Study on a high-efficiency catalyst for urea electrolysis

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Abstract: The Urea oxidation reaction (UOR) process has a slow four-electron transfer step, and it is necessary to design a catalyst with improved reaction kinetics and excellent mass transfer ability. Utilizing 316 stainless steel mesh (SSM) with mesoporous structure, A hydrothermal method and high temperature vapor phosphating methods were used for constructing a NiP₂-FeP₄(x:y)/SSM compounds, NiP₂.FeP₄(7:1)/SSM obtain the best performance with a potential of only 1.47 V at a current density of 100 mA·cm². Speculated that the exposure of active sites is ensured on the basis of retaining the Layered Double Hydroxide (LDH), and the synergistic effect of metal-like compounds NiP₂ and FeP₄ enhances the electron transfer ability, thereby improving the slow kinetics of UOR. Therefore, the NiP₂-FeP₄(7:1)/SSM complex is expected to be an effective catalyst for the electrooxidation of urea.

Keywords: LDH; nickel phosphide; Iron phosphide; UOR; catalyst

1. Introduction

Environmental and energy issues is a problem that human beings need to solve for decades [1]. The development of sustainable alternative energy sources and technologies has been gaining attention in both the scientific and the industrial communities, in order to satisfy the growing energy consumption, reduce the dependence on non-renewable fossil fuels, and protect the global environment [2].

At present, the mainstream renewable energy sources such as tidal energy, solar energy and wind energy are characterized by intermittency in space and time, and cannot be used as stable energy on a large scale. Hydrogen energy is an ideal candidate for fossil energy due to its environmentally friendly and high energy density [3]. However, the manufacture, storage and use of hydrogen are greatly challenged, which seriously limits the large-scale use of hydrogen energy.

Hydrogen can be obtained by electrolysis of water. Electrolysis of water, which can be divided into two half-reactions, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), the theoretical voltage of water splitting is 1.23 V. The actual operating voltage is usually above 1.8 V, and the reaction energy consumption is large, which is not conducive to large-scale development [4]. Urea $(CO(NH_2)_2)$ is stable, non-toxic, safe, and inexpensive. The theoretical electrolysis voltage of urea is only 0.37 V [5], the electrolysis products of urea under alkaline conditions are environmentally friendly N₂ and CO_3^{2-} , without considering environmental issues. The combination of wastewater treatment and energy production is a hot topic of sustainable development, industrial urea wastewater and a large amount of urea-containing wastewater produced by mammals need timely and scientific management. For these large amounts of urea-rich wastewater, as the original energy carrier for recycling and utilization, not only purify wastewater, achieve the purpose of reducing pollution and environmental protection, but also produce hydrogen and realize energy regeneration. In an alkaline electrolyte, the entire urea electrolysis reaction is a follows:

Anode:
$$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e^-$$
 (1)

Cathode:
$$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^-$$
 (2)

Overal:
$$CO(NH_2)_2 + H_2O \rightarrow N_2 + CO_2 + H_2$$
 (3)

Urea oxidation reaction (UOR) is similar to OER kinetics, involving multiple electron transfer, and the kinetic process is slow [6], requiring an effective catalyst to facilitate the oxidation process. Noble metal-based electrocatalysts such as RuO₂, IrO₂ show good performance in UOR process. However, the high cost of noble metal materials limits its industrial application [7].

Recent studies have found that compounds of transition metals with N, P, S, etc. have unique properties for UOR [5-7]. Among them, nickel-based phosphides are particularly regarded for their unique electronic properties, efficient electrocatalytic activity and anti-corrosion properties, as well as low cost. This work utilized SSM with mesoporous structure to synthesize NiP₂ FeP₄ (7:1)/SSM composites using hydrothermal and high-temperature vapor phase phosphating methods.

