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Effect of Pyrolysis Temperature on the Catalytic Performance of Nickel-nitrogen Doped Carbon Nanotubes for Oxygen Precipitation

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Abstract

In this experiment, nickel-nitrogen doped carbon nanotubes were prepared by using nickel oxide as a precursor, glucose as a carbon source, and urea as a nitrogen source, mixing the three and then using high-temperature in-situ reduction, and the effect of pyrolysis temperatures (750, 800, and 850 °C) on the electrochemical properties, such as OER activity and stability, was investigated. The experimental results show that the nickel-nitrogen doped carbon nanotubes prepared at 800 °C have better OER activity, better stability, smaller polarisation impedance and diffusion impedance, and larger active area, i.e. more active sites.

Keywords

Carbon Nanotubes; Water Electrolysis; Oxygen Precipitation Reaction.

1. Introduction

Energy is an important resource necessary for human survival and development, and the over-consumption of non-renewable fossil fuels and the deterioration of the environment are forcing people to vigorously develop new renewable energy sources that are safe, clean and efficient. Hydrogen energy is considered to be the best alternative to traditional fossil fuels due to its high combustion calorific value and clean combustion products. Hydrogen production by electrolysis of water is an important way of industrial hydrogen production, but it still cannot make hydrogen popularly used, the key problem is that its polarisation overpotential is too high and larger than the theoretical voltage of electrolysis of water [1]. The method to reduce the oxygen precipitation overpotential is generally through the use of electrode catalysts, however, the oxygen precipitation (OER) electrode catalysts with the best overall performance in acidic and alkaline aqueous solutions are RuO_2 and IrO_2, etc., which require the use of a number of precious metal oxides that have small reserves and high prices, severely restricting the large-scale commercial application of water electrolysis devices. Therefore, the development of OER electrocatalysts with abundant elements in the earth's reserves is an effective way to achieve efficient hydrogen production from electrolytic water [2]. Transition metal (Ni, Co, Fe, etc.) based compounds are abundant and inexpensive, possessing high OER electrocatalytic activity and stability, and have received extensive attention in the field of scientific research [3].

Water electrolysis is a technology that can effectively convert electrical energy into chemical energy. Water electrolysis involves two main reactions, i.e., OER reaction at the anode to produce oxygen and HER at the cathode to produce hydrogen. The OER reaction, which involves the transfer of four electrons, is a very slow kinetic process and requires the application of a very high overvoltage to drive the reaction [4]. The water electrolysis device consists of the following four parts respectively: external circuit, anode, cathode and electrolyte. The working principle of water electrolysis is that when a certain voltage is applied to the external circuit, H^+ migrates to the cathode and accumulates

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on the surface of the hydrogen electrode, and a reduction reaction occurs to produce H_2; at the same time, OH^- migrates to the anode and accumulates on the surface of the oxygen electrode, and an oxidation reaction occurs to produce O_2 [5].

From the development of water electrolysis until today, only IrO_2 and RuO_2, precious metals, can be used as reference standards for oxygen precipitation catalysts for water electrolysis. The properties of RuO_2 and IrO are also different, in terms of catalytic activity, RuO_2 shows better performance under alkaline conditions, and its overpotential measured at a current density of 10 mA cm^{-2} is 276 mV (1M NaOH), and from the aspect of stability test, IrO_2 shows better stability, and its overpotential is 340 mV. in practical application, although the oxygen precipitation catalytic activity of the noble metals is better, but the stability is better. In practical applications, although the oxygen precipitation catalytic activity of noble metals shows better performance, the overall poor stability, low mechanical strength, limited reserves and high price make it difficult to be applied on a large scale [7]. Transition metals, on the other hand, are also often used as catalysts due to their good OER performance in alkaline environments. Among them, nickel metal is often used as a catalyst for industrial electrolysis of water as it exhibits low overpotential in alkaline environments, excellent stability, and is much cheaper than precious metals [8].M. Plata-Torres et al. synthesised a variety of alloy catalysts such as Co_30Ni_{70}, Co_30Mo_{70}, $Ni_{30}Mo_{70}$ by using the mechanical milling method, $Co_{10}Ni_{20}Mo_70$, $Fe_{10}Co_{30}Ni_{60}$ and $Co_{10}Fe_{30}Ni_60$, and it was found that catalyst powders containing Ni and Co have better OER activity, such as $Co_{10}Ni_{20}Mo_{70}$.Carbon materials have the advantages of relative structural stability, excellent electrical conductivity, a large specific surface area, and low price, and have been widely used in many fields [9].

