

Preparation and electrocatalytic property of nickel plating graphene

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Graphene oxide (GO) was synthesized by a modified method. The different nickel plating graphene samples with diverse amount of nickel plating are synthesized by a novel method. The three-electrode system electrochemical workstation (CHI670) is used to test the electrochemical property through the cyclic voltammetry curve and time current curve. The samples' surface morphology is characterized respectively by the scanning electron microscope (SEM) and transmission electron microscope (TEM). The sol-gel method made distinct deep color surface layer growth tightly on original sheets. When the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ involved in the reaction was 0.65 g, the samples demonstrated superior catalytic activity in comparison to other concentrations. In 0.1 M NaOH electrolyte solution, methanol oxidation peak occurred at around 0.7 V with a higher and relatively stable electric current value. The most suitable loading quantity exhibited superior electro-catalytic performance.

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1. Introduction

An outlook on future power sources recently focuses on direct methanol fuel cells (DMFC), since the DMFC has the promising potential for clean and portable power sources. Although many studies have been carried out, the DMFC still has several problems: the slow reaction rate of methanol oxidation and the severely methanol infiltration. Most groups have paid attentions to improve catalytic reactions on anode. Pt and its alloys are the most commonly used as catalyst at present [1], while the electrocatalytic activity for methanol oxidation shows undesirability as well as some intermediate product of methanol oxidation may lead to catalyst poisoning [2, 3]. Then metal composite catalyst and noble metal doping as Pt-Ru [4], Pt-Sn [5], Pt-Wox [6] have been studied. As non-noble metal catalyst, nickel possesses high hydrogenation activity, excellent mechanical strength, and especially insensitive to toxicity [7, 8].

In the last ten years, large numbers of research has been focused on graphene since it was discovered in 2004 [9, 10]. For its ultrahigh theoretical specific surface area and excellent electronic transmission performance, graphene has widely been studied in the field of electronics recent years and graphene composite material is researched to pursue a more suited capability. Following chemical modified/doped, its performance could be improved in many fields. Fang et al prepared nickel plating graphene [11] with hydrophilic treatment and chemical plating. Hu et al synthesized Ni/graphene sheets

by electroless Ni-plating [12]. For a certain supported catalyst, loading amounts maybe one of the key points determining its final catalyst activity for the same substratum. Doping quantity controls the alterable performance, and the best property needs the most proper loading amount. Finding out the proper amount of nickel, instead of noble metal catalysts, for the best electrocatalytic performance would have the potential to reduce the cost and become more economical in the field of power sources, including the DMFC.

In this paper, graphene oxide (GO) was synthesized by a modified Hummers' methods [13, 14], and the nickel plating graphene was prepared by a novel sol-gel method, testing in 0.1M and 0.5M KOH electrolyte. We investigated the correlations between anode catalytic activity of DMFC and various quantity of nickel doped in the graphene and the better suited electrolyte concentration.

2. Experimental

2.1 Preparation of graphene oxide

Graphene oxide (GO) was prepared by the modified Hummers methods. The key points in this process were the precise dosage of flake graphite, H_2SO_4 , KMnO_4 , H_2O_2 , and the time control of three stages in different temperatures. Compared with Hummers methods, NaNO_3 was not used during this process.

2.2 Synthesis of nickel plating graphene

A certain amount of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in glycol solution with the concentration of 0.5 M, then hydrazine hydrate was added to form solution A; the homogeneous GO dispersion was blended with NaOH solution in the concentration of 1M to form the solution B. Turning the temperature of water bath to 60°C , solution A and B were mixed together in another beaker placed in the water bath, followed by stirring for 40 min.

Three different amount of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were added into the solution to obtain three types of graphene nickel plating: A, 0.50 g; B, 0.65 g; and C, 0.70 g, respectively named as Sample A, Sample B, Sample C.

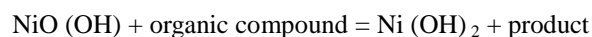
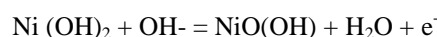
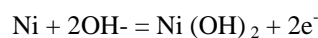
2.3 The electrocatalyst preparation

All the electrocatalyst were obtained by the same procedure: 1 mg of nickel plating graphene was dispersed in 175 μL of ethanol and sonicated for 30 min. Then 25 μL of ultrapure water and 5 μL of Nafion were added into the mixture above and sonicated for 10 min. 20 μL of final solution was spread on the electrode and dried at room temperature.