2. Experimental section

2.1 Synthesis of NiFe-LDH/SSM

Cut the 316 stainless steel mesh (SSM) into a rectangular shape of 5.5cm and 2.5cm in width, clean it with water and acetone, and activate it with acid etching in dilute nitric acid for 15 minutes. Finally, wash with water and ethanol [8].

40 ml solution containing 0.2 M urea (CO $(NH_2)_2$), 0.08 M ammonium fluoride(NH₄F) and 0.03 M (nickel nitrate $(Ni(NO_3)_2 \cdot 6H_2O)$ + iron nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$) was placed in a hydrothermal reactor and placed in a pretreated SSM. Then adjust the ratio of nickel to iron (3:1, 5:1, 7:1, 9:1, 11:1) and maintain it at a constant temperature of 120 ° C for 16 hours. After the reaction, the product was thoroughly washed with deionized water and ethanol and dried at 60 °C for 2 h to obtain NiFe-LDH(x :y)/SSM.

2.2 Synthesis of NiP2-FeP4(x:y)/SSM

A porcelain boat with the precursor of NiFe-LDH(x:y)/SSM was placed in the downwind, and another porcelain boat with hydrous NaH₂PO₂ was placed in the upwind in a furnace, where the mass ratio of NiFe-LDH(x:y)/SSM to NaH₂PO₂ was set as 1:3. The reaction was proceeded under an Ar atmosphere, and the furnace was heated to the desired temperature 300 °C with a heating rate of 2 °C min⁻¹ and maintained for 2 h. The NiP₂-FeP₄(x: y)/SSM were obtained after natural cooling [9].

2.3 Electrochemical and reaction kinetics testing

An electrochemical workstation is used to perform electrochemical tests for this experiment and to obtain the corresponding data. The electrochemical workstation is a typical three-electrode system. The precursor NiFe-LDH(x:y)/SSM and its phosphating NiP₂-FeP₄(x:y)/SSM were used as working electrode, Ag/AgCl electrode as reference electrode and platinum electrode as counter electrode. Cyclic voltammetry (CV) test and Linear sweep voltammetry (LSV) test were performed in 3.0 M KOH and 3.0 M KOH with 0.6 M urea added at a scan rate of 20 mV/s and calculate the Tafel slope test was performed after adding 0.6 M urea. In the potential range of 0.22-0.3 V, the scanning speed was adjusted for CV test, and the Electrical Double-Layer Capacitor (Cdl) and electrochemical active surface area (ECSA) were calculated. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHZ to 0.01 HZ. All potentials reported were calibrated to the RHE and All curves were tested with IR-compensation.

3. Results and discussion

3.1 Material characterization

The morphology of NiP₂-FeP₄(7:1)/SSM and NiFe-LDH(7:1)/SSM was characterized by scanning electron microscopy (SEM). Fig.1a, c, d and Fig.1b are SEM images of NiP₂-FeP₄(7:1) / SSM and NiFe-LDH (7:1) / SSM. NiP₂-FeP₄(7:1) was observed to grow uniformly on the surface of SSM from Fig.1(a, c), and a three-dimensional grid structure composed of longitudinal nanosheets was formed, it can be seen that the structure of the sample after phosphating did not change significantly compared with that before phosphating, indicating that the phosphating process did not destroy the structure of NiFe-LDH(7:1)/SSM.



Figure 1: a, c, d and b are SEM images of NiP_2 -FeP₄(7:1) / SSM and NiFe-LDH (7:1) / SSM.

The phase structures of the NiFe-LDH(7:1)/SSM and NiP₂-FeP₄(7:1)/SSM were further studied by XRD. Fig. 2 indicated XRD pattern of NiFe-LDH(7:1)/SSM and NiP₂-FeP₄(7:1)/SSM. A series of characteristic peaks were observed at 20 values of 11.5°, 23.2°, 34.6°, and 38.4°, were indexed to the (003), (006), (012) and (015), crystal planes of NiFe-LDHs, respectively, showing that NiFe-LDH(7:1)/SSM have typical hydrotalcite-like crystal structure. After phosphating, characteristic peaks are observed at 25.0°, 32.4°, 35.5° and 46.4° of 20 in the sample, which are indexed to the (121) and (131) crystal planes of FeP₄, as well as the 220 and 311 crystal planes of NiP₂. Indicating the successful synthesis of NiFe-LDH precursor and the formation of NiP₂-FeP₄ after phosphating.