Nickel-nitrogen doped carbon nanotubes have good electrical conductivity, large specific surface area and more active sites due to the carbon nanotubes as the carrier, plus the synergistic effect of nickel and nitrogen nano-co-doped carbon nanotubes make nickel-nitrogen doped carbon nanotubes have a good oxygen-removing catalytic performance. This experiment mainly focuses on the stability and OER activity of nickel-nitrogen doped carbon nanotubes to investigate the electrocatalytic performance, which is important for realising the large-scale application of hydrogen energy.

2. Experimental Materials and Methods

2.1 Catalyst Preparation

Firstly, 0.05 mol of NiO, 0.06 mol of C6H12O6·H2O and 4 mol of CO(NH2)2 were accurately weighed with an electronic balance, and then they were poured into a mortar, fully ground for 1h, mixed homogeneously, and recorded as A specimen. The Ar gas was first kept flowing into the multi-station tube furnace for 20 min, and then the A specimen was loaded into a corundum boat, which was slowly pushed into the tube furnace, and heat-treated at high temperatures (750, 800, and 850 °C) with the tube furnace. The corundum boat was heated with Ar as a protective gas at a rate of 8 °C min-1 , the tube furnace was heated from room temperature to the specified temperature after 100 min and held for 300 min, and then the corundum boat was removed after cooling naturally to room temperature, and the light green powder in the corundum boat was seen to have turned into black after the corundum boat was taken out, and finally, the black product obtained was ground in a mortar and pestle for 20 min, and the products generated by the different high-temperature heat treatments were recorded as: Sample-700, Sample-800, Sample-850 and Sample-850 respectively. The products generated by different high temperature heat treatments were recorded as: Sample-750°C, Sample-800°C and Sample-850°C, respectively.The growth process of nickel-nitrogen doped carbon nanotubes is shown schematically in Figure 1.

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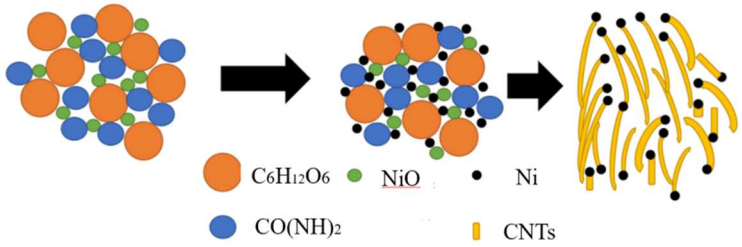

Figure 1. Schematic representation of the growth process of nickel-nitrogen doped carbon nanotubes

2.2 Material Characterisation

A Bruker D8 advance X-ray diffractometer was used to analyse the physical phase of the specimens. The experimental parameters were as follows: voltage 40 kV, Cukα rays, scanning angle from 10° to 90°, scanning speed 5°/min. The obtained data were analysed by JADE6.0 software to determine the changes in the physical phase and the integrated intensities of the different peaks.

2.3 Electrochemical Characterisation

The electrochemical properties of the materials were characterised using the Tatsunami CHI-660E electrochemical workstation, and the tests were all done under a three-electrode system electrolytic cell. The three electrode systems were working electrode (carbon paper loaded with catalyst), reference electrode (Ag/AgCl electrode) and counter electrode (Pt sheet electrode). The electrolyte was a 1 M KOH solution, and O_2 was continuously passed for at least 30 min before the test to ensure that the equilibrium potential for the O_2 reaction was constant. The corresponding response current density was measured and recorded by applying a linearly varying voltage to the working electrode. By applying a linearly varying voltage to the working electrode, the corresponding response current density was measured and recorded by linear scanning voltammetry (LSV), and the LSV was used to compare the activity of the catalysts to obtain information on their onset potentials, Tafel slopes, and reaction mechanisms [10]. The Tafel slope is used to indicate the increase of overpotential with current density, and the lower the value, the better the performance of the catalyst. The capacitance value of the bilayer calculated using cyclic voltammetry (CV) curves at different scan rates can be used to characterise the electrochemical active area (ECSA) of the catalyst [11].

