Electro-oxidation of Urea on the Nickel Phosphate-based Nanomaterials

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Nickel phosphate nanomaterials and multi-walled carbon nanotubes (MWCNTs) supported nickel phosphate nanomaterials were prepared by simple precipitate method. The nickel phosphate nanomaterials were tested the electrochemical activity of urea oxidation by cyclic voltammetry in alkaline solution. The nickel phosphate nanomaterials showed high catalytic performance towards the electro-oxidation of urea. Moreover, MWCNTs supported nickel phosphate nanomaterials showed higher catalytic current and lower onset potential due to the large specific surface and high electrical conductivity of MWCNTs.

Keywords: Nickel phosphate; Urea; Electro-oxidation; Multi-walled carbon nanotubes

1. INTRODUCTION

Fuel cells have attracted more and more attention because of their high energy conversion efficiency and environmental friendliness. Direct urea fuel cell is more attractive than conventional hydrogen fuel cell because urea has abundant sources and is easy to store and transport for its stability, non-toxic and non-flammable characteristics[1]. It is one of the high and new energy technologies that are developed preferentially in the world. High-efficiency electro-catalysts could determine the performance of fuel cell and its commercial application[2-7]. However, the catalytic materials are mainly composed of precious metal catalysts[8,9], while the expensive price of these materials hinders their wide application. Therefore, it is an important research direction to develop new catalysts with high efficiency, low cost and good stability. Nickel-based materials have attracted wide attention due to their low cost and high activity. They have been widely used as effective electro-oxidation catalysts for small compounds in alkaline medium[10-19]. Among them, nickel phosphate is a potential transition metal
material, which is widely used in oxidation electrocatalyst[20-22], supercapacitors[23, 24] and electrochemical sensors[25].

However, the nickel phosphates materials had low activity for their poor conductivity[26]. To overcome the disadvantages, conductive additives such as graphite, carbon nanotubes and graphene [27-29] can be used in the preparation of nickel phosphates materials. In this work, nickel phosphate nanomaterials and multi-walled carbon nanotubes (MWCNTs) supported nickel phosphate nanomaterials were prepared by simple precipitate method. Their electro-catalytic performance towards urea oxidation was investigated by cyclic voltammetry, which exhibited high electro-catalytic activity. Moreover, MWCNTs supported nickel phosphate nanomaterials showed higher catalytic current and lower onset potential due to the large specific surface and high electrical conductivity of MWCNTs. It is expected that nickel phosphate nanomaterials can be used as electrode catalysts for direct urea fuel cells.

2. EXPERIMENTAL SECTION

2.1 Reagents and instrumentation

Nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH), urea (H$_2$NCONH$_2$) and diammonium hydrogen phosphate ((NH$_4$)$_2$HPO$_4$) were obtained from China Pharmaceutical Group Chemical Reagents Co., Ltd. Multi-walled carbon nanotubes (MWCNTs) were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China).

The electrochemical experiments were performed on a CS350 Electrochemical Workstation (Wuhan Corrtest Instruments CO., LTD., Wuhan, China). A conventional three-electrode system was used for the electrochemical experiments. Nickel phosphate nanomaterials modified glassy carbon electrode (GCE) was used as the working electrode. The saturated calomel electrode (Saturated KCl) and platinum foil were used as the reference electrode and the counter electrode, respectively.

2.2 Preparation of nickel phosphate nanomaterials

0.25M nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O) and 0.25M diammonium hydrogen phosphate ((NH$_4$)$_2$HPO$_4$) were mixed together at room temperature in 50mL water with continuous stirring to form a greenish precipitate. Few drops of nitric acid were added to the mixture to get a uniform homogenous green solution. Then, the green solution was dropped to 40 mL 0.5M KOH solution with continuous stirring to form a greenish suspension. After filtered and washed several times with distilled water, the precipitate was left to dry in an oven at 110°C for 5h. The as-prepared material was named as NiPO.

The preparation of multi-walled carbon nanotubes (MWCNTs) supported nickel phosphate nanomaterials was similar to the preparation of NiPO. 75mg of MWCNTs were added to the as-prepared uniform homogenous green solution and was sonicated for 60 min to form black suspension. Then, the black suspension was dropped to 40 mL 0.5M KOH solution with continuous stirring to form a gray
suspension. After filtered and washed several times with distilled water, the precipitate was left to dry in an oven at 110 °C for 5h. The as-prepared material was named as NiPO-MWCNT.