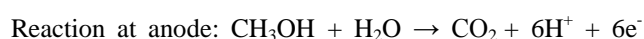
3. Results and discussion

3.1 The electrochemical performance test

All the samples were tested in two kinds of electrolyte concentration of KOH (0.1 M and 0.5 M), both of which were added with 1M NaOH (405 μL of methanol) with the scanning voltammetry conducted in the range of 0 to 1 V and the scanning rate in 0.01V/s. The process of nickel anode oxidation in alkaline solution may produce intermediate products as follows:



The CHI 760 electrochemical workstation of three-electrode system was used to measure electrochemical characteristics of anode catalyst we synthesized by cyclic voltammetry (CV) and time stability testing. Principal reactions of DMFC in alkaline condition:



3.2 Cyclic voltammetry curve

The samples were tested and results are revealed in Fig. 1. Compared with Fig. 1b, the CV curves in Fig. 1a demonstrate typical methanol oxidation cyclic voltammetry graph. When the electrolyte was 0.5M KOH, no obvious methanol oxidation peaks were observed, in contrast, the same samples presented preferably electro catalysis in the 0.1M KOH. The sample B has better catalytic activity than the others: the initial voltage is 0.445 V, the current peak reaches 0.730 mA/cm^2 in the potential of 0.847V.

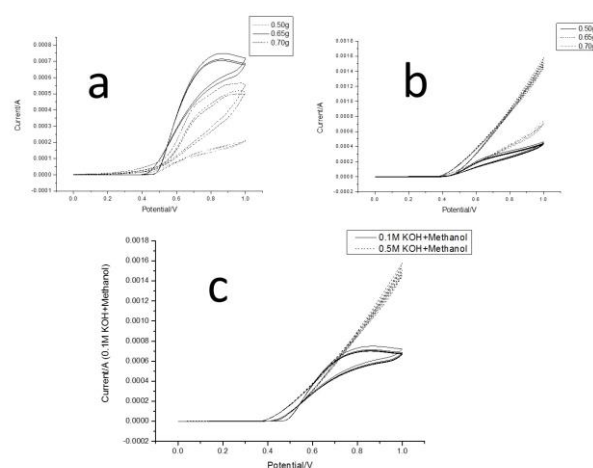


Fig. 1. Cyclic voltammetry curve of samples prepared. (a) all samples in 0.1M KOH electrolyte and 1 M methanol; (b) all samples in 0.5M KOH electrolyte and 1 M methanol; (c) sample B in methanol with different KOH concentrations: 0.1M and 0.5M.

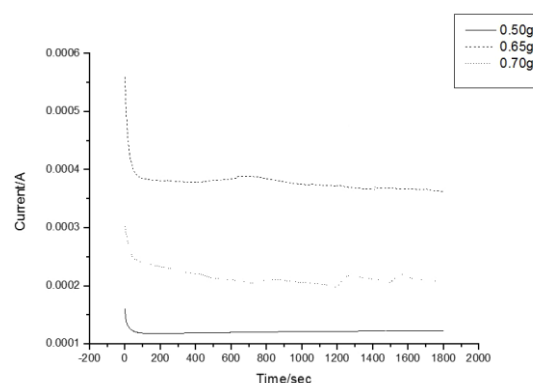


Fig. 2. Current time stability tests, all the samples in 0.1M KOH electrolyte and 1 M methanol

Current-time curves given in Fig. 2 were used to examine the stability of the samples. As shown in Fig. 2, Firstly they declined rapidly then current curve of sample B has a relatively higher current value than the others, indicating better stability.

The CV curve was measured in the speed of 0.05 V/S,

scanning from 0 V to 1 V, and the time of rest was 2s. Obviously, the oxidized peak turned up around 0.7V, which was the initial potential in current time testing.

In summary, Sample B shows the superior electro-catalytic performance.