3. Results and Discussion

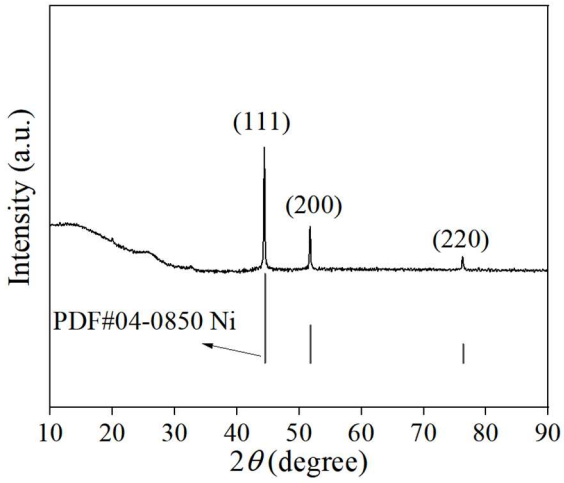

Figure 2. Schematic representation of the growth process of nickel-nitrogen doped carbon nanotubes

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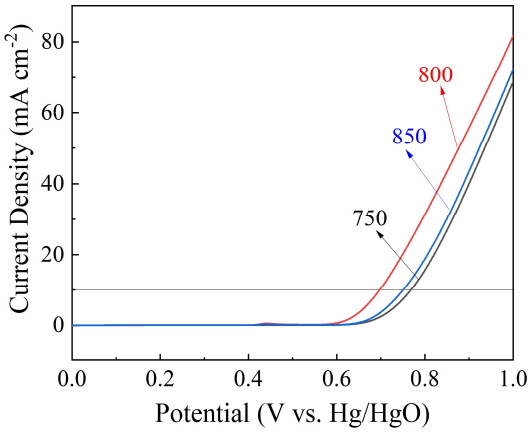
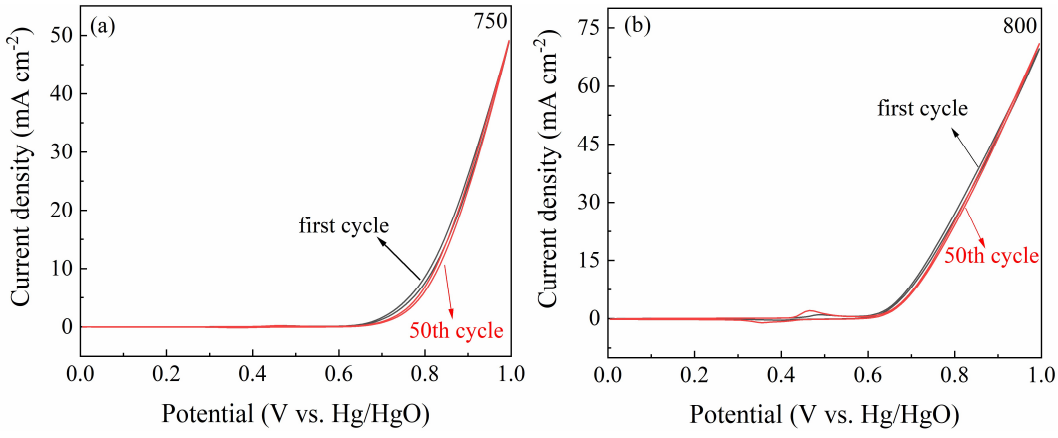


Figure 3. OER polarisation curves for Sample-750°C, Sample-800°C and Sample-850°C.

The prepared nickel-nitrogen doped carbon nanotubes were physically examined and the Xrd test results are shown in Figure 2. It can be seen from the figure that the characteristic peaks appeared at 44.5°, 51.8° and 76.3°, which can be seen from the XRD pattern corresponded to the (111), (200) and (220) crystal planes of the monolithic Ni, and the analysis of the XRD pattern can be obtained that the metallic Ni grown on the carbon nanotubes corresponded to the This indicates that the nickel nanoparticles have been successfully doped onto the carbon nanotubes.