2.3 Preparation of modified electrodes

The glassy carbon electrode (GCE, d = 2mm) was used here as the underlying substrate for nickel phosphate nanomaterials. It was mechanical polished with a leather containing 0.05 µm alumina slurry and then ordinal washed in ethanol and distilled water to obtain a clean surface.

The suspension of nickel phosphate nanomaterials, for being modified on the surface of GCE, was prepared as follows: 30 mg of nickel phosphate nanomaterials was added into a centrifuge tube with 0.5 mL 0.25 wt% nafion solution and 0.5 mL ethanol, then, ultrasonically treated for 1h to obtain a homogeneous suspension.

Finally, 3 uL of the suspension was dropped onto the surface of the GCE and then dried at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of nickel phosphate nanomaterials modified electrode

Figure 1. The cyclic voltammograms of NiPO/GCE(a) and NiPO-MWCNT/GCE(b) in 1M NaOH solution. Scan rate 20 mV/s.
The cyclic voltammetry technique was used for the investigation of electrochemical properties of nickel phosphate nanomaterials modified electrode. Figure 1 shows the cyclic voltammograms of NiPO/GCE and NiPO-MWCNT/GCE in 1M NaOH solution at the potential range of 0.1 to 0.6 V with scan rate of 20 mV/s. As can be seen from curve a, a pair of redox waves with a peak potential of 0.36 and 0.31 V was observed, which ascribed to the oxidation of Ni(OH)$_2$ to NiOOH and reduction of NiOOH to Ni(OH)$_2$. The electrochemical behavior of NiPO/GCE in alkaline solution is similar to that of Ni anode [30, 31]. The broad cathodic peak can be ascribed to the phase transformation of β-NiOOH to γ-NiOOH due to slow, irreversible overcharging during cycling, and the corresponding reduction to α-Ni(OH)$_2$. This phenomenon had been reported by Bode et al. [32]. A pair of well-fined redox peaks with a peak potential of 0.34 and 0.28 V was also observed in curve b, moreover, the current density is higher than that of curve a. It means that the large specific surface and high electrical conductivity of MWCNTs are favor of the oxidation of Ni(OH)$_2$ to NiOOH and reduction of NiOOH to Ni(OH)$_2$ at the electrode surface.

Figure 2 shows the cyclic voltammograms of NiPO/GCE and NiPO-MWCNT/GCE in 1M NaOH solution containing 0.1M urea. As can be seen from figure 2, with the presence of 0.1 M urea, it is evident to greatly enhance anode peak current and enlarge the peak region because of the overlapped of the anodic peak of nickel hydroxide and urea oxidation [33-35]. The electrode reaction could be explained as:

\[ \text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \]  \hspace{1cm} (1)

\[ 6\text{NiOOH} + \text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow 6\text{Ni(OH)}_2 + \text{N}_2 + \text{CO}_2 \]  \hspace{1cm} (2)

Firstly, Ni(OH)$_2$ is electro-oxidized to NiOOH and then NiOOH reacts with urea. At the same time, Ni(OH)$_2$ is regenerated. For the NiPO-MWCNT/GCE, it shows higher current density than that of NiPO/GCE. It means that NiPO-MWCNT/GCE has higher electroactivity toward urea oxidation due to the large specific surface and high electrical conductivity of MWCNTs.

![Figure 2. The cyclic voltammograms of NiPO/GCE(a) and NiPO-MWCNT/GCE(b)](image-url)
3.2. Voltammetric study of NiPO-MWCNT/GCE at different scan rates

Figure 3. (A) The cyclic voltammograms of NiPO-MWCNT/GCE in 1M NaOH solution at different scan rates. From 1-9: 10, 20, 30, 50, 80, 100, 150, 200, 300 mV/s. (B) Linear fit of peak current vs the square root of scan rate.
Figure 4. (A) The cyclic voltammograms of NiPO-MWCNT/GCE in 1M NaOH solution containing 0.1M urea at different scan rates. From 1 -9: 10, 20, 30, 50, 80, 100, 150, 200, 300 mV/s. (B) Linear fit of peak current vs the square root of scan rate.

Cyclic voltammetric responses of NiPO-MWCNT/GCE in 0.1M NaOH solution at different scan rates (from 10 to 300 mV/s) were depicted in Figure 3A. As shown in cyclic voltammograms, obvious oxidation peak and reduction peak in the potential range of 0.1–0.6V were observed, which is assigned for the redox transform of Ni(OH)$_2$/NiOOH. Both the oxidation peak current and reduction peak current
increase with the scan rate. Moreover, the difference of the oxidation and reduction peak potential ($\Delta E_p$) increases with the scan rate. The reduction peak current is less than the oxidation peak current. The results suggested a quasi-reversible process. Figure 3B shows the linear fit of peak current vs the square root of scan rate. The straight lines and excellent correlation coefficient ($R^2$) indicates a diffusion-controlled electrode reaction process.

