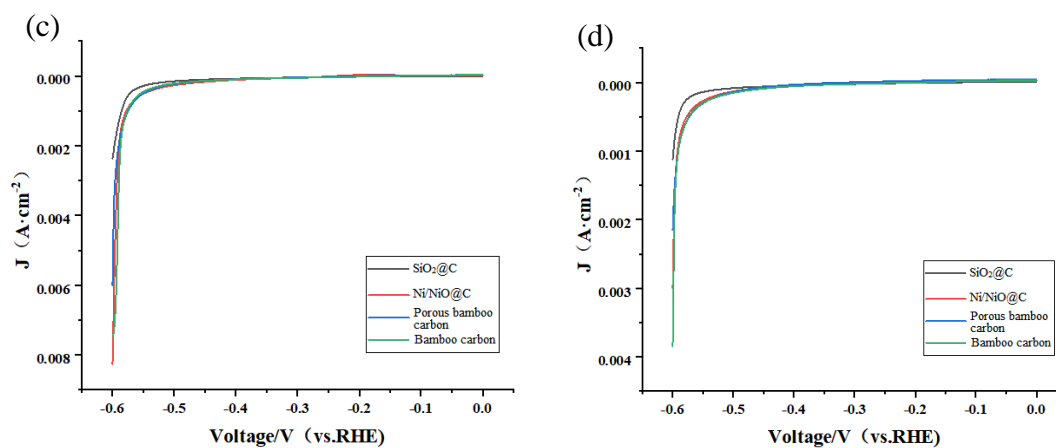
(a)

(b)

(c)　　　　　　　　　　　　　　　　　　(d)
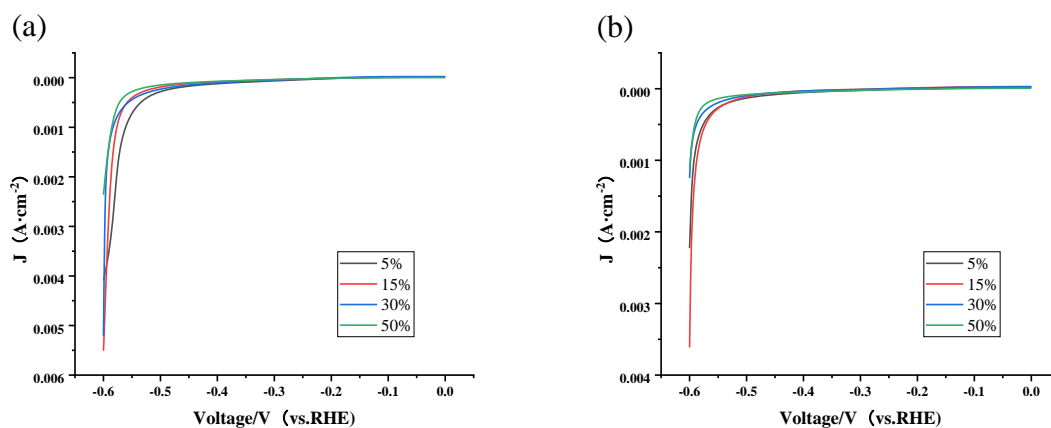
Figure 4. Linear scanning curves of bamboo carbon composites. (a) SiO_2@C composites at the initial test. (b) SiO_2@C composites after 100 cycles. (c) Bamboo carbon composites at the initial test. (d) Bamboo carbon composites after 100 cycles.

Compared with other carbon composites, as shown in Table 1. Bamboo carbon and its composites have higher overpotential. At the current of $1mA \cdot cm^{-2}$, the pure bamboo carbon, Si@C and Ni/NiO@C composites are 0.576V, 0.586V and 0.578V respectively. The polyphosphononitrile carbon sphere C-PZS is only 0.522 V, and the C-PZS@Si is 0.523V [31, 32]. The graphite carbon composites is the lowest. In conclusion, bamboo carbon and its transition metal composite materials as hydrogen evolution electrode can provide high overpotential and chemical stability, which is superior to graphite carbon and has potential application value.