Figure 3 shows the OER polarisation curves at Sample-750 °C, Sample-800 °C and Sample-850 °C. The nickel-nitrogen doped carbon nanotubes prepared at 750, 800, and 850 °C have overpotentials corresponding to current densities of 0.768, 0.7, and 0.751 V for a current density of 10 mA cm^{-2} , respectively. the current densities corresponding to a potential of 1 V are 67.13, 81.68, and 72.17 mA cm^{-2} , respectively. this suggests that the nickel-nitrogen doped carbon nanotubes prepared at 800 °C are the possessing the smallest potential of 0.7 V at 10 mA cm^{-2} among the three, and again possessing the largest current density of 81.68 mA cm^{-2} at a potential of 1 V, indicating that the nickel-nitrogen doped carbon nanotubes prepared at 800 °C exhibit better catalytic properties and the OER activity prepared at 800 °C is the best.

Figure 4 shows the comparison of the OER polarisation curves of Ni-N doped carbon nanotubes prepared at 750, 800, and 850 °C for the 1st and 50th turns after fifty turns of CV cycling, respectively, and the polarisation curves of the 1st and 50th turns after fifty turns of CV cycling for Sample-850 °C and Sample-800 °C show minimal deviation, indicating that the two have good stability. The potential corresponding to 10 mA cm-2 of Sample-750°C only deviated by 0.01 V after 50 turns of cyclic voltammetry, indicating that its stability is also good. This indicates that the Ni-N doped carbon nanotubes generated by pyrolysis in the range from 750 °C to 850 °C have good stability.



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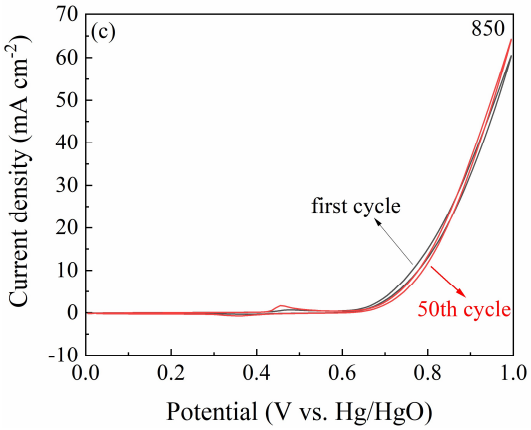

Figure 4. Comparison of 1st loop cyclic voltammetry and 50th loop cyclic voltammetry OER polarisation curves for Sample-750°C, Sample-800°C and Sample-850°C

Figure 5 shows the trend plot of potential versus time for nickel-nitrogen doped carbon nanotubes prepared at 750, 800, and 850 °C at a current of 10 mA. The change in electrode potential with time was recorded for 30 min at a constant current of 10 mA to assess the stability of the electrode material. From Fig. 4, it can be seen that the electrode potential of the nickel-nitrogen doped carbon nanotubes prepared at 750 °C decreases from 0.13 V to 0.008 V with a decline of 93.12 % at a current of 10 mA, the electrode potential of the nickel-nitrogen doped carbon nanotubes prepared at 800 °C decreases from 0.225 V to 0.208 V with a decline of 7.39 %, and the electrode potential of the nickel-nitrogen doped carbon nanotubes prepared at 850 °C decreased from 0.188 V to 0.1067 V with a decline of 43.08 %, and the comparison shows that the nickel-nitrogen doped carbon nanotubes prepared at 800 °C have the best stability [12].

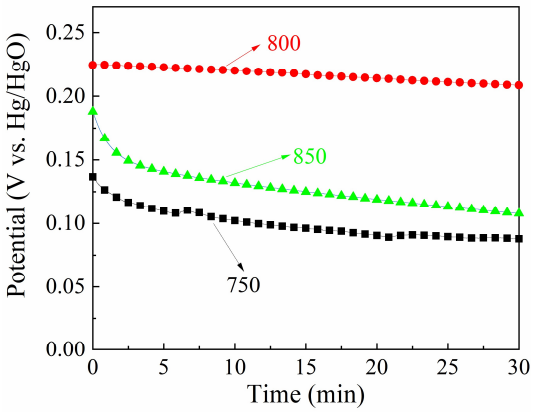

Figure 5. Trend of potential with time for Sample-750°C, Sample-800°C and Sample-850°C at a current of 10 mA