Figure 4A shows cyclic voltammograms of NiPO-MWCNT/GCE in 1M NaOH solution containing 0.1M urea at different scan rates. With the scan rate increases, the oxidation peak current of urea oxidation increases, and also with the reduction peak current. It is assigned for the reduction of the remaining Ni (III) species to Ni(II) increases with the scan rate. This may due to the fact that the remained Ni(III) increases with increasing the scan rate due to lower consumption of the Ni(III) species at higher scan rates. The reduction peak current is much less than the oxidation peak current because of the urea electro-oxidation, which suggests a completely irreversible process. The linear fit of peak current vs the square root of scan rate was illustrated in figure 4B. The results indicates a diffusion-controlled process, which is in accordance with the Randles-Sevcik equation for completely irreversible process [36]. The electrode reaction of NiPO-MWCNT/GCE in NaOH solution in the absence and presence of urea are diffusion-controlled process. Thus, it suggested that OH$^-$ and CO(NH$_2$)$_2$ diffuse to the electrode surface at the same time in the process of urea electro-oxidation.

3.3. Catalytic properties study at different concentration of urea and NaOH

![Figure 5](image-url)

Figure 5. The cyclic voltammograms of NiPO-MWCNT/GCE at different urea concentration in 1M NaOH solution. Scan rate 20 mV/s. From 1 -5: 0.05, 0.1, 0.15, 0.2, 0.25M. Inset : plot of peak current density vs urea concentration.
The cyclic voltammograms of NiPO-MWCNT/GCE at different NaOH concentration containing 0.1M urea. Scan rate 20 mV/s. From 1-5: 0.5, 1, 1.5, 2, 2.5M. Inset: plot of onset potential vs NaOH concentration.

The relationship between the peak current of urea oxidation and the urea concentration was investigated. Figure 5 shows cyclic voltammograms of NiPO-MWCNT/GCE at different urea concentration in 1M NaOH solution. As can be seen, the peak current increases with the increase of urea concentration (inset). When the urea concentration is higher than 0.2M, the current density not increase. In general, fuel such as urea chemically reacts with supporting electrolytes at a certain ratio. We can infer from equations (1) and (2), the best ratio of $[\text{OH}^-]/[\text{CO(NH}_2\text{)}_2]$ is 6. Therefore, the suitable concentration of urea for NaOH reaction is 0.17M. When the urea concentration is higher than 0.2M, the ratio of $[\text{OH}^-]/[\text{CO(NH}_2\text{)}_2]$ dropped below 6, suggesting that the amount of NaOH is insufficient. Excessive urea has many deep effects: Hydrolysis effect of excessive urea; Loss of fuel (urea); The consumption of supporting electrolyte (NaOH); Carbon dioxide on the surface of electrode hinders the reaction. Due to OH$^-$ and CO(NH$_2$)$_2$ diffuse to the electrode surface at the same time in the process of urea electro-oxidation, the oxidation current density could be affected by inappropriate $[\text{OH}^-]/[\text{CO(NH}_2\text{)}_2]$ ratio[37, 38].

The influence of NaOH concentration on the electro-oxidation of urea was also investigated. Figure 6 shows the cyclic voltammograms of NiPO-MWCNT/GCE at different NaOH concentration containing 0.1M urea. It can be seen that with the increase of NaOH concentration from 0.5-1.5M, the onset potential(inset) and the oxidation peak potential both move to the negative direction, and the oxidation peak current increase. Because the current density of oxidation peak is much higher than that of reduction peak, the reduction peak seems to be not obvious. When the NaOH concentration is more than 1.5M, the onset potential and the oxidation peak potential slowly shift, while the oxidation peak current decrease. It shows that excessive NaOH could not enhance the urea oxidation.
4. CONCLUSION

In this work, multi-walled carbon nanotubes (MWCNTs) supported nickel phosphate nanomaterials were prepared by simple precipitate method. The electrochemical activity of NiPO-MWCNT/GCE towards urea oxidation was investigated by cyclic voltammetry, which showed high catalytic current and low onset potential due to the large specific surface and high electrical conductivity of MWCNTs. The voltammetric responses of NiPO-MWCNT/GCE in different NaOH concentration and urea concentration were investigated. The effect of scan rate on the voltammetric responses of NiPO-MWCNT/GCE suggests a diffusion-controlled process in NaOH solution in the absence and presence of urea.

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References

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