3.2 Electrochemical and reaction kinetics analysis

The electrochemical performance of NiP₂-FeP₄(7: 1)/SSM and NiFe-LDH(7:1)/SSM was tested in 3 M KOH solution(Fig. 3b). Both CV curves have a pair of reversible redox peaks, which can be attributed to the valence transition between Ni (II) and Ni (III) species in KOH electrolyte [10]. Phosphating increases the current density of NiFe-LDH (7: 1) / SSM and also achieves superior reversibility.



Figure 2: XRD pattern of the NiFe-LDH(7:1)/SSM and NiP2-FeP4(7:1)/SSM.

Fig. 3b is the LSV curve after adding 0.3 M urea, as the proportion of Ni in NiP₂-FeP₄(7: 1)/SSM increases, the oxidation current density shows a trend of first increasing and then decreasing, reaching its optimum at x: y = 7: 1. Compared to NiFe-LDH (7: 1) / SSM, NiP₂-FeP₄(7: 1)/SSM exhibits a

significantly increased current density, despite an initial oxidation potential that does not significantly decrease (Fig. 3c). From Fig. 3d, the electrochemical impedance spectrum (EIS) also observes that NiP2-FeP4(7:1)/SSM exhibits the lowest charge transfer resistance.

As shown in Fig.4a, Cdl obtained by linear fitting of CV curve, and ECSA was 47.33 cm² calculated by the formula, indicating that NiP₂-FeP₄(x:y)/SSM has a considerable specific surface area. Fig.4b shows that the Tafel slope decreases with the increase of nickel-iron ratio, indicating that the increase of nickel content has a positive effect on the electron transfer ability of the catalytic process and improves the slow kinetics of UOR.

$$ECSA = \frac{Cdl}{Cs}; (Cs = 60\mu F/cm^2)$$

In summary, NiP₂-FeP₄(7:1)/SSM exhibits more excellent reversibility and higher current density. It may be that compared with NiFe-LDH, phosphating improves the electronic structure of Ni and Fe on the basis of maintaining the excellent three-dimensional grid structure of NiFe-LDH, the formed phosphide has metal-like properties, which is more conducive to the electron transfer of the UOR process, thereby improving its slow reaction kinetics.



Figure 3: CV diagram of the NiP2-FeP4(7:1)/SSM and NiFe-LDH(7:1)/SSM at 3 M KOH (a), and Added LSV diagram of 0.3M urea (c). Comparison of LSV between NiP2-FeP4(7:1)/SSM and NiFe-LDH(7:1)/SSM(b). During the UOR process EIS spectrum of NiP2-FeP4(x: y)/SSM (d).



Figure 4: (a) CV and Cdl of NiP2-FeP4 (7:1)/SSM. (b) The Tafel slope of NiP2-FeP4(x:y)/SSM.

4. Conclusion

A hydrothermal method and high temperature vapor phosphating approach were used for constructing a NiP₂-FeP₄(7:1)/SSM compounds. The excellent three-dimensional grid structure of NiP₂-FeP₄(7:1)/SSM exposed more electrochemical reaction active sites, which was more conducive to contact with the substrate and electron transfer for a rapid and efficient UOR process. Therefore, the NiP₂-FeP₄(7:1)/SSM compounds can be applied for a catalyst with Hydrogen production by electrooxidation of urea. The combination of Ni, Fe, and P, as well as their lower cost makes the NiP₂-FeP₄(7:1)/SSM compounds a very promising electrocatalyst for constructing urea electrooxidation hydrogen production electrolytic cell in practical applications.

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