3.3 SEM and TEM characterization

The graphene oxide synthesized by modified Hummer's method was characterized under electron microscope. Fig. 3a and b are scanning electron micrographs, which reveal wrinkling morphology of ultrathin layers of graphene oxides. Fig. 3c and d are transmission electron microscopy images, which demonstrate high quality of nanoscale thickness of graphene oxide.

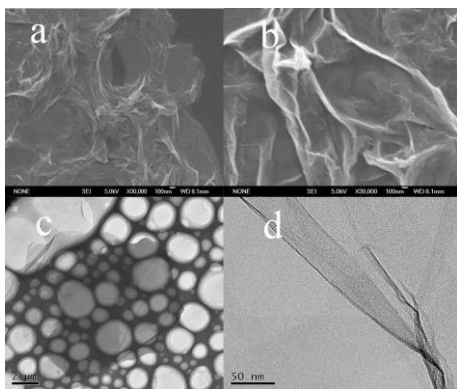


Fig. 3. (a) and (b): SEM of graphene oxide; (c) and (d): TEM of graphene oxide

The sheets size of Sample B increased a lot after Ni-plating process, while the thickness kept in nanoscale. The catalysts present cluster-like structure, as shown in Fig. 4a, b and c. Additional papery layer structure spreads on the original layer by layer, and with the increase of layer's number, the transparency decreases. Analyzed by energy dispersive x-ray spectrum (Fig. 4d), we found no other impurity elements except C, O, and Ni in the samples. The two big peaks are copper nets and silicon substrate which are necessary for the scanning test.

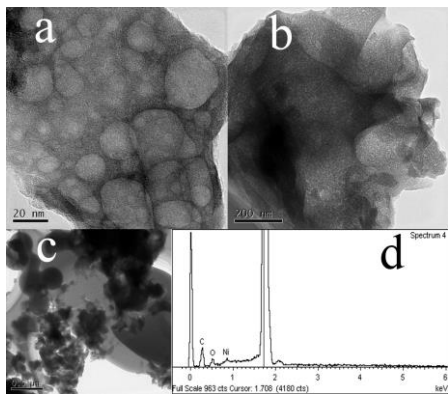


Fig. 4. (a), (b) and (c): TEM of sample B; (d): Spectrum of sample B

We choose two-dimensional graphene as the catalyst support material since it has ultrahigh specific surface area, making the electrode catalyst to have large and sufficient contact with electrolyte for electrochemical reactions [15]. Chemical reduction process of graphite oxide would leave some -OOH or -OH at the sheet edge, which will promote the catalysis [16] to eliminate the intermediate product caused by methanol oxidation, also improve the accessibility and wettability of methanol to the electroactive surface. Once contacting to alkaline solution, nickel would turn to $\text{Ni}(\text{OH})_2$, the crystal structure changing from $\alpha\text{-Ni}(\text{OH})_2$ to $\beta\text{-Ni}(\text{OH})_2$ irreversible, and the compounds with complex structure translate to $\beta\text{-NiOOH}$ and $\gamma\text{-NiOOH}$ [17]. Under the circulation of external current, they returned to Ni^{2+} finally. The conversion between Ni^{2+} and Ni^{3+} may produce some oxygen vacancy facilitating the release of adsorbed species like -OH etc, and make CO generated by methanol oxidation to CO_2 , accelerating catalytic process and enhancing catalytic performance.

Various doping amount results in the diversity of catalyst activity that was proved in our experiment. The low nickel content may have insufficient catalytic activity, while too high content may lead to non-uniform dispersion and to decrease the property. In this method, different amounts were 0.50 g, 0.65 g, and 0.70 g reacting with 0.05 g of GO separately, and 0.65 g had the best catalytic activity.

4. Conclusions

Novel nanoscale nickel/graphene samples as anode catalyst of DMFC were synthesized by a sol-gel method and their morphology and structure were characterized by electron microscopes. The sol-gel method made distinct deep color surface layer growth tightly on original sheets. When the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ involved in the reaction was 0.65 g, the samples demonstrated superior catalytic activity in comparison to other concentrations. In 0.1 M NaOH electrolyte solution, methanol oxidation peak occurred at around 0.7 V with a higher and relatively stable electric current value. The most suitable loading quantity exhibited superior electro-catalytic performance.

Acknowledgments

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