Table 1. The overpotential of some carbon materials at the current of $1mA \cdot cm^{-2}$

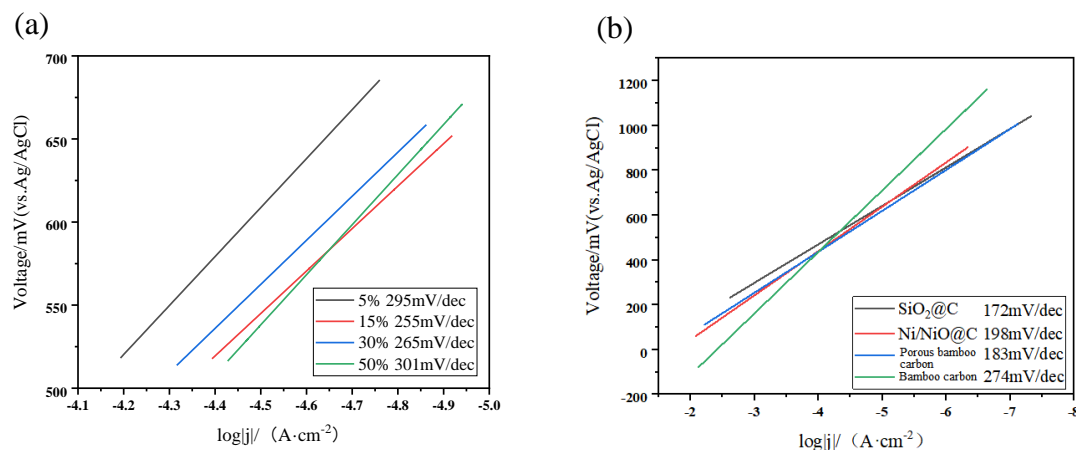| carbon materials	overpotential (V)
Bamboo carbon	0.576
Si@C composites	0.586
Ni/NiO@C composites	0.578
C-PZS composites	0.522
Ligin carbon composites [33]	0.451
Graphite carbon composites [34]	0.427

Figure 5. Tafel slope of different electrodes. (a) SiO_2@C composites with different contents. (b) Bamboo carbon composites.

Figure 5 shows the linear sweep voltammetry curve of the sample and the Tafel slope obtained by linear fitting according to the Tafel formula. Figure (a) is the Tafel slope diagram of SiO_2@C composites with different contents. It can be seen from the figure that the slope of 15%SiO_2@C composites is the smallest. This indicates that the current density increases fastest and the overpotential changes are small, and the electrocatalytic performance is the best. It can be seen from Figure (b) that the electrocatalytic performance of SiO_2@C composite is better than that of Ni/NiO@C composite. But, the Tafel slopes of all samples were greater than 116 mV·Dec^{-1} which indicating that chemical desorption was the main mechanism of hydrogen release in the electrocatalytic process [35].

4. CONCLUSIONS

At present, the production cost of electrolytic water catalysts for precious metals is high and difficult to produce in large scale. Porous bamboo carbon composites were prepared from bamboo with abundant resources as carbon sources, and combined with nickel oxide and silica respectively to study their electrochemical performance as electrolytic water hydrogen evolution catalyst. The main conclusions and novelty regarding electrochemical phenomena are summarized as follows:

SEM analysis of the carbon composites shows that nickel oxide is less loaded on the surface of bamboo carbon particles, however silica is more loaded and fully increases the specific surface area of bamboo carbon materials. Electrochemical performances of composites were analyzed by CV. Both Ni/NiO@C and SiO_2@C composites have better cyclic stability and reversibility. Although nickel oxide is less loaded, the specific capacitance of the electrode is improved and the electrochemical performance is better. The electrochemical performance of the 50% SiO_2@C composites with different contents of SiO_2@C is better. LSV was used to analyze the electrochemical performance of the samples. The results show that 15% SiO_2@C composites with different contents of SiO_2@C has more stable catalytic performance and longer catalytic life. In the same molar concentrated Ni/NiO@C and SiO_2@C

composites, the catalytic performance of $SiO_2@C$ composite is more stable and the catalytic life is longer.

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