Figure 6 shows the electrochemical impedance plots of nickel-nitrogen doped carbon nanotubes prepared at 750,800,850 °C at open circuit potential and 0.8 V potential. Figure 6(a) shows the impedance plots of nickel-nitrogen doped carbon nanotubes prepared at the three temperatures in the open-circuit state, showing that the intercepts in the x-axis are essentially the same, which suggests that the ohmic impedance of the nickel-nitrogen doped carbon nanotubes at 750,800,850 °C is about the same, and the straight line of the plots trends upwards due to the fact that it has a diffusion impedance, and the slopes of the nickel-nitrogen doped carbon nanotubes prepared at 800 °C are higher than that of the nickel-nitrogen doped carbon nanotubes prepared at The slope of Ni-N doped carbon nanotubes prepared at 800 °C is smaller than that of Ni-N doped carbon nanotubes prepared at 750,850 °C. From the magnitude of the slope, it can be judged that the Ni-N doped carbon

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nanotubes prepared at 800 °C have the smallest diffusion impedance. Fig. 6(b) shows the impedance plot at a potential of 0.8 V. The difference (absolute value) between the two intercepts in the x-axis of the nickel-nitrogen doped carbon nanotubes prepared at 750, 800, and 850 °C is 9.67, 7.59, and 9.35 Ω. This indicates that the nickel-nitrogen doped carbon nanotubes prepared at 800 °C have the smallest polarisation impedance as compared to the ones prepared at 750 °C, the ones prepared at 800 °C The performance of the nickel-nitrogen doped carbon nanotubes prepared at 800 °C is superior to that of the nickel-nitrogen doped carbon nanotubes prepared at 850 and at 750 °C.

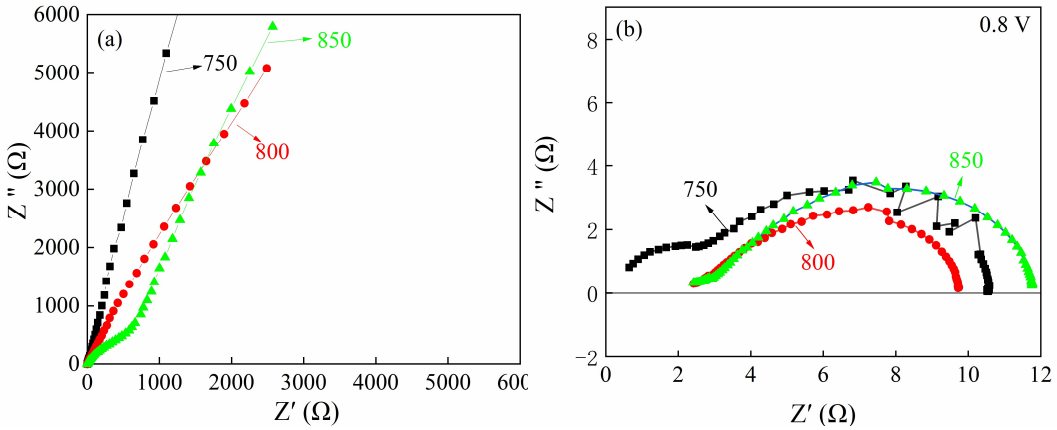

Figure 6. Electrochemical impedance plots of Sample-750°C, Sample-800°C and Sample-850°C at potentials of (a) open-circuit voltage (b) 0.8 V

4. Conclusion

1) Nickel-nitrogen doped carbon nanotubes can be successfully prepared by high-temperature in situ reduction with nickel oxide as the precursor, glucose as the carbon source, urea as the nitrogen source, and Ar as the protective gas.

2) By comparing the difference in activity of nickel-nitrogen doped carbon nanotubes prepared at 750, 800, and 850 °C, it was found that the prepared nickel-nitrogen doped carbon nanotubes at 800 °C have better oxygen precipitation catalytic performance compared to those prepared at 750 °C and at 850 °C.

Acknowledgments

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